THE PHYSICAL CHEMISTRY
OF
ELECTROLYTIC SOLUTIONS

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To those institutions which have fostered free inquiry through these troubled times, this book is gratefully dedicated.

GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical subareas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

Preface to Second Edition

During the years of the war, the tremendous emphasis upon technology caused a diminution in the volume of fundamental scientific research. The science of electrolytic solutions has not escaped this influence, but since 1945 the pre-war momentum of the laboratories is beginning to be restored. In view of this retardation and of the expense entailed in a thoroughgoing revision of the original text, a compromise has been adopted in preparing a second edition of this work. An appendix has been added which contains revisions of the tables of the theoretical functions, extensions of some of the tables of data, and discussions of some recent experimental and theoretical contributions.

While part of our original text was in press in 1941, revised tables of fundamental constants were published by Birge. At that time, it was decided to make no change in the numerical tables of physical constants, characteristic slopes and mathematical functions in Chapter (5). Had we decided to make this change, all of the numerical tables would have been inconsistent with the actual calculations in the book. In this edition we have not altered the tables in Chapter (5) for the same reason, but have incorporated in Appendix B revised values of those quantities affected by changes in the fundamental constants. This procedure leaves the original text representative of the calculations during the three decades preceding 1940, and we believe that this is the most unequivocal way of meeting this unfortunate complication.

Appendix B is comparatively short, so no subject index for it has been included. Instead, a detailed Table of Contents and a separate Author Index are supplied. The sections in Appendix B are designated consecutively, (B-1), (B-2), etc., and the equations are numbered, (B-1-1), (B-10-4), etc., where (B-1-1) is the first equation in Section (1), (B-10-4) is the fourth equation in Section (10), etc. The Figures and Tables are similarly designated. Cross references between tables in the main body of the book and Appendix B have been introduced.

Every effort has been made to eliminate the errors of typography, of sign, of factor omission, and of misstatements in the text. We are grateful to those of our colleagues who have called our attention to these mistakes. In particular we extend our thanks to Dr. Albert Sprague Coolidge of Harvard University, and to Dr. Roger G. Bates of the Bureau of Standards for lists of corrections which were the result of meticulous examination of many chapters of our work.

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New Haven, Conn.
June, 1949.

Preface

The science of solutions is very complex. It has evolved its own numerous experimental methods, and has required for its clarification many branches of mathematical physics, such as thermodynamics, statistical mechanics, electrostatics, and hydrodynamics. A great deal has been achieved by theory, but this achievement has been by no means enough to warrant the neglect of further experimental investigation. In writing this treatise on electrolytic solutions, we have tried to stress the importance of theory without neglecting that part of the subject which is empirical. At the same time, we have not hesitated to state the limitations of theory, or to criticize the accuracy of experimental data. We trust that the result approaches a well-balanced treatment, and hope that many of our readers will become aware of the many parts of the subject which are obscure, and which require further constructive effort. If we succeed in suggesting new and profitable fields of study to them, we shall be greatly repaid for our labor.

Although many of the important fundamental principles of electrochemistry had been discovered in the last decades of the eighteenth century and the first eighty years of the nineteenth century, it was not until 1887 that an organized theoretical and experimental investigation of conducting solutions was begun. This was brought about by the monumental discovery of van't Hoff[1] that solutions which readily conduct electric current possess freezing points, boiling points, osmotic pressures, and vapor pressures characteristic of a special class of systems, and the simultaneous and even more important discovery of Arrhenius[2] that such systems contain electrically charged particles, or ions.

It was van't Hoff who first applied the powerful methods of thermodynamics to solutions in a systematic manner. His treatment, however, lacked the generality which might have been achieved at that time if the system of thermodynamics developed by Gibbs[3] ten years earlier had been employed. Gibbs' great treatise provides all the essential basic principles required for the thermodynamics of solutions. The most important contribution of thermodynamics has been to reduce all measurements of systems in equilibrium to the determination of a single thermodynamic function.

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[1] J. H. van't Hoff, *Z. physik. Chem.*, **1**, 481 (1887).

[2] S. Arrhenius, *Z. physik. Chem.*, **1**, 631 (1887).

[3] J. W. Gibbs, *Transactions of Connecticut Academy of Sciences*, **2**, 309, 382 (1873); **3**, 108, 343 (1875–1878). "Scientific Papers of J. Willard Gibbs," Vol. I, New York, Longmans, Green and Co., 1906. "The Collected Work of J. Willard Gibbs," Vol. I, New York, Longmans, Green and Co., 1928.

Measurements of the elevation of the boiling point and the lowering of the freezing point and vapor pressure of a solvent, caused by the addition of solute, and measurements of solubility, osmotic pressure, and the electromotive forces of suitable cells may all be used to determine the Gibbs chemical potentials of electrolytes.

From 1887 to the present, the knowledge of ionic solutions has increased immensely. Steady improvement has been made in the experimental methods of measuring the properties associated with thermodynamic equilibrium, and those such as conductivity, viscosity, and diffusion, which involve ions under the influence of externally imposed fields. This development has led to an immense volume of information (some of very high accuracy) concerning a large number of ionic systems. Simultaneously with this more and more detailed study, an electrostatic and hydrodynamic theory, depending upon the methods of statistics, has been evolved.

Soon after the discovery that ions exist in solutions, it was realized that the electrostatic forces between the ions must play an important role in determining their properties. Although attempts were made to deduce a theory of interionic attraction in the first two decades of this century, it was not until 1923 that an exact theory of dilute solutions of electrolytes was evolved. After Debye's[4] formulation of the interionic attraction theory, a large literature developed, which includes theories of all the properties of electrolytic solutions.

The structure of this treatise is different from that of any other general treatment of the properties of ionic solutions. We are convinced that the interionic attraction theory is sufficiently well established to permit the development of the purely theoretical aspects of the subject before the discussion of the experimental methods and properties. This order of presentation has the advantage of allowing a logical development of the theory without the interpolation of extraneous material. Further, by presenting the basic theory first, the fundamental equations of theory become available both for the numerical treatment of the data and for subsequent discussions of the various properties of electrolytes.

The work is divided into three general parts of five chapters each. Chapters (1) to (5) are theoretical. The first chapter contains a thermodynamic introduction. Chapter (2) introduces the concept of the ionic atmosphere, and the foundations of the interionic attraction theory. Chapters (3) and (4) contain the theory of ionic solutions in equilibrium, and in perturbed states, respectively. A numerical summary of the theoretical results, in which the theoretical equations are reduced to their simplest form, is given in Chapter (5). For facilitating practical calculations, numerous tables of constants and theoretical functions are given.

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[4] P. Debye and E. Hückel, *Physik. Z.*, **24**, 185, 305 (1923).

We believe that a thorough understanding of this chapter will be of considerable practical value to those interested in numerical calculations which involve ionic solutions.

The second general division of the work [Chapters (6) to (10)] contains a discussion of experimental methods. No apparatus or experimental technique is described in detail. Chapters (6) and (7) contain a description of the use of the conductance method in the study of strong and weak electrolytes in aqueous and non-aqueous solutions, respectively. The effects of high frequencies and high fields upon conductances are also considered. Viscosity and diffusion of electrolytic solutions are included in this part. Chapter (8) contains a treatment of partial molal quantities with the exception of the partial molal free energy, work content, and entropy. In Chapter (9) freezing point, boiling point, and vapor pressure measurements are developed, and in Chapter (10) a general discussion of the electromotive force method is presented.

In the last third of the book, the emphasis is upon the properties of electrolytes rather than upon the methods by which they were obtained. Chapters (11), (12), and (13) deal with solutions of hydrochloric acid, 1-1 electrolytes, and polyvalent electrolytes, respectively. Thermodynamic properties, their interpretation, and special theories of these solutions are discussed. Mixtures of strong electrolytes in water form the subject of Chapter (14). Ionization constants of weak electrolytes, their temperature coefficients, and the ionization of weak electrolytes in salt solutions are considered in Chapter (15).

In all these discussions, we have tried to incorporate the most accurate results. Rather extensive tables of quantities derived from the best available data are given in an Appendix. These will prove useful for both theorists and experimental investigators. The former will find much to explain, and the latter will have at hand material which can be employed in practical calculations, and in comparisons with future data.

Each of the last ten chapters is of the nature of a short monograph. This has involved a certain amount of repetition which we felt was necessary to increase the value of the work as a reference book. Theoretical equations, deduced in the first part, have frequently been restated in subsequent sections. This procedure has been followed in order that the immediate subject under consideration may be more clearly discussed. The most pronounced example of such repetition occurs in Chapter (8) in which the properties of partial molal quantities are considered. Here, each section, devoted to the discussion of one of these quantities, is treated as a separate subject. This has the advantage of keeping the attention of the reader focussed on the immediate subject matter, although it may have the effect of rendering continuous reading of the chapter somewhat tiresome.

In the theoretical treatment of irreversible processes, we have had to remain content with the statement of fundamental principles and boundary conditions, and with the deduction of the differential equations. Detailed descriptions of the methods of integration would have led to a mathematical treatise. Our principal object has been the discussion and treatment of data, and both theoretical and empirical methods for computing them. Detailed descriptions of methods of extrapolation have been made with the risk that continued reading of these parts will be tedious. However, we trust that this procedure will be of help to experimenters in the calculation of their material.

Our original intention was to include a comprehensive discussion of ionic reaction velocities and homogeneous catalysis in liquid systems containing ions. This project was abandoned after careful consideration of the scope of the subject. It seemed that an adequate treatment could not be effected without increasing the volume of the book beyond convenient limits.

Some further restrictions have been imposed. Since we have devoted ourselves principally to the electrostatic theory and properties of ions in solutions, little attention has been paid to electrode processes, standard free energies and entropies of ions, or quantum theories of electrode processes. Nor have the Raman spectra and refractive indices of ionic solutions been considered. Further, we have omitted detailed discussion of solutions containing electrolytes of complicated structure, such as higher-order cobalt compounds, complex organic acids, bases, ampholytes, etc. The theory of the properties of dipolar ions is omitted because it has been thoroughly treated by Kirkwood in this series of monographs.[5] Even with these restrictions, an adequate treatment of all the excellent experimental material was found to be difficult to keep within the limits of a single volume.

The choice of symbols and conventions in a complicated field is always a source of considerable trouble. For the thermodynamic parts, we have used to a large extent the nomenclature of Lewis and Randall,[6] because it is commonly employed in this country. We have adopted, with modification, the symbols of Onsager and Fuoss[7] in developing the interionic attraction theory. These conform fairly well to those in general use. In a number of special deductions we have used symbols which conform closely to the original articles in the literature. In such cases, confusion has been avoided by careful explanatory notes. A complete glossary of symbols is given immediately before Chapter (1).

A large number of equations, figures and tables occur. All these are characterized by three numbers. The first number indicates the chapter, the second, the section of the chapter, and the third, the number of the

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[5] Chapter (12) of E. J. Cohn and E. T. Edsall, "Proteins, Amino Acids and Peptides," A. C. Monograph, No. 90, Reinhold Publishing Corporation, New York (1943).

[6] G. N. Lewis and M. Randall, "Thermodynamics," New York, McGraw-Hill Book Co., 1923.

[7] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

equation, etc., in this section [Equation (4-4-22), Fig. (13-9-1), Table (12-2-3), etc.]. Tables which occur in the appendix are indicated by an A following the last number, and refer to the chapter and section of the text in a similar manner [Table (12-6-1A)].

It is impossible to acknowledge all the help we have received from the publications, the private correspondence, and conversations with our colleagues in this and other countries. The influences from all these pleasant associations will appear in innumerable ways throughout the work. We are grateful for a number of suggestions and corrections made by members of the committee of the American Chemical Society Monograph Series and to Professor T. F. Young of the University of Chicago.

Among our immediate associates at Yale University, we are particularly aware of our indebtedness to Dr. Gösta Åkerlöf for his generous coöperation over many years in matters pertaining to the experimental side of the subject. We have been greatly influenced by our association with Dr. Lars Onsager, whose masterly treatment of the theory of irreversible processes has been closely followed. We are also greatly indebted to Dr. Robert A. Robinson of the University of New Zealand, who has allowed us access to experimental material on polyvalent electrolytes prior to publication, and who has generously helped with the calculation of the properties of weak electrolytes.

Above all, we thank our colleagues, the fellows and students, whose hard work and spirit of coöperation have made the last five chapters of this treatise possible.

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October, 1943.

Glossary of Symbols

The complexity of the subject has made it necessary frequently to use the same symbol for different quantities. For example, the principal use of A is to represent the work content, but in some instances, it is used to represent an area, special functions, or an empirical parameter. No confusion should arise from this source because all special uses are described carefully in the text.

In accordance with the procedure of Lewis and Randall, a bar over a thermodynamic quantity has been used to represent its partial derivative with respect to the number of mols at constant pressure and temperature. Thus $\bar{F}$ is the partial molal free energy, $\bar{V}$ the partial molal volume.

A circle directly over a symbol representing distance indicates that it is expressed in Ångström units. Thus, if "a" is used for distance in centimeters, $\mathring{a}$ will represent this distance in Ångströms.

All vectors are in bold face type with the exception of the operator ∇. The dot and cross representations of products of vectors are used. Only three scalar quantities, **E**, **F**, and **N**, representing electromotive force, Faraday charge and number of equivalents are printed in bold face type.

A few rules for subscripts and superscripts have been adopted.

Subscripts represent (a) ionic or molecular constituents. For example, $+$, $-$, i, j represent ionic constituents, $1, 2, \cdots c$, molecular components, w denotes water, v, vapor, etc. (b) The subscript $\pm$ is used to indicate a mean ionic quantity of an electrolyte. Thus, $\gamma_\pm$ is the mean molal activity coefficient, $m_\pm$ the mean molality. (c) The subscript zero is used to designate a property of the pure solvent. For example, d_0 and η_0 are the density and viscosity of a solvent.

The superscript zero has been used to indicate the value of a function in the standard state. The standard state is understood to be unit activity in aqueous solutions unless otherwise indicated (*e.g.*, by an asterisk).

There is, however, one use of the superscript zero which is not consistent with the above rules. We have represented the equivalent conductance of an electrolyte, and the equivalent conductance and transference number of an ion at infinite dilution by Λ^0, λ_i^0 and T_i^0, respectively. This choice of superscript rather than subscript was governed by the difficulty of describing all the conductance phenomena without multiple subscripts.

There is one innovation in symbols which is of considerable importance. A large number of the limiting theoretical equations reduce to a simple form. For example,

$$\log f_\pm = -\mathscr{S}_{(f)}\sqrt{\Gamma} = -\mathcal{S}_{(f)}\sqrt{c}$$

$$\bar{L}_2 = \mathscr{S}_{(L)}\sqrt{\Gamma} = \mathcal{S}_{(L)}\sqrt{c}$$

and so forth for many properties. In these equations $\mathcal{S}_{(f)}$, $\mathcal{S}_{(L)}$, $\mathcal{S}_{(f)}$, etc., are theoretical constants at constant pressure and temperature in a given medium. The subscript denotes the property under consideration. Since numerous graphs occur in which the left sides of these equations are plotted against the square root of concentration variables, these constants are limiting slopes and are referred to as such. We believe that the consistent use of this method of expression will avoid unnecessary confusion if generally adopted.

A, work content per mol.

$\bar{A}$, partial molal work content.

$\bar{A}_1$, $\bar{A}_2$, etc., $\bar{A}_i$, $\bar{A}_j$, etc., partial molal work content of components, etc., and ion constituents, etc., indicated by subscripts.

A, contribution to, (1) ΔA (el), electrical contribution to the work content [Equation (3–2–1)]; (2) $\Delta A_{(s)}$, contribution to the work content caused by addition of electrolyte [Equation (3–10–7)].

A^*_v, van der Waals co-volume contribution to the work content [Chapter (12), Section (8)].

A, A', characteristic parameters of equations (5–2–7) and (5–2–9). Important functions. Note that $A'_m = A'\sqrt{d_0}$.

A, area

A, special function given by equation (4–7–19).

A, special function [Chapter (12), Section (7)].

$A\Delta\alpha$, special function in Table (5–2–6), defined by equation (5–2–17).

A, A_n, A_{n-1}, A^*_{n-1}, A', A^*, etc., empirical coefficients.

a, activity.

a_1, a_2, $\cdots$, activities of components indicated.

a_+, a_-, a_i, a_j, conventional activities of ionic constituents indicated.

$a_\pm$, mean ionic activity of an electrolyte [Equation (1–6–3)].

a_R, activity of a component in a reference solution.

a_w, activity of water.

a_{H}, a_{OH}, etc., activities of ionic constituents indicated.

a_N, a_m, a_c, activity on N-, m-, and c-, concentration scales.

a'_s, activity of solid solvent at T'.

$a_1^{0'}$, activity of pure liquid solvent at T'.

a'_1, activity of solvent in solution at T'.

a'_2, activity of solute in solution at T'.

a'_v, activity of solvent vapor at T'.

a, mean distance of approach of ions defined by equation (14–1–5).

$\mathring{a}$, same in Ångström units.

a_i, a_j, mean ionic distances of approach of ions indicated.

$\mathring{a}_i$, $\mathring{a}_j$, same in Ångström units.

a, distance of approach of ions in theory of ionic pair formation [Chapter (3), Section (7)].

a_3, distance in triple ion formation equation (3–7–21).

a_4, distance in quadrupole formation equation (3–7–28).
a_{12}, a_{10}, a_{20}, mutual cohesive energy densities [Chapter (12), Section (7)].
a_{μ}^{λ}, element of rate of strain dyadic [Chapter (4), Section (2)].
a, a_0, a_1, a', a'', etc., coefficients of empirical equations.

$B_2(\kappa a)$, $B_2^*(\kappa a)$, $B_3(\kappa a)$, functions of extended theory [Equation (3–6–6)].
B, B', B'', B_{RI}, etc., coefficients of empirical equations.
b, characteristic parameter, Bjerrum's theory of ionic pair formation [Equation (3–7–7)].
b_3, characteristic parameter in theory of triple ion formation [Equation (3–7–21a)].
$\bar{b}$, function used in theory of effect of field on the dissociation of weak electrolytes, and given by equation (4–7-27).
b_j, ionic radius in salting theory [Chapter (3), Section (10)].
b, b_0, b_1, b', b'', b_c, b_m, etc., coefficients of empirical equations.

C_p, molal heat capacity at constant pressure.
C_{ps}, molal heat capacity of solid.
C_{pv}, molal heat capacity of vapor.
C_{p1}, molal heat capacity of solvent.
$\bar{C}_p$, partial molal heat capacity.
$\bar{C}_{p1}$, $\bar{C}_{p2}$, partial molal heat capacities of components indicated.
$\bar{C}_p^0$, $\bar{C}_{p1}^0$, $\bar{C}_{p2}^0$, standard partial molal heat capacities.
C_n, function defined by equation (9–2–9).
C_n^*, function defined by equation (9–3–6).
C_{-2}, C_{-1}, C_0, C_1, C_2, coefficients in equation (11–9–3).
C', C^*, etc., coefficients of empirical equations.
c_p, c_p^0, c_v, etc., specific heat capacities at constant pressure, or volume.
c, molar concentration in mols per 1000 cc. solution.
c_+, c_-, c_i, c_j, molar concentrations of constituents indicated.
$c_{\pm}$, mean molar concentration [Equation (1–8–8)].
c^*, concentration in equivalents per 1000 cc. solution.
c_u, molar concentration of undissociated electrolyte.
c_A^*, normality of ion constituent, A.
c_I^*, normality of indicator solution.
$c_I^{*\prime}$, initial normality of indicator solution.
$c(x)$, concentration of solute at a distance, x, from boundary of solution [Chapter (3), Section (11)].
c, number of components (Gibbs) in a system.
c_0, c_1, c_2, c_n, etc., coefficients defined by equations (4–3–52) and (4–3–53).
c, c_0, c', c'', c''', c_1, etc., coefficients of empirical equations.

D, dielectric constant of solution.
D_1, D_2, etc., dielectric constants of components indicated.
D_0, dielectric constant of solvent.
$\mathfrak{D}$, coefficient of diffusion [Equation (6–10–1)].

$\mathcal{D}^0$, coefficient of diffusion at infinite dilution.
$D^2_{\lambda\mu}$, second differential coefficients.
D', D^*, coefficients of empirical equations.
d, density of solution.
d_0, density of solvent.
$d(\quad)$, complete differential.
d_1, d_2, d_{12}, d_+, d_-, $d_\pm$, diameters of constituents indicated [Chapter (12), Section (8)].

$\mathbf{E}$, electromotive force of cell.
$\mathbf{E}^0$, standard electromotive force of cell.
$\mathbf{E}^0_N$, $\mathbf{E}^0_m$, $\mathbf{E}^0_c$, standard electromotive force of cell on the N-, m-, and c-scales.
$\mathbf{E}^{0*}$, standard electromotive force of cell in a mixed, or non-aqueous solvent.
$\mathbf{E}_{1(T)}$, $\mathbf{E}_{2(T)}$, electromotive forces of cells with transference.
$\mathbf{E}_{12}$, $\mathbf{E}_{21}$, etc., electromotive forces of certain cells without transference.
$\mathbf{E}_J$, liquid junction electromotive force.
$\mathbf{E}_{\mathrm{Ext.}}$, contribution of extended terms of electromotive force.
$\mathbf{E}^0_{\mathrm{pH}}$, constant in equation (10–7–2).
$\bar{E}_1$, $\bar{E}_2$, partial molal expansibilities of components indicated.
$\bar{E}^0_1$, $\bar{E}^0_2$, standard partial molal expansibilities.
$\bar{E}_2 - \bar{E}^0_2$, relative partial molal expansibility of component (2).
e, base of natural logarithm.
e, electrical charge.
e_1, e_2, $\cdots$. e_s, e_i, e_j, total electrical charge of ions indicated (carry sign).
$|e_1|$, $|e_2|$, $\cdots$ $|e_s|$, $|e_i|$, $|e_j|$, magnitudes of charges on ions.
$\mathfrak{E}$, light absorption coefficient [Equation (15–4–11a)].
$Ei(\quad)$, exponential integral function.

$\mathbf{F}$, Faraday charge.
F, molal free energy.
F^0, standard molal free energy.
F_1, F_2, $\cdots$ F_c, molal free energies of components indicated.
F^0_1, F^0_2, $\cdots$ F^0_c, standard molal free energies of components indicated.
$\bar{F}_1$, $\bar{F}_2$, $\cdots$ $\bar{F}_c$, partial molal free energies of components indicated.
$\bar{F}^0_1$, $\bar{F}^0_2$, $\cdots$ $\bar{F}^0_c$, standard partial molal free energies of components indicated.
$\bar{F}_i$, $\bar{F}_j$, conventional partial molal free energies of ions indicated.
$\bar{F}^0_i$, $\bar{F}^0_j$, same in standard states.
$\bar{F}^0_N$, $\bar{F}^0_m$, $\bar{F}^0_c$, standard partial molal free energies on the N-, m-, and c-scales.
F^*_w, van der Waals' co-volume contribution to free energy [Chapter (12), Section (8)].
$\mathcal{F}$, force.
$F(\bar{b})$, special function given by equation (4–7–30).
$F(Z)$, special function given by equation (7–2–5).
$F_{ji}(\Omega)$, number of ions leaving interior, Ω, of region, S [Equation (4–6–7)]

f, rational activity coefficient.

$f_{(s)}$, rational activity coefficient of non-electrolyte.

f_+, f_-, f_i, f_j, conventional rational activity coefficients of ions indicated.

$f_\pm$, mean rational activity coefficient [Equation (1–8–4)].

$f_{\pm(s)}$, rational activity coefficient of electrolyte in salting equation (3–10–10).

$f_{\pm(t)}$, rational activity coefficient of electrolyte in equation (3–10–13) for transfer of electrolyte.

$f_{ij}(\mathbf{r}_2, \mathbf{r}_{12}), f_{ji}(\mathbf{r}_1, \mathbf{r}_{21}), f_{ji}, f_{ij}$, distribution functions according to equation (2–1–4).

f^0_{ji}, f^0_{ij}, distribution functions for solution in unperturbed state.

f'_{ji}, f'_{ij}, distribution functions for perturbed solutions.

f_c, f_m, special functions given by equation (12–10–7).

$f(x)$, function in theory of Wien effect [Equation (4–6–45), Table (5–3–6)]

$G_{ji}, G_{ij}, G_{12}, G_{21}, G_{11}, G_{22}, G(\mathbf{r})$, functions used in theory of frequency and field effects (Wien effect) upon conductance [Chapter (4), Sections (5) and (6)].

g, rational osmotic coefficient [Equation (1–9–5)].

$g(x)$, function in theory of Wien effect [Equation (4–6–48), Table (5–3–5)].

$g(c)$, special function in equation (7–4–10).

g, special function [Chapter (4), Section (7)].

H, molal heat content.

$H_1, H_2, \cdots H_c$, molal heat contents of components indicated.

$\bar{H}_1, \bar{H}_2, \cdots \bar{H}_c$, partial molal heat contents of components indicated.

$\bar{H}_i, \bar{H}_j$, conventional partial molal heat contents of ions indicated.

H^0, standard molal heat content.

$H^0_1, H^0_2, \cdots H^0_c$, standard molal heat contents of components indicated.

$\bar{H}^0_1, \bar{H}^0_2, \cdots \bar{H}^0_c$, standard partial molal heat contents of components indicated.

$\bar{H}^0_i, \bar{H}^0_j$, conventional standard partial molal heat contents of ions indicated.

h, height.

h_{ji}, h'_{ji}, elements of matrix [Chapter (4), Section (3)].

H, changes in, ΔH_D, heat of dilution; $\Delta H_{D(s)}, \Delta H_{D(a)}, \Delta H_{D(b)}$, heats of dilution of salt, acid and base; ΔH_n, heat of neutralization; $\Delta H^*_n = \Delta H_n - \Delta H_{D(s)}(m \rightarrow m')$; ΔH^0_i, heat of ionization.

I_0, intensity of light before traversing solution.

I, intensity of light after traversing solution.

$I(b_3)$, special function in theory of triple ion formation [Equation (3–7–25), Table (5–2–4)].

, electric current.

, vector electric current.

, characteristic constant in equation (8–7–28b)

$\mathcal{J}(\equiv\bar{C}_p-\bar{C}_p^0)$, relative partial molal heat capacity.
$\mathcal{J}_1, \mathcal{J}_2, \cdots \mathcal{J}_c$, relative partial molal heat capacities of components indicated.
$\mathcal{J}_{2(T_R)}=\mathcal{J}_2$, at a reference temperature, T_R.
$\mathbf{J}$, flow of ions [Equation (4–4–1)].
$\mathbf{J}_i, \mathbf{J}_j$, flow of i ion, j ion.
$(J_j)_{\text{I}}, (J_j)_{\text{II}}, (J_j)_{\text{I}}(\kappa)$, special functions in Debye's theory of salting effect [Equations (3–10–44) to (3–10–49)].
$J(b_3, x)$, special function in theory of triple ion formation [Equation (3–7–26)].
j, function in freezing point theory [Equation (9–5–21)].

$\bar{K}_1, \bar{K}_2, \cdots \bar{K}_c$, partial molal compressibilities of components indicated.
$\mathbf{K}_i, \mathbf{K}_j$, total forces on ions.
K, equilibrium constant.
K_A, acid ionization constant.
K_B, base ionization constant.
K_w, ionization constant of water.
K_{2A}, second ionization constant of dibasic acid.
K_h, equilibrium constant of hydrolytic reaction.
K_θ, maximum value of ionization constant at temperature, θ.
K_A^*, specially defined ionization constants used in treatment of medium effects [Chapter (15), Section (7)].
K_3, dissociation constants for triple ions.
K_4, dissociation constants for quadruple ion aggregates.
$K(X), K(0)$, ionization constants with, and without external field.
K^2, special function given by equation (4–5–9).
$\mathcal{K}_{(H)}$, special function given by equation (3–8–8).
$\mathcal{K}_{(V)}$, special function given by equation (3–9–5).
k, Boltzmann constant.
$\mathbf{k}_i, \mathbf{k}_j$, external forces on ions.
$\mathbf{k}_0$, force acting in molecules of solvent.
k, k_0, bulk compression of solution and solvent [Equation (8–7–16)].
$k(\equiv 2.3026\, RT/\mathbf{NF})$ [Equation (11–2–3), etc.].
k_1, constant in equation (4–1–18).
k_1, k_2, kinetic constants in equation (14–1–3).
k_s, k_m, k_N, salting coefficients on c-, m-, and N-scales.
$k_w(\equiv m_{\text{H}} m_{\text{OH}})$.
$k_A(\equiv m_{\text{H}} m_{\text{R}}/m_{\text{HR}})$.
$k_h\ (\equiv m_{\text{HR}} m_{\text{OH}}/m_{\text{R}})$.
k'_A, k'_{0A}, special functions [Chapter (15), Section (7)].

$\bar{L}_1, \bar{L}_2$, relative partial molal heat contents of components indicated.
$\bar{L}_{2(T_R)}$, $\bar{L}_2$ at reference temperature, T_R.
L'_s, relative molal heat content of solid at T'.

$L_{s(0)}$, relative molal heat content of solid at T_0.
L_v', heat of vaporization at T'.
$L_{v(0)}$, heat of vaporization at T_0.
L, specific conductivity of solution.
L_0, specific conductivity of solvent.
$L^*(\equiv L-L_0)$.
L, constant in equation (8–7–28b).
l, length.
l, wave length [Equation (5–3–13)].

M, molecular weight.
M_1, M_2, molecular weight of components indicated.
M_X, M_Y, molecular weights of components of a binary mixture of solvents.
M_{XY}, mean molecular weight [Equation (1–8–16)].
$\mathfrak{M}$, $\Delta\mathfrak{M}$, $\mathfrak{M}_{ik}$, $\mathfrak{M}_{ki}$, $\Delta\overline{\mathfrak{M}}'$, $\Delta\overline{\mathfrak{M}}''$, functions in diffusion theory [Chapter (4), Section (4)].
m, molality (concentration in mols per 1000 g. of solvent).
m_R, reference molality.
m_1, $m_2, \cdots m_c$, molalities of components indicated.
m_i, m_j, m_+, m_-, molalities of ions indicated.
$m_\pm$, mean molality of ions of an electrolyte [Equation (1–8–7)].
m_{H}, m_{Cl}, $m_{\mathrm{HSO_4}}$, etc., molalities of ions indicated.
m_{H}', etc., apparent hydrogen ion. etc.. concentration.
N, number of Faraday equivalents.
N, Avogadro's number.
N_1, $N_2 \cdots N_c$, mol fractions of components indicated.
N_w, mol fraction of water.
$N_\pm$, mean mol fraction of electrolytic component [Equation (1–8–3)].
N_1^0, N_2^0, mol fractions at great distance from ion [Chapter (3), Section (10)].
n_1, n_2, $\cdots n_c$, number of mols of components indicated.
n_1, n_2, $\cdots$ n_s, number of ions of kind indicated per cc.
n, n', number of mols of non-electrolyte, and electrolyte [Chapter (3), Section (10)].
n_{ji}, number of i ions in the presence of j ion.
n_{ij}, number of j ions in the presence of i ion.
n_{ji}^0, n_{ij}^0, same (solution unperturbed)
n_{ji}', n_{ij}', same (solution perturbed).

P, total external pressure.
P_0, initial total external pressure [Chapter (8), Section (7)].
P_e, effective pressure [Chapter (8), Section (7)].
P_2, molecular polarization [Equation (7–4–22)].
P_i, experimental slope at x_i [Equation (8–2–17)].
$\bar{P}_i$, defined by equation (8–2–15).

$\mathcal{P}(\equiv m_+^{\nu_+} m_-^{\nu_-})$ where m_+, m_- are molalities of ions of saturating salt.
$\mathcal{P}_{(0)}(\equiv\mathcal{P})$ in pure solvent.
$\mathcal{P}_1(\equiv\mathcal{P})$ of component 1 in salt solution.
$\mathcal{P}_{1(0)}(\equiv\mathcal{P})$ of component 1 in pure solvent.
$p_1, p_2, \cdots p_c$, partial pressures of components indicated.
p_0, vapor pressure of solvent.
p, vapor pressure of solution.
pH$(\equiv \log 1/a_{H^+})$.
p, constant of equation (15–6–6).

Q, quantity of heat.
Q, special function given by equation (5–3–6).
$\bar{Q}$, special function given by equation (4–5–24).
$Q(b)$, function in theory of ion pair formation [Equation (3–7–10), Table (5–2–3)].
q, function in theory of ionic association [Equation (3–7–4)].
q^*, function in theory of irreversible processes [Equation (4–3–34)].

R, gas constant per mol.
$R_{\tilde{\omega}}$, electrical resistance at frequency, $\tilde{\omega}$.
R_∞, electrical resistance at infinite frequency.
$\bar{R}$, characteristic distance given by equation (3–10–27)
$\bar{R}_j$, special function given by (3–10–38).
$\bar{R}$, special function in theory of frequency effects given by equation (4–5–24).
R, distance in equation (3–7–21).
r, distance.
$\mathbf{r}$, vector distance.
$\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \cdots \mathbf{r}_{12}, \mathbf{r}_{21}$, variable vector distances.
r_+, r_-, ionic radii.
r_j, r_j^0, $r_j^{(n)}$, functions defined by equations (4–3–54) and (4–3–55).

S, entropy.
S, solubility of neutral molecule in salt solution.
S^0, solubility of neutral molecule in pure solvent.
S, experimental slope of plot.
S^0, experimental slope when $x_i=0$ [Equation (8–2–17)].
S_{C_p}, S_V, S_E, S_K, experimental slopes for partial molal heat capacity, apparent molal volume, apparent molal expansibility and apparent molal compressibility.
$\mathfrak{S}_{(\Lambda)}, \mathfrak{S}_{(L)}, \mathfrak{S}_{(J)}, \mathfrak{S}_{(\lambda)}, \mathfrak{S}_{(T+)}$, etc., limiting theoretical slopes of quantities indicated. Variable is $\sqrt{c}$.
$\boldsymbol{\mathfrak{S}}_{(\Lambda)}, \boldsymbol{\mathfrak{S}}_{(L)}, \boldsymbol{\mathfrak{S}}_{(J)}, \boldsymbol{\mathfrak{S}}_{(\lambda)}, \boldsymbol{\mathfrak{S}}_{(T+)}$, etc., limiting theoretical slopes of quantities indicated. Variable is $\sqrt{\Gamma}$.
$S_{xy}, S_{yx}, S_{mn}, S_{nm}$, etc., elements of stress dyadic.
$S^*_{xy}, S^*_{yx}, S^*_{mn}, S^*_{nm}$, etc., electrostatic contribution to stresses.

S^0_{xy}, S^0_{mn}, etc., stress elements between neutral solvent molecules.
$S(Z)$, special conductance function given by equation (7–2–13).

T, absolute temperature.
T', freezing point, or boiling point of solution.
T_0, freezing point, or boiling point of solvent.
T_R, reference temperature.
T_1, T_2, · · · T_+, T_-, T_i, T_j, transference numbers of constituents indicated.
T^0_+, T^0_-, T^0_i, T^0_j, limiting transference numbers of ions indicated.
T_A, transference number [Equation (6–5–2)].
T'_A, apparent transference number [Equation (6–5–1)].
T_R, transference number at reference concentration.
$T^{0\prime}_+$, transference number function given by equation (6–7–1).
t, degrees centigrade.
t, time in seconds.
t_i, t_j, time in which i ion, or j ion is in element of volume [Chapter (2), Section (1)].
t_{ij}, t_{ji}, time in which j ions or i ions are in given elements of volume, respectively [Chapter (2), Section (1)].
t_{ji}, matrix element defined by equation (4–3–56).

U, energy.
U^0, standard energy.
U_{ij}, U_{ji}, potential energy of j ion in presence of i ion, and vice versa.
U_0, energy of triple ion when $\theta=0$ [Equation (3–7–17)].
$U(\mathbf{r})$, function in theory of Wien effect [Equation (4–6–27)].
u, velocity of sound [Equation (8–7–29)].
u_i, u_j, mobilities of ions ($\equiv v_i/X$), for unit potential gradient (c.g.s. units).
$\bar{u}_i$, $\bar{u}_j$, mobilities of ions (practical units).
$\bar{u}^0_i$, $\bar{u}^0_j$, limiting mobilities of ions (practical units).

V, total volume.
V, molal volume.
V, potential in volts/cm.
V_1, V_2, · · ·, molal volumes of components indicated.
$\bar{V}_1$, $\bar{V}_2$, · · ·, partial molal volumes of components indicated.
$\bar{V}_i$, $\bar{V}_j$, conventional partial molal volumes of ions indicated.
$\bar{V}^0_1$, $\bar{V}^0_2$, · · ·, $\bar{V}^0_i$, $\bar{V}^0_j$, · · ·, partial molal volumes in standard states.
V^*, critical disruptive volume [(Chapter (8), Section (5)].
$V_s(\equiv\nu_1V_1+\nu_2V_2)$ [Chapter (12), Section (7)].
$\mathbf{V}(\mathbf{r}_1)$, $\mathbf{V}(\mathbf{r}_2)$, velocity of solution as a whole.
v, velocity.
$\mathbf{v}$, vector velocity.
$\mathbf{v}_i$, $\mathbf{v}_j$, velocities of ions indicated.
$\mathbf{v}_{ji}$, velocity of i ion in the presence of the j ion.

$\mathbf{v}_{ij}$, velocity of j ion in the presence of the i ion.

v_x, v_y, v_z, components of velocity.

v_1, v_2, volume constants in theory of salting effects [Chapter (3), Section (10)].

v, v_0, specific volume of solution, of pure solvent.

W, work.

$W(\text{el})$, electrical work.

$W_{ji}(r)$, mutual potential of the average forces between ions, i and j [Equation (4–7–3)].

$W(x)$, work required to bring a molecule, or ion, from interior of solution (depth $= x$) to surface [Equation (3–11–1)].

$W(n_j)$, $W'(n)$, $W(\kappa)$, electrical work expressions [Equations (3–10–1), (3–10–2), and (3–10–3)].

W_t, electrical work of transfer [Equation (3–10–12)].

$\mathfrak{W}_{(H)}$, special function defined by equation (3–8–7).

$\mathfrak{W}_{(V)}$, special function defined by equation (3–9–4).

w, function given by equation (5–2–1).

w', function given by equation (5–2–4).

w'', function given by equation (5–2–10).

w^*, function given by equation (5–3–7).

X, electrical field.

$\mathbf{X}$, vector electric field.

$X_{\bar{\omega}}$, electrical field strength at frequency, $\bar{\omega}$.

ΔX_j, field acting upon j ion due to both ionic atmosphere and electrophoresis effects.

$X_{2m+1}(\kappa a)$, $X_3(\kappa a)$, $X_5(\kappa a)$, $X_2(\kappa a)$, $X_3^*(\kappa a)$, functions in extended theory [Equations (3–6–4), (3–6–6), Table (5–2–2)].

X, represents various special functions given by equations (3–7–21), (3–8–12), (9–5–17), and (11–9–2).

X_T, special function given by equation (11–9–2).

X, Y, weight percentages of components of a mixture of two miscible solvents.

$x_1, y_1, \cdots X_1, Y_1, \cdots x_1', y_1', \cdots X_1', Y_1' \cdots$, numbers of mols. Special use [Chapter (1), Section (10)].

x, various functions used as variables.

x, special function given by equation (4–6–43).

$Y_{2m+1}(\kappa a)$, $Y_3(\kappa a)$, $Y_5(\kappa a)$, functions in extended term theory [Equations (3–6–4), (3–6–6), Table (5–2–2)].

Y, Y_e, Y_f, Y', Y_e', Y_f', y^2, function in surface tension theory [Equations (3–11–14), (3–11–15), Table (5–2–6)].

Y, variable defined by equation (3–7–6).

$Y(\mathbf{r})$, function given by equation (4–6–18).

y, molar activity coefficient.

y_+, y_-, y_1, y_2, y_H, etc., molar activity coefficients of constituents indicated.
$y_\pm$, mean molar activity coefficient of an electrolyte [Equation (1-8-6)].
y_u, molar activity coefficient of an undissociated molecule.
y, various functions used as variables.

Z, special function given by equation (7-2-6).
Z_2', average number of molecules surrounding an ion. [Chapter (3), Section (10)].
Z_2^0, number of molecules of component (2) at disposal of ion [Chapter (3), Section (10)].
Z_2, number of moleoules in solution after addition of electrolyte [Chapter (3), Section (10)].
z, valence.
z_i, z_j, valences of ions indicated (carry sign of charge).
$|z_i|$, $|z_j|$, $|z_+|$, $|z_-|$, magnitudes of valences of ions indicated.
z, function given by equation (12-4-5).

α, degree of dissociation in general.
α_0, degree of dissociation in absence of external field [Chapter (4), Section (7)].
α, coefficient of expansion of solution [Chapter (8)].
α_0, coefficient of expansion of solvent [Chapter (8)].
α^*, coefficient of conductance equation (5-3-4).
α, empirical coefficient in equations for heat data.
$\bar{\alpha}$, special function defined by equation (3-10-37).
α_{12}, α_{21}, empirical coefficients in equations for mixed electrolytes [Chapter (14)].

β, coefficient of compression of solution [Chapter (8)].
β_S, adiabatic coefficient of compression [Equation (8-7-29)].
β_0, coefficient of compression of solvent [Chapter (8)].
β^*, coefficient of conductance equation (5-3-5).
β, empirical coefficient in equations for heat data.
$\bar{\beta}$, $\bar{\beta}'$, empirical constants, salting theory [Chapter (3), Section (10)].
β_{12}, β_{21}, empirical coefficients in equations for mixed electrolytes [Chapter (14)].
β, special function defined by equation (4-7-14).

$\Gamma(\equiv\sum c_i z_i^2)$, ional concentration.
Γ_2, mols of solute negatively absorbed per unit increase in surface tension [Equation (1-11-1)].
$\Gamma(\mathbf{r})$, special function in theory of Wien effect [Equations (4-6-24)].
γ, molal activity coefficient.
γ_+, γ_-, γ_i, γ_j, conventional activity coefficients of ions indicated.
$\gamma_\pm$, mean molal activity coefficient of an electrolyte [Equation (1-8-5)].
γ_R, reference activity coefficient at a concentration, m_R.

γ_u, activity coefficient of an undissociated molecule.
$\gamma_{(s)}$, activity coefficient of a non-electrolyte.
$\gamma'_{\pm}$, $\gamma''_{\pm}$, activity coefficients at temperatures T' and T''.
$\gamma_{H(H)}$, $\gamma_{Cl(H)}$, $\gamma_{H(K)}$, etc., interaction coefficients [Chapter (14), Section (5)].
$\gamma_{(H+K)}$, $\gamma_{(Cl)}$, etc., salting out coefficient [Chapter (14), Section (5)].
$\gamma_{HCl(MCl)}$, etc., activity coefficient of HCl in a solution of MCl, etc., for other mixtures.
γ_0, $\overset{0}{\gamma}$, $\overset{0}{\gamma_0}$, γ^*, γ_A, γ_{0A}, γ_A^*, γ'_A, γ'_{0A}, specially defined activity coefficients used in theory of medium effects [Chapter (15), Section (7)].
$\gamma_{(0)1}$, $\gamma_{0(2)}$, $\gamma_{1(0)}$, $\gamma_{2(0)}$, special activity coefficients used in theory of mixed electrolytes [Equations (14–5–1) and (14–5–2)].
γ_a, special activity coefficient used in Chapters (11) and (13).

$\Delta(\quad)$, finite increase in quantity, ( ).
∇, ∇_1, ∇_2, vector operator, nabla or del.
$\nabla \cdot \nabla$, Laplacian operator.
Δ, conductance deficiency [Chapter (6), Section (3)].
Δ, deviation.
$\Delta_{ave.}$, average deviation.
$\partial(\quad)$, partial differential
$\delta(\quad)$, variation.
$\delta_{ji} = \begin{Bmatrix} 1; \, j=i \\ 0; \, j \neq i \end{Bmatrix}$, Kronecker symbol.
δ, special function given by equation (5–2–13).
δ_i, special function given by equation (8–2–18).

ϵ, electronic charge.

ζ, special activity coefficient, a/n [Chapter (4), Section (4)].

η, viscosity of solution.
η_0, viscosity of solvent.
η^*, contribution to viscosity of solution caused by ionic interaction.
η', special function defined by equation (4–6–35).

ϑ, freezing point depression.
ϑ, empirical constant [Equation (15–8–2)], temperature at which ionization constant is a maximum in salt solution.
θ, boiling point elevation.
θ, empirical constant [Equation (15–6–6)], temperature at which ionization constant is a maximum.
θ, angle variable.

κ, reciprocal of average radius of ionic atmosphere. Defined by equation (2–4–11).
$\kappa_1^2 (\equiv q^* \kappa^2)$ by equation (4–3–33).
κ_I, κ_{II}, functions in equation (4–5–14).

Λ, equivalent conductance of electrolyte.
Λ^0, limiting equivalent conductance of electrolyte at infinite dilution.
Λ_m, molar conductance.
Λ_m^0, limiting molar conductance.
$\Lambda_{\tilde{\omega}}$, molar conductance at frequency, $\tilde{\omega}$.
$\Lambda_{I\tilde{\omega}}$, contribution to molar conductance due to frequency, $\tilde{\omega}$.
Λ_{II}, contribution to molar conductance caused by electrophoresis.
$\Lambda_{I(0)}$ is $\Lambda_{I\tilde{\omega}}$ when $\tilde{\omega}=0$.
$\Lambda^{0\prime}$, special conductance function given by equation (6–3–7).
Λ', special conductance function given by equation (6–6–3).
Λ_X, conductance in field of strength, X.

λ_+, λ_-, λ_i, λ_j, λ_1, λ_2, equivalent conductance of ions indicated.
λ_+^0, λ_-^0, λ_i^0, λ_j^0, λ_1^0, λ_2^0, limiting equivalent conductances of ions indicated at infinite dilution.
λ, molal freezing point lowering.
λ^*, molal boiling point elevation.
λ, wave length of light.
λ_1, λ_2, λ_3, λ_4, special variables defined by equation (4–6–39) and (4–6–40).
λ, λ_1, λ_2, empirical constants in equations (12–6–3) and (12–6–4).

μ, chemical potential.
μ^0, chemical potential of standard state.
μ_1, μ_2, $\cdots$ μ_c, chemical potentials of components indicated.
μ_i, μ_j, conventional chemical potentials of ions indicated.
μ_1^0, μ_2^0, $\cdots$ μ_c^0, μ_i^0, μ_j^0, chemical potentials in standard states.
μ_1', μ_1'', $\cdots$ μ_1^p, chemical potentials of component (1) in each of p phases.
μ_2', μ_2'', $\cdots$ μ_2^p, same for component (2).
$\bar{\mu}_i$, $\bar{\mu}_j$, electrochemical potentials [Equation (10–6–19)].
$\bar{\mu}$, chemical potential in ergs per mol [Chapter (4), Section (4)].
μ, dipole strength [Chapter (7), Section (4)].
μ, contributions to, (1) $\Delta\mu_j(\mathrm{el})$, electrical contribution to chemical potential, (2) $\Delta\mu_{(s)}$, contribution to chemical potential of nonelectrolyte caused by addition of electrolyte [Equation (3–10–8)].
$\mu(\equiv\frac{1}{2}\sum_i m_i z_i^2)$, ionic strength.
μ', approximated "real" ionic strength [Equation (13–3–6) *et seq.* Frequently used].
$\mu'(\equiv eX/kT)$, special use in theory of Wien effect [Equation (4–6–36)].
$\mu_i(\equiv\Gamma_i/\Gamma)$ [Equation (4–3–57)].

ν_+, ν_-, numbers of cations, anions produced by dissociation of one molecule of electrolyte.
$\nu(\equiv\nu_+ + \nu_-)$.
ν_R, ν of a reference solute.
ν_{ji}, number of molecules which dissociate [Chapter (4), Sections (1) and (7)].

$\xi_1, \xi_2, \cdots \xi_6$, space coordinates.
$\dot{\xi}_1, \dot{\xi}_2, \cdots \dot{\xi}_6$, corresponding velocities.
$\xi(r)$, special function given by equation (4–2–20).

Π, product
$\pi(=3.1416)$.
π^0, standard electrode potential.

ρ, density in general.
ρ_i, ρ_j, coefficients of friction of ions indicated.
$\bar{\rho}, \bar{\rho}^2$, functions defined by equations (4–2–25) and (4–2–26).
$\overline{1/\rho}$, function defined by equation (4–1–9).

Σ, summation.
σ, as a subscript, represents summation.
σ, surface tension of solution.
σ_0, surface tension of solvent.
σ, electrical conductance, special use [Chapter (4), Sections (1) and (7)].
σ, special function given by equation (3–10–34).
σ, special function defined by equation (9–5–7).
σ_m, special function defined by equation (9–5–11).

τ, time of relaxation.
τ', Langevin time lags [Chapter (4), Sections (1) and (7)].
$\bar{\tau}(\equiv \tau q^*)$, equation (4–5–8).

Φ, total free energy in salting theory [Equation (3–10–17)].
ϕ, practical osmotic coefficient, defined by equation (1–9–6).
ϕ', osmotic coefficient at freezing, or boiling point.
ϕ_R, osmotic coefficient of reference solution.
$\phi_x, \phi_{2(0)}, \phi_{1(0)}$, osmotic coefficients used in describing mixtures [Chapter (14), Section (5)].
$\phi_H, \phi_L, \phi_{C_p}, \phi_V, \phi_K$, etc., apparent molal quantities as indicated.
ϕ_H^0, ϕ_V^0, etc., standard apparent molal quantities at infinite dilution.
$\phi'_{H(s)}, \phi_{H(a)}, \phi_{H(b)}$, apparent molal heat contents of salt, acid, and base [Equation (8–3–2)].
ϕ'_H, ϕ''_H, apparent molal heats of dilution at concentrations, m′ and m″.
ϕ_1, ϕ_2, free energies per molecule in salting effect theory [Chapter (3), Section (10)].
$\phi(\kappa a)$, special function given by equation (4–3–23a).
ϕ, special variable in equation (4–6–51).
ϕ_V^*, function in equation (8–5–14).
ϕ, angle variable.

$\psi^*(\equiv \phi_V^*/V^*)$, function used in Chapter (8), Section (5).
ψ, electrical potential.
$\psi' - \psi''$, difference in electrical potential.

ψ_i, ψ_j, electrical potentials of ions and their atmospheres.

ψ^0_i, ψ^0_j, electrical potentials of ions and their atmospheres for unperturbed solution.

ψ'_i, ψ'_j, electrical potentials of ions and their atmospheres for perturbed solution.

$\psi_{i(0)} = \psi_{i(r=0)}$.

ψ_{ij}, potential of *i* ion in the presence of *j* ions.

ψ_{ji}, potential of *j* ion in the presence of *i* ions.

ψ^0_{ij}, ψ^0_{ji}, same for unperturbed solutions.

ψ'_{ij}, ψ'_{ji}, same for perturbed solution.

ψ^{0*}_j, potential due to ionic atmosphere.

ψ_1, ψ_2, apparent specific volumes of solvent and solute in solution [Equation (8–7–21)].

$\psi(d)$, special function given by equation (6–10–5).

$\chi(q^*_j\tilde{\omega}\tau)$, function given by equation (4–5–19).

χ_R, function given by equation (4–5–23).

Ω, $\Omega_{\tilde{\omega}}$, functions used in conductance equations [Chapter (4), Section (5)].

ω, mobility in general.

ω_i, ω_j, mobilities of ions in general ($\omega_i = 1/\rho_i$; $\omega_j = 1/\rho_j$).

$\tilde{\omega}$, frequency of alternating electrical field.

Contents

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Chapter (1)

General Thermodynamic Introduction

The properties of electrolytic solutions fall naturally into two groups: (1) those determined by measurements of systems in equilibrium, and (2) those determined by measurements of systems in disturbed states. To the first group belong such properties as those derived from measurements of vapor pressure lowering, boiling point rise, freezing point lowering, solubility, specific heat, heat content, the potentials of galvanic cells, and surface tension. Properties derived from measurements of diffusion, electrical conductance, and viscosity comprise the second group, consideration of which will be reserved for later chapters. Since thermodynamics provides the formal method of treating systems in equilibrium, it is essential to state briefly those general conclusions of thermodynamics which will be used in subsequent developments. This will be done without making an attempt to develop the subject in a rigorous and detailed manner. Such a procedure will introduce and define the fundamental variables, and fix the symbolism and nomenclature.

(1) ENERGY, ENTROPY, AND THE CHEMICAL POTENTIALS OF GIBBS

The first law of thermodynamics will be expressed in a sufficiently general way if we regard the energy, U, of a phase as a function of the pressure, P, the volume, V, the temperature, T, the electrical charge, e, and the numbers of mols of each of the c components, $n_1, n_2, \cdots n_c$, in the phase. All other variables, such as surface, the force of gravity, external fields, etc., will be kept constant throughout the immediate discussions to follow. Later, the thermodynamic equation which involves surfaces of discontinuity will receive special attention. The energy of a phase in terms of these variables is

$$U = f(P, V, T, n_1, n_2, \cdots n_c, e) + U^0 \qquad (1\text{-}1\text{-}1)$$

in which U^0 is the energy in some arbitrary standard state. Since any one of the variables may be eliminated by the equation of state of the phase, the number of independent variables in the above expression is $c + 3$. The first law of thermodynamics requires that the increase in energy of a system, of constant composition and mass, is equal to the heat absorbed by the system plus the mechanical and electrical work done on the system by the surroundings. In the thermodynamic developments to follow, the mechanical work will be confined to the effect of changes in the volume of the system; therefore

$$dU = dQ - PdV + dW(el) \qquad (1\text{-}1\text{-}2)$$

By further limiting this treatment to reversible processes only, P represents the equilibrium pressure of the system, and $dW(el)$ is the reversible electrical work. The second law of thermodynamics requires that the reversible heat absorbed by the system is

$$dQ = TdS \qquad (1\text{-}1\text{-}3)$$

whereby the entropy, S, is introduced. The combination of equations (1-1-2) and (1-1-3) can be extended[1] to include variations in composition by introducing the chemical potentials, $\mu_1 = \frac{\partial U}{\partial n_1}$, $\mu_2 = \frac{\partial U}{\partial n_2}$, etc., representing rates of change in energy per mol. Accordingly, our generalized representation of the first and second laws becomes

$$dU = TdS - PdV + \mu_1 dn_1 + \cdots \mu_c dn_c + \frac{\partial U}{\partial e} de \qquad (1\text{-}1\text{-}4)$$

for reversible processes. The term $\frac{\partial U}{\partial e} de$ is the reversible electrical work expressed in terms of the charge as independent variable.

(2) HEAT CONTENT, WORK CONTENT, AND FREE ENERGY

The heat content, H, work content, A, and free energy, F,[2] are defined by the equations

$$H = U + PV \qquad (1\text{-}2\text{-}1)$$

$$A = U - TS \qquad (1\text{-}2\text{-}2)$$

$$F = U - TS + PV = H - TS \qquad (1\text{-}2\text{-}3)$$

The differentials of these quantities can be written in the forms

$$dH = +TdS + VdP + \mu_1 dn_1 + \cdots \mu_c dn_c + \frac{\partial H}{\partial e} de \qquad (1\text{-}2\text{-}4)$$

$$dA = -SdT - PdV + \mu_1 dn_1 + \cdots \mu_c dn_c + \frac{\partial A}{\partial e} de \qquad (1\text{-}2\text{-}5)$$

$$dF = -SdT + VdP + \mu_1 dn_1 + \cdots \mu_c dn_c + \frac{\partial F}{\partial e} de \qquad (1\text{-}2\text{-}6)$$

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[1] "The Scientific Papers of J. Willard Gibbs," Vol. I, p. 63, equation (12), and p. 338, equation (691). New York, Longmans, Green and Co. 1906.

[2] H, A, and F are the χ, ψ, and ζ functions of Gibbs, *loc. cit.*

consistent with the relations

$$\mu_1 = \left(\frac{\partial U}{\partial n_1}\right)_{S,V,n_2,\cdots n_c,e} = \left(\frac{\partial H}{\partial n_1}\right)_{S,P,n_2,\cdots n_c,e}$$
$$= \left(\frac{\partial A}{\partial n_1}\right)_{V,T,n_2\cdots n_c,e} = \left(\frac{\partial F}{\partial n_1}\right)_{P,T,n_2\cdots n_c,e} \cdots \qquad (1\text{-}2\text{-}7)$$

Analogous definitional equations may be written for $\mu_2, \cdots \mu_c$. Since μ_1 is less specific than any of the above differential coefficients, it is preferred as a basis for certain theoretical deductions.

By considering a system composed of p phases at constant temperature, pressure and charge, Gibbs was able to prove by equation (1-1-4), valid for each phase, that at equilibrium

$$\begin{array}{l} \mu_1' = \mu_1'' = \cdots \mu_1^p \\ \mu_2' = \mu_2'' = \cdots \mu_2^p \\ \cdots\cdots\cdots\cdots\cdots \\ \mu_c' = \mu_c'' = \cdots \mu_c^p \end{array} \qquad (1\text{-}2\text{-}8)$$

if $\mu_1', \mu_1'', \cdots \mu_1^p$ represent the chemical potentials of the first component, $\mu_2', \mu_2'', \cdots \mu_2^p$ those of the second component, etc., throughout the p phases.

(3) Systems at Constant Composition and Charge

Since U, H, A, F, and S are always referred to some standard state, which in almost all applications is arbitrarily selected, we are especially interested in changes in these quantities, and introduce the operator symbol Δ to indicate such changes. Thus, $\Delta F \equiv \int_1^2 dF$, where the integration is from state 1 to state 2, and ΔF, ΔH, etc., may replace F, H, etc., in the fundamental equations.

At constant composition and charge, equation (1-1-4) reduces to

$$dS = \frac{dU + PdV}{T} \qquad (1\text{-}3\text{-}1)$$

By completely differentiating equation (1-2-3) and combining it with the above, we obtain

$$\left(\frac{\partial F}{\partial T}\right)_P = -S, \text{ or } \left(\frac{\partial \Delta F}{\partial T}\right)_P = -\Delta S \qquad (1\text{-}3\text{-}2)$$

and

$$\left(\frac{\partial F}{\partial P}\right)_T = V, \text{ or } \left(\frac{\partial \Delta F}{\partial P}\right)_T = \Delta V \qquad (1\text{-}3\text{-}3)$$

As a consequence of (1-3-2), equation (1-2-3) may be written as

$$\Delta F = \Delta H + T\left(\frac{\partial \Delta F}{\partial T}\right)_P$$

or

$$\left(\frac{\partial(\Delta F/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2} \tag{1-3-4}$$

(4) Systems at Constant Pressure, Temperature, and Charge

Partial Molal Quantities

Under these conditions, equation (1-2-6) reduces to

$$dF = \mu_1 dn_1 + \mu_2 dn_2 + \cdots \mu_c dn_c = \sum_1^c \mu_i dn_i \tag{1-4-1}$$

Since this equation is homogeneous and of the first degree in the extensive variables, $n_1, n_2, \cdots n_c$, it may be integrated at constant $\mu_1, \mu_2, \cdots \mu_c$ to yield[3]

$$F = \mu_1 n_1 + \mu_2 n_2 + \cdots \mu_c n_c = \sum_1^c \mu_i n_i \tag{1-4-2}$$

If this be divided by $(n_1 + n_2 + \cdots n_c) = \sum_1^c n_i$, we obtain

$$\frac{F}{\Sigma n_i} = \mu_1 N_1 + \mu_2 N_2 + \cdots \mu_c N_c = \sum_1^c \mu_i N_i \tag{1-4-3}$$

where

$$N_i = \frac{n_i}{\Sigma n_i} \tag{1-4-3a}$$

$N_1, N_2, \cdots N_c$ are the mol fractions of the c components, and $(F/\Sigma n_i)$ is the free energy per mol of phase. Because the terms $\mu_1, \mu_2, \cdots \mu_c$, at constant temperature and pressure, are the partial derivatives of the free energy with respect to the number of mols, they are designated as the partial molal free energies, and written $\bar{F}_1, \bar{F}_2, \cdots \bar{F}_c$. For typographical reasons, $F/\Sigma n_i$ will be written F, since we are usually concerned with molal quantities. When this is not the case, it will be made clear by the context.[4]

Complete differentiation of equation (1-4-2) gives

$$dF = \sum_1^c \mu_i dn_i + \sum_1^c n_i d\mu_i \tag{1-4-4}$$

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[3] P. S. Epstein, "Textbook of Thermodynamics," p. 103, John Wiley and Sons, New York, 1937.

[4] This symbolism has been adopted to conform to the system of chemical thermodynamics most prevalent in the United States.

which, by combination with (1-4-1), yields the important equation

$$\sum_1^c n_i d\mu_i = 0, \quad \text{or} \quad \sum_1^c N_i d\mu_i = 0 \qquad (1\text{-}4\text{-}5)$$

interrelating the chemical potentials of the components of a phase, at constant temperature and pressure.

(5) Systems at Constant Temperature and Pressure

The Reversible Galvanic Cell[5]

Consider a cell consisting of two electrodes connected by a solution of an electrolyte. Let $(\psi' - \psi'')$ be the difference in electrical potential between two pieces of the same metal attached to the two electrodes. Thus, if the cell is charged reversibly at constant temperature and pressure, the electrical work done upon the system will be $(\psi' - \psi'')\, de$, and this will equal the total increase in free energy. At constant temperature, pressure, and composition equation (1-2-6) reduces to

$$dF = \sum_1^p \left(\frac{\partial F}{\partial e}\right)_{P,T,n_1 \cdots n_c} de = (\psi' - \psi'')de \qquad (1\text{-}5\text{-}1)$$

for the total change in free energy of p phases. It is important to note that the difference in potential, as defined above, is the quantity which is measured, and that the individual differences in potential between each of the two electrodes and the solution are not subject to separate measurement.[6]

At constant temperature and pressure, equation (1-2-6) yields for the total change in free energy of p phases the expression

$$dF = \sum_1^p \sum_1^c \mu_i\, dn_i + (\psi' - \psi'')de \qquad (1\text{-}5\text{-}2)$$

If all the changes in composition occur in one phase,

$$dF = \sum_1^c \mu_i dn_i + (\psi' - \psi'')\, de \qquad (1\text{-}5\text{-}2a)$$

As in the derivation of (1-4-2), this equation may be integrated to give

$$F = \sum_1^c \mu_i n_i + (\psi' - \psi'')e \qquad (1\text{-}5\text{-}3)$$

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[5] Such a cell, operating reversibly, has been termed "the perfect electrochemical apparatus" by Gibbs, *loc. cit.*, p. 338.

[6] The Scientific Papers of J. Willard Gibbs, Vol. I, pp. 338–349, New York, Longmans, Green and Co., 1906.

Complete differentiation of this expression yields

$$dF = \sum_1^c \mu_i dn_i + \sum_1^c n_i d\mu_i + (\psi' - \psi'')\, de + e d(\psi' - \psi'') \qquad (1\text{-}5\text{-}4)$$

which, by combination with (1-5-2a), becomes

$$\sum_1^c n_i d\mu_i + e d(\psi' - \psi'') = 0 \qquad (1\text{-}5\text{-}5)$$

This is the equation for concentration cells, from which the reversible electrical work may be calculated, under suitable conditions, from changes in composition.

An important feature of this equation is that only the whole of the electrical term is measurable. Consequently, the measurement of the electromotive force of a concentration cell permits the evaluation of the chemical potentials of the components as defined by Gibbs. It does not allow a similar evaluation of the potentials of each of the constituents of the components, or to be more specific, the potentials of the ions.

(6) THE ACTIVITY FUNCTION. THE ACTIVITY OF AN ELECTROLYTE

The equations appearing in the preceding sections contain all the variables, and are sufficiently general to provide thermodynamic background for all the systems which we shall discuss, except those which involve surface tension. By the use of the chemical potentials, it is possible to develop an adequate thermodynamics of solutions if suitable restrictions are imposed. In order to conform to the system most generally adopted in recent years, it is desirable to introduce additional, more restricted functions. In the application of thermodynamics to this subject, G. N. Lewis[7] introduced two new functions, *i.e.*, fugacity and activity. The latter has been employed extensively in solution thermodynamics, and its definition and general characteristics will be presented. For the sake of simplicity, we shall omit any considerations of the fugacity.[8] The activity, a_i, of a pure chemical species or constituent of a solution may be given general definition by the equation

$$\mu_i = RT \ln a_i + \mu_i^0 \qquad (1\text{-}6\text{-}1)$$

in which μ_i^0 is its chemical potential in some arbitrary standard state. We shall find that the value of μ_i^0 will depend on the concentration scales (molalities, mol fractions, etc.) in which a_i is expressed [Section (8)].

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[7] G. N. Lewis, *Proc. Am. Acad. Sci.*, **37**, 45 (1901); **43**, 259 (1907).

[8] Detailed discussions of the general thermodynamics of these functions may be found in the following works: G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923; J. N. Brönsted, *J. Am. Chem. Soc.*, **42**, 761 (1920); N. Bjerrum, *Z. physik. Chem.*, **104**, 406 (1923); H. S. Harned, Chap. XII in H. S. Taylor, "Treatise on Physical Chemistry," First Edition, 1924, Second Edition, 1930, New York, D. Van Nostrand Co.

Expressing equation (1-6-1) by its equivalent in the notation of Section (4), the activity of a constituent of a solution may be defined by

$$\bar{F}_i = RT \ln a_i + \bar{F}_i^0 \tag{1-6-2}$$

where $\bar{F}_i$ is the partial molal free energy of the constituent, and $\bar{F}_i^0$ is its value in some arbitrary standard state.

In solutions of an electrolyte, electro-neutrality imposes the condition that the number of mols of the individual ionic species cannot be varied independently. We must be careful, therefore, to refer to ionic species as constituents of the solution rather than as components, so that the latter term may retain the precise meaning assigned to it by Gibbs. A component is an independently variable constituent of a solution. Thus, in the system NaCl and H_2O there are two components whose chemical potentials can be measured by the application of thermodynamics alone. They are, of course, NaCl and H_2O. Although the ionic constituents Na^+ and Cl^- are of fundamental importance in determining the behavior and properties of the system, their concentrations are not independent variables. Thermodynamics does not permit the evaluation of the chemical potentials, free energies, activities, etc., of the individual ionic species. In spite of this limitation it is advantageous to express a number of thermodynamic developments in terms of "hypothetical" ionic activities, with the strict understanding that only certain ionic activity products, or ratios, have any real physical significance.

Convenient alternative expressions for the activity of an electrolyte are obtained upon consideration of the formal representation of its dissociation in solution.[9] This device has rendered important service in correlating the properties of electrolytes of different valence types. Thus, if an electrolyte, $C_{\nu_+}A_{\nu_-}$, dissociates into ν_+ cations and ν_- anions according to $C_{\nu_+}A_{\nu_-} \rightarrow \nu_+C + \nu_-A$, then its activity may be written

$$a = a_+^{\nu_+}a_-^{\nu_-} = a_\pm^{\nu} \tag{1-6-3}$$

where $\nu = \nu_+ + \nu_-$, a_+ and a_- are the conventional individual activities of the ionic constituents, and $a_\pm$ is termed the mean activity of the ions. Accordingly, the chemical potential and partial molal free energy of an electrolytic component of a solution may both be written

$$\mu - \mu^0 = RT \ln (a_+^{\nu_+}a_-^{\nu_-}) = \nu RT \ln a_\pm \tag{1-6-4}$$

and

$$\bar{F} - \bar{F}^0 = RT \ln (a_+^{\nu_+}a_-^{\nu_-}) = \nu RT \ln a_\pm \tag{1-6-5}$$

It is important to note that the activity function is more restricted than the chemical potential or partial molal free energy, because its definition

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[9] G. N. Lewis and M. Randall, "Thermodynamics," New York, McGraw-Hill Book Co., 1923.

usually involves the introduction of a separate standard state for each phase. Obviously the standard state must be clearly and unambiguously defined before the activity can be given a definite numerical value. To illustrate this matter, let us consider equation (1-2-8), which states that at constant temperature, pressure, and charge the chemical potential of a component is the same in every phase. The definition of activity, however, requires that the statement of a similar proposition regarding the activity of a component be accompanied by the proper proviso. Thus, the activity of a component of a system at constant temperature, pressure, and charge is the same in every phase, *provided that it is defined in each phase in reference to the same standard state.* If this proviso is borne in mind, no real difficulty will be experienced in the investigation of polyphase systems by solubility, distribution, freezing point lowering, and similar means.

(7) VARIATION OF THE ACTIVITY WITH TEMPERATURE AND PRESSURE

According to equation (1-4-3), the relative free energy of one mol of solution will be given by

$$F - F^0 = N_1(\bar{F}_1 - \bar{F}_1^0) + N_2(\bar{F}_2 - \bar{F}_2^0) + \cdots \qquad (1\text{-}7\text{-}1)$$

and likewise, the relative heat content per mol of solution, by

$$H - H^0 = N_1(\bar{H}_1 - \bar{H}_1^0) + N_2(\bar{H}_2 - \bar{H}_2^0) + \cdots \qquad (1\text{-}7\text{-}2)$$

respectively. The first of these equations may be combined with the definition of activity in the preceding section to give

$$F - F^0 = N_1RT \ln a_1 + N_2RT \ln a_2 + \cdots \qquad (1\text{-}7\text{-}3)$$

By substitution of these values for ΔF and ΔH in equation (1-3-4) and by performing the indicated partial differentiation with respect to temperature, we obtain

$$\left[\frac{N_1\partial \ln a_1 + N_2\partial \ln a_2 + \cdots}{\partial T}\right]_P = -\frac{N_1(\bar{H}_1 - \bar{H}_1^0) + N_2(\bar{H}_2 - \bar{H}_2^0) + \cdots}{RT^2} \qquad (1\text{-}7\text{-}4)$$

This general equation is rarely used. It is more usual to limit the investigation to each component separately. Thus,

$$\left(\frac{\partial \ln a_i}{\partial T}\right)_P = \frac{-(\bar{H}_i - \bar{H}_i^0)}{RT^2} \qquad (1\text{-}7\text{-}5)$$

The relative partial molal heat content of the component, i, $(\bar{H}_i - \bar{H}_i^0)$, will be represented by $\bar{L}_i$ according to

$$\bar{L}_i = \bar{H}_i - \bar{H}_i^0 \qquad (1\text{-}7\text{-}6)$$

Differentiation of this equation with respect to temperature at constant pressure serves to define the important quantities, the partial molal heat capacity, $\bar{C}_{p_i}$, and relative partial molal heat capacity, $\bar{C}_{p_i} - \bar{C}^0_{p_i}$, at constant pressure. Thus,

$$\left(\frac{\partial \bar{H}_i}{\partial T}\right)_P - \left(\frac{\partial \bar{H}^0_i}{\partial T}\right)_P = \bar{C}_{p_i} - \bar{C}^0_{p_i} = \left(\frac{\partial \bar{L}_i}{\partial T}\right)_P \equiv \bar{J}_i \tag{1-7-7}$$

At constant composition, temperature, and charge,

$$\left(\frac{\partial(F - F^0)}{\partial P}\right)_T = V - V^0 \tag{1-7-8}$$

according to equation (1-3-3), where V, the total volume of the phase, is given by

$$V = \sum_1^c N_i \bar{V}_i \tag{1-7-9}$$

in which $\bar{V}_1$, etc., are the partial molal volumes of the components. Combining these equations with equation (1-6-2), which defines the activity, we obtain

$$\left[\frac{N_1 \partial \ln a_1 + N_2 \partial \ln a_2 + \cdots}{\partial P}\right]_T = \frac{N_1(\bar{V}_1 - \bar{V}^0_1) + N_2(\bar{V}_2 - \bar{V}^0_2) + \cdots}{RT} \tag{1-7-10}$$

and for each individual component,

$$\left(\frac{\partial \ln a_i}{\partial P}\right)_T = \frac{\bar{V}_i - \bar{V}^0_i}{RT} \tag{1-7-11}$$

(8) VARIATION OF ACTIVITY WITH COMPOSITION AT CONSTANT TEMPERATURE AND PRESSURE. DEFINITIONS OF ACTIVITY COEFFICIENTS

By combining equation (1-4-5) with (1-6-1) or (1-6-4) we obtain the equation

$$\sum_1^c N_i d \ln a_i = 0 \tag{1-8-1}$$

at constant temperature, pressure and charge. This important relation permits the calculation of the activity of one component of a solution from the known activities of the remaining components. In binary solutions it is most frequently used to estimate the activity of the solute from measurements of the so-called colligative properties of the solvent.

In solutions of such high dilution that the mutual interaction between solute particles can be ignored, it has been shown experimentally[10] and by theoretical considerations[11] that the activities of solutes approach proportionality to their concentrations as the latter approach zero. Thus, as a limiting law for any electrolyte in infinitely dilute solution,

$$\bar{F} - \bar{F}^0_N = \nu RT \ln N_{\pm} \tag{1-8-2}$$

This equation has the same form as (1-6-5), and introduces the mean ionic mol fraction defined by the equation

$$N_{\pm} \equiv (N_{+}^{\nu_+} N_{-}^{\nu_-})^{1/\nu} \tag{1-8-3}$$

analogous to (1-6-3). The partial molal free energy in the standard state has been written $\bar{F}^0_N$ to indicate that activities have been expressed on the mol fraction scale. Mol fractional activities are of particular theoretical importance because equation (1-8-2) is used to define the behavior of the hypothetical "ideal" or "perfect" ionized solute at all concentrations. It is convenient to describe the departures of real solutes from ideality in terms of the factor

$$f_{\pm} \equiv \frac{a_{N\pm}}{N_{\pm}} = (f_{+}^{\nu_+} f_{-}^{\nu_-})^{1/\nu} \tag{1-8-4}$$

called the rational activity coefficient. This name will be retained for the sake of brevity, but a more adequate designation would be the stoichiometric mean ionic mol fractional activity coefficient.

For many purposes it will prove more convenient to employ activities expressed in terms of molalities (mols per 1000 g. solvent) or molarities (mols per 1000 cc. solution), and define the corresponding activity coefficients,

$$\gamma_{\pm} \equiv \frac{a_{m\pm}}{m_{\pm}} = (\gamma_{+}^{\nu_+} \gamma_{-}^{\nu_-})^{1/\nu} \tag{1-8-5}$$

and

$$y_{\pm} \equiv \frac{a_{c\pm}}{c_{\pm}} = (y_{+}^{\nu_+} y_{-}^{\nu_-})^{1/\nu} \tag{1-8-6}$$

The mean ionic molality and mean ionic molarity are defined by

$$m_{\pm} \equiv [m_{+}^{\nu_+} m_{-}^{\nu_-}]^{1/\nu} = [(\nu_{+}m)^{\nu_+}(\nu_{-}m)^{\nu_-}]^{1/\nu} = m[\nu_{+}^{\nu_+} \nu_{-}^{\nu_-}]^{1/\nu} \tag{1-8-7}$$

and

$$c_{\pm} \equiv [c_{+}^{\nu_+} c_{-}^{\nu_-}]^{1/\nu} = [(\nu_{+}c)^{\nu_+}(\nu_{-}c)^{\nu_-}]^{1/\nu} = c[\nu_{+}^{\nu_+} \nu_{-}^{\nu_-}]^{1/\nu} \tag{1-8-8}$$

respectively. The stoichiometric mean ionic molal activity coefficient, $\gamma_{\pm}$, is most often encountered in experimental work and is usually called

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[10] Cf., for example, H. S. Harned, Chapter XII, in H. S. Taylor, "Treatise on Physical Chemistry," New York, D. Van Nostrand and Co., 1930.

[11] E. A. Guggenheim, *Proc. Roy. Soc. London*, **A 135**, 181 (1932).

the practical activity coefficient. The stoichiometric mean ionic molar activity coefficient, $y_{\pm}$, has not come into sufficiently general use to acquire a scientific sobriquet. In later chapters, it will be possible without ambiguity to refer to any one of the three as "the" activity coefficient.

Following the discussion in Section (6), it is essential that the values of μ_i^0 or $\bar{F}_i^0$ in the reference state should be assigned so that the value of μ_i or $\bar{F}_i$ of a component is independent of the concentration scale in which a_i is expressed. Bearing this in mind, we may combine equation (1-6-2), (1-8-4), (1-8-5) and (1-8-6) and express the partial molal free energy of an electrolyte as follows:

$$\begin{aligned}\bar{F} = \bar{F}_N^0 + \nu RT \ln f_{\pm} N_{\pm} &= \bar{F}_m^0 + \nu RT \ln \gamma_{\pm} m_{\pm} \\ &= \bar{F}_c^0 + \nu RT \ln y_{\pm} c_{\pm}\end{aligned} \tag{1-8-9}$$

In practically all thermodynamic studies, except some of those in which mixed solvents are involved, it is customary to select the reference states so that $f_{\pm} = \gamma_{\pm} = y_{\pm} = 1$ at infinite dilution of solute. As long as this convention is adhered to, we may introduce the limiting values of $N_{\pm}/m_{\pm}$ and $c_{\pm}/m_{\pm}$ at infinite dilution, and obtain the relation

$$\bar{F}_N^0 = \bar{F}_m^0 + \nu RT \ln \frac{1000}{M_1} = \bar{F}_c^0 + \nu RT \ln \frac{1000\, d_0}{M_1} \tag{1-8-10}$$

from (1-8-9). Here M_1 is the molecular weight of the solvent, and d_0 is its density. The appearance of d_0 in the last member of this equation brings out an important distinction between the weight and volume concentration units. The concentration (composition) of a phase, in the sense in which the term is used in the development of fundamental thermodynamic relations, is an *independent* variable. When a process, or partial differentiation, takes place at constant composition, the weight concentration units, m, N, etc., remain constant, but the volume concentration unit c can, and usually does, vary. The constancy of c ordinarily imposes two conditions: constant composition and constant volume. Accordingly, when $\bar{F}_c^0$ (and other thermodynamic functions on the c-scale) are differentiated with respect to T or P at constant composition, it should not be forgotten that c is variable. The confusion which can be produced by overlooking this point makes it undesirable to use the c-scale except at constant temperature and pressure.

Combination of equations (1-8-9) and (1-8-10) leads to

$$\ln f_{\pm} = \ln \gamma_{\pm} + \ln \frac{m_{\pm}}{N_{\pm}} \left(\frac{M_1}{1000}\right) = \ln y_{\pm} + \ln \frac{c_{\pm}}{N_{\pm}} \left(\frac{M_1}{1000\, d_0}\right) \tag{1-8-11}$$

The concentration ratios are given at all dilutions by the general expressions

$$N_{\pm} = \frac{m_{\pm}}{\nu m + 1000/M_1} = \frac{c_{\pm}}{\nu c + (1000d - cM_2)/M_1} \tag{1-8-12}$$

in which m and c are the stoichiometric molality and molarity of the electrolyte, M_2 its molecular weight, and d is the density of the solution. Substitution of (1-8-12) in (1-8-11) leads to the important relationships

$$\ln f_{\pm} = \ln \gamma_{\pm} + \ln (1 + m\nu M_1/1000) \tag{1-8-13}$$

$$\ln f_{\pm} = \ln y_{\pm} + \ln (d/d_0 + c(\nu M_1 - M_2)/1000d_0) \tag{1-8-14}$$

$$\ln \gamma_{\pm} = \ln y_{\pm} + \ln (d/d_0 - cM_2/1000d_0) \tag{1-8-15}$$

Although the dependence of equations (1-8-13) to (1-8-15) upon (1-8-10) is of negligible interest in studies concerned only with the variation of the various activity coefficients with concentration, it will prove to be of fundamental importance in investigating the effects of changes in the solvent medium upon the thermodynamic behavior of the solute. Mixed solvents have come into general use in such investigations because their properties can be varied in a regular and continuous manner. If M_X and M_Y are the molecular weights of the components of a binary solvent mixture, and X and Y represent the composition in weight per cent, then the average molecular weight of the mixed solvent,

$$M_{XY} = \frac{100}{(X/M_X + Y/M_Y)} \tag{1-8-16}$$

must be substituted in the preceding equations for M_1.

(9) Activity Coefficient and Osmotic Coefficient of the Solvent

The rational activity coefficient of the solvent is defined by the equation

$$\bar{F}_1 - \bar{F}_1^0 = RT \ln f_1 N_1 \tag{1-9-1}$$

which is formally the same for any component of a solution, but the subscript 1 will always be used to designate the solvent. In dilute solutions, where the preponderance of the solvent is very pronounced, the activity coefficient of the solvent is subject to practical disadvantages for numerical computations. For the solute, represented by the subscript 2, we have according to (1-6-2) and the definition of rational activity coefficient, the equation

$$\bar{F}_2 - \bar{F}_2^0 = RT \ln f_2 N_2 \tag{1-9-2}$$

Differentiating these two equations, at constant temperature and pressure and combining with equation (1-8-1), we obtain

$$N_1 d \ln f_1 N_1 + N_2 d \ln f_2 N_2 = 0 \tag{1-9-3}$$

Since ($N_1 + N_2 = 1$), this readily reduces to

$$d \ln f_1 = -\frac{N_2}{N_1} d \ln f_2 \tag{1-9-4}$$

from which it follows that in dilute solutions the departure of f_1 from unity is much less than that of f_2. To obtain a more sensitive measure of the non-ideality of solutions in terms of the solvent, Bjerrum[12] introduced the concept of osmotic coefficient. The rational osmotic coefficient, g, is defined by

$$\bar{F}_1 - \bar{F}_1^0 = gRT \ln N_1 \tag{1-9-5}$$

and the practical osmotic coefficient, ϕ, by

$$\bar{F}_1 - \bar{F}_1^0 = -\phi RT \sum^{s} m_i M_1/1000 \tag{1-9-6}$$

where M_1 is molecular weight of solvent. The relation between the two coefficients is clearly

$$\phi = \frac{-g \ln N_1}{\sum\limits^{s} m_i M_1/1000} \tag{1-9-7}$$

which becomes

$$\phi = g[1 - \tfrac{1}{2} \sum^{s} m_i M_1/1000 + \tfrac{1}{3}(\sum^{s} m_i M_1/1000)^2 - \cdots] \tag{1-9-8}$$

in dilute solutions by introducing the relation $-\ln N_1 = \ln (1 + \sum^{s} m_i M_1/1000)$ and expanding the logarithm. The factor $\sum^{s} m_i$ represents the summation over all the solute species present. For a single electrolyte dissociating into ν ions, $\sum^{s} m_i$ equals νm. In this case, equation (1-9-6) reduces to

$$\ln a_1 = -\phi \nu m \frac{M_1}{1000} \tag{1-9-9}$$

Differentiating to obtain $d \ln a_1$ and substituting in equation (1-8-1) in the form

$$N_1 d \ln a_1 + N_2 d \ln a_2 = 0; \quad \text{or} \quad \frac{1000}{M_1} d \ln a_1 + \nu m d \ln \gamma_{\pm} m = 0 \tag{1-9-10}$$

leads to the important relation first derived by Bjerrum for the relation between the practical osmotic coefficient and the activity coefficient, namely

$$d[m(1 - \phi)] + md \ln \gamma_{\pm} = 0 \tag{1-9-11}$$

For the more general case, we obtain

$$d\left\{\sum^{s} m_i(1 - \phi)\right\} + \sum^{s} m_i d \ln \gamma_i = 0 \tag{1-9-11a}$$

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[12] N. Bjerrum, *Z. Elektrochem.*, **24**, 259 (1907); *Proc. Internat. Congr. Appl. Chem., Sect. X*, London, 1909.

In integrated form, these equations become

$$\phi = 1 + 1/m \int md \ln \gamma_{\pm} \tag{1-9-12}$$

and

$$\phi = 1 + 1/\sum^{i} m_i \int \sum^{i} m_i d \ln \gamma_i \tag{1-9-12a}$$

(10) THE EQUILIBRIUM CONSTANT OF A CHEMICAL REACTION

Consider any chemical reaction at constant temperature, pressure and charge in which $x_1, x_2, \cdots$ mols of $X_1, X_2, \cdots$ and $y_1, y_2, \cdots$ mols of $Y_1, Y_2, \cdots$ react to form $x'_1, x'_2, \cdots$ mols of $X'_1, X'_2, \cdots$ and $y'_1, y'_2, \cdots$ mols of $Y'_1, Y'_2, \cdots$ where the X's indicate pure substances and the Y's indicate the components of any polycomponent phases present. Then

$$\begin{aligned} x_1X_1 + x_2X_2 + \cdots + y_1Y_1 + y_2Y_2 + \cdots \\ = x'_1X'_1 + x'_2X'_2 + \cdots + y'_1Y'_1 + y'_2Y'_2 + \cdots \end{aligned} \tag{1-10-1}$$

and from the definition of activity we may write

$$\begin{aligned} (F - F^0)_{X_1} &= x_1RT \ln a_{X_1}, \text{ etc.,} \\ (\bar{F} - \bar{F}^0)_{Y_1} &= y_1RT \ln a_{Y_1}, \text{ etc.,} \\ \text{and} \qquad (F - F^0)_{X'_1} &= x'_1RT \ln a_{X'_1}, \text{ etc.,} \\ (\bar{F} - \bar{F}^0)_{Y'_1} &= y'_1RT \ln a_{Y'_1}, \text{ etc.} \end{aligned} \tag{1-10-2}$$

The total change in free energy for the reaction will be

$$\Delta F - \Delta F^0 = RT \ln \frac{(a_{X'_1})^{x'_1}(a_{X'_2})^{x'_2} \cdots (a_{Y'_1})^{y'_1} \cdots}{(a_{X_1})^{x_1}(a_{X_2})^{x_2} \cdots (a_{Y_1})^{y_1} \cdots} \tag{1-10-3}$$

where

$$\begin{aligned} \Delta F = (F_{X'_1} + F_{X'_2} \cdots + \bar{F}_{Y'_1} + \bar{F}_{Y'_2} \cdots) \\ - (F_{X_1} + F_{X_2} \cdots + \bar{F}_{Y_1} + \bar{F}_{Y_2} \cdots) \end{aligned} \tag{1-10-4}$$

and

$$\begin{aligned} \Delta F^0 = (F^0_{X'_1} + F^0_{X'_2} \cdots + \bar{F}^0_{Y'_1} + \bar{F}^0_{Y'_2} \cdots) \\ - (F^0_{X_1} + F^0_{X_2} \cdots + \bar{F}^0_{Y_1} + \bar{F}^0_{Y_2} \cdots) \end{aligned} \tag{1-10-5}$$

ΔF is obviously the free energy change of the reaction in general, and ΔF^0 the free energy change when all the products and reactants are in their standard states.

When the reaction is in equilibrium at constant temperature, pressure, and charge, the composition of each phase is fixed. Then, from equation (1-2-6), it follows that the condition

$$\Delta F = 0$$

must prevail. As a consequence,

$$\Delta F^0 = -RT \ln \frac{(a_{X'_1})^{x'_1}(a_{X'_2})^{x'_2} \cdots (a_{Y'_1})^{y'_1} \cdots}{(a_{X_1})^{x_1}(a_{X_2})^{x_2} \cdots (a_{Y_1})^{y_1} \cdots} \tag{1-10-6}$$

Since ΔF^0 is a constant[13] at constant temperature and pressure, we may write

$$K = \frac{(a_{X'_1})^{x'_1}(a_{X'_2})^{x'_2} \cdots (a_{Y'_1})^{y'_1} \cdots}{(a_{X_1})^{x_1}(a_{X_2})^{x_2} \cdots (a_{Y_1})^{y_1} \cdots} \tag{1-10-7}$$

where K is the equilibrium constant of the reaction. The relation stated in equation (1-10-7) forms the basis of the study of ionic equilibria. In another form it may be written

$$K = \frac{(a_{X'_1})^{x'_1}(a_{X'_2})^{x'_2} \cdots (m_{Y'_1})^{y'_1} \cdots \Pi\gamma'}{(a_{X_1})^{x_1}(a_{X_2})^{x_2} \cdots (m_{Y_1})^{y_1} \cdots \Pi\gamma} \tag{1-10-8}$$

where $\Pi\gamma'$ and $\Pi\gamma$ are the appropriate activity coefficient products. If we adopt the convention that all activity coefficients of pure phases (the species X_1, X_2, $\cdots$) are chosen so that their activities are unity, and the activity coefficients of all components of polycomponent phases (the species Y_1, Y_2, $\cdots$) are unity at infinite dilution of the corresponding components, then the classical mass action law,

$$K_m = \frac{(m_{Y'_1})^{y'_1} \cdots}{(m_{Y_1})^{y_1} \cdots} \tag{1-10-9}$$

results at infinite dilution.

Since the important relation

$$\Delta F^0 = -RT \ln K \tag{1-10-10}$$

follows from (1-10-6) and (1-10-7), the variations of the equilibrium constant with pressure and temperature are given by equations (1-3-3) and (1-3-4). Thus,

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V^0}{RT} \tag{1-10-11}$$

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[13] ΔF^0 is arbitrary to the extent that its value depends upon the selection of standard states for the components, and upon the units in which the activities are expressed. In the special case where the reaction is symmetrical, and confined to a single phase, ΔF^0 is independent of these arbitrary considerations.

and

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^0}{RT^2}. \tag{1-10-12}$$

The latter expression is sometimes referred to as the van't Hoff equation.

(11) SURFACE TENSION. THE ADSORPTION EQUATION OF GIBBS

In the subsequent treatment of the variation of surface tension with electrolyte concentration, we shall have occasion to use the adsorption equation of Gibbs in the form

$$\Gamma_2 = -\frac{\partial \sigma}{\partial F_2} = -\frac{\partial \sigma}{RT\,\partial \ln a_2}. \tag{1-11-1}$$

Here, Γ_2 is the number of mols of solute "negatively" adsorbed per unit increase in surface energy, and σ is the surface tension. The derivation and discussion of this relation would cause too great a digression from our principal objectives and will not be attempted.[14]

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[14] J. W. Gibbs, "Collected Works," Vol. I, pp. 219–233, Longmans, Green and Co., New York, 1928; "Commentary on the Scientific Writings of J. Willard Gibbs," Section by James Rice, Vol. I, pp. 504 ff., Yale University Press, New Haven, 1936; E. A. Guggenheim, *J. Chem. Phys.*, **4**, 689 (1936).

Chapter (2)

General Statement of the Interionic Attraction Theory and Properties of Ionic Atmospheres

Progress in developing the modern theory of ionic solutions has depended on one factor, namely, that the law of the force of attraction between ions is known. Upon the basis of this law, and by the specialized application of the fundamental concepts of electrostatics, hydrodynamics and statistical mechanics, an exact theory has been developed which will describe the properties of electrolytes under circumstances where these forces are the predominating factor and where other influences, such as intermolecular forces and short-range repulsive forces between ions, may be considered negligible. Consequently, the first step in constructing a theory requires a quantitative investigation of the effects of the forces between the ions on all the known properties of ionic solutions. If this is done correctly, and if under suitable conditions the results are verified experimentally, the next step in elucidating the electrolytic state of matter from the observed deviations from these laws may be undertaken with some hope of success.

Fortunately, it is possible to test the conclusions of the interionic attraction theory directly, since there exists a class of strong electrolytes which at moderate concentrations in water seem to be completely dissociated, and which conform to the simple electrostatic picture of charged ions in a medium of a given dielectric constant. It has been suspected for a long time that the behavior of strong electrolytes in dilute solution could be accounted for by the hypothesis of complete dissociation and an adequate consideration of the effects of interionic attraction. Sutherland,[1] Noyes,[2] and particularly Bjerrum[3] were among the first to adopt this point of view. Before this van Laar[4] had emphasized the importance of electrostatic forces in explaining the characteristics of ionic solutions. Hertz[5] and

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[1] W. Sutherland, *Phil. Mag.* (6), **3**, 167 (1902); **7**, 1 (1906).

[2] A. A. Noyes, *Congress Arts Sci., St. Louis Exposition*, **4**, 317 (1904).

[3] N. Bjerrum, *D. Kgl. Danske Vidensk. Selsk. Skrifter* (7), **4**, 1 (1906); Proc. 7th Intern. Congr. Applied Chemistry, Sect. X, London (1909); 16 *Skand. Naturforsk. Forhandl.*, 226, 1916; *Z. Electrochem.*, **24**, 321 (1918); *Meddel. Kgl. Vet. Akad. Nobelinst.*, **5**, No. 16 (1919); *Z. anorg. Chem.*, **109**, 275 (1920).

[4] J. J. van Laar, *Z. physik. Chem.*, **15**, 457 (1894); **17**, 245 (1895); **19**, 318 (1896); *Z anorg. Chem.*, **139**, 108 (1924).

[5] P. Hertz, *Ann. Physik.* (4), **37**, 1 (1912).

Ghosh[6] attempted to give the effects of interionic attraction mathematical expression, but the basis of their treatments proved to be inadequate. Milner[7] successfully analyzed the problem, but his mathematical treatment was exceedingly involved and did not yield an entirely satisfactory result.

The conception of the ionic "atmosphere" introduced by Debye, and his use of Poisson's equation, effected an ingenious mathematical short cut which leads to exact relations from which the behaviors of dilute solutions of electrolytes may be quantitatively predicted. In their first contribution to this theory, Debye and Hückel[8] computed successfully the limiting law for the activity coefficient, that is to say, an exact theoretical expression for the behavior of this property in extremely dilute solutions.

Upon the basis of their theory, they[9] were able also to make an important contribution to the theory of electrolytic conductance. Somewhat later, by developing a general treatment of the motion of ions, Onsager[10] derived the limiting law for electrolytic conductance. Later, Onsager's theory of conductance was extended by Debye and Falkenhagen[11] so that the effects of high frequency upon the conductance and dielectric constant were taken into account. The limiting law for the viscosity of an electrolytic solution has been deduced by Falkenhagen,[12] and the general laws of the diffusion of electrolytes have been investigated by Onsager and Fuoss.[13] Further, the Wien effect, or the influence of fields of high intensity upon the properties of these solutions, has been investigated from the theoretical point of view by Joos and Blumentritt.[14] More recently, Wilson[15] has obtained a complete solution of this problem for the case of electrolytes which dissociate into two ions. The theoretical treatment of the effects of high fields upon the ionization of weak electrolytes has been developed in a very interesting manner by Onsager.[16]

This brief survey of the history of the theory shows that it has now reached an advanced stage of development and has been applied successfully to most of the thermodynamic properties and irreversible processes

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[6] I. C. Ghosh, *J. Chem. Soc.*, **113**, 449, 627, 707, 790 (1918); *Trans. Faraday Soc.*, **15**, 154 (1919); *J. Chem. Soc.*, **117**, 823, 1390 (1920); *Z. physik. Chem.*, **98**, 211 (1921).

[7] R. Milner, *Phil. Mag.*, **23**, 551 (1912); **25**, 742 (1913).

[8] P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923). The statistical basis of this theory has been examined by R. H. Fowler, *Trans. Faraday Soc.*, **23**, 434 (1927); L. Onsager, *Chem. Rev.*, **13**, 73 (1933); H. A. Kramers, *Proc. Royal Acad. Sci. Amsterdam*, **30**, 145 (1927); J. G. Kirkwood, *J. Chem. Phys.*, **2**, 767 (1934).

[9] P. Debye and E. Hückel, *Physik. Z.*, **24**, 305 (1923).

[10] L. Onsager, *Physik. Z.*, **28**, 277 (1927).

[11] P. Debye and H. Falkenhagen, *Physik. Z.*, **29**, 121, 401 (1928).

[12] H. Falkenhagen and M. Dole, *Z. physik. Chem.*, **6**, 159 (1929); *Physik. Z.*, **30**, 611 (1929); H. Falkenhagen, *Physik. Z.*, **32**, 365, 745 (1931).

[13] L. Onsager and R. M. Fuoss, *J. Physical Chem.*, **34**, 2689 (1932).

[14] G. Joos and M. Blumentritt, *Physik. Z.*, **28**, 836 (1927).

[15] W. S. Wilson, *Dissertation*, Yale University, June, 1936.

[16] L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

in solutions. In this chapter, we shall examine the fundamental basis of the theory and derive the general equations for its application to various phenomena. In Chapters (3) and (4), we shall consider the reversible and irreversible properties, respectively.

THE IONIC ATMOSPHERE

In considering an ionic solution, two factors are of fundamental and equal importance. The first of these is the distribution of the ions with respect to one another, and the second the forces acting on the ions due to the presence of the ions themselves and external forces. These factors are not mutually exclusive, since the forces affect the distribution of the ions and the distribution of the ions determines the forces. The first step in developing the theory will be the formulation of distribution functions which are sufficiently general for the treatment of an ionic solution in equilibrium or in a perturbed state, the latter being caused by external disturbances such as imposed electrical fields or the flow of the solution as a whole.

Since the original contribution of Debye and Huckel, the theory for the solution in the absence of external fields has been frequently presented in a simple manner.[17] Although this simplified treatment is satisfactory for the equilibrium case, it is not general enough for the theory of solutions under the influence of external forces, *e.g.*, for the calculation of the conductance. Further, unless the symbolism is made more specific, a number of important fundamental theoretical assumptions are not brought to light. This situation may be remedied by employing the more elaborate symbolism of Onsager and Fuoss. Although the adoption of this symbolism increases the difficulty at the start, it ultimately leads to a more rigorous and a clearer understanding of the theory.

(1) The Distribution Functions

Consider an electrolytic solution containing $n_1, n_2, \cdots n_s$ ions per cc. of the ion species denoted by subscripts, and with charges, $e_1, e_2, \cdots e_s$, respectively. Since Coulomb forces, e_je_i/Dr^2, act between all pairs of ions of charges e_j and e_i, the motion of the ions is not entirely a random one. As a result, the presence of an ion at a given point in the solution will affect

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[17] A. A. Noyes, *J. Am. Chem. Soc.*, **46**, 1080 (1924).
H. S. Harned in Taylor, "Treatise on Physical Chemistry," p. 784, D. Van Nostrand and Company, New York, 1930.
A. Eucken, "Fundamentals of Physical Chemistry," Translated by E. R. Jette and V. K. LaMer, McGraw-Hill Book Co., New York, 1925.
M. Dole, "Principles of Experimental and Theoretical Electrochemistry," McGraw-Hill Book Co., New York, 1935.
D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, 1939.
W. M. Clark, "The Determination of Hydrogen Ions," 3rd Edition, Williams and Wilkins Co., Baltimore, 1928.

the space distribution of the other ions in its immediate vicinity. For example, each positive ion, by inducing a negative charge density in its vicinity, will be surrounded by an "atmosphere" which contains on the average more negative ions and less positive ions than the bulk of the solution. In a similar manner a negative ion will be surrounded with a positively charged "atmosphere." In order to treat the problem of ionic distribution in a manner sufficiently general for a theory of both the equilibrium conditions and of irreversible processes such as electrolytic conductance, diffusion, and viscosity, a function is required which will describe the chance of finding two ions in two given volume elements in the solution simultaneously.

This chance can readily be found if we specify two volume elements [Fig. (2-1-1)], located by the termini of the vectors, $\mathbf{r}_1$ and $\mathbf{r}_2$, drawn from

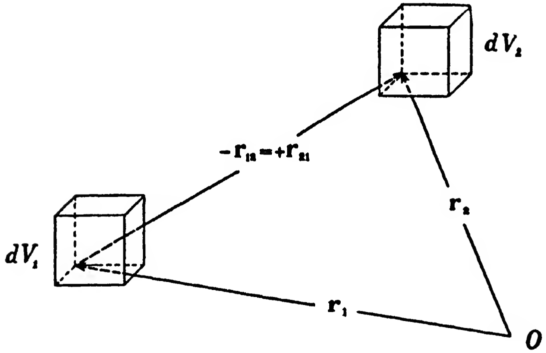

Fig. (2-1-1)
Definition of Vectors

some arbitrary origin. The distance between the two volume elements is given by

$$\mathbf{r}_{21} = \mathbf{r}_2 - \mathbf{r}_1 = -\mathbf{r}_{12} \tag{2-1-1}$$

We shall denote the concentrations (ions per cc.) of ions of kinds j and i by n_j and n_i, respectively. Further, we let n_{ji} be the time average concentration of i ions in dV_2 in the vicinity of a single j ion in dV_1; *vice versa* we let n_{ij} equal the time average concentration of j ions in dV_1 in the neighborhood of an ion of kind i in dV_2.

In general, these concentrations will depend on several variables.

(1) They will be a function of the distance r between the j ion and the point where the concentration of the i ion is required, and *vice versa.*

(2) When external forces act on the ions, a particular direction in space is specified, and n_{ji} and n_{ij} will depend on the direction of $\mathbf{r}$ as well as on its magnitude. For example, when an electrical field is applied, the ions may be considered to move in a specified direction, *i.e.*, the x direction.

Thus, the conductance will involve the direction x, as will the distance between the ions, r.

(3) If a variable velocity gradient is applied to the solution as a whole, n_{ji} will depend on the location of the j ion and n_{ij} on that of the i ion. These conditions may be expressed adequately by the functional expressions

$$\begin{aligned} n_{ji} &= n_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) \\ n_{ij} &= n_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) \end{aligned} \tag{2-1-2}$$

These general relations are required in the theory of viscosity.

It is now necessary to obtain the distribution functions. We consider the two volume elements, dV_1 and dV_2, temporarily fixed in space during a time t, and the two species of ions j and i. Out of the total time, t, we record a time, t_j, during which the j ion is in dV_1, and also the time, t_i, in which the i ion is in dV_2. The chance, t_j/t, of finding a j ion in dV_1 and the chance, t_i/t, of finding an i ion in dV_2 are related to the concentrations n_j and n_i by the expressions

$$\frac{t_j}{t} = n_j dV_1; \qquad \frac{t_i}{t} = n_i dV_2$$

Further, we note the time, t_{ji}, during which a j ion and an i ion are in dV_1 and dV_2 simultaneously. Then,

$$\frac{t_{ji}}{t_j} = n_{ji} dV_2; \qquad \frac{t_{ij}}{t_i} = n_{ij} dV_1$$

By eliminating t_j and t_i from the preceding two sets of equations, we find that

$$\frac{t_{ji}}{t} = n_j n_{ji} dV_1 dV_2 = \frac{t_{ij}}{t} = n_i n_{ij} dV_1 dV_2 \tag{2-1-3}$$

Since t_{ji}/t is the chance of finding a j ion in dV_1 and an i ion in dV_2 simultaneously, the foregoing relation can be employed to define the required distribution functions, namely

$$f_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) \equiv n_j n_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) = n_i n_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) \equiv f_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) \tag{2-1-4}$$

Note that f_{ji} is the concentration (number of ions per cc.) of the i ions at a distance $\mathbf{r}_{21}$ from the j ion multiplied by n_j, the number of ions per cc. of the kind j, located in space by $\mathbf{r}_1$. In other words, f_{ji} is the concentration of the i ions in the atmospheres of n_j ions of the kind j. Also note the important symmetry condition represented by the equality in this equation which causes f_{ji} to equal the reciprocal quantity f_{ij}. It is a quantity which must be known if the problem of the distribution of ions is to be solved. Now, n_j and n_i are known, but $n_{ji}(\mathbf{r}_1, \mathbf{r}_{21})$ and $n_{ij}(\mathbf{r}_2, \mathbf{r}_{12})$

must be found from further statistical considerations. In the equilibrium case, when the only forces considered are the Coulombic forces between the ions, the Maxwell-Boltzmann distribution law will be sufficient to determine these quantities.

A satisfactory conception of the "ionic atmosphere" may be obtained by considering a positive ion as fixed in dV_1. Due to the force of attraction between positive and negative ions, the latter (on the average) will be in dV_2 more frequently than the former. This excess of negative ions around a positive ion, or *vice versa*, constitutes an ionic atmosphere. In an electrolytic solution undisturbed by external forces, the field around an ion is the same in all directions and is therefore a function of the distance, r, and not the direction. In this case, the ionic atmosphere possesses spherical symmetry. When external forces act on the ions, as in the case of an applied electrical field, the ionic atmosphere is asymmetrical.

(2) The Time Rate of Change of the Distribution Function

We let $\mathbf{v}_{ji}$ equal the velocity of an i ion in the neighborhood of a j ion and write

$$\mathbf{v}_{ji} = \mathbf{v}_{ji}(\mathbf{r}_1, \mathbf{r}_{21})$$

Similarly

$$\mathbf{v}_{ij} = \mathbf{v}_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) \tag{2-2-1}$$

Further, if we let $\xi_1, \cdots \xi_6$ represent six space coördinates which locate two points in the solution, we can follow dV_1 and dV_2 simultaneously. Thus, the components of the velocity of the j ion in dV_1 are $\dot{\xi}_1$, $\dot{\xi}_2$, and $\dot{\xi}_3$, and of the i ion in dV_2 they are $\dot{\xi}_4$, $\dot{\xi}_5$, and $\dot{\xi}_6$, where the dots have the usual connotation of differentiation with respect to time. In this six-dimensional space, consider a six-dimensional element of volume whose center is located at $\xi_1, \cdots \xi_6$. Since f_{ji} is the concentration (in six-dimensional space) at this point, the flow of i ions, $f_{ji}\mathbf{v}_{ji}$, at ξ_1 through the five-dimensional area $d\xi_2 \cdots d\xi_6$ perpendicular to ξ_1 into the volume element is

$$\dot{\xi}_1 f_{ji}\, d\xi_2 \cdots d\xi_6$$

and at $\xi_1 + d\xi_1$ the flow out is

$$\left[\dot{\xi}_1 f_{ji} + \frac{\partial(\dot{\xi}_1 f_{ji})}{\partial \xi_1}\, d\xi_1\right] d\xi_2 \cdots d\xi_6$$

and hence the net increase in the number of ions in the volume element due to flow in the direction of the coördinate ξ_1 is

$$-\frac{\partial(\dot{\xi}_1 f_{ji})}{\partial \xi_1}\, d\xi_1 \cdots d\xi_6$$

per unit time. Division of the sum of the corresponding differences along the six coördinates by the volume of the element, $d\xi_1 \cdots d\xi_6$ gives the time rate of change of concentration in the volume element,

$$\frac{\partial f_{ji}}{\partial t} = -\sum_{r=1}^{6} \frac{\partial(\dot{\xi}_r f_{ji})}{\partial \xi_r} \tag{2-2-2}$$

Now, the differential operator on the right represents a six-dimensional divergence which may be written

$$\sum_{r=1}^{6} \frac{\partial}{\partial \xi_r} \equiv \nabla_1 \cdot + \nabla_2 \cdot$$

where the subscripts 1 and 2 represent differentiation with respect to the components of $\mathbf{r}_1$ and $\mathbf{r}_2$ respectively. Since $f_{ji}(\mathbf{r}_1,\mathbf{r}_{21}) = f_{ij}(\mathbf{r}_2,\mathbf{r}_{12})$, equation (2-2-2) may be written

$$-\frac{\partial f_{ji}(\mathbf{r}_1, \mathbf{r}_{21})}{\partial t} = \nabla_1 \cdot (f_{ij}\mathbf{v}_{ij}) + \nabla_2 \cdot (f_{ji}\mathbf{v}_{ji}) = -\frac{\partial f_{ij}(\mathbf{r}_2, \mathbf{r}_{12})}{\partial t} \tag{2-2-3}$$

which is the equation of continuity in an adequate form for the theory of ionic motion. In a steady state, $\frac{\partial f_{ij}}{\partial t} = 0$, and consequently

$$\nabla_1 \cdot (f_{ij}\mathbf{v}_{ij}) + \nabla_2 \cdot (f_{ji}\mathbf{v}_{ji}) = 0 \quad . \tag{2-2-4}$$

These fundamental hydrodynamic equations form the basis for the theory of irreversible processes. Before they can be used, however, it will be necessary to evaluate both the distribution functions and the velocities.

(3) The Equations of Motion

The factors which cause the ions to move can be reduced to three: (1) forces on the ions, (2) thermal (random) motion, and (3) flow of solution as a whole. The forces which influence the ions may be external (outside electrical field), and internal (concentration gradients and electrostatic forces due to the presence of the ions themselves). If the mobility of an i ion be ω_i, then a force, $\mathbf{K}_i$, acting upon it will produce a velocity equal to $\mathbf{K}_i\omega_i$. The coefficient of friction of this ion is given by $\rho_i = 1/\omega_i$. If the diffusion constant for an ion is taken to be $kT\omega$,[18] then a concentration gradient of ∇f will produce a current of strength $-kT\,\omega\,\nabla f$. Since this current is equal to $\mathbf{v}f$, the diffusion velocity is $-kT\,\omega\,\nabla \ln f$. Therefore, if the velocity of the solution as a whole at a point located by $\mathbf{r}_2$ is $\mathbf{V}(\mathbf{r}_2)$, then the total velocity, $\mathbf{v}_{ji}$, at this point is

$$\mathbf{v}_{ji} = \mathbf{V}(\mathbf{r}_2) + \omega_i(\mathbf{K}_{ji} - kT\nabla_2 \ln f_{ji}) \tag{2-3-1}$$

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[18] W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888); "Theoretical Chemistry," p. 368–374, Translation by H. T. Tizard, Macmillan Co., London, 1911; R. C. Tolman, "Statistical Mechanics," p. 231, Equation (535), Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1927.

Similarly

$$\mathbf{v}_{ij} = \mathbf{V}(\mathbf{r}_1) + \omega_j(\mathbf{K}_{ij} - kT\nabla_1 \ln f_{ij})$$

Substituting these values of the velocities, equation (2-2-4) for the steady state becomes

$$\nabla_1 \cdot [f_{ij}\mathbf{V}(\mathbf{r}_1) + \omega_j(f_{ij}\mathbf{K}_{ij} - kT\nabla_1 f_{ij})] + \nabla_2 \cdot [f_{ji}\mathbf{V}(\mathbf{r}_2) + \omega_i(f_{ji}\mathbf{K}_{ji} - kT\nabla_2 f_{ji})] = 0 \qquad (2\text{-}3\text{-}2)$$

In order to apply this equation to the theory of the irreversible processes, it will now be necessary to introduce considerations of the interionic forces. This will first require a careful examination of the electrolytic solution in the absence of external fields. We have delayed the discussion of this comparatively simple case because the expressions for the ionic velocities given by equation (2-3-1) are required to explain certain basic assumptions underlying the entire theory.

(4) The Fundamental Equations for the Potentials of an Ion and Its Atmosphere in the Absence of External Fields. Theory of Debye

If the electrolyte is stationary and not acted upon by external forces, the ionic atmospheres possess spherical symmetry and the distribution functions become functions of the distance $r = |\mathbf{r}_{12}| = |\mathbf{r}_{21}|$ only. The vertical bars indicate magnitude. The distribution functions for this case will be specified by the superscript zero, and therefore

$$f^0_{ji}(r) = n_j n^0_{ji}(r) = n_i n^0_{ij}(r) = f^0_{ij}(r) \qquad (2\text{-}4\text{-}1)$$

We shall now examine carefully the effects of Coulombic forces and thermal motion of the ions upon the distribution functions and the potentials. We shall assume that the ions are point charges, and reserve until later the computation of the effects due to the finite sizes of the ions. An ion of charge e_j in a liquid of dielectric constant D possesses an electrical potential e_j/Dr at a distance r from the ion. In a solution containing an electrolyte, ionic atmospheres are formed and the fields of the ions derivable from the potential superpose. The potential due to an ion and its atmosphere will be represented by $\psi_j(\mathbf{r}_1, \mathbf{r}_{21})$ in general, and by $\psi^0_j(r)$ in the static (unperturbed) case.

In a medium containing electrical charges (or other sources of fields) subject to forces which vary inversely as the square of the distance, the relation between the charge density, ρ, and the potential is given in general by Poisson's equation

This equation states th [illegible] space coördinates (x, y, [illegible] potential, or the total out [illegible] to the charge density at this point. In an electrolytic solution, the charge density (concentration or charge per cc.) at a distance r from the j ion is $\sum_{i=1}^{s} n_{ji}e_i$, where the summation is over all the kinds of ions in the solution. The potential at this point is that due to the j ion and its atmosphere. Thus, in general

$$\nabla\cdot\nabla\psi_j(\mathbf{r}_1, \mathbf{r}_{21}) = -\frac{4\pi}{D}\sum_{i=1}^{s} n_{ji}e_i \tag{2-4-2}$$

For the unperturbed electrolyte

$$\nabla\cdot\nabla\psi_j^0(r) = -\frac{4\pi}{D}\sum_{i=1}^{s} n_{ji}^0 e_i \tag{2-4-3}$$

ψ_j^0 is a function of r only.

From consideration of the thermal motion of the ions, we assume that the concentration of an ion in the neighborhood of another ion is determined by the Maxwell-Boltzmann distribution law in the forms

$$\begin{aligned} n_{ji}^0 &= n_i e^{-U_{ji}/kT} \\ n_{ij}^0 &= n_j e^{-U_{ij}/kT} \end{aligned} \tag{2-4-4}$$

U_{ji} is the potential energy of the i ion in the vicinity of the j ion and kT its kinetic energy.

An important insight into the fundamental assumption underlying the theory will appear upon examining these relations and the equations of motion. It is characteristic of the equilibrium case that the average values of the velocities $\mathbf{v}_{ji}$ and $\mathbf{v}_{ij}$ vanish. Hence, from equations (2-3-1), it follows that

$$\mathbf{K}_{ji} = kT\nabla \ln f_{ji}^0 = kT\nabla \ln f_{ij}^0 = \mathbf{K}_{ij} \tag{2-4-5}$$

According to equation (2-1-4), $f_{ji}^0 = n_j n_{ji}^0 = n_i n_{ij}^0 = f_{ij}^0$, and hence equations (2-4-4) yield

$$f_{ji}^0 = n_j n_i e^{-U_{ji}/kT} = n_i n_j e^{-U_{ij}/kT} = f_{ij}^0$$

Since n_j and n_i are constant concentrations, it follows by introducing this relation in equation (2-4-5) that

$$kT\nabla \ln f_{ji}^0 = -\nabla U_{ji} = -\nabla U_{ij} = kT\nabla \ln f_{ij}^0 \tag{2-4-6}$$

at constant temperature.

If it is assumed that the average force acting upon one ion is given by the potential of the other ion, which is equivalent to the assumption of the [illegible] superposition of the fields, then the potential energies, U_{ji}, and U_{ij} [illegible] $\psi_j^0(r)e_i$ and $\psi_i^0(r)e_j$, respectively, and according to equation

$$[illegible] = \psi_j^0(r)e_i = \psi_i^0(r)e_j = U_{ij} \tag{2-4-7}$$

must be found from further statistical considerations. In the equilibrium case, when the only forces considered are the Coulombic forces between the ions, the Maxwell-Boltzmann distribution law will be sufficient to determine these quantities.

A satisfactory conception of the "ionic atmosphere" may be obtained by considering a positive ion as fixed in dV_1. Due to the force of attraction between positive and negative ions, the latter (on the average) will be in dV_2 more frequently than the former. This excess of negative ions around a positive ion, or *vice versa*, constitutes an ionic atmosphere. In an electrolytic solution undisturbed by external forces, the field around an ion is the same in all directions and is therefore a function of the distance, r, and not the direction. In this case, the ionic atmosphere possesses spherical symmetry. When external forces act on the ions, as in the case of an applied electrical field, the ionic atmosphere is asymmetrical.

(2) The Time Rate of Change of the Distribution Function

We let $\mathbf{v}_{ji}$ equal the velocity of an i ion in the neighborhood of a j ion and write

$$\mathbf{v}_{ji} = \mathbf{v}_{ji}(\mathbf{r}_1, \mathbf{r}_{21})$$

Similarly

$$\mathbf{v}_{ij} = \mathbf{v}_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) \qquad (2\text{-}2\text{-}1)$$

Further, if we let $\xi_1, \cdots \xi_6$ represent six space coördinates which locate two points in the solution, we can follow dV_1 and dV_2 simultaneously. Thus, the components of the velocity of the j ion in dV_1 are $\dot{\xi}_1$, $\dot{\xi}_2$, and $\dot{\xi}_3$, and of the i ion in dV_2 they are $\dot{\xi}_4$, $\dot{\xi}_5$, and $\dot{\xi}_6$, where the dots have the usual connotation of differentiation with respect to time. In this six-dimensional space, consider a six-dimensional element of volume whose center is located at $\xi_1, \cdots \xi_6$. Since f_{ji} is the concentration (in six-dimensional space) at this point, the flow of i ions, $f_{ji}\mathbf{v}_{ji}$, at ξ_1 through the five-dimensional area $d\xi_2 \cdots d\xi_6$ perpendicular to ξ_1 into the volume element is

$$\dot{\xi}_1 f_{ji}\, d\xi_2 \cdots d\xi_6$$

and at $\xi_1 + d\xi_1$ the flow out is

$$\left[\dot{\xi}_1 f_{ji} + \frac{\partial(\dot{\xi}_1 f_{ji})}{\partial \xi_1}\, d\xi_1\right] d\xi_2 \cdots d\xi_6$$

and hence the net increase in the number of ions in the volume element due to flow in the direction of the coördinate ξ_1 is

$$-\frac{\partial(\dot{\xi}_1 f_{ji})}{\partial \xi_1}\, d\xi_1 \cdots d\xi_6$$

per unit time. Division of the sum of the corresponding differences along the six coördinates by the volume of the element, $d\xi_1 \cdots d\xi_6$ gives the time rate of change of concentration in the volume element,

$$\frac{\partial f_{ji}}{\partial t} = -\sum_{r=1}^{6} \frac{\partial(\dot{\xi}_r f_{ji})}{\partial \xi_r} \tag{2-2-2}$$

Now, the differential operator on the right represents a six-dimensional divergence which may be written

$$\sum_{r=1}^{6} \frac{\partial}{\partial \xi_r} \equiv \nabla_1 \cdot + \nabla_2 \cdot$$

where the subscripts 1 and 2 represent differentiation with respect to the components of $\mathbf{r}_1$ and $\mathbf{r}_2$ respectively. Since $f_{ji}(\mathbf{r}_1,\mathbf{r}_{21}) = f_{ij}(\mathbf{r}_2,\mathbf{r}_{12})$, equation (2-2-2) may be written

$$-\frac{\partial f_{ji}(\mathbf{r}_1, \mathbf{r}_{21})}{\partial t} = \nabla_1 \cdot (f_{ij}\mathbf{v}_{ij}) + \nabla_2 \cdot (f_{ji}\mathbf{v}_{ji}) = -\frac{\partial f_{ij}(\mathbf{r}_2, \mathbf{r}_{12})}{\partial t} \tag{2-2-3}$$

which is the equation of continuity in an adequate form for the theory of ionic motion. In a steady state, $\frac{\partial f_{ij}}{\partial t} = 0$, and consequently

$$\nabla_1 \cdot (f_{ij}\mathbf{v}_{ij}) + \nabla_2 \cdot (f_{ji}\mathbf{v}_{ji}) = 0 \tag{2-2-4}$$

These fundamental hydrodynamic equations form the basis for the theory of irreversible processes. Before they can be used, however, it will be necessary to evaluate both the distribution functions and the velocities.

(3) The Equations of Motion

The factors which cause the ions to move can be reduced to three: (1) forces on the ions, (2) thermal (random) motion, and (3) flow of solution as a whole. The forces which influence the ions may be external (outside electrical field), and internal (concentration gradients and electrostatic forces due to the presence of the ions themselves). If the mobility of an i ion be ω_i, then a force, $\mathbf{K}_i$, acting upon it will produce a velocity equal to $\mathbf{K}_i\omega_i$. The coefficient of friction of this ion is given by $\rho_i = 1/\omega_i$. If the diffusion constant for an ion is taken to be $kT\omega$,[18] then a concentration gradient of ∇f will produce a current of strength $-kT\,\omega\,\nabla f$. Since this current is equal to $\mathbf{v}f$, the diffusion velocity is $-kT\,\omega\,\nabla \ln f$. Therefore, if the velocity of the solution as a whole at a point located by $\mathbf{r}_2$ is $\mathbf{V}(\mathbf{r}_2)$, then the total velocity, $\mathbf{v}_{ji}$, at this point is

$$\mathbf{v}_{ji} = \mathbf{V}(\mathbf{r}_2) + \omega_i(\mathbf{K}_{ji} - kT\nabla_2 \ln f_{ji}) \tag{2-3-1}$$

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[18] W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888); "Theoretical Chemistry," p. 368–374, Translation by H. T. Tizard, Macmillan Co., London, 1911; R. C. Tolman, "Statistical Mechanics," p. 231, Equation (535), Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1927.

Similarly

$$\mathbf{v}_{ij} = \mathbf{V}(\mathbf{r}_1) + \omega_j(\mathbf{K}_{ij} - kT\nabla_1 \ln f_{ij})$$

Substituting these values of the velocities, equation (2-2-4) for the steady state becomes

$$\nabla_1\cdot[f_{ij}\mathbf{V}(\mathbf{r}_1) + \omega_j(f_{ij}\mathbf{K}_{ij} - kT\nabla_1 f_{ij})] + \nabla_2\cdot[f_{ji}\mathbf{V}(\mathbf{r}_2) + \omega_i(f_{ji}\mathbf{K}_{ji} - kT\nabla_2 f_{ji})] = 0 \qquad (2\text{-}3\text{-}2)$$

In order to apply this equation to the theory of the irreversible processes, it will now be necessary to introduce considerations of the interionic forces. This will first require a careful examination of the electrolytic solution in the absence of external fields. We have delayed the discussion of this comparatively simple case because the expressions for the ionic velocities given by equation (2-3-1) are required to explain certain basic assumptions underlying the entire theory.

(4) The Fundamental Equations for the Potentials of an Ion and Its Atmosphere in the Absence of External Fields. Theory of Debye

If the electrolyte is stationary and not acted upon by external forces, the ionic atmospheres possess spherical symmetry and the distribution functions become functions of the distance $r = |\mathbf{r}_{12}| = |\mathbf{r}_{21}|$ only. The vertical bars indicate magnitude. The distribution functions for this case will be specified by the superscript zero, and therefore

$$f^0_{ji}(r) = n_j n^0_{ji}(r) = n_i n^0_{ij}(r) = f^0_{ij}(r) \qquad (2\text{-}4\text{-}1)$$

We shall now examine carefully the effects of Coulombic forces and thermal motion of the ions upon the distribution functions and the potentials. We shall assume that the ions are point charges, and reserve until later the computation of the effects due to the finite sizes of the ions. An ion of charge e_j in a liquid of dielectric constant D possesses an electrical potential e_j/Dr at a distance r from the ion. In a solution containing an electrolyte, ionic atmospheres are formed and the fields of the ions derivable from the potential superpose. The potential due to an ion and its atmosphere will be represented by $\psi_j(\mathbf{r}_1, \mathbf{r}_{21})$ in general, and by $\psi^0_j(r)$ in the static (unperturbed) case.

In a medium containing electrical charges (or other sources of fields) subject to forces which vary inversely as the square of the distance, the relation between the charge density, ρ, and the potential is given in general by Poisson's equation

$$\nabla\cdot\nabla\psi = -\frac{4\pi\rho}{D}$$

This equation states that at any point in a medium located by three space coördinates (x, y, z; r, θ, ϕ) the divergence of the gradient of the potential, or the total outward flux of the force at this point, is proportional to the charge density at this point. In an electrolytic solution, the charge density (concentration or charge per cc.) at a distance r from the j ion is $\sum_{i=1}^{s} n_{ji}e_i$, where the summation is over all the kinds of ions in the solution. The potential at this point is that due to the j ion and its atmosphere. Thus, in general

$$\nabla \cdot \nabla \psi_j(\mathbf{r}_1, \mathbf{r}_{21}) = -\frac{4\pi}{D}\sum_{i=1}^{s} n_{ji}e_i \tag{2-4-2}$$

For the unperturbed electrolyte

$$\nabla \cdot \nabla \psi_j^0(r) = -\frac{4\pi}{D}\sum_{i=1}^{s} n_{ji}^0 e_i \tag{2-4-3}$$

ψ_j^0 is a function of r only.

From consideration of the thermal motion of the ions, we assume that the concentration of an ion in the neighborhood of another ion is determined by the Maxwell-Boltzmann distribution law in the forms

$$\begin{aligned} n_{ji}^0 &= n_i e^{-U_{ji}/kT} \\ n_{ij}^0 &= n_j e^{-U_{ij}/kT} \end{aligned} \tag{2-4-4}$$

U_{ji} is the potential energy of the i ion in the vicinity of the j ion and kT its kinetic energy.

An important insight into the fundamental assumption underlying the theory will appear upon examining these relations and the equations of motion. It is characteristic of the equilibrium case that the average values of the velocities $\mathbf{v}_{ji}$ and $\mathbf{v}_{ij}$ vanish. Hence, from equations (2-3-1), it follows that

$$\mathbf{K}_{ji} = kT\nabla \ln f_{ji}^0 = kT\nabla \ln f_{ij}^0 = \mathbf{K}_{ij} \tag{2-4-5}$$

According to equation (2-1-4), $f_{ji}^0 = n_j n_{ji}^0 = n_i n_{ij}^0 = f_{ij}^0$, and hence equations (2-4-4) yield

$$f_{ji}^0 = n_j n_i e^{-U_{ji}/kT} = n_i n_j e^{-U_{ij}/kT} = f_{ij}^0$$

Since n_j and n_i are constant concentrations, it follows by introducing this relation in equation (2-4-5) that

$$kT\nabla \ln f_{ji}^0 = -\nabla U_{ji} = -\nabla U_{ij} = kT\nabla \ln f_{ij}^0 \tag{2-4-6}$$

at constant temperature.

If it is assumed that the average force acting upon one ion is given by the potential of the other ion, which is equivalent to the assumption of the linear superposition of the fields, then the potential energies, U_{ji}, and U_{ij} will equal $\psi_j^0(r)e_i$ and $\psi_i^0(r)e_j$, respectively, and according to equation (2-4-6)

$$U_{ji} = \psi_j^0(r)e_i = \psi_i^0(r)e_j = U_{ij} \tag{2-4-7}$$

Thus, the potential energy of the i ion at a distance r from the j ion is assumed to be equal to the potential due to the j ion and its atmosphere at this point, multiplied by the charge on the i ion, and is equal to the work done in charging the i ion in a field of potential $\psi_j^0(r)$. The reciprocal relations given by equation (2-4-7) require that the potential of the ion and its atmosphere be proportional to its charge.

It is important to realize that the assumption of the linear superposition of the fields has always been employed in the development of the theory. For example, the theoretical calculation of the thermodynamic properties (chemical potentials, activity coefficients etc.) has been derived upon the assumption that $\psi_j^0(r) \propto e_j$. In the discussion which follows, we shall examine the conditions under which the relation of proportionality of potential to charge is compatible with the Maxwell-Boltzmann distribution.[19]

By the combination of equations (2-4-3) and (2-4-4) and by substitution of $\psi_j^0(r)e_i$ for U_{ji}, we obtain

$$\nabla \cdot \nabla \psi_j^0(r) = -\frac{4\pi}{D} \sum_{i=1}^{s} n_i e_i \exp\left(-\psi_j^0(r)e_i/kT\right) \tag{2-4-8}$$

Now this equation does not fulfil the requirement that $\psi_j^0(r)$ is proportional to e_j, since the term on the left is linear in e_j by hypothesis, while that on the right is not. This contradiction is remedied by making the approximation

$$\exp\left(-\psi_j^0(r)e_i/kT\right) \simeq 1 - \psi_j^0(r)e_i/kT \tag{2-4-9}$$

which neglects the terms in the expansion of higher order than the first. This approximation is justifiable only when $\psi_j^0(r)e_i$ is small, or when $\psi_j^0(r)$ is small, a condition approached at very low concentrations. For electrolytes of high-valence type and for electrolytes in media of low dielectric constant, $\psi_j^0(r)e_i$ becomes larger and the approximation is not good.

If we now substitute the approximation given by equation (2-4-9) in (2-4-8), we obtain

$$\nabla \cdot \nabla \psi_j^0(r) = \frac{4\pi}{DkT} \sum_{i=1}^{s} n_i e_i^2 \psi_j^0(r) \tag{2-4-10}$$

since electroneutrality of the solution as a whole requires that

$$\frac{4\pi}{D} \sum_{i=1}^{s} e_i n_i = 0 \tag{2-4-10a}$$

We now let $e_i^2 = z_i^2\epsilon^2$, where z_i is the valence of the ion and ϵ the electronic charge, and define the quantity κ by

$$\kappa^2 \equiv \frac{4\pi\epsilon^2}{DkT} \sum_{i=1}^{s} n_i z_i^2 \tag{2-4-11}$$

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[19] L. Onsager, *Chem. Rev.*, **13, 73 (1933).**

whence equation (2-4-10) reduces to

$$\nabla\cdot\nabla\psi_j^0(r) = \kappa^2\psi_j^0(r) \tag{2-4-12}$$

In the unperturbed electrolyte, the ionic atmospheres are spherical and it is most convenient to express $\nabla\cdot\nabla\psi_j^0(r)$ in spherical coördinates. Hence

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_j^0(r)}{\partial r}\right) = \kappa^2\psi_j^0(r) \tag{2-4-13}$$

since $\psi_j^0(r)$ is a function of r only. The integration of this equation will give $\psi_j^0(r)$ as a function of r and κ, where κ is seen to be a function of the dielectric constant of the medium, the temperature and the concentration of electrolyte.

A general solution of equation (2-4-13) is

$$\psi_j^0(r) = \frac{Ae^{-\kappa r}}{r} + \frac{A'e^{\kappa r}}{r} \tag{2-4-14}$$

where A and A' are integration constants. The constant A' must be zero since $\psi_j^0(r)$ equals zero when r is infinite, *i.e.*, $\psi_j^0(\infty) = 0$. For small values of κr, the equation remaining may be expanded to yield

$$\psi_j^0(r) = \frac{A}{r} - A\kappa \tag{2-4-14a}$$

if the higher terms be neglected. It will be shown in Chapter (3), Section (5), that A is independent of both r and κ. Hence A/r is a function of r only, and $A\kappa$ is a function of κ only, and vanishes at infinite dilution. Thus, A/r is the potential at a distance r from a point charge, e_j, of magnitude AD at the origin, and $\psi_j^0(r)$ is the potential corresponding to a point charge (ion) of magnitude AD at the origin, plus the potential due to the space charge of the atmosphere. Thus, A, may be replaced by e_j/D. From equations (2-4-3), (2-4-12), and (2-4-14), it follows that

$$\nabla\cdot\nabla\psi_j^0(r) = -\frac{4\pi}{D}\sum_{i=1}^{s} n_{ji}^0 e_i = \kappa^2\psi_j^0(r) = \kappa^2\frac{e_j e^{-\kappa r}}{Dr} \tag{2-4-15}$$

and hence the space charge of the i ion in the atmosphere of the j ion and at a distance r is given by

$$\sum_{i=1}^{s} n_{ji}^0 e_i = -\frac{D}{4\pi}\kappa^2\frac{e_j e^{-\kappa r}}{Dr} \tag{2-4-16}$$

The very important equations for the potentials follow from (2-4-14) upon substitution of e_j/D or $z_j\epsilon/D$ for A. Thus

$$\psi_j^0(r) = \frac{z_j\epsilon e^{-\kappa r}}{Dr} \tag{2-4-17}$$

or in another form

$$\psi_j^0(r) = \frac{z_j\epsilon}{Dr} - \frac{z_j\epsilon(1 - e^{-\kappa r})}{Dr} \tag{2-4-18}$$

The first term on the right of this equation is simply the potential at a distance r from an isolated ion in a medium of dielectric constant D. The second term is the potential of the ionic atmosphere. The first term will not be required in the expression for the variation of the thermodynamic properties of electrolytes with concentration of ions. However, in certain cases when the influence of change of media is required, the first term is retained. Since $(1 - e^{-\kappa r})$ approaches the value κr for small values of κr, the potential of the ion and its atmosphere becomes

$$\psi_j^0(r) = \frac{z_j \epsilon}{Dr} - \frac{z_j \epsilon \kappa}{D} \tag{2-4-18a}$$

an equation which also follows directly from (2-4-14a). The second term on the right is simply the potential of the ionic atmosphere, ψ_j^{0*}, for small values of κr, a condition fulfilled when, at a finite value of r, κ approaches 0, *i.e.*, the concentration approaches zero. It is apparent that $1/\kappa$ in the last term of equation (2-4-18a)

$$\psi_j^{0*} = -\frac{z_j \epsilon \kappa}{D} \tag{2-4-19}$$

is analogous to the distance r in the first term on the right of this equation and possesses the dimension of length. Thus, $1/\kappa$ is the mean radius of the ionic atmosphere, a property which makes κ an extremely important quantity in the theory.

In order to render the equation of continuity (2-3-2) suitable for the specialized theories of irreversible processes in electrolytes, the distribution functions f_{ji}^0 and f_{ij}^0 must be expressed as a function of r. The desired expressions may be obtained from equations (2-4-1), (2-4-4), (2-4-7), (2-4-9) and (2-4-17) and are

$$\begin{aligned} f_{ji}^0 = n_j n_{ji}^0 = n_j n_i \exp\left(-\psi_j^0(r)e_i/kT\right) &= n_j n_i \left(1 - \frac{\psi_j^0(r)e_i}{kT}\right) \\ &= n_j n_i \left(1 - \frac{e_j e_i}{DkTr} e^{-\kappa r}\right) \end{aligned} \tag{2-4-20}$$

Three of these equations are fundamental for various subsequent developments. Equation (2-4-19) is the basic equation of the theory for computing the limiting laws for activity and osmotic coefficients and, subsequently, partial molal heats of dilution and heat capacities [Chapter (3), Sections (1-4)]. Equation (2-4-17) is fundamental for the derivation of the Debye and Hückel equation for the activity coefficient which involves the mean distance of approach of the ions [Chapter (3), Section (5)]. The last of these equations (2-4-20) will be employed in the next section in adapting equation (2-3-2) to meet the requirements of the theory of irreversible processes in electrolytic solutions.

(5) General Equations for the Perturbations of Ionic Atmospheres

If the electrolyte is disturbed by external forces both the potentials and distribution functions become asymmetric. Thus

$$\begin{aligned} \psi_j(\mathbf{r}_1, \mathbf{r}_{21}) &= \psi_j'(\mathbf{r}_1, \mathbf{r}_{21}) + \psi_j^0(r) \\ f_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) &= f_{ji}'(\mathbf{r}_1, \mathbf{r}_{21}) + f_{ji}^0(r) \end{aligned} \qquad (2\text{-}5\text{-}1)$$

where the primed terms represent the effects of the perturbations. The potentials and distributions are related according to Poisson's equation in the following manner

$$\nabla\cdot\nabla\psi_j' = -\frac{4\pi}{D}\sum_{i=1}^{s}\frac{f_{ji}'e_i}{n_j} \qquad (2\text{-}5\text{-}2)$$

For simplicity, we frequently write ψ_j' and f_{ji}' in place of $\psi_j'(\mathbf{r}_1, \mathbf{r}_{21})$ and $f_{ji}(\mathbf{r}_1, \mathbf{r}_{21})$, respectively.

The perturbing factors bring about irreversible processes in the solution and the distribution is not given by the Maxwell-Boltzmann equation. We must therefore resort to the equation of continuity (2-3-2), since the average values of the velocities $\mathbf{v}_{ji}$ and $\mathbf{v}_{ij}$ do not equal zero.

The total force, $\mathbf{K}_{ji}$, acting on the i ion will be given by

$$\mathbf{K}_{ji} = \mathbf{k}_i - e_i\nabla_2\psi_i'(0) - e_i\nabla_2\psi_j(\mathbf{r}_1, \mathbf{r}_{21}) \qquad (2\text{-}5\text{-}3)$$

In this equation, $\mathbf{k}_i$ is the applied external force. The second term on the right is the force (gradient of potential) on the i ion due to the atmosphere of this ion. Note that it is the potential at the origin ($r = 0$) or at the point occupied by the i ion. The third term is the force acting on the i ion due to the potential of the j ion (as origin) and its atmosphere. It is important to note that this estimate of the total force involves the assumption that the total field due to the ions and their atmospheres may be obtained by linear superposition of the separate fields.

Upon substituting equation (2-5-3) in (2-3-1), multiplying by f_{ji} and taking the divergence, we obtain

$$\begin{aligned} \nabla_2\cdot(f_{ji}\mathbf{v}_{ji}) = \nabla_2\cdot[(f_{ji}\mathbf{V}(\mathbf{r}_2)) + \omega_i(f_{ji}\mathbf{k}_i - e_if_{ji}\nabla_2\psi_i'(0) \\ - e_if_{ji}\nabla_2\psi_j - kT\nabla_2f_{ji})] \end{aligned} \qquad (2\text{-}5\text{-}4)$$

Upon expansion, a few terms may be eliminated. For all cases to be considered, both the velocity of the solution as a whole and the external electrical field are maintained constant, and therefore, since $\nabla_2\cdot\mathbf{V}(\mathbf{r}_2) = 0$, and $\nabla_2\cdot\mathbf{k}_i = 0$, two terms vanish. The term containing $\nabla_2\psi_i'(0)$ may be neglected since it is of the order of e_i^2, and the terms retained are of the order e_i [See Equation (2-4-17)]. Further, according to equation (2-4-20), $f_{ji} - n_jn_i$ is of the order of e_i. Hence, in the expression $e_if_{ji}\nabla_2\psi_j$, f_{ji} may be replaced by n_jn_i, and since $\nabla_2 n_jn_i$ is zero, the term $\nabla_2\cdot[e_i\omega_in_jn_i\nabla_2\psi_j]$

reduces to $e_i\omega_i n_j n_i \nabla_2 \cdot \nabla_2 \psi_j$. Upon making these reductions, equation (2-5-4) becomes

$$\begin{aligned}\nabla_2 \cdot (f_{ji}\mathbf{v}_{ji}) = \mathbf{V}(\mathbf{r}_2)\cdot\nabla_2 f_{ji} + \omega_i(\mathbf{k}_i\cdot\nabla_2 f_{ji}) \\ - e_i\omega_i n_j n_i \nabla_2\cdot\nabla_2\psi_j - \omega_i kT\nabla_2\cdot\nabla_2 f_{ji}\end{aligned} \tag{2-5-5}$$

A similar equation for $\nabla_1\cdot(f_{ij}\mathbf{v}_{ij})$ may be obtained. In order to obtain the desired form of the equation of continuity, these values are substituted in equation (2-2-3), and some further reductions made. Both f_{ji}, f_{ij}, and ψ_j, ψ_i are replaced by use of equations (2-5-1). Since for the equilibrium state $\mathbf{k}_i = 0$, $\mathbf{k}_j = 0$, when $\mathbf{v}_{ji} = 0$ and $\mathbf{v}_{ij} = 0$, we find by use of equations (2-3-1) and (2-5-3) that $\omega_i kT\nabla_2\cdot\nabla_2 f^0_{ji} = -\omega_i n_j n_i e_i \nabla_2\cdot\nabla_2\psi^0_i$ and $\omega_j kT\nabla_1\cdot\nabla_1 f^0_{ij} = -\omega_j n_i n_j e_j \nabla_1\cdot\nabla_1\psi^0_j$, whence four terms disappear by cancellation. The final equation of continuity, which is sufficiently general for all further discussion of irreversible processes in electrolytic solutions, is

$$\begin{aligned}&\mathbf{V}(\mathbf{r}_2)\cdot\nabla_2 f_{ji} + \mathbf{V}(\mathbf{r}_1)\cdot\nabla_1 f_{ij} \\ &\quad + \omega_i(\mathbf{k}_i\cdot\nabla_2 f_{ji}) + \omega_j(\mathbf{k}_j\cdot\nabla_1 f_{ij}) \\ &\quad - e_i\omega_i n_j n_i \nabla_2\cdot\nabla_2\psi'_j - e_j\omega_j n_i n_j \nabla_1\cdot\nabla_1\psi'_i \\ &\quad - \omega_i kT\nabla_2\cdot\nabla_2 f'_{ji} - \omega_j kT\nabla_1\cdot\nabla_1 f'_{ij} \\ &\quad = -\frac{\partial f_{ji}(\mathbf{r}_1, \mathbf{r}_{21})}{\partial t} = -\frac{\partial f_{ij}(\mathbf{r}_2, \mathbf{r}_{12})}{\partial t} \qquad \text{(For non-stationary fields)} \\ &\quad = 0 \qquad \text{(For stationary fields)}\end{aligned} \tag{2-5-6}$$

With the exception of the theory of the Wien effect [Chapter (4), Section (5)], $\mathbf{V}(\mathbf{r}_1)$, $\mathbf{V}(\mathbf{r}_2)$, $\mathbf{k}_i$ and $\mathbf{k}_j$ are sufficiently small to permit the replacement of f by f^0 in the first four terms.

(6) General Consideration of the Behavior of Ionic Atmospheres in Perturbed States

Equation (2-5-6) is of sufficient generality for treating the theory of viscosity, conductance and diffusion of electrolytes. The first four terms contain the perturbing factors and the last four the asymmetric contributions to the potentials. The differential equations for the potentials, from which the forces causing the motion of the ions may be computed, can be obtained by elimination of the distribution functions f'_{ji} and f'_{ij} by means of the Poisson equation (2-5-2).

Equation (2-5-6) may be specialized for a particular problem. Thus, in the case of viscosity, the terms containing the bulk velocities $\mathbf{V}(\mathbf{r}_2)$ and $\mathbf{V}(\mathbf{r}_1)$ are retained, while those containing the external perturbing forces, $\mathbf{k}_i$ and $\mathbf{k}_j$, are omitted. The contribution to the viscosity due to the ions can be shown to be related to the potentials derivable from equation (2-5-6), and can be computed by suitable mathematical procedures.

In dealing with conductance and diffusion, the first two terms of equation (2-5-6), which contain the bulk velocities, may be omitted. The perturbing forces, $\mathbf{k}_i$ and $\mathbf{k}_j$, are the applied external fields in the case of conductance, and the gradients of the thermodynamic potentials in the case of diffusion. As the ion moves in the field, it drags its atmosphere with it and the resulting effect is a lowering of its mobility. The extent of this effect may be computed by evaluating the potentials by equation (2-5-6), and subsequently the forces upon the ions. However, there is another effect due to the motion of solvent with respect to the ion, called "electrophoresis," which must be computed independently and added to the influence of the asymmetric ionic atmospheres.

All these considerations apply to the stationary cases of constant external fields, where f_{ij} and f_{ji} do not vary with time. However, there are some phenomena which necessitate an investigation of the non-stationary case, and which require that the left side of equation (2-5-6) equal $\dfrac{-\partial f_{ji}(\mathbf{r}_1, \mathbf{r}_{21})}{\partial t}$ instead of zero.

If the ionic atmosphere becomes asymmetric because of a perturbing field and if this field is removed, the atmosphere will revert to its original spherical form. This reverse change will require a finite time which is denoted "the time of relaxation" of the atmosphere.

If the electrolytic solution is exposed to an alternating field of a frequency of the order of magnitude of this time of relaxation, the atmosphere will not have a chance to assume an asymmetric distribution, and the change in mobility of the ions, due to asymmetry of the atmospheres, will be less than in the stationary case. This idea is fundamental in the theory of Debye and Falkenhagen of the effect of high frequencies upon the conductances of the ions. Equation (2-5-6), modified for the non-stationary case, is the starting point for this theory.

There is still another important phenomenon which will require our attention. If a solution of an electrolyte is subjected to a high field, the central ions will be drawn out of their atmospheres. This will increase the conductances of the ions, since they no longer drag their atmospheres with them. This phenomenon, known as the Wien effect, may be treated theoretically by means of equation (2-5-5).

The application of equation (2-5-6) to the viscosity, conductance and diffusion will be undertaken in Chapter (4). The simpler theories of the thermodynamic properties will be presented in detail in the next chapter.

Chapter (3)

Theory of the Thermodynamic Properties of Electrolytic Solutions

A comprehensive theory of the thermodynamic properties of dilute ionic solutions will now be developed by combination and extension of the theoretical equations for the equilibrium case [Chapter (2), Section (4)] with the thermodynamic relations given in Chapter (1). The limiting laws for the variation with concentration of the activity and osmotic coefficients, relative partial molal heat content, heat capacity, expansibility and compressibility will be derived. Extension of the theory to include the effect of the finite sizes of the ions will be made. Further extension of the theory which avoids the approximation made in neglecting the higher terms in the expansion of the exponential function in equation (2-4-8) will be stated, and the theory which attempts to estimate the effect of ionic association will be discussed. The theory of the electrostatic contribution to the surface tension of the solution will be given in a condensed form. Finally, the theories of the salting effect of ions upon neutral molecules will be discussed.

(1) PROPERTIES OF $1/\kappa$

Considerations of the distribution of ions regarded as point charges have led to the conception that on the average each ion has in its neighborhood an excess of ions of opposite sign, and that this condition produces an electrical potential which, in the electrolyte solution undisturbed by external forces, we have designated ψ_j^{0*}. Upon the assumption that the Maxwell-Boltzmann distribution is maintained, and by employing the approximation represented by equation (2-4-9), we arrived at the very important first approximation of the Debye and Hückel theory represented by equation (2-4-19),

$$\psi_j^{0*} = \frac{-z_j \epsilon \kappa}{D} \tag{2-4-19}$$

where κ was defined by

$$\kappa^2 \equiv \frac{4\pi \epsilon^2}{DkT} \sum_{i=1}^{s} n_i z_i^2 \tag{2-4-11}$$

The quantity, κ, possesses the dimensions of a reciprocal distance, and $1/\kappa$ is related to the potential of the ionic atmosphere, ψ_j^{0*}, as r is related to the potential ψ of a lone particle of charge e_j in a medium of dielectric constant D.

The concentration, c_i, of an ion in mols per liter of solution is related to n_i (ions per cc.) by

$$c_i = \frac{1000\, n_i}{N} \tag{3-1-1}$$

where N is Avogadro's number. Consequently, by (2-4-11),

$$\kappa = \left(\frac{4\pi \epsilon^2 N}{1000\, DkT}\, \Gamma\right)^{1/2} \tag{3-1-2}$$

if we represent the so-called "ional" concentration by

$$\Gamma \equiv \sum_1^s c_i z_i^2 \tag{3-1-3}$$

Upon substitution of the numerical values of the constants, we find that

$$\frac{1}{\kappa} = 2.811 \times 10^{-10} \sqrt{\frac{DT}{\Gamma}}\ \text{cm} \tag{3-1-4}$$

in general, and for the particular case of a 1-1 electrolyte in water at 25°

$$\frac{1}{\kappa} = \frac{3.041 \times 10^{-8}}{\sqrt{c}} \tag{3-1-5}$$

Thus in a normal solution $1/\kappa$ is of the order of a molecular diameter. Owing to the relation involving the square root of c, we note that $1/\kappa$ increases ten times for a hundredfold decrease in concentration.

(2) METHODS OF COMPUTING THE WORK CONTENT AND CHEMICAL POTENTIAL

The electrical contribution to the work content, ΔA, [Equation (1-2-2)] of n_j ions and their atmospheres is given by

$$W(\text{el}) = \Delta A(\text{el}) = \sum_{j=1}^{n_j} \int_0^{e_j} \psi(e_j)\, de. \tag{3-2-1}$$

Thus, if an uncharged ion at constant composition is charged reversibly in a field of a potential, $\psi(e_j)$ depends on the instantaneous charge e. The charging process of Debye, which is represented by

$$W(\text{el}) = \Delta A(\text{el}) = \sum_{j=1}^{n_j} \int_{\lambda=0}^{\lambda=1} e_j \psi(\lambda e_j)\, d\lambda \tag{3-2-2}$$

follows directly from this equation if we represent the instantaneous charge by λe_j.

From the definition of the chemical potential, μ_j, given by equation

(1-2-7), another "charging process" follows immediately from (3-2-1) such that the electrical contribution to this quantity for an ion is

$$\Delta\mu_j(\mathrm{el}) = \left(\frac{\partial \Delta A(\mathrm{el})}{\partial n_j}\right)_{V,T} = \int_0^{z_j\epsilon} \psi(e_j)\,de \qquad (3\text{-}2\text{-}3)$$

which was pointed out by Güntelberg.[1] Provided the approximation represented by equation (2-4-9) and the first approximation for ψ_j^{0*} given by equation (2-4-19) are employed, these two charging processes lead to the same result. On the other hand, if the integration of the Poisson-Boltzmann equation (2-4-8) is made without using this approximation, the Debye and Güntelberg charging processes lead to somewhat different results. This fact was mentioned by Gronwall, LaMer and Sandved,[2] who developed the complete integration and employed the Debye charging process. They obtained a somewhat different result than Müller,[3] who used the simpler Güntelberg method. In a theoretical analysis of this difficulty, Onsager[4] arrived at the conclusion that the discrepancy is due to the limitation of the Poisson-Boltzmann equation at higher concentrations where the potentials of the ionic atmospheres can no longer be expected to be additive.

(3) THE CHARGING PROCESS AND THE CALCULATION OF THE ELECTROSTATIC CONTRIBUTION TO THE CHEMICAL POTENTIAL

From the fundamental assumption of the linear superposition of ionic atmospheres, it followed that the potential of the ionic atmosphere is proportional to the charge, or

$$a\psi_j^{0*} = e_j \qquad (3\text{-}3\text{-}1)$$

where a is a proportionality factor. If the charging process given by equation (3-2-3) is employed, the electrostatic contribution to the chemical potential of a j ion is given by

$$\Delta\mu_j(\mathrm{el}) = \int_0^{z_j\epsilon} \psi_j^{0*}(e_j)\,de_j = \int_0^{\psi_j^{0*}} a\psi_j^{0*}\,d\psi_j^{0*} = \frac{a\psi_j^{0*}\psi_j^{0*}}{2} = \frac{z_j\epsilon\psi_j^{0*}}{2} \qquad (3\text{-}3\text{-}2)$$

Upon substitution of the value of ψ_j^{0*} obtained from (2-4-19),

$$\Delta\mu_j(\mathrm{el}) = -\frac{(z_j\epsilon)^2\kappa}{2D} \qquad (3\text{-}3\text{-}3)$$

(4) THE LIMITING LAW FOR THE VARIATION OF THE ACTIVITY COEFFICIENT

According to equation (1-8-9), we have

$$\bar{F} = \nu RT \ln f_\pm + \nu RT \ln N_\pm + \bar{F}_N^0 \qquad (1\text{-}8\text{-}5)$$

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[1] E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

[2] T. H. Gronwall, V. K. LaMer and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

[3] H. Müller, *Ibid.*, **28**, 324 (1927); **29**, 78 (1928).

[4] L. Onsager, *Chem. Rev.*, **13**, 73 (1933).

$\bar{F}$ can be divided into two parts, as follows:

$$\bar{F}_N = \nu RT \ln N_\pm + \bar{F}_N^0 \tag{3-4-1}$$

$$\bar{F}_f = \nu RT \ln f_\pm \tag{3-4-2}$$

The first of these relations is of the form of the limiting law for dilute solutions of un-ionized solutes, and would presumably apply to solutions of electrolytes as well, were it not for the charges on the ions.

It is therefore assumed that, for completely ionized electrolytes in dilute solution, the deviation of electrolytic solutions from ideality can be attributed entirely to electrostatic forces between the ions. This is equivalent to identifying $\bar{F}_f$ with $N\Delta\mu(\text{el})$ for any ion. Hence,

$$\Delta\mu_j(\text{el}) = kT \ln f_j = -\frac{(z_j\epsilon)^2\kappa}{2D} \tag{3-4-3}$$

By substituting the value of κ from (3-1-2) and rearranging terms, we obtain

$$\ln f_j = -z_j^2\left(\frac{\pi N\epsilon^6}{1000\,(DkT)^3}\right)^{1/2}\sqrt{\Gamma} \tag{3-4-4}$$

as the limiting expression for the activity coefficient of an ion (of an arbitrary kind j) in a solution containing s kinds of ions at concentrations $n_1, n_2, \cdots n_s$ per cc.

The mean activity coefficient of an electrolyte dissociating into p kinds of ions is

$$\ln f_\pm = \frac{1}{\nu}\sum_1^p \nu_j \ln f_j \tag{3-4-5}$$

by (1-8-4), where the dissociation of one molecule of electrolyte produces a total number of ions, ν, of which ν_j are of the j kind. Combining this equation with (3-4-4), we obtain

$$\ln f_\pm = -\frac{1}{\nu}\sum_1^p \nu_j z_j^2\left(\frac{\pi N\epsilon^6}{1000\,(kDT)^3}\right)^{1/2}\sqrt{\Gamma} \tag{3-4-6}$$

For convenience we convert this equation to decadic logarithms, and introduce the numerical values of the constants, writing

$$\log f_\pm = -\mathfrak{S}_{(f)}\sqrt{\Gamma} \tag{3-4-7}$$

where

$$\mathfrak{S}_{(f)} = \frac{1}{\nu}\sum_1^p \nu_j z_j^2 (DT)^{-3/2}\, 1.283 \times 10^6 \tag{3-4-8}$$

The symbol $\mathfrak{S}$, with appropriate subscripts, will be used exclusively to represent the limiting slopes of the theoretical equations, in their most general form, which are derived from considerations of interionic attraction. $\mathfrak{S}$ is always associated with $\sqrt{\Gamma}$, and is usually applicable to solutions of mixed electrolytes. In solutions containing a single electrolyte, Γ is proportional to c, and it is convenient to rewrite the theoretical equations in terms of $\sqrt{c}$. This requires a redefinition of the limiting slopes, and we employ the symbol $\mathcal{S}$ for this purpose in Chapter (5).

In the very important, though special, case for which $p = 2$, the valence factor in $\mathfrak{S}_{(f)}$ reduces to $|z_1z_2|$†, and we write

$$\mathfrak{S}_{(f)} = |z_1z_2|(DT)^{-3/2}1.283 \times 10^6; \quad p = 2 \tag{3-4-8a}$$

Equations (3-4-6) to (3-4-8) represent the Debye-Hückel "limiting law" for activity coefficients in its most general form. It requires that the logarithm of the activity coefficient of an electrolyte, at extreme dilution, decreases linearly with the square root of Γ. It is important to remember that Γ is a function of *all* the ions $1, \cdots i, \cdots s$ in the solution, regardless of source, while the summation involved in $\mathfrak{S}$ is confined to the ions $1, \cdots j, \cdots p$ resulting from the dissociation of the electrolyte to which $f_\pm$ refers. Since we have retained only two terms in the expansion used to evaluate ψ_i^0, and assumed that the deviation in the behavior of electrolytic solutions from ideality may be attributed entirely to Coulomb forces between the ions, we cannot expect these equations to be *strictly* valid at measurable concentrations. We have, however, good reason to expect them to represent accurately the limiting behavior of electrolytes as the ional concentration is made to approach zero.

An important feature of "the limiting slope," $\mathfrak{S}_{(f)}$, is its unambiguous definition in terms of fundamental physical constants: the absolute temperature, the dielectric constant of the solvent, and the valence type of the electrolyte under consideration.

Before leaving this section it will be necessary to rewrite the limiting law in several very useful forms for future reference. For many purposes it is convenient to employ γ, the activity coefficient corresponding to molal concentrations (mols per kilo of solvent), rather than the rational activity coefficient f. By equations (1-8-13) and (3-4-7),

$$\log \gamma_\pm = -\mathfrak{S}_{(f)}\sqrt{\Gamma} - \log\left(1 + \frac{\nu m M}{1000}\right) \tag{3-4-9}$$

but for dilutions at which this equation approaches validity, the last term on the right‡ may be dropped. Since $c_i = m_i\left(d - \frac{c_i M}{1000}\right)$, $c_i = m_i d_0$,

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† The presence of bars in the expression $|z_1z_2|$ indicates the magnitude of the valence product irrespective of the signs of the valencies.

‡ This term is written for the single electrolyte in solution. If the solution contains several electrolytes of concentrations, $m_1, m_2, \cdots$, it may be generalized to read:

$$-\log\left(1 + \frac{\Sigma \nu m M}{1000}\right)$$

at extreme dilution. Γ, the ional concentration, is therefore related to the "ionic strength,"

$$\mu \equiv \frac{1}{2}\sum_{1}^{s} m_i z_i^2, \tag{3-4-10}$$

by

$$\Gamma = \sum_{1}^{s} c_i z_i^2 = d_0 \sum_{1}^{s} m_i z_i^2 = 2d_0\mu; \qquad c \ll 1 \tag{3-4-10a}$$

Consequently,

$$\log \gamma_{\pm} = -\mathcal{S}_{(f)}\sqrt{2d_0\mu} \tag{3-4-11}$$

Finally, by rearranging equation (3-4-6) or by combining (3-4-3) directly with (3-4-5) we may write

$$\ln f_{\pm} = -\left(\frac{1}{\nu}\sum_{1}^{p}\nu_j z_j^2\right)\frac{\epsilon^2\kappa}{2kDT} \tag{3-4-12}$$

in general, and

$$\ln f_{\pm} = -\frac{|z_1 z_2|\epsilon^2\kappa}{2kDT} \tag{3-4-13}$$

for an electrolyte dissociating into two kinds of ions only. In applying the limiting equations for calculating partial molal quantities, we shall require equation (3-4-6) in the form

$$\ln f_{\pm} = -\frac{1}{\nu}\sum_{1}^{p}\nu_j z_j^2\,\frac{2.457 \times 10^{14}}{R(DT)^{3/2}}\sqrt{\Gamma} \tag{3-4-14}$$

and, by combination with (3-4-8), obtain the useful relation

$$2.303\nu R\mathcal{S}_{(f)} = \sum_{1}^{p}\nu_j z_j^2\,\frac{2.457 \times 10^{14}}{(DT)^{3/2}} \tag{3-4-15}$$

(5) THE EFFECT OF THE APPARENT DIAMETERS OF THE IONS. EQUATIONS FOR THE ACTIVITY AND OSMOTIC COEFFICIENTS

In the previous discussion of the Debye and Hückel development of the Poisson-Boltzmann equation, we regarded the ions as point charges. We shall now consider a modification of the theory, which does not disregard the finite size of the ions, and introduce an ionic parameter "*a*." This parameter is the minimum average distance to which ions, both positive and negative, can approach one another. It has been pointed out that the primitive of the Poisson-Boltzmann equation is

$$\psi_j^0(r) = \frac{Ae^{-\kappa r}}{r} \tag{2-4-14}$$

$\psi_j^0(r)$ is the potential of the ion and its atmosphere, and may also be written

$$\psi_j^0(r) = \frac{z_j\epsilon}{Dr} + \psi^*(r) \tag{3-5-1}$$

where the first term on the right is the potential at r due to point charge $z_j\epsilon$ and $\psi^*(r)$ represents the potential of the ionic atmosphere at this distance.

Consequently,

$$\psi^*(r) = \frac{Ae^{-\kappa r}}{r} - \frac{z_j\epsilon}{Dr} \tag{3-5-2}$$

In order that the field be continuous when r equals the average minimum distance of approach a_j, it is necessary for the field of the ion and its atmosphere, $\partial\psi_j^0(r)/\partial r$, to equal the field of the ion alone, $-z_j\epsilon/Dr^2$ when $r = a_j$. This condition is satisfied if

$$\left(\frac{\partial\psi^*(r)}{\partial r}\right)_{r=a_j} = -\frac{Ae^{-\kappa a_j}}{a_j^2}(1 + \kappa a_j) + \frac{z_j\epsilon}{Da_j^2} = 0$$

whence

$$A = \frac{z_j\epsilon}{D}\frac{e^{\kappa a_j}}{1 + \kappa a_j} \tag{3-5-3}$$

Consequently,

$$\psi^*(r) = \frac{z_j\epsilon}{Dr}\left(\frac{e^{\kappa a_j}}{1 + \kappa a_j}e^{-\kappa r} - 1\right) \tag{3-5-4}$$

and

$$\psi^*(a_j) = -\frac{z_j\epsilon}{D}\frac{\kappa}{1 + \kappa a_j} \tag{3-5-5}$$

It is to be noted that this differs from the value of ψ_j^{0*} given by (2-4-19) by a factor $\dfrac{1}{1 + \kappa a_j}$. If we now assume that the potential is proportional to the charge, and employ the Güntelberg charging process [Equation (3-2-3)], we obtain

$$\Delta\mu_j(\text{el}) = -\frac{(z_j\epsilon)^2}{2D}\frac{\kappa}{1 + \kappa a_j} \tag{3-5-6}$$

for the chemical potential and

$$\ln f_j = -\frac{(z_j\epsilon)^2}{2DkT}\frac{\kappa}{1 + \kappa a_j} \tag{3-5-7}$$

for the activity coefficient of an ion. By the same procedure by which equation (3-4-7) was obtained, $\log f_\pm$ of an electrolyte (dissociating into two kinds of ions) is given by

$$\log f_{\pm} = -\frac{\mathfrak{S}_{(f)}\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} \qquad (3\text{-}5\text{-}8)$$

where $\mathfrak{S}_{(f)}$ is given by equations (3-4-8) and (3-4-8a) and

$$\begin{aligned} A \equiv \frac{a\kappa}{\sqrt{\Gamma}} &= \frac{35.57 \times 10^{8} a}{(DT)^{1/2}}; \quad a \text{ in cm.} \\ &= \frac{35.57 \times \mathring{a}}{(DT)^{1/2}}; \quad \mathring{a} \text{ in Ångstrom units} \end{aligned} \qquad (3\text{-}5\text{-}9)$$

It is important to note that as Γ approaches zero, equation (3-5-8) approaches the limiting law derived for point charges.

The theoretical equations for the osmotic coefficient may be derived by combining any of the above expressions for $\ln f_j$ with equation (1-9-12), or (1-9-12a). Thus, equation (1-9-12a) can be written

$$\phi = 1 + \frac{1}{\sum c_j}\int \sum c_j \, d\ln f_j \qquad (3\text{-}5\text{-}10)$$

because $c_j = m_j d_0$, and $\gamma_j = f_j$ at high dilution. Introducing the value of $d \ln f_j$ obtainable from (3-4-4), integration leads to the general limiting equation

$$\phi = 1 - \left(\frac{\pi N \epsilon^{6}}{1000\,(DkT)^{3}}\right)^{1/2} \frac{\left(\sum c_j z_j^2\right)^{3/2}}{3\sum c_j} \qquad (3\text{-}5\text{-}11)$$

for ϕ (or g) which is applicable to solutions containing any number of ionized solutes. This equation is rarely used. If we consider the important special case of solutions of a single electrolyte, where $\sum c_j = \nu c$, and $\sum c_j z_j^2 = c \sum \nu_j z_j^2 = \Gamma$, equations (3-4-6) and (3-4-8) may be introduced to simplify the result. In this case, equation (3-5-11) reduces to

$$\phi = 1 + (1/3)\ln f_{\pm} = 1 - (1/3)2.303\mathfrak{S}_{(f)}\sqrt{\Gamma} \qquad (3\text{-}5\text{-}12)$$

This result is also obtained by combining equations (3-4-6) and (3-4-8) directly with (1-9-12), and performing the integration.

A more detailed derivation and discussion of the theoretical equations for ϕ will be given in chapter (9), section (5), where the dependence of ϕ upon the parameter A of equation (3-5-8) is considered.

(6) THE DEVELOPMENT OF THE EXTENDED TERMS OF THE DEBYE AND HÜCKEL THEORY ACCORDING TO GRONWALL, LAMER AND SANDVED

The fundamental equation of the Debye and Hückel theory has been shown to be

$$\nabla \cdot \nabla \psi_j^0 = -\frac{4\pi}{D}\sum_{i=1}^{s} n_i e_i \exp\left(-\psi_j^0 e_i/kT\right) \qquad (2\text{-}4\text{-}8)$$

Up to the present, we have employed the approximation

$$\exp\left(-e_i\psi_j^0/kT\right) \simeq 1 - e_i\psi_j^0/kT \tag{2-4-9}$$

obtained from the first two terms of the expansion of the exponential function. Let us consider an electrolyte at a concentration of n molecules per cc. which dissociates into two kinds of ions. Then

$$\begin{aligned}\sum_1^2 n\nu_i e_i \exp\left(-e_i\psi_j^0/kT\right) &= n[\nu_1 \,|\, e_1 \,|\, \exp\left(-\,|\, e_1 \,|\, \psi_j^0/kT\right) - \nu_2 \,|\, e_2 \,|\, \exp\left(|\, e_2 \,|\, \psi_j^0/kT\right)] \qquad (3\text{-}6\text{-}1)\\ &= n\nu_1 \,|\, e_1 \,|\, [\exp\left(-\,|\, e_1 \,|\, \psi_j^0/kT\right) - \exp\left(|\, e_2 \,|\, \psi_j^0/kT\right)]\end{aligned}$$

since $\nu_1 \,|\, e_1 \,| = \nu_2 \,|\, e_2 \,|$.

Now if $|\, e_1 \,|$ equals $|\, e_2 \,|$, the expression in brackets is the negative of twice the hyperbolic sine of $|\, e_1 \,|\, \psi_j^0/kT$ and consequently, the summation is given by

$$-2n\nu \,|\, e_1 \,| \left[\frac{|\, e_1 \,|\, \psi_j^0}{kT} + \frac{1}{3}\left(\frac{|\, e_1 \,|\, \psi_j^0}{kT}\right)^3 + \frac{1}{5}\left(\frac{|\, e_1 \,|\, \psi_j^0}{kT}\right)^5 + \cdots\right] \tag{3-6-2}$$

It becomes apparent that for symmetrical types of electrolytes we have previously neglected the effects of terms of the 3rd, 5th and higher odd-numbered orders. Further, it is likewise apparent that for cases of unsymmetrical valence type electrolytes terms of even as well as odd-numbered orders must be considered. The complete treatment of this problem is to be found in the contributions of Gronwall, LaMer, and Sandved,[5] who developed the equation for the symmetrical type of electrolyte, and of LaMer, Gronwall, and Greiff,[6] who considered the unsymmetrical type. Because of the mathematical complexity, we shall not consider this development in detail, but shall write their final equations and discuss the character of the effects which can be attributed to the inclusion of the higher terms.

For electrolytes of symmetrical valence types, $(|\, z_1 \,| = |\, z_2 \,|)$, the extended equation for $\ln f_\pm$ is found to be

$$\begin{aligned}\ln f_\pm = &-\frac{(\epsilon z)^2}{2DkT}\frac{\kappa}{1+\kappa a}\\ &+ \sum_{m=1}^{\infty}\left(\frac{\epsilon^2 z^2}{DkTa}\right)^{2m+1}\left[\tfrac{1}{2}X_{2m+1}(\kappa a) - 2mY_{2m+1}(\kappa a)\right]\end{aligned} \tag{3-6-3}$$

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[5] T. H. Gronwall, V. K. LaMer, and K. Sandved, *Physik. Z.*, **29**, 358 (1929).

[6] V. K. LaMer, T. H. Gronwall and L. J. Greiff, *J. Physical Chemistry*, **35**, 2245 (1931).

which when expanded to include all terms up to the fifth order becomes

$$\ln f_{\pm} = -\frac{(\epsilon z)^2}{2DkT}\frac{\kappa}{1+\kappa a} + \left(\frac{\epsilon^2 z^2}{DkTa}\right)^3 [\tfrac{1}{2}X_3(\kappa a) - 2Y_3(\kappa a)] + \left(\frac{\epsilon^2 z^2}{DkTa}\right)^5 [\tfrac{1}{2}X_5(\kappa a) - 4Y_5(\kappa a)] \qquad (3\text{-}6\text{-}4)$$

The first term on the right is identical with (3-5-7) and (3-5-8), and represents the first approximation obtained by Debye and Hückel. The next two terms represent the contribution of the third and fifth order terms. $X_3(\kappa a)$, $Y_3(\kappa a)$, $X_5(\kappa a)$, and $Y_5(\kappa a)$ are complicated series functions of κa, the values of which have been obtained and tabulated by Gronwall, LaMer, and Sandved. The terms of the seventh order and higher were omitted by them.

From the character of the coefficients of the terms in brackets, the conditions for departure from the original Debye and Hückel theory become apparent. For electrolytes of high valence types (*e.g.*, 2-2, 3-3), and for electrolytes whose a values are small, deviations are to be expected. Further, in solvents of low dielectric constant, wide departure from the first approximation should be found.

For cases of unsymmetrical valence type electrolytes the situation, as found by LaMer, Gronwall and Greiff, is even more complicated. Thus,

$$\begin{aligned}\ln f_{\pm} = -\frac{|z_1 z_2|\,\epsilon^2}{2DkT}\frac{\kappa}{1+\kappa a} - |z_1 z_2| \Bigg\{ &\frac{1}{(10^8 a)^2}(z_1+z_2)^2 B_2(\kappa a) \\ &- \frac{1}{(10^8 a)^3}(z_1^2 - |z_1 z_2| + z_2^2)(z_1+z_2)^2 B_3^*(\kappa a) \\ &- \frac{1}{(10^8 a)^3}(z_1^2 - |z_1 z_2| + z_2^2)^2 B_3(\kappa a) - \cdots \Bigg\}\end{aligned} \qquad (3\text{-}6\text{-}5)$$

where

$$\begin{aligned} B_2(\kappa a) &= \left(\frac{10^8 \epsilon^2}{DkT}\right)^2 [\tfrac{1}{2}X_2(\kappa a) - Y_2(\kappa a)] \\ B_3^*(\kappa a) &= \left(\frac{10^8 \epsilon^2}{DkT}\right)^3 [\tfrac{1}{2}X_3^*(\kappa a) - 2Y_3^*(\kappa a)] \\ B_3(\kappa a) &= \left(\frac{10^8 \epsilon^2}{DkT}\right)^3 [\tfrac{1}{2}X_3(\kappa a) - 2Y_3(\kappa a)] \end{aligned} \qquad (3\text{-}6\text{-}6)$$

Numerical values of the bracketed terms have been tabulated by LaMer, Gronwall and Greiff. As a result of this equation, large departures from the Debye and Hückel first approximation are to be expected for cases of electrolytes of unsymmetrical types of higher valences, even in a medium of high dielectric constant such as water. Tables of all these special functions will be given in Chapter (5), Section (2).

(7) BJERRUM'S THEORY OF IONIC ASSOCIATION[7]

Soon after Debye and Hückel proposed their theory, Bjerrum, who realized the mathematical difficulties which would accompany the complete solution of the Poisson-Boltzmann equation as developed by Gronwall, LaMer and Sandved, suggested a much simpler improvement. The theory of Bjerrum develops from the consideration of the factors which determine the extent of ionic association or, more particularly, the formation of ion pairs under the influence of Coulombic forces. The simplest model is assumed. The ions are taken to be rigid unpolarizable spheres contained in a medium of a fixed macroscopic dielectric constant. Nonpolar quantum bonds between ions as well as ion-solvent interactions are excluded.

The probability that an i ion is at a distance r from a j ion is given according to the Maxwell-Boltzmann distribution law by

$$\text{Probability} = \frac{Nc_i}{1000} e^{U/kT} 4\pi r^2 dr \qquad (3\text{-}7\text{-}1)$$

$Nc_i/1000$ is the number of i ions per cc. of solution, and $4\pi r^2 dr$ is the volume of a spherical shell of thickness dr and radius r, circumscribing the j ion. U is the potential energy, or work of separating an i and j ion from r to infinity. At certain distances, U may be replaced by the simple Coulomb law,

$$U = -\frac{z_1 z_2 \epsilon^2}{Dr} \qquad (3\text{-}7\text{-}2)$$

with the result that the probability is given by

$$\text{Probability} = \frac{Nc_i}{1000}\left[\exp\left(\frac{-z_1 z_2 \epsilon^2}{DrkT}\right)\right] 4\pi r^2 dr \qquad (3\text{-}7\text{-}3)$$

This function possesses some interesting properties. If the ions are of like sign, the probability of ionic association is very low. If the ions are of opposite sign, the probability can be shown to possess a minimum at a distance q, such that,

$$r(\min) = q = \frac{\epsilon^2 |z_1 z_2|}{2DkT} \qquad (3\text{-}7\text{-}4)$$

from which it follows that q is the distance at which the energy of separation of the ions is $2kT$. For values of r less than q, the probability increases rapidly as r decreases. At values of r greater than q, the prob-

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[7] N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, 7, No. 9 (1926).

ability increases slowly. Bjerrum assumes that two ions at a distance of $r < q$ are associated. For 1-1 electrolytes in water at 18°, q equals 3.52 Å, and consequently electrolytes of this type, possessing values of the mean distance of approach of the ions, å, less than 3.5, will form short-range ion pairs. For 1-1 electrolytes, possessing values of å greater than 3.5 Å, the theory of Debye and Hückel is valid.[8]

Upon the basis of these considerations, two ions at a distance, r, less than q, will be associating, and the extent of ion pair formation will increase very rapidly with decreasing r. The degree of association, or $(1 - \alpha)$, will be given by the definite integral

$$(1 - \alpha) = \frac{4\pi Nc}{1000} \int_a^q e^{\frac{|z_1 z_2| \epsilon^2}{DrkT}} r^2 dr \tag{3-7-5}$$

The distance between the centers of the two ions forming the ion pair at their closest distance of approach is a. If we let

$$Y \equiv \frac{|z_1 z_2| \epsilon^2}{rDkT} \tag{3-7-6}$$

$$b \equiv \frac{|z_1 z_2| \epsilon^2}{aDkT} \tag{3-7-7}$$

and substitute in equation (3-7-5), we obtain

$$(1 - \alpha) = \frac{4\pi Nc}{1000} \left(\frac{|z_1 z_2| \epsilon^2}{DkT} \right)^3 \int_2^b e^Y Y^{-4}\, dY \tag{3-7-8}$$

$$= \frac{4\pi Nc}{1000} \left(\frac{|z_1 z_2| \epsilon^2}{DkT} \right)^3 Q(b). \tag{3-7-9}$$

where $Q(b)$ is defined by the integral

$$Q(b) \equiv \int_2^b e^Y Y^{-4}\, dY \tag{3-7-10}$$

From equations (1-10-7) and (1-10-8), the equilibrium constant, K^{-1}, for the formation of an ion pair is given by

$$K^{-1} = \frac{y_{12}(1 - \alpha)}{y_1 y_2 \alpha^2 c} \tag{3-7-11}$$

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[8] Long-range ion pairs, not considered by Bjerrum, have been discussed in a careful analysis of the whole theory by Fuoss.[9] For long-range pairs, the potential energy of an ion in relation to the nearest unpaired ion is very small compared to the energy of thermal motion. The total potential energy will be composed of a large number of small terms, which suggests the time average treatment of Debye and Hückel.

[9] R. M. Fuoss, *Chem. Rev.*, **17**, 27 (1935).

As the concentration decreases, the activity coefficient ratio approaches unity, α^2 approaches unity, and therefore

$$(1 - \alpha) = K^{-1}c \tag{3-7-12}$$

Thus, the reciprocal of the ionization constant of the associated ion pair is given by

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{|z_1 z_2| \epsilon^2}{DkT}\right)^3 Q(b) \tag{3-7-13}$$

Another deduction of this equation has been made by Fuoss and Kraus[10] by employing the somewhat less familiar, but more general, phase integral.

The integral $Q(b)$ reduces to

$$Q(b) = \int_2^b e^Y Y^{-4} dY = \frac{1}{6}\left\{e^2 - Ei(2) + Ei(b) - \frac{e^b}{b}\left(1 + \frac{1}{b} + \frac{2}{b^2}\right)\right\} \tag{3-7-14}$$

where $Ei(x)$ is the integral exponential function,

$$Ei(x) = \int_\infty^{-x} e^{-t} t^{-1}\, dt \tag{3-7-15}$$

Values of $Q(b)$ for the range, $1 \leq b \leq 15$, have been tabulated by Bjerrum from tables.[11] Values of $Q(b)$ in the range $15 \leq b \leq 80$ were obtained by Fuoss and Kraus by employing an asymptotic expansion of $Ei(x)$. The latter are not correct when b equals 15, but the error decreases rapidly with increasing b. Values of $Q(b)$ are given in Table (5-2-3).

In order to keep clearly in mind the various aspects of the phenomena of ionic association, or electrolyte dissociation, and to state the conditions under which Bjerrum's theory may be expected to be valid, a few general considerations will be of interest. We shall distinguish between two kinds of binding which will remove ions from the solution with the formation of neutral particles. For singly charged ions we may represent an association by

$$C^+ + A^- \rightleftharpoons [C^+A^-]^0 \rightleftharpoons CA$$

Here $[C^+A^-]^0$ denotes an ion pair and CA an undissociated molecule with a non-polar bond, the former being produced by the action of Coulombic forces only, and the latter by electronic linkage. Further reactions are possible such as the formation of a triple ion,

$$[C^+A^-]^0 + A^- \rightleftharpoons [A^-C^+A^-]^-$$
$$[C^+A^-]^0 + C^+ \rightleftharpoons [C^+A^-C^+]^+$$

and more complex ion aggregates.

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[10] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 1919 (1933).

[11] E. Jahnke and F. Emde, "Tables of Functions," Teubner, Berlin and Leipzig, 1938.

Bjerrum's theory is based entirely upon the range of validity of Coulombic forces, where the potential is given by $\psi(r) = \frac{e_1 e_2}{Dr}$, and upon the assumption that the ions act as rigid bodies. The variation of the potential as a function of r for this case is shown by Fig. (3-7-1) (a). Since e_1e_2 is negative and constant, $\psi(r)$ is negative and the plot is a hyperbola. At the minimum distance of approach of the positive and negative ions, $\psi(r)$ rises perpendicularly, indicating an infinite potential barrier. The distance for ion pair formation is that represented by $(q - a)$.

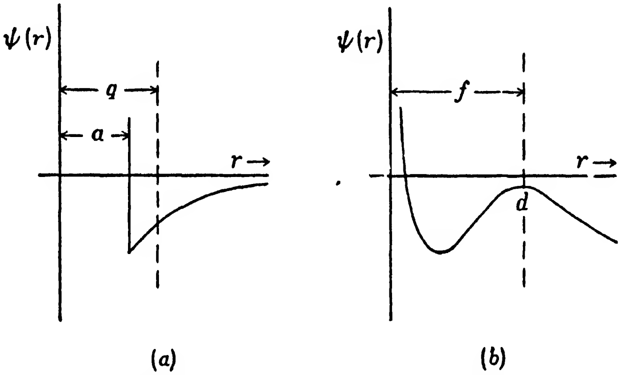

Fig. (3-7-1). Illustrating (a) Ionic association, and (b), Non-polar bond formation

Bjerrum's theory cannot be expected to be valid if undissociated molecules with non-polar linkages are found. For, consider a dissociation such as

$$HAc + H_2O \rightleftharpoons H_3O^+ + Ac^-$$

In this case, the variation of $\psi(r)$ with r, when $r < f$, is determined by quantum conditions, and is of the nature of the curve in Fig. (3-7-1) (b). Here, the molecular system on the left of the above reaction must possess sufficient energy to escape as ionic species, H_3O^+ and Ac^-, over the potential maximum at d.

These considerations lead to the conclusion that for weak electrolytes $\psi(r)$ is a much more complicated function of r than that postulated by Bjerrum's theory. On the other hand, we may expect this theory to hold in media of low dielectric constant for electrolytes which have sufficiently large a values. Indeed, we shall find numerous examples of its essential validity in subsequent discussions.

(7A) THE THEORY OF THE FORMATION OF TRIPLE IONS AND QUADRUPOLES ACCORDING TO FUOSS AND KRAUS[12]

By following the method of Bjerrum for the computation of ionic association, it is possible to obtain an expression for the dissociation constant, K_3, of the reactions

$$[A^-C^+A^-]^- \rightleftharpoons A^- + [A^-C^+]^0$$

$$[C^+A^-C^+]^+ \rightleftharpoons C^+ + [C^+A^-]^0$$

Consider a triple ion consisting of two negative and one positive ion, and assume the ions to be charged spheres. Of the various ways by which a triple ion can form, consider the approach of a negative ion to an ion pair. Let the distance between the ions of a pair be a; let θ be the angle between the extended axis of the pair and the line drawn to the center of the nearest negative ion from the center of the positive ion of the pair; and let r be the distance of the approaching negative ion from the positive ion. Then, the distance between the approaching negative ion and the negative ion of the pair will be $(r^2 + a^2 + 2ar \cos \theta)^{1/2}$, and the potential energy, U, of the negative ion will be

$$U = -\frac{e^2}{D}\left[\frac{1}{r} - \frac{1}{\sqrt{r^2 + a^2 + 2ar\cos\theta}}\right] \tag{3-7-16}$$

Considered as a function of θ, the minimum of potential energy, U_0, will occur when θ equals zero, so that

$$U_0 = -\frac{e^2}{D}\left[\frac{1}{r} - \frac{1}{a + r}\right] \tag{3-7-17}$$

Since the minimum in potential energy determines the maximum stability, the most favorable condition for triple ion formation occurs when all three ions lie in the same line.

The probability of finding a negative ion in dV_2 at a distance from the positive ion of an ion pair in dV_1 is given by

$$\begin{aligned}\text{Probability} &= ne^{-U/kT}dV_1dV_2 \\ &= ne^{-U_0/kT}e^{(U_0-U)/kT}dV_1dV_2\end{aligned} \tag{3-7-18}$$

where n is the number of free ions per unit volume. In polar coördinates, with the origin at the center of the positive ion, this expression may be changed to

$$\text{Probability} = ne^{-U_0/kT}e^{(U_0-U)/kT}2\pi r^2 \sin\theta d\theta dr dV_1 \tag{3-7-19}$$

The function $r^2e^{-U_0/kT}$ is a minimum at $r = R$, which is a root of the equation

$$\frac{1}{r} = \frac{2DkT}{e^2} + \frac{r}{(r+a)^2} \tag{3-7-20}$$

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[12] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 2387 (1933); **57**, 1 (1935).

If

$$x \equiv r/a_3\,; \qquad X \equiv R/a_3 \tag{3-7-21}$$

$$q = \frac{e^2}{2DkT}\,; \qquad b_3 \equiv \frac{e^2}{a_3DkT} \tag{3-7-21a}$$

be substituted in equation (3-7-20), we obtain

$$\frac{1 + 2x}{x(x + 1)^2} = \frac{a_3}{q} = \frac{2}{b_3} \tag{3-7-22}$$

The minimum corresponds to the root, X, of this equation. The parameters, a_3 and b_3, play the same part in triple ion formation as a and b in the theory of ion pairs.

In a manner analogous to that employed by Bjerrum for ion pair formation, we assume that triple ions are formed when $r \leq R$ and $\theta = 0$. When $r > R$, the triple ion is dissociated into an ion pair and an ion. The dissociation constant, K_3, of the triple ions is obtained from these considerations and equation (3-7-19) by the following integral:

$$K_3^{-1} = \frac{2\pi N}{1000}\int_{a_3}^{R} e^{-U_0/kT} r^2\, dr \int_0^{\pi} e^{(U_0-U)/kT} \sin\theta\, d\theta \tag{3-7-23}$$

Upon introducing the variable, x, defined by equation (3-7-21), this equation may be reduced to a form more suitable for numerical computation. Thus,

$$K_3^{-1} = \frac{2\pi N a_3^3}{1000}\int_1^{X} x^2 \exp\left(\frac{b_3}{x(x + 1)}\right) J(b_3, x)\, dx \tag{3-7-24}$$

$$= \frac{2\pi N a_3^3}{1000}\, I(b_3) \tag{3-7-25}$$

$J(b_3, x)$ includes the integration over θ, and is given by

$$J(b_3, x) = \int_{-1}^{+1} \exp\left[\frac{b_3}{x + 1}\left(1 - \frac{x + 1}{\sqrt{x^2 + 1 + 2xz}}\right)\right] dz \tag{3-7-26}$$

where $z = \cos\theta$. Fuoss and Kraus evaluated $J(b_3, x)$ as a function of x graphically, and then computed $I(b_3)$. In Table (5-2-4), their values of $I(b_3)$ are reproduced.

Fuoss and Kraus[13] have also developed a theory of ionic cluster dissociation represented by the scheme

$$\begin{bmatrix} C^+A^- \\ A^-C^+ \end{bmatrix}^0 \rightleftharpoons 2[C^+A^-]^0$$

Introducing the assumption that the quadrupole is an ellipsoid with axes a_4 and λa_4, with $\lambda < \sqrt{2}$, containing a dipole of strength μ at the center

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[13] R. M. Fuoss, J. Am. Chem. Soc., 56, 2017 (1934); R. M. Fuoss and C. A. Kraus, *Ibid.*, 57, 1 (1935).

and parallel to the major axis, they derived the expression

$$K_4^{-1} = \frac{N}{2000}\left(\frac{\pi}{3}\right)^{3/2}\frac{\mu^2}{DkT}\frac{e^y}{y^{7/2}}\left(\frac{1}{2\lambda^2} - 1\right)^{-1/2} \tag{3-7-27}$$

y is defined by the equation,

$$y \equiv \frac{\mu^2}{(\lambda a_4)^3 DkT} \tag{3-7-28}$$

(8) THE LIMITING EQUATIONS FOR THE RELATIVE PARTIAL MOLAL HEAT CONTENT AND RELATIVE PARTIAL MOLAL HEAT CAPACITY

From equation (1-7-5), and the definition of the activity coefficient, f, it follows that the relative partial molal heat content of one mol of electrolyte at a given temperature is given by

$$\bar{L}_2 \equiv \bar{H}_2 - \bar{H}_2^0 = -\nu RT^2\left(\frac{\partial \ln f_\pm}{\partial T}\right)_{P,N} \tag{3-8-1}$$

If we extend the concentration range of equation (3-5-8) by the addition of an empirical linear term, $B\Gamma$, the expression for $\ln f_\pm$ becomes

$$\ln f_\pm = -\frac{2.303\mathfrak{S}_{(f)}\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} + 2.303B\Gamma \tag{3-8-2}$$

where

$$\mathfrak{S}_{(f)} = \frac{1}{\nu}\sum_1^p \nu_j z_j^2 (DT)^{-3/2} 1.283 \times 10^6 \tag{3-8-3}$$

and

$$A = \mathring{a}(DT)^{-1/2} 35.57 \tag{3-8-4}$$

by equations (3-4-8) and (3-5-9). In performing the differentiation of equation (3-8-2) with respect to T and substitution into (3-8-1), the temperature variations of D, Γ, $\mathring{a}$ and B must all be considered, but it is convenient to have the familiar quantities $\mathfrak{S}_{(f)}$ and A appear in the final result. Accordingly,

$$\bar{L}_2 = \frac{\mathfrak{S}_{(H)}\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} + \frac{\mathcal{W}_{(H)}\Gamma}{(1 + A\sqrt{\Gamma})^2} + \mathcal{K}_{(H)}\Gamma \tag{3-8-5}$$

where

$$\mathfrak{S}_{(H)} = -2.303\nu RT^2\mathfrak{S}_{(f)}\frac{3}{2}\left\{\frac{1}{T} + \frac{\partial \ln D}{\partial T} + \frac{\alpha}{3}\right\} \tag{3-8-6}$$

$$\mathcal{W}_{(H)} = 2.303\nu RT^2\mathfrak{S}_{(f)}A\frac{1}{2}\left\{\frac{1}{T} + \frac{\partial \ln D}{\partial T} + \alpha - \frac{2\partial \ln \mathring{a}}{\partial T}\right\} \tag{3-8-7}$$

and

$$\mathcal{K}_{(H)} = -2.303\nu RT^2 B\left\{\frac{\partial \ln B}{\partial T} - \alpha\right\} \tag{3-8-8}$$

Numerical values of the above parameters in aqueous solutions are given in Table (5-2-5). The term α is the coefficient of thermal expansion of the solution, which by equation (8-6-5) has been written for $-\partial \ln \Gamma/\partial T$. Complete expressions analogous to equation (3-8-5) were derived by Harned and Ehlers[14] and Harned and Hecker[15] who demonstrated the importance of the contribution of the term containing B in moderately dilute solutions. At extreme dilutions the equation reduces to the limiting law

$$\bar{L}_2 = \mathcal{S}_{(H)} \sqrt{\Gamma} \tag{3-8-9}$$

which was originally derived by Bjerrum[16] without consideration for the variation of Γ with temperature, but later corrected for this effect.[17, 18] The sign of $\mathcal{S}_{(H)}$ is governed by the term $\partial \ln D/\partial T$, which is negative, and usually greater than $1/T$ by an amount exceeding $\alpha/3$. Therefore, for water and most (if not all) other solvents, the Debye-Hückel theory requires that $\bar{L}_2$ increases with the square root of the ional concentration at extreme dilution.

The relative partial molal heat capacity, $\bar{C}_{p_2} - \bar{C}^0_{p_2} \equiv \bar{J}_2$, is determined by differentiation of equations (3-8-1) or (3-8-5) with respect to temperature at constant pressure and composition. Thus, in general

$$\bar{J}_2 = \left(\frac{\partial \bar{L}_2}{\partial T}\right)_{P,N} = -\nu R \frac{\partial}{\partial T}\left\{T^2 \frac{\partial \ln f_\pm}{\partial T}\right\}$$

To avoid obtaining a too unwieldy expression for practical purposes, we shall consider only the limiting law

$$\bar{J}_2 = \mathcal{S}_{(C_p)} \sqrt{\Gamma} \tag{3-8-10}$$

derived by differentiation of (3-4-7) or (3-8-9). The limiting slope is given by

$$\mathcal{S}_{(C_p)} = 2.303\nu R\mathcal{S}_{(f)}\left\{X^2 - T\frac{\partial X}{\partial T} - \frac{1}{4}\right\} \tag{3-8-11}$$

where

$$X \equiv 1 + \frac{3}{2}T\frac{\partial \ln D}{\partial T} + \frac{1}{2}T\alpha \tag{3-8-12}$$

This expression is in suitable form for the evaluation of $\mathcal{S}_{(C_p)}$ in most solvents because it has been shown[19] that $\ln D$ is linear in T over a wide

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[14] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 2179 (1933).

[15] H. S. Harned and J. C. Hecker, *Ibid.*, **55**, 4838 (1933). The variable y which the authors define in their equation (11) should have an a written in the numerator.

[16] N. Bjerrum, *Z. physik. Chem.*, **119**, 145 (1926).

[17] G. Scatchard, *J. Am. Chem. Soc.*, **53**, 2037 (1931).

[18] O. Gatty, *Phil. Mag.* [7], **11**, 1082 (1931).

[19] G. Åkerlöf, *J. Am. Chem. Soc.*, **54**, 4125 (1932).

temperature range. The bracketed term of (3-8-11) may be written,

$$\frac{3}{4}\left\{1 + 2\frac{T}{D}\frac{\partial D}{\partial T} + 5\left(\frac{T}{D}\frac{\partial D}{\partial T}\right)^2 + \frac{2T^2}{DV}\frac{\partial D}{\partial T}\frac{\partial V}{\partial T} + \frac{2}{3}\frac{T}{V}\frac{\partial V}{\partial T} + \left(\frac{T}{V}\frac{\partial V}{\partial T}\right)^2 - \frac{2T^2}{D}\frac{\partial^2 D}{\partial T^2} - \frac{2}{3}\frac{T^2}{V}\frac{\partial^2 V}{\partial T^2}\right\} \tag{3-8-13}$$

which is the form usually appearing in the literature.[20, 21] In this expression α has been replaced by equivalent functions of V, which may be either the specific volume or the total volume of the solution.

(9) The Limiting Equations for the Relative Partial Molal Volume, Expansibility and Compressibility of an Electrolyte

According to equation (1-7-8), differentiated with respect to n_2, the partial molal volume of an electrolyte in solution is

$$\bar{V}_2 - \bar{V}_2^0 = \left(\frac{\partial(\bar{F}_2 - \bar{F}_2^0)}{\partial P}\right)_{T,N} = \nu RT\frac{\partial \ln f_\pm}{\partial P} \tag{3-9-1}$$

which by combination with (3-8-2) yields the general expression

$$\bar{V}_2 - \bar{V}_2^0 = \frac{\mathfrak{S}_{(v)}\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} + \frac{\mathcal{W}_{(v)}\Gamma}{(1 + A\sqrt{\Gamma})^2} + \mathcal{K}_{(v)}\Gamma \tag{3-9-2}$$

Equations (3-8-3) and (3-8-4) are used in evaluating the parameters

$$\mathfrak{S}_{(v)} = 2.303\nu RT\mathfrak{S}_{(f)}\cdot\frac{1}{2}\left\{\frac{3\partial \ln D}{\partial P} - \beta\right\} \tag{3-9-3}$$

$$\mathcal{W}_{(v)} = -2.303\nu RT\mathfrak{S}_{(f)}A\frac{1}{2}\left\{\frac{\partial \ln D}{\partial P} - \frac{2\partial \ln \mathring{a}}{\partial P} - \beta\right\} \tag{3-9-4}$$

and

$$\mathcal{K}_{(v)} = 2.303\nu RTB\left\{\frac{\partial \ln B}{\partial P} + \beta\right\} \tag{3-9-5}$$

The coefficient of compressibility, $\beta = \partial \ln \Gamma/\partial P$, is known for a number of solvents, but numerical values of $\partial \ln D/\partial P$ are generally not available. Fortunately, $\partial \ln D/\partial P$ is known for water at room temperatures. At present, we have no information whatever regarding the coefficients, $\partial \ln \mathring{a}/\partial P$ and $\partial \ln B/\partial P$, so that the last two terms of equation (3-9-2) cannot be evaluated. Accordingly, our use of this equation will be confined to extreme dilutions where the limiting law

$$\bar{V}_2 - \bar{V}_2^0 = \mathfrak{S}_{(v)}\sqrt{\Gamma} \tag{3-9-6}$$

is applicable.

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[20] V. K. LaMer and I. A. Cowperthwaite, *J. Am. Chem. Soc.*, **55**, 1004 (1933).

[21] F. T. Gucker, Jr., *Chem. Rev.*, **13**, 111 (1933).

The relative partial molal expansibility of an electrolyte in solution is defined by

$$\bar{E}_2 - \bar{E}_2^0 = \left(\frac{\partial(\bar{V}_2 - \bar{V}_2^0)}{\partial T}\right)_{P,N} \tag{3-9-7}$$

Differentiation of equation (3-9-6) with respect to temperature gives the corresponding limiting equation

$$\bar{E}_2 - \bar{E}_2^0 = \mathfrak{S}_{(E)}\sqrt{\Gamma} \tag{3-9-8}$$

in which[24]

$$\mathfrak{S}_{(E)} = -2.303\nu RT\mathfrak{S}_{(f)}\frac{1}{2}\left\{\frac{1}{2}\left(\frac{3\partial \ln D}{\partial P} - \beta\right)\left(\frac{3\partial \ln D}{\partial T} + \frac{1}{T} + \alpha\right) - \frac{\partial}{\partial T}\left(\frac{3\partial \ln D}{\partial P} - \beta\right)\right\} \tag{3-9-9}$$

At this point, it would be quite useless to derive a more general expression, similar to equation (3-9-2), because even the limiting slope, $\mathfrak{S}_{(E)}$, already contains the unknown temperature coefficient of $\partial \ln D/\partial P$. Gucker[24] has made an estimate of the order of magnitude of this term, and concludes that $\mathfrak{S}_{(E)}$ would be about $4 \times 10^{-13} \sum \nu_j z_j^2$ at 20°.

Similar considerations lead to a limiting expression for the apparent molal compressibility, defined by

$$\bar{K}_2 - \bar{K}_2^0 = -\frac{\partial(\bar{V}_2 - \bar{V}_2^0)}{\partial P} = \mathfrak{S}_{(K)}\sqrt{\Gamma} \tag{3-9-10}$$

The limiting slope[25] is given by

$$\mathfrak{S}_{(K)} = 2.303\nu RT\,\mathfrak{S}_{(f)}\frac{1}{4}\left\{\beta^2 + 2\frac{\partial\beta}{\partial P} - \frac{6\beta\,\partial \ln D}{\partial P} + 15\left(\frac{\partial \ln D}{\partial P}\right)^2 - \frac{6}{D}\frac{\partial^2 D}{\partial P^2}\right\} \tag{3-9-11}$$

Gucker has made a tentative estimate of the terms in this equation and obtained $\mathfrak{S}_{(K)} = 9.1 \times 10^{-4} \sum \nu_j z_j^2$ cc. per atmosphere at 25°.

(10) SALTING OUT AND SALTING IN OF MOLECULES OR ELECTROLYTES

It is well known that the addition of a salt to an aqueous solution containing a neutral molecule frequently tends to decrease its solubility. This corresponds to an increase in activity coefficient of the molecule. "Salting out" of this kind is not general, and examples of the reverse behavior of "salting in" may be found. A complete and reliable theory of these effects has not been developed, but it can be shown that the order

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[24] F. T. Gucker, Jr., *J. Am. Chem. Soc.*, **56**, 1017 (1934).

[25] F. T. Gucker, Jr., *Chem. Rev.*, **13**, 111 (1933).

of magnitude of the experimental results can be computed theoretically from the action of Coulombic forces without the inclusion of other factors.

Debye and McAulay[26] computed the partial free energy of a molecule relative to the pure solvent from the reversible electrical work. The ions are assumed to be rigid spheres. Later, Debye[27] developed a theory which is based upon the influence of ions on the distribution of the non-electrolyte molecules, and derived an expression for the concentration of these molecules as a function of the distance from an ion. This theory has been extended by Gross,[28] who incorporates the effect of the ionic atmosphere.

(a) Theory of Debye and McAulay

Consider an ion as a perfect sphere of radius b_j. Then, the potential at its surface will be given by e_j/Db_j. The work of charging n_j ions of this kind may be obtained from equation (3-2-2).

$$W(n_j) = \sum_1^{n_j} \int_{\lambda=0}^{\lambda=1} \frac{e_j^2 \lambda d\lambda}{Db_j} = \frac{n_j e_j^2}{2Db_j} \tag{3-10-1}$$

Let us consider a solution containing $n_1, \cdots n_j, \cdots n_s$ ions per cc., resulting from the dissociation of n' molecules of electrolyte, and compute the electrical work of discharging the ions at high dilution in a solvent (water) of dielectric constant D_0, and recharging them in a medium of dielectric constant D. The change in dielectric constant from D_0 to D may be produced by addition of either an electrolyte or a non-electrolyte to the solution. The net electrical work done on the system is

$$W'(n) = \sum_1^{s} \frac{n_j e_j^2}{2Db_j} - \sum_1^{s} \frac{n_j e_j^2}{2D_0 b_j} \tag{3-10-2}$$

Equation (2-4-19) permits a calculation of the additional electrical work done against the potential due to ionic atmospheres. Thus

$$\begin{aligned} W(\kappa) &= \sum_1^{s} \sum_1^{n_j} \int_{\lambda=0}^{\lambda=1} \psi_j^{0*}(e_j\lambda) e_j \, d\lambda \\ &= -\sum_1^{s} \sum_1^{n_j} \int_{\lambda=0}^{\lambda=1} (\kappa\lambda) \frac{\lambda e_j}{D_0} e_j \, d\lambda = -\frac{\kappa}{3D} \sum_1^{s} n_j e_j^2 \end{aligned} \tag{3-10-3}$$

The appearance of $\kappa\lambda$ in the next to last member of this expression results from the fact that κ is proportional to e. To a first approximation, the total electrical work of the charging process, obtained by adding the above equations, may be set equal to the increase in work content of the system. Thus

$$\Delta A = \frac{1}{2D} \sum_1^{s} \frac{n_j e_j^2}{b_j} - \frac{1}{2D_0} \sum_1^{s} \frac{n_j e_j^2}{b_j} - \frac{\kappa}{3D} \sum_1^{s} n_j e_j^2 \tag{3-10-4}$$

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[26] P. Debye and J. McAulay, *Physik. Z.*, **26**, 22 (1925).

[27] P. Debye, *Z. physik. Chem.*, **130**, 55 (1927).

[28] P. Gross, *Monatsh. d. Chem.*, **53**, 54 (1929).

Again, as a first approximation, we may represent the dielectric constant of the mixture by the equation

$$D = D_0(1 - \bar{\beta}n - \bar{\beta}'n') \tag{3-10-5}$$

where n and n' are the number of molecules of non-electrolyte and electrolyte respectively, and $\bar{\beta}$ and $\bar{\beta}'$ are empirical constants. From these last two equations, we obtain

$$\Delta A = \frac{\bar{\beta}n}{2D_0}\sum_{1}^{s}\frac{n_j e_j^2}{b_j} + \frac{\bar{\beta}'n'}{2D_0}\sum_{1}^{s}\frac{n_j e_j^2}{b_j} - \frac{\kappa}{3D_0}\sum_{1}^{s} n_j e_j^2 \tag{3-10-6}$$

if terms containing higher powers of n and n' are neglected. The last term leads to the limiting law of Debye and Hückel under the conditions, $n' = 0$ and $\bar{\beta} = 0$. In the discussion to follow we are concerned only with the "salting out" or "salting in" of electrolytes or non-electrolytes at extreme dilutions caused by alterations in dielectric constant according to equation (3-10-5). Under these conditions,

$$\Delta A_{(s)} = \frac{\bar{\beta}n}{2D_0}\sum_{1}^{s}\frac{n_j e_j^2}{b_j} + \frac{\bar{\beta}'n'}{2D_0}\sum_{1}^{s}\frac{n_j e_j^2}{b_j} \tag{3-10-7}$$

which represents a pure salting-out (-in) term independent of terms involving κ.

From this equation we may determine the contribution to the chemical potential of the non-electrolyte ($\Delta\mu_{(s)}$ per molecule) caused by the addition of electrolyte, or *vice versa*. Thus for a neutral molecule

$$\Delta\mu_{(s)} = \frac{\partial \Delta A_{(s)}}{\partial n} = \frac{\bar{\beta}}{2D_0}\sum_{1}^{s}\frac{n_j e_j^2}{b_j} = kT \ln f_{(s)} \tag{3-10-8}$$

or

$$\ln f_{(s)} = \frac{\bar{\beta}}{2kTD_0}\sum_{1}^{s}\frac{n_j e_j^2}{b_j} \tag{3-10-9}$$

which is the equation of Debye and McAulay. It is apparent that when $\bar{\beta}$ is positive the macroscopic dielectric constant of the medium is decreased. Accordingly, f is increased, and "salting out" occurs. When $\bar{\beta}$ is negative, "salting in" takes place. Considering the simplified picture, and the approximations made during the deduction, it is clear that (3-10-9) is a limiting equation, and can be regarded as only a first approximation.

An expression for the "salt effect" of an electrolyte upon itself may be readily obtained from equation (3-10-7) by differentiation with respect to n'. In performing this differentiation, it should be observed that $n_j = \nu_j n'$. Accordingly,

$$\ln f_{\pm(s)} = \frac{\bar{\beta}'n'\epsilon^2}{\nu kTD_0}\sum_{1}^{s}\frac{\nu_j z_j^2}{b_j} \tag{3-10-10}$$

Eliminating $\beta' n'$ by (3-10-5), we obtain

$$\ln f_{\pm(s)} = \frac{(D_0 - D)\epsilon^2}{\nu k T D_0^2} \sum_1^s \frac{\nu_j z_j^2}{b_j} \tag{3-10-11}$$

if no non-electrolyte is present except the solvent (water). This equation also gives the salt effect of one electrolyte upon another at high dilution. In this case the summation is taken over all the ions of both electrolytes.

Other equations for the salt effects of ions have been derived by means of a similarly simplified picture. Butler[29] obtained an equation identical with (3-10-9) except that D and not D_0 appears in the denominator. His equation for the mutual salting out of ions differs from (3-10-11) by the replacement of D_0^2 by D^2 in the denominator.

An expression for the effect of a non-electrolyte upon the activity coefficient of an electrolyte at extreme dilution is readily obtained from equation (3-10-2). Thus the electrical work, W_t, of transferring the charges from n' molecules of electrolyte from pure water, of dielectric constant D_0, to a water-non-electrolyte mixture of dielectric constant D, is

$$W_t = \frac{n'\epsilon^2}{2D} \sum_1^s \frac{\nu_j z_j^2}{b_j} - \frac{n'\epsilon^2}{2D_0} \sum_1^s \frac{\nu_j z_j^2}{b_j} \tag{3-10-12}$$

Setting this work equal to the increase in work content, and differentiating with respect to n', we obtain

$$\nu k T \ln f_{\pm(t)} = \frac{\epsilon^2}{2D} \sum_1^s \frac{\nu_j z_j^2}{b_j} - \frac{\epsilon^2}{2D_0} \sum_1^s \frac{\nu_j z_j^2}{b_j}$$

or

$$\ln f_{\pm(t)} = \frac{(D_0 - D)\epsilon^2}{2\nu k T D D_0} \sum_1^s \frac{\nu_j z_j^2}{b_j} \tag{3-10-13}$$

which is the equation derived by Born.[30] The quantity $\log f_{\pm(t)}$ is the primary medium effect, $\log f_0$, discussed in Chapter (15), Section (7).

(b) Theory of Debye

We shall now obtain an expression for the concentration of a neutral molecule in presence of an ion as a function of its distance from the ion by a method developed by Debye.[31] Consider a spherical ion of radius, b, in a medium composed of two miscible non-electrolytes. For an ideal mixture of these substances,

$$n_1 v_1 + n_2 v_2 = 1 \tag{3-10-14}$$

where v_1 and v_2 are the molal volumes of the pure components divided by Avogadro's number, and n_1 and n_2 the number of molecules of each species

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[29] J. A. V. Butler, *J. Phys. Chem.*, **33**, 1015 (1929).

[30] M. Born, *Z. Physik.*, **1**, 45 (1920). See also H. S. Harned and N. N. T. Samaras, *J. Am. Chem. Soc.*, **54**, 1 (1932).

[31] P. Debye, *Z. physik. Chem.*, **130**, 56 (1927).

per cc. The free energy of an element of volume, according to equation (1-9-1), is given by

$$[n_1(\phi_1 + kT\ln N_1) + n_2(\phi_2 + kT\ln N_2)]dV \tag{3-10-15}$$

where N_1 and N_2 are the mol fractions, and ϕ_1 and ϕ_2 are the standard free energies per molecule on the mol fraction scale. We are adhering to Debye's symbols to allow F_1, $\bar{F}_1^0$, etc. to be free energies or partial free energies per mol. Since the ideal solution is assumed, the activity coefficients are unity. In order to obtain the total free energy of the solution, it is necessary to add to this the contribution due to the field of the ion. From electrostatics, this quantity is found to be the energy of the volume element at a distance r from the ion, and is given by the expression

$$\frac{(DX)^2}{8\pi D}\,dV = \frac{\left[\frac{d}{dr}\left(\frac{e}{r}\right)\right]^2}{8\pi D}\,dV = \frac{e^2}{8\pi r^4 D}\,dV \tag{3-10-16}$$

where X is electric field strength, $\frac{e}{Dr^2}$. The total free energy of the system is, therefore,

$$\Phi = \int\left[n_1(\phi_1 + kT\ln N_1) + n_2(\phi_2 + kT\ln N_2) + \frac{e^2}{8\pi r^4 D}\right]dV \tag{3-10-17}$$

if the integration is extended over the entire volume of the solution. Let n_1 and n_2 be varied by δn_1 and δn_2. Then

$$\begin{aligned}\delta\Phi = \int\Bigg[\delta n_1\left(\phi_1 + kT\ln N_1 - \frac{e^2}{8\pi r^4}\frac{1}{D^2}\frac{\partial D}{\partial n_1}\right)&\\ + \delta n_2\left(\phi_2 + kT\ln N_2 - \frac{e^2}{8\pi r^4}\frac{1}{D^2}\frac{\partial D}{\partial n_2}\right)\Bigg]dV&\end{aligned} \tag{3-10-18}$$

The condition of equilibrium requires that $\delta\Phi = 0$, or Φ is a minimum subject to the condition that the total number of molecules does not change, or that

$\int n_1 dV$ and $\int n_2 dV$ are constant. From equation (3-10-14)

$$v_1\delta n_1 + v_2\delta n_2 = 0$$

Now let

$$\delta n_1 = v_2\delta x; \qquad \delta n_2 = -v_1\delta x$$

where δx is an arbitrary variation. As a result, equation (3-10-18) becomes

$$\begin{aligned}\delta\Phi = \int dV\delta x\Bigg[v_2\left(\phi_1 + kT\ln N_1 - \frac{e^2}{8\pi r^4}\frac{1}{D^2}\frac{\partial D}{\partial n_1}\right)&\\ - v_1\left(\phi_2 + kT\ln N_2 - \frac{e^2}{8\pi r^4}\frac{1}{D^2}\frac{\partial D}{\partial n_2}\right)\Bigg]&\end{aligned} \tag{3-10-19}$$

Since

$$\int \delta n_1 dV + \int \delta n_2 dV = (v_2 - v_1) \int \delta x dV = 0,$$

we find that

$$\int \delta x dV = 0 \tag{3-10-20}$$

This requires that for zero variation, ($\delta x = 0$) and ($\delta \Phi = 0$), the bracketed term under the integral in equation (3-10-19) equals a constant, or

$$\begin{aligned} v_2\left(\phi_1 + kT \ln N_1 - \frac{e^2}{8\pi r^4}\frac{1}{D^2}\frac{\partial D}{\partial n_1}\right) \\ - v_1\left(\phi_2 + kT \ln N_2 - \frac{e^2}{8\pi r^4}\frac{1}{D^2}\frac{\partial D}{\partial n_2}\right) = \text{constant} \end{aligned} \tag{3-10-21}$$

Let N_1^0 and N_2^0 represent the mol fractions at great distances from the ion ($r = \infty$). Then,

$$\text{constant} = v_2(\phi_1 + kT \ln N_1^0) - v_1(\phi_2 + kT \ln N_2^0)$$

and

$$v_2 \ln \frac{N_1}{N_1^0} - v_1 \ln \frac{N_2}{N_2^0} = \frac{e^2}{8\pi kTD^2}\left(v_2 \frac{\partial D}{\partial n_1} - v_1 \frac{\partial D}{\partial n_2}\right)\frac{1}{r^4} \tag{3-10-22}$$

From this result, it is clear that if D is known as a function of the composition, the concentrations of both components at a distance, r, from the ion may be computed. It is important to note that this theory excludes a variation of D as a function of r.

A simple and useful result may be obtained by considering a mixture which contains a small quantity of component (2). Since $N_1 = 1 - N_2$, and $N_1^0 = 1 - N_2^0$, the left of equation (3-10-22) becomes

$$v_2 \ln \frac{1 - N_2}{1 - N_2^0} - v_1 \ln \frac{N_2}{N_2^0}$$

We now assume that component (2) is salted out, and therefore $N_2/N_2^0 < 1$, and assume further that N_2^0 itself is small. Under these conditions, we retain only the term $-v_1 \ln N_2/N_2^0$, and equation (3-10-22) becomes

$$\ln \frac{N_2}{N_2^0} = -\frac{e^2}{8\pi kT}\frac{1}{v_1 D^2}\left(v_2 \frac{\partial D}{\partial n_1} - v_1 \frac{\partial D}{\partial n_2}\right)\frac{1}{r^4} \tag{3-10-23}$$

Let

$$R^4 = \frac{e^2}{8\pi kTv_1}\frac{1}{D^2}\left(v_2 \frac{\partial D}{\partial n_1} - v_1 \frac{\partial D}{\partial n_2}\right) \tag{3-10-24}$$

then

$$N_2 = N_2^0 e^{-(\bar{R}/r)^4} \tag{3-10-25}$$

and $\bar{R}$ is seen to be a characteristic length. The last two equations represent the basic result of Debye's theory. If D is a linear function of N_1 and N_2, or

$$D = N_1 D_1 + N_2 D_2 \tag{3-10-26}$$

then

$$\bar{R}^4 = \frac{e^2 V_1}{8\pi RT} \frac{(D_1 - D_2)}{D_1^2} \tag{3-10-27}$$

where V_1 is the volume of one mol of component (1).

From this result, it is clear that the salting out effect increases very rapidly with decreasing r. Salting out, or salting in, will depend upon whether $D_1 - D_2 < 0$, or $D_1 - D_2 > 0$.

Numerically useful equations for salting effects may be obtained from the preceding equations. From equation (3-10-14), we obtain in general,

$$n_1 = \frac{N_1}{v_1 N_1 + v_2 N_2}; \qquad n_2 = \frac{N_2}{v_1 N_1 + v_2 N_2} \tag{3-10-28}$$

which for small amounts of component (2) reduces to

$$n_2 = \frac{N_2}{v_1 N_1} \simeq \frac{N_2}{v_1} \tag{3-10-29}$$

Consider a solution saturated with component (2) in component (1), in he presence of $\sum n_i$ ions per unit volume. Then, according to equation 3-10-25), the average number of molecules surrounding an ion is given by

$$\begin{aligned} Z_2 = \int n_2 \, dV &= \frac{N_2^0}{v_1} \int e^{-(\bar{R}/r)^4} dV \\ &= \frac{N_2^0}{v_1} \left[\int dV - \int (1 - e^{-(\bar{R}/r)^4}) dV \right] \end{aligned} \tag{3-10-30}$$

'he integration is over the volume at the disposal of the ion. When r is o, N_2 equals N_2^0, and represents the concentration at any point containing o ions. The number of molecules of component (2), Z_2^0, at the disposal f one ion and before the addition of electrolyte will, consequently, be iven by

$$Z_2^0 = \frac{N_2^0}{v_1} \int dV \tag{3-10-31}$$

'he ratio of Z_2, the number of molecules present in the solution after the ldition of electrolyte, to Z_2^0 is therefore

$$\frac{Z_2}{Z_2^0} = 1 - \frac{\int (1 - e^{-(\bar{R}/r)^4}) dV}{\int dV} \tag{3-10-32}$$

The integration of the term in the numerator is over the volume at the disposal of one ion. Therefore

$$\sum n_j \int dV = 1 \tag{3-10-33}$$

where $\sum n_j$ is the total number of ions per cubic centimeter.

Let

$$\sigma = 4\pi \int_b^\infty (1 - e^{-(\bar{R}/r)^4}) r^2 dr \tag{3-10-34}$$

then

$$\frac{Z_2}{Z_2^0} = \frac{f_2^0}{f_2} = 1 - \sum \sigma n_j \tag{3-10-35}$$

where f_2 and f_2^0 are, respectively, the rational activity coefficients of component (2) in the presence and absence of ions. Since non-ionic solutions are assumed ideal in the study of salt effects, f_2^0 is usually set equal to unity.

In the statement and derivation of equation (3-10-35), we have closely followed Debye,[32] but in the numerical evaulation of the term $\sum \sigma n_j$ it seems preferable to modify it slightly so as to distinguish between the various physical conditions under which it will be used. According to equation (3-10-26)

$$D = D_1\left[1 - \left(\frac{D_1 - D_2}{D_1}\right) N_2\right] = D_1\left[1 - \left(\frac{D_1 - D_2}{D_1}\right) V_1 c\right] \tag{3-10-36}$$

since the concentration of component (2) in dilute solution is N_2/V_1. It is convenient to define the numerical magnitude

$$|\bar{\alpha}| = \left(\frac{D_1 - D_2}{D_1}\right) V_1 \tag{3-10-37}$$

so that

$$\bar{R}_j^4 = \frac{z_j^2 \epsilon^2 1000}{8\pi RTD_1} |\bar{\alpha}| \tag{3-10-38}$$

and the sign of the term $\sum \sigma n_j$ depends upon whether D_1 is greater or less than D_2. In the first case (I), $D_1 > D_2$

$$D = D_1(1 - |\bar{\alpha}| c) \tag{3-10-39}$$

and we define

$$(J_j)_\text{I} = \int_{b_j}^\infty (1 - e^{-(\bar{R}_j/r)^4}) r^2 dr \tag{3-10-40}$$

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[32] P. Debye, *Z. physik. Chem.*, **130**, 56 (1927).

In the second case (II), $D_1 < D_2$

$$D = D_1(1 + |\bar{\alpha}|c) \tag{3-10-41}$$

and we define

$$(J_j)_{\text{II}} = \int_{b_j}^{\infty} (1 - e^{+(\bar{R}_j/r)^4})r^2dr \tag{3-10-42}$$

The equation for the salt effect (3-10-35) therefore takes the form

$$\frac{f_2^0}{f_2} = 1 - \frac{4\pi N}{1000} \sum J_j c_j \tag{3-10-43}$$

The integrals involved in the evaluation of J_j are given by the series[33, 34]

$$(J_j)_{\text{I}} = \bar{R}_j^3\left[1.21 - \frac{1}{3}\left(\frac{b_j}{\bar{R}_j}\right)^3 \cdots\right]; \qquad \bar{R}_j > b_j \tag{3-10-44}$$

$$(J_j)_{\text{I}} = \frac{\bar{R}_j^4}{b_j}\left[1 - \frac{1}{\underline{|2}5}\left(\frac{\bar{R}_j}{b_j}\right)^4 \cdots\right]; \qquad \bar{R}_j < b_j \tag{3-10-45}$$

and

$$(J_j)_{\text{II}} = -\frac{\bar{R}_j^4}{b_j}\left[1 + \frac{1}{\underline{|2}5}\left(\frac{\bar{R}_j}{b_j}\right)^4 \cdots\right]; \qquad R_j < b_j \tag{3-10-46}$$

Gross[35] has extended this theory to include the effect of the ionic atmosphere. This effect requires that the energy of the volume element at a distance r from the ion [see equations (2-4-17) and (3-10-16)] increases by the amount

$$\frac{e^2}{8\pi D}\left[\frac{\partial}{\partial r}\left(\frac{e^{-\kappa r}}{r}\right)\right]^2 dV = \frac{e^2(1+\kappa a)e^{-2\kappa r}}{8\pi r^4 D}\,dV \tag{3-10-47}$$

The result of this inclusion is to change equations (3-10-44) and (3-10-45) to

$$(J_j)_{\text{I}}(\kappa) = \bar{R}_j^3\left[1.21 - \frac{1}{3}\left(\frac{a_j}{\bar{R}_j}\right)^3 - \frac{3}{2}\kappa\bar{R}_j + \cdots\right]; \qquad \bar{R}_j > a_j \tag{3-10-48}$$

and

$$(J_j)_{\text{I}}(\kappa) = \frac{\bar{R}_j^4}{a_j}\left[1 - \frac{3}{2}\kappa a_j\right]; \qquad \bar{R}_j < a_j \tag{3-10-49}$$

(11) THE THEORETICAL LIMITING LAW FOR SURFACE TENSION OF ELECTROLYTIC SOLUTIONS

Wagner,[36] and Onsager and Samaras[37] have developed the theory of the effect of interionic attraction on the surface tension of electrolytic

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[33] P. Gross and K. Schwarz, *Monats. Chem.*, **55**, 287 (1930); *Sitz. Akad. Wiss. Vien.*, **139**, 179 (1930).

[34] P. Gross, *Ibid.*, **138**, 449 (1929).

[35] P. Gross, *Monatsh. Chem.*, **53**, 445 (1929); **55**, 287 (1930).

[36] C. Wagner, *Physik. Z.*, **25**, 474 (1924).

[37] L. Onsager and N. N. T. Samaras, *J. Chem. Phys.*, **2**, 528 (1934).

solutions. The solution of this problem requires the computation of the deficiency of solute in the interfacial region

$$\Gamma_2 = -\frac{\partial\sigma}{\partial \bar{F}_2} = -\frac{\partial\sigma}{RT\partial \ln a_2} \tag{1-11-1}$$

and subsequently, the surface tension increase, $\sigma - \sigma_0$, by integration of this equation.

Owing to the forces of attraction of the ions in the interior of the solution, or, more specifically, the repulsion of the ions from the surface by the electrostatic image force, there will be a deficiency of the solute near the surface. The screening effect of the ionic atmospheres of radii, $1/\kappa$, limits the depth at which these forces are operative. Wagner's formulation led to equations which were very difficult to solve. Onsager and Samaras, by adding one further simplifying assumption to Wagner's treatment, were able to obtain an explicit solution which, upon analysis, appears to be a good first approximation.

The Interfacial Layer and the Adsorption Potential

The concentration of solute, $c(x)$, at a distance, x, from a boundary is given by the Maxwell-Boltzmann equation,

$$c(x) = ce^{-W(x)/kT} \tag{3-11-1}$$

Here, c is the concentration of solute in the interior of solution $[c = c(\infty)]$ and $W(x)$ is the work required to bring a molecule of solute, or ion, from the interior of the solution to a point at a depth, x, from the boundary. The quantity $W(x)$ is the "adsorption potential." Each ionic species will be considered to possess an adsorption potential to be designated $W_i(x)$.

To compute $W(x)$, Wagner employed the method of electrical images. Consider an ion of charge e at a distance, x, from a fixed boundary. The ion is in a medium of dielectric constant, D, in contact with air of dielectric constant, D', equal to unity. Construct its electrical image as in Fig. (3-11-1). The electrostatic potential, ψ, at any point in the medium will be given by

$$\psi = \frac{e_j}{Dr_1} + \frac{(D - D')}{(D + D')}\frac{e_j}{Dr_2} = \frac{e_j}{Dr_1} + \frac{(D - 1)}{(D + 1)}\frac{e_j}{Dr_2} \tag{3-11-2}$$

where r_1 is the distance from the ion and r_2 the distance from the electrical image.[38] The second term on the right of this equation is the potential caused by the presence of the boundary, and is expressed in terms of charge $[(D - 1)/(D + 1)]e_j$ of the image. This exerts a force

$$-\frac{\partial W(x)}{\partial x} = \left[\frac{(D - 1)e_j^2}{(D + 1)Dr_2^2}\right]_{r_2=2x} = \frac{(D - 1)}{(D + 1)}\frac{e_j^2}{4Dx^2}$$

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[38] A simple deduction of equation (3-11-2) is to be found in J. J. Thomson, "Elements of Electricity and Magnetism," Fourth Edition, p. 169–171, Cambridge University Press, 1909.

on the ion, and the potential of this force is

$$W(x) = \frac{(D - 1)}{(D + 1)} \frac{e_j^2}{4Dx} \tag{3-11-3}$$

Wagner showed that such an adsorption potential would cause an infinite increase in surface tension because the adsorbed amount of solute would be infinite

$$-\Gamma_2 = c \int_0^\infty (1 - e^{-W(x)/kT})\, dx = \infty \tag{3-11-4}$$

which is indeed a paradoxical situation. For ionic solutions, the screening effect of the ionic atmosphere limits the effective range of the electrostatic forces to a distance, $1/\kappa$, and, consequently, the above difficulty disappears. For electrolytic solutions, the potential has been found to obey equation (2-4-12)

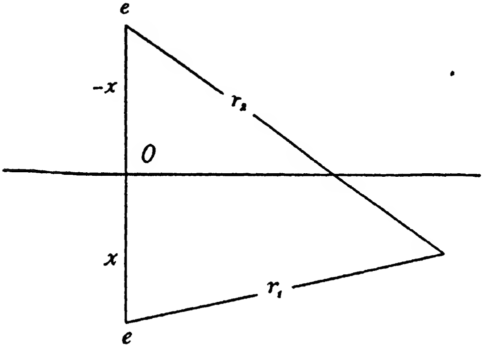

Fig. (3-11-1)
Diagram for computing electrostatic potential due to charge, e, and its image, $[(D - 1)/(D + 1)]e \simeq e$

$$\nabla \cdot \nabla \psi = \kappa^2 \psi \tag{3-11-5}$$

Further, since the concentration at the surface is different from that in the interior, κ^2 is a function of z if this equation is expressed in cylindrical coördinates, as follows

$$\nabla \cdot \nabla \psi = \frac{\partial^2 \psi}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial \psi}{\partial r}\right) = \kappa^2(z)\psi \tag{3-11-6}$$

The solution is restricted by the conditions that when $z = x$, $r = 0$; when $z = -x$, $r = 0$; when $z > 0$, $\kappa^2(z)$ is given by equation (3-11-1), and the equation for the definition of κ^2 [Equation (2-4-11)]; and when $z < 0$, $\kappa^2(z) = 0$. At the boundary, $z = 0$, ψ is continuous, and $\partial\psi/\partial z$ changes by a factor D.

To obtain an approximate solution of this equation, Wagner let $D' = 0$ instead of unity. Furthermore, he replaced $\kappa^2(z)$ by $\kappa^2(x)$. Onsager and Samaras simplified the problem by the additional approximation that

$$\kappa^2(z) \sim \kappa^2(\infty) = \kappa^2 \tag{3-11-7}$$

Under these conditions, $W(x)$ is given by

$$W(x) = \frac{e_j^2 e^{-2\kappa x}}{4Dx} \tag{3-11-8}$$

which is seen to differ from equation (3-11-3) by the factor $e^{-2\kappa x}$, provided that $D'(= 1)$ is neglected. By combining equation (3-11-8) with equation (3-11-1), we obtain for the concentration, at a depth x from the boundary, the expression,

$$c(x) = c \exp\left(\frac{-e_j^2}{4DkTx} e^{-2\kappa x}\right) = c \exp\left(\frac{-q}{2x} e^{-2\kappa x}\right) \tag{3-11-9}$$

where

$$q = e_j^2/2DkT \tag{3-11-10}$$

is the characteristic distance employed in Bjerrum's theory of ionic association [Equation (3-7-6)]. This is the simplest limiting equation. If the mean ionic distance of approach of the ions is introduced, then

$$W(x) = \frac{e^{\kappa a}}{1 + \kappa a} \frac{e_j^2}{4Dx} e^{-2\kappa x} \tag{3-11-11}$$

$$c(x) = c \exp\left(\frac{-qe^{\kappa a}}{1 + \kappa a} \frac{e^{-2\kappa x}}{2x}\right) \tag{3-11-12}$$

and

$$-\Gamma_2 = c \int_0^\infty \left[1 - \exp\left(\frac{-qe^{\kappa a}}{1 + \kappa a} \frac{e^{-2\kappa x}}{2x}\right)\right] dx \tag{3-11-13}$$

Onsager and Samaras succeeded in solving equation (3-11-13). Γ_2, obtained in this manner, was then substituted in equation (1-11-1). Upon integration, the increase in surface tension, $\Delta\sigma$, or $\sigma - \sigma_0$, where σ_0 is the surface tension of the solvent, was obtained.

In the limiting case (mean distance of approach of ions omitted), they expressed their result in the form

$$\sigma - \sigma_0 = \frac{kT}{16\pi q^2} (Y_c + Y_f) = \frac{kT}{16\pi q^2} Y \tag{3-11-14}$$

Similarly, the equation which includes the sizes of the ions is

$$\sigma - \sigma_0 = \frac{kT}{16\pi q^2} (Y'_c + Y'_f) = \frac{kT}{16\pi q^2} Y' \tag{3-11-15}$$

Y and Y' are complicated functions [Chapter 5, Table (5-2-6)].

For 1-1 electrolytes, the limiting law becomes

$$\sigma - \sigma_0 = \frac{79.517}{D} c \log \frac{1.143 \times 10^{-13} (DT)^3}{c} \tag{3-11-16}$$

With water as solvent at 25°

$$\sigma - \sigma_0 = 1.0124\, c \log \frac{1.467}{c} \tag{3-11-17}$$

Chapter (4)

The Theory of Irreversible Processes in Electrolytic Solutions

In Chapter (2), we discussed the fundamental theory necessary for the treatment of the dynamics of ionic atmospheres. By adaptation of the general equation of continuity (2-5-6) to the special problem under consideration, and by the addition of further important concepts, it is possible to deduce exact equations by means of which the electrostatic contribution of Coulomb forces to viscosity, conductance and diffusion of dilute electrolytic solutions may be computed. The development of this difficult theory is due to Debye and Hückel, Falkenhagen and Onsager. Since the solution of any of these problems requires considerable highly specialized mathematics, a complete treatment will not be given. However, a discussion of the fundamental physical foundations of the theory and an outline of the important steps of the deductions will be presented. This will introduce the reader to the literature which must be consulted if a thorough knowledge of the field is to be acquired. Following the theory of viscosity, conductance and diffusion, the theory of the effects of frequency and of high electrical fields upon the conductance will receive consideration. The final laws in forms adaptable for actual calculation will be stated. The more practical numerical aspects of the subject will receive detailed consideration in Chapter (5), where simplified equations and their numerical constants will be tabulated.

(1) TIME LAGS

(a) The Time of Relaxation of the Ionic Atmosphere (Debye and Hückel)

Whenever the ions of an electrolyte are subjected to a disturbance, such as an electrical field or a concentration gradient, the central ion moves relative to its atmosphere and the latter no longer will possess a symmetrical (spherical) structure. If the disturbing force is suddenly removed, the ionic atmosphere will tend to revert to its normal equilibrium condition. This change from the perturbed to the normal condition will require a finite time.

Let us suppose that a disturbance has taken place which causes a change in the density of charge, ρ. If the source of disturbance is suddenly removed, the system will revert to its original condition with a velocity, $\frac{d\rho}{dt}$, proportional to ρ

$$-\frac{d\rho}{dt} = k\rho = \frac{1}{\tau}\rho$$

The time, τ, which will be denoted the "time of relaxation," is the reciprocal of a velocity constant.

For consider a disturbance of electrical charges and the corresponding changes in density. If ψ is the disturbing potential and σ the conductance, then the current, according to Ohm's law, is

$$\mathbf{i} = -\sigma\nabla\psi \tag{4-1-1}$$

The time rate of density changes is given by the equation of continuity or

$$\frac{d\rho}{dt} = -\nabla\cdot\mathbf{i} = \sigma\nabla\cdot\nabla\psi \tag{4-1-2}$$

Further, according to Poisson's equation

$$\nabla\cdot\nabla\psi = -\frac{4\pi}{D}\rho \tag{4-1-3}$$

which relation, when combined with equation (4-1-2), yields

$$-\frac{d\rho}{dt} = +\frac{4\pi\sigma\rho}{D} = \frac{1}{\tau}\rho \tag{4-1-4}$$

Upon integration

$$\rho(t) = \rho(0)e^{-4\pi\sigma t/D} = \rho(0)e^{-t/\tau} \tag{4-1-5}$$

We note that

$$\tau = \frac{D}{4\pi\sigma} \tag{4-1-6}$$

a result first obtained by Maxwell.

From these considerations, we can readily obtain an expression for the time of relaxation of the ionic atmosphere. Since a force, $-\nabla\psi_j$, will cause an i ion to move with a velocity $-\omega_i e_i \nabla\psi_j$, or $-\frac{e_i\nabla\psi_j}{\rho_i}$, and since the current is equal to the velocity times the total charge,

$$\mathbf{i} = -\sum_{i=1}^{s}\frac{n_i e_i^2}{\rho_i}\nabla\psi_j \tag{4-1-7}$$

and consequently

$$\sigma = \sum_{i=1}^{s}\frac{n_i e_i^2}{\rho_i} \tag{4-1-8}$$

where ω_i and ρ_i represent the mobilities and frictional coefficients of the ion defined in Chapter (2), Section (3). Let

$$\overline{1/\rho} = \frac{\sum_{i=1}^{s} \frac{n_i e_i^2}{\rho_i}}{\sum_{i=1}^{s} n_i e_i^2} . \tag{4-1-9}$$

then

$$\sigma = \overline{1/\rho} \sum_{i=1}^{s} n_i e_i^2 = \frac{\kappa^2 DkT}{4\pi} \overline{1/\rho} \tag{4-1-10}$$

upon introducing the value of κ^2 given by equation (2-4-11). Consequently, the time of relaxation, according to equation (4-1-6), will be given by

$$\tau = \frac{1}{\kappa^2 kT \, \overline{1/\rho}} \tag{4-1-11}$$

If $\rho_1 = \rho_2 = \rho_3 = \rho_i$, then $\overline{1/\rho} = 1/\rho_i$, and

$$\tau = \frac{\rho_i}{\kappa^2 kT} \tag{4-1-12}$$

This simplified equation will prove useful in the preliminary discussion of viscosity. $\frac{kT}{\rho_i}$ is the coefficient of diffusion.

In order to estimate the magnitude of the time of relaxation, we shall write equation (4-1-11) in terms of known quantities for an electrolyte which dissociates into two kinds of ions. The equivalent conductance of an ion, λ_i, is equal to the current at a potential gradient of one volt per cm. produced by one gram equivalent of the ion. Hence,

$$\lambda_i = 96{,}500\bar{u}_i = 96{,}500 \, | e_i | / \rho_i = 96{,}500 \, | e_i | \, \omega_i \tag{4-1-13}$$

and consequently

$$1/\rho_i = \omega_i = u_i / | z_i | \, \epsilon = 300\bar{u}_i / | z_i | \epsilon \tag{4-1-14}$$

where the mobility, u_i, is in electrostatic units, and $\bar{u}_i$ refers to a potential gradient of one volt per cm. Therefore,

$$\omega_i = \frac{1}{\rho_i} = \frac{300 \, \lambda_i}{96500 \, | z_i | \, \epsilon} \tag{4-1-15}$$

Upon introducing this value of ρ_i in equation (4-1-9), we find that for a symmetrical electrolyte which dissociates into two ions,

$$\overline{1/\rho} = \frac{1}{\epsilon} \frac{300}{96{,}500} \left(\frac{\lambda_1 + \lambda_2}{| z_1 | + | z_2 |} \right) \tag{4-1-16}$$

whence by equation (4-1-11)

$$\tau = \left(\frac{|z_1| + |z_2|}{\lambda_1 + \lambda_2}\right) 15.34 \times 10^{-8}/kT\kappa^2 \qquad (4\text{-}1\text{-}17)$$

$z_1 = |z_1|$ times the sign of z_1; $z_2 = |z_2|$ times the sign of z_2.

It is apparent that, at a given temperature, this equation reduces to the simple form

$$\tau \simeq \frac{k_1}{c} 10^{-10} \text{ sec.} \qquad (4\text{-}1\text{-}18)$$

upon introducing the value of κ^2. The normal concentration is c, and k_1 is a constant characteristic of each electrolyte in a given solvent. Thus, for potassium chloride and hydrochloric acid at 18°, k_1 equals 0.55 and 0.19, respectively. In a $0.001N$ solution of electrolytes in water, τ is of the order of 10^{-7} to 10^{-8} sec.

(b) Time Lags of Processes of Ionic Combination

In some of our subsequent discussions of rates of dissociation and recombination of ions to form neutral molecules, we shall require a knowledge of the rate constant and time lags of such reactions. If n_i and n_j represent the number of the two species of ions which combine, and ν_{ji} the number of molecules which dissociate, then the chemical rate equations become

$$\frac{d\nu_{ji}}{dt} = -\frac{dn_j}{dt} = -\frac{dn_i}{dt} = An_jn_i - KA\nu_{ji} \qquad (4\text{-}1\text{-}19)$$

where A and KA are the rate constants for combination and dissociation, respectively, K is the ionization constant, $\frac{\alpha_0^2 n}{1 - \alpha_0}$, and, consequently α_0 is the degree of dissociation in the unperturbed state. If n is the number of molecules of electrolyte and α the degree of dissociation in general, then

$$\nu_{ji} = (1 - \alpha)n; \quad \text{and} \quad n_j = \alpha n = n_i$$

From equation (4-1-19) and these relations, it follows that

$$\frac{d\nu_{ji}}{An_jn_i - KA\nu_{ji}} = -\frac{d\alpha}{AK\left(\frac{n}{K}\alpha^2 + \alpha - 1\right)} = dt \qquad (4\text{-}1\text{-}20)$$

Upon integration, it is found that

$$\frac{(1 - \alpha_0)}{An(2 - \alpha_0)\alpha_0} \log \frac{\alpha - \alpha_0}{\alpha + \alpha_0/(1 - \alpha_0)} = -t + c', \quad \text{or} \qquad (4\text{-}1\text{-}21)$$

$$\frac{\alpha - \alpha_0}{\alpha + \alpha_0/(1 - \alpha_0)} = ce^{-t/\tau'} \qquad (4\text{-}1\text{-}22)$$

where

$$\tau' = \frac{1 - \alpha_0}{An(2 - \alpha_0)\alpha_0} \tag{4-1-23}$$

Thus, if an ionization equilibrium is disturbed by an external force, and if this disturbing influence is suddenly released, the system will proceed to a steady unperturbed state. The quantity, τ', is a measure of the time required for this process to take place and is analogous to the time of relaxation of the ionic atmosphere. Since the theory of such processes was originally studied by Langevin,[1] we shall refer to τ' as "the Langevin time lag." We shall find these fundamental considerations of value in discussions of the effect of high fields on the ionization of weak electrolytes. [This Chapter, Section (7)]

(2) VISCOSITY. THEORY OF FALKENHAGEN*

(a) A Preliminary Discussion of Viscosity

The theory of the change in viscosity of a medium brought about by the presence of Coulomb forces between the ions was first successfully developed by Falkenhagen[2] for the case of binary electrolytes. In the following outline of the theory, the method of treatment of Onsager and Fuoss[3] will be followed. They succeeded in obtaining a general solution applicable to mixtures as well as individual electrolytes. Since the equation for the potentials is of the same general form and somewhat simpler than the one involved in the computation of the conductance, the theory of viscosity will be treated first.

In the first place, a simplified treatment will be considered which will serve to show how the electrostatic forces between the ions influence the viscosity, and roughly estimate the order of magnitude of the effect. This procedure will serve to introduce the fundamentals of the theory of the dynamics of viscous fluids necessary for the development of the general theory.[4]

As illustrated by Fig. (4-2-1), we consider a solution between two parallel plates, A and B, which are h cms. apart. A is fixed and B moves with a

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[1] P. Langevin, *Ann. Chim. Phys.*, **28**, 433 (1903); L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

* The theory of conductance in Section (3) is easier to comprehend than this difficult theory of viscosity and can be studied without reference to the latter. The present order is that adopted for logical reasons by Onsager and Fuoss.

[2] H. Falkenhagen and M. Dole, *Z. physik. Chem.* [*B*], **6**, 159 (1929); *Physik. Z.*, **30**, 611 (1929); H. Falkenhagen, *Ibid.*, **30**, 611 (1929); H. Falkenhagen and E. L. Vernon, *Ibid.*, **33**, 140 (1932).

[3] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[4] An excellent and comprehensive presentation of this subject is to be found in L. Page, "Introduction to Theoretical Physics," pp. 225–229, Van Nostrand Co., New York, 1928.

constant velocity v' in the x direction. A constant velocity gradient in the y direction described by

$$\frac{v'}{h} = \frac{\partial v_x}{\partial y}; \qquad v_y = 0; \qquad v_z = 0, \tag{4-2-1}$$

will be assumed. The coefficient of the ij element of the stress dyadic[5], S_{xy}, is related to the corresponding element of the rate of strain dyadic[6] by the equation which defines the viscosity, η, namely,

$$S_{xy} = \eta\left(\frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y}\right) = S_{yx} \tag{4-2-2}$$

In the case of a simple laminar flow

$$S_{xy} = \eta\frac{\partial v_x}{\partial y} \tag{4-2-3}$$

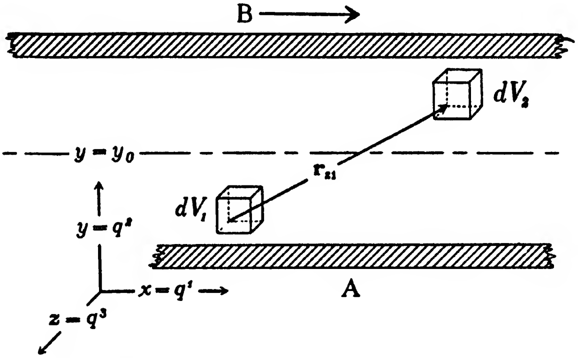

Fig. (4-2-1). Diagram for viscosity computation

The coefficient of viscosity, η, is the stress transferred per unit velocity gradient per unit area from each layer of liquid to the layer beneath it, or the force exerted by the portion of the medium above the plane on the portion of the medium below the plane per unit area of surface of separation.

In an electrolytic solution, part of the stress is caused by the deformation of the ionic atmosphere. In the unperturbed solution, each ion will be surrounded by an atmosphere of ions of opposite sign at an average distance of $1/\kappa$, and as previously shown [Chapter (2)], this distribution will possess a spherical symmetry. A velocity gradient in the solution will deform these atmospheres from a spherical to an ellipsoidal form. The electrostatic forces and thermal motion will tend to restore the atmospheres to their original form. As a result of these two opposite tendencies,

[5] L. Page, *loc. cit.*, Equation (43-13).
[6] L. Page, *loc. cit.*, Equation (71-3).

and because the time relaxation, τ, is finite, a stationary deformation will persist. If the relative rate of deformation is taken to be $\partial v_x/\partial y$, then a stationary deformation $\tau \partial v_x/\partial y$ will prevail. Since by equation (4-1-12), $\tau = \rho_i/\kappa^2 kT$, the deformation of the ionic atmospheres will be of the order of magnitude

$$\frac{\rho_i}{\kappa^2 kT} \frac{\partial v_x}{\partial y} \tag{4-2-4}$$

The forces between two ions of charge e at a distance $1/\kappa$ is $e^2\kappa^2/D$, and the total transfer of force between the ion and its atmosphere is $1/\kappa$ times this quantity, or $e^2\kappa/D$. This quantity, multiplied by the displacement of the ionic atmosphere, represented by equation (4-2-4), or,

$$\frac{e^2 \rho_i}{\kappa DkT} \frac{\partial v_x}{\partial y}$$

should be of the order of magnitude of the stress transferred between the ion and its atmosphere. Upon substitution of the value of κ^2 given by equation (2-4-11), we obtain for the electrostatic contribution to the stress, S^*_{yx},

$$S^*_{yx} \sim \kappa \rho_i \frac{\partial v_x}{\partial y} \tag{4-2-5}$$

This equation is correct except for a proportionality factor, $1/480\pi$ which can only be obtained by the more general consideration of the exact deformation of the ionic atmosphere. Thus for the case where $\frac{1}{\rho_i} = \omega_1 = \omega_2 = \cdots \omega_s$,

$$S^*_{yx} = \frac{1}{480\pi} \rho_i \kappa \frac{\partial v_x}{\partial y} \tag{4-2-6}$$

The stress between the solvent molecules is given by the equation

$$S^0_{yx} = \eta_0 \frac{\partial v_x}{\partial y} \tag{4-2-7}$$

where η_0 is the viscosity of the solvent. Hence, the ionic atmosphere contributes,

$$\eta^* = \frac{\rho_i \kappa}{480\pi} \tag{4-2-8}$$

to the viscosity. This is Falkenhagen's result, which verifies the conclusion reached experimentally by Jones and Dole[7] that in dilute solution η^* is proportional to the square root of the concentration.

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[7] G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).

(b) Outline of the General Solution of the Viscosity Problem

The general equation of motion of a viscous fluid[8] is

$$\frac{\partial \mathbf{v}}{\partial t} d + \mathbf{v} \cdot \nabla \mathbf{v} d = \mathbf{F} d - \nabla P + \tfrac{1}{3} \eta \nabla \nabla \cdot \mathbf{v} + \eta \nabla \cdot \nabla \mathbf{v} \qquad (4\text{-}2\text{-}9)$$

where $\mathbf{F}$ is the force per unit volume and P is the pressure. According to the equation of continuity, if the fluid is incompressible, $\nabla \cdot \mathbf{v} = \operatorname{div} \mathbf{v} = 0$. If the density "$d$" is taken to be unity, and the second term on the left is neglected for slow rates of flow since it involves the square of the velocity, $\mathbf{v}$, we obtain for constant rates of flow

$$\eta \nabla \cdot \nabla \mathbf{v} = \nabla P - \mathbf{F} \qquad (4\text{-}2\text{-}10)$$

For the case of the general motion at a point in a liquid located by $\mathbf{r}$, where the velocity $\mathbf{v}$ has the components v_x, v_y, v_z, the y component of the stress, S_{xy}, per unit area across a plane perpendicular to x, is given by equation (4-2-2). There are two factors which contribute to the stress. One is the friction of molecules of solvent on solvent molecules, and the second is the interaction of the electrostatic forces between the ions. As a result, if S^0_{mn} is the general coefficient of the stress matrix for force transfer in the pure solvent, and S_{mn} the same for motion in the solution, then

$$S_{mn} - S^0_{mn} = S^*_{mn} \qquad (4\text{-}2\text{-}11)$$

is the contribution by the ions to the stress. Further

$$\eta - \eta_0 = \eta^* \qquad (4\text{-}2\text{-}12)$$

is the increase in viscosity caused by the addition of solute. Upon substitution of this last relation in equation (4-2-10)

$$\eta_0 \nabla \cdot \nabla \mathbf{v} = \nabla P - (\mathbf{F} + \eta^* \nabla \cdot \nabla \mathbf{v}) \qquad (4\text{-}2\text{-}13)$$

is obtained. *This important result shows that the electrostatic forces between the ions may be interpreted as an addition to the volume force.*

Stresses are transferred from the ions to the solvent by friction, and there will be a relative motion between the ions and the solvent. Now, if in the interior of the solution $\nabla \cdot \nabla \mathbf{v}$ is 0, no stress is transferred between the solvent and the ions. In this case, the forces acting at the boundaries [A and B, Fig. (4-2-1)] equal $\pm \eta \, \partial v_x / \partial y$, and not $\pm \eta_0 \, \partial v_x / \partial y$. The difference, $\eta^* \, \partial v_x / \partial y$ can be explained if the ions move relative to the solvent along the boundaries up to distances, $1/\kappa$, and nowhere else.

These special considerations and the general equation of continuity (2-5-6) contain all the fundamental physical concepts for the solution of the viscosity problem. The mathematical treatment is quite complicated, and if the method of Onsager and Fuoss is to be followed a knowledge of the linear transformation of quadratic forms is essential. In this dis-

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[8] L. Page, *loc. cit.*, p. 229, Equation (71-18); note special use of $\mathbf{F}$ for total force.

cussion, a few steps of the deduction will be given, which will show how the computation of the stress, S^*_{yx}, as a volume force requires a knowledge of the potentials of the ionic atmospheres, which for the irreversible process in question can be evaluated only from the general equation of continuity.

We shall now calculate the stress by computing the total volume force. To accomplish this, we return to consideration of Fig. (4-2-1), and compute the total transfer of electrostatic force in the x direction, AS^*_{yx}, across an area, A, of a plane at $y = y_0$, and assume a constant velocity gradient of one component,

$$\frac{\partial v_x}{\partial y} = a_2^1$$

where the notations 1 and 2 characterize the variables x and y. The electrostatic force between any two ions is

$$\frac{e_j e_i}{D} \frac{\mathbf{r}_{21}}{r^3},$$

where $\mathbf{r}_{21}$ or r, is the distance separating them. Only those which are on opposite sides of the plane, $y = y_0$, contribute to the stress, so our considerations are limited to pairs of ions which satisfy the condition,

$$y_1 < y_0 < y_2 \tag{4-2-14}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ locate the ions, respectively. The force transferred from a j ion in dV_1 to the ions in dV_2 is

$$\frac{e_j}{D} \sum_i e_i n_{ji}(\mathbf{r}_{21}) dV_2 \frac{\mathbf{r}_{21}}{r^3}.$$

and the total force of all pairs of ions in dV_1 and dV_2 will be

$$\begin{aligned}\sum_j \frac{n_j e_j}{D} dV_1 \sum_i e_i n_{ji}(\mathbf{r}_{21}) dV_2 \frac{\mathbf{r}_{21}}{r^3} &= \sum_{ji} \frac{e_j e_i}{D} f_{ji}(\mathbf{r}_{21}) dV_1 dV_2 \frac{\mathbf{r}_{21}}{r^3} \\ &= -\sum_{ij} \frac{e_i e_j}{D} f_{ij}(\mathbf{r}_{12}) dV_1 dV_2 \frac{\mathbf{r}_{12}}{r^3}\end{aligned} \tag{4-2-15}$$

Thus, according to equation (2-1-4), the distribution function $f_{ji}(\mathbf{r}_{21})$ now appears in the equation. By integrating over all the volume elements which satisfy the restriction (4-2-14), the total stress may be computed. Thus, if $A = \int dxdz$, the x component of the force transferred is:

$$-AS^*_{yx} = \underset{y_1<y_0<y_2}{\int\int\int\int\int\int} \sum_{ji} \frac{e_i e_j}{D} f_{ji}(\mathbf{r}_{21}) \frac{x_{21}}{r^3} dV_1 dV_2 \tag{4-2-16}$$

Integration over x_1 and z_1 gives a factor A, and integration over y_1, keeping y_{21} constant, gives a factor y_{21}. By suitable manipulation of the limits of integration, and upon dropping the subscripts of x_{21}, y_{21}, dV_1, and dV_2, the integral becomes

$$S^*_{yx} = -\frac{1}{2}\iiint\limits_{-\infty}^{+\infty} \frac{xy}{r^3}\sum_{ji}\frac{e_j e_i}{D} f_{ji}(\mathbf{r})\,dV \tag{4-2-17}$$

Upon elimination of $f_{ji}(\mathbf{r})$ by Poisson's equation, the potential in the environment of the j ions may be introduced, and the integral

$$S^*_{yx} = \frac{1}{8\pi}\iiint\limits_{-\infty}^{+\infty} \sum_j n_j e_j \nabla\cdot\nabla\psi_j'(\mathbf{r})\,\frac{xy}{r^3}\,dV \tag{4-2-18}$$

is obtained. For purposes of mathematical convenience, another function, $\xi_j(r)$ which is related to the potential is introduced. The integral then becomes

$$S^*_{yx} = \frac{1}{8\pi}\iiint\limits_{-\infty}^{+\infty} \sum_j n_j e_j(a^\lambda_\mu D^2_{\lambda\mu}\nabla\cdot\nabla\xi_j(r))\,\frac{xy}{r^3}\,dV \tag{4-2-19}$$

in which a^λ_μ is the designated element of the rate of strain dyadic, and $D^2_{\lambda\mu}$ a second differential. For the case now under consideration a^1_2 is the only element of the strain dyadic, a^λ_μ, which does not vanish. Consequently,

$$\psi_j'(\mathbf{r}) = a^1_2\,\frac{\partial^2}{\partial x\partial y}\,(\xi_j(r)) \tag{4-2-20}$$

Therefore

$$S^*_{yx} = \frac{1}{8\pi}\iiint\limits_{-\infty}^{+\infty} \sum_j n_j e_j\,\frac{xy}{r^3}\,a^1_2\,\frac{\partial^2}{\partial x\partial y}\,\nabla\cdot\nabla\xi_j(r)\,dV$$

Upon changing to polar coördinates, and integrating the angles, we obtain

$$S^*_{yx} = \frac{a^1_2}{30}\sum_j n_j e_j \int_0^\infty \frac{d^2\nabla\cdot\nabla\xi_j(r)}{(r\,dr)^2}\,r^3 dr$$

which, upon integration by parts becomes

$$S^*_{yx} = \frac{a^1_2}{15}\sum_j n_j e_j \nabla\cdot\nabla\xi_j(0)$$

Consequently, the electrostatic contribution of the viscosity, η^*, is given by

$$\eta^* = \frac{1}{15}\sum_j n_j e_j \nabla\cdot\nabla\xi_j(0) \tag{4-2-21}$$

It is apparent from these considerations that the solution of the viscosity problem requires the evaluation of $\nabla\cdot\nabla\xi_j(0)$. This can be obtained only by means of the general equation of continuity (2-5-6). In order to obtain the differential equation for the potentials in a suitable form from equation (2-5-6), it is necessary to employ a few rather complicated transformations of variables.

Since this part of the deduction is concerned largely with matters of mathematical convenience, only a very brief outline is necessary for our purpose.

In the viscosity problem, the third and fourth terms of the general equation of continuity (2-5-6) are eliminated, since no external forces of the character of $\mathbf{k}_i$ and $\mathbf{k}_j$ are present. In order to convert equation (2-5-6) to a workable form, it is necessary to express the velocities in an appropriate manner. In the present case of the flow of the solution, both the distance between the ions, $\mathbf{r}_{21} = -\mathbf{r}_{12}$, and the distances $\mathbf{r}_1$ and $\mathbf{r}_2$ are independent variables. Since

$$\mathbf{r}_2 - \mathbf{r}_1 = \mathbf{r}_{21} = -\mathbf{r}_{12}$$

all the terms may be transformed to functions of two of these $(\mathbf{r}_1, \mathbf{r}_{21})$, or $(\mathbf{r}_2, \mathbf{r}_{12})$. Such transformation functions are devised. In all these problems, it turns out that it is more advantageous to employ the potentials, ψ'_j, instead of the distribution functions, f'_{ji}, since this substitution gives s functions, rather than $\frac{s(s+1)}{2}$. By means of Poisson's equation f'_{ji} and f'_{ij} are replaced by the potentials ψ'_j and ψ'_i, and these in turn are replaced by ξ'_j and ξ'_i by means of the relation

$$\nabla \cdot \nabla \psi'_j(\mathbf{r}) = a^{\lambda}_{\mu} D^2_{\lambda\mu} \nabla \cdot \nabla \xi_j(r) \tag{4-2-22}$$

With these transformations, the equation of continuity (2-5-6) reduces to the specialized form

$$\begin{aligned}(\nabla\cdot\nabla)^2\xi_j(r) - \frac{4\pi}{DkT}\sum_{i=1}^{s}\frac{n_i e_i^2 \omega_i}{\omega_i + \omega_j}\nabla\cdot\nabla\xi_j(r) - \frac{4\pi}{DkT}\sum_{i=1}^{s}\frac{e_i e_j \omega_j n_i}{\omega_i + \omega_j}\nabla\cdot\nabla\xi_i(r) \\ = -\frac{4\pi}{(DkT)^2}\frac{e^{-\kappa r}}{\kappa}\sum_{i=1}^{s}\frac{n_i e_i^2 e_j}{\omega_i + \omega_j}\end{aligned} \tag{4-2-23}$$

As we shall learn, the left side of this equation is identical with the left side of equation (4-3-27) for ψ'_j which appears in the conductance problem. This consideration shows the reason for the complicated transformations and the introduction of ξ_j.

The general solutions of some complicated differential equations involving summations can best be obtained by the use of matrix algebra.[9] By matrix methods, Onsager and Fuoss obtained a general solution of equation (4-2-23) subject to the natural boundary conditions of the prob-

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[9] Chapter I in R. Courant and D. Hilbert, "Methoden der Mathematischen Physik," Vol. I, Springer, Berlin, 1924, contains the necessary standard methods for the treatment of the present problem.

lem. An adequate treatment of the complicated algebra involved in the solution of this, and other differential equations resulting from the theory of irreversible processes in electrolytic solutions, would require much space and would divert attention from the physical aspects of the subject. Details are to be found in the contribution of Onsager and Fuoss, and in other papers to which we shall refer as occasion arises.

For the case of an electrolyte which dissociates into two kinds of ions ($s = 2$), the solution of equation (4-2-23) may be expressed in the form

$$\nabla\cdot\nabla\xi_j(0) = \frac{\kappa e_j}{2DkT}\left\{\frac{\bar{\rho}}{4\kappa^2} - \left(\rho_j - \frac{\overline{\rho^2}}{\bar{\rho}}\right)\frac{(1-\sqrt{q^*})}{(1+\sqrt{q^*})}\frac{1}{\kappa^2}\right\} \tag{4-2-24}$$

where $\bar{\rho}$, $\overline{\rho^2}$ and q^* are defined by the relations

$$\bar{\rho} = \frac{n_1 e_1^2/\omega_1 + n_2 e_2^2/\omega_2}{n_1 e_1^2 + n_2 e_2^2} \tag{4-2-25}$$

$$\overline{\rho^2} = \frac{n_1 e_1^2/\omega_1^2 + n_2 e_2^2/\omega_2^2}{n_1 e_1^2 + n_2 e_2^2} \tag{4-2-26}$$

$$q^* = \frac{n_1 e_1^2 \omega_1 + n_2 e_2^2 \omega_2}{(n_1 e_1^2 + n_2 e_2^2)(\omega_1 + \omega_2)} \tag{4-2-27}$$

From equation (4-2-24), the electrostatic contribution to the viscosity, η^*, given by equation (4-2-21) may readily be obtained. Thus,

$$\eta^* = \frac{1}{15}\sum_j n_j e_j \nabla\cdot\nabla\xi_j(0) = \frac{\kappa}{480\pi}\left\{\bar{\rho} + 4\left(\frac{\overline{\rho^2}}{\bar{\rho}} - \bar{\rho}\right)\frac{1-\sqrt{q^*}}{1+\sqrt{q^*}}\right\} \tag{4-2-28}$$

if equation (2-4-11) used to define κ, is employed to eliminate $\sum n_j e_j^2$.[10] We note that, if the second term on the right of equation (4-2-28) is omitted, the result is identical with equation (4-2-8), which we derived by approximate methods. The second term in the brackets involves $\overline{\rho^2}$, or the second power of the mobilities, or equivalent conductances. As stated, equation (4-2-28) is in a form convenient for conversion to practical units, and is the same as Falkenhagen's equation.[11] If $\omega_1 = \omega_2 = \cdots \omega_s = \omega$, the second term on the right vanishes, and Onsager and Fuoss convert this equation

$$\eta^* = \frac{\kappa}{480\pi\omega} \tag{4-2-29}$$

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[10] Equation (4-2-28) is not given in the article of Onsager and Fuoss. We are indebted to Professor Onsager for this symmetrical and convenient result which was obtained through consultation with him.

[11] H. Falkenhagen, "Electrolyte," Equations (580) and (581), S. Hirzel, Leipzig, 1932.

to an interesting form by substituting the value of the coefficient of friction ρ, given by Stokes formula [Equation (4-3-9)]. Thus

$$\frac{1}{\omega} = \rho = 6\pi\eta r$$

where r is the radius of the ion. Combining this relation with equation (4-2-29), we obtain

$$\frac{\eta^*}{\eta} = \frac{\kappa r}{80} = \frac{\eta - \eta_0}{\eta} \tag{4-2-30}$$

This shows that, in the first approximation, the relative increase in the viscosity is proportional to the ratio of the radius of the ion to that of its atmosphere.

(3) CONDUCTANCE. THEORY OF ONSAGER[12]

A. General Considerations and Preliminary Theory

In order to develop both the problems of conductance and diffusion from a common point of view, Onsager and Fuoss begin with a general treatment of the migration of ions in a homogeneous field of forces represented by $\mathbf{k}_1, \mathbf{k}_2, \cdots \mathbf{k}_s$ (per ion) acting upon the ionic species $1, \cdots s$ and a force, $\mathbf{k}_0$, acting upon molecules of the solvent, which balances the former according to

$$n_0 \mathbf{k}_0 = -\sum_{i=1}^{s} n_i \mathbf{k}_i \tag{4-3-1}$$

Such a system of forces is equivalent to a combination of an electric field, $E = -\nabla\psi$, where ψ is the electrical potential, and the concentration gradients, $\nabla n_1, \nabla n_2, \cdots \nabla n_s$, provided that electrical neutrality is maintained according to

$$\sum_{i=1}^{s} e_i \nabla n_i \equiv \nabla \sum_{i=1}^{s} n_i e_i = \nabla(0) = 0 \tag{4-3-2}$$

This can be shown by the following thermodynamic reasoning.

Equilibrium can be maintained with this system of electrical forces and gradients by superimposing forces of another nature, and of opposite sign, $-\mathbf{k}_0, -\mathbf{k}_1, \cdots -\mathbf{k}_s$, such that

$$\mathbf{k}_i = -\nabla\mu_i = -\nabla(\mu_i' + e_i\psi) \tag{4-3-3}$$

where μ_i' is the ordinary chemical potential, and μ_i the total chemical potential or the "electrochemical potential" [Chap. (10), Section (7)]. The velocities due to the various causes of migration may be assumed to be superimposable. Consequently, the velocities caused by the gradients, $-\nabla\mu_i$, must be the same as those caused by the forces, $\mathbf{k}_0, \mathbf{k}_1, \cdots \mathbf{k}_s$,

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[12] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

because they balance the superimposed forces, $-\mathbf{k}_0$, $-\mathbf{k}_1$, $\cdots -\mathbf{k}_s$. Since at constant pressure and temperature, the Gibbs-Duhem equation requires that $\sum_i n_i d\mu_i' = 0$, the equilibrium condition given by equation (4-3-1) can be shown to be consistent with the nature of the forces given by (4-3-3).

The very important part of the theory which is concerned with migration velocities of the ions will now be considered. If there were no Coulomb forces between the ions, or if the ion was isolated, the velocity relative to the medium in which the ion moves would be given by

$$\mathbf{v}_i = \frac{\mathbf{k}_i}{\rho_i} = \mathbf{k}_i \omega_i \tag{4-3-4}$$

This law would be valid for the ideal solution in which the forces between the ions are not sufficient to interfere. For actual electrolytic solutions, it is necessary to consider two effects:

(1) The direct transfer of forces between the ions. The complete treatment of this effect which includes allowance for the Brownian movement of the ions is due to Onsager.

(2) Electrophoresis, whereby an ion does not move in a medium at rest. Since it is surrounded by an ionic atmosphere which moves in the opposite direction, it migrates in respect to a moving medium. The effect of electrophoresis was first recognized by Debye and Hückel.

(a) **Preliminary Estimate of Force Transfer.** An ion under the influence of a force, **k**, will move with a velocity equal approximately to

$$\mathbf{v}_j = \frac{\mathbf{k}_j}{\rho_j} \tag{4-3-5}$$

When the force is applied, the ion tends to move away from its atmosphere, but the displaced ion will still attract the lagging atmosphere which will continue to form around the ion as it moves. If τ is the time of relaxation, the ion will be ahead of its atmosphere by a distance of the order

$$\mathbf{v}_j \tau = \frac{\mathbf{k}_j \tau}{\rho_j} \tag{4-3-6}$$

The ratio of this distance to the thickness of the ionic atmosphere, $\mathbf{k}_j \tau \kappa / \rho_j$, will measure the relative dissymmetry of the atmosphere. The directed force, $\Delta\mathbf{k}_j$, due to this dissymmetry, is obtained approximately by multiplying this quantity by the total force between the ion and its atmosphere. Thus,

$$\Delta\mathbf{k}_j \approx -\frac{e_j^2 \kappa^2}{D} \frac{\kappa \mathbf{k}_j \tau}{\rho_j} = -\frac{e_j^2 \kappa \mathbf{k}_j}{DkT} \tag{4-3-7}$$

upon substituting the value of τ given by equation (4-1-12). This value of $\Delta\mathbf{k}_j$, except for a numerical factor, will prove to be in agreement with the result obtained by the general method of procedure.

This force is caused by the dissymmetry of the atmosphere relative to the central ion. If some of the ions of the atmosphere migrate under the influence of external forces, the central ion becomes a part of the atmospheres of these. The relationship of these forces is reciprocal, and in order to take this reciprocity completely into account, the Brownian movement of the central ion must be considered, since it contributes to the relaxation of its own atmosphere. The fundamental equation (2-5-6) of Onsager takes care of this important effect.

(b) Preliminary Treatment of Electrophoresis. The calculation of electrophoresis is most easily made for electrical conductance, where the electrical field is $\mathbf{X}$, and where

$$\mathbf{k}_0 = 0; \qquad \mathbf{k}_j = e_j\mathbf{X}\ (j = 1, \cdots s) \tag{4-3-8}$$

The ion of charge e_j will possess an ionic atmosphere of charge $-e_j$, and this atmosphere will be subjected to a force, $-\mathbf{X}e_j$. This force will tend to move the atmosphere, and along with it liquid containing the atmosphere, in the direction of the force, $-\mathbf{X}e_j$. The central ion will also be carried by the medium in a direction opposite to its motion under the force, $-\mathbf{X}e_j$. The velocity of this counter-current may be calculated if it be assumed that the entire charge, $-e_j$, of the atmosphere is situated at a distance, $1/\kappa$, from the central ion, is distributed on a spherical shell of radius $1/\kappa$, and that the motion of this sphere is governed by Stokes law for the motion of a sphere in a viscous fluid. Thus,

$$\Delta\mathbf{v}_j = -\frac{\mathbf{k}_j\kappa}{6\pi\eta} = -\frac{\mathbf{X}e_j\kappa}{6\pi\eta}\ . \tag{4-3-9}$$

where $\Delta\mathbf{v}_j$ is the velocity of the interior of the shell, and η is the viscosity of the medium. We are led to the result that the medium in the interior of the shell will be travelling with this velocity, and that the central ion will migrate against a current of this magnitude. This expression is the correct equation for the most important part of the effect of electrophoresis although certain refinements are not present.

If the central ion possessed no atmosphere it would migrate with a velocity $\mathbf{k}_j/\rho_j$, but due to its atmosphere, the ion is subjected to a force, $\mathbf{k}_j - \Delta\mathbf{k}_j$, and will move with a velocity, relative to its environment, of a magnitude, $(\mathbf{k}_j - \Delta\mathbf{k}_j)/\rho_j$. Consequently, the net velocity, $\mathbf{v}_j$, is given by

$$\mathbf{v}_j = \Delta\mathbf{v}_j + \frac{(\mathbf{k}_j - \Delta\mathbf{k}_j)}{\rho_j} \tag{4-3-10}$$

For the case of electrical conduction, we obtain

$$\mathbf{v}_j = \frac{(\mathbf{X}e_j - \Delta\mathbf{k}_j)}{\rho_j} - \frac{\mathbf{X}e_j\kappa}{6\pi\eta} \tag{4-3-11}$$

Since both the equations of force transfer (4-3-7), and electrophoresis (4-3-9) involve the first power of κ, these effects are both proportional to the square root of the concentration. The above considerations serve as an introduction to the fundamental physical conceptions underlying the general theory.

B. Outline of the General Theory of Conductance According to Onsager

(a) Electrophoresis. The subsequent treatment of the general theory of conductance and diffusion will require a more general development of the theory of the electrophoretic effect than the one just reviewed. The volume force acting on the medium surrounding the ion is the cause of electrophoresis. If n_j is the average concentration of j ions, the average external force per unit volume will be

$$\sum_{j=1}^{s} n_j \mathbf{k}_j \equiv n_\sigma \mathbf{k}_\sigma$$

where the Greek index, σ, represents summation. These forces are transferred to the solvent molecules of concentration n_0 per unit volume. All the forces balance, according to equation (4-3-1), with the result that

$$n_\sigma \mathbf{k}_\sigma + n_0 \mathbf{k}_0 = 0 \tag{4-3-12}$$

In an element of volume dV near the j ion, the volume force is $n_{j\sigma}\mathbf{k}_\sigma dV$, since the presence of the j ion influences the average concentration of the ions in dV. The net force on dV will be given by

$$(n_{j\sigma}\mathbf{k}_\sigma + n_0\mathbf{k}_0)\, dV = (n_{j\sigma} - n_\sigma)\,\mathbf{k}_\sigma\, dV \tag{4-3-13}$$

In spherical coördinates the force acting on a spherical shell at a distance, r, from the central ion will be

$$4\pi r^2 (n_{j\sigma} - n_\sigma)\,\mathbf{k}_\sigma\, dr \tag{4-3-14}$$

This force is in the direction of the applied force, and is distributed uniformly over the surface. These conditions are comparable to those under which Stokes Law,

$$\mathbf{v} = \frac{\mathcal{F}}{6\pi\eta r} \tag{4-3-15}$$

is applicable,[13] and consequently, the latter may be employed. The force, $\mathcal{F}$, will cause the points within the sphere to move with the velocity, $\mathbf{v}$.

The next step is to express $(n_{ji} - n_i)$ as a function of r by means of the Maxwell-Boltzmann distribution, or

$$n_{ji} = n_i e^{-\frac{e_i\psi_j^0}{kT}} \simeq n_i\left[1 - \frac{e_i\psi_j^0}{kT} + \frac{1}{2}\left(\frac{e_i\psi_j^0}{kT}\right)^2\right] \tag{4-3-16}$$

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[13] Compare M. J. Polissar, *J. Chem. Phys.*, **6**, 833 (1938).

The second term of the expansion of the exponential function is retained by Onsager and Fuoss as it is of interest to the theory of diffusion. For the potential, the second approximation of Debye and Hückel,

$$\psi_j^0 = \frac{e_j}{D}\left[\frac{e^{\kappa a}}{(1+\kappa a)}\frac{e^{-\kappa r}}{r}\right] \tag{4-3-17}$$

is employed. This equation is easily derived from equations (2-4-14) and (3-5-3). Combining equations (4-3-14), (4-3-16) and (4-3-17), the desired force acting on the spherical shell is found by

$$\mathcal{F} dr = 4\pi r^2 \left\{ -\frac{e_j e_\sigma}{DkT}\frac{e^{\kappa a}}{(1+\kappa a)}\frac{e^{-\kappa r}}{r} + \frac{1}{2}\left(\frac{e_j e_\sigma}{DkT}\frac{e^{\kappa a}}{(1+\kappa a)}\right)^2 \frac{e^{-2\kappa r}}{r^2}\right\} n_\sigma \mathbf{k}_\sigma dr \tag{4-3-18}$$

which may be written in the simpler form

$$\mathcal{F} dr = 4\pi(-A_1 r e^{-\kappa r} + A_2 e^{-2\kappa r})\, dr \tag{4-3-19}$$

By introducing Stokes equation, we obtain for the velocity

$$d\mathbf{v}_j = \frac{\mathcal{F} dr}{6\pi\eta r} = \frac{2}{3\eta}\left(-A_1 e^{-\kappa r} + \frac{A_2 e^{-2\kappa r}}{r}\right) dr \tag{4-3-20}$$

The total velocity is obtained by integrating over all values of r from a to ∞, whence

$$\Delta \mathbf{v}_j = \frac{2}{3\eta}\left\{-\frac{A_1 e^{-\kappa a}}{\kappa} + A_2 \operatorname{Ei}(2\kappa a)\right\} \tag{4-3-21}$$

where Ei $(2\kappa a)$ is the exponential integral function

$$\operatorname{Ei}(x) = \int_x^\infty e^{-t}\frac{dt}{t} = -0.5772 - \ln x + x - \frac{x^2}{2\,\underline{|2}} + \cdots \tag{4-3-21a}$$

By resubstituting the values of A_1 and A_2, the final estimate of the effect of electrophoresis becomes

$$\Delta \mathbf{v}_j = -\frac{2}{3\eta}\frac{e_j e_\sigma n_\sigma \mathbf{k}_\sigma}{DkT\kappa(1+\kappa a)} + \frac{1}{3\eta}\left(\frac{e_j}{DkT}\frac{e_\sigma e^{\kappa a}}{(1+\kappa a)}\right)^2 n_\sigma \mathbf{k}_\sigma \operatorname{Ei}(2\kappa a) \tag{4-3-22}$$

For electrical forces, where $\mathbf{k}_i = Xe_i$, and at low concentrations, when κa is negligible, the first term on the right of this equation equals the term derived by the preliminary considerations and given by equation (4-3-9). This becomes apparent upon combining with equation (2-4-11) which defines κ.

For the case of diffusion of an electrolyte which dissociates into two kinds of ions, $s = 2$, and $\mathbf{k}_j = \mathbf{v}_j/\omega_j$. If $\mathbf{v}$ is the net velocity of diffusion, equation (4-3-22) reduces to

$$\Delta\mathbf{v}_j = -\frac{2}{3\eta}\left(\frac{n_1 e_1}{\omega_1} + \frac{n_2 e_2}{\omega_2}\right)\frac{e_j \mathbf{v}}{DkT}\frac{1}{\kappa(1+\kappa a)} + \frac{1}{3\eta}\left(\frac{n_1 e_1^2}{\omega_1} + \frac{n_2 e_2^2}{\omega_2}\right)\frac{\mathbf{v} e_j^2}{(DkT)^2}\phi(\kappa a) \tag{4-3-23}$$

where

$$\phi(\kappa a) = e^{2\kappa a}\,\mathrm{Ei}\,(2\kappa a)/(1+\kappa a)^2 \tag{4-3-23a}$$

In a subsequent discussion of diffusion, the contribution due to electrophoresis will be required. The product of the number of ions, n_j, into the electrophoretic velocity will give the flow, $\Delta\mathbf{J}_j$, or the number of ions passing unit area per second perpendicular to the direction of diffusion. Thus

$$\Delta\mathbf{J}_j = n_j \Delta\mathbf{v}_j = \left[-\frac{2}{3\eta}\frac{n_j e_j n_\sigma e_\sigma}{DkT\kappa(1+\kappa a)} + \frac{n_\sigma e_\sigma^2 n_j e_j^2 \phi(\kappa a)}{3\eta(DkT)^2}\right]\mathbf{k}_\sigma \tag{4-3-24}$$

If $\Delta\mathbf{J}_j = \Delta\mathfrak{M}_{j\sigma}\mathbf{k}_\sigma$, then $\Delta\mathfrak{M}_{ji} = \partial\Delta\mathbf{J}_j/\partial\mathbf{k}_i$, or the term in the brackets in the above equation. This completes the general treatment of electrophoresis.

(b) The General Theory of Ionic Forces Specialized for Conductance and Diffusion. For the treatment of conductance and diffusion, the first two terms of the general equation of continuity (2-5-6) involving the velocities, $V(\mathbf{r}_2)$ and $V(\mathbf{r}_1)$, which refer to flow of the solution as a whole, vanish. This equation for the stationary fields under consideration becomes

$$\begin{aligned}\omega_i[\mathbf{k}_i \cdot \nabla_2 f_{ji}^0(r)] &+ \omega_j[\mathbf{k}_j \cdot \nabla_1 f_{ij}^0(r)] \\ &- e_i\omega_i n_i n_j \nabla_2 \cdot \nabla_2 \psi_j'(\mathbf{r}_{21}) - e_j\omega_j n_i n_j \nabla_1 \cdot \nabla_1 \psi_i'(-\mathbf{r}_{21}) \\ &- \omega_i kT \nabla_2 \cdot \nabla_2 f_{ji}'(\mathbf{r}_{21}) - \omega_j kT \nabla_1 \cdot \nabla_1 f_{ij}'(-\mathbf{r}_{21}) = 0\end{aligned} \tag{4-3-25}$$

By consideration of certain symmetry relations among the variables, and because of the fact that $\mathbf{k}\cdot\nabla f_{ji}^0$ can be replaced by $k(\partial f_{ji}^0/\partial x)$, without loss of generality, this equation can be simplified to

$$(\omega_i k_i - \omega_j k_j)\frac{\partial f_{ji}^0}{\partial x} - e_i\omega_i n_i n_j \nabla\cdot\nabla\psi_j' + e_j\omega_j n_i n_j \nabla\cdot\nabla\psi_i' - (\omega_i + \omega_j)kT\nabla\cdot\nabla f_{ji}' = 0 \tag{4-3-26}$$

By means of the s Poisson equations

$$\nabla\cdot\nabla\psi_j' = -\frac{4\pi}{D}\sum_{i=1}^{s}\frac{e_i}{n_j}f_{ji}'$$

the distribution functions, f'_{ji}, may be eliminated from this equation. Further, since by equation (2-4-20),

$$f^0_{ji} = n_j n_i \left(1 - \frac{e_j e_i}{DkT} \frac{e^{-\kappa r}}{r}\right)$$

we can also eliminate f^0_{ji}. By performing this operation, and by employing some other simple relations involving ψ'_j and ψ'_i, the final differential equation for the potentials can be expressed in the form,

$$\begin{aligned}(\nabla\cdot\nabla)^2\psi'_j - \frac{4\pi}{DkT}\sum_{i=1}^{s}\frac{n_i e_i^2 \omega_i}{\omega_i+\omega_j}\nabla\cdot\nabla\psi'_j - \frac{4\pi}{DkT}\sum_{i=1}^{s}\frac{n_i e_i e_j \omega_i}{\omega_i+\omega_j}\nabla\cdot\nabla\psi'_i \\ = \frac{4\pi}{(DkT)^2}\sum_{i=1}^{s}\frac{\omega_i \mathbf{k}_i - \omega_j \mathbf{k}_j}{\omega_i+\omega_j} n_i e_i^2 e_j \frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r}\right)\end{aligned} \tag{4-3-27}$$

We note that the left side of this equation is identical in form with that of equation (4-2-23) for the potentials encountered in the general treatment of viscosity.

(c) **The Limiting Law of the Conductance of Electrolytes in Low Fields and at Low Frequency.**[14] **Electrolytes Which Dissociate into Two Kinds of Ions.** Before proceeding to an outline of the general solution of the conductance problem, valid for any number of ions, s, it will clarify matters somewhat to consider the case of an electrolyte which dissociates into two ions, or for $s = 2$. To this end, we shall expand equation (4-3-27), which for the case in question is

$$\begin{aligned}(\nabla\cdot\nabla)^2\psi'_1 - \frac{4\pi}{DkT}\frac{n_2 e_2^2 \omega_2}{\omega_1+\omega_2}\nabla\cdot\nabla\psi'_1 + \frac{4\pi}{DkT}\frac{n_2 e_1 e_2 \omega_1}{\omega_1+\omega_2}\nabla\cdot\nabla\psi'_2 \\ = \frac{4\pi X}{DkT}\cdot\frac{e_2\omega_2 - e_1\omega_1}{\omega_1+\omega_2}\frac{n_2 e_2^2 e_1}{DkT}\frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r}\right)\end{aligned} \tag{4-3-28}$$

We note that for conductance, $\mathbf{k}_i$ and $\mathbf{k}_j$ are replaced by Xe_2 and Xe_1, where X is the x-component of the external electrical field. Further, the condition

$$n_1 e_1 \psi'_1 + n_2 e_2 \psi'_2 = 0 \tag{4-3-29}$$

prevails, and also

$$\psi'_1 = \psi'_2. \tag{4-3-30}$$

must be true since electrical neutrality requires that

$$n_1 e_1 + n_2 e_2 = 0 \tag{4-3-31}$$

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[14] L. Onsager, *Physik. Z.*, **28**, 277 (1927).

Upon introducing these conditions, equation (4-3-28) becomes

$$(\nabla\cdot\nabla)^2\psi_1' - \frac{4\pi}{DkT}\left(\frac{n_1e_1^2\omega_1+n_2e_2^2\omega_2}{\omega_1+\omega_2}\right)\nabla\cdot\nabla\psi_1' = \frac{4\pi X}{DkT}\left(\frac{e_2\omega_2-e_1\omega_1}{\omega_1+\omega_2}\right)\frac{n_2e_2^2e_1}{DkT}\frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r}\right) \tag{4-3-32}$$

If we let

$$\kappa_1^2 = q^*\kappa^2 \tag{4-3-33}$$

$$q^* = \frac{e_1\omega_1-e_2\omega_2}{(e_1-e_2)(\omega_1+\omega_2)} \tag{4-3-34}$$

and

$$\Omega = \frac{Xe_1e_2}{DkT} \tag{4-3-35}$$

then equation (4-3-32) becomes

$$(\nabla\cdot\nabla)^2\psi_1' - \kappa_1^2\nabla\cdot\nabla\psi_1' = \Omega\kappa_1^2\frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r}\right) \tag{4-3-36}$$

Upon integration, ψ_1' may be expressed in a series of powers of r, as follows:

$$\psi_1' = \frac{\Omega\kappa_1^2x}{\kappa^2-\kappa_1^2}\left\{-\left(\frac{\kappa-\kappa_1}{3}\right)+\left(\frac{\kappa^2-\kappa_1^2}{8}\right)r-\cdots\right\} \tag{4-3-37}$$

From this the field due to the perturbation of the atmosphere, ΔX_1, is given by

$$\Delta X_1 = -\nabla\psi'_{1(r\to0)} = \frac{e_1e_2}{3DkT}\left(\frac{q^*}{1+\sqrt{q^*}}\right)\kappa X \tag{4-3-38}$$

which is the original expression of Onsager.[15]

This result, and the result obtained for the effect of electrophoresis, are all that we shall require for the computation of the mobility, ionic conductance, and equivalent conductance of an electrolyte. The total field acting on our ion is $X + \Delta X_j$. Because of electrophoresis, the velocity of the ion will be less than $e_j\omega_j(X + \Delta X_j)$. Introducing all the effects, we find that the net velocity in the x-direction is given by

$$v_j = X\left(e_j\omega_j + \frac{\Delta X_j}{X}e_j\omega_j - \frac{e_j\kappa}{6\pi\eta}\right) \tag{4-3-39}$$

where the last term is the correction for electrophoresis according to equation (4-3-11), or (4-3-22), upon neglecting the terms involving the squares.

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[15] L. Onsager, *Physik. Z.*, **28**, 277 (1927).

The mobility is the velocity for unit potential gradient, or $u_j = |v_j|/X$. Hence, in practical units,

$$\bar{u}_j = \frac{1}{300}\left(|e_j|\,\omega_j + \frac{\Delta X_j}{X}\,|e_j|\,\omega_j - \frac{|e_j|\,\kappa}{6\pi\eta}\right) \qquad (4\text{-}3\text{-}40)$$

Now, $|e_j|\,\omega_j/300$ is the limiting mobility $\bar{u}_j^0$ at infinite dilution, and further, $\lambda_j = 96{,}500\bar{u}_j$. Upon substituting these relations. and the value of κ given by equation (3-1-4), we obtain

$$\lambda_j = \lambda_j^0 + \frac{\Delta X_j}{X}\lambda_j^0 - \frac{96{,}500\,|e_j|\,\kappa}{1800\,\pi\eta}$$

or

$$\lambda_j = \lambda_j^0 + \frac{\Delta X_j}{X}\lambda_j^0 - \frac{28.98\,|z_j|}{\eta(DT)^{1/2}}\,\Gamma^{1/2} \qquad (4\text{-}3\text{-}41)$$

For this special case, where $s = 2$, we may substitute the value of $\Delta X_j/X$, given by equation (4-3-38), and introduce equation (3-1-4) for κ. We obtain,

$$\lambda_j = \lambda_j^0 - \mathfrak{S}_{(\lambda)}\Gamma^{1/2} \qquad (4\text{-}3\text{-}42)$$

where

$$\mathfrak{S}_{(\lambda)} = \frac{1.970 \times 10^6}{(DT)^{3/2}}\left(\frac{q^*}{1 + \sqrt{q^*}}\right)|z_1 z_2|\,\lambda_j^0 + \frac{28.98\,|z_j|}{\eta(DT)^{1/2}} \qquad (4\text{-}3\text{-}42a)$$

Expressing the ionic mobilities in equation (4-3-34) by the corresponding conductances, we may write,

$$q^* = \frac{|z_1 z_2|}{(|z_1| + |z_2|)}\,\frac{(\lambda_1^0 + \lambda_2^0)}{(|z_2|\,\lambda_1^0 + |z_1|\,\lambda_2^0)} \qquad (4\text{-}3\text{-}43)$$

Rewriting equation (4-3-42) for both kinds of ions of the electrolyte, and adding, we obtain,

$$\Lambda = \Lambda^0 - \mathfrak{S}_{(\Lambda)}\Gamma^{1/2} \qquad (4\text{-}3\text{-}44)$$

and

$$\mathfrak{S}_{(\Lambda)} = \frac{1.970 \times 10^6}{(DT)^{3/2}}\left(\frac{q^*}{1 + \sqrt{q^*}}\right)|z_1 z_2|\,\Lambda^0 + \frac{28.98\,(|z_1| + |z_2|)}{\eta\,(DT)^{1/2}} \qquad (4\text{-}3\text{-}45)$$

by virtue of the Kohlrausch relation,

$$\Lambda^0 = \lambda_+^0 + \lambda_-^0 \qquad (4\text{-}3\text{-}46)$$

This situation is further simplified if the electrolyte is a symmetrical valence type, for when $|z_1| = |z_2| = z$, $q^* = \frac{1}{2}$, $q^*/(1 + \sqrt{q^*}) = 0.2929$. and

$$\mathfrak{S}_{(\Lambda)} = \frac{5.770 \times 10^5}{(DT)^{3/2}}\,z^2\Lambda^0 + \frac{57.96\,z}{\eta(DT)^{1/2}} \qquad (4\text{-}3\text{-}47)$$

This result has proved to be of great importance, since it renders possible the interpretation of years of accurate experimental work upon the conductance of strong electrolytes, and with its help the determination of ionization constants of weak electrolytes may be performed with far greater certainty than was possible before the interionic attraction theory was developed.

Before turning to the general application of equation (4-3-41) in the next section, we shall consider the important special case where $s = 2$, and $| z_2 | = 2 | z_1 |$. In this case

$$\frac{q^*}{1 + \sqrt{q^*}} = \frac{0.2929 \times 2.2761}{1 + T_1^0 + 0.8165 \sqrt{1 + T_1^0}} \tag{4-3-48}$$

if we introduce the transference number, $T_1^0 = \lambda_1^0/(\lambda_1^0 + \lambda_2^0)$, of the ion constituent having the smaller valence z_1. The numerator, which is exactly 2/3, has been factored into 0.2929 × 2.2761 to simplify the use of Table (5-3-1). Accordingly, substitution in equation (4-3-45) gives

$$\mathfrak{S}_{(\Lambda)} = \frac{5.770 \times 10^5 \times 2.276 \, | z_1 z_2 | \, \Lambda^0}{(DT)^{3/2}(1 + T_1^0 + 0.8165 \sqrt{1 + T_1^0})} + \frac{28.98 \, (| z_1 | + | z_2 |)}{\eta (DT)^{1/2}} \tag{4-3-49}$$

Electrolytes Which Dissociate into any Number of Ions.[16] In order to obtain $\Delta X_j/X$, equation (4-3-41) for the general case of $s > 2$ ions, it is necessary to obtain a general solution of equation (4-3-27). This has been accomplished successfully by Onsager and Fuoss by the use of the matrix algebra in a manner similar to that employed in the case of viscosity. The final complete solution, which may be expanded into forms suitable for numerical computation, is given by

$$\frac{\Delta X_j}{X} = -\frac{1.970 \times 10^6 \, \Gamma^{1/2}}{(DT)^{3/2}} z_j \sum_{n=0}^{\infty} c_n r_j^{(n)} \tag{4-3-50}$$

If this is substituted in the equation for the ionic conductance (4-3-41), we obtain

$$\lambda_j = \lambda_j^0 - \left(\frac{1.970 \times 10^6}{(DT)^{3/2}} \lambda_j^0 z_j \sum_{n=0}^{\infty} c_n r_j^{(n)} + \frac{28.98 | z_j |}{\eta (DT)^{1/2}} \right) \Gamma^{1/2} \tag{4-3-51}$$

The series function, $\sum_{n=0}^{\infty} c_n r_j^{(n)}$, may be computed from the following relations. The coefficients c_n are given by

$$\begin{aligned} c_0 &= \tfrac{1}{2}(2 - \sqrt{2}) \\ c_n &= -\tfrac{1}{2}\sqrt{2} \binom{1/2}{n}; \qquad n \geq 1 \end{aligned} \tag{4-3-52}$$

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[16] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

where $\binom{1/2}{n}$ represents the coefficient of the terms of the expansion $(1 + x)^{1/2}$, or $-1/2$, $1/8$, $-1/16$, $+5/128$, $-7/256$ for n equal to 1, 2, 3, 4, 5. Therefore, the first six coefficients are

$$\begin{aligned} c_0 &= 0.2929 & c_3 &= -0.0442 \\ c_1 &= -0.3536 & c_4 &= 0.0276 \\ c_2 &= 0.0884 & c_5 &= -0.0193 \end{aligned} \tag{4-3-53}$$

Further,

$$r_j = r_j^{(0)} = z_j\left(1 - \frac{\sum \mu_i z_i}{\lambda_j \sum (\mu_i z_i/\lambda_i)}\right) \tag{4-3-54}$$

$$r_j^{(n)} = \sum t_{ji} r_j^{(n-1)} \tag{4-3-55}$$

and t_{ji} is an element of a matrix and is given by

$$t_{ji} = \delta_{ji} \sum_k \mu_k \frac{\mu_k - \mu_j}{\omega_k + \omega_j} + \frac{2\mu_i z_i}{\omega_j + \omega_i} \tag{4-3-56}$$

In these equations, μ_i is defined by

$$\mu_i = \frac{\Gamma_i}{\Gamma} = \frac{n_i e_i^2}{\sum n_j e_j^2} \tag{4-3-57}$$

and the Kronecker symbol, δ_{ji}, is given

$$\delta_{ji} = \begin{cases} 1, & \text{if } j = i \\ 0, & \text{if } j \neq i \end{cases} \tag{4-3-58}$$

t_{ji} is related to an element, h_{ji}, of a matrix H [Onsager and Fuoss, Equations (4-7-6) and (4-7-7)] according to

$$t_{ji} = 2h_{ji} - \delta_{ji} = 2h'_{ij} - \delta_{ji} \tag{4-3-59}$$

In employing these equations, it is important to observe that z_j carries the sign of the corresponding ionic charge. For the simplest case when $s = 2$ and $z_1 = -z_2$, it is clear that $r_j^0 = z_j$. It can also readily be shown that $r_j^{(n)} = 0$, and as a result $\sum c_n r_j^{(n)}$ reduces to $c_0 z_j$, or $0.2929 z_j$, and equation (4-3-51) reduces to equation (4-3-41). For the case when $s = 2$, $|z_1| = |z_2|$ and $q^* = 1/2$, the equivalent of equation (4-3-42) can be obtained from equations (4-3-51) to (4-3-56). In cases of mixtures when $s = 3$, or higher, the algebra involved becomes quite complicated. We shall have occasion to employ these expressions when some features of electrolytic conduction in mixtures of electrolytes come under consideration.

(4) DIFFUSSION OF ELECTROLYTES. THEORY OF ONSAGER[17,18]

(a) Some General Considerations

The coefficient of diffusion, $\mathfrak{D}$, is ordinarily defined by Fick's law, or by the relation

$$J = n\mathbf{v} = -\mathfrak{D}\nabla n \tag{4-4-1}$$

where $\mathbf{J}$ is the flow, $\mathbf{v}$ the velocity, and n is the number of molecules of solute per cc. The flow is usually defined relative to a fixed plane, assumed to be at rest. This definition is adequate for some purposes, but is not altogether convenient for the treatment of diffusion of electrolytes, since an appreciable volume change takes place upon mixing the solutions. In the present treatment, the flow of any solute species will be defined relative to a local frame of reference moving with the solvent. A bulk velocity may be defined by

$$\mathbf{v} = \sum \mathbf{J}_i\bar{V}_i = \sum n_i\mathbf{v}_i\bar{V}_i \tag{4-4-2}$$

where $\bar{V}_0, \bar{V}_1, \cdots \bar{V}_s$ are the partial volumes of the solvent molecule and the solute ions, $1, \cdots s$.

The law expressed by equation (4-4-1) may be written in the form

$$\mathbf{J} = -\mathfrak{D}\nabla n = -\mathfrak{M}\nabla\mu \tag{4-4-3}$$

where μ is the chemical potential, whence

$$\mathfrak{D} = \left(\frac{\partial\mu}{\partial n}\right)_{P,T}\mathfrak{M} \tag{4-4-4}$$

For the ideal solution,

$$\frac{\partial\mu}{\partial n} = \frac{RT}{n}$$

and, consequently,

$$RT\mathfrak{M} = n\mathfrak{D}$$

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[17] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932). See pp. 2759–2770.

[18] J. J. Hermans [*Rec. trav. chim.*, **56**, 635 (1937)] has developed a more general theory of diffusion which is not restricted to spherical symmetry of ionic atmospheres. We have not attempted to review his generalized equations because they reduce to those of Onsager under similar conditions. Although Hermans' equations may be valid at somewhat higher concentrations then Onsager's, they could hardly be expected to apply at the concentrations for which direct diffusion data are available. Hermans bases the experimental proof of his theory upon measurements of liquid junction potentials. See J. J. Hermans, *Rec. trav. chim.*, **56**, 658 (1937); **58**, 1, 259 (1939).

In concentrated solutions, the effect due to deviations from the ideal solution occurs, and the activity coefficient must be introduced, in which case

$$n\mathfrak{D} = RT\mathfrak{M}\left(1 + n\frac{\partial \ln \zeta}{\partial n}\right) \tag{4-4-5}$$

where ζ ($\equiv a/n$) is the activity coefficient of solute when n is in molecules per cc. If the variation of $\mathfrak{D}$ with the concentration could be entirely accounted for by the deviation from the ideal solution, $\mathfrak{M}/n$ would be a constant. The theory to be developed shows that this is not the case, nor do the facts bear out such a contention. $\mathfrak{M}/n$ is the mobility, or the velocity at unit potential gradient, produced by the force $\mathbf{k} = -\nabla\mu$.

Equation (4-4-3) may be converted to the general form

$$\mathbf{J}_i = -\sum_{k=1}^{s} \mathfrak{M}_{ik}\nabla\mu_k \tag{4-4-6}$$

upon the assumption of a linear relationship between the velocity and potential gradients of solute species. By a study of reciprocal relations in irreversible processes, Onsager,[19] on the basis of very general considerations involving the principle of microscopic reversibility, has shown that the matrix coefficients are symmetrical, or

$$\mathfrak{M}_{ik} = \mathfrak{M}_{ki} \tag{4-4-7}$$

This important result means that *the flow of the* i*th species of ion under unit force per unit amount of* k*th species equals the flow of the* k*th species under unit force per unit quantity of the* i*th species.*

(b) The Theory of Diffusion of a Simple Electrolyte

In the case of a solution of an electrolyte containing two kinds of ions, the condition for the absence of electric current is that both cations and anions possess the same velocity, or

$$\mathbf{v}_1 = \mathbf{v}_2 = \mathbf{v}; \qquad \mathbf{J}_1 = n_1\mathbf{v}; \qquad \mathbf{J}_2 = n_2\mathbf{v} \tag{4-4-8}$$

At low concentrations, we may neglect the interaction between the ions, and write

$$\mathbf{v} = \mathbf{k}_1\omega_1 = \mathbf{k}_2\omega_2 = -\omega_1\nabla\mu_1 = -\omega_2\nabla\mu_2 \tag{4-4-9}$$

If μ is the chemical potential of a molecule which dissociates into ν_1 anions and ν_2 cations, we obtain

$$\mathbf{k} = \nu_1\mathbf{k}_1 + \nu_2\mathbf{k}_2 = -\nabla\mu \tag{4-4-10}$$

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[19] L. Onsager, *Physical Review*, **37**, 405 (1931); L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932), pp. 2760–2762.

From the last two equations, it follows that

$$k_2 = \left(\frac{\rho_2}{\rho_1}\right) k_1 = \left(\frac{\omega_1}{\omega_2}\right) k_1 ;$$

$$\mathbf{k}_1 = \frac{-\rho_1}{\nu_1 \rho_1 + \nu_2 \rho_2} \nabla\mu = - \frac{\omega_2}{\nu_1 \omega_2 + \nu_2 \omega_1} \nabla\mu :$$

and that

$$\mathbf{v} = - \frac{\omega_1 \omega_2}{\nu_1 \omega_2 + \nu_2 \omega_1} \nabla\mu$$

If the solution is ideal,

$$\nabla\mu = (\nu_1 + \nu_2) kT \, \nabla n/n$$

and consequently

$$\mathbf{J} = n\mathbf{v} = - \frac{(\nu_1 + \nu_2)\omega_1 \omega_2}{\nu_1 \omega_2 + \nu_2 \omega_1} kT \nabla n \tag{4-4-11}$$

which is the simple law of diffusion of electrolytes first derived by Nernst.[20] When interionic forces are considered

$$\nabla\mu = (\nu_1 + \nu_2) kT \nabla \ln (\zeta_{\pm} n)$$

where $\zeta_{\pm}$ is the activity coefficient of electrolyte.

The observation that in the case of diffusion both positive and negative ions migrate with the same velocity is important. Since

$$\mathbf{k}_1 \omega_1 = \mathbf{k}_2 \omega_2$$

the perturbation terms in the equation of continuity (2-5-6) can readily be shown to cancel. A consequence of this simplification is that the ionic atmospheres remain symmetrical, a fact which considerably reduces the complexity of the problem.

On the other hand electrophoresis produces an effect, since it is the result of a volume force acting in the ionic atmosphere. Equation (4-3-23), upon substitution of $1/\rho_i$ for ω_i, gives the electrophoretic correction for the velocity, and may be written

$$\Delta\mathbf{v}_j = \mathbf{v} \left[- \frac{2}{3\eta} (n_1 e_1 \rho_1 + n_2 e_2 \rho_2) \frac{e_j}{DkT \, \kappa(1 + \kappa a)} + \frac{1}{3\eta} (n_1 e_1^2 \rho_1 + n_2 e_2^2 \rho_2) \left(\frac{e_j}{DkT}\right)^2 \phi(\kappa a) \right] \tag{4-4-12}$$

This influence upon the velocity alters the forces $\mathbf{k}_1$ and $\mathbf{k}_2$ in such a way that

$$\mathbf{k}_j = \rho_j(\mathbf{v} - \Delta\mathbf{v}_j); \qquad (j = 1, 2) \tag{4-4-13}$$

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[20] W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

Upon introduction of this consideration in equation (4-4-10), we find that

$$-\nabla\mu = \mathbf{k} = \nu_1\rho_1(\mathbf{v} - \Delta\mathbf{v}_1) + \nu_2\rho_2(\mathbf{v} - \Delta\mathbf{v}_2) \tag{4-4-14}$$

and if equation (4-4-12) is employed for the elimination of $\Delta\mathbf{v}_1$ and $\Delta\mathbf{v}_2$,

$$-\nabla\mu = \mathbf{v}\left[\nu_1\rho_1 + \nu_2\rho_2 + (\rho_1 - \rho_2)^2 \frac{\nu_1\nu_2}{(\nu_1 + \nu_2)} \frac{\kappa}{6\pi\eta(1 + \kappa a)} - \left(\frac{\nu_2\rho_1 + \nu_1\rho_2}{\nu_1 + \nu_2}\right)^2 \frac{\kappa^4\phi(\kappa a)}{48\pi^2\eta n}\right] \tag{4-4-15}$$

This is the force per molecule of solute at a concentration, $n = n_1/\nu_1 = n_2/\nu_2$ molecules per cc. The third term in the brackets on the right is the "first order" (electrophoretic) effect, and is proportional to the square root of the concentration. The last term is of the order of $n \log n$, and is negative.

By solving equation (4-4-15) for $\mathbf{v}$, and multiplying by n, we obtain $\mathbf{J}$. If the second and higher powers of $\Delta\mathbf{v}_1$ and $\Delta\mathbf{v}_2$ are neglected, we obtain

$$\mathbf{J} = n\mathbf{v} = -\mathfrak{M}\nabla\mu = -\left(\frac{n\omega_1\omega_2}{\nu_1\omega_2 + \nu_2\omega_1} + \Delta\mathfrak{M}\right)\nabla\mu \tag{4-4-16}$$

$\Delta\mathfrak{M}$ is given by

$$\Delta\mathfrak{M} = -\left(\frac{\omega_1 - \omega_2}{\nu_1\omega_2 + \nu_2\omega_1}\right)^2 \left(\frac{\nu_1\nu_2}{\nu_1 + \nu_2}\right) \frac{\kappa n}{6\pi\eta(1 + \kappa a)} + \frac{(\nu_1\omega_1 + \nu_2\omega_2)^2}{(\nu_1 + \nu_2)^2(\nu_1\omega_2 + \nu_2\omega_1)^2} \frac{\kappa^4\phi(\kappa a)}{48\pi^2\eta} \tag{4-4-17}$$

In order to convert to more familiar units, we employ the relations

$$n = N\bar{n}; \quad \mu N = \bar{\mu}$$

where N is Avogadro's number, $\bar{n}$ the concentration in mols per cc., and $\bar{\mu}$ the chemical potential in ergs per mol. Consequently, the flow per mol per cc. is given by

$$\bar{\mathbf{J}} = \bar{n}\mathbf{v} = -\bar{\mathfrak{M}}\nabla\bar{\mu} = -\left(\frac{\mathfrak{M}}{N^2}\right)\nabla\bar{\mu} \tag{4-4-18}$$

If we eliminate ω_1 and ω_2 from equation (4-4-17) by means of

$$\omega_j = \frac{300\lambda_j^0}{96{,}500\,|z_j|\,\epsilon} \tag{4-4-18a}$$

let $\Lambda^0 = \lambda_1^0 + \lambda_2^0$, and $c = 1000\bar{n}$, and introduce the numerical values of the universal constants given by Birge,[21] we obtain

$$\bar{\mathfrak{M}} = 1.074 \times 10^{-20} \frac{\lambda_1^0\lambda_2^0 c}{\nu_1\,|z_1|\,\Lambda^0} + \Delta\bar{\mathfrak{M}}' + \Delta\bar{\mathfrak{M}}'' \tag{4-4-19}$$

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[21] R. T. Birge, *Phys. Rev. Suppl.*, **1**, 1 (1929).

where

$$-\Delta\overline{\mathfrak{M}}' \equiv \frac{(|z_2|\lambda_1^0 - |z_1|\lambda_2^0)^2}{\Lambda^{0^2}|z_1 z_2|(\nu_1 + \nu_2)} \frac{3.111 \times 10^{-19}}{\eta_0(DT)^{1/2}} \frac{c\sqrt{\Gamma}}{(1 + \kappa a)} \tag{4-4-20}$$

and

$$\Delta\overline{\mathfrak{M}}'' \equiv \frac{(z_2^2\lambda_1^0 + z_1^2\lambda_2^0)^2}{\Lambda^{0^2}} \frac{9.18 \times 10^{-13}}{\eta_0(DT)^2} c^2\phi(\kappa a) \tag{4-4-21}$$

The function $\phi(\kappa a)$ is given by equation (4-3-23a).

According to equation (4-4-4), the coefficient of diffusion is given by

$$\mathfrak{D} = \overline{\mathfrak{M}} \frac{\partial\bar{\mu}}{\partial\bar{n}} = 1000\overline{\mathfrak{M}} \frac{\partial\bar{\mu}}{\partial c} \tag{4-4-22}$$

For a binary electrolyte,

$$c\frac{\partial\bar{\mu}}{\partial c} = 2RT\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) \tag{4-4-23}$$

and therefore $\mathfrak{D}$ is given by

$$\mathfrak{D} = 2000RT\frac{\overline{\mathfrak{M}}}{c}\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) \tag{4-4-24}$$

which is the equation[22] for the diffusion coefficient of an electrolyte which dissociates into only two ions. The value of R in this equation must be given in ergs per degree per mol.

(5) THE DEPENDENCE OF CONDUCTANCE AND DIELECTRIC CONSTANTS OF STRONG ELECTROLYTES UPON THE FREQUENCY. THEORY OF DEBYE AND FALKENHAGEN

(a) Equations for Potentials and Forces in an Alternating Field

We have developed the theory of the conductance of electrolytes, and computed the effect on the mobility of the ions caused by the asymmetry of their ionic atmospheres. So far no consideration has been given to the influence of the frequency of the alternating current upon the conductance, and the result obtained is valid at low frequencies and low electrical fields. The effect of high frequencies upon the conductance and dielectric constant has been successfully investigated from a theoretical point of view by Debye and Falkenhagen.[23]

In an alternating field the ions possess an oscillatory motion. At low

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[22] In comparing this equation with the final result given by Onsager and Fuoss (*loc. cit.* p. 2767), it should be noted that their equation (4-13-19) contains a typographical error, the numerical coefficient being 1000 times too small.

[23] P. Debye and H. Falkenhagen, *Physik. Z.*, **29**, 121, 401 (1928); *Z. Elektrochem.*, **34**, 562 (1928). H. Falkenhagen, "Electrolytes," p. 181–192, Clarendon Press, Oxford, 1934.

frequencies, the ionic atmospheres have an asymmetry caused by the external field. But if the frequency is so great that the period of oscillation is of the order of the time of relaxation of the atmosphere, then the asymmetric ionic atmospheres have less chance to form. As a result, the ionic atmospheres depart less and less from the spherical symmetry of the unperturbed state as the frequency is increased, and the conductance of the solution will increase accordingly.

Since the presence of an alternating external field produces a condition which is not stationary, we require the non-stationary form of the equation of continuity (2-5-6) in order to derive the equations for the potentials. Thus,

$$\begin{aligned} -\frac{\partial f_{ji}(\mathbf{r}_1,\mathbf{r}_{21})}{\partial t} &= \omega_i(\mathbf{k}_i\cdot\nabla_2 f^0_{ji}(\mathbf{r})) + \omega_j(\mathbf{k}_j\cdot\nabla_1 f^0_{ij}(\mathbf{r})) \\ &\quad - e_i\omega_i n_i n_j \nabla_2\cdot\nabla_2\psi'_j(\mathbf{r}) - e_j\omega_j n_i n_j \nabla_1\cdot\nabla_1\psi'_i(-\mathbf{r}) \\ &\quad - \omega_i kT\nabla_2\cdot\nabla_2 f'_{ji}(\mathbf{r}) - \omega_j kT\nabla_1\cdot\nabla_1 f'_{ij}(-\mathbf{r}) \end{aligned} \tag{4-5-1}$$

By the introduction of the relative coördinates, $q_{21} = q_2 - q_1$, etc., or, $x = x_2 - x_1$, $y = y_2 - y_1$, etc., it can be shown that

$$\begin{aligned} f^0_{ji}(\mathbf{r}) &= f^0_{ij}(\mathbf{r}), \\ \nabla_1 f^0_{ij}(\mathbf{r}) &= -\nabla_2 f^0_{ij}(\mathbf{r}) = -\nabla f^0_{ji}(\mathbf{r}) \\ \nabla_2\cdot\nabla_2 &= \nabla_1\cdot\nabla_1 = \nabla\cdot\nabla \\ f'_{ji}(\mathbf{r}) &= -f'_{ij}(\mathbf{r}) = f'_{ij}(-\mathbf{r}) \end{aligned}$$

Also since $\mathbf{k}_i$ and $\mathbf{k}_j$ have components in the x direction only, we have

$$\mathbf{k}\cdot\nabla f^0_{ji} = k\frac{\partial f^0_{ji}}{\partial x} = Xe_j\frac{\partial f^0_{ji}}{\partial x}$$

Upon employing these relations, and also by eliminating $\nabla_2\cdot\nabla_2\psi'_j$, and $\nabla_1\cdot\nabla_1\psi'_i$ by the corresponding Poisson equations, we may transpose equation (4-5-1), and obtain[24]

$$\begin{aligned} \frac{\partial f_{ji}}{\partial t} &= kT(\omega_i + \omega_j)\nabla\cdot\nabla f'_{ij} + (e_j\omega_j - e_i\omega_i)X\frac{\partial f^0_{ji}}{\partial x} \\ &\quad - \frac{4\pi}{D}\left[e_i\omega_i n_i \sum_i f'_{ji}e_i + e_j\omega_j n_j \sum_j f'_{ij}e_j\right] \end{aligned} \tag{4-5-2}$$

Now, we assume that the field strength, X, is small, and possesses a frequency $\bar{\omega}$, and let

$$X_{\bar{\omega}} = X_{(\bar{\omega}=0)}e^{i\bar{\omega}t} = Xe^{i\bar{\omega}t} \tag{4-5-3}$$

[24] (4-5-2) is equation (4-3-6) of Onsager and Fuoss, after introduction of the Poisson equation, with the difference that the nonstationary form is used. It is identical with equation (411) of H. Falkenhagen, "Electrolytes," p. 172, *loc. cit.*

Further, let

$$f_{ji} = f_{ji}^0 + g_{ji} = f_{ji}^0 + G_{ji}e^{i\bar{\omega}t} \tag{4-5-4}$$

where

$$f_{ji}^0 = n_i n_j \left(1 - \frac{e_i e_j}{D_0 kT}\frac{e^{-\kappa r}}{r}\right) \tag{2-4-20}$$

Upon substitution of these relations in equation (4-5-2), we obtain[25]

$$\begin{aligned}(\omega_i + \omega_j)kT\nabla\cdot\nabla G_{ji} - i\bar{\omega}G_{ji} - \frac{4\pi n_i e_i \omega_i}{D_0}\sum_i G_{ji}e_i \\ - \frac{4\pi n_j e_j \omega_j}{D_0}\sum_j G_{ij}e_j = (e_j\omega_j - e_i\omega_i)X\frac{\partial f_{ji}^0}{\partial x}\end{aligned} \tag{4-5-5}$$

For the case of an electrolyte which dissociates into two kinds of ions, the conditions which are of interest in the present problem are:

$$G_{12} = -G_{21}\,; \quad \text{and} \quad G_{11} = G_{22} = 0,$$

and, as a result, equation (4-5-5) reduces to

$$\begin{aligned}(\omega_1 + \omega_2)kT\nabla\cdot\nabla G_{12} - i\bar{\omega}G_{12} - \frac{4\pi}{D_0}(n_1 e_1^2\omega_1 + n_2 e_2^2\omega_2)G_{12} \\ = -(e_1\omega_1 - e_2\omega_2)X\frac{\partial f_{12}^0}{\partial x}\end{aligned} \tag{4-5-6}$$

We now use the relations given by equations (4-3-33) and (4-3-34), namely,

$$\kappa_1^2 = q^*\kappa^2; \tag{4-3-33}$$

$$q^* = \frac{e_1\omega_1 - e_2\omega_2}{(e_1 - e_2)(\omega_1 + \omega_2)} \tag{4-3-34}$$

From these relations, and equation (4-1-11), we obtain for the time of relaxation,

$$\tau = \left(\frac{\rho_1\rho_2}{\rho_1 + \rho_2}\right)\frac{1}{kT\kappa_1^2} \tag{4-5-7}$$

Further, we let

$$q^*\tau = \bar{\tau} \tag{4-5-8}$$

and define the complex quantity K^2 by

$$K^2 = \kappa_1^2(1 + i\bar{\omega}\tau) \tag{4-5-9}$$

By substitution of all these relations in equation (4-5-6), we obtain

$$\nabla\cdot\nabla G_{12} - K^2 G_{12} = -\frac{(e_1\rho_2 - e_2\rho_1)X\partial f_{12}^0}{(\rho_1 + \rho_2)kT\partial x} \tag{4-5-10}$$

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[25] This corresponds to equation (462), p. 184—H. Falkenhagen, "Electrolytes," *loc. cit.* Equation (4-5-6) is equation (465), p. 185 in this text.

Further, according to equation (2-4-20), the distribution function, f_{12}^0, is given by

$$f_{12}^0 = n_1 n_2 - \frac{n_1 n_2 e_1 e_2 e^{-\kappa r}}{D_0 kTr} \qquad (2\ 4\text{-}20)$$

and the asymmetric potentials, ψ_1', may be found from previous relations to be given by

$$-\frac{D_0 n_1}{4\pi e_2} \nabla \cdot \nabla \psi_1' = G_{12} e^{i\bar{\omega} t} \qquad (4\text{-}5\text{-}11)$$

Combining these last two relations with equation (4-5-10), we obtain the differential equation for the potential of the atmosphere around ion (1). Thus,

$$(\nabla \cdot \nabla)^2 \psi_1' - K^2 \nabla \cdot \nabla \psi_1' = \Omega\ \kappa_{\mathrm{I}}^2 \frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r}\right) e^{i\bar{\omega} t} \qquad (4\text{-}5\text{-}12)$$

where Ω is defined by equation (4-3-35) when $\bar{\omega}$ equals zero. We note that equation (4-5-12) has the same form as equation (4-3-36) derived by Onsager. K^2 is given by equation (4-5-9), or by

$$K^2 = \frac{\rho_1 \kappa_{\mathrm{II}}^2 + \rho_2 \kappa_{\mathrm{I}}^2}{\rho_1 + \rho_2} + \frac{2\rho_1 \rho_2}{(\rho_1 + \rho_2)} \frac{i\bar{\omega}}{2kT} \qquad (4\text{-}5\text{-}13)$$

and κ_{I}^2 and κ_{II}^2 are defined by

$$\kappa^2 = \kappa_{\mathrm{I}}^2 + \kappa_{\mathrm{II}}^2 = \frac{4\pi}{D_0 kT} n_1 e_1^2 + \frac{4\pi}{D_0 kT} n_2 e_2^2 \qquad (4\text{-}5\text{-}14)$$

When $\bar{\omega}$ equals zero, equation (4-5-12) reduces to equation (4-3-36) and is sufficiently general for the computation of the frequency effect upon the conductance and dielectric constant. ψ_1' is the asymmetric potential of the oscillating ion.

ψ_1' and the corresponding value of ψ_2' may be obtained by integration of equation (4-5-12), and the fundamental relations

$$n_1 e_1 \psi_1' + n_2 e_2 \psi_2' = 0,$$

$$n_1 e_1 = -n_2 e_2,$$

$$\psi_1' = \psi_2'$$

The asymmetric part of the potential in the immediate neighborhood of the ions turns out to be

$$\psi_1' = -\frac{\Omega_{\bar{\omega}} q^* \kappa^2}{3(\kappa + K)} e^{i\bar{\omega} t}[r \cos\theta + 0(r^2)] \qquad (4\text{-}5\text{-}15)$$

where θ is the angle between the radius vector, r, and the direction of the field.

From this equation, the field, at the position of ion 1 for $\theta = 0$, may be obtained according to the method indicated by equation (4-3-38). Thus,

$$\Delta X_{\bar{\omega}} = -\nabla\psi_1'(r = 0) = \frac{e_2}{3D_0kT}\left(\frac{q^*\kappa\rho_1 v_1 e^{i\bar{\omega}t}}{1 + \sqrt{q^*}\sqrt{1 + i\bar{\omega}t}}\right) \tag{4-5-16}$$

where $v_1 e^{i\bar{\omega}t}$ is the absolute velocity of ion 1.

(b) Equations for Conductance and Dielectric Constant Lowering in an Alternating Field

We now adopt a procedure similar to that which was employed in computing the conductance for the non-oscillating case. We are interested in the velocity $v_j e^{i\bar{\omega}t}$. If we modify equation (4-3-39) to meet the conditions now under consideration, we obtain

$$v_j e^{i\bar{\omega}t} = \left(Xe_j\omega_j + \Delta Xe_j\omega_j - \frac{Xe_j\kappa}{6\pi\eta}\right)e^{i\bar{\omega}t} \tag{4-5-17}$$

By employing equation (4-5-16), replacing $\rho_1 v_1$ by Xe_j,

$$v_j e^{i\bar{\omega}t} = X\left(e_j\omega_j + \frac{e_1e_2}{3D_0kT}\kappa e_j\omega_j\chi(q^*, \bar{\omega}\tau) - \frac{e_j\kappa}{6\pi\eta}\right)e^{i\bar{\omega}t} \tag{4-5-18}$$

is obtained, where

$$\chi(q^*, \bar{\omega}\tau) = \frac{q^*}{\sqrt{q^*}\sqrt{1 + i\bar{\omega}\tau} + 1} \tag{4-5-19}$$

From the above equation for the velocity, it is possible by suitable procedures to obtain final equations for the molar conductance, Λ_m, and the lowering of the dielectric constant, $D - D_0$. In practical units, the results may be expressed as follows:

$$\Lambda_{\bar{\omega}} = \Lambda_m^0 - \Lambda_{I\bar{\omega}} - \Lambda_{II} \tag{4-5-20}$$

$\Lambda_{\bar{\omega}}$ is the total molar conductance at a frequency $\bar{\omega}$, Λ_m^0 the molar conductance at infinite dilution, $\Lambda_{I\bar{\omega}}$ the contribution to $\Lambda_{\bar{\omega}}$ due to asymmetric ionic atmosphere, and Λ_{II} the contribution due to electrophoresis. $\Lambda_{I\bar{\omega}}$ and Λ_{II} are given by the equations,

$$\Lambda_{I\bar{\omega}} = \frac{|e_1e_2|\kappa}{3D_0kT}\Lambda_m^0\chi_R \tag{4-5-21}$$

and

$$\Lambda_{II} = \sum_j \frac{n_je_j^2\kappa}{6\pi\eta_0}\left(\frac{1000}{c}\right)\frac{1}{9 \times 10^{11}} \tag{4-5-22}$$

where χ_R, or the real part of χ, may be computed from

$$\chi_R = \frac{\sqrt{q^*}}{(1 - 1/q^*)^2 + \bar{\omega}^2\tau^2}[(1 - 1/q^*)(\bar{R} - 1/\sqrt{q^*}) + \bar{\omega}\tau\bar{Q}] \tag{4-5-23}$$

and where

$$\bar{R} = 2^{-1/2}[(1 + \tilde{\omega}^2\tau^2)^{1/2} + 1]^{1/2}; \quad \bar{Q} = 2^{-1/2}[(1 + \tilde{\omega}^2\tau^2)^{1/2} - 1]^{1/2} \qquad (4\text{-}5\text{-}24)$$

The increase in the dielectric constant caused by the alternating field turns out to be

$$D_{\tilde{\omega}} - D_0 = \frac{4\pi \mid e_1 e_2 \mid}{3D_0 kT} \kappa \sum n_j e_j^2 \omega_j \frac{\tau\sqrt{q^*}}{\tilde{\omega}\tau[(1 - 1/q^*)^2 + \tilde{\omega}^2 \tau^2]} \cdot [\bar{Q}(1 - 1/q^*) - \tilde{\omega}\tau(\bar{R} - 1/\sqrt{q^*})] \qquad (4\text{-}5\text{-}25)$$

Equations (4-5-20) to (4-5-24), and (4-5-25) represent the final formulation of the Debye-Falkenhagen theory of the dependence of conductance and dielectric constant upon high frequencies. For stationary fields ($\tilde{\omega} = 0$), χ_R becomes $\frac{q^*}{1 + \sqrt{q^*}}$ in agreement with the result of Onsager's theory of conductance. Simplified equations, and tables for practical computations will be found in Chapter (5), Section (3).[26]

(6) THEORY OF THE EFFECTS OF HIGH FIELDS ON THE PROPERTIES OF STRONG ELECTROLYTES. WIEN EFFECT

In the previous discussion of the behaviors of ionic atmospheres [Chapter (2)], we have pointed out that, in high fields, the ions are drawn out of their atmospheres, and as a result, when they are caused to migrate, they are not retarded by having to drag their atmospheres with them. A simple calculation by Falkenhagen[27] will serve to illustrate how this condition arises. According to equation (4-1-15), we find that

$$\rho_i = \frac{1.54 \times 10^{-7} \mid z_i \mid \cdot}{\lambda_i^0} \qquad (4\text{-}6\text{-}1)$$

Let us take the case of a solution of potassium chloride in water at 18°, and consider the potassium ion. Its mobility is 0.000675 cm/sec, and therefore its absolute velocity in a field of 100,000 volts/cm is 67.5 cm/sec. Since λ_1^0 equals 65, ρ_i equals 0.236×10^{-8}. If the concentration, c, is taken to be 0.0001, then according to equation (4-1-12), the time of relaxation is 0.276×10^{-6} sec. Now, at this concentration the mean thickness of the ionic atmosphere, $1/\kappa$, is 3.06×10^{-6} cm. During the time of relaxation, the ion will have migrated 18.6×10^{-6} cm, or six times the thickness of the atmosphere. Under such conditions, it is impossible for the atmosphere to form.

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[26] The extension of the theory of the influence of frequency upon conductance and dielectric constant to mixtures of strong electrolytes has been made by Falkenhagen and Fischer [H. Falkenhagen and W. Fischer, *Physik. Z.*, **33**, 941 (1932); **34**, 593 (1933); *Nature* **130**, 928 (1932)].

[27] H. Falkenhagen, "Electrolytes," p. 237, Clarendon Press, Oxford, 1934.

From these considerations, it is apparent that in the field the ions possess greater mobilities than in the absence of the field. Consequently, the conductance of the solution is increased, and Ohm's law can be expected to have only a limited range of validity.

Since the Debye-Hückel-Onsager theory of conductance was limited to low potentials, it must be modified to take into account the effects of high fields. The first attempt to extend the theory was made by Joos and Blumentritt.[28] They obtained an equation of the form

$$\frac{\Delta\Lambda}{\Lambda_{X=0}} \equiv \frac{\Lambda_X - \Lambda_{X=0}}{\Lambda_{X=0}} = AX^2(1 - BX^2) \tag{4-6-2}$$

where Λ_X and $\Lambda_{X=0}$ represent the molar conductances in fields of potential, X, and $X = 0$, respectively. The parameters A and B are functions of T, D, c, and the ionic conductances and valences. This result was applicable for the lower values of the applied potential. On account of the assumptions premised by Joos and Blumentritt, their theory possesses qualitative value only.

Proceeding in a different manner, Falkenhagen[29] developed a qualitative theory for fields varying in potential from 0 to ∞. Later, Falkenhagen and Fleischer,[30] on the basis of this theory, introduced the non-stationary field and computed the effect of frequency upon the Wien effect.

A more exact theory of the Wien effect for strong electrolytes which takes into account both the hydrodynamic effect and electrophoresis has been developed by Onsager and Wilson.[31] The general outline and final results of this theory will now be presented.

In terms of the variable $\mathbf{r}$, it follows from equation (2-5-5) that†

$$\begin{aligned}\nabla\cdot f_{ji}(\mathbf{r})[\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})] &= \omega_i[\mathbf{k}_i\cdot\nabla f_{ji}(\mathbf{r})] \\ &- \omega_j[\mathbf{k}_j\cdot\nabla f_{ij}(\mathbf{r})] - n_j n_i[e_i\omega_i\nabla\cdot\nabla\psi_j(\mathbf{r}) + e_j\omega_j\nabla\cdot\nabla\psi_i(-\mathbf{r})] \\ &- kT(\omega_i + \omega_j)\nabla\cdot\nabla f_{ji}(\mathbf{r}) = 0; \qquad (i, j = 1, 2, \cdots s)\end{aligned}$$

Only the case of the binary electrolyte will be considered. The forces, $\mathbf{k}_1$ and $\mathbf{k}_2$, will be expressed by

$$\mathbf{k}_1 = \mathbf{X}e_1\,; \qquad \mathbf{k}_2 = \mathbf{X}e_2$$

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[28] G. Joos and M. Blumentritt, *Physik. Z.*, **28**, 836 (1927); M. Blumentritt, *Ann. Physik.*, **85**, 812 (1928).

[29] H. Falkenhagen, *Physik. Z.*, **30**, 163 (1929); **32**, 353 (1931).

[30] H. Falkenhagen and H. Fleischer, *Ibid.*, **39**, 305 (1938); H. Falkenhagen, F. Fröhlich, and H. Fleischer, *Naturwiss.*, **25**, 446 (1937); H. Fleischer, "Dissertation," Dresden 1938; F. Fröhlich, *Physik. Z.*, **40**, 139 (1939).

[31] W. S. Wilson, "Dissertation," Yale University, 1936; also H. C. Eckstrom and C. Schmelzer, *Chem. Rev.*, **24**, 367 (1939).

† Note that the perturbation effects are large and that f, not f^0, appears in these equations.

where X is the component of the electric field acting in the direction of the positive x-axis. Further, for the restricted case of the binary electrolyte,

$$|e_1| = |e_2| = e$$

$$n_1 = n_2 = n \quad .$$

With these relations, the equations of motion become

$$n^2e\{\nabla\cdot\nabla(\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r}))\} + 2kT\nabla\cdot\nabla f_{11}(\mathbf{r}) = 0 \tag{4-6-3}$$

$$-n^2e\{\nabla\cdot\nabla(\psi_2(\mathbf{r}) + \psi_2(-\mathbf{r}))\} + 2kT\nabla\cdot\nabla f_{22}(\mathbf{r}) = 0 \tag{4-6-4}$$

$$\begin{aligned} Xe(\omega_1 + \omega_2)\frac{\partial f_{12}(\mathbf{r})}{\partial x} - n^2 e\{\omega_1\nabla\cdot\nabla\psi_2(\mathbf{r}) - \omega_2\nabla\cdot\nabla\psi_1(-\mathbf{r})\} \\ + kT(\omega_1 + \omega_2)\nabla\cdot\nabla f_{12}(\mathbf{r}) = 0 \end{aligned} \tag{4-6-5}$$

$$\begin{aligned} -Xe(\omega_1 + \omega_2)\frac{\partial f_{21}(\mathbf{r})}{\partial x} - n^2 e\{\omega_1\nabla\cdot\nabla\psi_2(-\mathbf{r}) - \omega_2\nabla\cdot\nabla\psi_1(\mathbf{r})\} \\ + kT(\omega_2 + \omega_1)\nabla\cdot\nabla f_{21}(\mathbf{r}) = 0 \end{aligned} \tag{4-6-6}$$

(a) The Boundary Conditions

(i) *Flow.* The number of ions, $F_{ji}(\Omega)$, leaving the interior, Ω, of a region S is

$$\begin{aligned} -\frac{\partial F_{ji}(\Omega)}{\partial t} &= \int_S f_{ji}(\mathbf{r})\{\mathbf{e}_n\cdot[\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})]\}\,dS \\ &= \int_\Omega \nabla\cdot(f_{ji}(\mathbf{r})[\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})])\,d\Omega = 0 \end{aligned} \tag{4-6-7}$$

where $\mathbf{e}_n$ is the unit vector normal to the surface, S. The laws of chemical conservation require that this integral vanish for any region, Ω. This fundamental condition is usually applied in the form

$$\lim_{\Omega(s)\to 0} \int f_{ji}(\mathbf{r})\{\mathbf{e}_n\cdot[\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})]\}\,dS = 0 \tag{4-6-8}$$

and states that the vector field of the flow, $f_{ji}(\mathbf{r})[\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})]$, must be without sources.

(ii) *Poisson Equations.* According to (2-4-1) and (2-4-2),

$$\begin{aligned} \nabla\cdot\nabla\psi_j(\mathbf{r}) &= -\frac{4\pi}{D}\rho_j(\mathbf{r}) = -\frac{4\pi}{D}\sum_{i=1}^{s} n_{ji}(\mathbf{r})e_i \\ &= -\frac{4\pi}{D}\frac{1}{n_j}\sum_{i=1}^{s} f_{ji}(\mathbf{r})e_i \end{aligned} \tag{4-6-9}$$

The expanded forms of these equations for a binary electrolyte are

$$\nabla\cdot\nabla\psi_1(\mathbf{r}) = \frac{4\pi e}{nD}[-f_{11}(\mathbf{r}) + f_{12}(\mathbf{r})] \tag{4-6-10}$$

$$\nabla\cdot\nabla\psi_2(\mathbf{r}) = \frac{4\pi e}{nD}[-f_{21}(\mathbf{r}) + f_{22}(\mathbf{r})] \tag{4-6-11}$$

(iii) *Ionic Fields.* The space charge within the region Ω is

$$-\frac{D}{4\pi}\int_\Omega \nabla\cdot\nabla\psi_j(\mathbf{r})\,d\Omega = \int_\Omega \rho_j(\mathbf{r})\,d\Omega$$

$\rho_j(\mathbf{r})$ is integrable except for the condition of point charge at the origin. The right side of this equation approaches zero as Ω approaches zero, unless Ω contains the origin, in which case

$$\lim_{\Omega\to 0}\int_\Omega \rho_j(\mathbf{r})\,d\Omega = e_j$$

Combining these equations and applying Gauss's theorem, we obtain

$$\lim_{\Omega\to 0}\int_{S(\Omega)} \nabla\psi_j(\mathbf{r})\cdot d\mathbf{S} = -\frac{4\pi e_j}{D}\,\delta \tag{4-6-12}$$

where δ is unity if the origin is at central ion, and zero if origin is elsewhere.

Very near a given ion, the screening effect of the ionic atmosphere becomes negligible, and the potential of the ion is given by e_j/Dr. The potential of the ion and its atmosphere, $\psi(\mathbf{r})$, will differ from the above potential by a finite amount, whence

$$\psi_j(\mathbf{r}) - e_j/Dr < \infty \tag{4-6-13}$$

At infinity

$$\psi_j(\mathbf{r}) = \psi_i(\mathbf{r}) = 0$$

whence for a binary electrolyte,

$$\psi_1(\mathbf{r}) - e_1/Dr < \infty$$

$$\psi_2(\mathbf{r}) - e_2/Dr < \infty \tag{4-6-14}$$

$$\psi_1(\infty) = \psi_2(\infty) = 0 \tag{4-6-15}$$

(iv) *Symmetry Conditions for the Potentials.* Two symmetry conditions may be derived for the potentials, one of which depends on the fact that $f_{11}(\mathbf{r})$ and $f_{22}(\mathbf{r})$ are even, and the other depends on the odd part of the distribution functions given by $f_{12}(\mathbf{r}) = f_{21}(-\mathbf{r})$. From this equality and the Poisson equations, (4-6-10) and (4-6-11), it follows that

$$\nabla\cdot\nabla[\psi_2(\mathbf{r}) - \psi_2(-\mathbf{r}) - \psi_1(\mathbf{r}) + \psi_1(-\mathbf{r})] = 0 \tag{4-6-16}$$

Since the differences, $\psi_i(\mathbf{r}) - \psi_i(-\mathbf{r})$, are finite, the quantity within the brackets is always finite. Further, this quantity is a constant, since from the theory of harmonic functions, any finite function which satisfies Laplace's equation is a constant. In addition, since $\psi_j(\infty) = \psi_i(\infty) = 0$,

$$\psi_2(\mathbf{r}) - \psi_2(-\mathbf{r}) - \psi_1(\mathbf{r}) + \psi_1(-\mathbf{r}) = 0 \tag{4-6-17}$$

or

$$\psi_2(\mathbf{r}) - \psi_2(-\mathbf{r}) = \psi_1(\mathbf{r}) - \psi_1(-\mathbf{r}) = 2Y(\mathbf{r}) \tag{4-6-18}$$

where $Y(\mathbf{r})$ is the odd part of the potential.

The symmetry conditions for the even part of the potential may be obtained in the following manner. From equation (4-5-1) the flow for $i = j = 1$ becomes

$$\begin{aligned} &f_{11}(\mathbf{r})[\mathbf{v}_{11}(\mathbf{r}) - \mathbf{v}_{11}(-\mathbf{r})] \\ &\qquad = \omega_1\nabla[-n^2e(\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r})) - 2kTf_{11}(\mathbf{r})] \end{aligned} \tag{4-6-19}$$

The boundary condition for the flow states that its vector field is sourceless. The gradient in the right-hand member is zero, and the bracketed term is constant. Since $f_{ji}(\infty) = n^2$, and $\psi_i(\infty) = \psi_j(\infty) = 0$, it follows that

$$f_{11}(\mathbf{r}) = f_{11}(-\mathbf{r}) = n^2 - \frac{n^2e}{2kT}[\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r})] \tag{4-6-20}$$

and, similarly,

$$f_{22}(\mathbf{r}) = f_{22}(-\mathbf{r}) = n^2 + \frac{n^2e}{2kT}[\psi_2(\mathbf{r}) + \psi_2(-\mathbf{r})] \tag{4-6-21}$$

By addition of the Poisson equations, (4-6-10) and (4-6-11), substitution of $f_{11}(\mathbf{r})$ and $f_{22}(\mathbf{r})$, further addition, and the use of the fundamental relation, equation (2-1-4), we obtain

$$\left(\nabla\cdot\nabla - \frac{\kappa^2}{2}\right)[\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r}) + \psi_2(\mathbf{r}) + \psi_2(-\mathbf{r})] = 0 \tag{4-6-22}$$

where, for the binary electrolyte,

$$\kappa^2 = \frac{8\pi ne^2}{DkT}$$

The boundary conditions require that the bracketed term containing the sum of the potentials be finite. Since equation (4-6-22) has no solution (other than 0) that is finite everywhere and possesses no singularities, it follows that

$$\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r}) + \psi_2(\mathbf{r}) + \psi_2(-\mathbf{r}) = 0$$

or

$$\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r}) = -[\psi_2(\mathbf{r}) + \psi_2(-\mathbf{r})] = 2\Gamma(\mathbf{r}) \tag{4-6-23}$$

where $\Gamma(\mathbf{r})$ is the even part of the potential.

Solving (4-6-18) and (4-6-23) leads to

$$\psi_1(\mathbf{r}) = -\psi_2(-\mathbf{r}) = \Gamma(\mathbf{r}) + Y(\mathbf{r}) \tag{4-6-24}$$

$$\psi_1(-\mathbf{r}) = -\psi_2(\mathbf{r}) = \Gamma(\mathbf{r}) - Y(\mathbf{r}) \tag{4-6-25}$$

which represent the fundamental symmetry conditions of the ionic fields for the binary electrolyte. Combining with (4-6-20) and (4-6-21), we obtain

$$f_{11}(\mathbf{r}) = f_{22}(\mathbf{r}) = n^2 - \frac{n^2 e}{kT}\Gamma(\mathbf{r}) \tag{4-6-26}$$

(b) Simplification of the Fundamental Differential Equations for the Distribution Functions and Potentials

The differential equations, (4-6-5) and (4-6-6), can be reduced to a convenient form by the symmetry relations, (4-6-24) and (4-6-25). Equations (4-6-3) and (4-6-4) are contained in (4-6-26), and this will serve for the elimination of $f_{11}(\mathbf{r})$ and $f_{22}(\mathbf{r})$. If we represent the even and odd parts of the distribution functions, $f_{12}(\mathbf{r})$, by $G(\mathbf{r})$ and $U(\mathbf{r})$, so that

$$f_{12}(\pm\mathbf{r}) = f_{21}(\mp\mathbf{r}) = G(\mathbf{r}) - n^2 \pm U(\mathbf{r}) \tag{4-6-27}$$

where $G(\mathbf{r}) - G(-\mathbf{r}) = U(\mathbf{r}) + U(-\mathbf{r}) = 0$, equations (4-6-5) and (4-6-6) reduce to

$$\frac{n^2 e}{kT}\nabla\cdot\nabla\Gamma(\mathbf{r}) - \nabla\cdot\nabla G(\mathbf{r}) = \frac{eX}{kT}\frac{\partial U(\mathbf{r})}{\partial x} \tag{4-6-28}$$

$$\frac{n^2 e}{kT}\nabla\cdot\nabla Y(\mathbf{r}) - \nabla\cdot\nabla U(\mathbf{r}) = \frac{eX}{kT}\frac{\partial G(\mathbf{r})}{\partial x} \tag{4-6-29}$$

In this formula of the stationary condition, the mobilities ω_1 and ω_2 do not appear.

Upon introducing the boundary conditions for the flow and utilizing the Poisson equations, the differential equations for the distribution functions and the potentials may be expressed in the following manner:

$$\left(\nabla\cdot\nabla - \frac{\kappa^2}{2}\right)U(\mathbf{r}) = -\mu'\frac{\partial G(\mathbf{r})}{\partial x} \tag{4-6-30}$$

$$\left(\nabla\cdot\nabla - \frac{\kappa^2}{2}\right)G(\mathbf{r}) - n^2\eta'\frac{\kappa^2}{2}\Gamma(\mathbf{r}) = -\mu'\frac{\partial U(\mathbf{r})}{\partial x} \tag{4-6-31}$$

$$\left(\nabla\cdot\nabla - \frac{\kappa^2}{2}\right)\Gamma(\mathbf{r}) = \frac{\kappa^2}{2n^2\eta'}G(\mathbf{r}) \tag{4-6-32}$$

$$\nabla\cdot\nabla Y(\mathbf{r}) = \frac{\kappa^2}{2n^2\eta'}U(\mathbf{r}) \tag{4-6-33}$$

By combining (4-6-30), (4-6-31) and (4-6-32), we obtain

$$\nabla\cdot\nabla(\nabla\cdot\nabla - \kappa^2)G(\mathbf{r}) = \mu'^2\frac{\partial^2 G(\mathbf{r})}{\partial x^2} \tag{4-6-34}$$

from which $G(\mathbf{r})$ may be calculated. Once $G(\mathbf{r})$ is known, $\Gamma(\mathbf{r})$, $Y(\mathbf{r})$ and $U(\mathbf{r})$ may be evaluated by equations (4-6-27) to (4-6-29). In the above expressions,

$$\eta' = e/kT \tag{4-6-35}$$

$$\mu' = eX/kT \tag{4-6-36}$$

(c) Solution of the Differential System

The differential system may be treated conveniently in cylindrical coördinates (x, ρ, θ), and is invariant to rotation around x, so that the angle variable, θ, may be dropped. Onsager and Wilson base their solution of these equations by expressing $G(\mathbf{r})$, $U(\mathbf{r})$, $\Gamma(\mathbf{r})$ and $Y(\mathbf{r})$ in terms of their Fourier transforms.[32] The final integrals for $f_{12}(\pm\mathbf{r})$ and $\psi_{12}(\pm\mathbf{r})$ are found to be,

$$\begin{aligned} f_{12}(\pm\mathbf{r}) = f_{21}(\mp\mathbf{r}) = \frac{2}{\pi}\frac{n^2\eta' e}{D}\Bigg[\int_0^\infty \frac{1}{\sqrt{\kappa^4 - 4\mu'^2\alpha^2}} \\ \{(\lambda_1^2 - \alpha^2)K_0(\lambda_1\rho) - (\lambda_2^2 - \alpha^2)K_0(\lambda_2\rho)\}\cos(\alpha x)d\alpha \\ \pm \int_0^\infty \frac{\mu'\alpha}{\kappa^4 - 4\mu'^2\alpha^2}\Bigg\{(\lambda_1^2 - \alpha^2)K_0(\lambda_1\rho) + (\lambda_2^2 - \alpha^2)K_0(\lambda_2\rho) \\ - \frac{\kappa^2}{2}K_0(\lambda_3\rho)\Bigg\}\sin(\alpha x)d\alpha\Bigg] \end{aligned} \tag{4-6-37}$$

$$\begin{aligned} \psi_{12}(\pm\mathbf{r}) = \frac{2}{\pi}\frac{e}{D}\Bigg[\int_0^\infty \frac{\kappa^2}{\kappa^4 - 4\mu'^2\alpha^2}\Bigg\{(\lambda_1^2 - \alpha^2)K_0(\lambda_1\rho) \\ + (\lambda_2^2 - \alpha^2)K_0(\lambda_2\rho) - \frac{4\mu'^2\alpha^2}{\kappa^2}K_0(\lambda_3\rho)\Bigg\}\cos(\alpha x)d\alpha \\ \pm \int_0^\infty \frac{\kappa^2\mu'\alpha}{\kappa^4 - 4\mu'^2\alpha^2}\{K_0(\lambda_1\rho) + K_0(\lambda_2\rho) - 2K_0(\lambda_3\rho)\}\sin(\alpha x)d\alpha\Bigg] \end{aligned} \tag{4-6-38}$$

where $K_0(\lambda\rho)$ is a modified Bessel's function of the second kind and zero order, and λ_1, λ_2 and λ_3 are given by

$$\lambda_1^2 = \lambda_2^2 = \alpha^2 + \kappa^2/2 \pm \sqrt{\kappa^4/4 - \mu'^2\alpha^2} \tag{4-6-39}$$

$$\lambda_3^2 = \alpha^2 + \kappa^2/2 \quad \text{and} \quad \lambda_4 = \alpha \tag{4-6-40}$$

The above integral forms can be used conveniently for both the solution of the ionic force effect and the effect of electrophoresis.

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[32] E. T. Whitaker and G. N. Watson, "Modern Analysis," Fourth Edition, Chapter IX, p. 160ff, Cambridge University Press, 1927. R. Courant and D. Hilbert, "Methoden der Mathematischen Physik," I, Chapter II, p. 65ff, Springer, Berlin, 1931.

(d) Electrophoresis

The effect of electrophoresis on the velocity of the ion in an external electric field of strength, **X**, is obtained by the solution of the hydrodynamic equations

$$\begin{aligned} \eta_0 \nabla \times (\nabla \times \mathbf{v}) &= -\nabla P + \mathbf{F} \\ \nabla \cdot \mathbf{v} &= 0 \end{aligned} \tag{4-6-41}$$

where $\mathbf{v}$ is the velocity, P the pressure, η_0 the viscosity, and $\mathbf{F}$ the force density which arises from the action of the external field upon the ionic atmosphere.

By utilizing the results of the preceding section, the velocity in the direction of the axis of the field is

$$\begin{aligned} v_x(0, 0, \theta) = -\frac{Xe}{2\pi^2\eta_0} \int_0^\infty \frac{1}{\kappa^4 - 4\mu'^2\alpha^2} \Bigg\{ &-\kappa^2\lambda_1^2 \ln\left(\frac{\lambda_1}{\alpha}\right) \\ &- \kappa^2\lambda_2^2 \ln\left(\frac{\lambda_2}{\alpha}\right) + \frac{\kappa^4 - 4\alpha^2\mu'^2}{2} \\ &+ \frac{4\alpha^2\mu'^2(2\alpha^2 + \kappa^2)}{\kappa^2} \ln\left(\frac{\lambda_3}{\alpha}\right)\Bigg\} \, d\alpha \end{aligned} \tag{4-6-42}$$

By employing the variable

$$x \equiv \mu'/\kappa \tag{4-6-43}$$

where $\mu' = Xe/kT$, and integrating, (4-6-42) may be expressed in the form

$$v_x(0, 0, \theta) = -\frac{Xe\kappa}{6\sqrt{2}\,\pi\eta_0} f(x) \tag{4-6-44}$$

where $f(x)$ is given by the equation

$$\begin{aligned} f(x) = 1 + \frac{3}{4\sqrt{2}\,x^3} \Bigg\{ &2x^2 \sinh^{-1} x + \sqrt{2}\,x - x\sqrt{1 + x^2} \\ &- (1 + 2x^2) \tan^{-1} (\sqrt{2}\,x) + (1 + 2x^2) \tan^{-1} \frac{x}{\sqrt{1 + x^2}} \Bigg\} \end{aligned} \tag{4-6-45}$$

We note that when $x = 0, f(x) = \sqrt{2}$ and (4-6-44) reduces to

$$v_0(0, 0, \theta) = -\frac{Xe\kappa}{6\pi\eta_0} \tag{4-3-9}$$

which is the result previously obtained [Equation (4-3-39)]. Further, for infinite field strengths, $x = \infty, f(x) = 1$, and

$$v_\infty(0, 0, \theta) = -\frac{Xe\kappa}{6\sqrt{2}\,\pi\eta_0} \tag{4-6-46}$$

and the electrophoretic effect does not disappear at infinite field.

(e) The Ionic Field

As in case of conductance in low fields [Section (3)], it is necessary to obtain the ionic field due to the perturbation of the atmosphere. This requires the evaluation of $-\nabla\psi(r)$ for $r = 0$. Thus, the total force

$$\mathbf{i}e\Delta X(0) = \mathbf{i}e\Delta X(0, 0, \theta) = \lim_{x=\rho=0} (\nabla\psi_j(0))$$

where $\mathbf{i}$ is unit vector in the x-direction. In terms of the variable $x = \mu'/\kappa$, and by utilizing the result given by equation (4-6-38),

$$\Delta X(0, 0, \theta) = \mp\frac{e\mu'\kappa}{2D}\, g(x) \tag{4-6-47}$$

where

$$g(x) = -\frac{1}{2x^3}\left\{-x\sqrt{1+x^2} + \tan^{-1}\frac{x}{\sqrt{1+x^2}} + \sqrt{2}\,x - \tan^{-1}\sqrt{2}\,x\right\} \tag{4 6-48}$$

and therefore

$$g(0) = \frac{2 - \sqrt{2}}{3}; \quad \text{and} \quad g(\infty) = 0 \tag{4-6-48a}$$

(f) The functions, $f(x)$ and $g(x)$, in Convenient Forms for Numerical Computation

Equations (4-6-45) and (4-6-48) may be transformed into convenient numerical forms by the following substitutions:

$$\tan\frac{\pi}{8} = \sqrt{2} - 1 = \frac{1}{\sqrt{2}+1};$$

$$\tan^{-1}s\left(\cot\frac{\pi}{8}\right) + \tan^{-1}s\left(\tan\frac{\pi}{8}\right) = \tan^{-1}\left(\frac{2s\sqrt{2}}{1-s^2}\right);$$

$$\tan^{-1}s\left(\cot\frac{\pi}{8}\right) - \tan^{-1}s\left(\tan\frac{\pi}{8}\right) = \tan^{-1}\left(\frac{2s}{1+s^2}\right);$$

where,

$$s = \frac{x}{1+\sqrt{1+x^2}}; \tag{4-6-49}$$

Then,

$$x = \frac{2s}{1-s^2}; \qquad \sqrt{1+x^2} = \frac{1+s^2}{1-s^2};$$

and

$$\tan^{-1}(\sqrt{2}\,x) - \tan^{-1}\frac{x}{\sqrt{1+x^2}}$$
$$= \tan^{-1}\left(\frac{2\sqrt{2}\,s}{1-s^2}\right) - \tan^{-1}\left(\frac{2s}{1+s^2}\right) = 2\tan^{-1}\left(s\tan\frac{\pi}{8}\right)$$

By utilizing these expressions, equation (4-6-48) may be written in the form

$$\begin{aligned} g(x) = {} & \left(\frac{1-s^2}{2}\right)\left\{\frac{1}{2} - \frac{1}{2}\tan\frac{\pi}{8}\left(\frac{1-s^2}{2}\right)\right. \\ & \left. - 4\tan^3\frac{\pi}{8}\left(\frac{1-s^2}{2}\right)^2\left\{\frac{1}{3} - \frac{\left(s\tan\frac{\pi}{8}\right)^2}{5} + \frac{\left(s\tan\frac{\pi}{8}\right)^4}{7}\cdots\right\}\right\} \end{aligned} \tag{4-6-50}$$

which reduces to the simple numerical equation

$$\begin{aligned} g(x) = {} & \frac{1}{\phi}\left\{\frac{1}{2} - \frac{0.20710688}{\phi} - \left(\frac{0.20710688}{\phi}\right)^2\left\{0.55228\right.\right. \\ & \left.\left. - 0.0569\left(\frac{x}{\phi}\right)^2 + 0.00695\left(\frac{x}{\phi}\right)^4\cdots\right\}\right\} \end{aligned} \tag{4-6-51}$$

if we replace $(1 - s^2)/2$ by $1/\phi$. In a like manner, equation (4-6-45) becomes

$$\begin{aligned} f(x) = 1 + {} & \frac{3}{4\sqrt{2}}\left(\frac{1-s^2}{2}\right)\left\{\frac{2}{s}\ln\left(\frac{1+s}{1-s}\right) - \cot\left(\frac{\pi}{8}\right)\right. \\ & \left. - \left(1 + s^2\cot^2\frac{\pi}{8}\right)\tan^3\frac{\pi}{8}\left(\frac{1}{1\times 3} - \frac{\left(s\tan\frac{\pi}{8}\right)^2}{3\times 5} + \frac{\left(s\tan\frac{\pi}{8}\right)^4}{5\times 7}\cdots\right)\right\} \end{aligned} \tag{4-6-52}$$

whence

$$f(0) = \sqrt{2}; \quad \text{and} \quad f(\infty) = 1 \tag{4-6-52a}$$

Plots of $f(x)$ and $g(x)$ are shown in Fig. (4-6-1). The limits approached by these functions at high and low fields are indicated in the diagram. Tables of these functions are given in Chapter (5), Section (3).

(g) The Conductance Equation Modified for the Wien Effect

The conductance equation for strong electrolytes in presence of the field can be derived readily from the preceding expressions. Introducing equations (4-6-44) and (4-6-47) for the effects of electrophoresis and the ionic fields, as in the derivation of equation (4-3-39), the ionic velocity becomes

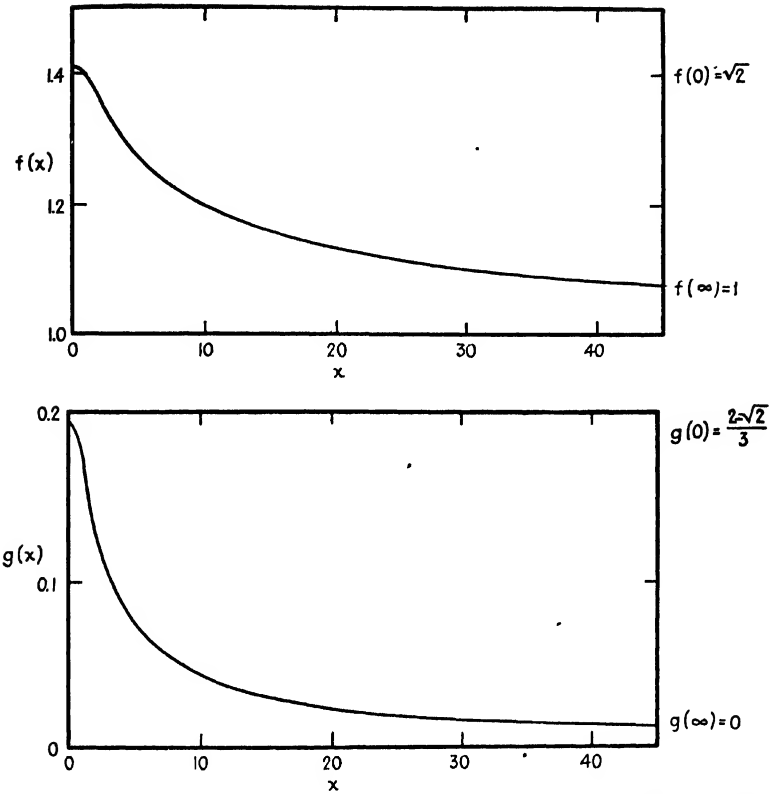

Fig. (4-6-1) (a and b). The functions, $f(x)$ and $g(x)$, for calculation of Wien effect for strong electrolytes.

$$v_j = X\left[e_j\omega_j - \frac{e_j^2\omega_j\mu'\kappa}{2DX}g(x) - \frac{e_j\kappa}{6\sqrt{2}\,\pi\eta_0}f(x)\right] \qquad (4\text{-}6\text{-}53)$$

and (4-3-40) may be expressed in the form

$$\bar{u}_j = \frac{1}{300}\left[|e_j|\,\omega_j - \frac{e_j^2\omega_j\mu'\kappa}{2DX}g(x) - \frac{|e_j|\,\kappa}{6\sqrt{2}\,\pi\eta_0}f(x)\right] \qquad (4\text{-}6\text{-}54)$$

Consequently, the equation for λ_j takes the form

$$\lambda_j = \lambda_j^0 - \frac{e_j^2\kappa}{2DkT}\lambda_j^0 g(x) - \frac{96{,}500\,|e_j|\,\kappa f(x)}{6\sqrt{2}\,\pi\eta_0 300} \qquad (4\text{-}6\text{-}55)$$

upon substitution of e_jX/kT for μ'. This equation reduces to (4-3-42) when x equals 0, since $f(x) = \sqrt{2}$ and $g(x) = \dfrac{2-\sqrt{2}}{3}$.

It is now possible from inspection of Fig. (4-6-1) to understand what happens to the conductance with increase in field. Since the magnitudes of both $g(x)$ and $f(x)$ decrease with increasing field strength, and since both effects [Equation (4-6-55)] of the ionic fields and electrophoresis are subtracted from the limiting conductance, λ_j will increase with increasing field strength. However, in very high fields λ_j will not approach λ_j^0 since $f(x)$ equals unity when $(x = \infty)$. The forms of the conductance curves as functions of the field and the quantitative proof of this theory will be discussed in Chapter (7), Section (8).

Falkenhagen, Frölich and Fleischer[33] have extended the Debye and Falkenhagen theory of frequency effects [This chapter, Section (5)] upon conductance and dielectric constant in the presence of high fields. It is not as complete as the preceding theory of Onsager and Wilson for zero frequency, since the effect of electrophoresis is omitted. The equations for the frequency effects are given in the forms

$$\frac{\Lambda_{X=\infty} - \Lambda_X}{\Lambda_{X=\infty}} = \frac{e^2\kappa^2}{2DkT}\frac{y'}{\mu'} = \frac{e\kappa^2}{X}y' \tag{4-6-56}$$

$$D_{\tilde{\omega}} - D_{\tilde{\omega}=\infty} = -\frac{\kappa^2 e y''}{X\tilde{\omega}\tau} \tag{4-6-57}$$

where μ' equals $2DkT/Xe$. The functions y' and y'', the real and imaginary parts of a complicated function y^*, are not given explicitly but are tabulated. Their tables contain values of y' and y'' as functions of $\mu'/\sqrt{DT/c}$ and $\tilde{\omega}\tau$.

(7) INFLUENCE OF HIGH FIELDS ON THE IONIZATION OF WEAK ELECTROLYTES. THEORY OF ONSAGER

Weak electrolytes in the presence of high fields exhibit deviations from Ohm's law which are many times greater than those of strong electrolytes.[34] The conductance is proportional to the absolute value of the field over a considerable range, and its limit corresponds to the complete dissociation of the weak electrolyte. Recently, upon the basis of the interionic attraction theory, Onsager[35] has developed a theory of this effect which promises to be a very close approach to the solution of the problem, and which has far-reaching implications.

The theory results from a detailed study of the rates of dissociation of electrolytes, and recombination of ions. The conventions regarding association of ions are obtained from an extension of Bjerrum's theory [Chapter (3), Section (7)]. Further, since in the presence of the field,

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[33] H. Falkenhagen, F. Frölich, and H. Fleischer, *Naturwiss.*, **25**, 446 (1937); H. Fleischer, "Dissertation," Dresden, 1938, Effect upon conductance; F. Fröhlich, *Physik. Z.*, **40**, 139 (1939), Effect upon dielectric constant.

[34] M. Wien and J. Schiele, *Physik. Z.*, **32**, 545 (1931).

[35] L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

X, the Boltzmann distribution law is no longer valid, the general laws of the Brownian movement of the ions as given by equation (2-5-6) for the non-stationary case are required. The complete development of this complicated problem of ionic motion requires considerable judgment regarding necessary simplifications, and involves an integral which had not previously been solved.

In the first place, Bjerrum's convention that a pair of ions of opposite sign at a distance $r < q$ is associated is assumed. Since our considerations will involve weak electrolytes, the concentration of free ions is small, and as a result, $1/\kappa$ is much greater than the "effective range" of the ions, q. Thus,

$$\kappa q = -\kappa e_1 e_2 / 2DkT \ll 1 \tag{4-7-1}$$

and

$$\kappa^2 = \frac{4\pi(n_1 e_1^2 + n_2 e_2^2)}{DkT} \tag{4-7-2}$$

where n_1 and n_2 are the concentrations of the free ions. In solutions of strong electrolytes, if κq is small as implied by equation (4-7-1), the effects of interionic forces are small. On the other hand, in the case of weak electrolytes, combination of ions may occur even though κq is small. Bjerrum showed that this effect is governed by the law of mass action no matter what forces are responsible for binding the ions. The variation of the mass action constant with the field becomes our primary concern.

Certain peculiarities of the ionic atmosphere, under the condition that $\kappa q \ll 1$, require examination. In the absence of an external field, the density of i ions in the presence of j ions, n_{ji}, is given by

$$n_{ji}(r) = n_i \exp\left(-W_{ji}(r)/kT\right) \tag{4-7-3}$$

where $W_{ji}(r)$ is the mutual potential of the average force between i and j. When $r > q$, the ions are free, and when $r < q$ the ions are bound. In the case $r > q$, $W_{ji}(r)$ may be derived from the Debye and Hückel theory, and by adapting equation (3-5-4) for the mutual potential between the ions, we obtain

$$W_{ji}(r) = \frac{e_j e_i}{D} \frac{e^{\kappa q - \kappa r}}{(1 + \kappa q) r}; \qquad r > q \tag{4-7-4}$$

Further, according to Bjerrum, the work of separation of the ions is*

$$W_{ji}(r) = \frac{e_j e_i}{Dr}; \qquad r < q \tag{4-7-5}$$

The concentration of associated ion pairs is given by

$$\nu_{ji} = \nu_{ij} = n_j \int_a^q n_{ji}(r) 4\pi r^2 \, dr \tag{4-7-6}$$

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* A correction term of the magnitude κqkT has been neglected, since we have adopted the assumption represented by equation (4-7-1).

where a is the closest distance of approach of the positive to a negative ion. For weak electrolytes, and for all electrolytes in media of low dielectric constant, the principal effect takes place at distances, r, just greater than a. While the upper limit of q is arbitrarily fixed, it can be shown that it may be replaced by $q/2$ or $2q$ without materially affecting the results.

Some important considerations regarding limits may be derived from equations (4-7-4) and (4-7-5). $e^{-\kappa r}$ in equation (4-7-4) represents the "screening off" of the field of an ion by its atmosphere, or by the space charge which surrounds it. If this factor is omitted from equation (4-7-4), and the resulting value for $W_{ji}(r)$ is employed in equation (4-7-3), this space charge can be shown to be infinite, since the integral of equation (4-7-3) with the upper limit of ∞ does not converge. Onsager points out, however, that $e^{-\kappa r}$ may be neglected if equation (4-7-1) is assumed up to a certain distance, $r' > q$, or to be specific

$$q \ll r' \ll 1/\kappa \tag{4-7-7}$$

These considerations make possible the extension of equation (4-7-5) to distances $r' > r$, so that

$$W_{ji}(r) = e_j e_i/Dr; \qquad r < r' \tag{4-7-8}$$

This approximation is particularly good for weak electrolytes, since incomplete dissociation depends principally on the innermost region of the field of the ions, while the region beyond r' is of no importance.

For strong electrolytes, equation (4-7-3) may be replaced [Equation (2-4-9)] by the approximation,

$$n_{ji}(r) \sim n_i(1 - W_{ji}(r)/kT) \tag{4-7-9}$$

which is good for large values of r, or when $W_{ji}(r)/kT \ll 1$. It is poor for small values of r. On the other hand, the approximation given by equations (4-7-8) and (4-7-6) is good at small distances, but leads to absurd consequences at $r = \infty$. Onsager finds, however, that, if r' is extended to infinity, and if the effects due to infinite total space charge at large distances are neglected, a convenient and significant solution may be obtained.

In order to compute the effects of an external field, $\mathbf{X}$, it is necessary to employ the general equations for the motion of the ions. Since the total force, $\mathbf{K}$, is the sum of the external force, $e\mathbf{X}$ acting on the ions, and $\mathbf{k}$, the average of the forces due to the ion atmosphere acting on the ions, we obtain from equation (2-3-1)

$$\begin{aligned}\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r}) = &-\omega_i[e_i\mathbf{X} + \mathbf{k}_{ji}(\mathbf{r}) - kT\nabla_2 \ln f_{ji}(\mathbf{r})] \\ &- \omega_j[e_j\mathbf{X} + \mathbf{k}_{ij}(-\mathbf{r}) - kT\nabla_1 \ln f_{ij}(-\mathbf{r})]\end{aligned} \tag{4-7-10}$$

Further, from equation (2-2-3),

$$\begin{aligned}\frac{\partial f}{\partial t} &= -\nabla_2\cdot[f_{ji}(\mathbf{r}_2-\mathbf{r}_1)\mathbf{v}_{ji}(\mathbf{r}_2-\mathbf{r}_1)] - \nabla_1\cdot[f_{ij}(\mathbf{r}_1-\mathbf{r}_2)\mathbf{v}_{ij}(\mathbf{r}_1-\mathbf{r}_2)] \\ &= \nabla_2\cdot[f_{ji}(\mathbf{r})\,\{\mathbf{v}_{ij}(-\mathbf{r})-\mathbf{v}_{ji}(\mathbf{r})\}] = 0\end{aligned} \tag{4-7-11}$$

This equation can be reduced to a suitable form upon the basis of the assumptions so far premised. (1) By the assumption $\kappa q \ll 1$, the effects of the ionic atmosphere are negligible. This is particularly applicable when a strong field is present, since the atmosphere around the ion is destroyed. (2) By letting $r' = \infty$ in equation (4-7-8), it becomes possible to replace W by the Coulomb potential, $e_j e_i/Dr$. (3) By choosing an external field, $\mathbf{X}$, parallel to the x axis with a potential $-\mathbf{X}x$, and assuming $\mathbf{X}e_j > 0$, $\mathbf{X}e_i < 0$, and dropping the indices of f, the flow is given by

$$\begin{aligned}f(\mathbf{r})\mathbf{v}(\mathbf{r}) &= f(\mathbf{r})[\mathbf{v}_{ji}(\mathbf{r})-\mathbf{v}_{ij}(-\mathbf{r})] \\ &= kT(\omega_j+\omega_i)\left(-\nabla f + f\nabla\left[\frac{2q}{r}+2\beta x\right]\right)\end{aligned} \tag{4-7-12}$$

where

$$q = -\frac{e_j e_i}{2DkT} \tag{4-7-13}$$

$$2\beta = \frac{X(e_j\omega_j - e_i\omega_i)}{kT(\omega_i+\omega_j)} \tag{4-7-14}$$

The stationary condition required by equation (4-7-11) is given by

$$\nabla\cdot\left[f\nabla\left(2\beta x+\frac{2q}{r}\right)\right] - \nabla\cdot\nabla f = 0$$

and since the field of the potential $\left(\frac{2q}{r}+2\beta x\right)$ has no divergence,

$$\nabla\cdot\nabla\left(\frac{2q}{r}+2\beta x\right) = 0,$$

and

$$\nabla\cdot\nabla f = \nabla f\cdot\nabla\left(\frac{2q}{r}+2\beta x\right) \tag{4-7-15}$$

The net rate at which pairs of ions enter any closed surface, S, may be obtained from equation (4-7-12). Thus,

$$\int\frac{\partial f}{\partial t}\,dV = kT(\omega_j+\omega_i)\int\left[\nabla_n f - f\nabla_n\left(\left(\frac{2q}{r}\right)+2\beta x\right)\right]dS \tag{4-7-16}$$

where ∇_n is the gradient normal to S.

In order to develop the theory of incomplete dissociation from the premises so far adopted, it becomes necessary to solve equation (4-7-15) with appropriate boundary conditions. Onsager has succeeded in performing for the first time the integration of this equation, but has not stated the mathematical details in his contribution to the theory of the Wien effect.* Since all the important assumptions have been stated in the preceding discussion, we shall merely outline the method and give the final results.

Onsager found it most convenient to separate the problem by computing the density, f, for the processes of combination and dissociation. The chemical rate of combination has already been given by equation (4-1-19), or

$$\frac{d\nu_{ji}}{dt} = -\frac{dn_j}{dt} = -\frac{dn_i}{dt} = An_jn_i - KA\nu_{ji} \tag{4-7-17}$$

where A and KA are velocity constants of combination and dissociation, respectively, and K the ionization constant. When complete dissociation exists, the distribution of the ions is given by equation (4-7-15), and $n_jn_i \doteq f(r) =$ constant. Consequently, the rate of combination of ions may be obtained from equation (4-7-16) as follows, if spherical co-ordinates, r, θ, and ϕ, are employed.

$$\begin{aligned} An_jn_i &= kT(\omega_j + \omega_i) \int n_jn_i \left(\frac{2q}{r^2} - 2\beta \sin\theta\right) r^2 \sin\theta \, d\theta \, d\phi \\ &= 8\pi qkT(\omega_j + \omega_i)n_jn_i \end{aligned} \tag{4-7-18}$$

For a binary electrolyte, $e_1 = -e_2$,

$$A = \frac{4\pi(e_1^2\omega_1 + e_2^2\omega_2)}{D} \tag{4-7-19}$$

Thus, the rate constant of the recombination of ions is unaffected by the field. When there is no field, and consequently β is zero, it follows from equations (4-7-8), (4-7-3) and the relation, $f(r) = n_jn_{ji}$, that the number of undissociated molecules, ν_{ji}, is given by

$$f(r) = \nu_{ji}K(0)(e^{2q/r} - 1) = n_jn_i(e^{2q/r} - 1) \tag{4-7-20}$$

where $K(0)$ denotes the dissociation constant in the absence of the field. This is the only solution of (4-7-15) which is satisfied by the boundary conditions, that $f = 0$ when $r = \infty$, and the flow from the origin through any space angle is finite.

When $X \neq 0$, the solution of equation (4-7-15) with these boundary conditions is complicated. Onsager has succeeded in obtaining a unique result in the form of a definite integral, namely

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* Solutions are given elsewhere by L. Onsager, Dissertation, Mathieu Functions of Period 4π, Yale University, June 1935.

$$f(r, \theta) = ge^{-\beta r + \beta r \cos\theta} \int_{s=0}^{s=2q} J_0[\sqrt{-4\beta s(1 + \cos\theta)}] \exp\left(\frac{2q - s}{r}\right) \frac{ds}{r} \tag{4-7-21}$$

where J_0 is a Bessel function of order zero. For small values of r, q may be replaced by ∞, and a good approximation

$$f(r, \theta) \simeq ge^{2q/r}e^{2\beta r \cos\theta} \tag{4-7-22}$$

is obtained. If, as mentioned in the preliminary discussion, we disregard the region $r > q$, and go a step further by replacing the second exponential term by unity, then

$$f(r) \sim ge^{2q/r} \tag{4-7-23}$$

which is the same distribution as that of the equilibrium case where $1 \ll \exp(2q/r)$. By comparison with equation (4-7-20), we find that

$$\nu_{ji} = g/K(0) \tag{4-7-24}$$

which gives the desired relation between g and $K(0)$.

In order to evaluate the rate of dissociation according to equation (4-7-21), it is necessary to substitute $f(r, \theta)$ in equation (4-7-16). If the integral is separated according to

$$\int_0^{2q} = \int_0^{\infty} - \int_{2q}^{\infty}$$

it happens that only the second integral on the right contributes anything. One obtains (most easily by specialization to small r),

$$-K(X)A\nu_{ji} = -8\pi qkT(\omega_j + \omega_i)g \frac{J_1(4\sqrt{-\beta q})}{2\sqrt{-\beta q}} \tag{4-7-25}$$

From equations (4-7-18) and (4-7-25), it is clear that the relative increase of the dissociation constant in the field is

$$\begin{aligned} \frac{AK(X)}{AK(0)} = \frac{K(X)}{K(0)} &= \frac{J_1(4\sqrt{-\beta q})}{2\sqrt{-\beta q}} \\ &= 1 + 2\beta q + \frac{(4\beta q)^2}{\underline{|2}\,\underline{|3}} + \frac{(4\beta q)^3}{\underline{|3}\,\underline{|4}} + \cdots \end{aligned} \tag{4-7-26}$$

where J_1 is a Bessel function of the order one. Referring to equation (4-7-19), we recall that the rate constant, A, of combination of ions turned out to be independent of the field.

Equation (4-7-26) represents the principal result of Onsager's theory. The present outline of the theory suffices merely to state the grounds upon which it has been developed, and to indicate the great difficulties. Onsager follows his outline of the derivation with a detailed critique of the approximations employed, and estimates the order of magnitude of the errors involved in these approximations. He notes that, for purposes of simplicity, the hydrodynamic interaction has been omitted, and he attempts to make an estimate of the order of magnitude of the hydrodynamic correction. His conclusion is that, in high fields, this effect may become important, but not sufficiently so to change the order of magnitude of the principal result.

According to equation (4-7-26), it appears that the relative increase of the dissociation constant is measured by the parameter $2\beta q$. From equation (4-7-14), this parameter $\bar{b}$ is given by

$$\bar{b} = 2\beta q = \frac{|z_1|\,\omega_1 + |z_2|\,\omega_2}{\omega_1 + \omega_2}\,|z_1 z_2|\,\frac{X\,\epsilon^3}{2Dk^2T^2} = \frac{z_1^2 z_2^2(\lambda_1 + \lambda_2)}{|z_2|\,\lambda_1 + |z_1|\,\lambda_2}\,9.636\,\frac{V}{DT^2} \tag{4-7-27}$$

where z_1, z_2 are the valences of the ions, λ_1 and λ_2 the equivalent conductances, ϵ the electronic charge, and V the field intensity in volts/cm. For 1–1 electrolytes, this reduces to the simple relation

$$\bar{b} = 9.636\,\frac{V}{DT^2} \tag{4-7-28}$$

The function on the right of equation (4-7-26) is given by a power series,

$$\frac{K(X)}{K(0)} = F(\bar{b}) = 1 + \bar{b} + \frac{\bar{b}^2}{3} + \frac{\bar{b}^3}{18} + \frac{\bar{b}^4}{180} + \frac{\bar{b}^5}{2700} + \frac{\bar{b}^6}{56700} + \cdots \tag{4-7-29}$$

or, for large values of $\bar{b}$, by asymptotic expansion

$$F(\bar{b}) \cong \sqrt{2/\pi}\,(8\bar{b})^{-3/4}e^{\sqrt{8\bar{b}}}\left\{1 - \frac{3}{8(8\bar{b})^{1/2}} - \frac{15}{128(8\bar{b})} - \frac{105}{1024(8\bar{b})^{3/2}}\cdots\right\} \tag{4-7-30}$$

where, for $\bar{b} \geq 3$, the remainder of the series is less than $1/130\bar{b}^2$, which is less than 10^{-3}.

We are now in a position to point out some important and far-reaching consequences of the theory.

(1) From equation (4-7-29), it is clear that the initial effect of the field is to cause $K(X)/K(0)$ to vary linearly with $\bar{b}$, or according to equation (4-7-27), linearly with the absolute value of the field, X.

(2) From these latter two equations, it is also apparent that the change in K with the field depends on two characteristics of the electrolyte, the valencies and the mobilities of its ions.

(3) From the law of mass action, it is possible to compute the effect of the field upon the concentration of the free ions, c_i. For binary electrolytes

$$\frac{c\alpha^2}{1-\alpha} = K(X) = K(0)F(\bar{b}) \tag{4-7-31}$$

where c is the concentration of the electrolyte, and α the degree of dissociation, c_i/c. Further,

$$\frac{\Lambda_X}{\Lambda_{X=0}} = \frac{c_i(X)}{c_i(0)} = \frac{\alpha}{\alpha_0} \tag{4-7-32}$$

where Λ is the conductance.

From the law expressed by equation (4-7-31), the important result is obtained that the change in equilibrium, corresponding to a given change in K, depends on the initial value of the degree of dissociation, α_0.

(4) It is important to note that α/α_0 decreases with increasing α_0. For the case of small values of $\bar{b}$, and for small changes of K,

$$\frac{\Delta\Lambda}{\Lambda_{X=0}} = \frac{\Delta\alpha}{\alpha_0} = \frac{(1-\alpha)}{(2-\alpha)}\frac{\cdot\Delta K}{K(0)} = \frac{(1-\alpha)}{(2-\alpha)}\bar{b} \tag{4-7-33}$$

if all the terms in equation (4-7-29) of order $\bar{b}^2$, or higher, are neglected. Δ denotes an increase caused by the field. When α is nearly unity, the change due to the field is proportional to $(1 - \alpha)$. When $\alpha << 1$, the effect approaches a maximum which is given by

$$\frac{\Lambda_X}{\Lambda_{X=0}} = \frac{\alpha}{\alpha_0} = \sqrt{\frac{K(X)}{K(0)}} = \sqrt{F(\bar{b})} = 1 + \tfrac{1}{2}\bar{b} + \tfrac{1}{24}\bar{b}^2 + \cdots \tag{4-7-34}$$

(5) Reference to equation (4-7-27) shows that b is proportional to the cube of the electronic charge, and inversely proportional to the dielectric constant. Equation (4-7-34), valid for binary electrolytes, is of particular importance in solutions of low dielectric constant where very small ionization is the rule. The magnitudes of the maximum effects in water ($D = 78.57$), and benzene ($D = 2.28$), in fields of the order of 5×10^5 volts/cm, is found to be $\Lambda_X/\Lambda_{X=0} = 1.37$ in water, and 121 in benzene.

(6) We have shown that the time lag of an ionization equilibrium, τ', for a binary electrolyte may be computed by means of equation (4-1-23). By substituting for A in this equation the value given by equation (4-7-19), we obtain the interesting relation,

$$\tau' = \frac{1-\alpha_0}{An(2-\alpha_0)\alpha_0} = \frac{(1-\alpha_0)D}{(2-\alpha_0)4\pi\sigma} \tag{4-7-35}$$

where σ is $\alpha_0 n(e_1^2\omega_1 + e_2^2\omega_2)$, or the specific conductance of the solution in electrostatic units. When $\alpha_0 \ll 1$, the Langevin time lag is

$$\tau' = D/8\pi\sigma = D/8\pi\,(9 \times 10^{11}L) \tag{4-7-36}$$

where L is the specific conductivity in practical units [Equation (6-1-2)]. Comparison with equation (4-1-6) indicates that τ' is just one-half the value of the Maxwell time of relaxation, or the time needed for the shielding of charges.

In equation (4-7-35), α_0 and σ refer to a steady state in a field of magnitude, X. Since our theory shows that both α_0 and σ increase with increasing field, τ' must decrease with the field.

This discussion of the dissociation field effect completes the brief outline of the interionic attraction theory and its applications to the reversible and irreversible phenomena of electrolytic solutions. These results will find repeated application in the subsequent treatment of the properties of these solutions. Since the laws deduced from the theory have not yet been reduced to the forms most suitable for numerical calculations, we shall devote the next chapter to their practical simplification.

Chapter (5)

Numerical Compilations of Physical Constants, Characteristic Slopes, and Mathematical Functions

As an unique feature of this monograph, we have collected, in this chapter, the final equations resulting from the interionic attraction theory, and reduced them to forms suitable for practical applications. Numerical values of important limiting and characteristic slopes have been tabulated under the appropriate equations, and physical constants and mathematical functions which occur frequently have also been recorded. We believe that a careful study of the contents of this chapter will be of considerable value to anyone concerned with applications of the theory, because many of the expressions are in more convenient forms than those previously given, and the tables have been assembled here for the first time.

(1) FUNDAMENTAL PHYSICAL CONSTANTS

In a work of this kind, which involves numerical calculations extending over a period of years, it was found to be necessary to adhere to the values of the physical constants originally selected, namely those given in the International Critical Tables[1] and reproduced in Table (5-1-1). The major changes in these values, necessitated by the use of an erroneous value of the viscosity of air in the earlier calculations, occur with the electronic charge and Avogadro's number. In the latest compilation of Birge,[2] 4.8025×10^{-10} esu. and 6.0228×10^{23} are given for these quantities, respectively. Further, the ice point has been altered to 273.16°. Minor changes are to be noted in the other constants. Although these changes will affect the calculations, they are generally less than the errors in the physico-chemical data with which they are combined.

In Table (5-1-2), we have tabulated functions of the absolute temperature, some of which involve the gas constant, R, and the value of the Faraday, **F**, throughout a temperature range from 0° to 100°.

Dielectric Constants

From the point of view of the interionic attraction theory, the most important physical property of a solvent is its dielectric constant. Several extensive studies of the dielectric constant of water have recently been

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[1] International Critical Tables, Vol. I, p. 17, McGraw-Hill Book Co., New York, 1930.

[2] R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

made. Measurement of a high dielectric constant, in a liquid possessing appreciable conductance, is not easy. The different methods do not show close agreement, especially at high temperatures. The data generally credited with the highest precision were obtained by Drake, Pierce, and Dow[3] and by Wyman,[4] who used resonance methods. Although there is

TABLE (5-1-1)*. FUNDAMENTAL PHYSICAL CONSTANTS EMPLOYED IN SUBSEQUENT NUMERICAL TABLES. ABSOLUTE ELECTRIC UNITS

Symbol	Constant	Value
ϵ	Electronic charge	4.774×10^{-10} esu
F	Faraday	9.6500×10^{4} coulomb
	“	23,060 cals (15°)
	“	2.89365×10^{14} esu
	Normal ideal gas volume	22.4115 liter mol^{-1}
T_0	Ice point 0° (1 atm)	273.1°Abs
R	Gas constant	8.316×10^{7} erg deg^{-1} mol^{-1}
	“	1.9869 cals (15°) deg^{-1} mol^{-1}
N	Avogadro's number	6.061×10^{23} mol^{-1}
k	Gas constant per molecule	1.372×10^{-16} erg deg^{-1}
	Normal atmosphere	1.01325×10^{6} dyne cm^{-2}
	“ (Lat. 45°)	1.01320×10^{6} dyne cm^{-2}
	Liter	1000.027 cm^3
15°	Gram calorie	4.185 joules
Mean	“ “	4.186 joules

* For recent values, see Appendix B, Table (B-1-1).

TABLE (5-1-2). SOME USEFUL FUNCTIONS OF THE ABSOLUTE TEMPERATURE. ($T = 273.10 + t$)

t°C	$\log T$	$\frac{1000}{T}$	$\frac{RT \ln 10}{\text{F}}$ (a)	$\frac{RT^2 \ln 10}{10^5}$ (a)	$y \times 10^8$ (b)	$z \times 10^8$ (c)
0	2.43632	3.66166	0.054191	3.4122	6712	86
5	2.44420	3.59583	.055183	3.5383	5273	54
10	2.45194	3.53232	.056175	3.6667	3885	30
15	2.45954	3.47102	.057168	3.7973	2545	13
18	2.46404	3.43525	.057763	3.8769	1763	6
20	2.46702	3.41181	.058160	3.9302	1251	3
25	2.47436	3.35458	.059151	4.0655	0	0
30	2.48159	3.29924	.060143	4.2030	−1210	3
35	2.48869	3.24570	.061135	4.3428	−2380	12
40	2.49568	3.19387	.062128	4.4849	−3513	26
45	2.50256	3.14367	.063120	4.6293	−4610	45
50	2.50934	3.09502	.064112	4.7760	−5674	69
55	2.51601	3.04785	.065104	4.9250	−6704	97
60	2.52257	3.00210	.066096	5.0762	−7704	130
70	2.53542	2.91460	.068081	5.3857	−9617	206
80	2.54790	2.83206	.070066	5.7043	−11421	296
90	2.56003	2.75406	.072050	6.0320	−13126	398
100	2.57183	2.68025	.074035	6.3688	−14740	511

(a) $\ln 10 = 2.3026$, $R \ln 10 = 4.575$

(b) $y = \dfrac{298.1 - T}{2.3026R \times 298.1T}$

(c) $z = 298.1y - \dfrac{1}{R} \log \dfrac{298.1}{T}$

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[3] F. H. Drake, G. W. Pierce and M. T. Dow, *Phys. Rev.*, **35**, 613 (1930).

[4] J. Wyman, Jr., *Ibid.*, **35**, 623 (1930).

little theoretical basis for choice between these two sets of data, practical considerations have led us to select Wyman's values. The temperature variation of his results for water were checked to better than 0.2 per cent by Åkerlöf.[5] Both these investigators extended their measurements over a wide range of mixtures of non-electrolytes and water. Wyman expressed his results for water by the equation

$$D = 78.54[1 - 0.00460(t - 25) + 0.0000088(t - 25)^2] \qquad (5\text{-}1\text{-}1)$$

from which the values given in Table (5-1-3) were calculated. Åkerlöf's results for water-organic solvent mixtures at 25° are given in Table (5-1-4).

Because of its low dielectric constant, neutral character, and complete miscibility with water, dioxane (1,4-diethylene oxide) has become an important solvent in studying the effect of varying dielectric constant upon the properties of ionic solutions. For this reason special tables (11-1-1A), (11-3-1A) and (11-9-1A), applicable to thermodynamic and conductance calculations in dioxane-water mixtures, appear in later chapters. The dielectric constants of these dioxane-water mixtures may be calculated at any temperature between 0° and 80° by the equation[6]

$$\log D = A - Bt \qquad (5\text{-}1\text{-}2)$$

for which the parameters are recorded in Table (5-1-5).

Ionic Radii

Table (5-1-6) contains values of the ionic radii for some ions of simple structure taken from the recent compilation of Pauling.[7] Frequent references to these values will occur in later discussions.

(2) EQUATIONS DERIVED IN CHAPTER (3) FOR THE CALCULATION OF THERMODYNAMIC PROPERTIES FROM THE ELECTROSTATICS OF IONIC ATMOSPHERES

The limiting equation for the mean rational activity coefficient of a strong electrolyte which dissociates into p kinds of ions was shown to be

$$\log f_\pm = -\mathfrak{S}_{(f)}\sqrt{\Gamma} \qquad (3\text{-}4\text{-}7)$$

where

$$\mathfrak{S}_{(f)} = \frac{1}{\nu}\sum_{1}^{p} \nu_j z_j^2 \frac{1.283 \times 10^6}{(DT)^{3/2}} \qquad (3\text{-}4\text{-}8)$$

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[5] G. Akerlöf, *J. Am. Chem. Soc.*, **54**, 4125 (1932). More recently J. Wyman, Jr., and E. N. Ingalls [*J. Am. Chem. Soc.*, **60**, 1182 (1938)] have re-evaluated $\partial D/\partial T$.

[6] G. Akerlöf and O. A. Short, *J. Am. Chem. Soc.*, **58**, 1241 (1936).

[7] L. Pauling, "Nature of the Chemical Bond," Chapter X, Cornell University Press, Ithaca, New York, 1939; See also: A. Lande, *Z. Physik.*, **1**, 191 (1920); J. A. Wasastjerna, *Soc. Sci. Fenn. Comm. Phys. Math.*, **38**, 1 (1923); V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente," Skrifter det Norske Videnskaps. Acad. Oslo I. Matem.—Naturvid. Klasse, 1926.

TABLE (5-1-3). DIELECTRIC CONSTANT OF WATER AND USEFUL DERIVED FUNCTIONS.

t°C	D	$\log D$	$\log DT$	$-\frac{dD}{dT}$	$-\frac{TdD}{DdT}$
0	88.00	1.94450	4.38082	0.3958	1.228
5	86.04	1.93471	4.37891	.3889	1.257
10	84.11	1.92487	4.37681	.3820	1.286
15	82.22	1.91499	4.37453	.3751	1.314
18	81.10	1.90904	4.37308	.3710	1.332
20	80.36	1.90506	4.37208	.3682	1.343
25	78.54	1.89509	4.36945	.3613	1.371
30	76.75	1.88508	4.36667	.3544	1.400
35	75.00	1.87504	4.36373	.3475	1.428
40	73.28	1.86496	4.36064	.3406	1.455
45	71.59	1.85486	4.35742	.3337	1.483
50	69.94	1.84472	4.35406	.3268	1.510
55	68.32	1.83457	4.35058	.3199	1.536
60	66.74	1.82440	4.34697	.3130	1.562
70	63.68	1.80401	4.33943	.2991	1.611
80	60.76	1.78362	4.33152	.2853	1.658
90	57.98	1.76325	4.32328	.2715	1.700
100	55.33	1.74297	4.31480	.2576	1.737

TABLE (5-1-4). DIELECTRIC CONSTANTS AT 25° OF MIXTURES OF WATER AND (1) METHANOL, (2) ETHANOL, (3) *n*-PROPANOL, (4) ISO-PROPANOL, (5) *ter*-BUTANOL, (6) ETHYLENE GLYCOL, (7) GLYCEROL, (8) ACETONE, (9) MANNITOL, (10) SUCROSE, AND (11) DIOXANE.

Water Wt. %	(1)*	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
90	74.1	72.8	71.8	71.4	70.0	75.6	75.5	73.0	77.1	76.3	69.69
80	69.2	67.0	64.9	64.1	61.3	72.8	72.9	67.0	75.5	73.6	60.79
70	64.3	61.1	57.7	56.9	52.6	69.8	70.0	61.0		70.9	51.90
60	59.6	55.0	50.3	49.7	43.9	66.6	67.1	54.6		67.9	42.98
50	54.9	49.0	43.0	42.5	35.4	63.2	64.0	48.2		64.2	34.26
40	50.1	43.4	36.4	35.3	27.9	59.4	60.0	41.8		59.9	25.85
30	45.0	38.0	30.7	28.7	21.4	54.7	55.6	35.7		54.2	17.69
20	40.1	32.8	26.1	23.7	16.5	49.3	50.6	29.6			10.71
10	35.7	28.1	22.7	20.3	12.4	43.7	45.5	24.0			5.605
0	31.5	24.3	20.1	18.0	9.9	37.7	40.1	19.1			2.101

* Compare T. T. Jones and R. M. Davies, *Phil. Mag.* [7], **28**, 289, 307 (1939).

TABLE (5-1-5). PARAMETERS FOR THE CALCULATION OF DIELECTRIC CONSTANTS OF DIOXANE-WATER MIXTURES BY EQUATION (5-1-2).

Wt. % Dioxane	A	B
0*	1.9461	0.00205
10	1.8969	.00215
20	1.8398	.00224
30	1.7734	.00233
40	1.6935	.00241
50	1.5965	.00247
60	1.4747	.00249
70	1.3090	.00245
80	1.0860	.00225
90	0.7896	.00164
95	0.5923	.00100
100	0.3234	.00004

* Åkerlöf's results for pure water are included here for comparison. In subsequent calculations we shall always use those given in Table (5-1-3).

TABLE (5-1-6). IONIC RADII FROM CRYSTALLOGRAPHIC DATA.[8]
(Ångstrom Units)

	Li^+ 0.607	Be^{++} 0.31	
F^- 1.341	Na^+ 0.958	Mg^{++} 0.65	
Cl^- 1.806	K^+ 1.331	Ca^{++} 0.99	
	Cu^+ 0.96	Zn^{++} 0.74	
Br^- 1.951	Rb^+ 1.484	Sr^{++} 1.13	
	Ag^+ 1.26	Cd^{++} 0.97	In^{+++} 0.81
I^- 2.168	Cs^+ 1.656	Ba^{++} 1.35	La^{+++} 1.15
	Au^+ 1.37	Hg^{++} 1.10	Tl^{+++} 0.95

TABLE (5-2-1)*. DEBYE AND HÜCKEL CONSTANTS FOR AQUEOUS SOLUTIONS.†

t°C	$\mathfrak{S}_{(f)} = \frac{-\log f_\pm}{\sqrt{\Gamma}}$	$\mathcal{S}_{(f)} = \frac{-\log f_\pm}{\sqrt{C}}$	$A/å = \frac{\kappa\, 10^{-8}}{\sqrt{\Gamma}}$	$A'/å = \frac{\kappa\, 10^{-8}}{\sqrt{C}}$
0	0.3446w	0.4870w'	0.2294	0.3244w''
5	.3466w	.4902w'	.2299	.3251w''
10	.3492w	.4938w'	.2305	.3260w''
15	.3519w	.4977w'	.2311	.3268w''
18	.3538w	.5002w'	.2315	.3274w''
20	.3549w	.5019w'	.2318	.3278w''
25	.3582w	.5065w'	.2325	.3288w''
30	.3616w	.5114w'	.2332	.3298w''
35	.3653w	.5166w'	.2340	.3309w''
40	.3692w	.5221w'	.2348	.3321w''
45	.3733w	.5280w'	.2357	.3333w''
50	.3777w	.5341w'	.2366	.3346w''
55	.3823w	.5406w'	.2376	.3360w''
60	.3871w	.5474w'	.2386	.3374w''
70	.3973w	.5619w'	.2407	.3403w''
80	.4083w	.5774w'	.2429	.3434w''
90	.4200w	.5940w'	.2452	.3467w''
100	.4325w	.6116w'	.2476	.3501w''

* For definitions of the valence factors w, w' and w'', see equations (5-2-1), (5-2-4), and (5-2-10).

† The corresponding limiting slopes in some important mixed solvents are given in Table (11-3-1A). See Appendix B, Table (B-1-2), for revised values.

and

$$\Gamma = \sum_{1}^{s} c_i z_i^2 \qquad (3\text{-}1\text{-}3)$$

Values of the theoretical limiting slope, $\mathfrak{S}_{(f)}$, for aqueous solutions at various temperatures are given in Table (5-2-1). The values of (DT) employed in the calculation of these slopes were taken from column (4) of Table (5-1-3). For simplicity in tabulation the valence factor has been written

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[8] L. Pauling, "Nature of the Chemical Bond," Chapter X, Cornell University Press, Ithaca, New York, 1939.

$$w \equiv \frac{1}{\nu}\sum_{1}^{p} \nu_j z_j^2 \qquad (5\text{-}2\text{-}1)$$

If the electrolyte dissociates into only two kinds of ions ($p = 2$), w reduces to $| z_1 z_2 |$ in general, and becomes unity for 1-1 electrolytes.

In the important special case of solutions containing only a single electrolyte, Γ equals $c \sum_{1}^{p} \nu_j z_j^2$, and the limiting law may be written

$$\log f_{\pm} = -\mathcal{S}_{(f)}\sqrt{c} \qquad (5\text{-}2\text{-}2)$$

where

$$\mathcal{S}_{(f)} = \frac{1}{\nu}\left(\sum_{1}^{p} \nu_j z_j^2\right)^{3/2} \frac{1.283 \times 10^6}{(DT)^{3/2}} \qquad (5\text{-}2\text{-}3)$$

The values of $\mathcal{S}_{(f)}$ given in Table (5-2-1) are expressed in terms of the valence factor

$$w' \equiv \frac{1}{\nu\sqrt{2}}\left(\sum_{1}^{p} \nu_j z_j^2\right)^{3/2} \qquad (5\text{-}2\text{-}4)$$

The term $\sqrt{2}$ was introduced into this factor so that w' becomes unity for 1-1 electrolytes.

At the high dilutions postulated in the derivation of the limiting law, the ratio of the volume and weight concentrations becomes d_0, the density of the pure solvent. Thus, by equation (3-4-10a)

$$\log f_{\pm} = -\sqrt{2d_0}\,\mathfrak{S}_{(f)}\sqrt{\mu} \qquad (5\text{-}2\text{-}5)$$

in general, and

$$\log f_{\pm} = -\sqrt{d_0}\,\mathcal{S}_{(f)}\sqrt{m} \qquad (5\text{-}2\text{-}6)$$

for solutions containing only a single electrolyte.

At moderate dilutions where the ionic parameter "a" (the "mean distance of nearest approach" of the ions) can no longer be neglected, the activity coefficient is given by

$$\log f_{\pm} = -\frac{\mathfrak{S}_{(f)}\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} \qquad (3\text{-}5\text{-}8)$$

The term $A\sqrt{\Gamma}$ is equal to κa. It is convenient to express the ionic parameter in Ångstrom units, in which case it is written $\mathring{a}$. Accordingly,

$$A = \mathring{a}\kappa \frac{10^{-8}}{\sqrt{\Gamma}} = \mathring{a}\,\frac{35.57}{(DT)^{1/2}} \qquad (5\text{-}2\text{-}7)$$

Values of $\kappa 10^{-8}\Gamma^{-1/2}$ calculated by (3-1-2) are recorded in Table (5-2-1).

In solutions containing only a single electrolyte equation (3-5-8) may be used in the restricted form

$$\log f_{\pm} = -\frac{\mathfrak{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} \tag{5-2-8}$$

where

$$A' = \mathring{a}\,\frac{\kappa 10^{-8}}{\sqrt{c}}\ . \tag{5-2-9}$$

The values of $\kappa 10^{-8} c^{-1/2}$ given in Table (5-2-1) are expressed in terms of the valence factor

$$w'' \equiv \left(\frac{1}{2}\sum_{1}^{p} \nu_j z_j^2\right)^{\frac{1}{2}} = \frac{w'}{w} \tag{5-2-10}$$

It should be noted that for binary electrolytes ($|z_1| = |z_2| = z$), the valence factor w'' reduces to z.

Computations involving the so-called "extended terms" of the Debye-Hückel theory are carried out with equations (3-6-4) to (3-6-6), containing the contributions to $\log f_{\pm}$ of higher terms in the expansion of the function, $\exp(-e_i\psi_i^0/kT)$, which were neglected in the derivation of equation (3-4-7). Symmetrical valence types of electrolytes are treated by equation (3-6-4). Values of

$$10^3[\tfrac{1}{2}X_3(\kappa a) - 2Y_3(\kappa a)]$$

and

$$10^5[\tfrac{1}{2}X_5(\kappa a) - 4Y_5(\kappa a)]$$

are recorded as functions of (κa) in Table (5-2-2) for values of κa varying from 0.005 to 0.4.[9] Equations (3-6-5) and (3-6-6) are used for unsymmetrical types of electrolytes. Values of

$$10^2[\tfrac{1}{2}X_2(\kappa a) - Y_2(\kappa a)]$$

and

$$10^3[\tfrac{1}{2}X_3^*(\kappa a) - 2Y_3^*(\kappa a)]$$

are also given in Table (5-2-2) for values of κa varying from 0.005 to 0.4.[10] Calculation of the extended terms is complicated by the necessity of successive arithmetical approximations. The magnitude of "a" must be known to evaluate the functions, and they in turn must be known to determine "a." In later discussions some applications of these terms will be considered in detail. The ratios recorded in the last two columns of Table (5-2-1) readily permit the estimation of κ from Γ or c.

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[9] T. H. Gronwall, V. K. LaMer, and K. Sandved, *Physik. Z.*, **29**, 358 (1928). Note that in this paper, $x_i = \kappa a$.

[10] V. K. LaMer, T. H. Gronwall, and L. J. Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

TABLE (5-2-2). EXTENDED TERMS OF THE DEBYE-HÜCKEL THEORY

$x = \kappa a$	$10^3[\frac{1}{2}X_3 - 2Y_3]$	$10^5[\frac{1}{2}X_5 - 4Y_5]$	$10^2[\frac{1}{2}X_2 - Y_2]$	$10^3[\frac{1}{2}X_3^* - 2Y_3^*]$
0.	0.00000	0.00000	0.000000	0.000000
.005	− .00092	− .00107	− .001482	.000009
.01	− .00351	− .00416	− .004797	.000071
.02	− .01239	− .01487	− .014784	.000423
.03	− .02497	− .02985	− .027666	.001264
.04	− .04014	− .04725	− .042363	.002693
0.05	− .05711	− .06564	− .058209	.004750
.06	− .07522	− .08394	− .074748	.007457
.07	− .09403	− .10138	− .091660	.010809
.08	− .11316	− .11737	− .108703	.014766
.09	− .13231	− .13153	− .125699	.019291
0.10	− .15130	− .14363	− .142514	.024335
.11	− .16992	− .15356	− .15905	.02986
.12	− .18802	− .16126	− .17522	.03580
.13	− .20355	− .16680	− .19097	.04211
.14	− .22240	− .17023	− .20626	.04874
0.15	− .23853	− .17166	− .22105	.05563
.16	− .25391	− .17123	− .23533	.06274
.17	− .26851	− .16910	− .24908	.07002
.18	− .28231	− .16543	− .26230	.07743
.19	− .29530	− .16037	− .27497	.08493
0.20	− .30750	− .15409	− .28710	.09248
.21	− .31892	− .14674	− .29870	.10005
.22	− .32953	− .13847	− .30977	.10761
.23	− .33943	− .12942	− .32032	.11513
.24	− .34859	− .11973	− .33036	.12258
0.25	− .35703	− .10953	− .33991	.12994
.26	− .36478	− .09895	− .34896	.13720
.27	− .37187	− .08804	− .35755	.14433
.28	− .37832	− .07696	− .36567	.15132
.29	− .38416	− .06577	− .37335	.15816
0.30	− .38942	− .05453	− .38060	.16482
.31	− .39411	− .04335	− .38743	.17132
.32	− .39827	− .03222	− .39386	.17762
.33	− .40193	− .02131	− .39990	.18374
.34	− .40510	− .01053	− .40557	.18965
0.35	− .40780	− .00001	− .41087	.19536
.36	− .41007	+ .01027	− .41583	.20087
.37	− .41193	+ .02022	− .42045	.20617
.38	− .41339	+ .02986	− .42475	.21116
.39	− .41448	+ .03917	− .42875	.21613
0.40	− .41525	+ .0481	− .43244	.22080

Functions of Bjerrum's Theory[11] of the Association of Ions

Equation (3-7-13) relates the ionization constant with the dielectric constant and the function $Q(b)$. Thus

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{|z_1 z_2|\epsilon^2}{kDT}\right)^3 Q(b) \tag{3-7-13}$$

where b and $Q(b)$ are given by

$$b = \frac{|z_1 z_2|\epsilon^2}{aDkT} \tag{3-7-7}$$

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[11] N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, 7, No. 9 (1926).

$$Q(b) = \int_2^b e^Y Y^{-4}\,dY = \frac{1}{6}\left\{e^2 - Ei(2) + Ei(b) - \frac{e^b}{b}\left(1 + \frac{1}{b} + \frac{2}{b^2}\right)\right\} \tag{3-7-14}$$

and

$$Ei(x) = \int_\infty^{-x} e^{-t} t^{-1}\,dt \tag{3-7-15}$$

Values of $Ei(b)$ to $b = 15$ were obtained by Bjerrum from tables.[12] Values of b from 15 to 80 were obtained by Fuoss and Kraus,[13] who used the asymptotic expansion

$$Ei(x) = \frac{e^x}{x}\left(1 + \frac{1}{x} + \frac{1\cdot 2}{x^2} + \frac{1\cdot 2\cdot 3}{x^3} + \cdots\right) \tag{5-2-11}$$

Taking the logarithm and neglecting the term, $(1/6\{e^2 - Ei(2)\}) = 0.41$, the equation for $\log Q(b)$ becomes

$$\log Q(b) \simeq 0.4343b - 4\log b + \log(1 + \delta) \tag{5-2-12}$$

where

$$\delta = \frac{4}{b} + \frac{4\cdot 5}{b^2} + \frac{4\cdot 5\cdot 6}{b^3} + \cdots \tag{5-2-13}$$

This approximation causes an error in $\log Q(b)$ for b equal to 15, but this error decreases rapidly with increasing b. Values of $\log Q(b)$ in Table (5-2-3) were obtained from these results.

TABLE (5-2-3). THE FUNCTION $\log Q(b)$ OF BJERRUM'S THEORY.

b	$\log Q(b)$	b	$\log Q(b)$	b	$\log Q(b)$
2	$-\infty$	10	0.655	40	11.01
2.5	−0.728	12	1.125	45	12.99
3	−0.489	14	1.680	50	14.96
4	−0.260	16	2.275	55	16.95
5	−0.124	18	2.92	60	18.98
6	+0.016	20	3.59	65	21.02
7	0.152	25	5.35	70	23.05
8	0.300	30	7.19	75	25.01
9	0.470	35	9.08	80	27.15

Functions of the Fuoss and Kraus Theory of Triple Ion Formation

We have shown [Chapter (3), Section (7)] that the constant, K_3, of triple ion dissociation represented by

$$[C^+A^-C^+]^+ \rightleftharpoons [C^+A^-]^0 + C^+$$

$$[A^-C^+A^-]^- \rightleftharpoons [C^+A^-]^0 + A^-$$

may be computed by the equation

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[12] E. Jahnke and F. Emde, "Tables of Functions," p. 83–85, Teubner, Leipzig and Berlin, 1933.

[13] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 1019 (1933).

$$K_3^{-1} = \frac{2\pi N a_3^3}{1000} I(b_3) \tag{3-7-25}$$

where

$$b_3 = \frac{\epsilon^2}{a_3 DkT} \tag{3-7-7}$$

Table (5-2-4) contains $I(b_3)$ and $\log I(b_3)$ at values of b_3 from 3.5 to 36.6. The last column contains values of $X = R/a_3$ where R is the characteristic distance which determines whether or not triple ions can form.

TABLE (5-2-4). LOG $I(b_3)$, $I(b_3)$ AND $X = R/a_3$ AS FUNCTIONS OF b_3.

b_3	$\log I(b_3)$	$\log I(b_3) - 3\log b_3$	$I(b_3)$	X
8/3	$-\infty$	$-\infty$	0	1.0
3.5	0.096	−1.536	1.25	1.225
5	.668	−1.429	4.66	1.56
10	1.534	−1.466	34.2	2.46
15	2.183	−1.345	152.4	3.17
20	2.894	−1.009	784.	3.76
25	3.732	−0.462	5.40×10^3	4.28
30	4.634	+0.203	4.30×10^4	4.75
35	5.565	+0.933	3.67×10^5	5.19
36.6	5.878	+1.187	7.55×10^5	5.33

$I(b_3) = 0$, when $X = 1$, so that on a plot of $\log I(b_3)$ versus b_3, $\log I(b_3)$ is asymptotic to the vertical line at $b_3 = 8/3$. This means that triple ions form when $b_3 > 8/3$, and are unstable when $b_3 \leq 8/3$.

Limiting Slopes for the Relative Partial Molal Heat Content and Heat Capacity in Aqueous Solutions

The relative partial molal heat content and heat capacity of an electrolyte have been shown to vary with the concentration according to the equations

$$\bar{L}_2 = \bar{H}_2 - \bar{H}_2^0 = \mathcal{S}_{(H)}\sqrt{\Gamma} \tag{3-8-9}$$

and

$$\bar{J}_2 = \bar{C}_{p_2} - \bar{C}_{p_2}^0 = \mathcal{S}_{(C_p)}\sqrt{\Gamma} \tag{3-8-10}$$

According to equation (3-8-6), $\mathcal{S}_{(H)}$ is a function of D, T and α, the coefficient of expansion of the solution. $\mathcal{S}_{(C_p)}$ is a more complicated function of the same variables, and is calculated by equations (3-8-11) to (3-8-13). The nature of these functions is such that the magnitudes of $\mathcal{S}_{(H)}$ and $\mathcal{S}_{(C_p)}$ are very sensitive to experimental uncertainties in measuring the temperature coefficient of D. Consequently the values of these slopes given in the literature show considerable discrepancy, depending upon the sources of the dielectric constant data. The slopes recorded in Table (5-2-5) were computed[14] from Wyman's dielectric constants, given in Table (5-1-3),

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[14] H. S. Harned and J. C. Hecker, *J. Am. Chem. Soc.*, **55**, 4838 (1933).

and values of the density of water, given in the "International Critical Tables."[15]

It is also convenient to write the limiting equations in the forms

$$\bar{L}_2 = \bar{H}_2 - \bar{H}_2^0 = \mathcal{S}_{(H)}\sqrt{c} \tag{5-2-14}$$

and

$$\bar{J}_2 = \bar{C}_{p_2} - \bar{C}_{p_2}^0 = \mathcal{S}_{(C_p)}\sqrt{c} \tag{5-2-15}$$

which apply to solutions containing only a single electrolyte. Values of $\mathcal{S}_{(H)}$ and $\mathcal{S}_{(C_p)}$ are recorded in Table (5-2-5). For 1-1 electrolytes ($\nu = 2$) the valence factors w and w' become unity.

TABLE (5-2-5).* DEBYE AND HÜCKEL SLOPES FOR THE RELATIVE PARTIAL MOLAL HEAT CONTENT AND HEAT CAPACITY IN AQUEOUS SOLUTIONS.†

t°C	$\mathfrak{S}_{(H)} = \bar{L}_2/\sqrt{\Gamma}$	$\mathcal{S}_{(H)} = \bar{L}_2/\sqrt{c}$	$\mathfrak{S}_{(C_p)} = \bar{J}_2/\sqrt{\Gamma}$	$\mathcal{S}_{(C_p)} = \bar{J}_2/\sqrt{c}$
0	$153\nu w$	$216\nu w'$	$3.40\nu w$	$4.81\nu w'$
5	$169\nu w$	$239\nu w'$	$3.67\nu w$	$5.19\nu w'$
10	$190\nu w$	$269\nu w'$	$3.96\nu w$	$5.60\nu w'$
15	$210\nu w$	$297\nu w'$	$4.22\nu w$	$5.97\nu w'$
20	$231\nu w$	$327\nu w'$	$4.48\nu w$	$6.34\nu w'$
25	$254\nu w$	$359\nu w'$	$4.72\nu w$	$6.68\nu w'$
30	$278\nu w$	$393\nu w'$	$4.96\nu w$	$7.01\nu w'$
35	$303\nu w$	$429\nu w'$	$5.19\nu w$	$7.34\nu w'$
40	$329\nu w$	$465\nu w'$	$5.44\nu w$	$7.69\nu w'$
45	$357\nu w$	$505\nu w'$	$5.67\nu w$	$8.02\nu w'$
50	$385\nu w$	$544\nu w'$	$5.89\nu w$	$8.33\nu w'$
55	$414\nu w$	$585\nu w'$	$6.08\nu w$	$8.60\nu w'$
60	$446\nu w$	$631\nu w'$	$6.30\nu w$	$8.91\nu w'$

* For definitions of the valence factors w and w' see equations (5-2-1) and (5-2-4).

† The corresponding limiting slopes in some important mixed solvents are given in Table (11-8-1A). See Appendix B, Table (B-1-2), for revised values.

Limiting Slopes for the Relative Partial Molal Volume, Expansibility, and Compressibility of an Electrolyte

It is clear from the equations given in Chapter (3) Section (9) that $\mathfrak{S}_{(V)}$, $\mathfrak{S}_{(E)}$ and $\mathfrak{S}_{(K)}$ are functions of both the temperature and pressure coefficients of the dielectric constant of the solvent. These derivatives of the dielectric constant of water may be estimated by equations discussed in Appendix B, Section (1). Tentative values of the theoretical slopes are given in Table (B-1-2).

Theoretical Laws for the Increase of Surface Tension

The limiting law for surface tension for binary electrolytes was found to be

$$\Delta\sigma = \sigma - \sigma_0 = \frac{kT}{16\pi q^2}(Y_e + Y_f) = \frac{kT}{16\pi q^2} Y \tag{3-11-14}$$

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[15] "International Critical Tables," Vol. III, p. 25, McGraw-Hill Book Co., New York, 1930.

where

$$q = \frac{\epsilon^2 z^2}{2DkT} \tag{3-7-4}$$

If the mean distance of approach of the ions is included, then

$$\Delta\sigma = \sigma - \sigma_0 = \frac{kT}{16\pi q^2}(Y_c' + Y_f') = \frac{kT}{16\pi q^2} Y' \tag{3-11-15}$$

Let

$$y^2 = \kappa^2 q^2 = \frac{1.746 \times 10^{13}}{(DT)^3} z^6 c \equiv Bc \tag{5-2-16}$$

and

$$\frac{Y}{y^2} = \frac{Y_c + Y_f}{y^2} = \frac{2 \times 10^3 \sigma_0 D}{N\epsilon^2 z^2}\left(\frac{\sigma - \sigma_0}{c\sigma_0}\right) \equiv A\Delta\alpha \tag{5-2-17}$$

where $\Delta\alpha$ is defined as the relative surface tension increase per mol of solute.

TABLE (5-2-6). FUNCTIONS FOR THEORETICAL COMPUTATION OF SURFACE TENSION INCREASE FOR 1-1 ELECTROLYTES AT 25°.

I				II			
y^2	Y_c/y^2	Y_f/y^2	$A\Delta\alpha$	y^2	Y_c'/y^2	Y_f'/y^2	$A\Delta\alpha$
0			∞	0			∞
0.0063	3.048	−0.076	2.972				
0.0126	2.747	−0.097	2.650				
0.0189	2.576	−0.111	2.465				
0.0315	2.367	−0.134	2.233				
0.0378	2.295	−0.141	2.154	0.0378	2.308	−0.107	2.201
0.0630	2.095	−0.163	1.932	0.0850	2.003	−0.125	1.878
0.0944	1.944	−0.184	1.760				
0.1259	1.840	−0.203	1.637	0.1259	1.867	−0.132	1.735
0.1574	1.760	−0.217	1.543				
0.1889	1.697	−0.228	1.469	0.1963	1.718	−0.139	1.579
0.2014	1.675	−0.232	1.443				
0.2266	1.634	−0.241	1.394				

Numerical values of Y_c, Y_f, Y_c', and Y_f' have been obtained by Onsager and Samaras[16] for 1-1 electrolytes. Values of these quantities divided by y^2 at given values of y^2 are given in Table (5-2-6). Values of $A\Delta\alpha$ are also included. We note that the effect caused by introducing the mean distance of approach of the ions is not great.

(3) EQUATIONS DERIVED IN CHAPTER (4) INVOLVING THE DYNAMICS OF IONIC ATMOSPHERES

Limiting Law for Viscosity.—The limiting law for the increase in the viscosity of a solution with addition of electrolyte dissociating into two kinds of ions is

$$\eta^* = \eta - \eta_0 = \frac{\kappa}{480\pi}\left\{\bar{\rho} + 4\left(\frac{\bar{\rho^2}}{\bar{\rho}} - \bar{\rho}\right)\frac{1 - \sqrt{q^*}}{1 + \sqrt{q^*}}\right\} \tag{4-2-28}$$

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[16] L. Onsager and N. N. T. Samaras, *J. Chem. Phys.*, **2**, 528 (1934).

where

$$\bar{\rho} = \frac{n_1 e_1^2/\omega_1 + n_2 e_2^2/\omega_2}{n_1 e_1^2 + n_2 e_2^2} \tag{4-2-25}$$

$$\bar{\rho}^2 = \frac{n_1 e_1^2/\omega_1^2 + n_2 e_2^2/\omega_2^2}{n_1 e_1^2 + n_2 e_2^2} \tag{4-2-26}$$

and

$$q^* = \frac{n_1 e_1^2 \omega_1 + n_2 e_2^2 \omega_2}{(n_1 e_1^2 + n_2 e_2^2)(\omega_1 + \omega_2)} \tag{4-2-27}$$

In all these expressions, it is important to remember that e_1 and e_2 carry the sign of the charge. Thus, for a binary electrolyte $e_1 = -e_2$. To convert to practical units, we substitute for κ and ω_i the values

$$\kappa = \left(\frac{4\pi\epsilon^2 N}{1000\,DkT}\right)^{1/2} \sqrt{\Gamma} = \frac{35.57 \times 10^8 \sqrt{\Gamma}}{(DT)^{1/2}} \tag{3-1-2}$$

and

$$\omega_i = \frac{300\,\lambda_i^0}{96500\,|z_i|\,\epsilon} \tag{4-1-15}$$

where Γ equals $\sum c_i z_i^2$, λ_i^0 is the limiting ionic conductance and $|z_i|$ the magnitude of the valence. Further, for electro-neutrality,

$$n_1 e_1 = -n_2 e_2; \qquad n_1\,|z_1|\,\epsilon = n_2\,|z_2|\,\epsilon$$

where ϵ is the electronic charge, and n_i is given by

$$n_i = \frac{c_i N}{1000}$$

Here c_i is the concentration of the i ion in mols per liter of the solution. For binary electrolytes, $n_1 = n_2$, and $|z_1| = |z_2|$. Consequently, $q^* = 1/2$, $\bar{\rho} = 1/2(1/\omega_1 + 1/\omega_2)$, and $\bar{\rho^2} = 1/2(1/\omega_1^2 + 1/\omega_2^2)$, which considerably simplifies equation (4-2-28) for this special case.

Limiting Slope for the Equivalent Conductance of a Strong Electrolyte

Computation of the limiting slope for the general case of conductance in solutions of mixed electrolytes is very complicated. It may be accomplished by means of equations (4-3-51) to (4-3-56) inclusive. Particular examples are discussed in Chapters (6) and (7).

In the important special case of a single electrolyte dissociating into two kinds of ions only, equation (4-3-44) for the equivalent conductance mav be written

$$\Lambda = \Lambda^0 - \mathcal{S}_{(\Lambda)}\sqrt{c} \tag{5-3-1}$$

and the limiting slope expressed in the convenient form

$$\mathcal{S}_{(\Lambda)} \doteq \alpha^*\Lambda^0 + \beta^* \tag{5-3-2}$$

The constants

$$\alpha^* = \left(\frac{1.970 \times 10^6 \times 0.2929\sqrt{2}}{(DT)^{3/2}}\right) w'Q \tag{5-3-4}$$

and

$$\beta^* = \left(\frac{28.98 \times 2\sqrt{2}}{\eta(DT)^{1/2}}\right) w^* \tag{5-3-5}$$

are recorded in Table (5-3-1). The viscosities used in the calculation of β^* are given in the last column. The quantities $0.2929\sqrt{2}$ and $2\sqrt{2}$ were introduced within the parentheses so that the factors

TABLE (5-3-1).[a] VALUES OF THE CONSTANTS APPEARING IN THE LIMITING SLOPE FOR CONDUCTANCE IN AQUEOUS SOLUTIONS.[b]

t°C	α^*	β^*	$10^3\eta_0$[c]
0	$0.2198w'Q$	$29.47w^*$	17.938
5	$.2205w'Q$	$34.87w^*$	15.188
10	$.2220w'Q$	$40.56w^*$	13.097
15	$.2237w'Q$	$46.53w^*$	11.447
18	$.2249w'Q$	$50.31w^*$	10.603
20	$.2257w'Q$	$52.95w^*$	10.087
25	$.2277w'Q$	$59.86w^*$	8.949
30	$.2299w'Q$	$67.15w^*$	8.004
35	$.2322w'Q$	$74.81w^*$	7.208
40	$.2348w'Q$	$82.79w^*$	6.536
45	$.2374w'Q$	$90.99w^*$	5.970
50	$.2401w'Q$	$99.28w^*$	5.492
55	$.2431w'Q$	$107.93w^*$	5.072
60	$.2461w'Q$	$116.98w^*$	4.699

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[a] For definitions of the valence factors w', Q and w^*, see equations (5-3-6) to (5-3-8) inclusive. See Appendix B, Table (B-1-2), for revised values.

[b] The values of α^* and β^* for some important mixed solvents are given in Table (11-1-1A).

[c] "International Critical Tables," V, p. 10, McGraw-Hill Book Co., New York, 1931.

$$Q = \frac{q^*}{0.2929(1 + \sqrt{q^*})} \tag{5-3-6}$$

and

$$w^* = \left(\frac{|z_1| + |z_2|}{2}\right)\left(\frac{\nu\,|z_1 z_2|}{2}\right)^{1/2} \tag{5-3-7}$$

become unity for 1-1 electrolytes. The valence factor w' defined by equation (5-2-4) becomes

$$w' = |z_1 z_2|(|z_1 z_2|\,\nu/2)^{1/2} \tag{5-3-8}$$

for the case under consideration. The parameter q^* which appears in the definition of Q is given by equation (4-3-43), or

$$q^* = \frac{|z_1 z_2| (\lambda_1^0 + \lambda_2^0)}{(|z_1| + |z_2|)(|z_2| \lambda_1^0 + |z_1| \lambda_2^0)} \tag{4-3-43}$$

Q may also be expressed in terms of the limiting transference numbers of the ion constituents. Thus

$$Q = \frac{3.4141\, S^2}{(T_2^0 + vT_1^0) + S(T_2^0 + vT_1^0)^{1/2}} \tag{5-3-9}$$

where $v \equiv |z_2|/|z_1|$ and $S^2 \equiv v/(1 + v)$. In this equation it is immaterial whether the anion or cation is assigned the subscript 2. Consequently Q has the same form for sodium sulfate as for barium chloride. Q is unity for all symmetrical electrolytes.

The equation (4-3-42) for the equivalent conductance of the individual ion constituents in solutions containing only two kinds of ions can be written

$$\lambda_j = \lambda_j^0 - \mathfrak{S}_{(\lambda)}\sqrt{c} \tag{5-3-10}$$

where

$$\mathfrak{S}_{(\lambda)} = \alpha^* \lambda_j^0 + \frac{\beta^* |z_j|}{|z_1| + |z_2|}; \qquad j = 1, 2 \tag{5-3-10a}$$

Theory of Diffusion

In Chapter (4), Section (4), it was shown that the Onsager and Fuoss theory of diffusion led to the expression

$$\mathfrak{D} = 16.632 \times 10^{10}\, T \frac{\overline{\mathfrak{M}}}{c}\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) \tag{4-4-24}$$

for the coefficient of diffusion of an electrolyte which dissociates into two kinds of ions. $\overline{\mathfrak{M}}$ is a complicated function which may be evaluated by means of equations (4-4-19), (4-4-20), (4-4-21), (4-3-21a) and (4-3-23a). For symmetrical electrolytes this function may be written

$$\left(\frac{\overline{\mathfrak{M}}}{c}\right) 10^{20} = \frac{1.074}{z}\left(\frac{\lambda_+^0 \lambda_-^0}{\Lambda^0}\right) - \frac{0.4373}{\mathring{a}\eta_0}\left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda^0}\right)^2 \frac{\kappa a}{1 + \kappa a} + \left(\frac{z}{\mathring{a}}\right)^2 \frac{36280}{\eta_0 D T} (\kappa a)^2 \cdot \phi(\kappa a) \tag{5-3-11}$$

which is a convenient form for numerical calculations. Values of $(\kappa a)^2 \cdot \phi(\kappa a)$ are recorded in Table (5-3-2). An equivalent equation, written in terms of $\sqrt{c}$, will be found in Chapter (6), Section (10), where the expression for the limiting slope of $\mathfrak{D}$ against $\sqrt{c}$ is also given [see equations (6-10-2) and (6-10-7)].

Theory of Frequency Effects

The molar conductance $\Lambda_{\tilde{\omega}}$ in the presence of a field of frequency, $\tilde{\omega}$, has been split into three parts according to equation (4-5-20), or

$$\Lambda_{\tilde{\omega}} = \Lambda_m^0 - \Lambda_{I\tilde{\omega}} - \Lambda_{II} \qquad (4\text{-}5\text{-}20)$$

Λ_m^0 is the molar conductance at infinite dilution, $\Lambda_{I\tilde{\omega}}$ the contribution to $\Lambda_{\tilde{\omega}}$ due to asymmetric ionic atmosphere, and Λ_{II} is the contribution due to electrophoresis. $\Lambda_{I\tilde{\omega}}$ is given by equation (4-5-21), and is a complicated function of the frequency, time of relaxation, and the quantity q^*. When $\tilde{\omega}$ is zero, $\Lambda_{I(0)}$ is the contribution to the molecular conductance due to the asymmetric ionic atmosphere computed by Onsager. The numerical values of $\Lambda_{I\tilde{\omega}}/\Lambda_{I(\tilde{\omega}=0)}$ as a function of $\tilde{\omega}\tau$ and q^*, computed by Falkenhagen,[17] are given in Table (5-3-3).

The effect of frequency on the dielectric constant is given by equation (4-5-24) which measures $D_{\tilde{\omega}} - D_0$ as a function of q^*, $\tilde{\omega}\tau$, T, and c. Falkenhagen has also computed $(D_{\tilde{\omega}} - D_0)/(D_{\tilde{\omega}=0} - D_0)$ as a function of $\tilde{\omega}\tau$ and q^*, and these results are compiled in Table (5-3-4).[18]

TABLE (5-3-2). VALUES OF THE FUNCTIONS $\phi(\kappa a)$ AND $(\kappa a)^2\phi(\kappa a)$ FOR USE IN EQUATIONS (4-4-21) AND (6-10-2).

(κa)	$\phi(\kappa a)$	$(\kappa a)^2\phi(\kappa a)$	(κa)	$\phi(\kappa a)$	$(\kappa a)^2\phi(\kappa a)$
0	∞	0	.5	.2651	.06628
.010	3.3550	.00034	.6	.2054	.07394
.025	2.4695	.00154	.7	.16304	.07989
.05	1.8273	.00457	.8	.13194	.08444
.10	1.2342	.01234	.9	.10844	.08784
.15	.9245	.02080	1.0	.09033	.09033
.20	.7277	.02911	1.2	.06477	.09327
.25	.5907	.03692	1.4	.04813	.09433
.30	.4899	.04409	1.6	.03676	.09411
.35	.4130	.05059	1.8	.02876	.09318
.40	.3527	.05643	2.0	.02292	.09168
.45	.3044	.06164	2.5	.01391	.08694
.50	.2651	.06628	3.0	.00908	.08172

The time of relaxation, required for these calculations, may be computed from a simple formula readily obtained from equation (4-1-17), namely,

$$\tau = \frac{8.85 \times 10^{-11}}{\Lambda^\circ c^*} D_0 \qquad (5\text{-}3\text{-}12)$$

Here, $\Lambda^0 = \lambda_1^0 + \lambda_2^0$, $c^* = \nu_1 \mid z_1 \mid c = \nu_2 \mid z_2 \mid c$, and D_0 is the dielectric constant of the solvent; q^* is given by equation (4-3-43),

$$q^* = \frac{\mid z_1 z_2 \mid (\lambda_1^0 + \lambda_2^0)}{(\mid z_1 \mid + \mid z_2 \mid)(\mid z_2 \mid \lambda_1^0 + \mid z_1 \mid \lambda_2^0)} \qquad (4\text{-}3\text{-}43)$$

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[17] H. Falkenhagen, "Electrolytes," Table 31, p. 213. English Translation by R. P. Bell, Oxford Press, 1934.

[18] H. Falkenhagen, *loc. cit.*, Table 37, p. 219.

calculations of $\Lambda_{I\bar\omega}/\Lambda_{I(\bar\omega=0)}$ and $\Lambda_{\bar\omega}$, as well as of $(D_{\bar\omega} - D_0)/(D_{\bar\omega=0} - D_0)$, can be made if the valences, limiting ionic conductances, concentration of electrolyte, dielectric constant of solvent and temperature are known.

TABLE (5-3-3). $\dfrac{\Lambda_{I\bar\omega}}{\Lambda_{I(\bar\omega=0)}}$

$\bar\omega\tau$	$q^* = 0.5$	$q^* = 0.45$	$q^* = 0.40$	$q^* = 0.35$	$q^* = 0.30$
0.	1.	1.	1.	1.	1.
0.2	0.997	0.997	0.997	0.997	0.997
.5	.980	.981	.981	.981	.981
.75	.956	.959	.962	.965	.963
1.	.930	.934	.938	.942	.946
1.25	.904	.909	.913	.918	.922
1.5	.876	.882	.888	.894	.900
2.	.826	.833	.841	.848	.856
2.5	.783	791	.799	808	.817
3.	.745	.753	.763	.773	.785
4.	.682	.691	.701	.713	.727
6.	.593	.603	.614	.628	.643
8.	.531	.540	.553	.565	.582
10.	.486	.496	.507	.520	537
15.	.409	.417	.428	.442	.458
20.	.360	.368	.378	.390	.406
25.	.326	.334	.344	.354	.369
30.	.299	.307	.317	.327	.342
35.	.279	.286	.295	.305	.318
40.	.261	.267	.272	.287	.299
45.	.247	.254	.263	.272	.288
50.	.235	.242	.250	.259	.271
75.	.193	.199	.206	.214	.223
100.	.168	.173	.179	.186	.195
150.	.138	.142	.147	.153	.160
200.	.1195	.1232	.1278	.1328	.1394
300.	.0983	.1011	.1046	.1088	.1145
500.	.0759	.0783	.0812	.0844	.0888
700.	.0643	.0663	.0688	.0716	.0751
1000.	.0538	.0555	.0576	.0599	.0629
5000.	.0241	.0249	.0258	.0269	.0282
10000.	.0171	.01755	.0182	.0190	.0199

Since the wave-length, l, in meters is sometimes used in these calculations, the equation for its computation

$$l = \frac{2\pi \times 3 \times 10^{10}}{\bar\omega 100} = \frac{18.85 \times 10^{8}}{\bar\omega} \tag{5-3-13}$$

will be useful.

Effect of High Fields on Conductance of Electrolytes

Equation (4-6-55) of the Onsager-Wilson theory of the Wien effect on the conductance of strong electrolytes gives for the equivalent conductances of a binary electrolyte,

$$\Lambda = \Lambda^0 - \frac{|e_j|^2 \kappa \Lambda^0}{2DkT} g(x) - \frac{96500\, k\, |e_j|\, 2\kappa}{6\sqrt{2}\,\pi\eta 300} f(x) \tag{5-3-14}$$

where

$$x = \frac{\mu'}{\kappa} = \frac{Xz\epsilon}{kT\kappa} \tag{4-6-43}$$

TABLE (5-3-4). $(D_{\tilde{\omega}} - D_0)/(D_{\tilde{\omega}=0} - D_0)$.

$\tilde{\omega}\tau$	$q^* = 0.5$	$q^* = 0.45$	$q^* = 0.4$	$q^* = 0.35$	$q^* = 0.3$
0.0	1.	1.	1.	1.	1.
.1	0.999	0.999	0.999	0.999	0.999
.2	.989	.989	.989	.9895	.990
.35	.974	.974	.974	.975	.975
.5	.940	.941	.943	.944	.946
.75	.879	.882	.885	.887	.890
1.	.813	.816	.820	.824	.830
1.25	.748	.752	.757	.763	.768
1.5	.689	.694	.700	.706	.713
2.	.585	.591	.598	.605	.615
2.5	.502	.510	.517	.525	.535
3.	.437	.444	.452	.406	.471
4.	.342	.349	.356	.365	.375
6.	.231	.237	.244	.251	.261
8.	.1703	.1753	.1811	.1877	.1957
10.	.1326	.1369	.1419	.1477	.1546
15.	.0822	.0853	.0889	.0931	.0983
20.	.0576	.0600	.0627	.0660	.0700
25.	.0434	.0453	.0475	.0501	.0533
30.	.0343	.0358	.0376	.0398	.0425
35.	.0280	.0293	.0316	.0327	.0350
40.	.0235	.0246	.0259	.0275	.0298
45.	.0201	.0210	.0222	.0236	.0253
50.	.01741	.01826	.0193	.0205	.0220
75.	.01001	.01053	.01114	.01190	.01284
100.	.00672	.00707	.00750	.00803	.00869
150.	.00380	.00401	.00426	.00457	.00497
200.	.00252	.00267	.00284	.00302	.00332
300.	.001411	.001493	.001592	.001714	.001870
500.	.000674	.000713	.000762	.000822	.000899
700.	.000413	.000437	.000467	.000505	.000553
1000.	.000245	.000259	.000268	.000300	.000329
5000.	.0000227	.0000241	.0000258	.0000280	.0000308
10000.	.00000808	.00000859	.00000922	.00000999	.0000110

For practical computations, values of $g(x)$ and $f(x)$ in Tables (5-3-5) and (5-3-6) may be used. In terms of the constants α^* and β^* given in Table (5-3-1), equation (5-3-14) becomes

$$\Lambda = \Lambda^0 - \left(\frac{\alpha^* 3 g(x)}{2-\sqrt{2}}\Lambda^0 + \frac{\beta^*}{\sqrt{2}} f(x)\right)\sqrt{c} \tag{5-3-15}$$

The Dissociation Field Effect

According to the theory of Onsager, the effects of high fields on the ionization constants are given by equations (4-7-29) and (4-7-30). Thus,

$$\frac{K(X)}{K(0)} = F(\bar{b}) = 1 + \bar{b} + \frac{\bar{b}^2}{3} + \frac{\bar{b}^3}{18} + \frac{\bar{b}^4}{180} + \cdots \tag{4-7-29}$$

or, for large values of $\bar{b}$, by the asymptotic expansion

TABLE (5-3-5).[19] THE FUNCTION $g(x)$. SEE TABLE (B-1-3).

x	$g(x)$	x	$g(x)$	x	$g(x)$	x	$g(x)$
0.0	0.19526	2.5	0.11977	10.0	0.04354	24.	0.01965
.1	.19492	2.6	.11721	10.5	.04173	25.	.01891
.2	.19391	4.2	.08656	11.0	.04007	26.	.01822
.3	.19228	4.4	.08376	11.5	.03853	27.	.01758
.4	.19009	4.6	.08113	12.0	.03711	28.	.01698
.5	.18742	4.8	.07865	12.5	.03579	29.	.01643
.6	.18437	5.0	.07632	13.0	.03456	30.	.01590
.7	.18102	5.2	.07411	13.5	.03341	31.	.01541
.8	.17745	5.4	.07203	14.0	.03233	32.	.01495
.9	.17373	5.6	.07005	14.5	.03132	33.	.01452
1.0	.16992	5.8	.06818	15.0	.03037	34.	.01413
1.1	.16607	6.0	.06640	15.5	.02948	35.	.01372
1.2	.16223	6.2	.06472	16.0	.02864	38.	.01269
1.3	.15842	6.4	.06311	16.5	.02784	41.	.01178
1.4	.15466	6.6	.06158	17.0	.02709	44.	.01101
1.5	.15098	6.8	.06012	17.5	.02638	47.	.01032
1.6	.14740	7.0	.05873	18.0	.02570	50.	.00972
1.7	.14390	7.2	.05740	18.5	.02506	55.	.00886
1.8	.14051	7.4	.05613	19.0	.02444	60.	.00814
1.9	.13723	7.5	.05551	19.5	.02387	65.	.00753
2.0	.13406	7.6	.05491	20.0	.02331	70.	.00700
2.1	.13099	8.0	.05262	20.5	.02278	75	.00654
2.2	.12803	8.5	.05002	21.0	.02227	80.	.00614
2.3	.12518	9.0	.04766	22.	.02133	85.	.00579
2.4	.12242	9.5	.04550	23.	.02045		

TABLE (5-3-6). THE FUNCTION $f(x)$.

x	$f(x)$	x	$f(x)$	x	$f(x)$
0.0	1.4142	4.2	1.2895	15.5	1.1531
.1	1.4139	4.4	1.2845	16.0	1.1502
.2	1.4133	4.6	1.2797	16.5	1.1475
.3	1.4121	4.8	1.2750	17.0	1.1449
.4	1.4104	5.0	1.2705	17.5	1.1424
.5	1.4085	5.2	1.2662	18.0	1.1399
.6	1.4061	5.4	1.2622	18.5	1.1376
.7	1.4035	5.6	1.2583	19.0	1.1354
.8	1.4006	5.8	1.2545	19.5	1.1332
.9	1.3975	6.0	1.2507	20.0	1.1312
1.0	1.3942	6.2	1.2471	20.5	1.1291
1.1	1.3907	6.4	1.2437	21.0	1.1272
1.2	1.3872	6.6	1.2403	22	1.1235
1.3	1.3836	6.8	1.2370	23	1.1201
1.4	1.3799	7.0	1.2338	24	1.1168
1.5	1.3762	7.2	1.2308	25	1.1138
1.6	1.3724	7.4	1.2278	26	1.1109
1.7	1.3687	7.5	1.2263	27	1.1082
1.8	1.3650	7.6	1.2249	28	1.1057
1.9	1.3613	8.0	1.2193	29	1.1032
2.0	1.3576	8.5	1.2129	30	1.1010
2.1	1.3539	9.0	1.2068	31	1.0988
2.2	1.3503	9.5	1.2011	32	1.0969
2.3	1.3468	10.0	1.1958	33	1.0947
2.4	1.3433	10.5	1.1908	34	1.0928
2.5	1.3398	11.0	1.1860	35	1.0910
2.6	1.3364	11.5	1.1815	38	1.0861
2.8	1.3298	12.0	1.1773	41	1.0816
3.0	1.3234	12.5	1.1733	44	1.0780
3.2	1.3172	13.0	1.1695	47	1.0742
3.4	1.3112	13.5	1.1659	50	1.0710
3.6	1.3055	14.0	1.1625	55	1.0664
3.8	1.2999	14.5	1.1592	60	1.0623
4.0	1.2946	15.0	1.1561	65	1.0588

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[19] The authors are indebted to Dr. William S. Wilson for these values, which do not occur in his Dissertation.

$$F(\bar{b}) \cong \left(\frac{2}{\pi}\right)^{1/2} (8\bar{b})^{-3/4} e^{\sqrt{8\bar{b}}} \left\{1 - \frac{3}{8(8\bar{b})^{1/2}} - \frac{15}{128(8\bar{b})} - \frac{105}{1024(8\bar{b})^{3/2}} \cdots \right\} \tag{4-7-30}$$

where $\bar{b}$ is given by the equation

$$\bar{b} = \frac{z_1^2 z_2^2(\lambda_1 + \lambda_2)}{|z_2|\lambda_1 + |z_1|\lambda_2} \frac{9.636V}{DT^2} \tag{4-7-27}$$

For the important case where $\alpha \ll 1$, the equivalent conductance, degree of ionization, and ionization constant in the field may be computed by

$$\frac{\Lambda_X}{\Lambda_{X=0}} = \frac{\alpha}{\alpha_0} = \sqrt{\frac{K(X)}{K(0)}} = 1 + \frac{1}{2}\bar{b} + \frac{1}{24}\bar{b}^2 \cdots \tag{4-7-34}$$

Λ_X, α, and $K(X)$ are the conductance, the degree of dissociation, and ionization constant in the field of V (volts/cm), and $\Lambda_{X=0}$, α_0, and $K(0)$, are these quantities in the absence of the field.

Chapter (6)

Experimental Investigation of Irreversible Processes in Solutions of Strong Electrolytes. Conductance, Transference Numbers, Viscosity and Diffusion

In the preceding chapters, the theoretical equations necessary for the interpretation of dilute ionic solutions have been developed and summarized. We shall now undertake to utilize the experimental methods which have proved most fruitful in this field, considering first the conductance measurements [Chapters (6) and (7)], and then the measurements of thermodynamic properties [Chapters (8), (9) and (10)] in suitable order. From the very beginning of the study of electrolytes, conductance measurements have proved of great value, and their importance has increased as the subject has developed. This is because of the great accuracy attainable, and of the generality of the method, which can be applied to the study of strong and weak electrolytes in any stable medium which will dissolve them. Further, the conductance of electrolytic solutions has been studied as a function of the frequency and potential gradient of external electrical fields. This extends the range of variables beyond that considered by thermodynamic methods.

(1) EQUIVALENT CONDUCTANCE, Λ. PRIMARY STANDARDS

The equivalent conductance of an electrolyte in solution is defined by the equation

$$\Lambda = \frac{1000\, L^*}{c^*} \qquad (6\text{-}1\text{-}1)$$

in which c^* is the concentration of the electrolyte in equivalents per liter, and L^* is that part of the specific conductivity of the solution which is due to the electrolyte. In the simplest case, L^* is obtained by subtracting the specific conductivity of the pure solvent, L_0, from that of the solution, L. If L_0 is not very small compared to L, it may be necessary to consider the effect of the dissolved electrolyte upon the conductivity of the solvent. For example, if much of the solvent conductivity is due to the ions formed from dissolved carbon dioxide, it is clear that this quantity would be greatly decreased in the presence of a strong acid such as hydrochloric. Thus the proper estimation of L^* from observed values of L and L_0 must take account of the nature of the electrolyte as well as the solvent. The details of such calculations are discussed elsewhere.[1]

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[1] C. W. Davies, "The Conductivity of Solutions," John Wiley and Sons, New York, 1930; *Trans. Faraday Soc.*, **28**, 607 (1932). W. F. K. Wynne-Jones, *J. Phys Chem.*, **31**, 1647 (1927).

Measurement of the conductivity of solutions of electrolytes depends upon the use of some modification of the Wheatstone bridge. Except in very rare cases,[2] polarization at the electrodes in contact with the solution must be reduced by the use of alternating currents[3] and platinization of the electrodes.[4] Even at moderate frequencies, alternating currents complicate the measurement of resistance by including the effects of the capacitance of the cell, and the inductance and capacitance of various parts of the bridge network. The elimination or accurate compensation of these effects requires considerable ingenuity. Since the initial development of the alternating current conductivity bridge by Kohlrausch,[5] many technical advances have been made in bridge design, and in the source and detection of the alternating current signal.[6] A large proportion of the most precise conductivity data now available was obtained with equipment based upon the designs of Jones and Josephs,[7] and of Shedlovsky.[8] In most studies of electrolytes at high dilution, the errors due to limitations of the best modern bridges are considerably less than those due to capacitance effects in conductivity cells, and uncertainty in the estimation of the proper solvent conductivity.

The problem of cell design has been very thoroughly investigated by Jones and Bollinger[9] and by Shedlovsky.[10] The capacitance of the cell is ordinarily compensated by a variable condenser in the opposite bridge arm, but Jones and Bollinger showed that if the leads to the electrodes are not widely separated from certain parts of the cell which contain solution, there is produced a capacitance by-path of such a nature that compensation is not practicable. It was shown that this fault in cell design would

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[2] J. N. Brönsted and R. F. Nielsen, *Trans. Faraday Soc.*, **31**, 1478 (1935); R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 21, 3614 (1933); L. V. Andrews and W. E. Martin, *Ibid.*, **60**, 871 (1938); H. E. Gunning and A. R. Gordon, *J. Chem. Phys.*, **10**, 126 (1942).

[3] Polarization is not eliminated at audio frequencies, but may be corrected for by extrapolating resistance readings, $R_{\bar{\omega}}$ (at various frequencies $\bar{\omega}$), to give the resistance, R_∞, at infinite frequency. G. Jones and S. M. Christian [*J. Am. Chem. Soc.*, **57**, 272 (1935)] showed that the extrapolation is linear if $R_{\bar{\omega}}$ is plotted against $1/\sqrt{\bar{\omega}}$.

[4] The conditions under which polarization is reduced by platinization of the electrodes have been investigated by G. Jones and D. M. Bollinger [*J. Am. Chem. Soc.*, **57**, 280 (1935)].

[5] F. Kohlrausch, *Z. physik. Chem.*, **2**, 561 (1888).

[6] A comprehensive review of the subject is given by B. Hague, "A. C. Bridge Methods," Pitman, New York, 1938.

[7] G. Jones and R. C. Josephs, *J. Am. Chem. Soc.*, **50**, 1049 (1928); P. H. Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[8] T. Shedlovsky, *J. Am. Chem. Soc.*, **52**, 1793 (1930). These investigators make use of a ground similar to that of K. W. Wagner [*Elektrotech. Z.*, **32**, 1001 (1911)]. A. V. Astin [*Bur. Standards J. Research*, **21**, 425 (1938)] and W. F. Luder [*J. Am. Chem. Soc.*, **62**, 89 (1940)] have recently proposed a separate detector terminal balance to ground for increasing the sensitivity in measuring high resistances.

[9] G. Jones and G. M. Bollinger, *J. Am. Chem. Soc.*, **53**, 411 (1931).

[10] T. Shedlovsky, *Ibid.*, **52**, 1806 (1930).

produce an error which must vary with the specific resistance of the solution.[11] This offered a ready explanation for the observation that the cell constants of certain cells show a slight variation[12] with the conductivity of the solution.

The relation between the measured resistance across the terminals of a conductivity cell and the specific conductivity of the solution depends upon the geometry of the cell. In the simple case, where the electrodes form the parallel ends of a cylindrical cell, X, of length, l, and uniform cross-section, a, the specific conductivity is given by

$$L = K_X/R_X \tag{6-1-2}$$

The term K_X equals l/a, is a property of the particular cell, and is called the cell constant.[13] To avoid the necessity of always constructing cells of uniform and accurately known dimensions, K_X is calculated by equation (6-1-2) from the measured value of R_X when the cell contains a standard solution of known specific conductivity, L. The primary standard for this purpose is pure mercury, by virtue of its use in defining the international ohm. The specific conductivity of mercury is so high that solutions of potassium chloride are used as secondary standards in determining the cell constants of cells designed for the study of electrolytes. Kohlrausch[14] was the first to determine the specific conductivity of standard potassium chloride solutions in absolute units, and his results were used for many years without being seriously questioned. There was, however, some ambiguity in the manner in which Kohlrausch described the composition of his standard solutions. Parker and Parker[15] redetermined the specific conductance of potassium chloride solutions, and eliminated an inconsistency in units by defining a *demal* (written $1D$) solution as one containing one gram molecule of salt dissolved in one cubic decimeter of solution at 0°. The Parker and Parker results were chosen as standards for the tabulation of conductance values in the "International Critical Tables," but objections were soon raised regarding this choice.

Jones and Bradshaw[16] made new absolute measurements of the specific conductivity of solutions of the same composition used by Parker and Parker, and Jones and Prendergast[17] reinvestigated the solutions described

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[11] Compare C. W. Davies, *J. Chem. Soc.*, **138**, 432 (1937).

[12] H. C. Parker, *J. Am. Chem. Soc.*, **45**, 1366, 2017 (1923).

[13] If the cross-section, a, is not uniform, but is known as a function of the distance from one of the electrodes, the cell constant is given by

$$K_X = \int_0^l \frac{dl}{a}$$

[14] F. Kohlrausch, L. Holborn and H. Diesselhorst, *Wien. Ann.*, **64**, 417 (1898).

[15] H. C. Parker and E. W. Parker, *J. Am. Chem. Soc.*, **46**, 312 (1924).

[16] G. Jones and B. C. Bradshaw, *J. Am. Chem. Soc.*, **55**, 1780 (1933).

[17] G. Jones and M. J. Prendergast, *J. Am. Chem. Soc.*, **59**, 731 (1937).

by Kohlrausch. The results of these new measurements tend to confirm the values of Kohlrausch rather than those of Parker and Parker, but differ substantially from both. The results of Jones are now generally accepted as the most reliable secondary standards available for solution conductivity, and all the conductances which we compile in the text and tables have been referred to the Jones standards. As an aid in making the conversion from one of the common standards to another, we have recorded the Kohlrausch, Parker, and Jones values of the specific conductivity for various potassium chloride solutions in Table (6-1-1). In the lower half of this table, the concentrations are expressed as 1 demal (1*D*), tenth demal (0.1*D*), etc. Jones has eliminated all sources of ambiguity by expressing the composition of his solutions in terms of the actual weights of salt and solution in vacuo.

TABLE (6-1-1).† SPECIFIC CONDUCTIVITY OF STANDARD POTASSIUM CHLORIDE SOLUTIONS IN OHMS^{-1} CM.$^{-1}$

	0°	18°	20°	25°
	1*N* KCl 71.3828 g KCl per kg of solution in vacuum			
Kohlrausch	0.06541	0.09822	0.10207	0.11180
Parker	.06531$_2$	.09811$_6$		.11168$_7$
Jones	.06543$_0$	.09820$_1$	.10202$_4$	.11173$_3$
	0.1*N* KCl 7.43344 g KCl per kg of solution in vacuum			
Kohlrausch	0.00715	0.01119	0.01167	0.01288
Parker	.007141$_6$	.011184$_6$		.012876$_5$
Jones	.007154$_3$	.011191$_9$	.011667$_6$	.012886$_2$
	0.01*N* KCl 0.746558 g KCl per kg of solution in vacuum			
Kohlrausch	0.000776	0.001225	0.001278	0.001413
Parker	.0007742$_2$	.0012223$_8$		.0014103$_7$
Jones	.0007751$_2$	.0012226$_9$	.0012757$_2$	.0014114$_5$
	1*D* KCl 71.1352 g KCl per kg of solution in vacuum			
Parker	0.06509$_8$	0.09779$_0$		0.11132$_2$
Jones	.06517$_6$*	.09783$_8$*		.11134$_2$*
	0.1*D* KCl 7.41913 g KCl per kg of solution in vacuum			
Parker	0.007129$_5$	0.011163$_6$		0.012852$_4$
Jones	.007137$_9$*	.011166$_7$*		.012856$_0$*
	0.01*D* KCl 0.745263 g KCl per kg of solution in vacuum			
Parker	0.00077284	0.0012202$_3$		0.0014078$_9$
Jones	.0007736$_4$*	.0012205$_2$*		.0014087$_7$*

† A discrepancy of several parts in 10,000 between the conductivities of the normal and demal standard solutions has been pointed out by H. E. Gunning and A. R. Gordon, *J. Chem. Phys.*, **10**, 130 (1942), footnote (14).

* These values of Jones and Bradshaw are used as standards for all conductances recorded in this book.

(2) THE ONSAGER CONDUCTANCE EQUATION. COMPARISON WITH EXPERIMENT

In the derivation of the theoretical equation (5-3-1) for the equivalent conductance,

$$\Lambda = \Lambda^0 - \mathcal{S}_{(\Lambda)}\sqrt{c} = \Lambda^0 - (\alpha^*\Lambda^0 + \beta^*)\sqrt{c} \tag{6-2-1}$$

the treatment was confined to completely dissociated electrolytes at extreme dilutions. The equation will now be tested under these conditions. Later, it will be shown that the theory is also applicable to the *ions* of incompletely dissociated electrolytes.

Onsager[18] originally compared the theoretical limiting slopes with numerous experimental slopes, calculated by Debye and Hückel[19] from the data of Kohlrausch. The results for concentrations between 0.001 and $0.005N$ were used to evaluate the arbitrary constants A and B of the equation

$$\Lambda = \Lambda^0 - A\sqrt{c} + Bc \tag{6-2-2}$$

by the method of least squares. The agreement between the experimental slopes,[20] A, and the theoretical slopes, $\mathcal{S}_{(\Lambda)}$, was of the order of 5 to 10 per cent for 1-1 electrolytes, and within 13 per cent for 2-1 electrolytes. Fortunately, later very accurate measurements are available for a more rigorous test of the theory. For a comprehensive test, see Appendix B.

The data for some 1-1 electrolytes are compared with the theoretical limiting functions in Fig. (6-2-1). The dependence of the slope of these graphs upon the temperature and the magnitude of Λ^0 is very striking indeed. The value of Λ^0 for hydrochloric acid at 25° is almost three times that for potassium chloride at the same temperature. The temperature appears explicitly in the theoretical slope as the product, D_0T, which decreases only about 18 per cent in water between 0 and 100°. The most pronounced temperature effect is the rapid decrease in viscosity, which acts to increase both Λ^0 and β^*.

The influence of valence type upon conductance is illustrated in Fig. (6-2-2). The data used in this figure were all obtained at 25°, and the values of Λ^0 for the various salts are roughly equal. All the results except those for zinc sulfate are in excellent accord with theory. Throughout the entire experimental concentration range, the decrease in the conductance of zinc sulfate with $\sqrt{c}$ is more rapid than the theory predicts. This behavior is characteristic of weak electrolytes. Figure (6-2-2) shows that

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[18] L. Onsager, *Physik. Z.*, **28**, 277 (1927); J. Lange, *Z. Physik. Chem.*, **A188**, 284 (1941).

[19] P. Debye and E. Hückel, *Physik. Z.*, **24**, 305 (1923).

[20] P. Walden [*Z. physik. Chem.*, **144**, 297, 434 (1929); *Ibid.*, **147A**, 1 (1930)] showed that $A \simeq 65.7/D_0\eta_0$ by an extension of the empirical Ostwald-Walden-Bredig rule. This relation gives values of the same order as $\mathcal{S}_{(\Lambda)}$ for a surprising variety of electrolytes in various solvents.

at moderate concentrations the conductance of potassium nitrate also falls below the limiting function, but to a less marked degree. This effect will be considered later.

Smoothed values of the equivalent conductances of electrolytes of various valence types are recorded in Table (6-2-1A).

As a further direct test of the theory, the effect of dielectric constant is shown in Fig. (6-2-3), where $(\Lambda - \Lambda^0)\eta_0$ for tetraethylammonium picrate in nitromethane,[21] methanol,[22] ethanol,[23] and acetone[24] is plotted against $\sqrt{c}$. The temperature of each system is 25°. The inclusion of the factor η_0 in the ordinates eliminates the effect of the widely different viscosities of the solvents, since both $\Lambda^0\eta_0$ and $\mathfrak{S}_{(\Lambda)}\eta_0$ are independent of η_0 for solutes, such as tetraethylammonium picrate, which obey Walden's rule [Equation (7-1-4)]. Consequently, the differences in the limiting slopes and in the character of the plots in the figure are almost entirely due to differences in dielectric con-

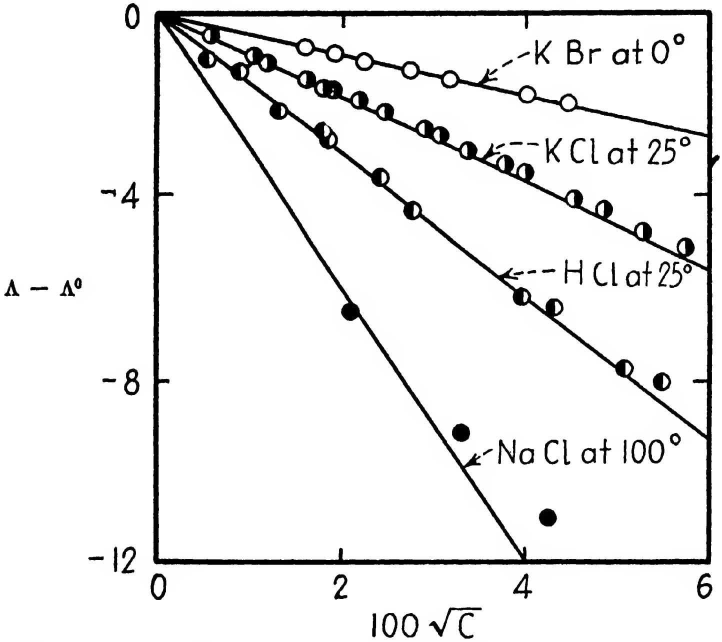

Fig. (6-2-1). Comparison of theoretical equation (6-2-1) with data for 1-1 electrolytes. The straight lines represent the theoretical equation (6-2-1).

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[21] C. P. Wright, D. M. Murray-Rust and H. Hartley, *J. Chem. Soc. (London)*, **134**, 199 (1931).

[22] A. Unmack, E. Bullock, D. M. Murray-Rust and H. Hartley, *Proc. Roy. Soc. London*, **A132**, 427 (1931).

[23] M. Barak and H. Hartley, *Z. physik. Chem.*, **A165**, 272 (1933).

[24] P. Walden, H. Ulich and G. Busch, *Ibid.*, **123**, 429 (1926).

stants. Specific solvent effects, which strongly influence the conductance of small ions, are minimized by our choice of solute.[25]

Figure (6-2-3) emphasizes the point that the predictions of the theoretical equation are verified by experimental results obtained under the conditions postulated in the theory, namely high dilution and complete dissociation. A number of phenomena indicate that ionization is far from complete in media of low dielectric constants. The tendency of Λ to fall more and more below the theoretical function as the dielectric constant is decreased must be due largely to incomplete dissociation. These negative departures from the limiting equation are discussed in the following section and in Chapter (7).

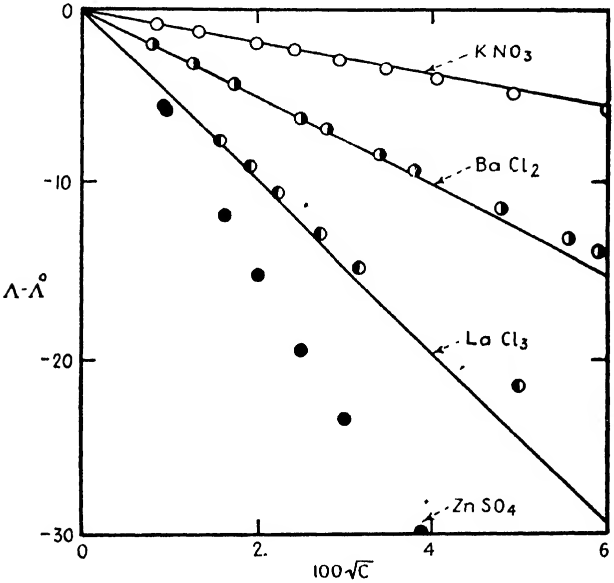

Fig. (6-2-2). The influence of valence upon the equivalent conductance in aqueous solutions at 25°. The straight lines represent the theoretical equation (6-2-1). Note that $\mathfrak{S}_{(\Lambda)}$ for $LaCl_3$ and $ZnSO_4$ are indistinguishable on this scale.

The general equation (4-3-51) for the equivalent conductance of an ion constituent in the presence of an arbitrary mixture of ions is

$$\lambda_j = \lambda_j^0 - \left[\frac{1.970 \times 10^6}{(D_0T)^{3/2}} \lambda_j^0 \; z_j \sum_0^\infty c_n r_j^{(n)} + \frac{28.98\, z_j}{\eta_0 (DT)^{1/2}}\right] \sqrt{\Gamma} \quad (6\text{-}2\text{-}3)$$

In this equation $z_j \sum\limits_0^\infty c_n r_j^{(n)}$ replaces the factor $|z_1 z_2| q^*/(1 + \sqrt{q^*})$ in equation (4-3-42), derived for only two kinds of ions. The difference

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[25] H. Ulich, *Z. angew. Chem.*, **41**, 1141 (1928).

between the effects of these two factors upon the numerical value of λ_j is not large in any case, and becomes zero as the mobilities of the various ions of like charge approach equality. Therefore, a rigorous experimental test of the "mixture effect" is more difficult than the tests of equation (6-2-1). The most readily verified prediction of equation (6-2-3) is that wide departures from the Kohlrausch principle of independent ionic mobilities should appear in mixtures containing ions of like sign but very different mobilities. In a mixture of hydrochloric acid and potassium chloride, the theory predicts that the hydrogen-ion mobility will be smaller, and the potassium-ion mobility larger than in solutions of the pure single electrolytes at the same ionic strength. This effect is clearly shown in Figs. (6-2-4) and (6-2-5). The ordinates represent the difference (in % of λ_j) between the cation conductance in the mixture and in a solution of the single electrolyte at the same ionic strength. The solid lines are the theoretical curves at 25° calculated by Onsager and Fuoss.[26] The circles represent the observed[27] effects at the same temperature. The

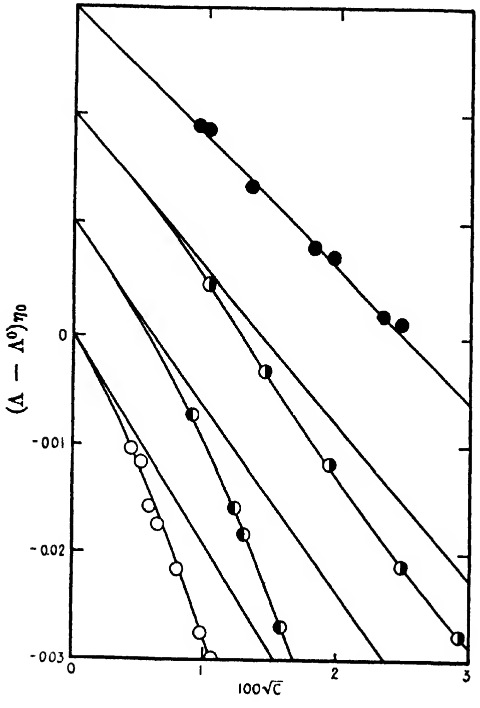

Fig. (6-2-3)
The influence of dielectric constant upon the conductance of tetraethylammonium picrate at 25°. ●, Nitromethane, $D = 37$, $\eta = 0.00627$; ◑, Methanol, $D = 30.3$; $\eta = 0.00545$; ◐, Ethanol, $D = 25$, $\eta = 0.01078$; ○, Acetone, $D = 21$, $\eta = 0.00316$. The intercepts are separated by 0.01.

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[26] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).
[27] L. G. Longsworth, *J. Am. Chem. Soc.*, **52**, 1897 (1930).

crosses represent an independent series of measurements[28] at 18°. The observed and theoretical effects are seen to agree in sign and order of magnitude. Exact numerical agreement could not be expected at the concentration involved ($\Gamma = 0.2$). The results given in Table (6-2-1) indicate more complete concordance at high dilution. The measurements upon which this table is based could not be expressed in terms of individual ionic conductances, because the transference numbers are not known in sodium chloride-hydrochloric acid mixtures. The comparison with theory was therefore made on the basis of specific conductivities. In the column headed % obs., we have recorded the percentage difference between observed specific conductivities of the mixtures and values calculated by the

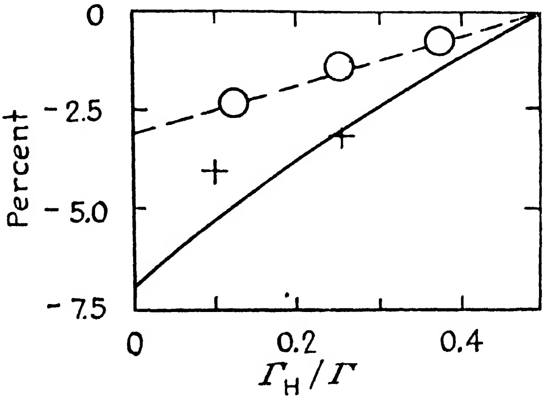

Fig. (6-2-4). Variation in hydrogen ion conductance in HCl-KCl mixtures

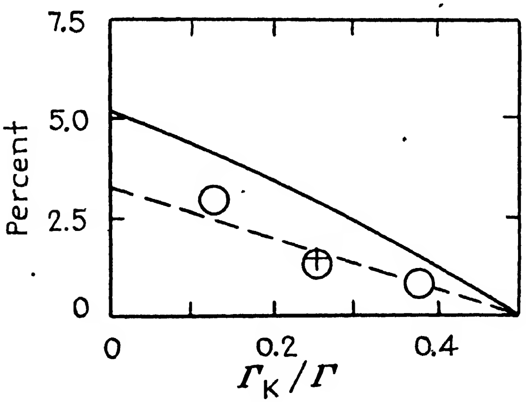

Fig. (6-2-5). Variation in potassium ion conductance in HCl-KCl mixtures

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[28] K. Bennewitz, C. Wagner and K. Küchler, *Physik. Z.*, **30**, 623 (1929).

Kohlrausch law from measurements on solutions of the pure electrolytes. The % calc. column contains the corresponding changes in specific conductivity predicted by equation (6-2-3). The last column shows that the difference between the observed and calculated mixture effects disappears at high dilution. Similar results were obtained in mixtures of lithium and potassium chlorides by Krieger and Kilpatrick.[29]

The careful measurements of Renholm[30] on mixtures of potassium chloride with barium nitrate or copper sulfate, clearly demonstrate a "mixture effect" of the conductance at quite low concentrations (10^{-3} to 10^{-4}). A comparison of his results with the predictions of equation (6-2-3) has not been attempted because of the incomplete ionization of barium nitrate and copper sulfate.

TABLE (6-2-1).* COMPARISON OF OBSERVED WITH CALCULATED MIXTURE EFFECTS ON THE SPECIFIC CONDUCTIVITY OF HCl-NaCl MIXTURES AT 25°.

$\frac{c_{NaCl}}{c_{HCl}}$	Γ	% obs.	% calc.	Δ
1	0.400	1.99	3.31	1.32
1	.080	1.02	1.38	.36
1	.020	.76	.66	−.10
2	.300	1.72	3.29	1.57
2	.060	.98	1.35	.37
2	.015	.62	.65	.03
5	.240	1.44	2.50	1.06
5	.048	.88	1.03	.15
5	.012	.49	.49	.00

* Taken from Table VII in the paper of L. Onsager and R. M. Fuoss [*J. Phys. Chem.*, **36**, 2689 (1932)]. The measurements are by W. C. Bray and F. L. Hunt [*J. Am. Chem. Soc.*, **33**, 781 (1911)].

(3) EXTENSIONS OF THE ONSAGER EQUATION. EVALUATION OF Λ^0

Three distinct methods have been used for extending the range of the Onsager equation to somewhat higher concentrations. The first applies only to electrolytes for which the conductance falls below the limiting law in dilute solutions, and interprets this "conductance deficiency" in terms of finite ionization constants. The second assumes infinite ionization constants (complete dissociation), and attempts to account for all departures from the limiting equation by more elaborate theoretical treatments designed to include higher terms in the mathematical approximations, or inclusion of the "mean distance of closest approach" in the physical picture. The third method is the purely empirical addition of terms in higher powers of c than the one-half. To prevent confusion, these methods will be discussed separately.

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[29] K. A. Krieger and M. Kilpatrick, *J. Am. Chem. Soc.*, **59**, 1878 (1937); Correction, *Ibid.*, **60**, 3601 (1938).

[30] J. E. Renholm, "Dissertation," Helsingfors, 1925.

The Introduction of Finite Dissociation Constants

The manner in which the limiting law is approached in dilute solutions is of considerable theoretical importance. Onsager[31] pointed out that completely dissociated electrolytes should approach the limiting tangent asymptotically from above, whereas incompletely dissociated electrolytes should approach it from below. Ionic association restricts the concentration range over which the limiting slope may be used, but does not influence its numerical value because the effect of association is proportional to the first power of the concentration at high dilution. This can be readily shown by combining the expression

$$K = \frac{(y_{\pm}\alpha)^2 c}{(1 - \alpha)} \tag{6-3-1}$$

for the dissociation constant of a binary electrolyte, with equation (6-2-1). At extreme dilution, it is permissible to set both α^2 and the activity coefficient, $y_{\pm}^2$, equal to unity in the numerator, so that

$$1 - \alpha \doteq c/K \tag{6-3-2}$$

Since the decrease in conductance due to ionic association is $\Lambda(1 - \alpha)$, or $\Lambda^0(1 - \alpha)$ in the limit, we may write

$$\Lambda = \Lambda^0 - (\alpha^*\Lambda^0 + \beta^*)\sqrt{c} - c\Lambda^0/K \tag{6-3-3}$$

which is equation (62) given by Onsager.[32] Although equation (6-3-3) is of theoretical interest, its use in the evaluation of ionization constants is subject to serious difficulties. This equation can represent the conductance of a partially dissociated electrolyte only throughout the concentration range in which (6-2-1) is valid for completely dissociated electrolytes. Reference to Figs. (6-2-1) and (6-2-2) shows that, in the region where the experimental curves for potassium nitrate and zinc sulfate are clearly concave downward, the curves for the typical strong electrolytes become concave upward. Any determination of the degree of dissociation of potassium nitrate, or zinc sulfate, should therefore take both of these effects into account. The first method of doing this is illustrated below.

Onsager assumed that the curve for potassium chloride represents the normal deviation of strong 1-1 electrolytes from the limiting law. On this assumption, the difference, $\Lambda_{(\text{obs.})} - \Lambda_{(\text{lim. law.})}$, for potassium nitrate subtracted from the corresponding difference for potassium chloride, at the same concentration, would be the "conductance deficiency" attributed to the association of potassium nitrate. In terms of this deficiency, Δ, the associated fraction of the electrolyte would be

$$1 - \alpha = \Delta/\Lambda_{(\text{obs.})} \tag{6-3-4}$$

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[31] L. Onsager, *Physik. Z.*, **28**, 277 (1927).

[32] L. Onsager, *Ibid.*

From this, K may be evaluated by (6-3-1) if the activity coefficient is known. In this connection, it should be noted that the stoichiometric activity coefficients calculated from freezing-point depressions, and other colligative properties, are actually the product, $y_{\pm}\alpha$, occurring in (6-3-1). The activity coefficient of un-ionized potassium nitrate is assumed to be unity.

Table (6-3-1) gives the values of K, and the data required in their calculation. K is seen to be essentially constant over the whole concentration range considered. This independence of K upon concentration is a necessary, but not a sufficient, condition for the validity of the hypothesis that the conductance of potassium nitrate (in dilute solutions) falls below the limiting law because of ionic association. This is an important point, and will be referred to later in this section.

TABLE (6-3-1).* ESTIMATION OF THE DISSOCIATION CONSTANT OF KNO_3 AT 25° BY ONSAGER'S METHOD.

c	.005	.01	.02	.05	.07	.1
$\Lambda_{(obs.)}$; KNO_3	138.48	135.82	132.41	126.31	123.55	120.39
$\Lambda_{(obs.)} - \Lambda_{(L.L)}$; KCl	0.45	0.89	1.79	4.50	6.22	8.77
$\Lambda_{(obs.)} - \Lambda_{(L.L)}$; KNO_3	0.08	0.14	0.56	2.08	3.13	4.77
"Deficiency", Δ	0.37	0.75	1.23	2.42	3.09	4.00
Degree of Association $1 - \alpha$.	.0027	.0055	.0093	.0192	.0250	.0332
$y_{\pm}\alpha$; KNO_3†	.927	.899	.862	.794	.763	.726
K	1.59	1.47	1.60	1.64	1.63	1.59

* All conductances are the smoothed values of T. Shedlovsky [*J. Am. Chem. Soc.*, **54**, 1411 (1932)] corrected to the standard of G. Jones and B. C. Bradshaw.

† G. Scatchard, S. S. Prentiss and P. T. Jones, *J. Am. Chem. Soc.*, **54**, 2690 (1932).

Davies[33] has made a large number of calculations of this nature,[34] and has tabulated[35] the dissociation constants of a variety of salts, especially complex valence types. Some typical results are given in Table (6-3-2). Judging from the magnitude of K for many of these salts, it appears that dissociation is far from complete in solutions of electrolytes of high valence types. However, we do not wish to accept this view entirely without reservation, because the evaluation of K depends upon the arbitrary selection of some conductance curve to represent the behavior of the

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[33] C. W. Davies, *Trans. Faraday Soc.*, **23**, 351 (1927). Later references are given in Table (6-3-2).

[34] If the conductance of the salt departs seriously from the limiting law (*e.g.*, zinc sulfate), an accurate value of Λ^0 cannot be obtained from the simple extrapolation of Λ against $\sqrt{c}$. In this case, Davies determines, by trial, the value of Λ^0, which leads to the most nearly constant values of K at low concentrations. If accurate activity coefficients are not available, this process yields no completely consistent values of Λ^0 and K over any experimental concentration range, and therefore allows considerable latitude in evaluating either of these constants.

[35] C. W. Davies, *J. Chem. Soc.*, **140**, 2093 (1938); W. H. Banks, E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **27**, 621 (1931).

hypothetical completely dissociated electrolyte. In our calculations, we used the curve for potassium chloride and obtained very self-consistent values of K for potassium nitrate. If we had used almost any other experimental curve as standard, the values of K would have shown more variation with concentration. This difficulty is magnified in the case of a salt such as zinc sulfate, because no 2-2 electrolyte has yet been found to have a conductance curve which approaches the limiting law from above.

TABLE (6-3-2). DISSOCIATION CONSTANTS OF SALTS AND COMPLEX IONS IN WATER ESTIMATED FROM CONDUCTANCE DATA AT 25°* AND 18°. SEE TABLE (B-9-1).

	K	Ref.		$100K$	Ref.
$KClO_3$	1.4	(1)	$(Ca\ Acetate)^+$	100*	(3)
KNO_3	1.4	(1)	$(CaOH)^+$	3.1*	(4)
$AgNO_3$	1.2	(1)	$(BaOH)^+$	23*	(4)
$TlNO_3$	.52	(1)	$MgSO_4$	0.78	(5)
$TlCl$	.300	(1)	$CaSO_4$	.53	(6)
$(CdNO_3)^+$	.394	(2)	$CuSO_4$	.50	(5)
$(CdCl)^+$	.0101	(2)	$ZnSO_4$	.53	(5)
$(PbNO_3)^+$	.0647	(2)	$CdSO_4$	.49	(5)
$(PbCl)^+$	.0304	(2)	$MgSO_4$	.63*	(6)
$(CaNO_3)^+$	.521	(2)	$CoSO_4$	.34*	(6)
$(SrNO_3)^+$	.150	(2)	$NiSO_4$	.40*	(6)
$(BaNO_3)^+$	.121	(2)	$CuSO_4$	.43*	(7)
$(LiSO_4)^-$	.229	(2)	$ZnSO_4$	.49*	(7)
$(NaSO_4)^-$	.198	(2)	Cu Malonate	.00025*	(6)
$(KSO_4)^-$	.151	(2)	Zn Malonate	.021*	(6)
$(AgSO_4)^-$	.05	(2)	Cd Malonate	.051*	(6)
$(TlSO_4)^-$	.0472	(2)	$(KFe(CN)_6)^{\equiv}$	.55*	(8)

* Values followed by an asterisk were estimated at 25°.

(1) C W Davies, *Trans. Faraday Soc*, **23**, 351 (1927)

(2) E C Righellato and C. W Davies, *Ibid*, **26**, 592 (1930); compare J. Zirkler, *Z. physik. Chem.*, **163A**, 1 (1932).

(3) C. W. Davies, *J. Chem. Soc (London)*, **140**, 277 (1938) The ionization of calcium acetate is exceptionally high. The values of $100K$ for the calcium ions of nine other monobasic organic acids lie between 2 and 30. The association of alkaline-earth metal cations with carboxylic acid radicals has been investigated potentiometrically by R K Cannan and A Kibrick, [*J Am Chem Soc.*, **60**, 2314 (1938)] and by N. E. Topp and C. W. Davies, *J. Chem Soc*, **142**, 87 (1940).

(4) C. W. Davies, *Ibid*, **141**, 349 (1939).

(5) C. W. Davies, *Ibid*, **140**, 2093 (1938). Compare Ref (1).

(6) R. W. Money and C. W. Davies, *Trans. Faraday Soc*, **28**, 609 (1932).

(7) B. B. Owen and R. W. Gurry, *J. Am. Chem Soc.*, **60**, 3074 (1938).

(8) C. W. Davies, *Ibid.*, **59**, 1760 (1937).

We are therefore at a loss to decide just what constitutes the normal behavior of the completely dissociated 2-2 electrolyte. Until this decision can be made with some assurance, the physical interpretation of these values of K must remain doubtful.

This situation is greatly improved if we are not required to calculate K at experimental concentrations, but may evaluate K and Λ^0 simultaneously by a suitable extrapolation to infinite dilution. Two similar and convenient extrapolation functions have been proposed by Fuoss[36] and by Shedlovsky.[37] These are considered in detail in Chapters (7), (11) and

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[36] R. M. Fuoss, *J. Am. Chem. Soc.*, **57**, 488 (1935).

[37] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(13). Fuoss assumes that the hypothetical completely ionized electrolyte would obey the Onsager limiting law at all concentrations; but Shedlovsky uses equation (6-3-10), which allows small departures above the limiting law in the experimental concentration range. Both of these procedures, in common with that of Onsager and Davies, require some knowledge of the activity coefficient of the electrolyte as a function of the concentration. In calculations involving 1-1 electrolytes, the Debye-Hückel limiting law may be satisfactorily employed in many cases, but for high valence type electrolytes it is not yet possible to estimate sufficiently trustworthy activity coefficients for this purpose from theory alone. Furthermore, the experimental determinations of the activity coefficients of complex electrolytes are neither so accurate nor so numerous as those for simpler salts. For this reason, it is particularly desirable to avoid the introduction of activity coefficients, and to evaluate Λ^0 for complex electrolytes from conductivity data alone. It will now be shown how this can be done by means of a theoretical extension of the limiting law (6-3-5).

Theoretical Extensions Based Upon The Assumption of Complete Dissociation

In one of his earlier papers,[38] and later with Fuoss,[39] Onsager estimated the effect of the mathematical simplifications involved in the derivation of his limiting equation. The deviation of Λ from linearity with $\sqrt{c}$ is represented by the addition of two terms. Thus in dilute solutions[40]

$$\Lambda = \Lambda^0 - \mathcal{S}_{(\Lambda)}\sqrt{c} + Ac \log c + Bc \qquad (6\text{-}3\text{-}5)$$

As originally proposed, this expression was semi-empirical in that the numerical values of the constants A and B had not been evaluated from theoretical considerations. Fuoss[41] has obtained expressions for these constants for 1-1 electrolytes by neglecting the effects of electrophoresis, and the Brownian motion of the central ion. Since we have no numerical indications of the effect of these approximations, the constants A and B will be evaluated empirically from the conductance data to show the formal agreement between this equation and experiment. For dilute solutions of 1-1 electrolytes, such a test will require data of extreme precision, but it can be readily made on electrolytes of higher valence types because the predicted[42] and observed deviations from the limiting slope are more pronounced. Rearranging equation (6-3-5) to read

$$\left[\frac{\Lambda + (\alpha^*\Lambda^0 + \beta^*)\sqrt{c} - \Lambda^0}{c}\right] = A \log c + B \qquad (6\text{-}3\text{-}6)$$

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[38] L. Onsager, *Physik. Z.*, **28**, 277 (1927).

[39] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36** 2689 (1932).

[40] This equation applies to completely dissociated electrolytes. The linear term, Bc, is not to be confused with the additional term, $-c\Lambda^0/K$, resulting from ionic association. [*Cf.* equation (6-3-3)].

[41] R. M. Fuoss, *Physik. Z.*, **35**, 59 (1934).

[42] L. Onsager, *Physik. Z.*, **28**, 277 (1927).

the constants A and B can be evaluated from a plot of the bracketed terms against log c. It is clear that when the correct value of Λ^0 is used, a plot of the left-hand member of this equation against log c must be a straight line of slope A and intercept B. The selection of the correct value of Λ^0 can be done very readily by trial, because the value used in calculating the term $\alpha^*\Lambda^0$ is not a very important factor in determining the shape of the plot. A preliminary value of Λ^0 (and α^*) is therefore obtained from a rough extrapolation of a plot of Λ against $\sqrt{c}$. This value is used to calculate values of $\Lambda + (\alpha^*\Lambda^0 + \beta^*)\sqrt{c}$, which remain unaltered during the selection of a value of Λ^0 roughly satisfying the graphical requirements of equation (6-3-2). The latter value is then used to calculate more accurate values of $\Lambda + (\alpha^*\Lambda^0 + \beta^*)\sqrt{c}$, and the process repeated until a self-consistent value of Λ^0 is found which will express the data by equation (6-3-6) up to about 0.01N within the probable experimental error. The final plots[43] for potassium, barium, and lanthanum chlorides are shown in Fig. (6-3-1). In order to make it possible to plot all three curves in a small space we have expressed the concentration c^* as equivalents per liter in the abscissa and in the denominator of the ordinate. It is apparent

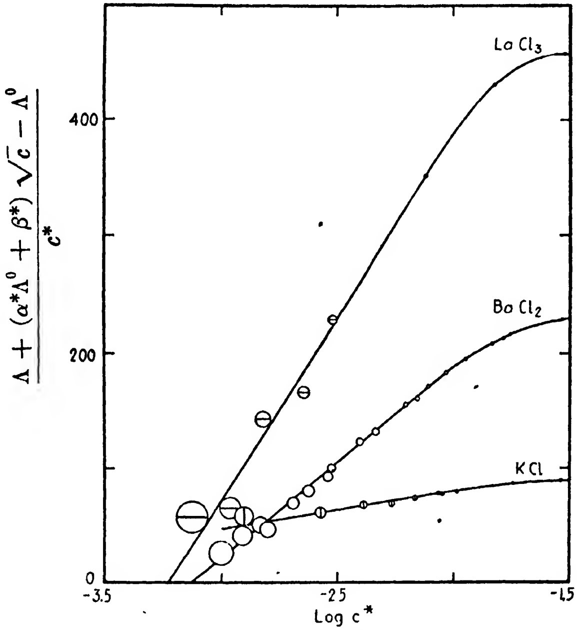

Fig. (6-3-1). Graphical evaluation of the parameters A and B of equation (6-3-5). The radii of circles correspond to an experimental error of 0.01 in Λ.

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[43] B. B. Owen, *J. Am. Chem. Soc.*, **61**, 1393 (1939).

from the figure that equation (6-3-5) fits the experimental results very closely in dilute solutions. The diameters of the circles representing the data correspond to an error of only 0.02 unit in the determination of $\Lambda^0 - \Lambda$. The plots are all linear below $0.008N$,[44] and pass through a maximum at about $0.03N$.

The values of A, B, and Λ^0, obtained from Fig. (6-3-1) and similar plots for other electrolytes, are recorded in Table (6-3-3). Because of the magnitudes[45] of the parameters for the last three electrolytes, the best method of illustrating the accuracy of equation (6-3-5) is to use it to calculate Λ^0 from A and B and each experimental value of Λ. Figure (6-3-2) shows the difference between the values of Λ^0 calculated in this manner and the values of Λ^0 used in the graphical evaluation of A and B. Since the diameters of the circles in the figure represent an uncertainty

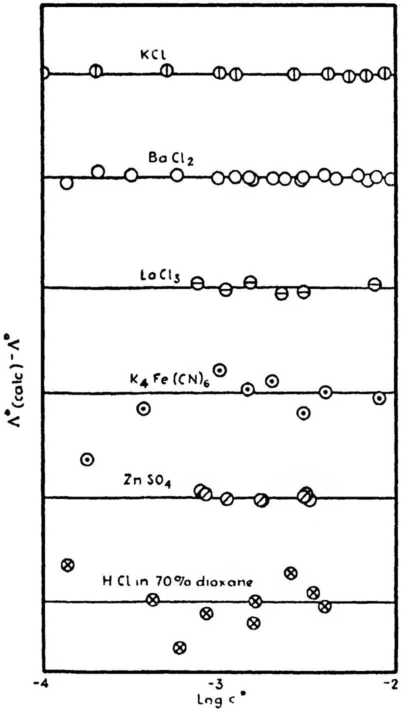

Fig. (6-3-2)
Deviations: Diameters of circles are 0.06 conductance unit; distance between plots is 0.6 unit.

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[44] Five results are available for barium chloride below $0.000985N$, but were omitted from the figure because the apparent uncertainty in $\Lambda^0 - \Lambda$ was several times greater than at higher concentrations.

[45] For reasons to be discussed later, the physical significance of the numerical values of these parameters is obscure.

of 0.06 conductance unit, it is clear that equation (6-3-5) fits the data for potassium, barium and lanthanum chlorides and zinc sulfate within about 0.02 unit. For the other two electrolytes, the deviations are as much as five to ten times as great, but are apparently without consistent trends. For the most part, these larger deviations result from the fact that the data for potassium ferrocyanide were combined from two different sources, and the data for hydrochloric acid involve measurements in two independent preparations of the 70 per cent dioxane solutions used as solvent. From this, it appears that equation (6-3-5) satisfactorily expresses the results for electrolytes of widely different valence types at high dilutions. Recalling that equation (6-3-5) is based upon the assumption of complete dissociation, we note that the conductance of several of these electrolytes can also be interpreted in terms of finite ionization constants [Table (6-3-2)]. This ambiguity in interpretation arises from the arbitrary selection of a standard conductance curve in the calculation of K, and from the purely empirical evaluation of A and B. For this reason, it is difficult to distinguish between the effects of non-conducting ion pairs, postulated in the estimation of K, and the higher electrostatic terms represented by $Ac \log c$ and Bc in (6-3-5), until A and B are evaluated theoretically. If the theoretical values of A and B were known, the standard conductance curve for the hypothetical completely dissociated electrolyte would no longer be arbitrary. Under this condition, the association of salts such as potassium nitrate and zinc sulfate could be investigated with greater assurance.

TABLE (6-3-3).* PARAMETERS OF EQUATION (6-3-5) AT 25°.

Electrolyte	A	B	Λ^0
KCl	31.8	144	149.87
$BaCl_2$	175	540	140.00
$LaCl_3$	320	1030	145.8
$K_4Fe(CN)_6$	3345	6170	185.0
$ZnSO_4$	5736	10627	132.92
HCl (70% dioxane)	4800	9800	93.1

* In evaluating A and B by equation (6-3-5), the concentration in the terms, $Ac^* \log c^* + Bc^*$, was arbitrarily expressed in equivalents per liter. All results are consistent with the primary standard of G. Jones and B. C. Bradshaw [*J. Am. Chem. Soc.*, **55**, 1780 (1933)].

Two independent attempts have been made to explain the specificity of conductance curves in terms of differences in ionic radii, or the mean distance of nearest approach. Since the most recent[46] of these is not an extension of the Onsager equation, it will be discussed in the next section.

Kaneko[47] derived a conductance equation which reduces to the limiting law (6-2-1) at infinite dilution. At moderate concentrations, it can be

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[46] M. H. Gorin, *J. Chem. Phys.*, **7**, 405 (1939).

[47] S. Kaneko, *J. Chem. Soc. Japan*, **56**, 793, 1320 (1935); **58**, 985 (1937).

put in the form of the empirical extensions considered in the next part of this section. One of its features is the inclusion of the factor, $1/(1 + \kappa a)$, which appears somewhat arbitrary.

Purely Empirical Extensions

In studying the conductance of 1-1 electrolytes, Shedlovsky[48] noted that, if the limiting equation (6-2-1) is rearranged so that Λ^0 may be calculated directly from individual values of Λ, the difference between successive values of Λ^0 is proportional to the difference in concentration. The values of Λ^0 computed in this manner will henceforth be designated $\Lambda^{0\prime}$, so as to differentiate them from the true limiting conductances, Λ^0, obtained by extrapolation to infinite dilution. In mathematical form, Shedlovsky's observation can be written

$$\Lambda^{0\prime} \equiv \frac{\Lambda + \beta^*\sqrt{c}}{1 - \alpha^*\sqrt{c}} = \Lambda^0 + Bc \qquad (6\text{-}3\text{-}7)$$

or

$$\Lambda = \Lambda^0 - \mathcal{S}_{(\Lambda)}\sqrt{c} + Bc - \alpha^* Bc^{3/2} \qquad (6\text{-}3\text{-}8)$$

The positive empirical constant, B, is characteristic of each electrolyte, and of the same order of magnitude as $\mathcal{S}_{(\Lambda)}$. The conductance of strong 1-1 electrolytes can usually be expressed by this equation up to $0.1N$ within experimental error. Potassium chloride is a noteworthy exception. The conductance of high valence type electrolytes cannot be expressed by the equation, but it is apparent from Figure (6-3-3) that a plot of $\Lambda^{0\prime}$ against concentration allows a satisfactory extrapolation of the data for barium and lanthanum chlorides. This figure also illustrates the slight, though measurable, departure of the values of $\Lambda^{0\prime}$ for potassium chloride from the linear relationship (6-3-7). The approximately linear portion of the curves is the result of an inflection. At high concentrations, the curves are strongly concave downward. These plots permit the evaluation of Λ^0 within very narrow limits, even though the curvatures cause extra weight to be given to the data at the lowest concentrations. For higher valence types, such as potassium ferrocyanide and zinc sulfate, this extrapolation is impractical. Figure (6-3-4) shows that the plots for these salts are sharply curved as they approach the axis.

The initial decrease in $\Lambda^{0\prime}$ with concentration, observed in Figure (6-3-4), is predicted theoretically by equation (6-3-5) for all valence types,[49] because when c approaches zero as a limit, we find that

$$\frac{d\Lambda^{0\prime}}{dc} = \frac{\Lambda^{0\prime} - \Lambda^0}{c} = \frac{A \log c - B}{1 - \alpha^*\sqrt{c}} = -\infty \qquad (6\text{-}3\text{-}9)$$

Fortunately this result does not seriously affect the usefulness of the extrapolations illustrated in Figure (6-3-3). Calculations based upon the

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[48] T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1405 (1932).

[49] B. B. Owen, *J. Am. Chem. Soc.*, **61**, 1393 (1939).

values of A and B, given in Table (6-3-3), for potassium, barium and lanthanum chlorides show that $\Lambda^{0'}$ passes through a rather flat minimum at a concentration just below the experimental range. Furthermore, the value of $\Lambda^{0'}$, corresponding to this minimum, is only slightly less than the

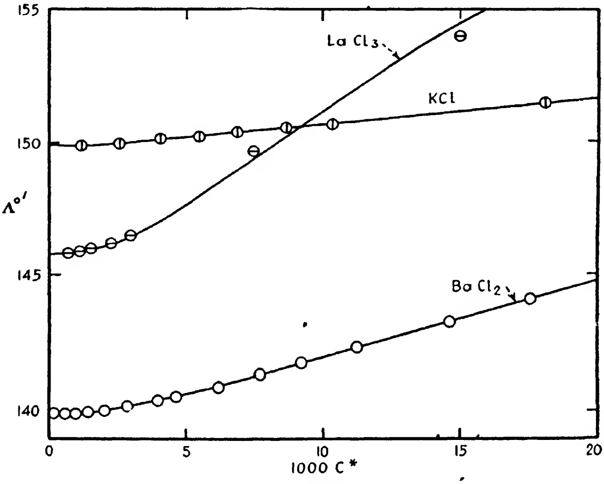

Fig. (6-3-3). Variation of $\Lambda^{0'}$ with concentration (equivalents per liter) in aqueous solutions at 25°; evaluation of Λ^0 by extrapolation

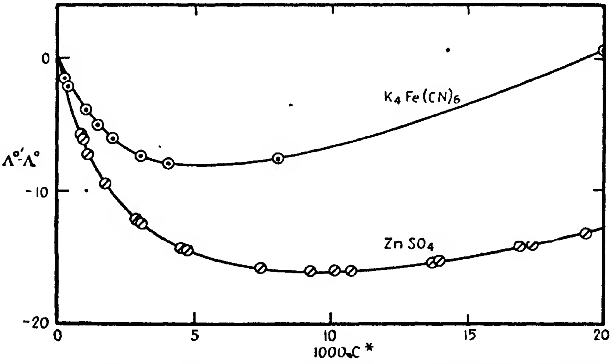

Fig. (6-3-4). Variation of $\Lambda^{0'}$ with concentration (equivalents per liter) in aqueous solutions at 25°.

value of Λ^0 which satisfies equation (6-3-5). The difference is approximately 0.00015, 0.021 and 0.031 conductance unit for potassium, barium and lanthanum chlorides, respectively. This indicates that satisfactory values of Λ^0 are obtained for these salts by simply extending the curves in Figure (6-3-3) horizontally beyond the lowest experimental points.

Shedlovsky[50] has proposed another extension of the Onsager equation which may be more readily applied to certain calculations than equation (6-3-8). He found that, up to $c \simeq 0.01$, the conductance of typical 1-1 strong electrolytes in water may be very accurately represented by the equation

$$\Lambda = \Lambda^0 - \frac{\Lambda}{\Lambda^0}(\alpha^*\Lambda^0 + \beta^*)c^{1/2} \qquad (6\text{-}3\text{-}10)$$

which allows for a gradual decrease in slope with increasing concentration. In the above form, this equation is not suitable for interpolation, but it may be rearranged as the series

$$\Lambda = \Lambda^0 - \mathcal{S}_{(\Lambda)}c^{1/2} + \frac{\mathcal{S}^2_{(\Lambda)}}{\Lambda^0}c - \frac{\mathcal{S}^3_{(\Lambda)}}{\Lambda^{02}}c^{3/2} + \cdots \qquad (6\text{-}3\text{-}11)$$

which, for the number of terms shown, is formally equivalent to (6-3-8), and has the advantage of avoiding the empirical parameter, B.

As an extrapolation function, equation (6-3-10) can be used in the form[51]

$$\frac{1}{\Lambda} = \frac{1}{\Lambda^0} + \left(\frac{\alpha^*\Lambda^0 + \beta^*}{\Lambda^{02}}\right)c^{1/2} \qquad (6\text{-}3\text{-}12)$$

according to which $1/\Lambda^0$ may be obtained by extrapolating a plot of $1/\Lambda$ against $c^{1/2}$. The obvious convenience of such a plot does not, however, make it superior to those shown in Figure (6-3-3), because extrapolation by (6-3-12) is longer and steeper.

(4) OTHER CONDUCTANCE EQUATIONS. CRITICAL SUMMARY

Among the numerous empirical equations which have been suggested for the extrapolation of conductivity data for strong electrolytes, the square root law of Kohlrausch[52]

$$\Lambda = \Lambda^0 - A\sqrt{c} \qquad (6\text{-}4\text{-}1)$$

has rendered the most noteworthy service in aqueous solutions, and is formally in agreement with the interionic attraction theory. Because of the success of this equation at extreme dilutions, most of the interpolation equations proposed for use at higher concentrations reduce to (6-4-1) in the limit. The simplest of these is the relation

$$\Lambda = \Lambda^0 - A\sqrt{c} + Bc \qquad (6\text{-}4\text{-}2)$$

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[50] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

[51] R. Lorenz [*Z. anorg. Chem.*, **108**, 191 (1919)] proposed a similar equation which can be written, $1/\Lambda = 1/\Lambda^0 + (A\Lambda^{p-1})c^{1/2}$. Unfortunately, he found the value of p characteristic of the electrolyte at moderate concentrations ($c \leq 0.1$), thereby missing a very important feature of equation (6-3-10), namely, $p = 1$ at high dilutions.

[52] For a comprehensive discussion of the application of this equation, consult F. Kohlrausch and L. Holborn "Das Leitvermögen der Elektrolyte," Teubner, Leipzig, 1916.

previously referred to in section (2). Walden[53] proposed the equation

$$\Lambda = \frac{\Lambda^0}{1 + B\sqrt{c}} \tag{6-4-3}$$

containing only two constants. This is considerably less accurate than (6-4-2), but covers the same concentration range ($<0.01M$). Lattey[54] combined features of both of these equations by writing

$$\Lambda = \Lambda^0 - \frac{A\sqrt{c}}{1 + B\sqrt{c}} \tag{6-4-4}$$

This expression is fairly successful at concentrations below $0.1N$. By the addition of a linear term in concentration, Jones and Dole[55] showed that the relation

$$\Lambda = \Lambda^0 - \frac{A\sqrt{c}}{1 + B\sqrt{c}} + Dc \tag{6-4-5}$$

will describe their data for barium chloride up to $2N$ within the very small experimental error. The results for potassium bromide[56] can be expressed with equal success at 0° and 25°. All the foregoing equations have the property in common that

$$\left(\frac{d\Lambda}{d\sqrt{c}}\right)_{c\to 0} = -(\text{constant}) \tag{6-4-6}$$

but the value of this constant differs for each equation, and differs in general from the theoretical limiting slope given by equation (6-2-1). In view of the evident validity of the Onsager equation, none of the foregoing empirical equations should be used for extrapolation. Since the interionic attraction theory has demonstrated the inapplicability of the Ostwald dilution formula,[57]

$$K = \frac{\Lambda^2 c}{\Lambda^0(\Lambda^0 - \Lambda)} \tag{6-4-7}$$

to aqueous solutions of strong electrolytes, the numerous conductance equations incorporating this relation[58] have dropped into disuse.

The general equation

$$\Lambda = \Lambda^0 - Ac^n \tag{6-4-8}$$

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[53] P. Walden, *Z. physik. Chem.*, **108**, 341 (1924).

[54] R. T. Lattey, *Phil. Mag.* [7], **4**, 831 (1927).

[55] G. Jones and M. Dole, *J. Am. Chem. Soc.*, **52**, 2245 (1930).

[56] G. Jones and C. F. Bickford, *J. Am. Chem. Soc.*, **56**, 602 (1934).

[57] W. Ostwald, *Z. physik. Chem.*, **2**, 36 (1888).

[58] Most of these equations are discussed by C. A. Kraus and W. C. Bray, *J. Am. Chem. Soc.*, **35**, 1315 (1913). See also E. W. Washburn, *Ibid.*, **40**, 150 (1918); and J. R. Partington in H. S. Taylor "Treatise on Physical Chemistry," Vol. I, p. 657, Van Nostrand Co., New York, 1931.

in which the exponent, n, is treated as an empirical parameter characteristic of each electrolyte (or group of electrolytes) was studied by Lorenz,[59] and, in spite of the success of the Onsager equation, is still used to some extent.[60] According to (6-4-8), a plot of log $(\Lambda^0 - \Lambda)$ against log c should be a straight line of slope n if Λ^0 is properly chosen. Ferguson and Vogel[61] have fitted this equation to their data for a large number of electrolytes, and find that both A and n are characteristic of the electrolyte. The individuality of A is in accord with theory, since the theoretical slope $(\alpha^*\Lambda^0 + \beta^*)$ contains the term Λ^0. Davies[62] has pointed out that, with few exceptions, the supposed variation of n, from one electrolyte to another $(0.4 < n < 0.6)$, is of the same order as that observed between duplicate series of measurements on a single electrolyte. This emphasizes the futility of using such an equation for extrapolation.

As an illustration of the large errors which may be produced by purely empirical extrapolation, we shall apply the foregoing equations to the data for a typical 2-1 electrolyte at 25°. Jones and Dole[63] found that, at high dilution, their measured molecular conductivities of barium chloride could be represented numerically as follows:

$$\Lambda_m = 278.75 - 449.9\sqrt{c} \tag{6-4-1a}$$

$$\Lambda_m = 280.64 - 550.12\sqrt{c} + 1265.1c \tag{6-4-2a}$$

$$\Lambda_m = 278.69/(1 + 1.715\sqrt{c}) \tag{6-4-3a}$$

$$\Lambda_m = 281.22 - 602.8\sqrt{c}/(1 + 4.069\sqrt{c}) \tag{6-4-4a}$$

$$\Lambda_m = 282.13 - 636.3\sqrt{c}/(1 + 4.628\sqrt{c}) - 31.13c \tag{6-4-5a}$$

$$\Lambda_m = 288.18 - 227.32c^{0.3276} \tag{6-4-8a}$$

Table (6-4-1) shows the concentration ranges throughout which the equations will reproduce the data. The figures in parentheses are the values of the limiting molecular conductivities, Λ_m^0, which satisfy these equations. The discordance of these values is proof enough of the im-

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[59] R. Lorenz, *Z. anorg. Chem.*, **108**, 191 (1919); **114**, 209 (1920). The theoretical deductions of P. Hertz [*Ann. Phys.* [4], **37**, 37 (1912)] and of I. C. Ghosh [*J. Chem. Soc.*, **113**, 449 *et seq.* (1918)] gave considerable impetus to the study of the equation $\Lambda = \Lambda^0 - Ac^{1/3}$. *Cf.* R. Lorenz (*loc. cit.*), R. Lorenz and P. Osswald, [*Z. anorg. Chem.*, **114**, 209 (1920)], R. Lorenz and W. Michael, [*Ibid.*, **116**, 161 (1921)], and P. Walden and H. Ulich [*Z. physik. Chem.*, **106**, 49 (1923)].

[60] A. Ferguson and I. Vogel, *Phil. Mag.* [4], **50**, 971 (1925); [7], **4**, 1, 233, 300 (1927).

[61] A. Ferguson and I. Vogel, *Trans. Faraday Soc.*, **33**, 404, 414 (1927); I. Vogel, *Phil. Mag.* [7], **5**, 199 (1928).

[62] C. W. Davies, "The Conductivity of Solutions," Chapman and Hall, London, p. 84, 1930. Further discussion of the applicability of (6-4-8) may be found in the polemical papers of A. Ferguson and I. Vogel [*Trans. Faraday Soc.*, **27**, 285 (1927)], C. W. Davies, A. R. Martin, and A. W. Porter [*Ibid.*, **27**, 547 (1927)].

[63] G. Jones and M. Dole, *J. Am. Chem. Soc.*, **52**, 2245 (1930).

portance of an exact theoretical limiting function. The correct value[64] of Λ_m^0 is undoubtedly close to 280.00, which is twice the equivalent conductance recorded in Table (6-3-3). We note that the greatest departure from this value is the result (288.18) obtained by equation (6-4-8), which involves an arbitrary power of c. It is also significant that, among the remaining equations, the average discrepancy is 1.3 units in spite of their common property expressed by (6-4-6). Equation (6-4-5), which contains the greatest number of empirical constants, leads to an error of over 2 units in Λ_m^0.

Table (6-4-1). Representation of the Molecular Conductance of Barium Chloride at 25° by Empirical Equations.

c	Λ_m(obs)	(6-4-1a)	(6-4-2a)	(6-4-3a)	(6-4-4a)	(6-4-5a)	(6-4-8a)
0		(278.75)	(280.64)	(278.69)	(281.22)	(282.13)	(288.18)
.001	264.53	264.53	264.51	264.25	264.33	264.55	264.53
.0025	256.25	256.25	256.30	256.65	256.16	256.22	256.25
.005	248.11	246.94	248.07	248.56	248.10	248.03	248.11
.01	238.27	233.76	238.28	237.89	238.37	238.32	237.89
.025	223.25	207.61	225.29	219.24	223.22	223.26	220.29
.05	210.65		220.89	201.44	210.64	210.65	202.99
.1	197.36		233.19	180.69	197.86	197.36	181.27
.25	178.39				181.90	178.35	
.5	161.20				171.28	161.26	
1.00	137.96					137.94	

Gorin[65] has made an interesting addition to the list of conductance equations which do not reduce to the Onsager limiting law. In the derivation of his equation

$$\Lambda = \frac{\Lambda^0 + (a_-\lambda_+^0 + a_+\lambda_-^0)\kappa}{1 + (a_+ + a_-)\kappa} \tag{6-4-9}$$

for binary electrolytes, Gorin makes use of the Debye-Hückel theory to calculate the potential at the surface of an ion, but he assumes that an applied external field does not sensibly distort the ionic atmospheres. This assumption neglects the asymmetry potential, ψ_j'. It will be recalled that ψ_j' is an essential feature of the Onsager equation, and leads to a satisfactory description of high field and frequency effects. In spite of its theoretical inadequacy, Gorin's equation is capable of representing conductance and transference data over a considerable concentration range. This is undoubtedly caused by the inclusion of two additional constants, the ionic radii, a_+ and a_-.

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[64] Values between the limits 279.6 and 280.0 are obtained from three different plots based upon the Onsager equation. Two of these are illustrated in Figures (6-3-1) and (6-3-3). The third is a simple plot of Λ against $\sqrt{c}$ which is made to approach the theoretical limiting slope at extreme dilution. The latter plot involves a relatively long extrapolation, and yields 279.8 with an uncertainty of two or three tenths of a unit.

[65] M. H. Gorin, *J. Chem. Phys.*, **7**, 405 (1939).

In common with the other equations in this section, (6-4-9) reduces to equation (6-4-6) in the limit. The limiting slope, in this case, becomes

$$\frac{d\Lambda}{d\kappa} = -(a_+\lambda_+^0 + a_-\lambda_-^0) \tag{6-4-10}$$

in terms of the variable κ. Table (6-4-2) shows the results of some calculations based upon the application of equation (6-4-9) to the data of Shedlovsky[66] and Longsworth.[67] The values of a_+ are not unreasonable for hydrated radii, and a_{Cl} is practically independent of the nature of the cation. Gorin has pointed out that the order and variation in a_+ is consistent with classic hydrodynamic theory.

TABLE (6-4-2). IONIC RADII (IN ÅNGSTROMS) ESTIMATED BY EQUATION (6-4-9) AT 25°.

Electrolyte	Λ^0	λ_+^0	λ_-^0	$\frac{d\Lambda}{d\sqrt{c}}$ $c \to 0$	$\mathring{a}_+$	$\mathring{a}_-$
HCl	426.06	349.73	76.33	−156.5	0.945	1.921
KCl	149.86	73.53	76.33	−96.1	1.978	1.933
NaCl	126.45	50.12	76.33	−90.6	2.562	1.937
LiCl	115.03	38.70	76.33	−88.7	3.095	1.976

(5) TRANSFERENCE NUMBERS* BY THE MOVING BOUNDARY METHOD. FUNDAMENTAL EQUATIONS

Lodge[68] demonstrated the possibility of directly observing ionic motion, and Whetham,[69] Nernst,[70] Masson,[71] and particularly Denison and Steele[72] have developed the method by which transference numbers can be quantitatively determined from the observed velocities of moving boundaries. In subsequent investigations by Cady,[73] E. R. Smith,[74] MacInnes,[75] and

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[66] T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1411 (1932).

[67] L. G. Longsworth, *Ibid.*, **54**, 2741 (1932); see also D. A. MacInnes, T. Shedlovsky and L. G. Longsworth, *Ibid.*, **54**, 2758 (1932).

* For a complete bibliography of literature bearing upon the general subject of transference numbers, see D. J. LeRoy, Univ. Toronto Studies, Papers Chem. Lab., No. 156, (1939); J. W. McBain, *Ibid.*, No. 67 (1907).

[68] O. Lodge, *Brit. Assn. Advancement Sci.*, p. 389, Birmingham, (1886).

[69] W. C. D. Whetham, *Phil. Trans.*, **184A**, 337 (1893); *Z. physik. Chem.*, **11**, 220 (1893).

[70] W. Nernst, *Z. Elektrochem.*, **3**, 308 (1897).

[71] D. O. Masson, *Phil. Trans.*, **192A**, 331 (1899).

[72] R. B. Denison, and B. D. Steele, *J. Chem. Soc.*, **89**, 999 (1906).

[73] E. C. Franklin and H. P. Cady, *J. Am. Chem. Soc.*, **26**, 499 (1904); H. P. Cady and L. G. Longsworth, *Ibid.*, **51**, 1656 (1929).

[74] E. R. Smith and D. A. MacInnes, *J. Am. Chem. Soc.*, **46**, 1398 (1924); *Ibid.*, **47**, 1009 (1925); E. R. Smith, *Bureau of Standards J. Research*, **6**, 917 (1931).

[75] D. A. MacInnes and E. R. Smith, *J. Am. Chem. Soc.*, **45**, 2246 (1923); D. A. MacInnes, I. A. Cowperthwaite, and T. C. Huang, *Ibid.*, **49**, 1710 (1927); L. G. Longsworth and D. A. MacInnes, *Rev. Sci. Inst.*, **19**, 50 (1929).

Longsworth,[76] the method has been subjected to steady technical improvement, and is now capable of yielding data of very high accuracy. In view of the importance of these results for verifying[77] the interionic attraction theory, and their practical application to conductance and electromotive force studies, we shall outline the calculation of transference numbers from observed boundary velocities relative to the apparatus.

The first step is the calculation of a preliminary or apparent transference number by neglecting the effects of conductance of the solvent and volume changes at the electrodes. Then the true transference number is obtained by the application of appropriate corrections for these effects. Figure (6-5-1) represents a vertical section through a tube in which the boundary at x_0 is formed by juxtaposition of two solutions of electrolytes, *AR* and *IR*, with a common ion, *R*. After the passage of a steady current, *i*, for *t* seconds, the boundary attains the position indicated by x_t. If c_A^* is the normality of the ion constituent *A*, and *V* the volume (in liters) swept out by the boundary in passing from x_0 to x_t, then the migration of *A* ions up the tube must have transferred $\mathrm{F}c_A^*V$ coulombs past an arbitrary reference plane across the tube above x_t. Accordingly, the apparent transference number, T'_A, of the *A* ion is given by

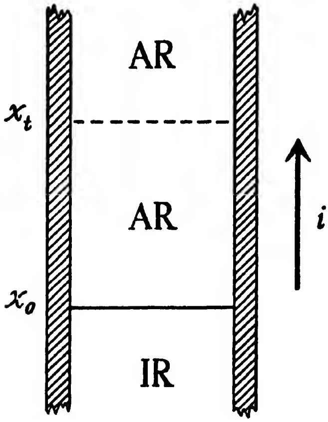

Fig. (6-5-1)
Schematic representation of tube and boundary

$$T'_A = \frac{\mathrm{F}c_A^*V}{it} \tag{6-5-1}$$

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[76] L. G. Longsworth, *J. Am. Chem. Soc.*, **54**, 2741 (1932).

For a comprehensive review of the theory, technique, and results of the modern moving boundary method, see D. A. MacInnes and L. G. Longsworth, *Chem. Rev.*, **11**, 171 (1932).

[77] With the exception of a few isolated data, transference numbers determined by the well known Hittorf analytical method are generally of insufficient accuracy for this purpose.

where the product (*it*) is the total quantity of electricity passed through the tube.

At very low concentrations an appreciable portion of the current is carried by ions resulting from ionization of the solvent and traces of impurities such as carbonic acid. The recognition of this effect and the calculation of its magnitude is due to Longsworth.[78] For a 1-1 electrolyte, AR, at concentration c^*, it can be shown that, if a is the area of the tube, the true transference number, $T_A = \bar{u}_A/(\bar{u}_A + \bar{u}_R)$, is given by

$$T_A = \frac{\mathrm{F}\bar{u}_A c^*/1000}{i/a} + T_A \frac{L_0}{L} \tag{6-5-2}$$

Since mobilities are referred to a stationary solvent, $\bar{u}_A$ is the distance traveled by the A ions per second through the solution in unit field. If volume changes caused by electrolysis and ion migration produce motion of the solvent relative to the tube in which the boundary positions are determined, the volume which appears in equation (6-5-1) is given by

$$V = \frac{\bar{u}_A ta}{1000} + \Delta V \tag{6-5-3}$$

Here ΔV represents the contribution (in liters) of the motion of the solvent to the observed volume swept out by the boundary in t seconds. Combination of equations (6-5-1) and (6-5-3) with (6-5-2) gives the expression

$$T_A = T'_A - \frac{\mathrm{F}c^*\Delta V}{it} + T_A \frac{L_0}{L} \tag{6-5-4}$$

The necessity of the correction term containing ΔV was pointed out by Miller.[79] ΔV can be measured experimentally,[80] or estimated from the densities of the solutions and the components of the electrodes.[81]

If the leading and indicator solutions are properly chosen, restorative effects limit the extent of diffusion across the boundary.[82]

Although the moving boundary method as just described is limited to the study of ions for which suitable (slower) indicator ions are available, it is capable of an interesting extension by which the transference numbers of the latter may also be directly determined. Kohlrausch[83] showed that one of the conditions of a stable boundary is proportionality between the concentrations and transference numbers of the leading and indicator ions. Since these ions must have the same velocity at the boundary,

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[78] L. G. Longsworth, *J. Am. Chem. Soc.*, **54**, 2741 (1932).

[79] W. L. Miller, *Z. physik. Chem.*, **69**, 436 (1909).

[80] E. R. Smith, *Bur. Standards J. Research*, **8**, 457 (1932).

[81] G. N. Lewis, *J. Am. Chem. Soc.*, **32**, 862 (1910); L. G. Longsworth, *Ibid.*, **54**, 2741 (1932).

[82] D. A. MacInnes and I. A. Cowperthwaite, *Proc. Nat. Acad. Sci.*, **15**, 18 (1929); L. G. Longsworth, *J. Am. Chem. Soc.*, **52**, 1897 (1930); W. L. Miller, *Z. physik. Chem.*, **69**, 436 (1909).

[83] F. Kohlrausch, *Ann. Physik.*, **62**, 209 (1897).

the volume swept out per faraday is not only equal to T_A/c_A^*, but must also equal T_I/c_I^*. Therefore

$$\frac{T_A}{c_A^*} = \frac{T_I}{c_I^*} \quad . \tag{6-5-5}$$

If the boundary was initially formed with an indicator solution of concentration $c_I^{*\prime}$, not very different from c_I^*, the concentration in the region swept out by the motion of the boundary will be automatically adjusted to c_I^* in accordance with equation (6-5-5). The concentration disturbance produced by this adjustment remains in the vicinity of the initial boundary position, because T_I is very nearly the same at $c_I^{*\prime}$ as at c_I^*.

If the specific conductances of the solutions are known as functions of concentration, the Kohlrausch concentration, c_I^*, can be determined conductometrically.[84] Hartley[85] has developed an ingenious "balanced boundary" apparatus, and has used equation (6-5-5) to compare the cation transference numbers of hydrochloric acid, potassium chloride and sodium chloride solutions with that of a lithium chloride indicator solution. The results agree with those of Longsworth[86] within 0.5 per cent. The practical importance of the balanced boundary method is its ability to determine directly the transference numbers of ions of very low mobility. It has been applied to the study of salts with paraffin chain cations containing as many as sixteen carbon atoms,[87] and furnishes an interesting experimental basis for interpreting the behavior of colloidal electrolytes.[88]

Although the Hittorf[89] method of determining transference numbers presents serious difficulties of chemical analysis when high precision is required, MacInnes and Dole[90] obtained values by this method with an accuracy of about 0.2 per cent. Within this experimental error, their results were in complete agreement with the corresponding moving boundary values. Jones and Bradshaw[91] reported data on lithium chloride which agree with moving boundary results to within ±0.7 per cent.

[84] H. P. Cady and L. G. Longsworth, *J. Am. Chem. Soc.*, **51**, 1656 (1929).

[85] G. S. Hartley, *Trans. Faraday Soc.*, **30**, 648 (1934); E. Drew and G. S. Hartley, *idem.*, p. 653; B. Collie and G. S. Hartley, *idem.*, p. 657.

[86] L. G. Longsworth, *J. Am. Chem. Soc.*, **54**, 2741 (1932).

[87] G. S. Hartley, B. Collie, and C. S. Samis, *Trans. Faraday Soc.*, **32**, 795 (1936).

[88] J. C. Moilliet, C. R. Collie, and G. S. Hartley, *Trans. Faraday Soc.*, **31**, 120 (1935).

[89] W. Hittorf, *Ann. Physik.*, **89**, 177 (1853); **98**, 1 (1856); **103**, 1 (1858); **106**, 337, 513 (1859). An extensive bibliography of the method is given by J. R. Partington in H. S. Taylor, "A Treatise on Physical Chemistry," Vol. I, pp. 678–683, Van Nostrand Co., New York, 1931.

[90] D. A. MacInnes and M. Dole, *J. Am. Chem. Soc.*, **53**, 1357 (1931).

[91] G. Jones, and B. C. Bradshaw, *J. Am. Chem. Soc.*, **54**, 138 (1932).

The true transference numbers are obtained by correcting[92] these Hittorf numbers for net transfer, per faraday, of ΔN_w mols of water, from anode to cathode. Thus

$$T_+ = T_{+(\text{Hittorf})} + 0.018\Delta N_w c^* \tag{6-5-6}$$

Since ΔN_w is of the order of unity,[93] this correction becomes important at moderate concentrations.

(6) THE ONSAGER LIMITING EQUATION FOR TRANSFERENCE NUMBERS. COMPARISON WITH EXPERIMENTAL RESULTS

The definition of the transference number of an ion constituent, in a solution containing a single electrolyte, can be written

$$T_j \equiv \lambda_j/\Lambda; \qquad T_j^0 \equiv \lambda_j^0/\Lambda^0 \tag{6-6-1}$$

By limiting the discussion to electrolytes composed of only two kinds of ions (i, j) the values of λ_j and Λ given by equations (5-3-10) and (6-2-1) may be combined with the above to give the expression

$$T_j = T_j^0 + \mathcal{S}_{(T_j)}\sqrt{c}(\Lambda^0/\Lambda') \tag{6-6-2}$$

predicted by the Onsager theory. In this and subsequent equations, values of the equivalent conductance calculated by (6-2-1) are written Λ', so as to differentiate them from observed values, Λ. Thus,

$$\Lambda' \equiv \Lambda^0 - (\alpha^*\Lambda^0 + \beta^*)\sqrt{c} \tag{6-6-3}$$

Since Λ^0/Λ' approaches unity at high dilution, the limiting equation is

$$T_j = T_j^0 + \mathcal{S}_{(T_j)}\sqrt{c} \tag{6-6-4}$$

where

$$\mathcal{S}_{(T_j)} = \left(\frac{T_j^0(|z_j| + |z_i|) - |z_j|}{(|z_j| + |z_i|)\Lambda^0}\right)\beta^* \tag{6-6-4a}$$

Note that the slope does not contain the parameter α^*. Since only the numerical magnitudes of the valences appear in $\mathcal{S}_{(T_j)}$, it is immaterial whether the j ion is chosen to represent the anion or cation. In either case the condition, $T_j + T_i = 1$, requires that $\mathcal{S}_{(T_j)} = -\mathcal{S}_{(T_i)}$.

Some of the most accurate experimental values, obtained by the moving boundary method at 25°, are given in Table (6-6-1A). Figures (6-6-1) and (6-6-2) show the observed variation of the cation transference number, T_+, with $\sqrt{c}$ in aqueous solutions of electrolytes at 25°. The limiting expressions given by (6-6-4) are represented by straight lines with inter-

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[92] E. W. Washburn, "Principles of Physical Chemistry", p. 277, McGraw-Hill Book Co., New York, 1921; *J. Am. Chem. Soc.*, **31**, 322 (1909); A. A. Noyes and K. G. Falk, *ibid.*, **33**, 1436 (1911).

[93] *E.g.*, $1/4 < \Delta N_w < 3/2$ for the chlorides of hydrogen and the alkalies.

cepts, T^0_+. The data for the chlorides are in striking agreement with theory, and this result is typical of 1-1 electrolytes which show positive departures from the limiting conductance equation (6-2-1) in dilute solutions. For such salts, the limiting law is approached from below if $\mathcal{S}_{(T)}$ is positive, and from above if $\mathcal{S}_{(T)}$ is negative. In the case of potassium nitrate, the observed transference numbers do not merge with the theoretical expression at experimental concentrations, and although $\mathcal{S}_{(T_+)}$ is positive, the limiting law is approached from above. The conductance of this salt shows negative departures from the conductance equation (6-2-1), as can be seen in Figure (6-6-2). The behavior of the transference numbers and conductance of silver nitrate is similar to that of potassium nitrate in all respects.

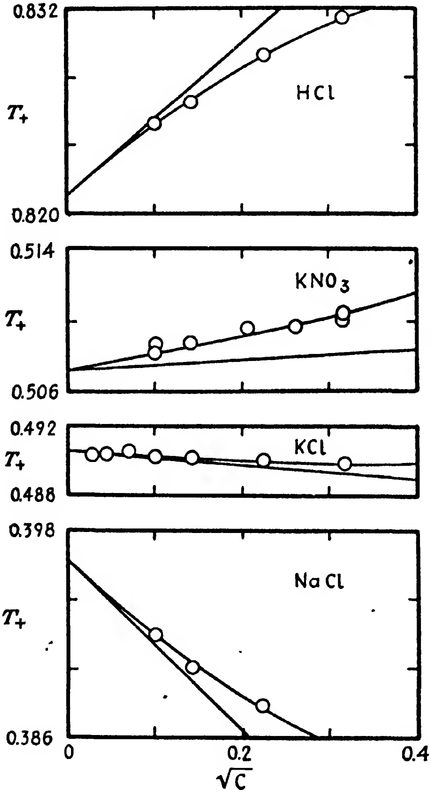

Fig. (6-6-1)
Cation transference numbers in aqueous solutions of 1-1 electrolytes at 25°

Figure (6-6-2) shows the experimental results for two complex valence type electrolytes, calcium and lanthanum chlorides. In these examples, $\mathcal{S}_{(T_+)}$ is negative and the limiting law is approached from above, but the departures from the theoretical equations are pronounced, even in the most dilute solutions. On the other hand, the conductance curves for both of these electrolytes are in accord with theory, and approach the limiting law from above. No satisfactory explanation has yet been found for this anomaly. A theoretical evaluation of the coefficients, A and B, of the terms in $c \log c$ and c of equation (6-3-5), would be interesting in this connection. These terms undoubtedly make significant contributions to the transference numbers of high valence type electrolytes at the lowest concentrations studied experimentally. It has been suggested that ion association is responsible for the anomalous transference numbers, and indeed the data for the alkali sulfates[94] and alkaline-earth chlorides have been satisfactorily represented on this basis.[95] Unfortunately, this evidence of association in alkaline-earth chloride solutions is contradicted by the conductance data, and the transference data of potassium and silver nitrates have not yet been represented numerically in terms of association.

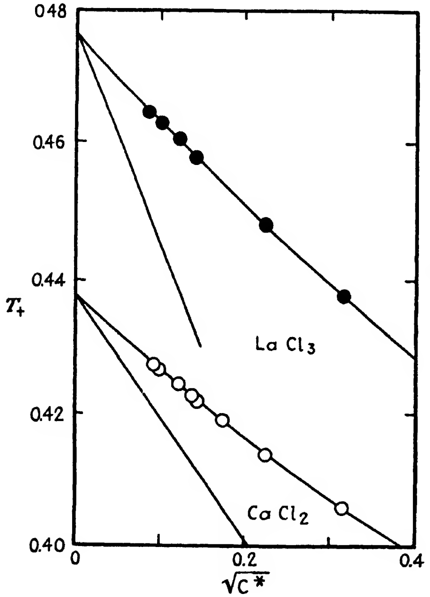

Fig. (6-6-2)
Cation transference numbers of unsymmetrical electrolytes (in aqueous solutions) at 25°

The results of the tests of the theoretical equation (6-6-4) may be summarized as follows. The experimental results for most of the 1-1 elec-

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[94] The curve for sodium sulfate must pass through an inflection at high dilution if it is to merge with the theoretical slope. L. G. Longsworth, *J. Am. Chem. Soc.*, **57**, 1185 (1935). See also G. S. Hartley and G. W. Donaldson, *Trans. Faraday Soc.*, **33**, 457 (1937).

[95] E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

trolytes investigated by the moving boundary method merge with the theoretical limiting slope.[96] This coincidence of experimental and theoretical limiting slopes will be shown more strikingly in the next section where extensions of the theoretical equations are discussed. The available data for other electrolytes show no indication of merging with the theoretical slopes at the highest dilutions studied. In those cases in which the theory is not in accord with experiment, the discordance seems to bear no simple relation to the sign of the theoretical slope, $\mathfrak{S}_{(T)}$, or to the form of the conductance curves of the electrolytes.

TABLE (6-6-1).* CATION TRANSFERENCE NUMBERS IN AQUEOUS POTASSIUM CHLORIDE SOLUTIONS.

t°C	Λ^0†	$\mathfrak{S}_{(T_+)}$	T_+^0	Concentration (mols/liter)				
				.005	.01	.02	.05	.10
15	121.1	-0.0027_7	0.4928	0.4926	0.4925	0.4924	0.4923	0.4921
25	149.9	$-.0037_9$	.4905	.4903	.4902	.4901	.4900	.4900
35	180.5	$-.0046_0$	.4889	.4887	.4886	.4885	.4885	.4888
45	212.5	$-.0054_8$	.4872	.4869	.4868	.4868	.4869	.4873

* R. W. Allgood, D. J. LeRoy and A. R. Gordon, *J. Chem. Phys.*, **8**, 418 (1940).
† H. E. Gunning and A. R. Gordon, *Ibid.*, **10**, 126 (1942).

TABLE (6-6-2).* CATION TRANSFERENCE NUMBERS IN AQUEOUS SODIUM CHLORIDE SOLUTIONS.

t°C	Λ^0†	$\mathfrak{S}_{(T_+)}$	T_+^0	Concentration (mols/liter)				
				.005	.01	.02	.05	.10
15	101.2	-0.0492_4	0.3929	0.3897	0.3885	0.3870	0.3846	0.3820
25	126.5	$-.0491_3$	.3962	.3930	.3918	.3903	.3878	.3853
35	153.9	$-.0485_3$	.4002	.3970	.3958	.3943	.3919	.3892
45	182.7	$-.0478_6$	.4039	.4008	.3996	.3982	.3957	.3932

* R. W. Allgood and A. R. Gordon, *J. Chem. Phys.*, **10**, 124 (1942).
† H. E. Gunning and A. R. Gordon, *Ibid.*, **10**, 126 (1942).

Although independent measurements of transference numbers at higher temperatures than 25° are not completely in accord, there is good evidence that those electrolytes which obey equation (6-6-4) in the limit of 25° do likewise at other temperatures. Cation transference numbers in aqueous potassium chloride and sodium chloride[97a] solutions[97] at several temperatures are given in Tables (6-6-1) and (6-6-2), and similar results for hydrochloric acid[98] in various media are collected in Table (11-9-1A). The

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[96] C. S. Samis [*Trans. Faraday Soc.*, **33**, 469 (1937)] found that the behavior of hydrochloric acid and potassium chloride is the same at 40 and 50° as at 25°.

[97] R. W. Allgood, D. J. LeRoy and A. R. Gordon, *J. Chem. Phys.*, **8**, 418 (1940).

[97a] R. W. Allgood and A. R. Gordon, *Ibid.*, **10**, 124 (1942).

[98] Two of these electrolytes were studied by C. S. Samis, *Trans. Faraday Soc.*, **33**, 469 (1937). His results have not been included because it was pointed out in Reference 97 that they may contain inaccuracies due to peculiarities of the indicator solutions at high temperatures.

effect of temperature upon the transference numbers in potassium chloride solutions is exceptional, in that the difference between T_+ and T_- increases with temperature. As a rule,[99] the higher ionic mobilities have the lower temperature coefficients, so that transference numbers generally become more nearly equal[100] with rising temperature.

(7) EQUATIONS FOR TRANSFERENCE NUMBERS AT MODERATE DILUTIONS. EVALUATION OF T_j^0

A number of useful equations have been proposed for representing transference data from the lowest experimental concentrations (~ 0.01 N) up to 0.2 N, or higher. Three of these equations reduce to the theoretical limiting law at extreme dilution, and will be considered first.

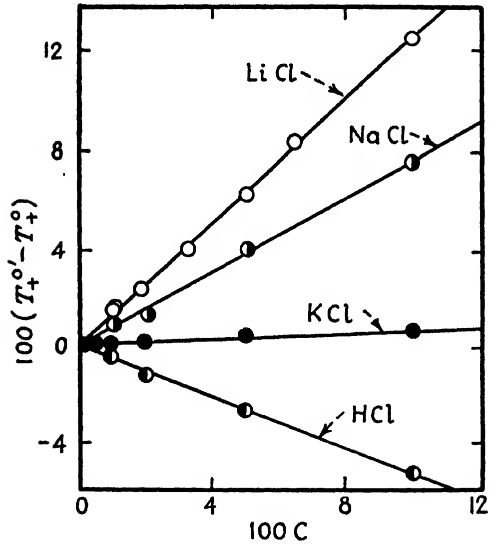

Fig. (6-7-1)
Verification of equation (6-7-1) for aqueous solutions of 1-1 chlorides at 25°

(a) Longsworth[101] found that values of T_+^0, calculated by equation (6-6-2), from experimental values of T_+ for the alkali chlorides and hydrochloric acid, vary linearly with c. Representing such calculated values by $T_+^{0\prime}$, so as to retain the usual meaning for the symbol T_+^0, Longsworth's observation can be written

$$T_+^{0\prime} \equiv \frac{T_+\Lambda' + (1/2)\beta^*\sqrt{c}}{\Lambda' + \beta^*\sqrt{c}} = T_+^0 + Bc \qquad (6\text{-}7\text{-}1)$$

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[99] F. Kohlrausch and L. Holborn, "Das Leitvermögen der Elektrolyte," Teubner, Leipzig and Berlin, 1916.

[100] See H. S. Taylor, *J. Chem. Phys.*, **6**, 331 (1938) and Reference 97.

[101] L. G. Longsworth, *J. Am. Chem. Soc.*, **54**, 2741 (1932).

for 1-1 electrolytes. The empirical constant B is characteristic of each electrolyte. Solution of this equation for T_+ gives

$$T_+ = T_+^0 + \mathcal{S}_{(T_+)}\sqrt{c}(\Lambda^0/\Lambda') + B(1 + \beta^*\sqrt{c}/\Lambda')c \qquad (6\text{-}7\text{-}2)$$

Figure (6-7-1) shows the high accuracy with which equation (6-7-1) fits those experimental results which merge with the theoretical limiting law. Tables (6-6-1) and (6-6-2) confirm this result at other temperatures. The extrapolated values of T_+^0, obtained from this figure, are completely in accord with the limiting conductances of the electrolytes and the principle of independent limiting mobilities. For the particular electrolytes involved, these considerations confirm the predictions of theory. On the other hand, equation (6-7-1) cannot be applied to potassium and silver nitrates, or to electrolytes of higher valence types.

(b) Shedlovsky[102] proposed the general empirical equation

$$\frac{1}{T_j} = \frac{1}{T_j^0} + A\sqrt{c} - B^*c \qquad (6\text{-}7\text{-}3)$$

which fits the data up to 0.2 N for a variety of electrolytes. When this equation is applied to the results for electrolytes such as calcium chloride and silver nitrate, both of the parameters, A and B^*, must be evaluated from the transference data. A theoretical value of A, consistent with equation (6-6-4), can be used in dealing with the alkali halides and other 1-1 electrolytes. In this case

$$A = -\mathcal{S}_{(T_j)}(1/T_j^0)^2 \qquad (6\text{-}7\text{-}4)$$

Since equation (6-7-3) contains only one arbitrary constant, B^*, under this condition, a plot of $[1/T_j + \mathcal{S}_{(T_j)}(1/T_j^0)^2\sqrt{c}]$ *vs.* c may be used to obtain $1/T_j^0$ by extrapolations involving a series of successive approximations. All of the limiting transference numbers obtained in this manner are in excellent agreement with those obtained by Longsworth's extrapolation. If the theoretical value of A, given by (6-7-4) is disregarded, correct values of T_j^0 for calcium chloride and silver nitrate can be derived from equation (6-7-3) by the method of least squares.

(c) The equation[103]

$$T_j = T_j^0 + \mathcal{S}_{(T_j)}\sqrt{c}(\Lambda^0/\Lambda')[1 - (1 - \alpha^*\sqrt{c})\sqrt{2c}] \qquad (6\text{-}7\text{-}5)$$

has been proposed for estimating T_j in dilute solutions of 1-1 electrolytes for which direct measurements are not available. The right-hand member contains no terms which cannot be determined from conductivity measurements and known limiting ionic conductance. Equation (6-7-5) yields values of T_j at 25° with an accuracy of 0.2 to 0.3 per cent when applied to dilute solutions ($c < 0.15$) of the 1-1 electrolytes for which equation

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[102] T. Shedlovsky, *J. Chem. Phys.*, **6**, 845 (1938).

[103] B. B. Owen, *J. Am. Chem. Soc.*, **57**, 2441 (1935).

(6-6-2) is valid as a limit. It is unsatisfactory for other electrolytes. The most interesting feature of equation (6-7-5) is the fact that the empirical bracketed term accounts for the deviations of a whole group of electrolytes from the limiting equation. These deviations are more accurately represented by equations (6-7-2) and (6-7-3) because they contain an additional empirical parameter, B, or B^*, characteristic of each electrolyte. A comparison of equations (6-7-2) and (6-7-5) leads to the relation

$$B = -\sqrt{2}\mathcal{S}_{(T_j)} \tag{6-7-6}$$

at 25°. Insufficient data are available to determine to what extent this equation is independent of temperature, but the indications are that it fails at higher temperatures. It is probable that the factor $\sqrt{2}$ which appears in equations (6-7-5) and (6-7-6) must be replaced by a parameter which varies with the temperature (and the nature of the solvent), if these equations are to have more general application.

(d) Gorin[104] deduced the equation

$$\frac{T_+}{T_-} = \frac{T_+^0}{T_-^0}\left(\frac{1 + a_-\kappa}{1 + a_+\kappa}\right) \tag{6-7-7}$$

for the ratio of the transference numbers of a symmetrical electrolyte. The derivation of this equation is based upon the same assumptions involved in equation (6-4-9). The values of a_+ and a_- can be calculated by equation (6-4-10) from a knowledge of the experimental limiting slopes of conductance curves and the limiting ionic mobilities. It is significant that, in spite of the two parameters, a_+ and a_-, equation (6-7-7) will not represent the experimental results over as wide a concentration range as the three equations, (6-7-2), (6-7-3), and (6-7-5), which reduce to the theoretical limiting law.

(e) Jones and Dole[105] found that the empirical equation

$$T_j = \frac{A}{1 + B\sqrt{c}} - 1 \tag{6-7-8}$$

represented their results for barium chloride at 25° with an average deviation of only 0.0002 up to a concentration of one molar. Such high accuracy and long range make this two-constant equation useful for interpolation, but it is not suitable for extrapolation. The value $T_j^0 = A - 1$ derived from the data on barium chloride is not in accord with the known limiting conductances of the barium and chloride ions.

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[104] M. H. Gorin, *J. Chem. Phys.*, **7**, 405 (1939).

[105] G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 1073 (1929).

(8) LIMITING IONIC CONDUCTANCE. KOHLRAUSCH'S LAW

As a result of the classic investigation of the conductance of electrolytic solutions, Kohlrausch[106] showed that the limiting equivalent conductance of an electrolyte is the sum of two independent factors characteristic of the anion and cation respectively. Thus the relation

$$\Lambda^0 = \lambda_+^0 + \lambda_-^0 \qquad (6\text{-}8\text{-}1)$$

is known as the Kohlrausch law. The complete independence of the limiting ionic conductances is demonstrated by Figure (6-8-1) based upon the results of MacInnes, Shedlovsky and Longsworth[107] for some 1-1 electrolytes. The quantity $\lambda_i^{0\prime}$ used as ordinate in this figure represents

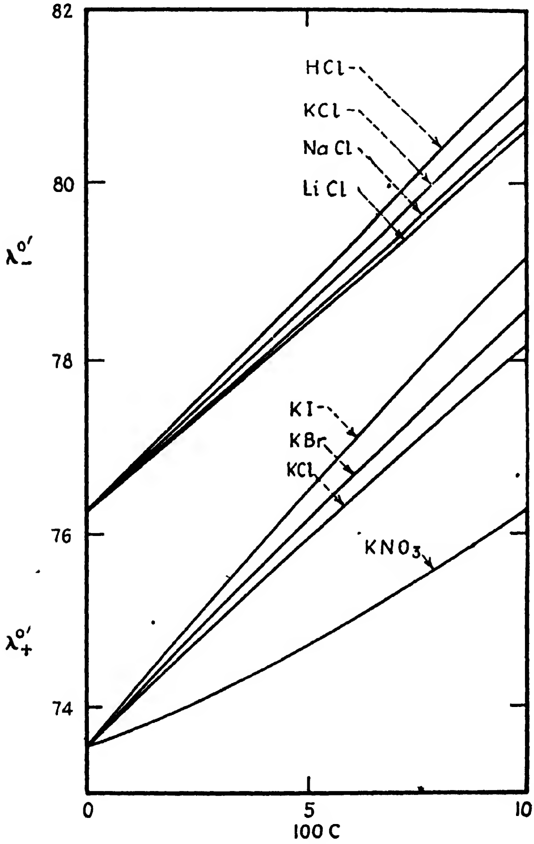

Fig. (6-8-1)
The variation of $\lambda^{0\prime}$ with concentration at 25°

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[106] F. Kohlrausch, *Ann. Physik.*, **50**, 385 (1893); **66**, 785 (1898).

[107] D. A. MacInnes, T. Shedlovsky, and L. G. Longsworth, *J. Am. Chem. Soc.*, **54**, 2758 (1932); *Chem. Rev.*, **13**, 29 (1933).

an "apparent" value of λ_j^0, calculated directly from the Onsager equation (5-3-10) by the introduction of an experimental value, $\lambda_j = T_j\Lambda$. At infinite dilution, $\lambda_j^{0\prime}$ equals the true limiting conductances, λ_j^0. The plots are all practically straight, except for potassium nitrate, indicating that $\lambda_j^{0\prime}$ is linear in c at low concentrations. Accordingly, the relation

$$\lambda_j^{0\prime} \equiv \frac{\lambda_j + (1/2)\beta^*\sqrt{c}}{1 - \alpha^*\sqrt{c}} = \lambda_j^0 + bc \qquad (6\text{-}8\text{-}2)$$

for ionic conductances in 1-1 electrolyte solutions has the same form as equation (6-3-7) for the equivalent conductance. The empirical constant b is determined by the slopes of the curves.

The most important result to be derived from Figure (6-8-1) is the determination of λ_{Cl}^0 and λ_{K}^0 from a number of concordant and independent studies. All these values of λ^0, obtained by extrapolation of the individual curves, agree within ±0.02 per cent, and the sum of the mean values, $\lambda_{\text{Cl}}^0 = 76.34$ and $\lambda_{\text{K}}^0 = 73.52$, is exactly equal to $\Lambda_{\text{KCl}}^0 = 149.86$ determined by direct experiment. The limiting conductances of all the ions must therefore be known to ±0.02 per cent by virtue of their common intercepts. This figure also demonstrates that the additivity expressed by equation (6-8-1) is very closely maintained up to a concentration as high as $c = 0.02$ for all the electrolytes shown, except potassium nitrate. This observation is of importance, as the applicability of the Kohlrausch principle to solutions at finite dilution is assumed in the determination of the ionization constants of weak electrolytes from conductivity measurements. It should be kept in mind that only 1-1 electrolytes are represented in Figure (6-8-1).

TABLE (6-8-1). λ_{Cl} IN 0.05N SOLUTIONS OF SODIUM AND LITHIUM CHLORIDES IN METHANOL-WATER MIXTURES AT 25°.

Mol fraction of alcohol	0	0.1	0.2	0.4	0.6	0.8
λ_{Cl} (in NaCl)............	68.01	45.87	36.19	30.45	29.69	30.82
λ_{Cl} (in LiCl)............	67.99	45.85	36.24	30.46	29.77	30.82

The additivity of univalent ionic conductances has also been found to exist in mixed solvents of relatively high dielectric constants. The results of Longsworth and MacInnes[108] given in Table (6-8-1) show that the chloride ion conductance in methanol-water solutions of sodium and lithium chloride is practically independent of the univalent cation.

The dependence of conductance of an ion constituent upon the valence of its co-ion is shown[109] in Figure (6-8-2). The theoretical limiting laws for the chloride ion conductance in the three salt solutions are

[108] L. G. Longsworth and D. A. MacInnes, *J. Phys. Chem.*, **43**, 239 (1939).

[109] L. G. Longsworth and D. A. MacInnes, *J. Am. Chem. Soc.*, **60**, 3070 (1938).

$$\lambda_{\text{Cl}}^{\text{NaCl}} = 76.34 - 47.2\sqrt{c^*} \tag{6-8-3}$$

$$\lambda_{\text{Cl}}^{\text{CaCl}_2} = 76.34 - 74.0\sqrt{c^*} \tag{6-8-4}$$

$$\lambda_{\text{Cl}}^{\text{LaCl}_3} = 76.34 - 99.1\sqrt{c^*} \tag{6-8-5}$$

in terms of the concentration, c^*, in equivalents per liter. This concentration unit is used to prevent the curves from crowding on the figure. They are brought much closer together if the ionic strength is used as abscissa, but they do not superpose in any concentration range. In addition to the individuality of these curves in dilute solutions which is predicted by theory, the departures from the theoretical relation depend to a high degree upon the valence of the co-ion. It clearly follows from this, and from the discussion of mixtures [Section (2)] that the principle of independent ionic mobilities can be used only as a rough approximation at experimental concentrations of high valence type, or mixed electrolytes.

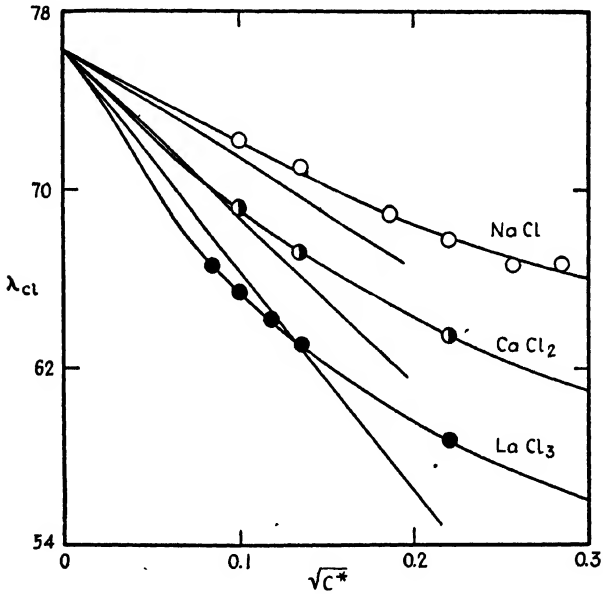

Fig. (6-8-2). Variation of chloride-ion conductance with concentration at 25°

In Table (6-8-2), we have collected representative values of limiting ionic conductances determined recently. The values for most of the univalent ions and for the alkaline earths are accurate to a few hundredths of one per cent. Some of the values for polyvalent ions are in considerable doubt, as is indicated by the number of significant figures.

TABLE (6-8-2).* LIMITING IONIC CONDUCTANCES IN WATER AT 25°.

Cation	λ_+^0	Ref.	Anion	λ_-^0	Ref.
H^+	349.8	(1), (13), (19)	OH^-	197.6	(8), (22)
Li^+	38.69	(1)	Cl^-	76.34	(1), (19), (21)
Na^+	50.11	(1), (13), (21)	Br^-	78.3	(9), (2)
K^+	73.52	(1), (21)	I^-	76.8	(10), (2)
NH_4^+	73.4	(2)	NO_3^-	71.44	(1)
Ag^+	61.92	(1)	ClO_4^-	68.0	(3)
Tl^+	74.7	(3)	HCO_3^-	44.5	(11)
			HCO_2^-	54.6	(18)
$\frac{1}{2}\ Mg^{++}$	53.06	(4)	$CH_3CO_2^-$	40.9	(1), (13)
$\frac{1}{2}\ Ca^{++}$	59.50	(4)	$ClCH_2CO_2^-$	39.8	(12), (13)
			$CNCH_2CO_2^-$	41.8	(18)
			$CH_3CH_2CO_2^-$	35.8	(14)
$\frac{1}{2}\ Sr^{++}$	59.46	(4)	$CH_3(CH_2)_2CO_2^-$	32.6	(14), (18)
$\frac{1}{2}\ Ba^{++}$	63.64	(4)	$C_6H_5CO_2^-$	32.3	(15), (16)
			$HC_2O_4^-$	40.2	(20)
			$\frac{1}{2}\ C_2O_4^{--}$	74.2	(20)
$\frac{1}{2}\ Cu^{++}$	54.	(5)	$\frac{1}{2}\ SO_4^{--}$	80	(2), (7)
$\frac{1}{2}\ Zn^{++}$	53.	(5)	$\frac{1}{3}\ Fe(CN)_6^{---}$	101	(7)
$\frac{1}{3}\ La^{+++}$	69.5	(6), (2)	$\frac{1}{4}\ Fe(CN)_6^{----}$	111	(17)
$\frac{1}{3}\ Co(NH_3)_6^{+++}$	102.	(7)			

* All values have been corrected to conform to the standard of G. Jones and B. C. Bradshaw. See Table (6-1-1). For values at other temperatures, see Appendix B, Table (B-2-2).

(1) D. A. MacInnes, T. Shedlovsky and L. G. Longsworth, *J. Am. Chem. Soc.*, **54**, 2758 (1932).
(2) D. A. MacInnes, *J. Franklin Inst.*, **225**, 661 (1938).
(3) R. A. Robinson and C. W. Davies, *J. Chem. Soc.*, **139**, 574 (1937).
(4) T. Shedlovsky and A. S. Brown, *J. Am. Chem. Soc.*, **56**, 1066 (1934).
(5) B. B. Owen and R. W. Gurry, *Ibid.*, **60**, 3074 (1938).
(6) G. Jones and C. F. Bickford, *Ibid.*, **56**, 602 (1934). See Table (6-3-3).
(7) G. S. Hartley and G. W. Donaldson, *Trans. Faraday Soc.*, **33**, 457 (1937).
(8) V. Sivertz, R. E. Reitmeier, and H. V. Tartar, *J. Am. Chem. Soc.*, **62**, 1379 (1940).
(9) G. Jones and C. F Bickford, *J. Am Chem. Soc.*, **56**, 602 (1934).
(10) P. A. Lasselle and J. G. Aston, *Ibid.*, **55**, 3067 (1933).
(11) T. Shedlovsky and D. A. MacInnes, *Ibid.*, **57**, 1705 (1935).
(12) T. Shedlovsky, A. S. Brown and D. A. MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1935).
(13) B. Saxton and T. W. Langer, *J. Am. Chem. Soc.*, **55**, 3638 (1933).
(14) D. Belcher, *Ibid.*, **60**, 2744 (1938).
(15) B. Saxton and H. F. Meier, *Ibid.*, **56**, 1918 (1934). These authors also report 30.3 and 31.0 for the *ortho*- and *meta*-chlorobenzoate ions respectively.
(16) F. G. Brockman and M. Kilpatrick, *Ibid.*, **56**, 1483 (1934).
(17) G. Jones and F. C. Jelen, *Ibid.*, **58**, 2561 (1936); C. W. Davies, *Ibid.*, **59**, 1760 (1937). See Table (6-3-3).
(18) B. Saxton and L. S. Darken, *J. Am. Chem. Soc.*, **62**, 846 (1940).
(19) Values at 10° intervals from 5 to 65° are given by B. B. Owen and F. H. Sweeton, *Ibid.*, **63**, 2811 (1941).
(20) L. S. Darken, *Ibid.*, **63**, 1007 (1941).
(21) Values at 15, 25, 35, and 45° are given by H. E. Gunning and A. R. Gordon, *J. Chem. Phys.*, **10**, 126 (1942). See also N. C. Li and W. Brüll, *J. Am. Chem. Soc.*, **64**, 1635 (1942), and A. R. Gordon, *Ibid.*, **64**, 2517 (1942).
(22) L. S. Darken and H. F. Meier, *J. Am. Chem. Soc.*, **64**, 621 (1942).

(9) VISCOSITY OF SOLUTIONS OF STRONG ELECTROLYTES AND ITS DEPENDENCE UPON CONCENTRATION

Since the pioneer investigations of Poiseuille,[110] a very extensive literature[111] dealing with the viscosity, or its reciprocal, the fluidity, of solutions

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[110] J. L. M. Poiseuille, *Ann. chim. phys.* [3], **21**, 76 (1847).

[111] See E. C. Bingham, "Fluidity and Plasticity", McGraw-Hill Book Co., New York, 1922; E. Hatschek, "The Viscosity of Liquids", D. Van Nostrand Co., New York, 1928.

has appeared. With the development of the interionic attraction theory much of the interest in this subject has been directed toward very accurate determinations[112] of the viscosities of dilute solutions of electrolytes, and the theoretical interpretation of the results. Grüneisen[113] appears to have been the first to make very accurate measurements at high dilutions, and he showed, in contradiction to earlier views,[114] that the viscosity is not a linear function of the concentration in dilute solutions. Moreover, the departures from linearity increase rapidly as the concentration is reduced. This behavior of electrolytes appears to be general,[115] and has been termed[116] the Grüneisen effect. It is absent in solutions of nonelectrolytes.

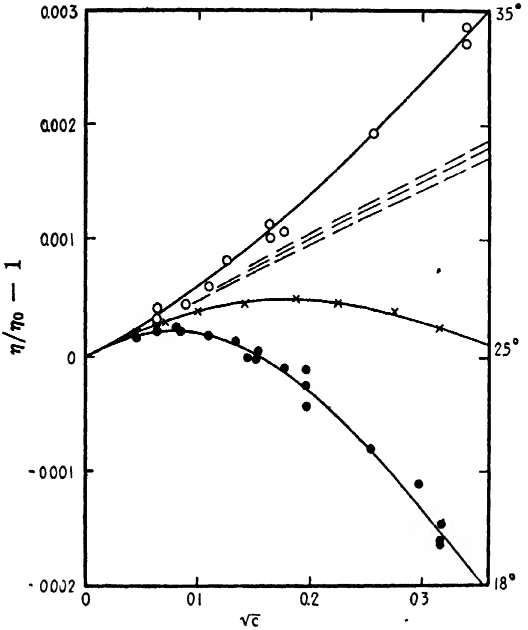

Fig (6-9-1) Relative viscosity of aqueous KCl solutions at 18, 25, and 35°; the theoretical limiting law gives the broken lines

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[112] E. Grüneisen, *Wiss. Abh. phys. tech. Reichsanstalt*, **4**, 159, 241 (1904); E. W. Washburn and G. V. Williams, *J. Am. Chem. Soc.*, **35**, 737 (1913); E. C. Bingham and R. F. Jackson, *Bull. Bureau of Standards*, **14**, 59 (1918-19); G. Jones and S. K. Talley, *Physics*, **4**, 215 (1933); G. Jones and H. J. Fornwalt, *J. Am. Chem. Soc.*, **60**, 1683 (1938); G. Jones and R. E. Stauffer, *Ibid.*, **59**, 1630 (1937).

[113] E. Grüneisen, *Wiss. Abh. phys. techn. Reichsanstalt*, **4**, 151, 237 (1905).

[114] A. Sprung, *Pogg. Ann. Phys. Chem.*, **159**, 1 (1876); S. Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887).

[115] M. P. Appelbey, *J. Chem. Soc.*, **97**, 2000 (1910); T. R. Merton, *Ibid.*, **97**, 2454 (1910).

[116] G. Jones and S. K. Talley, *J. Am. Chem. Soc.*, **55**, 624 (1933).

It was shown experimentally by Jones and Dole,[117] and Joy and Wolfenden[118] that the viscosities of solutions of strong electrolytes vary linearly with the square root of the concentration at high dilutions. This result is illustrated in Figure (6-9-1) and its generality is supported by recent studies of a large number of salts. It was pointed out[117] that the viscosities of many solutions can be accurately represented by the equation

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc \tag{6-9-1}$$

up to concentrations as high as $0.1N$.

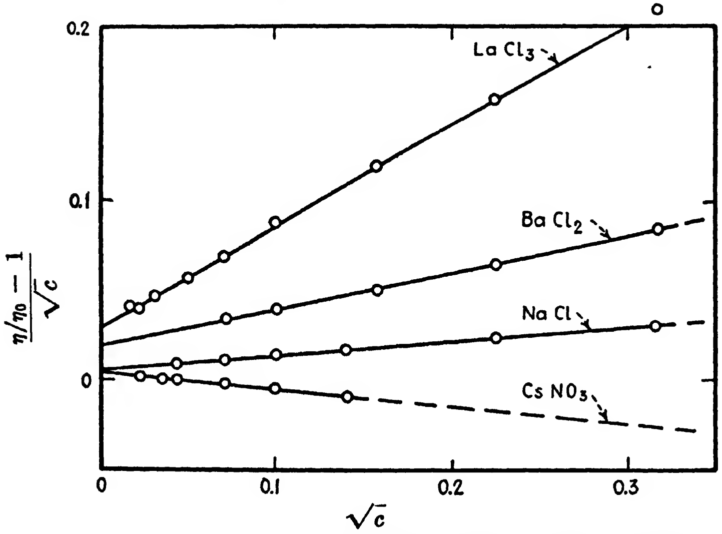

Fig. (6-9-2). Evaluation of the limiting slopes for relative viscosity at 25°

The experimental values of the parameters A and B are determined by plotting the left-hand member of the equation

$$\frac{\eta/\eta_0 - 1}{\sqrt{c}} = A + B\sqrt{c} \tag{6-9-2}$$

against $\sqrt{c}$. Figures (6-9-2) and (6-9-3) illustrate such plots for a variety of electrolytes. The intercepts and slopes of the linear plots are A and B, respectively. The curved plots [Figure (6-9-3)] can be used to obtain satisfactory values of A if the data extend to very high dilutions, but it is clear that B is not constant within the experimental concentration range. Fortunately, such plots are unusual for aqueous solutions and are confined

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[117] G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929). See also G. Jones and S. K. Talley, *Ibid.*, **55**, 624 (1933).

[118] W. E. Joy and J. H. Wolfenden, *Proc. Roy. Soc. London*, **A 134**, 413 (1931).

to partially dissociated, or high valence type (particularly 2-2) electrolytes. The behavior of electrolytes in non-aqueous solvents is similar, but the range of validity of equation (6-9-1) is limited to more dilute solutions.

The constant B is highly specific, and is an approximately additive[119, 120] property of the ions. Note that B is negative for cesium nitrate at 25°. Negative B-values are obtained at low temperatures for many salts composed of large, relatively unhydrated, ions. On the other hand, the observed temperature coefficients of B are always positive, so the effect of salts at high temperatures would be to increase the viscosity of the solution throughout the entire range covered by equation (6-9-1). Figure (6-9-1) shows that, for potassium chloride, this change of B from minus to plus takes place between 25 and 35°. So far, no satisfactory theoretical interpretation of the B parameter has been found, but its approximate additivity can be used to develop empirical methods for calculating the viscosities of solutions containing one[121] or more[122] electrolytes. Ionic "fluidities" can also be used for this purpose.[123]

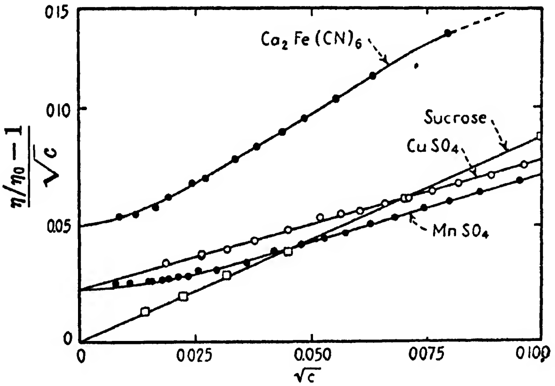

Fig. (6-9-3) Evaluation of the limiting slopes for relative viscosity at 25°

Although the individuality of A, and its variation with temperature, are much less pronounced than for those of B, the numerical values of A are of very great theoretical interest. Since $\eta/\eta_0 = 1 + \eta^*/\eta_0$, the theoretical value of the parameter, A, is obtainable from equation (4-2-28), which applies to solutions of a single electrolyte dissociating into only two kinds of ions. By combination of equations (3-1-2), (4-1-15) and

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[119] W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc. London*, **A 145**, 475 (1934).

[120] V. D. Laurence and J. H. Wolfenden, *J. Chem. Soc.*, **136**, 1144 (1934).

[121] W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc. London*, **A 145**, 475 (1934).

[122] H. Tollert, *Z. physik. Chem.*, **A 172**, 129 (1935); **A 174**, 239 (1935); **A 180**, 383 (1937).

[123] E. C. Bingham, *J. Phys. Chem.*, **45**, 885 (1941).

(4-2-25) to (4-2-28), the limiting law for the relative viscosity can be written

$$\eta/\eta_0 = 1 + \mathcal{S}_{(\eta)}\sqrt{c} \tag{6-9-3}$$

where

$$\mathcal{S}_{(\eta)} = \frac{\beta^*}{80(|z_1| + |z_2|)^2}\left\{\frac{\lambda_1^0 z_2^2 + \lambda_2^0 z_1^2}{\lambda_1^0 \lambda_2^0} - \frac{4}{\lambda_1^0 \lambda_2^0}\left[\frac{|z_2|\,\lambda_1^0 - |z_1|\,\lambda_2^0}{(\Lambda^0)^{1/2} + (\Lambda^0 + \lambda_1^0\,|z_2/z_1| + \lambda_2^0\,|z_1/z_2|)^{1/2}}\right]^2\right\} \tag{6-9-4}$$

This is the equation, in slightly altered form, for the limiting slope as originally derived by Falkenhagen and Vernon.[124] Numerical values of the coefficient β^* are given in Tables (5-3-1) and (11-1-1A). For binary electrolytes

$$\mathcal{S}_{(\eta)} = \frac{\beta^*}{320}\,\frac{\Lambda^0}{\lambda_1^0 \lambda_2^0}\left[1 - 0.6863\left(\frac{\lambda_1^0 - \lambda_2^0}{\Lambda_0}\right)^2\right] \tag{6-9-5}$$

and in the special case where $\lambda_1^0 = \lambda_2^0$ this equation reduces to the relation,

$$\mathcal{S}_{(\eta)} = \frac{\beta^*}{160\,\lambda^0} \tag{6-9-6}$$

derived by Falkenhagen and Dole.[125]

A comparison of the observed and theoretical limiting slopes is made in Table (6-9-1) for aqueous solutions at 25°. The agreement is very satisfactory indeed, and appears to be as good for complex valence types as for simple 1-1 salts. The relative viscosity can be calculated, within the experimental error, from the values of A and B and equation (6-9-1) up to, and often beyond, the concentrations indicated in the next to the last column. The non-electrolytes, sucrose and urea, are included in the table to show that the limiting slope is zero for solutes of zero charge. The influence of temperature upon the limiting slope has been shown to be completely in accord with theory.[126] The effect of the dielectric constant in non-aqueous solvents is more difficult to verify. The experi-

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[124] H. Falkenhagen and E. L. Vernon, *Physik. Z.*, **33**, 140 (1932); *Phil. Mag.* [7] **14**, 537 (1932). See also H. Falkenhagen, *Nature*, **127**, 439 (1931); *Physik. Z.*, **32**, 745 (1931); *Z. physik. Chem.*, **B 6**, 159 (1931).

[125] H. Falkenhagen and M. Dole, *Physik. Z.*, **30**, 611 (1929); *Z. physik. Chem.*, **B 6**, 159 (1929).

[126] Results are available at 0° for all the salts in Table (6-9-1) which were studied by G. Jones and his students. W. E. Joy and J. H. Wolfenden [*Proc. Roy. Soc. London*, **A 134**, 413 (1913)] and W. M. Cox and J. H. Wolfenden [*Ibid.*, **A 145**, 475 (1934)] investigated a number of electrolytes, including nitric acid, at 18 and 35°. Data at 35° and higher temperatures are given by A. S. Chakravarti and B. Prasad [*Trans. Faraday Soc.*, **35**, 1466 (1939)], J. D. Ranade and G. R. Paranjpe [*J. Univ. Bombay*, **7**, 41 (1938)] and in standard handbooks.

mental limiting slopes are subject to errors caused by accidental absorption of moisture by hygroscopic solvents, and the theoretical slopes them-

TABLE (6-9-1). PARAMETERS A AND B OF THE VISCOSITY EQUATION (6-9-1) FOR AQUEOUS SOLUTIONS AT 25°. THE THEORETICAL LIMITING SLOPES.

Solute*	Type	$\mathfrak{S}_{(\eta)}10^4$	$A\ 10^4$	B	Range	Ref.
Sucrose	0	0	0	0.8786	0.02	(g)
Urea	0	0	0	0.0378	0.2	(g)
NH_4Cl	1-1	50	57	−0.0144	0.2	(g)
$NaCl$	1-1	60	67	0.0244	0.2	(c)
KCl	1-1	50	52	−0.0140	0.2	(g)
KBr	1-1	49	47.4	−0.0480	0.1	(f)
KNO_3	1-1	52	50	−0.053	0.1	(g)
$KClO_3$	1-1	55	50	−0.031	0.1	(g)
$KBrO_3$	1-1	58	58	−0.001	0.1	(g)
$KMnO_4$	1-1	56	58	−0.066	0.1	(e)
CsI	1-1	48	39	−0.118	0.2	(e)
$CsNO_3$	1-1	51	43	−0.092	0.02	(g)
$AgNO_3$	1-1	56	63	0.045	0.1	(a)
K_2SO_4	1-2	131	140.6	0.194	0.1	(a)
K_2CrO_4	1-2	131	133	0.152	0.1	(a)
$BaCl_2$	2-1	147	201	0.207	0.1	(h)
$LaCl_3$	3-1	284	304	0.567	0.1	(b)
$K_4Fe(CN)_6$	1-4	330	370	0.366	0.1	(d)
$MgSO_4$	2-2	228	225	—	—	(i)
$MnSO_4$	2-2	227	231	—	—	(i)
$CuSO_4$	2-2	228	230	0.540	0.01	(i)
$ZnSO_4$	2-2	225	229	—	—	(i)
$CdSO_4$	2-2	225	232	—	—	(i)
$Cr_2(SO_4)_3$	3-2	507	495	—	—	(i)
$Ca_3[Fe(CN)_6]_2$	2-3	464	467	—	—	(i)
$Ca_2Fe(CN)_6$	2-4	490	495	—	—	(i)

* For additional solutes see V. D. Laurence and J. H. Wolfenden, *J. Chem. Soc.*, **136**, 1144 (1934).

(a) G. Jones and J. H. Colvin, *J. Am. Chem. Soc.*, **62**, 338 (1940).
(b) G. Jones and R. E. Stauffer, *Ibid.*, **62**, 335 (1940).
(c) G. Jones and S. M. Christian, *Ibid.*, **59**, 484 (1937).
(d) G. Jones and R. E. Stauffer, *Ibid.*, **58**, 2548 (1936).
(e) G. Jones and H. J. Fornwalt, *Ibid.*, **58**, 619 (1936).
(f) G. Jones and S. K. Talley, *Ibid.*, **55**, 4124 (1933).
(g) G. Jones and S. K. Talley, *Ibid.*, **55**, 624 (1933).
(h) G. Jones and M. Dole, *Ibid.*, **51**, 2950 (1929).
(i) E. Asmus, *Ann. Physik*, **35**, 1 (1939).

TABLE (6-9-2). LIMITING SLOPES FOR VISCOSITY IN NON-AQUEOUS SOLVENTS AT 25°.

Salt	Solvent	$A\ 10^4$	$\mathfrak{S}_{(\eta)}10^4$	Ref.
$LiCl$	acetone	240	237	(a)
KCl	methanol	151	173	(b)
KBr	"	142	165	(b)
KI	"	159	158	(b)
NH_4Cl	"	183	165	(b)
NaI	ethanol	270	255	(c)

(a) G. R. Hood and L. P. Hohlfelder, *J. Phys. Chem.*, **38**, 979 (1934).
(b) G. Jones and H. J. Fornwalt, *J. Am. Chem. Soc.*, **57**, 2041 (1935).
(c) W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc. London*, **A145**, 475 (1934).

selves may be inaccurate because the limiting ionic conductivities are not known with certainty in these media. Table (6-9-2) shows some representative results obtained in acetone and alcohols. In attempting to evaluate A in these solvents, it is necessary to obtain measurements at very low concentrations. Dalian and Briscoe[127] found that the extrapolation of their data at relatively high concentrations ($c \geq 0.04$) leads to negative values of A for solutions of nickel and aluminum chlorides in ethanol, and zero values of A for the chlorides of cobalt, copper, iron, tin, cadmium and mercury[128] in this solvent. Reference to Fig. (6-9-3) strongly suggests that the anomalous A-values reported by Dalian and Briscoe are without physical significance.

(10) DIFFUSION OF ELECTROLYTES

The determination of the differential diffusion coefficient, $\mathfrak{D}$, at high dilutions is so difficult experimentally that Onsager and Fuoss[129] were unable to find results below $0.05N$ with which to test their theoretical equation (4-4-24). The recent development of the Northrop-McBain[130] diffusion cell, in which solutions of two concentrations are separated by a horizontal diaphragm of sintered glass, has made it relatively easy to determine "integral" diffusion coefficients. Unfortunately, the estimation of the true differential coefficients from such results appears impractical at high dilutions. Therefore, we are unable to make a significant comparison of the theoretical limiting law with experiment, but a discussion of the results at higher concentrations will serve to illustrate the use of the equations, and to introduce some experimental results.

According to equations (4-4-24) and (4-4-19), the differential diffusion coefficient is given by

$$\mathfrak{D} = 16.632 \times 10^{10}\, T \left(\frac{\overline{\mathfrak{M}}}{c}\right)\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) \tag{6-10-1}$$

where $y_\pm$ is the mean activity coefficient and the mobility term, $\overline{\mathfrak{M}}/c$, can be written

$$\left(\frac{\overline{\mathfrak{M}}}{c}\right) 10^{20} = 1.074\left(\frac{\lambda_+^0 \lambda_-^0}{\Lambda^0}\right) - \frac{22.00}{\eta_0 (DT)^{1/2}}\left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda^0}\right)^2 \frac{\sqrt{c}}{1 + A'\sqrt{c}} + \frac{9.18 \times 10^7}{\eta_0 (DT)^2}\, c\phi(A'\sqrt{c}) \tag{6-10-2}$$

for 1-1 electrolytes. In aqueous solutions, the factors, $22/\eta_0(DT)^{1/2}$ and $9.18 \times 10^7/\eta_0(DT)^2$, are 16.07 and 18.71 at 25°, and 13.50 and 15.53 at 18°.

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[127] F. E. Dalian and H. T. Briscoe, *J. Phys. Chem.*, **41**, 1129 (1937).

[128] Even in dilute aqueous solutions mercuric chloride behaves as a typical non-electrolyte. See F. Prasad, A. S. Chakravarti and B. Prasad, *J. Indian Chem. Soc.*, **15**, 301 (1938).

[129] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[130] J. H. Northrop and M. L. Anson, *J. Gen. Physiol.*, **12**, 543 (1929); J. W. McBain, and T. H. Liu, *J. Am. Chem. Soc.*, **53**, 59 (1931); J. W. McBain and C. R. Dawson, *Ibid.*, **56**, 52, 1021 (1934); *Proc. Roy. Soc. London*, **148 A**, 32 (1935).

The first term of the right-hand member of equation (6-10-2) is constant, and always greater than $\Lambda^0/4$. For many salts, the difference $(\lambda_+ - \lambda_-)$ is so small that the second term is negligible. Inspection of Table (5-3-2) shows that $c\phi(A'\sqrt{c})$, which equals $(1/A')^2(\kappa a)^2\phi(\kappa a)$, is practically constant at high concentrations, and never exceeds 0.1 in any case. Consequently, the variation of $\mathfrak{M}/c$ is usually so small that the change in the diffusion coefficient with concentration is governed by the thermodynamic factor $(1 + c\partial \ln y_\pm/\partial c)$. This factor may be evaluated graphically, or by differentiation of the equation

$$\log y_\pm = -\frac{\mathcal{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} + B2c - \log\left[\frac{d + 0.001c(2M_1 - M_2)}{d_0}\right] \tag{6-10-3}$$

which results from the combination of equations (3-8-2) and (1-8-14). In the latter case, we obtain the relation

$$\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{1.1514\mathcal{S}_{(f)}\sqrt{c}}{(1 + A'\sqrt{c})^2} + 2.303B2c - c\psi(d) \tag{6-10-4}$$

The term

$$\psi(d) \equiv \frac{\partial d/\partial c + 0.001(2M_1 - M_2)}{d + 0.001c(2M_1 - M_2)} \tag{6-10-5}$$

is not negligible except at high dilutions.

If we combine equations (6-10-1), (6-10-2) and (6-10-4), and note that the function, $c\phi(A'\sqrt{c})$, and its first derivative with respect to $\sqrt{c}$, approach zero as c approaches zero, we obtain the limiting equation

$$\mathfrak{D} = \mathfrak{D}^0 - \mathcal{S}_{(\mathfrak{D})}\sqrt{c} \tag{6-10-6}$$

where

$$\mathcal{S}_{(\mathfrak{D})} = \frac{3.732 \times 10^{-3}}{D^{3/2}T^{1/2}}\left(\frac{\lambda_+^0\lambda_-^0}{\Lambda^0}\right) + \frac{3.659 \times 10^{-8}}{\eta_0 D^{1/2}T^{-1/2}}\left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda^0}\right)^2 \tag{6-10-7}$$

and

$$\mathfrak{D}^0 = 17.863 \times 10^{-10}T\left(\frac{\lambda_+^0\lambda_-^0}{\Lambda^0}\right) \tag{6-10-8}$$

$\mathfrak{D}^0$, the diffusion coefficient for infinitely dilute solutions, was first calculated by Nernst.[131] For aqueous solutions, $17.863 \times 10^{-10}T$ equals 5.325×10^{-7} at 25°, and 5.200×10^{-7} at 18°. The factors, $3.732 \times 10^{-3}/D^{3/2}T^{1/2}$ and $3.659 \times 10^{-8}T^{1/2}/\eta_0 D^{1/2}$, are 0.03104 and 0.7965×10^{-5} at 25°, and 0.02995 and 0.7781×10^{-5} at 18°. The above three equations follow from Hermans'[132] general treatment of diffusion, if we impose the condition of

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[131] W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

[132] J. J. Hermans, Dissertation (Leiden), p. 27 (1937); *Rec. trav. chim.*, **56**, 635, 658 (1937).

spherical symmetry upon the ionic atmospheres, and neglect concentration terms higher than $c^{1/2}$.

As an illustration of the calculation of $\mathfrak{D}$ for a typical electrolyte, we shall consider sodium chloride solutions at 18°. From the results of Harned and Cook,[133] we obtain $A' = 1.310$, $2B = 0.0502$, and $\mathcal{S}_{(f)} = 0.5002$ at this temperature. The densities[134] can be expressed by

$$d = 0.99862 + 0.0428c - 0.00145c^{3/2} \tag{6-10-9}$$

Accordingly

$$\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{0.5759\sqrt{c}}{(1 + 1.31\sqrt{c})^2} + 0.1156c - c\psi(d) \tag{6-10-10}$$

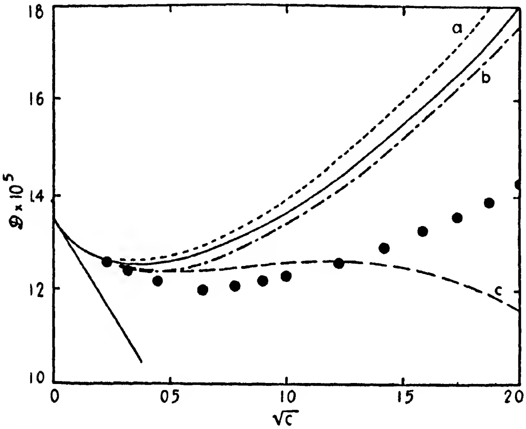

Fig. (6-10-1) Diffusion coefficient of sodium chloride in water. Curves calculated at 18°. Experimental points obtained near 18.5°

and

$$\psi(d) = \frac{0.0204 - 0.00217\sqrt{c}}{0.9986 + 0.0204c - 0.00145c^{3/2}} \tag{6-10-11}$$

Introducing the proper numerical coefficients into equation (6-10-2) at 18°, we obtain

$$\left(\frac{\mathfrak{M}}{c}\right) 10^{20} = 27.92 - \frac{0.608\sqrt{c}}{1 + 1.31\sqrt{c}} + 15.53c\phi(\kappa a) \tag{6-10-12}$$

if we use 66.0 and 42.9 for the limiting ionic mobilities.[135] The solid line in Fig. (6-10-1) is a plot of $\mathfrak{D}$ calculated from these equations. Curve (a) shows the effect of neglecting the term $\psi(d)$, and curve (b) the effect of omitting the last two terms in equation (6-10-2). In this example, the effect of $\psi(d)$ is more pronounced than the theoretical variation of

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[133] H. S. Harned and M. A. Cook, *J. Am. Chem. Soc.*, **61**, 495 (1939).

[134] Landolt-Börnstein, "Tabellen," p. 378, Erg. III-a, (1935).

[135] $\Lambda^0_{NaCl} = 108.9$; $\Lambda^0_{KCl} = 129.9$; and $T^0_K = 0.492$ at 18° from Table (6-6-1).

$\overline{\mathfrak{M}}/c$ with concentration. The experimental differential diffusion coefficients, measured by Clack,[136] are represented by circles. At high concentrations, they depart widely from the calculated curve, and although Onsager and Fuoss[137] have suggested a qualitative explanation of this behavior, it is apparent that the present theory is inadequate in the experimental concentration range.

On the other hand, the results do approach[138] the theoretical curve at the lower concentrations, and are not inconsistent with the limiting slope[139] given by equation (6-10-7). Recent data on hydrochloric acid[140] solutions at 25° agree more closely with the theory at high concentrations than at $0.01N$, and appear to extrapolate to a value of $\mathfrak{D}^0$ about 6 per cent lower than that required by equation (6-10-8). Since these data were obtained in a McBain-Northrup cell, and are considered[141] only a "good approximation" to the true $\mathfrak{D}$ at the mean concentrations of the experiments, the measurements at the highest dilutions are of doubtful value in testing the theory.

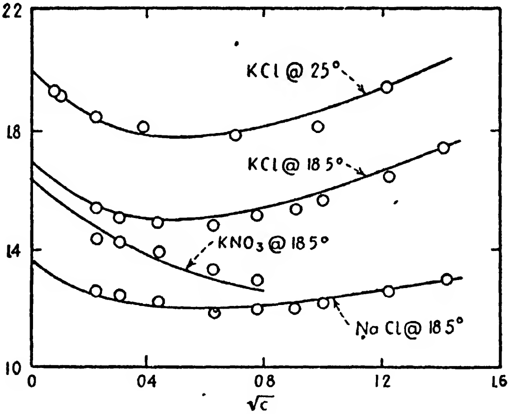

Fig. (6-10-2). Comparison of equation (6-10-13) with experiment

Onsager and Fuoss pointed out that at moderate concentrations the change in viscosity caused by the presence of the ions would have an

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[136] B. W. Clack, *Proc. Phys. Soc. London*, **36**, 313 (1924). The temperature was maintained near 18.5°.

[137] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, p. 2769 (1932).

[138] The results for potassium chloride behave similarly at *ca.* 18.5° (Clack) and at 25° (McBain and Dawson).

[139] L. Friedman and P. G. Carpenter [*J. Am. Chem. Soc.*, **61**, 1745 (1939)] found that the diffusion coefficient of the non-electrolyte, glucose, varies linearly with $\sqrt{c}$ over a considerable range.

[140] W. A. James, E. A. Hollingshead and A. R. Gordon, *J. Chem. Phys.*, **7**, 89 (1939). See also W. A. James and A. R. Gordon, *Ibid.*, **7**, 963 (1939).

[141] A. R. Gordon, *J. Chem. Phys.*, **5**, 522 (1937).

appreciable effect upon the mobility term, and that, as a first approximation, this effect should be inversely proportional to the macroscopic viscosity. Curve (c) in Figure (6-10-1) shows the effect of multiplying $\overline{\mathfrak{M}}/c$ in equation (6-10-2) by η_0/η. This factor produces a shift in the calculated curve toward the experimental points in dilute solutions, but seriously over corrects at the higher concentrations. Van Rysselberghe[142] has made an extensive study of this and similar viscosity corrections.

Gordon[143] has proposed the semi-empirical equation

$$\mathfrak{D} = 2000RT\left[1.074 \times 10^{-20}\left(\frac{\lambda_+^0 \lambda_-^0}{\Lambda^0}\right)\frac{V}{n_1 \bar{V}_1}\frac{\eta_0}{\eta}\right]\left(1 + m\frac{\partial \ln \gamma_\pm}{\partial m}\right) \quad (6\text{-}10\text{-}13)$$

in which the mobility factor contains both the partial molal volume of the solvent and the viscosity of the solution. This equation does not reduce to (6-10-6) in the limit, but does yield the theoretical value of $\mathfrak{D}^0$ [Equation (6-10-8)], and represents the data[144] for a number of electrolytes within the probable experimental error. The success of Gordon's equation is illustrated in Figure (6-10-2). It is noteworthy that for sodium chloride solutions at 18°, η_0/η is less than unity, while η_0/η is greater than unity for potassium chloride and nitrate solutions in all but the most dilute solutions. The application of equation (6-10-13) to higher valence type electrolytes is not so successful.[145]

Another attempt to express diffusion data at moderate concentrations in mathematical terms is due to Vinograd and McBain.[146] They neglect activity coefficients and collision effects at all concentrations, and extend the classical Nernst[147] relation to include mixtures of electrolytes. Their final equations express the integral diffusion coefficient of any given ion in terms of the individual mobilities and concentration gradients of all the ions. The direct effect of concentration gradients is explicitly kept separate from the effect of the diffusion potential. When the latter is zero, the ions diffuse at their true characteristic rates; otherwise, fast ions are accelerated and slow ions are retarded by the electrical effect of the diffusion potential. Experimental results in mixtures of electrolytes are shown to verify this acceleration and retardation, and to agree closely in magnitude with the effects calculated from the theoretical equations upon the assumption of linear concentration gradients for diffusion into pure water. For further discussion of diffusion, see Appendix B, Section (3).

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[142] P. Van Rysselberghe, *J. Am. Chem. Soc.*, **60**, 2326 (1938).

[143] A. R. Gordon, *J. Chem. Phys.*, **5**, 522 (1937).

[144] A. R. Gordon, *J. Chem. Phys.*, **5**, 522 (1937). See also W. A. James and A. R. Gordon, *Ibid.*, **7**, 963 (1939).

[145] E. A. Hollingshead and A. R. Gordon, *J. Chem. Phys.*, **9**, 152 (1941).

[146] J. R. Vinograd and J. W. McBain, *J. Am. Chem. Soc.*, **63**, 2008 (1941).

[147] W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888); S. Arrhenius, *Ibid.*, **10**, 51 (1892).

Chapter (7)

Coulomb Forces and Ion Association; Weak Electrolytes; Frequency and Field Effects

In the preceding chapter, the conductance of highly ionized electrolytes in a medium of high dielectric constant was discussed in considerable detail. On the basis of the Onsager conductance equation, the behaviors of most of these solutions indicated complete ionization of the solute at low concentrations. In media other than water, Bjerrum's theory of ionic association [Chapter (3), Section (7)] has indicated, and the experimental results about to be discussed will confirm, that the ions of all electrolytes tend to associate more and more as the dielectric constants of the solvent media decrease. Accordingly, all electrolytes are partially associated, or "weak," in media of low dielectric constants, and classification of electrolytes into strong and weak becomes somewhat arbitrary. Nevertheless, the characterization of electrolytes as strong and weak, depending upon whether they are highly or slightly ionized in aqueous solutions, is commonly retained in describing the electrolytes, regardless of the medium in which they may be dissolved. The title of the present chapter, dealing with non-aqueous solutions of the alkali halides, quarternary ammonium salts, etc., conforms with this convention.

(1) STOKES' LAW AND WALDEN'S RULE

When strong electrolytes are dissolved in solvents of very low dielectric constants, the simple Coulomb forces are sufficient to cause ionic association at extremely low ionic concentrations. In this case, the ions not acting as part of an associated ion-pair, or more complex aggregate, are so far apart that short-range repulsive forces are negligible and the effect of the ionic atmospheres is also very small. For example, in a dioxane-water mixture having a dielectric constant of 2.3 (0.343 per cent H_2O), the ionic concentration present in a 10^{-3} N solution of tetraisoamyl ammonium nitrate (a strong electrolyte in water) is only of the order of 10^{-8}. In spite of the large limiting slopes, $\mathcal{S}_{(\Lambda)}^*$, resulting from the low dielectric constant, the total effect of the ionic atmosphere is less than 0.2 per cent of Λ and may be neglected.

Exceedingly low ionic dissociation precludes the determination of Λ^0 by direct extrapolation of experimental data. In aqueous solutions, Λ^0 is indirectly evaluated for weak electrolytes by combining the data for suitable strong electrolytes in accordance with Kohlrausch's law. This procedure is obviously impossible in solvents of such low dielectric constants that all electrolytes dissolved in them are highly associated. In this case, it has generally been necessary to employ an approximation known as Walden's rule. This rule, as originally[1] proposed, was empirical, but it can be shown to be a direct consequence of the application of Stokes' law [Equation (4-3-9)] to the motion of ions. Since Walden's rule is most strictly applicable to systems which closely approach the conditions postulated in the derivation of Stokes' law, it will be of interest to consider these two relationships together.

According to Stokes' law, an electric force, $\mathbf{X}z_j\epsilon$, acting upon a spherical ion of radius a_j, would maintain it at a velocity[2]

$$\mathbf{v}_j = \frac{\mathbf{X}z_j\epsilon}{6\pi\eta_0 a_j} \tag{7-1-1}$$

in a homogeneous medium of viscosity, η_0. Ions are often far from spherical, and since they are of the same order of magnitude as the solvent molecules, it is questionable whether the retarding effect of the latter can be accurately described by the macroscopic viscosity. As a first approximation, we can regard the conditions required by equation (7-1-1) as fulfilled by large, spherical ions. By combining this equation with (4-1-15) and $\omega_j = \mathbf{v}_j/\mathbf{X}z_j\epsilon$, we obtain the relation,

$$\lambda_j^0\eta_0 = \frac{96{,}500\,|z_j|\,\epsilon}{1800\pi a_j} = \frac{0.8147 \times 10^{-8}\,|z_j|}{a_j} \tag{7-1-2}$$

Therefore, if Λ^0 is the limiting equivalent conductance of an electrolyte dissociating into p kinds of ions, we write

$$\Lambda^0\eta_0 = 0.8147 \times 10^{-8} \sum_{j=1}^{p} \frac{|z_j|}{a_j} \tag{7-1-3}$$

Ionic radii calculated by (7-1-2) are of the order of one to three Ångstroms for the elementary ions,[3] which is in agreement with estimates of (solvated) ionic radii deduced from other data.[4] Since solvation of ions is clearly indicated by a variety of phenomena, a_j (and hence $\lambda_j^0\eta_0$) would be expected to depend to some extent upon the nature of the solvent, and to

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[1] P. Walden, *Z. physik. Chem.*, **55**, 207, 246 (1906).

[2] J. J. Hermans [*Z. physik.*, **97**, 681 (1935)] derived a more exact equation for the velocity of an ion by taking the interaction of solvent dipoles into account.

[3] The value thus calculated for the hydrogen ion is a noteworthy exception, being about ¼Ångstrom in water. Since there is independent evidence that the high conductance of these ions is mainly due to successive exchanges between solvent molecules, the inapplicability of Stokes' law could be anticipated. In this connection, the experiments of L. E. Baker and V. K. La Mer [*J. Chem. Phys.*, **3**, 406 (1935)] are of particular interest. See also L. G. Longsworth and D. A. MacInnes, *J. Am. Chem. Soc.*, **59**, 1666 (1937).

[4] H. Ulich, *Z. Elektrochem.*, **36**, 497 (1930).

a lesser degree upon the temperature. This subject has been thoroughly investigated by Walden,[5] who showed that the products, $\lambda_j^0\eta_0$ and $\Lambda^0\eta_0$, are practically independent of the temperature,[6] and exhibit less than a twofold variation from solvent to solvent. This approximate constancy,

TABLE (7-1-1).* THE EFFECT OF TEMPERATURE UPON $\lambda_j^0\eta_0$ AND $\Lambda^0\eta_0$.

Ion	Solvent	$\lambda_j^0\eta_0$		
H^+	Water	3.99 (0°)	3.14 (25°)	1.81 (100°)
Na^+	"	0.466 "	0.459 "	0.43 "
Cl^-	"	.741 "	.682 "	.59 "
$(C_2H_5)_4N^+$	"	.287 "	.295 "	.293 "
Picrate⁻	"	.269 "	.274 "	.27 "
$\frac{1}{2}SO_4^{--}$	"	.73 "	.724 "	—
Electrolyte		$\Lambda^0\eta_0$		
NaI	Ethanol	.529 (0°)	.524 (25°)	.527 (50°)
$(CH_3)_4NCl$	"	.524 "	.549 "	.555 (56°)
$(C_2H_5)_4N$ Picrate	"	.567 "	559 "	.564 "
$(C_2H_5)_4N$ Picrate	Acetone	.568 "	.568 "	.560 (50°)
NaI	"	557 "	.578 "	.570 (40°)
NaI	Isobutanol	.489 "	.488 "	.471 (50°)
NaI	Pyridine	.638 "	.637 (20°)	.640 "
KI	Nitromethane	.765 "	.77 (25°)	.75 (55°)

* H. Ulich, *Fortschritte Chem.*, **18**, No. 10 (1926).

TABLE (7-1-2).* THE PRODUCT $\lambda_j^0\eta_0$ IN VARIOUS SOLVENTS AT 25°.

Solvent	K^+	Na^+	I^-	CNS^-	$(C_2H_5)_4N^+$	Picrate⁻
Water	0.668	0.459	0.686	0.598	0.295	0.269
Methanol	.292	.251	.332	.327	.294	.267
Ethanol	.267	.238	.285	.28	.295	.263
Acetone	.222	.217	.366	.40	.294	.266
Furfural	.215	.190	.424	—	.293	—
Acetonitrile	.31	.28	.38	.44	.294	—
Pyridine	.27	.22	.42	.45	.294	—

* H. Ulich and E. R. Birr, *Z. Angew. Chem.*, **41**, 443 (1928). See also H. Ulich, *Trans. Faraday Soc.*, **23**, 388 (1927).

$$\left.\begin{aligned}\lambda_j^0\eta_0 &= \\ \Lambda^0\eta_0 &= \end{aligned}\right\}\text{constant} \qquad (7\text{-}1\text{-}4)$$

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[5] A comprehensive review is given by P. Walden, "Elektrochemie nicht-wässeriger Lösungen," Barth, Leipzig, 1924. For more recent discussions, consult P. Walden and H. Ulich, *Z. physik. Chem.*, **114**, 297 (1925); P. Walden, H. Ulich, and G. Busch, *Ibid.*, **113**, 429 (1926); H. Ulich, *Fortschritte Chem.*, **18**, No. 10 (1926); H. Schmick, *Z. physik.*, **24**, 56 (1924); R. T. Lattey, *Phil. Mag.*, **6**, 258 (1928). *Cf.* M. Born, *Z. Physik.*, **1**, 221 (1920).

[6] P. Walden and H. Ulich, *Z. physik. Chem.*, **107**, 219 (1923); H. Ulich, *Fortschritte Chem.*, **18**, No. 10 (1926). The most pronounced variations with temperature are found in systems containing hydrogen ions, or highly associated or highly viscous solvents.

was discovered experimentally,[7] and is known as Walden's rule. Very large spherical ions would be nearly free from solvation because of the low charge density on their surfaces, and the magnitude of their radii would be independent of the nature of the solvent. Such ions would most nearly approximate the ideal condition of spheres moving through homogeneous media, as required by Stokes' law. Ions of small size, or of unsymmetrical shape or distribution of charge, would be expected to show most serious departures from Walden's rule, especially when compared in solvents of widely differing polarizability and molecular volume. An idea of the magnitudes of the effects of these factors may be gained from inspection of Tables (7-1-1) and (7-1-2).

(2) ASSOCIATION INTO ION PAIRS. ESTIMATION OF DISSOCIATION CONSTANTS

Although the Ostwald dilution function

$$K = \frac{\Lambda^2 c}{\Lambda^0(\Lambda^0 - \Lambda)} \tag{7-2-1}$$

is unsatisfactory when applied to aqueous solutions of strong electrolytes, it is a close approximation to the behaviors of dilute solutions of weak electrolytes in water, or of strong electrolytes in solvents of low dielectric constants. In these solvents, strong electrolytes are all highly associated, even at the lowest experimentally attainable concentrations. This condition makes it necessary to determine Λ^0 and K simultaneously from the same data. This can be done by assigning successive values to Λ^0 until K, calculated by (7-2-1), is independent of the concentration in dilute solution; but graphical methods are more satisfactory. Kraus and Bray[8] rearranged equation (7-2-1) to read

$$\frac{1}{\Lambda} = \frac{1}{\Lambda^0} + \frac{c\Lambda}{K(\Lambda^0)^2} \tag{7-2-2}$$

and determined $1/\Lambda^0$ and $1/K(\Lambda^0)^2$ as intercept and slope, respectively, of a plot of $1/\Lambda$ against $c\Lambda$. They prepared plots of this nature for a large number of salts, both organic and inorganic, in liquid ammonia, liquid sulfur dioxide, and in many organic solvents. They surveyed the literature up to 1912, and concluded that the mass action expression [Equation (7-2-1)] is obeyed in *all* solutions of electrolytes in which the ion concentration is less than 10^{-3} or 10^{-4} N. They also pointed out that the divergence from the equation, which becomes increasingly apparent at higher concentrations, is a function of the ion concentration rather than of the total concentration of the solute.*

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[7] P. Walden, *Z. physik. Chem.*, **55**, 207, 249 (1906). *Cf.* G. Angel, *Ibid.*, **A 170**, 81 (1934).

[8] C. A. Kraus and W. C. Bray, *J. Am. Chem. Soc.*, **35**, 1315 (1913).

* On the basis of insufficiently precise transference numbers, they rejected the suggestion of A. Schanov [*Z. physik. Chem.*, **83**, 129 (1913)] that the presence of complex ions and molecules,

Precise modern measurements, as well as theory, show that equation (7-2-1) is not exact, even at ionic concentration as low as $10^{-4}N$, because of the neglect of long-range interionic attraction upon the conductance and the activities of the ion. Fuoss and Kraus[9] developed a graphical method which took account of these effects by successive approximation. Since much of the laboriousness of this method is eliminated by the use of a table given by Fuoss,[10] the original method will not be given.

For a completely dissociated electrolyte, the conductance would be $\Lambda^0 - \mathcal{S}_{(\Lambda)}\sqrt{c}$ at high dilution [Equation (5-3-1)]. If the fraction of the electrolyte present as ions is α, then the mean ionic concentration is αc, and the equivalent conductance would be

$$\Lambda = \alpha(\Lambda^0 - \mathcal{S}_{(\Lambda)}\sqrt{\alpha c}) \tag{7-2-3}$$

and the degree of dissociation is

$$\alpha = \frac{\Lambda}{\Lambda^0(1 - \mathcal{S}_{(\Lambda)}\sqrt{\alpha c}/\Lambda^0)} \tag{7-2-4}$$

In the limit, these equations reduce to $\alpha = \Lambda/\Lambda^0$ upon which (7-2-1) is based. By the simple expedient of successive substitution of equation (7-2-4) back into its own correction term, $1 - \mathcal{S}_{(\Lambda)}\sqrt{\alpha c}/\Lambda^0$, the latter may be replaced by the continued fraction

$$F(Z) = 1 - Z\{1 - Z[1 - Z(\text{etc.})^{-1/2}]^{-1/2}\}^{-1/2} \tag{7-2-5}$$

in which

$$Z = \mathcal{S}_{(\Lambda)}\sqrt{\Lambda c}(\Lambda^0)^{-3/2} \tag{7-2-6}$$

Fuoss[11] tabulated numerical values of $F(Z)$, for $0 \leq Z \leq 0.209$, by intervals of 0.001, so that α can be calculated by

$$\alpha = \frac{\Lambda}{\Lambda^0 F(Z)} \tag{7-2-7}$$

$$(\mathrm{CA})_2 \rightleftharpoons 2(\mathrm{CA}) \tag{A}$$
$$(\mathrm{CA})_2 \rightleftharpoons \mathrm{C}^+ + \mathrm{CA}_2^- \tag{B}$$
$$\mathrm{CA} \rightleftharpoons \mathrm{C}^+ + \mathrm{A}^- \tag{C}$$

might explain the deviation from the mass action law for the simple ionization represented by (C). Twenty years later, Kraus, with Fuoss, brilliantly applied these equilibria to the interpretation of the conductance curves of salts in solvents of low dielectric constants.

[9] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 476 (1933).

[10] R. M. Fuoss, *J. Am. Chem. Soc.*, **57**, 488 (1935).

[11] R. M. Fuoss, *J. Am. Chem. Soc.*, **57**, 488 (1935).

$$F(Z) = \frac{4}{3}\cos^2\frac{1}{3}\cos^{-1}\left(\frac{-3\sqrt{3}Z}{2}\right)$$

Cf. D. J. Mead, R. M. Fuoss and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

when Λ^0 is known. The evaluation of Λ^0 usually requires a short series of approximations, which may begin with a rough value of Λ^0 obtained by free-hand extrapolation of the conductance data, or the application of Walden's rule. This preliminary value of Λ^0 leads to approximate values of $F(Z)$ and α. These values of α are used to estimate the activity coefficient by the limiting law*

$$\log y_{\pm} = -\mathcal{S}_{(f)}\sqrt{\alpha c} \tag{7-2-8}$$

or by equation (5-2-8). The expression

$$\frac{F(Z)}{\Lambda} = \frac{1}{\Lambda^0} + \frac{[c\Lambda y_{\pm}^2/F(Z)]}{K(\Lambda^0)^2} \tag{7-2-9}$$

obtained by combining the thermodynamic ionization constant

$$K = \frac{c\alpha^2 y_{\pm}^2}{1 - \alpha} \tag{7-2-10}$$

with equation (7-2-7), requires that $1/(K(\Lambda^0)^2)$ be the slope of a plot[12] of $F(Z)/\Lambda$ against $c\Lambda y_{\pm}^2/F(Z)$, and that $1/\Lambda^0$ be the intercept obtained by extrapolation. Such an extrapolation, based on the first approximate values of $F(Z)$ and $y_{\pm}$, yields a value of Λ^0 from which more accurate values of $F(Z)$ and $y_{\pm}$ may be obtained and a new plot constructed. This process is repeated until a final value of Λ^0 is found to satisfy all the equations (7-2-7), (7-2-8) and (7-2-9), and then K is derived from the plot based upon this value of Λ^0.

The use of equation (7-2-9) is illustrated in Figure (7-2-1). The plot is based upon the final values of α calculated by Shedlovsky and Uhlig[13] from their measurements of the conductance of sodium guaiacolate in wet guaiacol solutions at 25°. The experimental data are represented by a straight line whose intercept is 0.143 and whose slope is 416. These values correspond to $\Lambda^0 = 7.5$ and $K = 4.27 \times 10^{-5}$. Although the linearity of the plot is a strong argument in support of the general validity of the method, Shedlovsky and Uhlig offer independent confirmation of equation (7-2-4) by showing that the variation of α with concentration is consistent with their distribution measurements.[14]

Although the method just described is quite satisfactory under proper conditions, its application is restricted by the use of the limiting conductance equation (5-3-1), and the practical necessity of having Fuoss' tabulation of $F(Z)$ at hand. If equation (6-3-10) is used to represent the

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* Compare equations (5-2-2) and (1-8-14).

[12] Fuoss concluded that this plot should be linear for concentrations less than $3 \times 10^{-7}D^3$.

[13] T. Shedlovsky and H. H. Uhlig, *J. Gen. Physiol.*, **17**, 549 (1934).

[14] T. Shedlovsky and H. H. Uhlig, *J. Gen. Physiol.*, **17**, 570 (1934).

conductance of the hypothetical completely dissociated electrolyte, the concentration range is extended considerably beyond that covered by the limiting law, and Shedlovsky[15] has shown that $F(Z)$ may be replaced by a much simpler function. Thus, if we set the observed conductance equal to the degree of dissociation times the conductance given by (6-3-10), we obtain a quadratic equation

$$\alpha = \frac{\Lambda}{\Lambda^0} + \left(\frac{\mathcal{S}_{(\Lambda)}}{(\Lambda^0)^2}\right)\Lambda\sqrt{\alpha c} \qquad (7\text{-}2\text{-}11)$$

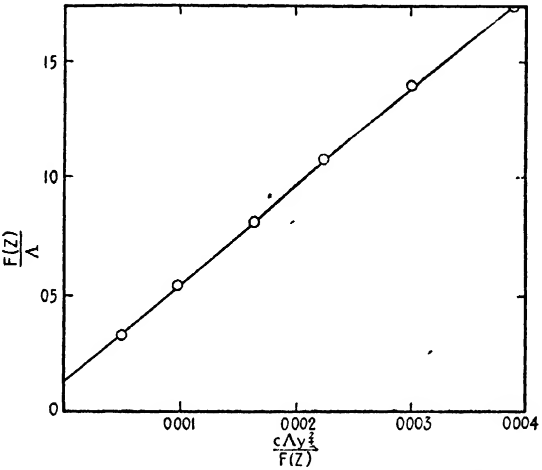

Fig. (7-2-1). Evaluation of K and $\Lambda°$ by equation (7-2-9). Sodium guaiacolate in wet guaiacol solutions at 25°.

instead of the cubic equation (7-2-4). Solution of (7-2-11) for α in terms of the variable Z, defined by (7-2-6), leads to

$$\alpha = \frac{\Lambda}{\Lambda^0}\left[\frac{Z}{2} + \sqrt{1 + \left(\frac{Z}{2}\right)^2}\right]^2 \equiv \frac{\Lambda}{\Lambda^0}S(Z) \qquad (7\text{-}2\text{-}12)$$

The bracketed term may be used in the expanded form

$$S(Z) = 1 + Z + \frac{Z^2}{2} + \frac{Z^3}{8} - \cdots \qquad (7\text{-}2\text{-}13)$$

for small values of Z. Ordinarily, it is not necessary to employ terms higher than Z^2 in evaluating $S(Z)$.

Combination of equation (7-2-12) with (7-2-10) gives the expression

$$\frac{1}{\Lambda S(Z)} = \frac{1}{\Lambda^0} + \frac{(c\Lambda y_\pm^2 S(Z))}{K(\Lambda^0)^2} \qquad (7\text{-}2\text{-}14)$$

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[15] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

corresponding to (7-2-9). In comparing the use of this equation with that of (7-2-9), we shall rearrange them both as follows:

$$\Lambda/F(Z) = \Lambda^0 - (c\alpha^2 y_\pm^2)\Lambda^0/K \tag{7-2-15}$$

$$\Lambda S(Z) = \Lambda^0 - (c\alpha^2 y_\pm^2)\Lambda^0/K \tag{7-2-16}$$

Figure (7-2-2) contains plots of the conductance data of zinc sulfate[16] in water at 25°. The lower curve is based upon equation (7-2-16) and, being very nearly linear, affords a better extrapolation than the upper curve based upon (7-2-15). The intercept and limiting slope of the lower curve yield 132.8 and 0.0049 for Λ^0 and K, respectively. If the same data are treated by the method of Davies [Chapter (6) Section (2)], K is found[17] to lie within the limits 0.0044 and 0.0047. All things considered, equation (7-2-16) appears to furnish the most satisfactory basis for estimating ionization constants from a single series of conductance measurements.[18]

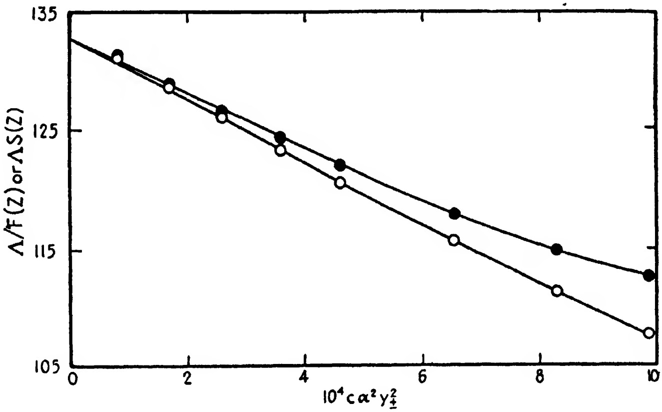

Fig. (7-2-2). Evaluation of Λ^0 and K for zinc sulfate in water at 25°. ●, by equation (7-2-15); ○, by equation (7-2-16); The product, $\alpha y_\pm$, was made equal to the stoichiometrical activity coefficient [Table (13-5-2)]. For further discussion of the extrapolation, see Appendix B, Section (2).

(3) CONFIRMATION OF BJERRUM'S EXTENSION OF THE THEORY OF INTERIONIC ATTRACTION. IONIC PAIR FORMATION AS A FUNCTION OF THE DIELECTRIC CONSTANT

Bjerrum's equation

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{|z_1 z_2|\epsilon^2}{DkT}\right)^3 Q(b) \tag{3-7-13}$$

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[16] B. B. Owen and R. W. Gurry, *J. Am. Chem. Soc.*, **60**, 3074 (1938).

[17] B. B. Owen, *J. Am. Chem. Soc.*, **61**, 1393 (1939).

[18] This is borne out by the calculations of D. Belcher, *J. Am. Chem. Soc.*, **60**, 2745 (1938). The limitations of this procedure have been carefully analyzed by M. L. Kilpatrick, *J. Chem. Phys.*, **8**, 306 (1940).

was deduced [Chapter (3) Section (7)] by considering the effect of Coulomb forces upon ion pair formation. K is the equilibrium constant for the ion pair dissociation,

$$[C^+A^-]^0 \rightleftharpoons C^+ + A^-$$

and b is the parameter

$$b = \frac{|z_1 z_2| \epsilon^2}{aDkT} \tag{3-7-7}$$

Numerical values of the function $Q(b)$ are giv 2-3).

A very important experimental verification of Bjerrum's theory and a proof of the validity of equation (3-7-13) have been presented by Fuoss and Kraus.[19] Their investigations have proved particularly important because, through them, the theory of ionic interaction has been extended to media varying from that of water ($D = 78.54$) to that of dioxane ($D = 2.1$). For this purpose, they employed their extensive conductance data on tetraisoamyl ammonium nitrate in dioxane-water mixtures. Ionic association was noticeable, but not very pronounced in a solution containing 53 per cent H_2O ($D = 38$ at 25°). It was therefore practicable to extrapolate the data according to Onsager's approximate equation (6-3-3) to obtain Λ^0, and a rough estimate of K. A more accurate value of K was then obtained by consideration of activity coefficients at several low concentrations. In the solvent mixtures in which the dielectric constant was 11.9 and 8.5 (20.2 and 14.95 per cent H_2O), Λ^0 and K were evaluated by the intercept method described in the preceding section. Their data did not extend to sufficiently high dilutions to use this method at lower dielectric constants, so for the mixtures in which the dielectric constant is 5.84, or less, they assumed "reasonable values" of Λ^0 based on Walden's rule (7-1-4), and estimated the corrections due to interionic attraction. Values of K calculated in this manner increased with concentration, because of triple ion formation, and had to be extrapolated to zero concentration.

These values of K may be used to calculate the parameter a by equations (3-7-13) and (3-7-7) in conjunction with a plot of $\log Q(b)$ against $\log b$ [Table (5-2-3)]. By substitution of the numerical values of the constants, these equations become

$$-\log K = 6.120 - 3 \log D + \log Q(b) \tag{7-3-1}$$

and

$$-\log b = 5.254 + \log D + \log a \tag{7-3-2}$$

at 25°. The results of these calculations of Fuoss and Kraus are given in Table (7-3-1). In spite of the difficulties involved in the estimation of

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[19] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 1019 (1933).

K in the solvents of lowest dielectric constants, the variation of K with D is sufficiently pronounced in these media to permit a significant test of the theory. It will be observed that the calculated values of a are fairly constant over the entire range of the mixtures. The maximum difference between any two values is 11 per cent, so it seems possible that the average value of a ($= 6.4 \times 10^{-8}$) would represent all the data within the combined uncertainties of the calculations and the experimental measurements. Fuoss and Kraus point out that, in all the solvent mixtures included in the table, the molar water concentration is always much greater than that of the solute, and in view of the high polar moment of water (1.85) compared to that of dioxane (<0.4), we might expect the relative hydration of the solute ions and, therefore, their effective diameter, a, to be practically constant.

TABLE (7-3-1). CONSTANTS FOR TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE-WATER MIXTURES AT 25°.

Wt. % H_2O	D*	$-\log K$	K	$a \times 10^8$
0.60	2.38	15.7	2×10^{-16}	6.01
1.24	2.56	14.0	1×10^{-14}	6.23
2.35	2.90	12.0	1×10^{-12}	6.36
4.01	3.48	9.6	2.5×10^{-10}	6.57
6.37	4.42	7.53	3.0×10^{-8}	6.65
9.50	5.82	5.78	1.65×10^{-6}	6.45
14.95	8.50	4.00	1.00×10^{-4}	6.50
20.2	11.9	3.08	9.0×10^{-4}	6.70
53.0	38.0	0.60	2.5×10^{-1}	6.15

* These values of D used by Fuoss and Kraus are somewhat higher than those in Table (5-1-4).

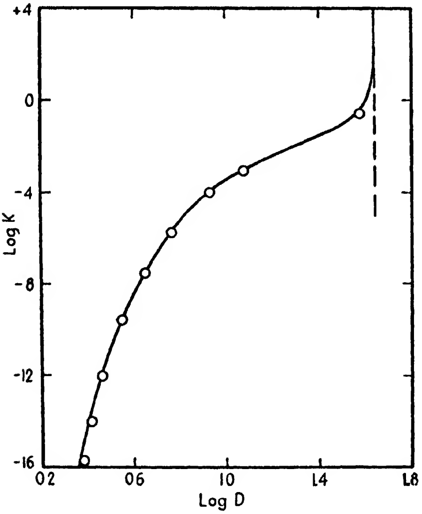

Fig. (7-3-1) Dissociation of ion pairs as a function of the dielectric constant. Tetraisoamylammonium nitrate in dioxane-water mixtures at 25°

Accordingly the single value a ($= 6.4 \times 10^{-8}$) was used to calculate K by equations (7-3-1) and (7-3-2) for various values of D. These calculated values are represented graphically by the smooth curve in Fig. (7-3-1). The experimental points taken from Table (7-3-1) are seen to be in striking agreement with the general course of this curve throughout a range of fifteen powers of ten in the constant K. The curve has a vertical asymptote corresponding to $D = 43.6$, which implies that tetraisoamylammonium nitrate cannot form stable ion pairs in dioxane-water mixtures when the dielectric constant is equal to, or greater than, this critical value.

(4) ASSOCIATION INTO COMPLEX AGGREGATES. TRIPLE IONS, QUADRUPOLES, AND THE CONDUCTANCE MINIMUM

As shown by Figure (7-4-1), when the dielectric constant of the solvent is of the order of 10 or less, a minimum is observed in the conductance curves in dilute solution. With further decrease in dielectric constant, the minimum becomes more distinct and its position shifts in the direction of increasing dilution. To account for the increase in the number of ions, per mol, as the solute concentration increases, Fuoss and Kraus[20] postulated the combination of ions with ion pairs to form "triple ions" according to the scheme

$$[A^+B^-A^+]^+ \rightleftharpoons A^+ + [A^+B^-]^0 \qquad (7\text{-}4\text{-}1)$$

$$[B^-A^+B^-]^- \rightleftharpoons B^- + [A^+B^-]^0 \qquad (7\text{-}4\text{-}2)$$

They pointed out that triple ions should be stable because the excess potential energy due to the third ion is several times as great as the mean thermal energy of the ions in a solvent of low dielectric constant.

If the simple ions are spherical, and the same size, the two triple-ion combinations should be formed to an equal extent, and we may write[21]

$$\frac{(AB)(B^-)}{(BAB^-)} = \frac{(AB)(A^+)}{(ABA^+)} = K_3 \qquad (7\text{-}4\text{-}3)$$

If we consider the simple equilibrium,

$$[A^+B^-]^0 \rightleftharpoons A^+ + B^-; \qquad y_\pm^2 \frac{(A^+)(B^-)}{(AB)} = K \qquad (7\text{-}4\text{-}4)$$

and let $\alpha = (A^+)/c$ and $\alpha_3 = (ABA^+)/c$, then all the equilibria may be considered simultaneously, and the concentrations of single ions, double ions, and triple ions will be $c\alpha$, $c(1 - \alpha - 3\alpha_3)$, and $c\alpha_3$, respectively. Sub-

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[20] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 2387 (1933).

[21] The assumption of equal ion size avoids the complication of considering two different triple-ion constants, which could not, at present, be independently evaluated. Whatever approximation is involved in this assumption will appear in the average ion size computed from K_3. See M. Dole, *Trans. Electrochem. Soc.*, **77**, 385 (1940). C. B. Wooster, *J. Am. Chem. Soc.*, **60**, 1609 (1938).

stituting these terms in the above equations, and solving for α and α_3, we obtain

$$\alpha_3 = \frac{c\alpha}{K_3}(1 - \alpha - 3\alpha_3) = (\sqrt{Kc}/K_3)(1 - \alpha - 3\alpha_3)^{3/2} y_\pm^{-1} \qquad (7\text{-}4\text{-}3a)$$

and

$$\alpha = \sqrt{K/c}\,(1 - \alpha - 3\alpha_3)^{1/2} y_\pm^{-1} \qquad (7\text{-}4\text{-}4a)$$

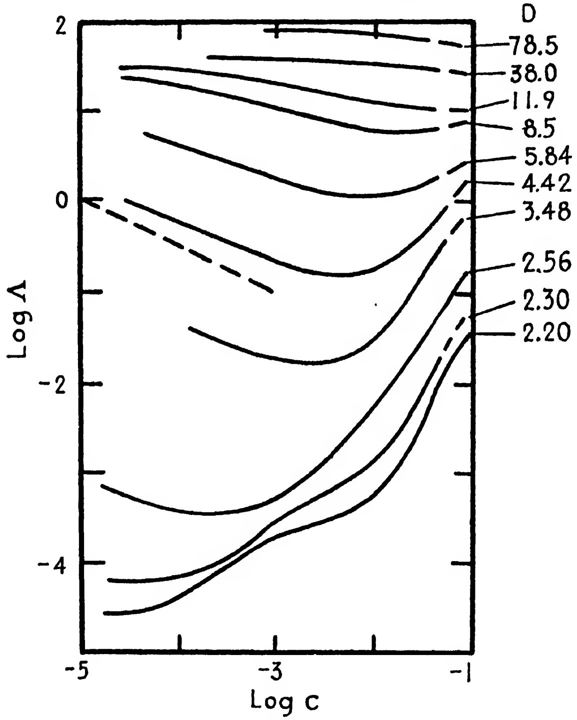

Fig. (7–4–1). The influence of dielectric constant upon the variation of conductance with concentration. Tetraisoamylammonium nitrate in dioxane-water mixtures at 25°. Dielectric constants are indicated at the right hand margin. Experimental curves after Fuoss and Kraus

Writing Λ_3^0 for the sum of the limiting conductances of the two kinds of triple ions, the function

$$\Lambda = (\alpha\Lambda^0 + \alpha_3\Lambda_3^0)(1 - \mathfrak{S}_{(\Lambda)}\sqrt{c(\alpha + \alpha_3)}/\Lambda^0) \qquad (7\text{-}4\text{-}5)$$

should approximately express the conductance in dilute solutions. According to equation (7-2-8),

$$y_\pm^{-1} = \exp\,(2.303\mathfrak{S}_{(f)}\sqrt{c(\alpha + \alpha_3)}) \qquad (7\text{-}4\text{-}6)$$

In order to combine these four equations, it will be necessary to introduce an additional approximation. Fuoss and Kraus assume that

$$c(\alpha + \alpha_3) \simeq c\Lambda/\Lambda^0 \qquad (7\text{-}4\text{-}7)$$

and

$$(1 - \alpha - 3\alpha_3) \simeq (1 - \Lambda/\Lambda^0) \qquad (7\text{-}4\text{-}8)$$

so that their final combined equation, rearranged for extrapolation, becomes

$$\Lambda\sqrt{c}\cdot g(c) = \sqrt{K}\Lambda^0 + (\sqrt{K}\Lambda_3^0/K_3)(1 - \Lambda/\Lambda^0)c \qquad (7\text{-}4\text{-}9)$$

where

$$g(c) \equiv \frac{\exp(-2.303\,\mathcal{S}_{(f)}\sqrt{c\Lambda/\Lambda^0})}{(1 - \mathcal{S}_{(\Lambda)}\sqrt{c\Lambda/\Lambda^0}/\Lambda^0)(1 - \Lambda/\Lambda^0)^{1/2}} \qquad (7\text{-}4\text{-}10)$$

Since both c and Λ/Λ^0 are ordinarily much less than unity, this equation may be used in the approximate form[22]

$$\log g(c) \simeq \left[\frac{0.4343\,\mathcal{S}_{(\Lambda)} - \mathcal{S}_{(f)}\Lambda^0}{(\Lambda^0)^{3/2}}\right]\sqrt{c\Lambda} + \frac{0.2171\Lambda}{\Lambda^0} \qquad (7\text{-}4\text{-}10a)$$

The term $g(c)$ accounts for the effects of the ionic atmosphere upon the mass action expression and the conductance. If the conductance minimum occurs above $10^{-3}N$, the approximations involved in equation (7-4-9) are too crude for a quantitative treatment of the data unless the measurements extend to very low concentrations.

It is apparent from equation (7-4-9) that a plot of $\Lambda\sqrt{c}g(c)$ against $(1 - \Lambda/\Lambda^0)c$ will be a straight line with intercept, $\Lambda^0\sqrt{K}$, and slope, $\Lambda_3^0\sqrt{K}/K_3$. Such a plot is shown in Fig. (7-4-2). In order to estimate the individual values of K and K_3, Λ^0 and Λ_3^0 must be known. Λ^0 cannot be directly determined in solvents of very low dielectric constants, but Walden's rule (7-1-4) yields a good approximation for Λ^0. The product, $\Lambda^0\eta_0$, can be determined in solvents of sufficiently high dielectric constants to allow extrapolation. The value of Λ_3^0 cannot be directly determined in any medium, but the ratio Λ_3^0/Λ^0 may be estimated from a study of the temperature coefficient of the conductance,[23, 24] if it be assumed that Λ_3^0/Λ^0 is independent of T. Since the variation of K_3 with temperature and dielectric constant is of greater theoretical interest than its absolute magnitude, it is sufficient for most purposes to set Λ_3^0/Λ^0 equal to some

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[22] Compare D. J. Mead and R. M. Fuoss, *J. Am. Chem. Soc.*, **62**, 1720 (1940), footnote (5).

[23] R. M. Fuoss, *J. Am. Chem. Soc.*, **56**, 1857 (1934); footnote (7).

[24] G. S. Bien, C. A. Kraus and R. M. Fuoss, *Ibid.*, **56**, 1860 (1934).

"reasonable" constant fraction, say 1/3 or 1/2, in all media and at all temperatures.[25]

A simpler, but somewhat less accurate, estimate of K_3 in terms of Λ^0/Λ_3^0 depends upon the numerical values of the minimum conductance and the concentration at which it appears. If we neglect $g(c)$ and the factor, $1 - \Lambda/\Lambda^0$, in equation (7-4-9), differentiate, and impose the condition for a minimum, we obtain the relation

$$K_3 = c_{\min}\Lambda_3^0/\Lambda^0 \tag{7-4-11}$$

which, upon recombination with (7-4-9), yields

$$\sqrt{K} = \frac{(c\Lambda)_{\min}}{2\Lambda^0} \tag{7-4-12}$$

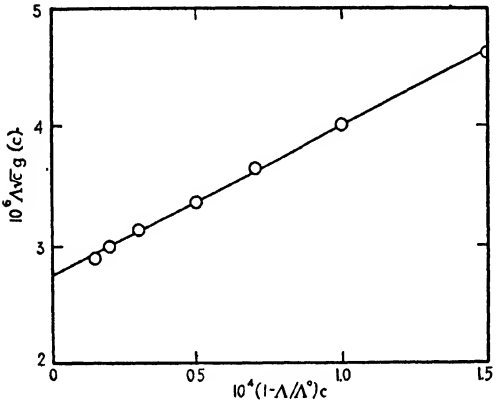

Fig. (7-4-2)
Plot according to equation (7-4-9) with $g(c)$ estimated by equation (7-4-10a). Tetraisoamylammonium nitrate in dioxane solutions containing 1.24 per cent water ($t = 25°$, $D = 2.56$)

Since the graphical determination of $c_{\min}$ and $\Lambda_{\min}$ is not very precise, and the correction term, $g(c)$, is neglected in the derivation of equation (7-4-11), K_3 is more accurately evaluated from the slopes and intercepts of plots such as the one illustrated in Figure (7-4-2). The experimental values of $-\log K_3$ given in Table (7-4-1) were obtained in this manner. Note that K_3 and the concentration at the minimum increase rapidly with the dielectric constant.

We are now in a position to apply the theory of "triple ion formation" developed in Chapter (3), Section (7). According to this theory, K_3 may be computed by the equation

$$K_3^{-1} = \frac{2\pi N a_3^3}{1000} I(b_3) \tag{7-4-13}$$

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[25] M. Born, *Z. Physik.*, **1**, 221 (1920); H. Schmick, *Ibid.*, **24**, 56 (1924); R. T. Lattey, *Phil. Mag.*, **6**, 258 (1928). The coefficient $d\lambda_j^0/dT$ is practically the same for most large ions.

where

$$b_3 = \frac{|z_+ z_-| \epsilon^2}{a_3 DkT} \tag{7-4-14}$$

and $I(b_3)$ as a function of b_3 is given in Table (5-2-4). Consideration of boundary conditions leads to the conclusion that triple ions are unstable ($K_3 = \infty$) with respect to thermal agitation when $b_3 \leq 8/3$. Therefore, according to equation (7-4-14), triple ion formation can not take place in solvents in which

$$D \geq \frac{3|z_+ z_-| \epsilon^2}{8 a_3 kT} \tag{7-4-15}$$

The existence of such a critical value of D is indicated in Figure (7-4-1) by the disappearance of the conductance minimum with increasing dielectric constant.

TABLE (7-4-1).* TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE-WATER MIXTURES AT 25°.

Wt. % H_2O	D	$-\log c_{(\min)}$	$-\log K_{3(\exp)}$	$-\log K_{3(\text{calc})}$
0.60	2.38	4.10	4.68	4.34
1.24	2.56	3.60	4.12	4.03
2.35	2.90	3.15	3.50	3.56
4.01	3.48	2.60	3.00	3.02
6.37	4.42	2.30	2.5	2.50
9.50	5.84	2.05	2.0	2.06
14.95	8.50	1.60	—	1.56

* Taken from Table III of the paper by R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 2387 (1933).

In fitting equation (7-4-13) to the data for tetraisoamylammonium nitrate in dioxane-water mixtures, Fuoss and Kraus[26] used the value $a_3 = 9 \times 10^{-8}$ cm. The figures recorded in the last column of Table (7-4-1) as $-\log K_{3(\text{calc})}$ are based upon this value. They are in very good agreement with $-\log K_{3(\exp)}$. Referring to Table (7-3-1), we note that it was necessary to use the value $a \simeq 6.4 \times 10^{-8}$ cm to represent ion pair formation in the same solutions. In Figure (7-4-3), the values of $\log K_{3(\exp)}$ given in Table (7-4-1) are shown as circles. The curve is derived from equation (7-4-13) for $a_3 = 9 \times 10^{-8}$ cm. According to equation (7-4-15), the theoretical limit of triple ion formation for this value of a_3 should appear at a dielectric constant of 23.2.

By combination with equations (7-4-11) and (7-4-14), equation (7-4-13) may be put in the form

$$\frac{D^3}{c_{\min}} = \left(\frac{\Lambda_3^0 2\pi N\epsilon^6}{\Lambda^0 1000 k^3 T^3}\right) \frac{I(b_3)}{b_3^3} \tag{7-4-16}$$

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[26] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 2387 (1933).

Fuoss and Kraus suggested this relation as a probable explanation of the empirical rule, $D^3/c_{\min} = \text{constant} \ (\simeq 3 \times 10^4)$, discovered by Walden,[27] because the ratio $I(b_3)/b_3^3$ is not very sensitive to the value of b_3 within the region of the inflection [Fig. (7-4-3)].*

Association into more complex aggregates than triple ions would be expected in solvents of very low dielectric constant, and progress has already been made in the numerical consideration of quadrupole formation from ion pairs. The existence of quadrupoles is implied by inflections just above the minima in the conductance concentration curves for alkylammonium salts in benzene[28] and dioxane,[29] and by the apparent molecular weights of the solutes derived from cryoscopic data.[30] Moreover, the observed conductance is so small that it can be assumed, as a first approximation, that the concentrations of single ions, triple ions, and other charged aggregates are negligible compared to the concentrations of neutral ion pairs and quadrupoles. Over the limited concentration range in which this approximation is valid, we need only consider the equilibrium

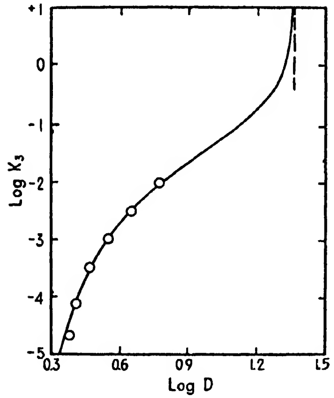

Fig. (7-4-3)
The influence of dielectric constant upon the dissociation of triple ions. Tetraisoamylammonium nitrate in dioxane-water mixtures at 25°

$$[A^+B^-]^0[A^+B^-]^0 \rightleftharpoons 2[A^+B^-]^0 \qquad (7\text{-}4\text{-}17)$$

[27] P. Walden, *Z. physik. Chem.*, **147A,** 1 (1930).

* Numerically, (7-4-16) becomes

$$\frac{D^3}{c_{\min}} = 0.66 \times 10^6 \frac{\Lambda_3^0}{\Lambda^0} \frac{I(b_3)}{b_3^3} \text{ at } 25°$$

For large ions, say $a_3 = 10^{-7}$ cm and $D = 3$, or 4, $I(b_3)/b_3^3$ is of the order of 0.1 to 0.5. Since Walden found that $D^3/c_{\min} \simeq 3 \times 10^4$, it follows that Λ_3^0/Λ^0 is of the order ½ to 1. This is certainly a physically reasonable result.

[28] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55,** 3614 (1933); W. F. Luder and C. A. Kraus, *Ibid.*, **58,** 255 (1936).

[29] R. M. Fuoss and C. A. Kraus, *Ibid.*, **55,** 21 (1933).

[30] F. M. Batson and C. A. Kraus, *J. Am. Chem. Soc.*, **56,** 2017 (1934); C. A. Kraus and R. A. Vingee, *Ibid.*, **56,** 511 (1934).

which defines the constant

$$K_4 = \frac{(\mathrm{AB})^2}{([\mathrm{AB}][\mathrm{AB}])} \tag{7-4-18}$$

By introducing the assumption that a quadrupole can be represented by an ellipsoid (of axes a and λa), containing a point dipole of strength μ at its center, and parallel to the major axis, Fuoss and Kraus[31] derived the expression

$$K_4^{-1} = \frac{N}{2000}\left(\frac{\pi}{3}\right)^{3/2} \frac{\mu^2}{DkT}\frac{e^y}{y^{7/2}}(1/(2\lambda^2) - 1)^{-1/2} \tag{7-4-19}$$

previously given as equation (3-7-27). The function, y, is defined by

$$y = \frac{\mu^2}{(\lambda a)^3 DkT} \tag{7-4-20}$$

Freezing point measurements[32] on benzene solutions of tri-isoamylammonium picrate can be satisfactorily represented in terms of equation (7-4-18), leading to the relation[33]

$$K_4 = \frac{c(1-2j)^2}{j} \tag{7-4-21}$$

where j, for an undissociated solute, is given by equation (9-5-21) when $\nu = 1$. It was found graphically that $K_4 = 0.105$ mol per liter at 5.5°. Substitution of this value in (7-4-19) results in the physically reasonable value, $\lambda a = 5.54 \times 10^{-8}$. In this case, the approximations underlying equation (7-4-21) seem justified by the data throughout the concentration range, 0.002 to 0.03N.

Making use of the same elliptical model postulated in the derivation of equation (7-4-19), Fuoss[34] showed that the limiting slope for a plot of the molecular polarization, P_2, of the solute against concentration should be

$$\left(\frac{dP_2}{dc}\right)^{\cdot}_{c\to 0} = -\frac{4\pi}{D}\left(\frac{\pi}{3}\right)^{3/2}\left(\frac{N\mu}{3kT}\right)^2 \frac{\mu^2}{1000}\frac{e^y}{y^{7/2}}\left(\frac{1}{2\lambda^2} - 1\right)^{-1/2} \tag{7-4-22}$$

This equation may be combined with (7-4-19) to express K_4 as a function of P_2, but the numerical value of K_4 is too sensitive to errors in estimating μ and dP_2/dc to be of much interest. The results derived from some of these dielectric constant studies in benzene solutions are recorded in Table (7-4-2). The large limiting molecular polarizations, P_2^0, of the solutes, and the corresponding polar moments (in Debye units) are given in the second and third columns. The limiting slopes dP_2/dc were obtained

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[31] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **57**, 1 (1935).

[32] F. M. Batson and C. A. Kraus, *J. Am. Chem. Soc.*, **56**, 2017 (1934).

[33] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **57**, 1 (1935).

[34] R. M. Fuoss, *J. Am. Chem. Soc.*, **56**, 1031 (1934).

graphically. The lengths, λa, of the minor axes depend upon the assumption that $\lambda = \frac{1}{2}$. The values obtained from dielectric constant data and equation (7-4-22) are given in the next to last column. They are of the expected order of magnitude, and agree satisfactorily with the two values derived from freezing point data by the use of equations (7-4-21) and (7-4-19). Unfortunately, no quantitative application of the ion pair-quadrupole equilibrium to the interpretation of conductance data has yet been made.

Fuoss[35] has derived the approximate equation

$$\frac{d \ln \Lambda}{d \ln T} = -\frac{d \ln \eta_0}{d \ln T} + \frac{1}{2}\left(1 + \frac{d \ln D}{d \ln T}\right)\left(b - 1 - \frac{4}{b}\right) - \frac{\frac{1}{2}}{(1 + K_3\Lambda^0/\Lambda_3^0 c)}\left(1 + \frac{d \ln D}{d \ln T}\right)\left(b_3 - 4 - \frac{16}{3b_3}\right) \quad (7\text{-}4\text{-}23)$$

TABLE (7-4-2).[1] PROPERTIES OF ELLIPSOIDAL DIPOLE MODELS.

Electrolyte	P_2^0(cc)	$\mu \times 10^{18}$	$\left(\frac{dP_2}{dc}\right)_{c\to 0} \times 10^{-6}$	$a \times 10^8$	
				(D)	(F.P.)
Tetra-n-butylammonium hydroxytriphenylboron	8270	19.7	−14.30	6.37	—
Tetra-iso-amylammonium picrate	7090	18.3	−2.86	6.28	—
Tetra-n-butylammonium picrate	6740	17.8	−1.52	6.28	—
Tri-iso-amylammonium picrate	3830	13.3	−1.12	5.05	5.54[2]
Tri-n-butylammonium picrate	3670	13.1	−0.71	5.02	5.59[3]
Tetra-n-butylammonium acetate	2690	11.2	−0.27	4.59	—

[1] J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, 32, 585 (1936); See also G. S. Hooper and C. A. Kraus' *J. Am. Chem. Soc.*, 56, 2265 (1934); *Proc. Nat. Acad. Sci.*, 19, 939 (1933).

[2] R. M. Fuoss and C. A Kraus, *J. Am. Chem. Soc.*, 57, 1 (1935).

[3] D. A. Rothrock and C. A. Kraus, *Ibid.*, 59, 1699 (1937).

for the temperature dependence of the conductance of strong electrolytes in media of low dielectric constants. It is based upon equation (7-4-9), and is therefore valid only when $\alpha \ll 1$, and at values of c less than the concentration at which Λ is a minimum. It is further restricted to systems for which $b_3 > 10$, because use is made of an asymptotic expansion of equation (7-4-13). The assumption of three physical restrictions is also made, namely

$$\frac{d(\Lambda^0 \eta_0)}{dT} = \frac{d(\Lambda_3^0 \eta_0)}{dT} = 0 \quad (7\text{-}4\text{-}24)$$

$$\frac{da}{dT} = \frac{da_3}{dT} = 0 \quad (7\text{-}4\text{-}25)$$

and

$$\frac{d(\Lambda^0/\Lambda_3^0)}{dT} = 0 \quad (7\text{-}4\text{-}26)$$

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[35] R. M. Fuoss, *J. Am. Chem. Soc.*, 56, 1857 (1934).

The application of equation (7-4-23) to conductance data requires a series of plots and successive approximations, and also involves Walden's rule (7-1-4) in the estimation of Λ^0. The details of this calculation are given by Bien, Kraus and Fuoss,[36] who verified equation (7-4-23) with their measurements of the conductance of tetrabutylammonium nitrate and picrate in anisole ($D = 4.29$ at 25°) at temperatures between −33 and 95°. They plotted their data, as in Figure (7-4-2), and obtained $\Lambda_3^0\sqrt{K}/K_3$ and $\Lambda^0\sqrt{K}$ from the slopes and intercepts. These quantities are recorded in Table (7-4-3) for tetrabutylammonium nitrate. Λ^0 was estimated by the relation, $\Lambda^0\eta_0 = 0.508$, based on measurements in ethylene chloride[37] at 25°. The values of K were calculated from the figures given in columns (2) and (4) of the table, and the corresponding values of a computed by equations (3-7-13) and (3-7-7). The constancy of a may be taken as an indication of the correctness of the values of Λ^0.

The estimation of K_3 was performed in such a manner that the ratio, Λ_3^0/Λ^0, assumed to be independent of the temperature, could be determined from the data. The average value of Λ_3^0/Λ^0 (= 0.82) was then employed to calculate K_3 from each experimental value of $K_3\Lambda^0/\Lambda_3^0$. These values of K_3, together with the corresponding values of a_3, calculated from them, are given in the last two columns of Table (7-4-3). The constancy of a_3 is very satisfactory.

TABLE (7-4-3).* CONSTANTS FOR TETRABUTYLAMMONIUM NITRATE IN ANISOLE.

t°C	$\Lambda^0\sqrt{K} \times 10^4$	$\Lambda_3^0\sqrt{K}/K_3$	Λ^0	$K \times 10^{11}$	$a \times 10^8$	$K_3 \times 10^4$	$a_3 \times 10^8$
−33	0.650	0.115	14.22	2.08	4.88	4.61	5.79
0	2.34	.324	31.8	5.42	4.95	5.89	5.79
25	4.75	.550	49.5	9.20	4.96	7.05	5.84
61.3	10.50	.950	82.1	16.30	4.91	9 04	5.82
80.2	14.70	1.145	102.1	20.65	4 89	10.47	5.88
95.1	18.10	1.288	118.9	23.2	4.85	11.48	5.88

* Taken from Table III of the paper by G. S. Bien, C. A. Kraus and R. M. Fuoss *J. Am. Chem. Soc.*, **56**, 1860 (1934).

With the aid of empirical equations, fitted to their data on the fluidity and molecular polarization of anisole, Bien, Kraus and Fuoss estimated analytically the terms $d \ln \eta_0/dT$ and $d \ln D/d \ln T$. Using the average values of a and a_3, it was then possible to calculate $d \ln \Lambda/dT$ by equation (7-4-23) and compare the results with experimental values read directly (as chord slopes) from a plot of $\ln \Lambda$ against T. This comparison is illustrated by curve I in Fig. (7-4-4). Although the theoretical curve only represents the general course of the experimental values, this is all that could be expected in the light of the complexity of the calculation and the approximations involved. The slope of the theoretical curve is mainly

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[36] G. S. Bien, C. A. Kraus and R. M. Fuoss, *J. Am. Chem. Soc.*, **56**, 1860 (1934).
[37] N. L. Cox, C. A. Kraus and R. M. Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

due to the term $d \ln \eta_0/dT$, which suggests that departures from equation (7-4-24) may be an important factor in the observed discrepancy.

The combination of equation (7-4-23) with (7-4-11) and (7-4-12) permits a comparison with values of $\log c_{\min}$ and $\log \Lambda_{\min}$, read from logarithmic plots of the original data at each temperature. Curves II and III in Fig. (7-4-4) are derived from the foregoing equations, and the observed $\log (c_{\min})$ and $\log (\Lambda_{\min})$ are represented by dots and circles, respectively.

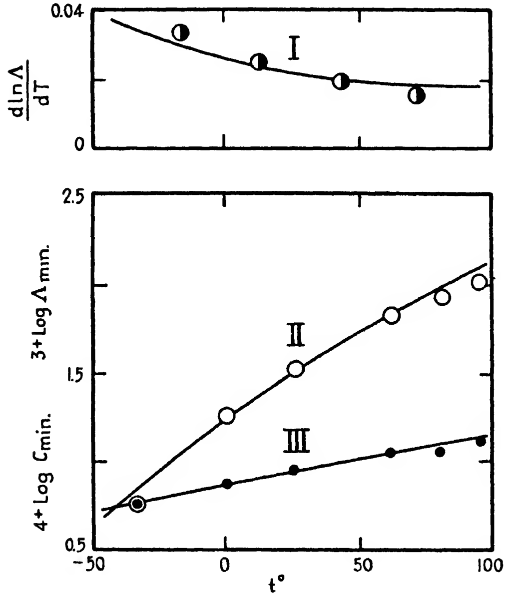

Fig. (7-4-4)
The effect of temperature upon the conductance of tetrabutylammonium nitrate in anisole

(5) THE INFLUENCE OF IONIC SIZE AND STRUCTURE UPON CONDUCTANCE AND ASSOCIATION

Since the extent of ionic association depends upon the potential energy of an ion pair (or more complex aggregate), and this in turn depends upon how close the charges on the ions may be brought together, ionic size is a very important factor in determining the individuality of dissociation constants. The effect of the "a" parameter has been given quantitative expression in the equations of Bjerrum (3-7-13), and of Fuoss and Kraus (7-4-13).

Unfortunately, it is not possible to check the equations by precise independent determination of "a", and this quantity has not been clearly defined in terms of actual ionic dimensions, or structure. In the derivation of the equations, "a" is interpreted as the distance between centers (charges) of uniformly charged spheres in contact. Ions are, in general, neither spherical nor uniformly charged, especially when in contact. The difficult questions of solvation, and the correct value of the dielectric constant in the immediate vicinity of an ion, or between an ion pair, have not yet been satisfactorily answered. Nevertheless, it is possible to draw several qualitative conclusions from the systematic comparison of the magnitude of the "a" parameters, calculated from equations (3-7-13) and (7-4-13), with the results of studies of unrelated properties, such as crystal lattice constants, ionic mobilities, polar moments, and freezing-point lowerings.

In a qualitative way, we would expect this over-simplified physical picture to be most nearly approached in systems composed of large spherically symmetrical ions in media of low polarizability. Systems of this type have been investigated by Fuoss and Kraus,[38] who measured the conductance of tetraisoamylammonium halides in benzene. By locating the conductance minimum graphically, they could determine $K(\Lambda^0)^2$, and $K_3\Lambda^0/\Lambda_3^0$ by equation (7-4-12) and (7-4-11). Λ^0, and of course Λ_3^0, could not be determined experimentally because of the minuteness of the degree of dissociation of electrolytes in benzene. The results for the halides, as well as for the thiocyanate and two picrates,[39] are given in Table (7-5-1). In a non-polar solvent such as benzene, where solvation is presumably absent, the size of the halide ions in solution should vary with atomic number in the same order as ionic radii calculated from X-ray crystal studies [Table (5-1-6)]. It is apparent from the table that $K(\Lambda^0)^2$ decreases steadily from iodide to fluoride, which may be taken as proof that K decreases in the same order, because Λ^0 should increase somewhat in passing from the large iodide ion to the small (hence more mobile) fluoride ion. Since the values of log K given in the table are calculated on the assumption that $\Lambda^0 = 100$ for all the salts, the "observed" variation of K with electrolyte is undoubtedly too small.

TABLE (7-5-1). CONSTANTS FOR SALTS IN BENZENE AT 25°.

	$-\log K(\Lambda^0)^2$	$-\log K$†	$a \times 10^8$	$-\log (K_3\Lambda^0/\Lambda_3^0)$	$-\log K_3$*	$a_3 \times 10^8$
$(C_5H_{11})_4NI$	13 30	17.30	5.67	4.90	5.40	7.36
$(C_5H_{11})_4NBr$	13.45	17.45	5.62	4.80	5.30	7.52
$(C_5H_{11})_4NCl$	13.90	17.90	5.47	4.70	5.20	7.67
$(C_5H_{11})_4NF$	14 20	18 20	5 25	4.60	5.10	7.85
$(C_5H_{11})_4NSCN$	13.25	17.25	5.68	4.65	5.15	7.76
$(C_5H_{11})_4NOC_6H_2(NO_2)_3$	13.05	17.05	5.75	4.35	4.85	8.34
$(C_5H_{11})_3HNOC_6H_2(NO_2)_3$	16.60	20.60	4.74	2.90	3.40	16.3

† Λ^0 assumed equal to 100.
* Λ^0/Λ_3^0 assumed equal to 3.

Λ^0/Λ_3^0 probably varies but slightly in any series of similar salts. There-

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[38] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 3614 (1933).

[39] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 21 (1933).

fore K_3 varies as $K_3\Lambda^0/\Lambda_3^0$, which is seen to increase with decreasing atomic number of the halide ion. This is to be expected because the larger ions should be most loosely bound (lower potential energy) into triple ions, and therefore have the lowest value of K_3. It should be remarked that the values of a_3 differ from those of "a" in both magnitude and order of increase with composition of electrolyte. A similar difference is illustrated in Table (7-4-3), where a single system is considered at various temperatures. In view of the simplicity of the physical picture of triple-ion formation upon which the theoretical equation (7-4-13) is based, we are hardly justified in attaching more significance to "observed" values of a_3 than to note that dimensions within the range 5 to 10 Å are physically reasonable for the ions under discussion. Certainly, the theory in its present form is inadequate to account for the observation[40] that a_3 for n-tetrabutylammonium picrate increases by 1 Å between −33 and 95°.

TABLE (7-5-2). THE DISSOCIATION CONSTANT AND a-PARAMETER OF n-TETRABUTYLAMMONIUM PICRATE IN VARIOUS SOLVENTS.

Solvent	t	D	Λ^0	K	$a \times 10^8$
Ethylene chloride[1]	25	10.23	57.40	2.28×10^{-4}	5.75
Tricresyl phosphate[2]	40	6.92	1.92	1.014×10^{-5}	5.80
Chlorobenzene[3]	25	5.63	60	1.88×10^{-8}	4.75
Anisole[4]	25	4.29	43	1.16×10^{-9}	5.61
Diphenylether[5]	50	3.53	24.5	2.70×10^{-11}	5.33

[1] C. A. Kraus, *J. Franklin Inst.*, **225**, 687 (1938).
[2] M. A. Elliott and R. M. Fuoss, *J. Am. Chem. Soc.*, **61**, 294 (1939).
[3] L. R. McIntosh, D. J. Mead and R. M. Fuoss, *Ibid.*, **62**, 506 (1940).
[4] N. L. Cox, C. A. Kraus and R. M. Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).
[5] D. J. Mead and R. M. Fuoss, *J. Am. Chem. Soc.*, **61**, 2047 (1939).

Although values of "a" are practically independent of temperature, there is no doubt that they depend upon the nature of the solvent as well as that of the solute. The variation of "a" shown in Table (7-5-2) is one of several examples which might have been selected to show that ion-solvent interaction[41] must be considered in any adequate theory dealing with polarizable solvents. Specific solvent effects are generally more pronounced when the solute is an incompletely substituted ammonium salt. The a-value of n-tributylammonium picrate is 4.66 Å in tricresyl phosphate,[42] but only 2.4 Å in ethylene chloride.[43]

The influence of ion structure upon this type of electrolytic dissociation

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[40] G. S. Bien, C. A. Kraus and R. M. Fuoss, *J. Am. Chem. Soc.*, **56**, 1860 (1934).

[41] See R. L. McIntosh, D. J. Mead and R. M. Fuoss, *J. Am. Chem. Soc.*, **62**, 506 (1940); E. Swift, Jr., *Ibid.*, **60**, 2611 (1938); W. F. Luder, P. B. Kraus, C. A. Kraus and R. M. Fuoss, *Ibid.*, **58**, 255 (1936).

[42] M. A. Elliott and R. M. Fuoss, *J. Am. Chem. Soc.*, **61**, 294 (1939).

[43] D. J. Mead, C. A. Kraus and R. M. Fuoss, *Ibid.*, **61**, 3257 (1939).

has been brought out in a number of studies.[44] Some indications of structural effects may be obtained from Table (7-5-1) by considering the substitution of the larger, but more unsymmetrical, picrate ion for one of the halide ions. The localization of negative charge around the oxygen atom at one end of the picrate ion will decrease the tendency to form ion pairs because of the unsymmetrical screening effect of the trinitrobenzene group. This same localization of charge would, on the other hand, endow ion pairs, once formed, with additional stability, because the charges could be brought more closely together than if symmetrically distributed over the ionic surfaces. The net result of these opposing effects is not always clearly predictable in terms of K; but since the screening effect would be doubly effective in the formation of triple ions, and would decrease the potential energy contributed by the addition of a third ion to an ion pair, we expect a considerable increase in K_3 with the introduction of pronounced dissymmetry. The transition from quaternary ammonium iodide to thiocyanate to picrate is accompanied by an almost four-fold increase in K_3, and a two-fold increase in K. The substitution of ternary for quaternary ammonium picrate introduces dissymmetry into both ions with the result that the increase in K_3 is thirty-fold, while K is decreased by a factor of 3,500. The high increase in stability, accompanying the replacement of the large isoamyl radical by hydrogen, can be attributed partly to the ability of the charge-bearing atoms (O and N) to approach each other very closely, and partly to proton interaction with the solvent.[45]

The absolute magnitude of "a" is more significant than that of a_3, because "a" is associated with a simpler physical process, and can be evaluated by independent experimental methods. Thus, for tri-isoamylammonium picrate in benzene, $a \times 10^8$ was found to be 4.74 by conductance, 5.05 by dielectric constant, and 5.54 by freezing-point measurements [Tables (7-5-1) and (7-4-2)]. According to Table (7-1-2), the Stokes' law constant is 0.265 for the picrate ion, and about 0.295 for the tri-isoamylammonium ion (assuming the conductance of this ion equal to that of the tetraethylammonium ion). Substitution of these values into equation (7-1-2) yields 3.1 and 2.7 Å for the individual ionic radii, or 5.8 Å for the a-value estimated from mobilities. Since "a" is rather loosely defined in a physical sense, and approximations, as well as experimental errors of various kinds, are involved in its several determinations, the discordance of these independently derived values does not appear excessive. Our discussion of the effects of differences in ion size and structure is not concerned with this uncertainty in absolute magnitude, because

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[44] C. A. Kraus, *J. Franklin Inst.*, **225**, 687 (1938); C. A. Kraus and E. G. Johnson, *J. Am. Chem. Soc.*, **55**, 3542 (1933); C. A. Kraus and W. W. Hawes, *Ibid.*, **55**, 2776 (1933); D. L. Fowler and C. A. Kraus, *Ibid.*, **62**, 2237 (1940).

[45] C. A. Kraus, *Science*, **90**, 281 (1939).

the observed effects are larger than the relative accuracy with which "a" can be determined conductometrically.

(6) THE IONIZATION OF WEAK ELECTROLYTES

The transformation of the thermodynamic mass action expression for the ionization of a binary weak electrolyte,

$$K = \frac{y_{\pm}^2 \alpha^2 c}{y_u(1 - \alpha)} \tag{7-6-1}$$

into the Ostwald dilution law, [Equation (7-2-1)], involves the approximations, $y_{\pm}^2/y_u = 1$ and $\alpha = \Lambda/\Lambda^0$, which ignore ionic interaction. At high dilutions, these approximations introduce small errors of the same order of magnitude and of opposite sign, so that the agreement of the Ostwald dilution law with the earlier measurements on weak electrolytes was sufficiently close to be considered a triumph of the Arrhenius[46] theory of electrolytic dissociation. Ostwald[47] recognized that there was a slight but reproducible trend in the values of K with c when calculated by his equation. He suggested that the assumption of constant ionic mobilities, introduced by setting $\alpha = \Lambda/\Lambda^0$, might be improved by considering the change in the viscosity of the solutions with concentration. In some cases, the trend in K could be eliminated over a considerable concentration range by the use of $\alpha = \Lambda\eta/\Lambda^0\eta_0$, but the improvement was by no means general. Before the advent of the interionic attraction theory, many other modifications of the original dilution law were proposed[48] on empirical grounds, but none of these was important in the final development of the subject.

Any exact determination of ionization constants of weak electrolytes by the conductance method must take into account the dependence of both activity coefficients and mobilities upon concentration. Sherrill and Noyes,[49] and MacInnes[50] were the first to perfect the method. They evaluated K in dilute solutions by employing the limiting law of Debye and Hückel for $y_{\pm}$, and defined the degree of ionization by

$$\alpha = \Lambda/\Lambda_e \tag{7-6-2}$$

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[46] S. Arrhenius, *Z. physik. Chem.*, **1**, 631 (1887); M. Planck, *Ibid.*, **1**, 577 (1887).

[47] W. Ostwald, *Z. physik. Chem.*, **2**, 270 (1888).

[48] For a complete account of these "dilution laws" see J. R. Partington, Chapter XI, in H. S. Taylor's "Treatise on Physical Chemistry", Vol. I, D. Van Nostrand Co., New York.

[49] M. S. Sherrill and A. A. Noyes, *J. Am. Chem. Soc.*, **48**, 1861 (1926).

[50] D. A. MacInnes, *Ibid.*, **48**, 2068 (1926). See also C. W. Davies, *J. Phys. Chem.*, **29**, 977 (1925).

Λ_e is the equivalent conductance of the hypothetical completely ionized electrolyte at the ion concentration[51]

$$c_i = \alpha c \tag{7-6-2a}$$

corresponding to the observed equivalent conductance, Λ. The evaluation of Λ_e is based upon the assumption[52] that the ionic mobilities are additive at the concentrations involved. For a weak acid, HR, dissociating as

$$\mathrm{HR} \rightleftharpoons \mathrm{H}^+ + \mathrm{R}^-$$

the value of Λ_e can be obtained by combination of the measured conductances of the strong electrolytes, HCl, NaR, and NaCl, all at the concentration c_i, as follows:

$$\Lambda_{e_{\mathrm{HR}}} = \Lambda_{\mathrm{HCl}} + \Lambda_{\mathrm{NaR}} - \Lambda_{\mathrm{NaCl}} \tag{7-6-3}$$

The determination of the ionic concentration, c_i, is performed by a short series of successive approximations. A first approximation to c_i is obtained as $c_i' = c\Lambda/\Lambda^0$, and a value Λ_e' calculated from (7-6-3) at this concentration. A second approximation is then given by $c_i'' = c\Lambda/\Lambda_e'$, from which, in turn, a value of Λ_e'' is obtained. Since Λ_e does not change very rapidly with c_i, a third or fourth approximation is seldom required to yield self-consistent values of c_i and Λ_e, within the experimental error of the best measurements.

For convenience in calculation, MacInnes expressed the conductances of the strong electrolytes by means of equation (6-3-8). Thus,

$$\Lambda_{\mathrm{HCl}} = \Lambda^0_{\mathrm{HCl}} - \mathfrak{S}_{\mathrm{HCl}}\sqrt{c_i} + B_{\mathrm{HCl}}c_i(1 - \alpha^*\sqrt{c_i}) \tag{7-6-4}$$

$$\Lambda_{\mathrm{NaR}} = \Lambda^0_{\mathrm{NaR}} - \mathfrak{S}_{\mathrm{NaR}}\sqrt{c_i} + B_{\mathrm{NaR}}c_i(1 - \alpha^*\sqrt{c_i}) \tag{7-6-5}$$

$$\Lambda_{\mathrm{NaCl}} = \Lambda^0_{\mathrm{NaCl}} - \mathfrak{S}_{\mathrm{NaCl}}\sqrt{c_i} + B_{\mathrm{NaCl}}c_i(1 - \alpha^*\sqrt{c_i}) \tag{7-6-6}$$

From these, the parameters in the equation,

$$\Lambda_{e_{\mathrm{HR}}} = \Lambda^0_{\mathrm{HR}} - \mathfrak{S}_{\mathrm{HR}}\sqrt{c_i} + B_{\mathrm{HR}}c_i(1 - \alpha^*\sqrt{c_i}) \tag{7-6-7}$$

are obtained by linear combination according to equation (7-6-3). This analytical expression of $\Lambda_{e_{\mathrm{HR}}}$ has come into general use, and appears to give satisfactory results.* Before closing the discussion of the evaluation

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[51] The first substitution of a hypothetical conductance of this nature for Λ^0 seems to have been due to F. Kohlrausch [*Z. physik. Chem.*, **64**, 129 (1908)] who determined the solubility of silver chloride from the relation, $c = 1000\ \kappa/\Lambda_e$, instead of $c = 1000\ \kappa/\Lambda^0$. Here κ is the specific conductivity of the saturated solution, and c is the solubility.

[52] F. Kohlrausch, *Wied. Ann.*, **6**, 1 (1879); **26**, 161 (1885). See Chapter (6) Section (8).

* The objection might be raised that, in the preceding chapter, it was shown that equation (6-3-8) is not strictly valid at extreme dilutions. This objection is more academic than practical, however, as this equation satisfactorily expresses the results for 1-1 electrolyte within the concentration range employed in the determination of ionization constants. This procedure is therefore just as accurate, and presumably more convenient than a more refined analytical treatment.

of c_i, it should be made clear that, although Λ/Λ_e is a much closer approximation to the true ionic concentration than Λ/Λ^0, it cannot be considered exact, because the quantity Λ is measured in a medium containing $c_u = c - c_i$ mols per liter of undissociated weak electrolyte, whereas Λ_e is evaluated in pure water. It might appear at first glance that the effect of this variation in the solvent medium could be taken into account by writing $c_i = \Lambda\eta/\Lambda^0\eta_0$. As variations from Stokes' law are most pronounced where hydrogen ions are concerned, and the viscosity of a c_u normal solution of the weak electrolyte *free from ions* is unmeasurable, conductance measurements lead to apparent values of c_i. These values, however, will yield an accurate extrapolation of K_A. In addition to these objections to the use of the viscosity ratio, it has the property of being very helpful in certain cases[53] and superfluous in others. It is generally avoided because it requires additional experimental data.

The evaluation of K_A from a series of values of c and c_i can be conveniently performed in a number of ways. If experimental results are available at very high dilutions, it is sufficient to calculate

$$k_A = \frac{c_i^2}{c - c_i} = \frac{c_i^2}{c_u} \tag{7-6-8}$$

for various values of c_i, and extrapolate to infinite dilution by a plot of $\log k_A$ against $\sqrt{c_i}$. Fig. (7-6-1) shows a plot of this kind used by MacInnes and Shedlovsky[54] to obtain the ionization constant of acetic acid at 25°. The equation for the straight line drawn through the experimental points at high dilution is

$$\log k_A = \log K_A + 1.013\sqrt{c_i} \tag{7-6-9}$$

and a comparison of this equation with (7-6-1) and (7-6-8) shows that

$$2\log y_\pm - \log y_u = -1.013\sqrt{c_i} \tag{7-6-10}$$

At the high dilutions concerned, the activity coefficient of a neutral solute would be expected to be so close to unity[55] that $\log y_u$ can be safely disregarded, and we see that the limiting slope of the plot is in exact numerical agreement with the limiting slope predicted by the Debye-Hückel theory for aqueous solutions at 25°.

The departures of the experimental results from the limiting tangent in the more concentrated range cannot be accounted for by experimentally determined values of $\log y_u$, or by the introduction of reasonable ionic radii into the expression for $\log y_\pm$. Assuming $\mathring{a} = 4$ for ionized acetic acid, MacInnes and Shedlovsky calculated $\log y_\pm^2$ by equation (3-5-8), and $\log y_u$ from freezing-point measurements. The variation of $\log k_A$ with

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[53] C. W. Davies, *J. Am. Chem. Soc.*, **54**, 3776 (1932).

[54] D. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429 (1932).

[55] W. D. Larson and W. J. Tomsicek, *J. Am. Chem. Soc.*, **61**, 65 (1939).

$\sqrt{c_i}$, predicted by this calculation, falls slightly below the dashed line in Fig. (7-6-1), but departs widely from the experimental curve at the higher concentrations.

Although the failure of the Kohlrausch law and the increasing lack of exact physical definition of c_i at these concentrations undoubtedly account for some of the descrepancies observed above, an important factor is the neglect of the "medium effect" of the neutral molecules of acetic acid upon $\log y_{\pm}^2$ of its ions. Quantitative information regarding this particular effect is not available. The effect is probably not very different from that of acetic acid molecules upon $\log y_{\pm}^2$ of hydrochloric acid, which is known[56] to be about $0.106c_u$. Without stressing the numerical magnitude of the effect, we may merely assume that it is proportional to c_u and write

$$\log\ (y_{\pm}^2/y_u) = -1.013\sqrt{c_i} + \beta c_u \tag{7-6-11}$$

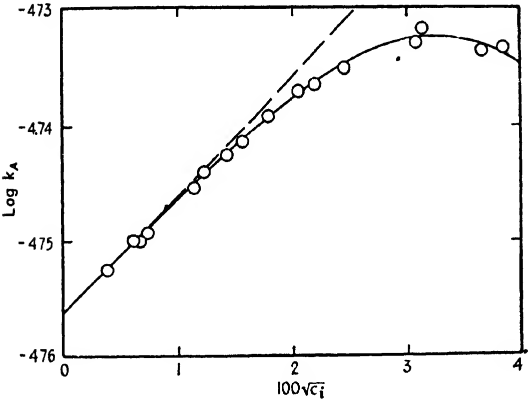

Fig. (7-6-1)
Graphical evaluation of the ionization constant of acetic acid in water at 25° according to equation (7-6-9)

where $\log y_u$ has also been assumed linear in c_u. Combination of this equation with equation (7-6-1) leads to[57, 58]

$$\log k_A - 1.013\sqrt{c_i} = \log K_A - \beta c_u \tag{7-6-12}$$

In Fig. (7-6-2), the left-hand member of this equation is plotted for the data of MacInnes and Shedlovsky at concentrations above 0.0005*N*. The radii of the circles represent an uncertainty of 0.1 per cent in k_A, which seems to be the experimental reproducibility of this quantity. It is

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[56] B. B. Owen, *J. Am. Chem. Soc.*, **54**, 1758 (1932). By the conditions of the measurements, the ionization of the acetic acid, at the concentrations with which we are here concerned, was so depressed by the presence of HCl that we may consider its stoichiometrical concentration equal to c_u. 0.106 c_u has been written for 5.87 times the mole fraction of acetic acid.

[57] B. Saxton and T. W. Langer, *J. Am. Chem. Soc.*, **55**, 3638 (1933).

[58] B. Saxton and H. F. Meier, *Ibid.*, **56**, 1918 (1934); B. Saxton and L. S. Darken, *Ibid.*, **62**, 846 (1940).

apparent that the linearity predicted by equation (7-6-12) is fulfilled over the concentration range considered, and the value of β is about 0.134, the expected order of magnitude.

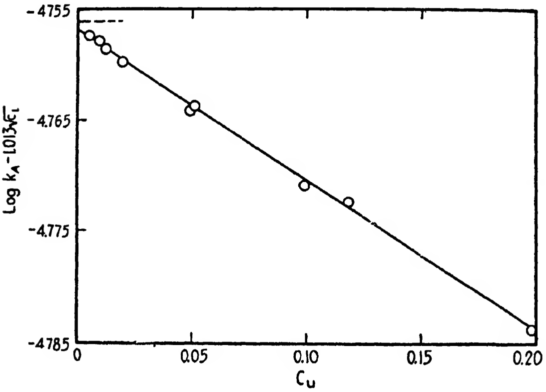

Fig. (7-6-2)
Graphical evaluation of the ionization constant of acetic acid at 25° according to equation (7-6-12).

TABLE (7-6-1). IONIZATION CONSTANTS OF WEAK ELECTROLYTES DETERMINED CONDUCTOMETRICALLY IN WATER AT 25°.

	K (*m*-scale)	Ref.
Formic acid	1.830×10^{-4}	1
Acetic acid	1.758×10^{-5}	2
n-Propionic acid	1.347×10^{-5}	3
n-Butyric acid	1.512×10^{-5}	3, 1
Chloroacetic acid	1.400×10^{-3}	4, 5
Cyanoacetic acid	3.370×10^{-3}	1
Lactic acid	1.391×10^{-4}	6
Sulfuric acid (K_{2A})	1.18×10^{-2}	7
Phosphoric acid (K_{1A}, 18°)	8.31×10^{-3}	7
α-Crotonic acid	1.981×10^{-5}	8
Benzoic acid	6.313×10^{-5}	9, 10
o-Chlorobenzoic acid	1.200×10^{-3}	9, 10
m-Chlorobenzoic acid	1.510×10^{-4}	9, 10
p-Chlorobenzoic acid	1.043×10^{-4}	9, 10
Carbonic acid (K_{1A})	4.323×10^{-7}	11
Monoethanolammonium hydroxide	3.19×10^{-5}	12
Oxalic acid (K_{1A})	5.376×10^{-2}	13

1. B. Saxton and L. S. Darken, *J. Am. Chem. Soc.*, **62**, 846 (1940).
2. D. A. MacInnes and T. Shedlovsky, *Ibid.*, **54**, 1429 (1932).
3. ✓ D. Belcher, *Ibid.*, **60**, 2744 (1938).
4. T. Shedlovsky, A. S. Brown and D. A. MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1935).
5. ✓ B. Saxton and T. W. Langer, *J. Am. Chem. Soc.*, **55**, 3638 (1933).
6. ✓ A. W. Martin and H. V. Tartar, *Ibid.*, **59**, 2672 (1937), 0 to 50°.
7. M. S. Sherrill and A. A. Noyes, *Ibid.*, **48**, 1861 (1926).
8. ✓ B. Saxton and G. W. Waters, *Ibid.*, **59**, 1048 (1937).
9. ✓ B. Saxton and H. F. Meier, *Ibid.*, **56**, 1918 (1934).
10. ✓ F. G. Brockman and M. Kilpatrick, *Ibid.*, **56**, 1483 (1934).
11. T. Shedlovsky and D. A. MacInnes, *Ibid.*, **57**, 1705 (1935).
12. V. Sivertz, R. E. Reitmeier and H. V. Tartar, *Ibid.*, **62**, 1379 (1940).
13. L. S. Darken, *Ibid.*, **63**, 1007 (1941).

The extrapolated value of K_A derived from this plot is 1.750×10^{-5}, while the value derived from Fig. (7-6-1) is 1.753×10^{-5}. The difference between these values is 0.17 per cent, almost twice the apparent experimental reproducibility of the individual data, but well within the agreement which we might expect between values of K_A determined by different investigators, or by different methods, under the best conditions. The choice between the two extrapolations is mainly a matter of experimental convenience, rather than of accuracy, and on this basis the method of Fig. (7-6-2) is unquestionably to be preferred. It can be observed from the plots that the concentration range that might be used to determine the straight line is *below* 0.003 in Fig. (7-6-1), but *above* 0.005 in Fig. (7-6-2), and the latter extrapolation is much shorter.

Table (7-6-1) contains ionization constants derived from conductance data by the methods outlined in this section.

(7) EXPERIMENTAL INVESTIGATIONS OF THE EFFECT OF FREQUENCY ON CONDUCTANCE AND DIELECTRIC CONSTANT

Wien[59] was the first to demonstrate the variation of conductivity with the frequency. Sack,[60] however, was the first to obtain sufficiently accurate data at high frequencies to show that the increase in conductivity with frequency is of the order predicted by theory. A number of different experimental methods have been employed by Sack,[61] Zahn,[62] Deubner,[63] Wien[64] and Malsch.[65] The method of Wien measures the effect of high frequency on either the conductance or the dielectric constant.

The theory of Debye and Falkenhagen[66] is verified by these experiments for cases of many electrolytes. Magnesium sulfate in water has been selected by Falkenhagen as the best example available. In Fig. (7-7-1), $100\Lambda_{I\bar{\omega}}/\Lambda_m^0$ has been plotted against $\sqrt{c^*}$, where c^* is the equivalent concentration and Λ_m^0 is the molecular conductance when $\bar{\omega}$ is zero. According to equation (4-5-20),

$$\Lambda_{\bar{\omega}} = \Lambda_m^0 - \Lambda_{I\bar{\omega}} - \Lambda_{II} \qquad (7\text{-}7\text{-}1)$$

The solid line in the figure represents the plot of $100\Lambda_{I(\bar{\omega}=0)}/\Lambda_m^0$ for the stationary case derived from Onsager's equation. The dotted line is that

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[59] M. Wien, *Ann. Phys.*, [4], **83**, 840 (1927).

[60] H. Sack, *Physik. Z.*, **29**, 627 (1928).

[61] B. Brendel, O. Mittelstaedt, and H. Sack, *Physik. Z.*, **30**, 576 (1929); H. Sack and B. Brendel, *Ibid.*, **31**, 345 (1930); B. Brendel, *Ibid.*, **32**, 327 (1931).

[62] H. Zahn, *Z. Physik.*, **51**, 350 (1928); H. Rieckhoff and H. Zahn, *Ibid.*, **53**, 619 (1929).

[63] A. Deubner, *Physik. Z.*, **30**, 946 (1929); *Ann. Physik.* [5], **5**, 305 (1930); *Physik. Z.*, **33**, 223 (1932).

[64] M. Wien, *Physik. Z.*, **31**, 793 (1930); **32**, 183 (1931); *Ann. Physik.* [5], **11**, 429 (1931).

[65] J. Malsch, *Physik. Z.*, **33**, 19 (1932); *Ann. Physik.* [5], **12**, 865 (1932).

[66] P. Debye and H. Falkenhagen, *Physik. Z.*, **29**, 121, 401 (1928); *Z. Elektrochemie*, **34**, 562 (1928).

calculated by the Debye and Falkenhagen theory. The latter is in good agreement with the experimental results of Wien which are given by the circles.

In Fig. (7-7-2) the frequency effect on the conductance of a 0.001 N magnesium sulfate solution is illustrated. Here the solid line represents the plot of the percentage dispersion effect against the wave length in meters. The solid line is the calculated effect, and the points represent the experimental results of various investigators. This leaves little doubt of the fundamental validity of the theory.

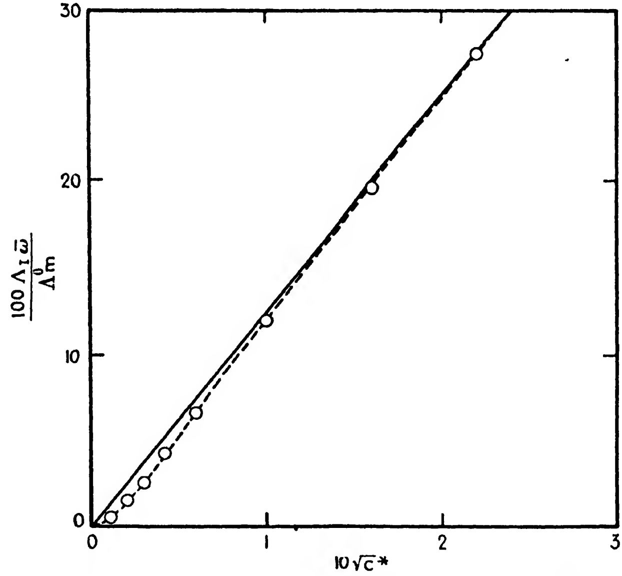

Fig. (7-7-1). Frequency effect upon the conductance of magnesium sulfate solutions at 18°. —— $\frac{100\,\Lambda_{I(0)}}{\Lambda^0_m}$, or $l = \infty$; ---- $\frac{100\,\Lambda_I(\bar{\omega})}{\Lambda^0_m}$, theoretical, $l = 10$; ○ experimental, $l = 10$

The theory of Debye and Falkenhagen of the lowering of the dielectric constant is interesting since it goes beyond the Onsager theory of conductance, and predicts a change in dielectric constant with the concentration at zero frequency. Equation (4-5-25) may be reduced to

$$D_{(\bar{\omega}=0)} - D_0 = \frac{1.97 \times 10^6 |z_1 z_2| (|z_1| + |z_2|)^{1/2}}{2D_0^{1/2} T^{3/2} (1 + 1/\sqrt{q^*})^2} (q^* c^*)^{1/2} \tag{7-7-2}$$

for the special case when $\bar{\omega} = 0$. Equation (4-3-43) defines q^*, and $c^* = \nu_1 |z_1| c = \nu_2 |z_2| c$. For simplicity, this equation may be written,

$$D_{(\bar{\omega}=0)} - D_0 = \mathfrak{S}_{(D)} \sqrt{c} \tag{7-7-3}$$

In water at 18°, $\mathfrak{S}_{(D)}$ was found by Falkenhagen to be 3.79, 10.9, 13.8 and 30.3 for potassium, magnesium, and lanthanum chlorides, and magnesium sulfate solutions, respectively.

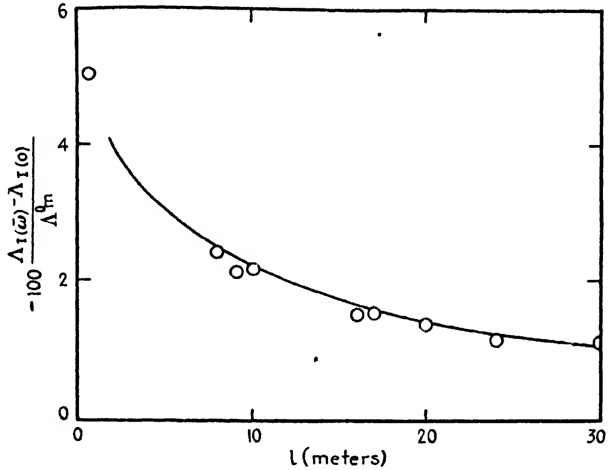

Fig. (7-7-2). Frequency effect upon the conductance of magnesium sulfate solutions at 18°; $c^* = 0.001$; —— theoretical

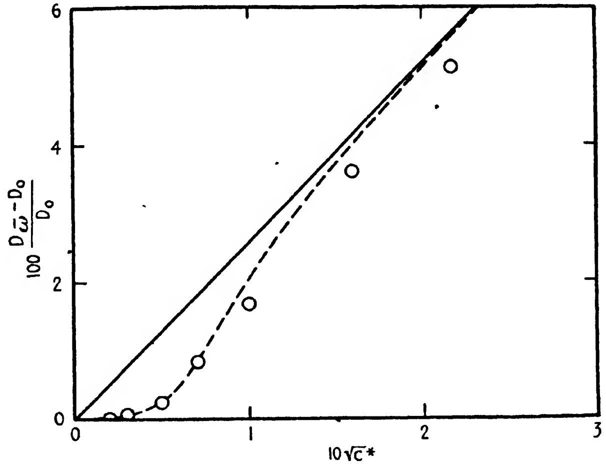

Fig. (7-7-3). Frequency effect upon the dielectric constant of magnesium sulfate solutions at 18°. —— $100(D_{(\bar\omega=0)} - D_0)/D_0$; ---- $100(D_{\bar\omega} - D_0)/D_0$; theoretical, $l = 10$; ○, experimental, $l = 10$

A good agreement with the theory is again obtained by comparison with measurements of Wien of the dielectric constant in dilute magnesium sulfate solutions. Fig. (7-7-3) contains a plot of $100\,(D_{\bar\omega} - D_0)/D_0$ against

$\sqrt{c^*}$. The solid line represents the effect at zero frequency, and the dotted line that calculated from Table (5-3-4) at a wave length of 10 meters. The circles represent the values of Wien. Considering the difficulties of measuring dielectric constants in dilute salt solutions, the agreement is satisfactory.

(8) THE EFFECT OF HIGH ELECTRIC FIELDS UPON THE CONDUCTANCE OF ELECTROLYTES

In 1927 Wien[67] announced the important generalization that the conductivities of electrolytic solutions always increase with electrical field strength. He showed that this increase was a function of the concentration, the valence, and the specific nature of the solution. Furthermore, the equivalent conductance of strong electrolytes seems to approach a constant limiting value asymptotically in very high fields. In solutions containing weak electrolytes,[68] it was found that the relative increase in conductance with the field strength was many times greater than for strong electrolytes. Gemant[69] observed a similar effect in solvents of very low dielectric constant ($D \simeq 3$). Wien correctly interpreted this behavior by suggesting that the field increased the dissociation of the electrolyte.

Since high fields produce considerable heating effects, the ordinary method of conductance measurement must be replaced by impulse methods whereby the field is applied for very short periods of time ($\sim 10^{-5}$ to 10^{-7} sec.). The difficulties of measurement have been largely overcome by Wien and his collaborators, so that accurate results are available. An excellent discussion of the experimental methods can be found in a review by Eckstrom and Schmelzer.[70]

The Wien Effect for Strong Electrolytes

In Fig. (7-8-1) the observed[71] relative increase in the equivalent conductance of various strong electrolytes is plotted against the field strength in kilovolts per cm. These plots refer to solutions of such concentrations that they have a common value of $\Lambda_{(X=0)}$. The relative increase in equivalent conductance is roughly proportional to $(z_+z_-)^2$, and seems to approach a constant value in very high fields.

The effect of concentration and the general character of the phenomenon are illustrated by Fig. (7-8-2), which shows the theoretical behavior predicted by equation (4-6-55) for a hypothetical 2-2 strong electrolyte in water. In low fields the Wien effect is vanishing small, as the curves are horizontal when $X = 0$. As the field strength is increased, the conductance

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[67] M. Wien, *Ann. Physik.* [4], **83**, 327 (1927); *Ibid.*, **85**, 795 (1928); *Physik. Z.*, **28**, 834 (1927); *Ibid.*, **29**, 751 (1928).

[68] M. Wien and J. Schiele, *Physik. Z.*, **32**, 545 (1931).

[69] A. Gemant, *Physik. Z.*, **29**, 289 (1928).

[70] H. C. Eckstrom and C. Schmelzer, *Chem. Rev.*, **24**, 367 (1939).

[71] M. Wien, *Ann. Physik.*, **83**, 327 (1927).

increases more and more rapidly, passes through an inflection, and finally approaches a limiting value asymptotically. This limiting value, $\Lambda_{(X=\infty)}$, is less than Λ^0, the limiting conductance at infinite dilution, because the destruction of the ionic atmosphere by the high field is not accompanied

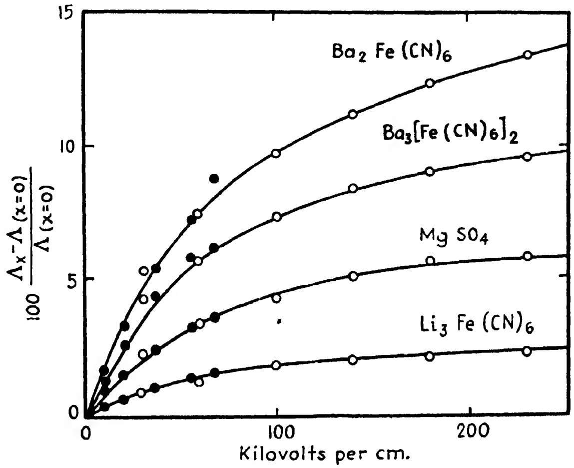

Fig. (7-8-1). Wien effect on strong electrolytes. $L_{(X=0)} = 4.5 \times 10^{-5}$; ● and ○ refer to results obtained with two different cells

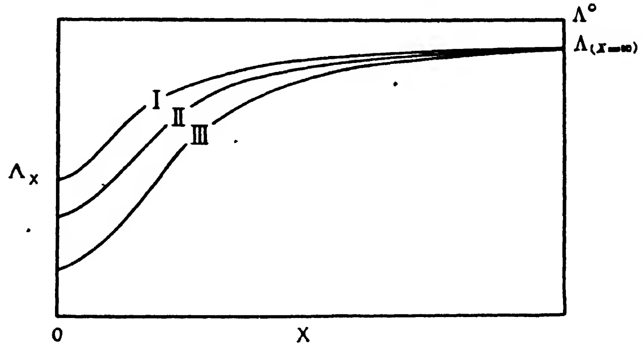

Fig. (7-8-2). General characteristics of Wien effect. Curves I, II and III represent effects for solutions of three different concentrations of an electrolyte, $C_{III} > C_{II} > C_I$

by complete elimination of the electrophoretic effect. The theoretical equation (5-3-14) for the conductance of symmetrical electrolytes in a field of strength, X, can be written,

$$\Lambda_X = \Lambda^0 - \left[\frac{\epsilon^2 |z_1 z_2| \Lambda^0}{2kDT} g(x) + \frac{96500\epsilon(|z_1| + |z_2|)}{6\pi\eta_0 300} \frac{f(x)}{\sqrt{2}}\right]\kappa \qquad (7\text{-}8\text{-}1)$$

and recalling [Chapter (4), Section (6)] that $g(\infty) = 0$, and $f(\infty) = 1$, we see that the difference between Λ^0 and Λ_X is given by

$$\Lambda^0 - \Lambda_{(X=\infty)} = \frac{96500\epsilon(|z_1| + |z_2|)}{6\pi\eta_0 300\sqrt{2}}\kappa \tag{7-8-2}$$

In low fields, equation (7-8-1) can be reduced to the quadratic form originally found by Joos and Blumentritt.[72] Thus, for $x^2 < 1$, and neglecting higher powers in x, Eckstrom and Schmelzer[72a] obtained

$$\frac{\Lambda_X - \Lambda_{(X=0)}}{\Lambda_{(X=0)}} = \left[\frac{(0.0172)(z\epsilon)^2\Lambda^0\kappa}{\Lambda_{(X=0)}DkT} + \frac{(0.0243)(643.34)\,|z\epsilon|\kappa}{\Lambda_{(X=0)}6\sqrt{2}\pi\eta_0}\right]x^2 \tag{7-8-3}$$

in formal agreement with the first term of the Joos and Blumentritt[72] equation* (4-6-2):

$$\frac{\Lambda_X - \Lambda_{(X=0)}}{\Lambda_{(X=0)}} = AX^2(1 - BX^2) \tag{7-8-4}$$

Since the derivation of equation (7-8-3) limits it to binary electrolytes, the measurements of Wien[73] on magnesium sulfate yield the only data on high valence type electrolytes available for a comparison of theory with experiment. Eckstrom and Schmelzer have made the necessary calculations in both the high and the low field regions. The constants employed in the high fields are $c = 3.7 \times 10^{-4}$ and $\Lambda_{(X=0)} = 105.5$; and in the low fields $c = 1.22 \times 10^{-3}$ and $\Lambda_{(X=0)} = 99.0$. Further, $T = 291$, $D = 81$, $\eta_0 = 0.0105$, and $\Lambda^0 = 114$. The required values of $g(x)$ and $f(x)$ calculated by Wilson are given in Tables (5-3-5) and (5-3-6). The comparison is illustrated graphically in Fig. (7-8-3), where the circles represent the experimental data in low fields, and the dots those in high fields. The solid curves, representing the predictions of equations (7-8-1) and (7-8-3), are in remarkably good agreement with experiment below 50 kv./cm.

Falkenhagen, Frölich and Fleischer[74] have found that their theory of the effects of frequency upon conductance in high fields are in qualitative agreement with the data of Michels.[75] Since the experimental results in this field are very few, further investigation will be interesting.

The Wien Effect for Weak Electrolytes, or The Dissociation Field Effect

The Onsager theory of the effect of high fields on the dissociation of weak electrolytes led to the quantitative expression (4-7-29),

$$\frac{K(X)}{K(0)} = 1 + \bar{b} + \frac{\bar{b}^2}{3} + \frac{\bar{b}^3}{18} + \frac{\bar{b}^4}{180} + \cdots \tag{7-8-5}$$

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[72] G. Joos and M. Blumentritt, *Physik. Z.*, **28**, 836 (1927); M. Blumentritt, *Ann. Physik.*, **85**, 812 (1928).

[72a] H. C. Eckstrom and C. Schmelzer, *Chem. Rev.*, **24**, 367 (1939).

* The numerical coefficients in their equation correspond to 0.0133 and 0.0973 instead of 0.0172 and 0.0243 which appear in (7-8-3).

[73] M. Wien, *Ann. Physik.*, **85**, 795 (1928); *Physik. Z.*, **29**, 751 (1928).

[74] H. Falkenhagen, F. Frölich and H. Fleischer, *Naturwiss.*, **25**, 446 (1937).

[75] F. Michels, *Ann. Physik.*, **22**, 735 (1935).

where $K(X)$ and $K(0)$ represent the ionization constant with and without external field, respectively. The variable, $\bar{b}$, is given by equation (4-7-28),

$$\bar{b} = 9.636\, V/DT^2 \tag{7-8-6}$$

for 1-1 electrolytes when V is in volts per centimeter. When the degree of ionization is small ($\alpha \ll 1$), then, by equation (4-7-34),

$$\frac{\Lambda_X}{\Lambda_{(X=0)}} = \frac{\alpha}{\alpha_0} = \sqrt{\frac{K(X)}{K(0)}} = 1 + \tfrac{1}{2}\bar{b} + \tfrac{1}{24}\bar{b}^2 + \cdots \tag{7-8-7}$$

These equations have been verified by Onsager[76] with data in media of high and low dielectric constant.

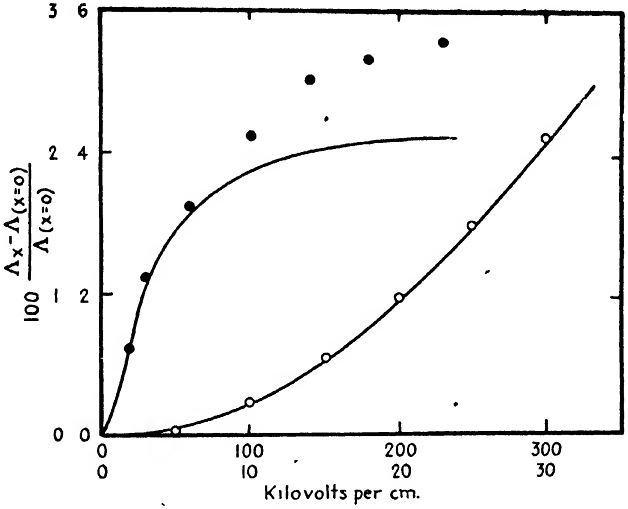

Fig. (7-8-3). Wien effect on magnesium sulfate solutions. —— Theory; ○ Weak fields; ● Strong fields

In Fig. (7-8-4), due to Onsager, the points represent the experimental results of Schiele[77] for acetic acid and chloroacetic acid in water ($D = 78.57$). The lines represent theoretical computations of the relative change in conductance. Here the effect depends largely on the value of α, and is greater the weaker the acid. In fields greater than 50 kilovolts per cm, the agreement is excellent. In lower fields, the lack of agreement is explained by the fact that the ionic atmosphere effect was omitted in the development of the theory which can be expected to be valid only in fields strong enough to destroy the ionic atmospheres. This discrepancy is in the right direction, but a theoretical calculation of this effect would be very difficult.

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[76] L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

[77] J. Schiele, *Ann. Physik* [5], **13**, 811 (1932).

Onsager first showed that his theory is confirmed in media of low dielectric constant by the data of Gemant[77a] who measured the effects of high fields upon a solution of picric acid in a mixture of 5 per cent ethyl alcohol and 1 per cent mineral oil in benzene ($D = 2.7$).

Mead and Fuoss[78] measured the conductance at 60 cycles of solutions of tetrabutylammonium picrate in diphenyl ether ($D = 3.53$) at 50° in fields ranging from 0 to 20 kv/cm. Measurements were made at a sufficient number of concentrations for the evaluations of the dissociation constants of both $[C^+A^-]^0$, and $[C^+A^-C^+]^+$ by the methods described in Sections (2) and (4). They obtained 2.70×10^{-11} and 1.00×10^{-3} for K and K_3, respectively.

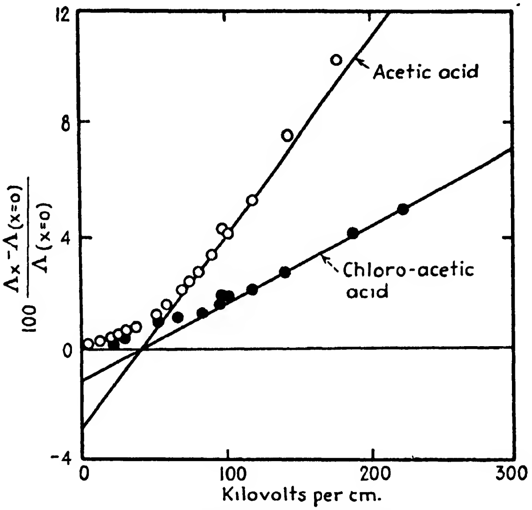

Fig. (7-8-4). Wien effect for acetic and chloroacetic acids; ——, theoretical

The field effects at a very low, and at a higher concentration, are shown in Figs. (7-8-5) and (7-8-6) in which specific conductance is plotted against field. When the solute is present at very low concentrations, the plot is very nearly linear, but as the concentration is increased, the initial part of the curve (Fig. 7-8-6) is concave upward and approaches linearity at higher field strengths. As previously mentioned, this deviation from linearity is due to the presence of ionic atmospheres which are broken up in the higher fields. If the linear parts of the graphs are extrapolated to zero field, the low voltage conductance which the ions would have if the

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[77a] A. Gemant, "Electrophysik der Isolierstoffe," pp. 78–80, Springer, Berlin (1930); *Physik. Z.*, **29**, 289 (1928).

[78] D. J. Mead and R. M. Fuoss, *J. Am. Chem. Soc.*, **61**, 2047 (1939); Correction, *Ibid.*, **61**, 3589 (1939).

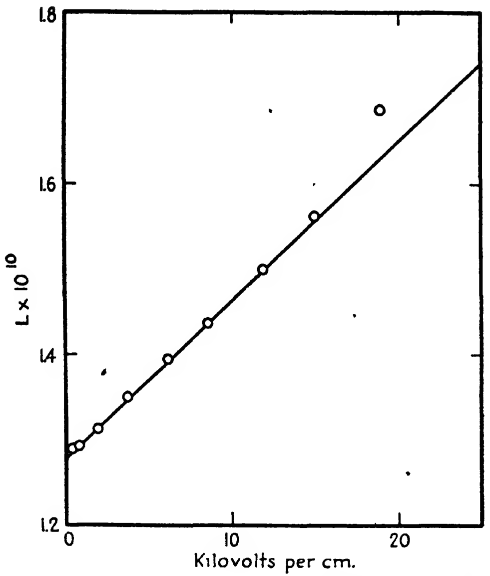

Fig. (7-8-5). Wien effect at low concentration. Tetrabutyl ammonium picrate in diphenyl ether. $D = 3.53$; $t = 50°$ $c = 1.03 \times 10^{-6}$

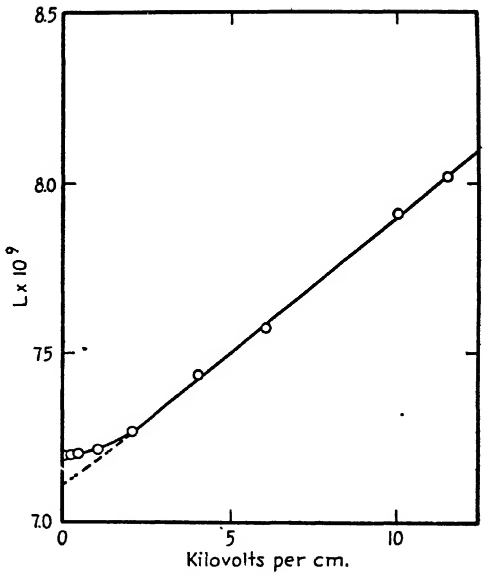

Fig. (7-8-6). Wien effect at higher concentration. Tetrabutyl ammonium picrate in diphenyl ether. $D = 3.53$; $t = 50°$; $c = 9.73 \times 10^{-4}$

activity coefficients were unity (dashed line) is obtained. The ratio of the conductance obtained from the actual results at zero field to the linearly extrapolated values is a measure of the activity coefficient. Mead and Fuoss computed the activity coefficient in this manner with the result shown in Fig. (7-8-7). The dashed line represents the limiting function, $\log f_{\pm} = -33.8c_i^{1/2}$, and the experimental results are indicated by the circles. The correct order of magnitude is obtained proving that Onsager's interpretation of the curvature in lower fields (Fig. 7-8-6) is correct.

According to equation (7-8-7)

$$\Lambda_X/\Lambda_{(X=0)} = 1 + \tfrac{1}{2}\bar{b} + \cdots = 1 + 0.0132(10^{-3}V) + \cdots \qquad (7\text{-}8\text{-}8)$$

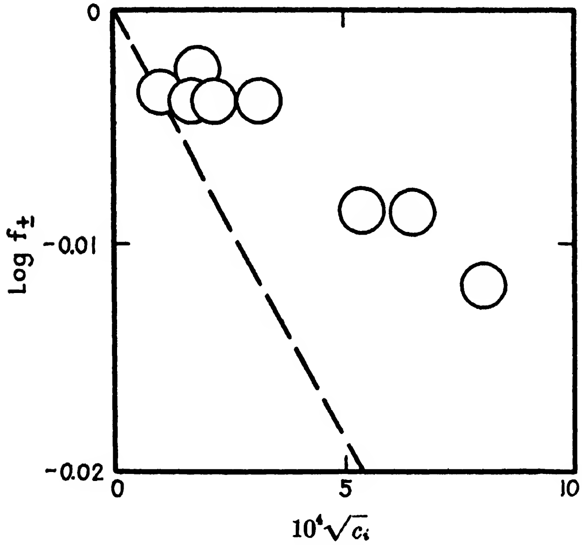

Fig. (7-8-7) Activity coefficient of tetrabutylammonium picrate in diphenyl ether, estimated from the Wien effect

when $D = 3.53$, and $T = 323$. Mead and Fuoss found that the limiting value of their slopes at zero electrolyte concentration was in exact agreement with theory.

The slopes of the curves of conductance against field were found to decrease with increasing electrolyte concentration. This departure from the theoretical prediction occurs at a concentration where triple ion formation causes the log Λ vs. log c plot to begin to deviate from linearity. The theory does not include the effects of field on triple ion formation. Several series of measurements, made at 500 to 1500 cycles, showed that the slopes of the conductance-field strength curves decreased considerably with increasing frequency. Mead and Fuoss[79] have investigated this effect more thoroughly.

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[79] D. J. Mead and R. M. Fuoss, *J. Am. Chem. Soc.*, **62**, 1720 (1940).

The change in slope with frequency is illustrated in Figure (7-8-8) for a single concentration. The ordinates are the ratios of the high voltage conductivity to the low voltage* conductivity at the same frequency. The abscissae are the field strengths in kilovolts per centimeter. The effect of frequency† is most pronounced at high dilutions, and gradually disappears as the concentration is increased. The influence of concentra-

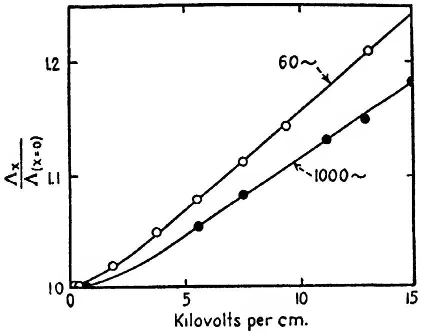

Fig. (7-8-8)
Influence of frequency on Wien effect: tetrabutyl ammonium bromide in diphenyl ether at 50°. $c = 1.5 \times 10^{-4}$

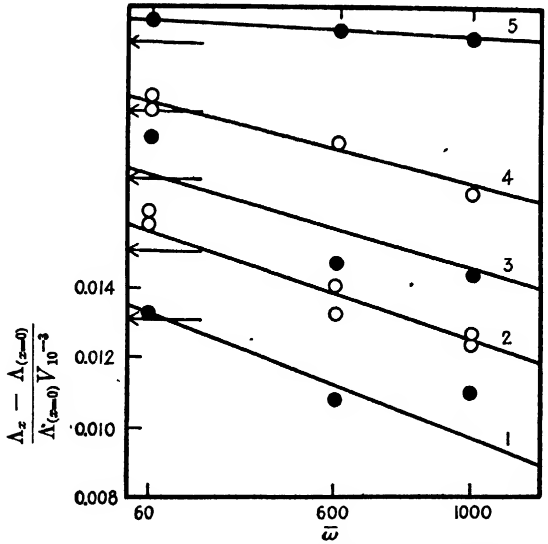

Fig (7-8-9). Influence of frequency and concentration upon Wien effect. Tetrabutyl ammonium bromide in diphenyl ether at 50°. The ordinate scale is shifted vertically (0.02 unit) for each concentration. The numbers on the right-hand margin represent $c \times 10^4$

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* A voltage so low that doubling it causes no detectable change in conductivity.

† Note that at low voltages the conductivity becomes independent of frequency, which indicates that polarization is negligible.

tion is observable in Figure (7-8-9) which shows the variation in the slope, $(\Lambda_X/\Lambda_{(X=0)} - 1)/(10^{-3}V)$ with frequency. The theoretical value (0.0132) is indicated, for each concentration, by the horizontal line at the left.

At low frequencies the observed slopes[80] are in excellent agreement with the theoretical, and for the highest concentration this agreement persists at 1000 cycles. This behavior is predictable from consideration of the Langevin time lag [Equation (4-7-36)]. For the most dilute solutions ($c = 10^{-4}$), τ' is about 5×10^{-4} sec, and the field-sensitive ionization reaction is unable completely to follow the field alternating at intervals of the same order (1000 cycles). Consequently, the field effect decreases sharply with increasing frequency. At higher concentrations, the time lag is shorter, and the ionic distribution can more completely adjust itself to the field. When $c = 5 \times 10^{-4}$, $\tau' \simeq 8 \times 10^{-5}$ sec, and the normal low frequency Wien effect is approximately maintained up to 1000 cycles.

[80] The slopes in Fig. (7-8-9) have been multiplied by $\frac{3}{4}$ to allow for the harmonic analysis made by the filter and amplifier which were used in the measuring circuit. See D. J. Mead and R. M. Fuoss, *J. Am. Chem. Soc.*, **61**, 3589 (1939).

Chapter (8)

Thermochemical Quantities, Partial Molal Volumes, and the Coefficients of Expansion and Compressibility

(1) INTRODUCTION

This chapter marks the beginning of a systematic discussion of the thermodynamics of electrolytic solutions. As indicated by the formal treatment of this subject in Chapter (1), this will require a study of all the partial molal quantities of the components of the solutions. These partial quantities may be divided into two types. (1) Those which may be derived from the determination of the pressure and temperature coefficients of the relative partial molal free energy or activity, such as the relative partial molal heat content, heat capacity, and volume [Equations (1-7-5), (1-7-7) and (1-7-11)]; these can be measured without the knowledge of the partial molal free energy, but it is impossible to derive this latter quantity from them without further information. (2) The partial molal free energy of the solute or the solvent.

Although it may seem somewhat arbitrary, we have found it to be more convenient to reserve the treatment of the free energy for later chapters, and to consider first the quantities which can be derived from it. The most important of these, the relative partial molal heat content, and its integral counterpart, the relative apparent molal heat content (heat of dilution) will be discussed first. Then, the partial molal heat capacity, which may be evaluated in an absolute sense, will be treated in considerable detail. Heats of neutralization will also be included so that all these calorimetric quantities can be discussed in immediate relation with one another. The concluding sections will deal with partial molal volumes, expansibility and compressibility.

(2) THE RELATIVE APPARENT MOLAL HEAT CONTENT, HEAT OF DILUTION, AND RELATIVE PARTIAL MOLAL HEAT CONTENT

Thermochemical measurements have always been a major concern of physical chemists, but it is only by the recent development of multi-junction thermocouples, and successive refinements of the adiabatic thermal balance technique, that the small heat changes occurring in dilute solutions have been satisfactorily measured. For many purposes, it is necessary to know the heat contents of the components of a solution relative to their corresponding values at infinite dilution. The determination of such quantities requires the extrapolation of experimental data in very dilute solutions. By the application of the Debye-Hückel equation, a theoretical limiting slope has been derived [Equation (5-2-14)] which increases the reliability of these extrapolations. Conversely, the verification of the limiting slope has magnified the importance of measurements at extreme dilutions. Before we can give an account of such measurements and their interpretation, it will be necessary to extend the treatment of partial molal quantities, given in Chapter (1), by defining several new quantities.

Dropping the generalized formulation of equation (1-7-2), we obtain for two components,

$$H = n_1\bar{H}_1 + n_2\bar{H}_2 \qquad (8\text{-}2\text{-}1)$$

which gives the total heat content of a solution, composed of n_1 mols of solvent and n_2 mols of solute, in terms of the partial molal heat contents of its components. A similar equation,

$$H = n_1\bar{H}_1^0 + n_2\phi_H \qquad (8\text{-}2\text{-}2)$$

gives the heat content in terms of the partial molal heat content of the solvent at infinite dilution, $\bar{H}_1^0$, and the apparent molal heat content of the solute, ϕ_H. Comparison of these equations shows that

$$\phi_H^0 = \bar{H}_2^0 \qquad (8\text{-}2\text{-}3)$$

at infinite dilution. Since the absolute values of heat contents are experimentally undefined, it is necessary to employ the corresponding relative properties, which, unless otherwise noted, will be referred to the infinitely dilute solution. Thus, by equation (1-7-6), the expression

$$H - H^0 = n_1(\bar{H}_1 - \bar{H}_1^0) + n_2(\bar{H}_2 - \bar{H}_2^0) = n_2(\phi_H - \phi_H^0) \qquad (8\text{-}2\text{-}4)$$

follows from equations (8-2-1) and (8-2-2). Upon substituting the definitions, $L \equiv H - H^0$, $\bar{L}_1 \equiv \bar{H}_1 - \bar{H}_1^0$, $\bar{L}_2 \equiv \bar{H}_2 - \bar{H}_2^0$, and $\phi_L \equiv \phi_H - \phi_H^0$, this equation becomes

$$L = n_1\bar{L}_1 + n_2\bar{L}_2 = n_2\phi_L \qquad (8\text{-}2\text{-}5)$$

The relative apparent molal heat content, $\phi_H - \phi_H^0$, is equal to, and of opposite sign to, the heat of dilution, ΔH_D, for the isothermal isobaric addition of an infinite quantity of pure solvent to a solution containing one mol of solute in n_1/n_2 mols of solvent. Consequently,

$$n_2\Delta H_D = -n_1\bar{L}_1 - n_2\bar{L}_2 = -n_2\phi_L \qquad (8\text{-}2\text{-}6)$$

According to this definition ΔH_D is positive when the dilution process is accompanied by the absorption of heat. This convention regarding sign is contrary to that adopted by Lange and other European writers to whom we shall presently refer.

Differentiating the first and last members of equation (8-2-5) with respect to n_2 at constant temperature, pressure, and n_1, and recalling that $\frac{\partial L}{\partial n_2}$ defines $\bar{L}_2$ under these conditions, we obtain

$$\bar{L}_2 = \phi_L + n_2 \frac{\partial \phi_L}{\partial n_2} \tag{8-2-7}$$

This is the fundamental equation upon which calorimetric determination of $\bar{L}_2$ is based. The quantity ϕ_L cannot be measured directly, but is readily obtained by measuring the heat changes accompanying successive finite dilutions, and by extrapolating from the lowest experimental concentrations to infinite dilution. Thus for the dilution of a binary solution, from a solute concentration m (mols per kilogram of solvent) to m', and from m' to m'', etc., the corresponding heat effects may be written,

Table (8-2-1). The Heat of Dilution of NaCl at 25°.

c (mols/liter)		$\Delta H_D(c_{\mathrm{In}} \rightarrow c_{\mathrm{Fi}})$ cals/mol	Final concs.		$\Delta H_{(0.1 \rightarrow c)}$	ΔH_D
Initial	Final		c	$\sqrt{c}$		
0.1	0.00308	−61.5	0.05	0.2236	−12.8	−70.2
.1	.00605	−52.9	.025	.1581	−27.8	−55.2
.05	.00154	−54.9	.0125	.1118	−42.9	−40.1
.05	.00302	−48.7	.00605	.0778	−52.9	−30.1
.025	.000770	−45.6	.00305*	.0552	−61.5	−21.5
.025	.001515	−39.9	.00153	.0391	−67.4	−15.6
.0125	.000385	−33.1	.00076	.0276	−73.1	−9.9
.0125	.000754	−30.5	.00039	.0197	−75.7	−7.3
			0	0	(−83.0)	0

* The heat effect from $c = 0.00308$ to $c = 0.00302$ is negligible; hence both of these concentrations are set equal to their mean, and lower concentrations in the table are treated likewise.

$$\Delta H_{(m \rightarrow m')} = \phi'_H - \phi_H \tag{8-2-8}$$

$$\Delta H_{(m' \rightarrow m'')} = \phi''_H - \phi'_H \tag{8-2-9}$$

and so on, for successive dilutions. Linear combination of these equations leads to values of $\phi'_H - \phi_H$, $\phi''_H - \phi_H$, $\phi'''_H - \phi_H$, etc., which may be extrapolated to infinite dilution in order to evaluate $\phi^0_H - \phi_H$. Finally, by subtracting $\phi'_H - \phi_H$, $\phi''_H - \phi_H$, etc., from this extrapolated value, the corresponding heats of dilution at m', m'', etc., are obtained throughout the whole experimental range. An example of such a calculation is given in Table (8-2-1). The data are for sodium chloride in aqueous solutions at 25°, the first three columns in the table being taken from the computations of Robinson.[1]

The extrapolation by which the value, $\Delta H_{(0.1 \rightarrow 0)} = -83.0$, is obtained,

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[1] A. L. Robinson, *J. Am. Chem. Soc.*, **54**, 1311 (1932).

quantities requires the extrapolation of experimental data in very dilute solutions. By the application of the Debye-Hückel equation, a theoretical limiting slope has been derived [Equation (5-2-14)] which increases the reliability of these extrapolations. Conversely, the verification of the limiting slope has magnified the importance of measurements at extreme dilutions. Before we can give an account of such measurements and their interpretation, it will be necessary to extend the treatment of partial molal quantities, given in Chapter (1), by defining several new quantities.

Dropping the generalized formulation of equation (1-7-2), we obtain for two components,

$$H = n_1\bar{H}_1 + n_2\bar{H}_2 \tag{8-2-1}$$

which gives the total heat content of a solution, composed of n_1 mols of solvent and n_2 mols of solute, in terms of the partial molal heat contents of its components. A similar equation,

$$H = n_1\bar{H}_1^0 + n_2\phi_H \tag{8-2-2}$$

gives the heat content in terms of the partial molal heat content of the solvent at infinite dilution, $\bar{H}_1^0$, and the apparent molal heat content of the solute, ϕ_H. Comparison of these equations shows that

$$\phi_H^0 = \bar{H}_2^0 \tag{8-2-3}$$

at infinite dilution. Since the absolute values of heat contents are experimentally undefined, it is necessary to employ the corresponding relative properties, which, unless otherwise noted, will be referred to the infinitely dilute solution. Thus, by equation (1-7-6), the expression

$$H - H^0 = n_1(\bar{H}_1 - \bar{H}_1^0) + n_2(\bar{H}_2 - \bar{H}_2^0) = n_2(\phi_H - \phi_H^0) \tag{8-2-4}$$

follows from equations (8-2-1) and (8-2-2). Upon substituting the definitions, $L \equiv H - H^0$, $\bar{L}_1 \equiv \bar{H}_1 - \bar{H}_1^0$, $\bar{L}_2 \equiv \bar{H}_2 - \bar{H}_2^0$, and $\phi_L \equiv \phi_H - \phi_H^0$, this equation becomes

$$L = n_1\bar{L}_1 + n_2\bar{L}_2 = n_2\phi_L \tag{8-2-5}$$

The relative apparent molal heat content, $\phi_H - \phi_H^0$, is equal to, and of opposite sign to, the heat of dilution, ΔH_D, for the isothermal isobaric addition of an infinite quantity of pure solvent to a solution containing one mol of solute in n_1/n_2 mols of solvent. Consequently,

$$n_2\Delta H_D = -n_1\bar{L}_1 - n_2\bar{L}_2 = -n_2\phi_L \tag{8-2-6}$$

According to this definition ΔH_D is positive when the dilution process is accompanied by the absorption of heat. This convention regarding sign is contrary to that adopted by Lange and other European writers to whom we shall presently refer.

Differentiating the first and last members of equation (8-2-5) with respect to n_2 at constant temperature, pressure, and n_1, and recalling that $\frac{\partial L}{\partial n_2}$ defines $\bar{L}_2$ under these conditions, we obtain

$$\bar{L}_2 = \phi_L + n_2 \frac{\partial \phi_L}{\partial n_2} \tag{8-2-7}$$

This is the fundamental equation upon which calorimetric determination of $\bar{L}_2$ is based. The quantity ϕ_L cannot be measured directly, but is readily obtained by measuring the heat changes accompanying successive finite dilutions, and by extrapolating from the lowest experimental concentrations to infinite dilution. Thus for the dilution of a binary solution, from a solute concentration m (mols per kilogram of solvent) to m', and from m' to m'', etc., the corresponding heat effects may be written,

TABLE (8-2-1). THE HEAT OF DILUTION OF NaCl AT 25°.

c (mols/liter)		$\Delta H_D(c_{\text{In}} \rightarrow c_{\text{Fi}})$ cals/mol	Final concs.		$\Delta H_{(0.1\rightarrow c)}$	ΔH_D
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			0	0	(−83.0)	0

* The heat effect from $c = 0.00308$ to $c = 0.00302$ is negligible; hence both of these concentrations are set equal to their mean, and lower concentrations in the table are treated likewise.

$$\Delta H_{(m\rightarrow m')} = \phi_H' - \phi_H \tag{8-2-8}$$

$$\Delta H_{(m'\rightarrow m'')} = \phi_H'' - \phi_H' \tag{8-2-9}$$

and so on, for successive dilutions. Linear combination of these equations leads to values of $\phi_H' - \phi_H$, $\phi_H'' - \phi_H$, $\phi_H''' - \phi_H$, etc., which may be extrapolated to infinite dilution in order to evaluate $\phi_H^0 - \phi_H$. Finally, by subtracting $\phi_H' - \phi_H$, $\phi_H'' - \phi_H$, etc., from this extrapolated value, the corresponding heats of dilution at m', m'', etc., are obtained throughout the whole experimental range. An example of such a calculation is given in Table (8-2-1). The data are for sodium chloride in aqueous solutions at 25°, the first three columns in the table being taken from the computations of Robinson.[1]

The extrapolation by which the value, $\Delta H_{(0.1\rightarrow 0)} = -83.0$, is obtained,

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[1] A. L. Robinson, *J. Am. Chem. Soc.*, **54**, 1311 (1932).

is illustrated in Fig. (8-2-1). The theoretical limiting slope is derived from equation (5-2-14),

$$\bar{L}_2 = \mathcal{S}_{(H)}\sqrt{c} = \sqrt{d_0}\,\mathcal{S}_{(H)}\sqrt{m} \tag{8-2-10}$$

applied to a 1-1 strong electrolyte at such high dilutions that c may be replaced by d_0m. Combination of this equation with (8-2-7) leads to

$$\phi_L = (2/3)\sqrt{d_0}\,\mathcal{S}_{(H)}\sqrt{m} \tag{8-2-11}$$

or, in simpler terms

$$\Delta H_D = -(2/3)\,\mathcal{S}_{(H)}\sqrt{c} \tag{8-2-12}$$

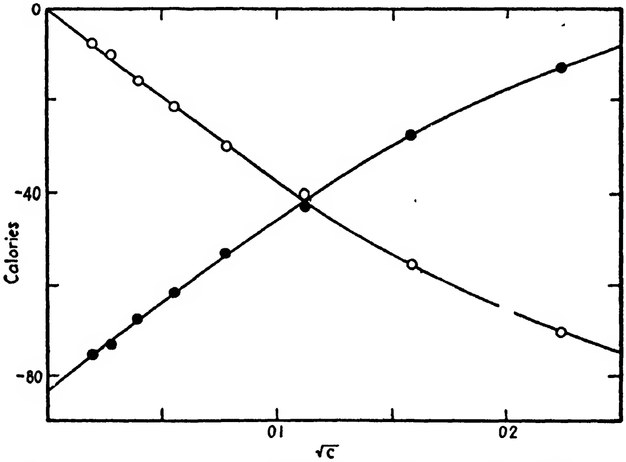

Fig. (8-2-1). Heats of dilution of sodium chloride in water at 25°; ● $\Delta H_{D(0.1\rightarrow c)}$ ○ ΔH_D. Compare Fig. (B-4-2).

This is the limiting function which the plot of ΔH_D should approach as c decreases. Accordingly, the limiting law for the experimental quantity $\Delta H_{(0.1\,\rightarrow\,c)}$ is the equation,

$$\Delta H_{(0.1\rightarrow c)} = \Delta H_{(0.1\rightarrow 0)} + (2/3)\,\mathcal{S}_{(H)}\sqrt{c} \tag{8-2-13}$$

which can be obtained by subtracting $\phi_{H(0.1)}$ from both sides of equation (8-2-11) and rearranging terms.

The method of extrapolation just described is that used by Lange.* Although his estimate of an error in extrapolation of ±2 calories per mol is usually justified, the "experimental" limiting slopes which he derived from his most dilute measurements show considerable deviations from the theoretical values. This contradiction to theory has been eliminated by more recent methods of computation. Before discussing these, it will

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* Table (8-2-1A).

be profitable to describe briefly the remarkable experimental technique employed in these measurements.

The first accurate measurement of heats of dilution at very low concentrations were made by Nernst and Orthmann,[2] but the development of the method to its present high precision is largely due to Lange[3] who applied a number of ingenious refinements to the Joule-Pfaundler twin calorimeter technique. Their most striking innovation is the use of a flat thermocouple as a partition separating the two halves of the calorimeter.[4] A 1000 to 1500 junction iron-constantan thermel, employed in this manner, is capable of measuring small temperature differences with an accuracy of about 2 × 10^{-7} degree. Since the heat conductivity of such a thermel precludes the measurement of temperature differences greater than 10^{-3} in dilute solutions, the rise in temperature, accompanying the dilution of the solution in one half of the calorimeter, must be largely counterbalanced by electrical heating of the pure solvent in the other half. The function of the thermel is to determine the difference between the heat of dilution and the precisely measured electrical heating. In the ideal case, the thermel would operate as a null instrument. Making use of a Paschen galvanometer and a specially constructed potentiometer, Gucker, Pickard and Planck[5] have been able to decrease the heat conduction by employing a copper-constantan thermel of only 60 junctions. This permits a greater separation of the two halves of the calorimeter system. By delicate regulation of the thermostat, the temperature difference between the calorimeter and its surroundings is reduced to about 10^{-4} degree, and since this is the order of the temperature changes produced by dilutions at the lower concentrations, the measurements may properly be considered adiabatic and isothermal. A good example of the sensitivity of the measurements and the reproducibility of the data is furnished by a comparison of the work of Lange and Streeck,[6] and Lange and Monheim[7] on calcium sulfate at extreme dilutions. A plot of their results is given in Fig. (8-2-2) which shows the two independent series fitted to a common curve. The plot for magnesium sulfate is distinguishable from that for calcium sulfate at concentrations as low as $0.0005M$.

The specificity of heats of dilution at the lowest accessible concentrations is a general phenomenon not confined to any particular valence type

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[2] W. Nernst and W. Orthmann, *Sitzber. preuss. Akad. Wiss.*, 51, (1926); *Z. physik. Chem.*, **135**, 199 (1928).

[3] A review of this technique is given by E. Lange and A. L. Robinson [*Chem. Rev.*, **9**, 89 (1931)], and a complete bibliography of earlier developments can be found in the paper by T. W. Richards and F. T. Gucker, Jr. [*J. Am. Chem. Soc.*, **47**, 1876 (1925)].

[4] E. Lange and J. Monheim, *Z. physik. Chem.*, **149A**, 51 (1930).

[5] F. T. Gucker, Jr., H. G. Pickard and R. W. Planck, *J. Am. Chem. Soc.*, **61**, 459 (1939).

[6] E. Lange and H. Streeck, *Z. physik. Chem.*, **157A**, 1 (1931).

[7] E. Lange and J. Monheim, *Z. physik. Chem.*, **150A**, 349 (1930).

electrolytes. Fig. (8-2-3) illustrates the behavior of some typical 1-1 electrolytes studied by Lange.[8] These results raise two important questions. Is the theoretical slope actually approached by all of the curves at infinite dilution, and why is the individuality of the salts at high dilution so much more pronounced for heat data than for activity coefficients? The answer to the latter question is obtained by differentiation of the complete Debye-Hückel equation (3-8-2),

$$\log f_{\pm} = -\frac{\mathfrak{S}_{(f)}\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} + B\Gamma \qquad (8\text{-}2\text{-}14)$$

from which it appears that the temperature coefficients of both A and B make important contributions at high dilutions.* Earlier attempts[9] to explain the specificity of heat data on the basis of the A parameter alone, either in the above form, or including the extended terms of equations (3-6-4) and (3-6-5), led to some curious anomalies in the magnitudes of the ionic parameter, $\mathring{a}$. It was found[10] that if a series of electrolytes with a common ion is arranged in the order of increasing $\mathring{a}$-values, derived from heats of dilution, the order is usually the reverse of that which would have

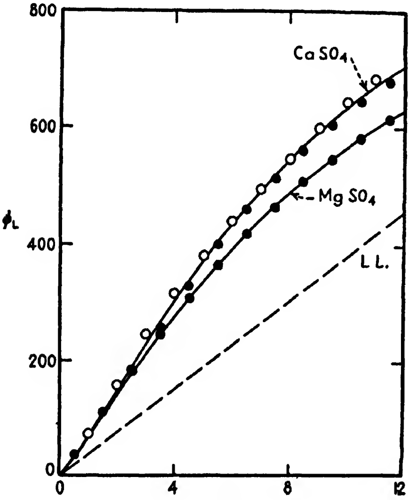

Fig. (8-2-2)
Relative apparent molal heat contents of calcium sulfate and magnesium sulfate in water at 25°. ○ Lange and Monheim; ● Lange and Streeck

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[8] Bibliography of experimental papers will be given in connection with tables of ΔH_D and L_2 in this chapter, and in the appendix.

* See Chapters (11) and (12).

[9] G. B. Bonino and V. Vaglio [*Nuovo Cimento*, **5**, 4 (1928)] attempted to account for the individuality of heats of dilution curves by a semi-empirical treatment.

[10] E. Lange and H. Streeck, *Naturwiss.*, **19**, 359 (1931). E. Lange and A. L. Robinson, *Chem. Rev.*, **9**, 89 (1931).

been obtained if $\mathring{a}$-values, derived from activity coefficient data, had been used. Furthermore, the nature of the common ion plays an important part in this connection, and may even reverse the order in certain series. Thus, $\mathring{a}_{MgSO_4}$ is greater than $\mathring{a}_{CaSO_4}$, while $\mathring{a}_{MgCl_2}$ is less than $\mathring{a}_{CaCl_2}$. These considerations threw some doubt upon the validity of the Debye-Hückel equation, and made it apparent that the actual approach of the experimental curves to the theoretical limiting slopes must be definitely established. A detailed discussion of this matter will be found in Appendix B, Section (4).

The reported discrepancies between the "experimental" limiting slopes and those required by theory were largely due to the difficulty of reading off a truly representative limiting slope from plots such as the one illustrated by Fig. (8-2-1). Graphs of this nature seemed to be linear over a considerable range within the accuracy of the data, but since pronounced departures from linearity appear at higher concentrations [Fig. (8-2-3)], the experimental limiting slope was a function of the concentration range employed in its evaluation. From their data on sodium chloride at 10, 15, 20 and 25°, Gulbransen and Robinson[11] concluded that the heat of dilution was linear with $\sqrt{m}$ up to $\sqrt{m} = 0.1$, although they state that "there is some evidence of continuously changing slope to $m = 0$, but the heat effects below $\sqrt{m} = 0.1$ are too small to decide this question definitely." According to their treatment of these results, Gulbransen and Robinson found that the limiting slopes are from 33 per cent (at 10°) to 12 per cent (at 25°) smaller than the theoretical. Later, by an analytical adaptation of the chord-area method,[12] Young and Groenier[13] found that the same data yielded slopes within 5 per cent of the theoretical.

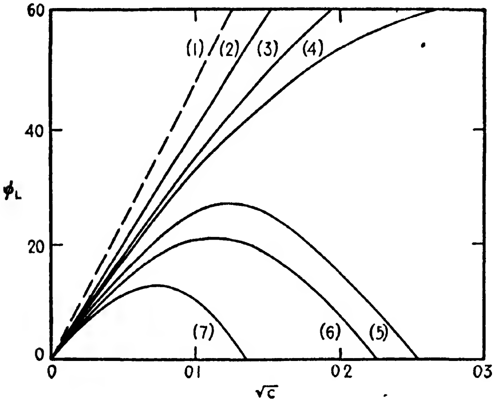

Fig. (8-2-3)
Relative apparent molal heat contents of potassium salts in water at 25°. (1) Theoretical limiting law; (2) KF; (3) KCl; (4) KBr; (5) $KClO_3$; (6) KNO_3; (7) $KClO_4$

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[11] E. A. Gulbransen and A. L. Robinson, *J. Am. Chem. Soc.*, **56**, 2637 (1934).

[12] T. F. Young and O. G. Vogel, *J. Am. Chem. Soc.*, **54**, 3030 (1932).

[13] T. F. Young and W. L. Groenier, *Ibid.*, **58**, 187 (1936).

In the application of this method, the chord

$$\bar{P}_i = \frac{\Delta H_{(m_1 \rightarrow m_2)}}{\sqrt{m_2} - \sqrt{m_1}} \tag{8-2-15}$$

represents the average value of the slope, S, of the ΔH_D *vs.* $\sqrt{m}$ curve throughout the concentration range, $\sqrt{m_2} \rightarrow \sqrt{m_1}$. The expansion of equation (3-8-5) implies that S may be represented in dilute solutions by

$$S = S^0 + B''\sqrt{m} + C''m \tag{8-2-16}$$

and preliminary plots show that the inclusion of higher powers of $\sqrt{m}$ are unnecessary below $\sqrt{m} = 0.64$. S^0, B'' and C'' are empirical constants which are to be evaluated from the experimental data after S has been properly expressed in terms of $\bar{P}_i$. If the data are in accord with theory, the value of S^0 so determined should be equal to $(2/3)\sqrt{d_0}\,\mathfrak{S}_{(H)}$. Representing the value of $(1/2)(\sqrt{m_2} + \sqrt{m_1})$ for the *i*th chord by x_i, and the value of S at x_i by P_i, then

TABLE (8-2-2). CONSTANTS FOR SODIUM CHLORIDE.

	Chord-area method			Theory S^0	Gulbransen and Robinson S^0
	$-B''$	C''	S^0		
25°	1452.2	730.4	476.1	477(478)*	418
20°	1585.7	894.8	451.3	434(435)	370
15°	1650.8	924.5	413.6	393(396)	340
10°	1531.5	591.8	355.7	355(358)	239

* Values in parentheses were calculated from $\mathfrak{S}_{(H)}$ given in Table (5-2-5). All other values are those reported by Young and Groenier.

$$P_i = S^0 + B''x_i + C''x_i^2 \tag{8-2-17}$$

and the difference between P_i and $\bar{P}_i$ is given by

$$P_i - \bar{P}_i = -\frac{d^2S}{d(\sqrt{m})^2}\frac{\delta_i^2}{24} = -\frac{C''\delta_i^2}{12} \tag{8-2-18}$$

where δ_i is the change in $\sqrt{m}$ corresponding to the *i*th dilution. Elimination of P_i between equations (8-2-18) and (8-2-17) results in the desired equation,

$$\bar{P}_i = S^0 + B''x_i + C''(x_i^2 + \delta_i^2/12) \tag{8-2-19}$$

which allows the evaluation of S^0, B'' and C'' by the method of least squares. In carrying out this operation, Young and Groenier used m_2 as a weighting factor.

The constants obtained by this procedure are given in Table (8-2-2), where the values of S^0 are compared with those originally derived from the same data by Gulbransen and Robinson,[14] and the theoretical values,

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[14] E. A. Gulbransen and A. L. Robinson, *J. Am. Chem. Soc.*, **56**, 2637 (1934).

$(2/3)\sqrt{d_0}\mathfrak{S}_{(H)}$. To show that this excellent agreement between the theoretical slopes and those calculated by the chord-area method is not fortuitous, Young and Seligmann[15] extended the application of this method to all the salts of the alkali metals for which adequate data are available. In these later calculations, m was replaced by c in equations (8-2-15) to (8-2-19). Since this alters the numerical values of B'' and C'', we shall designate these constants B' and C' when the c-scale is used. Their plots of P_i, calculated by equation (8-2-17) from the experimental values of $\bar{P}_i$ and empirical values of C', are reproduced in Figs. (8-2-4) and (8-2-5). The smooth curves represent the equations (8-2-16) for S obtained by the procedure described above. The intercepts, S^0, obtained in this manner are in good agreement with theory, the average of the deviations being only ±6.3 per cent. The sum of the positive and negative deviations for twenty-one salts is only +10.8 per cent. The individual values of the deviation, $\Delta = 100\,[S^0_{(\text{exp})} - S^0_{(\text{theo})}]/S^0_{(\text{theo})}$, are given in the sixth column of Table (8-2-3). In view of this concordance, Young and Seligmann considered the theory completely verified within the probable error of the data and the extrapolation method. They therefore accepted the theoretical value of S^0 in all cases, and re-evaluated the constants B' and C' by the method of least squares. The values obtained in this manner are recorded in Table (8-2-3). The use of these parameters in the expression,

$$\phi_L = -\Delta H_D = S^0\sqrt{c} + (1/2)B'c + (1/3)C'c^{3/2} \qquad (8\text{-}2\text{-}20)$$

leads to accurate values of the relative apparent molal heat content, or heat of dilution, up to $\sqrt{c} = 0.2$ in general, and up to $\sqrt{c} = 0.4$ for sodium and potassium chlorides. For all the salts considered in Table (8-2-3), the limiting slope is given by

$$S^0 = (2/3)\mathfrak{S}_{(H)} \qquad (8\text{-}2\text{-}21)$$

in accordance with theory. With regard to the remaining salts for which data are available at high dilution, Young and Seligmann found that the few measurements on lithium chloride[16] and potassium fluoride[17] are in accord with equation (8-2-21), although the data are insufficient to justify least squaring. They also reported, "An incomplete investigation of salts of the alkaline earth metals of the 2-1 valence type indicates similar agreement, at least at 25°. The extrapolations seem to be of poorer precision, and afford less definite support of the Debye-Hückel theory, but no data point to failure of the theory. Existing data for salts of the 2-2 valence type *if treated by the methods described above*, certainly do not lead to limiting values in agreement with theory."[18] Since there is evidence

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[15] T. F. Young and P. Seligmann, *J. Am. Chem. Soc.*, **60**, 2379 (1938).

[16] E. Lange and J. Messner, *Z. Elektrochem.*, **33**, 431 (1927).

[17] E. Lange and A. Eichler, *Z. physik. Chem.*, **129**, 285 (1927).

[18] T. F. Young and P. Seligmann, *J. Am. Chem. Soc.*, **60**, 2379 (1938), footnote 19. *Cf.* T. F. Young, *Science*, **85**, 48 (1937).

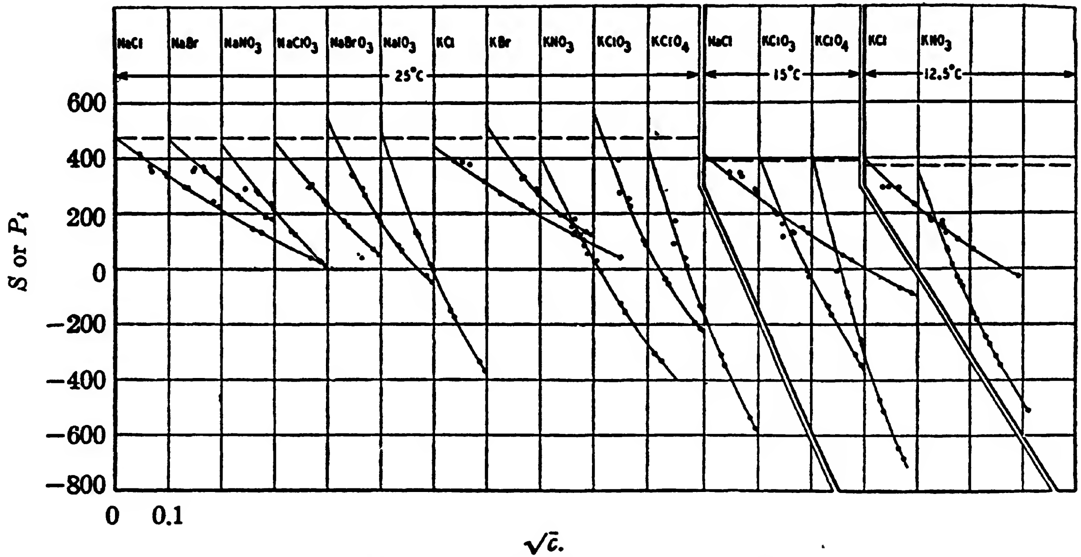

Fig. (8-2-4). Evaluation of the experimental limiting slopes, $S°$, for the relative apparent molal heat contents of 1-1 electrolytes in water at several temperatures that salts of the 2-2 valence type are incompletely dissociated in solution [Table (6-3-2)], the behavior of these salts does not constitute a serious exception to the general conformity of heat of dilution data with theory.

The evaluation of the relative partial molal heat content, $\overline{L}_2$, from heats of dilution follows from equation (8-2-7) in the form

$$\overline{L}_2 = -\Delta H_D - n_2 \frac{\partial \Delta H_D}{\partial n_2} = -\Delta H_D - \tfrac{1}{2}\sqrt{m}\frac{\partial \Delta H_D}{\partial \sqrt{m}} \qquad (8\text{-}2\text{-}22)$$

In dilute solutions, where m is proportional to c, this equation may be combined with (8-2-20) to yield

$$\overline{L}_2 = (3/2)S^0\sqrt{c} + B'c + (5/6)C'c^{3/2} \qquad (8\text{-}2\text{-}23)$$

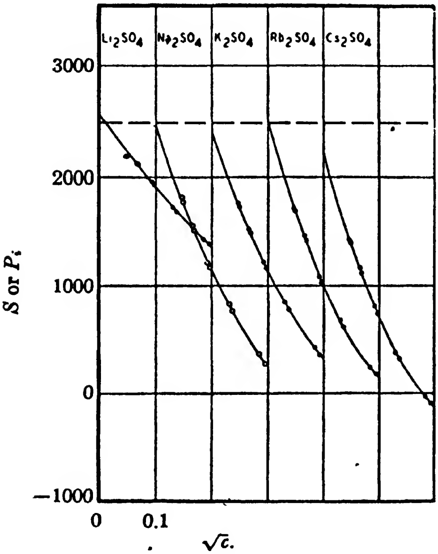

Fig. (8-2-5)
Evaluation of the experimental limiting slopes, S^0, for the relative apparent molal heat contents of 1-2 electrolytes in water at 25°

This expression may be used to calculate $\overline{L}_2$ up to concentrations of the order 0.05N.

For practical reasons, particularly in relating the results of freezing-point measurements to a standard temperature, it is often necessary to calculate $\overline{L}_1$. The general relation for this quantity is

$$\overline{L}_1 = \frac{n_2^2}{n_1}\frac{\partial \Delta H_D}{\partial n_2} = \frac{M_1 m^{3/2}}{2000}\frac{\partial \Delta H_D}{\partial \sqrt{m}} \qquad (8\text{-}2\text{-}24)$$

and follows from equations (8-2-6) and (8-2-7). In sufficiently dilute solutions md_0 may replace c and this equation becomes

$$\overline{L}_1 = -\frac{M_1}{2000d_0}(S^0c^{3/2} + B'c^2 + C'c^{5/2}) \qquad (8\text{-}2\text{-}25)$$

when ΔH_D is eliminated by (8-2-20).

In Tables (8-2-1A) and (8-2-2A), we have compiled values of ϕ_L and $\bar{L}_2$ derived from calorimetric data on strong electrolytes at 25°. Additional values, derived from electromotive force measurements, are given in Chapters (11) and (12). Comprehensive tabulations at other temperatures, particularly at 18°, can be found in standard handbooks, and in the monograph of Bichowsky and Rossini.[19]

Since the theoretical limiting slope was disregarded in the original extrapolations of most of the data used in the preparation of Table (8-2-1A), we have re-extrapolated the results for all salts, to make the curves of ϕ_L against $\sqrt{m}$ approach the origin with the theoretical slope, $(2/3)\sqrt{d_0}\mathfrak{S}_{(H)}$. This slope is greater than most of those previously employed, so it was usually necessary to bend the curves more strongly as the axis was approached. The resulting curves were then displaced vertically until they passed through the origin, and values of ϕ_L and $d\phi_L/d\sqrt{m}$ read off at round concentrations. $\bar{L}_2$ was calculated by equation (8-2-22) from these

TABLE (8-2-3). PARAMETERS OF EQUATION (8-2-20).

Salt	$t°$	S^{0a}	$-B'$	C'	Δ	Ref.[c]
$NaCl^b$	25	477	1,532	1,154	−0.2	(1)
$NaCl^b$	15	393	1,411	335	+5.3	(1)
NaBr	25	477	1,888	1,770	−1.5	(2)
$NaNO_3$	25	477	2,961	2,834	−4.8	(3)
$NaClO_3$	25	477	2,708	2,701	−3.1	(3)
$NaBrO_3$	25	477	3,562	4,831	+13.2	(3)
$NaIO_3$	25	477	5,635	6,913	+5.0	(3)
KCl	25	477	1,893	2,144	−6.9	(4)
KCl	12.5	374	1,569	273	+5.3	(4)
KBr	25	477	2,541	3,902	+7.8	(2)
KNO_3	25	477	5,006	6,079	−14.5	(5)
KNO_3	12.5	374	5,753	7,522	−6.4	(5)
$KClO_3$	25	477	4,527	5,334	+19.1	(6)
$KClO_3$	15	393	4,681	4,602	+4.1	(6)
$KClO_4$	25	477	7,492	10,510	−7.8	(6)
$KClO_4$	15	393	8,086	11,011	+3.6	(6)
Li_2SO_4	25	2,481	6,022	2,305	+2.7	(7)
Na_2SO_4	25	2,481	15,576	21,482	−2.0	(7)
K_2SO_4	25	2,481	16,022	25,599	−3.3	(7)
Rb_2SO_4	25	2,481	17,896	31,381	+5.3	(7)
Cs_2SO_4	25	2,481	22,169	44,570	−10.1	(7)

[a] $S^0 = (2/3)\mathfrak{S}_{(H)}$.

[b] The parameters for NaCl refer to concentrations expressed as molality. The parameters for all of the other salts refer to concentrations expressed in mols per liter of solution.

[c] The references listed below give the origin of the data.

(1) E. A. Gulbransen and A. L. Robinson, *J. Am. Chem. Soc.*, **56**, 2637 (1934).
(2) H. Hammerschmid and A. L. Robinson, *Ibid.*, **54**, 3120 (1932).
(3) E. Lange and A. L. Robinson, *Z. physik. Chem.*, **148A**, 97 (1930).
(4) E. Lange and P. A. Leighton, *Z. Elektrochem.*, **34**, 566 (1928).
(5) E. Lange and J. Monheim, *Z. physik. Chem.*, **150A**, 349 (1930).
(6) M. Andauer and E. Lange, *Ibid.*, **165A**, 89 (1933).
(7) E. Lange and H. Streeck, *Ibid.*, **157A**, 1 (1931).

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[19] F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, 1936.

values, and smoothed graphically to eliminate irregularities due to the difficulty of estimating $d\phi_L/d\sqrt{m}$. Part I of Table (8-2-2A) contains these recalculated and smoothed values of $\bar{L}_2$. The results given in Part II of this table were not all recalculated, but were adjusted in every case to fall smoothly upon the extensions of plots of the corresponding values in Part I.

In dilute solutions, our values of ϕ_L and $\bar{L}_2$ agree closely with those calculated by equations (8-2-20) and (8-2-23) and the constants given in Table (8-2-3). In concentrated solutions, our values are usually greater than those[20] derived from the original extrapolations. This difference is recorded as Δ in the last column in Table (8-2-1A), and positive values of Δ represent the upward displacement required to bring the new extrapolation curves to the origin.

It will be seen that Δ does not exceed 7 cal except for lithium chloride, and the 2-2 salts. The large displacement for lithium chloride is due to the absence of data below 0.139*M*. Our extrapolation is based upon the close similarity of the curves for lithium chloride and lithium bromide at moderate dilutions, and, although it is much less certain than those for the other 1-1 salts, it is to be preferred to that of Lange and Dürr.[21]

The extrapolation of the heat data for 2-2 salts is very uncertain, because the slopes of the experimental curves at the highest dilutions are two or three times greater than the theoretical. In forcing the extrapolation curves to conform with theory in the limit, it is necessary to introduce so much curvature[22] in the region below the experimental concentration range that the estimation of Δ is a rough approximation at best. Furthermore, the experimental results for these hydrolyzable salts are subject to corrections which may seriously influence the extrapolations.

Doehlemann and Lange[23] pointed out that measureable heat effects

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[20] Some of the thermodynamic quantities, tabulated in the various German papers by Lange and his collaborators, can be simply transposed into the conventional American nomenclature used in these chapters by the relations,

$$-\phi_L = \Delta H_D = L_m - L_0 = -V_m$$

$$L_2 = \Lambda_0 - \Lambda_m = V_m + \frac{55.51}{m}\phi_m$$

$$L_1 = -\phi_m; \qquad L_{2(s)} = L_0 = \Lambda_0$$

Here $-L_m$ is the total (integral) heat of solution, and $-\Lambda_m$ is the partial (differential) heat of solution, and $L_{2(s)}$ is the relative partial heat content of the solid solute. For a more complete comparison of the American and German nomenclature and conventions, compare G. N. Lewis and M. Randall, "Thermodynamics", McGraw-Hill Book Co., New York, 1923, with W. Schottky, "Thermodynamik", Julius Springer, Berlin, 1929.

[21] E. Lange and F. Dürr, *Z. physik. Chem.*, **121**, 361 (1926).

[22] Experimental evidence of such curvature is provided by the calculations of A. L. Robinson and W. E. Wallace, *J. Am. Chem. Soc.*, **63**, 1582 (1941).

[23] E. Doehlemann and E. Lange, *Z. physik. Chem.*, **170A**, 391 (1934).

are produced by changes in ionic equilibria which accompany the process of dilution. In dilute neutral salt solutions, the effect of changing the ionization of water is small (<2 cal per mol of salt), but the heat effects produced by changes in the hydrolysis or dissociation of a salt, such as zinc sulfate, are unknown, and may be quite large. For the completely dissociated salt, ammonium chloride, the hydrolysis correction is of the same order as the displacement ($\Delta = 7$) involved in the re-extrapolation. It is probable that the effects of the hydrolysis of potassium and rubidium fluorides are only partially compensated by the displacements recorded for these salts. As an extreme example of the uncertainty which may be involved in the extrapolation of heat data which are influenced by changes in ionic equilibria, it is shown in Chapter (13), Section (13), that a displacement of the order of −450 cal is required to bring the calorimetric values of $\bar{L}_2$ for sulfuric acid into agreement with theory. Values of $\bar{L}_2$ for this acid may be computed at various temperatures from the parameters given in Table (13-13-1A).

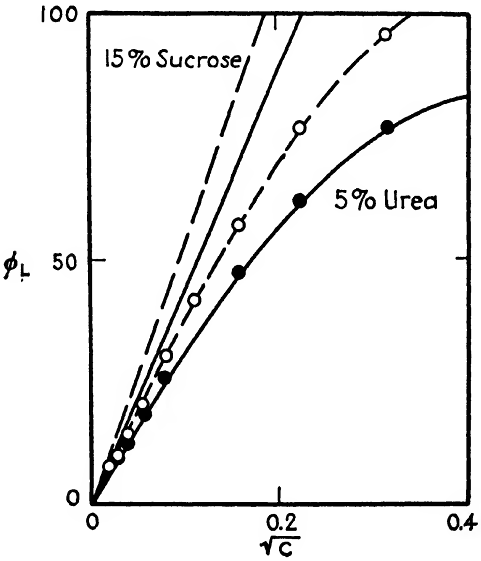

Fig (8-2-6)
Relative apparent molal heat content of KCl in mixed solvents at 25°; straight lines represent theoretical limiting law

Lange and Robinson[24] measured the heat of dilution of potassium chloride in aqueous sugar and urea solutions to see if variation of the dielectric constant by the presence of non-electrolytes would have the effect predicted by theory. Their results are shown in Fig. (8-2-6) along with the appropriate limiting slopes. In calculating the latter, the

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[24] E. Lange and A. L. Robinson, *J. Am. Chem. Soc.*, **52**, 4218 (1930).

dielectric constants of Wyman were used for water[25] and the urea solution.[26] Wyman has published no data on sucrose solutions, but we may take Åkerlöf's[27] experience as an indication that Kockel's data are, in this case, consistent with Wyman's other measurements. Kockel's[28] data have, therefore, been used in calculating this theoretical slope for the sugar solution. Since dV/dT is not known with certainty for urea solutions, this term was omitted in evaluating all three slopes. It can be seen from the figure that the observed slopes are all about 25 per cent lower than required by theory, but this simple regularity must be regarded as fortuitous until dD/dT is more accurately known.[29] We note that the experimental limiting slopes estimated in this manner for 1-1 electrolytes in pure water were generally found to be from 10 to 50 per cent lower than the theoretical, and that the success of the chord-area method in clearing up this discrepancy would presumably extend to sucrose and urea solutions as well.

The heats of dilution and relative partial molal heat contents of a few non-electrolytes have been determined in dilute solutions. Because of the lack of charge, the square root term in the expression for the heat of dilution of an electrolyte should vanish for a non-electrolyte. There is no adequate theory by which the numerical magnitude of the coefficients of the linear or higher concentration terms may be predicted. For this reason, there has been but little interest in the calorimetry of solutions of non-electrolytes, and we are fortunate in having data on the sucrose-water system of an accuracy comparable to that attained with solutions of electrolytes. Gucker, Pickard and Planck[30] have measured the heat of dilution of sucrose at high dilutions in water at 20 and 30°, and Naudé[31] has made similar measurements at 18°. Data are available at higher concentrations through the work of Porter and Wood,[32] Pratt,[33] and Vallender and Perman.[34] Gucker[30] determined the chords $\Delta H/\Delta m$ experimentally and treated his results by an adaptation of the method of

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[25] J. Wyman, Jr., *Phys. Rev.*, **35**, 623 (1930).

[26] J. Wyman, Jr., *J. Am. Chem. Soc.*, **55**, 4116 (1933).

[27] G. Åkerlöf, *J. Am. Chem. Soc.*, **54**, 4125 (1932).

[28] L. Kockel, *Ann. Physik.*, **77**, 417 (1925).

[29] Above 30 to 35°, urea solutions undergo a slow, irreversible change in conductivity and dielectric constant, and it was only by rapid manipulation that Wyman obtained reproducible temperature coefficients. An earlier value of dD/dT, obtained by L. Kockel [*Ann. Physik.*, **77**, 417 (1925)], actually gave a slope of opposite sign to that shown in Fig. (8-2-6).

[30] F. T. Gucker, Jr., H. G. Pickard and R. W. Planck, *J. Am. Chem. Soc.*, **61**, 459 (1939). See also the study of urea solutions by F. T. Gucker, Jr., and H. G. Pickard, *Ibid.*, **62**, 1464 (1940).

[31] F. M. Naudé, *Z. physik. Chem.*, **135**, 209 (1928).

[32] Results quoted by A. W. Porter, *Trans. Faraday Soc.*, **13**, 123 (1917).

[33] F. R. Pratt, *J. Franklin Inst.*, **185**, 663 (1918).

[34] R. B. Vallender and E. P. Perman, *Trans. Faraday Soc.*, **27**, 124 (1931).

Young and Vogel.[35] He found that, between $m = 0.002$ and $m = 0.2$, $\Delta H/\Delta m$ was constant within the experimental accuracy, the average deviation from the mean corresponding to about 3 micro-degrees. The limiting equations are

$$-\Delta H_D = \phi_L = 128.9m; \quad \text{at } 20° \tag{8-2-26}$$

and

$$-\Delta H_D = \phi_L = 140.2m; \quad \text{at } 30° \tag{8-2-27}$$

When the available data at higher concentrations were consistently treated to yield values of ϕ_L, it was found necessary to add a term in m^2 to the analytical expression for ϕ_L, but the coefficient of the linear term in m was practically the same as that evaluated from the data at high dilutions alone. Terms in m^2 were added to equations (8-2-26) and (8-2-27), and the coefficients adjusted to give a satisfactory representation of all the data. The final equations are

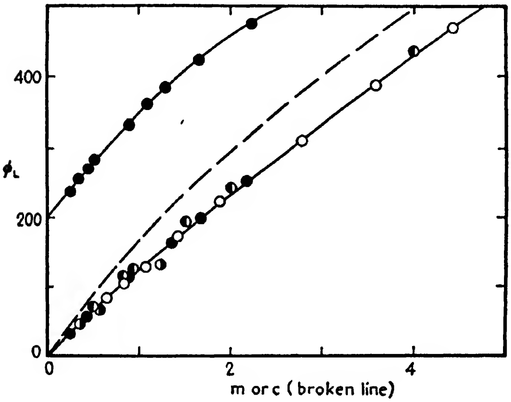

Fig. (8-2-7)
Relative apparent molal heat content of sucrose in aqueous solutions at 20 and 30°. The plot for 30° has been shifted upward 200 cals.

$$-\Delta H_D = \phi_L = 128.9m - 6.917m^2; \quad \text{at } 20° \tag{8-2-28}$$

up to $m = 5.9$, and

$$-\Delta H_D = \phi_L = 140.2m - 7.08m^2; \quad \text{at } 30° \tag{8-2-29}$$

up to $m = 2.2$. In Fig. (8-2-7) Gucker, Pickard and Planck[36] plot values calculated by these equations as heavy solid lines which may be compared with the experimental results. The broken line represents the results at 20° plotted against c instead of m. This change in the concentration scale has little effect upon the curvature in concentrated solutions.

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[35] T. F. Young and O. G. Vogel, *J. Am. Chem. Soc.*, **54**, 3030 (1932).

[36] F. T. Gucker, Jr., H. G. Pickard and R. W. Planck, *J. Am. Chem. Soc.*, **61**, 459 (1939).

(3) HEATS OF NEUTRALIZATION AND HEATS OF IONIZATION

In considering the heats of neutralization of various acids and bases, we shall deal with both strong and weak electrolytes. The latter are discussed in Chapter (15), Section (6). Our chief concern will be with the determination of the limiting values approached by these quantities at infinite dilution. In the case of heats of neutralization of strong acids by strong bases, this limiting value is the heat of formation of water from its ions, or the negative of the heat of ionization of water, as determined from the temperature coefficient of its ionization constant. We shall now show how calorimetric data are employed to evaluate the heat of ionization of water, and record the best values so obtained for comparison with those derived from electromotive force measurements of the ionization constant.

The reaction between a strong acid and a strong base at finite and equal concentrations is given by

$$HB \cdot xH_2O + MOH \cdot xH_2O = MB \cdot (2x + 1)H_2O \qquad (8\text{-}3\text{-}1)$$

where $x = 55.5/m$. This reaction represents the formation of one mol of water from its ions at the initial concentration, $m = 55.5/x$, and also the dilution of one mol each of M^+ and B^- ions from m to $m' = 55.5/(2x + 1)$. The increase in heat content for the process is

$$\Delta H_n = \phi'_{H(s)} + \bar{H}^0_{H_2O} - \phi_{H(a)} - \phi_{H(b)} \qquad (8\text{-}3\text{-}2)$$

The subscripts refer to salt, water, acid and base, respectively, and the prime indicates that the salt concentration is m'. If we rewrite this equation for infinite dilution, and subtract from equation (8-3-2), we obtain

$$\Delta H_n = \Delta H^0_n - \Delta H'_{D(s)} + \Delta H_{D(a)} + \Delta H_{D(b)} \qquad (8\text{-}3\text{-}3)$$

Since the hydrogen and hydroxyl ions are uninfluenced by the ions of the salt at infinite dilution, we may write,

$$-\Delta H^0_n \equiv \Delta H^0_i \qquad (8\text{-}3\text{-}4)$$

where ΔH^0_i is the heat of ionization of water. This quantity is readily obtained from a single heat of neutralization if the corresponding heats of dilution are known. Richards and Hall[37] found that $\Delta H_n = -13{,}924$ for the combination of $HCl \cdot 100H_2O$ with $NaOH \cdot 100H_2O$ at 20°. Using heats of dilution which they considered most reliable, equation (8-3-3) becomes $-13{,}924 = -\Delta H^0_i + 15 - 266 - 20$, or $\Delta H^0_i = 13{,}653$. Rossini[38] has made a careful recalculation of fifty-two heats of neutralization obtained by Richards and Rowe,[39] and seven obtained by Gillespie, Lam-

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[37] T. W. Richards and L. P. Hall, *J. Am. Chem. Soc.*, **51**, 731 (1929).

[38] F. D. Rossini, *Bur. Standards J. Research*, **6**, 847 (1931).

[39] T. W. Richards and A. W. Rowe, *J. Am. Chem. Soc.*, **44**, 684 (1922).

bert, and Gibson.[40] By combining these with appropriate values of ΔH_D and $\bar{C}_{p_2}$, which he obtained from a critical examination of all of the available data,[41] he derived a "best" value of 13,721 for ΔH_i^0 at 18°. The average individual deviation from this "best" value is less than 20 cals. At 20°, ΔH_i^0 becomes 13,606, according to Rossini.

The consistency of these results, derived from a large number of experiments with different combinations of reagents, is a strong indication of the essential accuracy of their mean. There is, however, an element of uncertainty introduced into the calculations by the use of individual heats of dilution, each of which involves extrapolation to infinite dilution. The data upon which we base our estimates of ΔH_D for acids and bases are either confined to concentrations above $0.1M$, or are too erratic at high dilutions to allow reliable extrapolation, except in a few isolated cases. Sulfuric acid has been studied calorimetrically at high dilution by Lange, Monheim, and Robinson[42] at 25°, and their results have been closely checked by the electromotive force measurements of Harned and Hamer.[43] Hydrochloric acid[44] and sodium hydroxide[45] have been studied electrometrically over a wide range of temperatures.

ΔH_i^0 can be calculated from the same neutralization data of Richards and Rowe by a method which employs only directly measurable (intermediate) heats of dilution, and a single extrapolation of ΔH_n to infinite dilution. If we substitute the limiting law [Equation (8-2-12)] for the heats of dilution in equation (8-3-3), and remember that $m' = 0.5\, m$ in dilute solution, we obtain

$$\Delta H_n = -\Delta H_i^0 - (2 - \sqrt{0.5})\,[(2/3)\,\sqrt{d_0}\,\mathcal{S}_{(H)}]\,\sqrt{m} \qquad (8\text{-}3\text{-}5)$$

Thus, if we have a series of observed (or calculated) values of ΔH_n at various concentrations, the plot of ΔH_n against $\sqrt{m}$ should be a straight line at extreme dilutions, and its intercept is $-\Delta H_i^0$. The slope of this line may be reduced, and the curvature somewhat modified by introducing the observed intermediate heat of dilution of the salt from m to m'. Lambert and Gillespie[46] calculated $\Delta H_n - \Delta H_{D(s)(m \to m')}$ at the five concentrations investigated, and plotted this function against $\sqrt{m}$ as illustrated in Fig. (8-3-1). Their plots are moderately curved, and converge toward a common tangent for which the equation is

$$\Delta H_n^* \equiv [\Delta H_n - \Delta H_{D(s)(m \to m')}]$$
$$= -\Delta H_i^0 - [(2/3)\,\sqrt{d_0}\,\mathcal{S}_{(H)}]\,\sqrt{m} \qquad (8\text{-}3\text{-}6)$$

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[40] L. J. Gillespie, R. H. Lambert, and J. A. Gibson, Jr., *J. Am. Chem. Soc.*, **52**, 3806 (1930).

[41] F. D. Rossini, *Bur. Standards J. Research*, **6**, 791 (1931); *Ibid.*, **7**, 47(1931).

[42] E. Lange, J. Monheim, and A. L. Robinson, *J. Am. Chem. Soc.*, **55**, 4733 (1933).

[43] H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 27 (1935).

[44] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 2179 (1933).

[45] H. S. Harned and J. C. Hecker, *J. Am. Chem. Soc.*, **55**, 4838 (1933).

[46] R. H. Lambert and L. J. Gillespie, *J. Am. Chem. Soc.*, **53**, 2632 (1931).

We have introduced ΔH_n^* to represent the bracketed terms for which Lambert and Gillespie have coined the expression "heat of neutralization at constant concentration." From the intercept in Fig. (8-3-1), they obtain the value $\Delta H_i^0 = 13{,}650$ at 20°, which is 44 cal. above the value obtained from the same data by the use of extrapolated heats of dilution, and 42 cal. below that derived from electromotive force measurements in Chapter (15), Section (3). As we might expect from the behavior of heats of dilution, the individuality of the curves persists well below $0.1M$.

Although the heat of ionization of pure water is equal to $-\Delta H_n^*$ at infinite dilution, $-\Delta H_n^*$ has no clear-cut physical significance at finite concentrations because, in writing $\Delta H_{D(s)(m \to m')}$ for $\phi'_{H(B)} + \phi'_{H(M)} - \phi_{H(B)} - \phi_{H(M)}$, it is tacitly assumed that $\phi_{H(MB)}$, in the neutral salt solution, is equal to the sum of the terms $\phi_{H(M)}$ and $\phi_{H(B)}$, in the basic and acid solution, respectively. A similar assumption is also made regarding $\phi_{H(H)}$ and $\phi_{H(OH)}$. We have no means of verifying this assumption because individual ionic heat contents are not thermodynamically defined.

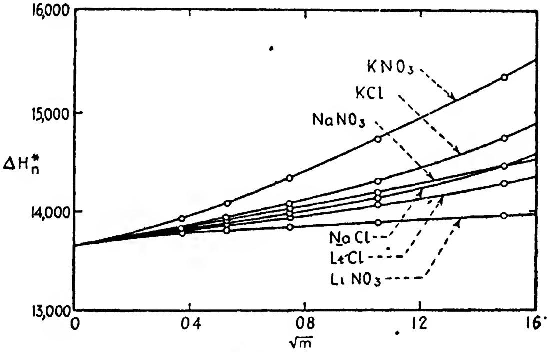

Fig. (8-3-1). Extrapolation of heats of neutralization at constant concentration to obtain the heat of ionization of water at 20°; the salt produced by neutralization is indicated on each curve

(4) The Partial Molal Heat Capacity at Constant Pressure

The fundamental equations relating the total heat capacity, C_p, of a binary solution of the partial molal heat capacities, $\bar{C}_{p_1}$ and $\bar{C}_{p_2}$, of both components, or to the molal heat capacity, $\bar{C}^0_{p_1}$, of the pure solvent, and the apparent molal heat capacity, ϕ_{C_p}, of the solute, are analogous to those already discussed in section (2), and can be derived from them by partial differentiation with respect to temperature at constant pressure. Thus, referring to equations (8-2-1) and (8-2-2), the heat capacity of the solution is given by

$$C_p = n_1\bar{C}_{p_1} + n_2\bar{C}_{p_2} \tag{8-4-1}$$

or

$$C_p = n_1\bar{C}^0_{p_1} + n_2\phi_{C_p} \tag{8-4-2}$$

and it is clear that

$$\phi_{C_p}^0 = \bar{C}_{p_2}^0 \tag{8-4-3}$$

at infinite dilution. The corresponding relative quantities are connected by the equation,

$$C_p - C_p^0 = n_1(\bar{C}_{p_1} - \bar{C}_{p_1}^0) + n_2(\bar{C}_{p_2} - \bar{C}_{p_2}^0) = n_2(\phi_{C_p} - \phi_{C_p}^0) \tag{8-4-4}$$

obtained by combinations of equations (8-4-1) and (8-4-2), or by differentiation of equation (8-2-4). Although the absolute values of C_p, $\bar{C}_{p_1}$, and $\bar{C}_{p_2}$ may be determined from available specific heat data, it is only the relative values which can be obtained from the temperature variation of activities. For these quantities, we shall employ the symbols given by the definitions $J \equiv C_p - C_p^0$, $\bar{J}_1 \equiv \bar{C}_{p_1} - \bar{C}_{p_1}^0$, $\bar{J}_2 \equiv \bar{C}_{p_2} - \bar{C}_{p_2}^0$ and $\phi_J \equiv \phi_{C_p} - \phi_{C_p}^0$, and rewrite equation (8-4-4) as

$$J = n_1\bar{J}_1 + n_2\bar{J}_2 = n_2\phi_J \tag{8-4-5}$$

J, $\bar{J}_1$ and $\bar{J}_2$ are the partial derivatives, $(\partial L/\partial T)_P$, $(\partial \bar{L}_1/\partial T)_P$ and $(\partial \bar{L}_2/\partial T)_P$, of the corresponding relative heat contents [Equation (1-7-7)]. The determination of these quantities from relative molal heat contents is therefore too simple to need elaboration, but the determination of absolute values of $\bar{C}_{p_1}$, $\bar{C}_{p_2}$, and ϕ_{C_p} requires discussion.

According to equation (8-4-2), the apparent molal heat capacity of the solute is given by

$$\phi_{C_p} = \frac{(1000 + mM_2)c_p - 1000\,c_p^0}{m} \tag{8-4-6}$$

if m is the molality of the solute of molecular weight, M_2, and c_p and c_p^0 are the specific heats of the solution and pure solvent respectively.

The calculation of $\bar{C}_{p_1}$ and $\bar{C}_{p_2}$ from ϕ_{C_p} is so similar to that described in section (2) that we need only record the fundamental equations

$$\bar{C}_{p_2} = \phi_{C_p} + n_2\frac{\partial \phi_{C_p}}{\partial n_2} = \phi_{C_p} + m\frac{\partial \phi_{C_p}}{\partial m} \tag{8-4-7}$$

or

$$\bar{C}_{p_2} = \phi_{C_p} + \frac{\sqrt{m}}{2}\frac{\partial \phi_{C_p}}{\partial \sqrt{m}} \tag{8-4-8}$$

and

$$\bar{J}_1 = -\frac{n_2^2}{n_1}\frac{\partial \phi_{C_p}}{\partial n_2} = -\frac{m^2}{1000/M_1}\frac{\partial \phi_{C_p}}{\partial m} \tag{8-4-9}$$

or

$$\bar{J}_1 = -\frac{m\sqrt{m}}{2000/M_1}\frac{\partial \phi_{C_p}}{\partial \sqrt{m}} \tag{8-4-10}$$

Since ϕ_{C_p}, as well as other apparent molal quantities, is often expressed in terms of c rather than m, the equations[47]

$$\bar{C}_{p_2} = \phi_{C_p} + \left[\frac{1000 - c\phi_V}{2000 + c^{3/2}\,\partial\phi_V/\partial\sqrt{c}}\right]c^{1/2}\frac{\partial \phi_{C_p}}{\partial \sqrt{c}} \tag{8-4-11}$$

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[47] F. T. Gucker, Jr., *J. Phys. Chem.*, **38**, 312 (1934); F. T. Gucker, Jr., F. D. Ayres and T. R. Rubin, *J. Am. Chem. Soc.*, **58**, 2118 (1936).

and

$$\bar{C}_{p_1} = \bar{C}^0_{p_1} - \frac{M_1}{d_0}\left[\frac{c}{2000 + c^{3/2}\,\partial\phi_V/\partial\sqrt{c}}\right]c^{1/2}\,\frac{\partial\phi_{C_p}}{\partial\sqrt{c}} \qquad (8\text{-}4\text{-}12)$$

are found to be convenient. These equations may be adapted for the estimation of $\bar{L}_2$, and other partial molal quantities. The differential coefficients are, for the most part, determined graphically from plots of ϕ_{C_p} against m for non-electrolytes, or against $\sqrt{m}$ for electrolytes. In the latter case, the limiting slopes of the plots are given by theory according to equation (5-2-15), which may be written

$$\mathcal{J}_2 = \mathcal{S}_{(C_p)}\sqrt{c} = \mathcal{S}_{(C_p)}\sqrt{d_0 m} \qquad (8\text{-}4\text{-}13)$$

for (1-1) electrolytes. Combination of this equation with equations (8-4-8) and (8-4-3) yields

$$\phi_J = 2/3\ \mathcal{S}_{(C_p)}\sqrt{d_0 m} = 2/3\ \mathcal{S}_{(C_p)}\sqrt{c} \qquad (8\text{-}4\text{-}14)$$

upon integration and subsequent rearrangement.

The accurate determination of specific heats of solutions utilizes the twin calorimeter method of Joule[48] and Pfaundler,[49] greatly improved by later investigators.* This method is essentially a thermal balance. Two practically identical calorimeters, equipped with similar electrical heating elements, are submerged in a thermostat. One calorimeter contains water, and the other contains the solution under investigation. The relative weights of water and solution are adjusted so that the passage of a current through the heating elements, connected in series, produces the same rise in temperature in the two calorimeters. At the same time, the temperature of the thermostat is carefully increased in such a way that heat transfer through the calorimeter walls is practically eliminated, making the process adiabatic.

The calculation of c_p for a solution from such an experiment requires very accurate values of the ratio of the resistances of the heating elements, and of the water equivalent of each calorimeter system. The resistance ratio can be determined with high precision,[50] but completely satisfactory values for the water equivalents of the calorimeter systems are not readily obtainable. This difficulty can be eliminated by always using the same amount of water in one calorimeter, designated the tare, and determining

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[48] J. P. Joule, *Mem. Manchester Lit. Phil. Soc.*, **2**, 559 (1845).

[49] L. Pfaundler, *Sitzsb. Akad. Wiss. Wien.*, **59**, 2145 (1869).

* A bibliography of over fifty references in this connection may be found in the paper by Richards and Gucker [*J. Am. Chem. Soc.*, **47**, 1876 (1925)], and a number of more recent papers will be referred to later in this section.

[50] F. T. Gucker, Jr., F. D. Ayres and T. R. Rubin [*J. Am. Chem. Soc.*, **58**, 2118 (1936)] employed variable heating elements whose resistance ratio could be accurately measured *during the course of* the experiments. This innovation has important technical advantages in the adjustment of the system to produce equal increases in temperature in the two calorimeters.

successively the weights of water and of solution which will produce a temperature rise in the other (working) calorimeter equal to that produced in the tare. If the absolute magnitude of the specific heat is to be determined with high precision, it is necessary to employ air-free water.[51] The complete numerical treatment of the experimental data, including the several small correction terms is considered in detail by Randall and Rossini.[52]

Although the twin calorimeter technique is capable of yielding specific heats with an accuracy of 0.01 per cent, or better, the values of ϕc_p and $\bar{C}_{p_2}$ which may be derived from these data are far from satisfactory at high dilutions. The unavoidable magnification of the experimental error which results from the use of equation (8-4-6) can be readily seen by differentiating this equation, and rearranging it in the forms

$$\delta\phi c_p = \left[\frac{1000}{m}(c_p^0 - c_p)\right]\frac{\delta m}{m} \tag{8-4-15}$$

and

$$\delta\phi c_p = \left[\frac{1000}{m}c_p^0 + \phi c_p\right]\frac{\delta c_p}{c_p} \tag{8-4-16}$$

which show that ϕc_p is much more sensitive to errors in c_p than in m. Gucker and Schminke[53] point out that the term, $\frac{1000}{m}(c_p^0 - c_p)$, is nearly constant over a wide range in aqueous solutions, and is approximately equal to 50. An error of 0.1 per cent in m would therefore amount to only 0.05 calorie per degree in ϕc_p. On the other hand, the factor corresponding to the bracketed terms in equation (8-4-16) is of the order $1000/m$, which requires that an error of only 0.01 per cent in c_p would cause an uncertainty of 10 calories per degree in ϕc_p, when $m = 0.01$. Because of this magnification of the experimental errors, it is practically useless to carry out heat capacity measurements as low as $0.01M$ by present methods.

One practical solution of this difficulty is the combination of $\bar{C}_{p_2}$ with the corresponding values of $\bar{J}_2$, derived from the temperature coefficient of $\bar{L}_2$, or the second temperature derivative of activity coefficients. Since

$$\bar{C}_{p_2}^0 = \bar{C}_{p_2} - \bar{J}_2 \tag{8-4-17}$$

must be independent of m, we may confine the calculations to the concentration range in which both sets of data are most trustworthy. Table (8-4-1) contains the results of this calculation for the several electrolytes which yield essentially constant values of $\bar{C}_{p_2}^0$. It appears probable from inspection of the table that $\bar{C}_{p_2}^0$ is known to better than 0.5 cal. for the

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[51] R. Jessel, *Proc. Phys. Soc. London*, **46**, 759 (1934).

[52] M. Randall and F. D. Rossini, *J. Am. Chem. Soc.*, **51**, 323 (1929).

[53] F. T. Gucker, Jr., and K. H. Schminke, *J. Am. Chem. Soc.*, **54**, 1358 (1932).

first three electrolytes, and to about 1 cal. for sodium hydroxide. It may be remarked that several theoretical attempts[54] to estimate $\bar{C}^0_{p_2}$ for electrolytes, on the basis of the electrostriction[55] of the solvent, have predicted the order of magnitude of this quantity without allowing for the specific differences observed experimentally.

It is a convenient experimental fact that $\bar{C}_{p_2}$, and many other partial molal properties of strong electrolytes vary linearly with $c^{1/2}$ or $m^{1/2}$ over a concentration range (0.2 to $3M$) far beyond the dilutions at which the limiting laws might be expected to hold. This behavior permits the expression of the experimental results in terms of the parameters of the equation,

$$\bar{C}_{p_2} = \bar{C}^0_{p_2} + S_{C_p} m^{1/2} \tag{8-4-18}$$

TABLE (8-4-1). VALUES OF $\bar{C}^0_{p_2}$ CALCULATED BY EQUATION (8-4-17) AT 25°.

m	HCl[a,b]	KCl[c,d]	KOH[e,b]	NaOH[f,g]
0.2	−29.50	−28.30	......	.....
.25	....	....	−30.3	−28.08
.5	−29.15	−28.75	−30.2	−27.74
1.0	−29.25	−29.25	−30.62	−28.37
1.5	−29.17	−28.78	−30.85	−27.52
2.0	−29.75	−30.05	−31.36	−26.24
2.5	......	−28.45	......	−26.30
ave.	−29.4	−28.8	−30.7	−27.4

[a] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 2179 (1933).
[b] F. T. Gucker Jr. and K. H. Schminke, *Ibid.*, **54**, 1358 (1932).
[c] H. S. Harned and M. A. Cook, *Ibid.*, **59**, 1290 (1937).
[d] M. Randall and F. D. Rossini, *Ibid.*, **51**, 323 (1929).
[e] H. S. Harned and M. A. Cook, *Ibid.*, **59**, 496 (1937).
[f] H. S. Harned and J. C. Hecker, *Ibid.*, **55**, 4838 (1933).
[g] F. T. Gucker Jr. and K. H. Schminke, *Ibid.*, **55**, 1013 (1933).

although the experimental slopes, S_{C_p}, may differ considerably from the theoretical, $\mathfrak{S}_{(C_p)}$. This equation will represent the observed values of $\bar{C}_{p_2}$ for the electrolytes included in Table (8-4-2) within the experimental error throughout the concentration range $m = 0.2$ to $m = 3$. Since the parameters are not evaluated from data at high dilutions, the intercept and slope may differ numerically from the correct value of the property, $\bar{C}^0_{p_2}$, and the limiting slope given by theory. For the intercept, this difference is usually small, as is indicated by comparison of the values of $\bar{C}^0_{p_2}$ in Table (8-4-1) with those in Table (8-4-2). On the other hand, the experimental slopes, S_{C_p}, for these 1-1 electrolytes differ widely among themselves and from the theoretical limiting slope, $\mathfrak{S}_{(C_p)}$, which is about 13.36 at 25°. These differences are not in contradiction with theory, as determinations of $\bar{J}_2$ from $\partial\bar{L}_2/\partial T$ and $\partial^2 \ln \gamma_\pm/\partial T^2$ show that S_{C_p} varies

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[54] F. Zwicky, *Physik Z.*, **26**, 664 (1925); *Ibid.*, **27**, 271 (1926); *Proc. Nat. Acad. Sci.*, **12**, 86 (1926); H. M. Evjen and F. Zwicky, *Phys. Rev.*, **33**, 860 (1929).

[55] T. J. Webb, *J. Am. Chem. Soc.*, **48**, 2589 (1926).

considerably with concentration below $c = 0.2$, and approaches the predicted limiting value at high dilutions. This is clearly demonstrated by the calculations of Young and Machin,[56] and is illustrated in Figs. (11-8-1) and (12-2-2).

Only a few precise calorimetric studies of the heat capacities of electrolytes of higher valence types have been reported, and the results of these investigations do not, in general, follow the simple linear relationship of equation (8-4-18). The smoothed values of $\bar{C}_{p_2}$ have been recorded in Table (8-4-3), along with the intercepts and apparent limiting slopes, obtained from the experimental data at high dilutions. The results for barium chloride were obtained from two different sources, and were considered adequately represented by equation (8-4-18).

Table (8-4-2). Parameters of the Interpolation Equation $\bar{C}_{p_2} = \bar{C}^0_{p_2} + S_{C_p}\sqrt{m}$ Valid at 25° from 0.2 to 3 M.

Electrolyte*	S_{C_p}	$\bar{C}^0_{p_2}$
HCl[a]	7.50	−29.20
$LiCl$[a]	7.88	−15.63
$NaCl$[b]	21.6	−23.8
KCl[b]	16.8	−29.0
$NaBr$[b]	20.4	−24.3
KBr[b]	16.2	−29.5
NaI[b]	24.9	−25.0
KI[b]	20.4	−30.2
$NaNO_3$[b]	30.0	−12.6
KNO_3[b]	28.65	−17.8
NH_4NO_3[c]	12.1	−2.5
$LiOH$[d]	18.80	−19.98
$NaOH$[d]	26.24	−26.59
KOH[a]	19.88	−32.10

[a] F. T. Gucker Jr. and K. H. Schminke, *J. Am. Chem. Soc.*, **54**, 1358 (1932).

[b] F. D. Rossini, *Bur. Standards J. Research*, **7**, 47 (1931) recalculated from M. Randall and F. D. Rossini, *J. Am. Chem. Soc.*, **51**, 323 (1929). See also C. M. White, *J. Phys. Chem.*, **44**, 494 (1940), and C. B. Hess, *Ibid.*, **45**, 755 (1941).

[c] F. T. Gucker Jr., F. D. Ayres and T. R. Rubin, *J. Am. Chem. Soc.*, **58**, 2118 (1936).

[d] F. T. Gucker Jr. and K. H. Schminke, *Ibid.*, **55**, 1013 (1933).

* A similar table for these and several additional electrolytes at 18°, 21.5°, and 25° is given in Reference (b).

Table (8-4-3). $\bar{C}_{p_2}$ for High Valence Type Electrolytes at 25°.

m	Na_2SO_4[a]	K_2SO_4[a]	$BaCl_2$[b]
0	(−50)	(−60.6)	(−74.36)
0.1	−22.6	−41.0	−57.5
.2	−8.5	−31.8	−50.5
.35	5.8	−21.4	−42.9
.5	15.8	−13.4	−36.7
1.0	39.0	.....	−21.1
1.5	55.0	......	......
Slope	76	62	54

[a] M. Randall and F. D. Rossini, *J. Am. Chem. Soc.*, **51**, 323 (1929).

[b] C. M. White, *Ibid.*, **58**, 1615 (1936).

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[56] T. F. Young and J. S. Machin, *J. Am. Chem. Soc.*, **58**, 2254 (1936).

The pronounced variation observed in the values of S_{c_p}, [Table (8-4-2)], in a series of electrolytes of the same valence type, is illustrated graphically in Fig. (8-4-1) taken from a paper by Gucker and Rubin.[57] Those authors estimated the difference between the isopiestic and isochoric apparent molal heat capacities by means of the equation

$$\phi c_p - \phi c_v = \frac{\alpha^2}{\beta} vT - \frac{\alpha_0^2}{\beta_0} v_0 T \tag{8-4-19}$$

in which α and β represent the coefficients of expansibility and compressibility respectively. The subscript zero refers to pure solvent. Their results are summarized in Table (8-4-4). The limiting values were derived from the equation

$$\phi^0_{c_p} - \phi^0_{c_v} = \frac{\alpha_0 T}{\beta_0}\left[2\phi^0_E - \frac{\alpha_0}{\beta_0}\phi^0_K\right] \tag{8-4-20}$$

TABLE (8-4-4). VALUES OF $\phi c_p - \phi c_v$ AT 25°.

Solute	$\sqrt{c} = 0$	0.25	0.50	0.75	1.00	1.25	1.50
HCl	2.90	2.91	2.71	2.85	3.01	3.10	3.23
LiCl	2.94	2.74	2.70	2.57	2.49	2.41	2.31
NaCl	8.60	8.33	8.14	8.11	8.25	8.48	8.71
KCl	7.82	7.32	7.16	6.98	6.89	6.82	6.72
LiOH	5.36	4.92	4.71	4.44	4.23	3.99	3.69
NaOH	11.36	10.66	10.59	10.63	10.78	10.98	11.12

TABLE (8-4-5). OBSERVED VALUES OF $\left(\frac{\partial \phi c_p}{\partial \sqrt{c}} - \frac{\partial \phi c_v}{\partial \sqrt{c}}\right)_{c \to 0}$ AT 25°.

HCl	LiCl	NaCl	KCl	LiOH	NaOH
−0.081	−0.72	−1.94	−2.04	−1.82	−3.27

in which ϕ^0_E and ϕ^0_K are the limiting values of the apparent molal expansibility and apparent molal compressibility. Gucker and Rubin also deduced the equation

$$\frac{\partial \phi c_p}{\partial \sqrt{c}} - \frac{\partial \phi c_v}{\partial \sqrt{c}} = \frac{\alpha_0 T}{\beta_0}\left[2\frac{\partial \phi_E}{\partial \sqrt{c}} - \frac{\alpha_0}{\beta_0}\frac{\partial \phi_K}{\partial \sqrt{c}}\right] \tag{8-4-21}$$

for the condition $c \to 0$, which gives the difference in the limiting slopes of the isopiestic and isochoric systems. The observed values of this difference are highly specific, as can be seen in Table (8-4-5). Their magnitudes and signs are such that the limiting slopes of the plots in the isochoric system would show even more individuality than those in the isobaric system. In the experimental concentration range, however, the isopiestic system exhibits greater individuality in slopes. The most pronounced difference

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[57] F. T. Gucker, Jr., and T. R. Rubin, *J. Am. Chem. Soc.*, **57**, 78 (1935).

in the two systems is that ϕ_{C_v} is always more negative than ϕ_{C_p} and there is a much greater spread in the values of $\phi^0_{C_v}$. Both of these effects are clearly indicated by a comparison of Fig. (8-4-1) with Fig. (8-4-2).

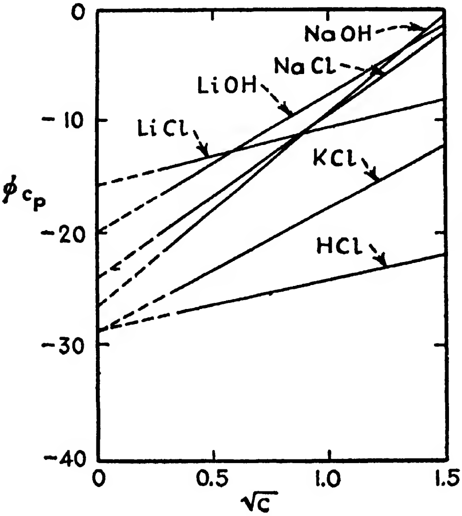

Fig. (8-4-1)
Apparent molal isopiestic heat capacities in water at 25°

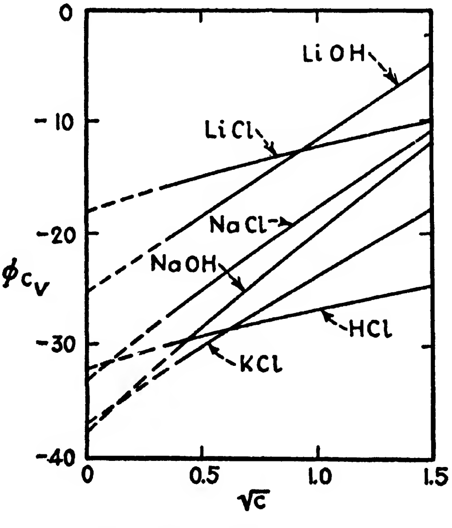

Fig. (8-4-2)
Apparent molal isochoric heat capacities in water at 25°

By way of contrast with the properties of solutions of electrolytes, it will be useful to consider the behavior of a typical non-electrolyte. For this purpose we have reproduced in Fig. (8-4-3) a plot of ϕ_{C_p} for sucrose from a paper by Gucker and Ayres,[58] which represents the most accurate series of measurements available over a wide concentration range. The limiting slope of the plot against $\sqrt{c}$ is apparently zero. This is in accord with theory which attributes the $\sqrt{c}$ term to the effect of ionic interaction. The plot against c is linear within the experimental error up to about $c = 1$.[59] Essentially the same situation is maintained if the concentration scale is changed to mol fraction or molality, but the curvature is reversed and increased about 50 per cent. For convenience in computing $\bar{C}_{p_2}$ and $\bar{C}_{p_1}$, the results were expressed as a function of m according to the equation

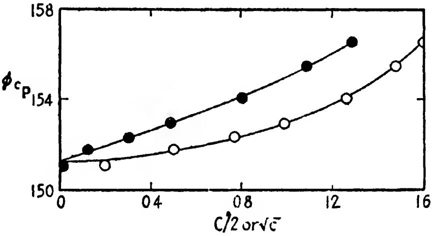

Fig. (8-4-3). Apparent molal heat capacity of sucrose at 25° plotted against $c/2$ (upper curve), and $\sqrt{c}$ (lower curve)

$$\phi_{c_p} = 145.87 + 1.950m - 0.1182m^2 \qquad (8\text{-}4\text{-}22)$$

at 20°, and

$$\phi_{c_p} = 151.20 + 1.325m - 0.0704m^2 \qquad (8\text{-}4\text{-}23)$$

at 25°. The coefficient of the linear term is small, and decreases with temperature so fast that, at about 40°, ϕ_{c_p} would be nearly independent of concentration in dilute solutions. In this respect sucrose would behave as an ideal solute. This matter is considered in some detail by Gucker and Ayres, and especially by Bennewitz and Kratz.[60]

Although the limiting slopes, $(\partial\phi_{c_p}/\partial m)_{c\to0}$, obtained from equations (8-4-22) and (8-4-23), were derived from experimental results above $0.04M$, the slope at 25° is in close agreement with the value derived from the temperature coefficient of heats of dilution at lower concentrations. Thus, from equations (8-2-28) and (8-2-29) for ϕ_L at 20 and 30°,

$$\frac{\partial\phi_{c_p}}{\partial m} = \frac{\partial}{\partial T}\left(\frac{\partial\phi_L}{\partial m}\right) \cong \frac{140.2 - 128.9}{10} = 1.13 \qquad (8\text{-}4\text{-}24)$$

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[58] F. T. Gucker, Jr., and F. D. Ayres, *J. Am. Chem. Soc.*, **59**, 447 (1937).

[59] Similar plots for urea solutions show no such clear cut differentiation between the c and $\sqrt{c}$ plots. F.T. Gucker, Jr., and F. D. Ayres, [*J. Am. Chem. Soc.*, **59**, 2152 (1937)], and C. M. White, [*Ibid.*, **58**, 1620 (1936)].

[60] K. Bennewitz and L. Kratz, *Physik. Z.*, **37**, 496 (1936).

Gucker, Pickard and Planck[61] considered this a more accurate determination of the limiting slope, and used this value to re-evaluate the other parameters in equation (8-4-23) from the specific heat data. Their final equation,

$$\phi_{c_p} = 151.50 + 1.130m - 0.0466m^2 \qquad (8\text{-}4\text{-}25)$$

represents the experimental specific heats to within 1 part in 20,000 on the average.

(5) PARTIAL MOLAL VOLUMES, APPARENT MOLAL VOLUMES AND THE DENSITIES OF SOLUTIONS OF ELECTROLYTES

Partial molal and apparent molal volumes are derived from the densities of solutions. The apparent molal volume is given by

$$\phi_V = \frac{V - n_1 \bar{V}_1^0}{n_2} \qquad (8\text{-}5\text{-}1)$$

in general, which becomes

$$\phi_V = \frac{1000}{cd_0}(d_0 - d) + \frac{M_2}{d_0} \qquad (8\text{-}5\text{-}2)$$

if $n_2 = c$, the number of mols of solute in $V = 1000$ cc. of solution. Also,

$$\phi_V = \frac{1000}{mdd_0}(d_0 - d) + \frac{M_2}{d} \qquad (8\text{-}5\text{-}3)$$

if $n_2 = m$, the number of mols of solute per 1000 grams of solvent.

It was found by Masson[62] that ϕ_V varies linearly with $\sqrt{c}$ in dilute solutions, and that this simple relationship often extends to concentrated solutions. Thus, if

$$\phi_V = \phi_V^0 + S_V\sqrt{c} \qquad (8\text{-}5\text{-}4)$$

over the range in which the densities are known, the latter must be given by the equation

$$d = d_0 + \frac{(M_2 - d_0\phi_V^0)c}{1000} - \frac{(S_V d_0)c^{3/2}}{1000} \qquad (8\text{-}5\text{-}5)$$

which follows by combination of equations (8-5-2) and (8-5-4). This equation was first derived by Root.[63] According to theory, the coefficient, $S_V d_0/1000$, should be common to all strong electrolytes of the same valence type in a given solvent, and the coefficient of the c term should be an

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[61] F. T. Gucker, Jr., H. G. Pickard and R. W. Planck, *J. Am. Chem. Soc.*, **61**, 459 (1939).

[62] D. O. Masson, *Phil. Mag.* [7], **8**, 218 (1929). See also A. F. Scott, *J. Phys. Chem.*, **35**, 2315 (1931); W. Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931); and O. Redlich and P. Rosenfeld, *Z. Elektrochem.*, **37**, 705, (1931); *Z. physik. Chem.*, **A155**, 65 (1931).

[63] W. C. Root, *J. Am. Chem. Soc.*, **55**, 850 (1933).

additive property of the ions. The experimental values of S_V, however, show considerable individuality within a series of similar electrolytes, and are only of the order of magnitude of the theoretical slope [Equation (3-9-6)]. Root reported that the experimental coefficients are both additive.

Wirth[64] determined the apparent (and partial) molal volumes of potassium chloride, bromide, and sulfate in sodium chloride solutions, and found that equation (8-5-4) would express the results for the 1-1 type salt mixtures up to $1N$, if c represents the total solute concentration. The results for potassium sulfate can also be represented by this equation if $c^{1/2}$ is replaced by $\Gamma^{1/2}$. This confirms the theoretical equation (3-9-6) insofar as the variable, $\Gamma^{1/2}$, is concerned.

ϕ_V is not seriously influenced by ordinary experimental errors in the determination of concentration, but is very sensitive to experimental uncertainties in the density at high dilutions. Differentiation of equation (8-5-2) at constant d, and combination with (8-5-5), shows that

$$\delta\phi_V = \left[\frac{M_2}{d_0} - \phi_V^0\right]\frac{\delta c}{c} \tag{8-5-6}$$

in dilute solutions. The bracketed terms are independent of c, and of the order, M_2 to $1/2\ M_2$. At constant c, the corresponding equation is

$$\delta\phi_V = -\frac{1000}{c}\frac{\delta d}{d_0} \tag{8-5-7}$$

so that an error of 0.001 per cent in d would cause an uncertainty of 1 cc. in ϕ_V when $c = 0.01$.

Because of the linear relationship [Equation (8-5-4)], the most convenient calculation of partial molal volumes makes use of the c-scale. The equations are[65, 66, 67]

$$\bar{V}_2 = \phi_V + \left[\frac{1000 - c\phi_V}{2000 + c^{3/2}\,\partial\phi_V/\partial\sqrt{c}}\right]c^{1/2}\frac{\partial\phi_V}{\partial\sqrt{c}} \tag*{(8-5-8)*}$$

and

$$\bar{V}_1 = \left[\frac{2000\,\bar{V}_1^0}{2000 + c^{3/2}\,\partial\phi_V/\partial\sqrt{c}}\right] \tag{8-5-9}$$

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[64] H. E. Wirth, *J. Am. Chem. Soc.*, **59**, 2549 (1937); **62**, 1128 (1940).

[65] W. Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931).

[66] F. T. Gucker, Jr., *J. Phys. Chem.*, **38**, 311 (1934). *Cf. J. Am. Chem. Soc.*, **60**, 2582 (1938).

[67] R. E. Gibson, *J. Phys. Chem.*, **38**, 320 (1934).

* At $c = 1$, the error caused by neglecting the concentration terms within the brackets is less than 0.1 cc. for most 1-1 and 2-1 electrolytes.

which follow from the more familiar equations

$$\bar{V}_2 = \phi_V + \frac{m^{1/2}\,\partial\phi_V}{2\partial\sqrt{m}} \tag{8-5-10}$$

and

$$\bar{V}_1 = \bar{V}_1^0 - \frac{M_1}{2000} m^{3/2} \frac{\partial\phi_V}{\partial\sqrt{m}} \tag{8-5-11}$$

by combination with the useful relationship

$$\frac{c}{m} = d_0\left[1 - \frac{c\phi_V}{1000}\right] \tag{8-5-12}$$

Equation (8-5-12) is deduced from (8-5-2).

Values of the parameters, S_V and ϕ_V^0, derived by several investigators from density data at 25°, are recorded in Table (8-5-1). The values for all of the alkali halides, except potassium fluoride, were derived by Scott[68] from the data of Baxter and Wallace.[69] Geffcken[70] combined the same data with his own and some from other sources.[71, 72, 73, 74] The values obtained by Scott and by Geffcken are nearly identical. We have selected Scott's values wherever possible because they have been used in the estimation of some derived quantities which appear later in Table (8-5-2). Both authors tabulated values of S_V and ϕ_V^0 at 0, 25, 50 and 70°, and Geffcken includes some at 35 and 45°. Further results at 25° are given elsewhere.[75]

Table (8-5-1) shows that the difference between S_V and ϕ_V^0 for any pair of 1-1 type salts with a common ion is practically independent of the nature of the common ion. This additivity of ϕ_V^0 persists, less accurately, for salts of higher valence types. Scott[76] showed that the average deviation from additivity, derived from all possible combinations of alkali halides with a common ion, was about 0.07 cc. Geffcken's values lead to about the same figure, but the corresponding deviation derived by LaMer and Gronwall,[77] from the same data, is about twice as great. Instead of equation (8-5-4), a power series of the third order in m was used by the latter investigators, and it appears that this more complicated treatment

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[68] A. F. Scott, *J. Phys. Chem.*, **35**, 2315 (1931).

[69] G. P. Baxter and C. C. Wallace, *J. Am. Chem. Soc.*, **38**, 70 (1916).

[70] W. Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931).

[71] H. Hüttig, *Z. Elektrochem.*, **34**, 14 (1928).

[72] H. Köhner, *Z. physik. Chem.*, **B1**, 427 (1928).

[73] P. Hölemann and H. Köhner, *Ibid.*, **B13**, 338 (1931).

[74] Z. Shibata and P. Hölemann, *Ibid.*, **B13**, 347 (1931).

[75] L. G. Longsworth, *J. Am. Chem. Soc.*, **57**, 1185 (1935); B. B. Owen and S. R. Brinkley Jr., *Chem. Rev.*, **29**, 461 (1941); K. Fajans and O. Johnson, *J. Am. Chem. Soc.*, **64**, 668 (1942).

[76] A. F. Scott, *J. Phys. Chem.*, **35**, 2315 (1931).

[77] V. K. LaMer and T. H. Gronwall, *J. Phys. Chem.*, **31**, 393 (1927).

tends to exaggerate the deviations. In any event, the additivity of ϕ_V^0 is surprisingly exact when it is recalled that all the extrapolations are made from relatively concentrated solutions ($c \geq 0.25$). This matter will be discussed later in connection with the approximate additivity of S_V.

The theoretical limiting slope is not accurately known because of the uncertainty in the experimental value of $\partial D/\partial P$ required in equation (3-9-2). The experimental slopes, S_V, determined from the results above $0.25N$, are specific, and do not yield an experimental verification of the limiting law. For this reason it is important to have precise measurements of densities at higher dilutions. To overcome the unfavorable magnification of the experimental error, according to equation (8-5-7), Geffcken, Beckmann and Kruis[78] developed a differential float method for deter-

TABLE (8-5-1)*. VALUES OF THE PARAMETERS OF EQUATION (8-5-4) FOR AQUEOUS SOLUTIONS AT 25°.

Electrolyte	$\phi_V^0 (= \bar{V}_2^0)$	S_V	Electrolyte	$\phi_V^0 (= \bar{V}_2^0)$	S_V
LiCl[a]	17.00	1.488	HCl[b]	18.20	0.83
	(17.06)[b]			(18 07)[g]	
LiBr[a]	24.08	1.159	LiOH[i]	−6.0	3.00
LiI[a]	35.50	0.841	NaOH[e]	−6.7	4.18
NaCl[a]	16.40	2.153	KOH[e]	2.9	4.35
	(16.61)[d]		NH_4Cl[j]	35.98	1.45†
NaBr[a]	23.51	1.760	NH_4NO_3[h]	47.56	0.97
	(23.48)[c]			(47.24)[c]	
NaI[a]	35.10	1.346	$AgNO_3$[l]	28.01	2.61†
KF[b]	6.60	3.35	KNO_3[e]	38.18	2.30
KCl[a]	26.52	2.327	K_2CrO_4[l]	37.13	11.70
	(26.81)[c]		K_2SO_4[f]	32.28	18.11
KBr[a]	33.73	1.939	Na_2SO_4[c]	11.47	12.16
KI[a]	45.36	1.556		(11.52)[c]	
RbCl[a]	31.87	2.219	Na_2CO_3[c]	−6.70	11.30
RbBr[a]	38.71	2.038		(−6.74)[c]	
RbI[a]	50.31	1.607	$CaCl_2$[i]	18.25	5.99
CsCl[a]	39.15	2.172	$SrCl_2$[d]	17.94	9.90†
CsBr[a]	46.19	1.901	$BaCl_2$[i]	23.60	4.83
CsI[a]	57.74	1.579	$LaCl_3$[k]	16.02	11.87

* Where two values of ϕ_V^0 are given, the one in parentheses was evaluated from data at high dilution, and is the most accurate value of the physical quantity, ϕ_V^0. Such values were not used in evaluating S_V, and therefore should not be used for estimating ϕ_V at high concentrations by equation (8-5-4).

† Evaluated in dilute solutions, $c < 0.5$.

[a] A. F. Scott, *J. Phys. Chem.*, 35, 2315 (1931).
[b] W. Geffcken, *Z. physik. Chem.*, 155A, 1 (1931); *Naturwiss.*, 19, 321 (1931).
[c] W. Geffcken and D. Price, *Z. physik. Chem.*, 26B, 81 (1934).
[d] A. Kruis, *Ibid.*, 34B, [illegible] (1936)
[e] R E. Gibson and J. F. Kincaid, *J. Am. Chem. Soc.*, 59, 25 (1937).
[f] H. E. Wirth, *Ibid*, 59, 2549 (1937).
[g] H. E. Wirth, *Ibid.*, 62, 1128 (1940).
[h] F. T. Gucker Jr. and T. R. Rubin, *Ibid.*, 58, 2118 (1936).
[i] F. T. Gucker Jr., *Chem. Rev.*, 13, 111 (1933).
[j] G. Jones and S. K. Talley, *J. Am. Chem. Soc.*, 55, 624 (1933).
[k] G. Jones and R. E. Stauffer, *Ibid.*, 62, 335 (1940).
[l] G. Jones and J. H. Colvin, *Ibid.*, 62, 338 (1940).

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[78] W. Geffcken, C. Beckmann and A. Kruis, *Z. physik. Chem.*, B20, 398 (1933).

mining relative densities with very high precision. The method is a refinement of the procedure used by Lamb and Lee,[79] and others,[80, 81] in which the bouyancy of a submerged float containing an iron core is delicately counterbalanced by the pull of a solenoid. The differential method, making use of duplicate float systems in the same thermostat, minimizes the effect of uncertainties in temperature control by simultaneously measuring the densities of solution and pure solvent. In addition, modern pycnometric studies of high precision have led to reliable values of ϕ_V in dilute solutions.[82] Geffcken and Price[83] have collected and analyzed the best data from various sources, and conclude that, for potassium and sodium chlorides and sodium bromide, there is convergence toward a common limiting slope at high dilutions. The value of this slope is 1.9, in agreement with theory.[84] They showed graphically that $\phi_V - 1.9c^{1/2}$ varies linearly with the first power of c at high dilutions. In Fig. (8-5-1) we have plotted $\phi_V - 2/3\ \mathcal{S}_{(V)}c^{1/2}$ against concentration for several salts. In this plot the data obtained by the differential float method are seen to be in excellent agreement with results obtained by an ingenious dilatometric method used by Kruis[85] and by Geffcken, Kruis and Solana.[86] Although the data for the salts shown in Fig. (8-5-1) are in satisfactory accord with theory, the results for sodium sulfate, sodium carbonate and ammonium nitrate, obtained by the same authors, are doubtful in this respect. The plot of $\phi_V - 1.9c^{1/2}$ for ammonium nitrate[87] against c is curved in dilute solutions, and the corresponding plots for sodium carbonate (corrected for hydrolysis) and sodium sulfate cannot be made to appear linear at high dilutions without assigning different values, 11.3 and 12.2, to the limiting slopes.* The theoretical slope for the 1-2 type electrolytes should be $(3)^{3/2}$ times the value for 1-1 type salts, or 9.9, which is the value used in Fig. (8-5-1) for strontium chloride. Considered

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[79] A. B. Lamb and R. E. Lee, *J. Am. Chem. Soc.*, **35**, 1666 (1913).

[80] F. Kohlrausch and W. Hallwach, *Wied. Ann.*, **53**, 14 (1894).

[81] N. Reggiani, *Rend. Reale Accad. dei Lincei* [4], **6**, 99 (1890).

[82] Several very sensitive methods of detecting small density differences have been developed for estimating the isotopic composition of water. So far as we know, these methods have not yet been applied to the determination of ϕ_V at high dilutions. For bibliography see P. C. Vincent, *Proc. Phys. Soc. London*, **45**, 833 (1933); H. E. Wirth, T. G. Thompson and C. L. Utterback, *J. Am. Chem. Soc.*, **57**, 400 (1935); and O. E. Frivold, *Physik. Z.*, **21**, 529 (1920).

[83] W. Geffcken and D. Price, *Z. physik. Chem.*, **B26**, 81 (1934).

[84] O. Redlich, *J. Phys. Chem.*, **44**, 619 (1940).

[85] A. Kruis, *Z. physik. Chem.*, **B34**, 1 (1936).

[86] W. Geffcken, A. Kruis and L. Solana, *Ibid.*, **B35**, 317 (1937).

[87] F. T. Gucker, Jr., and T R. Rubin [*J. Am. Chem. Soc.*, **58**, 2118 (1936)] found that their data for this salt at somewhat higher concentrations indicated a limiting slope of only 0.966.

* The slopes here given conform to our equation (8-5-4) in which ϕ_V is the apparent *molal* volume and c is in *mols* per liter.

as a whole, the results obtained by the float and dilatometer methods appear to support the interionic attraction theory for typical strong electrolytes. On the other hand the hydrolyzable salts show significant departures at the most dilute solutions studied. In the case of sodium carbonate, in which hydrolysis is most pronounced, the values of ϕ_V, calculated from the densities of Lamb and Lee,[88] pass through a minimum at about 0.01N. The plot of ϕ_V against $\sqrt{c}$ approaches the axis at zero concentration with a *negative* slope. Lamb and Lee attributed this effect to hydrolysis, and Geffcken and Price[89] estimated its numerical magnitude at each experimental concentration. At the lowest concentration, the hydrolysis correction is about 1.7 cc.; this not only eliminates the minimum but also brings the results into approximate agreement with theory. The agreement is within the estimated uncertainty of the hydrolysis corrections, and it is quite possible that the relatively small departures noted in the case of ammonium nitrate, and sodium sulfate might be eliminated

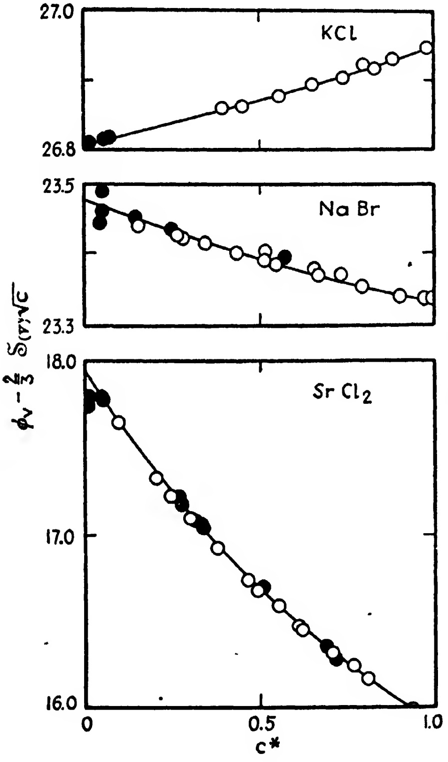

Fig. (8-5-1)
Evaluation of apparent molal volumes at infinite dilution. Verification of the theoretical limiting equation for aqueous solutions at 25°; c^* = equivalent per liter. ○ Dilatometer method; ● Differential float method. Compare Fig. (8-4-1).

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[88] A. B. Lamb and R. E. Lee, *J. Am. Chem. Soc.*, **35**, 1666 (1913).

[89] W. Geffcken and D. Price, *Z. physik. Chem.*, **B26**, 81 (1934).

in the same way.* With higher valence type salts such as zinc sulfate, the correction would have to take ionic association as well as hydrolysis into account. Geffcken and Price, and others,[90] have shown that ϕ_V for weak acids may be quantitatively interpreted in terms of their known dissociation constants.

In Fig. (8-5-2), we have plotted ϕ_V against $c^{1/2}$ for strontium chloride to show the S-shaped character of the curves in the transition from the limiting law, at high dilution, to Masson's equation (8-5-4), in more concentrated solutions. It appears that the first significant departures from Masson's equation take place at such low concentrations that it makes little difference whether the data extend to extreme dilutions or not. More satisfactory extrapolations, which involve both the å-parameter and a linear term in c, are discussed in Appendix B, and illustrated by Fig. (B-4-1).

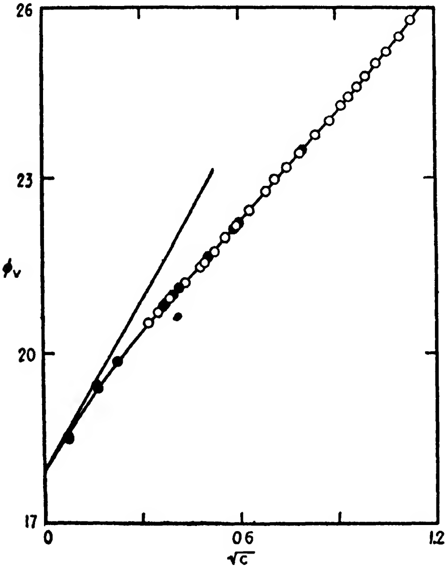

Fig. (8-5-2)
Apparent molal volume of strontium chloride in water at 25°; departures from theoretical limiting law at moderate dilutions. ○ Dilatometer method; ● Differential float method

No satisfactory explanation of the validity of equation (8-5-4) has yet been proposed, but a number of interesting speculations regarding it may be noted. Masson[91] postulated that, if the plots of ϕ_V against $c^{1/2}$ were to remain linear for supersaturated solutions, the hypothetical maximum

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[90] R. C. Hoather and C. F. Goodeve, *Trans. Faraday Soc.*, **30**, 630 (1934); I. M. Klotz and C. F. Eckert, *J. Am. Chem. Soc.*, **64**, 1878 (1942).

* Cationic hydrolysis tends to reduce ϕ_V contrary to the effect produced by anionic hydrolysis (Na_2CO_3).

[91] D. O. Masson, *Phil. Mag.* [7], **8**, 218 (1929).

value of ϕ_V would occur when c became the concentration of electrolyte in the pure crystalline salt. Using the subscript max. for this maximum, we have,

$$\phi_{V_{\text{max.}}} = \phi_V^0 + S_V\sqrt{c_{\text{max.}}} \tag{8-5-13}$$

where $1000/c_{\text{max.}}$ is the molal volume, V_2, of the pure crystalline salt. A plot of $\phi_{V_{\text{max.}}}$ against V_2 for the alkali halides yields two straight lines, with the lithium and cesium salts on one line, and the remaining salts on the other. The intercepts of both lines are about 6 cc. The slope of the lithium and cesium plot is unity, while the other is 0.86 ($\cong \sqrt{3/4}$), which suggests a purely geometrical interpretation of the volume relationships in solutions. Scott[92] pointed out that equation (8-5-4) is valid for lithium salts over a limited range, and that, if the data at the highest concentrations only are used in evaluating ϕ_V^0 and S_V, the lithium salts would have lower values of $\phi_{V_{\text{max.}}}$. This would place them more nearly in line with the other alkali halides of the rock salt (face-centered cubic) crystalline structure than with the cesium salts, which have a body-centered cubic lattice. Furthermore, if hypothetical values of V_2 are calculated for cesium salts on the basis of a rock-salt lattice, these salts lie on the common plot with the sodium, potassium and rubidium salts.

Scott goes an important step further. He objects to the use of the pure crystalline solid as the hypothetical upper limit to the concentration of the solution, maintaining that if the properties of the solid salt are to be included in the interpretation of this limiting solution we should use the "critical disruptive volume," V^*, of the solid. The method of estimating V^*, is given by Scott.[93] For our purposes it will be sufficient to remark that the cohesive forces reach a maximum when the crystal is expanded from its normal equilibrium volume to V^*, and decrease thereafter with further expansion. Hence V^* marks the transition from rigid crystalline structure to the more mobile condition of liquids, and may be assumed to correspond to the hypothetical maximum concentration attainable in a (supersaturated) solution of a given salt.

In Table (8-5-2) we have given Scott's values of V^* for the alkali halides at 25°, and the corresponding values of

$$\phi_V^* = \phi_V^0 + S_V\sqrt{1000/V^*} \tag{8-5-14}$$

derivable from equation (8-5-4), and the parameters in Table (8-5-1). To these, we have added values for potassium fluoride at 25°, and for the function

$$\psi^* \equiv \frac{\phi_V^*}{V^*} = \frac{S_V\sqrt{1000/V^*} + \phi_V^0}{V^*} \tag{8-5-15}$$

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[92] A. F. Scott, *J. Phys. Chem.*, **35**, 3379 (1931).

[93] See A. F. Joffé, "The Physics of Crystals," McGraw-Hill Book Co., New York, 1928.

at other temperatures. This fraction was estimated from values of S_V and ϕ_V^0 obtained from the work of Scott,[94] Geffcken[95] and Pesce,[96] and upon the assumption that

$$V^* \cong V_{25}^*[1 + 1.2 \times 10^{-4}(t - 25)] \qquad (8\text{-}5\text{-}16)$$

for all the salts. The effect of the temperature variation of V^* upon ϕ_V^* and ψ^* is so small that the coefficient of expansion need not be known accurately.

TABLE (8-5-2). PROPERTIES OF THE CRITICAL DISRUPTIVE CONDITION.

Salt	$V^*(25°)$	$\phi_V^*(25°)$	$\psi^* = \phi_V^*/V^*$					
			0°	25°	35°	45°	50°	70°
LiCl	32.4	25.3		0.78				
LiBr	39.1	30.0		.77				
LiI	51.2	39.2		.77				
NaCl	41.6	26.9	0.68	.65	0.64	0.65	0.64	0.64[b]
NaBr	49.0	31.5	.66	.64	.64	.64	.64	.65
NaI	61.1	40.6		.66				
KF	37.2	24.0		.65				
KCl	56.6	36.3	.65	.64	.64	.64	.64	.64[b]
KBr	64.7	41.3	.65	.64	.64	.64	.64	
KI	78.0	51.0		.65				
RbCl	63.8	40.7	.65	.64			.64	
RbBr	72.7	46.3	.64	.64			.64	
RbI	86.7	55.9		.64				
CsCl[a]	73.4	47.2		.64				
CsBr[a]	82.6	52.8		.64				
CsI[a]	97.5	62.7		.64				
CsCl	62.4	48.0		.77				
CsBr	70.4	53.4		.76				
CsI	83.3	63.2		.76				

[a] Hypothetical rock-salt type lattice structure.
[b] 85°.

From equation (8-5-15) we obtain

$$S_V = (\psi^* V^* - \phi_V^0)\sqrt{V^*/1000} \qquad (8\text{-}5\text{-}17)$$

for the rate of change of ϕ_V with $c^{1/2}$. This result is peculiar since it makes no provision for the effect of an ionic atmosphere in the usual sense. The terms ψ^* and V^* apply to such a close-packed system of ions that their distribution presumably follows a crystal lattice pattern, and ϕ_V^0 implies the disappearance of the atmosphere by infinite separation of the ions. Two consequences of this empirical equation are of considerable interest. In the first place, it follows from the data in Tables (8-5-1) and (8-5-2), that both ϕ_V^0 and ϕ_V^* are additive. Therefore, for salts of the same crystalline structure (identical ψ^* values), it follows from equation (8-5-17) that $S_V\sqrt{1000/V^*}$ must be additive in so far as V^* fulfills this condition

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[94] A. F. Scott, *J. Phys. Chem.*, **35**, 3379 (1931).
[95] W. Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931).
[96] B. Pesce, *Gazz. chim. ital.*, **66**, 99 (1936).

[Table (8-5-2), column 2]. The approximate additivity of S_V, noted by Root and others, should, however, be used with caution because the presence of ψ^* in equation (8-5-17) may completely obliterate this additivity if ψ^* varies considerably with crystal structure. A second consequence of equation (8-5-17) follows from the fact that ψ^* and V^* are nearly independent of the temperature over a considerable range, and therefore the relation

$$\frac{\partial S_V}{\partial T} \cong -\left(\frac{V^*}{1000}\right)^{1/2} \frac{\partial \phi_V^0}{\partial T} \qquad (8\text{-}5\text{-}18)$$

is a fairly close approximation.

Fig. (8-5-3) shows a plot of ϕ_V^* against V^* at 25°. The arrows indicate the effect of using rough values of S_V and ϕ_V^0 for the lithium salts obtained from data at the highest concentrations only,[97] and the effect of calculating V^* for the cesium salts on the basis of a rock-salt structure. It seems evident from the plot that ψ^*, the slope of the solid line, is a function of the spatial arrangement in the lattice, and this is supported by the fact that ψ^* is quite insensitive to variations in temperature. This conclusion is important, because, if the relationship between S_V and ϕ_V^0 given by equation (8-5-15) is governed only by the geometry of the critical disruptive state, it suggests that the geometry of this state is maintained, statistically at least, over the entire range of validity of equation (8-5-4). If this is the case, the concept of the ionic atmosphere might be replaced by a statistical lattice structure, except at high dilutions. This point deserves more detailed investigation, since X-ray studies also indicate a corre-

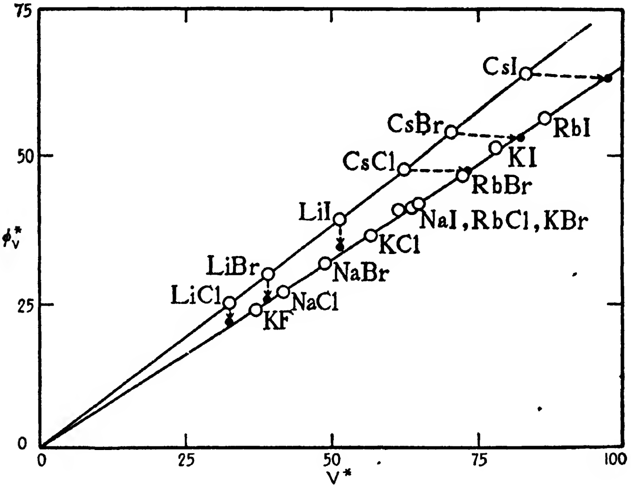

Fig. (8-5-3) Plots of ϕ_V^* against V^* for the alkali halides in aqueous solutions at 25°

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[97] There is evidence of abrupt changes in S_V in passing from low to high concentrations. *Cf.* A. F. Scott and G. L. Bridger, *J. Phys. Chem.*, **39**, 1031 (1935).

spondence between S_V and the rate of variation of the liquid structure of the solvent with ionic concentration.[98]

Precise density measurements on dilute solutions of urea[99] and sucrose[100] have been used to show that ϕ_V for non-electrolytes varies linearly with c rather than $c^{1/2}$ in dilute solutions. Examination of Fig. (8-5-4), from the work of Gucker, Gage and Moser,[99] will leave little doubt as to the validity of this conclusion.

So far our attention has been focussed upon ϕ_V rather than $\bar{V}_2$ because the former quantity is more directly obtained from the density data, and is more simply expressed by empirical equations, such as (8-5-4). The quantity $\bar{V}_2$ is no less important, but since its behavior is so similar to that of ϕ_V, it will be discussed briefly.

At extreme dilutions $\bar{V}_2$ varies linearly with $c^{1/2}$ wherever ϕ_V exhibits this behavior, and the slope $\partial \bar{V}_2/\partial c^{1/2}$ is 3/2 times the corresponding slope, $\partial \phi_V/\partial c^{1/2}$, a result obtained by differentiation of equation (8-5-8). Consequently, agreement with the theoretical limiting law in one case requires agreement in both. At moderate dilutions the S-shaped feature of ϕ_V shown in Fig. (8-5-2) is somewhat exaggerated by the requirements of equation (8-5-8), and in concentrated solutions, where ϕ_V is again linear with $c^{1/2}$ for many salts, the plot of $\bar{V}_2$ shows a slight curvature, which usually becomes quite pronounced at high concentrations.

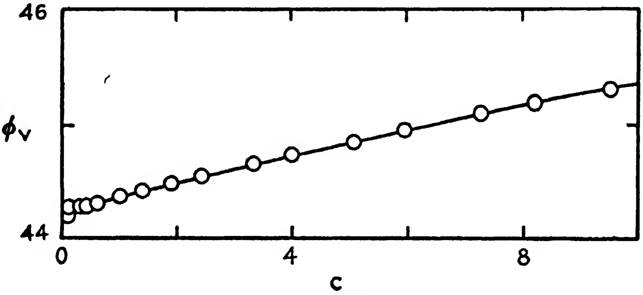

Fig. (8-5-4). Apparent molal volume of urea in aqueous solutions at 25°

The values of ϕ_V^0 given in Table (8-5-1) are equal to the corresponding values of $\bar{V}_2^0$. For many practical purposes $\bar{V}_2$ may be estimated at moderate concentrations by multiplying the last term in equation (8-5-4) by 3/2 and using the values of S_V ($= \partial \phi_V/\partial c^{1/2}$) recorded in the same table.

The temperature and pressure variations of $\bar{V}_2$ are considered in detail

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[98] G. W. Stewart, *J. Chem. Phys.*, **7**, 869 (1939).

[99] F. T. Gucker, Jr., F. W. Gage and C. E. Moser, *J. Am. Chem. Soc.*, **60**, 2582 (1938). Cf. O. K. Skarre, S. G. Demidenko and A. I. Brodskiĭ, *Acta Physicochim. U.R.S.S.*, **6**, 297 (1937).

[100] F. Plato, J. Domke and H. Harting, *Wiss. Abh. Normaleichungskommission*, 2 Hefte, Berlin, Springer, 1900, quoted by O. Redlich and H. Klinger, *Monatshefte für Chemie*, **65**, 137 (1934).

in Sections (6) and (7) which deal with expansibility and compressibility, but there are several interesting effects of these variations which are relevant to the present discussion. A number of recent studies[101–105] suggest the generalization that ϕ_V^0 for electrolytes in aqueous solutions passes through a maximum between 60 and 70°. This maximum also appears in plots of ϕ_V, and the effect of increasing concentration is usually a small increase in the temperature of the maximum, and a considerable decrease in the curvature of the plot in its neighborhood. The behavior of $\bar{V}_2$ is quite similar. The maximum values of ϕ_V^0 or $\bar{V}_2^0$ are approximately additive.

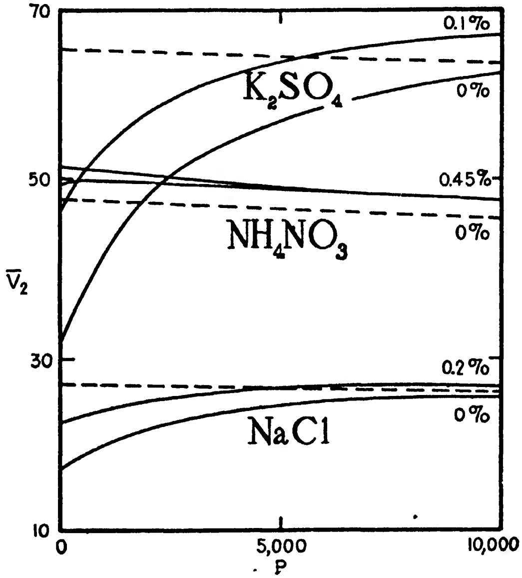

Fig. (8-5-5). The effect of pressure upon the partial molal volumes of salts in aqueous solutions at 25°. Molal volumes of pure solid salts are represented by broken lines. The numbers at the right-hand margin indicate the salt concentrations in weight per cent.

The effect of pressure on ϕ_V and $\bar{V}_2$ is particularly interesting because an increase in pressure increases the apparent molal and partial molal volumes. The negative sign and order of magnitude of $\partial \bar{V}_2^0/\partial P$ is predictable[106, 107]

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[101] W. R. Bousfield and T. M. Lowry, *Trans. Faraday Soc.*, **6**, 15 (1910).

[102] W. Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931).

[103] A. F. Scott, *J. Phys. Chem.*, **35**, 2315 (1931).

[104] B. Pesce, *Gazz. chim. ital.*, **66**, 99 (1936).

[105] O. Redlich and H. Klinger, *Monatsh.*, **65**, 137 (1934).

[106] W. Geffcken, *Z. phys. Chem.*, **A167**, 240 (1933).

[107] I. R. Krichevskii, *Acta Physico-chem. U.R.S.S.*, **8**, 181 (1938); *J. Phys. Chem. (U.S.S.R.)*, **11**, 305 (1938).

from the simple electrostatic theory which led to equation (3-10-13). Adams[108] has shown that this curious effect persists at pressures as high as 10,000 atmospheres for solutions of sodium chloride and potassium sulfate, but becomes less pronounced at high pressures and high concentrations. Fig. (8-5-5) illustrates the behavior of these salts in comparison with that of ammonium nitrate.[109] The broken lines in the figure, representing the molal volumes of the pure crystalline salts, are approached by the partial molal volumes at high concentrations and high pressures. The increase in partial molal volume with pressure presumably results from a compression of the solvent caused by the solute when the process of solution is accompanied by a net contraction in volume. Equation (8-5-1) shows that, if an increase in pressure decreases $\bar{V}_1^0$ much more rapidly than V, ϕ_V may increase with pressure. This is the case in dilute aqueous solutions of electrolytes at low pressures, for the compressibility of water decreases rapidly with pressure under this condition. At high pressures, where the compressibility decreases very little with pressure, or in concentrated solutions, where the magnitude of P_e[110] approaches that of P, the change in ϕ_V with P will decrease, and eventually become negative. Furthermore these excessive conditions of high pressure, or high concentrations, should allow the compressibility of the pure salt to be an important factor in characterizing the compressibility of the solution. The fact that ϕ_V and its variation with pressure approach the corresponding molal values of the pure solute under these conditions should therefore not be regarded as a sufficient condition of ideality.[111]

(6) THE PARTIAL MOLAL EXPANSIBILITY, APPARENT MOLAL EXPANSIBILITY, AND THE COEFFICIENT OF THERMAL EXPANSION OF SOLUTIONS OF ELECTROLYTES

The partial molal expansibilities of the components of a binary solution are defined by

$$\bar{E}_1 \equiv \left(\frac{\partial \bar{V}_1}{\partial T}\right)_P \qquad (8\text{-}6\text{-}1)$$

and

$$\bar{E}_2 \equiv \left(\frac{\partial \bar{V}_2}{\partial T}\right)_P \qquad (8\text{-}6\text{-}2)$$

The apparent molal expansibility of the solute is defined by

$$\phi_E \equiv \left(\frac{\partial \phi_V}{\partial T}\right)_P \qquad (8\text{-}6\text{-}3)$$

[108] L. H. Adams, *J. Am. Chem. Soc.*, **53**, 3769 (1931); *Ibid.*, **54**, 2229 (1932).

[109] L. H. Adams and R. E. Gibson, *J. Am. Chem. Soc.*, **54**, 4520 (1932).

[110] The effective pressure, P_e, is defined in the text immediately before equation (8-7-21).

[111] R. E. Gibson, *J. Am. Chem. Soc.*, **59**, 1521 (1937).

Combination of this equation with (8-5-1) leads to

$$\phi_E = \frac{\left(\frac{\partial V}{\partial T}\right)_P - n_1\left(\frac{\partial \bar{V}_1^0}{\partial T}\right)_P}{n_2} = \frac{\alpha V - \alpha_0 n_1 \bar{V}_1^0}{n_2} \tag{8-6-4}$$

where

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{d}\left(\frac{\partial d}{\partial T}\right)_P = -\frac{1}{c}\left(\frac{\partial c}{\partial T}\right)_P \tag{8-6-5}$$

is the coefficient of thermal expansion of the solution, and

$$\alpha_0 \equiv \frac{1}{\bar{V}_1^0}\left(\frac{\partial \bar{V}_1^0}{\partial T}\right)_P = -\frac{1}{d_0}\left(\frac{\partial d_0}{\partial T}\right)_P \tag{8-6-6}$$

is the coefficient of thermal expansion of the pure solvent. The apparent molal expansibility may be readily calculated from densities and their temperature coefficients by the equations

$$\begin{aligned} \phi_E &= \frac{1000}{cd_0}(d_0\alpha - d\alpha_0) + \frac{M_2}{d_0}\alpha_0 \\ &= \frac{1000}{c}(\alpha - \alpha_0) + \alpha_0\phi_V \end{aligned} \tag{8-6-7}$$

and

$$\begin{aligned} \phi_E &= \frac{1000}{mdd_0}(d_0\alpha - d\alpha_0) + \frac{M_2}{d}\alpha \\ &= \frac{1000}{md_0}(\alpha - \alpha_0) + \alpha\phi_V \end{aligned} \tag{8-6-8}$$

obtained by combination of equations (8-6-5) and (8-6-6) with (8-5-2) or (8-5-3). In practice the density data available for this purpose have usually been used to obtain ϕ_V, and therefore it is a simple matter to calculate ϕ_E from the latter by equation (8-6-3). Gucker[112] constructed plots of the values of ϕ_V calculated from the density data[113] for sodium and potassium chlorides. The tangents were estimated graphically, and are plotted against $\sqrt{c}$ at three temperatures in Fig. (8-6-1). With the exception of the results for sodium chloride at 0°, the points are satisfactorily represented by straight lines. Accordingly, ϕ_E is given by

$$\phi_E = \phi_E^0 + S_E\sqrt{c} \tag{8-6-9}$$

within the experimental concentration range. Because of the wide difference in S_E exhibited by salts of the same valence type, the values of ϕ_E^0, obtained by fitting this equation to the available data, may differ considerably from the true limiting partial molal expansibilities.

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[112] F. T. Gucker, Jr., *J. Am. Chem. Soc.*, **56**, 1017 (1934).

[113] W. Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931); G. P. Baxter and C. C. Wallace, *J. Am. Chem. Soc.*, **38**, 70 (1916).

In dilute solutions, equation (8-6-9) follows from differentiation of (8-5-4). Thus,

$$\phi_E = \frac{\partial \phi_V^0}{\partial T} + \left[\frac{\partial S_V}{\partial T} - \frac{\alpha S_V}{2}\right] c^{1/2} \tag{8-6-10}$$

within the range of validity of (8-5-4). Further, Gucker[114] points out that the effect of replacing α by α_0 in this equation is negligible for most 1-1 electrolytes up to concentrations as high as "several molal". Consequently we may write

$$S_E \cong \left[\frac{\partial S_V}{\partial T} - \frac{\alpha_0 S_V}{2}\right] \tag{8-6-11}$$

as a close approximation. The graphical advantages of a linear plot could be extended to more concentrated solutions by transferring the concentration dependent term in α to the left side of equation (8-6-10), and plotting $[\phi_E + 1/2\ \alpha S_V c^{1/2}]$ against $c^{1/2}$. The estimation of S_E by substitution of the approximate relation (8-5-18) in (8-6-1) yields values .001 to .002 unit too low in the few cases for which the data are available.

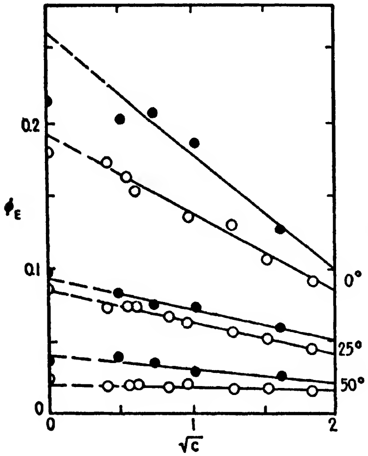

Fig. (8-6-1)
Variation of the apparent molal expansibility with temperature and composition in aqueous solutions. ● NaCl; ○ KCl

Combination of equations (8-6-9) and (8-5-4) with the second form of (8-6-7) yields the expression

$$\alpha = \alpha_0 + \left[\frac{\phi_E^0 - \alpha_0 \phi_V^0}{1000}\right] c + \left[\frac{S_E - \alpha_0 S_V}{1000}\right] c^{3/2} \tag{8-6-12}$$

similar to the density equation (8-5-5). The values of the bracketed coefficients in this equation are readily determined from the slope and intercept of a plot of $(\alpha - \alpha_0)/c$ against $c^{1/2}$, and ϕ_E^0 and S_E can be estimated if ϕ_V^0 and S_V are known. These latter quantities are recorded for a number of electrolytes in Table (8-5-1), and Gucker[114] has added other values calculated from densities given in the "International Critical Tables", and from Gibson's[115] data on sodium sulfate. Gucker's values for the coefficients of equations (8-6-9) and (8-6-12) at 25° are given in Table (8-6-1). Values at 0° and 50° for lithium, sodium and potassium chlorides have also been compiled by Gucker. A plot of the apparent molal expansibility of these electrolytes is given in Fig. (8-6-2). At 25°, it is seen that ϕ_E^0 is positive and ϕ_E decreases with concentration. At lower temperatures, ϕ_E^0 becomes more positive, and the decrease with concentration is more pronounced. At higher temperatures, the opposite is true. Thus, at 50°, Gucker found that ϕ_E^0 was negative, and S_E was

TABLE (8-6-1). NUMERICAL COEFFICIENTS FOR ϕ_E AND α AT 1 ATMOSPHERE AND 25°

Electrolyte	$\phi_E = \phi_E^0 + S_E c^{1/2}$		$\alpha = \alpha_0 + Ac + Bc^{3/2}$[a]	
	$10^2\phi_E^0$	$10^2 S_E$	$10^4 A$	$10^4 B$
HCl	3.4	−0.02	0.29	−0.004
LiCl	2.5	− .65	.21	− .069
LiOH[b]	4.5	−1.8	.47	− .19
NaCl	9.30	−2.10	.89	− .216
KCl	8.50	−2.20	.78	− .226
NaOH	11.7	−3.5	1.19	− .36
Na_2SO_4	22.19	−9.33	2.19	− .966

[a] $\alpha_0 = 2.55 \times 10^{-4}$.

[b] Values for LiOH must be considered rather tentative.

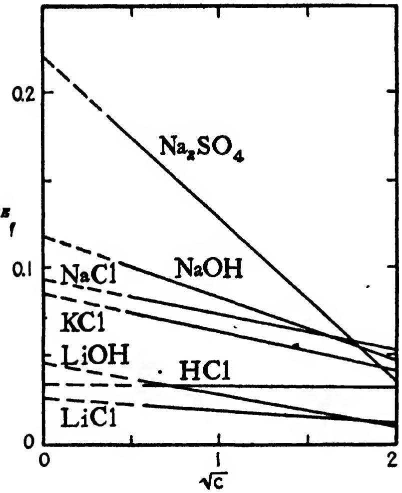

Fig. (8-6-2)
Apparent molal expansibilities in water at 25°

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[114] F. T. Gucker, Jr., *J. Am. Chem. Soc.*, **56**, 1017 (1934).

[115] R. E. Gibson, *J. Phys. Chem.*, **31**, 496 (1927); *Ibid.*, **38**, 319 (1934).

positive for lithium chloride. At the concentrations used in evaluating S_E, the electrolytes of the same valence type exhibit no tendency to share a common slope.

$\bar{E}_2$ and $\bar{E}_1$ may be obtained in terms of ϕ_E and $\partial\phi_E/\partial m^{1/2}$ by differentiation of equations (8-5-10) and (8-5-11). If it is more convenient to use the c-scale for this purpose, the corresponding equations are

$$\bar{E}_2 = \phi_E + \left[\frac{1000 - c\phi_V}{2000 + c^{3/2}\,\partial\phi_V/\partial\sqrt{c}}\right] c^{1/2}\,\frac{\partial\phi_E}{\partial\sqrt{c}} \qquad (8\text{-}6\text{-}13)$$

and

$$\bar{E}_1 = \bar{E}_1^0 - \frac{M_1}{d_0}\left[\frac{1}{2000 + c^{3/2}\,\partial\phi_V/\partial\sqrt{c}}\right] c^{3/2}\,\frac{\partial\phi_E}{\partial\sqrt{c}} \qquad (8\text{-}6\text{-}14)$$

Both of these equations are general, but Gucker[114] expresses equation (8-6-13) in the form

$$\bar{E}_2 = \phi_E^0 + \left[\frac{3000 - c\phi_V^0}{2000 + c^{3/2}\,\partial\phi_V/\partial\sqrt{c}}\right] c^{1/2}\,\frac{\partial\phi_E}{\partial\sqrt{c}} \qquad (8\text{-}6\text{-}15)$$

which is valid only over a concentration range in which both ϕ_E and ϕ_V vary linearly with $c^{1/2}$. Consequently, if ϕ_E is linear in $c^{1/2}$, $\bar{E}_2$ cannot be. For the electrolytes for which data are available the departures of $\bar{E}_2$ from linearity would be only 3 or 4 per cent up to $c = 9$, and it is difficult to decide which, if either, of the quantities, ϕ_E and $\bar{E}_2$, is strictly linear in $c^{1/2}$. In any case, the plots of $\bar{E}_2$ against $(3/2)c^{1/2}$ would fall so closely upon those shown in Fig. (8-6-2) that no further illustration is necessary.

The quantities α, ϕ_E, $\bar{E}_2$ and $\bar{E}_1$ have been estimated[116] for aqueous solutions of urea at 27.5° from density data at 25 and 30°. Since the densities at both temperatures were expressed by

$$d = d_0 + A_1c + A_2c^2 + A_3c^3 + \cdots \qquad (8\text{-}6\text{-}16)$$

it follows [Equation (8-6-5)] that the equation for α must take the same form. The relationships between the coefficients of the similar equations for d and α have been derived by Gucker and Moser.[117] Their final expressions for the coefficient of thermal expansion and apparent molal volume of urea at 27.5° are

$$\alpha \times 10^6 = 281.2 + 52.0c - 4.71c^2 \qquad (8\text{-}6\text{-}17)$$

and

$$\phi_V = 44.385 + 0.1203c \qquad (8\text{-}6\text{-}18)$$

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[116] F. T. Gucker, Jr., and C. E. Moser, *J. Am. Chem. Soc.*, **61**, 1558 (1939).

[117] F. T. Gucker, Jr., and C. E. Moser, *J. Am. Chem. Soc.*, **61**, 1558 (1939). The numerical factor of the third term in the coefficient of c^3 in their equation (6) should be unity.

Hence, by equation (8-6-7),

$$\phi_E = 0.0645 - 0.00468c \tag{8-6-19}$$

When account is taken of this linearity in c instead of $c^{1/2}$, these equations lead to

$$\bar{E}_2 = 0.0645 - 0.00936c + 0.00208c^2 \tag{8-6-20}$$

and

$$\bar{E}_1 = 0.005085 + 0.0000846c^2 - 10^{-8}c^4 \tag{8-6-21}$$

The absence of a term in $c^{1/2}$, in the expressions for $\bar{E}_2$, ϕ_E and ϕ_V, or of a term in $c^{3/2}$, in the expressions for $\bar{E}_1$, α and d, was to be expected for a solution of a non-electrolyte. The fact that the numerical values of ϕ_E and $\bar{E}_2$ for urea are approximately the same as the corresponding magnitudes for 1-1 type strong electrolytes is without explanation at present, and is probably coincidental. This non-ideal behavior of urea is very peculiar since the behavior of ϕ_V [Equation (8-6-18)] is almost ideal. The molal volume of solid urea is 45.19 cc. at 25°, and $\bar{V}_2$, at the same temperature, is within 2 per cent of this value up to $c = 10$.

(7) THE PARTIAL MOLAL COMPRESSIBILITY, APPARENT MOLAL COMPRESSIBILITY, AND COEFFICIENT OF COMPRESSIBILITY OF SOLUTIONS OF ELECTROLYTES

The partial molal compressibilities of the components of a binary solution are defined by

$$-\bar{K}_1 \equiv \left(\frac{\partial \bar{V}_1}{\partial P}\right)_T \tag{8-7-1}$$

and

$$-\bar{K}_2 \equiv \left(\frac{\partial \bar{V}_2}{\partial P}\right)_T \tag{8-7-2}$$

The apparent molal compressibility is

$$-\phi_K \equiv \left(\frac{\partial \phi_V}{\partial P}\right)_T \tag{8-7-3}$$

which, by combination with (8-5-1), becomes

$$-\phi_K = \frac{\left(\frac{\partial V}{\partial P}\right)_T - n_1\left(\frac{\partial \bar{V}_1^0}{\partial P}\right)_T}{n_2} = \frac{-V\beta + n_1\bar{V}_1^0\beta_0}{n_2} \tag{8-7-4}$$

The coefficients of compressibility are defined by

$$\beta \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{d}\left(\frac{\partial d}{\partial P}\right)_T = \frac{1}{c}\left(\frac{\partial c}{\partial P}\right)_T \tag{8-7-5}$$

and

$$\beta_0 \equiv -\frac{1}{\bar{V}_1^0}\left(\frac{\partial \bar{V}_1^0}{\partial P}\right)_T = \frac{1}{d_0}\left(\frac{\partial d_0}{\partial P}\right)_T \tag{8-7-6}$$

for the solution and pure solvent respectively.

In practice, the apparent molal compressibility may be calculated from compressibility and density data by one of the equations,

$$\begin{aligned}\phi_K &= \frac{1000}{cd_0}(d_0\beta - d\beta_0) + \beta_0\frac{M_2}{d_0} \\ &= \frac{1000}{c}(\beta - \beta_0) + \beta_0\phi_V\end{aligned} \tag{8-7-7}$$

and

$$\begin{aligned}\phi_K &= \frac{1000}{mdd_0}(d_0\beta - d\beta_0) + \beta\frac{M_2}{d} \\ &= \frac{1000}{md_0}(\beta - \beta_0) + \beta\phi_V\end{aligned} \tag{8-7-8}$$

as well as by equation (8-7-3).

As in the case of ϕ_E, we would expect the concentration dependence of ϕ_K to follow closely the simple form

$$\phi_K = \phi_K^0 + S_K\sqrt{c} \tag{8-7-9}$$

because differentiation of equation (8-5-4) leads to

$$\phi_K = \phi_K^0 - \left[\left(\frac{\partial S_V}{\partial P}\right)_T + \frac{\beta S_V}{2}\right]c^{1/2} \tag{8-7-10}$$

Furthermore

$$S_K = -\left[\left(\frac{\partial S_V}{\partial P}\right)_T + \frac{\beta_0 S_V}{2}\right] \tag{8-7-11}$$

so long as β may be replaced by β_0 in equation (8-7-10) without causing a large error. For 1-1 electrolytes, this condition is fulfilled below $3N$, at which concentration the difference in ϕ_K, as calculated by equation (8-7-9) and (8-7-10) amounts to approximately 1 per cent. A linear relationship with $\sqrt{c}$ may be maintained up to the highest concentrations, if equation (8-7-10) is rearranged to read

$$[\phi_K + \tfrac{1}{2}\beta S_V c^{1/2}] = \phi_K^0 - \left(\frac{\partial S_V}{\partial P}\right)_T c^{1/2} \tag{8-7-12}$$

and the bracketed member considered the dependent variable instead of ϕ_K. Scott[118, 119] uses this equation almost exclusively for both numerical

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[118] A. F. Scott and R. W. Wilson, *J. Phys. Chem.*, **38**, 951 (1934).

[119] A. F. Scott and G. L. Bridger, *Ibid.*, **39**, 1031 (1935).

and theoretical purposes, and there can be no doubt as to its advantages over equation (8-7-9), if one considers Masson's rule strictly vailid. At the present stage of the subject, we feel justified in using the simpler equation (8-7-9) for purposes of tabulation. We shall see later that, for some electrolytes, it is preferable to avoid the c-scale altogether, and make use of molalities or weight fractions.

Through the range in which both ϕ_K and ϕ_V vary as $c^{1/2}$, the combination of equations (8-7-9), (8-7-11) and (8-5-4) with (8-7-7) leads to an expression of the form

$$\beta = \beta_0 + Ac + Bc^{3/2} \tag{8-7-13}$$

in which

$$1000A = \phi_K^0 - \beta_0\phi_V^0 \tag{8-7-14}$$

and

$$1000B = S_K - \beta_0 S_V \tag{8-7-15}$$

If equation (8-7-10) had been used instead of equations (8-7-9) and (8-7-11), the right-hand member of (8-7-15) would be increased by $\frac{1}{2}S_V$ $(\beta_0 - \beta)$. The addition of this term would cause a difference of only about $\frac{1}{2}$ per cent in the calculated value of β in $3N$ solutions of 1-1 electrolytes.

In Table (8-7-1), we have recorded the parameters from which ϕ_K and β may be calculated by means of equations (8-7-9) and (8-7-13). The values of A and B were computed by Gucker and Rubin[120], who converted the mean compressibility data of Lanman and Mair,[121] between 100 and 300 bars, to compressibility coefficients at one bar. For this calculation they employed the accurate method of Gibson[122] which will be considered later. ϕ_K^0 and S_K were estimated by equations(8-7-14) and (8-7-15) from the values of A and B given in the same table. The required values of ϕ_V^0 and S_V were taken from Table (8-5-1). ϕ_K^0 and S_K, for the salts and bases given in Table(8-7-1), are all about 16 and 23 per cent higher respectively than those obtained by Gucker[123] before he had converted the compressibility results from 200 bars to one atmosphere. Our values of ϕ_K^0 and S_K for hydrochloric acid are 26 and 30 per cent higher than his. The behavior of ϕ_K at high concentrations is illustrated in Fig. (8-7-1). A discussion of the results in more dilute solutions will be reserved for the end of this section [Table (8-7-5)].

The problem of calculating the compressibility coefficient at one atmosphere from direct measurement of the pressure-volume relationships of solutions is a difficult one. The pressure dependence of β is such that β

[120] F. T. Gucker, Jr., and T. R. Rubin, *J. Am. Chem. Soc.*, **57**, 78 (1935).

[121] E. H. Lanman and B. J. Mair, *J. Am. Chem. Soc.*, **56**, 390 (1934).

[122] R. E. Gibson, *J. Am. Chem. Soc.*,**56**, 4 (1934).

[123] F. T. Gucker, Jr., *Chem. Rev.*, **13**, 111 (1933).

decreases most rapidly at low pressures, where it is most difficult to obtain experimental results of high accuracy. The usual measurement involves determining the contraction in volume attending an increase in pressure of the order of 200 to 1000 atmospheres. If the initial pressure is P_0, usually one atmosphere, the result of a single measurement is the bulk compression, k_0, defined by*

TABLE (8-7-1). PARAMETERS FOR EQUATIONS (8-7-9) AND (8-7-13) AT 25° AND 1 ATMOSPHERE*

Electrolyte	$\phi_K^0 \times 10^4$†	$S_K \times 10^4$	$A \times 10^6$	$B \times 10^6$
HCl	−8.3	3.0	−1.66	0.26
LiCl	−42.0	9.1	−4.97	0.84
NaCl	−51.6	11.4	−5.91	1.04
KCl	−45.2	12.4	−5.73	1.13
LiOH	−77.9	17.0	−7.52	1.56
NaOH	−89.0	20.9	−8.59	1.90

* $\beta_0 = 45.5 \times 10^{-6}$.

† Additional values of ϕ_K^0 are tabulated by B. B. Owen and S. R. Brinkley Jr., *Chem. Rev.*, **29**, 461 (1941).

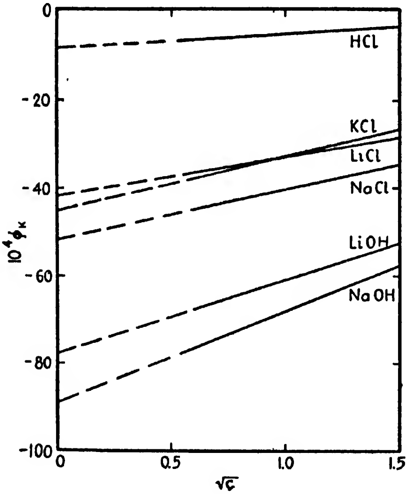

Fig. (8-7-1)
Apparent molal compressibilities of 1-1 electrolytes in water at 25° and one atmosphere.

$$k_0 \equiv -\frac{v_0^{(P)} - v_0^{(P_0)}}{v_0^{(P_0)}} \tag{8-7-16}$$

for a pure liquid. By dropping the subscript, 0, this equation becomes the definition of the bulk compression, k, of a solution. If k_0 is accurately

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* From this point to the end of the chapter, we shall use specific volumes, etc., rather than the corresponding molal quantities, so that our treatment will not differ too greatly from Gibson's.

determined at a large number of pressures, it should be possible to express its pressure dependence by a power series in the pressure increase, such as

$$k_0 = a_1(P - P_0) + a_2(P - P_0)^2 + a_3(P - P_0)^3 + \ldots \quad (8\text{-}7\text{-}17)$$

and evaluate the parameters by suitable means.[124, 125] Furthermore, it follows from equation (8-7-17) that

$$\left(\frac{\partial k_0}{\partial P}\right)_T = a_1 + 2a_2(P - P_0) + 3a_3(P - P_0)^2 + \cdots \quad (8\text{-}7\text{-}18)$$

at any pressure. The true compressibility, β_0, at atmospheric pressure ($P = P_0 = 1$) is equal to a_1. The difficulty of obtaining the numerous data essential to the success of this simple empirical treatment is very great. In the following paragraphs, the equations described are possibly less convenient for numerical computation, but they allow a very satisfactory estimation of β_0 over a wide pressure range from a single experimental value of k_0.

In 1888 Tait[126] discovered a simple P-V relationship for water which may be written

$$\beta_0^{(P)} v_0^{(P)} = -\left(\frac{\partial v_0}{\partial P}\right)_T^{(P)} = \frac{0.4343C}{B + P} \quad (8\text{-}7\text{-}19)$$

or, in integrated form,

$$k_0 v_0^{(P_0)} = -(v_0^{(P)} - v_0^{(P_0)}) = C \log\left(\frac{B + P}{B + P_0}\right) \quad (8\text{-}7\text{-}20)$$

where C and B are positive constants. Gibson[127,128] has made a very thorough study of the Tait equation, and reports that it closely fits the experimental results of Adams[129] on water at 25° up to 10,000 bars, and Bridgman's[130] data on numerous non-volatile liquids at different temperatures over the same range. It also fits Bridgman's data for fifteen volatile liquids between 4,000 and 12,000 bars, and the data for some solids as well.

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[124] A. L. T. Moesveld, *Z. physik. Chem.*, **105**, 442, 450 (1923).

[125] T. W. Richards and W. N. Stull, Carnegie Inst. Pub. #7 (1903); *Ibid.*, #76 (1907).

[126] P. G. Tait, "Report on some of the physical properties of fresh-water and of sea-water." 1888. From the "Physics and Chemistry" of the voyage of H. M. S. *Challenger*. Vol. II, Part IV. S. P. LXI.

[127] R. E. Gibson, *J. Am. Chem. Soc.*, **56**, 4 (1934); *Ibid.*, **57**, 284 (1935).

[128] R. E. Gibson and J. F. Kincaid, *Ibid.*, **60**, 511 (1938). See also J. F. Kincaid and H. Eyring, *J. Chem. Phys.*, **5**, 587 (1937) and L. J. Hudleston, *Trans. Faraday Soc.*, **33**, 98 (1937).

[129] L. H. Adams, *J. Am. Chem. Soc.*, **53**, 3769 (1931).

[130] P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **66**, 185 (1931); *Ibid.*, **67**, 1 (1932); *Ibid.*, **68**, 1 (1933).

Some of Gibson's most recent* values, B and C/v_0, are given in Table (8-7-2). Note that C/v_0 varies very little with composition of the liquid, and is independent of the temperature.[131] The theoretical significance of the parameters has been discussed by Gibson and Kincaid.[132] The term

TABLE (8-7-2). PARAMETERS OF EQUATIONS (8-7-19) AND (8-7-20).

Substance	$\frac{C}{v_0}$	B (in bars)			
		25°	45°	65°	85°
Water[a,e]	0.3150	2,996	3,081	3,052.2	2,939.0
Methanol[b]	.2208	764	...	...	...
Ethylene glycol[a]	.21763	2,544	2,363	2,186	2,011
Benzene[c]	.21591	970	829	701	...
Chlorobenzene[d]	.21591	1,249.1	1,097.8	960.9	835.0
Bromobenzene[d]	.21591	1,404.4	1,247.3	1,103.3	972.0
Nitrobenzene[d]	.21591	1,865.2	1,678.8	1,504.5	1,341.6
Aniline[d]	.21591	2,006.6	1,798.3	1,605.6	1,429.4
Carbon tetrachloride[a]	.21290	867.0	737.7	622.1	...

[a] Private communication from Dr. Gibson.

[b] R. E. Gibson, *J. Am. Chem. Soc.*, **59**, 1525 (1937).

[c] R. E. Gibson and J. F. Kincaid, *Ibid.*, **60**, 511 (1938). $B = 970 - 7.37\,(t - 25) + 0.016\,(t - 25)^2$.

[d] R. E. Gibson and O. H. Loeffler, *Ibid.*, **61**, 2517 (1939).

[e] R. E. Gibson, *Am. J. Sci.* [5], **35A**, 49 (1938).

Note that by our choice of symbols it is C/v_0, and not C, that is independent of temperature.

TABLE (8-7-3). COMPARISON OF VALUES OF $\beta_0 \times 10^6$ AT ONE BAR CALCULATED BY EQUATION (8-7-19) WITH VALUES DERIVED FROM MEASUREMENTS OF THE VELOCITY OF SOUND

Liquid	t	Equation	Sound
Benzene	10	86.5	86.4[a]
Benzene	20	93.1	93.7[a]
Benzene	30	100.4	101.2[a]
Benzene	40	108.6	108.6[a]
Benzene	50	117.8	118.3[a]
Methanol	25	125.3	125.6[a]
Water	25	45.7	45.2[b] 45.9[c]

[a] E. B. Freyer, J. C. Hubbard and D. H. Andrews, *J. Am. Chem. Soc.*, **51**, 759 (1929). High frequencies.

[b] J. C. Hubbard and A. L. Loomis, *Phil. Mag.* [7], **5**, 1177 (1928). High frequencies.

[c] L. G. Pooler, *Phys. Rev.*, **35**, 832 (1930). Low frequencies.

0.4343C may be regarded as the compression produced by a pressure interval, $B + P$, and B represents the difference between the expansive

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* In Gibson's earlier papers, B and C should be replaced by $B + 1$ and $0.4343\,C$ to conform with the present meaning attached to these symbols.

[131] H. Carl, *Z. physik. Chem.*, **101**, 238 (1922).

[132] R. E. Gibson and J. F. Kincaid, *J. Am. Chem. Soc.*, **60**, 511 (1938). See also J. F. Kincaid and H. Eyring [*J. Chem. Phys.*, **6**, 587 (1938)], and L. J. Hudleston [*Trans. Faraday Soc.*, **33**, 98 (1937)] for discussions of equations of state similar to (8-7-19).

pressure, due to thermal energy, and the cohesive pressure, due to temperature-independent attraction between the molecules. Therefore, B decreases with the temperature, and increases with the intermolecular forces, as can be seen from Table (8-7-2).

The results in Table (8-7-3) illustrate the ability of equation (8-7-19) to represent the properties of liquids at atmospheric pressure by means of constants derived from compression measurements at high pressures. Values of β_0 at one bar are calculated from the constants given in Table (8-7-2), and compared with results derived from measurements of the velocity of sound through liquids at atmospheric pressures [Equations (8-7-29) and (8-7-30)]. The value for water, 45.7×10^{-6}, calculated by equation (8-7-19), is only 1/3 per cent higher than the mean of the results obtained from velocity measurements. A slightly lower value, 45.5×10^{-6}, previously reported by Gibson,[133] will be used in subsequent calculations.

Gibson[134] has applied the Tait equation to solutions by the introduction of a single additional parameter. This important extension is based upon Tammann's[135] hypothesis that, in the presence of an ionized solute, the water in an aqueous solution behaves as though it were subjected to a constant effective pressure, P_e, in addition to the atmospheric. The contraction in volume and decrease in compressibility which accompanies the solution of an electrolyte is thereby ascribed to a compression of the water rather than to any alteration in the properties of the solute (as a liquid).

In accordance with this idea the volume of one g. of solution containing x_1 g. of solvent and x_2 g. of solute may be represented by

$$v^{(P)} = x_1\psi_1^{(P)} + x_2\psi_2^{(P)} \tag{8-7-21}$$

where ψ_2 is the specific volume of the pure solute (as a liquid), and ψ_1 is the apparent specific volume of the solvent in solution.* Further, the addition of an ionic solute (as a liquid) to one g. of pure water would cause the contraction, $v_0^{(P)} - \psi_1^{(P)}$, in the total volume of the system. In terms of the Tait equation (8-7-20), this volume change becomes

$$-[\psi_1^{(P)} - v_0^{(P)}] = C \log\left(\frac{B + P + P_e}{B + P}\right) \tag{8-7-22}$$

at any pressure, P. This useful expression will be referred to as the Tait-Gibson equation.

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[133] R. E. Gibson, *J. Am. Chem. Soc.*, **56**, 4 (1934).

[134] R. E. Gibson, *J. Am. Chem. Soc.*, **56**, 4 (1934); *Ibid.*, **57**, 284 (1935).

[135] G. Tammann, "Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Losungen," p. 36, Voss, Leipzig, 1907.

* For moderate pressures and concentrations, where $x_2\psi_2$ is considerably less than $x_1\psi_1$, it is not essential to be able to evaluate ψ_2 exactly. The interpretation of this quantity will be referred to later.

Eliminating $\psi_1^{(P)}$ between the foregoing equations, we obtain

$$-v^{(P)} = x_1 C \log(B + P + P_e) - x_2\psi_2^{(P)} - x_1[v_0^{(P)} + C \log(B + P)] \tag{8-7-23}$$

According to equation (8-7-20), the last term on the right drops out for variations in pressure at constant composition; hence

$$kv^{(P_0)} = -[v^{(P)} - v^{(P_0)}] = x_1 C \log \frac{(B + P + P_e)}{(B + P_0 + P_e)} - x_2[\psi_2^{(P)} - \psi_2^{(P_0)}] \tag{8-7-24}$$

By differentiation at constant temperature and composition, we obtain

$$\beta^{(P)} v^{(P)} = \frac{0.4343\, x_1 C}{B + P + P_e} - x_2 \frac{\partial \psi_2^{(P)}}{\partial P} \tag{8-7-25}$$

for the compressibility of the solution at any pressure, P. At moderate pressures and concentrations the terms containing ψ_2 are negligible. Since B and C are characteristic of the solvent alone, P_e is the only parameter dependent upon the properties of the solution, and may be evaluated from the measurement of a single compression over any convenient pressure range. P_e is directly related to the partial molal volume of the solute. From the definition, $\bar{v}_1 M_1 = (\partial V/\partial n_1)_{P,T,n_2}$, the proportion $x_1/x_2 = n_1M_1/n_2M_2$, and equation (8-7-21) it follows that

$$\bar{v}_1^{(P)} = x_1 x_2 \frac{\partial \psi_1^{(P)}}{\partial x_1} + \psi_1^{(P)} \tag{8-7-26}$$

By combining this equation with the fundamental relation

$$v^{(P)} = x_1\bar{v}_1^{(P)} + x_2\bar{v}_2^{(P)} \tag{8-7-27}$$

and equations (8-7-21) and (8-7-22), Gibson[136] derived the expressions

$$\bar{v}_2^{(P)} - \psi_2^{(P)} = \frac{0.4343\, x_1^2 C}{B + P_e + P} \frac{\partial(B + P_e)}{\partial x_1} \tag{8-7-28}$$

and

$$\bar{V}_2^{(P)} - M_2\psi_2^{(P)} = \frac{-434.3C}{B + P_e + P} \frac{\partial(B + P_e)}{\partial m} \tag{8-7-28a}$$

The last equation shows that the magnitude of the partial molal volume of the solute is largely governed by two factors. The first, $\partial(B + P_e)/\partial m$, is the rate of change of total internal pressure with concentration, and is a function of both solvent and solute. The second, $C/(B + P_e + P)$, is related to the compressibility of the solvent at the pressure, $P + P_e$, and is independent of the solute.

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[136] R. E. Gibson, *Am. J. Sci.*, [5], **35A**, 49 (1938).

In the calculation of the values of β, corresponding to the parameters given in Table (8-7-1), the pressure increment of 200 bars was from an initial pressure, P_0, of 100 bars instead of atmospheric. In this case, the argument of the logarithmic term in equation (8-7-24) is $(B + P_e + 300)/(B + P_e + 100)$, and the last term represents the compression of the pure liquid solute between 100 and 300 bars. The interval 1 to 1000 bars was used by Gibson[137] in his investigation of the concentration dependence of P_e for a large number of electrolytes. Some of his results[138] are reproduced in Fig. (8-7-2). Since the term P_e evidently arises from attractive forces between the ions and the induced or residual charges on the water molecules, it would be expected to increase with the charge density on the ions.

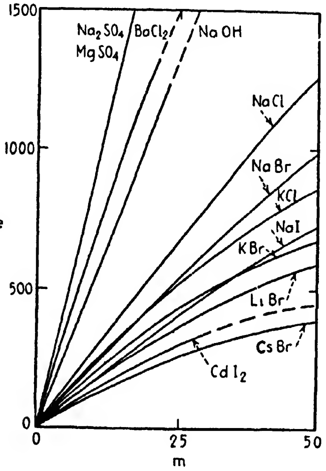

Fig. (8-7-2)
Effective pressure (bars) of salts in aqueous solutions at 25°

This expectation is borne out, with a few exceptions, by the curves in the figure, where it can be seen that in a series of salts with a common ion the value of P_e is highest for the salts with the smaller, or more highly charged uncommon ion. It should be remarked, however, that the *smallest* ions, Li^+, Be^{++} and Mg^{++}, constitute exceptions to these rules. The polarization produced by small ions of high charge density has been shown by Bernal and Fowler[139] to strengthen the forces responsible for the relatively open structure of water, in which each molecule is surrounded tetrahedrally by four others. This would counteract some of the normal tendency of the ions to compress the solvent, and give rise to abnormally low values of P_e. A more detailed description of this process is given by Gibson,[138] who also suggests that much of the specificity exhibited by P_e for similar

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[137] R. E. Gibson, *J. Am. Chem. Soc.*, **57**, 290 (1935).
[138] R. E. Gibson, *Sci. Monthly*, **46**, 103 (1938).
[139] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 540 (1933).

ions may be due simply to the effect of the volumes of the ions in increasing the average distance between water molecules. This diminishes the contribution of water-water molecule interaction to the total internal pressure, $B + P_e$, of the solution. This volume effect would increase with the size of the ions. He proposed to take this effect into account by comparing the total internal pressures of solutions divided by the square of the water concentration rather than comparing the effective pressures alone. Thus, if the function, $(B + P_e)/C_W^2$, is plotted as ordinate in Fig. (8-7-2) instead of P_e, the individuality of the plots is greatly reduced. Indeed, the results for all of the 1-1 salts, except those of lithium, are surprisingly well represented by a single curve. This fact leaves little doubt as to the importance of pure ionic volume effects.

The role of the solvent is emphasized by the fact that the anomalous behavior of lithium salts in respect to P_e in water disappears in glycol solutions, and the plots of P_e against m for dilute solutions of sodium and lithium bromides, and sodium and cadmium iodides superimpose in methanol, but are widely divergent in water and in glycol.[140]

Another empirical relation governing the variation of P_e with composition is[141]

$$P_e = Lc_1c_2 + i \tag{8-7-28b}$$

where L and i are characteristic of the electrolyte. The constant i is so small that it may be neglected for most purposes. It is introduced into the equation to call attention to the fact that plots of P_e against c_1c_2 do not pass exactly through the origin for all salts. This equation suggests that P_e may be considered a measure of the departure of the volume relationships of solutions from ideality, because it has been shown[141] that the relative departures from the simple law of mixtures for the compressions of a number of solutions are also directly proportional to the product c_1c_2. It follows from equation (8-7-28b) that P_e varies inversely with the square of the volume. This brings out the analogy between P_e and the cohesive pressure in gases, which are responsible for the a/v^2 term in the van der Waals equation. It also implies that P_e is a function of the pressure. This may become an important consideration in the study of liquids of relatively high compressibilities. Under the conditions of the present applications of equations (8-7-24) and (8-7-25), P_e is considered a constant characteristic of a given system at constant composition and temperature. This simplification is justified by the ability of the equations to represent compression data over the entire experimental range, and to effect extrapolations to atmospheric pressure. In Table (8-7-4) some compressibilities, calculated at 1 bar by equation (8-7-25) from values of P_e derived

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[140] R. E. Gibson, *J. Am. Chem. Soc.*, **59**, 1521 (1937).

[141] R. E. Gibson, *J. Am. Chem. Soc.*, **57**, 284 (1935). The concentrations of the water, c_1, and the electrolyte, c_2, are in mols per liter of solution.

from compressions at 1000 bars, are compared with values determined at one atmosphere from the velocity of sound[142] through the solutions. The agreement leaves little to be desired.

In concluding this discussion of the Tait equation, and its extension to solution of electrolytes, some implications regarding the actual volume of the dissolved solute will be briefly noted. Equation (8-7-23) may be used to compute ψ_2 at one atmosphere from values of P_e estimated from the contraction accompanying the process of solution. Values of ψ_2 obtained in this manner[143] are practically independent of the concentration, and are equal to, or a little greater (5 to 30 per cent) than the specific volume of the pure crystalline solute. If equation (8-7-28a) is used to estimate ψ_2 from P_e and $\bar{V}_2$, it is found that ψ_2 diminishes slightly with concentration. If, however, it is assumed that the compressibility of the solute in solution is three times as great as in the solid state, then ψ_2 is quite independent of concentration.[144] Thus, the specific volume of the pure solute, or more accurately the pure melted solute, appears to be closely associated with the "actual" volume of the solute in solution. The same conclusion is to be drawn from the discussion [Section (5)] of the critical disruptive volume, V^*, but it should be noted that V^* is considerably larger than the calculated values of $M_2\psi_2$. The exact relationship between these two quantities is by no means obvious.

TABLE (8-7-4).* COMPARISON OF COMPRESSIBILITIES ESTIMATED BY TWO INDEPENDENT METHODS AT 1 BAR AND 25°.

$100x_2$ (Wt.%)	$\beta \times 10^6$ (From compressions at 1000 bars)				$\beta \times 10^6$ (From sound velocities at 1 bar)			
	KCl	KBr	KI	NaCl	KCl	KBr	KI	NaCl
6	41.8	43.2	44.3	40.6	41.7	43.5	44.3	40.4
10	39.5	41.7	.	37.6	39.4	41.9	..	37.5
16	36.3	. ..	41.7	33.2	36.2	..	41.7	33.4
20	34.3	38.1	...	30.7	34.2	38.4	....	31.0
24	32.4	....	.. .	28.4	32.4	..	. .	28.8
30	....	34.6	37.8	...	. .	34.8	38.0	...
40	....	31.1	.		.	31.4		....
45	....	....	33.4	. ..	....	. ..	33.7	.. .

* R. E. Gibson, *J. Am. Chem. Soc.*, **57**, 284 (1935). Table IV, p. 291.

So far the experimental data under consideration have been confined to relatively concentrated solutions ($c \geq 0.5$). Direct compression measurements are not well suited to the investigation of dilute solutions, so other means have been resorted to in an effort to determine accurate compressibilities, at sufficiently high dilutions, to make a significant comparison of the experimental results with the predictions of the interionic attraction

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[142] E. B. Freyer, *J. Am. Chem. Soc.*, **53**, 1313 (1931).

[143] R. E. Gibson, *J. Am. Chem. Soc.*, **56**, 4 (1934); *Ibid.*, **57**, 284 (1935).

[144] R. E. Gibson, *Am. J. Sci.* [5], **35A**, 49 (1938).

theory. As was the case for the other second derivatives of the Debye-Hückel equation, $\bar{J}_2$ and $\bar{E}_2$, we are prepared not to expect close agreement of ϕ_K or $\bar{K}_2$ with the theoretical limiting law at dilutions within the present experimental range. However, it is a matter of some interest to ascertain whether there is any tendency of the experimental curves to converge toward the predicted slopes at the highest accessible dilutions, or at least to group themselves unambiguously with regard to valence type. It will be recalled that the experimental slopes S_K given in Table (8-7-1) show a seven-fold variation among the few 1-1 electrolytes represented.

The most accurate method of determining compressibilities at atmospheric pressure and low concentrations depends upon measurements of the velocity of sound through the solutions. The adiabatic compressibility β_S in bars^{-1}, is related to the velocity of sound, u, in cm. sec.$^{-1}$, through a medium of density, d, by the equation

$$\beta_S = \frac{10^6}{u^2 d} \tag{8-7-29}$$

The isothermal compressibility β can be calculated from β_S by the familiar thermodynamic formula

$$\beta = \beta_S c_p / c_v = \beta_S + 0.02391 \alpha^2 T / c_p d \tag{8-7-30}$$

in which c_p and c_v are the specific heats of the medium, and α is its coefficient of thermal expansion. In aqueous solutions at 25°, the difference between β and β_S is only about 1 per cent, but the effect of this difference on ϕ_K may amount to as much as 10 per cent for a 1-1 electrolyte. In Tables (8-7-3) and (8-7-4), this difference has been taken into account, and isothermal coefficients are recorded. In the following discussion, values of β_S will be used directly. The small correction in dilute solutions does not effect the conclusions to be drawn from the data, and the necessary factors are not known with sufficient accuracy for some of the solutions to justify making the corrections. In the literature dealing with measurements of sound velocity, β_S is usually expressed in cgs units. We have converted these values to reciprocal bars.

The experimental method has steadily developed from the relatively crude experiments of Kundt[145] to the acoustic interferometer technique of Hubbard and Loomis,[146] for which an absolute accuracy of 0.06 per cent is claimed. Relative accuracies of a few thousandths of one per cent are reported by more recent investigators[147–155] who have made use of the im-

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[145] A. Kundt and D. Lehmann, *Pogg. Ann.*, **127**, 497 (1866).

[146] J. C. Hubbard and A. L. Loomis, *Nature*, **120**, 189 (1927); *Phil. Mag.* [7], **5**, 1177 (1928); *Phys. Rev.*, **31**, 158 (1928). See also E. B. Freyer, J. C. Hubbard and D. H. Andrews, *J. Am. Chem. Soc.*, **51**, 759 (1929); E. B. Freyer, *Ibid.*, **53**, 1313 (1931) and E. Klein and W. D. Hershberger, *Phys. Rev.*, **37**, 760 (1931).

[147] L. Bergmann, *Physik. Z.*, **34**, 761 (1933).

[148] A. Szalay, *Ibid.*, **35**, 639 (1934).

portant discovery of Debye and Sears[156] and Lucas and Biquard[157] that ultrasonic waves traversing a liquid set up a periodical inhomogeneity which acts as an optical grating. Szalay[158] was one of the first to apply this technique, but it would be unsafe to draw any conclusions regarding the agreement of his published results with the theoretical valence effect, because he records only the values of $(\beta_0 - \beta)/\beta_0$ at the single concentration, $0.1N$. Reference to equations (8-7-13) to (8-7-15) shows that $(\beta_0 - \beta)$ is composed of two terms, the first of which, $(\beta_0 \phi_V^0 - \phi_K^0)10^{-3}c$, contains no valence factor whatever. Consequently, the ratio of the values of $(\beta_0 - \beta)$ for two salts of different types will not necessarily equal the ratio of the corresponding valence factors $(\Sigma\nu_i z_i^2)^{3/2}$. The valence effect is correctly considered by Gucker,[159] and by Falkenhagen and Bachem.[160,161] Bachem's measurements extend from 0.5 to $0.03N$, and include a considerable variety of salts. His values of ϕ_K, calculated directly from β_s, are linear with $\sqrt{c}$, but the slopes, reproduced in Table (8-7-5), are in no

TABLE (8-7-5). COMPARISON OF EXPERIMENTAL SLOPES, S_K, WITH THE THEORETICAL.*

Electrolyte	$S_K\, 10^4$	$(2/3)\, \mathfrak{S}_{(K)}\, 10^4$[c]
$NaCl$	9.0	6.3
KBr	8.2	6.3
$BaCl_2$	26.8	32.6
$CaCl_2$[a]	26.0	32.6
Na_2CO_3	48.8	32.6
$MgSO_4$	35.2	50.3
$K_3Fe(CN)_6$	58.0	92.4
$K_4Fe(CN)_6$	100.8	199.4
$Ca_2Fe(CN)_6$[b]	139.	*ca.* 260.

* C. Bachem, *Z. Physik.*, **101**, 541 (1936).

[a] F. T. Gucker Jr., *Chem. Rev.*, **13**, 111 (1933), at 30°.

[b] F. T. Gucker Jr., *Idem*, at 0°.

[c] $\mathfrak{S}_{(K)} = \mathfrak{S}^*_{(K)} \sqrt{\nu}\, |z_+z_-|$; $p = 2$.

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[149] R. Wyss, *Helv. Phys. Act.*, **7**, 406 (1934).

[150] C. Bachem and E. Hiedemann, *Z. Physik*, **89**, 502 (1934); *Ibid.*, **91**, 418 (1934); *Ibid.*, **94**, 68 (1935).

[151] E. Hiedemann and N. Siefen, *Ibid.*, **91**, 413 (1934).

[152] E. Hiedemann, H. R. Asbach and K. H. Hoesch, *Ibid.*, **90**, 322 (1934).

[153] C. Bachem, E. Hiedemann and H. R. Asbach, *Ibid.*, **87**, 734 (1934); *Ibid.*, **88**, 395 (1934).

[154] H. Falkenhagen and C. Bachem, *Z. Elektrochem.*, **41**, 570 (1935).

[155] C. Bachem, *Z. Physik*, **101**, 541 (1936).

[156] P. Debye and F. W. Sears, *Proc. Nat. Acad.*, **18**, 409 (1932); P. Debye, *Physik. Z.*, **33**, 849 (1932).

[157] R. Lucas and P. Biquard, *J. Phys. Radium*, **3**, 464 (1932).

[158] A. Szalay, *Physik. Z.*, **35**, 639 (1934).

[159] F. T. Gucker, Jr., *Chem. Rev.*, **13**, 111 (1933).

[160] H. Falkenhagen and C. Bachem, *Z. Elektrochem.*, **41**, 570 (1935).

[161] C. Bachem, *Z. Physik.*, **101**, 541 (1936).

better agreement with theory than the slopes derived by Gucker[162,163] [Table (8-7-1)] from data at higher concentrations. It is true that the halogen salts of the alkali and alkaline-earth metals are in substantial accord with theory throughout the experimental concentration range, but the other electrolytes exhibit large discrepancies at the highest dilutions. The same situation was found at higher concentrations in the study of apparent molal volumes in section (5), and it was only by extending the measurements to very low concentrations, and applying hydrolysis corrections, that ϕ_V for a salt, such as sodium carbonate, gave definite indications of conformity with theory.

The compressibilities of some non-electrolyte solutions appear to possess the same concentration dependence as solutions of electrolytes. Gucker[164] obtained linear plots of ϕ_K against $\sqrt{c}$ from the data of Perman and Urry[165] on urea and sucrose. Bachem's[166] data on sucrose are more nearly linear in c than in $\sqrt{c}$, but two points at the lowest concentrations are inconsistent with either plot. Gibson found that, within the experimental error, the apparent molal compressibility of resorcinol[167] is linear in $\sqrt{c}$. In methanol-water mixtures this relationship definitely does not apply to the methanol but is very closely followed by the water.[167] In solutions of partially ionized electrolytes the results are contradictory. The apparent compressibility of acetic acid[168] in aqueous solutions is linear in $c^{1/2}$ up to about 40 per cent acid, while the values for cadmium iodide[169] in glycol and in methanol are linear in c up to 50 per cent salt.

In the face of the material presented in this and the two preceding sections, it seems evident that the interionic attraction theory in its present form is inadequate to deal with the volume relationships of aqueous solutions within the experimentally accessible concentration range. It is true that, by the development of an elaborate precision technique, partial molal volumes have been shown to agree with the Debye-Hückel theory at high dilutions, but the explanation of Masson's rule and the similar linear relationships obeyed by the expansibility and compressibility seem to require an intimate knowledge concerning the structure of liquids and quite possibly a much more detailed concept of ionic distribution than the ionic atmosphere.

[162] F. T. Gucker, Jr., *J. Am. Chem. Soc.*, **55**, 2709 (1933); *Chem. Rev.*, **13**, 111 (1933).

[163] F. T. Gucker, Jr., and T. R. Rubin, *J. Am. Chem. Soc.*, **57**, 78 (1935).

[164] F. T. Gucker, Jr., *Chem. Rev.*, **13**, 111 (1933). Cf. Ref. 30 and 90.

[165] E. P. Perman and W. D. Urry, *Proc. Roy. Soc. London*, **A126**, 44 (1929).

[166] C. Bachem, *Z. Physik*, **101**, 541 (1936).

[167] R. E. Gibson, *J. Am. Chem. Soc.*, **57**, 1551 (1935).

[168] R. E. Gibson, *J. Am. Chem. Soc.*, **57**, 284 (1935).

[169] R. E. Gibson, *J. Am. Chem. Soc.*, **59**, 1521 (1937).

Chapter (9)

The Calculation of Activity and Osmotic Coefficients from Freezing Points, Boiling Points and Vapor Pressures

All the partial molal quantities except $\Delta\bar{F}$ and $\Delta\bar{S}$† were considered in the preceding chapter. Changes in the partial molal free energy, or activity, of dissolved electrolytes may be directly investigated by measurements of the electromotive forces of suitable cells, or calculated by the Gibbs-Duhem equation (1-4-5) from observed changes in the free energy, or activity, of the solvent. The present chapter is concerned with the most important methods of determining free energy changes of the solvent, and the derived quantities, the activity and osmotic coefficients. The electromotive force method will be considered in Chapter (10).

(1) INTRODUCTION

When the solute is non-volatile, the activity of the solvent can be determined from measurements of the lowering of its vapor pressure caused by the presence of the solute. This method has the advantage of not being limited to any particular temperature, but cannot attain the accuracy of the freezing-pont or boiling-point methods without elaborate experimental precautions. Accurate determinations of vapor pressure lowerings can be made with a sensitive differential manometer,[1,2,3] or calculated from the amount of solvent vapor required to saturate a given volume of inert gas.[4] The development of the static (manometric) method of studying solutions is largely due to Frazer and Lovelace.[5] The dynamic (air-saturation) method is simpler experimentally, and has been used in a large

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† $\Delta\bar{S}$ is too rarely used to require detailed consideration. The variation of $\Delta\bar{F}$ with temperature is almost invariably expressed in terms of $\Delta\bar{H}$ rather than $\Delta\bar{S}$.

[1] C. Dieterici, *Ann. Physik* [3], **50**, 47 (1893); **62**, 616 (1897); **67**, 859 (1899).

[2] Lord Rayleigh, *Z. physik. Chem.*, **37**, 713 (1901); *Trans. Roy. Soc. London*, **196**, 205 (1901).

[3] A. Smits, *Z. physik. Chem.*, **39**, 386 (1906).

[4] J. Walker, *Z. physik. Chem.*, **2**, 602 (1888).

[5] J. C. W. Frazer and B. F. Lovelace, *Z. physik. Chem.*, **89**, 155 (1914); *J. Am. Chem. Soc.*, **36**, 2439 (1914); J. C. W. Frazer, B. F. Lovelace and E. Miller, *Ibid.*, **38**, 515 (1916); J. C. W. Frazer, B. F. Lovelace and T. H. Rogers, *Ibid.*, **42**, 1793 (1920); J. C. W. Frazer, B. F. Lovelace and V. B. Sease, *Ibid.*, **43**, 102 (1921); J. C. W. Frazer. B. F. Lovelace and W. H. Bahlke, *Ibid.*, **45**, 2930 (1923).

number of investigations, among which those of Berkeley,[6] Washburn[7] and Pearce[8] are particularly noteworthy.

The determination of freezing point depression is highly developed. The first investigator to abandon the original supercooling method of Raoult,[9] and Beckmann,[10] appears to have been Roloff,[11] and the use of thermocouples was introduced by Hausrath,[12] and Osaka.[13] More recently, the measurement of freezing point lowering has become a precision method through continuous improvements in technique and in potentiometer design. Some of the more important refinements are due to White,[14] Adams,[15] Randall,[16] Harkins,[17] and Scatchard.[18] The various sources of experimental errors and their magnitudes have been reviewed by these investigators.[19] Certain minor errors inherent in the calculation of activity coefficients from the experimental data will be discussed in this chapter.

The precise determination of boiling point elevations is much more difficult than the measurement of freezing-point depressions because of the phenomenon of super-heating, and the necessity of close pressure control. Furthermore, the molal boiling point elevation is less than the corresponding freezing-point depression, and, therefore, the uncertainties in temperature measurement produce greater errors in the calculated thermodynamic properties. The development of the successful method of overcoming the most serious difficulty, super-heating, began with the work of Cottrell,[20] and of Washburn and Read,[21] and culminated in that of Smith.[22] We need not discuss the many contributions of the intervening twenty years in detail, as they are exhaustively reviewed in a recent monograph,[23] and have progressed on a parallel course with the development of the freezing-point technique.

[6] Earl of Berkeley, E. G. J. Hartley and C. V. Burton, *Phil. Trans. Roy. Soc. London*, **A209**, 177 (1909); *Ibid.*, **A218**, 295 (1919).

[7] E. W. Washburn and E. O. Heuse, *J. Am. Chem. Soc.*, **37**, 309 (1915).

[8] J. N. Pearce and R. D. Snow, *J. Phys. Chem.*, **31**, 231 (1927); J. N. Pearce and A. F. Nelson, *J. Am. Chem. Soc.*, **54**, 3544 (1932); *Ibid.*, **55**, 3075 (1933); J. N. Pearce and L. E. Blackman, *Ibid.*, **57**, 24 (1935); J. N. Pearce and H. C. Eckstrom, *Ibid.*, **59**, 2689 (1937); *J. Phys. Chem.*, **41**, 563 (1936).

[9] F. M. Raoult, *Ann. chim. phys.* [5], **20**, 217 (1880).

[10] E. Beckmann, *Z. physik. Chem.*, **2**, 638 (1888); **7**, 323 (1891).

[11] M. Roloff, *Z. physik. Chem.*, **18**, 572 (1895).

[12] H. Hausrath, *Ann. Physik.* [4], **9**, 522 (1902).

[13] Y. Osaka, *Z. physik. Chem.*, **41**, 560 (1902).

[14] W. P. White, *J. Am. Chem. Soc.*, **36**, 1859, 1876, 2011, 2292, 2313 (1914).

[15] L. H. Adams, *Ibid.*, **37**, 481 (1915).

[16] M. Randall and A. P. Vanselow, *J. Am. Chem. Soc.*, **46**, 2418 (1924).

[17] R. E. Hall and W. D. Harkins, *Ibid.*, **38**, 2658 (1916).

[18] G. Scatchard, P. T. Jones and S. S. Prentiss, *Ibid.*, **54**, 2676 (1932).

[19] See also, C. Robertson and V. K. LaMer, *J. Phys. Chem.*, **35**, 1953 (1931).

[20] F. G. Cottrell, *J. Am. Chem. Soc.*, **41**, 721 (1919).

[21] E. W. Washburn and J. W. Read, *J. Am. Chem. Soc.*, **41**, 729 (1919).

[22] R. P. Smith, *Ibid.*, **61**, 497 (1939).

[23] W. Swietoslawski, "Ebulliometry," Chemical Publishing Co. New York, 1937.

(2) GENERAL EQUATIONS FOR CALCULATING THE ACTIVITY OF THE SOLVENT AND THE OSMOTIC COEFFICIENT FROM FREEZING-POINT DEPRESSIONS

At the temperature T', corresponding to the freezing point of a solution containing m mols of solute per kilogram of solvent, we shall represent the activity of the solid solvent by a'_s, the activity of the liquid solvent by $a_1^{0\prime}$, and the activities of the solvent and solute in the solution by a'_1 and a'_2, respectively. The increase in $\bar{F}_1$ accompanying the isothermal transfer of one mole of solvent from pure liquid to solid is $RT' \ln a'_s/a_1^{0\prime}$, and from pure liquid to solution is $RT' \ln a'_1/a_1^{0\prime}$ [Equations (1-6-1) and (1-6-2)]. Adopting the pure solvent as the common standard state to which all activities are referred, we may write $a_1^{0\prime} = 1$. Accordingly*

$$a'_s = a'_1 \tag{9-2-1}$$

and

$$\left(\frac{a'_2}{m^\nu}\right)_{m\to 0} = 1 \tag{9-2-2}$$

The application of equation (1-7-5) to the transfer of one mol of solvent from pure liquid to solid permits the derivation of a functional relationship between a'_s, and hence a'_1, and the freezing point depression,

$$\vartheta \equiv T_0 - T' \tag{9-2-3}$$

T_0 is the freezing point of the pure solvent. ΔH for this transfer is the difference between the relative molal heat contents of the solid and pure solvent. Since the pure solvent is in the standard state, its relative molal heat content is zero. Therefore,

$$d \ln a'_s = -\frac{L'_s}{RT'^2}dT' = \frac{L'_s\,d\vartheta}{R(T_0 - \vartheta)^2} \tag{9-2-4}$$

where L'_s is the relative molal heat content of the solid at T'. Although temperature is a variable in this equation, we shall persist in the use of the primes as a constant reminder that the calculations are carried out at the freezing point of the solution. L'_s must be expressed as a function of T', or ϑ, before integrating this equation.

If the molal heat capacities of solid and pure liquid solvent are expressed as power series in ϑ, then

$$C_{p_s} - \bar{C}^0_{p_1} = \sum_1^\infty A_{n-1}\vartheta^{n-1} \tag{9-2-5}$$

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* Since the conditions of the measurements require only that solid solvent and a certain solution be in equilibrium at T', it is immaterial that solid and pure liquid solvent cannot exist in equilibrium at any temperature but T_0. It is necessary to employ pure solvent as standard state so that the usual conventions represented by (9-2-1) and (9-2-2) may be retained at all temperatures.

if A_n is the difference between the numerical coefficients of the nth terms in the two series. A_0 is identical with $\Delta\bar{C}_{p_1}$ at T_0. Then, by the application of equation (1-7-7),

$$\int_{T_0}^{T'} dL_s = \int_{T_0}^{T'} (C_{p_s} - \bar{C}^0_{p_1})\,dT = -\int_0^{\vartheta} \sum_1^{\infty} A_{n-1}\vartheta^{n-1}\,d\vartheta \qquad (9\text{-}2\text{-}6)$$

whence*

$$L_s' = L_{s(0)} - \sum_1^{\infty} \frac{1}{n} A_{n-1}\vartheta^n \qquad (9\text{-}2\text{-}7)$$

Substituting this value in equation (9-2-4), replacing a_s' by a_1', and expanding $(T_0 - \vartheta)^{-2}$, we obtain

$$d\ln a_1' = \frac{L_{s(0)}}{RT_0^2} \sum_1^{\infty} nC_n\vartheta^{n-1}\,d\vartheta = \frac{-M_1}{1000\lambda} \sum_1^{\infty} nC_n\vartheta^{n-1}\,d\vartheta \qquad (9\text{-}2\text{-}8)$$

where

$$C_n = T_0^{1-n} - \frac{T_0^{1-n}}{L_{s(0)}} \sum_{s=1}^{s=n} \left(\frac{n-s}{ns}\right) T_0^s A_{s-1} \qquad (9\text{-}2\text{-}9)$$

and

$$\lambda = \frac{-M_1RT_0^2}{1000\,L_{s(0)}} \qquad (9\text{-}2\text{-}10)$$

It can be shown [Equation (9-5-22)] that $\nu\lambda$ is the lowering of the freezing point per mol of solute as m approaches zero. Numerical values† of this important quantity are given in Table (9-2-1) for several solvents. For aqueous solutions, the first four coefficients, calculated by equation (9-2-9) are $C_1 = 1$, $C_2 = 5.2 \times 10^{-4}$, $C_3 = -8.5 \times 10^{-6}$, and $C_4 \backsimeq -5 \times 10^{-8}$.

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* Perhaps the first attempt to generalize equation (9-2-4) (using N_1 for a_1) by combining it with an equation analogous to (9-2-7) was that of J. J. van Laar, [*Kon. Akad. Wetten. Amsterdam, Verslog Wis.-en Natuur.*, **11,** 478 (1902)]. He expressed the variation of L_s as a power series in N_2, and determined the numerical coefficients from the freezing-point data themselves. Later [*Ibid.*, **11,** 576 (1903)], by an elaborate derivation, he expressed this variation in terms of the coefficients of the van der Waals equation of state for a binary mixture [*Z. physik. Chem.*, **8,** 188 (1891)]. E. W. Washburn [*J. Am. Chem. Soc.*, **32,** 653 (1910)] employed a power series in temperature similar to equation (9-2-7), but upon substitution in equation (9-2-4) (N_1 replacing a_1), his expansion included the logarithmic term, and is therefore not directly comparable with ours. His subsequent "general integration", retaining the logarithmic form, unfortunately neglects all coefficients beyond the second in equation (9-2-7). In comparing Washburn's equations with ours, we must remark the errata [*Ibid.*, p. 1636]. The signs of ΔC_p and L must be changed to conform with the present conventions.

† The necessary values of T_0 and $L_{s(0)}$ are taken from the "International Critical Tables," Vol. V, p. 130, McGraw-Hill Book Co., New York, 1931.

TABLE (9-2-1). FREEZING-POINT CONSTANTS OF VARIOUS SOLVENTS AT ONE ATMOSPHERE.

Solvent	t (F.P.)	λ[a]
Ammonia	−75	0.72
Water	0	1.858
Acetic acid	16.6	3.73
Dioxane	11.7	4.63[b]
Benzene	5.4	5.08
Phenol	25.4	6.11
Stannic chloride	−33	13.6
Carbon tetrachloride	−24	29.6
Camphor	178.4	37.7[c]
Cyclohexanol	23.2	41.6[d]

[a] Evaluated by equation (9-2-10).

[b] Determined from freezing points by C. A. Kraus and R. A. Vingee, *J. Am. Chem. Soc.*, **56**, 511 (1934).

[c] Determined from freezing points by M. Frandsen, *Bur Standards J. Research*, **7**, 477 (1931).

[d] Compare E. Schreiner and O. E. Frivold, *Z. physik. Chem.*, **124**, 1 (1926).

In integrated form equation (9-2-8) becomes

$$\ln a_1' = \frac{-M_1}{1000\lambda} \sum_1^{\infty} C_n \vartheta^n \tag{9-2-11}$$

and comparison with equation (1-9-9) leads to the expression

$$\phi' = \frac{1}{\nu m \lambda} \sum_1^{\infty} C_n \vartheta^n \tag{9-2-12}$$

for the osmotic coefficient at the freezing point of the solution. For dilute aqueous solutions the first two terms in the summation yield

$$-\ln a_1' = 9.696 \times 10^{-3}\vartheta + 5.1 \times 10^{-6}\vartheta^2 \tag{9-2-13}$$

and

$$\phi' = \frac{\vartheta}{1.858\,\nu m}(1 + 0.54 \times 10^{-3}\vartheta) \tag{9-2-14}$$

(3) GENERAL EQUATIONS FOR CALCULATING THE ACTIVITY OF THE SOLVENT AND THE OSMOTIC COEFFICIENT FROM BOILING-POINT ELEVATIONS

At the boiling point, T', of a solution containing m mols of solute per kilogram of solvent, the activity of the solvent vapor is represented by a_v', and that of the solvent in solution by a_1'. Choosing the pure liquid solvent as reference state for both phases, a_v' is made equal to a_1' under the vapor pressure, p_0, of the pure solvent at T_0. According to equation (1-7-5), the activity of the solvent is therefore given by

$$d \ln a_1' = -\frac{L_v'\,dT'}{RT'^2} = -\frac{L_v'\,d\theta}{R(T_0 + \theta)^2} \tag{9-3-1}$$

in terms of the heat of vaporization, L'_v, of the solvent, and the elevation in the boiling point

$$\theta \equiv T' - T_0 \tag{9-3-2}$$

If the power series

$$C_{p_v} - C_{p_1} = \sum_1^\infty A^*_{n-1}\theta^{n-1} \tag{9-3-3}$$

represents the difference between the molal heat capacities of vapor and pure solvent under the constant[24] pressure, p_0, equation (1-7-7) requires that

$$L'_v = L_{v(0)} + \sum_1^\infty \frac{1}{n} A^*_{n-1}\theta^n \tag{9-3-4}$$

Substituting this equation in equation (9-3-1), and expanding $(T_0 + \theta)^{-2}$, we obtain

$$d \ln a'_1 = -\frac{L_{v(0)}}{RT_0^2} \sum_1^\infty nC^*_n \theta^{n-1}\, d\theta = -\frac{M_1}{1000\lambda^*} \sum_1^\infty nC^*_n \theta^{n-1}\, d\theta \tag{9-3-5}$$

where

$$C^*_n = (-T_0)^{1-n} + \frac{(-T_0)^{1-n}}{L_{v(0)}} \sum_{s=1}^{s=n} \left(\frac{n-s}{ns}\right) A^*_{s-1}(-T_0)^s \tag{9-3-6}$$

and

$$\lambda^* = +\frac{M_1RT_0^2}{1000\,L_{v(0)}} \tag{9-3-7}$$

Table (9-3-1) contains the molal elevation of the boiling point, λ^*, for common organic solvents at their normal boiling points. Values of λ^* and

TABLE (9-3-1). BOILING-POINT CONSTANTS[a] OF SOLVENTS AT ONE ATMOSPHERE.

Solvent	t (B.P.)	λ^*
Ammonia	−33.4	0.349
Water	100.0	0.513
Methanol	64.7	0.862
Ethanol	78.3	1.214
Sulfur dioxide	−10.1	1.45
Carbon disulfide	46.3	2.41
Benzene	80.2	2.628
Cyclohexanol	116.1	2.78
Acetic acid	118.3	3.15

[a] Calculated by equation (9-3-7) from data in "International Critical Tables," Vol. V, p. 135, McGraw-Hill Book Co., New York, 1931.

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[24] The computation of the temperature dependence of L_v at a fixed pressure, p_0, from the results obtained at the continuously varying saturation pressure, is carefully described by George C. Johnson, Dissertation, Yale University (1940). The results of this computation are given by G. C. Johnson and R. P. Smith, *J. Am. Chem. Soc.*, **63**, 1351 (1941).

the first three coefficients, C_n^*, for water at several pressures are given in Table (9-3-2).

TABLE (9-3-2). BOILING-POINT CONSTANTS[a] FOR WATER AT VARIOUS PRESSURES.

t	p_0	λ^*	C_1^*	$10^5 C_2^*$	$10^8 C_3^*$	$10^{10} C_4^*$
60	149.4	0.39108	1	−347.900	1072.12	−325.2
70	233.7	.41931	1	−339.201	992.13	−284.1
80	355.2	.44905	1	−331.029	915.88	−245.9
90	525.8	.48007	1	−323.132	822.64	−198.2
100	760.0	.51276	1	−316.017	784.24	−184.4

[a] Calculated from the numerical constants used by R. P. Smith, *J. Am. Chem. Soc.*, **61**, 500 (1939); Table I: $T = 273.1 + t$; $R = 8.3126$ int. joules.

Integrating equation (9-3-5) and recalling equation (1-9-9), we obtain

$$\ln a_1' = -\frac{M_1}{1000\lambda^*}\sum_1^\infty C_n^*\theta^n \tag{9-3-8}$$

and

$$\phi' = \frac{1}{\nu m\lambda^*}\sum_1^\infty C_n^*\theta^n \tag{9-3-9}$$

(4) GENERAL EQUATIONS FOR CALCULATING THE ACTIVITY OF THE SOLVENT AND THE OSMOTIC COEFFICIENT FROM VAPOR PRESSURE MEASUREMENTS AND FROM ISOPIESTIC COMPARISONS

Equation (1-2-6) and the definitional equation for the activity of a pure gas at constant temperature, $RT\,d\ln a = dF$, lead to

$$\left(\frac{\partial \ln a_v}{\partial P}\right)_T = \frac{V}{RT} \tag{9-4-1}$$

for the variation of the activity of water vapor with pressure. At equilibrium, the total pressure P is equal to the vapor pressure p. The molal volume is conveniently expressed by

$$V = \frac{RT}{P} - \alpha \tag{9-4-2}$$

where α is, in general, a function of P and T, but reduces to a function of T alone when P is small. Combining the above equations and making use of the proportionality between the activity of the solvent in the vapor phase and in a solution in equilibrium with it, we obtain

$$d\ln a_1 = d\ln P - \frac{\alpha}{RT}dP \tag{9-4-3}$$

Integrating between p and p_0, the vapor pressure of the pure solvent, gives

$$\ln a_1 = \ln p/p_0 - \int_{p_0}^{p}\frac{\alpha dP}{RT} \tag{9-4-4}$$

The osmotic coefficient [Equation (1-9-9)] is therefore given by

$$\phi = -\frac{1000}{\nu m M_1} \ln \frac{p}{p_0} + \frac{1000}{\nu m M_1 RT} \int_{p_0}^{p} \alpha dP \qquad (9\text{-}4\text{-}5)$$

In practice the terms containing α are neglected as being smaller than the experimental errors in vapor pressure measurements at room temperatures.*

If the osmotic coefficient or activity of the solvent is known as a function of concentration in some reference solution, it may be readily determined in other solutions by isopiestic comparison.[25] Samples of a reference solution and of a solution under investigation are weighed into silver dishes, and kept in good thermal contact in a vacuum desiccator. After equilibrium is attained, the vapor pressure of the solvent is the same for all solutions. The equilibrium concentrations are determined by re-weighing the dishes and their contents. The properties of the solution being studied, at the concentration m, are given by

$$a_{1(m)} = a_{1R(m_R)} \qquad (9\text{-}4\text{-}6)$$

and

$$\phi_{(m)} = \frac{\nu_R m_R}{\nu m} \phi_{R(m_R)} \qquad (9\text{-}4\text{-}7)$$

in terms of the corresponding properties of the reference solution at the concentration m_R. Values of ϕ_R for important reference solutions are given in Table (9-4-1). Potassium chloride, or sodium chloride, forms the usual reference solution for comparison with other electrolytes.

(5) CALCULATION OF THE ACTIVITY COEFFICIENT OF THE SOLUTE FROM THE OSMOTIC COEFFICIENT OR ACTIVITY OF THE SOLVENT

This calculation, which involves the integration of equation (1-8-1), has been performed by a variety of analytical and graphical methods. We shall illustrate representative methods by their applications to data from several sources. Rearrangement of equations (1-9-10) and (1-9-11) gives the fundamental relations

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* It is also customary to disregard the fact that the values of a_1 and ϕ calculated from direct manometric measurements are derived under a pressure, p, which varies with the composition of the solution. Considering the magnitude of $\bar{V}_1/RT$, it is clear from equation (1-7-11) that the correction required to bring these values to a constant pressure, p_0, or to one atmosphere, is much less than the experimental error.

[25] D. A. Sinclair, *J. Phys. Chem.*, **37**, 495 (1933); R. A. Robinson and D. A. Sinclair, *J. Am. Chem. Soc.*, **56**, 1830 (1934).

$$d \ln \gamma_{\pm} = -\frac{1000}{\nu m M_1} d \ln a_1 - d \ln m \tag{9-5-1}$$

and

$$d \ln \gamma_{\pm} = -\frac{1}{m} d\{m(1 - \phi)\} \tag{9-5-2}$$

which are to be integrated. Since the values of $\ln a_1$, or ϕ, may be expressed empirically as functions of m, they may be eliminated from these equations.

TABLE (9-4-1). OSMOTIC COEFFICIENTS OF REFERENCE SOLUTIONS AT 25°.

m	NaCl[a]	KCl[a]	H_2SO_4[b]	Sucrose[c]
0.1	0.9319	0.9257	0.6800	1.0073
.2	.9246	.9129	.6680	1.0151
.3	.9212	.9062	.6672	1.0234
.5	.9217	.9002	.6748	1.0410
.7	.9265	.8979	.6888	1.0596
1.0	.9378	.8994	.7195	1.0897
1.5	.9594	.9056	.7823	1.1415
2.0	.9862	.9148	.8488	1.1929
2.5	1.0170	.9274	.9185	1.2436
3.0	1.0498	.9409	.9960	1.2923
3.5	1.0847	.9552	1.0725	1.3379
4.0	1.1219	.9698	1.1523	1.3805
4.5	......	.9854	1.2298	1.4186
5.0	......	.9958*	1.3041	1.4541
5.5	......	.....	1.3766	1.4881
6.0	......	.....	1.4485	1.5216
7.0	......	.....	1.5817	......
8.0	......	..	1.6998	..

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[a] These values were kindly furnished by Dr. R A. Robinson. They have been adjusted to conform as closely as possible with the best electromotive force and vapor pressure determinations of the activity coefficients of the chlorides and bromides of sodium and potassium (ten independent series), and with the most recently determined isopiestic ratios The values are given to four places as an aid to drawing consistent smooth curves The last place is not physically significant.

[b] Calculated from the values in columns (2) and (3) and the isopiestic ratios of G. Scatchard, W J. Hamer and S. E. Wood, *J. Am. Chem Soc*, **60**, 3061 (1938); H Scheffer, A. A. Janis and J. B. Ferguson, *Canadian J. Research*, **17B**, 338 (1939); and R. A. Robinson, *Trans Faraday Soc*, **35**, 1229 (1939). Above 3*M*, the values of ϕ are based upon the data of S Shankman and A R. Gordon, *J. Am Chem Soc*, **61**, 2370 (1939).

[c] Calculated from the values in column (3) and the isopiestic ratios of G Scatchard, W J Hamer and S. E. Wood (*loc. cit.*); and R. A. Robinson and D. A. Sinclair, *J. Am Chem Soc*, **56**, 1830 (1934); and recent unpublished results of R. A. Robinson.

* $m = 4.81$.

Unfortunately, the absolute accuracy with which $\ln \gamma_{\pm}$ is determined by this procedure is strongly influenced by the form of these functions, if the lower limit of the integration is $m = 0$. The Debye-Hückel equation supplies a logical basis for the selection of proper functions by which the properties of solutions may be expressed from infinite dilution up to the lowest experimental concentrations.

Combination of equations (5-2-8) and (1-8-13) leads to

$$\log \gamma_{\pm} = -\frac{\mathfrak{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} - \log\left(1 + \frac{\nu m M_1}{1000}\right) \tag{9-5-3}$$

Since the present use of this equation is confined to dilute solutions, the last term may be neglected. Accordingly, if we let $x = A' \sqrt{c}$, and $k' = 2.303\ \mathcal{S}_{(f)}/A'$, then

$$d \ln \gamma_{\pm} = -k'(1 + x)^{-2}\, dx \tag{9-5-4}$$

Substitution of this equation into (9-5-2) gives

$$1 - \phi = \frac{k'}{m} \int_0^x m \frac{dx}{(1 + x)^2} = \frac{k'}{x^2} \int_0^x x^2 \frac{dx}{(1 + x)^2} \tag{9-5-5}$$

since m is proportional to x^2 at high dilution.

Integration and rearrangement yield

$$1 - \phi = \frac{k'x}{3}\left\{\frac{3}{x^3}\left(1 + x - 2 \ln (1 + x) - \frac{1}{1 + x}\right)\right\} \equiv \frac{k'x\sigma}{3} \tag{9-5-6}$$

The function σ defined by this equation may be expressed by

$$\sigma = \sum_{n=1}^{\infty} \frac{3n}{n + 2} (-x)^{n-1} = \sum_{n=1}^{\infty} \frac{3n}{n + 2} (-A' \sqrt{c})^{n-1} \tag{9-5-7}$$

when $x \leq 1$. Substituting the value of k' into (9-5-6), we obtain

$$1 - \phi = 0.7676 \mathcal{S}_{(f)} \sigma \sqrt{c} \tag{9-5-8}$$

Any expression which is used to represent experimental values of $1 - \phi$ as a function of composition should reduce to this equation at high dilutions. Numerical values of $\mathcal{S}_{(f)}$ and A' are given in Table (5-2-1) and values of σ are given in Table (9-5-1).

Since the above equation is restricted to dilute solutions, we may write $\sqrt{c} = \sqrt{md_0}$, and define

$$\mathcal{S}_{m(f)} \equiv \mathcal{S}_{(f)} \sqrt{d_0} \tag{9-5-9}$$

$$A'_m \equiv A' \sqrt{d_0} \tag{9-5-10}$$

and

$$\sigma_m = \sum_{n=1}^{\infty} \frac{3n}{n + 2} (-A'_m \sqrt{m})^{n-1} \tag{9-5-11}$$

Accordingly,

$$1 - \phi = 0.7676 \mathcal{S}_{m(f)} \sigma_m \sqrt{m} \tag{9-5-12}$$

This convenient expression reduces to (9-5-8) in the limit, and differs from it by a negligible amount at moderate dilutions.

Smith[26] calculated ϕ' at the boiling points of solutions of sodium chloride, and used the expression

$$1 - \phi' = 0.7676 \mathcal{S}_{m(f)} \sigma_m \sqrt{m} - 0.5Bm \tag{9-5-12a}$$

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[26] R. P. Smith, *J. Am. Chem. Soc.*, **61**, 500 (1939).

The term $0.5Bm$ is included to represent the data at high concentrations [Compare equation (3-8-2)]. Numerical values of A'_m and B can be chosen so that the deviation

$$\delta\phi' = -(1 - \phi') + 0.7676\mathcal{S}_{m(f)}\sigma_m\sqrt{m} - 0.5Bm \qquad (9\text{-}5\text{-}13)$$

is not large at any concentration. Comparison of equations (9-5-13) and (9-5-12) shows that $\delta\phi'$ must become zero at infinite dilution. Combining equations (9-5-13) with (9-5-2) and integrating, we obtain

$$\ln \gamma'_\pm = -\frac{2.303\mathcal{S}_{m(f)}\sqrt{m}}{1 + A'_m\sqrt{m}} + Bm + \int_0^m \frac{\delta\phi'}{m}\,dm + \delta\phi' \qquad (9\text{-}5\text{-}14)$$

TABLE (9-5-1)* THE FUNCTION σ. SEE TABLE (B-4-1)

$A'\sqrt{c}$	σ	$A'\sqrt{c}$	σ	$A'\sqrt{c}$	σ
0.00	1.0000	0.40	0.5986	0.80	0.4036
.05	.9293	.45	.5668	.85	.3863
.10	.8662	.50	.5377	.90	.3703
.15	.8097	.55	.5108	.95	.3552
.20	.7588	.60	.4860	1.00	.3411
.25	.7129	.65	.4631	1.05	.3279
.30	.6712	.70	.4418	1.10	.3154
.35	.6332	.75	.4220	1.15	.3037

* The column heading may be replaced by $A'_m\sqrt{m}$ and σ_m for use on the m-scale.

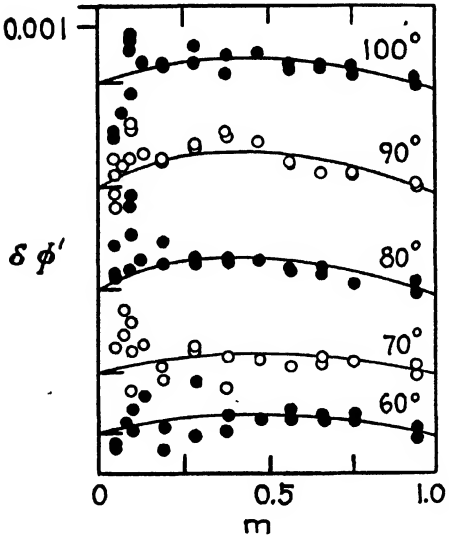

Fig. (9-5-1)
The deviation function, $\delta\phi'$, for sodium chloride in water at various temperatures. Diameter of circles equals 0.0005

The two terms containing $\delta\phi'$ are evaluated graphically. From Fig. (9-5-1) which contains Smith's values of $\delta\phi'$ for sodium chloride solutions

(T_0 = 60, 70, 80, 90 and 100°), it appears that the maximum contribution of these terms to $\gamma'_{\pm}$ is only 2 or 3 per cent.

It should be noted that the quantity designated $\gamma'_{\pm}$ is not a true activity coefficient because equation (9-5-2) was used under non-isothermal conditions. It is converted to a true activity coefficient by correcting all values of ϕ' to some standard temperature, T'', before integrating equation (9-5-2). Writing equation (1-7-5) in the integrated forms

$$\log a''_1 = \log a'_1 + X \qquad (9\text{-}5\text{-}15)$$

and

$$\phi'' = \phi' - \frac{2{,}303X}{\nu m M_1} \qquad (9\text{-}5\text{-}16)$$

where

$$X \equiv -\int_{T'}^{T''} \frac{\bar{L}_1 dT}{2.303RT^2} \qquad (9\text{-}5\text{-}17)$$

we obtain the expression

$$\log \gamma'' = \log \gamma' - \frac{1000}{\nu M_1} \int_0^X \left(\frac{1}{m}\right) dX \qquad (9\text{-}5\text{-}18)$$

used by Lewis and Randall.[27]

The calculation of activity coefficients from equations (9-5-14) and (9-5-18) is largely analytical, because the terms in $\delta\phi'$ and dX contribute very little to the final result. Although a formal and completely analytical method of calculating osmotic and activity coefficient is described by Scatchard,[28] it is more usual to emphasize graphical procedures. Integrating equation (9-5-2), the activity coefficient is given by

$$\ln \gamma_{\pm} = -(1 - \phi) - 2 \int_0^m \left(\frac{1 - \phi}{m^{1/2}}\right) dm^{1/2} \qquad (9\text{-}5\text{-}19)$$

when dm is replaced by $2m^{1/2}dm^{1/2}$. A plot of $(1 - \phi)/m^{1/2}$ against $m^{1/2}$ is sufficient to evaluate both terms in ϕ. The value of $(1 - \phi)/m^{1/2}$ is so sensitive to experimental errors in dilute solutions that some form of the Debye-Hückel equation must be used to extend the plot from about 0.1M to infinite dilution. Equation (9-5-12) leads to

$$(1 - \phi)/m^{1/2} = 0.7676\mathcal{S}_{m(f)}\sigma_m \qquad (9\text{-}5\text{-}20)$$

in dilute solutions. In using this equation to complete the plot of $(1 - \phi)/m^{1/2}$ against $m^{1/2}$, it is necessary to know A'_m in order to calculate

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[27] G. N. Lewis and M. Randall, "Thermodynamics," p. 350, McGraw-Hill Book Co., New York, 1923. See also M. Randall and L. E. Young, *J. Am. Chem. Soc.*, **50**, 989 (1928).

[28] G. Scatchard, *Chem. Rev.*, **8**, 321 (1931); G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **56**, 1486 (1934).

σ_m. Since $\mathring{a}$ is usually unknown, a value of A'_m is selected, by trial, which makes equation (9-5-20) fit the experimental data at the lowest concentrations. The evaluation of A'_m is illustrated in connection with the j-function [Equations (9-5-21)]. Equations (9-5-19) and (9-5-20) are usually employed in calculating activity coefficients from osmotic coefficients derived from vapor pressures, or isopiestic comparisons. Tables (12-3-1A) and (13-1-2A) contain values of $\gamma_\pm$ obtained in this manner.

In the estimation of activity coefficients from freezing-point depression, the graphical integration of the Gibbs-Duhem equation commonly involves the variable*

$$j \equiv 1 - \frac{\vartheta}{\nu m \lambda} \tag{9-5-21}$$

of Lewis and Randall.[29] Combining equations (9-2-8), (9-5-1) and (9-5-18), we obtain

$$d \log \gamma''_\pm = 0.4343 \frac{d\vartheta}{\nu m \lambda} \sum_1^\infty n C_n \vartheta^{n-1} - d \log m - \frac{1000}{\nu M_1} \frac{dX}{m} \tag{9-5-22}$$

Since differentiation of equation (9-5-21) gives

$$\frac{d\vartheta}{\nu m \lambda} = (1 - j)\, d \ln m - dj \tag{9-5-23}$$

and the coefficient C_1 is unity, equation (9-5-22) may be written

$$\begin{aligned} d \log \gamma''_\pm = {} & -0.4343 dj - j d \log m \\ & + \frac{0.4343 d\vartheta}{\nu m \lambda} \sum_2^\infty n C_n \vartheta^{n-1} - \frac{1000}{\nu M_1} \frac{dX}{m} \end{aligned} \tag{9-5-24}$$

whence

$$\begin{aligned} \log \gamma''_\pm = {} & -0.4343 j - 0.8686 \int_0^m \left(\frac{j}{m^{1/2}}\right) d\sqrt{m} \\ & + \frac{0.4343}{\nu \lambda} \int_0^\vartheta \frac{1}{m} \sum_2^\infty n C_n \vartheta^{n-1}\, d\vartheta - \frac{1000}{\nu M_1} \int_0^X \frac{dX}{m} \end{aligned} \tag{9-5-25}$$

Calorimetric data are generally not available for evaluating C_n beyond C_1, or C_2. For water the data justify the use of C_3 when accurate freezing-point measurements are considered at moderate concentrations.[30] For

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* The quantity $j^* \equiv 1 - \theta/\nu m \lambda^*$ may be applied to boiling-point calculations in an analogous manner.

[29] G. N. Lewis and M. Randall, "Thermodynamics," p. 347, McGraw-Hill Book Co., New York, 1923.

[30] T. F. Young [*Chem. Rev.*, **13**, 103 (1933)] has shown that the effect of the various terms upon the activity coefficient of 5.2*M* sodium chloride is about 0.58 per cent for the C_3 term, 0.06 per cent for C_4, and 0.006 per cent for C_5. These effects decrease rapidly with dilution.

most purposes the summation is neglected beyond C_2, and equation (9-5-25) takes the approximate but more familiar form

$$\log \gamma''_{\pm} = -0.4343j - 0.8686 \int_0^m \left(\frac{j}{m^{1/2}}\right) d\sqrt{m} + 0.8686C_2 \int_0^{\vartheta} (1 - j)\, d\vartheta - \frac{1000}{\nu M_1} \int_0^x \frac{dX}{m} \qquad (9\text{-}5\text{-}26)$$

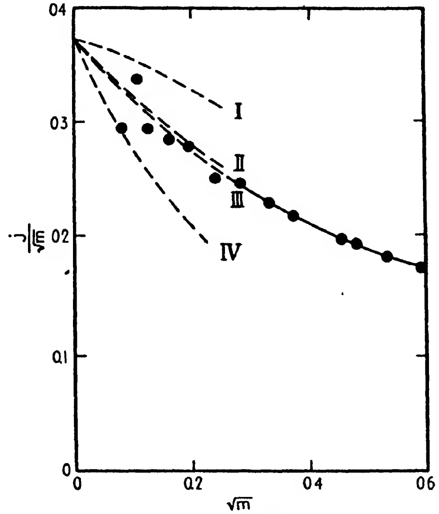

Fig. (9-5-2). Extrapolation of $j/m^{1/2}$ for potassium chloride solutions. Broken curves I, II, and IV by equation (9-5-29) with å = 2, 3.6, 7, respectively. Broken curve III by equation (9-5-28) with å = 3.6

In dilute solutions, where the right-hand member of equation (9-5-24) may be represented by the first two terms, $d \log \gamma''_{\pm}$ can be eliminated by (9-5-4), and we obtain

$$j = 0.7676\mathfrak{S}_{(f)}\sigma\sqrt{c} \qquad (9\text{-}5\text{-}27)$$

and

$$j = 0.7676\mathfrak{S}_{m(f)}\sigma_m\sqrt{m} \qquad (9\text{-}5\text{-}28)$$

by the procedure used to derive equations (9-5-8) and (9-5-12). Obviously, $j = 1 - \phi$ within the concentration range covered by these equations.

The use of these equations and the selection of a proper value of A'_m from which to calculate σ_m are illustrated in Figure (9-5-2). The experimental[31] values of $j/m^{1/2}$ for aqueous potassium chloride solutions are plotted against $m^{1/2}$. The solid curve representing these values can be located with high accuracy down to concentrations as low as $m^{1/2} = 0.3$,

[31] G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, 55, 4355 (1933).

and with reasonable certainty down to $m^{1/2} = 0.2$. Below the latter concentration the experimental results are of little value in determining the shape of the curve which must bridge the gap between $m^{1/2} = 0.2$ and infinite dilution. This portion of the curve, represented by a broken line, was calculated by equation (9-5-28) for a value of A'_m corresponding to $\mathring{a} = 3.6$. In selecting the proper value of $\mathring{a}$, or A'_m, the experimental value of $j/m^{1/2}$, read from the plot at about $m^{1/2} = 0.2$, can be used to calculate $A'_m m^{1/2}$, and hence A'_m, from equations (9-5-11) and (9-5-28) by successive approximations. Spencer[32] published a table of theoretical values of $j/m^{1/2}$ and $m^{1/2}$ in aqueous solutions corresponding to various values of $\mathring{a}$ (1 to 8 Å). The equation he used was

$$j = 0.3738\sigma_m\sqrt{m} - 0.1640(z^2/\mathring{a})^3 10^3[X_3(x) - 6Y_3(x)] - 0.0780(z^2/\mathring{a})^5 10^5[X_5(x) - 10Y_5(x)] \qquad (9\text{-}5\text{-}29)$$

which includes the contributions of the extended terms of equation (3-6-4) for symmetrical electrolytes. The three dashed curves in Figure (9-5-2) were constructed from Spencer's values corresponding to $\mathring{a} = 2$, 3.6, and 7 Å, respectively. The effect of the extended terms in aqueous potassium chloride solutions can be seen in the figure, where the curves based on equations (9-5-29) and (9-5-28) are clearly distinguishable. It is apparent from the figure that, if equation (9-5-29) had been used to extrapolate the experimental curve, we would have chosen a value of $\mathring{a}$ greater than 3.6. The difference between the values of $\mathring{a}$ (actually about 0.1 Å) derived from these two equations is not physically important, because both equations are employed at such high concentrations ($m^{1/2} = 0.2$) that the $\mathring{a}$ parameter has been forced to absorb the effect of writing $c \doteq d_0 m$, and the effect of neglecting the last two terms in equation (9-5-25). To this extent, the extrapolation in Figure (9-5-2) is empirical except for the theoretical value of the intercept. Scatchard[33] has recently emphasized the empirical aspects of this calculation by employing the function

$$j = \frac{0.3738m^{1/2}}{1 + Bm^{1/2}} + Cm \qquad (9\text{-}5\text{-}30)$$

for 1-1 electrolytes which, although reducing to equation (9-5-28) at infinite dilution, does not agree with the Debye-Hückel theory at higher concentrations. This function has the merit, however, of conveniently approximating the freezing-point data up to $1M$. When used in conjunction with a plot of the deviation, δj, of values calculated by (9-5-30) from the experimental values, it puts a minimum of burden upon theory.

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[32] H. M. Spencer, *J. Am. Chem. Soc.*, **54**, 4490 (1932).

[33] G. Scatchard, P. T. Jones and S. S. Prentiss, *J. Am. Chem. Soc.*, **54**, 2676, 2690 (1932).

This procedure has certain advantages. It is usually a simple matter to assign values to the empirical constants, B and C, such that the deviation

$$\delta j = j - \frac{0.3738m^{1/2}}{1 + Bm^{1/2}} - Cm \tag{9-5-31}$$

is less than 0.01, or 0.02. A plot of δj against m, or $m^{1/2}$, therefore affords a very sensitive and compact means of smoothing the data, and obtaining representative j-values for use in evaluating the integrals of equation (9-5-25), or (9-5-26).

Figure (9-5-3) was constructed from the data of Scatchard and Prentiss[34] on potassium chloride. The solid curve was considered by them to represent their data, shown as circles. For comparison, the j-values, obtained by Spencer[35] from a composite plot of earlier data, have been used to construct the broken curve. The agreement between the two curves is nearly everywhere better than ±0.001 in j, which is quite satisfactory for data derived from different sources.

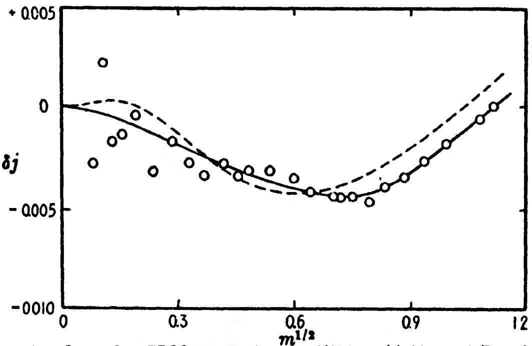

Fig. (9-5-3). δj values for KCl; $\delta j = j - (0.3738\, m^{1/2})/(1 + 1.7\, m^{1/2}) + 0.0149\, m$; Solid line used by Scatchard to obtain smoothed j-values from experimental data; broken line from Spencer's computation of earlier data

From this and similar figures, the extensive measurements of Scatchard and Prentiss have been used to calculate the values of $-\log \gamma'_{\pm}$ for numerous 1-1 electrolytes. These are given in Table (9-5-1A), and will be referred to in the general discussion in Chapter (12).

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[34] G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **55**, 4355 (1933).

[35] H. M. Spencer, *J. Am. Chem. Soc.*, **54**, 4490 (1932).

Chapter (10)

The Thermodynamics of Galvanic Cells

This chapter will begin with the elementary principles of the electromotive force method. The symbols for the representation of cells and the conventions regarding the signs of the electromotive force and standard electrode potentials will be stated. The thermodynamics of cells, without and with liquid junctions, in its relation to solution investigations will be developed. The hypothetical liquid-junction potential, the concept of electrical potential at phase boundaries, and the problem of individual ionic chemical potentials and activities will receive close attention. Finally, limitations of the use of cells with liquid junctions and a suitable method of eliminating liquid-junction potentials will be discussed.

(1) GENERAL THERMODYNAMIC PROPERTIES OF CELLS. DEFINITION OF THE STANDARD ELECTRODE POTENTIAL

It has been shown that, at constant pressure, temperature and composition, the free energy change is related to the reversible electrical work according to equation (1-5-1), or

$$(dF)_{P,T,n} \mp (\psi' - \psi'')de \qquad (1\text{-}5\text{-}1)$$

The mechanism which fulfills the conditions required by this equation is a galvanic cell, consisting of two reversible electrodes connected by a solution of appropriate electrolytes. The difference, $(\psi' - \psi'')$, is the electrical potential between two pieces of identical metal connected to the electrodes, and de is the charge transferred, which corresponds to a change in free energy dF. Equation (1-5-1) is valid for reversible changes only, a condition rigorously fulfilled if:

(1) No changes take place within the cell without the passage of the current.

(2) Every change which actually takes place during the passage of the current may be reversed by reversing the direction of the current.

Furthermore a cell is valuable for thermodynamic investigations only when the net result of all the chemical changes which take place is known. When all these conditions are fulfilled, we are in a position to measure the reversible electrical work, $(\psi' - \psi'')de$, and hence the free energy change, dF, corresponding to a known reaction. If a cell with an electromotive force, $\pm\mathbf{E}$, is exactly balanced against an external electromotive force, so that no charging or discharging of the cell is taking place, then $\pm\mathbf{E}$

is the electromotive force of the cell when the entire system is in equilibrium. If we imagine the cell to discharge against this electromotive force until a quantity of electricity, de, has passed through, the cell process will have taken place reversibly, performing the reversible electrical work, $\pm\mathbf{E}de$. The difference in potential, $(\psi' - \psi'')$, is equal to $+\mathbf{E}$ or $-\mathbf{E}$, depending on the convention adopted concerning the sign of the electromotive force. Equation (1-5-1) now becomes

$$(dF)_{P,T,n} = \pm\mathbf{E}de \tag{10-1-1}$$

In dealing with chemical reactions, we are interested in changes of molar quantities of the substances and, therefore, according to Faraday's laws, are concerned with the passage of a Faraday, **F**, of electricity, or a simple multiple of a Faraday, **NF**, through the cell. Since dF is proportional to de, by equation (10-1-1),

$$(-\Delta F)_{P,T,n} = \mathbf{NFE} \tag{10-1-2}$$

if **NF** coulombs pass through the cell. In writing this equation, we have now adopted the convention of Lewis and Randall that a positive **E** corresponds to a decrease in free energy.

The total free energy change of any chemical reaction in terms of the activities of the reactants and reaction products is given by equation (1-10-3). If we write $\Pi'a$ and Πa for the appropriate activity products of the resultants and reactants, respectively, and $\Pi'\gamma$, $\Pi\gamma$, $\Pi'm$, and Πm for the corresponding activity coefficients and concentration products, equation (1-10-3) may be written

$$\Delta F - \Delta F^0 = RT \ln \frac{\Pi'a}{\Pi a} = RT \ln \frac{\Pi'\gamma\Pi'm}{\Pi\gamma\Pi m} \tag{10-1-3}$$

ΔF is the free energy of the reaction in general, and ΔF^0 is the free energy change when the activities of all reacting and resulting species are unity.

If the free energy of reaction is measured by means of a cell, then this equation may be combined with equation (10-1-2) to yield

$$\mathbf{E} = \mathbf{E}^0 - \frac{RT}{\mathbf{NF}} \ln \frac{\Pi'a}{\Pi a} = \mathbf{E}^0 - \frac{RT}{\mathbf{NF}} \ln \frac{\Pi'\gamma\Pi'm}{\Pi\gamma\Pi m} \tag{10-1-4}$$

where

$$\mathbf{E}^0 = -\Delta F^0/\mathbf{NF} \tag{10-1-4a}$$

$\mathbf{E}^0$ is termed the standard electromotive force of the cell. Obviously, **E** equals $\mathbf{E}^0$ when the activities of all constituents are equal to unity. Since the composition of the solid components (or pure liquid phase) of the cell are ordinarily independent of the concentration of the electrolyte solution, it is customary to assign the value unity to the activities of such components, and consider them in their standard states at all temperatures under a pressure of one atmosphere.* The standard state for the components of liquid solutions is ordinarily selected so that $m = a$, or $\gamma = 1$, for each solute at infinite dilution. Since partial pressures are proportional to concentrations in gaseous mixtures, and the perfect gas law may be applied for practical purposes over small pressure changes in the neighborhood of one atmosphere, the activity of a gaseous component will be written equal to its partial pressure. Therefore, a gas is in its standard state at any temperature when its partial pressure is one atmosphere.† On the basis of this selection of standard states it will be seen, by rearranging equation (10-1-4) to the form

$$\mathbf{E} + \frac{RT}{\mathbf{NF}} \ln \frac{\Pi' m}{\Pi m} = \mathbf{E}^0 - \frac{RT}{\mathbf{NF}} \ln \frac{\Pi' \gamma}{\Pi \gamma} \qquad (10\text{-}1\text{-}5)$$

that $\mathbf{E}^0$ is numerically equal to the sum of the terms on the left-hand side of the equation at infinite dilution of the electrolyte solution, for under this condition the term in γ is zero. Various methods of evaluating the important quantity,

$$\left[\mathbf{E} + \frac{RT}{\mathbf{NF}} \ln \frac{\Pi' m}{\Pi m}\right]_{(m \to 0)} = \mathbf{E}^0 \qquad (10\text{-}1\text{-}5a)$$

will be discussed in Section (3) and in later chapters.

(2) CONVENTIONS REGARDING THE REPRESENTATION OF CELLS AND ELECTRODES, AND THE SIGNS OF THEIR ELECTROMOTIVE FORCES

Since most American chemists are accustomed to the system of conventions adopted by Lewis and Randall[1] for writing electrode and cell reactions, and the signs of their corresponding electromotive forces, their system will be adhered to. Regarding the schematic representation of cells by chemical symbols, etc., some variations will be introduced, and several additional conventions are required to describe the more complex cells recently appearing in the literature. Conventions of limited use will be announced at the time of their introduction, but those of general application will now be summarized.

(a) Contact between separate phases (electrode and solution) is usually indicated by a vertical line, but, in the representation of individual elec-

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* Because of the small molal volumes of solids (and liquids), they may be considered to have unit activity at any pressure of the order of one atmosphere, [Equation (1-7-11)]. For gases, the pressure must be designated.

† These conventional standard states will always be implied except in a few special studies where the proper alternatives will be specifically mentioned.

[1] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923.

trodes,* a hyphen is used between the phases. Thus, Pt-Ag-AgCl | MCl(m) represents a silver-silver chloride electrode in contact with a chloride solution.

(b) The physical nature of a phase, when not self-evident, is indicated by (s), (l), or (g) for solid, liquid, or gas. The symbols (m), (c), etc., expressing concentration, indicate liquid solutions. Solid solutions are seldom used for electrodes except when mercury is a component and then two saturated solid solutions are usually present. In such cases, the expression "two-phase amalgam" is used. Thus, Pt-Pb-Hg(2-phase)-$PbSO_4$(m) | represents an electrode composed of saturated solutions of Hg in Pb, and of Pb in Hg.

(c) The partial pressure of a gas is indicated by (p), or (1 atm.), etc. The omission of a specific designation of pressure implies a partial pressure of one atmosphere.

(d) The concentration of solutes will usually be expressed in mols per kilogram of solvents, and represented by (m). When several solutes are present in solution, their concentrations will be differentiated as (m_1), (m_2), etc., or sometimes m_{KCl}, m_{H^+}, etc. Co-solutes are separated by commas to indicate that they are present in the same phase.

(e) Unless otherwise specified, the solvent is water. When mixed solvents are employed, their composition will usually be expressed in weight percentages, X and Y. X will represent the non-aqueous component if water is present.

(f) A positive sign over an electrode of a cell indicates that negative electricity is transferred from the electrode to the electrolyte during the spontaneous operation of the cell in its standard state. The positive sign will frequently be omitted, because cells written in general terms without specifying the numerical value of $\mathbf{E}^0$, or limiting the concentrations in any way, cannot be given a definite polarity.

(g) The electromotive force, **E**, will be taken as positive when the spontaneous operation of the cell involves the transfer of negative electricity from right to left within the cell as written.

Most of the conventions so far enumerated can be illustrated by the cell,

$$\mathrm{H_2(1\ atm.)} \mid \mathrm{HA}(m_0), \mathrm{NaA}(m_1), \mathrm{NaCl}(m_2), \mathrm{CH_3OH}(X), \mathrm{H_2O}(Y) \mid \overset{+}{\mathrm{AgCl\text{-}Ag}}$$

containing sodium chloride and some weak acid, HA, and its sodium salt. The solvent is X per cent methanol, and Y per cent water. The silver-silver chloride electrode is indicated as positive. Thus, by (10-1-4),

$$\mathbf{E} = \mathbf{E}^0 - \frac{RT}{\mathbf{NF}} \ln a_{\text{H}^+} a_{\text{Cl}^-}$$

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* In representing these electrodes, Pt- is customarily omitted. Thus, Ag-AgCl | MCl(m); Pb-Hg(2-phase)-$PbSO_4$ | etc. Furthermore, amalgam electrodes are often written, M-Hg(sat.) and M_xHg, to differentiate between a 2-phase and single-phase amalgam.

$\mathbf{E}^0$ would be the electromotive force of this cell if we could make $a_{\mathrm{H}}a_{\mathrm{Cl}} = 1$. As we shall see later, $\mathbf{E}^0$ is also the electromotive force of the cell,

$$\mathrm{H_2(1\ atm.)} \mid \mathrm{HCl}(m),\ \mathrm{CH_3OH}(X),\ \mathrm{H_2O}(Y) \mid \mathrm{AgCl\text{-}Ag}$$

at the same temperature when $a_{\mathrm{H}}a_{\mathrm{Cl}} = 1$.

(h) All single electrodes will be written with the electrolyte on the right. Thus, for the hydrogen electrode,

$$\mathrm{H_2}(p\ \mathrm{atm.}) \mid \mathrm{H^+}(m_{\mathrm{H^+}})$$

or, more simply

$$\mathrm{H_2}(p) \mid \mathrm{H^+}(m)$$

the electromotive force will be positive when negative electricity is transferred from right to left through the electrode. The operation of the above electrode corresponds to the reaction,

$$\tfrac{1}{2}\mathrm{H_2}(p) = \mathrm{H^+}(m) + \ominus \qquad (10\text{-}2\text{-}1)$$

where the symbol, $\ominus$, represents one Faraday of negative electricity. By always writing electrode reactions so that $\ominus$ appears as a product of the reaction, the general equation for the potential, π, of a single electrode is given by

$$\pi = \pi^0 - \frac{RT}{\mathbf{NF}} \ln \frac{\Pi' a}{\Pi a} \qquad (10\text{-}2\text{-}2)$$

and for the electrode just considered, this becomes

$$\pi = \pi^0 - \frac{RT}{\mathbf{F}} \ln \frac{a_{\mathrm{H^+}}}{p_{\mathrm{H}}^{1/2}} \qquad (10\text{-}2\text{-}3)$$

since $\mathbf{N} = 1$.

(i) The standard (or normal) electrode potential, π^0, is the potential when all the activities involved in the electrode reaction are unity. Since single electrode potentials are incapable of independent measurement, it is customary to compute their values relative to $\pi^0_{\mathrm{H}} = 0$.

(j) In combining any two single electrodes to form a galvanic cell, the electromotive force of the cell is the algebraic difference between the potentials of the electrodes. The electrode potential of the right-hand electrode is subtracted from that on the left. Thus, if we combine the electrode,

$$\mathrm{Ag\text{-}AgCl} \mid \mathrm{Cl^-}(m)$$

with the hydrogen electrode, we may write

$$\mathrm{H_2}(p) \mid \mathrm{HCl}(m) \mid \mathrm{AgCl\text{-}Ag}, \qquad \mathrm{I}$$

The electrode reactions are

$$\tfrac{1}{2}H_2(p) = H^+(m) + \ominus \tag{10-2-4}$$

and

$$Ag + Cl^-(m) = AgCl(s) + \ominus \tag{10-2-5}$$

The corresponding potentials are

$$\pi_{H(p)} = 0 - \frac{RT}{F} \ln \frac{a_H}{p^{1/2}} \tag{10-2-6}$$

and

$$\pi_{AgCl} = \overset{0}{\pi}_{AgCl} - \frac{RT}{F} \ln \frac{1}{a_{Cl}} \tag{10-2-7}$$

The cell reaction and electromotive force are

$$\tfrac{1}{2}H_2(p) + AgCl(s) \rightarrow Ag + HCl(m) \tag{10-2-8}$$

and

$$\pi_{H(p)} - \pi_{AgCl} = 0 - \overset{0}{\pi}_{AgCl} - \frac{RT}{F} \ln \frac{a_H a_{Cl}}{p^{1/2}} \tag{10-2-9}$$

or

$$E_{I(p)} = E_I^0 - \frac{RT}{F} \ln \frac{a_H a_{Cl}}{p^{1/2}} \tag{10-2-10}$$

for cell I as written. Under ordinary conditions, the spontaneous tendency for negative electricity to pass through this cell is from right to left, and therefore E_I and E_I^0 are positive. If we had chosen to combine the same two electrodes in the order,

$$Ag\text{-}AgCl \mid HCl(m) \mid H_2(p) \qquad \text{II}$$

it would be necessary to write

$$HCl(m) + Ag \rightarrow AgCl(s) + \tfrac{1}{2}H_2(p) \tag{10-2-11}$$

and

$$E_{II(p)} = E_{II}^0 + \frac{RT}{F} \ln \frac{a_H a_{Cl}}{p^{1/2}} \tag{10-2-12}$$

In this case, $E_{II(p)} = -E_{I(p)}$, and $E_{II}^0 = -E_I^0$. Obviously, it is immaterial whether we write cell I or cell II, so long as we associate the electromotive force and its sign with the appropriate cell reaction.

It should be emphasized at this point that the nature of the chemical reaction, corresponding to a particular electrode or cell, cannot be determined by electromotive force measurements alone. Cell reactions, no matter how simple and obvious, must be treated as hypothetical until it can be shown that thermodynamic quantities calculated from the electromotive force, ΔF, ΔH, equilibrium constants, etc., have been checked by other evidence.

To avoid the necessity of recording the partial pressures of gases involved in cell reactions, it has become customary to convert electromotive forces, measured at a partial pressure, p, to values corresponding to a partial pressure of exactly one atmosphere, and record the latter as an "observed" electromotive force. If we arrange equation (10-2-10) for cell I in the form

$$\mathbf{E}^0 - \frac{RT}{\mathbf{F}} \ln a_{\mathrm{H}} a_{\mathrm{Cl}} = \left[\mathbf{E}_{(p)} - \frac{RT}{2\mathbf{F}} \ln p\right] = \mathbf{E} \qquad (10\text{-}2\text{-}13)$$

it is seen that the bracketed expression equals the electromotive force of the cell when $p = 1$. This electromotive force is designated **E**.

TABLE (10-2-1). BAROMETRIC CORRECTION: $\frac{RT}{2\mathbf{F}} \ln [760/(P - p_W)]$ FOR DILUTE AQUEOUS SOLUTIONS (VOLTS × 10^5).

P	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
780	−24	−21	−17	−12	−4	7	20	40	64	98	140	195	269
770	−8	−6	−1	4	12	24	38	58	82	115	160	217	291
760	7	10	15	21	29	41	56	76	101	136	181	239	314
750	23	26	31	38	46	59	74	95	121	156	202	261	338
740	39	43	48	55	64	76	92	113	141	176	223		

Table (10-2-1) contains values of the correction factor

$$-\frac{RT}{2\mathbf{F}} \ln p = \frac{RT}{2\mathbf{F}} \ln \frac{760}{P - p_w} \qquad (10\text{-}2\text{-}14)$$

for aqueous solution. This quantity, sometimes written $\mathbf{E}_{(\mathrm{Bar.})}$, should be added to $\mathbf{E}_{(p)}$ to obtain **E**. Here, the total barometric pressure, P, and the vapor pressure of pure water, p_w, are expressed in millimeters. The vapor pressure of water over a dilute solution does not differ enough from that of pure water to affect **E** appreciably, since a change of ½ mm. in p_w affects the figures in Table (10-2-1) by about 0.01 mv. at room temperature. Linear interpolation is satisfactory. For concentrated solutions, however, it is necessary to employ equation (10-2-14) for each concentration, and make use of the appropriate values of p_w.

There remains one further matter. Since no boundary between two solutions of the same electrolyte at different concentrations, or between two solutions of different electrolytes, is specified in cells of the type considered in this section, these cells are designated "cells without liquid junction." However, such cells are not absolutely free from concentration gradients since the silver halide is slightly soluble. If the solution is saturated throughout with the halide, silver will deposit on the hydrogen electrode, and affect its electromotive force. If the solution is not saturated with the halide, a concentration gradient of silver and halide ions will be present which will give rise to a liquid junction potential of a small magnitude. This condition prevails in all cells containing electrodes of this kind. Obviously, the lower the solubility of the salt under consideration, the more nearly the actual cell approaches the ideal cell without liquid junction.

(3) EXTRAPOLATION OF ELECTROMOTIVE FORCE DATA AND EVALUATION OF THE STANDARD MOLAL ELECTRODE POTENTIAL

In general, the electromotive force of a cell is given by equation (10-1-4). We shall be particularly interested in a specialized form of this equation. In the first place, we shall consider the electromotive force, **E**, to be that at which any gas involved in the cell reaction is at unit pressure [Equation (10-2-13)]. Secondly, we shall consider only that kind of cell reaction in which the electrolyte is formed at a concentration, m [Equation (10-2-8)]. In this case, equation (10-1-4) reduces to

$$\mathbf{E} = \mathbf{E}^0 - \frac{RT}{\mathbf{NF}} \ln \gamma_+^{\nu_+} \gamma_-^{\nu_-} m_+^{\nu_+} m_-^{\nu_-}$$

or

$$\mathbf{E} = \mathbf{E}^0 - \frac{\nu RT}{\mathbf{NF}} \ln \gamma_\pm m_\pm \tag{10-3-1}$$

according to the definitional equations (1-6-3) and (1-8-5). Upon rearrangement of this equation, we obtain

$$\left[\mathbf{E} + \frac{\nu RT}{\mathbf{NF}} \ln m_\pm\right] = \mathbf{E}^0 - \frac{\nu RT}{\mathbf{NF}} \ln \gamma_\pm \tag{10-3-2}$$

The bracketed terms must equal $\mathbf{E}^0$ when $m = 0$, since $\gamma_\pm = 1$ at infinite dilution. Therefore, the problem of extrapolation reduces to the evaluation of the left side of this equation when $m = 0$. Since the equation (3-4-9), without the logarithmic term on the right,

$$\log \gamma_\pm = -\mathfrak{S}_{(f)} \sqrt{\Gamma} \tag{10-3-3}$$

permits the elimination of $\gamma_\pm$ from equation (10-3-2), $\mathbf{E}^0$ might be calculated from a single, accurate measurement at very high dilution, or a series of measurements at various concentrations. In the latter case, the left side of equation (10-3-2) can be plotted against $\sqrt{\Gamma}$, and extrapolated to $c = 0$ so as to approach the limiting slope of the theory asymptotically. Such a plot was originally used by Lewis and Randall[2] before the advent of the

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[2] G. N. Lewis and M. Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921).

Debye and Hückel theory. They assumed the linearity of the left side of equation (10-3-2) with $\sqrt{m}$ at infinite dilution, and extrapolated with an arbitrary slope which seemed to fit the data at high dilution. This type of extrapolation is not very satisfactory because it exhibits a curvature at the lowest concentrations, and too much weight must be given to the most dilute solutions where the measurements are least trustworthy.

A simple practical extrapolation[3] which fits the data closely at moderate concentrations may be obtained by using equation (10-3-3) with an additional term, or

$$\log \gamma_{\pm} = -\mathfrak{S}_{(f)}\sqrt{\Gamma} + B'm \qquad (10\text{-}3\text{-}4)$$

When combined with equation (10-3-2) and arranged in a suitable manner,

$$\left[\mathbf{E} + \frac{\nu RT}{\mathbf{NF}} \ln m_{\pm} - \frac{\nu RT}{\mathbf{NF}} \mathfrak{S}_{(f)} \sqrt{\Gamma}\right] = \mathbf{E}^0 - \frac{\nu RT}{\mathbf{NF}} B'm \qquad (10\text{-}3\text{-}5)$$

According to this equation, a plot of the bracketed term against m should be linear, and the intercept at $m = 0$ must be $\mathbf{E}^0$. Numerous examples of this and similar kinds of extrapolations will be found in Chapters (11) to (15).

We have made no attempt to compile comprehensive tables of standard potentials, but have recorded values of $\mathbf{E}^0$ which have a direct bearing on the immediate subject matter. Tables[4] of standard ionic free energies and entropies have been omitted entirely.

(4) DETERMINATION OF ACTIVITY COEFFICIENTS BY EXTRAPOLATION OF THE ELECTROMOTIVE FORCES OF CONCENTRATION CELLS WITHOUT LIQUID JUNCTIONS

There is another type of extrapolation which, although not as important as that just described, has proved useful in the development of this subject. Sometimes for experimental purposes it is convenient to combine two cells of the kind described above. An important example is the amalgam cell of the type

$$\mathrm{M}_x\mathrm{Hg} \mid \mathrm{M}X(m_1) \mid \mathrm{Ag}X\text{-}\mathrm{Ag} \qquad (10\text{-}4\text{-}1)$$

where M is an alkali metal, and MX an alkali halide. The cell reaction is taken to be

$$\mathrm{M}(\mathrm{M}_x\mathrm{Hg}) + \mathrm{Ag}X = \mathrm{Ag} + \mathrm{M}X(m_1) \qquad (10\text{-}4\text{-}2)$$

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[3] D. I. Hitchcock, *J. Am. Chem. Soc.*, **50**, 2076 (1928); N. Bjerrum and A. Unmack, *Det. Kg. Danske Videnskab. Math. fys. Medd.*, **9**, 1 (1929).

[4] For recent tabulations see W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, New York, 1938. See also W. M. Latimer, K. S. Pitzer and W. V. Smith, *J. Am. Chem. Soc.*, **60**, 1829 (1938).

Consider another cell of this type,

$$\mathrm{M}_x\mathrm{Hg} \mid \mathrm{M}X(m_2) \mid \mathrm{Ag}X\text{-}\mathrm{Ag} \tag{10-4-3}$$

in which the electrolyte is at a different concentration, m_2. The cell reaction is

$$\mathrm{M}(\mathrm{M}_x\mathrm{Hg}) + \mathrm{Ag}X = \mathrm{Ag} + \mathrm{M}X(m_2) \tag{10-4-4}$$

If these two cells are combined to form

$$\mathrm{Ag}\text{-}\mathrm{Ag}X \mid \mathrm{M}X(m_2) \mid \mathrm{M}_x\mathrm{Hg} \mid \mathrm{M}X(m_1) \mid \mathrm{Ag}X\text{-}\mathrm{Ag} \tag{10-4-5}$$

the cell reaction is obtained by subtracting (10-4-4) from (10-4-2) so that the net effect of the cell reaction corresponds to the transfer of $\mathrm{M}X$ from a solution of concentration, m_2, to a solution of concentration m_1. This is represented by

$$\mathrm{M}X(m_2) = \mathrm{M}X(m_1) \tag{10-4-6}$$

From equation (1-6-2), we immediately obtain for the transfer of one mol,*

$$-\mathrm{NFE} = \int_{\bar{F}_2}^{\bar{F}_1} dF = \bar{F}_1 - \bar{F}_2 = RT \ln \frac{\gamma_1 m_1}{\gamma_2 m_2} \tag{10-4-7}$$

This equation also results by applying equation (10-1-4) to cells (10-4-1) and (10-4-3), and subtracting. Since the ratio m_1/m_2 is known, the measurement of the electromotive force of a double cell of this kind yields an activity coefficient ratio. In order to determine γ, it is usually customary to keep m_1 constant at a reference concentration ($0.1M$), and determine $\gamma/\gamma_{0.1}$, where γ is the activity coefficient at any other concentration, m. The extrapolation is then effected by means of Hückel's extended Debye and Hückel equation, which is derived by adding a linear term in c to equation (3-5-8). Thus, recalling equation (1-8-13), we may write

$$\log \gamma = -\frac{\mathfrak{S}_{(f)}\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} + Bc - \log(1 + 0.01802\nu m) \tag{10-4-8}$$

A and B are empirical constants at a given temperature. This equation has been shown to fit activity data with high precision from low concentrations to $1M$, or sometimes to $2M$, and for this reason is suitable for extrapolating data obtained at high concentrations.[5] A and B may be determined in a number of ways, the simplest of which is the solution of two

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* For remainder of this section, γ will represent the mean activity coefficient, $\gamma_\pm$, and the subscripts 1 and 2 simply represent two different concentrations of the same electrolyte.

[5] E. Hückel, *Physik. Z.*, **26**, 93 (1925); G. Scatchard, *J. Am. Chem. Soc.*, **47**, 2098 (1925); H. S. Harned, *Ibid.*, **48**, 326 (1926); **51**, 416 (1929); H. S. Harned and G. Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

simultaneous equations for activity coefficient ratios. Thus, according to equation (10-4-8),

$$\log \frac{\gamma_2}{\gamma_1} = - \frac{\mathfrak{S}_{(f)} \sqrt{\Gamma_2}}{1 + A\sqrt{\Gamma_2}} + \frac{\mathfrak{S}_{(f)} \sqrt{\Gamma_1}}{1 + A\sqrt{\Gamma_1}} + B(c_2 - c_1) - \log \left(\frac{1 + 0.01802\nu m_2}{1 + 0.01802\nu m_1} \right) \tag{10-4-9}$$

If γ_2/γ_1 is written for two different values of c_2, c_1 and γ_1 remaining constant, two simultaneous equations are obtained from which A and B may be evaluated. Upon substituting these values of A and B in equation (10-4-8), γ may be computed at any desired concentration.

If good data are available at concentrations from 0.1 to $1M$, γ can be extrapolated by this method with an accuracy of the order of ± 0.002 in the activity coefficient, which corresponds to an error of ± 0.1 mv. The failure of equation (10-4-8) to represent the data accurately at concentrations much greater than $1M$ will sometimes result in an extrapolation error considerably in excess of this estimate.

(5) THE COMPUTATION OF THE RELATIVE PARTIAL MOLAL HEAT CONTENT, AND RELATIVE PARTIAL MOLAL HEAT CAPACITY OF ELECTROLYTES FROM ELECTROMOTIVE FORCE DATA

According to equations (3-8-1) and (10-3-1)

$$\frac{\nu \partial \ln \gamma_\pm}{\partial T} = - \frac{\bar{L}_2}{RT^2} \tag{3-8-1}$$

and

$$\frac{(\mathbf{E} - \mathbf{E}^0)\mathbf{NF}}{\nu RT} = - \ln \gamma_\pm - \ln m. \tag{10-3-1}$$

Therefore, at constant composition,

$$\frac{\partial \ln \gamma_\pm}{\partial T} = - \frac{\mathbf{NF}}{\nu R} \frac{\partial}{\partial T} \frac{(\mathbf{E} - \mathbf{E}^0)}{T} = - \frac{\bar{L}_2}{\nu RT^2} \tag{10-5-1}$$

and

$$\bar{L}_2 = \mathbf{NF}T^2 \frac{\partial}{\partial T} \left(\frac{\mathbf{E} - \mathbf{E}^0}{T} \right) \tag{10-5-2}$$

which is the Gibbs-Helmholtz equation analogous to (1-3-4). Upon differentiation, this equation reduces to the more familiar form

$$\bar{L}_2 = - \mathbf{NF}(\mathbf{E} - \mathbf{E}^0) + \mathbf{NF}T \frac{\partial(\mathbf{E} - \mathbf{E}^0)}{\partial T} \tag{10-5-3}$$

These equations show that the determination of $\bar{L}_2$ from electromotive-force measurements depends on the accuracy with which the temperature coefficient of electromotive force can be determined.

The relative partial molal heat capacity may be computed from these relations by equation (1-7-7), or

$$\bar{J}_2 \equiv (\bar{C}_p - \bar{C}_p^0) = \frac{\partial \bar{L}_2}{\partial T} \tag{10-5-4}$$

Upon substituting the value of $\bar{L}_2$ given by equation (10-5-3), and performing the differentiation, we obtain

$$\bar{J}_2 = \mathbf{NF}T\frac{\partial^2(\mathbf{E} - \mathbf{E}^0)}{\partial T^2} \tag{10-5-5}$$

The question now arises as to the kind of function which should be employed for the computation of the variation of $(\mathbf{E} - \mathbf{E}^0)$ with the temperature. Although it is known that $\bar{J}_2$ does not vary rapidly with temperature, we shall assume as a first approximation that it varies linearly, or that

$$\bar{J}_2 = \bar{J}_{2(0)} + c'''(T - T_0) \tag{10-5-6}$$

where $\bar{J}_{2(0)}$ refers to some reference temperature, T_0, and c''' is a constant. By integrating (10-5-4) between the limits of T and T_0, we obtain

$$\bar{L}_2 = \bar{L}_{2(0)} + \int_{T_0}^{T} \bar{J}_2\, dT \tag{10-5-7}$$

which when combined with equation (10-5-6) yields

$$\bar{L}_2 = a'' + b''T + c''T^2 \tag{10-5-8}$$

where

$$\left.\begin{aligned} a'' &= \bar{L}_{2(0)} - \bar{J}_{2(0)}T_0 + c'''\,T_0^2/2 \\ b'' &= \bar{J}_{2(0)} - c'''\,T_0 \\ c'' &= c'''/2 \end{aligned}\right\} \tag{10-5-9}$$

Upon substitution of the value of $\bar{L}_2$ given by equation (10-5-8) in equation (10-5-2), and subsequent integration, we obtain

$$(\mathbf{E} - \mathbf{E}^0) = \frac{1}{\mathbf{NF}}(-a'' + IT + b''T\ln T + c''T^2) \tag{10-5-10}$$

$$= (a' - a_0') + (b' - b_0')T + (c' - c_0')T^2 + (d' - d_0')T\ln T \tag{10-5-11}$$

where I is an integration constant.

In actual practice it has been found that, over limited temperature ranges

(0° to 50°), both $\mathbf{E}$ and $\mathbf{E}^0$ for many cells may be expressed to within ±0.05 mv. by the quadratic equations

$$\mathbf{E} = a + bT + cT^2 \tag{10-5-12}$$

$$\mathbf{E}^0 = a_0 + b_0T + c_0T^2 \tag{10-5-13}$$

without the logarithmic term.

If $(\mathbf{E} - \mathbf{E}^0)$ is expressed by equation (10-5-11), then according to (10-5-2)

$$\bar{L}_2 = -\mathbf{NF}[(a' - a_0') - (d' - d_0')T - (c' - c_0')T^2] \tag{10-5-14}$$

and if the quadratic equations (10-5-12) and (10-5-13) are employed,

$$\bar{L}_2 = -\mathbf{NF}[(a - a_0) - (c - c_0)T^2] \tag{10-5-15}$$

The corresponding equations for $\bar{J}_2$ are

$$\bar{J}_2 = \mathbf{NF}[(d' - d_0') + 2(c' - c_0')T] \tag{10-5-16}$$

and

$$\bar{J}_2 = 2\mathbf{NF}(c - c_0)T \tag{10-5-17}$$

If we are dealing with a concentration cell without liquid junction [Equation (10-4-5)], then $\bar{L}_2$ and $\bar{J}_2$ can be computed only relative to a reference concentration. If the electromotive force of this cell is expressed by a quadratic formula as follows

$$\mathbf{E}_m - \mathbf{E}_R = a + bT + cT^2$$

then

$$\bar{H}_{2(m)} - \bar{H}_{2(R)} = \bar{L}_{2(m)} - \bar{L}_{2(R)} = -\mathbf{NF}(a - cT^2) \tag{10-5-18}$$

where $\bar{L}_{2(m)}$ is the relative partial molal heat content at a concentration, m, and $\bar{L}_{2(R)}$ is its value at the reference concentration. The partial molal heat capacity relative to the reference concentration is given by

$$\bar{C}_{p_2(m)} - \bar{C}_{p_2(R)} = \bar{J}_{2(m)} - \bar{J}_{2(R)} = 2\mathbf{NF}cT \tag{10-5-19}$$

Since the constants a, b, c, etc., are usually obtained by the method of least squares, the labor of calculation is greatly reduced by using the simpler quadratic equations. If the accuracy of the electromotive forces is not greater than ±0.05 mv., and the temperature range not greater than 40°, the use of a term in $T \ln T$, or higher powers of T is scarcely justified.

(6) THE CONCENTRATION CELL WITH LIQUID JUNCTION

The general equation for the electromotive force of a concentration cell with transference across a liquid junction may be obtained in the following manner as shown by Taylor.[6] We represent such a cell by

$$\text{Electrode (1)} \,|\, m_1, m_2, \cdots m_i, \cdots m_s \,|\, m_1', m_2', \cdots m_i', \cdots m_s' \,|\, \text{Electrode (1)} \tag{10-6-1}$$

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[6] P. B. Taylor, *J. Phys. Chem.*, **31**, 1478 (1927).

where $m_1, \cdots m_s$, and $m_1', \cdots m_s'$ are the molalities of the ions on the two sides of the boundary of the two solutions, and where electrode (1) is reversible to ion (1). The odd subscripts refer to cations and the even to anions. A reversible discharge of the cell involving the passage of one Faraday would correspond to the transfer of one equivalent of ion (1) from one solution to the other. In addition to this, every ion in the solution is transferred across the boundary in amounts determined by their concentrations and transference numbers. Therefore, if the concentrations on the two sides of the boundary differ by infinitesimals, we obtain

$$\mathbf{F}\,d\mathbf{E}_{1(T)} = d\bar{F}_1 - T_1 d\bar{F}_1 + T_2 d\bar{F}_2 - T_3 d\bar{F}_3 + \cdots \tag{10-6-2}$$

$$= d\bar{F}_1 - \sum_1^s T_i d\bar{F}_i \tag{10-6-3}$$

$$= d\bar{F}_1 - \mathbf{F}d\mathbf{E}_J \tag{10-6-4}$$

$\mathbf{E}_{1(T)}$ is the electromotive force of the cell and can be obtained by direct measurement. $\mathbf{E}_J$ is commonly called the liquid-junction potential. In regard to the "hypothetical" partial free energies of the ions on the right of equation (10-6-3), it is important to recall the discussion in Chapter (1) in which it was stressed that thermodynamics permits the evaluation of only partial free energies, activities, etc., of the molecular components in the sense in which Gibbs defined them, and does not allow the actual determination of these quantities for the individual ionic species.

The above expression for $d\mathbf{E}_{1(T)}$ is very convenient for obtaining the relation between the electromotive forces of concentration cells with and without liquid junctions. For suppose we place an electrode reversible to ion (2) between the two solutions of the above cell (10-6-1), and thus construct the cell without liquid junction, namely

Electrode (1) | $m_1, \cdots m_s$ | Electrode (2) | $m_1', \cdots m_s'$ |

Electrode (1) (10-6-5)

it follows that the electromotive force corresponds to a transfer of ions (1) and (2) from one solution to the other. Therefore, if the concentrations of the two solutions differ by infinitesimals, the electromotive force, $d\mathbf{E}_{12}$, is given by

$$\mathbf{F}d\mathbf{E}_{12} = d\bar{F}_1 + d\bar{F}_2, \quad \text{or} \quad d\bar{F}_2 = -d\bar{F}_1 + \mathbf{F}d\mathbf{E}_{12} \tag{10-6-6}$$

Similarly, if electrode (2) is replaced by an electrode (3) reversible to ion 3, the electromotive force of the resulting cell, $d\mathbf{E}_{13}$, will be

$$\mathbf{F}d\mathbf{E}_{13} = d\bar{F}_1 - d\bar{F}_3, \quad \text{or} \quad d\bar{F}_3 = d\bar{F}_1 - \mathbf{F}d\mathbf{E}_{13} \tag{10-6-7}$$

Similar equations may be obtained for the other ions.

By substituting these values of $d\bar{F}_2$, $d\bar{F}_3$, etc., in equation (10-6-2), we obtain

$$\mathbf{F}d\mathbf{E}_{1(T)} = d\bar{F}_1 - T_1 d\bar{F}_1 - T_2 d\bar{F}_1 + T_2\mathbf{F}d\mathbf{E}_{12} - T_3 d\bar{F}_1 + T_3\mathbf{F}d\mathbf{E}_{13} \pm \cdots \quad (10\text{-}6\text{-}8)$$

or

$$\mathbf{F}d\mathbf{E}_{1(T)} = d\bar{F}_1 - (T_1 + T_2 + \cdots + T_s)d\bar{F}_1 + T_2\mathbf{F}d\mathbf{E}_{12} + T_3\mathbf{F}d\mathbf{E}_{13} + \cdots \quad (10\text{-}6\text{-}9)$$

and, therefore,

$$d\mathbf{E}_{1(T)} = T_2 d\mathbf{E}_{12} + T_3 d\mathbf{E}_{13} + \cdots \quad (10\text{-}6\text{-}10)$$

since the sum of the transference numbers of all the ions is unity. A similar formula may be obtained when the ion transferred is an anion if the cation and anion subscripts are permuted. Thus, if the electrode in cell (10-6-1) is reversible to ion (2), then

$$d\mathbf{E}_{2(T)} = T_1 d\mathbf{E}_{21} + T_3 d\mathbf{E}_{23} + \cdots \quad (10\text{-}6\text{-}11)$$

The result expressed by equations (10-6-10) and (10-6-11) is important, because we find that all ionic partial free energies, $d\bar{F}_i$, have been eliminated, and the electromotive forces of the cells have been expressed in terms of the quantities, $\mathbf{E}_{21}$, $\mathbf{E}_{23}$, etc., corresponding to sums of the partial free energies of the positive and negative ions. Such sums are simply the molecular free energies of the electrolytes.

Since we have shown that equation (10-6-2) will not yield ionic partial free energies, we are forced to the conclusion that measurements of the electromotive forces of cells with transference can yield no information whatsoever regarding ionic activities and partial free energies.

The exact thermodynamic result expressed by equations (10-6-10) and (10-6-11) is an important one, since it enables us to determine the transference number from measurements of cells with and without a liquid junction.[7] Suppose we consider cells of these kinds which contain a single electrolyte. If the electrode is reversible to the anion, equation (10-6-11) yields

$$d\mathbf{E}_{2(T)} = T_1 d\mathbf{E}_{21} \quad (10\text{-}6\text{-}12)$$

where T_1 is the cation transference number. It is apparent from this equation that if $\mathbf{E}_{2(T)}$ is known as a function of $\mathbf{E}_{21}$, T_1 may be evaluated. If such a function is not known, $\mathbf{E}_{2(T)}$ may be plotted against $\mathbf{E}_{21}$ and the slope, T_1, determined. This method of determining the transference number was developed with a fair degree of accuracy by MacInnes and

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[7] See H. v. Helmholtz, *Wied. Ann.*, **3**, 201 (1878); *Ber.*, **7**, 27 (1882); *Ges. Abhl.*, **1**, 840; **2**, 979.

Parker[8] and MacInnes and Beattie.[9, 10] Since the limiting equation of Onsager for the transference was available, Jones and Dole[11] and others[12] have also applied this method, but the results so far obtained are of a much lower order of accuracy than those derived by the moving-boundary method [Chapter (6)].

Brown and MacInnes[13] have taken advantage of the high precision of moving boundary data by developing a method for determining the activity coefficient of a halide from measurements of cells with transference. They employed the cell

$$\text{Ag-AgCl} \mid \text{NaCl}(c_1) \mid \text{NaCl}(c_2) \mid \text{AgCl-Ag} \qquad (10\text{-}6\text{-}13)$$

Upon integration of equation (10-6-12), the electromotive force of this cell is

$$\mathbf{E}_{2(T)} = T_{\text{Na}} \int_{\text{I}}^{\text{II}} d\mathbf{E}_{21} = -\frac{2RT}{\mathbf{F}} \int_{\text{I}}^{\text{II}} T_{\text{Na}}\, d \ln y_{\pm} c \qquad (10\text{-}6\text{-}14)$$

If T_{Na} is known at various concentrations, $y_{\pm}$ can be very accurately determined by this relation. The details of the calculation will be discussed in chapter (12), section (1).

The preceding discussion of cells with liquid-junction potentials, although adequate for our purposes, is too brief to exhaust this complicated and profound subject. Recently contributions have been made by Hermans,[14] and especially by Koenig,[15] who has extended the theory to include the effects of gravitational, electrical and magnetic fields.

The Hypothetical Liquid Junction Potential

The deductions in the preceding paragraphs have shown that the measurements of cells with liquid junctions lead to the determination of partial molal free energies, or linear combinations of "hypothetical" ionic free energies. This thermodynamic result is very important in its relation to the so-called liquid-junction potential. Equations (10-6-3) and (10-6-12) lead to

$$\begin{aligned} \mathbf{F}T_2 d\mathbf{E}_{12} &= \mathbf{F}d\mathbf{E}_{1(T)} \\ &= d\bar{F}_1 - \sum_{1}^{s} T_i d\bar{F}_i = d\bar{F}_1 - RT \sum_{1}^{s} T_i d \ln a_i \end{aligned} \qquad (10\text{-}6\text{-}15)$$

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[8] D. A. MacInnes and K. Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915).

[9] D. A. MacInnes and J. A. Beattie, *Ibid.*, **42**, 1117 (1920).

[10] W. W. Lucasse, *Ibid.*, **47**, 743 (1925).

[11] G. Jones and M. Dole, *Ibid.*, **51**, 1073 (1929).

[12] W. J. Hamer, *Ibid.*, **57**, 662 (1935); H. S. Harned and E. C. Dreby, *Ibid.*, **61**, 3113 (1939).

[13] A. S. Brown and D. A. MacInnes, *J. Am. Chem. Soc.*, **57**, 1356 (1935).

[14] J. J. Hermans, *Rec. trav. chim.*, **56**, 635, 658 (1937); *Ibid.*, **58**, 99, 2419 (1939).

[15] F. O. Koenig, *J. Phys. Chem.*, **44**, 101 (1940); F. O. Koenig and S. W. Grinnell, *Ibid.*, **44**, 463 (1940); **46**, 980 (1942).

The only quantity which can be measured by the cell with liquid junction is $\mathbf{F}d\mathbf{E}_{1(T)}$, where $d\mathbf{E}_{1(T)}$ is the difference in potential between two wires of the same metal attached to the electrodes. $d\bar{F}_1$ is purely hypothetical, and impossible to evaluate by any thermodynamic method. Therefore, $\sum_{1}^{s} T_i d\bar{F}_i$ is equally arbitrary, and the liquid-junction potential given by the second term on the right of these equations is also entirely arbitrary. If a convention be adopted to fix the ionic free energy of one of the ions in the solution, then the ionic free energies of the other ions are also fixed through knowledge of the molecular free energies. So we are at liberty to adopt such a convention, whether or not it serves any useful end. For example, it has been proposed[16] to let $\bar{F}_K = \bar{F}_{Cl}$, and refer other ionic free energies to this conventional standard. But according to the relations given by (10-6-15), any other convention such as $\bar{F}_K = n\bar{F}_{Cl}$, where n is any finite positive number, would serve equally well. This was proved to be the case by Harned[17] by a numerical method, and by Taylor[18] by means of the analytical method just developed. Since this is the case, there is no more reason to choose the potassium and chloride ions as reference than the ions of any other electrolyte.

Equations for liquid-junction potentials, such as Planck's and Henderson's, do not solve the difficulties. This can be shown in a simple manner by writing the equation for the hypothetical liquid-junction potential, $\mathbf{E}_J$, in the integrated form

$$\mathbf{E}_J = -\frac{RT}{\mathbf{F}}\sum_{1}^{s}\int_{\mathrm{I}}^{\mathrm{II}} T_i\, d\ln\gamma_i - \frac{RT}{\mathbf{F}}\sum_{1}^{s}\int_{\mathrm{I}}^{\mathrm{II}} T_i\, d\ln m_i \qquad (10\text{-}6\text{-}16)$$

where the integration is between the limits corresponding to the two solutions (I and II) forming the liquid junction. Planck's[19] and Henderson's[20] formulas for $\mathbf{E}_J$ were obtained by evaluating the last term on the right of this equation. Assuming such an evaluation to be correct, only part of the liquid-junction potential would be evaluated, as the part involving the hypothetical ionic activity coefficients would still remain. This is true at all finite concentrations of ions, and the difficulty only disappears when the solutions on the two sides of the junctions have the same composition.

The use of salt bridges consisting of solutions of electrolytes at high concentrations (sat. KCl) may reduce the numerical value of the second term on the right of equation (10-6-16), but again leaves us with the purely arbitrary first term.

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[16] D. A. MacInnes, *J. Am. Chem. Soc.*, **41**, 1086 (1919); H. S. Harned, *Ibid.*, **42**, 1808 (1920); *J. Phys. Chem.*, **30**, 433 (1926).

[17] H. S. Harned, *J. Phys. Chem.*, **30**, 433 (1926).

[18] P. B. Taylor, *J. Phys. Chem.*, **31**, 1478 (1927).

[19] M. Planck, *Wied. Ann.*, **39**, 161 (1890); **40**, 561 (1890).

[20] P. Henderson, *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908); Compare J. J. Hermans, *Rec. trav. chim.*, **57**, 1373 (1938).

THE CONCEPT OF ELECTRICAL POTENTIAL AT PHASE BOUNDARIES

The conclusion of Taylor that measurements of cells with or without liquid junctions can yield no information whatsoever concerning ionic free energies has been extended by Guggenheim.[21] He has analyzed the concept of electric potential difference between two points in different media, and has arrived at the negative result that such a quantity is entirely arbitrary, and has not yet been defined in terms of physical realities (measurable quantities). Guggenheim shows the difference between this electrostatic potential and the one which is defined in electrostatics. The latter science is based "on a mathematical theory of an imaginary fluid electricity, whose equilibrium and motion is determined entirely by the electric field. 'Electricity' of this kind does not exist; only electrons and and ions have physical existence, and these differ fundamentally from the hypothetical fluid electricity in that the particles are at all times in movement relative to one another; their equilibrium is thermodynamic, not static." The criteria of thermodynamic equilibria in these systems at constant temperature and pressure may be developed from equation (1-5-2),

$$dF = \sum^{p} \sum^{s} \mu_i \, dn_i + (\psi' - \psi'') \, de \tag{1-5-2}$$

We recall that $(\psi' - \psi'')$, applied to the reversible cell, is the difference in electrical potential of two wires attached to the electrodes of the cell; $(\psi' - \psi'')\, de$ represents the electrical work; and the μ_i are the chemical potentials of the components in a given phase. We shall now express that part of the work term corresponding to a phase as $\sum_1^{\sigma} \psi e_j \, dn_j$, where ψ is the potential at a particle, ion or electron, of charge e_j, and the summation is for all such particles in the phase. The potential ψ is purely conventional. $(\psi' - \psi'')\, de$ is equal to the summation, $\sum_1^{p} \sum_1^{\sigma} \psi e_j \, dn_j$. Equation (1-5-2) for a single phase becomes

$$dF_p = \sum_1^{s} \mu_i \, dn_i + \sum_1^{\sigma} \psi e_j \, dn_j \tag{10-6-17}$$

where the first summation is over all the molecular and electrical species (s), and the second summation is over all the electrical species (σ). If we now consider a process which involves only the electrified particles, we may divide the chemical potential of the molecular component, μ_i, into arbitrary chemical potentials of the electrified species, μ_j, and write,

$$dF_e = \sum_1^{\sigma} \mu_j \, dn_j + \sum_1^{\sigma} \psi e_j \, dn_j$$

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[21] E. A. Guggenheim, *J. Phys. Chem.*, **33**, 842 (1929); **34**, 1540 (1930).

or

$$dF_e = \sum_1^{\sigma} (\mu_j + \psi e_j)\, dn_j \tag{10-6-18}$$

Now let, $\bar{\mu}_j \equiv \mu_j + \psi e_j$; then (10-6-19)

$$dF_e = \sum_1^{\sigma} \bar{\mu}_j\, dn_j \tag{10-6-20}$$

analogous to

$$dF = \sum_1^{c} \mu_i\, dn_i \tag{1-4-2}$$

whence it is apparent that $\bar{\mu}_j$ plays a role in the electrochemical system similar to that of μ_i in the molecular system. Applied to equilibria in a polyphase system at constant pressure, temperature and charge, this latter relation leads to the equality of the chemical potential of a component throughout all the phases, as shown by equation (1-2-8). Analogously, $\bar{\mu}_j$, the electrochemical potential (Guggenheim-Brönsted) of a given electrified species, determines the equilibria in the electrochemical systems, provided that it is distributed throughout all phases. Thus

$$\begin{array}{ccccc} \bar{\mu}_1' & = & \bar{\mu}_1'' & = \cdots & \bar{\mu}_1^p \\ | & & | & & | \\ \bar{\mu}_\sigma' & = & \bar{\mu}_\sigma'' & = \cdots & \bar{\mu}_\sigma^p \end{array} \tag{10-6-21}$$

if $\bar{\mu}_1', \bar{\mu}_1'' \cdots \bar{\mu}_1^p$, represent the electrochemical potentials of the first species, and $\bar{\mu}_2', \bar{\mu}_2'' \cdots \bar{\mu}_2^p$, those of the second species, etc. throughout the p-phases.[22] For a single ionic species, the partial molal free energy, or μ_j, has been shown in the preceding discussion to be entirely arbitrary; consequently, ψe_j has no thermodynamic significance.

These relations will lead directly to the previous conclusion that, although μ_j is arbitrary, certain linear combinations of μ_j are not. For suppose we consider an electrolyte dissociating into two ions in the same phase. Then, as shown by Guggenheim,

$$\begin{aligned} \bar{\mu}_j &= \mu_j + e_j\psi \\ \bar{\mu}_k &= \mu_k + e_k\psi \end{aligned} \tag{10-6-22}$$

from which it follows by elimination of ψ that

$$\frac{\bar{\mu}_j}{e_j} - \frac{\bar{\mu}_k}{e_k} = \frac{\mu_j}{e_j} - \frac{\mu_k}{e_k} \tag{10-6-23}$$

so that $\left(\dfrac{\mu_j}{e_j} - \dfrac{\mu_k}{e_k}\right)$ is definitely defined in terms of measurable quantities. Guggenheim shows that it is a simple matter to prove that the phenomena

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[22] The above treatment of the electrochemical potential is essentially the same as that given by J. N. Brönsted, who uses the symbol λ for this quantity. [*Z. physik. Chem.*, **143**, 301 (1929)].

of diffusion, partition between two media, membrane equilibria, cells with and without liquid junctions, and reaction velocities can all be completely described in terms of the electrochemical potentials, and that the chemical potentials, μ_i, and the ψe_i terms never occur separately. This proves that no known measurements yield any knowledge regarding these latter quantities. Guggenheim goes as far as to say that "the electrical potential difference between two points in different media can never be measured."

These considerations are of great interest in relation to the century-old problem of the seat of the electrical potential in a galvanic cell, as for example the Daniell cell,

$$\mathrm{Cu} \mid \mathrm{Zn} \mid \mathrm{ZnSO_4}\ (m) \mid \mathrm{CuSO_4}\ (m) \mid \mathrm{Cu}$$

The total measured electrical potential may be regarded as the sum of the differences of potentials at the boundaries, Cu | Zn, Zn | $ZnSO_4$ (m), $ZnSO_4$ (m) | $CuSO_4$ (m), and $CuSO_4$ (m) | Cu. Since we have shown that the potentials at points within the phases are neither defined nor capable of measurement by known methods, it is impossible at present to estimate the contributions at any individual phase boundary.

The point of view resulting from this analysis was anticipated by Gibbs[23] when he wrote, "Again, the consideration of the electrical potential in the electrolyte, and especially the consideration of the difference of potential in electrolyte and electrode, involves the consideration of quantities of which we have no apparent means of physical measurement, while the difference of potential in pieces of metal of the same kind attached to the electrodes is exactly one of the things which we can and do measure."

(7) THE USE OF CELLS WITH LIQUID JUNCTIONS. DETERMINATION OF pH. ELIMINATION OF LIQUID-JUNCTION POTENTIALS

There are two types of liquid junctions commonly encountered in electrochemical studies: homoionic junctions formed by juxtaposition of solutions differing only in ionic concentrations; and heterionic junctions involving differences in ionic species, or in both ionic species and concentrations. It was shown in section (6) that homoionic junction potentials are subject to exact thermodynamic definition [Equation (10-6-14)] and that cells containing them may be used in thermodynamic calculations [Chapter (11), Section (9), and Chapter (12), Section (1)]. The present section deals with the use of cells with heterionic liquid junctions. Their measurement has widespread applications in pH control procedures, and may, under very special conditions, yield results of thermodynamic significance. These special conditions are experimental, and are concerned with the elimination of liquid-junction potentials, but not with their evaluation.

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[23] "The Collected Works of J. Willard Gibbs," Vol. I, p. 429, Longmans Green Co., New York, 1928.

We shall discuss first the modern measurement[24] of pH, and the uncertainty that liquid junctions produce in the definition of this quantity. It will then be shown that the junction potentials of certain cells, or combinations of cells, may be reduced to negligible values by causing the two solutions comprising the junction to approach identity. In this case the cells may be said to come under the usual definition* of cells without liquid junctions. Finally, we shall examine the limiting case in which complete identity of these two solutions may be attained only by extrapolations based upon a series of measurements. The use of such extrapolated results is thermodynamically rigorous, but the possibility of a practical extrapolation method must be established experimentally.

The pH of a solution was originally defined[25] as the negative of the common logarithm of the hydrogen-ion concentration, but it later became identified with this function of the hydrogen-ion activity.[26] We employ the equation

$$\mathrm{pH} = -\log a_{\mathrm{H}^+} \qquad (10\text{-}7\text{-}1)$$

with the understanding that this is a purely formal relationship, because a_{H^+} is itself undefined [Section (6)]. The ultimate definition of pH is made in terms of the method used in determining it. For this purpose the cell

$$\mathrm{H_2} \mid \text{Test Solution} \mid \mathrm{KCl_{(sat.)}} \mid \text{Reference Electrode} \qquad \mathrm{I}$$

is typical. The reference electrode is usually a saturated, or $N/10$ calomel electrode.[27] For special purposes, the hydrogen gas electrode is replaced by secondary standards such as the quinhydrone, antimony-antimony trioxide, and glass electrodes. In any case, the pH may be defined by

$$\mathrm{pH} = \frac{\mathbf{E} - \mathbf{E}^0_{\mathrm{pH}}}{2.3RT/F} = \frac{\mathbf{E} - \mathbf{E}^0_{\mathrm{pH}}}{k} \qquad (10\text{-}7\text{-}2)$$

where **E** is the observed electromotive force of Cell I. If $\mathbf{E}^0_{\mathrm{pH}}$ is a constant which depends only upon the temperature, the pressure, and the nature of

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[24] For comprehensive digests of earlier methods, see W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1928; E. Mislowitzer, "Die Bestimmung der Wasserstoffionenkonzentration von Flüssigkeiten," Julius Springer, Berlin, 1928; H. T. S. Britton, "Hydrogen Ions," Van Nostrand Co., New York, 1929.

* See the concluding paragraph of Section (2), p. 303.

[25] S. P. L. Sørensen, *Compt. Rend. Lab. Carlsberg*, **8**, 1 (1909).

[26] S. P. L. Sørensen and K. Linderstrøm-Lang [*Compt. Rend. Lab. Carlsberg*, **15**, 40 (1924)] proposed the term paH for use when hydrogen-ion activity is involved but we shall designate this quantity pH in keeping with current usage.

[27] This selection is arbitrary, and is governed largely by convenience. D. I. Hitchcock [*J. Am. Chem. Soc.*, **58**, 855 (1936)], and O. Redlich and H. Klinger [*Ibid.*, **61**, 2983 (1939)] discussed the possible advantage of employing reference electrodes which are reversible with respect to a univalent cation.

the electrodes, this equation completely defines a useful pH number, about which no confusion need arise unless an attempt is made to interpret it in terms of equation (10-7-1). It is clear that the numerical value of this pH number depends upon the nature of the liquid junction, and the manner in which it is formed. This number cannot be identified with $-\log a_{\text{H}^+}$ by equation (10-7-1) without also imputing a dependence of a_{H^+} upon the properties of the junction. In the effort to eliminate this difficulty in interpreting pH, or a_{H^+}, without eliminating the liquid junction itself,[28] attempts have been made to correct either $\mathbf{E}$ or $\mathbf{E}^0_{\text{pH}}$ for the liquid-junction potentials. Neither of these is thermodynamically sound, and the "correction" of each measured $\mathbf{E}$ by Henderson's[29] equation, for example, is always laborious and usually impractical in routine control work.

Recently, new values of $\mathbf{E}^0_{\text{pH}}$ have been proposed, for the various types of calomel electrodes, which presumably include the greater part of the junction potential. They should prove very convenient and useful in determining ionization and other equilibrium constants where the greatest accuracy is not required. These values of $\mathbf{E}^0_{\text{pH}}$ were determined by replacing the test solution in Cell I by buffer solutions of acids, for which the ionization constants have been accurately evaluated conductometrically, or from cells without liquid junctions. This may be illustrated by considering a buffer solution of the weak acid, HA, and its sodium salt. If $\text{p}K_{\text{A}}$ is the negative logarithm of its thermodynamic ionization constant,* then, by equations (10-7-1) and (7-2-10),

$$\text{pH} = \text{p}K_{\text{A}} + \log \frac{c_{\text{A}^-}}{c_{\text{HA}}} + \log \frac{y_{\text{A}^-}}{y_{\text{HA}}} \qquad (10\text{-}7\text{-}3)$$

MacInnes, Belcher and Shedlovsky[30] write $-S\sqrt{\mu}$ for $\log y_{\text{A}^-}/y_{\text{HA}}$ and rearrange this equation to read

$$\frac{\mathbf{E} - \mathbf{E}^0_{\text{pH}}}{k} - \log \frac{c_{\text{A}^-}}{c_{\text{HA}}} = \text{p}K_{\text{A}} - S\sqrt{\mu} \qquad (10\text{-}7\text{-}4)$$

They select a value of $\mathbf{E}^0_{\text{pH}}$ by trial, so that a plot of the left-hand member against $\sqrt{\mu}$ is linear in dilute solutions ($\mu \sim 0.001$ to 0.01) and yields the intercept, $\text{p}K_{\text{A}}$. Two such plots are illustrated in Fig. (10-7-1). The val-

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[28] The definition of pH in terms of cells without liquid junctions has been urged by D. I. Hitchcock [*J. Am. Chem. Soc.*, **58**, 855 (1936)], W. J. Hamer [*Trans. Electrochem. Soc.*, **72**, 45 (1937)], W. J. Hamer and S. F. Acree [*Bur. Standards J. Research*, **23**, 647 (1939)], E. A. Guggenheim [*J. Phys. Chem.*, **34**, 1758 (1930)], and others.

[29] P. Henderson, *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908). *Cf.* N. Bjerrum and A. Unmack, *K. Danske Videnskab. Selskab Math-fys. Medd.*, **9**, 1 (1929), and E. A. Guggenheim and T. D. Schindler, *J. Phys. Chem.*, **38**, 533 (1934).

* It appears unnecessary to consider the difference between the values of K_{A} on a molality or a molarity basis because its effect on $\mathbf{E}^0_{\text{pH}}$ is ordinarily less than 0.1 mv.

[30] D. A. MacInnes, D. Belcher and T. Shedlovsky, *J. Am. Chem. Soc.*, **60**, 1094 (1938).

ues of S determined from the slopes of the plots are 10 to 25 per cent higher than the Debye-Hückel slope, $\mathbb{S}_{(f)}$, for an univalent ion.

Hitchcock and Taylor[31] replace $\log (y_{A^-}/y_{HA})$ in equation (10-7-3) by $-\mathbb{S}_{(f)}\sqrt{\mu} + B\mu$, and rearrange this equation in the form

$$\mathrm{E}^{0\prime}_{\mathrm{pH}} \equiv \mathrm{E} - k\mathrm{p}K_{\mathrm{A}} - k \log \frac{c_{\mathrm{A}^-}}{c_{\mathrm{HA}}} + k\mathbb{S}_{(f)}\sqrt{\mu} = \mathrm{E}^0_{\mathrm{pH}} + kB\mu \qquad (10\text{-}7\text{-}5)$$

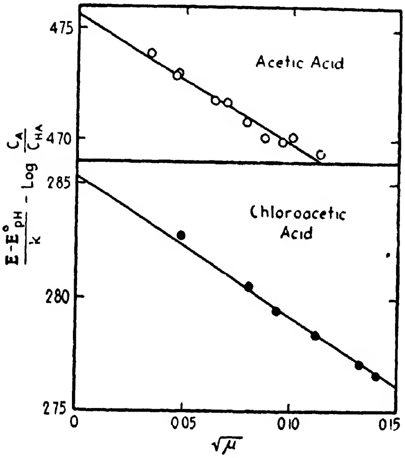

Fig. (10-7-1)
Evaluation of E^0_{pH} at 25° by equation (10-7-4). The ratio, c_A/c_{HA}, is variable

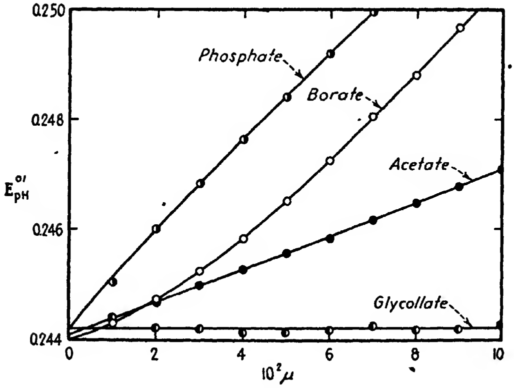

Fig. (10-7-2)
Evaluation of E^0_{pH} at 25° by equation (10-7-5). The ratio c_A/c_{HA} is unity

$\mathrm{E}^0_{\mathrm{pH}}$ is determined as the intercept of the plot of the left-hand member against μ. For this purpose, values of μ between 0.01 and 0.1 are used, and the plots exhibit some curvature, as can be seen in Fig. (10-7-2).

Table (10-7-1) contains values of $\mathrm{E}^0_{\mathrm{pH}}$ at 25° obtained by both of these

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[31] D. I. Hitchcock and A. C. Taylor, *J. Am. Chem. Soc.*, **59**, 1812 (1937).

methods. The hydrogen electrode, in various buffer solutions, is used with the saturated calomel electrode[*] as reference.

The variation observed in the values of E^0_{pH} given in Table (10-7-1) is presumably a measure of the difference between the liquid-junction potentials produced by the various test solutions in contact with saturated potassium chloride. The first seven values determined in buffered solutions are all within 0.1 mv of their average (0.2441). Hydrochloric acid, in the presence of nine parts of sodium chloride, also leads to this value. Pure hydrochloric acid solutions give a much higher result. There is a significant difference between the values of E^0_{pH} obtained in essentially the same acetic acid buffers by the two different methods. Some of this discordance may be due to minor differences in the saturated calomel electrodes used in the two sets of measurements.

TABLE (10-7-1). E^0_{pH} AT 25° FOR THE CELL:
H_2 | ACID(m_1), SALT(m_2) | KCl(sat), HgCl, Hg

Acid	Salt	m_2/m_1[*]	E^0_{pH}
CH_3CO_2H	CH_3CO_2K	1	0.2442[a]
CH_3CO_2H	CH_3CO_2Na	4	.2441[a]
CH_3CO_2H	CH_3CO_2Na	1	.2441[a]
CH_3CO_2H	CH_3CO_2Na	1/4	.2440[a]
KH_2PO_4	Na_2HPO_4	1	.2442[a]
HBO_2	$NaBO_2$	1	.2440[a]
HCl	CH_2OHCO_2Li	2	.2442[a]
HCl	....	..	.2450[a]
HCl	KCl	9	.2445[a]
HCl	NaCl	9	.2441[a]
CH_3CO_2H	CH_3CO_2Na	1	.2446[b]
$ClCH_2CO_2H$	$ClCH_2CO_2Na$	1	.2445[b]

[*] The values of m_2/m_1 are only approximate.
[a] D. I. Hitchcock and A. C. Taylor, *J. Am. Chem. Soc.*, **59**, 1812 (1937).
[b] D. A. MacInnes, D. Belcher and T. Shedlovsky, *Ibid.*, **60**, 1094 (1938).

To avoid preparing reference electrodes according to exact specifications, it is recommended that E^0_{pH} of each electrode system used be determined at the time. The standard solutions given in Table (10-7-2) are to be used for this purpose. The pH of these solutions has been calculated from the values of E^0_{pH} given in Table (10-7-1), and constitute a new scale of standard values, which makes it possible to evaluate thermodynamic ionization constants with greater accuracy than was formerly attained by pH measurements. In determining the value of E^0_{pH} for any particular electrode system, it is desirable to employ a standard solution for which the pH is comparable with that in the test solutions to be investigated.

If the standard and test solutions are of equal ionic strength, and very

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[*] The results by MacInnes, Belcher and Shedlovsky were actually determined with the $N/10$ calomel electrode, but they have been reduced to conform with the common reference electrode by subtracting their value (0.0912) for the difference between the saturated and N/10 electrode potentials.

similar in composition,* the junction potentials against the reference electrode systems will be essentially equal, and may be assumed to cancel for most practical purposes. This experimental method of overcoming the effect of liquid junctions was used by Harned and Robinson,[32] Güntelberg and Schiödt,[33] and Larsson and Adell,[34] and may be illustrated by the following cells:

$$\mathrm{H_2}\left|\begin{matrix}\mathrm{HA}(m_1)\\ \mathrm{NaCl}(m - m_{\mathrm{H}})\end{matrix}\right|\mathrm{KCl_{(sat.)}},\ \mathrm{HgCl\text{-}Hg} \qquad \mathrm{II}$$

$$\mathrm{H_2}\left|\begin{matrix}\mathrm{HCl}(m_0)\\ \mathrm{NaCl}(m - m_0)\end{matrix}\right|\mathrm{KCl_{(sat.)}},\ \mathrm{HgCl\text{-}Hg} \qquad \mathrm{III}$$

TABLE (10-7-2). THE pH VALUES OF SOME STANDARD SOLUTIONS FOR USE IN DETERMINING E^0_{pH} BY EQUATION (10-7-2)

Solution Composition in mols/liter*		pH (25°)		pH (38°)	
		a, b	c	b	c
0.1	HCl	1.085		1.082	
.1	$KH_3(C_2O_4)_2\cdot 2H_2O$ (tetroxalate)	1.480		1.495	
.01	HCl + 0.09 NaCl	2.058			
.01	HCl + 0.09 KCl	2.078		2.075	
.03	$KHC_4H_4O_6$ (tartrate)	3.567			
.1	$KH_2C_6H_5O_7$ (citrate)	3.719			
.05	$KHC_8H_4O_4$ (phthalate)	4.008	4.000	4.025	4.015
.1	$HC_2H_3O_2$ + 0.1 $NaC_2H_3O_2$ (acetate)	4.648	4.640	4.655	4.635
.01	$HC_2H_3O_2$ + 0.01 $NaC_2H_3O_2$	4.714	4.700		4.710
.025	KH_2PO_4 + 0.025 Na_2HPO_4	6.857		6.835	
.05	$Na_2B_4O_7$	9.180		9.070	

* Compositions of solutions used by [a] and [b] were determined at 21 to 23°C.

[a] D. I. Hitchcock and A. C. Taylor, *J. Am. Chem. Soc.*, **59**, 1812 (1937).

[b] D. I. Hitchcock and A. C. Taylor, *Ibid.*, **60**, 2710 (1938).

[c] D. A. MacInnes, D. Belcher and T. Shedlovsky, *Ibid.*, **60**, 1094 (1938).

Since the electromotive force of Cell II yields a rough value of m_{H} in the solution of the weak acid, HA, by the application of equations (10-7-1) and (10-7-2), it is possible to adjust the concentrations in Cell III so that the ionic strengths in both acid solutions are equal to m.† The combination of these cells leads to the cell

$$\mathrm{H_2}\left|\begin{matrix}\mathrm{HA}(m_1)\\ \mathrm{NaCl}(m - m_{\mathrm{H}})\end{matrix}\right|\begin{matrix}\mathrm{HCl}(m_0)\\ \mathrm{NaCl}(m - m_0)\end{matrix}\left|\mathrm{H_2}\right. \qquad \mathrm{IV}$$

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* The preponderant electrolytes are identical, and at equal concentrations in the two solutions.

[32] H. S. Harned and R. A. Robinson, *J. Am. Chem. Soc.*, **50**, 3157 (1928).

[33] E. Güntelberg and E. Schiödt, *Z. physik. Chem.*, **135**, 393 (1928).

[34] E. Larsson and B. Adell, *Z. physik. Chem.*, **A156**, 352 (1931).

† In practice, m_0 may be kept constant at about 0.01*M*, as it is sufficient that $m_{\mathrm{H}} \backsimeq m_0$. Cell III is likely to give erratic results if $m_0 < 0.001$, but this is an experimental, not a theoretical, limitation of the method.

for which the electromotive force is practically free from liquid-junction potential if m_0 is small, and m is relatively large.

Assuming that the hydrochloric acid is completely ionized, the electromotive force of Cell IV is a measure of the hydrogen-ion concentration in the solution of the weak acid. Thus

$$\mathbf{E}_{\mathrm{IV}} = -k \log \frac{m_{\mathrm{H}}}{m_0} \tag{10-7-6}$$

since the activity coefficients of the hydrogen ions in the two solutions cancel because of the symmetry of the cell. Values of

$$k_{\mathrm{A}} = \frac{m_{\mathrm{H}} m_{\mathrm{A}}}{m_{\mathrm{HA}}} = \frac{m_{\mathrm{H}}^2}{m_1 - m_{\mathrm{H}}} \tag{10-7-7}$$

in salt solutions, determined by this method,[34] are in close agreement with those obtained from cells without liquid junctions.[35] The corresponding thermodynamic ionization constants,

$$K_{\mathrm{A}} = k_{\mathrm{A}}(\mu \rightarrow 0) \tag{10-7-8}$$

are also in accord with values obtained by other methods [Table (15-6-2)].

The practically complete elimination of liquid-junction potential attained in Cell IV, by making m_1 and m_0 small, can be made absolutely complete if it is possible to obtain the value of an appropriate function of **E** and of the concentrations as m_1 and m_0 approach zero as a limit.[36] The experimental determination of this limiting value of the function involves the study of a series of cells containing solutions of varying compositions, but maintained at constant total ionic strength by the presence of an electrolyte which takes no part in the electrode reactions.[37] Extrapolation to zero concentration of the dissimilar ions eliminates the junction potential. The conditions of extrapolation have been analyzed by Owen and Brinkley.[36a] The effect of the inert electrolyte is eliminated by subsequent extrapolation to zero ionic strength. The method will be illustrated by considering the cell

$$\text{Ag-AgCl}\left|\begin{array}{l}\mathrm{KCl}(x)m\\ \mathrm{KNO_3}(1-x)m\end{array}\right|\mathrm{KNO_3}(m)\left|\begin{array}{l}\mathrm{AgNO_3}(x)m\\ \mathrm{KNO_3}(1-x)m\end{array}\right|\text{AgCl-Ag} \qquad \mathrm{V}$$

The total ionic strength in each solution is m, but a fraction, x, of this is composed of chloride ion in the left-hand compartment, and silver ion in the right. The electromotive force of the cell is given by

$$\mathbf{E} = k \log a'_{\mathrm{Ag}}/a_{\mathrm{Ag}} \pm \mathbf{E}_J \tag{10-7-9}$$

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[35] H. S. Harned and G. M. Murphy, *J. Am. Chem. Soc.*, **53**, 8 (1931).

[36] This notion was implied in the work of G. A. Linhart [*J. Am. Chem. Soc.*, **38**, 2356 (1916)], and used by S. Popoff and A. H. Kunz [*Ibid.*, **51**, 382 (1929)].

[36a] B. B. Owen and S. R. Brinkley, Jr., *Ibid.*, **64**, 2171 (1942).

[37] B. B. Owen, *J. Am. Chem. Soc.*, **60**, 2229 (1938).

$\mathbf{E}_J$ is the sum of the unknown liquid-junction potentials, $k = 2.303RT/F$, and a'_{Ag} and a_{Ag} represent the activities of the silver ion in the right-hand and left-hand solutions, respectively. The solubility product

$$K_{AgCl} = a_{Ag}a_{Cl} \qquad (10\text{-}7\text{-}10)$$

can be used to eliminate a_{Ag}, and equations (10-7-9) becomes

$$\mathbf{E} - k \log a'_{Ag}a_{Cl} = -k \log K_{AgCl} \pm \mathbf{E}_J \qquad (10\text{-}7\text{-}11)$$

The introduction of the concentrations, xm, and the individual activity coefficients leads to

$$\mathbf{E} - 2k \log xm = -k \log K_{AgCl} + k \log \gamma_{Cl}\gamma'_{Ag} \pm \mathbf{E}_J \qquad (10\text{-}7\text{-}12)$$

Note that the last two terms of this equation are not independently defined by thermodynamics alone.

Inspection of equation (10-7-12), and consideration of the symmetry of the electrochemical system it represents, shows that if m is held constant while x is varied, extrapolation to $x = 0$ must yield

$$[\mathbf{E} - 2k \log xm]_{x=0} = -k \log K_{AgCl} + [k \log \gamma_{Cl}\gamma'_{Ag}]_{x=0} \qquad (10\text{-}7\text{-}13)$$

because $\mathbf{E}_J$ becomes zero under this condition. Since it is no longer necessary to retain the prime on γ'_{Ag} when $x = 0$, the last term is amenable to thermodynamic treatment, and can be expressed as a function of m, similar to that for any 1-1 strong electrolyte. Accordingly, $k \log \gamma_{Cl}\gamma_{Ag}$ is replaced by $-2k\mathcal{S}_{(f)}\sqrt{md_0}$, and equation (10-7-13) takes the form

$$[\mathbf{E} - 2k \log xm + 2k\mathcal{S}_{(f)}\sqrt{md_0}]_{x=0} = -k \log K'_{AgCl} \qquad (10\text{-}7\text{-}14)$$

The determination of the bracketed member of this equation by extrapolation at several values of m is illustrated in Figure (10-7-3).[37] The determination of $-k \log K_{AgCl}$, by subsequent extrapolation of these intercepts ($-k \log K'_{AgCl}$) to $m = 0$, is shown in Figure (10-7-4). Both of these extrapolations appear to be linear* within the estimated uncertainty of ±0.1 mv, which corresponds to the radii of the circles on the plots. Similar linear relationships were found to represent the results obtained with the cells[38]

$$\mathrm{H_2} \,|\, \mathrm{HAc}(m), \mathrm{NaAc}(m) \,|\, \begin{matrix} \mathrm{AgAc}(x)m \\ \mathrm{HAc}(m), \mathrm{NaAc}(1-x)m \end{matrix} \,|\, \mathrm{Ag} \qquad \mathrm{VI}$$

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* The linearity apparent in Figure (10-7-3) is probably a consequence of equation (14-4-3), and the high symmetry of the electrolyte systems. The linearity of the plots in Figure (10-7-4) is predicted from consideration of equations (10-3-4) and (10-3-5).

[38] B. B. Owen and S. R. Brinkley Jr., *J. Am. Chem. Soc.*, **60**, 2233 (1938).

and[30]

$$\text{Ag-AgCl}\left|\begin{matrix}\text{KCl}(x)m\\ \text{KNO}_3(1-x)m\end{matrix}\right|\begin{matrix}\text{KBr}(x)m\\ \text{KNO}_3(1-x)m\end{matrix}\left|\text{AgBr-Ag}\right. \qquad \text{VII}$$

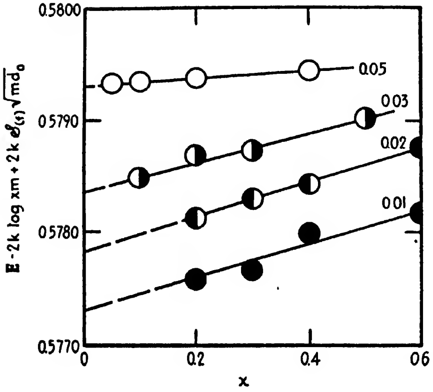

Fig. (10-7-3)
Elimination of E_J at 25° at constant total molalities indicated on the right

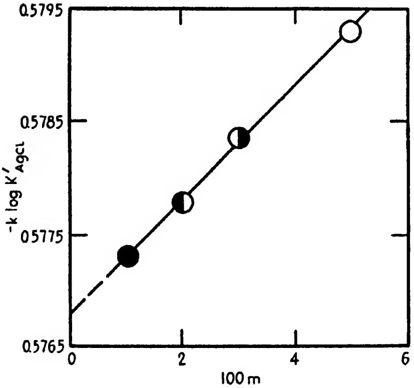

Fig. (10-7-4)
Evaluation of $(-k \log K_{AgCl})$ at 25°.

TABLE (10-7-3). STANDARD ELECTRODE POTENTIAL OF SILVER DERIVED FROM CELLS V AND VI

t	Cell V	Cell VI	Equation (10-7-16)
5	-0.8185_5	-0.8187	-0.8185_8
15	$-\ .8087$	$-\ .8090$	$-\ .8089_1$
25	$-\ .7990$	$-\ .7992$	$-\ .7991_0$
35	$-\ .7891$	$-\ .7892$	$-\ .7891_5$
45	$-\ .7788$	$-\ .7791_5$	$-\ .7790_6$

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[30] B. B. Owen and E. J. King, *J. Am. Chem. Soc.*, **63**, 1711 (1941).

The simplicity of the function plotted in Figure (10-7-3) is important, as its form and the possibility of its extrapolation constitute the essential extra-thermodynamic hypothesis upon which this method of eliminating liquid-junction potentials is based.

The validity of the extrapolation by which the liquid-junction potentials are eliminated can be verified by comparing the calculated thermodynamic quantities with those obtained by independent procedure. Where such comparisons are possible, the agreement appears quite satisfactory.[37,38] The difference between the values of the standard potentials of the silver-silver chloride and silver-silver bromide electrodes, obtained from Cell VII, is in exact agreement with the difference between the corresponding values, directly obtained from cells without liquid junctions. It was also found that the results obtained from Cells V and VI are in excellent agreement, although the slopes of the extrapolations employed in the two systems differ in sign, and in order of magnitude. The standard electrode potential of silver may be calculated by the equation

$$\pi^0_{\mathrm{Ag}} = k \log K_{\mathrm{AgCl}} + \pi^0_{\mathrm{Ag-AgCl}} \qquad (10\text{-}7\text{-}15)$$

from the values of K_{AgCl} obtained from Cell I. Cell II yields π^0_{Ag} directly. The comparison is illustrated in Table (10-7-3). These results are well represented by the quadratic equation

$$\pi^0_{\mathrm{Ag}} = -0.7991 + 0.000988(t - 25) + 7 \times 10^{-7}(t - 25)^2 \qquad (10\text{-}7\text{-}16)$$

The temperature coefficient derived from this equation leads to a value of the entropy of the silver ion at 25°, in excellent agreement with the most recent calorimetric[40] determinations.

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[40] W. M. Latimer, K. S. Pitzer and W. V. Smith, *J. Am. Chem. Soc.*, **60**, 1829 (1938); K. S. Pitzer and W. V. Smith, *Ibid.*, **59**, 2633 (1937).

Chapter 11

Hydrochloric Acid

The properties of hydrochloric acid in aqueous and nonaqueous solutions, and in water-nonaqueous solvent mixtures have been investigated more comprehensively than those of any other electrolyte, and they may be used to illustrate the fundamental characteristics of ionic solutions without introducing the difficulties caused by the presence of ions of charge greater than unity. The subject will be introduced with a discussion of the extent of ionization of this acid in media of varying dielectric constant as derived from conductance data. The thermodynamics of hydrochloric acid, as determined from the electromotive force of the cell,

$$H_2 \,|\, HCl(m) \,|\, AgCl\text{-}Ag$$

will then be developed in considerable detail. Comparison of the results obtained from electromotive forces will be made with similar results from freezing point, heat of dilution, and specific heat data. In this way, a comprehensive view of the properties of a single electrolyte as a function of its concentration, the temperature, and the dielectric constant may be obtained. All these results will be considered in relation to the predictions of the interionic attraction theory.

(1) CONDUCTANCE OF HYDROCHLORIC ACID IN DIOXANE-WATER MIXTURES

Previous discussion [Chapter (6) Section (2)] of the conductance of hydrochloric acid in water showed that it is a typically strong electrolyte. The criterion for this conclusion is that the equivalent conductance, Λ, is greater than that predicted by Onsager's equation,

$$\Lambda = \Lambda^0 - (\alpha^*\Lambda^0 + \beta^*\sqrt{c}) \qquad (6\text{-}2\text{-}1)$$

in dilute solutions, and approaches the result predicted by this equation in the limit. The behavior of this acid in media of lower dielectric constant is illustrated clearly by the results of Owen and Waters,[1] who measured the conductance in dioxane-water mixtures of 20, 45, 70 and 82 per cent dioxane from 15 to 45°. At 25°, the dielectric constants of these mixtures, according to Åkerlöf and Short,[2] are 60.79, 38.48, 17.69 and 9.53, respectively. Fig. (11-1-1) contains plots of the equivalent conductance, Λ, against $c^{\frac{1}{2}}$. The experimental points are represented by the circles,

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[1] B. B. Owen and G. W. Waters, *J. Am. Chem. Soc.*, **60**, 2371 (1938).

[2] G. Åkerlöf and O. A. Short, *J. Am. Chem. Soc.*, **58**, 1241 (1936).

whereas the straight lines are the theoretical plots of Onsager's equation. In the 20 per cent dioxane mixtures, the result is very similar to that in water, since the observed curve lies above the theoretical one [Fig. (6-2-1)]. Even the result for the most dilute solution (0.0004*N*) is slightly above the theoretical result. In the 45 per cent mixtures ($D \sim 40$), there is evidence for ionic association. The theoretical result is approached from below, although this effect is barely noticeable. In the case of the 70 per cent dioxane solutions, ionic association appears to be present to a considerable extent. In the 82 per cent dioxane mixtures, hydrochloric acid shows the characteristic behavior of a weak electrolyte.

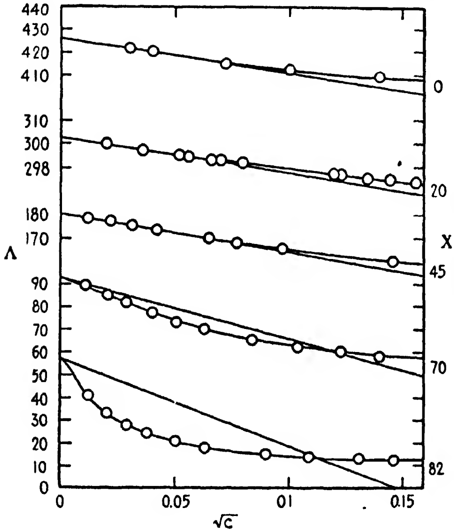

Fig. (11-1-1)
Equivalent conductance of hydrochloric acid in dioxane-water mixtures at 25°. Straight lines represent theoretical limiting law; *X* equals per cent dioxane by weight

To evaluate the limiting conductance in the 20 and 45 per cent mixtures, the extrapolation which utilizes the function,

$$\Lambda^{0'} = \frac{(\Lambda + \beta^* \sqrt{c})}{(1 - \alpha^* \sqrt{c})} \tag{6-3-7}†$$

was employed. For the 70 and 82 per cent mixtures, the method of Fuoss and Kraus,[3] improved by Fuoss,[4] which involves the use of equations (7-2-3) to (7-2-9), was used.

The dissociation constants obtained by Owen and Waters are given in Table (11-1-1). No accurate estimate can be made of the results in the 20 and 45 per cent dioxane solutions, although these investigators judge that *K* is of the order of unity in the latter.

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† Values of α^* and β^* for these dioxane-water mixtures are given in Table (11-1-1A).

[3] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 476 (1933).

[4] R. M. Fuoss, *J. Am. Chem. Soc.*, **57**, 488 (1935).

The general nature of these results is in accord with Bjerrum's theory of ionic association. By employing this theory [Equation (3-7-13)], Owen and Waters obtained the values in Ångstroms of the sums of the ionic radii given in the table. Greater weight should be given to the values in the case of 82 per cent mixtures, since the values of K are somewhat more certain than those in the more dilute dioxane mixtures.

TABLE (11-1-1). DISSOCIATION CONSTANTS OF HYDROCHLORIC ACID IN DIOXANE-WATER MIXTURES*

t	70% Dioxane			82% Dioxane		
	D_0	$K \times 10^2$	$a \times 10^8$	D_0	$K \times 10^4$	$a \times 10^8$†
15	18.72	11	9.1	10.01	2.5	6.6
25	17.69	8	7.9	9.53	2.0	6.3
35	16.72	7	7.7	9.06	1.6	6.2
45	15.80	6	7.4	8.62	1.1	5.8

* Values of parameters α^* and β^*, and the required viscosities are to be found in Table (11-1-1A).

† Sum of ionic radii.

(2) THE STANDARD POTENTIAL OF THE CELL: H_2 | HCl (m) | AgCl-Ag IN AQUEOUS SOLUTIONS

The reaction corresponding to the cell,

$$H_2 \mid HCl\ (m) \mid AgCl\text{-}Ag \tag{11-2-1}$$

is taken to be

$$\tfrac{1}{2}H_2 + AgCl = Ag + HCl\ (m) \tag{11-2-2}$$

Since one mol of hydrochloric acid is formed, the electromotive force of the cell is given by equation (10-3-2). Thus, for a 1-1 electrolyte,

$$\mathbf{E} + 2k \log m = \mathbf{E}^0 - 2k \log \gamma_\pm \tag{11-2-3}$$

where k has been substituted for the factor 2.3026 $RT/\mathbf{F}$. For purposes of extrapolation, equation (10-3-5) will be employed, namely,

$$\mathbf{E} + 2k \log m - 2k\, \mathcal{S}_{(f)} \sqrt{\Gamma} = \mathbf{E}^0 - 2kB'm \tag{11-2-4}$$

In Fig. (11-2-1), the left side of this equation has been plotted against m. It is clear that these data can be represented by straight lines at the lower concentrations, and that the extrapolation can be made with high precision. Since the electrode potential of the hydrogen electrode at one atmosphere is taken to be zero at all temperatures, the value of $\mathbf{E}^0$, thus obtained, becomes the standard potential of the silver-silver chloride electrode merely by changing its sign.

Many attempts have been made to determine this standard electrode potential. We shall discuss those which appear to be the most accurate.

Several different kinds of electrodes have been used. Linhart[5] employed an electrode made by introducing a platinum wire into a mixture of precipitated silver chloride, and silver prepared by electrolysis of silver nitrate at high current density. Carmody[6] used a platinum gauze electrode upon which silver had been deposited electrolytically. Silver chloride was formed on this by electrolysis of hydrochloric acid.[7] Ellis,[8] Roberts,[9] and Harned and Ehlers[10] used electrodes prepared by heating silver oxide on a platinum spiral to 500°. The silver thus formed was coated with silver chloride by electrolysis in hydrochloric acid solution.[11]

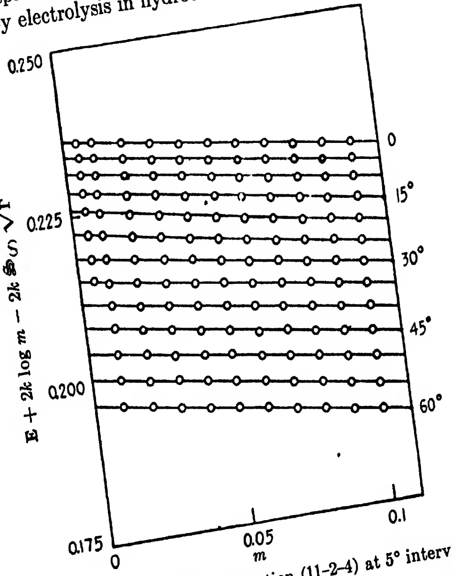

Fig. (11-2-1). Evaluation of E^0 by equation (11-2-4) at 5° intervals.

The values of $\mathbf{E}^0$ have usually been determined by graphical methods. Prentiss and Scatchard[12] have recently computed $\mathbf{E}^0$ from the measure-

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[5] G. A. Linhart, *J. Am. Chem. Soc.*, **41**, 1175 (1919).

[6] W. R. Carmody, *J. Am. Chem. Soc.*, **51**, 2905 (1929).

[7] A similar electrode was employed by G. Scatchard, *J. Am. Chem. Soc.*, **47**, 641 (1925).

[8] A. A. Noyes and J. H. Ellis, *Ibid.*, **39**, 2532 (1917).

[9] E. J. Roberts, *Ibid.*, **52**, 3877 (1930).

[10] H. S. Harned and R. W. Ehlers, *Ibid.*, **54**, 1350 (1932).

[11] Somewhat different types of this electrode are described by E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); H. S. Harned, *J. Am. Chem. Soc.*, **51**, 416 (1929); D. A. MacInnes and J. A. Beattie, *Ibid.*, **42**, 1117 (1920); A. S. Brown, *Ibid.*, **56**, 646 (1934).

[12] S. S. Prentiss and G. Scatchard, *Chem. Rev.*, **13**, 139 (1933).

ments of the above investigators by using the method of least squares. In Table (11-2-1), we have compiled the results at 25°.

Considering the variety in technique and in type of electrodes used, the agreement between the results of the different investigators is excellent. Further, the results obtained graphically compare favorably with those computed by the least squares method.

TABLE (11-2-1). THE STANDARD POTENTIAL OF THE SILVER-SILVER CHLORIDE ELECTRODE AT 25°

Observer	Graphical	Least Square (7)
Carmody	−0.2223 (1)	
"	−0.2222 (2)	−0.22222
Linhart	−0.2226 (3)	− .22253
"	−0.2224 (4)	
Roberts	−0.22240 (5)	− .22241
"	....	− .22237
Harned and Ehlers	−0.22239 (6)	− .22244
MacInnes	−0.2225 (8)	....

Computed by: (1) W. R. Carmody, *loc. cit.*; (2) H. M. Spencer, *J. Am. Chem. Soc.*, **54**, 3647 (1933); (3) G. Scatchard, *J. Am. Chem. Soc.*, **47**, 641 (1925); (4) D. I. Hitchcock, *Ibid.*, **50**, 2076 (1928); (5) E. J. Roberts, *loc. cit.*; (6) H. S. Harned and R. W Ehlers, *loc. cit.*; (7) S. S. Prentiss and G. Scatchard, *loc. cit.*; (8) D. A. MacInnes, "The Principles of Electrochemistry," p. 187, Reinhold Publishing Corp., New York, 1939 from the data of Harned and Ehlers, *loc. cit.*

TABLE (11-2-2). THE STANDARD POTENTIAL OF THE SILVER-SILVER CHLORIDE ELECTRODE FROM 0° TO 60°

t	$-\pi^0_{Ag\text{-}AgCl} = E^0$	Dev. (mv)*
0	0.23634	−0.02
5	.23392	− .01
10	.23126	+ .04
15	.22847	+ .04
20	.22551	+ .04
25	.22239	.00
30	.21912	− .04
35	.21563	− .02
40	.21200	.00
45	.20821	+ .04
50	.20437	− .01
55	.20035	− .02
60	.19620	.00

* Minus deviation indicates that calculated value is less than observed.

It is important to note that these values are influenced considerably by the choice of numerical values for the constant, k, and the Debye-Hückel limiting slope. Harned and Wright[13] have computed E^0 from the data of Harned and Ehlers: (a) using $k = 0.00019844T$, and $T = t + 273.1$, in conformity with International Critical Constant Table data; and (b)

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[13] H. S. Harned and D. D. Wright, *J. Am. Chem. Soc.*, **55**, 4849 (1933).

using the values of Birge,[14] according to which $k = 0.00019848T$ and $T = t + 273.18$. From (a), $\mathbf{E}^0$ was found to be 0.22239 volt at 25°, and from (b), $\mathbf{E}^0$ was 0.22223 volt.

By employing a consistent technique, Harned and Ehlers have determined the standard potentials of the silver-silver chloride electrode from 0 to 60° at 5° intervals. They employed equation (11-2-4), and evaluated $\mathbf{E}^0$ graphically. In Table (11-2-2), their observed values are given, as well as the deviations of the observed results from those computed by the equation,

$$-\pi^0_{\text{Ag-AgCl}} = \mathbf{E}^0 = 0.22239 - 645.52 \times 10^{-6}(t - 25) \\ -3.284 \times 10^{-6}(t - 25)^2 + 9.948 \times 10^{-9}(t - 25)^3 \qquad (11\text{-}2\text{-}6)$$

obtained by the method of least squares. In subsequent calculations, these values will be employed, since they were determined over a wide temperature range by a technique which is consistent with most of the experimental material to be considered. The deviations are less than the combined errors of the measurements and the extrapolation, which is estimated to be ±0.05 mv.

(3) THE STANDARD POTENTIAL OF THE CELL: $H_2 \mid HCl(m), S(X), H_2O\ (Y) \mid AgCl\text{-}Ag$ IN ORGANIC SOLVENT-WATER MIXTURES

The electromotive forces of these cells in methanol-water mixtures, containing 10 and 20 per cent methanol, have been determined by Harned and Thomas.[15] They have also been investigated in pure methanol and ethanol solutions by Nonhebel and Hartley[16] and by Woolcock and Hartley,[17] respectively. Similar measurements at 25° in pure ethanol have been made by Danner,[18] and in 50 and 99.9 per cent ethanol by Harned and Fleysher.[19] Lucasse[20] has measured the cell in 1 mol per cent and 5 mol per cent glycerol-water mixtures and Scatchard[21] in sucrose solutions. The most comprehensive series of measurements of this kind has recently been made using dioxane-water mixtures.[22] These include the measure-

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[14] R. T. Birge, *Phys. Rev. Supplement*, **1**, 1 (1929).

[15] H. S. Harned and H. C. Thomas, *J. Am. Chem. Soc.*, **57**, 1666 (1935); **58**, 761 (1936).

[16] G. Nonhebel and H. Hartley, *Phil. Mag.*, (6), **50**, 729 (1925).

[17] J. W. Woolcock and H. Hartley, *Ibid.*, (7), **5**, 1133 (1928).

[18] P. S. Danner, *J. Am. Chem. Soc.*, **44**, 2832 (1922).

[19] H. S. Harned and M. H. Fleysher, *J. Am. Chem. Soc.*, **47**, 82 (1925).

[20] W. W. Lucasse, *Z. physik. Chem.*, **121**, 254 (1926).

[21] G. Scatchard, *J. Am. Chem. Soc.*, **48**, 2026 (1926).

[22] H. S. Harned and J. O. Morrison, *Am. J. Sci.*, **33**, 161 (1937); *J. Am. Chem. Soc.*, **58**, 1908 (1936).

H. S. Harned and C. Calmon, *Ibid.*, **60**, 334 (1938). Densities.

H. S. Harned, *Ibid.*, **60**, 336 (1938). Extrapolations (20% and 45%).

H. S. Harned and J. G. Donelson, *Ibid.*, **60**, 339 (1938). Properties (20%); **60**, 2128 (1938). Properties (45%).

ments of the cells at 5° intervals from 0 to 50°, at concentrations of acid from $0.001M$ to the highest practical concentration in 20, 45, 70, and 82 per cent dioxane-water mixtures, which correspond to values of the solvent dielectric constant of approximately 60, 40, 20, and 10. The dielectric constants of the media have been determined by Åkerlöf and Short,[23] and the vapor pressures by Hovorka, Shaefer, and Dreisbach.[24]

As the dielectric constant of the solvent decreases, the effect of the higher-order terms of the interionic attraction theory, given by equations (3-6-4) and (3-6-5), must be taken into consideration in the extrapolations. In order to illustrate this effect, and at the same time show this method of extrapolation for media containing 20, 45 and 70 per cent dioxane, we shall employ the function, $\mathbf{E}^{0'}$, defined by

$$\mathbf{E}^{0'} \equiv \mathbf{E} + 2k \log m - \frac{2k\mathfrak{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} - 2k \log(1 + 0.002M_{XY}m) = \mathbf{E}^0 + f(m) \tag{11-3-1}$$

$\mathbf{E}$ is the observed electromotive force of the cell at a concentration m, $\mathbf{E}^0$ the standard potential of the cell, A' is the parameter which involves the apparent ionic diameter, $\mathring{a}$ [(Equation (3-5-9)], and M_{XY} is the average molecular weight of the solvent [Equation (1-8-16)]. $\mathbf{E}^{0'}$ was first calculated by employing a preliminary value of $\mathring{a}$. Then, the Gronwall, LaMer and Sandved extended-term contribution, corresponding to this value of $\mathring{a}$, was computed from their functions in Table (5-2-2). This quantity, multiplied by $2k$, will be denoted as $\mathbf{E}_{\text{Ext.}}$. The functions, $\mathbf{E}^{0'}$ and $\mathbf{E}^{0'} - \mathbf{E}_{\text{Ext.}}$, were plotted, and, if $\mathbf{E}^{0'} - \mathbf{E}_{\text{Ext}}$ was not constant at the lower concentrations ($m < 0.02M$), other values of $\mathring{a}$ were employed until constancy was obtained. Values of c were obtained from Table (11-3-2A).

Fig. (11-3-1) clearly shows the extrapolation and the extended-term effects. In it are the plots of $\mathbf{E}^{0'}$, and $\mathbf{E}^{0'} - \mathbf{E}_{\text{Ext.}}$ versus the molality, m, at 25° for solvents containing 20, 45, and 70 per cent dioxane. The dielectric constants of these solutions are 60.79, 38.48, and 17.69, respectively. We note that the plots of $\mathbf{E}^{0'}$ have "humps" near the origin which are characteristic of this function. Their magnitude increases with decreasing dielectric constant. That the extended-term theory accounts

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H. S. Harned and C. Calmon, *Ibid.*, **60**, 2130 (1938). Extrapolations. (70%)

H. S. Harned, J. G. Donelson, and C. Calmon, *Ibid.*, **60**, 2133 (1938). Properties (70%).

H. S. Harned, F. Walker, and C. Calmon, *Ibid.*, **61**, 44 (1939). Extrapolations (82%).

H. S. Harned and F. Walker, *Ibid.*, **61**, 48 (1939). Properties (82%).

H. S. Harned, J. O. Morrison, F. Walker, J. G. Donelson, and C. Calmon, *Ibid.*, **61**, 49 (1938). Summary and Critique.

[23] G. Åkerlöf and O. A. Short, *J. Am. Chem. Soc.*, **58**, 1241 (1936).

[24] F. Hovorka, R. A. Schaefer, and D. Dreisbach, *J. Am. Chem. Soc.*, **58**, 2264 (1936).

for these results at low concentrations is shown by the graphs of the function $E^{0'} - E_{Ext.}$, which for the values of å of 5.0, 5.4, and 5.6, respectively, are straight with zero slopes [$f(m) = 0$] below $0.02M$. The contribution of the extended terms in the case of the 20 per cent solutions is so small that the extrapolation without them yields the same E^0 within very narrow limits (~0.1 mv). These values of å agree closely with 5.6, obtained by Shedlovsky and MacInnes[25] from measurements of cells with liquid junction in water, and with 5.3, obtained from the data of Harned and Ehlers from cells without liquid junction in the same medium. The constancy of the function, $E^{0'} - E_{Ext.}$, in the concentration range from $0.002M$ to $0.02M$ is shown clearly by the data in Table (11-3-1).

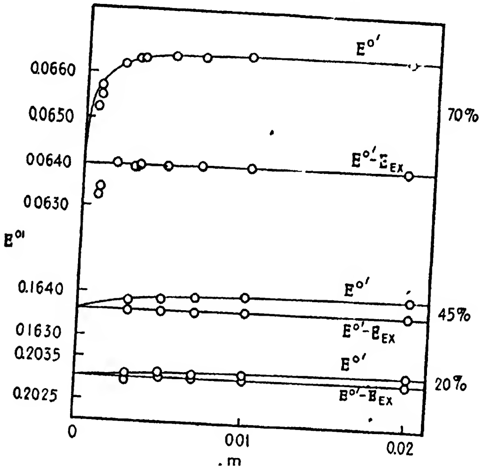

Fig. (11-3-1). Extrapolation in dioxane-water mixtures (at 25°) according to equation (11-3-1). Weight percent of dioxane is indicated at right.

The evaluation of the standard potential in solutions of dielectric constant as low as those containing 82 per cent dioxane cannot be carried out with certainty. There are a number of reasons for this. The Gronwall, LaMer and Sandved extension of the Debye and Hückel theory is not satisfactory in media of dielectric constant of the magnitude 10 or less, since the second term of the extended term series is large. In fact, it is greater than the first term at acid concentrations of the order of $0.001M$. In the second place, reliable electromotive forces at acid concentrations less than $0.001\,M$ have not yet been obtained. For an empirical extrapolation, results in the region of concentrations as low as $0.00005M$, or less, will be required. In view of these difficulties, a tentative method, which involves the law of mass action and dissociation constants derived from

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[25] T. Shedlovsky and D. A. MacInnes, *J. Am. Chem. Soc.*, **58**, 1970 (1936).

conductance measurements, will be employed. This procedure is not altogether satisfactory, but seems as good as any method available at the moment.

According to equation (11-3-1), the deviation function, $\mathbf{E}^{0\prime} - \mathbf{E}^0$ is given by

$$\mathbf{E}^{0\prime} - \mathbf{E}^0 = \mathbf{E} - \mathbf{E}^0 + 2k \log m - \frac{2k\mathcal{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} = f(m) \qquad (11\text{-}3\text{-}2)$$

if we neglect the term containing M_{XY}. If $\mathbf{E}^{0\prime} - \mathbf{E}^0$ can be computed by some means which is theoretically sound when m equals 0, then $\mathbf{E}^0$ may be evaluated from the known values of $\mathbf{E}^{0\prime}$. In order to utilize the known

TABLE (11-3-1). VALUES OF EXTRAPOLATION FUNCTION, $\mathbf{E}^{0\prime} - \mathbf{E}^0_{\text{Ext.}}$[b]

m	$X = 20\%$ $d = 5.0$	$X = 45\%$ $d = 5.4$	$X = 70\%$ $d = 5.6$
0.000	(0.20303)	(0.16358)	(0.06395)
.001	....	....	(.0634)[a]
.002	....	....	.06400
.003	.20298	.16357	.06393
.005	.20304	.16358	.06389
.007	.20303	.16359	.06391
.01	.20305	.16361	.06399
.02	.20305	.16360	.06400

[a] At concentrations below 0.002 M, the accuracy of the results decreases greatly, as indicated by this result. This matter has been discussed in detail by H. S. Harned and C. Calmon, *J. Am. Chem. Soc.*, **60**, 2130 (1938).

[b] Values of $\mathcal{S}_{(f)}$, used in these computations, are given in Table (11-3-1A). Densities of solutions are given in Table (11-3-2A).

values of the dissociation constant, K, we may express the cell electromotive force by the equation,

$$\mathbf{E} - \mathbf{E}^0 = -2k \log \alpha m \gamma_\alpha \qquad (11\text{-}3\text{-}3)$$

where α is the degree of dissociation, and γ_α, the activity coefficient of the acid as a strong electrolyte at an ionic concentration, αm. Combining this equation with equation (11-3-2), the deviation factor becomes

$$\mathbf{E}_\alpha \equiv \mathbf{E}^{0\prime} - \mathbf{E}^0 = -2k \log \alpha\gamma_\alpha - \frac{2k\mathcal{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} = f(m) \qquad (11\text{-}3\text{-}4)$$

so that the problem becomes one of computing α and γ_α. In terms of the thermodynamic dissociation constant [Equation (7-6-1)], α is given by

$$\alpha = \frac{1}{2}\left[-\frac{K}{\gamma_\alpha^2 m} \pm \sqrt{\frac{K^2}{\gamma_\alpha^4 m^2} + \frac{4K}{\gamma_\alpha^2 m}}\right] \qquad (11\text{-}3\text{-}5)$$

By employing the theoretical equation with extended terms, γ_α was computed and a suitable plot of γ_α versus $\sqrt{m}$ drawn. The above equation was then solved by arithmetical approximation, using the values of K† determined from conductance data in Table (11-1-1). The characteristics of the extrapolation at 25° are illustrated by Fig. (11-3-2) where both $\mathbf{E}^{0'}$ and $\mathbf{E}^{0'} - \mathbf{E}_\alpha$ are plotted against m. Both of these functions equal $\mathbf{E}^0$ when m equals zero. The plot of the Debye and Hückel function, $\mathbf{E}^{0'}$, is deceptive because it is nearly straight, and, if the effect of ionic association is not taken into consideration, would be extrapolated as shown by the upper dashed line. This would lead to a value of $\mathbf{E}^0$ roughly 10 mv too high. The lower dashed line indicates the character of the curve to be expected, but so far no reliable results have been obtained at such low acid concentrations ($<0.001M$).

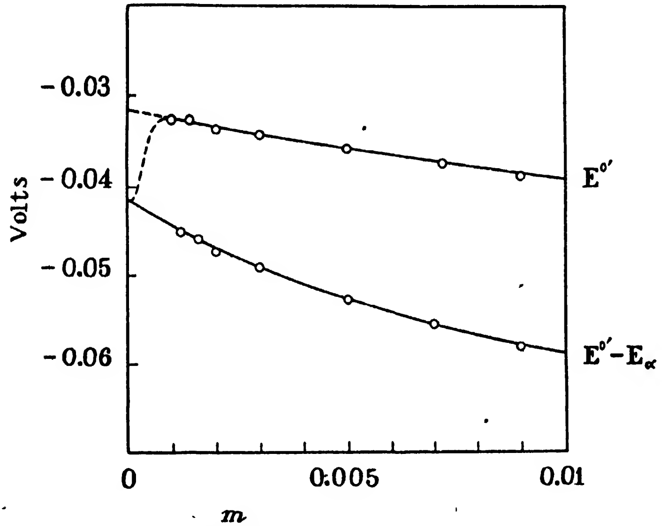

Fig. (11-3-2). Extrapolation in 82% dioxane-water mixtures at 25° according to equations (11-3-4) and (11-3-5)

The plot of $\mathbf{E}^{0'} - \mathbf{E}_\alpha$ is not all that is to be desired because it possesses a slope of considerable magnitude, a factor which decreases the accuracy of the extrapolation. The value of the mean ionic diameter was taken to be 6Å, in agreement with the result of Owen and Waters [Table (11-1-1)]. We note that this value is nearly the same as that found for the mean distance of approach of the ions in water, and in 20, 45, and 70 per cent dioxane-water mixtures, as determined by cell measurements.

Values of the standard potentials at 25° on the m-, c-, and N-scales in some of these media are collected in Table (11-3-2) and specially designated

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† Since at best this calculation is crude, the distinction between K on the c- and m-scales has been ignored.

by a superscript asterisk to conform with equations (11-3-8) and (11-3-9). According to equation (1-8-10), these three quantities, $\mathbf{E}_m^{0*}$, $\mathbf{E}_c^{0*}$, and $\mathbf{E}_N^{0*}$, are related at 25° by the equations,

$$\mathbf{E}_c^{0*} = \mathbf{E}_m^{0*} + 0.1183 \log d_0 \tag{11-3-6}$$

$$\mathbf{E}_N^{0*} = \mathbf{E}_m^{0*} - 0.1183 \log (1000/M_{XY}) \tag{11-3-7}$$

In Fig. (11-3-3), $\mathbf{E}_m^{0*}$ is plotted against $1/D$ for media of high dielectric constant ($D \sim 80$ to 60). The origin of the plots on the left of the figure represents $\mathbf{E}_m^0$ for pure water. None of these plots is a straight line. Further, they exhibit pronounced individual behavior. Plots of $\mathbf{E}_c^{0*}$, or $\mathbf{E}_N^{0*}$, versus $1/D$ have similar characteristics.

Table (11-3-2). Standard Potentials of the Cells: H_2 | HCl (m), Solvent (N_2), H_2O (N_1) | AgCl-Ag at 25°. N_1, N_2 = Mol Fraction

	N_2	D_0	$\mathbf{E}_m^{0*}$	$\mathbf{E}_c^{0*}$	$\mathbf{E}_N^{0*}$
Water	0	78.54	0.22239	0.22151	0.01602
Methanol-Water*	0.0588	74.0	.21535	.21431	.01124
" "	.1233	69.2	.20881	.20692	.00710
" "	1.	31.5	− .0101		
Ethanol-Water	.0417	72.8	.21442	.21340	.01123
" "	.0891	67.0	.20736	.20561	.00763
" "	1.	24.3	− .0740		
Glycerol-Water	.01	77	.2196	.2201	.0153
" "	.05	72	.2082	.2106	.0107
Isopropanol-Water	.0323	71.4	.21363	.21266	.01095
Dioxane-Water*	.0487	60.8	.20303	.20375	.00554
" "	.1433	38.5	.16352	.16513	− .02002
" "	.3231	17.7	.06395	.06584	− .10049
" "	.4823	9.5	− .0413	− .0396	− .19339

* Standard potentials at other temperatures may be obtained from Table (11-3-3A).

The phenomenon of transfer of the acid from water to the water-solvent mixture can be treated conveniently in the following manner. The electromotive force of these cells may be represented by two fundamental equations [Equation (11-2-3)] at 25°

$$\mathbf{E} = \mathbf{E}_m^0 - 0.05915 \log m_H m_{Cl} - 0.05915 \log \gamma_H \gamma_{Cl} \tag{11-3-8}$$

$$\mathbf{E} = \mathbf{E}_m^{0*} - 0.05915 \log m_H m_{Cl} - 0.05915 \log \overset{*}{\gamma}_H \overset{*}{\gamma}_{Cl} \tag{11-3-9}$$

In these, $\mathbf{E}_m^0$ is the standard potential in water, $\gamma_H \gamma_{Cl}$ is the activity coefficient in any of these solutions relative to unity at infinite dilution in water, $\mathbf{E}_m^{0*}$ is the standard potential in any mixture relative to unit activity coefficient, $\gamma^*_{H}\gamma^*_{Cl}$, at infinite dilution in that solvent. Combination of these equations yields,

$$E^0_m - E^{0*}_m = 0.05915 \log \frac{\gamma_H \gamma_{Cl}}{\gamma^*_H \gamma^*_{Cl}} \tag{11-3-10}$$

The superscript star is a special symbol used when a transfer of an electrolyte from one medium to another is under consideration. It appears in this section and in Chapter (15), Section (7).

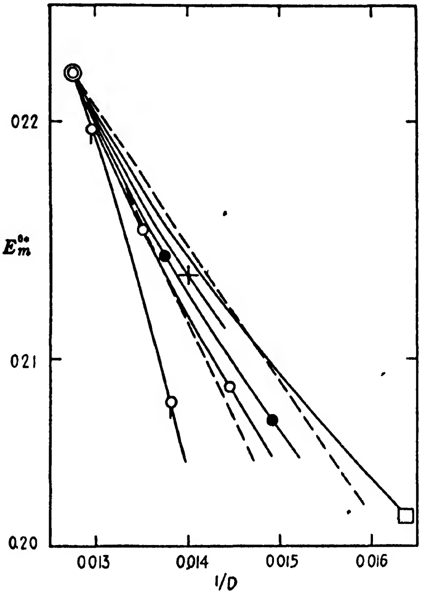

Fig. (11-3-3). Plots of E^{0*}_m against $1/D$ in media of high dielectric constant. **O**, water, ♀, glycerol-water; ○, methanol-water; ●, ethanol-water; +, isopropanol-water; □, dioxane-water. Dashed lines are plots of equation (11-3-13).

Further, by using the thermodynamic relationships of the reaction, $H^+ + Cl^- + H_2O \rightleftharpoons H_3O^+ + Cl^-$, which prevails in solutions of high water content, equations (11-3-8) and (11-3-9) may be converted to

$$E^0_m - (E^{0*}_m - 0.05915 \log a_w) = 0.05915 \log \frac{\gamma_{H_3O} \gamma_{Cl}}{\gamma^*_{H_3O} \gamma^*_{Cl}} \tag{11-3-11}$$

where a_w is the activity of the water in any mixture. Similarly,

$$E^0_N - (E^{0*}_N - 0.05915 \log a_w) = 0.05915 \log \frac{f_{H_3O} f_{Cl}}{f^*_{H_3O} f^*_{Cl}} \tag{11-3-12}$$

The activity of pure water is always taken to be unity. Partial vapor pressure data indicate that as an approximation, N_1, the mol fraction of water, may be substituted for a_w in solutions of high water content. This suggests the plot of (E_N^{0*} − 0.05915 log N_1) versus $1/D$, shown in Figure (11-3-4). In contradistinction to the result shown in Figure (11-3-3), the points for all solvents fall very nearly on the same line. This striking result may prove of considerable importance in organizing data of this kind, if it is verified by future experimental investigations.

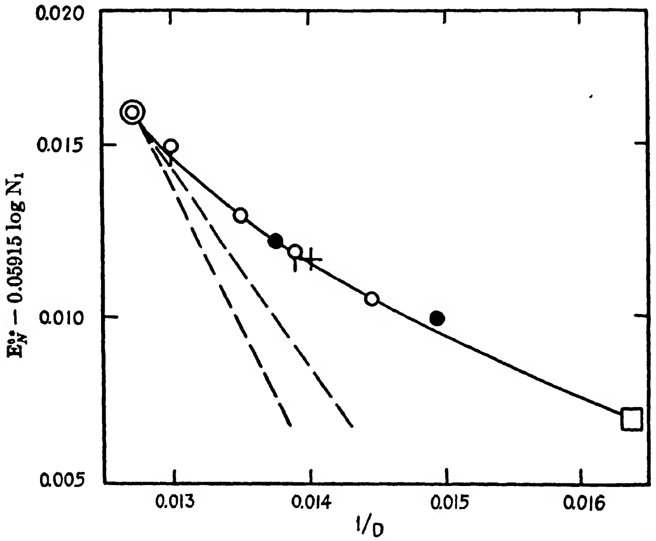

Fig. (11-3-4). Plots of the function, $E_N^{0*} - 0.05915 \log N_1$, against $1/D$ ⊙, water; ♀, glycerol-water; ○, methanol-water; ●, ethanol-water; + isopropanol-water; □, dioxane-water. Dashed lines are plots of equation (11-3-13)

The transfer corresponding to equations (11-3-10), (11-3-11), and (11-3-12) is at unit activity and activity coefficient (hypothetical ideal solution at unit molality) and is therefore independent of the effect of the ionic atmosphere. The electrostatic theory of this effect has been developed in Chapter (3), Section (10), and shown to lead to the Born equation (3-10-13). For a 1-1 electrolyte at 25°, this equation becomes

$$\frac{E_N^0 - E_N^{0*}}{0.05915} = 1.210 \times 10^2 \frac{D_1 - D_2}{D_1 D_2} \sum \frac{1}{b_j} \qquad (11\text{-}3\text{-}13)$$

if $\ln f_{\pm(c)}$ be replaced by the corresponding expression for the electromotive force. Results given by this equation are indicated by the dashed lines in Figures (11-3-3) and (11-3-4). The lower plots have been computed using 1.2 for $\sum 1/b_j$, which corresponds roughly to values derived from crystallographic radii. The upper dashed graphs represent the result obtained from equation (11-3-13) when $\sum 1/b_i = 0.8$, which results from a mean ionic diameter 5 Å, if the radii of both ions are assumed to be equal. Although the agreement with this rough procedure is not good, the result shows that the theoretical result is of the right order of magnitude. The phenomenon is too complicated to be completely explained by so simple an electrostatic theory.

The characteristics of the variation of E_m^{0*} over wider ranges of dielectric constants are shown in Fig. (11-3-5). Curve (2) represents E_m^{0*} versus $1/D$ for ethanol-water mixtures, from pure water to pure alcohol. The intermediate values of E_m^{0*}, not given in Table (11-3-2), were derived from the data of Harned and Fleysher.[26] Curve (1) for methanol-water mixtures was drawn tentatively to the value in pure alcohol. Curve (3) represents the results of the dioxane-water mixtures. The final point is in solution of dielectric constant 9.6, and is still quite far from a pure dioxane solution which possesses a dielectric constant of 2.1. The dashed straight line represents the result computed from Born's equation. We note that this equation is more than sufficient to account for the large change of E_m^{0*} in media containing from 100 to 2 per cent water. The very rapid decrease of E_m^{0*} with $1/D$, as the water content of the mixture becomes small, takes place under conditions where the oxonium ion, H_3O^+, is being replaced by (solvent)H^+ according to the reaction, $H_3O^+ + \text{(solvent)} \rightleftharpoons H_2O + \text{(solvent)}H^+$. The concentration of the dioxane in the dioxane-water

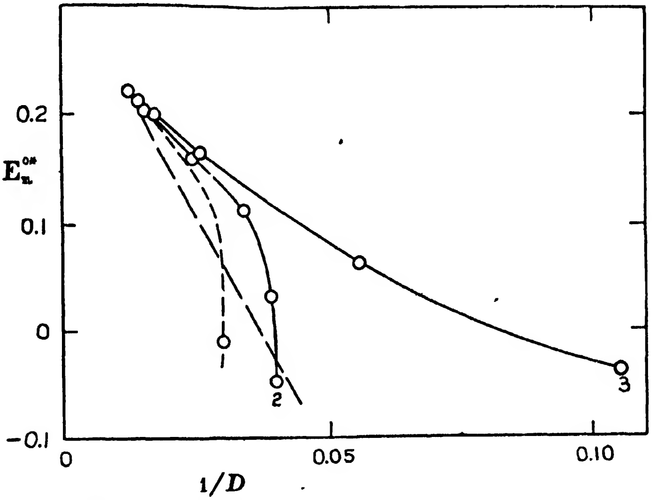

Fig. (11-3-5). E_m^{0*} versus $1/D$ over wide variation of dielectric constant. Curve (1), methanol-water; Curve (2), ethanol-water; Curve (3), dioxane water. Dashed line is a plot of equation (11-3-13)

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[26] H. S. Harned and M. H. Fleysher, *J. Am. Chem. Soc.*, 47, 82 (1925).

mixtures is not sufficient to show this effect. This subject will be further amplified in subsequent discussions of medium effects [Chapter (15)].

(4) THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN AQUEOUS SOLUTIONS

A comprehensive discussion of the activity coefficient and other thermodynamic properties of hydrochloric acid, computed from electromotive measurements, will now be undertaken. The results will indicate to what extent the interionic attraction theory applies, and what additional parameters are required to express the actual results.

The most extensive investigation of cell (11-2-1) has been carried out by Harned and Ehlers.[27] They extended their measurements from 0 to 60° at 5° intervals, and from 0.004 to 4 *M* concentration. The accuracy obtained by them was of the order of ±0.05 mv. The smoothed results, over the temperature range, were expressed by the equation

TABLE (11-4-1). OBSERVED AND CALCULATED MEAN ACTIVITY COEFFICIENTS

m	0°			25°†		60°	
	(E.M.F.)	(F.P.)	(Calc.)	(E.M.F.)	(Calc.)	(E.M.F.)	(Calc.)
0.001	0.9668	0.9661	0.9667	0.9656	0.9654	0.9632	0.9628
.002	.9541	.9534	.9541	.9521	.9524	.9491	.9489
.005	.9303	.9300	.9311	.9285	.9285	.9235	.9235
.01	.9065	.9064	.9080	.9048	.9045	.8987	.8975
.02	.8774	.8772	.8798	.8755	.8751	.8666	.8660
.05	.8346	.8341	.8366	.8304	.8299	.8168	.8170
.1	.8027	.8021	.8032	.7964	.7946	.7813	.7780
.2	.7756	.7754	.7749	.7667	.7650	.7437	.7437
.5	.7761	.774	.7753	.7571	.7563	.7237	.7234
1.	.8419	.840	.8415	.8090	.8091	.7541	.7567
1.5	.9452	.....	.9465	.8962	.8960	.8178	.8196
2.	1.078	.....	1.081	1.0090	1.0085	.9072	.9059
3.	1.452	.....	1.454	1.316	1.313	.....	.....
4.	2.006	.....	2.005	......	......	....	.....

† T. Shedlovsky and D. A. MacInnes, *J. Am. Chem. Soc.*, **58**, 1970 (1936), have obtained values at 25° below 0.1 *M* from cells with liquid junctions.

$$E = E_{25} + a(t - 25) + b(t - 25)^2 + c(t - 25)^3 \qquad (11\text{-}4\text{-}1)$$

and the constants of this equation are given in Table IV of their second communication. The results from 0.0001 to 0.002 *M* inclusive were obtained from the graphs of the left side of equation (11-2-4) which were employed in evaluating E^0.

Upon rearrangement of equation (11-2-3), we obtain,

$$\log \gamma_\pm = -\log m - \frac{(E - E^0)}{2k} \qquad (11\text{-}4\text{-}2)$$

The values of $\gamma_\pm$ given in Table (11-4-1A) were computed from E obtained by equation (11-4-1), and E^0 from Table (11-2-2). The results in parenthe-

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[27] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **54**, 1350 (1932); **55**, 652 (1933); **55**, 2179 (1933).

sis were obtained from extrapolated electromotive forces, and are not in the range of concentration of the observed results. Values at intermediate temperatures may be obtained by interpolation. An error of ±0.05 mv corresponds to an error of the order of ±0.001 in the activity coefficient. The values at 20 and 25° agree very closely with those obtained from electromotive force measurements by Güntelberg,[28] and by Randall and Young.[29] Åkerlöf and Teare[30] have extended the measurements of cell (11-2-1) to include acid concentrations from 3 to 16 M. Their values of $\log \gamma_\pm$ from 0 to 50° are given in Table (14-9-1A).

An important confirmation of the reliability of these results is obtained by comparing them with values of the activity coefficient, at the freezing point, $\gamma'_\pm$, computed by Randall and Young from the freezing point measurements of Randall and Vanselow.[31] Table (11-4-1) shows the agreement between values computed from electromotive force and freezing point data and leaves little doubt that our assumption regarding the nature of the cell reaction is a very close approximation to the actual cell process.

(5) Calculation of the Activity Coefficient of Hydrochloric Acid in Water by the Extended Debye and Hückel Theory

By combining equations (1-8-13), (3-5-8), and (3-6-4), we obtain for a 1-1 electrolyte

$$\log \gamma_\pm = -\frac{\mathcal{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} + \text{Ext.} - \log(1 + 0.01802\nu m) \qquad (11\text{-}5\text{-}1)$$

where Ext. represents the total contribution of the extended terms. This equation represents the total effect of Coulomb forces on the activity coefficient of a completely dissociated electrolyte, if the dielectric constant of the medium, acid and water, remains constant. The activity coefficient of an actual electrolyte approaches the theoretical prediction as its concentration approaches zero. To describe the behavior of a real electrolyte, it is necessary to add a linear term in c, [Equation (10-4-8)], or terms of a power series in c. Thus,

$$\begin{aligned}\log \gamma_\pm = {} & -\frac{\mathcal{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} + \text{Ext.} + Bc \\ & + \sum_{n>2} A_n c^{n/2} - \log(1 + 0.01802\nu m)\end{aligned} \qquad (11\text{-}5\text{-}2)$$

where B and A_n are constants at constant temperature and pressure. Experimental values of activity coefficients of strong electrolytes up to 1 M concentration can be represented with high accuracy without the terms

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[28] E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

[29] M. Randall and L. E. Young, *J. Am. Chem. Soc.*, **50**, 989 (1928).

[30] G. Åkerlöf and J. W. Teare, *J. Am. Chem. Soc.*, **59**, 1855 (1937).

[31] M. Randall and A. P. Vanselow, *J. Am. Chem. Soc.*, **46**, 2418 (1924).

of powers higher than unity.[32] The determination of the parameters A' and B can be accomplished by solving two equations as outlined in Chapter (10), Section (4) [Equation (10-4-9)]. In the earlier calculations of these parameters, Hückel,[33] Harned,[34] and Harned and Åkerlöf[35] used results from 0.1 to 3 M, and the equation with the term linear in c only. Their values for A', and consequently [Equation (3-5-9)] their values of the mean distance of approach, $\mathring{a}$, are somewhat low. Better values of $\mathring{a}$ may be obtained if the constants of the equation be derived from the experimental results in the region from 0.01 to 1 M. This determination is very sensitive since, for example, a change in $\mathring{a}$ from 4.2 to 4.3 causes a change in the first term on the right of equation (11-5-1) of only one in the third decimal place of the activity coefficient at 0.1 M.

Harned and Ehlers solved the equation for $\mathring{a}$ directly from the experimental results at temperatures from 0 to 60°, at 5° intervals. All their values for $\mathring{a}$ were in the range 4.3 ± 0.2, while nine of the thirteen results (from 10 to 50° inclusive) were 4.33 ± 0.03. This is an important result since it indicates that the mean distance of approach varies little, if at all, with the temperature. We note that this value of $\mathring{a}$ is considerably greater than the sum of the ionic radii determined from crystallographic data. This result is to be expected in dilute solutions since the ions are hydrated. Shedlovsky and MacInnes[36] obtained 4.6 from cells with liquid junction when they used equation (11-5-2) with the first, third and fifth terms only. By using the expression $D'c^2$ in place of $\Sigma A_n c^{n/2}$ in equation (11-5-2), Harned and Ehlers obtained a very close fit with the results from 0 to 60°, and from 0.005 M to 2, or 4 M. Their computations were made by employing the values of $\mathfrak{S}_{(f)}$ and $\kappa/c^{1/2}$ given in Table (5-2-1), and $\mathring{a} = 4.3$. B and D' were found to vary linearly with the temperature. Thus,

$$B = 0.1390 - 0.000392t \qquad (11\text{-}5\text{-}3)$$

$$D' = 0.0070 - 0.000033t \qquad (11\text{-}5\text{-}4)$$

In Table (11-4-1), the observed activity coefficients, and the values computed by equation (11-5-2) are given at 0, 25 and 60°. In Table (11-5-1), an equation and constants, a_1 and b_1, are given by means of which c may be computed from m. This table also includes values of the parameters A', B and D', and the slopes $\mathfrak{S}_{(f)}$ at 5° intervals from 0 to 60°. This completes the data necessary for the employment of equation (11-5-2). The concordance of calculated and observed results shown in Table (11-4-1) is excellent, since with very few exceptions the maximum deviation is of

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[32] Scatchard and Prentiss have employed a power series in c of the form, $\mathfrak{S}_{(f)}\sqrt{c} + Bc + Cc^{3/2} + Dc^2 + \cdots$

[33] E. Huckel, *Physik. Z.*, **26**, 93 (1925).

[34] H. S. Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926).

[35] H. S. Harned and G. Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[36] T. Shedlovsky and D. A. MacInnes, *J. Am. Chem. Soc.*, **58**, 1970 (1936).

TABLE (11-5-1). DATA FOR THE CALCULATION OF THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID ACCORDING TO EQUATION (11-5-2),

$$\log \gamma_{\pm} = -\frac{\mathcal{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} + \text{Ext.} + Bc + D'c^2 - \log(1 + 0.03604\, m)$$

where

$$\frac{c}{m} = a_1 - b_1 m$$

Valid from 0 to 4 M (0 to 25°); from 0 to 2 M (30 to 60°)

t	0	5	10	15	20	25	30	35	40	45	50	55	60
$\mathcal{S}_{(f)}$	0.487	0.490	0.494	0.498	0.502	0.506	0.512	0.517	0.522	0.528	0.534	0.541	0.547
A'	1.395	1.398	1.402	1.405	1.409	1.414	1.418	1.423	1.428	1.433	1.439	1.445	1.450
B	.1390	.1371	.1351	.1332	.1312	.1292	.1272	.1253	.1233	.1214	.1194	.1175	.1155
D'	.0070	.0068	.0067	.0065	.0063	.0061	.0060	.0058	.0057	.0055	.0054	.0052	.0050
a_1	0.9998	1.0000	0.9995	0.9990	0.9982	0.9972	0.9958	0.9941	0.9922	0.9901	0.9879	0.9855	0.9832
$b_1 \times 10^2$	1.707	1.742	1.760	1.782	1.805	1.817	1.822	1.825	1.825	1.815	1.815	1.805	1.805

Values of Ext.

m	0°	25°	60°	m	0°	25°	60°
0.001	−0.00009	−0.00010	−0.00011	0.2	−0.00067	−0.00072	−0.00085
.002	− .00015	− .00018	− .00019	.5	− .00045	− .00049	− .00057
.005	− .00027	− .00030	− .00036	1	− .00027	− .00028	− .00032
.01	− .00041	− .00045	− .00053	1.5	− .00017	− .00019	− .00020
.02	− .00055	− .00061	− .00072	2	− .00012	− .00013	− .00015
.05	− .00071	− .00077	− .00091	3	− .00007	− .00007	− .00008
.1	− .00075	− .00080	− .00094	4	− .00004	− .00005	− .00006

the order of ±0.001 in $\gamma_\pm$, which corresponds to ±0.05 mv error. The results at the lower temperatures (0 and 5°, from 0.01 to 0.1 *M*) are not quite as good as those at the higher temperatures. In view of the agreement of the observed results with the results from freezing point measurements, we are not inclined to ascribe this discrepancy to experimental error only.

From a few general considerations of equation (11-5-2), it is possible to describe the behaviors of highly dissociated electrolytes. For 1-1 electrolytes in water, Ext., the contribution of the extended terms is very small, amounting at most to about one in the third decimal place of the activity coefficient, and neet not concern us for the present. A typical completely dissociated 1-1 electrolyte will possess a mean distance of approach, $\mathring{a}$, of about 4. If we consider a number of electrolytes with this value of $\mathring{a}$, the first term on the right of equation (11-5-2) will be the same for each of them. On the other hand, the values of *B* may vary widely (from 0.01 to 0.2 for halides), and may be used to distinguish the individual characteristics of electrolytes in the more concentrated solutions. This behavior is very well illustrated in Fig. (11-5-1), in which are plotted the total contributions to log $\gamma_\pm$, due to the limiting law [Equation (3-4-9)], to the first term on the right of equation (11-5-2), and to the sum of this term and the linear term, *Bc*. It is to be noticed that the higher the value of *B*, the sharper the minimum characteristic of many strong electrolytes.

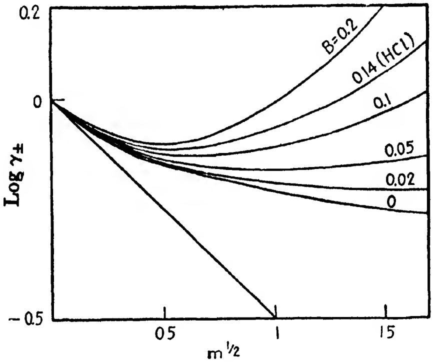

Fig. (11-5-1). Illustrating the magnitudes of the different terms of equation (11-5-1) at 25° ($\mathring{a}$ = 4)

It is also a matter of importance to consider the order of magnitude of the terms in equation (11-5-2) in the case of an actual electrolyte such as hydrochloric acid. In very dilute solutions, the terms in *c*, or higher powers of *c*, are very small compared to the Debye and Hückel contribution, but even at 0.001 *M*, they are detectable. For example, at 0.002 *M* and 0° the first, second, and remaining terms contribute −0.02050, −0.00015, and +.00028, respectively. Thus, the terms, $Bc + \cdots$, are twice the magnitude of Ext. At 0.1 M, these terms contribute −0.10680, −0.00075, +0.01394, respectively, while at 4 M the respective contributions are −0.25458, −0.00004, and +0.6153. We note that at 0.1 M, the term linear in c is about fifteen times the contribution of the extended terms.

(6) THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN MEDIA CONTAINING ORGANIC SOLVENTS

The characteristics of the variation of the activity coefficient with acid concentration, temperature, and dielectric constant (or solvent composition) may be illustrated strikingly by the extensive investigations of dioxane-water mixtures [Data in Table (11-6-1A)]. In Fig. (11-6-1), all of the values of log $\gamma_\pm$ at 25°, and some of those, given in Table (11-6-1A) at 0 and 50°, have been plotted against $m^{1/2}$ for mixtures containing 0, 20, 45, 70 and 82 per cent dioxane. The straight lines represent the plots of the limiting law of the interionic attraction theory at 25°. Values of the limiting slopes, $\mathcal{S}_{(f)}$, are given in [Table (11-3-1A)].

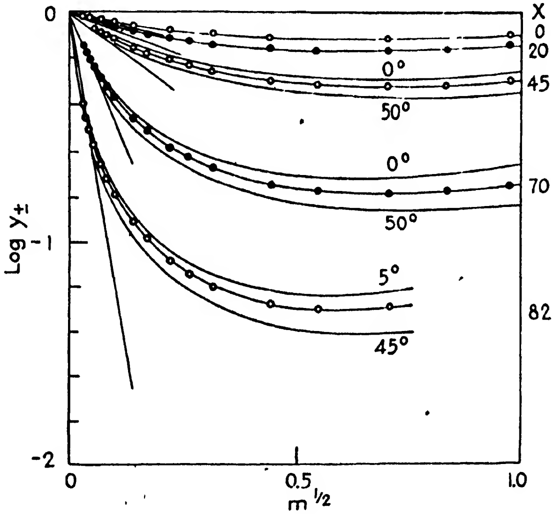

Fig. (11-6-1). Mean activity coefficient of hydrochloric acid in dioxane-water mixtures. X = weight percent of dioxane. Dots and circles represent results at 25°.

The most striking characteristic of these results is the general agreement of the observed values with those predicted by theory in dilute solutions. The limiting slope, $\mathcal{S}_{(f)}$, in the 82 per cent dioxane solutions ($D = 9.53$; $\mathcal{S}_{(f)} = 11.98$) is 23 times that in water ($D = 78.54$; $\mathcal{S}_{(f)} = 0.506$), so that the term $\mathcal{S}_{(f)}\sqrt{c}$, due to Coulombic forces is very large in the former. Thus, the theory predicts a change of a ten-fold variation in $\gamma_\pm$ between 0 and 0.1 N acid. If no ionic association occurs, the observed plot lies above the limiting slope, an effect predicted by the theory which includes the mean distance of approach of the ions. In media containing 0, 20, and 45 per cent, the results conform with this prediction, and at all concentrations lie above the limiting slope. As the dielectric constant decreases, the observed plot in dilute solutions approaches the theoretical curve until, as illustrated by the 70 per cent dioxane mixtures, it superimposes at acid concentrations below 0.002 M. In the 82 per cent dioxane mixtures, the plot of log $\gamma_{\pm}$ may lie below the limiting slope, as indicated by the results at 0.001 and 0.0015 M acid. This behavior parallels that observed from conductance, shown in Fig. (11-1-1). The activity coefficients at all concentrations and temperatures decrease with increasing temperature. Consequently, the relative partial molal heat content, $\bar{L}_2$, is always positive.

In the more concentrated solutions, all the plots in Fig. (11-6-1) show minima. This indicates that the combined effect of restriction of Coulomb forces due to the sizes of the ions, and the concentrated solution effect, which increases the activity of the acid, is very large in the 82 per cent solutions. For example, the limiting law predicts a value log $\gamma_{\pm}$ of -8.569 at 0.5 M, whereas the observed value is -1.2173. If $\mathring{a}$ is taken to be 6, log $\gamma_{\pm}$ equals -1.697 which helps considerably to reduce this discrepancy.

The activity coefficient of hydrochloric acid has been determined in some methanol-, ethanol-, isopropanol-, and glycerol-water mixtures, and in pure methanol and ethanol solutions [Table (11-6-2A)]. The characteristics of this function in these media seems to be normal, and conforms to a pattern similar to that found in aqueous solutions. The results may be computed from 0 to 1 M by the equation,

$$\log \gamma_{\pm} = -\frac{\mathfrak{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} + B'm - \log\,(1 + 0.002M_{XY}m) \qquad (11\text{-}6\text{-}1)$$

In the solutions of higher dielectric constant ($D \geq 60$), the accuracy of the computation is ± 0.002 in $\gamma_{\pm}$, if 4.3 is employed for $\mathring{a}$. The values of B' for 10 and 20 per cent methanol-, 10 and 20 per cent ethanol-, and 10 per cent isopropanol-water mixtures suitable for the calculation are 0.1315, 0.1293, 0.1345, 0.1376, and 0.1373, respectively. In pure methanol and ethanol solutions, other values of the parameters $\mathring{a}$ and B' are required.[37,38]

(7) THE RELATIVE PARTIAL MOLAL HEAT CONTENT OF HYDROCHLORIC ACID. NUMERICAL METHODS FOR COMPUTING $\bar{L}_2$ FROM ELECTROMOTIVE FORCES

The calculation of heat data from electromotive force measurements is very sensitive to experimental errors. If, for 1-1 electrolytes, the temperature coefficient of electromotive force be determined to within ±0.001

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[37] G. Scatchard, *J. Am. Chem. Soc.*, **47**, 2098 (1925).

[38] W. W. Lucasse, *Z. physik. Chem.*, **121**, 254 (1926).

mv/deg., then the error in $\bar{L}_2$ is ±7 cal. The best results are not as accurate as this. If an accuracy of ±30 cal. is obtained, the result may be considered very satisfactory. Since the best calorimetric values have a relative accuracy in $\bar{L}_2$ of ±10 cal., they are better than those derived from electromotive force.

The customary procedure for evaluating $\bar{L}_2$ from electromotive forces requires measurements at many temperatures. The results are smoothed graphically against concentration, and values are obtained at convenient round concentrations. The constants of some suitable function, such as equation (10-5-12), are obtained from these results at each concentration by the method of least squares, or by plotting first order differences.[39] In the case of hydrochloric acid, Harned and Ehlers employed equations (10-5-12), and evaluated $\bar{L}_2$ by equation (10-5-15). They also computed $\bar{L}_2$ by the differentiation of the Debye and Hückel equation (11-5-2) in a manner similar to that by which equation (3-8-5) was derived. The resulting equation is

$$\bar{L}_2 = \frac{2\mathcal{S}_{(\bar{H})}\sqrt{2c}}{1 + A\sqrt{2c}} - \frac{2.3481 \times 10^7 T^{1/2}}{(1 + A\sqrt{2c})^2 D^{3/2}}\left[c\frac{\partial A}{\partial T} + \frac{A}{2}\frac{\partial c}{\partial T}\right]$$
$$- 4.6052 \times RT^2\left[(B + 2D'c)\frac{\partial c}{\partial T} + c\left(\frac{\partial B}{\partial T} + c\frac{\partial D'}{\partial T}\right)\right] \quad (11\text{-}7\text{-}1)$$

Table (11-7-1) contains values of $\bar{L}_2$ at 10, 25, 40, and 60°, obtained by the two methods of calculation. Table (11-7-2) contains an equation and parameters by means of which $\bar{L}_2$ may be computed at all temperatures from 0 to 60°. The values obtained by the first method were smoothed by plotting against $m^{1/2}$. At all temperatures from 10 to 60°, the two series of results exhibit a maximum deviation of 40 cal. At 0°, the discrepancy is somewhat greater. The second method is more complicated, but yields more reliable results. The term, $\partial c/\partial T$, is readily computed from density data, $\partial B/\partial T$ and $\partial D'/\partial T$ are known from equations (11-5-3) and (11-5-4), and we have shown that $\mathring{a}$ may be considered independent of the temperature.

It is instructive to investigate the contribution to $\bar{L}_2$ due to the first, second, and final terms of equation (11-7-1). The first term, designated (1) in Fig. (11-7-1), is always positive, and contributes the most to $\bar{L}_2$ in the dilute solutions. The second term is negative in the case of hydrochloric acid, since $c\partial A/\partial T > A\partial c/2\partial T$. The sum of the first and second terms is indicated by (1) + (2) in the figure. Since both $\partial B/\partial T$ and $\partial D'/\partial T$ are negative in the case of hydrochloric acid, the third term is positive, and constitutes the major contribution to $\bar{L}_2$ in concentrated solutions. The curve designated (1) + (2) + (3) represents the right member of equation (11-7-1).

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[39] H. S. Harned and L. F. Nims, *J. Am. Chem. Soc.*, **54**, 423 (1932).

TABLE (11-7-1). THE RELATIVE PARTIAL MOLAL HEAT CONTENT OF HYDROCHLORIC ACID. (1) COMPUTED BY EQUATION (10-5-15); (2) COMPUTED BY EQUATION (11-7-1)

m	10°	25°	40°	60°
0.001 (1)	16	22	27	39
.005 (1)	18	37	60	90
(2)	34	45	59	79
.01 (1)	19	46	75	117
(2)	48	63	81	108
.02 (1)	27	64	101	155
(2)	64	85	109	145
.05 (1)	74	120	169	238
(2)	99	130	165	219
.1 (1)	101	160	221	300
(2)	135	175	222	295
.2 (1)	172	238	307	414
(2)	189	242	306	395
.5 (1)	319	402	488	614
(2)	319	391	483	608
1. (1)	502	626	748	944
(2)	503	611	728	900
1.5 (1)	676	840	1000	1230
(2)	698	831	975	1184
2.0 (1)	866	1040	1236	1506
(2)	900	1059	1230	1470
3.0 (1)	1264	1510	....	....
(2)	1302	1507	....	....
4.0 (1)	1696	1982	....	....
(2)	1735	1991	....	....

TABLE (11-7-2)[a]. CONSTANTS OF THE EQUATION $\bar{L}_2 = \bar{L}_2(0°) + \alpha t + \beta t^2$ Valid from 0 to 60°[b]

m	$\bar{L}_2$ (0°)	α	β
0.005	28	0.70	0.003
.01	39	1.00	.003
.02	52	1.30	.004
.05	82	1.85	.006
.1	113	2.50	.008
.2	159	3.20	.009
.5	272	4.70	.011
1.	427	6.80	.015
1.5	615	8.20	.019
2.	791	10 00	.023
3.	1175	12.45	.031
4.	1604	14.70	.040

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[a] G. Åkerlöf and J. W. Teare [*J. Am. Chem. Soc.*, **59**, 1855 (1937)] have evaluated $\bar{L}_2$ from 0 to 50°, and from 3 to 16 *M* from electromotive for data.

[b] Values of $\bar{L}_2$ obtained from cells are in good agreement with the recent calorimetric results of J. M. Sturtevant [*J. Am. Chem. Soc.*, **62**, 584 (1940)]. Maximum deviation is 31 cal. at 3 *M*.

Further consideration of the variation of the B and D' parameters with temperature is helpful in summarizing the general behavior of $\bar{L}_2$ for different electrolytes in concentrated solutions. For hydrochloric acid, $\partial B/\partial T$ and $\partial D'/\partial T$ are both negative, and the third term is positive. It is sometimes found that these coefficients are positive, and the third term of equation (11-7-1) is negative. The curve designated by (1) + (2) − (3) illustrates an electrolyte which possesses values of these coefficients equal in magnitude, but opposite in sign to the values for hydrochloric acid, and which possesses an å-value equal to 4.3. Curves (1) + (2) + (3) and (1) + (2) − (3) represent extreme cases. The values of $\bar{L}_2$ for most 1-1 electrolytes are between these curves. As an example, we have included on the graph the values of $\bar{L}_2$ for sodium hydroxide in aqueous solution. Since the å value is approximately 3.5, the curve is slightly higher than the corresponding hydrochloric acid curve in dilute solution. The curve passes through a maximum when $m^{1/2}$ equals 0.4 ,indicating that $\partial B/\partial T$ is positive. Then, there appears a minimum when $m^{1/2}$ equals 1.2, which indicates that $\partial D'/\partial T$ is negative. This illustrates, in a general way, the behavior of $\bar{L}_2$ for 1-1 electrolytes in water.

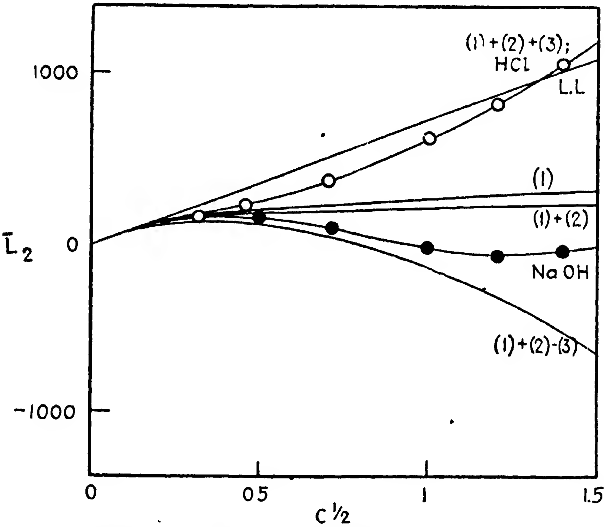

Fig. (11–7–1). Variation of $\bar{L}_2$ with $c^{1/2}$ at 25° according to equation (11–7–1). å = 4.

The characteristic behavior of the relative partial molal heat content as a function of the dielectric constant is apparent from the graphs in Fig. (11-7-2). $\bar{L}_2$ at 25° in dioxane-water mixtures is plotted against $m^{1/2}$. The straight lines, drawn from the origin, represent values computed by the limiting theoretical equation, $\bar{L}_2 = \mathfrak{S}_{(H)} \sqrt{c}$. Values of $\mathfrak{S}_{(H)}$, computed by equation (3-8-6), are to be found in Table (11-7-1A). We note that there is an increasing tendency for the experimental curves to be higher than the limiting values in dilute solution as the dioxane content of the mixtures increases. All the curves have similar characteristics. After the first rapid rise in dilute solutions, their slopes decrease, and rise again as the solutions become more concentrated.

The uncertainty, due chiefly to the difficulties of extrapolation, increases with increasing dioxane concentration. In the 82 per cent dioxane mixture, the error may amount to several hundred calories. The accuracy relative to a given concentration is better than this, and is estimated to be of an order of 100 cal. Equations for the calculation of $\bar{L}_2$ in these mixtures are given in Table (11-7-2A).

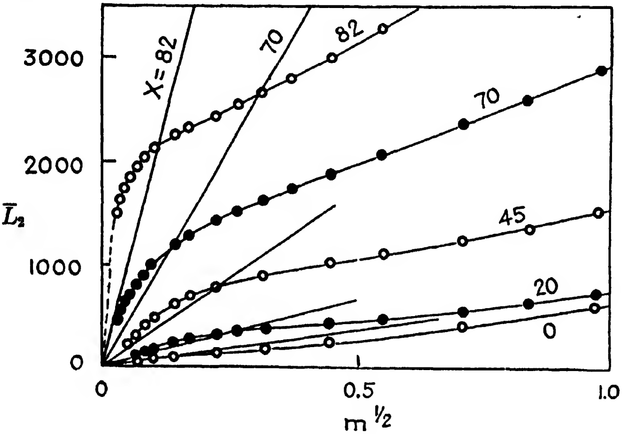

Fig. (11-7-2). Relative partial molal heat content of hydrochloric acid in dioxane-water mixtures at 25°. Straight lines represent limiting law. X = weight percent of dioxane.

(8) THE RELATIVE PARTIAL MOLAL HEAT CAPACITY OF HYDROCHLORIC ACID

The relative partial molal heat capacity may be determined by equation (10-5-17),

$$\bar{J}_2 = 46{,}120(c - c_0)T \qquad (11\text{-}8\text{-}1)$$

where c and c_0 are the constants of equations (10-5-12) and (10-5-13). Since the determination of this quantity involves the second differential coefficient of the original electromotive force data, high accuracy cannot be expected. On the other hand, values obtained by this method are of real interest for purposes of comparison with calorimetric determinations. In Table (11-8-1) values of $(c - c_0)$ are given from which $\bar{J}_2$ may be computed at temperatures from 0 to 60°. Harned and Ehlers also computed this quantity from values of $\bar{L}_2$, calculated by equation (11-7-1). The results at 25° are given in the table.

TABLE (11-8-1). THE RELATIVE PARTIAL MOLAL HEAT CAPACITY OF HYDROCHLORIC AND HYDROBROMIC ACIDS

m	HCl $(c - c_0) \times 10^6$	HBr $(c - c_0) \times 10^6$	$\bar{J}_2(25°)$		
			HCl[1]	HCl[2]	HCl[3]
0.001	0.03	0.04	0.3	...	0.3
.005	.08	.10	.9	...	1.1
.01	.11	.15	1.2	...	1.5
.02	.15	.20	1.5	...	2.1
.05	.22	.26	2.1	...	3.1
.1	.28	.31	2.9	2.4	3.8
.2	.34	.35	3.7	3.4	4.8
.5	.43	...	5.3	5.3	6.0
1.	.58	..	7.5	7.5	8.1
1.5	.74	...	9.1	9.2	10.1
2.	.87	...	11.2	10.6	12.0
3.	1.14	...	14.1	13.0	15.8
4.	1.4	...	16.7	15.0	19.1

[1] Equation (11-7-1).

[2] Equation (11-8-1).

[3] Calorimetric Values. F. T. Gucker Jr., and K. H. Schminke, *J. Am. Chem. Soc.*, **54**, 1358 (1932).

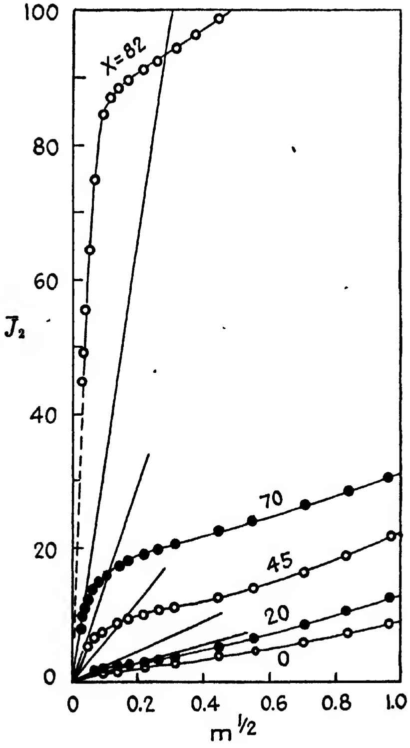

Fig. (11-8-1).

Relative partial molal heat capacity of hydrochloric acid in dioxane-water mixtures at 25°. Straight lines represent limiting law. X = weight percent of dioxane.

Gucker and Schminke[40] have determined this quantity in concentrated solutions at 25° by calorimetric measurements. Their results may be represented by the equation, $\bar{J}_2(25°) = 7.5m^{1/2}$, and values computed by this expression are included in the table. The agreement between these results and those derived from the electromotive forces is very good, considering the difficulties encountered in obtaining these quantities.

Values of $\bar{J}_2(25°)$ in water, and in the dioxane-water mixtures designated, are plotted against $m^{1/2}$ in Fig. (11-8-1). The straight lines represent the limiting equation (5-2-15), $\bar{J}_2(25°) = \mathcal{S}_{(c_p)}\sqrt{c}$, for the relative partial molal heat capacity, resulting from the interionic attraction theory. Relative to a given acid concentration, these results are valid to within a few calories (± 2). The extrapolation in the case of the 82 percent dioxane mixtures, represented by the dashed line, may be subject to a large error ($\sim$ 10 cal.). The rapid increase in this quantity in the media of low dielectric constant is illustrated strikingly by these results.

(9) THE TRANSFERENCE NUMBERS OF HYDROCHLORIC ACID IN WATER AND DIOXANE-WATER MIXTURES FROM 0 TO 50°

In Chapter (6), Section (6), the transference numbers of a few electrolytes determined by the very accurate moving boundary method, were discussed in relation to the limiting equation of the interionic attraction theory. In Chapter (10), Section (6), it was shown that the transference number of an electrolyte may be obtained from measurements of the electromotive forces of cells with and without liquid junctions by equation (10-6-12). This method has been employed by Harned and Dreby[41] in an extensive study of the cation transference number of hydrochloric acid in water, and in dioxane-water mixtures from 0 to 50°. The results constitute the most extensive survey of the transference number of an electrolyte as a function of its concentration, the temperature, and solvent composition.

The required data were obtained from the electromotive forces, $\mathbf{E}_T$ and $\mathbf{E}$, of the cells,

$$\text{Ag-AgCl} \mid \text{HCl } (m), \text{ Dioxane } (X), \text{ } H_2O \text{ } (Y) \mid \text{HCl } (m_R), \text{ Dioxane } (X), \text{ } H_2O \text{ } (Y) \mid \text{AgCl-Ag};$$

and

$$\text{Ag-AgCl} \mid \text{HCl } (m), \text{ Dioxane } (X), \text{ } H_2O \text{ } (Y) \mid H_2 \mid \text{HCl } (m_R), \text{ Dioxane } (X), \text{ } H_2O \text{ } (Y) \mid \text{AgCl-Ag};$$

with and without liquid junctions, respectively. The electromotive forces of the cells with liquid junction were measured by Harned and Dreby,

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[40] F. T. Gucker Jr. and K. H. Schminke, *J. Am. Chem. Soc.*, **54**, 1358 (1932).

[41] H. S. Harned and E. C. Dreby, *J. Am. Chem. Soc.*, **61**, 3113 (1939).

and those of the cells without liquid junction were computed by them from the measurements of the cells

$$H_2 \mid HCl\ (m),\ \text{Dioxane}\ (X),\ H_2O\ (Y) \mid AgCl\text{-}Ag$$

discussed in section (3). HCl (m_R) denotes a fixed reference concentration.

According to equation (10-6-12), the cation transference number, T_+, is given by

$$T_+ = d\mathbf{E}_T/d\mathbf{E} \qquad (11\text{-}9\text{-}1)$$

T_+, at any particular concentration, is the slope of the plot of $\mathbf{E}_T$, the electromotive force of the cell with liquid junction, versus $\mathbf{E}$, the electromotive force of the cell without liquid junction. It is well known that the accuracy of this method, which requires the evaluation of a slope, is not as great as that of the moving boundary method, but it is reliable and rapid, and therefore suitable for an extensive investigation.

The actual evaluation of the slope of $\mathbf{E}$ against $\mathbf{E}_T$ may be carried out by expressing these quantities by empirical functions, and performing the differentiation,[42] or by a purely graphical method. Hamer,[43] and Harned and Dreby[41] found the following graphical method to be more satisfactory than any other method, graphical or analytical, which they could devise.

Since the range of values of $\mathbf{E}_T$ and $\mathbf{E}$ is large, plotting them directly causes the loss of significant figures, necessary for the accurate determination of the slope. Harned and Dreby used a method whereby values of $\mathbf{E}$ at equally spaced intervals of $\mathbf{E}_T$ were determined without the loss of significant figures. Furthermore, the results in this form made it possible to determine the slope analytically, and hence improve the accuracy.

Deviation functions, defined by the relations,

$$X \equiv \mathbf{E} + 2k \log m/m_R; \qquad X_T \equiv \mathbf{E}_T + 2k \log m/m_R \qquad (11\text{-}9\text{-}2)$$

gave values of X_T and X corresponding to the values of $\mathbf{E}_T$ and $\mathbf{E}$. These values of X_T and X covered a very small range, so that they could be plotted very accurately with no loss of significant figures. Values of X_T were interpolated graphically to the round concentrations at which values of X were known. These results were then used to make a plot of $X - X_T$ versus X. It is to be noted that $X - X_T$ is simply $\mathbf{E} - \mathbf{E}_T$. From this graph, $X - X_T$ was read off for values of X_T corresponding to values of $\mathbf{E}_T$ spaced at equal intervals of 0.01 v. The latter were obtained from a plot of $\mathbf{E}_T$ against X_T. Adding together the appropriate values of $X - X_T$ and $\mathbf{E}_T$ gave the desired results, namely, $\mathbf{E}$ corresponding to $\mathbf{E}_T$, spaced at intervals of 0.01 v. The data were then in a form for the analytical determination of the slope.

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[42] D. A. MacInnes and J. A. Beattie, *J. Am. Chem. Soc.*, **42**, 1117 (1920).

[43] W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 662 (1935).

A derivative function obtained by Rutledge[44] was employed for the determination. It is of the form

$$\frac{d\mathrm{E}}{d\mathrm{E}_T} = f(\mathrm{E}) = \frac{1}{12h}(C_{-2}\mathrm{E}_{-2} + C_{-1}\mathrm{E}_{-1} + C_0\mathrm{E}_0 + C_1\mathrm{E}_1 + C_2\mathrm{E}_2) \qquad (11\text{-}9\text{-}3)$$

where $d\mathrm{E}/d\mathrm{E}_T$ is the slope at a value, E, of the dependent variable; h is the magnitude of the chosen interval in the independent variable; E_{-2}, E_{-1}, etc., are consecutive values of the dependent variable; and C_{-2}, C_{-1}, etc., are constants. There are three sets of constants, the choice of any one being dependent on whether the slope is to be determined at E_{-1}, E_0, or E_1. Except at the extremes, the values of the slope were determined by taking the average of the results obtained by placing the Rutledge formula in the three possible positions.

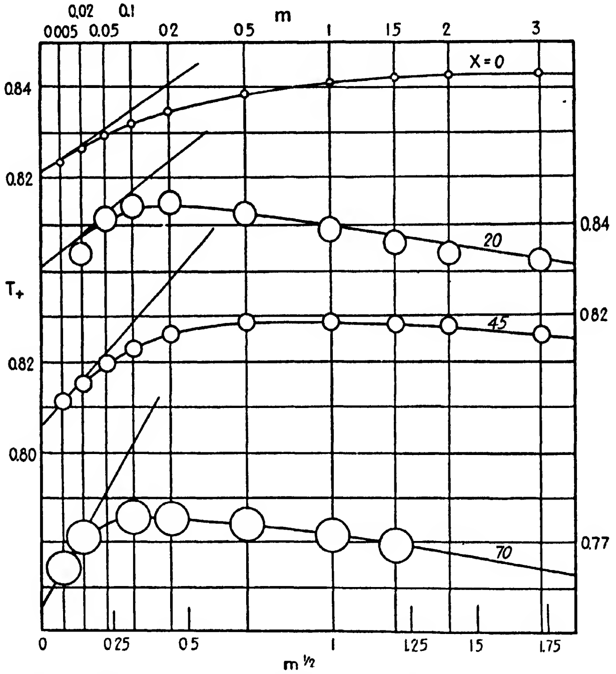

Fig. (11-9-1). The cation transference number of hydrochloric acid in dioxane-water mixtures at 25°. Gross error equals diameter of circles. X = % dioxane by weight. Limiting theoretical law is represented by the straight lines from the origin of each plot.

T_+ obtained in this manner were plotted against E_T, and from this graph, smoothed values of T_+ at round acid concentrations were obtained.

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[44] G. Rutledge, *J. Math. Phys. M. I. T.*, **8**, 1 (1929); *Phys. Rev.*, **40**, 262 (1932).

From these results, the limiting value of the transference number was determined by the method of Longsworth,[45] described in Chapter (6), Section (7). This consists in plotting the function

$$T_+^{0\prime} = \frac{T_+\Lambda' + 1/2\beta^*\sqrt{c}}{\Lambda' + \beta^*\sqrt{c}.} \tag{11-9-4}$$

where

$$\Lambda' = \Lambda^0 - (\alpha^*\Lambda^0 + \beta^*)\sqrt{c} \tag{11-9-5}$$

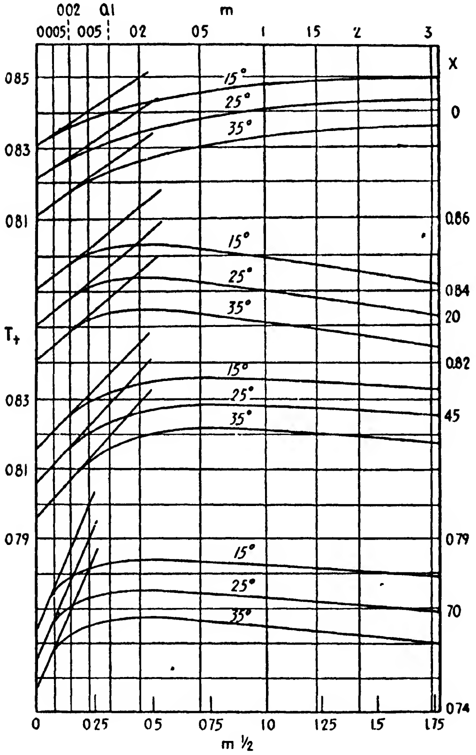

Fig. (11-9-2)
The cation transference number of hydrochloric acid at 15°, 25°, and 35° in dioxane-water mixtures. Straight lines represent theoretical limiting law. X = weight percent of dioxane.

against the acid concentration, c, and extrapolating to zero concentration. The actual plots of Harned and Dreby were straight lines at concentrations from 0.01 to $0.1N$,[46] and were satisfactory for extrapolation. The values of T_+ at concentrations less than $0.01N$ were more erratic. This behavior is due to the difficulty of obtaining slopes at the extreme ends of the curve.

From a consideration of the Rutledge derivative function, it can be shown

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[45] L. G. Longsworth, *J. Am. Chem. Soc.*, **54**, 2741 (1932).

[46] In the case of the 20 percent dioxane solution, this plot was straight from 0.03 to $0.1N$. The results below $0.03N$ were erratic.

that an error of 0.01 mv. in **E**, or $\mathbf{E}_T$, causes an error of 0.001 in T_+. From the mean deviations of the observed electromotive forces, or from the average deviations of the observed points from the smoothed graphs, the average error in T_+ may be estimated. A representation of extent of error is contained in Fig. (11-9-1). T_+ at 25° is plotted for pure water, and 20, 45 and 70 percent dioxane-water mixtures. The estimated gross error is given by the diameters of the circles, and is 0.002 in water, and 0.005, 0.004 and 0.008 for the three dioxane-water mixtures, respectively.

The final smoothed values of T_+^0 and T_+ in these solvents and at 5° intervals from 0 to 50° are contained in Table (11-9-1A), and plots of this quantity at 15, 25, and 35° are shown in Fig. (11-9-2). The straight lines represent values calculated by the Onsager limiting equation for the transference number,

TABLE (11-9-1). T_+ OF HYDROCHLORIC ACID FROM ELECTROMOTIVE FORCES AND BY THE MOVING BOUNDARY METHOD AT 25°

c	0.005	0.01	0.02	0.05	0.100
T_+ (M.B.)	0.8239	0.8251	0.8266	0.8292	0.8314
T_+ (E.M.F.)	(.824)	(.825)	(.827)	(.830)	(.830)

$$T_+ = \mathcal{S}_{(T)}\sqrt{c} = \frac{(2T_+^0 - 1)\beta^*}{2\Lambda^0}\sqrt{d_0}\sqrt{m} \tag{11-9-6}$$

Values of $\mathcal{S}_{(T)}$ are given at the bottom of Table (11-9-1A). The results conform with theory since all the curves converge towards the predicted slopes as the concentration of electrolyte decreases.

According to Fig. (11-9-1), the best results were obtained with solutions of the acid in pure water. That the error is no greater than one or two in the third decimal place is shown in Table (11-9-1), in which the values obtained by Longsworth, by the more accurate moving boundary method, are compared with those obtained by Harned and Dreby from electromotive forces. In this, the most favorable case, the agreement is good, and the deviations are of the order of magnitude predicted from the mean deviations of the original electromotive forces.

Harned and Dreby also measured the electromotive forces of the cells with liquid junction in 82 percent dioxane-water mixtures. The results were less accurate than those in the mixtures of lower dioxane content, particularly when the cells contained acid at concentrations less than 0.05M. Since no transference number data are available in media of dielectric constant as low as these ($D(25°) = 9.57$), the results have a value, and are included in Table (11-9-1A).

Chapter (12)

Strong 1-1 Electrolytes in Aqueous Solution

In Chapter (9), the important and extensive determinations of freezing point lowerings of 1-1 electrolytes have been described, and in Chapter (8), the recent very valuable determinations of the heat data of these solutions have been discussed. In the present survey, a more general discussion of the results obtained from measurements of the thermodynamic properties of these solutions will be given.

The importance of a systematic study of the activity coefficients of electrolytes was first emphasized by Lewis.[1] By the use of an empirical extrapolation function, containing two constants, Lewis and Linhart,[2] and Lewis and Randall[3] made the first systematic attempt to compute activity coefficients from the existing data. A similar attempt was made by Harned,[4] who employed an empirical equation for $\gamma_{\pm}$ which contained three empirical constants. These investigations, made before the limiting law of the Debye and Hückel theory was known, were subject to large errors in extrapolation, and the activity coefficients computed at that time had an accuracy not greater than ±0.01.

When the limiting law of Debye and Hückel was used, rapid advances were made in improving the accuracy of the extrapolations. Hückel,[5] Scatchard,[6] Harned[7] and Randall and Young,[8] by employing the limiting law, or extended forms of the Debye and Hückel theory, were able to improve considerably the accuracy of the extrapolations. A general survey of the results obtained before 1929 was made by Harned.[9]

In the following discussion, a summary based on the available data on 1-1 electrolytes will be given. Further, the heat data in relation to activity coefficients will be discussed. Sodium and potassium chlorides will be

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[1] G. N. Lewis, *J. Am. Chem. Soc.*, **34**, 1631 (1912).

[2] G. N. Lewis and G. A. Linhart, *J. Am. Chem. Soc.*, **41**, 1951 (1919).

[3] G. N. Lewis and M. Randall, *Ibid.*, **43**, 1112 (1921). See also "Thermodynamics," McGraw-Hill Book Company, New York (1923).

[4] H. S. Harned, *J. Am. Chem. Soc.*, **42**, 1808 (1920); **44**, 252 (1922). See also H. S. Harned, H. S. Taylor, "Treatise on Physical Chemistry," 1st Edition, p. 744-747, Van Nostrand and Company, New York, (1924).

[5] E. Huckël, *Physik. Z.*, **26**, 93 (1925).

[6] G. Scatchard, *J. Am. Chem. Soc.*, **47**, 648 (1925); **47**, 2098 (1925).

[7] H. S. Harned, *Ibid.*, **48**, 326 (1926).

[8] M. Randall and L. E. Young, *Ibid.*, **50**, 989 (1928).

[9] H. S. Harned, H. S. Taylor, "Treatise on Physical Chemistry," 2nd Edition, Table IX, p. 772.

treated first, since they have been investigated most thoroughly, both at 25° and at other temperatures. The activity coefficients of these electrolytes may then be employed as reference for the computation of the activity coefficients of other electrolytes by the isopiestic vapor pressure method [Section (3)]. Sections (5) to (8) include a survey of the behaviors of the activity coefficients of 1-1 electrolytes in relation to the theory of Debye and Hückel, its modifications, and extensions to concentrated solutions.

In addition, Section (10) is devoted to the "salting effects" of electrolytes upon neutral molecules, and Section (11) to the surface tension of ionic solutions. Both of these phenomena are discussed in relation to the theories developed in Chapter (3), Sections (10) and (11).

(1) THE THERMODYNAMICS OF SODIUM CHLORIDE SOLUTIONS FROM ELECTROMOTIVE FORCE AND CALORIMETRIC DATA

(a) The Activity Coefficient in Dilute Solutions at 25°

Extensive measurements of electromotive forces of cells without liquid junction containing 1-1 halides and hydroxides have been made.[10] It was found that the flowing amalgam electrodes behaved very well in solutions at concentrations higher than $0.05M$. At lower concentrations, these electrodes exhibit erratic behaviors.

In order to avoid this difficulty, Brown and MacInnes[11] have measured very carefully the cell

$$\text{Ag-AgCl} \mid \text{NaCl}\ (c_1) \mid \text{NaCl}\ (c_2) \mid \text{AgCl-Ag}$$

It has been shown [Equation (10-6-14)] that the electromotive force of this cell is given by

$$\mathbf{E} = -\frac{2RT}{\mathbf{F}} \int_{\mathrm{I}}^{\mathrm{II}} T_+ \, d \ln a_\pm \tag{12-1-1}$$

where the integration extends from the concentration of the solution at electrode (I) to the solution at electrode (II). Due to the very accurate knowledge of transference numbers obtained by MacInnes and Longsworth [Chapter (6)], and to the fact that the above cells may be measured

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[10] D. A. MacInnes and K. Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915); D. A. MacInnes and J. A. Beattie, *Ibid.*, **42**, 1117 (1920); M. Knobel, *Ibid.*, **45**, 70 (1923); H. S. Harned and F. E. Swindells, *Ibid.*, **48**, 126 (1926); H. S. Harned, *Ibid.*, **47**, 676 (1925); **51**, 416 (1929); H. S. Harned and S. M. Douglas, *Ibid.*, **48**, 3095 (1926); H. S. Harned and O. E. Schupp Jr., *Ibid.*, **52**, 3886 (1930); H. S. Harned and L. F. Nims, *Ibid.*, **54**, 423 (1932); H. S. Harned and J. C. Hecker, *Ibid.*, **55**, 4838 (1933); H. S. Harned and M. A. Cook, *Ibid.*, **59**, 497 (1937), H. S. Harned and C. C. Crawford, *Ibid.*, **59**, 1903 (1937); G. Åkerlöf and G. Kegeles, *Ibid.*, **62**, 620 (1940).

[11] A. S. Brown and D. A. MacInnes, *J. Am. Chem. Soc.*, **57**, 1356 (1935); similar measurements from 15 to 45° have been made by G. J. Janz and A. R. Gordon, *Ibid.*, **65**, 218 (1943).

at low concentrations, a good extrapolation can be made, and accurate activity coefficients obtained.

In differential form, equation (12-1-1) at 25° becomes

$$dE = -0.1183T_+ \,(d\log c + d\log y_\pm) \tag{12-1-2}$$

Instead of expressing T_+ as a function of c and performing the integration, a simpler method due to Longsworth was employed. The transference number at any concentration is given by

$$T_+ \equiv T_R + \Delta T_+ \tag{12-1-3}$$

where T_R is its value at a reference concentration, in this case, $0.1N$. By substituting this value of T_+ in (12-1-2), rearranging the terms and integrating, we obtain

$$\begin{aligned} -\Delta \log y_\pm \equiv \log y_\pm - \log y_R = -\frac{E}{0.1183T_R} - \log\frac{c}{c_R} \\ - \frac{1}{T_R}\int_{c_R}^{c} \Delta T_+ \, d\log c - \frac{1}{T_R}\int_{y_R}^{y_\pm} \Delta T_+ \, d\log y_\pm \end{aligned} \tag{12-1-4}$$

The first two terms on the right of this equation may be evaluated immediately from the experimental data. The third term may be obtained by graphical integration. The last term, which is relatively small, was obtained by graphical integration, using preliminary values of Δ log $y_\pm$ obtained from the first three terms. The preliminary values of Δ log $y_\pm$ were then corrected, and the process repeated until further approximations were found unnecessary. Since $y_\pm$ equals unity at infinite dilution, we may write

$$\log y_\pm = C' - \Delta\log y_\pm \tag{12-1-5}$$

where C' is the constant, log y_R. Substituting for log $y_\pm$ the value given for log $f_\pm$ in equation (5-2-8), and rearranging terms, we obtain

$$\Delta \log y_\pm - \mathfrak{S}_{(f)}\sqrt{c} = C' + A'(C' - \Delta\log y_\pm)\sqrt{c} \tag{12-1-6}$$

By plotting the left-hand member of this equation against $(C' - \Delta\log y_\pm)\sqrt{c}$, the constants C' and A' can be evaluated after a few approximations. By this procedure Brown and MacInnes obtained -0.1081 and -0.1088 for log $y_\pm$ and log $\gamma_\pm$, respectively, at the concentration $0.1M$. Their values of $y_\pm$ and $\gamma_\pm$ are given in Table (12-1-1). The last column contains values of $y_\pm$ computed by equation (10-4-8).

(b) The Relative Partial Molal Heat Content of Sodium Chloride in Water

In Table (8-2-2A) we have given values of $\bar{L}_2$ of sodium chloride in aqueous solution at 25°. These data have been supplemented by Gulbransen and Robinson[12] who reported calorimetric measurements at 10, 15, 20, and 25°. Their results are given in Table (12-1-2).

[12] E. A. Gulbransen and A. L. Robinson, *J. Am. Chem. Soc.*, **56**, 2637 (1934).

(c) The Activity Coefficient of 0.1M Sodium Chloride from 0 to 100°

From the value of 0.7784 for $\gamma_{\pm}$ at $0.1M$ and 25°, and the values of $\bar{L}_2$ at this concentration, given in Table (12-1-2), $\gamma_{0.1}$ may be calculated at other temperatures by means of the equation

$$\frac{2\partial \ln \gamma_{0.1}}{\partial T} = -\frac{\bar{L}_{2(0.1)}}{RT^2} \tag{3-8-1}$$

TABLE (12-1-1). ACTIVITY COEFFICIENT OF SODIUM CHLORIDE AT 25°

m	$y_{\pm}$	$\gamma_{\pm}$	$y_{\pm}$ (calc.)[1]
.005	0.9283	0.9283	0.9281
.007	.9171	.9171	.9169
.01	.9034	.9032	.9034
.02	.8726	.8724	.8724
.03	.8513	.8509	.8515
.04	.8354	.8348	.8354
.05	.8221	.8215	.8224
.06	.8119	.8111	.8115
.08	.7940	.7927	.7938
.1	.7796	.7784	.7796

[1] Calculated by equation in (10-4-8); $\mathring{a} = 4$; $B = 0.047$.

TABLE (12-1-2). THE RELATIVE PARTIAL MOLAL HEAT CONTENT OF SODIUM CHLORIDE FROM HEATS OF DILUTION†

$$\bar{L}_2\left(\frac{\text{cal}}{\text{mol}}\right)$$

m	10°	15°	20°	25°
0.0001	3.0	4.7	5.3	6.3
.0005	8.3	12.0	13.1	14.8
.001	11.5	16.5	17.9	20.1
.005	25.6	35.8	38.1	42.2
.01	34.8	46.0	51.0	55.8
.05	43.2	65.0	76.3	93.7
.1	30.2	57.7	76.6	99.6
.2	−20.	9.4	54.2	85.0
.404	−130.	−89.9	−19.4	30.0
.816	......	......	−169.7	−123.3

† These are the values originally reported by Gulbransen and Robinson. The results at 25° differ slightly from those in Table (8-2-2A).

$\bar{L}_{2(0.1)}$ is given as a function of the temperature by the equation

$$\bar{L}_{2(0.1)} = -1277 + 4.62T \tag{12-1-7}$$

Upon substitution of $\bar{L}_{2(0.1)}$ in equation (3-8-1), integration, and evaluation of the integration constant by employing the value of 0.7784 for $\gamma_{0.1}$ at 25°, we obtain

$$-\log \gamma_{0.1} = \frac{139.56}{T} + 1.1625 \log T - 3.2358 \tag{12-1-8}$$

This should yield an accurate value of $\gamma_{0.1}$ over a wide temperature range, provided that the relative partial heat capacity (= 4.62) changes not at all or little with temperature. Values of $\gamma_{0.1}$ computed in this manner at various temperatures are given in Table (12-1-3).

Harned and Nims[13] have measured the cells without liquid junction

$$\text{Ag-AgCl} \mid \text{NaCl } (m) \mid \text{Na}_x\text{ Hg} \mid \text{NaCl } (0.1) \mid \text{AgCl-Ag}$$

at 5° intervals from 0 to 40°. These flowing amalgam cells are not reliable at concentrations below 0.05*M*, and, therefore, the extrapolation must be made from the results at higher concentrations. To this end the Debye and Hückel functions [Equations (10-4-8) or (10-4-9)] may be used. Experience has shown that a good extrapolation can be effected by this method if the results from 0.1 to 1*M* are employed. If these equations are applied over a greater concentration range (0.1 to 3*M*), somewhat low values of $\mathring{a}$ and $\gamma_\pm$ will be obtained. In the third column of Table (12-1-3) are given the results obtained from these data by Harned and Cook.[14] The value of the mean distance of approach of the ions was found to be 4.0 ± 0.1 Å at all temperatures. The agreement of these values of $\gamma_{0.1}$ with those in the first column is satisfactory.

TABLE (12-1-3). $\gamma_{0.1}$ OF SODIUM CHLORIDE BY INDEPENDENT METHODS

t	Eq. (12-1-8)†	Eq. (10-4-9)	B.P‡
0	0.7809	0.781	.....
5	.7809	.782	.....
10	.7807	.782	.....
15	.7802	.7815	.....
20	.7793	.781	.....
25	.7784	.779	.....
30	.7773	.776	.....
35	.7757	.774	.....
40	.7743	.773	.....
50	.770	.....	.....
60	.766	.....	0.766
70	.761	.....	.762
80	.756	.....	.757
90	.751	.....	.752
100	.745	.....	.746

† H. S. Harned, *J. Franklin Inst.*, **226**, 623 (1938); E. R. Smith and J. K. Taylor, *Bur. Standards J. Res.*, **25**, 731 (1940).

By employing equation (10-4-9), in combination with the equations for the osmotic coefficient obtained from elevation of the boiling point, Smith[15] obtained the values in the last column of Table (12-1-3). He also employed 4.0 for the mean distance of approach of the ions. The agreement with the results obtained by equation (12-1-8) is very satisfactory.

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[13] H. S. Harned and L. F. Nims, *J. Am. Chem. Soc.*, **54**, 423 (1932).

[14] H. S. Harned and M. A. Cook, *J. Am. Chem. Soc.*, **61**, 495 (1939).

[15] R. P. Smith, *J. Am. Chem. Soc.*, **61**, 500 (1939).

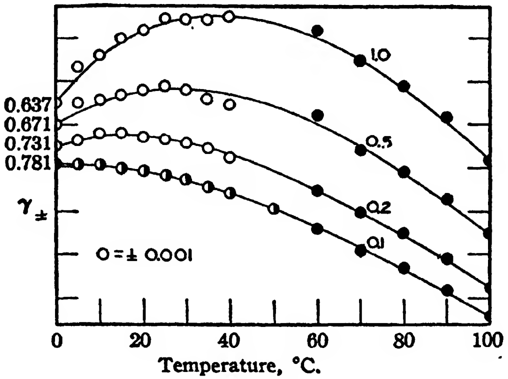

Fig. (12-1-1). The mean activity coefficient of sodium chloride in 0.1, 0.2, 0.5 and 1*M* solutions as a function of temperature. ◑, Calculated by equation (12-1-8); ○, electromotive force; ●, boiling point. Diameter of circles equals 0.002.

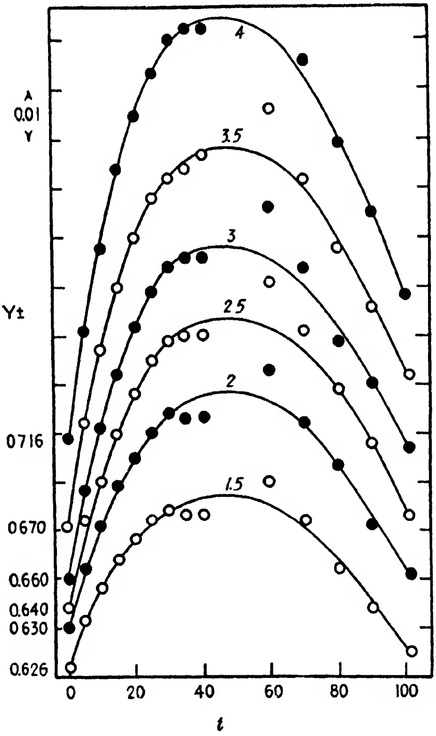

Fig. (12-1-2). The mean activity coefficient of sodium chloride from 1.5 to 4 molal concentration as a function of temperature. 0 to 40°, Electromotive force; 60 to 100°, Boiling point. Diameter of circles equals 0.002.

In Table (12-1-1A), simple equations and their constants for computing c from m are given for solutions of 1-1 electrolytes. These will be found useful in certain theoretical computations.

(d) The Osmotic and Activity Coefficients of Sodium Chloride from 0 to 100°

From the electromotive force data,[16] and boiling point data,[17,18] the activity coefficient and osmotic coefficient of sodium chloride from 0 to 100° and from 0.1 to 4M have been computed. The activity coefficient is plotted against the temperature in Figs. (12-1-1) and (12-1-2), respectively. Similar plots for the osmotic coefficients are given in Fig. (12-1-3). The results from 0 to 40° were obtained from the electromotive forces, and those from 60 to 100° from the boiling points. We note that the results indicate a small error in both types of measurement. At 35 and 40, the values of $\gamma_{\pm}$ from the electromotive force measurements appear to be too low in some cases, while at 60 and 70° the values obtained by

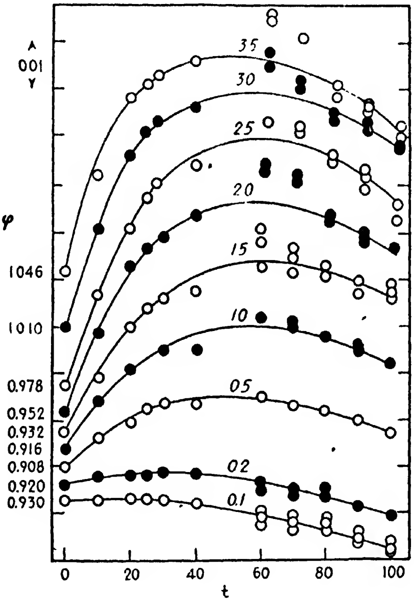

Fig. (12-1-3). Osmotic coefficients of sodium chloride solutions from 0.1 to 3.5M. 0 to 40°, Electromotive force; 60 to 100°, Boiling point. Diameter of circles equals 0.002.

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[16] H. S. Harned and L. F. Nims, *J. Am. Chem. Soc.*, **54**, 423 (1932).

[17] R. P. Smith, *Ibid.*, **61**, 497 (1939).

[18] R. P. Smith and D. S. Hirtle, *Ibid.*, **61**, 1123 (1939).

the boiling point method appear somewhat too high. This is most apparent for the results at 60°, and at high concentrations (1.5 to $4M$). The same remarks apply to the osmotic coefficients. Values of $\gamma_\pm$ are given in Table (12-1-2A). These results were smoothed in the range of 35 to 70° according to the plots shown in the figures so that the graphs may be reproduced. The diameter of the circles in these plots equals 0.002 in $\gamma_\pm$, which corresponds to about 0.15 mv, or 0.0003° in the boiling point rise. At 40° the maximum deviation of the observed results from the curve is 0.004, or about 0.3 mv.

(e) Relative Partial Molal Heat Content and Heat Capacity of Sodium Chloride

The best estimate of the relative partial molal heat content from the electromotive force and boiling point measurements has been made by Smith and Hirtle.[18] Equation (3-8-1) may be written in the form

$$\frac{\partial \ln \gamma_\pm}{\partial(1/T)} = \frac{\bar{L}_2}{2R} \tag{3-8-1}$$

from which it is apparent that $\bar{L}_2$ may be determined from the slopes of the tangents to the curves of ln $\gamma_\pm$ plotted against $1/T$. The results at 0° are practically the same as those determined from the electromotive force measurements by Harned and Cook. The results at 100° are not so reliable since the slope at the end of the curve is not well defined. Fig. (12-1-4) contains the plots of these results together with the calorimetric results of Robinson,[19] Gulbransen and Robinson[20] and Rossini.[21] These data are given in (12-1-3A). The values obtained from the electromotive forces and boiling points are represented in the figure by circles, and the calorimetric results by dots. The dotted line was obtained from Rossini's values at 18°. The agreement between the results derived by these entirely independent methods is very satisfactory from 10 to 25°. At the higher temperatures no calorimetric data are available for comparison. The results at the higher temperatures are only an approximate estimate, but they serve to give a comprehensive view of the behavior of $\bar{L}_2$ over a wide temperature range.

The values of relative partial molal heat capacity, $\bar{J}_2$, obtained by Smith and Hirtle from the temperature coefficient of $\bar{L}_2$ are given with those obtained by calorimetric methods in Table (12-1-4). Up to $1M$, the results obtained from the boiling point and electromotive force measurements agree with those of Gulbransen and Robinson, and at higher temperatures show a trend towards those obtained by Rossini.[22]

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[19] A. L. Robinson, *J. Am. Chem. Soc.*, **54**, 1311 (1932).

[20] E. A. Gulbransen and A. L. Robinson, *Ibid.*, **56**, 2637 (1934).

[21] F. D. Rossini, *Bur. Standards J. Research*, **7**, 47 (1931); *Ibid.*, **6**, 791 (1931).

[22] F. D. Rossini, *Bur. Standard J. Research*, **7**, 47 (1931).

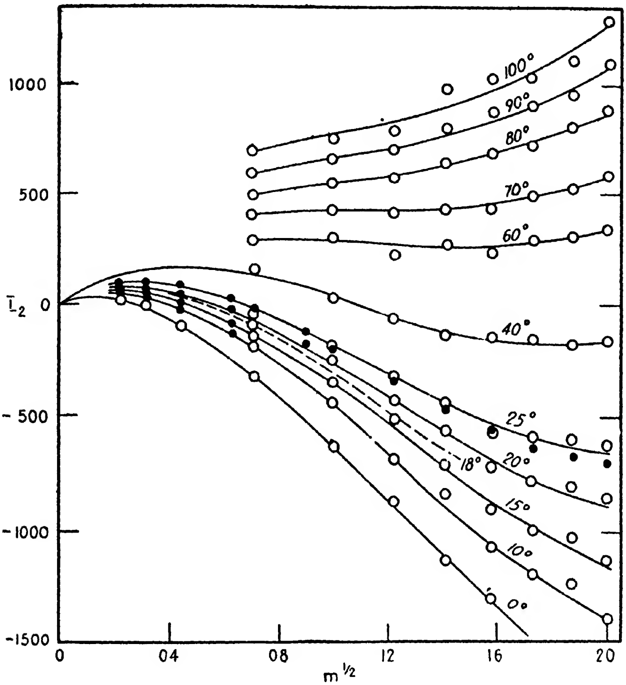

Fig. (12-1-4). L_2 of sodium chloride in aqueous solution. ○, Electromotive force and boiling point (diameter = 50 cal.); ●, Calorimetric (diameter = 30 cal.)

Table (12-1-4). The Relative Partial Molal Heat Capacity of Sodium Chloride

m	$\bar{J}_2$[1]			$\bar{J}_2$[2]	$\bar{J}_2$[3]
	0°	25°	60°	25°	25°
.05	....	3.3	....	3.5	4.8
.1	....	5.4	....	5.	6.8
.2	....	7.	....	7.1	9.6
.5	10	10.	10	11.2	15.3
1.	20	16.	12	15.6	21.6
1.5	25	20.	15	....	26.4
2.	33	24.	19	....	31.0
2.5	35	32.	21	....	34.2
3.	45	35.	21	....	37.2
3.5	51	38.	22	....	40.5
4.	53	41.	24	....	43.2

[1] Boiling point and electromotive force.

[2] Derived by Gulbransen and Robinson from values of L_2 determined calorimetrically.

[3] Derived by Rossini from heat capacity measurements of M. Randall and F. D. Rossini, *J. Am. Chem. Soc.*, **51**, 323 (1929).

(2) THE THERMODYNAMICS OF HYDROBROMIC ACID, POTASSIUM CHLORIDE, SODIUM BROMIDE, AND SODIUM AND POTASSIUM HYDROXIDES IN AQUEOUS SOLUTION

(a) The Standard Potential of the Cell H_2 | HBr (m) | AgBr-Ag

Since the earlier work of Lewis and Storch,[23] and Harned and James[24] on cells with hydrogen and silver-silver bromide electrodes at 25°, extensive measurements have been made[25] over a wide temperature range of the cells containing the acid solutions only,[26] or acid solutions containing a bromide.[27, 28] Two kinds of silver-silver bromide electrodes have been employed. One of these was prepared by heating a mixture of 90 per cent silver oxide and 10 per cent silver bromate to 650°. The other was prepared by heating silver oxide on a platinum spiral to 450°, and then forming silver bromide by electrolyzing hydrobromic acid or a bromide solution. Harned, Keston and Donelson showed that if oxygen is excluded these two types of electrodes give essentially the same result.

Three independent determinations of the standard potential of the silver-silver bromide electrode have been made recently.

(i) E^0 of the above cell, containing hydrobromic acid only, was determined by the method of graphical extrapolation described in Chapter (11), Section (2).

(ii) From the cells

$$H_2 \mid HBr\ (0.01),\ LiBr\ (m) \mid AgBr\text{-}Ag$$

Harned and Donelson obtained E^0 by a similar method.

(iii) That a direct comparison between the silver-silver bromide and chloride electrodes can be made in buffered solutions has been shown by Owen.[29] Consider the cells,

$$H_2 \mid HBO_2\ (m),\ NaBO_2\ (m),\ NaBr\ (m) \mid AgBr\text{-}Ag$$

$$H_2 \mid HBO_2\ (m),\ NaBO_2\ (m),\ NaCl\ (m) \mid AgCl\text{-}Ag$$

measured by Owen and Foering.[30] Their electromotive forces, E^m_{HBr} and E^m_{HCl} are given by the equations

$$E^m_{HBr} = E^0_{HBr} - \frac{RT}{F} \ln \gamma_H \gamma_{Br} m_H m_{Br}$$

$$E^m_{HCl} = E^0_{HCl} - \frac{RT}{F} \ln \gamma_H \gamma_{Cl} m_H m_{Cl}$$

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[23] G. N. Lewis and H. Storch, *J. Am. Chem. Soc.*, **35**, 2544 (1917).

[24] H. S. Harned and G. M. James, *J. Phys. Chem.*, **30**, 1060 (1926).

[25] A. S. Keston, *J. Am. Chem. Soc.*, **57**, 1671 (1935).

[26] H. S. Harned, A. S. Keston and J. G. Donelson, *Ibid.*, **58**, 989 (1936).

[27] H. S. Harned and W. J. Hamer, *Ibid.*, **55**, 4496 (1933).

[28] H. S. Harned and J. G. Donelson, *Ibid.*, **59**, 1280 (1937).

[29] B. B. Owen, *J. Am. Chem. Soc.*, **57**, 1526 (1935).

[30] B. B. Owen and L. Foering, *J. Am. Chem. Soc.*, **58**, 1575 (1936).

Upon eliminating $\gamma_H m_H$ from these equations by means of the thermodynamic equation for the boric acid equilibrium,

$$K_A = \frac{\gamma_H \gamma_{BO_2}}{\gamma_{HBO_2}} \frac{m_H m_{BO_2}}{m_{HBO_2}}$$

and rearranging, we obtain

$$\mathbf{E}^0_{HBr} - f(\gamma) = \mathbf{E}^m_{HBr} + \frac{RT}{\mathbf{F}} \ln K_A + \frac{RT}{\mathbf{F}} \ln m$$

and

$$\mathbf{E}^0_{HCl} - f(\gamma) = \mathbf{E}^m_{HCl} + \frac{RT}{\mathbf{F}} \ln K_A + \frac{RT}{\mathbf{F}} \ln m$$

TABLE (12-2-1). THE STANDARD POTENTIAL OF THE SILVER-SILVER BROMIDE ELECTRODE BY THREE METHODS

$-\pi^0_{Ag\text{-}AgBr} = \mathbf{E}^0_{HBr}$

t	(i)	(ii)	(iii)
0	0.0813	0.08165	....
5	.0796	.07991	0.07986
10	.0777	.07801	.07800
15	.0756	.07593	.07596
20	.0734	.07377	.07374
25[a]	.0711	.07127	.07134[a]
30	.0685	.06872	.06876
35	.0658	.06602	.06600
40	.0629	.06300	.06306
45	.0600	.05995	....
50	.0569	.05666	....

[a] G. Jones and S. Baeckström [*J. Am. Chem. Soc.*, **56**, 1524 (1934)] found 0.0712 at 25°.

These equations may be employed individually to obtain K_A, and then $\mathbf{E}^0_{HBr}$, or K_A may be eliminated, provided that all three electrolytic components are at the same concentration. Thus, subtraction of the second of these equations from the first gives

$$\mathbf{E}^0_{HBr} = \mathbf{E}^0_{HCl} + \mathbf{E}^m_{HBr} - \mathbf{E}^m_{HCl} \tag{12-2-1}$$

Knowing the standard potential of the silver-silver chloride electrode, $-\mathbf{E}^0_{HCl}$, and measuring $\mathbf{E}^m_{HBr}$ and $\mathbf{E}^m_{HCl}$ at one low concentration, $\mathbf{E}^0_{HBr}$ can readily be evaluated. In this connection, see Fig. (15-4-2). The values of $\mathbf{E}^0$ determined by these methods are given in Table (12-2-1). The values of $\mathbf{E}^0_{HCl}$, necessary for the computation by equation (12-2-1), were obtained by equation (11-2-6). Excellent agreement is found between the results in the last two columns, while those in the first column are somewhat lower. The equation

$$-\pi_{Ag-AgBr} = \mathbf{E}^0_{HBr} = 0.07131 - 4.99 \times 10^{-4}(t - 25) - 3.45 \times 10^{-6}(t - 25)^2 \tag{12-2-2}$$

expresses the results in columns (ii) and (iii) to within a few hundredths of a millivolt.

(b) The Thermodynamics of Hydrobromic Acid from Electromotive Force Measurements

The activity coefficient, relative partial molal heat content, and heat capacity of hydrobromic acid have been measured up to $1M$ concentration and from 0 to 60° by Harned, Keston, and Donelson.[31] Values of $\gamma_\pm$ over these temperature and concentration ranges are given in Table (12-2-1A) as well as values of $\bar{L}_2$ and $\bar{J}_2$ at 25°. Since the properties of this acid are very similar in magnitude and character to those of hydrochloric acid, further discussion is not required.

(c) The Thermodynamics of Potassium Chloride in Aqueous Solution

Aqueous solutions of potassium chloride have been investigated by various methods. The electromotive force of the cells

$$\text{Ag-AgCl} \mid \text{KCl}(m) \mid \text{K}_x\text{Hg} \mid \text{KCl}(m_0) \mid \text{AgCl-Ag}$$

have been measured at 25° by MacInnes and Parker,[32] and Harned,[33] at 0° by Smith,[34] and from 0 to 40° by Harned and Cook.[35] The cell

$$\text{Ag-AgCl} \mid \text{KCl}(c_1) \mid \text{KCl}(c_2) \mid \text{AgCl-Ag}$$

has been investigated by Shedlovsky and MacInnes[36] at 25°.

Spencer[37] has computed the activity coefficient from freezing point data at 0°, and Scatchard and Prentiss[38] have made a similar calculation of their own results. Saxton and Smith[39] have computed $\gamma_\pm$ at 100° from boiling determinations. The vapor pressures of potassium chloride solutions at 20° have been measured by Lovelace, Frazer and Sease.[40]

Comparisons of results by these methods are shown in Table (12-2-2). The agreement between the results obtained by the various methods is very good. A more complete set of values of the activity coefficient covering a wider range in temperature is given in Table (12-2-2A).

In Table (12-2-3A), the constants of equations by means of which $\bar{L}_2$ and $\bar{J}_2$ may be computed from 0 to 40° have been compiled. This material will be considered later in this section.

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[31] H. S. Harned, A. S. Keston and J. G. Donelson, *J. Am. Chem. Soc.*, **58**, 989 (1936).

[32] D. A. MacInnes and K. Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915).

[33] H. S. Harned, *Ibid.*, **51**, 416 (1929).

[34] R. P. Smith, *J. Am. Chem. Soc.*, **55**, 3279 (1933).

[35] H. S. Harned and M. A. Cook, *Ibid.*, **59**, 1290 (1937).

[36] T. Shedlovsky and D. A. MacInnes, *J. Am. Chem. Soc.*, **59**, 503 (1937).

[37] H. M. Spencer, *J. Am. Chem. Soc.*, **54**, 4490 (1932).

[38] G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **55**, 4355 (1933).

[39] B. Saxton and R. P. Smith, *J. Am. Chem. Soc.*, **44**, 2826 (1932).

[40] B. F. Lovelace, J. C. W. Frazer and V. B. Sease, *J. Am. Chem. Soc.*, **43**, 102 (1921).

TABLE (12-2-2). THE ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE BY VARIOUS METHODS

m	0°				20°		25°	
	$\gamma_{\pm}$ (E.M.F.)[1]	$\gamma_{\pm}$ (E.M.F.)[2]	$\gamma_{\pm}$ (F.P.)[3]	$\gamma_{\pm}$ (F.P.)[4]	$\gamma_{\pm}$ (E.M.F.)[1]	$\gamma_{\pm}$ (V.P.)[5]	$\gamma_{\pm}$ (E.M.F.)[1]	$\gamma_{\pm}$ (E.M.F.)[6]
0.005	(0.929)		0.929	0.929			(0.927)	(0.9275)
.01	(.904)		.903	.904			(.901)	.902
.05	(.819)		.818	.819	(0.816)		(.815)	.817
.1	.768	.770	.771	(.770)	.770		.769	.770
.2	.717	.717	.719	.717	.718	.721	.719	.719
.3	.683				.688		.688	
.5	.642	.642	.645	.644	.651	.651	.651	.652
.7	.613	.615		.618	.627		.628	
1.	.588	.589	.590	.588	.604	(.604)	.606	.607
1.5	.563	.562	.561		.582		.585	
2.	.547	.548			.573	.573	.576	.578
2.5	.540	.541			.568		.572	
3.	.539	.540			.567	.569	.573	.574
3.5	.540	.542			.571		.574	.576
4.					.574	.572	.582	.581

[1] H. S. Harned and M. A. Cook, cells without liquid junction, *J. Am. Chem. Soc.*, **59**, 1290 (1937); H. S. Harned, *Ibid.*, **41**, 416 (1929).

[2] R. P. Smith, cells without liquid junction, *Ibid.*, **55**, 3279 (1933).

[3] H. M. Spencer, freezing point, *Ibid.*, **54**, 4490 (1932).

[4] G. Scatchard and S. S. Prentiss, freezing point, *Ibid.*, **55**, 4355 (1933).

[5] B. F. Lovelace, J. C. W. Frazer and V. B. Sease, vapor pressure, *Ibid.*, **43**, 102 (1921).

[6] T. Shedlovsky and D. A. MacInnes, cells with liquid junction, *Ibid.*, **59**, 503 (1937).

TABLE (12-2-3). ACTIVITY COEFFICIENTS OF ALKALI HYDROXIDES AT 25°

m	LiOH[1]	NaOH[2]	KOH[3]	CsOH[4]
0.05	(0.803)	(0.818)	(0.824)	(0.831)
.1	.760	.766	.798	.802
.2	.702	.727	.757	.761
.5	.616	.693	.728	.748
1.	.554	.679	.756	.780
1.5	.528	.683	.814	....
2.	.513	.698	.888	....
2.5	.501	.729	.974	....
3.	.494	.774	1.081	....
3.5	.487	.826	1.215	....
4.	.481	.888	1.352	....

[1] H. S. Harned and F. E. Swindells, *J. Am. Chem. Soc.*, **48**, 126 (1926).

[2] H. S. Harned and J. C. Hecker, *Ibid.*, **55**, 4838 (1933) (0.05 to 2 *M*); G. Åkerlöf and G. Kegeles, *Ibid.*, **62**, 620 (1940) (2 to 4 *M*).

[3] H. S. Harned and M. A. Cook, *Ibid.*, **59**, 496 (1937).

[4] H. S. Harned and O. E. Schupp, Jr., *Ibid.*, **52**, 3886 (1930).

(d) The Thermodynamics of Sodium Bromide in Aqueous Solutions from Electromotive Force Measurements

The flowing amalgam cell with silver-silver bromide electrodes has been employed in obtaining the activity coefficient, relative partial molal heat content, and heat capacity by Harned and Crawford.[41] The activity

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[41] H. S. Harned and C. C. Crawford, *J. Am. Chem. Soc.*, **59**, 1903 (1937).

coefficients obtained by them are given in Table (12-2-4A). Equations and their constants are given in Table (12-2-5A) from which $\bar{L}_2$ and J_2 can be computed from 0 to 40°.

(e) The Activity Coefficients of the Alkaline Hydroxides at 25°

The reaction of the cell

$$H_2 \mid MOH(m_2) \mid M_xHg \mid MOH(m_1) \mid H_2; \qquad M = \text{Li, Na, etc.}$$

may be represented by

$$MOH(m_2) + H_2O(m_1) = MOH(m_1) + H_2O(m_2)$$

and its electromotive force by

$$E = 2k \log \frac{\gamma_2 m_2}{\gamma_1 m_1} + k \log \frac{a_{w(m_1)}}{a_{w(m_2)}} \tag{12-2-4}$$

where k equals $2.3026RT/F$, and $a_{w(m_1)}$ and $a_{w(m_2)}$ are the activities of water in the two solutions designated.

The activity coefficients of potassium, sodium, lithium and cesium hydroxides have been computed from measurements of these cells at 25° by Knobel,[42] Harned,[43] Harned and Swindells,[44] and Harned and Schupp.[45] More recently, Harned and Hecker[46] investigated cells containing sodium hydroxide, and Harned and Cook[47] cells containing potassium hydroxide from 0 to 35°. Harned has shown how the correction for the water transfer may be computed from the electromotive forces by employing an equation for $\gamma_\pm$. Harned and Hecker, and Harned and Cook employed a graphical method which is somewhat similar. According to equation (1-8-1), the relation between the activity of the solvent and that of the solute is given by

$$d \ln a_w = -\frac{N_2}{N_1} d \ln a_2 \tag{12-2-5}$$

Since $d \ln a_2 = \nu d \ln \gamma m$

$$d \ln a_w = -\frac{2m}{55.51} d \ln \gamma m \tag{12-2-6}$$

for 1-1 electrolytes in water, and consequently

$$-\frac{1}{2} d \ln a_w = \frac{dm}{55.51} + \frac{m}{55.51} d \ln \gamma \tag{12-2-7}$$

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[42] M. Knobel, *J. Am. Chem. Soc.*, **45**, 70 (1923).

[43] H. S. Harned, *J. Am. Chem. Soc.*, **47**, 676 (1925).

[44] H. S. Harned and F. E. Swindells, *Ibid.*, **48**, 126 (1926).

[45] H. S. Harned and O. E. Schupp Jr., *Ibid.*, **52**, 3886 (1930).

[46] H. S. Harned and J. C. Hecker, *J. Am. Chem. Soc.*, **55**, 4838 (1933).

[47] H. S. Harned and M. A. Cook, *J. Am. Chem. Soc.*, **59**, 496 (1937).

Upon integration between the limits m_1 and m_2, the desired logarithm of the activity ratio is given by

$$\frac{1}{2}\log\frac{a_{w(m_R)}}{a_{w(m)}} = \frac{m - m_R}{2.303 \times 55.51} + \frac{1}{55.51}\int_{m_R}^{m} md \log\frac{\gamma_\pm}{\gamma_R} \tag{12-2-8}$$

Let γ_R and m_R represent a reference activity coefficient and molality. Harned and Hecker used $0.05M$ as a fixed reference concentration. The desired term on the left of this equation may be evaluated by arithmetical approximation. As a first approximation the second term on the right is omitted. The values of the left side at various concentrations are computed and substituted in equation (12-2-4), along with **E** and m. Provisional values of $\log \gamma_\pm/\gamma_R$ are calculated by equation (12-2-4), and used to evaluate the second term of (12-2-8) by graphical integration. This process gives new values of the left side of equation (12-2-8), which may be employed in obtaining more accurate values of the activity coefficient ratio. This procedure is repeated until the equations are satisfied.* Three or four repetitions will satisfy the equations to within 0.01 mv, which is considerably less than the experimental error. This leads to final values of the ratio $\gamma_\pm/\gamma_R$. By appropriate application of the equation of the Debye and Hückel theory (10-4-8), these results may be extrapolated, and a value of γ_R, at the reference concentration, and subsequently $\gamma_\pm$ at the other concentrations, may be found.

Values of $\gamma_\pm$ at 25° determined by this method are given in Table (12-2-3). The extrapolation should be reliable for all but the lithium hydroxide, for which the results are relatively inaccurate.

(f) The Thermodynamics of Aqueous Sodium and Potassium Hydroxides from Electromotive Force Measurements

The activity coefficient, relative partial molal heat content, and heat capacity of sodium hydroxide in water up to $4M$ and from 0 to 35° have been determined by Harned and Hecker.[48] Åkerlöf and Kegeles[49] have made a very extensive investigation of these solutions which covers concentration and temperature ranges from 0.1 to $17M$ and 0 to 70°. Potassium hydroxide solutions from 0 to 40° and up to $4M$ have been studied by Harned and Cook.[50] The activity coefficients of these hydroxides are given in Tables (12-2-6A) and (12-2-7A). Constants of equations by means of which $\bar{L}_2$ and $\bar{J}_2$ may be computed are given in Tables (12-2-8A) and (12-2-9A).

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* G. Åkerlöf and G. Kegeles [*J. Am. Chem. Soc.*, **62**, 620 (1940)] employ an analytical procedure which avoids successive approximations, but which requires the representation of **E** as a function of m by the method of least squares.

[48] H. S. Harned and J. C. Hecker, *J. Am. Chem. Soc.*, **55**, 4838 (1933).

[49] G. Åkerlöf and G. Kegeles, *Ibid.*, **62**, 620 (1940).

[50] H. S. Harned and M. A. Cook, *J. Am. Chem. Soc.*, **59**, 496 (1937).

(g) Comparison of the Relative Partial Molal Heat Content and Heat Capacity as Determined from Electromotive Force and Calorimetric Measurements

In Fig. (12-2-1), $\bar{L}_2$ obtained from heat of dilution data and electromotive forces is plotted against $m^{1/2}$ for hydrochloric acid, potassium chloride, and sodium and potassium hydroxides at 18°. The solid lines represent the values determined by electromotive forces, and the dashed lines those obtained calorimetrically. The maximum discrepancy between the two sets of data is about 60 cals. This agreement is good since the flowing amalgam cells employed in the three cases are among those most difficult to operate. The straight line represents the limiting law of the interionic attraction theory. Similarly, $\bar{L}_2$ for sodium bromide solutions, determined from the electromotive forces, is in good agreement with the calorimetric results of Hammerschmid and Robinson,[51] if allowance is made for a difference of 25 cals., due to the difficulty of extrapolation.

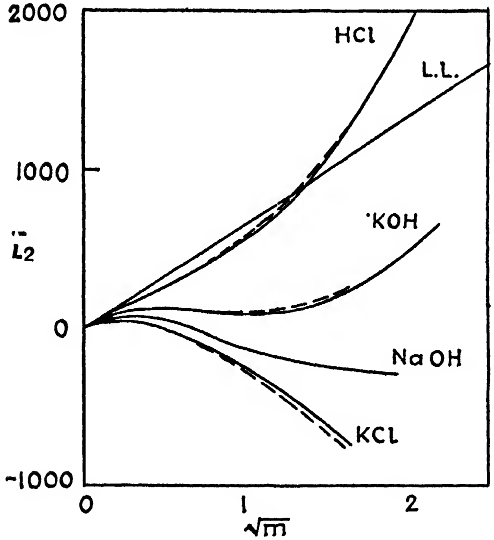

Fig. (12-2-1)
The relative partial molal heat contents of some 1-1 electrolytes at 18°. ——, electromotive force; ----, calorimetry.

Fig. (12-2-2) contains plots of $\bar{J}_2$ of potassium chloride, potassium hydroxide and hydrochloric acid as determined by the two methods. The dashed lines represent the calorimetric results whereas the solid lines represent the values obtained from suitable cells. The agreement is excellent since the maximum deviation is of the order of two calories. The values for sodium hydroxide, not included in the figure, agree equally well.

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[51] A. L. Robinson, *J. Am. Chem. Soc.*, **60**, 1265 (1938); H. Hammerschmid and A. L. Robinson, *Ibid.*, **54**, 3120 (1932).

These illustrations suffice to show that the electromotive force method can be used for obtaining a comprehensive view of the behaviors of $\bar{L}_2$ and $\bar{J}_2$ for quite a number of electrolytes. It should be borne in mind that the electromotive method measures directly $(\bar{F}_2 - \bar{F}_2^0)$ and $\gamma_\pm$. When attempt is made to determine $\bar{L}_2$ and $\bar{J}_2$ by this method, the original data are subjected to a very severe test, since these determinations involve the first and second differential coefficients of the original data. For this reason, the calorimetric determinations should yield the better result, except in cases where the electromotive forces can be measured with extreme accuracy. The agreement noted in the preceding illustrations indicates that the postulated cell mechanisms approach very closely the actual ones.

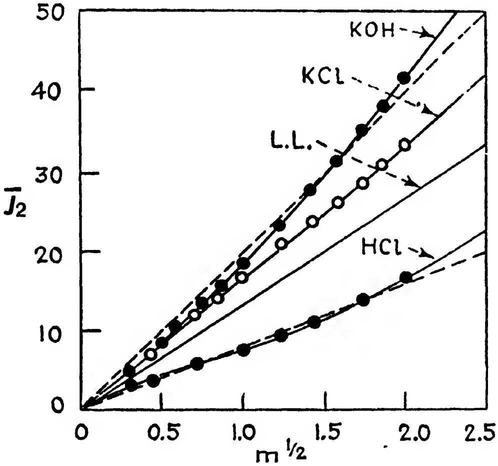

Fig. (12-2-2)
The relative partial molal heat capacities of some 1-1 electrolytes at 25°. ——, electromotive force; ----, calorimetry.

(3) The Activity Coefficients of 1-1 Electrolytes from Isopiestic Vapor Pressure Measurements

(a) Activity Coefficients at 25°

The electromotive force method has been shown to be good when applicable, but is limited to the electrolytes which possess ions for which reversible electrodes may be found. For concentrated solutions, a vapor pressure method is generally applicable, but so far the absolute vapor pressures of only a few electrolytic solutions have been accurately measured. A very valuable contribution to this subject has been made by Robinson and Sinclair,[52] and Robinson,[53] who have greatly improved the isopiestic

[52] D. A. Sinclair, *J. Phys. Chem.*, **37**, 495 (1933).

[53] R. A. Robinson and D. A. Sinclair, *J. Am. Chem. Soc.*, **56**, 1830 (1934); R. A. Robinson, *Ibid.*, **57**, 1161 (1935); **57**, 1165 (1935); **59**, 84 (1937); *Trans. Faraday Soc.*, **35**, 1217 (1939).

vapor pressure comparison method of Bousfield[54] [Chapter (9), Section (4)]. If solutions of two different salts are allowed to equilibrate through the vapor phase and then analyzed, and if the activity of one of the salts at its concentration is known, then the activity coefficient of the other salt may be computed. Let m_R, γ_R, m, and $\gamma_\pm$ be the molalities and activity coefficients of the two salts under the above isopiestic condition, and let a_R represent the activity of the reference salt. Then, since the solvent activities of the two solutions are the same, we have [Equation (1-8-1)]

$$\frac{m_R}{55.51}\,d\ln a_R = -d\ln a_w = \frac{m}{55.51}\,d\ln a_2 \tag{12-3-1}$$

or

$$d\ln \gamma_\pm = d\ln \gamma_R + d\ln \frac{m_R}{m} + \left(\frac{m_R}{m} - 1\right) d\ln \gamma_R m_R \tag{12-3-2}$$

Since

$$d\ln \gamma_R m_R = 2\frac{d\sqrt{a_R}}{\sqrt{a_R}}$$

we obtain upon integration

$$\ln \gamma_\pm = \ln \gamma_R + \ln \frac{m_R}{m} + 2\int_0^{a_R} \left(\frac{m_R}{m} - 1\right) \frac{d\sqrt{a_R}}{\sqrt{a_R}} \tag{12-3-3}$$

from which $\gamma_\pm$ may be evaluated provided that γ_R and a_R are known. The ratio of the concentrations of the isopiestic solutions, m_R/m, may be plotted against m, and the second term on the right evaluated at round concentrations. The third term on the right may be evaluated graphically from a plot of $(m_R/m - 1)/\sqrt{a_R}$ versus $\sqrt{a_R}$. Since $a_R = 0$ when $m = 0$, the plot proceeds to zero.

The problem of obtaining a suitable reference electrolyte still remains. Robinson and Sinclair employed potassium chloride solutions as reference, whereas Scatchard, Hamer and Wood[55] used sodium chloride solutions. The latter placed more weight on vapor pressure measurements and less on electromotive force measurements than the former, and their standard values differ considerably from Robinson's [Table (9-4-1)]. In Table (12-3-1A) Robinson's values of $\gamma_\pm$ at 25° for all the alkali metal halides, nitrates, acetates, p-toluene sulphonates and thallous salts are compiled. These are based on potassium or sodium chloride solutions as standards. The values of $\gamma_\pm$ which he employed for these salts are practically the same as those recorded in Tables (12-1-2A) and (12-2-2A). Robinson's is the most extensive work of this kind at 25°.

The isopiestic vapor pressure measurement is quite accurate, and the results obtained by it agree satisfactorily with those obtained by the

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[54] W. R. Bousfield and E. Bousfield, *Proc. Roy. Soc.* (*London*), **A, 103,** 429 (1923).

[55] G. Scatchard, W. J. Hamer and S. E. Wood, *J. Am. Chem. Soc.*, **60,** 3061 (1938).

electromotive force method. This is clearly illustrated by the data in Table (12-3-1), in which the ratios of the activity coefficients of several salts to that of potassium chloride, determined by both methods, are compiled. From 0.1 to $3M$, the agreement is excellent. The discrepancies at the higher concentrations may be due to solubility effects on the electrodes. This is not certain since this region of concentration has not been investigated as thoroughly with flowing amalgam cells as the region 0.1 to $3M$. Lithium amalgam electrodes are not as reproducible as those of the other alkali metals. Consequently, the agreement with the isopiestic measurements for lithium chloride and bromide is not as good.[56]

TABLE (12-3-1). MEAN ACTIVITY RATIOS AT 25° DETERMINED BY THE ISOPIESTIC VAPOR PRESSURE AND ELECTROMOTIVE FORCE METHODS

m	$\frac{\gamma_{NaCl}}{\gamma_{KCl}}$[c]		$\frac{\gamma_{NaBr}}{\gamma_{KCl}}$		$\frac{\gamma_{KBr}}{\gamma_{KCl}}$		$\frac{\gamma_{CsCl}}{\gamma_{KCl}}$	
	V.P.	E.M.F.	V.P.	E.M.F.	V.P.	E.M.F.[a]	V.P.	E.M.F.[b]
0.1	1.012	1.013	1.016	1.017	1.003	1.004	0.982	0.984
.2	1.024	1.020	1.031	1.029	1.006	1.004	.967	.966
.3	1.033	1.032	1 044	1.044	1.007	1.006	....	....
.5	1.049	1.046	1.069	1.068	1.011	1.013	.929	.931
.7	1.067	1.068	1.097	1.094	1.018	1.018	.915	.916
1.	1.088	1.084	1.136	1.132	1.020	1.019	.898	.898
1.5	1.126	1.122	1.203	1.202	1.027	1.026	.879	.879
2.	1.167	1.165	1.273	1.274	1.037	1.032	.861	.859
2.5	1.210	1.210	1.346	1.352	1.042	1.039	.848	.843
3.	1.257	1.261	1.426	(1.447)	1.047	1.043	.838	.829
3.5	1.307	1.312	1.512	(1 530)	1.052	1.053	....	....
4.	1.361	1.368	1.612	1.613	1.057	1.061	....	....

[a] H. S. Harned, *J. Am. Chem. Soc.*, **51**, 416 (1929).
[b] H. S. Harned and O. E. Schupp Jr., *Ibid.*, **52**, 3886 (1930).
[c] Similar comparisons at 15 and 40° have been made by R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1222 (1939) and P. Olynyk and A. R. Gordon, *J. Am. Chem. Soc.*, **65**, 224 (1943).

(4) CALCULATION OF THE ACTIVITY COEFFICIENT AT VARIOUS TEMPERATURES AND PRESSURES FROM VALUES AT 25° AND ONE ATMOSPHERE

In Tables (8-2-2A) and (8-4-2) and (8-4-3), values of $\bar{L}_2$ and $\bar{J}_2$ are compiled. If the small variation of $\bar{J}_2$ with temperature be neglected, the approximate equation for $\bar{L}_2$,

$$\bar{L}_2 = \bar{L}_{2(T_R)} + \bar{J}_{2(T_R)}(T - T_R) \qquad (12\text{-}4\text{-}1)$$

follows. T_R is some reference temperature. This result can be used to compute activity coefficients at various temperatures from values determined at a given temperature. Thus, according to equation (3-8-1),

$$\left(\frac{\partial \ln \gamma_\pm}{\partial T}\right)_{P,m} = \left(\frac{\partial \ln f_\pm}{\partial T}\right)_{P,m} = -\frac{\bar{L}_2}{\nu RT^2} \qquad (3\text{-}8\text{-}1)$$

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[56] For other similar comparisons see R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

If this equation be combined with (12-4-1) and integrated, we obtain

$$\log \gamma_\pm = \frac{\bar{L}_{2(T_R)} - J_{2(T_R)}T_R}{\nu 2.303RT} - \frac{J_{2(T_R)}}{\nu R}\log T + I \qquad (12\text{-}4\text{-}2)$$

If γ_R at a given temperature, T_R, is known, the integration constant, I, may be computed. [See Section (1) of this chapter]. If the reference temperature is 25°, $T_R = 298.1$ may be substituted into the above equation, and the integration constant expressed in terms of $\log \gamma_\pm$ at this temperature. Thus

$$\log \gamma_\pm = \log \gamma_\pm(25°) + \frac{y}{\nu}\bar{L}_2(25°) - \frac{z}{\nu}J_2(25°) \qquad (12\text{-}4\text{-}3)$$

when

$$y = \frac{298.1 - T}{2.303R\,298.1T} \qquad (12\text{-}4\text{-}4)$$

$$z' = 298.1y - \frac{1}{R}\log\left(\frac{298.1}{T}\right) \qquad (12\text{-}4\text{-}5)$$

Values of the variables, y and z, are given in Table (5-1-2) for temperatures between 0 to 100°C.

According to equation (3-9-1) the variation of the activity coefficient with pressure is given by

$$\left(\frac{\partial \ln f_\pm}{\partial P}\right)_{T,m} = \left(\frac{\partial \ln \gamma_\pm}{\partial P}\right)_{T,m} = \frac{\bar{V}_2 - \bar{V}_2^0}{\nu RT} \qquad (12\text{-}4\text{-}6)$$

Table (8-5-1) contains values of $\bar{V}_2^0$ and S_V at 25°, and $\bar{V}_2$, at this temperature, can be calculated from these quantities by the approximate equation

$$\bar{V}_2 = \bar{V}_2^0 + (3/2)S_V\sqrt{c} \qquad (12\text{-}4\text{-}7)$$

or by the more exact relation

$$\bar{V}_2 = \frac{\bar{V}_2^0 + (3/2)S_V\sqrt{c}}{1 + S_V\,c^{3/2}/2000} \qquad (12\text{-}4\text{-}8)$$

obtained from equation (8-5-8). $\bar{V}_2^0$ and $\bar{V}_2$ can be estimated at other temperatures by equations (8-6-2), (8-6-9), and (8-6-13), and the data given in Table (8-6-1).

In order to express $\bar{V}_2 - \bar{V}_2^0$ as a function of pressure before integrating equation (12-4-6), we may consider the partial molal compressibilities at one atmosphere, $\bar{K}_2$ and $\bar{K}_2^0$, to be constant over a small pressure range, and write

$$\bar{V}_2 - \bar{V}_2^0 = (\bar{V}_2 - \bar{V}_2^0)_{P=1} - (P - 1)(\bar{K}_2 - \bar{K}_2^0)_{P=1} \qquad (12\text{-}4\text{-}9)$$

by equation (8-7-2). Accordingly, equation (12-4-6) yields

$$\log \gamma_{\pm} = (\log \gamma_{\pm})_{P=1} + \frac{(P-1)(\bar{V}_2 - \bar{V}_2^0)_{P=1}}{2.303\nu RT} - \frac{(P-1)^2(\bar{K}_2 - \bar{K}_2^0)_{P=1}}{2 \times 2.303\nu RT} \qquad (12\text{-}4\text{-}10)$$

from which activity coefficients can be estimated at moderate pressures. For higher pressures, or greater accuracy, the variation of $\bar{K}_2 - \bar{K}_2^0$ with pressure must be taken into account. $\bar{K}_2 - \bar{K}_2^0$ is closely represented up to $1M$ by

$$\bar{K}_2 - \bar{K}_2^0 = (3/2)S_K\sqrt{c} \qquad (12\text{-}4\text{-}11)$$

and values of S_K for some salts are to be found in Table (8-7-1).

Robinson and Harned[67] have employed equation (12-4-2) in the form

$$\log \gamma_{\pm} = -\frac{A}{T} - B\log T + I \qquad (12\text{-}4\text{-}2a)$$

for the computation of the activity coefficient of sodium chloride from 0 to 100°. From the heat data discussed in Section (1) and the values of $\gamma_{\pm}$ at 25°, the values of A, B and I in Table (12-4-1) were obtained. The use of this equation is limited by the paucity of reliable thermal data at high concentrations. A comparison of the activity coefficients calculated by this equation with the values given in Table (12-1-2A) is made in Table (12-4-2) where the deviations of calculated from observed values are recorded. It will be observed that the equation represents the results with accuracy from 0 to 100° although, as is to be expected, somewhat greater discrepancies are to be found at the higher concentrations.

TABLE (12-4-1). DATA FOR CALCULATING THE ACTIVITY COEFFICIENT OF SODIUM CHLORIDE BETWEEN 0 AND 100°C.

$$\log \gamma_{\pm} = I - \frac{A}{T} - B \log T$$

m	I	A	B
0.1	3.5083	152.06	1.2557
0.2	5.0010	221.15	1.7755
0.3	6.1564	275.49	2.1748
0.5	7.9970	364.47	2.8051
0.7	9.5163	440.34	3.3199
1.0	11.4326	535.45	3.9679
1.5	14.0912	668.38	4.8619
2.0	16.3294	779.34	5.6128

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[67] R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

TABLE (12-4-2). COMPARISON OF OBSERVED ACTIVITY COEFFICIENTS OF SODIUM CHLORIDE WITH THOSE COMPUTED BY EQUATION (12-4-2a)

$(\gamma_{\text{obsd.}} - \gamma_{\text{calcd.}}) \times 10^3$

t	$m = 0.1$	$m = 0.2$	$m = 0.5$	$m = 1.0$	$m = 1.5$	$m = 2.0$
0	+1	−2	−2	−1	−2	−2
10	+1	−1	−2	0	−1	0
20	0	−2	−2	−2	−3	−1
30	0	−2	−2	−3	−4	−1
40	0	−2	−2	−4	−4	−4
60	0	−1	0	0	−2	−2
80	+1	+2	+3	+1	+1	0
100	+2	+3	+4	+1	+4	+2

By elimination of $(\bar{V}_2 - \bar{V}_2^0)$ and $(\bar{K}_2 - \bar{K}_2^0)$ from equation (12-4-10) by means of equation (12-4-7) and (12-4-11), we obtain

$$\begin{aligned}\log \gamma_\pm = (\log \gamma_\pm)_{P=1} &+ 0.888 \times 10^{-5}(\tfrac{3}{2}S_V)(P - 1)\sqrt{c} \\ &- 0.444 \times 10^{-5}(\tfrac{3}{2}S_K)(P - 1)^2\sqrt{c}\end{aligned} \qquad (12\text{-}4\text{-}12)$$

for a 1-1 electrolyte at 25°.

The magnitudes of the pressure effects upon the activity coefficients of hydrochloric acid at 1, 100 and 1000 atmospheres at four concentrations and for potassium chloride, sodium chloride and sodium hydroxide at unit concentration are illustrated in Table (12-4-3). At 100 atmospheres, the contribution due to the term containing the square of the pressure is negligible, but at 1000 atmospheres, it must be included. The last two rows of the table contain values of $3/2S_V$ and $3/2S_K$ from Tables (8-5-1) and (8-7-1).

TABLE (12-4-3). EFFECT OF PRESSURE ON ACTIVITY COEFFICIENTS AT 25°

Activity Coefficients

P	HCl				KCl $c = 1$	NaCl $c = 1$	NaOH $c = 1$
	$c = 0.1$	$c = 0.5$	$c = 1.0$	$c = 2.0$			
1	0.797	0.757	0.807	0.991	0.605	0.6545	0.6775
100	0.7975	0.759	0.809	0.995	0.609	0.659	0.686
1000*	0.803	0.771	0.828	1.0275			
1000**	0.802	0.768	0.829	1.021	0.637	0.687	0.745
$(3/2)\,S_V$	1.25				3.49	3.23	6.27
$(3/2)\,S_K 10^4$	4.5				18.6	17.1	31.3

* Equation (12-4-12) neglecting term containing $(P - 1)^2$.
** Equation (12-4-12) complete.

The activity coefficient of hydrochloric acid is not influenced greatly by a change in pressure. Even in a $2M$ solution, only a 3 per cent change in $\gamma_\pm$ is produced by a change in pressure of 1000 atmospheres. For the other electrolytes, the influence of pressure is somewhat greater. The largest effect, of 10 per cent, occurs with the activity coefficient of sodium hydroxide.

(5) GENERAL DISCUSSION OF THE ACTIVITY COEFFICIENTS OF 1-1 ELECTROLYTES IN RELATION TO THE THEORY OF DEBYE AND HÜCKEL

(a) The Mean Distances of Approach of the Ions, $\mathring{a}$

Numerous examples have been cited which show the agreement of the observed results with the limiting laws of the interionic attraction theory. Further, the equations resulting from the theory have been employed repeatedly for purposes of extrapolation. The limiting laws, however, are valid at infinite dilution only, and do not apply rigidly to a real ionic solution. The factors which cause deviations from the limiting laws are of great interest as are also the various theoretical interpretations of the properties of electrolytes at moderate or high concentrations.

Debye and Hückel realized that a restriction due to the finite sizes of the ions must be put on Coulombic forces, and introduced the parameter, $\mathring{a}$, defined as the "mean distance of approach of the ions, positive or negative." This led to the extension of the limiting law for activity coefficients, represented by equations (3-5-8) and (3-5-9), and may be written

$$\log f_{\pm} = -\frac{\mathfrak{S}_{(f)}\sqrt{\Gamma}}{1 + 35.57\mathring{a}(DT)^{-1/2}\sqrt{\Gamma}} \tag{12-5-1}$$

Later Hückel[58] extended this theory by assuming that the dielectric constant of the medium varies linearly with the concentration of ions. Upon introducing this relation, Hückel deduced an equation of the form of (10-4-8), or

$$\log f_{\pm} = -\frac{\mathfrak{S}_{(f)}\sqrt{\Gamma}}{1 + 35.57\,\mathring{a}(DT)^{-1/2}\sqrt{\Gamma}} + Bc \tag{12-5-2}$$

which we have frequently employed for the purpose of extrapolating electromotive force data. According to his theory, the term Bc represents the effect of change of dielectric constant with salt concentration. A lowering of D, produced by the addition of ions, has the effect of "salting out the ions," and causes an increase in the activity coefficient. This result corresponds to an effect of repulsive force between the ions, and is opposite in sign to the interionic attraction effect expressed by the first term on the right of equation (12-5-2). If, on the other hand, the dielectric constant is increased by salt addition, the ions are "salted in," Bc is negative, and the activity coefficient is decreased. These behaviors correspond to the salting effects which, according to Debye and McAulay [Chapter (3), Section (10)], vary directly as the sum of the reciprocals of the ion radii, $\Sigma\, 1/b_i$. Although there is no doubt that the dielectric con-

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[58] E. Hückel, *Physik. Z.*, **26**, 93 (1925).

stant is altered by addition of ions, it is also certain that this effect is not the only important factor in concentrated solutions. Therefore, this equation must be regarded as mainly empirical.

When the parameters, $\mathring{a}$ and B are determined from the data, they are found to be different for each electrolyte. However, no exact significance can be attached to the values of $\mathring{a}$, although they are always of the right order of magnitude. In Table (12-5-1), values of $\mathring{a}$ for a few electrolytes evaluated from data over various concentration ranges by a number of different equations are compiled. In column (1), values[59] determined by equation (12-5-1), without the linear term, are given. In the next three columns values obtained by fitting equation (12-5-2) to the data over different concentration ranges are given. In column (5) are given values of $\mathring{a}$ computed from the equation

$$\log f_{\pm} = -\frac{\mathfrak{S}_{(f)}\sqrt{\Gamma}}{1 + 35.57\mathring{a}(DT)^{-1/2}\sqrt{\Gamma}} + Bc + D'c^2 \qquad (12\text{-}5\text{-}3)$$

TABLE (12-5-1). MEAN DISTANCES OF APPROACH OF IONS, $\mathring{a}$

	(1) Equation (12-5-1)	(2)	(3)	(4)	(5)	(6)
		Equation (12-5-2)			Equation (12-5-3)	Equation (12-8-8)
		(0.005 – 0.1 M)	(0.1 – 1 M)	(0.1 – 3 M)	(0.1 – 4 M)	(0.1 – 3 M)
HCl	5.6	4.6	4.3	3.6	4.3	
KCl	4.1	4.1	3.6	3.4	3.95	3.2
NaCl	4.4	4.4	4.0	3.6	4.2	3.7

which contains an additional term in c^2 and which was used [Chapter (11), Section (5)] for computing the activity coefficient of hydrochloric acid. The last column contains values computed by Van Rysselberghe and Eisenberg[60] by equation (12-8-8) which is similar in form to (12-5-3). We note that the different methods of computation do not lead to the same result, but that the values obtained are always of the right magnitude, usually somewhat larger than crystal dimensions, and that the values of $\mathring{a}$ are in the same order, HCl > NaCl > KCl, whichever way the calculation is made.

In the above cases, the simple equation without the linear term, and with a constant value of $\mathring{a}$, expresses the data over a considerable range of concentration (0.005 to 0.1M). This is not always the case. Gronwall, LaMer and Sandved[61] have shown that for potassium nitrate, $\mathring{a}$ varies

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[59] A. S. Brown and D. A. MacInnes, *J. Am. Chem. Soc.*, **57**, 1356 (1935); T. Shedlovsky and D. A. MacInnes, *Ibid.*, **59**, 503 (1937).

[60] P. Van Rysselberghe and S. Eisenberg, *J. Am. Chem. Soc.*, **61**, 3030 (1939).

[61] T. H. Gronwall, V. K. LaMer and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

with concentration when computed by this equation, and that a constant value of $\mathring{a}$ was obtained when their extended theory was employed.

In Table (12-5-2), values of the parameters $\mathring{a}$ and B of equation (12-5-2) and $\mathring{a}$, B' and D' of equation (12-5-3) for the 1-1 halides, halide acids and sodium and potassium hydroxides at 25° are recorded. We have pointed out in Section (1) that good extrapolations may be obtained by equation (12-5-2), if it be fitted to the experimental results at concentrations up to $1M$, but not to higher concentrations of electrolytes. Activity coefficients at $0.1M$ computed by the use of these parameters are identical with those in Table (12-3-1A). From 0.1 to $1M$, the agreement between the observed activity coefficients and those computed by equation (12-5-2) is within ±0.002 in $\gamma_\pm$ with three exceptions. For lithium iodide, the agreement is not good; for lithium bromide and cesium chloride, the calculated and observed results are within the above limit up to $0.7M$.

TABLE (12-5-2). PARAMETERS OF EQUATIONS (12-5-2) AND (12-5-3) AT 25°

	Equation (12-5-2) Valid to $1M$		Equation (12-5-3) Valid to $4M$				$(r_+ + r_-)$
	$\mathring{a}$	B	$\mathring{a}$	B	D'	Max. Dev.	
HI	5 0	0.197	5.5	0.1725	0.0128	0.007	
HBr	4.4	.165					
HCl	4.3	.133	4.3	.1292	.00615	.003	
LiI	5.05	.165	5.0	.155	.0113	.015	2 77
LiBr	4 3	.130	4.3	.126	.0099	.002	2.56
LiCl	4 25	121	4 25	.111	0070	.002	2.41
NaI	4 2	.100	4.2	.090	.0058	.008	3.13
NaBr	4 1	0687	4 2	.0590	.0064	.002	2.91
NaCl	4.0	0521	4 2	.0410	.0053	.001	2.76
KI	3.94	.0462	3 95	.0140	.0016	.002	3.50
KBr	3 84	.0282	3.85	0247	.0035	.001	3.28
KCl	3 8	.0202	3.85	.0187	.0034	.001	3.14
RbCl	3.6	.010	3 2	.0235	.0023	.003	3.29
RbBr	3 55	.010	3.2	.0193	.0021	.005	3.43
RbI	3.5	.0085	3.2	0162	.0031	004	3.65
CsCl	3.0	0	2 5	0229	0024	.006	3 46
CsBr	2.93	0	2.5	.0162	0033	.008	3.61
CsI	2.87	0	2.5	.0140	0	.006	3.82
NaOH	3.24	.0460					
KOH	3.7	.1294					

The middle columns of Table (12-5-2) contain the parameters $\mathring{a}$, B and D' of equation (12-5-3). The next to last column records the maximum deviations of the observed results [Table (12-3-1A)] from those calculated by this equation whose range of validity extends to $4M$. It will be observed that in nearly all cases the agreement is excellent, and is particularly good for the results in which most confidence may be placed. The most serious discrepancies are found with lithium and sodium iodide, both of which salts require further experimental investigation.[62]

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[62] R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

The last column of this table contains the sum of the crystallographic radii of the salts. The values of $\mathring{a}$ are all of the expected order of magnitude. For most of the salts, $\mathring{a}$ is greater than the sum of the crystallographic radii. This can be explained by the effect of the hydration of the ions. For cesium, salts, $\mathring{a}$ is less than $(r_+ + r_-)$. Since there is some doubt as to the absolute magnitude of $\mathring{a}$, it is inadvisable to draw any inference from this result.

Judging from Bjerrum's theory of ionic association [Chapter (3), Section (7)] all of these electrolytes are strong, because most of the $\mathring{a}$ values are greater than q (= 3.5), indicating that the probability of ionic association is very small. Ion pair formation may occur to some extent in the cases of the cesium salts, but even in these solutions, it is doubtful.

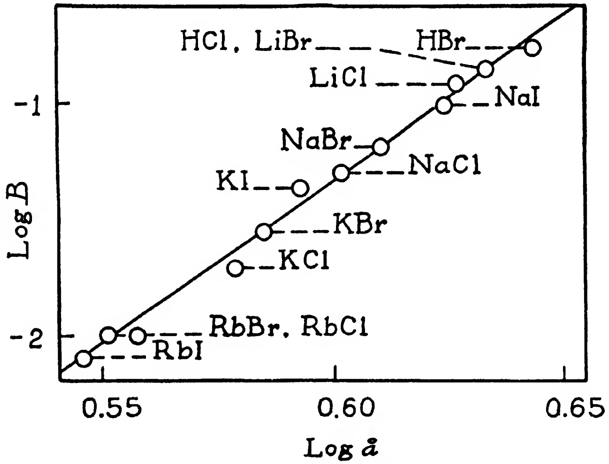

Fig. (12-5-1). Log B against log $\mathring{a}$ for 1-1 halides at 25°.

It will be observed from Table (12-5-2) that $\mathring{a}$ and B obtained from equation (12-5-2) are in the same order and it is probable that some relation can be found between them. If this is so, then all these results can be expressed up to $1M$ by a single parameter equation and constitute a single family of curves. In Fig. (12-5-1) we have plotted log $\mathring{a}$ against log B and find that a linear relation between the two holds within the limits within which $\mathring{a}$ and B can be evaluated. The equation of this straight line is

$$\log B = 14 \log \mathring{a} - 9.75 \qquad (12\text{-}5\text{-}4)$$

which leads to the result that B is proportional to the 14th power of $\mathring{a}$, a very sensitive relation indeed if we desire to compute B from values of $\mathring{a}$. The reverse calculation of $\mathring{a}$ from B is satisfactory. We do not consider significant the exact numerical value found for the power of $\mathring{a}$. It merely suggests that the repulsive forces between the ions depend on a power of $\mathring{a}$ and that two equations, such as equations (12-5-2) and (12-5-4) are sufficient for the representation of the single family of curves for the alkali and hydrogen halides between 0.1 and 1.0 M.*

Any relationship between $\mathring{a}$ and B, calculated from data between 0.1 and $4M$ by means of equation (12-5-3), is obscured by the introduction of the third term, $D'c^2$. Nor does this constant D' appear to be related to B but, with so sensitive a three-parameter equation, it is doubtful if any quantitative relation can be found by induction. The tendency of $\mathring{a}$ and B to increase together, however, is still found. We shall return in Section (8) to a consideration of a relation similar in form to equation (12-5-3) which has some theoretical support.

If the B values are plotted against $\Sigma\ 1/r_i$, separate curves are obtained from the chlorides, bromides and iodides, respectively Although the result does not confirm the Debye and McAulay equation (3-10-10), it indicates that the activity coefficients in concentrated solutions may be largely determined by the ionic radii. More careful consideration of this possibility will be reserved for Section (7).

(b) Specific Behaviors of 1-1 Electrolytes

In Fig. (12-5-2), $\gamma_\pm$ is plotted against $\sqrt{m}$ for the chlorides, bromides and iodides of the alkali metals up to high concentrations. The spread of the results is great, and very pronounced individual differences, corresponding to large differences in the B-values, occur as the concentration increases. Since all the plots lie above that which represents the limiting law of the theory, there is no definite evidence of ionic association. The graphs show regularity except in one respect. The order for the cations is lithium, sodium, potassium, rubidium, and cesium. For the anions it is iodide, bromide and chloride for the lithium, sodium, and potassium salts, but the reverse for the rubidium and cesium salts. The situation would have been more complicated had the less accurate results of the fluorides been included, because the cation order appears to be reversed for the fluorides.

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* H. I. Stonehill and M. A. Berry, [*J. Am. Chem. Soc.*, **64**, 2724 (1942)] express doubt that any relation, such as equation (12-5-4), would exist if $\mathcal{S}_{(f)}$ were altered from 0.5065 to 0.5103. The calculations which they present are misleading, in that the concentration range which they have chosen, 0.01 to 0.10, is not suitable for the determination of B because the contribution of the linear term is less than the experimental error at $0.01M$, and of the order of the experimental error at $0.10M$. Had they chosen the range 0.1 to $1.0M$ employed by us, the effect of this change in $\mathcal{S}_{(f)}$ would have been 0.138 in $\mathring{a}$ and -0.0034 in B instead of 0.63 and -0.0528 as given in their example. In calculations of this kind using other values of $\mathcal{S}_{(f)}$, we have always found, for a series of 1-1 halides, that B is a fairly smooth, rapidly increasing function of $\mathring{a}$. Any equation which will express this function will serve to represent the results as a single family of curves.

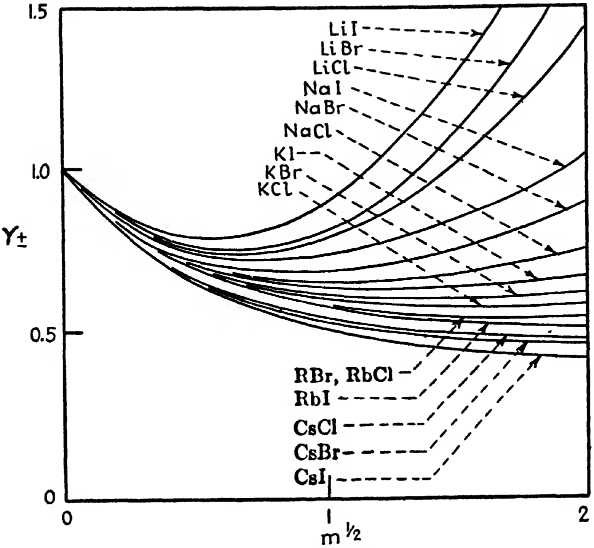

Fig. (12-5-2). Mean activity coefficients of 1-1 halides at 25°.

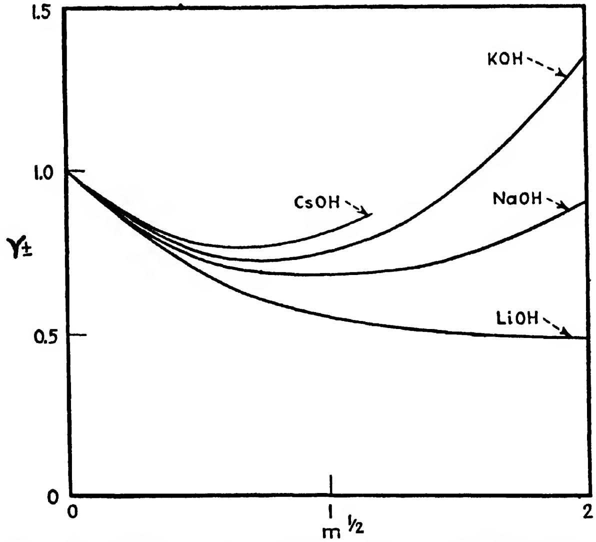

Fig. (12-5-3). Mean activity coefficients of 1-1 hydroxides at 25°.

The most pronounced example of reversal of order occurs with the hydroxides, as demonstrated by the graphs in Fig. (12-5-3). These plots show a wide spread with cesium hydroxide possessing the highest, and lithium hydroxide the lowest activity coefficient. This is exactly opposite to the behavior of the chlorides, bromides and iodides. This behavior may be interpreted partially by ionic interaction, and formation of associated ion pairs. According to Bjerrum's theory of ionic association [Chapter (3), Section (7)], a 1-1 electrolyte is strong if the distance of approach of the ions is equal to or greater than 3.5Å. The above values of $\gamma_\pm$ are consistent with values of mean distances of approach of 3, 3.5, 4, and 4.2Å, for lithium, sodium, potassium and cesium hydroxides, respectively. On the basis of this theory, all these hydroxides are strong electrolytes, although some ionic association may occur in the case of lithium hydroxide. This observation agrees with indications derived from conductance measurements. A similar order of results is found with the acetates although the spread is not so great.

We suggest that the "normal order" for the halides and the reversal of this order for the hydroxides, acetates etc. has its explanation in solvent interaction with the ions. Owing to the more intense fields of the smaller ions (*i.e.*, the lithium ion), there will be strong interaction with the solvent dipoles. The formation of a sheath of water molecules around the ion will result in high values of $\mathring{a}$, compared with crystallographic radii. With the halides, the values of B [Equation (12-5-2)] are in the same order as the values of $\mathring{a}$, and the activity coefficients will be in the same order. Therefore, the hydration which decreases in the order Li > Na > K > Rb > Cs will account for the order of the activity coefficients found for the halides. But this kind of ion-solvent interaction can also lead to a "localized hydrolysis" by reaction with anions which are proton acceptors. The protons in these water molecules will be repelled from the hydration sheath and will tend to form linkages with proton acceptors such as hydroxyl or acetate ions. This tendency may be represented by

$$M^+ + H_2O \rightleftharpoons M^+ \cdots OH^- \cdots H^+$$

where the dotted lines represent the linkages due to ion-solvent molecule forces. The interaction with a proton acceptor may be represented by

$$M^+ \cdots OH^- \cdots H^+ + A^- \rightleftharpoons M^+ \cdots OH^- \cdots H^+ \cdots A^-$$

and the proton regarded as oscillating between extreme positions on the hydroxyl group and proton acceptor. Addition of these expressions gives

$$M^+ + H_2O + A^- \rightleftharpoons M^+ \cdots OH^- \cdots H^+ \cdots A^-$$

which resembles ion pair formation of the type

$$M^+ + A^- \rightleftharpoons M^+ \cdots + \cdots A^-$$

in that both lead to a reduction of the number of free ions in the solution. This mechanism leads to a lower activity coefficient than that calculated upon the basis of complete ionization, and this lowering will be greater the smaller the radius of the cation. Thus, for compounds of the proton accepting hydroxides, acetates etc., the order of activity coefficients will be Cs > Rb > K > Na > Li. In some of these cases ordinary hydrolysis may occur but this does not lead to a change in the number of free ions.

(6) BRÖNSTED'S POSTULATES OF SPECIFIC IONIC INTERACTION, AND GUGGENHEIM'S METHOD OF COMPUTATION OF OSMOTIC AND ACTIVITY COEFFICIENTS AT LOW CONCENTRATIONS

The specificity of the properties of electrolytes has been amply illustrated by the behaviors of their activity coefficients, relative heat contents and heat capacities. The theory of Debye and Hückel does not account for such varied behaviors. Bjerrum's theory of ionic pair formation, supplemented by the theory of Fuoss and Kraus of triple ion formation [Chapter (7)], has proved of great value for interpreting the characteristics of ionic solutions in media of low dielectric constant, but adds little to the interpretation of ionic interaction of strong electrolytes in media of high dielectric constant.

An important contribution to the elucidation of the specific effects of ions of different kinds upon the activity coefficients of other electrolytes was made by Brönsted[63] before the advent of the Debye and Hückel theory. His investigations of the solubilities of higher valence type cobalt compounds in various salt solutions culminated in a generalization known as "the theory of specific ionic interaction". The fundamental postulate of Brönsted's theory is that "in dilute salt solutions of constant total concentrations, ions will be uniformily influenced by ions of like sign." Specific electrical effects take place between the ions and, in dilute solution, only the ions of unlike sign approach each other closely enough to produce these specific effects. Besides the interaction effect, Brönsted also recognizes that there are present solvent, or "salting out" effects. Since most of the experimental evidence in support of the principle of specific ionic interaction was obtained from the investigation of solutions of mixtures of two electrolytes, the detailed discussion of this theory will be reserved for Chapter (14), which deals with the properties of such mixtures.

Guggenheim[64] has employed a combination of the Debye and Hückel theory and a simplified theory of specific interaction for the treatment of 1-1 electrolytes at concentrations from 0 to $0.1M$. A standard electrolyte is chosen which has the characteristics of a "perfect Debye and Hückel electrolyte," or an electrolyte whose rational activity coefficient is deter-

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[63] J. N. Brönsted, *J. Am. Chem. Soc.*, **42**, 761 (1920); **44**, 877 (1922); **44**, 938 (1922); **45**, 2898 (1923).

[64] E. A. Guggenheim, Rep. of Scandinavian Science Congress, Copenhagen (1929) p. 296; *Phil. Mag.* [7], **19**, 588 (1935); *Ibid.*, [7], **22**, 322 (1936); E. A. Guggenheim and L. A. Wiseman, *Ibid.*, [7], **25**, 45 (1938).

mined by the equation

$$\log f_{\pm} = -\frac{\mathfrak{S}_{(f)}\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} \tag{3-5-8}$$

This electrolyte obeys Coulomb's law at all distances and its ions are rigid non-polarizable spheres. Further, for purposes of numerical simplicity, let the mean distance of approach of the ions be equal to 3.05 Å. at 25°. Then

$$\log f_{\pm} = -\frac{\mathfrak{S}_{(f)}\sqrt{\Gamma}}{1 + \sqrt{\Gamma/2}} \tag{12-6-1}$$

or, for 1-1 electrolytes,

$$\log f_{\pm} = -\frac{\mathcal{S}_{(f)}\sqrt{c}}{1 + \sqrt{c}} \tag{12-6-2}$$

Guggenheim adds to this a linear term to account for the contribution due to all the specific effects which give the electrolyte its individual characteristics. Thus, the very simple and easily applied equation

$$\log f_{\pm} = -\frac{\mathcal{S}_{(f)}\sqrt{c}}{1 + \sqrt{c}} + \lambda c \tag{12-6-3}$$

is obtained. The term λc will include the contributions due to lowering of the dielectric constant (Hückel), to ionic pair formation (Bjerrum), to effects due to ion size, polarizability, etc. Guggenheim applied this equation to the computation of osmotic and activity coefficients from freezing point and electromotive force data at concentrations less than $0.1M$. The agreement with the freezing data is within ±0.0002 to ±0.0005°C.

This equation is useful for the calculation of the activity coefficients in dilute solution because of its simplicity. Since at a given temperature the first term on the left is the same for all 1-1 electrolytes, it need only be computed once for each concentration, so that the calculation of $f_{\pm}$ merely involves that of the linear term. In Table (12-6-1A), Guggenheim's values of λ for a large number of electrolytes, and $f_{\pm}(\lambda = 0)$ of the standard electrolyte are tabulated at a number of concentrations. From these, $f_{\pm}$ may be computed up to $0.1M$ with an estimated accuracy of the order of 0.5 per cent, which is sufficient for most practical purposes.

From a theoretical point of view, this treatment is over simplified, even in the range of concentration specified ($\nless 0.1M$). Applied to the activity coefficients of two electrolytes at the same concentration, equation (12-6-3) leads to the relation

$$\log \frac{f_1}{f_2} = \log \frac{\gamma_1}{\gamma_2} = (\lambda_1 - \lambda_2)c = B_{12}c \tag{12-6-4}$$

where $(\lambda_1 - \lambda_2)$ and hence B_{12} is not a function of c. The Debye and Hückel theory does not lead to this result unless the mean distance of approach of the ions is the same for all electrolytes. This would indeed be an unexpected result. According to this theory equation (3-5-8) would lead to

$$\log f_1/f_2 = -\mathfrak{S}_{(f)}\sqrt{\Gamma}\left(\frac{1}{1 + A_1\sqrt{\Gamma}} - \frac{1}{1 + A_2\sqrt{\Gamma}}\right) \qquad (12\text{-}6\text{-}5)$$

$$\neq B_{12}c$$

an expression which is not linear, but which requires B_{12} to vary with the concentration. The behavior of this function for two 1-1 electrolytes possessing $\mathring{a}$ values of 4.0 and 3.5, respectively, is shown by the curve in Fig. (12-6-1). Here, $\frac{\log (f_1/f_2)}{c}$ is plotted against c, and it is clear that it is a function of c.

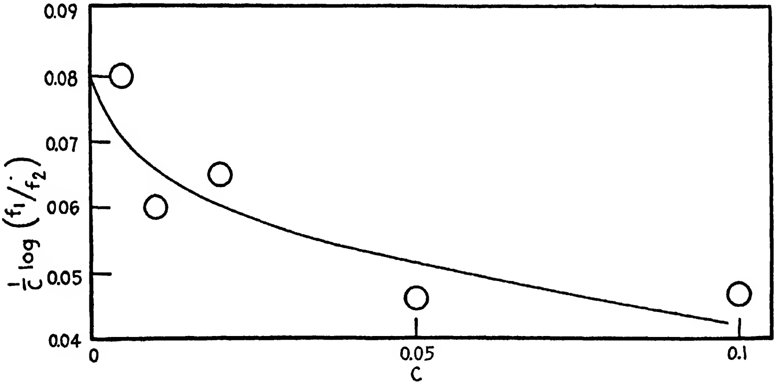

Fig. (12-6-1). Theoretical and experimental variation of $1/c \log (f_1/f_2)$. ——, theoretical; ○, experimental, (1) NaCl; (2) KCl.

Brown and MacInnes, and Shedlovsky and MacInnes obtained $\mathring{a}$ values of 5.6, 4.1, and 4.4 for hydrochloric acid, potassium chloride, and sodium chloride, respectively, when they fitted their accurate data to the Debye and Hückel equation [Table (12-5-1)], and 4.6, 3.7 and 4.0 by using this formula with a linear term [Equation (12-5-2)]. The range of concentration was from 0.005 to 0.1 M. This result is not in accord with Guggenheim's simplified equation. $(\lambda_{\mathrm{HCl}} - \lambda_{\mathrm{KCl}})$, computed from the observed values of $\log (\gamma_{\mathrm{HCl}}/\gamma_{\mathrm{KCl}})$, varies from 0.24 to 0.15. In the case of $\log (\gamma_{\mathrm{HCl}}/\gamma_{\mathrm{NaCl}})$, $(\lambda_{\mathrm{HCl}} - \lambda_{\mathrm{NaCl}})$ varies from 0.16 to 0.11 from 0.005 to 0.1M. The circles in Fig. (12-6-1) are the values of $(\lambda_{\mathrm{NaCl}} - \lambda_{\mathrm{KCl}})$ obtained from these results. Even though the computed $\mathring{a}$-values differ by only 0.3, there is an indication that this quantity decreases with increasing concentration.

These computations are extremely sensitive, and can only be verified by the most accurate experiments. We believe that these experiments are sufficiently accurate to indicate that Guggenheim's method is approximate, and of value for practical calculations where simplicity is desired.[65]

(7) THE THEORY OF CONCENTRATED SOLUTIONS OF ALKALI HALIDES ACCORDING TO SCATCHARD

In Section (5), we have mentioned the extension of the original Debye and Hückel theory by the addition of a "salting out" term produced by the change in dielectric constant of the medium with ionic concentration. We have also pointed out that although this factor must be considered in a theory of concentrated solutions, it alone is inadequate for their explanation. Indeed, Hückel's formula led to the result that in a hydrochloric acid solution at about $4M$, the dielectric constant would be zero and negative at higher concentrations.[66,67]

The most comprehensive theoretical study of concentrated solutions of strong electrolytes, particularly, the alkali halides, has been made by Scatchard.[68] The simplest case, ions of the noble gas type, is the one best suited for numerical treatment. Scatchard's equation for the activity coefficient is

$$\begin{aligned}\ln \gamma_{\pm} = -\ln\,(1 + \nu_s N_s/N_0) + \frac{\epsilon^2 N}{2RTD_0}\Bigg[\frac{z_1 z_2 \kappa}{1 + \kappa a} \\ + \left(\frac{\kappa}{1 + \kappa a} + X\right) z_1 z_2 V_s m d_0 + \frac{4\nu_1\nu_2}{\nu_s}\left(\frac{V_2 z_1^2}{b_1} + \frac{V_1 z_2^2}{b_2}\right) m d_0\Bigg] \\ + \frac{A m d_0(2 + \nu_s m\, d_0)}{RT(1 + V_s m\, d_0)^2}\end{aligned} \qquad (12\text{-}7\text{-}1)$$

The extended terms of Gronwall, LaMer and Sandved are omitted. N_s is number of mols of electrolyte, and N_0 is the number of mols of solvent. V_1 and V_2 are the molal volumes of the ions, and V_0 is the molal volume of solvent. The parameters, b_1 and b_2, are the radii of the ions which are effective for "salting out". The other symbols are defined by the following equations in which "a" is the sum of the ionic radii effective in ionic collisions (mean distance of approach), and a_{12}, a_{10}, and a_{20} are the mutual cohesive energy densities.

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[65] Additional evidence for this conclusion is discussed by R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

[66] H. S. Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926).

[67] E. Guntelberg, *Z. Physik. Chem.*, **123**, 199 (1926).

[68] G. Scatchard, *Physik. Z.*, **33**, 22 (1932); *Chem. Rev.*, **19**, 309 (1936). For the development leading to the deduction of equation (12-7-1), see Chapter (3) on "Thermodynamics and Electrostatic Theory" by G. Scatchard in E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corporation, New York (1943).

$$md_0 = N_s/V_0N_0$$

$$\nu_s = \nu_1 + \nu_2$$

$$V_s = \nu_1 V_1 + \nu_2 V_2$$

$$D = D_0 V_0 N_0/V$$

$$\kappa^2 = -\frac{8\pi N^2 \epsilon^2 z_1 z_2 \nu_s N_s}{1000RTDV} = -\frac{8\pi N^2 \epsilon^2 z_1 z_2 \nu_s md_0}{1000RTD_0}$$

$$X = \frac{\kappa}{1 + \kappa a} - Y$$

$$Y = \left[1 + \kappa a - \frac{1}{1 + \kappa a} - 2 \ln (1 + \kappa a)\right] \Big/ \kappa^2 a^3$$

$$A = 2\nu_1 \nu_2 V_1 V_2(2a_{12} - a_{10} - a_{20})/\nu_s$$

We shall not go into detail in the discussion of this complicated expression, but simply describe the significance of each term.

Equation (12-7-1) represents an extension of the Debye and Hückel theory. The first term on the right is merely the usual expression for converting the rational activity coefficient, $f_\pm$, to the stoichiometrical activity coefficient, $\gamma_\pm$. The first two terms within the bracket are essentially those of Debye and Hückel for charge-charge interaction, except that κ is defined for changing dielectric constant, D, rather than for constant dielectric constant, D_0. Whereas Hückel assumes a linear variation of dielectric constant with molarity of electrolyte, Scatchard employs the relation, $D = D_0V_0N_0/V$ found by Wyman[69] for nonelectrolytic solutions. The influence of this difference in κ turns out to be small. The effect is proportional to the number of ions in unit volume of solvent. The third term within the brackets is the salting out term, or the charge-molecule term, and corresponds to the Debye and McAulay expression for this effect. These terms are similar to those of the Hückel extension of the theory. The final term outside the brackets is introduced to represent the non-electrolyte molecule-molecule interaction, or the departure of purely non-electrolyte solutions from the ideal solution.

For the application of the theory, it is necessary to know the temperature, the molal volume, and the dielectric constant of solvent, the valence, molal volume in solution, and the radius effective in salting out for each ion, the effective collision diameter of the pair of ions, a, and their molecule-molecule interaction coefficient, A. For alkali halides, the ions are assumed to be spheres. In this, $b = r$, and $a = r_1 + r_2$. The values of the radii were those obtained by Pauling[70] from crystallographic data. The ionic volume in solution was taken to be somewhat less than $4\pi r^3/3$, and the constant, A, was assumed to be the same for all these halides. Brönsted's

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[69] J. Wyman Jr., *J. Am. Chem. Soc.*, **58**, 1482 (1936).

[70] L. Pauling, *J. Am. Chem. Soc.*, **50**, 1036 (1928). See Table (5-1-6).

theory of ionic interaction, which excludes short range interaction between ions of like sign, was also employed to simplify certain substitutions. Two parameters were determined empirically from osmotic coefficient data. These were the ratio of the volume in solution to the actual volume of the ions, and the coefficient A. Of these, the first agreed with the theoretically expected value while the second agreed approximately.

The calculations by this theory of the osmotic coefficients of the alkali halides agree, in general, satisfactorily with the data of Robinson and Sinclair, and Robinson. The most important result is that the properties of these noble gas type ions are characterized by their valences, and sizes as determined from crystallographic data. The order and magnitude of the results for the iodides, bromides and chlorides are in good agreement with theory. Further, the theory also predicts the reversal in order of cationic effects in the case of the fluorides as judged from freezing point data.

This investigation of Scatchard is the most determined attempt to obtain a theoretical knowledge of concentrated solutions by a detailed extension of the Debye and Hückel theory. Charge-charge, charge-molecule, and molecule-molecule interaction are considered separately, and relations between the individual thermodynamic properties of the electrolytes and the ionic radii, as determined by crystallographic data, are indicated.

(8) INTERPRETATION OF CONCENTRATED SOLUTIONS OF ELECTROLYTES IN TERMS OF A VAN DER WAALS' CO-VOLUME EFFECT

We have shown [Section (5)] that the activity coefficients of many 1-1 electrolytes from 0 to $4M$, may be calculated very accurately by the equation,

$$\log f_{\pm} = -\frac{\mathfrak{S}_{(f)}\sqrt{\Gamma}}{1 + 35.57\mathring{a}(DT)^{-1/2}\sqrt{\Gamma}} + Bc + D'c^2 \qquad (12\text{-}8\text{-}1)$$

The numerator of the first term on the right represents the effect of Coulomb forces between ions considered as point charges. The denominator represents the effect of the restriction on Coulomb forces, imposed by the finite sizes of the ions. The terms Bc and $D'c^2$ are positive, and opposite in sign to the first term, and may be interpreted in terms of the short range repulsive forces which cause such large effects in very concentrated solutions.

As a result of an interesting analysis of the theory of concentrated solutions, Onsager[71] suggested that these repulsive force terms might be expressed as an ordinary van der Waals co-volume correction

$$\Delta\mu_i \approx kT\left(\sum \frac{4\pi}{3}\frac{\mathring{a}^3}{V}\right) \qquad (12\text{-}8\text{-}2)$$

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[71] L. Onsager, *Chem. Rev.*, **13**, 73 (1933).

where $\mathring{a}$ is the "mean distance of approach of the ions" and V is the total volume. This amounts to the assumption that the repulsive forces decrease rapidly with the distance, and that these forces may be represented "by a large discontinuity of the potential energy at some distance ($r = \mathring{a}$)." Since the parameter $\mathring{a}$ in the excluded volume term [Equation (12-8-2)] is the same as in the first term on the right of equation (12-8-1), this theory raises the possibility, mentioned in Section (5), of expressing the thermodynamic properties of electrolytes in terms of an equation with only one parameter.

This suggestion has been developed in greater detail by Van Rysselberghe and Eisenberg.[72] The problem of computing a suitable function, which represents the mutual exclusion from certain portions of space, in the case of N_1 and N_2 molecules of two kinds with diameters, d_1 and d_2, respectively, is a difficult one. The best treatment so far is that of Ursell[73] who has developed the theory of the general case for any number of molecules, and has obtained a complete solution for the case of two kinds of molecules. His result is greatly simplified by assuming that

$$d_1 = d_2 = d_{12} = d_+ = d_- = d_\pm = a$$

and by the relations

$$N_1 = N_+ = \nu_+ N; \qquad N_2 = N_- = \nu_- N$$

$$\nu_+ + \nu_- = \nu$$

$$N_i = (\nu_+ + \nu_-)N = \nu N$$

d_+, d_- and $d_\pm$ denote the cationic, anionic, and mean ionic diameters of the ions and electrolyte, respectively. We note that $d_\pm$ is equated to the mean distance of closest approach a, of the ions, and appears as a parameter, not a mean diameter derived from crystallographic data. For the case of a binary electrolyte, the excluded volume term (ln Y of Van Rysselberghe) is simply

$$\ln Y = -\frac{1}{2}\frac{N_i^2}{V}v - \frac{5}{64}\frac{N_i^3}{V^2}v^2 \tag{12-8-3}$$

where V is the volume, and $v = \frac{4}{3}\pi a^3$. The excluded volume effect contributes to the total van der Waals work content of the solution, A_w^*, the amount,

$$A_w^* = N_i \Delta\mu_i^* + N_0 \Delta\mu_0^* = -kT \ln Y$$

$$= N_i kT\left[\frac{1}{2}\frac{N_i}{V}v + \frac{5}{64}\left(\frac{N_i}{V}\right)^2 v^2\right] \tag{12-8-4}$$

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[72] P. Van Rysselberghe and S. Eisenberg, *J. Am. Chem. Soc.*, **61**, 3030 (1939); Correction, *Ibid.*, **62**, 451 (1940).

[73] H. D. Ursell, *Proc. Camb. Phil. Soc.*, **23**, 685 (1927); See R. H. Fowler, "Statistical Mechanics," 2nd edition, pp. 241 *et seq.*, Cambridge University Press (1936).

If, taking into consideration the small compressibility of ionic solutions, A_w^* be replaced by F_w^*, the van der Waals contribution to the activity coefficient, $\ln f_\pm^*$, may be obtained by differentiating with respect to N_i at constant P, T, and N_0. Thus,

$$\begin{aligned}\ln f_\pm^* &= \frac{\Delta\mu_i^*}{kT} = \frac{1}{kT}\frac{\partial F_w^*}{\partial N_i} \\ &= \frac{N_i}{V}v + \frac{15}{64}\left(\frac{N_i}{V}\right)^2 v^2 - \left[\frac{1}{2}\left(\frac{N_i}{V}\right)^2 v + \frac{10}{64}\left(\frac{N_i}{V}\right)^3 v^2\right]\frac{\partial V}{\partial N_i}\end{aligned} \tag{12-8-5}$$

Similarly, the activity coefficient of the solvent is given by

$$\log f_1^* = \frac{\partial F^*}{\partial V}\frac{\partial V}{\partial N_0} = -\left[\frac{1}{2}\left(\frac{N_i}{V}\right)^2 v + \frac{10}{64}\left(\frac{N_i}{V}\right)^3 v^2\right]\frac{\partial V}{\partial N_0} \tag{12-8-6}$$

Expressing 'a' in Ånstrom units, converting to molar concentrations, and neglecting the last term in $\partial V/\partial N_i$, we obtain from equation (12-8-5) the result

$$\log f_\pm^* = 2.2063 \times 10^{-3}\mathring{a}^3 c + 2.6269 \times 10^{-6}\mathring{a}^6 c^2 \tag{12-8-7}$$

for binary electrolytes. This is the theoretical result corresponding to the terms $Bc + D'c^2$ in equation (12-8-1).

It is hardly to be expected that this simplified picture is sufficient to give an accurate representation of the results. In the case of hydrochloric acid, we found that the experimental results at 25° could be expressed with an accuracy of ±0.001 in γ if $\mathring{a}$, B and D' were 4.3, 0.1292 and 0.00615, respectively. Using 4.3 for $\mathring{a}$, the theoretical equation (12-8-7) yields 0.1754 and 0.01661 for B and D', respectively. This indicates that the van der Waals co-volume effect is more than sufficient to account for the contribution corresponding to the net repulsive forces between the ions. Quantitatively, the result is not good. Similar results occur with other 1-1 electrolytes. We have found [Table (12-5-2)] that the experimental results up to $1M$ for hydrobromic acid, sodium bromide, and sodium and potassium chlorides may be computed if $\mathring{a}$ equals 4.4, 4.1, 4.0 and 3.8, and B equals 0.165, 0.059, 0.041, and 0.019, respectively. The theoretical values of B are 0.1879, 0.1521, 0.1412 and 0.1259, respectively. Therefore the theoretical results are considerably too high. This suggests the possibility that a combination of the co-volume effect and ionic association, which is very likely to occur in solutions of high concentration, would give a closer representation of the real conditions.

We have noted in Section (5) the possibility of obtaining a single parameter equation for the computation of activity coefficients of 1-1 electrolytes at a given temperature. Van Rysselberghe and Eisenberg found that the empirical equation

$$\log f_\pm = -\frac{0.5059\sqrt{c}}{1 + \dfrac{\mathring{a}}{3.042}\sqrt{c}} + 1.1031 \times 10^{-3}\mathring{a}^3 c + 8.7564 \times 10^{-7}\mathring{a}^6 c^2 \tag{12-8-8}$$

similar in form to (12-8-1), nearly satisfies this possibility from 0.1 to $4M$. The application of this equation to 1-1 halides yields values of $\mathring{a}$ which do not differ greatly from those obtained by equation (12-5-2) from data in the concentration range from 0.05 to $3M$.[74] They are lower than those evaluated from the best data from 0.005 to $1M$ [Table (12-5-2)], and lead to values of $\gamma_{\pm}$ at $0.1M$ which are somewhat too low. However, considering the complexity of the situation, the single parameter equation is a surprisingly good approximation.

(9) Thermodynamic Properties of Ions in Relation to Their Size and Structure

As a result of the recent comprehensive investigations of the freezing points by Scatchard and Prentiss [Chapter (9)], and the isopiestic vapor pressure measurements of Robinson, sufficient knowledge of the thermodynamic coefficients of many 1-1 electrolytes has been obtained to permit a crude classification of them in terms of the structure of the ions.[75] For convenience, the following scheme may be adopted:

Group I. Noble gas type cations with
    (1) Noble gas type anions.
    (2) Anions which are proton acceptors.
        (a) Small anions, F^-, OH^-, etc.
        (b) Unsymmetrical anions, $HCOO^-$, CH_3COO^-, etc.
    (3) Polyatomic anions of the type, NO_3^-, ClO_3^-, ClO_4^-, etc.
Group II. Polyatomic Cations, H_3O^+, NH_4^+, and organo-substituted ammonium ions.

The first class in Group I has been discussed in the preceding sections, and it appeared that the individual properties depended very largely on the size of the ions. The peculiar interaction which causes the reversal of the cationic effects in the presence of the fluoride and hydroxide ions depends also on the very small size of these according to Scatchard and Prentiss. Although little is known accurately about the fluorides, it would appear that the fluoride ion is a proton acceptor since the osmotic coefficient of $1M$ hydrofluoric acid is about the same as that of formic acid at this concentration. If this is the case, the mechanism of cationic reaction with the solvent water, discussed in Section (5), may be an important factor. An anion of large size such as the acetate probably has its charge at a considerable distance from its center. This would account for its proton accepting capability, and the reversal in the order of the cationic effects.

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[74] H. S. Harned and G. Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[75] Similar attempts have been made when fewer data were available by H. S. Harned [H. S. Taylor, "Treatise on Physical Chemistry," 2nd Edition, Chapter XII, p. 823 ff. Van Nostrand and Co., New York, (1929)]. The present discussion follows closely the summary given by G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **56**, 807 (1934).

The behavior of the salts of the polyatomic anions which are not proton acceptors (their acids are strong electrolytes) is more difficult to explain. The characteristics of the alkaline nitrates, chlorates or perchlorates are illustrated by Fig. (12-9-1), in which the activity coefficients of the nitrates are compared with the chlorides. Although the anion is complex, the cationic order is the same, but the spread of the curves for the nitrates is a little greater. Scatchard and Prentiss have pointed out that since the cationic order is the reverse of that of the acetates, etc., the effects cannot be explained by an unsymmetrical ionic charge distribution. Further, in regard to effects of dipole moments, Scatchard and Prentiss say, "The fact that the difference from the halide ions is no greater for the chlorate, which should have a dipole, than for the nitrate and perchlorate which have no dipoles unless the structure in solution is very different from that in the crystal, eliminates the dipole moment as an important factor."

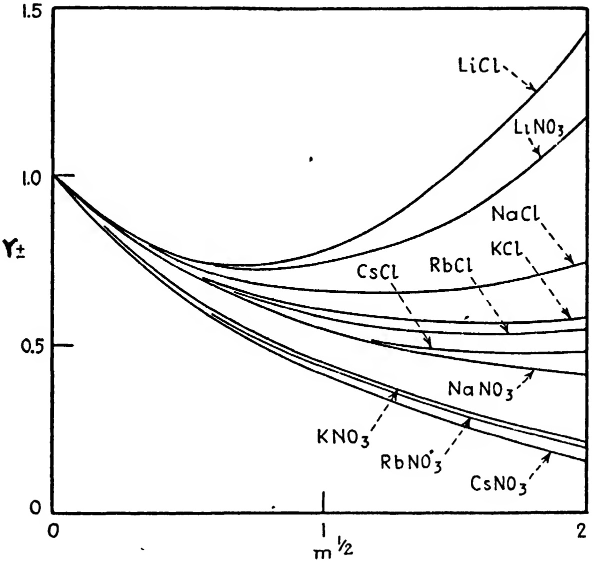

Fig. (12-9-1). Mean activity coefficients of 1-1 chlorides and nitrates at 25°.

There is not sufficient knowledge of the properties of the polyatomic cations to throw much light on their behavior. The hydronium ion in strong acid solutions behaves nearly the same as the lithium ion, even though their sizes appear to be quite different.

The symmetrical ammonium ion in concentrated solutions acts similarly to the smaller sodium or potassium ions. Scatchard and Prentiss[76] found that the ammonium halides and nitrates behave uniquely in dilute solution

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[76] G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **54**, 2696 (1932).

($< 0.04M$). They all show an effect similar to that of ionic association, which at higher concentrations disappears due to factors which increase the activity coefficient. No other 1-1 electrolytes have been found which possess this characteristic ion interaction. So far, a satisfactory explanation of the effect has not been found.

The freezing points of solutions of alkyl ammonium fluorides and chlorides have been measured accurately by Ebert and Lange,[77] and Lange.[78] Their values of the osmotic coefficients of these strong electrolytes are plotted in Fig. (12-9-2). The dashed line represents the Debye and Hückel limiting law. The chlorides are all strong electrolytes, whereas the fluoride ion appears to form ion pairs with these polyatomic cations, since their curves all lie below the limiting law.

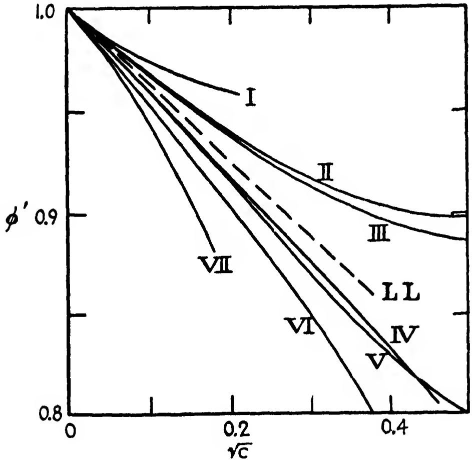

Fig. (12-9-2). Osmotic coefficients of alkyl ammonium chlorides and fluorides at the freezing point. I, $N(C_4H_9)_4Cl$; II, $N(C_3H_7)_4Cl$, III, $N(CH_3)_4Cl$; IV, $N(CH_3)_4F$; V, $N(CH_3)_3(C_6H_{11})F$; VI, $N(C_3H_7)_4F$; VII, $N(C_4H_9)_4F$. L.L., theoretical limiting law.

That the effect of ionic association may appear in the case of a monoatomic ion of a high electron complexity is evidenced by the behavior of thallous chloride. Cowperthwaite, LaMer and Barksdale[79] have measured the electromotive force of the cells,

$$\text{Tl}(s) \mid \text{TlCl}(m) \mid \text{AgCl-Ag}$$

from 0 to 50°. They found that the results were fitted by the Gronwall, LaMer and Sandved extension of the theory if $\mathring{a}$ was assigned the value of

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[77] L. Ebert and J. Lange, *Z. Physik. Chem.* **A, 139,** 584 (1928).

[78] J. Lange, *Ibid.,* **A, 168,** 147 (1934).

[79] I. A. Cowperthwaite, V. K. LaMer and J. Barksdale, *J. Am. Chem. Soc.*, **56,** 544 (1934).

0.93. They also found that by assigning the more probable value of 3.0 to $\mathring{a}$, and supplementing the Gronwall, LaMer and Sandved function by the mass action law, an equally good fit was obtained when the constant of equilibrium was assigned the value of 0.31. This latter result is the same as that derived by Onsager[80] from consideration of the deviation of conductance data from his limiting equation.

(10) Activity Coefficients of Neutral Molecules in Aqueous Salt Solutions

The computation of the activity coefficient of a neutral molecule in a salt solution may be made most readily from solubility determinations, or from partition measurements. Consider a gas in equilibrium with its aqueous solution according to a reaction such as: $O_2(g) = O_2(\text{aq.})$. The equilibrium constant at constant P and T is

$$K = \frac{a_2(\text{aq.})}{a_2(\text{g})} = \frac{f_{(s)} N_{(s)}}{p} \tag{12-10-1}$$

if the pressure of the gas, p, is low enough to equal its fugacity. $N_{(s)}$ and $f_{(s)}$ are the mol fraction and activity coefficient of the gas in the salt solution. In pure water, let $f_{(s)} = f_{(0)} = 1$, and $\gamma_{(s)} = m_{(0)}/m_{(s)}$. Then, $f_{(s)}N_{(s)} = N_{(0)}$, and

$$f_{(s)} = \frac{N_{(0)}}{N_{(s)}} = \gamma_{(s)} \frac{55.5 + m_{(s)}}{55.5 + m_{(0)}} \tag{12-10-2}$$

Exactly the same relation would be obtained for the activity coefficient of a liquid or a solid solute in a salt solution, provided that the activity coefficients are taken to be unity in the saturated solution in pure water.

An exhaustive survey of the data previous to 1927 has been made by Randall and Failey.[81] This material, and more recent determinations of the activity coefficients of helium, argon, and more complicated molecules such as ethyl acetate[82] and diacetone alcohol, will be employed to illustrate the complicated nature of the effects.

Empirical equations for the salt effect upon neutral molecules have been proposed by a number of investigators.[83] Of these, we mention particularly that of Setchénow,

$$\log \frac{S^0}{S} = k_s c \tag{12-10-3}$$

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[80] L. Onsager, *Physik. Z.*, **28**, 277 (1927).

[81] M. Randall and C. F. Failey, *Chem. Rev.*, **4**, 271 (1927); **4**, 285 (1927); **4**, 291 (1927).

[82] G. Åkerlöf, *J. Am. Chem. Soc.*, **57**, 1198 (1935), He, A; *Ibid.*, **51**, 984 (1929), Diacetone alcohol; S. Glasstone and A. Pound, *J. Chem. Soc.*, **127**, 2660 (1925), S. Glasstone, D. W. Dimond and E. C. Jones, *Ibid.*, **128**, 2935 (1926), Ethyl acetate.

[83] M. Setchénow, *Ann. chim. phys.*, [6] **25**, 226 (1892); V. Gordon, *Z. Physik. Chem.*, **18**, 8 (1895); V. Rothmund, *Ibid.*, **33**, 401 (1900).

where S^0 and S are the solubilities of the neutral molecule in the pure solvent and the salt solution, respectively, c is the concentration in mols per liter, and k_s is a constant. Comparison with equation (12-10-2) indicates that the relations,

$$\log f_{(s)} = k_N\mu \qquad (12\text{-}10\text{-}4)$$

$$\log \gamma_{(s)} = k_m\mu \qquad (12\text{-}10\text{-}5)$$

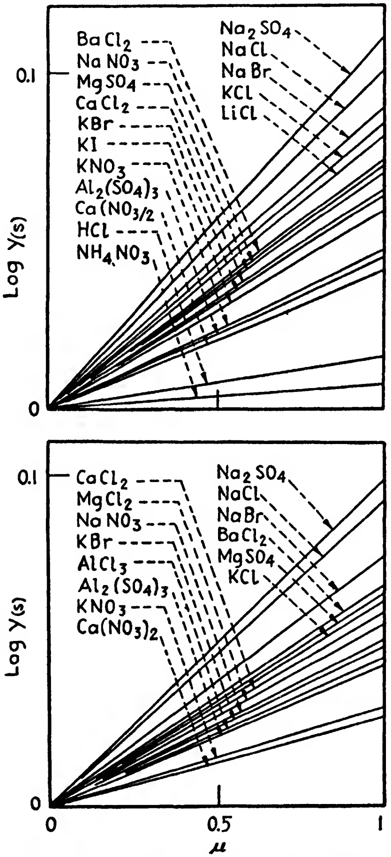

Fig. (12-10-1a). Various salt effects. Upper figure, N_2O; lower figure, C_2H_4.

where μ is the ionic strength, should serve as a useful means of expressing the results. That such a linear relationship is a first approximation, and not strictly valid, has been shown by Randall and Failey. On the other hand, it gives a fair representation of the data, and will be used as a basis for the present discussion.

In Table (12-10-1A), the salting coefficients, k_m [Equation (12-10-5)] for helium,[84] argon,[84] hydrogen,[85] oxygen,[85] nitrous oxide,[85] carbon dioxide,[85] iodine,[85] acetylene[85] in many salt solutions are compiled. Similar constants for the liquids ethyl acetate,[86] diacetone alcohol,[87] phenyl thiourea,[88] and phenol[89] are also given. The general nature of the phenomenon is shown in Fig. (12-10-1), in which log $\gamma_{(s)}$ for two gases and two liquid molecules in many salt solutions are plotted against the ionic strength.

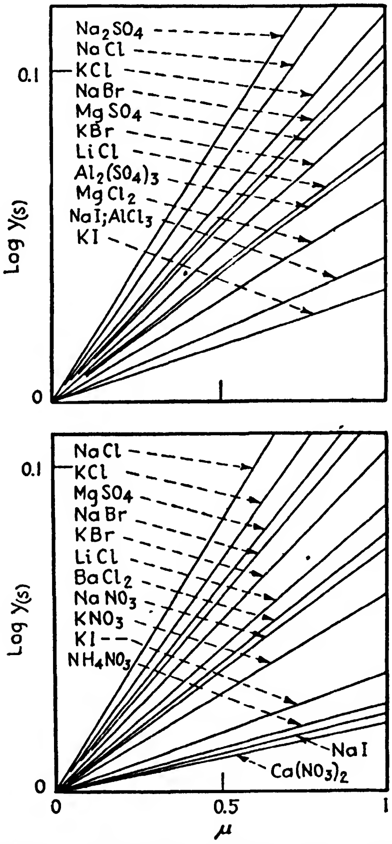

Fig. (12-10-1b). Various salt effects. Upper figure, diacetone alcohol; lower figure, ethyl acetate.

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[84] G. Åkerlöf, *J. Am. Chem. Soc.*, **57**, 1196 (1935).

[85] M. Randall and C. F. Failey, *Chem. Rev.*, **4**, 271 (1927); **4**, 285 (1927).

[86] S. Glasstone and A. Pound, *J. Chem. Soc.*, **127**, 2660 (1925); S. Glasstone, D. W. Dimond and E. C. Jones, *Ibid.*, **128**, 2935 (1926).

[87] G. Åkerlöf, *J. Am. Chem. Soc.*, **51**, 984 (1929).

[88] W. Biltz, *Z. physik. Chem.*, **43**, 41 (1903); V. Rothmund, *Ibid.*, **33**, 401 (1900).

[89] W. Herz and F. Hiebenthal, *Z. anorg. Chem.*, **177**, 363 (1929).

We note immediately the similarity in nature of the graphs. The order of magnitude of the salting out is the same, and the order of the salt effects is approximately the same. Minor changes in order of the salt effects may be observed. The similarity between the order and magnitude of the effects upon such dissimilar molecules as nitrous oxide and diacetone alcohol should be noted.

In Chapter (3), Section (10), the Debye and McAulay equation (3-10-9) for the salting effect on neutral molecules by electrolytes,

$$\ln f_{(s)} = \frac{\bar{\beta}}{2kTD_0} \sum_{1}^{s} \frac{n_j e_j^2}{b_j} \tag{12-10-6}$$

was obtained. The derivation showed that this equation is an approximation for dilute solutions, and cannot be expected to yield quantitative results at high concentrations. It will be interesting, however, to compare qualitatively the results of this theory with the experimental data.

We recall that $\bar{\beta}$ is a constant characteristic of the non-electrolyte, defined by the relation, $D = D_0 - \bar{\beta}n$, where n is the number of molecules of non-electrolyte. D is the dielectric constant of the mixture of non-electrolyte and solvent (water), D_0 is that of pure solvent. n_j is the number of ions of the kind, j, of radius, b_j. The summation is over all the ions present. The coefficient, $\bar{\beta}$, is positive when the non-electrolyte has a lower dielectric constant than that of the solvent. Since water has a high dielectric constant, $f_{(s)}$ of most neutral substances, should be increased in aqueous solutions. The data in Fig. (12-10-1) bear out this prediction. Further, the theory predicts that $\log f_{(s)}$ varies linearly with the ional concentration which again conforms with experimental observation, since $\Gamma \cong 2\mu$. Finally, the salt effects should be in the order of the sum of the reciprocals of the ionic radii. If crystallographic radii [Table (5-1-6)] are employed, this prediction is not followed, and many exceptions may be noted.

The salt effects of sodium and barium chlorides upon a number of neutral molecules are shown in Fig. (12-10-2). In the case of barium chloride solutions, the spread of the results is much smaller than in that of the sodium chloride, a fact which indicates that the constant $\bar{\beta}$ must vary from salt to salt in order to satisfy the results.

We may sum up this complicated situation in the following manner. The equation of Debye and McAulay has the form of the empirical equation (12-10-5), and leads to results of the right order of magnitude.[90] This shows that the electrostatic influence is an important part of the salting out effect. The role of the ionic radius is confused, and the theoretical prediction of the order of effects does not agree with the observed results. The theory requires salting out in aqueous solution, while numerous examples of salting in (ethyl acetate in cesium iodide) occur. These discrepancies might be partially eliminated if the investigations were confined to dilute solutions of both neutral molecules and salts.

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[90] G. Scatchard, *Trans. Far. Soc.*, **23**, 454 (1927).

The Activity Coefficient of the Undissociated Part of Some Weak Acids in Salt Solutions

In Table (12-10-2A), the salting coefficients, k_m, of benzoic, o-toluylic, o-nitrobenzoic, salicylic, acetic and chloroacetic acids, as computed by Randall and Failey,[91] are recorded. The results for the first four of these acids were obtained from the solubility data of Rördam,[92] and Hoffmann and Langebeck,[93] while those for acetic acid were compiled from the

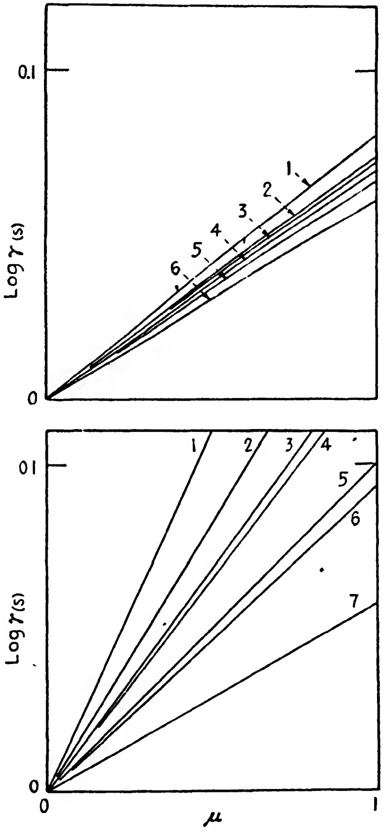

Fig. (12–10–2). Salt effects of barium and sodium chlorides upon various substances. Upper figure, barium chloride: 1, ethyl acetate; 2, phenylthiourea; 3, N_2O; 4, argon, phenol; 5, C_2H_4; 6, CO_2. Lower figure, sodium chloride: 1, phenol; 2, ethyl acetate; 3, phenylthiourea, diacetone alcohol; 4, O_2; 5, N_2O; 6, H_2, C_2H_4; 7, argon.

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[91] M. Randall and C. F. Failey, *Chem. Rev.*, **4**, 291 (1927).

[92] H. N. K. Rördam, Thesis, Copenhagen (1926).

[93] F. Hoffmann and K. Langebeck, *Z. physik. Chem.*, **51**, 385 (1905).

results of Sugden,[94] and McBain and Kam.[95] Sugden determined the distribution of acetic acid between amyl alcohol and water, whereas McBain and Kam obtained a quantity which was proportional to the partial pressure of acid over the solution, divided by the concentration of the undissociated molecules of the acid in the solution. Randall and Failey investigated the distribution of monochloro- and dichloro-acetic acids between dibutyl ether and aqueous salt solutions.

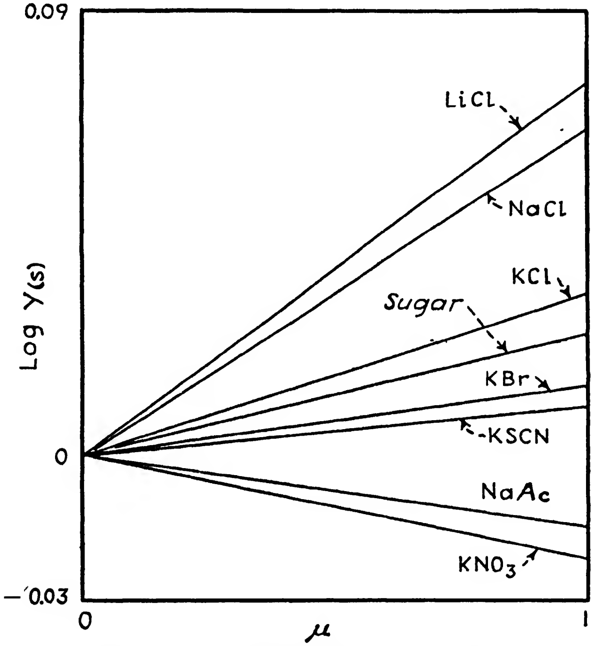

Fig. (12-10-3). Salt effects upon acetic acid.

In Fig. (12-10-3), values of log $\gamma_{(s)}$ of acetic acid are plotted against the ionic strength. We note that these results are similar to those of other non-electrolytes shown in Figs. (12-10-1), and (12-10-2). Minor dissimilarities in order of the curves may be noted as well as salting in effects in sodium acetate and potassium nitrate solutions.

Partition of Acetone and Hydrocyanic Acid Between Aqueous Salt Solutions and Benzene. The Debye Theory of Salt Effects

A thorough investigation of the effects of salts on the activity coefficients of acetone and hydrocyanic acid has been conducted by Gross,[96] by measur-

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[94] J. N. Sugden, *J. Chem. Soc.*, **128**, 174 (1926).

[95] J. W. McBain and J. Kam, *J. Chem. Soc.*, **115**, 1332 (1919).

[96] P. Gross and K. Schwarz, *Sitz. Akad. Wiss. Wien*, **139**, 179 (1930); P. Gross and M. Iser, *Ibid.*, **139**, 221 (1930).

ing the distribution of these substances between water, or aqueous salt solutions, and benzene. These measurements are particularly suitable for testing the Debye theory of the salting effect [Chapter (3), Section (11)], since acetone lowers, and hydrocyanic acid raises the dielectric constant of water.

From the partition coefficients between benzene and pure water, and freezing point measurements of the solutions in benzene combined with calorimetric data, the activity coefficients in benzene were calculated as a function of the concentration. From these, the activity coefficients of the compounds in the salt solutions may be computed. Gross tabulates the functions

$$f_c \equiv \left(\frac{c_B}{c_0}\right)_s \Big/ \left(\frac{c_B}{c_0}\right)_0; \qquad f_m = \left(\frac{m_B}{m_0}\right)_s \Big/ \left(\frac{m_B}{m_0}\right)_0 \tag{12-10-7}$$

where the subscripts s and 0 indicate the presence and the absence of electrolytes, respectively, and B refers to the benzene solutions. In the partition experiments with dilute salt solutions, $[c_B]_s \cong [c_B]_0$, and the above ratios are nearly equal to the ratio of the activity coefficient in the salt solution to that in pure water. At higher concentrations of salt, a small correction can be made for the variation of the activity coefficient with concentration of the salted out substance in the benzene layer.

The salting effects were found to be dependent upon the nature of the non-electrolyte, but practically independent of its concentration and the temperature. Further, the equations

$$\frac{1}{f_c} = 1 - b_c c; \qquad \frac{1}{f_m} = 1 - b_m c \tag{12-10-8}$$

in which c is the salt concentration, represent the results approximately.[97] In Fig. (12-10-4), some of Gross's results are plotted. The full and dashed lines represent the salting of acetone and hydrocyanic acid, respectively. For cesium and potassium nitrates, sodium chloride, and magnesium and lanthanum sulphates, a striking reversal in salt effect is observed. Acetone is salted out, and hydrocyanic acid is salted in. As an exception, we note the behavior in lithium nitrate solutions. Similar reversal in effects were found in the cases of lithium and potassium chloride, sodium nitrate and potassium sulphate solutions, but in magnesium chloride solutions another exception was found.

These results conform in a general way with the Debye theory of salt effects. In Chapter (3), Section (10), the equation

$$\frac{f^0}{f} = 1 - \frac{4\pi N}{1000} \Sigma J_j c_j \tag{3-10-43}$$

was obtained. The functions, J_j, given by equations (3-10-44) to (3-10-46),

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[97] This is approximately the same as equation (12-10-5) since $k_{m\mu} = \log \gamma_{(s)} \simeq 1 - 1/\gamma_{(s)}$.

are themselves functions of the ionic radii, and a quantity, $\bar{R}_j$, defined by equation (3-10-38),

$$\bar{R}_j^4 = \frac{z_j^2 \epsilon^2 1000}{8\pi RTD_1} |\bar{\alpha}| \tag{3-10-38}$$

The constant, $|\bar{\alpha}|$, is defined by equation (3-10-37),

$$|\bar{\alpha}| = \frac{(D_1 - D_2)}{D_1} V_1 \tag{3-10-37}$$

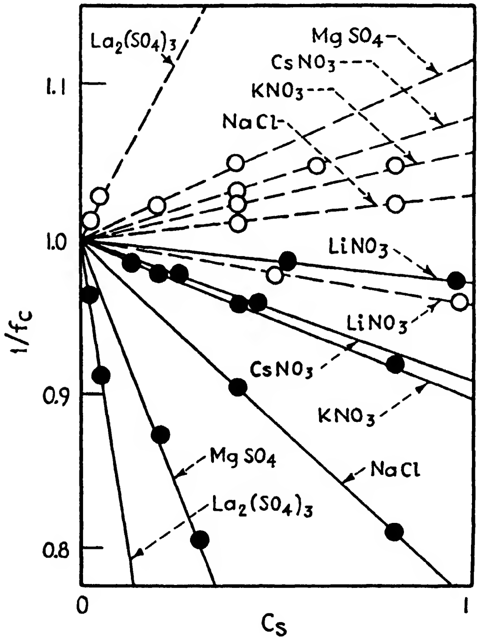

Fig. (12-10-4)
Salting in and out of hydrocyanic acid and acetone. ●, acetone; O, hydrocyanic acid.

D_1 and D_2 are the dielectric constants of components (1) and (2), and V_1 is the molal volume of component (1). The component (2) is salted out or in. Applied to the systems under discussion, component (1) is water and component (2) is either acetone or hydrocyanic acid.

Since the functions J_j are constant functions depending on the values of $|\bar{\alpha}|$ and $\bar{R}_j$, and since f^0, the activity coefficient of the component (2), is taken to be unity in pure water, equation (3-10-43) is formally equivalent to (12-10-8). Consequently, the theory predicts the observed linear variation of $1/f_c$. Further, according to theory, hydrocyanic acid should be salted in, since its dielectric constant is greater than water while the reverse is true for acetone. With the exception of lithium nitrate and magnesium chloride, this prediction is verified by the results.

From measurements of the dielectric constants, Gross obtained

$$D = D_1(1 - 0.0367c) \tag{12-10-9}$$

and

$$D = D_1(1 + 0.0039c) \tag{12-10-10}$$

for solutions of acetone and hydrocyanic acid, respectively. Therefore, according to equations (3-10-39) and (3-10-41), $|\bar{\alpha}|$ equals 0.0367 and 0.0039, respectively, and $\bar{R}_j$ (acetone) $= 2.03 \times 10^{-8}$ cm., and $\bar{R}_j$ (HCN) $= 1.2 \times 10^{-8}$ cm., according to equation (3-10-38). For the limiting salting effects (dilute salt solutions), these values lead to the equations

$$1/f = 1 - \frac{0.13}{\mathring{a}}\Gamma \tag{12-10-11}$$

$$1/f = 1 + \frac{0.0135}{\mathring{a}}\Gamma \tag{12-10-12}$$

for acetone and hydrocyanic acid, respectively, where $1/\mathring{a} = \Sigma\, 1/\mathring{a}_j$.

These equations cannot be expected to hold quantitatively since they are limiting equations for very dilute solutions, and since, as evidenced by the anomalous results for lithium nitrate and magnesium chloride, they are probably complicated by chemical effects which are not purely electrostatic. The theoretical predictions are of the right order of magnitude since they yield values of $\mathring{a}$ of the order of 0.5 to 2 for many of the salts. The large effects for lanthanum sulphate and magnesium sulphate are striking, and agree approximately with theory.

The salting out of water from water-dioxane mixtures by potassium, sodium, and lithium chlorides has been investigated by Scatchard and Benedict[98] by freezing point measurements. Mixtures of dioxane with the salts in 1 to 2 and 2 to 1 ratios in water at concentrations from 0.01 to $2M$ were used. From the values of the osmotic coefficient, the salting out coefficients (molecule-salt interaction coefficients) were evaluated. Using crystallographic radii [Table (5-1-6)], excellent agreement was found between the results and Debye's theory of salting out, whereas the Debye and McAulay theory proved to be less satisfactory.

(11) The Surface Tension of Dilute Solutions of Electrolytes

The increase in surface tension caused by the addition of electrolytes was first observed by Heydweiller.[99] Schwenker[100] has also measured the surface tension of some 1-1 electrolytes at concentrations from 6.015 to $0.2N$, and obtained similar results.

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[98] G. Scatchard and M. A. Benedict, *J. Am. Chem. Soc.*, **58**, 837 (1936).

[99] A. Heydweiller, *Ann. Physik.* [4] **33**, 145 (1910); *Physik. Z.*, **3**, 329 (1902).

[100] G. Schwenker, *Ann. Physik.*, **11**, 525 (1931).

The theoretical treatment of surface tension according to Wagner, and Onsager and Samaras, has been shown [Chapter (3), Section (11)], to lead to

$$\frac{\sigma}{\sigma_0} = 1 + \frac{1.012c}{\sigma_0} \log \frac{1.467}{c} \tag{12-11-1}$$

for the effect of 1-1 electrolyte addition upon the relative surface tension of water at 25°. We note first that the theory leads to an increase in σ/σ_0. However, this predicted change is small. For example, in water, σ/σ_0 equals 1, 1.00004, 1.0003, and 1.0016 at values of c equal to 0, 0.001, 0.01 and 0.1, respectively. Onsager and Samaras found that their theory agreed in order of magnitude with the results of Heydweiller and Schwenker. Exact agreement was not obtained, but this was probably due to experimental error, because the results of Heydweiller were not in exact agreement with those of Schwenker.

Jones and Ray,[101] by employing a silica capillarimeter, have succeeded in measuring the relative capillary rise with a very high degree of accuracy. From their measurements, they derived a quantity $(\sigma/\sigma_0)'$ which we shall designate as an "apparent relative surface tension". The reproducibility of the measurements was extraordinary. The greatest deviation for any solution was 0.005 percent, and the average deviation was 0.002 percent.

Some of their results in very dilute solutions are illustrated in Fig. (12-11-1), in which the apparent relative surface tension is plotted against the concentration for potassium chloride, cesium nitrate and potassium sulphate. In each case, the upper curve represents the theoretical result according to equation (12-11-1). In the extremely dilute solutions, there is a rapid decrease in $(\sigma/\sigma_0)'$ until a sharp minimum occurs. After this, the curves rise at approximately the rate predicted by theory. It is obvious that if $(\sigma/\sigma_0)'$ is a relative surface tension, and nothing else, the theory is erroneous in very dilute solutions. Jones and Ray showed that this rapid decrease was a property of ionic solutions, and does not occur in solutions of sucrose in water.

Langmuir[102] has pointed out that, in very dilute solutions, the zeta potential of quartz causes the formation of a wetting layer in the fine quartz capillaries. This is of such a thickness as to reduce the diameters of the capillaries sufficiently to affect the measurements of the surface tension. As a result, the effect observed by Jones and Ray is not a measure of relative surface tension alone, but is an effect which includes both surface tension and the influence of the zeta-potential. Onsager[103] has made an extended theoretical investigation of wetting of surfaces with electrolytic

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[101] G. Jones and W. A. Ray, *J. Am. Chem. Soc.*, **59**, 187 (1937); *Ibid.*, **63**, 288 (1941).

[102] I. Langmuir, *Science*, **88**, 430 (1937); *J. Chem. Phys.*, **6**, 873 (1938); An attempt to interpret the results as a pure surface tension effect has been made by M. Dole *J. Am. Chem. Soc.*, **60**, 904 (1938).

[103] L. Onsager, Private communication.

solutions, and has developed a quantitative theory of the influence of the zeta-potential on the capillary rise. His theory accounts largely for the difference between the results shown in Fig. (12-11-1), the rapid decrease in $(\sigma/\sigma_0)'$ in dilute solutions, and the minimum in the curves. It does not yet include the possible effects of London forces. However, from the actual surface tension measurements of Jones and Ray, Onsager calculates with accuracy the zeta-potential of quartz.

These considerations lead to the conclusion that the interionic attraction theory for the surface tension as developed by Wagner, and Onsager and Samaras, is a good first approximation.

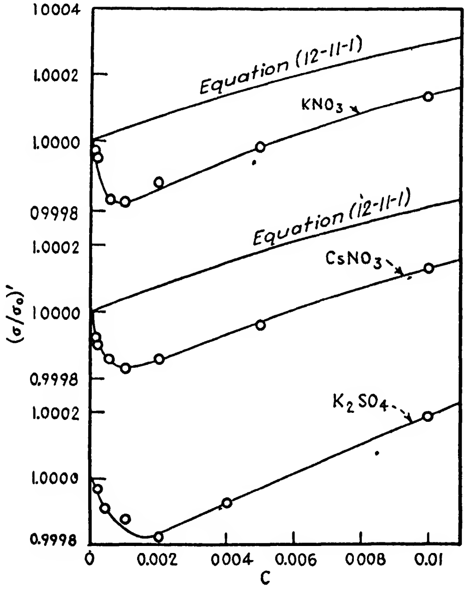

Fig. (12-11-1). Apparent relative surface tension of potassium nitrate, cesium nitrate, and potassium sulphate solutions at 25°. Theoretical curves for relative surface tension according to equation (12-11-1).

(12) CRITICAL CONSIDERATIONS

In the preceding review of the properties of 1-1 electrolytes, it has proved difficult to organize the data. Examination of this material will show that discrepancies exist between the results obtained by different investigators. For example, the values of $f_{0\,1}$ obtained by Guggenheim [Table (12-6-1A)] for some electrolytes differ considerably from those obtained by Scatchard and Prentiss [Table (9-5-3A)] from the same freezing point data. Guggenheim's analytical extrapolation in nearly all cases yields lower values for $\gamma_\pm$ than the graphical method used by Scatchard and

Prentiss. Further, Robinson's results [Table (12-3-1A)], obtained by the isopiestic vapor pressure method, are for many electrolytes lower than Guggenheim's. In the cases of potassium and sodium chloride, the measurements of cells with liquid junction by Brown and MacInnes, and Shedlovsky and MacInnes, help considerably in establishing $f_{0.1}$ at 25°, and the concordance of the results obtained for these electrolytes by various methods has been stressed.

So far, sodium chloride is the only electrolyte which has been investigated from 0 to 100°, and, unfortunately, the methods employed were not accurate in the dilute solutions ($< 0.1M$). Even in more concentrated solutions at 25°, there is still doubt as to the values of $\gamma_\pm$. The results [Table (12-1-2A)] derived from combined electromotive force, boiling point, and heat of dilution data are not in complete agreement with the values chosen by Scatchard, Hamer and Wood[104] as standard for their isopiestic vapor pressure measurements.

The theory of concentrated solutions of electrolytes, or individual ionic effects, is seen to be very difficult, and no exact quantitative treatment of the complicated factors is available. We have shown [Section (5)] that determination of the mean distance of approach of the ions, $\mathring{a}$, from experimental data is subject to ambiguity. This is equivalent to the statement that up to the present no observed departure from the limiting law has been exactly interpreted.

The extended theory of Scatchard, which includes his estimates of charge-charge, charge-molecule, and molecule-molecule effects, is important because it shows that the properties of the simplest "noble gas type ions" may be interpreted as functions of the ionic radii. It is doubtful, however, that the linear combination of the terms representing these effects with the Debye and Hückel limiting term [Equation (12-7-1)] can give more than a reasonable qualitative interpretation and classification of the specific characteristics of the ions.

Onsager[105] has made a thoughtful critique and summary of the theory of concentrated solutions. We have shown [Chapters (2) and (3)] that the computations of thermodynamic properties depends on the assumption of "linear superposition of ionic atmospheres", which leads to the proportionality between the charge and the potential. Onsager shows that owing to the fact that the Poisson-Boltzmann equation is an approximation, the ionic atmospheres can no longer be expected to be additive when the higher (extended) terms of the Poisson-Boltzmann equation become important.

The effects of ion-solvent interaction upon the thermodynamic properties of electrolytic solutions are not definitely understood. Bjerrum[106] and

[104] G. Scatchard, W. J. Hamer and S. E. Wood, *J. Am. Chem. Soc.*, **60**, 3061 (1938).

[105] L. Onsager, *Chem. Rev.*, **13**, 73 (1933).

[106] N. Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920).

Huckel[107] have shown that ionic hydration would be expected to increase the activity coefficient in the concentrated solutions. A modern extension of the theory of Bjerrum will receive more detailed consideration in Appendix B, Section (7).

Bernal and Fowler[108] from fundamental considerations concerning the structure of water and the interactions of ions with water have given a theoretical treatment of such properties as the apparent molal volumes and heats of hydration of the ions. They show that the molecules in liquid water tend to orient in groups with the oxygen atoms at the corners of a tetrahedron. The arrangement is similar to the open tetrahedral structure of ice.[109] In crystals, water molecules are coordinated around the ions and the number of water molecules in this state is determined by the space allowed by the relative volumes of the water molecules and ions. In aqueous solutions, the degree of hydration of an ion is determined by the number of water molecules which find room to pack around the ion and the field exerted at the surface of the ion.

By applying these considerations to the partial molal volumes, Bernal and Fowler's computations show that the hydration of monovalent cations is in the order: $Li^+ > Na^+ > K^+ > Rb^+, Cs^+$. Indeed, due to their size, the fields of Rb^+ and Cs^+ are too weak to attract the water di-poles, and their hydration is negligible. This prediction is in accord with the fact that the volume of a solution of cesium iodide in water is considerably larger than the sum of the volumes of the pure salt and liquid water at the same temperature. With the exception of F^-, monovalent anions are large and unhydrated. Polyvalent cations are hydrated and the expected order of some divalent cations is: $Mg^{++} > Ca^{++} > Sr^{++} > Ba^{++}$. Applications of these considerations will be found in Appendix B, Sections (6) and (7).

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[107] E. Hückel, *Physik. Z.*, **26**, 92 (1925).

[108] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1931); See also T. J. Webb, *J. Am. Chem. Soc.*, **48**, 2589 (1926).

[109] L. Pauling, *J. Am. Chem. Soc.*, **57**, 2680 (1935).

Chapter (13)

Polyvalent Electrolytes in Aqueous Solution

The presence of ions of higher valence types introduces further complications in the thermodynamic properties, even in media of high dielectric constants. The theoretical considerations in Chapter (3), Sections (6) and (7), prove that, upon the basis of Coulomb's forces only, deviations from the original Debye and Hückel theory are to be expected. The higher order terms of the complete solution of the Poisson-Boltzmann equation are a function of the valences of the ions. As shown by Gronwall, LaMer and Sandved for symmetrical electrolytes, the contribution to $\ln f_{\pm}$ caused by the second and third terms on the right of equation (3-6-4), though practically negligible for 1-1 electrolytes in water, varies very markedly with the magnitude of z, since the terms which multiply the functions within the brackets involve z^6 and z^{10}, respectively. A similar result was obtained for the extended terms for unsymmetrical valence type electrolytes as indicated by equation (3-6-6). The exact determination of the effect of the extended terms is a matter of considerable difficulty, since it may be somewhat obscured and confused by other effects such as those caused by the series terms, $\sum_{n>2} A_n c^{n/2}$ [Equation (11-5-2)], which have been found necessary for the computation of the activity coefficients of 1-1 electrolytes.

It is illuminating to consider polyvalent electrolytes from the alternative point of view of Bjerrum's theory of ionic association [Chapter (3), Section (7)]. We have learned that if b, the minimum distance of approach of positive to negative ions, is greater than $q = \epsilon^2 |z_1 z_2|/2DkT$, then the probability of ionic association is negligible. For a 1-1 electrolyte in water at 25°, $q = 3.5$ Å. Therefore for 2-1, 3-1, 2-2, 3-2, and 3-3 electrolytes, q equals 7, 10.5, 14, 21, and 31.5 Å, respectively. Since these values are much greater than $\mathring{a}$ for many high valence type electrolytes, considerable ionic association of the Bjerrum type is to be expected. Judging from conductance data in dilute solution, calcium chloride and like electrolytes are strong, but electrolytes like zinc and magnesium sulphate are associated.

Other electrolytes which are unquestionably incompletely dissociated are the cadmium halides. In these cases, there is the possibility of equilibrium of the kind represented by

$$MCl_2 \rightleftharpoons Cl^- + MCl^+ \rightleftharpoons M^{++} + 2Cl^-$$

where the ionization is not completely determined by Coulomb's forces but by more complex fields such as those discussed in Chapter (3), Section (7).

In these cases, mass action type calculations have been found to fit the experimental results.

Of the abundant but scattered material in this field, we shall consider a limited amount which will illustrate the best attempts yet employed for treating the results. Examples of 2-1, 3-1, 2-2, and 3-2 electrolytes will first be discussed. The properties of solutions of the weaker electrolytes will then be considered with particular emphasis on cadmium halide solutions. Finally, the properties of aqueous sulphuric acid solutions will be considered in some detail.

(1) THE THERMODYNAMICS OF MAGNESIUM, CALCIUM, STRONTIUM AND BARIUM HALIDE SOLUTIONS

Lucasse[1] has measured the electromotive forces at 25° of the cells,

$$\text{Ag-AgCl} \mid \text{MCl}_2(m) \mid \text{M}_x\text{Hg} \mid \text{MCl}_2(m_R) \mid \text{AgCl-Ag}$$

containing calcium, strontium, and barium chlorides. Scatchard and Tefft[2] also employed this cell in order to investigate calcium chloride solutions at 25°. More recently, Tippetts and Newton[3] have extended the study of barium chloride solutions over the temperature range from 0 to 45° by the same kind of measurement.

From considerations similar to those employed in deriving equation (10-4-7), the electromotive force of this cell is given by

$$\mathrm{E} = \frac{3RT}{2\mathrm{F}} \ln \frac{\gamma_{\pm} m}{\gamma_R m_R} \tag{13-1-1}$$

from which it is clear that $\gamma_{\pm}$ relative to its value, γ_R, at a reference concentration may be computed. These data have been extrapolated in conformity with theory by Harned,[4] Scatchard and Tefft,[2] Jones and Dole,[5] and Tippetts and Newton by employing equation (10-4-9), or a similar function. The extended terms were not employed in any of these treatments. So far, experience indicates that both barium and strontium amalgam electrodes are reproducible, and that calcium amalgam electrodes are extremely erratic and lead to erroneous results. Tippetts and Newton report an average deviation of ±0.2 mv. with the barium amalgam electrodes, while Scatchard and Tefft's average deviation with the calcium electrodes was ±0.4 mv. Lucasse, and Scatchard and Tefft employed flowing amalgams, while stationary electrodes covered with an oil layer were used by Tippetts and Newton. Results at salt concentrations less than $0.01M$ have not been reported, since the consistency of the results decreases with decreasing concentration. Values of $\gamma_{\pm}$ at 25° for barium

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[1] W. W. Lucasse, *J. Am. Chem. Soc.*, **47**, 743 (1925).

[2] G. Scatchard and R. F. Tefft. *J. Am. Chem. Soc.*, **52**, 2265 (1930).

[3] E. A. Tippetts and R. F. Newton, *J. Am. Chem. Soc.*, **56**, 1675 (1934).

[4] H. S. Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926).

[5] G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 1084 (1929).

and strontium chlorides obtained from the amalgam cell measurements are given in Table (13-1-1). Tippetts and Newton's values for barium chloride from 0 to 45° are contained in Table (13-1-1A).

That cells containing barium amalgam can be accurately reproduced is shown by the agreement of the values of the activity coefficient at 25°, as determined by Tippetts and Newton, in column (3) with those computed from Lucasse's data in column (4). Newton and Tippetts[6] have also computed the activity of water in barium chloride solutions from their electromotive force measurements at 25°, and have compared the results obtained with values determined directly from their dynamic vapor pressure measurements. The agreement is a good indication of the fundamental correctness of both methods at this temperature.

TABLE (13-1-1). THE ACTIVITY COEFFICIENTS OF ALKALINE EARTH CHLORIDES AT 25°

m	$BaCl_2$			$SrCl_2$		$CaCl_2$
	V.P.[c]	E.M F.		V.P.[c]	E M F.[b]	V.P.[c]
	$\gamma_\pm$	$\gamma_\pm$[a]	$\gamma_\pm$[b]	$\gamma_\pm$	$\gamma_\pm$	$\gamma_\pm$
0.01	.....	0.723	0.723	. ..	0 729	.....
.05	...	.559	.554	..	.571	.
.1	(0.492)	.492	.495	(0 514)	.512	(0.531)
.2	.438	.436	.439	.463	.465	.482
.3	.411	.411	.....	440	.....	.462
.4	.398	.....	....	.430	.....	.456
.5	.390	.390	.395	.425	.427	.457
.6	.386	. ...	.....	.426	.....	.462
.7	.384	.384	. .	430	.....	.469
.8	.385	.....	.....	.436	.....	.479
.9	.388	....	...	444	. .	.493
1.0	.392	389	.395	.455	449	.509
1.1	.397	....	. ..	.467	....	.528
1.2	.402	. ...	.. .	.480	....	.550
1.3	.409	....	....	.494	.....	573
1.4	.416	.	...	510	... .	.599
1.5	.423	.425	.425	527	.526	626
1.6	.431	.....	.....	.546	. ..	657
1.7	.440	.....	....	.566	....	.690
1.8	.450	.....	....	.587	.....	.726
1.9	...	.. .	.....	611	.....	.764
2.0	.....	.....	...	.636	.638	.807
2.1	.....	....	... .	.664	. .	.853
2.2	.....	.....	.....	.694	.....	.901
2.5	.....	.....	.....	....	.772	.....
3.	.....	.....	.....	.. .	1 003	....

[a] E. A. Tippetts and R. F. Newton, *J. Am. Chem. Soc.*, **56**, 1675 (1934).
[b] H. S. Harned, *Ibid.*, **48**, 326 (1926) from the data of Lucasse, *Ibid*, **47**, 743 (1925).
[c] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **36**, 735 (1940).

The relative partial molal heat content, $\bar{L}_2$, of barium chloride has been computed from electromotive force measurements by Tippetts and Newton, and the result is in good agreement with values obtained from the

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[6] R. F. Newton and E. A. Tippetts, *J. Am. Chem. Soc.*, **58**, 280 (1936); M. F. Bechtold and R. F. Newton, *Ibid.*, **62**, 1390 (1940).

calorimetric measurements of Richards and Dole[7] at 25°. On the other hand, their values at the other temperatures cannot be reliable, particularly those at their extreme temperatures, 0 and 45°, since values of the relative partial molal heat capacity, $\bar{J}_2$, computed from them, differ greatly from the calorimetric measurements. At 25° and $0.1M$, Tippetts and Newton obtained 61 for $\bar{J}_2$, whereas the calorimetric value of White[8] is 17.1. This discrepancy may be caused largely by the difficulties of extrapolation of the electromotive force results rather than by large errors in the original measurements.

The osmotic and activity coefficients of manganese, cobalt, nickel, copper, magnesium, calcium, strontium and barium chlorides and magnesium bromide and iodide have been determined from isopiestic vapor pressure measurements by Robinson[9] from 0.1 to 1.6 or $2M$. The standard solution to which all these isopiestic measurements are referred is sodium chloride [See pages 289 and 375]. The values of $\gamma_{\pm}$ at 25° are compiled in Table (13-1-2A). The agreement of the isopiestic measurements with the results obtained from electromotive forces for barium and strontium chlorides is made apparent by the results in Table (13-1-1). On the other hand, the values of $\gamma_{\pm}$ determined by the use of calcium amalgam differ greatly from those obtained from the vapor pressures.

(2) THE THERMODYNAMICS OF AQUEOUS LITHIUM, SODIUM AND POTASSIUM SULPHATE SOLUTIONS

Cells of the type,

$$\text{Hg-Hg}_2\text{SO}_4 \mid \text{M}_2\text{SO}_4(m) \mid \text{M}_x\text{Hg} \mid \text{M}_2\text{SO}_4(m_R) \mid \text{Hg}_2\text{SO}_4\text{-Hg}$$

have been employed by Åkerlöf[10] for determining the activity coefficients of lithium, sodium, and potassium sulphates at 25°. More recently, Harned and Hecker[11] have measured the electromotive forces of the cells,

$$\text{Pb-Pb}_x\text{Hg-PbSO}_4 \mid \text{Na}_2\text{SO}_4(m) \mid \text{Na}_x\text{Hg} \mid \text{Na}_2\text{SO}_4(0.05) \mid \text{PbSO}_4\text{-Pb}_x\text{Hg-Pb}$$

in a more thorough investigation of the thermodynamics of aqueous sodium sulphate solutions. For this salt, accurate freezing point, heat of dilution, and specific heat data have been obtained by Randall and Scott,[12] Lange and Streeck,[13] and Randall and Rossini,[14] respectively.

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[7] T. W. Richards and M. Dole, *J. Am. Chem. Soc.*, **51**, 794 (1931).

[8] C. M. White, *J. Am. Chem. Soc.*, **58**, 1620 (1936).

[9] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **36**, 733 (1940); R. A. Robinson, *Ibid.*, **36**, 735 (1940); R. A. Robinson and R. H. Stokes, *Ibid.*, **36**, 1137 (1940).

[10] G. Åkerlöf, *J. Am. Chem. Soc.*, **48**, 1160 (1926); H. S. Harned and G. Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[11] H. S. Harned and J. C. Hecker, *J. Am. Chem. Soc.*, **56**, 650 (1934).

[12] M. Randall and G. N. Scott, *J. Am. Chem. Soc.*, **49**, 647 (1927).

[13] E. Lange and H. Streeck, *Z. physik. Chem.* A., **157**, 1 (1931).

[14] M. Randall and F. D. Rossini, *J. Am. Chem. Soc.*, **51**, 323 (1929).

Since the alkali metal amalgams are inaccurate in the dilute solutions ($m < 0.05M$), extrapolation to zero molality by the use of equation (10-4-9) is uncertain. In Table (13-2-1), the values of $\gamma_\pm$ from amalgam cell measurements are given. The reference values obtained by extrapolation with equation (10-4-9) are shown in brackets. In the third column, values of $\gamma'_\pm$ at the freezing point, computed by Randall and Scott, with the use of the Debye and Hückel limiting equation are given. Their value of 0.537 at $0.05M$ is not widely different from 0.532, obtained from electromotive forces by Harned and Hecker. This discrepancy is caused principally by the difficulties of extrapolation. Values at 25° determined by the isopiestic vapor pressure method, are in good agreement with those from the electromotive forces.

Harned and Hecker computed $\bar{L}_2$ and $\bar{J}_2$ from 0 to 35° and up to $2M$ from their electromotive forces. These results are of value in giving a general view of the behavior of these quantities as functions of electrolyte concentration and temperature, but are subject to large errors. Accurate determinations of these quantities by calorimetric measurements have been made at 15, 20 and 25° from very dilute solutions to $0.4M$ by Wallace and Robinson.[15] Their results for sodium sulphate may be computed by the following empirical equations:

$$15°;\quad \bar{L}_2 = 2650m^{1/2} - 11382m + 7080m^{3/2} \tag{13-2-1}$$

$$20°;\quad \bar{L}_2 = 3100m^{1/2} - 12164m + 8340m^{3/2} \tag{13-2-2}$$

$$25°;\quad \bar{L}_2 = 3644m^{1/2} - 15468m + 22475m^{3/2} - 15108m^2 \tag{13-2-3}$$

$$25°;\quad \bar{J}_2 = 84m^{1/2} \tag{13-2-4}$$

$$25°;\quad \bar{C}_{p_2} = 84m^{1/2} - 50 \tag{13-2-5}$$

(3) HALIDES OF ZINC, CADMIUM, AND LEAD IN AQUEOUS SOLUTION

The properties of solutions of these salts have been investigated by means of cells of the type,

$$M_xHg \text{ (single or 2-phase)} \mid MX_2(m) \mid AgX\text{-}Ag$$

According to equation (10-3-2) their electromotive force is given by

$$\mathbf{E} = \mathbf{E}^0 - \frac{3}{2}\frac{RT}{\mathbf{F}} \ln \gamma_\pm m_\pm = \mathbf{E}^0 - \frac{3}{2}\frac{RT}{\mathbf{F}} \ln \gamma_\pm m(4)^{1/3} \tag{13-3-1}$$

Upon rearrangement and substitution of the limiting law of Debye and Hückel with an added linear term, we obtain the particularized form of equation (10-3-5)

$$\mathbf{E}^{0'} \equiv \mathbf{E} + \frac{3RT}{2\mathbf{F}} \ln m(4)^{1/3} - \frac{3RT}{2\mathbf{F}} 2.303\mathcal{S}_{(f)}\sqrt{c} = \mathbf{E}^0 - \frac{3RT}{2\mathbf{F}} Bm \tag{13-3-2}$$

which at 25° becomes

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[15] W. E. Wallace and A. L. Robinson, *J. Am. Chem. Soc.*, **63**, 958 (1941).

TABLE (13-2-1). THE MEAN ACTIVITY COEFFICIENTS OF SODIUM, LITHIUM, AND POTASSIUM SULPHATES

m	Na_2SO_4							Li_2SO_4		K_2SO_4		$Na_2S_2O_3$
	0^a	0^b	15^a	25^a	25^d	25^c	35^a	25^a	25^d	25^a	25^d	25^d
0.01		(0.719)	.....	....	....			.....	...			
.05	(0.532)	.537	(0.530)	(0.529)	....	(0.529)	(0.523)					
.075	.482		.482	.480		.480	.475					
.1	.446	.449	.447	.445	(0.445)	.445	.440	(0.468)	(0.468)	(0.441)	(0.441)	0.455
.2	.359	.374	.364	.365	.365	.366	.363	.398	.398	.361	.361	.382
.3	.310	...	.319	.322	.320	.322	.321		.362	.313	.317	.340
.5	.250		.263	.268	.267	.271	.270	.323	.322	.265	.264	.292
.7			.230	.234	.234	.237	.238		.299		.233	.263
1.				.204	.202	.204	.208	.276	.281			.236
1.2				.189	.187	.187	.194					
1.3				.182	.182	.180	.187					
1.5					.171			.272	.269			.212
2.					.153			.267	.269			.200

[a] Electromotive force.

[b] $\gamma'_{\pm}$ from freezing point.

[c] Calculated by equation (10-4-9) with parameters, $A = 0.809$; $B = -0.014$; $\mathring{a} = 3\ 63$.

[d] Isopiestic vapor pressure measurements. R. A. Robinson, J. M. Wilson and R. H. Stokes, *J. Am. Chem. Soc.*, **63**, 1011 (1941).

$$\mathbf{E}^{0\prime} = \mathbf{E} + 0.08873 \log m + 0.01783 - 0.155\sqrt{m} = \mathbf{E}^0 - f(m) \qquad (13\text{-}3\text{-}3)$$

if m is taken equal to c as a simplifying approximation. The behavior of $\mathbf{E}^{0\prime} - \mathbf{E}^0$ as a function of the concentration for some cadmium, lead and zinc halides are shown in Fig. (13-3-1). These curves are similar to those of Scatchard and Tefft,[16] whose method of treatment of these solutions will in a general way be followed. The measurements of cadmium chloride are those of Horsch,[17] and Harned and Fitzgerald,[18] and those on lead chloride were made by Carmody.[19] The zinc chloride results are those of Scatchard and Tefft. The zinc iodide,[20] cadmium bromide[21] and iodide[22]

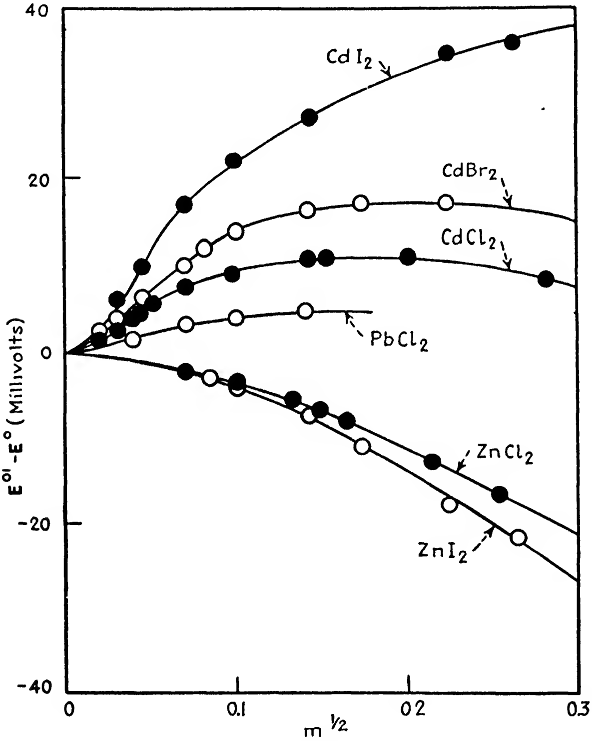

Fig. (13-3-1). Plots of $\mathbf{E}^{0\prime} - \mathbf{E}^0$ for halides of lead, zinc, and cadmium at 25°.

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[16] G. Scatchard and R. F. Tefft, *J. Am. Chem. Soc.*, **52**, 2272 (1930).

[17] W. G. Horsch, *J. Am. Chem. Soc.*, **41**, 1787 (1919).

[18] H. S. Harned and M. E. Fitzgerald, *J. Am. Chem. Soc.*, **58**, 2624 (1936).

[19] W. R. Carmody, *J. Am. Chem. Soc.*, **51**, 2905 (1929).

[20] R. G. Bates, *J. Am. Chem. Soc.*, **60**, 2983 (1938).

[21] R. G. Bates, *J. Am. Chem. Soc.*, **61**, 308 (1939).

[22] R. G. Bates *J. Am. Chem. Soc.*, **63**, 399 (1941).

plots were constructed from the data of Bates, and Bates and Vosburgh.[23] It is to be observed that the zinc chloride and zinc iodide plots possess no maxima, and as we proceed from this salt to cadmium chloride, bromide and iodide, a maximum appears which becomes increasingly pronounced.

There are two ways of treating these data. One is to employ the extended Debye and Huckel theory. LaMer, Gronwall, and Greiff have done this, and obtained for the mean distances of approach of the ions of zinc, lead, and cadmium chloride the values, 3.8, 1.75 and 1 Å, respectively. More recently, Bates[24] has applied the extended term theory for the purpose of extrapolating his electromotive force data of the cells containing cadmium bromide. Log $\gamma_\pm$ was computed by equations (3-6-3) and (3-6-5), and the data in Table (5-2-2) for a number of values of $\mathring{a}$.

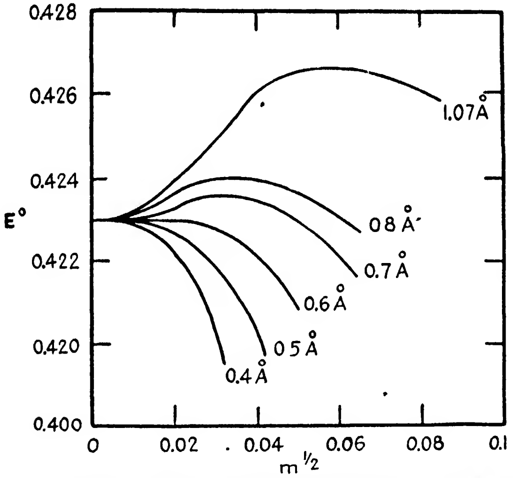

Fig. (13-3-2). Tentative values of E° of the cadmium amalgam-silver bromide cell at 25°, calculated by the extended equation (3-6-5).

By substitution in equation (13-3-1), tentative values of E^0 were computed at concentrations from 0.0005 to 0.01*M* salt. These are shown plotted versus $m^{1/2}$ in Fig. (13-3-2). The data are best represented by a value of $\mathring{a}$ equal to 0.6. Constant values of the tentative E^0 are obtained only at concentrations below 0.001*M*. Since the theory only describes the results at such low concentrations, and since a value of $\mathring{a}$ of 0.6 seems to have little physical significance, it seems probable that factors other than those deducible from simple Coulombic interaction of the ions must be considered. The second method described by Scatchard and Tefft,[25] and modified by

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[23] R. G. Bates and W. C. Vosburgh, *J. Am. Chem. Soc.*, **59**, 1188 (1937).

[24] R. G. Bates, *J. Am. Chem. Soc.*, **61**, 308 (1939).

[25] G. Scatchard and R. F. Tefft, *J. Am. Chem. Soc.*, **52**, 2272 (1930).

Harned and Fitzgerald,[26] is to assume that the effect is caused by incomplete dissociation of a kind represented by

$$MX_2 \rightarrow MX^+ + X^-$$

and

$$MX^+ \rightleftharpoons M^{++} + X^- \quad \text{or} \quad MX^+ + X^- \rightleftharpoons M^{++} + 2X^-$$

and then apply the law of mass action. In the cases of cadmium chloride and bromide, it is probable that both MX_2 and MX^+ are incompletely dissociated, but we shall assume that the first dissociation is complete. This assumption is not justifiable for cadmium iodide solutions. If α is the degree of dissociation of MX^+, and K the dissociation constant of this equilibrium, then the former is given by

$$\alpha = \frac{1}{2}\left\{-\left(1 + \frac{K}{m\gamma_{\alpha(M)}}\right) + \sqrt{\left(1 + \frac{K}{m\gamma_{\alpha(M)}}\right)^2 + 4\frac{K}{m\gamma_{\alpha(M)}}}\right\} \tag{13-3-4}$$

if $\gamma_{\alpha(X)}$ is taken equal to $\gamma_{\alpha(MX)}$. $\gamma_{\alpha(M)}$ is the real activity coefficient of the M^{++} ion, or $a_M/\alpha m$, where αm is the actual concentration of the ion. This means that $\gamma_{\alpha(M)}$ will have a value comparable to that found for strong electrolytes such as barium chloride. Therefore, we may compute $\gamma_{\alpha(M)}$ in dilute solution according to the Debye and Hückel equation,

$$\log \gamma_{\alpha(M)} = -\frac{2\mathfrak{S}_{(f)}\sqrt{2\mu'}}{1 + A\sqrt{2\mu'}} \tag{13-3-5}$$

We assign to $\mathring{a}$ the value of 5, which is of the order of magnitude found for barium chloride. Such a value of $\mathring{a}$ reduces the contribution of the extended terms of the theory to a magnitude small enough to be negligible for these computations. Note that $2\mu'$ equals $\Sigma m_i' z_i^2$ where m_i' is an estimated actual ionic concentration to be distinguished from stoichiometrical.† Values of α corresponding to given values of K and m may be obtained by the following procedure. An initial value of α is assumed for values of K and m. From this μ' is calculated by the relation,

$$\mu' = (2\alpha + 1)m \tag{13-3-6}$$

$\gamma_{\alpha(M)}$ is then obtained by equation (13-3-5). Then α is recalculated by equation (13-3-4) using this value of $\gamma_{\alpha(M)}$. From this value of α, $\gamma_{\alpha(M)}$ and μ' are recomputed, and equation (13-3-5) reapplied. This process is repeated until the same value of α, to 0.1 percent, is obtained.

Equation (13-3-1) has been written in terms of the stoichiometrical activity coefficient and molality. **E** may also be expressed by the alternative equation,

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[26] H. S. Harned and M. E. Fitzgerald, *J. Am. Chem. Soc.*, **58**, 2624 (1936).

† This symbolism is used in Chapter (15).

$$\mathbf{E} = \mathbf{E}^0 - \frac{RT}{2\mathbf{F}} \ln \alpha(1 + \alpha)^2 m^3 \gamma_\alpha^3 \tag{13-3-7}$$

where γ_α is the "real" mean activity coefficient, and $\alpha(\alpha + 1)^2 m^3$ is the product of the real concentrations. According to the definition of $\mathbf{E}^{0\prime}$ in equation (13-3-2)

$$\mathbf{E}^{0\prime} - \mathbf{E}^0 = \mathbf{E} - \mathbf{E}^0 + \frac{1}{2}\frac{RT}{\mathbf{F}} \ln 4m^3 - \frac{3}{2}\frac{RT}{\mathbf{F}} 2.303\mathfrak{S}_{(f)}\sqrt{2\mu} \tag{13-3-8}$$

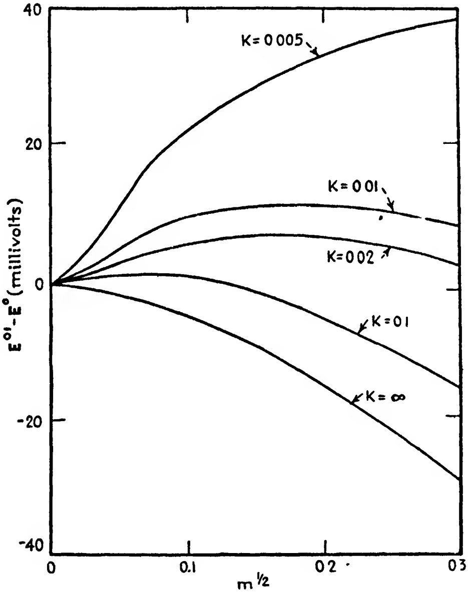

Fig. (13-3-3).
Plots of $\mathbf{E}^{0\prime}$-$\mathbf{E}^0$ according to equation (13-3-9) for various values of K.

which when combined with equation (13-3-7) gives

$$\mathbf{E}^{0\prime} - \mathbf{E}^0 = \frac{1}{2}\frac{RT}{\mathbf{F}} \ln 4 - \frac{1}{2}\frac{RT}{\mathbf{F}} \ln \alpha(1 + \alpha)^2 - \frac{3}{2}\frac{RT}{\mathbf{F}} \ln \gamma_\alpha - \frac{3}{2}\frac{RT}{\mathbf{F}} 2.303\mathfrak{S}_{(f)}\sqrt{2\mu} \tag{13-3-9}$$

From the values of α, computed as above described for different values of K, and values of γ_α assumed to equal those derived from measurements on a strong 2-1 electrolyte such as barium chloride, the deviation factor, $\mathbf{E}^{0\prime} - \mathbf{E}^0$, may be computed. Such calculations are represented in Fig. (13-3-3) for values of K ranging from 0.01 to ∞. By comparison with Fig. (13-3-2), we note a close similarity, which indicates that barium, zinc, lead and cadmium chlorides in dilute solutions may be explained by this theory provided we assign ionization constants for the reaction, $MX^+ \rightleftharpoons M^{++} + X^-$, of the order ∞, 0.1, 0.04, 0.01, respectively.

An illustration of the more careful application of this method is to be found in the work of Harned and Fitzgerald,[27] who made a comprehensive investigation of aqueous cadmium chloride solutions. In Fig. (13-3-4) are shown plots of the deviation factors, $E^{0\prime} - E^0$, at 0, 25, and 40°, calculated by this method, and which fitted closely the values of $E^{0\prime}$, computed from the experimental results expressed by equation (13-3-3). The values of the ionization constants employed, which seemed to agree best with the results, are given.[28]

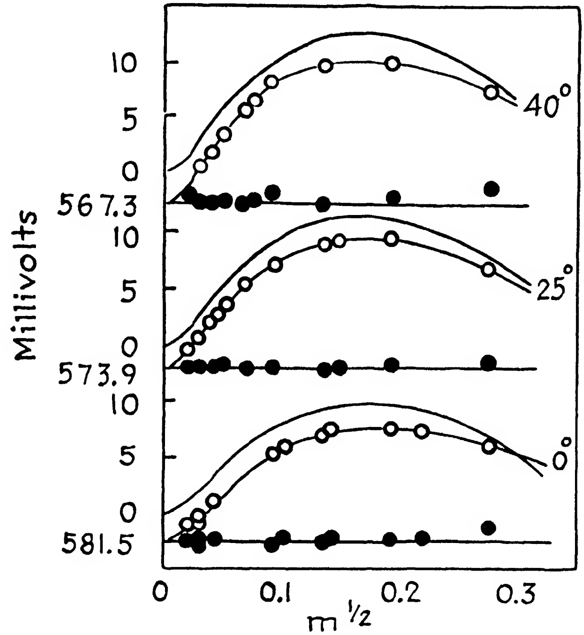

Fig. (13-3-4). Extrapolation functions at 0°, 25°, and 40° (scale in mv., diameters of circles equal 1 mv. Curves without points are calculated by equation (13-3-9). $E^{0\prime} - E^0$ is plotted. Circles represent plots of $E^{0\prime}$ according to equation (13-3-2). Dots represent E^0 according to equation (13-3-10). The ionization constants are 0.01, 0.011, and 0.013 at 40°, 25°, and 0°, respectively.

Upon rearrangement of equation (13-3-7), E^0 is given by

$$E^0 = E + \frac{3}{2}\frac{RT}{F} \ln \alpha(1 + \alpha)^2 m^3 \gamma_\alpha^3 \tag{13-3-10}$$

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[27] H. S. Harned and M. E. Fitzgerald, *J. Am. Chem. Soc.*, **58**, 2624 (1936).

[28] They are in approximate agreement with the value, 0.010, estimated from conductance data by E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

The straight line plots used for extrapolation of E^0 were obtained by adding to the experimental values of E the second term on the right of this equation. This fit shows that the simple expedient of combining the law of mass action and the Debye and Hückel limiting law affords a satisfactory extrapolation method.

Bates[29] in an equally comprehensive investigation of cadmium bromide solutions by means of the cell,

$$\text{Cd-Cd}_x\text{Hg} \mid \text{CdBr}_2(m) \mid \text{AgBr-Ag}$$

has also determined the standard potential from 0 to 40°. By combining these with the standard potentials of the silver-silver chloride, and silver-silver bromide electrodes [Equations (11-2-6) and (12-2-2), respectively], the standard potential of the electrode, $\text{Cd-Cd}_x\text{Hg} \mid \text{Cd}^{++}$ $(a = 1)$, may be obtained. In Table (13-3-1A), the standard potentials obtained from these results are compiled. The last two columns contrast the values obtained by Harned and Fitzgerald, and Bates. The agreement at 25, 30, 35 and 40° is excellent, but an increasing difference is observed with decreasing temperature. This discrepancy is still unexplained.

Bates and Vosburgh measured the cell,

$$\text{Cd-Cd}_x\text{Hg} \mid \text{CdI}_2(m) \mid \text{Hg}_2\text{I}_2\text{-Hg}$$

containing cadmium iodide solutions only, and also cells containing cadmium iodide-sulphate mixtures, and cadmium iodide-potassium iodide mixtures. The standard potential of the mercury-mercurous iodide electrode was obtained,[30] the activity coefficient of cadmium iodide[31] was evaluated, and the numerous equilibria involved in these solutions[32] were investigated at 25°.[33] The thermodynamic properties, $\gamma_\pm$, $\bar{L}_2$, and $\bar{J}_2$, have been determined by Bates[34] from measurements of the cells,

$$\text{Cd-Cd}_x\text{Hg} \mid \text{CdI}_2(m) \mid \text{AgI-Ag}$$

from 5 to 40°.

Zinc chloride,[35] bromide[36] and iodide[37] solutions have been studied by means of the cells,

$$\text{Zn-Zn}_x\text{Hg} \mid \text{ZnX}_2(m) \mid \text{AgX-Ag}$$

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[29] R. G. Bates, *J. Am. Chem. Soc.*, **61**, 308 (1939).

[30] R. G. Bates and W. C. Vosburgh, *J. Am. Chem. Soc.*, **59**, 1188 (1937).

[31] R. G. Bates and W. C. Vosburgh, *J. Am. Chem. Soc.*, **59**, 1583 (1937).

[32] R. G. Bates and W. C. Vosburgh, *J. Am. Chem. Soc.*, **60**, 136 (1938).

[33] For earlier work on cadmium halides, see, W. G. Horsch, *J. Am. Chem. Soc.*, **41**, 1787 (1919); F. H. Getman, *J. Phys. Chem.*, **35**, 588 (1931); W. W. Lucasse, *J. Am. Chem. Soc.*, **51**, 2597 (1929)

[34] R. G. Bates, *J. Am. Chem. Soc.*, **63**, 399 (1941).

[35] G. Scatchard and R. F. Tefft, *J. Am. Chem. Soc.*, **52**, 2272 (1930); R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **36**, 740 (1940); Transference numbers from cells with liquid junction are given by A. C. Harris and H. N. Parton, *Ibid.*, **36**, 1139 (1940).

[36] H. N. Parton and J. W. Mitchell, *Trans. Faraday Soc.*, **35**, 758 (1939); R. H. Stokes and J. M. Stokes, *Ibid.*, **41**, 488 (1945).

[37] R. G. Bates, *J. Am. Chem. Soc.*, **60**, 2983 (1938)

The work of Robinson and Stokes on zinc chloride, and of Bates on zinc iodide covers the temperature range from 5 to 40°, while that of Parton and Mitchell on zinc bromide is at 25° only. The standard potentials of these cells, as well as that of the two phase zinc amalgam electrode, are given in Table (13-3-2A). The agreement between the standard potentials of the latter electrode obtained from the different sources is excellent. From the standard potentials of the cells and their electromotive forces, values of $\gamma_\pm$ were computed by equation (13-3-1). These have been compiled in Table (13-3-3A).

By means of equations (10-5-15) and (10-5-17), the relative partial molal heat content, $\bar{L}_2$, and the relative partial molal heat capacity, $\bar{J}_2$, of zinc chloride and iodide, and cadmium chloride, bromide, and iodide, have been derived from electromotive forces. For zinc chloride and iodide, these quantities may be computed from the data in Table (13-3-4A).

Robinson and Wallace[37a] have determined $\bar{L}_2$ and $\bar{J}_2$ up to 0.2M from heat of dilution data. Their results differ considerably from those computed from the electromotive forces and, being unquestionably more accurate, are given in Table (13-3-5A). A re-examination of the methods employed for computing these quantities from electromotive force data may clarify the situation.

(4) General Considerations Regarding 1-2 and 2-1 Electrolytes in Aqueous Solutions

The activity coefficients at 25° of 1-2 and 2-1 halides and sulphates and barium hydroxide[38] are plotted against $m^{1/2}$ in Fig. (13-4-1). The upper group from barium chloride to magnesium iodide inclusive are strong electrolytes. Values of $\mathring{a}$, the mean distance of approach of the ions, for these salts are roughly between 4 for barium chloride and 6 for magnesium and zinc iodides. These are less than the value of $q = 7$ Å of Bjerrum's theory of ionic association for 2-1 or 1-2 electrolytes, and consequently, some ionic association may be expected to occur. $[M^{++}X^-]$ or $[MX]^+$ ions are not excluded in any of these solutions, and may be present to a considerable extent in concentrated solutions of barium chloride. The high activity coefficients of zinc iodide and cobalt chloride should be noted. The middle group containing the alkali sulphates and barium hydroxide, with $\mathring{a}$ values from 3 to 4, show more evidence of some kind of ionic association such as the presence of $[MSO_4]^-$, $[Ba(OH)]^+$ ions. Lead chloride and the incompletely ionized cadmium halides form a third group. By the method of treatment of electromotive forces outlined in the preceding section, Harned and Fitzgerald obtained 0.011 for the ionization constant of $[CdCl]^+$ at 25°. Similarly, Bates,[39] and Bates and Vosburgh,[40] obtained

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[37a] A. L. Robinson and W. E. Wallace, *Chem. Rev.*, **30**, 195 (1942).

[38] H. S. Harned and C. M. Mason, *J. Am. Chem. Soc.*, **54**, 1439 (1932).

[39] R. G. Bates, *J. Am. Chem. Soc.*, **61**, 308 (1939).

[40] R. G. Bates and W. C. Vosburgh, *J. Am. Chem. Soc.*, **60**, 136 (1938).

0.006 and 0.004 for the ionization constants of $[CdBr]^+$ and $[CdI]^+$, respectively. Carmody's[41] results with lead chloride cells leads to a value of the ionization constant of $[PbCl]^+$ of the order of 0.03.

These observations are in accord with Onsager's and, particularly, with Righellato and Davies' interpretation of conductance data [Chapter (6), Section (3)]. They found that the group, barium chloride to magnesium chloride, was composed of very strong electrolytes. The estimated ionization constants of $[LiSO_4]^-$, $[NaSO_4]^-$, and $[KSO_4]^-$ were 0.23, 0.20, and 0.15, respectively, and are in the same order as indicated by their activity coefficients. $[CaNO_3]^+$, $[SrNO_3]^+$, and $[BaNO_3]^+$ possess ionization constants of the same order of magnitude. Finally, the values of 0.03 and 0.01 for $[PbCl]^+$ and $[CdCl]^+$ are in close agreement with those evaluated from the thermodynamic measurements.

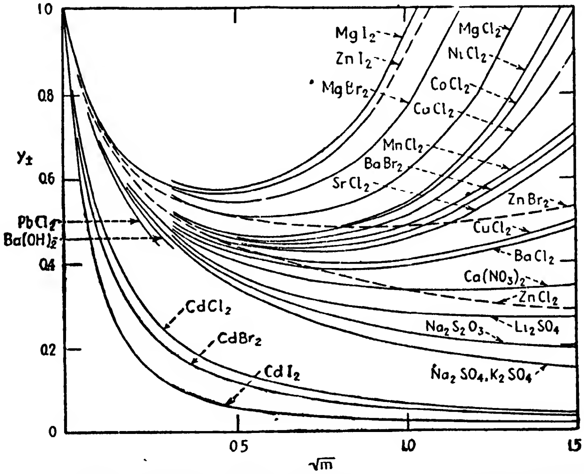

Fig. (13–4–1). Mean activity coefficients of 1-2 and 2-1 electrolytes at 25°.

The curves for zinc chloride and zinc bromide exhibit a curious feature. In dilute solutions both salts behave as strong electrolytes, electromotive force experiments leading to $\mathring{a}$ values of approximately 5 to 6, but above about $0.3M$ the activity coefficient curves begin to descend in such a way as to intersect the curves for many other electrolytes; the reason for this behavior is not clear.

(5) The Thermodynamics of Aqueous Zinc Sulphate Solutions

Bray[42] has measured the cells,

$$Zn\text{-}Zn_xHg \mid ZnSO_4(m) \mid PbSO_4\text{-}Pb_xHg\text{-}Pb$$

at 25° over a wide concentration range. More recently, Cowperthwaite

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[41] W. R. Carmody, *J. Am. Chem. Soc.*, **51**, 2905 (1929).

[42] U. B. Bray, *J. Am. Chem. Soc.*, **49**, 2372 (1972).

and LaMer[43] investigated this cell at low concentrations (0.0005 to 0.01M) at temperatures from 0 to 50°. The relative partial heat content, $\bar{L}_2$, has been determined at low concentrations by Lange, Monheim, and Robinson.[44] These investigations will serve to illustrate some important characteristics of 2-2 electrolytes.

We shall employ the quantity, $\mathbf{E}^{0\prime}$, defined in terms of the equation for the cell by

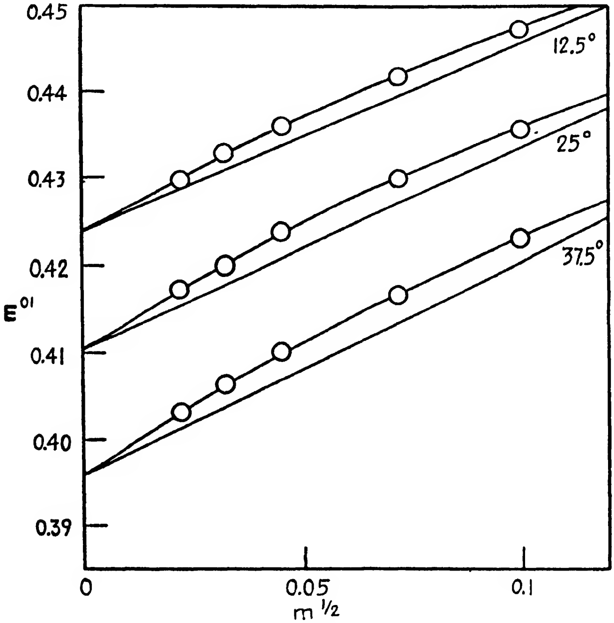

Fig. (13-5-1). Plots of $\mathbf{E}^{0\prime}$ [Equation (13-5-1)] for zinc sulfate solutions. Straight lines represent limiting law.

$$\mathbf{E}^{0\prime} \equiv \mathbf{E} + \frac{\nu RT}{\mathbf{NF}} \ln m = \mathbf{E}^0 - \frac{\nu RT}{\mathbf{NF}} \ln \gamma_\pm \tag{13-5-1}$$

In Fig. (13-5-1), $\mathbf{E}^{0\prime}$, obtained from Cowperthwaite and LaMer's results, is plotted against $m^{1/2}$. The straight line represents the limiting equation of the Debye and Hückel theory. The noticeable departure from the limiting law, characterized by a "hump" agrees with the expectation of the extended Debye theory as developed by Gronwall, LaMer and Sandved. Indeed, this probably constitutes the most rigorous verification of the extended theory in aqueous solutions.

By employing equations (3-6-4), Cowperthwaite and LaMer obtained

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[43] I. A. Cowperthwaite and V. K. La Mer, *J. Am. Chem. Soc.*, **53**, 4333 (1931).

[44] E. Lange, J. Monheim, and A. L. Robinson, *J. Am. Chem. Soc.*, **55**, 4733 (1933).

a value of $\mathring{a}$ which led to an exact agreement between the theory and their data, since their computed value of E^0 was constant throughout the concentration range, 0.0005 to 0.01*M*. Furthermore $\mathring{a}$ was found to have the constant value, 3.64, at all temperatures from 0 to 50°. Although the inclusion of additional effects, linear in concentration, might alter the numerical results slightly, the concentrations are too low for such effects to be comparable in magnitude to the contribution of the extended terms.

The values of $\bar{L}_2$ derived from these electromotive forces[45] are in good agreement with those obtained from the calorimetric data by Lange, Monheim and Robinson from 0.001 to 0.01*M* as shown by Table (13-5-1). The latter have been decreased uniformily by 25 cal. in accordance with our re-extrapolation explained in Chapter (8), Section (2).

The activity coefficients in concentrated solutions have been determined by the electromotive force method by Bray,[46] and the isopiestic vapor pressure method by Robinson and Jones.[47] In Table (13-5-2), values of this quantity at 25° are given. The value of $\gamma_\pm$ (0.387) at 0.01*M* from Cowperthwaite and LaMer's computations, is used for the recalculation of Bray's values. The vapor pressure results are based on the value of 0.150 at 0.1*M* also determined from electromotive forces. The agreement is quite good throughout the concentration range in which measurements by both methods were obtained.

TABLE (13-5-1). THE RELATIVE PARTIAL MOLAL HEAT CONTENT OF ZINC SULFATE AT 25° FROM ELECTROMOTIVE FORCE AND CALORIMETRIC DATA

m	0.0005	0.001	0.002	0.005	0.01
$\bar{L}_2$ (E.M.F.)	(198)	385	480	674	772
$\bar{L}_2$ (Cal.)	227	327	463	655	765

For 2-2 electrolytes, q = 14 Å. Since Cowperthwaite and LaMer found $\mathring{a}$ to be 3.6 for zinc sulphate, it is to be expected that this salt will be incompletely dissociated. With this value of $\mathring{a}$, Bjerrum's equation (3-7-13) leads to 0.003 for K. Owen and Gurry[48] have measured the conductances of zinc and copper sulphates in water at 25°, and obtained 0.0049 and 0.0043 for the dissociation constants, respectively. Davies[49] reported 0.0045 at 18° for both these salts.

(6) ACTIVITY COEFFICIENTS OF THE SULFATES OF BIVALENT METALS IN AQUEOUS SOLUTION

Although the thermodynamics of aqueous solutions of cadmium, copper, magnesium, manganese, and nickel sulphates have not been studied as

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[45] H. S. Harned, *J. Am. Chem. Soc.*, **58**, 360 (1937).

[46] U. B. Bray, *J. Am. Chem. Soc.*, **49**, 2372 (1927).

[47] R. A. Robinson and R. S. Jones, *J. Am. Chem. Soc.*, **58**, 959 (1936).

[48] B. B. Owen and R. W. Gurry, *J. Am. Chem. Soc.*, **60**, 3074 (1938).

[49] C. W. Davies, *Trans. Faraday Soc.*, **23**, 351 (1927).

comprehensively as zinc sulphate solutions, sufficient data are available to indicate that the behavior of their activity coefficients is of considerable interest. In the first place the freezing point data in dilute solutions show that the activity coefficients of each of these electrolytes have nearly the same value. Thus, at $0.1M$ different investigators have obtained values of 0.149, 0.150, 0.166 and 0.160 for the activity coefficients of copper, cadmium, magnesium and zinc sulphate, respectively. Further, LaMer and Parks[49a] obtained, from electromotive force measurements, values of $\gamma_\pm$ for cadmium sulphate (0.699, 0.476, and 0.383 at $0.001M$, $0.005M$, and $0.01M$) which are nearly identical with those for zinc sulphate given in Table (13-5-2). The present uncertainty in the data, and also in the methods of extrapolation, is probably as great as the spread of the values of $\gamma_\pm$, obtained from the freezing point results. In any case, the individuality is very slight indeed.

TABLE (13-5-2). THE MEAN ACTIVITY COEFFICIENT OF ZINC SULFATE IN AQUEOUS SOLUTION AT 25°

m	$\gamma_\pm$(E.M.F)	$\gamma_\pm$(V.P.)
0.0005	0.780	.....
.001	.700	.....
.002	.608	.....
.005	.477	.....
.01	.387	.....
.02	.298	.....
.05	.202	.....
.1	.150	(0.150)
.2	.104	.104
.5	.0634	.0626
1.	.0438	.0434
1.5	.0372	.0378
2.	.0354	.0350
2.5	.0368	.0360
3.	.0409	.0397
3.5	.0478	.0467

This conclusion is also substantiated by the isopiestic vapor pressure data of Robinson and Jones[50] in solutions of high concentration (0.1 to $4M$). If, for the purpose of illustration, we let $\gamma_\pm$ be 0.150 at $0.1M$ and 25° for all these sulphates, the result shown in Table (13-6-1) is obtained. Inspection of these values shows that, even in concentrated solutions, the individuality is very much less pronounced than that observed for 1-1 and 2-1 electrolytes.

(7) 1-3, 3-1, 3-2, AND 1-4 ELECTROLYTES

Accurate data on these unsymmetrical types of electrolytes are fragmentary. Only in one case, lanthanum chloride, have results been ob-

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[49a] V. K. LaMer and W. G. Parks, *J. Am. Chem. Soc.*, **53**, 2040 (1931); *Ibid.*, **55**, 4343 (1933).

[50] R. A. Robinson and R. S. Jones, *J. Am. Chem. Soc.*, **58**, 959 (1936).

tained in solutions sufficiently dilute for extrapolation.[51] From freezing point measurements, the activity coefficients of lanthanum nitrate,[52] potassium ferri-,[53] and cobalti-cyanide,[54] and lanthanum sulphate[55] have been computed. Isopiestic vapor pressure data on solutions of lanthanum chloride,[56, 57, 58] potassium ferrocyanide,[56] aluminum sulphate,[56] and some 3-1 rare earth chlorides[58] have been made. Aqueous indium sulphate solutions have been investigated from 0 to 35° by the use of the cell,

$$\mathrm{In} \mid \mathrm{In_2(SO_4)_3}(m) \mid \mathrm{Hg_2SO_4\text{-}Hg}$$

by Hattox and DeVries.[59]

From measurements of the cells,

$$\mathrm{Ag\text{-}AgCl} \mid \mathrm{LaCl_3}(c_1) \mid \mathrm{LaCl_3}(c_2) \mid \mathrm{AgCl\text{-}Ag}$$

and the transference numbers, Shedlovsky and MacInnes[60] have supplied the data for the determination of the activity coefficient of lanthanum chloride from 0.0006 to 0.03333 molar by the method described in Chapter (12), Section (1). Due to an error in calculation, the erroneous conclusion was made that lanthanum chloride in water does not conform to theory in dilute solutions. We have repeated the computation and find that, as a first approximation, the observed results may be calculated by the Debye

TABLE (13-6-1). THE MEAN ACTIVITY COEFFICIENTS OF BIVALENT METAL SULFATES AT 25°

m	$ZnSO_4$	$CdSO_4$	$MnSO_4$	$MgSO_4$	$CuSO_4$	$NiSO_4$
0.1	(0.150)	(0.150)	(0.150)	(0.150)	(0.150)	(0.150)
.2	.104	.102	.1056	.1077	.1043	.1049
.3	.0831	.0815	.0850	.0877	.0834	.0841
.4	.0708	.0692	.0728	0760	.0708	.0713
.5	.0626	.0609	.0643	.0678	.0624	.0628
.7	.0520	.0501	.0532	.0574	.0515	.0516
1.	.0434	.0411	0441	.0488	...	.0426
1.5	0368	.0342	0373	.0430	.....	.0360
2.	.0350	.0318	.0351	.0419	.....	.0343
2.5	.0360	.0315	.0353	.0441	.....	.0357
3.	.0397	.0327	.0375	0495	.....	.....
3.5	.0467	.0351	.0416	. ...	.....	.....
4.	.....	.....	.0478	.....	.....	.....
4.25	.....	.....	.0518	.....	.....	.....

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[51] T. Shedlovsky and D. A. MacInnes, *J. Am. Chem. Soc.*, **61**, 200 (1939).

[52] R. E. Hall and W. D. Harkins, *J. Am. Chem. Soc.*, **38**, 2658 (1916).

[53] G. T. Bedford, *Proc. Roy. Soc.*, **83A**, 454 (1909).

[54] C. Robertson and V. K. LaMer, *J. Phys. Chem.*, **35**, 1953 (1931).

[55] F. Hovorka and W. H. Rodebush, *J. Am. Chem. Soc.*, **47**, 1614 (1925); W. H. Rodebush, *Ibid.*, **48**, 709 (1926).

[56] R. A. Robinson, *J. Am. Chem. Soc.*, **59**, 84 (1937).

[57] R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1229 (1939).

[58] C. M. Mason, *J. Am. Chem. Soc.*, **60**, 1638 (1938).

[59] E. M. Hattox and T. DeVries, *J. Am. Chem. Soc.*, **58**, 2126 (1936).

[60] T. Shedlovsky and D. A. MacInnes, *J. Am. Chem. Soc.*, **61**, 200 (1939).

and Hückel formula

$$\log y_{\pm} = -\frac{3.7446\sqrt{c}}{1 + 4.75\sqrt{c}} \tag{13-7-1}$$

which yields the reasonable value of 5.9Å. for the mean distance of approach of the ions. The theoretical functions in this equation were computed from the recent values of the universal constants given in Appendix B, Table (B-1-1). The average difference between the calculated and observed results is 0.0015 in $y_{\pm}$. The character of this deviation from theory indicates that this difference could be reduced by employing the extended terms of the theory.† Since there is no large difference between $y_{\pm}$ and $\gamma_{\pm}$ at the low concentrations, this equation has been employed to compute the value of 0.392 for $\gamma_{\pm}$ at 0.05*M*.

TABLE (13-7-1). MEAN ACTIVITY COEFFICIENTS OF LANTHANUM CHLORIDE, POTASSIUM FERROCYANIDE, ALUMINUM AND INDIUM SULFATES AT 25°

m	$LaCl_3$	$K_4Fe(CN)_6$[a]	$Al_2(SO_4)_3$[a]	$In_2(SO_4)_3$[b]
0.001	0.788	.....	.....	.....
.005	.637	.....	....	.....
.01	.559	.....	. ..	0.142
.02	.484	.....	.....	.095
.03	.442	.....	.....	.071
.05	.392	(0.189)	. .	.054
.1	.336	.138	(0.0350)	.035
.2	.293	.107	.0223	.022
.3	.281	.088	.0174	.017
.4	.280	.076	.0151	.015
.5	.285	.067	.0115	....
.7	.305	.055	.0133	.....
1.	.366	.048	.0176	.....
1.2	.426	.....	.....	.....
1.4	.503	.....	.....	.....
1.5	.554	.....	....	.....

[a] R. A. Robinson. *J. Am. Chem. Soc.*, **59**, 84 (1937).

[b] E. M. Hattox and T. DeVries, *J. Am. Chem. Soc.*, **58**, 2126 (1936). Results obtained at 0°, 15° and 30°. L_2 estimated.

Robinson[61] and Mason[62] made isopiestic vapor pressure measurements on lanthanum chloride solutions at high concentrations (0.05 to 2*M*). Activity coefficients derived from these results have been brought into accord with the values at low concentration.[63] These are recorded in Table (13-7-1). Chlorides of aluminum, scandium, yttrium, cerium, praseo- and neodymium have also been investigated by this method in concentrated solutions by Mason. These are compiled in Table (13-7-1A).

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† Dr. Shedlovsky has informed us that he has recomputed his results. By using the Debye and Hückel formula with an additional term, $Dc \log c$, he is able to reduce the average deviation to 0.0002

[61] R. A. Robinson, *J. Am. Chem. Soc.*, **59**, 84 (1937).

[62] C. M. Mason, *J. Am. Chem. Soc.*, **60**, 1638 (1938).

[63] R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1229 (1939).

The 1-4 and 3-2 electrolytes are represented in Table (13-7-1) by potassium ferrocyanide, aluminium sulphate[64] and indium sulphate.[65] In these cases, the extrapolations are uncertain, but the results are of the right order of magnitude, and serve to illustrate the behavior of electrolytes of these valence types. Further advance in this field will require much additional data in very dilute solutions.

(8) THE IONIZATION CONSTANT OF HSO_4^- FROM ELECTROMOTIVE FORCE MEASUREMENTS

The following sections will be devoted principally to a discussion of the activity coefficient, the relative partial molal heat content and heat capacity of sulphuric acid in aqueous solutions, derived from measurements of the cells,

$$H_2 \mid H_2SO_4(m) \mid PbSO_4\text{-}PbO_2\text{-}Pt$$

$$H_2 \mid H_2SO_4(m) \mid Hg_2SO_4\text{-}Hg$$

Since sulphuric acid is a partially weak electrolyte, difficulties arise in the determination of the standard potentials of these cells which can be overcome if the ionization constant

$$K_{2A} = \frac{m_H m_{SO_4} \gamma_H \gamma_{SO_4}}{m_{HSO_4} \gamma_{HSO_4}} \qquad (13\text{-}8\text{-}1)$$

is known.

Recently, this quantity has been determined by Hamer[66] from measurements of the cells

$$H_2 \mid NaHSO_4(m_1),\ Na_2SO_4(m_2),\ NaCl(m_3) \mid AgCl\text{-}Ag$$

and by Young, Klotz and Singleterry[67] who used a spectrophotometric method. Values determined by both these methods are recorded at various temperatures in Table (13-8-1). The values at 25° are in good agreement with 0.0118(m-scale) obtained by Sherill and Noyes[68] from the combined conductance and transference data of Noyes and Stewart[69] who took into consideration the mobility and activity coefficient corrections given by the interionic attraction theory. We note that this value is considerably below 0.03, 0.02, and 0.017 previously reported by investigators[70] who did not make all the required corrections.

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[64] R. A. Robinson, *J. Am. Chem. Soc.*, **59**, 84 (1937).

[65] E. M. Hattox and T. DeVries, *J. Am. Chem. Soc.*, **58**, 2126 (1936).

[66] W. J. Hamer, *J. Am. Chem. Soc.*, **56**, 866 (1934).

[67] Private communication from Professor T. F. Young based on the Dissertations of I. M. Klotz and C. R. Singleterry, University of Chicago (1940).

[68] M. S. Sherrill and A. A. Noyes, *J. Am. Chem. Soc.*, **48**, 1861 (1926).

[69] A. A. Noyes and M. A. Stewart, *J. Am. Chem. Soc.*, **32**, 1133 (1910).

[70] R. S. Livingston, *J. Am. Chem. Soc.*, **48**, 45 (1926); C. Drucker, *Z. physik. Chem.*, **96**, 381 (1920); I. M. Kolthoff, *Rec. trav. chim.*, **43**, 207 (1924).

The calculation of K_{2A} from electromotive force measurements is difficult and involves complicated arithmetical approximations.[71] We shall find [Chapter (15)] that accurate values of ionization constants of magnitudes less than 10^{-3} can be made from cells without liquid junctions. When the ionization constant is greater than this, it becomes more difficult to obtain accurate results. Since K_{2A} for HSO_4^- is approximately 10^{-2}, the values recorded are necessarily approximations.

The values obtained by the optical method change more rapidly with temperature than those derived from the electromotive forces and lead to a value for the heat of ionization, $-\Delta H_i^0$, of 5200 ± 100 cals. This agrees with 5200 cals. obtained recently by Pitzer,[72] whereas $-\Delta H_i^0$ from the electromotive forces is found to be 2200. A reexamination of the methods of computing K_{2A} from the electromotive forces may remove this discrepancy.

Table (13-8-1). The Ionization Constant of HSO_4^-

t	K_{2A}(E.M.F.)[a]	K_{2A}[b]
0	0.0148	.....
5	.0143	0.0180
10	.0139	.....
15	.0134	.0136
20	.0127	.....
25	.0120	.0101
30	.0113	.....
35	.0105	.0075
40	.0097	.....
45	.0089	.0056
50	.0079	.....
55	.0070	.0041
60	.0060	.....

[a] W. J. Hamer, *J. Am. Chem. Soc.*, **56**, 866 (1934).
[b] See Reference 67.

(9) The Standard Potential of the Cell,[73]

$$H_2 \mid H_2SO_4\ (m) \mid PbSO_4\text{-}PbO_2\text{-}Pt$$

(a) Evaluation of the Standard Potential, E^0, by an Empirical Method.

The chemical reaction represented by the cell in question is taken to be

$$H_2 + PbO_2(s) + H_2SO_4(m) = PbSO_4(s) + 2H_2O$$

and the electromotive force is given by the equation,

$$\mathbf{E} = \mathbf{E}^0 + (RT/2\mathbf{F}) \ln m_H^2 m_{SO_4} + (RT/2\mathbf{F}) \ln \gamma_H^2 \gamma_{SO_4} - (RT/2\mathbf{F}) \ln a_w^2 \qquad (13\text{-}9\text{-}1)$$

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[71] W. J. Hamer, *J. Am. Chem. Soc.*, **56**, 866 (1934).
[72] K. S. Pitzer, *J. Am. Chem. Soc.*, **59**, 2365 (1937).
[73] W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 9 (1935).

where **E** is the measured electromotive force of the cell, and $\mathbf{E}^0$ is its standard potential. The activity of the water in a solution of m molal sulphuric acid is represented by a_w.

We shall first employ an empirical method of extrapolation.[74] Equation (13-9-1) may be rearranged in the form,

$$\mathbf{E} - (RT/2\mathbf{F}) \ln m_{\mathrm{H}}^2 m_{\mathrm{SO_4}} = \mathbf{E}^0 + (RT/2\mathbf{F}) \ln \gamma_{\mathrm{H}}^2 \gamma_{\mathrm{SO_4}} - (RT/2\mathbf{F}) \ln a_w^2$$

(13-9-2)[75]

and if the left side is plotted against the square root of the molality, a straight line may be obtained in dilute solution. At zero concentration this function equals $\mathbf{E}^0$, since by definition the last two terms on the right vanish.

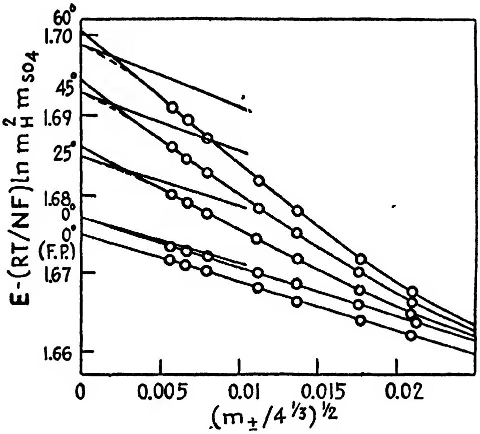

Fig. (13-9-1). Plots of left side of equation (13-9-2) against $(m_\pm/4^{1/3})^{1/2}$.

As a comparison with this extrapolation, the activity coefficients at 0° of Randall and Scott,[76] obtained from freezing point determinations, were used to evaluate the second term on the right of equation (13-9-2). The difference between this term and the left side of the same equation gives $\mathbf{E}^0$, when a_w, a very small term, is neglected. The electromotive force measurements are parallel to their curve as found for other electrolytes by Randall and Young.[77] The extrapolations of the left side of equation (13-9-2) against $(m_\pm/4^{1/3})^{1/2}$ are given in Fig. (13-9-1) at 0, 25, 45, and 60° from 0.0005 to 0.01M. The lower curve is the one given by freezing point

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[74] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Company, New York (1923), p. 334.

[75] In very dilute solutions, these electromotive forces were corrected for the solubility of $\mathrm{PbSO_4}$. W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 9 (1935).

[76] M. Randall and G. N. Scott, *J. Am. Chem. Soc.*, **49**, 647 (1927).

[77] M. Randall and L. E. Young, *J. Am. Chem. Soc.*, **50**, 989 (1928).

measurements. For clear comparison with electromotive force measurements, 0.002v. has been subtracted from the function computed from freezing point measurements. The freezing point curve has a slight "hump" below 0.002*M*, but this may be due to the somewhat arbitrary extrapolation by Randall and Scott of their function, $j/m^{1/2}$, in dilute solutions. The points computed from the electromotive forces are not accurate enough to justify this slight "hump", and consequently straight lines have been drawn at the other temperatures. The standard potentials, determined in this manner, are given in the second column of Table (13-9-1). These were least squared to fit a quadratic equation, and the equation with numerical values is

$$\mathbf{E}^0 = 1.6769_4 + 342.17 \times 10^{-6}t + 83.11 \times 10^{-8}t^2 \qquad (13\text{-}9\text{-}3)$$

Values of $\mathbf{E}^0$, calculated by this equation, agree with the observed values to less than 0.1 mv.

TABLE (13-9-1). STANDARD POTENTIALS OF THE CELL, $H_2 \mid H_2SO_4(m) \mid PbSO_4\text{-}PbO_2\text{-}Pt$

t	[Equation (13-9-2)]	[Equation (13-9-6)]	Δ(mv.)
0	1.67694	1.67694	0
5	1.67870	1.67846	0.24
10	1.68045	1.67998	.47
15	1.68228	1.68159	.69
20	1.68411	1.68322	.89
25	1.68597	1.68488	1.09
30	1.68800	1.68671	1.29
35	1.68991	1.68847	1.45
40	1.69196	1.69036	1.60
45	1.69396	1.69231	1.65
50	1.69616	1.69436	1.80
55	1.69831	1.69649	1.82
60	1.70044	1.69861	1.83

(b) Evaluation of the Standard Potential, $\mathbf{E}^0$, by a Method Employing the Ionization Constant of HSO_4^-.

In the previous method of extrapolation, we have employed stoichiometrical concentrations. Sulfuric acid is known to be a moderately strong electrolyte, the second step in its ionization being incomplete. This is shown to be true in Fig. (13-9-1), since the experimental slopes are greater than those predicted by the limiting law of Debye and Hückel for a completely dissociated electrolyte.

This method of extrapolation possesses the advantage of simplicity, but is subject to two major criticisms. When $m^{1/2}$ is plotted, the extrapolation from the last experimental point to zero concentration is long. Secondly, for an electrolyte which is partially dissociated, the straight line extrapolation does not conform to the law of Debye and Hückel at zero concentration.

An alternative method, which has the advantage of including the limiting law, will now be described.

If the value of the real concentration of the hydrogen ion, given by the equation

$$K_{2A} = (m_{\mathrm{H}} m_{\mathrm{SO_4}} \gamma_{\mathrm{H}} \gamma_{\mathrm{SO_4}})/(m_{\mathrm{HSO_4}} \gamma_{\mathrm{HSO_4}}) \tag{13-9-4}$$

is substituted in equation (13-9-1), we obtain

$$\mathbf{E} = \mathbf{E}^0 + (RT/2\mathbf{F}) \ln m_{\mathrm{H}} m_{\mathrm{HSO_4}} + (RT/2\mathbf{F}) \ln \gamma_{\mathrm{H}} \gamma_{\mathrm{HSO_4}} + (RT/2\mathbf{F}) \ln (K_{2A}/a_w^2) \tag{13-9-5}$$

In making this step a number of considerations are involved. In the first place, the assumption that sulfuric acid dissociates completely into the hydrogen and hydrosulfate ions is made. In the second place, we regard m as representing the true concentration of a species present, and not the stoichiometrical concentration. This permits the substitution of the limiting law of Debye and Hückel for the activity coefficients. Upon substitution of this law with an additional term, $\beta\mu'$, for the third term on the right of equation (13-9-5), the equation

$$\begin{aligned} \mathbf{E}^{0\prime} &= \mathbf{E} - (RT/2\mathbf{F}) \ln m_{\mathrm{H}} m_{\mathrm{HSO_4}} + 2.303\,(RT/2\mathbf{F}) \mathfrak{S}_{(f)} \sqrt{2\mu'} \\ &\qquad - (RT/2\mathbf{F}) \ln K_{2A} \\ &= \mathbf{E}^0 - (RT/2\mathbf{F}) \ln a_w^2 + \beta\mu' \end{aligned} \tag{13-9-6}$$

results. Since at very low concentrations all quantities on the left side may be either obtained experimentally or evaluated, an extrapolation of the left side against μ' gives $\mathbf{E}^0$. The ionic strength, μ', is computed from the real concentrations of the ionic species.

The ionic concentrations of each of the ions (H^+, HSO_4^- and $SO_4^=$) were estimated from equation (13-9-4), and the logarithm of the activity coefficient ratio was obtained from the limiting law of Debye and Hückel. In equation (13-9-4), $m_{\mathrm{H}} = m + m'_{\mathrm{H}}$, $m_{\mathrm{SO_4}} = m'_{\mathrm{H}} + S$, and $m_{\mathrm{HSO_4}} = m - m'_{\mathrm{H}}$, where m is the stoichiometrical concentration, and m'_{H} is the concentration of the sulfate or hydrogen ion produced in the ionization of HSO_4^-. S is the additional molality of the sulfate ion caused by the slight solubility of lead sulfate. The ionic strength is equal to $(m + 2m'_{\mathrm{H}} + 4S)$. The values of m'_{H}, and the ionic strength were obtained by successive approximations. In these calculations, the experimental values of K_{2A}, given in Table (13-8-1), were employed. The values of the concentrations obtained by this method are only approximations in solutions of appreciable ionic strength, but in dilute solutions they approach the correct values, and should yield a correct extrapolation.

The extrapolation is shown by Fig. (13-9-2) in which the left side of equation (13-9-6), $\mathbf{E}^{0\prime}$, is plotted against μ'. The final results are given in the third column of Table (13-9-1). These results may be computed by the equation

$$E^0 = 1.67699 + 0.000285t + 1.2467 \times 10^{-6}t^2 \qquad (13\text{-}9\text{-}7)$$

obtained by the method of least squares. The fourth column contains the differences between these values and those obtained by the first method of extrapolation. At 0° the plots have a slight curvature, but at higher temperatures they are straight lines, and it is a comparatively simple matter to make the short extrapolation.

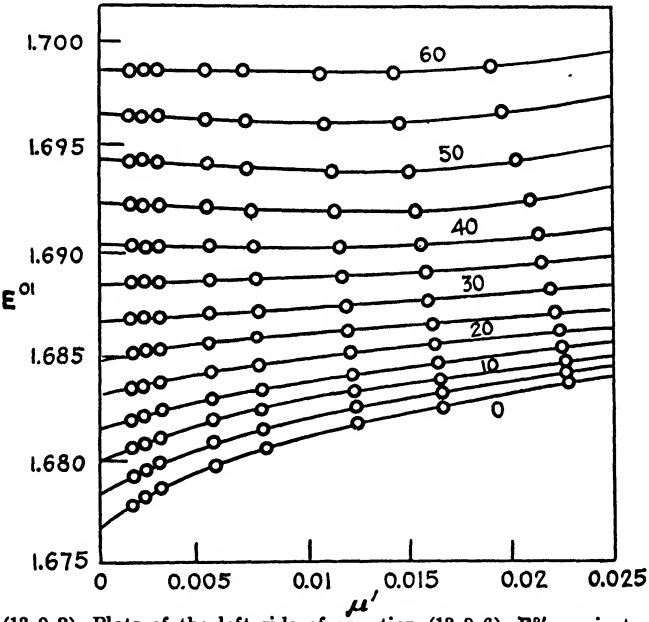

Fig. (13-9-2). Plots of the left side of equation (13-9-6), E°', against μ' at 5° intervals.

We are now in a position to compare the two methods of extrapolation. In Fig. (13-9-1), we have drawn lines (L. L.) to the values of E°, obtained by the second method of extrapolation, which show the requirement of the limiting law of Debye and Hückel. First, it is to be noticed that at zero degrees the slope of the Lewis and Randall extrapolation happens to be nearly the same as that required by the limiting law. Consequently, at this temperature both methods of extrapolation give the same values of E°. At the higher temperatures, most noticeable at 60°, the slope of the Lewis and Randall graph is greater than that required by theory. It is obvious that if we do not abandon the theory, the values of E° must be lower than those obtained by the first method. Such conformity with theory is represented by the dotted lines drawn to the values of $\mathbf{E}^0$, obtained by the second method. Somewhere in the region of concentration below $0.0005M$, the results should show a curvature, and the slopes of experimental graphs should approach the limiting slopes. Although the present results show no tendency to approach the limiting law, we think that this is simply due to the fact that reliable experiments have not been obtained from the cells in question at such extreme dilutions. In view of this well established theoretical requirement, there is no doubt that the values of $\mathbf{E}^0$, obtained by the second method of extrapolation, are the better.

(10) THE ACTIVITY OF WATER IN AQUEOUS SULFURIC ACID FROM ELECTROMOTIVE FORCE AND VAPOR PRESSURE MEASUREMENTS

As pointed out in the preceding section, the electromotive forces of cells with the lead sulfate-dioxide electrode are given by equation (13-9-1), and the corresponding cell reaction by

$$H_2 + PbO_2 + H_2SO_4(m) = PbSO_4 + 2H_2O$$

To evaluate a_w, from the electromotive forces and equation (13-9-1), γ', a preliminary activity coefficient, obtained by neglecting the term containing a_w, was first computed. From these values of γ', a preliminary value of a_w may be computed by graphical integration of the general thermodynamic equation (1-8-1) which becomes

$$-\ln a_w = \ln \frac{p_0}{p} = \frac{m}{55.5}\left[\nu + \frac{\nu}{m}\int_0^{\ln \gamma} m\, d\ln \gamma\right] \qquad (13\text{-}10\text{-}1)$$

when the vapor pressures are introduced. These values of a_w were then substituted in equation (13-9-1), and new values of γ' computed. This process was repeated until the values of a_w satisfied this equation. This procedure was most convenient for concentrations below $0.1M$. At higher concentrations a simpler method was adopted.

The electromotive forces of the cells,

$$H_2 \mid H_2SO_4(m) \mid Hg_2SO_4\text{-}Hg \qquad \text{I}$$

are given by the equation[78]

$$\mathbf{E}_\text{I} = \mathbf{E}_\text{I}^0 - \frac{RT}{2\mathbf{F}} \ln m_\text{H}^2 m_{\text{SO}_4} - \frac{RT}{2\mathbf{F}} \ln \gamma_\text{H}^2 \gamma_{\text{SO}_4} \qquad (13\text{-}10\text{-}2)$$

where $\mathbf{E}_\text{I}^0$ is the molal electrode potential of the cell. Upon addition of equations (13-9-1) and (13-10-2), we obtain

$$\mathbf{E} + \mathbf{E}_\text{I} - \mathbf{E}^0 - \mathbf{E}_\text{I}^0 = -\frac{RT}{2\mathbf{F}} \ln a_w^2 \qquad (13\text{-}10\text{-}3)$$

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[78] The subscript, I, differentiates the cell containing mercurous sulfate from that containing lead dioxide. It is used in this section only.

from which a_w may be computed easily. By employing the values of E^0 in Table (13-9-1), of E and E_I^0 given by Hamer,[79] and Harned and Hamer,[80] and E_I^0 in Table (13-12-1), a_w was computed. These are given at several temperatures in Table (13-10-1).

These results are in excellent agreement with the values from the direct vapor pressure measurements of Grollman and Frazer[81] for dilute solutions, and with the data of Collins[82] at somewhat higher concentrations (0.5 to 4*M*), as shown by Fig. (13-10-1). On the other hand, the vapor pressure measurements of Shankman and Gordon[83] do not agree well with results derived from the electromotive forces in regions of concentration from 5 to 8*M*, and from 12 to 17.5*M*. Up to 4*M*, the agreement is good as shown by the fourth column of Table (13-10-1), while at 5, 6 and 7*M* the deviations are of the order of 1 per cent in a_w.

TABLE (13-10-1). THE ACTIVITY OF WATER IN SULFURIC ACID SOLUTIONS

$m(H_2SO_4)$	0°	25°	25°(V P.)[a]	40°	60°
0.0005	0.99998	0 99998	.....	0 99998	0.99998
.01	.99959	99960	.....	.99961	.99962
.05	.99809	.99819	...	.99822	.99823
.1	.99620	.9961	.	.9964	.9964
.5	.9817	9821	9821	.9822	.9823
1	.9613	.9620	(9620)	9624	.9630
1 5	.9374	.9391	.9389	9402	.9415
2	.9105	9136	9129	.9155	.9180
3	8438	.8506	8514	.8548	8602
4	.7650	.7775	7795	.7850	7950
5	.6801	.6980	.7030	.7086	.7229
6	5968	.6200	6252	.6288	.6505
7	.5184	.5453	.5197	5608	.5815

[a] S. Shankman and A. R. Gordon, *J. Am. Chem. Soc.*, **61**, 2370 (1939).

(11) THE ACTIVITY COEFFICIENT OF SULFURIC ACID

Upon eliminating the last term on the right of equation (13-9-1) and rearranging, we obtain,

$$E = E^0 - \frac{3RT}{2F} \ln m\gamma_{\pm}4^{1/3} \qquad (13\text{-}11\text{-}1)$$

which may be used to compute $\gamma_{\pm}$ from the data of either cells containing the lead dioxide-lead sulfate-platinum electrode, or the mercurous sulfate-mercury electrode. The cells with the mercurous sulfate-mercury electrodes are not satisfactory at concentrations below 0.05*M*, but from this concentration up to 17.5*M*, they are quite reproducible. The values

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[79] W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 9 (1935).

[80] H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 27 (1935).

[81] A. Grollman and J. C. W. Frazer, *J. Am. Chem. Soc.*, **47**, 712 (1925).

[82] E. M. Collins, *J. Phys. Chem.*, **37**, 1191 (1933).

[83] S. Shankman and A. R. Gordon, *J. Am. Chem. Soc.*, **61**, 2370 (1939).

of $\gamma_\pm$, computed from the combined results, are given in Table (13-11-1) at several temperatures. The second column contains values obtained by Randall and Scott[84] from freezing point measurements. It is apparent that the agreement is excellent. At 25°, the values are much lower than those given by Lewis and Randall.[85] This is due principally to the fact that they employed in their calculation values of the relative partial molal heat content which were unquestionably too low. The present results are 2.4 per cent higher than those obtained by Baumstark,[86] and those computed by Sherrill and Noyes.[87]

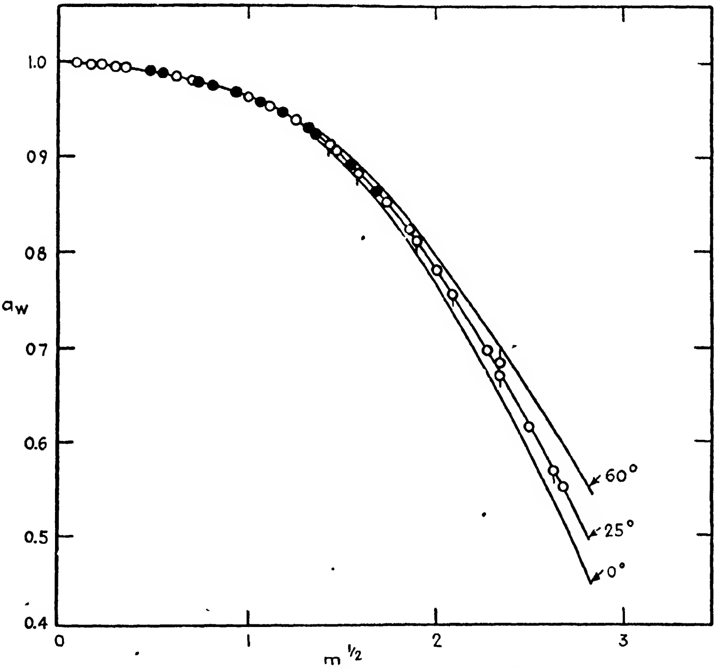

Fig. (13-10-1). Water activity in sulfuric acid solutions from electromotive force and vapor pressure measurements. ●, Grollman and Frazer (V.P.); ȹ, Collins (V.P.); ○, Harned and Hamer (E.M.F.)

Values of $\gamma_\pm$ at 25°, computed from the vapor pressures of Shankman and Gordon using a common reference value at 1 *M*, are also given in Table

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[84] M. Randall and G. N. Scott, *J. Am. Chem. Soc.*, **49**, 647 (1927).

[85] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, pp. 354 and 356.

[86] G. Baumstark Dissertation, Catholic University of America. Baltimore, Md., 1933.

[87] M. S. Sherrill and A. A. Noyes, *J. Am. Chem. Soc.*, **48**, 1861 (1926).

(13-11-1). The agreement is satisfactory from 1 to 4*M* and from 9 to 11*M* inclusive, but is poor from 5 to 8*M* and from 12 to 16*M*. The last column contains values of $\gamma_\pm$ obtained by the isopiestic vapor pressure method, using sodium chloride as standard. Good agreement is obtained between 0.1 and 4*M*. In Table (13-11-1A), the activity coefficient from 0 to 60° at 5° intervals derived from the electromotive forces is given.

TABLE (13-11-1). MEAN ACTIVITY COEFFICIENT OF SULFURIC ACID IN AQUEOUS SOLUTION

m	0°(F.P.)[1]	0°(E.M.F.)[2]	25°(E.M.F.)[2]	25°(V.P.)[3]	25°(V.P.)[4]
0.0005	0.912	0.908	0.885	.....	.....
.001	.876	.873	.830	.....	.....
002	.825	.825	.757	.....	.....
.005	.734	.734	.639	.....	.....
.01	.648	.649	.544	.....	.....
.02	.553	.554	.453	.....	.....
.05	.424	.426	.340	.....	.....
.1	.341	.341	.265	.....	(0.265)
.2	.272	.271	.209	.....	.207
.5	....	.202	.154	.....	.154
1.	....	.173	.130	(0.130)	.131
1.5	....	.167	.124	.124	.125
2	....	.170	.124	.125	.126
3	....	.201	.141	.141	.142
4	....	.254	.171	.168	.172
5	....	.330	.212	.206	....
6	....	.427	.264	.254	....
7	....	.546	.326	.315	....
8	....	.686	.397	.385	....
9	....	.843	.470	.466	....
10	....	1.012	.553	.557	....
11	....	1.212	.643	.643	....
12	....	1.431	.743	.763	....
13	....	1.676	.851	.850	....
14	....	1.958	.969	1.009	....
15	....	2.271	1.093	1.123	....
16	....	2.612	1.235	1.270	....
17	....	3.015	1.387	.....	....
17.5	....	3.217	1.473	.....	....

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[1] M. Randall and G. N. Scott, *J. Am. Chem. Soc.*, **49**, 647 (1927).

[2] H. S. Harned and W. J. Hamer, *Ibid.*, **57**, 27 (1935).

[3] S. Shankman and A. R. Gordon, *Ibid.*, **61**, 2370 (1939).

[4] R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1229 (1939). From isopiestic ratios $m_{H_2SO_4}/m_{NaCl}$. G. Scatchard, W. J. Hamer and S. E. Wood, *J. Am. Chem. Soc.*, **60**, 3061 (1938).

(12) THE STANDARD POTENTIAL OF THE CELL, $H_2 \mid H_2SO_4\ (m) \mid Hg_2SO_4$-Hg

Since the electromotive forces of the cells of this type were insufficiently accurate in dilute solutions for suitable extrapolation, we employed the values of $\gamma_\pm$, derived from cells with lead sulphate-oxide electrodes, for the purpose of computing the molal electrode potential. The values of $\gamma_\pm$ at 0.05, 0.07 and 0.1*M* were substituted in equation (13-11-1) as were also the values of **E**, and $\mathbf{E}^0$ was computed at each concentration. The mean value of the three determinations is given in Table (13-12-1). They may be expressed to within approximately ±0.05 mv. by the quadratic equation

$$\mathbf{E}^0 = 0.63495 - 781.44 \times 10^{-6}t - 426.89 \times 10^{-9}t^2 \quad (13\text{-}12\text{-}1)$$

The constants of this equation were computed by the method of least squares.

The result at 25° is 6 mv. lower than that computed by Lewis and Randall[88] from the data of Randall and Cushman.[89] It is also lower than the value calculated by Brodsky.[90] We are certain that the present value is better since the activity coefficients of the acid computed from the electromotive forces of the cells with mercurous sulphate electrodes agree with those of cells containing lead oxide from 0.05 to 7*M*. These activity coefficients at 0° agree very well with those obtained from freezing point data of Randall and Scott.

TABLE (13-12-1). THE STANDARD POTENTIAL OF THE CELL, $H_2 \mid H_2SO_4(m) \mid Hg_2SO_4\text{-}Hg$

t	$\mathbf{E}^0$	t	$\mathbf{E}^0$
0	0.63495	35	0.60701
5	.63097	40	.60305
10	.62704	45	.59900
15	.62307	50	.59487
20	.61930	55	.59051
25	.61515	60	.58659
30	.61107	..	......

(13) THE RELATIVE PARTIAL MOLAL HEAT CONTENT AND HEAT CAPACITY OF SULFURIC ACID IN AQUEOUS SOLUTION

Values of $\bar{L}_2$ from 0 to 60° were computed from the electromotive forces by Harned and Hamer. The results were expressed by the equation

$$\bar{L}_2 = \bar{L}_2(0°) + \alpha t + \beta t^2 \quad (13\text{-}13\text{-}1)$$

in which α and β are constants, and $\bar{L}_2(0°)$ is the value of $\bar{L}_2$ at 0°. The constants of this equation are given in Table (13-13-1A).

Lange, Monheim, and Robinson[91] determined $\bar{L}_2$ calorimetrically from 0.0001 to 0.05*M*. In Fig. (13-13-1), their results (dots), and values of $\bar{L}_2 - \bar{L}_2(0.05)$, computed from the electromotive forces (circles), have been plotted against $m^{1/2}$. The agreement is excellent since most of the values agree within 20 cal.

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[88] G. N. Lewis and M. Randall, "Thermodynamics," p. 407, McGraw-Hill Book Co., New York (1923).

[89] M. Randall and O. E. Cushman, *J. Am. Chem. Soc.*, **40**, 393 (1918).

[90] A. E. Brodsky, *Z. Elektrochem.*, **35**, 833 (1929).

[91] E. Lange, J. Monheim, and A. L. Robinson, *J. Am. Chem. Soc.*, **55**, 4733 (1938).

In this figure, two extrapolations are shown. The straight line represents an empirical extrapolation which Lange, Monheim, and Robinson used. This is in agreement with the empirical extrapolation of the electromotive forces [Equation (13-9-2); Fig. (13-9-1)]. The curved line represents an extrapolation consistent with theory, and the standard potentials obtained by the use of the limiting law [Equation (13-9-6); Fig. (13-9-2)]. We note that the theoretical requirement is approached only in very dilute solutions ($m < 0.0001M$). The difference between the two methods of extrapolation amounts to 460 cal. at 25°. In our opinion, the extrapolation in agreement with theory is preferable, although no measurements of electromotive force, or heats of dilution have been obtained at sufficiently low concentrations to prove the contention.

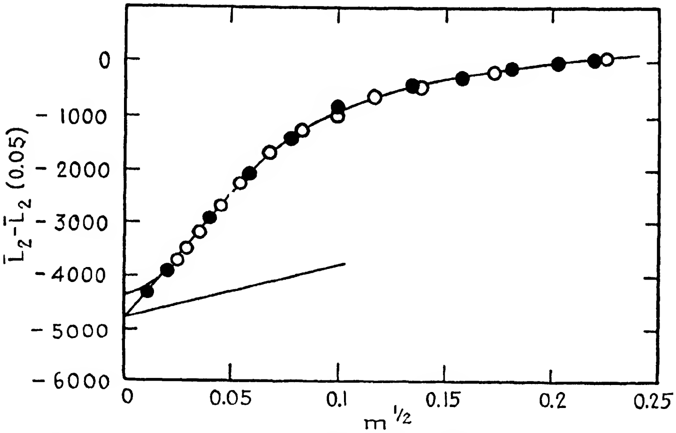

Fig. (13-13-1). $\bar{L}_2 - \bar{L}_2$ (0.05) of sulfuric acid in dilute aqueous solutions at 25°. ○, electromotive force; ●, calorimetry.

For further comparison, $\bar{L}_2$ at 25° has been plotted against $m^{1/2}$ over the entire concentration range in Fig. (13-13-2). The circles represent the results derived from electromotive forces, the dots the results of Lange, Monheim and Robinson, and the circles with vertical lines represent values computed by Brönsted from electromotive force measurements. Since Brönsted's data were not determined in sufficiently dilute solutions for purposes of extrapolation, it was necessary to add 2530 cal. to each of his results. The present results and those of Brönsted[92] possess the same characteristics although the maximum deviation is of the order of 300 cal. The dashed plot represents values determined from the calorimetric data

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[92] J. N. Brönsted, *Z, physik. Chem.*, **68**, 693 (1910); G. N. Lewis and M. Randall, "Thermodynamics," p. 95, McGraw-Hill Book Co., New York, 1923.

by Craig and Vinal.[93] They employed the experimental method of extrapolation and for this reason the curve lies about 400 cal. higher than the one obtained from the electromotive forces. If allowance is made for the difference in method of extrapolation, the agreement is quite satisfactory.

The relative partial molal heat capacity, obtained from equation (13-13-1) by differentiation, is given by

$$\bar{J}_2 = \alpha + 2\beta t \qquad (13\text{-}13\text{-}2)$$

Craig and Vinal have computed $\bar{J}_2$ at 25° from calorimetric data.[94] Values of this quantity at 25° from both the electromotive force and calorimetric data are given in Table (13-13-1A). The results from these sources are plotted in Fig. (13-3-3). Both series of results are characterized by a very rapid increase in $\bar{J}_2$ with $m^{1/2}$ in dilute solutions after which $\bar{J}_2$ decreases, passes through a minimum and then increases again in very concentrated solutions. The agreement is not good. Both series of results may be considerably in error. The calorimetric values were derived from older data of uncertain accuracy, and high accuracy is not to be expected from

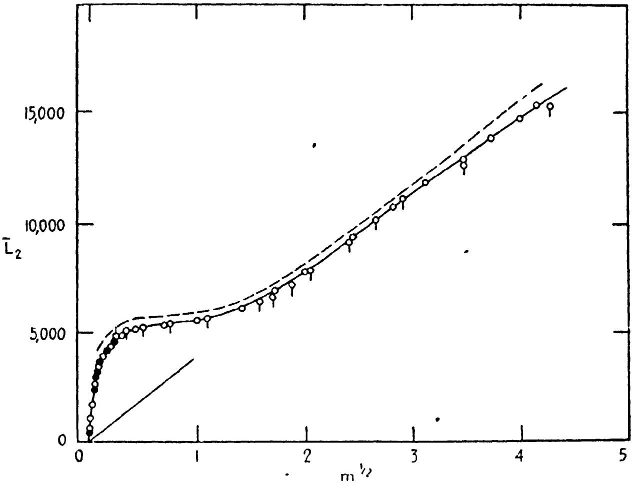

Fig. (13-13-2). $\bar{L}_2$ of sulphuric acid in aqueous solutions at 25°. ○, Electromotive force; ●, Calorimetry; ♀, Electromotive force (Bronsted). Straight line from origin represents limiting law. Dashed line represents values computed by Craig and Vinal from calorimetric data.

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[93] D. N. Craig and G. W. Vinal, *Bur. Standards J. Research*, **24**, 475 (1940).

[94] E. Biron, *Russkoe Fiziko-Khimicheskoe Obshchestvo*, **31**, 201 (1899); S. Socolik, *Z. physik. Chem.*, **158**, 305 (1932); F. Bode, *Z. Angw. Chem.*, **2**, 244 (1889); P. Pascal and Garnier, *Bull. Soc. Chim.*, **27**, 8 (1920); M. D. Taylor, Thesis; University of California (1931).

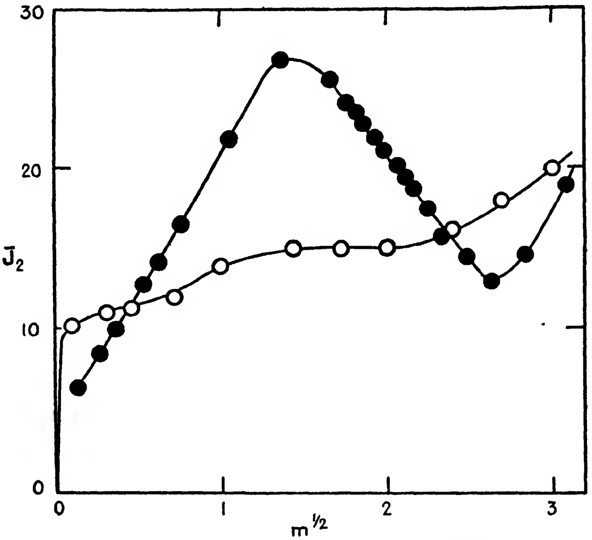

Fig. (13-13-3). Relative partial molal heat capacity of sulfuric acid in aqueous olutions at 25°. ○, electromotive force; ●, calorimetry.

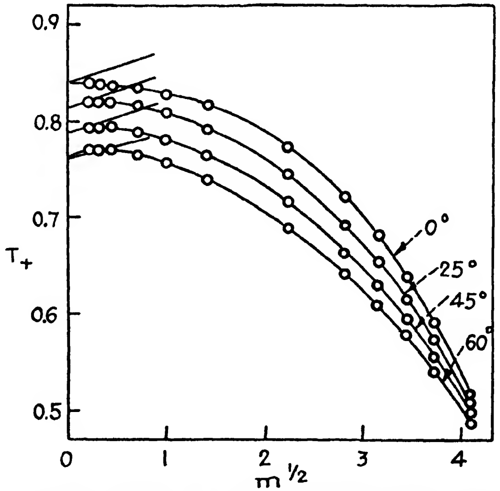

Fig. (13-14-1). Cation transference number of sulfuric acid in aqueous solutions. Straight lines represent limiting law.

results derived from the second differential coefficient of electromotive force.

(14) THE CATION TRANSFERENCE NUMBER OF SULFURIC ACID IN AQUEOUS SOLUTIONS

From the electromotive forces of the cells,

$$\text{Hg-Hg}_2\text{SO}_4 \mid \text{H}_2\text{SO}_4(m) \mid \text{H}_2 \mid \text{H}_2\text{SO}_4(m_R) \mid \text{Hg}_2\text{SO}_4\text{-Hg};\ \mathbf{E},$$

derived from the results discussed in the preceding sections, and those of the cells,

$$\text{Hg-Hg}_2\text{SO}_4 \mid \text{H}_2\text{SO}_4(m) \mid \text{H}_2\text{SO}_4(m_R) \mid \text{Hg}_2\text{SO}_4\text{-Hg};\ \mathbf{E}_T,$$

Hamer[95] has determined the cation transference number of sulphuric acid. The method he employed to evaluate T_+ by means of equation (10-6-12), or $T_+ = d\mathbf{E}_T/d\mathbf{E}$, was essentially the same as that described in Chapter (11), Section (9). The slopes of the graph of $\mathbf{E}$ versus $\mathbf{E}_T$ at various acid concentrations were determined by the Rutledge derivative function [Equation (11-9-3)]. These values of T_+ from 0.05 to 17M, and from 0 to 60° are contained in Table (13-14-1A). This table also contains values of the limiting transference number, computed from conductance data and other transference number data, and values of the limiting slopes, $\mathcal{S}_{(T)}\sqrt{d_0}$, of the Onsager equation,

$$T_+ = T_+^0 + \mathcal{S}_{(T)}\sqrt{d_0}\sqrt{m} \qquad (13\text{-}14\text{-}1)$$

Plots of T_+ versus $m^{1/2}$ are shown in Fig. (13-14-1). The theoretical limiting functions represented by the straight lines predict an increase in T_+ as the concentration increases. The experimental results were not obtained in solutions dilute enough to verify the theoretical prediction, nor can they be used satisfactorily for purposes of extrapolation. The results all show a tendency to approach a maximum as the concentration of acid decreases, and it is reasonable to suppose that they should approach the theoretical results in more dilute solutions. The theoretical lines have been drawn to values of the limiting transference numbers obtained from other sources.[95]

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[95] W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 662 (1935).

Chapter (14)

Mixtures of Strong Electrolytes

The determination of a thermodynamic property such as the activity coefficient of one electrolyte in a solution of another electrolyte has been of considerable value in establishing the theory of interionic attraction, and in extending our knowledge of ionic equilibria. Two experimental methods have proved to be of prime importance in this field. The first is the determination of the solubility of salts in salt solutions, and the second the determination of the activity coefficient of one electrolyte in the presence of another by electromotive force measurements.

The investigation of the solubility of salts in salt solutions was begun by Noyes,[1] and continued by Bray,[2] and Harkins.[3] These results were employed by Lewis and Randall[4] to illustrate the value of their concept of ionic strength, and by Noyes[5] in his discussion of the Debye and Hückel theory.

The solubilities of the salts employed in these first studies were somewhat too great for an exact proof of the validity of the equations of the interionic attraction theory. This difficulty was surmounted by Brönsted[6] and his collaborators who determined the solubilities of many higher order cobalt compounds of very low solubility ($\sim 0.00005M$) in various salt solutions. These investigations were the first to illustrate in a very striking manner the effects on the activity coefficients caused by the different valences of the ions. They also brought to light many complicated specific effects of electrolytes upon the properties of other electrolytes, and led Brönsted[6] to his theory of specific ionic interaction.

The cell without liquid junction containing a mixture of electrolytes was first employed by Harned,[7] who investigated the effect of varying concentrations of potassium chloride on the activity coefficient of $0.1M$ hydrochloric acid. Loomis, Essex and Meacham,[8] and Ming Chow[9] also in-

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[1] A. A. Noyes, *Z. physik. Chem.*, **6**, 241 (1890); A. A. Noyes and W. C. Bray, *J. Am. Chem. Soc.*, **30**, 1643 (1908).

[2] W. C. Bray and W. J. Winninghof, *J. Am. Chem. Soc.*, **33**, 1663 (1911).

[3] W. D. Harkins and W. J. Winninghof, *J. Am. Chem. Soc.*, **33**, 1827 (1911); W. D. Harkins and H. M. Paine, *Ibid.*, **41**, 1155 (1919); W. D. Harkins and W. T. Pearce, *Ibid.*, **38**, 2679 (1916).

[4] G. N. Lewis and M. Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921).

[5] A. A. Noyes, *J. Am. Chem. Soc.*, **46**, 1098 (1924).

[6] J. N. Brönsted, *J. Am. Chem. Soc.*, **42**, 761 (1920); **44**, 877 (1922); **44**, 938 (1922); **45**, 2898 (1923); J. N. Brönsted and A. Petersen, *Ibid.*, **43**, 2265 (1921).

[7] H. S. Harned, *J. Am. Chem. Soc.*, **38**, 1986 (1916); **42**, 1808 (1920).

[8] N. E. Loomis, J. L. Essex, and M. R. Meacham, *J. Am. Chem. Soc.*, **39**, 1133 (1917).

[9] Ming Chow, *J. Am. Chem. Soc.*, **42**, 497 (1920).

vestigated a similar cell for the purpose of measuring the activity coefficient of hydrochloric acid in potassium chloride solutions at $0.1M$ total ionic strength. One result, shown by Harned to follow from these measurements, is that the activity coefficient, and also the relative partial molal heat content of a strong electrolyte in a solution of another electrolyte, is primarily a function of the total electrolyte concentration, or, as shown by Lewis and Randall, the total ionic strength. This conclusion is in accord with the general theoretical equations of the interionic attraction theory, because $\Gamma^{1/2}$, a function of all the ions and their valences, always appears. Since these earlier studies and the advent of the interionic attraction theory, very comprehensive electromotive force investigations of mixtures have been made. These results form a basis for an exact study of ionic equilibria of weak electrolytes which involve hydronium ions in salt solutions [Chapter (15)].

(1) Solubility Measurements and the Interionic Attraction Theory

The activity coefficient relationships of strong electrolytes in the presence of salts (co-solutes) of various types and concentrations can be deduced in a very simple manner from solubility measurements. The presence of the solid phase of the saturating solute requires that

$$\mathcal{P}_{(0)}\gamma_{(0)}^{\nu} = \mathcal{P}\gamma_{\pm}^{\nu} = (m_{+}^{\nu_{+}})(m_{-}^{\nu_{-}})(\gamma_{+}^{\nu_{+}}\gamma_{-}^{\nu_{-}}) \qquad (14\text{-}1\text{-}1)$$

where $\mathcal{P}_{(0)}$ and $\mathcal{P}$ have been written for its stoichiometrical solubility product in water, and in the presence of the co-solute, respectively, and $\gamma_{(0)}$ and $\gamma_{\pm}$ are the corresponding mean activity coefficients. Therefore,

$$\frac{1}{\nu}\log\frac{\mathcal{P}}{\mathcal{P}_{(0)}} = \log\gamma_{(0)} - \log\gamma_{\pm} \qquad (14\text{-}1\text{-}2)$$

in general. If the co-solute is a non-electrolyte, or has no ion in common with the saturating electrolyte, the left side of this equation may be replaced by $\log (S/S_{(0)})$, where S and $S_{(0)}$ are the stoichiometrical solubilities in the salt solution and pure water, respectively. We shall now discuss some results of solubility measurements, which we regard as particularly significant in their relation to the interionic attraction theory.

Immediately after the Debye and Hückel development of the interionic attraction theory, solubility data were employed extensively to test its validity. The measurements of Brönsted and LaMer[10] with cobaltammines of 1-1, 2-1, and 3-1 valence types, and more recent experiments with 2-2 and 3-3[11] types, leave little doubt as to the correctness of the valence factor in the theoretical equation, and show that $\log \gamma_{\pm}$ is very closely proportional to the square root of the ionic strength. In selected cases[12], the data confirm the numerical value of the theoretical slopes.

[10] J. N. Brönsted and V. K. LaMer, *J. Am. Chem. Soc.*, **46**, 555 (1924).

[11] J. N. Brönsted and N. J. Brumbaugh, *J. Am. Chem. Soc.*, **48**, 2015 (1926).

[12] V. K. LaMer, C. V. King, and C. F. Mason, *J. Am. Chem. Soc.*, **49**, 363 (1927).

Later LaMer and others have observed abrupt changes in slope at the concentration of the saturating solute in water. Baxter[13] has confirmed the theory at 75° from measurements of the solubility of silver iodate in salt solutions. Solubility measurements in organic solvents of low dielectric constant have not, in general, led to agreement with theory except in a qualitative manner.

Even when the complication of ionic association is reduced to a minimum, as in very dilute aqueous solutions, the activity coefficient relationships are highly specific in certain combinations of complex valence type electrolytes. This effect was first investigated by Brönsted and Petersen[14] and more recently by LaMer.[15] Fig. (14-1-1) illustrates the results obtained by LaMer and Mason for the solubility of the 1-3 salt, luteodinitrodiammino-oxalo cobaltiate, in various aqueous salt solutions at 25°. It will be observed that the co-solutes, potassium nitrate and barium chloride, yield curves which converge satisfactorily with the theoretical limiting slope, while the other salts produce characteristic "humps". The most abrupt changes in slope are observed with systems in which the ion of the highest valence in the saturating solute is of opposite sign to the ion of highest valence in the co-solute.[14] Pronounced "humps" are common to (3-1, 1-2) systems such as lanthanum iodate in potassium sulfate,[16] cerium

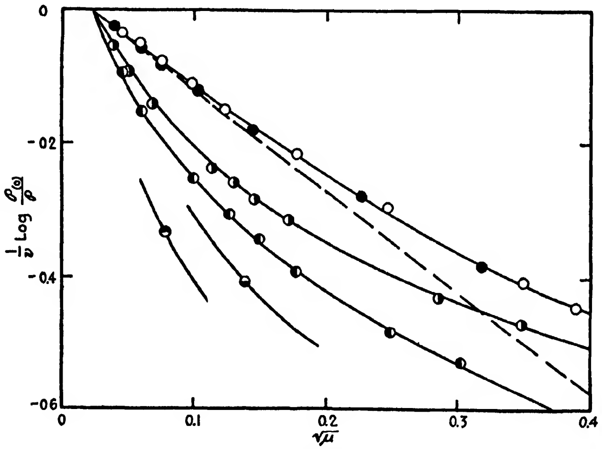

Fig. (14-1-1). The influence of various salts upon the solubility of $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_2C_2O_4]$ in water at 25°. ●, KNO_3; ○, $BaCl_2$; ◐, K_2SO_4; ◑, $MgSO_4$; ◒, $K_3Fe(CN)_6$; ◓, $K_4Fe(CN)_6$. The broken line represents the limiting law.

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[13] W. P. Baxter, *J. Am. Chem. Soc.*, **48**, 615 (1926).

[14] J. N. Brönsted and A. Petersen, *J. Am. Chem. Soc.*, **43**, 2265 (1921).

[15] V. K. LaMer and C. F. Mason, *J. Am. Chem. Soc.*, **49**, 410 (1927).

[16] V. K. LaMer and F. H. Goldman, *J. Am. Chem. Soc.*, **51**, 2632 (1929).

iodate in potassium sulfate,[17] and 3-1 valence type cobaltammines in potassium sulfate.[15,18] Replacement of the potassium sulfate in these systems by a symmetrical valence type sulfate, such as magnesium sulfate, reduces the hump considerably, and it is absent in the presence of magnesium chloride. When no ions of valence greater than two are involved, the hump is small, and sometimes experimentally unrealizable. Thus, in the system calcium iodate-potassium sulfate, no hump was observed,[19] but it is definitely present in other (2-1, 1-2) systems.[20]

When the ions of highest valence of the saturating salt and co-solute are of the same sign, the hump is generally absent.[21] The most striking exception to this rule is the (3-3, 2-2) system studied by LaMer, King and Mason.[22]

Incomplete ionization would account for some of the above results in a qualitative way, and LaMer has found a close correlation between certain features of his results and Brönsted's principle of specific ionic interaction, but no quantitative treatment has been found. The relationships shown in Figs. (14-1-2) and (14-1-3) give some notion of the complexity of these ionic interactions, even at concentrations of the order of μ equal to 0.01, and for combinations of valence types as simple as (1-1, 1-2). Although it has been shown [Chapters (12) and (13)] that the Debye and Hückel equation in its extended form can closely account for the humps observed in the activity coefficients of simple electrolytes, it is inadequate for mixtures of salts of varying proportions if $\mathring{a}$ is to retain any physical significance. The specific parameter, $\mathring{a}_0$, of the saturating salt is generally different from that, $\mathring{a}_s$, of the co-solute, and the calculation, or even a satisfactory definition of $\mathring{a}$ in the mixtures in terms of $\mathring{a}_0$ and $\mathring{a}_s$ has not been made.[23] Since this is the case, it is not particularly significant that a constant value of $\mathring{a}$ can sometimes be found which will approximately fit the data. A more illuminating use of the theory would be to assume its validity in mixtures of any given concentration ratio, and calculate the values of $\mathring{a}$ which would give exact agreement with the observed solubilities in these mixtures. In this way, the variation in $\mathring{a}$ with the ionic strength may be studied.

In order to carry out such a computation, $\log \gamma_{(0)}$ is obtained by the extended equation for some arbitrary value of $\mathring{a}_0$, such as 1, and is com-

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[17] J. B. Chloupek, V. Z. Daneš and B. A. Danešova, *Coll. Czech.*, **5**, 21 (1933).

[18] V. K. LaMer and R. G. Cook, *J. Am. Chem. Soc.*, **51**, 2622 (1929).

[19] J. B. Chloupek, V. Z. Daneš, and B. A. Danešova, *Coll. Czech.*, **6**, 116 (1934).

[20] E. W. Neuman, *J. Am. Chem. Soc.*, **55**, 879 (1933); V. K. LaMer and F. H. Goldman, *Ibid.*, **51**, 2632 (1929).

[21] L. O'Neill and J. R. Partington, *Trans. Faraday Soc.*, **30**, 1134 (1934); V. K. LaMer and C. F. Mason, *J. Am. Chem. Soc.*, **49**, 410 (1927); J. B. Chloupek, V. Z. Daneš and B. A. Danešova, *Coll. Czech.*, **6**, 116 (1934).

[22] V. K. LaMer, C. V. King, and C. F. Mason, *J. Am. Chem. Soc.*, **49**, 363 (1927).

[23] J. R. Partington and H. J. Stonehill, *Phil. Mag.* [7], **22**, 857 (1936).

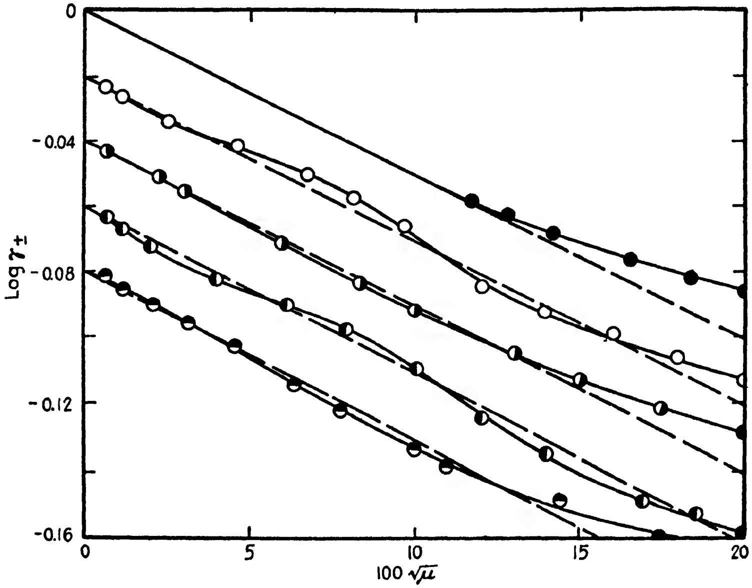

Fig. (14-1-2). Mean activity coefficients of silver chloride in aqueous salt solutions at 25°. ●, KNO_3; ○, K_2SO_4; ◑, $La(NO_3)_3$; ◐, $La_2(SO_4)_3$; ⊖, $MgSO_4$. The ordinates have been displaced by multiples of 0.02.

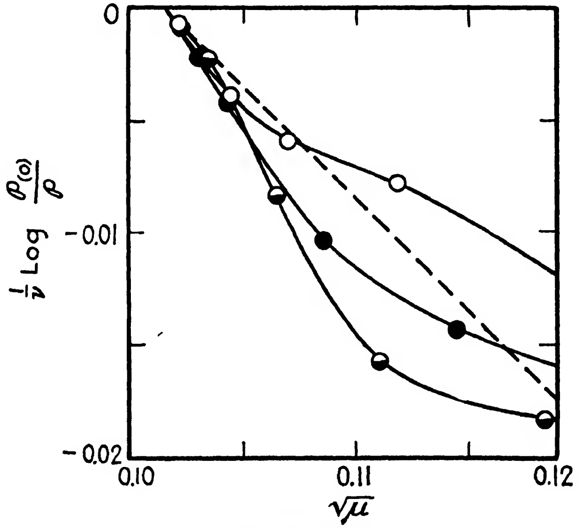

Fig. (14-1-3). The influence of various salts upon the solubility of $[Co(NH_3)_5NCS][NO_3]_2$ in water at 25°. ○, KCNS; ●, NaCNS; ⊖, $Ba(CNS)_2$. The broken line represents the limiting law.

bined with solubility data in equation (14-1-2) to give values of log $\gamma_{\pm}$. The extended equation is then solved, by successive approximations, for a-values corresponding to each log $\gamma_{\pm}$. The whole process is then repeated for values of $\mathring{a}_0$ equal to 2, 3, 4 etc. Partington and Stonehill[23] have made extensive calculations of this type on their data for 2-1 cobaltammines. They ascertained the value of $\mathring{a}_0$ for a given saturating salt which produced the minimum variation of $\mathring{a}$ in the presence of the given co-solute. These values of $\mathring{a}_0$, and the average of the corresponding $\mathring{a}$-values obtained in the mixtures, are recorded in Table (14-1-1). The numbers given in the second column are the cationic radii of the co-solutes derived from crystallographic data. Although the thiocyanate ion is common to all the co-solutes, it is seen that the order of $\mathring{a}$ is not the same as that of the crystallographic radii, and also varies with the nature of the saturating salt. The mean $\mathring{a}$ is therefore a function of both salts, without being characteristic of either one separately. This conclusion is not limited to cobaltamminethiocyanate systems, for a similar situation was found by Chloupek, Daneš, and Danešova with cerium iodate and calcium iodate in the presence of a variety of salts, although in these cases the variations of $\mathring{a}$ were not so pronounced.

TABLE (14-1-1). MEAN VALUES OF $\mathring{a}$ (EXTENDED EQUATION)

Co-Solute		Saturating Salt	
$\mathrm{M(SCN)_n}$	r_M	$\left[\mathrm{Co}\begin{smallmatrix}\mathrm{NCS}\\(\mathrm{NH_3})_5\end{smallmatrix}\right](\mathrm{NO_3})_2$ ($\mathring{a}_0 = 3.0$)	$\left[\mathrm{Co}\begin{smallmatrix}\mathrm{NCS}\\(\mathrm{NH_3})_5\end{smallmatrix}\right]\mathrm{I_2}$ ($\mathring{a}_0 = 4.0$)
NaSCN	0.96	$\mathring{a}$ = 2.85	4.86
KSCN	1.33	3.03	4.07
$\mathrm{Ba(SCN)_2}$	1.35	2.84	5.11
$\mathrm{La(SCN)_3}$	1.15	3.88	5.34

Crockford and Thomas[24] derived a definition of $\mathring{a}$ in mixtures, based upon considerations of collision frequencies. Their expression,

$$\mathring{a} = \frac{\mathring{a}_1 k_1 c_1^2 + \mathring{a}_2 k_2 c_2^2}{k_1 c_1^2 + k_2 c_2^2} \qquad (14\text{-}1\text{-}3)$$

contains kinetic constants, k_1 and k_2, whose evaluation would require a knowledge of individual ionic radii in solutions. If k_1, $\mathring{a}_1$ and k_2, $\mathring{a}_2$ were characteristic of the individual salts, this equation predicts that the order of the $\mathring{a}$, obtained for a given series of co-solutes, would be independent of the saturating salt. This contradicts the results in Table (14-1-1). The same objection applies to the simpler equation,

$$\mathring{a} = \frac{\mathring{a}_1 c_1 + \mathring{a}_2 c_2}{c_1 + c_2} \qquad (14\text{-}1\text{-}4)$$

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[24] H. D. Crockford and H. C. Thomas, *J. Am. Chem. Soc.*, **55**, 568 (1933).

suggested by MacDougall.[25] Therefore, neither equation properly defines $\mathring{a}$ in terms of parameters characteristic of the individual salts. It is possible that equation (14-1-3) would be satisfactory if data were available for evaluating k_1 and k_2 as properties of the mixtures.

The "a" parameter, which appears in the Debye-Hückel equation (3-5-9), is related to the individual values of a_j by

$$\frac{\sum_1^p \nu_j z_j^2}{1 + \kappa a} = \sum_1^p \frac{\nu_j z_j^2}{1 + \kappa a_j} \tag{14-1-5}$$

At high dilutions, where $(1 + \kappa a)^{-1}$ may be replaced by $(1 - \kappa a)$, this equation may be written

$$\mathring{a} = \frac{\sum_1^p \nu_j z_j^2 \mathring{a}_j}{\sum_1^p \nu_j z_j^2} \tag{14-1-6}$$

Neither of these relations gives a satisfactory physical picture of $\mathring{a}$, because $\mathring{a}_j$ is not clearly defined.

(2) THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC, HYDROBROMIC, AND SULFURIC ACIDS, AND OF ALKALI METAL HYDROXIDES IN SALT SOLUTIONS FROM ELECTROMOTIVE FORCE MEASUREMENTS

One very important advantage of the electromotive force method, as applied to the measurement of the activity coefficient of one electrolyte in the presence of another, is that the concentrations of both electrolytes may be varied at will. The solubility method has the disadvantage that one concentration, that of the saturating electrolyte, is fixed. It is possible to employ electromotive forces either to determine the activity coefficient of one electrolyte, at a fixed concentration, in the presence of another electrolyte of varying concentration, or to measure this quantity, at varying concentration of both electrolytes, in a medium of constant total molality.

The fundamental equations of the cells,

$$H_2 \mid HX(m_1), MX_n(m_2) \mid AgX\text{-}Ag$$

$$H_2 \mid H_2SO_4(m_1), M_2SO_4(m_2) \mid Hg_2SO_4\text{-}Hg$$

are

$$E = E^0 - \frac{2.303RT}{F} \log \gamma_H \gamma_X m_1(nm_2 + m_1) \tag{14-2-1}$$

$$E = E^0 - \frac{2.303RT}{2F} \log \gamma_H^2 \gamma_{SO_4} (2m_1)^2 (m_1 + m_2) \tag{14-2-2}$$

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[25] F. H. MacDougall, *Thermodynamics and Chemistry*, p. 279, John Wiley and Sons, New York (1926).

respectively. Thus, if their standard potentials are known, γ_{HX} and $\gamma_{H_2SO_4}$ may be readily determined in the halide and sulfate solutions.

We have already shown [Chapter (11), Section (2) and Chapter (13), Section (12)] that these standard potentials may be evaluated from measurements of the cells of these types containing acid solutions only. Although the salt-free cells are most favorable for this purpose, good determinations of $\mathbf{E}^0$ may be effected by the cells containing salts. By rearranging equation (14-2-1), and introducing the Debye and Hückel limiting equation, we obtain a modified form of equation (11-2-4), suitable for this purpose. Thus,

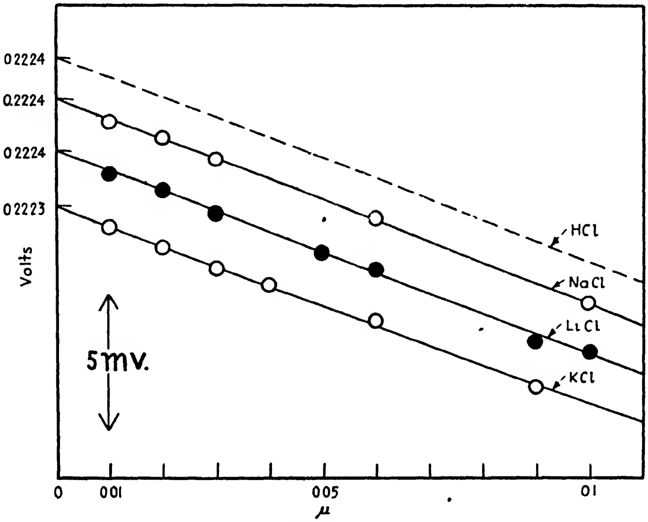

Fig. (14-2-1). Extrapolation of $\mathbf{E}^0$ at 25° according to equation (14-2-3).

$$\mathbf{E}^{0\prime} \equiv \mathbf{E} + \frac{2.303RT}{\mathbf{F}} \log m_1(nm_2 + m_1) - \frac{4.605RT\mathfrak{S}_{(f)}\sqrt{\mu d_0}}{\mathbf{F}} \qquad (14\text{-}2\text{-}3)$$

$$= \mathbf{E}^0 + f(\mu)$$

where $\mathbf{E}^{0\prime} = \mathbf{E}^0$, when $\mu = 0$. In Figure (14-2-1), plots of $\mathbf{E}^{0\prime}$ against μ for cells containing lithium, sodium, and potassium chlorides are shown. Since these plots are practically superimposable, they have been separated in the figure. We note that they all extrapolate to nearly the same value of $\mathbf{E}^0$, and that this value agrees with that previously obtained with the cell containing acid alone. The plot for this latter cell is represented by the dashed line. The cell employed for determining the thermodynamics of hydroxide solutions [Chapter (12), Section (2)];

$$\mathrm{H_2} \left| \mathrm{MOH}(m_1), \begin{Bmatrix} \mathrm{MX,} \quad \mathrm{or} \\ \mathrm{M_x(SO_4)_y} \end{Bmatrix} (m_2) \right| \mathrm{M_xHg} \,|\, \mathrm{MOH}(m_R) \,|\, \mathrm{H_2}$$

may be utilized for measuring the activity coefficients of hydroxides in halide and sulfate solutions. Its electromotive force in a halide solution is given by

$$\mathbf{E} = \frac{2.303RT}{\mathbf{F}} \log \frac{\gamma_{\mathrm{M}} \gamma_{\mathrm{OH}} a_{\mathrm{H_2O}(m_{\mathrm{R}})} m_1(m_1 + m_2)}{\gamma_{\mathrm{M}(m_{\mathrm{R}})} \gamma_{\mathrm{OH}(m_{\mathrm{R}})} a_{\mathrm{H_2O}} m_{\mathrm{R}}^2} \qquad (14\text{-}2\text{-}4)$$

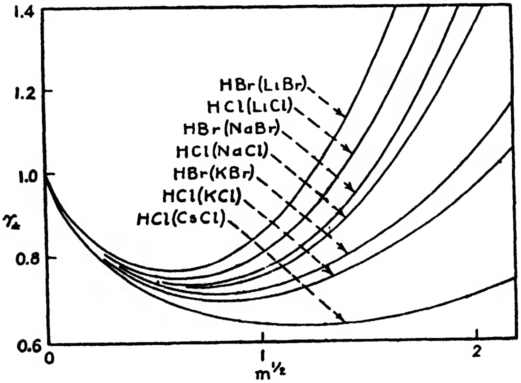

Fig. (14-2-2). Mean activity coefficients of hydrochloric and hydrobromic acids in alkali halide solutions at 25°.

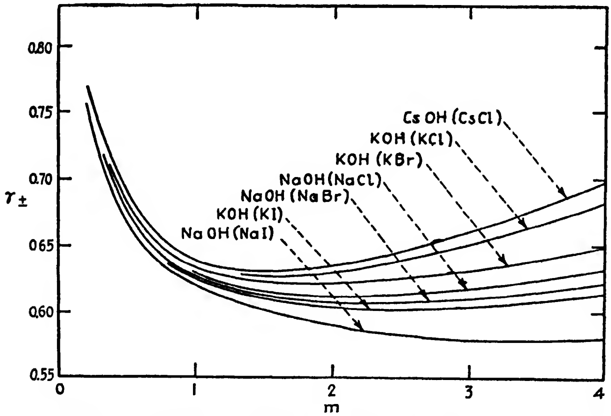

Fig. (14-2-3). Mean activity coefficients of hydroxides in corresponding halide solutions at 25°.

The characteristics of these results are illustrated in Figs. (14-2-2), (14-2-3), and (14-2-4) where the activity coefficients of the acids and bases are plotted at low concentrations (0.1 or 0.01*M* or less) in the salt solutions of the strengths designated.[26] In general, these curves are similar

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[26] The sources of the material used in these figures are: H. S. Harned, *J. Am. Chem. Soc.*, **42**, 1808 (1920); H. S. Harned and N. J. Brumbaugh, *Ibid.*, **44**, 2729 (1922); H. S.

in form to those of the single electrolytes. They show characteristic minima, and many increase very rapidly in concentrated solutions.

The specific behaviors of the activity coefficients may be summarized in a general way by two statements.

(i) At a given ionic strength and acid concentration, the activity coefficient of a strong acid is greater in the solutiòn of a salt, of a given valence type, which in the pure solvent possesses the greater activity coefficient. Thus, from Fig. (14-2-2), it is seen that

$$\gamma_{HCl(LiCl)} > \gamma_{HCl(NaCl)} > \gamma_{HCl(KCl)} > \gamma_{HCl(CsCl)}$$

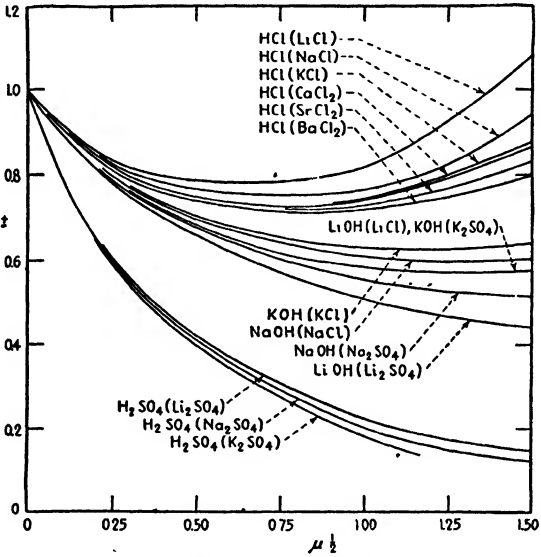

Fig. (14-2-4). Mean activity coefficients of acids and hydroxides in salt solutions at 25°.

and, from Fig. (12-5-2)

$$\gamma_{LiCl} > \gamma_{NaCl} > \gamma_{KCl} > \gamma_{CsCl}$$

Also, from Fig: (14-2-4),

$$\gamma_{H_2SO_4(Li_2SO_4)} > \gamma_{H_2SO_4(Na_2SO_4)} > \gamma_{H_2SO_4(K_2SO_4)}$$

and, from Fig. (13-4-1)

$$\gamma_{Li_2SO_4} > \gamma_{Na_2SO_4} > \gamma_{K_2SO_4}$$

Harned and F. E. Swindells, *Ibid.*, **48**, 126 (1926); H. S. Harned and G. M. James, *J. Phys. Chem.*, **30**, 1060 (1926); G. Åkerlöf, *J. Am. Chem. Soc.*, **48**, 1160 (1926); M. Randall and C. T. Langford, *Ibid.*, **49**, 1445 (1927); M. Randall and G. F. Breckenridge, *Ibid.*, **49**, 1435 (1927); H. S. Harned and O. E. Schupp, Jr., *Ibid.*, **52**, 3892 (1930); H. S. Harned and G. Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

(ii) Strong hydroxides in the halide solutions exhibit the opposite behavior. As shown in Fig. (14-2-3),

$$\gamma_{MOH(CsCl)} > \gamma_{MOH(KCl)} > \gamma_{MOH(KBr)} > \gamma_{MOH(NaCl)} >$$
$$\gamma_{MOH(NaBr)} > \gamma_{MOH(KI)} > \gamma_{MOH(NaI)}$$

which is in the reverse order to the activity coefficients of the individual salts in water. Further, Fig. (14-2-4) indicates that

$$\gamma_{MOH(K_2SO_4)} > \gamma_{MOH(Na_2SO_4)} > \gamma_{MOH(Li_2SO_4)}$$

which also conforms to this rule. Ionic interaction in solutions containing hydroxides and acids is a very interesting one, and will receive further attention. Recently, the activity coefficients of hydrochloric and hydrobromic acid in solutions containing lithium, sodium, potassium and barium chlorides, and lithium, sodium and potassium bromides, respectively, have been evaluated over wide temperature ranges (~ 0 to 50°) with an accuracy of ±0.001. These results will appear later to be of considerable importance in the calculation of the ionization of water and weak electrolytes in salt solutions [Chapter (15), Sections (2) and (8)]. Therefore, they are incorporated in Table (14-2-1A) along with the bibliography.

(3) The Relative Partial Molal Heat Content of 0.01M Hydrochloric and Hydrobromic Acids in Halide Solutions

From the electromotive force data of the cells considered in the last section, it is possible to compute the partial molal heat content, $\bar{L}_2 - \bar{L}_2(0.01)$, of the acid relative to its value at 0.01M, by employing equation (3-8-1), or a suitable form of the Gibbs-Helmholtz equation. In Fig. (14-3-1), plots of $\bar{L}_2$ of these acids in some of their corresponding halide solutions are shown as well as the values for hydrochloric acid in pure water. The similarity in form and magnitude of these results should be noted. Indeed, the relative heat contents of the acids in lithium chloride and bromide solutions are nearly the same as that of hydrochloric acid in water.

(4) The Variation of the Activity Coefficient of One Electrolyte in the Presence of Another at Constant Total Ionic Strength

Extensive measurements have been made with cells of the type,

$$H_2 \mid HX(m_1),\ MX_n(m_2) \mid AgX\text{-}Ag$$

in which the ionic strength, μ, is maintained constant. From these measurements, the activity coefficient of the halide acid in the mixtures has been determined, and surprisingly simple empirical relationships have been discovered in both dilute and concentrated solutions.

At 0.1M total concentration and at 20 and 25°, Güntelberg[27] has made

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[27] E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); *Studier over Elektrolyt-Activiteter* G. E. C. Gads Forlag, København (1938).

extraordinarily accurate measurements of the above cell containing lithium, sodium, potassium and cesium chlorides. Owing to the fact that Güntelberg found an error due to presence of traces of bromide ion in the chloride solutions, the earlier work was repeated except for the cells containing cesium chloride. In this work, two types of silver-silver chloride electrodes were used which differed from each other by a constant amount (0.185 mv.). The one which gave the higher electromotive force was prepared from silver obtained by precipitation from a silver nitrate solution upon addition of ferrous sulphate. The second by electrolytic precipitation of silver from a silver nitrate solution. The cell, containing the first of these types of electrodes and 0.1*M* hydrochloric acid, had an electromotive force of 0.35316 at 20° and 0.35233 at 25°. Harned and Ehlers[28] obtained 0.35322 and 0.35239 at these temperatures using electrodes made by electrolytic formation of silver chloride upon silver, obtained by thermal decomposition of silver oxide. The reproducibility of Güntelberg's cells was of the order of ±0.02 mv. and the mean values possessed a relative accuracy within ±0.01 mv.

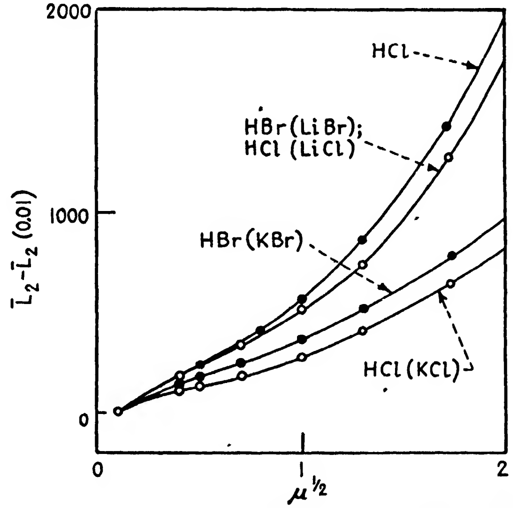

Fig. (14-3-1). Relative partial molal heat contents of halide acids in some halide solutions.

From the equation for the cell, we may define $E^{0'}$ by the equation,

$$E^{0'} \equiv E + \frac{RT}{F} \ln m_H m_{Cl} = E^0 - \frac{2RT}{F} \ln \gamma_{\pm} \qquad (14\text{-}4\text{-}1)$$

where E is the electromotive force of the cell at constant total molality, and varying acid and salt composition. If $m_{MCl} = 0.1\, x$, where x has all

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[28] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 2179 (1933).

values between zero and 1, then the results may be expressed by the simple relation,

$$E^{0'} = E^{0'}_{(x=0)} + kx \tag{14-4-2}$$

where k is an isothermal constant. Table (14-4-1) contains the values of $E^{0'}_{(x=0)}$ and k, which Güntelberg found satisfied his results obtained with the electrodes prepared from chemically precipitated silver. The excellent agreement between the observed results and those computed by equation (14-4-2) is illustrated in the lower part of the table. The values of k obtained in the earlier contribution were 0.00008, 0.00049, and 0.00098 at 25°. By employing similar cells with calomel electrodes, Harned[29] obtained results of less accuracy which lead to values of k at 25° of 0.0002, 0.0005 and 0.0009 for lithium, sodium and potassium chloride with an error of the order of 0.0001.

TABLE (14-4-1). CONSTANTS OF EQUATION (14-4-2), AND PROOF OF THE LINEAR VARIATION OF $E^{0'}$

	$t = 20°$	$t = 25°$
LiCl	$E^{0'} = 0.23683_0 + 0.00014x$	$E^{0'} = 0.23401_5 + 0.00011x$
NaCl	$E^{0'} = .23683_0 + .00054x$	$E^{0'} = .23401_5 + .00051x$
KCl	$E^{0'} = .23683_0 + .00096x$	$E^{0'} = .23401_5 + .00093x$
CsCl	$E^{0'} = .23683_0 + .00170x^a$	

Salt	x	$t = 25°$ $E^{0'}$(calc.)	$t = 25°$ $E^{0'}$(obs.)
	0	0.23401_5	0.23402_0
LiCl	0.5	$.23407_0$	$.23407_0$
	.9	$.23411_4$	$.23411_0$
NaCl	.5	$.23427_0$	$.23427_0$
	.9	$.23447_4$	$.23445_5$
KCl	.5	$.23448_0$	$.23448_5$
	.9	$.23485_2$	$.23485_2$

[a] 0.00170 was taken from Güntelberg's earlier contribution. $2RT/F$ 0.4343 = 0.116324 and 0.118310 at 20 and 25°, respectively.

Since E^0 is a constant at a given temperature, it is apparent from equation (14-4-1) that the observed linear variation of $E^{0'}$ requires that log $\gamma_\pm$ vary linearly with acid, or salt concentration at constant total molality. This simple empirical rule is not restricted to dilute solutions in many cases.

Fig. (14-4-1) shows the variation of $\gamma_\pm$ of hydrochloric acid, in a few chloride solutions at total molalities of $1M$ and $3M$, with the logarithm of the acid concentration. It is important to note that as the concentration of the acid decreases, $\gamma_\pm$ approaches constancy. In Fig. (14-4-2), log $\gamma_\pm$ for the acid is plotted against the acid concentration. These plots are straight lines. In fact, Hawkins[30] has shown that, for hydrochloric acid-uniunivalent halide mixtures, this linearity persists at constant total

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[29] H. S. Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926).

[30] J. E. Hawkins, *J. Am. Chem. Soc.*, **54**, 4480 (1932).

molalities as high as $6M$. Bates and Urmston,[31] and Murdock and Barton[32] have also found a linear variation for hydrochloric acid in sodium and potassium perchlorates, and perchloric acid. The error of these experiments is of the order of ±0.1 mv. It is very important to note that these results can be extrapolated to zero acid concentration. This permits the

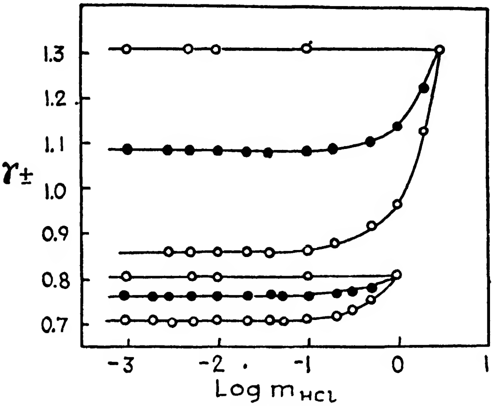

Fig. (14–4–1). Mean activity coefficients of hydrochloric acid in chloride solutions against the logarithm of its molality at 1 and 3 total molalities. Upper three curves at $3M$, lower three curves at $1M$. The upper curve of each series of three refers to lithium chloride; the center (dots) to sodium chloride and the lower to potassium chloride.

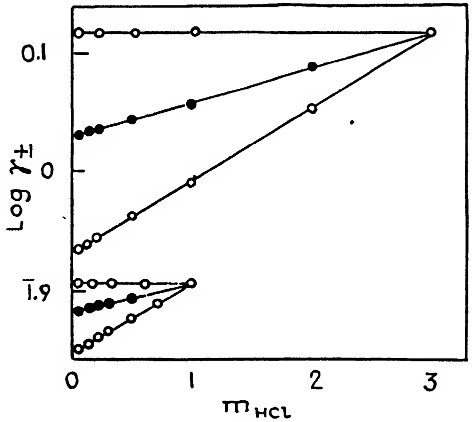

Fig. (14–4–2). Linear variation of log $\gamma_\pm$ of hydrochloric acid in 1–1 chloride solutions at constant total molality. Upper three plots at $3M$, lower three at $1M$. The upper curve of each series of three refers to lithium chloride; the center (dots) to sodium chloride and the lower to potassium chloride.

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[31] S. R. Bates and J. W. Urmston, *J. Am. Chem. Soc.*, **55**, 4068 (1933).

[32] P. G. Murdock and R. C. Barton, *J. Am. Chem. Soc.*, **55**, 4074 (1933).

evaluation of log $\gamma_\pm$ of the acid at zero concentration in the pure salt solution.

In Fig. (14-4-3), log $\gamma_\pm^2$ of hydrochloric acid in pure aqueous solutions (curve), and in cesium chloride solutions[33] of fixed total concentrations (straight lines), are plotted against μ. The straight lines are drawn through the corresponding points at the same total molality. These

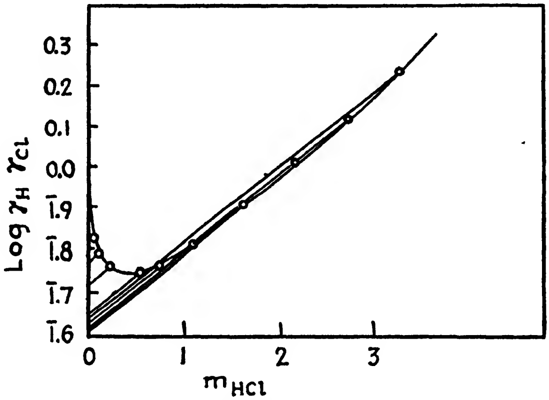

Fig. (14-4-3). Plots of log $\gamma_H\gamma_{Cl}$ versus m_{HCl} in hydrochloric acid-cesium chloride solutions. Straight lines represent variations at constant total molalities.

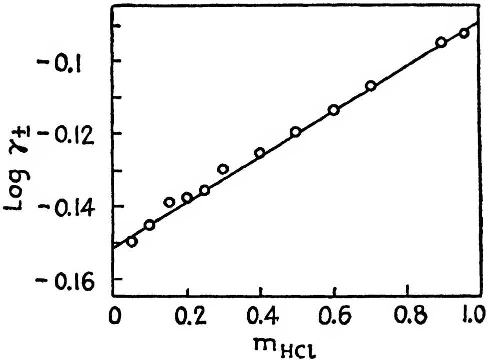

Fig. (14-4-4). Plot of log $\gamma_\pm$ of hydrochloric acid against acid concentration in hydrochloric acid-aluminum chloride solutions at constant ionic strength (unity).

plots appear to be parallel, and indeed are nearly so at the higher concentrations. This behavior is characteristic of hydrochloric acid in halide solutions.

The same linear variation is found frequently in cases of solutions containing electrolytes of higher valence types. This is verified by Fig. (14-4-4) in which the activity coefficient of hydrochloric acid in aluminum

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[33] H. S. Harned and O. E. Schupp, Jr., *J. Am. Chem. Soc.*, **52**, 3892 (1930).

chloride solutions[34] at constant total ionic strength is plotted against its molality (ionic strength). Similar results have been obtained for the activity coefficient of this acid in cerium chloride,[35] barium and lanthanum chlorides[36] and sodium dithionate.[37] Determinations of the solubility of silver sulfate[38] in mixtures of salts also indicate a linear variation of log $\gamma_\pm$ of the saturating salt at constant total ionic strength. It is important to observe that the linear relationship is valid only when the ionic strengths of the salts are plotted. Thus, log $\gamma_\pm$ of silver sulfate in magnesium and cadmium sulfate mixtures, in magnesium and lithium sulfate mixtures, and in aluminum and zinc sulfate solutions varies linearly with the ionic strength of the silver sulfate.

The linear variation of log $\gamma_\pm$ of each of two electrolytes in a mixture may be represented in detail by the equations,

$$\log \gamma_1 = \log \gamma_{(0)1} + \alpha_{12}\mu_1 = \log \gamma_{1(0)} - \alpha_{12}\mu_2 \qquad (14\text{-}4\text{-}3)$$

$$\log \gamma_2 = \log \gamma_{(0)2} + \alpha_{21}\mu_2 = \log \gamma_{2(0)} - \alpha_{21}\mu_1 \qquad (14\text{-}4\text{-}4)$$

where the subscripts (1) and (2) refer to electrolytes (1) and (2), respectively. The mean activity coefficients of electrolytes (1) and (2) in a mixture of any composition at constant total molality are written γ_1 and γ_2. In these expressions, $\gamma_{(0)1}$ is the activity coefficient of electrolyte (1) at zero concentration in the presence of electrolyte (2) at a given ionic strength μ, and $\gamma_{(0)2}$ is the activity coefficient of electrolyte (2) at zero concentration in the presence of electrolyte (1) at the same ionic strength, μ. Further, $\gamma_{1(0)}$ and $\gamma_{2(0)}$ are the activity coefficients of electrolytes (1) and (2) in the pure solutions of (1) and (2), respectively. The constants, α_{12} and α_{21}, represent the slopes of the plots shown in the figures. This symbolism is important, and necessary for the subsequent theoretical developments.

An interesting and valuable extension of this behavior of concentrated solutions of mixtures is to be found in an investigation of Åkerlöf, Teare and Turck[39]. In Fig. (14-4-5) the logarithm of the activity coefficient of hydrochloric acid in sodium chloride solutions at $1M$ total ionic strength, and, at the temperatures indicated, is plotted against the molality of the acid. The six solvents are 10, 20, 30, 40, 50 and 60% by weight methyl alcohol-water mixtures. The plots are straight lines within an error of ±0.1 mv. Further, at a given temperature the slopes of these lines $(-\alpha_{12})$ are independent of the alcohol concentration, which is an unexpectedly simple result. It is obvious that α_{12} is a function of the temperature.

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[34] H. S. Harned and C. M. Mason, *J. Am. Chem. Soc.*, **53**, 3377 (1932).
[35] C. M. Mason and D. B. Kellam, *J. Phys. Chem.*, **38**, 689 (1934).
[36] M. Randall and G. F. Breckenridge, *J. Am. Chem. Soc.*, **49**, 1435 (1927).
[37] P. G. Murdock and R. C. Barton, *J. Am. Chem. Soc.*, **55**, 4074 (1933).
[38] G. Åkerlöf and H. C. Thomas, *J. Am. Chem. Soc.*, **56**, 593 (1934).
[39] G. Åkerlöf, J. W. Teare and H. E. Turck, *J. Am. Chem. Soc.*, **59**, 1916 (1937).

The linear relationship expressed by equation (14-4-3) is not a universal law, and cases are known where it is necessary to employ equations with higher powers of μ_2 and μ_1 to account for the results. This has been shown by Harned and Harris,[40] and Harned and Cook,[41] who measured the activity coefficients of sodium and potassium hydroxides in their corresponding chloride solutions by means of the cells,

$$H_2 \mid MOH(m_1), MCl(m_2) \mid M_xHg \mid MOH(m_R) \mid H_2$$

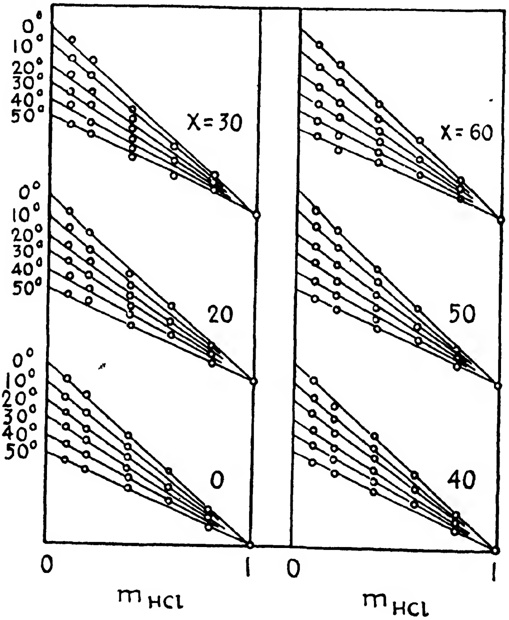

Fig. (14-4-5). Plots of log $(\gamma_{(0)}/\gamma_{\pm})$ for hydrochloric acid in sodium chloride solutions at 1 M total molality against molality of acid. The activity coefficient in the salt-free acid solutions is $\gamma_{(0)}$. X = weight per cent of methanol. Diameter of circles equals 0.002.

In Fig. (14-4-6), log $\gamma_{\pm}$ of sodium hydroxide in sodium chloride solutions at 3 and 5 total molalities is plotted against the hydroxide concentration. The deviations from the linear variation of this quantity are clearly seen.

All these results indicate that the linear variation of log $\gamma_{\pm}$, as expressed by equations (14-4-3) and (14-4-4), affords a first approximation which can be utilized in the treatment of many such mixtures. Certainly, a considerable simplification of a complicated subject is made possible by this fact.

[40] H. S. Harned and J. M. Harris, *J. Am. Chem. Soc.*, **50**, 2633 (1928).

[41] H. S. Harned and M. A. Cook, *Ibid.*, **59**, 1890 (1937).

In cases where incompletely ionized electrolytes are present, deviations from the above empirical relationship may be expected. As an illustration, Güntelberg[42] has measured the cells,

$$\mathrm{Pb}_x\mathrm{Hg} \mid \mathrm{PbCl}_2(m_1),\ \mathrm{MCl}(m_2) \mid \mathrm{AgCl\text{-}Ag}$$

at $\mu = 0.1$. He found that instead of the linear relationship given by equation (14-4-2), $\mathrm{E}^{0'}$ could be expressed by the equation

$$\mathrm{E}^{0'} = \mathrm{E}^{0'}_{(x=0)} - ax + bx^{3/2} \qquad (14\text{-}4\text{-}5)$$

where a and b are constants. The degree of ionization of lead chloride in the halide solutions was estimated.

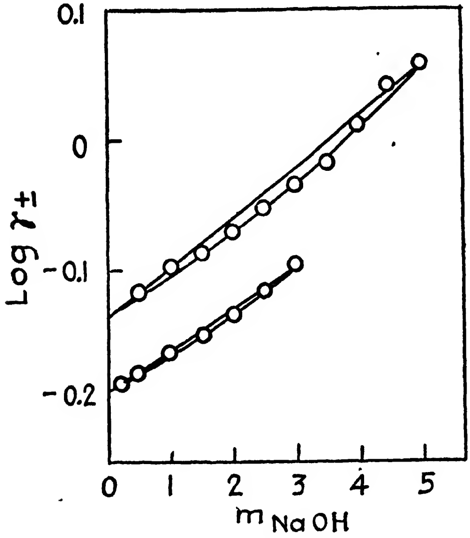

Fig. (14-4-6). Log $\gamma_\pm$ of sodium hydroxide, in sodium hydroxide-chloride mixtures of 5 molal (upper curves), and 3 molal (lower curves) total concentrations, against molality of hydroxide.

(5) Thermodynamic Theory of Mixtures at Constant Total Molality*

For the purpose of reducing our discussion to its simplest form, we shall consider only solutions of mixtures of two 1-1 electrolytes, denoted (1) and (2), at constant total molality. Further, we shall consider only those mixtures where the logarithm of the activity coefficient of each electrolyte may be assumed to vary linearly with its molal concentration. According

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[42] E. Güntelberg, *Studier over Elektrolyt-Activiteter*, G. E. C. Gads Forlag, København (1938).

* The following treatment follows closely that of H. S. Harned [*J. Am. Chem. Soc.*, **51**, 1865 (1935)]. A number of important ramifications suggested by the excellent work of E. Güntelberg [*Studier over Elektrolyt-Actitiviteter*, G. E. C. Gads Forlag København (1938)] have been incorporated.

to equations (14-4-3) and (14-4-4), the linear variation of log $\gamma_\pm$ for electrolytes (1) and (2) is given by the equations,

$$\log \gamma_1 = \log \gamma_{(0)1} + \alpha_{12} m_1 = \log \gamma_{1(0)} - \alpha_{12} m_2 \tag{14-5-1}$$

$$\log \gamma_2 = \log \gamma_{(0)2} + \alpha_{21} m_2 = \log \gamma_{2(0)} - \alpha_{21} m_1 \tag{14-5-2}$$

Relations between α_{12} and α_{21}, and other thermodynamic quantities may be obtained from the Gibbs-Duhem equation (1-8-1), or

$$N_1\, d \ln a_1 + N_2\, d \ln a_2 + N_w\, d \ln a_w = 0 \tag{1-8-1}$$

where N_1, N_2, N_w and a_1, a_2, a_w are the mol fractions and activities of electrolytes, (1), (2), and water, respectively. This equation becomes

$$2m_1\, d \log \gamma_1 + 2m_2\, d \log \gamma_2 = -55.51\, d \log a_w' \tag{14-5-3}$$

upon substitution of activity coefficients and molalities. According to equations (14-5-1) and (14-5-2), $d \log \gamma_1 = \alpha_{12}\, dm_1$, $d \log \gamma_2 = \alpha_{21}\, dm_2$, whence equation (14-5-3) becomes

$$2\alpha_{12} m_1\, dm_1 + 2\alpha_{21} m_2\, dm_2 = -55.51\, d \log a_w \tag{14-5-4}$$

Let $m = m_1 + m_2$, and $m_1 = mx$, where x can have any value between 0 and 1. Then $m_2 = (1 - x)m$. Substitution of these in the last equation leads to,

$$2(\alpha_{12} + \alpha_{21})x\, dx - 2\alpha_{21}\, dx = -\frac{55.51}{m^2}\, d \log a_w = \frac{2\, d\phi}{2.303m} \tag{14-5-5}$$

since

$$d \log a_w = -\frac{2m\, d\phi}{55.51(2.303)}$$

by differentiation of equation (1-9-9) at constant m and T. Upon integration of the left side of equation (14-5-5), we obtain

$$\begin{aligned}(\alpha_{12} + \alpha_{21})x^2 - 2\alpha_{21} x &= -\frac{55.51}{m^2} \int_0^x d \log a_w \\ &= -\frac{55.51}{m^2} \log \frac{a_{w(x)}}{a_{w(0)}} \qquad (14\text{-}5\text{-}6) \\ &= \frac{2}{2.303m} \int_0^x d\phi = \frac{2}{2.303m} (\phi_x - \phi_0)\end{aligned}$$

which is fundamental to much of the subsequent discussion.

If either α_{12} or α_{21} is known (by experiment), the other may be evaluated from osmotic and activity coefficients by the following simple procedures. Substituting the upper limit ($x = 1$) into equation (14-5-6), we obtain

$$\alpha_{21} = \alpha_{12} + \frac{55.51}{m^2} \log \frac{a_{w(1)}}{a_{w(2)}} = \alpha_{12} + \frac{2}{2.303m} (\phi_{2(0)} - \phi_{1(0)}) \tag{14-5-7}$$

where $a_{w(1)}$, $a_{w(2)}$, $\phi_{1(0)}$ and $\phi_{2(0)}$ are the activities of water and the osmotic coefficients in pure binary solutions of the electrolytic components, (1) or (2), respectively.

Further, we have found [Chapter (1), Section (9)] that the osmotic coefficient is related to the activity coefficient of the solute by the equation,

$$\phi = 1 + \frac{1}{m}\int_{1}^{\gamma_{\pm}} m\, d\ln\gamma_{\pm} \tag{1-9-12}$$

Upon substitution for ϕ in equation (14-5-7), we readily obtain

$$\begin{aligned}\alpha_{21} &= \alpha_{12} + \frac{2}{m^2}\left[\int_{1}^{\gamma_{2(0)}} m\, d\ln\gamma_{2(0)} - \int_{1}^{\gamma_{1(0)}} m\, d\ln\gamma_{1(0)}\right] \\ &= \alpha_{12} + \frac{2}{m^2}\left[\int_{0}^{m} m\, d\ln\frac{\gamma_{2(0)}}{\gamma_{1(0)}}\right]\end{aligned} \tag{14-5-8}$$

Equations (14-5-7) and (14-5-8) show the relation between the slopes, α_{12} and α_{21}, and the osmotic coefficients and activity coefficients of the solutions of the unmixed electrolytes at a total concentration, m. The validity of these relationships is determined by the accuracy of the linear variation of the logarithms of the activity coefficients of the solutes at constant total molality, as expressed by equations (14-5-1) and (14-5-2). The deductions from these relations depend on exact thermodynamic methods.

(a) In general, we see from equation (14-5-6) that the linear variation of $\log\gamma_{\pm}$ with x, at constant total molality, leads to a quadratic variation of the osmotic coefficient except for the case when $\alpha_{12} = -\alpha_{21}$. For the latter it is obvious that,

$$(\phi_x - \phi_0) = 2.303 m\alpha_{21}x \tag{14-5-9}$$

which represents a linear variation of ϕ. The general result without any additional restriction is illustrated by Fig. (14-5-1) (a). Here $\alpha_{12} \neq -\alpha_{21}$, $\log\gamma_{(0)1} \neq \log\gamma_{(0)2}$, and ϕ is quadratic in x.

(b) If we superimpose the restriction that

$$\log\frac{\gamma_{1(0)}}{\gamma_{2(0)}} = B_{12}m \tag{14-5-10}$$

where $B_{12} \neq f(m)$, a relation which Åkerlöf and Thomas[43] have found to be approached at high concentrations, we obtain the result shown in Fig. (14-5-1) (b). By substituting this relation in equation (14-5-8), and integrating, we obtain

$$\alpha_{12} - \alpha_{21} = B_{12} \neq f(m) \tag{14-5-11}$$

Further, from this and equations (14-5-1) and (14-5-2), we find that

$$(\alpha_{12} - \alpha_{21})m = \log\frac{\gamma_{1(0)}}{\gamma_{2(0)}} \tag{14-5-12}$$

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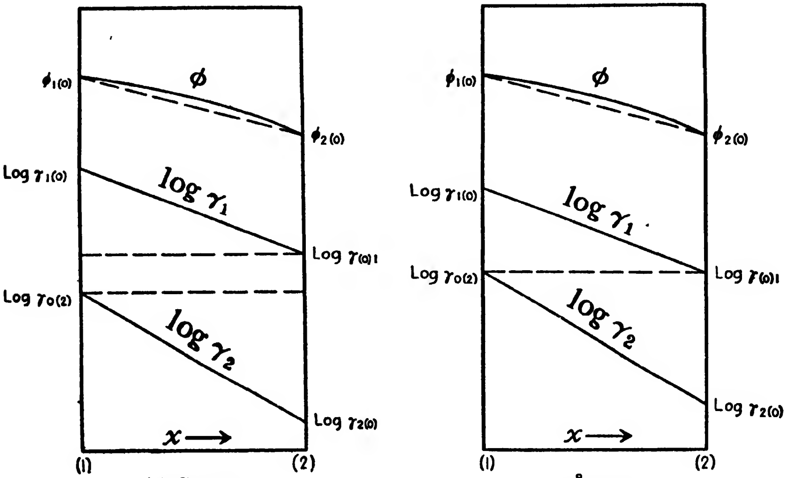
[43] G. Åkerlöf and H. C. Thomas, *J. Am. Chem. Soc.*, **56**, 593 (1934).

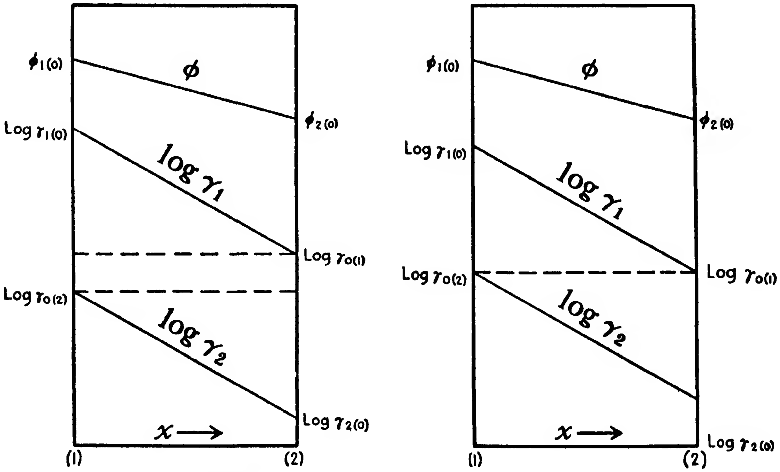
and

$$\log \gamma_{0(1)} = \log \gamma_{0(2)} \qquad (14\text{-}5\text{-}13)$$

a relation shown in Fig. (14–5–1b).



(a) General (b) Åkerlöf



(c) Brönsted (d) Guggenheim

Fig. (14–5–1). Illustrating various interpretations of the properties of two electrolytes in solution.

(c) Brönsted's theory of specific ionic interaction [Chapter (12) Section (6)] introduces different restrictions. In order to understand clearly the application of this theory, it is convenient to choose a concrete case, for example, a mixture of hydrochloric acid and potassium chloride. We may write for the logarithm of the activity coefficients of hydrochloric acid and potassium chloride in solutions of potassium chloride and hydrochloric acid, respectively, the following expressions,

$$\ln \gamma_{\mathrm{HCl(KCl+HCl)}} = \ln \gamma_{\mathrm{H(H)}}\gamma_{\mathrm{Cl(Cl)}}\gamma_{\mathrm{H(K)}}\gamma_{\mathrm{Cl(K)}}\gamma_{\mathrm{H(Cl)}}\gamma_{\mathrm{Cl(H)}}\gamma^2_{\mathrm{(H+K)}}\gamma^2_{\mathrm{(Cl)}} \tag{14-5-14}$$

$$\ln \gamma_{\mathrm{KCl(HCl+KCl)}} = \ln \gamma_{\mathrm{K(H)}}\gamma_{\mathrm{Cl(Cl)}}\gamma_{\mathrm{K(K)}}\gamma_{\mathrm{Cl(K)}}\gamma_{\mathrm{K(Cl)}}\gamma_{\mathrm{Cl(H)}}\gamma^2_{\mathrm{(K+H)}}\gamma^2_{\mathrm{(Cl)}} \tag{14-5-15}$$

where $\gamma_{\mathrm{H(H)}}$, $\gamma_{\mathrm{Cl(K)}}$, etc. are specific interaction coefficients, and $\gamma_{\mathrm{(H+K)}}$ and $\gamma_{\mathrm{(Cl)}}$ are salting out coefficients. Brönsted's theory may be summarized by two postulates:

(i) Ions of unlike sign react differently upon one another, while ions of like sign react identically with one another.

(ii) Each ion has a characteristic "salting out effect" which acts upon all other ions in the solution.

Consider a change in $x = m_{\mathrm{HCl}}/m$ at constant molality, m. According to postulate (i), $\gamma_{\mathrm{H(H)}} = \gamma_{\mathrm{H(K)}} = \gamma_{\mathrm{Cl(Cl)}} = \gamma_{\mathrm{K(K)}} =$ a constant. Further, at constant chloride concentration, the interaction coefficients of the chloride ion on the cations, $\gamma_{\mathrm{H(Cl)}}$ and $\gamma_{\mathrm{K(Cl)}}$, will remain constant with change in composition. Differentiation of equations (14-5-14) and (14-5-15) will yield, respectively, the relations,

$$d \ln \gamma_{\mathrm{HCl(HCl+KCl)}} = d \ln \gamma_{\mathrm{Cl(K)}}\gamma_{\mathrm{Cl(H)}} + 2d \ln \gamma_{\mathrm{(H+K)}}\gamma_{\mathrm{(Cl)}} \tag{14-5-16}$$

$$d \ln \gamma_{\mathrm{KCl(HCl+KCl)}} = d \ln \gamma_{\mathrm{Cl(K)}}\gamma_{\mathrm{Cl(H)}} + 2d \ln \gamma_{\mathrm{(K+H)}}\gamma_{\mathrm{(Cl)}} \tag{14-5-17}$$

at any given value of x from 0 to 1. Therefore,

$$d \ln \gamma_{\mathrm{HCl(HCl+KCl)}} = d \ln \gamma_{\mathrm{KCl(HCl+KCl)}} \tag{14-5-18}$$

Referring to our earlier treatment, this is equivalent to the statement that $\alpha_{12} = -\alpha_{21}$. This result always follows from the Brönsted theory of specific ionic interaction.

Let us now consider the limiting values of $\ln \gamma_{\mathrm{HCl(KCl)}}$ and $\ln \gamma_{\mathrm{KCl(HCl)}}$, where the subscripts indicate that the acid and salt are at zero concentrations in the solutions of the salt and acid, respectively. For this extreme case, equations (14-5-14) and (14-5-15) reduce to

$$\ln \gamma_{\mathrm{HCl(KCl)}} = \ln \gamma_{\mathrm{H(K)}}\gamma_{\mathrm{H(Cl)}}\gamma_{\mathrm{Cl(K)}}\gamma_{\mathrm{Cl(Cl)}}\gamma^2_{\mathrm{(KCl)}} \tag{14-5-19}$$

$$\ln \gamma_{\mathrm{KCl(HCl)}} = \ln \gamma_{\mathrm{K(H)}}\gamma_{\mathrm{K(Cl)}}\gamma_{\mathrm{Cl(H)}}\gamma_{\mathrm{Cl(Cl)}}\gamma^2_{\mathrm{(HCl)}} \tag{14-5-20}$$

where $\gamma_{\mathrm{(KCl)}}$ and $\gamma_{\mathrm{(HCl)}}$ are the salting out coefficients of the electrolytes, $\gamma_{\mathrm{(K)}}\gamma_{\mathrm{(Cl)}}$ and $\gamma_{\mathrm{(H)}}\gamma_{\mathrm{(Cl)}}$, respectively. From these equations, it is clear that

$$\ln \gamma_{\mathrm{HCl(KCl)}} - \ln \gamma_{\mathrm{KCl(HCl)}} = 2 \ln \gamma_{\mathrm{(KCl)}} - 2 \ln \gamma_{\mathrm{(HCl)}} \tag{14-5-21}$$

if we introduce the postulated relations, $\gamma_{\mathrm{H(K)}} = \gamma_{\mathrm{Cl(Cl)}} = \gamma_{\mathrm{K(H)}}$, and if we assume that $\gamma_{\mathrm{H(Cl)}} = \gamma_{\mathrm{Cl(H)}}$, and $\gamma_{\mathrm{K(Cl)}} = \gamma_{\mathrm{Cl(K)}}$. Güntelberg[44] has dis-

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[44] E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

cussed the fundamental nature and plausibility of this assumption. It depends on the basic assumption of the linear superposition of ionic atmospheres which requires that the average force acting upon the ion is given by the potential of atmosphere of the other ion [Equation (2-4-7)].

Equation (14-5-21) shows that Brönsted's postulates do not require that $\ln \gamma_{HCl(KCl)}$ equal $\ln \gamma_{KCl(HCl)}$, the result obtained from Åkerlöf's relation, and expressed by (14-5-13). Another result from Brönsted's theory may be readily obtained by integrating equation (14-5-18) from $x = 0$ to $x = 1$. By this means, we find that,

$$\ln \gamma_{HCl(KCl)} + \ln \gamma_{KCl(HCl)} = \ln \gamma_{KCl} + \ln \gamma_{HCl} \qquad (14\text{-}5\text{-}22)$$

The Brönsted result is represented by Fig. (14-5-1) (c). Here, $\alpha_{12} = -\alpha_{21}$, ϕ is linear with change in composition according to (14-5-7), and $\log \gamma_{0(1)} \neq \log \gamma_{0(2)}$.

(d) If we neglect the salting out coefficients of Brönsted in equation (14-5-21), it follows immediately from equation (14-5-22) that

$$\ln \gamma_{HCl(KCl)} = \ln \gamma_{KCl(HCl)} = \tfrac{1}{2}(\ln \gamma_{HCl} + \ln \gamma_{KCl}) \qquad (14\text{-}5\text{-}23)$$

which in our general symbolism means that, $\alpha_{12} = -\alpha_{21}$, and $\log \gamma_{0(1)} = \log \gamma_{0(2)}$. This condition is represented by Fig. (14-5-1) (d), and follows from Guggenheim's treatment of the theory of specific interaction. Guggenheim's[45] equation (12-6-3) leads to the expression, for the logarithm of the ratio of the activity coefficients of two electrolytes, which is the same as the Åkerlöf and Thomas relation (14-5-10), except that it is in c units, not m units, and the rational activity coefficient is employed. Thus,

$$\log \frac{f_{1(0)}}{f_{2(0)}} = Bc \qquad (12\text{-}6\text{-}4)$$

where B is a constant. This will lead to the result given by equation (14-5-13), namely, $\log \gamma_{0(1)} = \log \gamma_{0(2)}$.

(6) GENERAL SURVEY OF THE EXPERIMENTAL INVESTIGATIONS OF 1-1 HALIDE MIXTURES

As an introduction to the discussion of the theories and rules developed in the preceding section, the extensive experimental investigations of hydrochloric acid in chloride solutions will be reviewed. From the measurements cited in Sections (2) and (4), $\log \gamma_1$ of the acids in the halide solutions is obtained, and, consequently, the characteristic slopes, α_{12}, may be evaluated at different concentrations and temperatures. From these and the activity, or osmotic coefficients of the acids and the salts in pure water, α_{21} may be computed by means of equations (14-5-7), or (14-5-8).[46] Since α_{12} is computed from only two experimental values, that

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[45] E. A. Guggenheim, *Phil. Mag.* [7], **19**, 588 (1935).

[46] H. S. Harned, *J. Am. Chem. Soc.*, **37**, 1865 (1935).

in pure acid and that in the 0.01M acid-salt solution of the same molality, the highest accuracy is not to be expected. Further, the error in the computation of α_{12} is proportional to $1/m$, and consequently its evaluation at concentrations below 0.5M is not of a high order of accuracy, and has been omitted. Errors in the electromotive forces of ±0.1, ±0.2 and ±0.2 mv. at 0.5, 1 and 3M, respectively, cause an error in α_{12} equal to ±0.0034, ±0.0034, and ±0.0011 at these concentrations. Since the results come from many sources, it is difficult to estimate the errors, but judging from the consistency of the results, an accuracy of ±0.001 is probably obtained. The evaluation of α_{21} is less certain and is of the order of ±0.002 in the most favorable cases. Table (14-6-1) contains these values, and the sources of the data from which α_{12} and α_{21} were obtained. The effects of temperature may be seen from the values of these quantities for sodium chloride-hydrochloric acid mixtures given in Table (14-6-2). That ±0.001 is the magnitude of the error in determining α_{12} from these measurements is proved by the more recent results of Åkerlöf, Teare and Turck,[47] who obtained values at 1M from 0 to 40° which agree with those in the table to within this limit.

TABLE (14-6-1).* VALUES OF α_{12} AND α_{21} FOR 1-1 CHLORIDE-HYDROCHLORIC ACID MIXTURES AT 25°

m	LiCl[b]		NaCl[c]		KCl[d]		CsCl[e]	
	α_{12}	$-\alpha_{21}$	α_{12}	$-\alpha_{21}$	α_{12}	$-\alpha_{21}$	α_{12}	$-\alpha_{21}$
0.1	0.0013[a]	....	0.043[a]	...	0.077[a]	....	0.143[b]	...
.5	.006	0.011	.037	0.057	.062	0.074	.105	0.070
1.	.005	.012	.032	.058	.056	.072	.100	.060
1.5	.005	.011	....	.058	.055	.069	.099	.053
2.	.005	.012	.031	.058	.057	.064	.099	.046
3.	.004	.013	.031	.058	.062	.054	.098	.041
4.[f]	− .0025	.....	.030	....	.066	.050	....	.....
5.[f]	....	.....	.030	....	.072	.....	....	.....
6.[f]	− .0086	.....	.029	.....	....	.....	.....	.....

[a] E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).
[b] H. S. Harned and H. R. Copson, *J. Am. Chem. Soc.*, **55**, 2206 (1933).
[c] H. S. Harned, *Ibid.*, **57**, 1865 (1935).
[d] H. S. Harned and W. J. Hamer, *Ibid.*, **55**, 2194 (1933).
[e] H. S. Harned and O. E. Schupp Jr., *Ibid.*, **52**, 3892 (1930).
[f] J. E. Hawkins, *Ibid.*, **54**, 4480 (1932).
* The values employed for log $\gamma_\pm$ for hydrochloric acid and the halides were those in Tables (11-4-1A) and (12-3-1A), respectively.

The characteristics of the behaviors of α_{12} and α_{21} as functions of the concentration are shown in Figs. (14-6-1) and (14-6-2). As the concentration increases, it appears [Fig. (14-6-1)] that in some cases (CsCl, NaBr, NaCl) that α_{12} approaches constancy. This tendency led Åkerlöf and Thomas to the rule that this quantity as well as α_{21} are not functions of the concentration in concentrated solutions. Due to the fact, however,

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[47] G. Åkerlöf, J. W. Teare and H. E. Turck, *J. Am. Chem. Soc.*, **59**, 1916 (1937).

that there is distinct evidence that this rule is not valid in all cases (KBr, KCl, etc.), it must be regarded as a first approximation. At the lower concentrations ($<0.5M$), it is obvious that the rule is invalid for all of these mixtures.

TABLE (14-6-2). VALUES OF α_{12} AND α_{21} FOR HYDROCHLORIC ACID-SODIUM CHLORIDE MIXTURES FROM 10 TO 40°

t	α_{12}					
	m = 0.1	0.3	0.5	1	2	3
10	.....	.044	.040	.038	.037	.037
20	0.046[a]	.040	.036	.034	.033	.033
25	.043[a]	.038	.034	.032	.031	.031
30	.....	.035	.032	.030	.029	.029
40	.....	.030	.028	.026	.025	.025
	$-\alpha_{21}$					
10	.....	.068	.070	.069	.066	.064
20	.....	.060	.062	.062	.060	.064
25	.....	.057	.059	.058	.058	.059
30	.....	.054	.055	.055	.055	.057
40	.....	.047	.047	.048	.049	....

[a] E. Guntelberg, *Z. physik. Chem.*, **123**, 199 (1926)

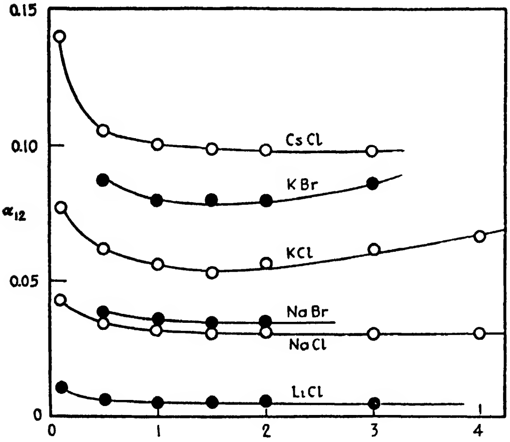

Fig. (14-6-1). Variation of the parameter, α_{12}, with molality:

In Fig. (14-6-2), plots of both α_{12} and α_{21} are given for cesium chloride and sodium chloride. The parameter, α_{12} is not equal to $-\alpha_{21}$ although in the case of sodium, the value of α_{12} appears to approach that of $-\alpha_{21}$ as the concentration decreases.

If we consider these results in relation to the theory of the preceding section, we find that they comform to the case which we have designated as general [Fig. (14-5-1) (a)]. This fact is illustrated by Fig. (14-6-3) in which both $(\alpha_{12} - \alpha_{21})$ and B_{12}, defined by the equation,

$$\log \frac{\gamma_{1(0)}}{\gamma_{2(0)}} = B_{12} m \tag{14-5-10}$$

are plotted against m. We note that B_{12} is a function of m in dilute solutions, and hence according to theory, $\log \gamma_{0(1)}$ does not equal $\log \gamma_{0(2)}$, nor does $\alpha_{12} - \alpha_{21}$ equal B_{12} except in the cases of lithium bromide and chloride. This equality may not be exact but is well within the experimental error. As the concentration increases, B_{12} and $\alpha_{12} - \alpha_{21}$ approach each other in magnitude, a fact which indicates that the empirical rule that $B_{12} \neq f(m)$ is a good approximation in the very concentrated solutions, and that the condition represented by Fig. (14-5-1) (b) is approached.

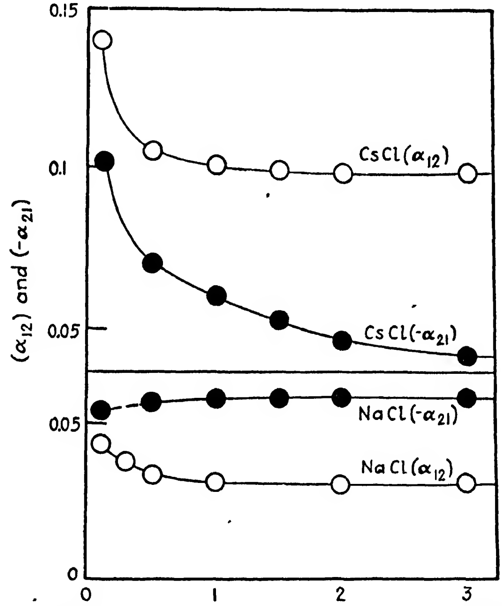

Fig. (14-6-2). Variation of parameters, α_{12} and $(-\alpha_{21})$, with molality for cesium and sodium chloride solutions.

A direct proof that the osmotic coefficient does not vary linearly in lithium chloride-potassium chloride mixtures at total molalities of 1, 2 and $3M$, has been obtained by Owen and Cooke.[48] By utilizing the iso-

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[48] B. B. Owen and T. F. Cooke, Jr., *J. Am. Chem. Soc.*, **59**, 2273 (1937).

piestic vapor pressure method, they obtained directly the change in osmotic coefficient, and were able to test equation (14-5-6), or

$$(\phi_x - \phi_0) = -2.303\alpha_{21}mx + 1.151(\alpha_{12} + \alpha_{21})mx^2 \qquad (14\text{-}6\text{-}1)$$

In this system, the concentration of the lithium chloride is mx, and of potassium chloride is $m(1 - x)$, where m is the total molality. In terms of the vapor pressure, this equation may be rearranged to read

$$\frac{\log p_0 - \log p_x}{xm^2} = -0.036\alpha_{21} + 0.018(\alpha_{12} + \alpha_{21})x \qquad (14\text{-}6\text{-}2)$$

If a plot of the left side of this equation versus x is a straight line, then a quadratic variation of the osmotic coefficient will express the results. In Fig. (14-6-4), this function is plotted. The diameters of the circles represent an error of ±0.1 percent in m, which is the estimated error of the measurements. The plots are evidently linear within this limit of error, which indicates a formal agreement with equations (14-6-1) and (14-6-2).

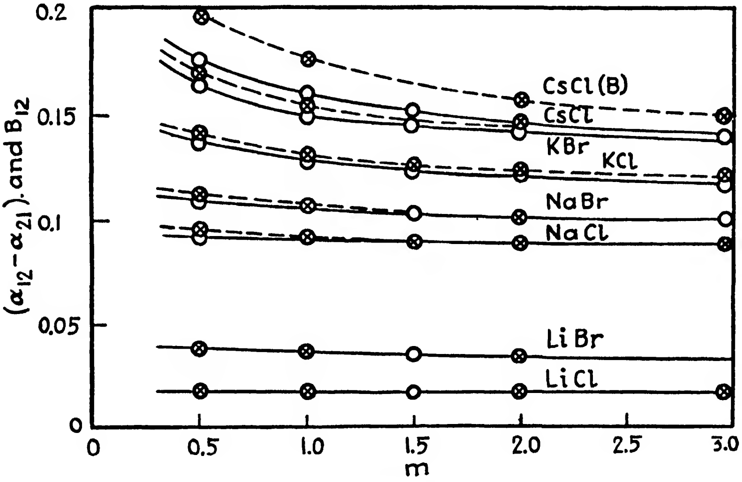

Fig. (14-6-3). Plots of B_{12} and $(\alpha_{12}-\alpha_{21})$ against molality for 1-1 halide solutions; ⊗, B_{12}; ○, $(\alpha_{12}-\alpha_{21})$.

Since α_{12} does not equal $-\alpha_{21}$ in the concentrated solutions (0.5*M* or greater), the theory of specific ionic interaction in its simplest form [Figs. (14-5-1) (c) or (d)] is not strictly valid. This fact is illustrated by Fig. (14-6-5) in which $\alpha_{12} + \alpha_{21}$ is plotted against m for hydrochloric acid-chloride mixtures. Since $\alpha_{12} + \alpha_{21}$ does not equal zero, the conditions superimposed by specific interaction do not hold. This, of course, is not surprising in solutions of these concentrations.

Although the computation becomes very sensitive at 0.1*M*, it seems from the present data that the correct distribution of the curves is obtained at this concentration. Thus, taking values of 0.0980, 0.1135, 0.1088, and 0.1238 for $-\log \gamma_{0.1}$ of hydrochloric acid, potassium chloride, sodium

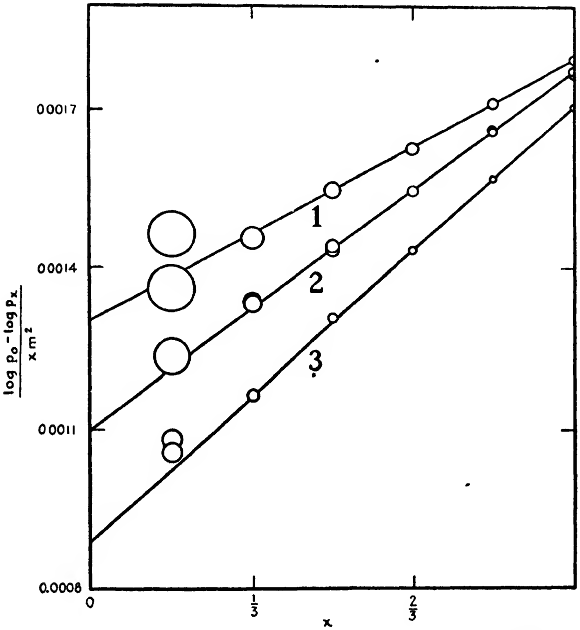

Fig. (14-6-4). Formal verification of equations (14-6-1) and (14-6-2). The numbers indicate the total molality for each series. The ordinates of the 3 *M* series have been lowered by 0.0001 to avoid overlapping.

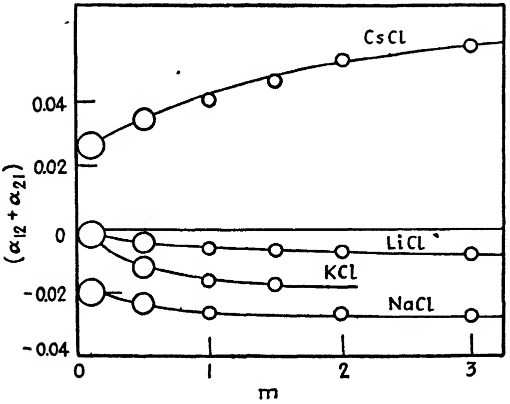

Fig. (14-6-5). Plots of $(\alpha_{12} + \alpha_{21})$ against *m*. Radii of circles represent the magnitudes of the errors.

chloride and cesium chloride, respectively [Tables (11-4-1A) and (12-3-1A)], and the values of α_{12} in Table (14-6-1), we obtain +0.028, −0.001 and

-0.020 for $\alpha_{12} + \alpha_{21}$ in the cases of cesium, potassium, and sodium chloride mixtures. The small difference between $\alpha_{12} - \alpha_{21}$ and B_{12} has been neglected in this computation. As seen by the plots in Fig. (14-6-5), these results show the same distribution as those at higher concentrations. There seems to be a tendency for $\alpha_{12} + \alpha_{21}$ to approach zero, but this condition is not reached at $0.1M$, although it is very nearly valid in the lithium and potassium chloride mixtures.

Owen and Cooke[49] have determined $\log \gamma_{\pm}$ for hydrobromic acid in hydrochloric acid solutions from the cells,

$$H_2 \mid HBr(m_1),\ HCl(m_2) \mid AgBr\text{-}Ag$$

at $m_1 + m_2$ equal to 0.5 from 0 to 45°. Log γ_{HBr} was found to vary linearly with the molality of hydrobromic acid. The slopes, α_{12}, were evaluated, and the slopes, α_{21}, for the variation of hydrochloric acid in these mixtures was estimated and found to be nearly equal in magnitude but opposite in sign to α_{12}. The sum, $\alpha_{12} + \alpha_{21}$, is small at all temperatures.

The preceding considerations indicate that the original treatment of specific ionic interaction of Brönsted, developed in the preceding section, is somewhat oversimplified. This point is established by the comprehensive analysis of the freezing measurements of mixtures of potassium nitrate, potassium chloride, lithium nitrate, and lithium chloride carried out by Scatchard and Prentiss.[50] By application of his extended equation (12-7-1), which includes the effects of change in dielectric constant with salt concentration, ion-molecule salting out, and molecule-molecule effect to the mixtures, Scatchard's investigations indicate that the theory of specific ionic interaction is confirmed at concentrations above $0.1M$, and possibly at concentrations of $1M$.

(7) FURTHER CONSIDERATIONS OF THE THEORY OF SPECIFIC IONIC INTERACTION

Although the results in the last section show the extremely complicated nature of these systems, and the difficulty of obtaining exact verification of the theory of specific ionic interaction, Brönsted and Guntelberg have obtained much evidence for its essential validity. Of this, we shall choose a few illustrations from experimental results of a high degree of accuracy.

One of the requirements which follows readily from the application of the theory is that

$$\log \frac{\gamma_{TlCl(HCl)}}{\gamma_{TlCl(MCl)}} = \log \frac{\gamma_{AgCl(HCl)}}{\gamma_{AgCl(MCl)}} = \log \frac{\gamma_{RCl(HCl)}}{\gamma_{RCl(MCl)}} = \log \frac{\gamma_{HCl(HCl)}}{\gamma_{HCl(MCl)}} \quad (14\text{-}7\text{-}1)$$
$$= \text{etc.}$$

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[49] B. B. Owen and T. F. Cooke, Jr., *J. Am. Chem. Soc.*, **59**, 2277 (1937).

[50] G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **56**, 2320 (1924); G. Scatchard, *Chem. Rev.*, **19**, 309 (1936).

By measuring the solubility of the slightly soluble salt, $[Co(NO_2)(CNS)(NH_3)_4]Cl$, in chloride solutions, Güntelberg[51] was able to relate solubility determinations with his electromotive force measurements of hydrochloric acid in the same halide solutions. From the last two of these relations, we obtain,

$$\frac{1}{2}[\log S_{RCl(MCl)} - \log S_{RCl(HCl)}] = \log \gamma_{HCl(HCl)} - \log \gamma_{HCl(MCl)} = \alpha_{12} m \qquad (14\text{-}7\text{-}2)$$

The results at 20° are shown in Table (14-7-1), where the left side of this equation divided by m is given in the third column, and the values of α_{12} from electromotive force measurements are given in the last column. The agreement between the results from these entirely different sources is good.

TABLE (14-7-1). PROOF OF EQUATION (14-7-2). $m = 0.1$

	S_{RCl}	$\frac{1}{2m}[\log S_{RCl(MCl)} - \log S_{RCl(HCl)}]$	α_{12}
HCl	0.01216	....	....
LiCl	.01219	0.006	0.012
NaCl	.01238	.039	.046
KCl	.01264	.084	.081
CsCl	.01301	.147	.146

TABLE (14-7-2). RATIO OF THE SOLUBILITY OF TETRANITRO-DIAMMINE-COBALTIATES IN 0.1 M KNO_3 TO THAT IN 0.1 M $NaNO_3$ AT 20°

Cations	$r = S_{RX_n(KNO_3)}/S_{RX_n(NaNO_3)}$
$Co(NH_3)_4(C_2O_4)^+$	1.034
$Co(NH_3)_4CO_3^+$	1.032
Ag^+	1.034
$N(CH_3)_4^+$	1.033
$Co(NH_3)_5Cl^{++}$	1.041
$Co(NH_3)_5NO_2^{++}$	1.041
$Co(NH_2C_2H_4NH_2)_3^{+++}$	1.045
$Co(NH_3)_5H_2O^{+++}$	1.047

Another excellent example of the proof of the relationship given by equation (14-7-1) is the solubility measurements of complex salts with the common anion, $[Co(NH_3)_2(NO_2)_4]^-$. According to theory, r, the ratio of the solubilities of these salts, of a given valence type, in potassium and sodium nitrates should be the same. This is shown clearly by the results in Table (14-7-2)[52]. Further, it follows from Guggenheim's[53] treatment of the theory that

$$r_0 = (r_{RX})^2 = (r_{RX_2})^{3/2} = (r_{RX_3})^{4/3} \qquad (14\text{-}7\text{-}3)$$

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[51] E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

[52] J. N. Brönsted, *J. Am. Chem. Soc.*, **44**, 877 (1922).

[53] E. A. Guggenheim, *Phil. Mag.*, [7] **19**, 588 (1935).

where r_0 is a constant, which, if assigned the value 1.064, satisfies this relation. This procedure yields 1.032, 1.042 and 1.047 for r for uni-, bi-, and trivalent cations, respectively. This checks well with the results in Table (14-7-2).

(8) HYDROXIDE-CHLORIDE MIXTURES

As pointed out in Section (4) [Fig. (14-4-6)], Harned and Harris showed that in some hydroxide-chloride mixtures, the logarithm of the activity coefficients of the hydroxides did not vary linearly with the concentration of hydroxide at constant total molality. Recently, Harned and Cook[54] by measurements of the cells,

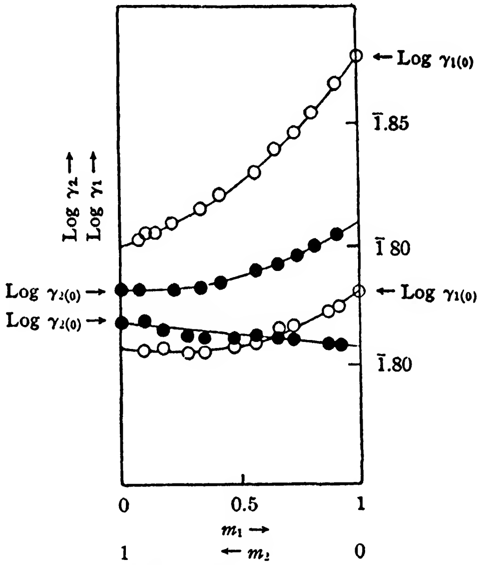

Fig. (14-8-1). Log γ_1 and log γ_2 against m_2 and m_1 at a constant molality of 1M Two curves at top represent KOH-KCl mixtures; two curves at bottom NaOH-NaCl mixtures. Diameter of circles equals 0.5 mv.

$$H_2 \mid MOH(m_1), MX(m_2) \mid M_xHg \mid MOH(m_R) \mid H_2$$

and

$$Ag\text{-}AgX \mid MOH(m_1), MX(m_2) \mid M_xHg \mid MX(m_R) \mid AgX\text{-}Ag$$

have been able to determine the activity coefficients of both the hydroxide and chloride in the mixtures. This is the first time that the activity coef-

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[54] H. S. Harned and M. A. Cook, *J. Am. Chem. Soc.*, **59**, 1890 (1937).

ficients of both electrolytic components in a mixture have been directly evaluated. Indeed, there are not many cells suitable for such a determination.

The characteristics of the results are illustrated in Fig. (14-8-1). The two curves at the upper part of the figure represent the behavior of the potassium hydroxide-chloride mixtures while the two curves at the bottom of the figure represent the sodium hydroxide-chloride mixtures, both at $1M$. At the top (circles) the logarithm of the activity coefficient of potassium hydroxide in the chloride solutions is plotted against its concentration. The curve below this (dots) represents the logarithm of the activity coefficient of the chloride in the hydroxide solution. Log $\gamma_{1(0)}$, the activity coefficient of the hydroxide, and log $\gamma_{2(0)}$, that of the chloride, both in pure water, are indicated on the margins. Similarly, the two lower curves represent the behavior of the sodium hydroxide-chloride system. The circles represent the values of the logarithm of the activity coefficient of sodium hydroxide in the chloride solution, and the dots represent the activity coefficient of the sodium chloride in the same mixtures.

It is clear that neither log γ_1 nor log γ_2 vary linearly with m_2 or m_1. Harned and Cook were able to express the variation within the error of experiment by the quadratic equations,

$$\begin{aligned} \log \gamma_1 &= \log \gamma_{1(0)} - \alpha_{12}m_2 - \beta_{12}m_2^2 \\ \log \gamma_2 &= \log \gamma_{2(0)} - \alpha_{21}m_1 - \beta_{21}m_1^2 \end{aligned} \qquad (14\text{-}8\text{-}1)$$

Upon substitution in equation (14-5-4) and integration, the change in osmotic coefficient becomes

$$\begin{aligned} \frac{\phi_{(x_1=0)} - \phi_{(x_1=x)}}{2.303m} = \alpha_{21}x_1 - \frac{1}{2}(\alpha_{12} + \alpha_{21})x_1^2 - m(\beta_{12} - \beta_{21})x_1^2 \\ + \frac{2}{3}m(\beta_{12} - \beta_{21})x_1^3 \end{aligned} \qquad (14\text{-}8\text{-}2)$$

where $m = m_1 + m_2$ is constant, and $x_1 = m_1/m$.

There is one peculiarity of the sodium hydroxide-chloride mixtures. The curves slope in the opposite direction, a fact which leads to the same sign for α_{12} and α_{21}. This has not proved to be characteristic of most of the other systems, although there is evidence that the lithium hydroxide chloride mixtures behave in like manner.

Harned and Cook computed by equation (14-8-2) the change in osmotic coefficients between the pure hydroxides and chlorides, or $(\phi_{(x_1=1)} - \phi_{(x_1=0)})$. They compared these differences with values computed from electromotive force measurements by graphical integration of equation (14-5-8), and with similar values calculated from freezing point measurements. The differences, computed from these entirely independent series of results, agreed within satisfactory limits.

(9) Extrapolation of Activity Coefficients to Saturated Solutions. Calculation of the Solubility of Highly Soluble Salts in Solutions of Electrolytes

The knowledge of the thermodynamic properties of electrolytes and their mixtures may be applied to the calculation of the solubility of highly soluble salts in salt solutions. This calculation requires some method of extrapolation by which the activity coefficient of the saturating solute may be estimated at the high total ionic strengths of the mixed salt solutions. For this purpose, Åkerlöf and Thomas,[55] and Åkerlöf[56] employed the approximate empirical equation (14-5-10), which we write in the form[57]

$$\log \frac{\gamma_{1(0)}}{\gamma_{R(0)}} = B_{R1}\,\mu \qquad (14\text{-}9\text{-}1)$$

The subscript (0) serves as a reminder that this equation applies only to simple binary solutions of the individual electrolytes, (1) and (R), at the same ionic strength, μ.[58] Hydrochloric acid is used as the reference electrolyte (R) because its activity coefficient is known over a very wide concentration range. Åkerlöf and Teare[59] have determined this quantity from 0 to 50°, and from 3 to 16M. Their values are given in Table (14-9-1A). The isothermal constant, B_{R1}, may be determined from known values of $\gamma_{1(0)}$ and $\gamma_{R(0)}$ in simple unsaturated solutions, or from solubility data by a method outlined later.

The solubility product of an electrolyte which dissociates into two kinds of ions will be written

$$\mathcal{P}_{(0)} = (m_+^{\nu_+} m_-^{\nu_-})_{(0)} = (\nu_+^{\nu_+} \nu_-^{\nu_-}) m_{(0)}^{\nu} \qquad (14\text{-}9\text{-}2)$$

when the solvent is pure water, and

$$\mathcal{P} = (m_+^{\nu_+} m_-^{\nu_-}) \qquad (14\text{-}9\text{-}3)$$

when the solvent is a solution containing other electrolytes. If these other electrolytes have no ions in common with the saturating salt, $\mathcal{P}$ is also equal to $(\nu_+^{\nu_+} \nu_-^{\nu_-}) m^{\nu}$.

In saturated solutions of electrolyte (1), the ionic activity product of this electrolyte is constant at a given temperature, and therefore

$$\frac{1}{\nu_1} \log K_1 = \frac{1}{\nu_1} \log \mathcal{P}_{1(0)} + \log \gamma_{1(0)} = \frac{1}{\nu_1} \log \mathcal{P}_1 + \log \gamma_1 \qquad (14\text{-}9\text{-}4)$$

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[55] G. Åkerlöf and H. C. Thomas, *J. Am. Chem. Soc.*, **56**, 593 (1934).

[56] G. Åkerlöf, *Ibid.*, **56**, 1439 (1934); *J. Phys. Chem.*, **41**, 1053 (1937). See also G. Åkerlöf and H. E. Turck, *J. Am. Chem. Soc.*, **56**, 1875 (1934); H. S. Harned, *J. Franklin Institute*, **225**, 623 (1938).

[57] In some cases, it is necessary to include a small constant term, because the plot of $\log \gamma_{1(0)}/\gamma_{R(0)}$ extrapolated from high concentrations to $\mu = 0$, does not always pass through the origin. Occasionally, the plot exhibits a distinct curvature at high concentrations, and a term in μ^2 should be added to equation (14-9-1).

[58] In solutions of mixed electrolytes the subscript (0) is omitted.

[59] G. Åkerlöf and J. W. Teare, *J. Am. Chem. Soc.*, **59**, 1855 (1937).

Since $\log \gamma_{1(0)}$ in this equation refers to a saturated solution of electrolyte (1) in pure water, this term is given directly by equation (14-9-1).[60] Denoting the ionic strength of this solution by $\mu_{1(0)}$, we obtain

$$\frac{1}{\nu_1}\log K_1 = \frac{1}{\nu_1}\log \mathcal{P}_{1(0)} + \log \gamma_{R(0)} + B_{R1}\,\mu_{1(0)} \qquad (14\text{-}9\text{-}5)$$

The term $\log \gamma_1$ in equation (14-9-4) refers to a saturated solution of (1) in the presence of one or more additional electrolytes at a total ionic strength, μ_T. For simplicity, we shall consider only a single co-solute, designated electrolyte (2), so that $\mu_T = \mu_1 + \mu_2$. The calculation of $\log \gamma_1$ involves two steps. Equation (14-9-1) is assumed to hold in supersaturated solutions of (1) in pure water, so that it may be used to calculate $\log \gamma_{1(0)}$ at the ionic strength, μ_T. At this ionic strength equation (14-5-1) is used to express $\log \gamma_1$ in terms of $\log \gamma_{1(0)}$ and μ_2. Thus,

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_{12}\mu_2 \qquad (14\text{-}9\text{-}6)$$

Combination with equation (14-9-1), also at μ_T, yields[61]

$$\log \gamma_1 = \log \gamma_{R(T)} + B_{R1}\mu_T - \alpha_{12}\mu_2 \qquad (14\text{-}9\text{-}7)$$

Accordingly, equation (14-9-4) becomes

$$\begin{aligned}\frac{1}{\nu_1}\log K_1 &= \frac{1}{\nu_1}\log \mathcal{P}_{1(0)} + \log \gamma_{R(0)} + B_{R1}\,\mu_{1(0)} \\ &= \frac{1}{\nu_1}\log \mathcal{P}_1 + \log \gamma_{R(T)} + B_{R1}\,\mu_T - \alpha_{12}\,\mu_2\end{aligned} \qquad (14\text{-}9\text{-}8)$$

This equation contains three independent constants, B_{R1}, α_{12}, and $\mathcal{P}_{1(0)}$ (or K_1), which must be evaluated before $\mathcal{P}_1$, and subsequently the solubility of electrolyte (1), can be calculated in the presence of the co-solute (2). There are many possible combinations of data from which these constants can be evaluated. The following three are of particular interest.

(i) If B_{R1} and α_{12} are known from measurements in dilute solutions, and $\mathcal{P}_{1(0)}$ is obtained by a single solubility determination in pure water, equation (14-9-8) predicts[62] the solubility of electrolyte (1) in mixed solutions containing the co-solute at any ionic strength, μ_2. This is an interesting

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[60] In this equation μ is any experimental ionic strength within the range of validity of the equation. The use of equation (14-9-1) at $\mu_{1(0)}$ usually constitutes an extrapolation, as activity coefficients of highly soluble salts are rarely measured up to saturation.

[61] The validity of equation (14-9-6) appears less general in concentrated solutions than that of (14-9-1). It is frequently necessary to add a term $\beta_{12}\mu_2^2$ to equations (14-9-6) to (14-9-8). We have avoided a completely general formulation of these relationships because each additional empirical parameter tends to obscure the physical significance of the rest.

[62] The solution of this equation is obtained by a short series of successive approximations because, in this calculation, μ_T is not known at the start.

result because no solubility measurements in the mixtures would be required.

(ii) If the activity coefficient of electrolyte (1) is known in pure water over a sufficiently high concentration range to evaluate B_{R1}, then $\mathcal{P}_{1(0)}$ and α_{12} can be determined from one solubility measurement in the pure solvent, and one in the presence of the co-solute. These activity coefficient data are frequently available.

(iii) If B_{R1} is not known, the constants can be obtained from three solubility measurements in the presence of the co-solute. This result is noteworthy because, through B_{R1} and equation (14-9-1), solubility data in mixtures at high ionic strength are seen to predict the activity coefficient of the saturating solute in pure water. Unfortunately, activity coefficients obtained in this manner are subject to large errors, because uncertainties in the data and departures from equation (14-9-8) are magnified by the form of this equation.

It is important to note that the application of equation (14-9-8) to actual solubility calculations requires that neither B_{R1} nor α_{12} varies with the total ionic strength, μ_T. In Section (6), we have shown that for some electrolytes at high concentrations, B_{R1} fulfills this condition very closely [Fig. (14-6-3)]. That part of the computations which depends upon this equation may be expected to be quite accurate for many electrolytes. On the other hand, the assumption that α_{12} is not a function of the concentration may introduce considerable error in some cases. For example, Tables (14-6-1) and (14-6-2), and Figs. (14-6-1) and (14-6-2) show that although α_{12} and α_{21} very little with m at high concentrations in sodium chloride-hydrochloric acid mixtures, they vary considerably in potassium chloride-hydrochloric acid mixtures. These facts are in agreement with the recent calculations of Åkerlöf[63] of the solubility of sodium and potassium chlorides in hydrochloric acid solutions. He found that the equations,

$$\tfrac{1}{2}\log m_{\mathrm{NaCl}} = 0.7782 + 0.0875\mu_T - \tfrac{1}{2}\log\mu_T - \log\gamma_{\mathrm{R}(T)} - 0.0530m_{\mathrm{HCl}} + 0.0005m^2_{\mathrm{HCl}} \tag{4-9-9}$$

and

$$\tfrac{1}{2}\log m_{\mathrm{KCl}} = 0.4621 + 0.118\mu_T - \tfrac{1}{2}\log\mu_T - \log\gamma_{\mathrm{R}(T)} - 0.0512m_{\mathrm{HCl}} + 0.00167m^2_{\mathrm{HCl}} \tag{4-9-10}$$

will represent accurately the solubilities, m_{NaCl} and m_{KCl}, at 25°. These are identical with (14-9-8) except for the additional terms in m^2_{HCl}. The first terms on the right of these equations are the values of $1/2 \log K_1$, and -0.0875 and -0.118 are the values of B_{R1} for these systems, respectively. The last two terms in each of these equations replace the last term in

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[63] G. Åkerlöf, Private communication.

equation (14-9-8). This not only indicates that the parameter, α_{12}, varies with concentration, but that it changes more rapidly in the potassium than in the sodium chloride system. This result is in accord with the data in Table (14-6-1) which indicate the $(-\alpha_{21})$[64] decreases more rapidly in the potassium than in the sodium chloride system. The numerical values of these quantities, determined from the solubility data and the data in more dilute solutions, are in rough agreement, but, up to the present, an accurate fit of the material from these two sources has not been obtained.

Åkerlöf[65] has applied extended forms of equations (14-9-8) to a number of ternary and quaternary systems, and the quinary system, NaCl-KCl-$MgCl_2$-$MgSO_4$-water.

[64] Note that α_{21} in Table (14-6-1) corresponds to α_{12} in equation (14-9-8).

[65] G. Åkerlöf, *J. Phys. Chem.*, **41**, 1053 (1937).

Chapter (15)

The Ionization and Thermodynamic Properties of Weak Electrolytes*

In Chapter (7), the most recent methods of computing the ionization constants of strong electrolytes in media of low dielectric constant, and of weak electrolytes in aqueous solution from conductance measurements were considered. In most cases, the ionization constants from this source are known accurately at 25° only and, therefore, yield no knowledge regarding heats of ionization or other thermochemical quantities associated with the ionization reactions.

Most of the accurate data on the variation of ionization constants with temperature have been derived from measurements of cells without liquid junction containing weak electrolytes. Also, the only accurate ionization constants yet obtained in water-non-aqueous solvent mixtures, over considerable temperature ranges, have been derived from cells without liquid junction. In this chapter, the basis of this method and its application to the determination of the ionization constants of water, weak acids, and ampholytes in water, in aqueous salt solutions, and in organic solvent-water mixtures, will be discussed. Methods of computing the variation of ionization constants with temperature will be described, and tables of the thermochemical quantities associated with ionization reactions will be considered.

In general, two types of cells without liquid junction may be employed. The first type, which contains a buffer solution, is especially adapted for the determination of ionization constants in pure solvents, in mixed solvents and in salt solutions. The second type, containing unbuffered solutions yields additional information concerning medium effects. In several of these respects the electromotive force method is superior to the conductance method.

Cells involving unknown liquid junctions have been used in the study of weak electrolytes, but since these are usually unsuitable for rigorous thermodynamic purposes, they will be used in the present discussion as an occasional source of information to supplement that now available from the cells without liquid junction.†

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* Parts of this chapter follow closely a review by H. S. Harned and B. B. Owen, *Chem. Rev.*, **25**, 31 (1939).

† Note discussion of the use of cells with liquid junction in Chapter (10), Section (7).

Quite recently, with the development of completely objective photoelectric technique, accurate determinations of ionization constants and ionization in salt solutions have been made. Some of these results will be discussed, and contrasted with those derived from electromotive force measurements.

(1) The Ionization Constant of Water

Since water is the most important weak electrolyte, the thermodynamics of its ionization process has received much attention. Early accurate determinations of its ionization constant were made by conductance measurements[1] and by electrometric measurements of cells with liquid junctions. In view of the great experimental difficulties, the values of K_w (0.59×10^{-14} at 18° and 1.04×10^{-14} at 25°) estimated conductometrically are in remarkable agreement with the most recent electrometric values (0.58×10^{-14} at 18° and 1.008×10^{-14} at 25°). Cells with liquid junctions similar to the one originally used by Arrhenius

$$H_2 \mid NaOH(m) \mid NaCl(m) \mid HCl(m) \mid H_2$$

have frequently been employed.[2] By the use of the Lewis and Sargent[3] equation for liquid junction potentials and the substitution of mean for individual ionic activities, Lewis, Brighton and Sebastian[4] obtained the value 1.012×10^{-14} for K_w at 25° in good agreement with 1.008×10^{-14} derived from cells without liquid junctions.

The first application of cells without liquid junction to the study of the ionization of water was the determination of the ionization product, $m_H m_{OH}$, and the activity coefficient function, $\gamma_H \gamma_{OH}/a_{H_2O}$, in salt solutions at 25°.[5] This latter quantity was shown to approach the limiting law for activity coefficients in dilute salt solutions.[6] The calculations involved the use of an ionization constant determined from other data. In subsequent investigations, the cells without liquid junction,

$$H_2 \mid HX(m) \mid AgX\text{-}Ag \qquad \text{I}$$

$$H_2 \mid MOH(m_1),\ MX(m_2) \mid AgX\text{-}Ag \qquad \text{II}$$

$$H_2 \mid HX(m_1),\ MX(m_2) \mid AgX\text{-}Ag \qquad \text{III}$$

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[1] F. Kohlrausch and A. Heydweiller, *Z. physik. Chem.*, **14**, 317 (1894); *Ann. Physik.*, **53**, 209 (1894); F. Kohlrausch, *Z. physik. Chem.*, **42**, 193 (1903); A. Heydweiller, *Ann. Physik.*, [4], **28**, 503 (1909).

[2] S. Arrhenius, *Z. physik. Chem.*, **11**, 808 (1893); A summary of the early determinations of K_w is given by H. T. Beans and E T. Oakes, *J. Am. Chem. Soc.*, **42**, 2116 (1920).

[3] G. N. Lewis and L. W. Sargent, *J. Am. Chem. Soc* , **31**, 363 (1909).

[4] G. N. Lewis, T. B. Brighton, and R. L. Sebastian, *J. Am. Chem. Soc.*, **39**, 2245 (1917).

[5] H. S. Harned, *J. Am. Chem. Soc.*, **47**, 930 (1925); H. S. Harned and F. E. Swindells, *Ibid.*, **48**, 126 (1926); H. S. Harned and G. M. James, *J. Phys. Chem.*, **30**, 1060 (1926).

[6] H. S. Harned, *Trans. Faraday Soc.*, **23**, 462 (1927).

were employed in certain combinations for the determination of the ionization constant itself, as well as $m_H m_{OH}$ and $\gamma_H \gamma_{OH}/a_{H_2O}$ in salt solutions.

The electromotive forces of these cells are all expressed by the equivalent relations

$$\mathbf{E} = \mathbf{E}^0 - \frac{RT}{\mathbf{F}} \ln a_H a_X \tag{15-1-3}$$

and

$$\mathbf{E} = \mathbf{E}^0 - \frac{RT}{\mathbf{F}} \ln \gamma_H \gamma_X m_H m_X \tag{15-1-4}$$

where the subscript X refers to chloride, bromide, or iodide. The meaning to be attached to the quantities, γ_H, γ_X, m_H, and m_X, is largely derived from extra-thermodynamical considerations. Consider cell I containing only the halide acid. All of the evidence discussed in chapter (11) indicates that the halide acids are very strong electrolytes. We shall assume that they are completely ionized at all ionic strengths, and consequently that m_H is the sum of the (molal) concentrations of protons and solvated protons, and that m_X is the sum of the concentrations of the halide ion and solvated halide ion. Any deviations from this hypothesis will require corrections to the values we shall obtain for $m_H m_{OH}$ and $\gamma_H \gamma_{OH}/a_{H_2O}$ in salt solutions, but will not affect the determination of the ionization constant, K_w. Further, since m_H and m_X are actual stoichiometrical molalities, $\gamma_H \gamma_X$ is the activity coefficient product of a completely ionized electrolyte, obeying the limiting law of the interionic attraction theory.

These considerations are equally applicable to the cell

$$H_2 \mid MOH(m_1), MX(m_2) \mid AgX\text{-}Ag \qquad \text{II}$$

used to determine the ionization constant of water. It is assumed that the strong base, MOH (usually an alkali hydroxide), and MX are completely ionized, so that m_{OH} is the sum of the molalities of the hydroxyl ions and hydrated hydroxyl ions. The electromotive force of this cell is given by equation (15-1-4). In this case, the hydrogen ion concentration is determined by the equation for ionization of water,

$$K_w = \frac{\gamma_H \gamma_{OH}}{a_{H_2O}^x} m_H m_{OH} \tag{15-1-5}$$

and is now expressed in terms of the independent variable, m_{OH}. Since the subscripts, H and OH, include the hydrated ions, the exponent x is unity, or greater, depending upon the extent of hydration. There is evidence that the hydration of the proton is virtually complete in aqueous solutions, but in the absence of exact information regarding the hydration of ions, we shall adopt the convention of writing $x = 1$. This convention will introduce no error in subsequent thermodynamic computations, but should not be overlooked in interpreting the mechanism of the ionization. Thus, if x is made unity, the elimination of m_H between equations (15-1-4) and (15-1-5), results in the expression

$$\frac{(E_{II} - E^0)F}{2.303RT} + \log \frac{m_X}{m_{OH}} = \log \frac{\gamma_{OH}}{\gamma_X a_{H_2O}} - \log K_w \qquad (15\text{-}1\text{-}6)$$

Since the term, $\log \gamma_{OH}/\gamma_X a_{H_2O}$, is proportional to the ionic strength in dilute solutions, a plot of the left-hand member against μ should yield $(-\log K_w)$ by linear extrapolation to infinite dilution. In Figure (15-1-1) six independent extrapolations of this type are shown. If the experiment is limited to the evaluation of K_w only, it may be convenient to keep m_X/m_{OH} constant[7] throughout a series of dilutions. In the measurements represented in the figure,[8–13] however, m_X was varied, while m_{OH} was kept

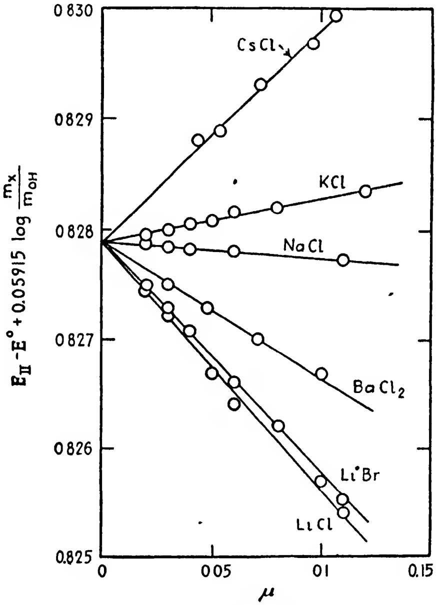

Fig. (15-1-1). Evaluation of $(-0.05915 \log K_w)$ by measurements in various salt solutions at 25°.

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[7] E. J. Roberts, *J. Am. Chem. Soc.*, **52**, 3877 (1930).

[8] H. S. Harned and O. E. Schupp Jr., *J. Am. Chem. Soc.*, **52**, 3892 (1930): CsOH-CsCl.

[9] H. S. Harned and W. J. Hamer, *Ibid.*, **55**, 2194 (1933): KOH-KCl.

[10] H. S. Harned and H. R. Copson, *Ibid.*, **55**, 2206 (1933): LiOH-LiCl.

[11] H. S. Harned and G. E. Mannweiler, *Ibid.*, **57**, 1873 (1935): NaOH-NaCl.

[12] H. S. Harned and J. G. Donelson, *Ibid.*, **59**, 1280 (1937): LiOH-LiBr.

[13] H. S. Harned and C. G. Geary, *Ibid.*, **59**, 2032 (1937): $Ba(OH)_2$-$BaCl_2$.

constant and equal to 0.01, so that the data could also be used in subsequent calculations of other quantities. The plots are all linear within the range shown, and their intercepts have been made identical without injustice to the data. The reproducibility of the electromotive forces is about 0.05 mv., and it is probable that the extrapolated value of K_w is accurate to 0.2% at 25°.

There is another combination of cells which yields the ionization constant of water without recourse to the standard potential, $\mathbf{E}^0$. By combining cells of types II and III,

$$\mathrm{H_2} \mid \mathrm{HX}(m_1),\ \mathrm{MX}(m_2) \mid \mathrm{AgX\text{-}Ag} \qquad \mathrm{III}$$

we obtain the expression

$$\frac{(\mathbf{E}_{\mathrm{II}} - \mathbf{E}_{\mathrm{III}})\mathbf{F}}{2.303RT} = \log \frac{(\gamma_{\mathrm{H}}\gamma_{\mathrm{X}}m_{\mathrm{H}}m_{\mathrm{X}})_{\mathrm{III}}}{(\gamma_{\mathrm{H}}\gamma_{\mathrm{X}}m_{\mathrm{H}}m_{\mathrm{X}})_{\mathrm{II}}} = \log \frac{(m_{\mathrm{H}}m_{\mathrm{X}})_{\mathrm{III}}}{(m_{\mathrm{H}}m_{\mathrm{X}})_{\mathrm{II}}} \qquad (15\text{-}1\text{-}7)$$

The second equality involves the premise that the activity coefficient of the acid is the same in the acid-salt solution as in the hydroxide-salt solution. This assumption is closely approximated under the experimental conditions, since both the acid and hydroxide concentrations are only $0.01M$. In the next section, a method is presented by which these concentrations may be made zero by a series of extrapolations at constant ionic strengths, but the correction is usually less than 0.03 mv. when $m_1 = 0.01$, and may be safely neglected. Accordingly the value of the function, $\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}/a_{\mathrm{H_2O}}$, in either of the cells II or III may be identified with its value in a pure solution of the salt, MX, at an ionic strength corresponding to $m_1 + m_2$. With this in mind, the elimination of $(m_{\mathrm{H}})_{\mathrm{II}}$ between equations (15-1-7) and (15-1-5) leads to the expression

$$\frac{(\mathbf{E}_{\mathrm{II}} - \mathbf{E}_{\mathrm{III}})\mathbf{F}}{2.303RT} - \log \frac{(m_{\mathrm{H}}m_{\mathrm{X}})_{\mathrm{III}}}{(m_{\mathrm{X}}/m_{\mathrm{OH}})_{\mathrm{II}}} = \log \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}{a_{\mathrm{H_2O}}} - \log K_w \qquad (15\text{-}1\text{-}8)$$

in which $\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}/a_{\mathrm{H_2O}}$ appears without the designation II. According to the Debye-Hückel theory, this quantity can be represented by

$$\log \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}{a_{\mathrm{H_2O}}} = -\frac{3.629 \times 10^6}{(DT)^{3/2}}\sqrt{\mu} + f(\mu) \qquad (15\text{-}1\text{-}9)$$

hich, upon combination with (15-1-8), yields

$$-\log K'_w \equiv \frac{(\mathbf{E}_{\mathrm{II}} - \mathbf{E}_{\mathrm{III}})\mathbf{F}}{2.303RT} - \log \frac{(m_{\mathrm{H}}m_{\mathrm{X}})_{\mathrm{III}}}{(m_{\mathrm{X}}/m_{\mathrm{OH}})_{\mathrm{II}}} + \frac{3.629 \times 10^6}{(DT)^{3/2}}\sqrt{\mu} = -\log K_w + f(\mu) \qquad (15\text{-}1\text{-}10)$$

Since all of the terms making up the left side of this equation are known experimentally, a plot of this member against μ leads to $(-\log K_w)$ by extrapolation to infinite dilution. Several plots of this nature are shown in Figure (15-1-2), where it will be noticed that the slopes differ from those of the corresponding curves in Figure (15-1-1). This difference is a decided advantage in determining the intercept.[14] The most important property of the extrapolation represented by Figure (15-1-2) is its independence of standard electrode potentials. It will be seen that the value of K_w is the same as that obtained from Figure (15-1-1).

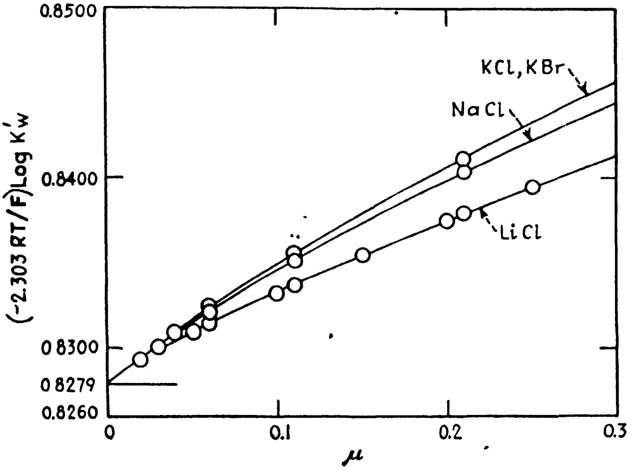

Fig. (15-1-2). Evaluation of K_w at 25° according to equation (15-1-10).

TABLE (15-1-1). THE IONIZATION CONSTANT OF WATER (p = 1 atm.)
$K_w \times 10^{14}$

t	KCl[1]	NaCl[2]	BaCl$_2$[3]	LiBr[4]	Weighted Mean
0	0.1142[a]	0.1134	(0.1125)	(0.1132)	0.1139
5	(.1860)	.1850	(1834)	.1842	.1846
10	(293)	.2919	(2890)	2921	.2920
15	(.452)	.4505	.4506	.4504	.4505
20	.681	6806	.6815	.6806	.6809
25	1.008	1 007	1.009	1 007	1.008
30	1.471	1 470	1 466	1 467	1.469
35	2 088	2 091	2 090	(2.068)	2.089
40	2.916	2.914	2 920	....	2.919
45	4.016	4.017	4 023	....	4.018
50	5.476	5.482	5.465	....	5.474
55	7.297	......	....	....	7.297
60	9.614	......	....	....	9.614

[1] H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).
[2] H. S. Harned and G. E. Mannweiler, *Ibid* , **57**, 1875 (1935).
[3] H. S. Harned and C. G. Geary, *Ibid.*, **59**, 2032 (1937).
[4] H. S. Harned and J. G. Donelson, *Ibid.*, **59**, 1280 (1937).
[a] Recalculated.

A comparison of the values of K_w, obtained independently in several of the investigations quoted above, is given in Table (15-1-1). Those re-

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[14] H. S. Harned and H. R. Copson, *J. Am. Chem. Soc.*, **55**, 2206 (1933).

sults which we believe to be of most doubtful accuracy are enclosed by parentheses, and are not included in estimating the mean value given in the last column.

(2) THE ACTIVITY COEFFICIENT FUNCTION, $\gamma_H\gamma_{OH}/a_{H_2O}$, AND THE IONIZATION PRODUCT, m_Hm_{OH}, IN AQUEOUS SALT SOLUTIONS

The first determinations[15–18] of the quantity, $\gamma_H\gamma_{OH}/a_{H_2O}$, required measurements on cells of the types

$$H_2 \mid MOH(m_1), MX(m_2) \mid M_xHg \mid MOH(m_3) \mid H_2 \qquad \text{IV}$$

and

$$Ag\text{-}AgX \mid MX(m_2) \mid M_xHg \mid MX(m_1) \mid AgX\text{-}Ag \qquad \text{V}$$

in addition to those discussed in the preceding section. The method depends upon the evaluation of the three quantities, $\gamma_H\gamma_X$, $\gamma_M\gamma_{OH}/a_{H_2O}$, and $\gamma_M\gamma_X$, in solutions of the pure salt, MX, at the same concentration. The combination of these quantities yields $\gamma_H\gamma_{OH}/a_{H_2O}$ in the salt solution at this particular concentration. Thus

$$(\gamma_H\gamma_X)(\gamma_M\gamma_{OH}/a_{H_2O})/(\gamma_M\gamma_X) = \gamma_H\gamma_{OH}/a_{H_2O} \qquad (15\text{-}2\text{-}1)$$

The evaluation of $\gamma_M\gamma_X$ is carried out with the aid of Cell V by methods outlined in Chapter (10), section (4). Cells I and III, or Cell III, and the value of E^0 derived from Cell I, can be used to determine $\gamma_H\gamma_X$ in the mixture, HX-MX, in various proportions at a given constant total molality. Then, by making use of the linear variation of log $\gamma_H\gamma_X$ with m_{HX}, discussed in Chapter (14), Section (4), it is a simple matter to obtain $\gamma_H\gamma_X$ in the pure salt solution by extrapolation to zero concentration of acid. The application of the same procedure to the results derivable from Cell IV yields values of $\gamma_M\gamma_{OH}/a_{H_2O}$ in salt solutions at zero concentration of hydroxide.

The method just described is accurate and thermodynamically sound, but it is laborious since it requires the use of the inconvenient flowing amalgam electrode. This inconvenience is now avoided by the use of cells of types II and III. Since K_w is known, equation (15-1-8) may be rewritten

$$\frac{(E_{II} - E_{III})F}{2.303RT} - \log\frac{(m_H\,m_X)_{III}}{(m_X/m_{OH})_{II}} + \log K_w = \log\frac{\gamma_H\,\gamma_{OH}}{a_{H_2O}} \qquad (15\text{-}2\text{-}2)$$

to give $\gamma_H\gamma_{OH}/a_{H_2O}$ directly. The ionization product, m_Hm_{OH}, is obtained by dividing this quantity into K_w, in accordance with equation (15-1-5). This method has been used to determine the ionization of water in aqueous

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[15] H. S. Harned, *J. Am. Chem. Soc.*, **47**, 930 (1925).

[16] H. S. Harned and F. E. Swindells, *Ibid.*, **48**, 126 (1926).

[17] H. S. Harned and G. M. James, *J. Phys. Chem.*, **30**, 1060 (1926).

[18] H. S. Harned and O. E. Schupp Jr., *J. Am. Chem. Soc.*, **52**, 3892 (1930).

solutions of the chlorides and bromides of sodium, potassium and lithium, and the chlorides of cesium, strontium and barium, over the concentration range 0 to 3*M*, and at temperatures ranging from 0 to 50, or 60°.

It is very important to recall that in these calculations, we have assumed that all the strong electrolytes in the cells (HX, MOH and MX) are completely ionized at all concentrations. If this assumption is not true, then the values of $m_H m_{OH}$ are not strictly the product of the actual molalities of these ions in the salt solutions. The present results, however, may be corrected in the future for any deviations found from the assumption of complete ionization. However, the value of $m_H m_{OH}$ when the salt concentration is zero, or K_w, will not be altered because these deviations vanish on extrapolation.

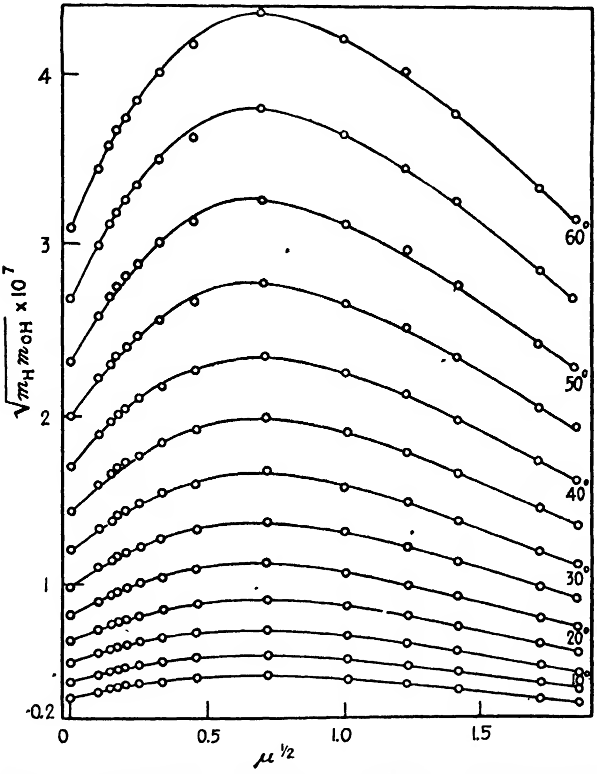

Fig. (15-2-1). The dissociation of water in potassium chloride solutions at 5° intervals.

The effect of temperature and concentration upon $m_H (= \sqrt{m_H m_{OH}})$ in potassium chloride solutions[19] is illustrated in Figure (15-2-1). It is seen

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[19] H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).

that the ionization attains a maximum at about 0.7*M*, and this maximum becomes increasingly pronounced at higher temperatures.

Values of both $\gamma_H\gamma_{OH}/a_{H_2O}$ and m_Hm_{OH} in a series of salt solutions at 25° are plotted against $\sqrt{\mu}$ in Figure (15-2-2). The complete results at various temperatures are compiled in Table (15-2-1A). They have been partially summarized by Harned and Cook[20] in terms of the Debye-Hückel equation,

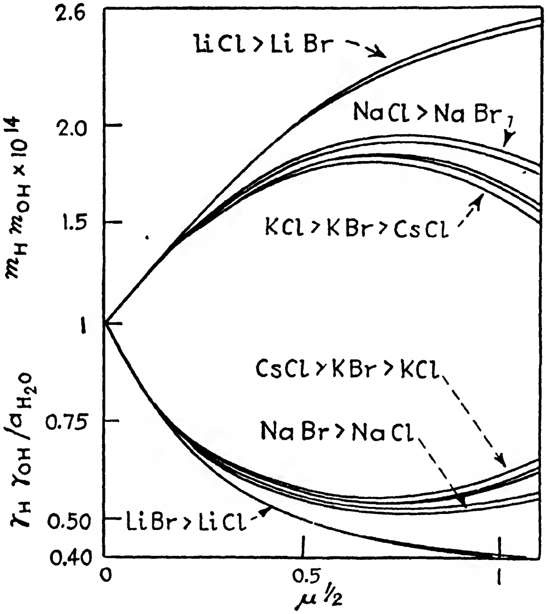

Fig. (15-2-2). The ionic activity coefficient product and ionization of water in some halide solutions at 25°.

TABLE (15-2-1). CONSTANTS FOR EQUATIONS (15-2-5) TO (15-2-7)

Salt	d	b_0	$b_1 \times 10^4$	c_0	$c_1 \times 10^4$	$\Delta_{ave.}$
KCl..............	3.6	0.266	5.20	−0.0350	−4.88	0.0027
NaCl.............	3.6	.198	2.00	− .0085	−2.0	.0032
LiCl	3.6	.039	2.00	+ .0325	−4.0	.0025
KBr..............	4.2	.205	12.75	− .016	−9.0	.0022
NaBr	4.2	.157	6.75	+ .010	−6.57	.0035
LiBr.	4.2	.000	0.000	+ .0475	−2.20	.0041

$$\log \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} = \frac{-2\mathcal{S}_{(f)}\sqrt{\mu}}{1 + A'\sqrt{\mu}} + B\mu + C\mu^{3/2} \qquad (15\text{-}2\text{-}3)$$

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[20] H. S. Harned and M. A. Cook, *J. Am. Chem. Soc.*, **59**, 2304 (1937).

in which

$$\mathcal{S}_{(f)} = 1.814 \times 10^6/(DT)^{3/2} \qquad (15\text{-}2\text{-}4)$$

and

$$A' = \mathring{a}50.30/(DT)^{1/2} \qquad (15\text{-}2\text{-}5)$$

Values of D are given in Table (5-1-3). For convenience in calculation and tabulation, it was assumed that the empirical parameters, B and C, vary linearly with temperature

$$B = b_0 + b_1 t \qquad (15\text{-}2\text{-}6)$$

$$C = c_0 + c_1 t \qquad (15\text{-}2\text{-}7)$$

and that $\mathring{a}$ is independent of temperature. The constants are recorded in Table (15-2-1). In spite of the arbitrary selection of common $\mathring{a}$-values for the chlorides and bromides, respectively, and a simple temperature dependence for the parameters, the constants given in Table (15-2-1) will reproduce the experimental results within ½ to 1 percent at all concentrations up to $3M$, and at any temperature between 0 and 40°, except in lithium chloride solutions where the errors exceed 1% below 10°. In sodium and potassium chloride solutions, the representation may be satisfactorily extended to 50°. The average deviations, Δ_{ave}, between the observed values of log $\gamma_H\gamma_{OH}/a_{H_2O}$ and those calculated by equation (15-2-3) are recorded in the last column of Table (15-2-1). If we had allowed all of the parameters to be unrestricted, these deviations would not have exceeded the experimental errors.

The order in which the curves in Figure (15-2-2) arrange themselves deserves some comment. At a given concentration, the ionization of water is greater in solutions containing ions of smaller radii in the crystalline state. This effect could be predicted, qualitatively at least, from the greater polarization of the water molecules under the immediate influence of the high charge density of the smaller ions. The data are not sufficiently consistent to allow a determination of the exact functional dependence of solvent dissociation upon ionic radii, but the regular and inverse nature of this dependence can be seen in Figure (15-2-3). This effect has already been illustrated by Harned and Mannweiler[21] who arbitrarily used $\Sigma 1/a_i (\equiv 1/a_+ + 1/a_-)$ as the abscissa. We have used $\Sigma 1/a_i^2$ as a variable because the average charge density on the ions is proportional to this quantity. The ionic radii were taken from Table (5-1-6).

Although it would be unwise to draw any quantitative conclusions from Figure (15-2-3), the equation,

$$\log \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} = \log \frac{K_w}{m_H m_{OH}} = A - B\Sigma \frac{1}{a_i^2} \qquad (15\text{-}2\text{-}8)$$

[21] H. S. Harned and G. E. Mannweiler, *J. Am. Chem. Soc.*, **57**, 1873 (1935).

representing the straight lines through the points, suggests that results of this kind may eventually be used to separate the effect of the salt into two distinct parts. The effect of interionic forces may be associated with the term A, while the effect of polarization of the solvent molecules may appear only in the term, $B\Sigma 1/a_i^2$, which is proportional to the mean charge densities. The plausibility of such a separation is increased by the fact that the parameter B increases steadily with concentration, while A first decreases with concentration, passes through a minimum at about 0.4M, and thereafter increases with concentration according to the familiar behavior of the activity coefficient of a strong 1-1 electrolyte.

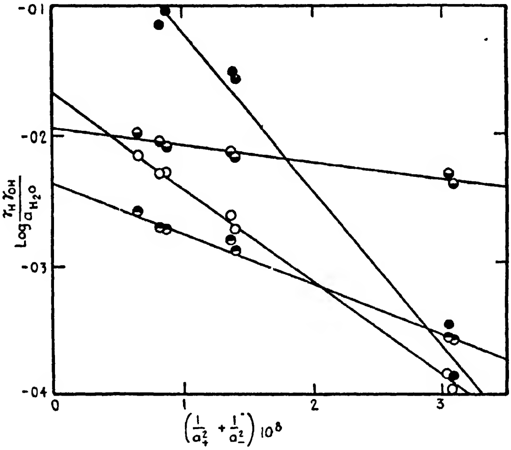

Fig. (15-2-3). Dependence of $\gamma_H\gamma_{OH}/a_{H_2O}$ in salt solutions upon ionic radii of the salts. ●, 2.01 M; ○, 1M; ◒, 0.5 M; ◓, 0.11 M (t = 25°).

(3) THE EFFECT OF TEMPERATURE AND PRESSURE ON THE IONIZATION OF WATER. THERMOCHEMICAL QUANTITIES*

In view of the lack of an exact theoretical equation for expressing the ionization constant as a function of the temperature, and of the fact that ionization constants are known accurately only over comparatively short temperature ranges (0 to 60° at most), it is difficult to know which of the possible empirical equations to use. The usual method has been to assume that ΔH_i^0 can be expressed as a power series in T,

$$\Delta H_i^0 = A - BT - CT^2 + \cdots \tag{15-3-1}$$

$$\Delta C_{p_i}^0 = -B - 2CT + \cdots \tag{15-3-2}$$

whence

$$\ln K_w = -\frac{A}{RT} - \frac{B}{R}\ln T - \frac{C}{R}T + D + \cdots \tag{15-3-3}$$

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* H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

by substitution in equation (1-10-12), and subsequent integration. The signs of the terms are chosen so that the constants obtained from the experimental values are positive. For a series of results over a limited temperature range, it is never necessary to use terms beyond T^2 in the first of these equations. The evaluation of the constants of equation (15-3-3) from the experimental results by least squares is laborious, and therefore simpler expressions are desirable. One satisfactory simplification is to assume that $\Delta C^0_{p_i}$ is independent of T, or that ΔH^0_i varies linearly with T. Thus,

$$\Delta H^0_i = A - BT \tag{15-3-4}$$

$$\Delta C^0_{p_i} = -B \tag{15-3-5}$$

$$\ln K_w = -\frac{A}{RT} - \frac{B}{R}\ln T + D \tag{15-3-6}$$

Another equation for ln K, which follows immediately from the nature of the original electromotive forces, deserves consideration. We have found that over the temperature range in question, the observed electromotive forces obey a quadratic equation in t within the error of experiment (±0.05 mv.). Inspection of equation (15-1-6) shows immediately that if both $\mathbf{E}_{\text{II}}$ and $\mathbf{E}^0$ are quadratic in T, $\ln K_w$ may be expressed by

$$\ln K_w = -\frac{A}{RT} - CT + D \tag{15-3-7}$$

and, consequently,

$$\Delta H^0_i = A - CT^2 \tag{15-3-8}$$

$$\Delta C^0_{p_i} = -2CT \tag{15-3-9}$$

It is certainly not likely that $\Delta C^0_{p_i}$ is absolutely independent of T, nor that it varies linearly with T, as expressed by equations (15-3-5) and (15-3-9), respectively. We shall show, however, that both equations (15-3-6) and (15-3-7) may be used with equal accuracy for the computation of K_w from 0 to 60°. This will demonstrate that these calculations can not be used to prove or disprove how $\Delta C^0_{p_i}$ varies with T.

The constants in equations (15-3-3), (15-3-6) and (15-3-7) were evaluated by the method of least squares from the values of K_w in Table (15-1-1). The resulting numerical equations and those derived from equation (15-3-3) for computing ΔF^0_i, ΔH^0_i, $\Delta C^0_{p_i}$ and ΔS^0_i are given in the Table (15-3-1). A striking agreement is found with all three equations. Thus the mean deviations are only 0.00045, 0.0005, and 0.0005 in ($-\log K_w$) for the three equations, respectively, and the maximum deviations are 0.0014. The mean deviation corresponds to an error of 0.03 mv. and the maximum deviation to an error of 0.08 mv. which are no greater than the reproducibility of the original electromotive forces. This proves that these results cannot be used to decide whether $\Delta C_{p_i}^0$ is constant, or how this quantity varies with temperature.

The maximum variation in ΔH_i^0 computed by the three equations is 40 cal. at 0°. At 25°, the values of $\Delta C_{p_i}^0$ obtained from equations (15-3-2), (15-3-5) and (15-3-9) are -46.7, -47.0, and -46.5, respectively. However, at higher or lower temperatures, the differences are considerable. Thus at 0° the three equations yield -44.8, -47.0, and -42.6. Since all the equations fit the experiments equally well, it is impossible to say which one of these results is nearest the true value.

In Fig. (15-3-1), values of $(-\log K_w)$, calculated by equations (15-3-3a), (15-3-6a), and (15-3-7a), have been plotted against T. Each of these plots has a maximum in the neighborhood of 550°. The only determinations of K_w at such high temperatures were obtained by Noyes and Kato[22] and Sosman[23] from investigations of the hydrolysis of ammonium acetate. These are represented by the circles in the figure, and indicate definitely that a maximum occurs in K_w at the temperature predicted by these equations.

TABLE (15-3-1). NUMERICAL VALUES FOR THE COMPUTATION OF $(-\log K_w)$ BY EQUATIONS (15-3-3), (15-3-6) AND (15-3-7), AND OF ΔF_i^0, ΔH_i^0, $\Delta C_{p_i}^0$ AND ΔS_i^0 BY THE EQUATIONS RELATED TO (15-3-3)

(1) Equation (15-3-3) etc.

$$\log K_w = -\frac{5242.39}{T} + 35.3944 - 0.008530T - 11.8261 \log T \qquad (15\text{-}3\text{-}3a)$$

(Average deviation of observed from calculated results is 0.00045 in log K. Maximum deviation 0.0014).

$$\Delta F_i^0 = 23984.15 + 54.1047T \log T - 161.9308T + 0.039025T^2$$

$$\Delta H_i^0 = 23984.15 - 23.497T - 0.039025T^2 \qquad (15\text{-}3\text{-}1a)$$

$$\Delta C_{p_i}^0 = -23.497 - 0.07805T \qquad (15\text{-}3\text{-}2a)$$

$$\Delta S_i^0 = -54.1047 \log T - 0.07805T + 138.4338$$

(2) Equation (15-3-6)

$$\log K_w = -\frac{6013.79}{T} - 23.6521 \log T + 64.7013 \qquad (15\text{-}3\text{-}6a)$$

(Average deviation is 0.0005; maximum deviation 0.0014).

(3) Equation (15-3-7)

$$\log K_w = -\frac{4470.99}{T} + 6.0875 - 0.017060T \qquad (15\text{-}3\text{-}7a)$$

(Average deviation is 0.0005; maximum deviation 0.0014).

Another unique application of these results is the calculation of ΔH_i, the heat of ionization of water in salt solutions. In a solution of concentration m, the heat of ionization of water is

$$\Delta H_i = \bar{H}_{\mathrm{H}^+} + \bar{H}_{\mathrm{OH}^-} - \bar{H}_{\mathrm{H_2O}} \qquad (15\text{-}3\text{-}10)$$

or, in terms of the corresponding relative quantities

$$\Delta H_i = \Delta H_i^0 + \bar{L}_{\mathrm{H}^+} + \bar{L}_{\mathrm{OH}^-} - \bar{L}_{\mathrm{H_2O}} \qquad (15\text{-}3\text{-}11)$$

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[22] A. A. Noyes and Y. Kato, *Publications Carnegie Institution*, **63**, 153 (1907).

[23] R. B. Sosman, *Publications Carnegie Institution*, **63**, 193 (1907).

Thus, ΔH_i may be divided into two parts. The first part, ΔH_i^0, is independent of the salt concentration, and is related to the temperature coefficient of ln K by equation (1-10-12). The second part ($\bar{L}_{H^+} + \bar{L}_{OH^-} - \bar{L}_{H_2O}$) varies with the concentration, and is calculable by equation (1-7-5) from the temperature coefficient of the function, ln $(\gamma_H \gamma_{OH}/a_{H_2O})$. Accordingly,

$$\Delta H_i = RT^2 \frac{\partial \ln K_w}{\partial T} - RT^2 \frac{\partial \ln (\gamma_H \gamma_{OH}/a_{H_2O})}{\partial T} \qquad (15\text{-}3\text{-}12)$$

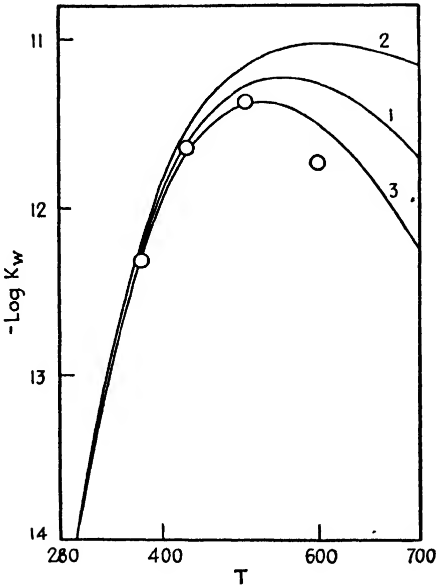

Fig. (15-3-1).
Ionization constant of water as a function of temperature. ○, Experimental; 1, Equation (15-3-3a); 2, Equation (15-3-6a); 3, Equation (15-3-7a).

Comparison of this equation with (15-1-8) shows that ΔH_i can be obtained directly from the electromotive force data by the relation

$$\Delta H_i = \mathbf{F}T^2 \frac{[\partial(\mathrm{E_{II}} - \mathrm{E_{III}})/T]}{\partial T} \qquad (15\text{-}3\text{-}13)$$

Similarly, the other quantities are given by

$$\Delta S_i = \mathbf{F} \frac{\partial(\mathrm{E_{II}} - \mathrm{E_{III}})}{\partial T} \qquad (15\text{-}3\text{-}14)$$

and

$$\Delta C_{p_i} = \mathbf{F}T \frac{\partial^2(\mathrm{E_{II}} - \mathrm{E_{III}})}{\partial T^2} \qquad (15\text{-}3\text{-}15)$$

The heats of ionization of water in various salt solutions have been calculated,[24-26] and found to vary linearly with $\mu^{1/2}$ at all concentrations within the experimental uncertainty of 30 to 80 calories. Such a relationship is predicted theoretically for $\bar{L}_{H^+} + \bar{L}_{OH^-} - \bar{L}_{H_2O}$ at high dilutions. Its unexpected validity at higher concentrations permits the determination of ΔH_i^0 by extrapolation of ΔH_i to infinite dilution. Figure (15-3-2) illustrates the behavior of ΔH_i in five different salt solutions at 20°. When the data in the individual salt solutions are extrapolated independently, the intercepts all occur within about ±30 calories of the value of ΔH_i^0 equal to 13,710, and the agreement is of the same order at other temperatures. To avoid confusion in the figure the data are omitted, and the results are represented by straight lines with the experimentally observed slopes. The theoretical limiting slope is indicated by the broken line.

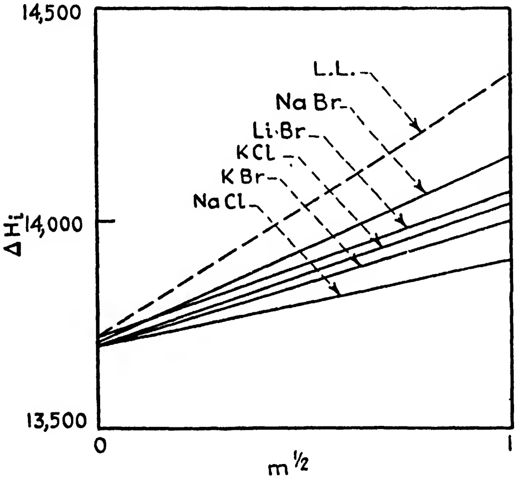

Fig. (15-3-2)
Total heat of ionization of water in some halide solutions at 20°.

In comparing Figure (15-3-2) with the corresponding calorimetric determination illustrated in Figure (8-3-1), it will be noted that the intercepts, ΔH_i^0, obtained by the two independent methods, differ by 40 calories, which appears within the combined uncertainties of the two determinations. The discussion in Chapter (8), Section (3) showed that $(-\Delta H_i)$ in a salt solution can not be identified with ΔH_n, a directly measured heat of neutralization, because of the dilution of the salt ions accompanying neutralization. Furthermore, although ΔH_n^* is ostensibly the heat of neutralization, corrected for the heat of dilution of the salt, it is not the

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[24] H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **55**, 4496 (1933).

[25] H. S. Harned and G. E. Mannweiler, *Ibid.*, **57**, 1873 (1935).

[26] H. S. Harned, *J. Franklin Inst.*, **225**, 623 (1938).

same as $(-\Delta H_i)$ unless the individual ionic heat contents are additive at all concentrations. Therefore, we have refrained from attempting to compare $(-\Delta H_i)$ with ΔH_n^* at any point other than their common limiting value at infinite dilution.[27]

According to equation (1-10-11), the effect of pressure upon the ionization of water is given by

$$\left(\frac{\partial \log K_w}{\partial P}\right)_T = \frac{-\Delta V_i^0}{2.3RT} \tag{15-3-16}$$

where

$$\Delta V_i^0 = \bar{V}^0_{\mathrm{H}^+} + \bar{V}^0_{\mathrm{OH}^-} - \bar{V}^0_{\mathrm{H_2O}} \tag{15-3-17}$$

The quantity, $\bar{V}^0_{\mathrm{H_2O}}$, is equal to the molal volume of pure water, or 18.07 cc. at 25° and one atmosphere. The partial molal volume of ionized water may be calculated by linear combination of values of $\bar{V}_2^0$ for strong acids, bases, and salts, since ionic volumes are additive at infinite dilution. For example, we may write

$$\bar{V}^0_{\mathrm{H}^+} + \bar{V}^0_{\mathrm{OH}^-} = \bar{V}^0_{2(\mathrm{HCl})} + \bar{V}^0_{2(\mathrm{KOH})} - \bar{V}^0_{2(\mathrm{KCl})}$$

In the same way, $\bar{K}^0_{\mathrm{H}^+} + \bar{K}^0_{\mathrm{OH}^-}$ can be obtained by combination of values of $\bar{K}_2^0$ for strong acids, bases and salts, and $\bar{K}^0_{\mathrm{H_2O}}$ is equal to $18.02\,\beta_0/d_0$. If $\bar{K}_2^0$ be considered independent of P, then

$$\bar{V}_{2(P)} = \bar{V}_2^0 - \bar{K}_2^0(P-1) \tag{15-3-18}$$

by equation (8-7-2). Here $\bar{V}^0_{2(P)}$ represents a partial molal volume at any pressure, P, and $\bar{V}_2^0$ and $\bar{K}_2^0$ refer to values at $P = 1$. Combination of the preceding three equations leads to the approximate relation

$$\log \frac{K_w}{K_{w(P-1)}} = -\frac{\Delta V_i^0(P-1)}{2.3RT} + \frac{\Delta K_i^0(P-1)^2}{4.6RT} \tag{15-3-19}$$

valid for low pressures.

Fortunately, it is not necessary to neglect the variation of ΔK_i^0 with pressure, for it has been shown[28] that, so long as $\bar{K}_2^0$ is large compared to the molal compression of the pure solute, the limiting partial molal volume of a solute at any pressure is given by

$$\bar{V}^0_{2(P)} = \bar{V}_2^0 - \bar{K}_2^0\left(\frac{B+1}{B+P}\right)(P-1) \tag{15-3-20}$$

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[27] Comparison of $(-\Delta H_i)$ and ΔH_n^*, however, shows a close correspondence. H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **55**, 4496 (1933); H. S. Harned and G. E. Mannweiler, *Ibid.*, **57**, 1873 (1935); H. S. Harned, *J. Franklin Inst.*, **225**, 623 (1938).

[28] B. B. Owen and S. R. Brinkley Jr., *Chem. Rev.*, **29**, 461 (1941).

The factor, $(B + 1)/(B + P)$, which distinguishes this equation from (15-3-18), accounts for the pressure dependence of $\bar{K}_2^0$ over a considerable range. Combination of this equation with (15-3-16) and (15-3-17) yields the expression

$$\log\left(\frac{K_w}{K_{w(P-1)}}\right) = -\frac{\Delta \bar{V}_i^0(P-1)}{2.3RT} + \frac{\Delta \bar{K}_i^0(B+1)}{2.3RT}\left\{(P-1) - (B+1)\ln\left(\frac{B+P}{B+1}\right)\right\} \tag{15-3-21}$$

which may be used over a pressure range of several thousand atmospheres.

Table (15-3-2) contains average values of $\Delta \bar{V}_i^0$ and $\Delta \bar{K}_i^0$, and shows the results obtained by substituting these values into equation (15-3-21).

TABLE (15-3-2).[a] THE EFFECT OF PRESSURE UPON THE IONIZATION OF PURE WATER

P(bars)[c]	$K_w/K_{w(P-1)}$						
	5°	15°	25°	35°	45°	$\Delta \bar{H}_i^0$(25°)	$\Delta \bar{S}_i^0$(25°)
1	1	1	1	1	1	13,500	−18 7
200	1.246	1.225	1 202	1.180	1 163	13,200	−19 4
400	1.543	1.490	1.435	1 384	1 345	12,900	−20 1
600	1.896	1.800	1.703	1 612	1.545	12,600	−20 8
800	2.317	2 163	2.009	1.868	1 766	12,200	−21.8
1000	2 816	2.585	2 358	2.154	2.009	11,800	−22.8
$\Delta \bar{V}_i^0$	−26.1	−24.9	−23 4	−21.8	−20.6	.....	...
$\Delta \bar{K}_i^0$	......	.....	−0.00522[b]	......	.....	....	......

[a] B. B. Owen and S. R. Brinkley Jr., *Chem. Rev.*, **29**, 461 (1941).

[b] The value of $\Delta \bar{K}_i^0$ at 25° was used at all temperatures.

[c] One bar = 0.9869 normal atms.

The ionization constant increases with pressure, and the relative increase is the greater the lower the temperature. At zero degrees, K_w undergoes a threefold increase between 1 and 1000 bars. The positive temperature coefficient of $\Delta \bar{V}_i^0$ (and $\Delta \bar{V}^0$ for some other ionization reactions) indicates that, at sufficiently high temperatures, $\Delta \bar{V}_i^0$ may become positive and cause a decrease in K_w with pressure. The effect of pressure upon ΔH_i^0 and ΔS_i^0 at 25° is shown in the last two columns of Table (15-3-2). These thermochemical quantities, as well as $\Delta C_{p_i}^0$, become more negative with increasing pressure.

Unfortunately, the data at hand are not sufficiently accurate to give us unambiguous information about the effect of pressure upon the temperature of the maximum value of K_w, or K_i for weak electrolytes in general. A brief discussion of this matter, and the effect of pressure upon ionization reactions in salt solutions, is given by Owen and Brinkley.[28]

(4) DETERMINATION OF THE IONIZATION CONSTANTS OF WEAK ACIDS AND BASES

Ionization constants of weak acids can be derived from measurements of cells without liquid junction containing either an unbuffered solution, or a buffered solution. The unbuffered cell,

$$H_2 \mid HR(m_1),\ MX(m_2) \mid AgX\text{-}Ag \qquad \text{VI}$$

was first used to determine the ionization function, $m_H^2/(m_1 - m_H)$, and the activity coefficient function, $\gamma_H \gamma_{Ac}/\gamma_{HAc}$, in salt solutions,[29] and later for the determination of the ionization constant, K_A.[30] These results yielded a value of 1.75×10^{-5} for K_A for acetic acid at 25°, and further determinations[31] showed that this quantity varied little if at all between 20 and 30°. These values are consistent with recent ones of greater accuracy determined by means of cells containing buffered solutions. A comprehensive analysis of the unbuffered cell will be given in Section (7). It will be shown that activity coefficient, and ionization functions of weak acids in salt solutions as well as ionization constants may be determined by this cell. Further, the medium effects on the properties of the substances in the cells will be thoroughly investigated.

The most direct electrometric determination of the ionization constant of a weak acid makes use of cells of the type[32]

$$H_2 \mid HR(m_1),\ MR(m_2),\ MCl(m_3) \mid AgCl\text{-}Ag \qquad \text{VII}$$

Although such cells are limited to the determination of ionization constants only, they are peculiarly well adapted to this purpose. Buffer action permits accurate and easy measurements of small hydrogen ion concentrations at relatively low ionic strengths. The necessary extrapolation is short and practically linear. The concentrations of the weak acid, HR, and of the two salts, MR and MCl, are made approximately equal, and the cation, M, is usually sodium or potassium. The use of the silver-silver chloride electrode has many practical advantages, but other combinations can be used when this electrode is unsuitable.

The electromotive force of this cell is given by equation (15-1-4), in which $\gamma_H m_H$ may be eliminated by combination with the expression,

$$K_A = \frac{\gamma_H \gamma_R}{\gamma_{HR}} \frac{m_H m_R}{m_{HR}} \qquad (15\text{-}4\text{-}1)$$

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[29] H. S. Harned and R. A. Robinson, *J. Am. Chem. Soc.*, **50**, 3157 (1928).

[30] H. S. Harned and B. B. Owen, *J. Am. Chem. Soc.*, **52**, 5079 (1930).

[31] H. S. Harned and G. M. Murphy *J. Am. Chem. Soc.*, **53**, 8 (1931).

[32] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **54**, 1350 (1932).

for the ionization of the weak acid. The resulting equation is

$$\frac{(\mathrm{E_{VII}} - \mathrm{E}^0)\mathrm{F}}{2.303RT} + \log \frac{m_{\mathrm{Cl}} m_{\mathrm{HR}}}{m_{\mathrm{R}}} = -\log K_{\mathrm{A}} - \log \frac{\gamma_{\mathrm{Cl}}\gamma_{\mathrm{HR}}}{\gamma_{\mathrm{R}}} \qquad (15\text{-}4\text{-}2)$$

Since $m_{\mathrm{Cl}} = m_3$, $m_{\mathrm{HR}} = m_1 - m_{\mathrm{H}}$, and $m_{\mathrm{R}} = m_2 + m_{\mathrm{H}}$, the left-hand member of this equation is known if m_{H} is negligible compared to m_1 and m_2. If m_{H} is too large to be neglected, it may be estimated as follows.[33-35] A preliminary value of K_{A} is obtained from equation (15-4-2) by using the limiting law for activity coefficients, and writing $m_{\mathrm{HR}}/m_{\mathrm{R}} = m_1/m_2$. If this value is less than 10^{-4}, m_{H} is given with sufficient accuracy by $m_{\mathrm{H}} \simeq K_{\mathrm{A}} m_1/m_2$. If necessary, more accurate values of m_{H} can be derived from a more exact value of K_{A}, obtained by extrapolation as described below. The number of such successive approximations required increases with the magnitude of K_{A}. Ionization constants of the order of 10^{-4}, or greater, can also be determined by this method, but the relatively large values of m_{H} encountered make it necessary either to employ a very long series of approximations,[36] or to avoid the use of equation (15-4-2) altogether. In the latter case, the procedure is based upon the calculation of "apparent" hydrogen ion concentrations[37] directly from the electromotive forces [Section (7)] and equation (15-1-4). Thus, if we rearrange this equation and express the activity coefficients by the limiting law, we obtain

$$-\log m'_{\mathrm{H}} = \frac{(\mathrm{E_{VII}} - \mathrm{E}^0)\mathrm{F}}{2.303\,RT} + \log m_{\mathrm{Cl}} - 2\mathcal{S}_{(f)}\sqrt{\mu d_0} \qquad (15\text{-}4\text{-}3)$$

The ionic strength is approximately

$$\mu \simeq m_2 + m_3 + m'_{\mathrm{H}} \qquad (15\text{-}4\text{-}3)$$

The approximation introduced by the use of the limiting law, which neglects the medium effect of the unionized weak electrolyte, prevents the determination of the true m_{H} by this method, but the difference between m_{H} and m'_{H} decreases rapidly with dilution, and vanishes in the limit. Accordingly, we may calculate an apparent ionization constant, k'_{A}, corresponding to m'_{H}, from equation (15-4-1) and the limiting law. Thus,

$$\log k'_{\mathrm{A}} = -2\mathcal{S}_{(f)}\sqrt{\mu d_0} + \log \frac{m'_{\mathrm{H}}(m_2 + m'_{\mathrm{H}})}{(m_1 - m'_{\mathrm{H}})} \qquad (15\text{-}4\text{-}5)$$

Log K_{A} may be obtained by extrapolation[38] of values of log k'_{A}.

[33] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **54**, 1350 (1932).

[34] L. F. Nims, *Ibid.*, **55**, 1946 (1933).

[35] B. B. Owen, *Ibid.*, **56**, 1695 (1934).

[36] W. J. Hamer, *J. Am. Chem. Soc.*, **56**, 860 (1934); See Chapter (13), Section (8).

[37] H. S. Harned and B. B. Owen, *J. Am. Chem. Soc.*, **52**, 5079 (1930).

[38] L. F. Nims, *J. Am. Chem. Soc.*, **56**, 1110 (1934).

If, as in the case of boric acid, $K_A < 10^{-9}$, the hydrolysis of the acid anion, R, must be considered at high dilutions. Since m_H is quite negligible in solutions of such weak acids, we may write, $m_{HR} = m_1 + m_{OH}$, and, $m_R = m_2 - m_{OH}$, and estimate m_{OH} from the hydrolysis constant,

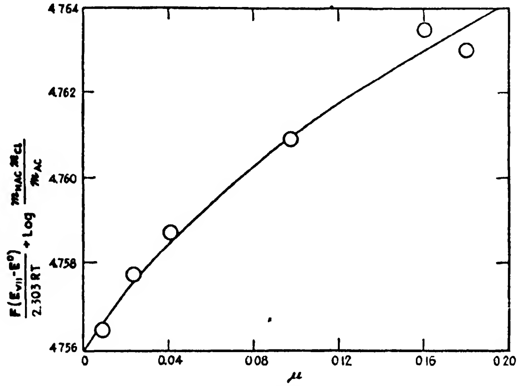

Fig. (15-4-1). Evaluation of ionization constant of acetic acid at 25° according to equation (15-4-2). Diameters of circles equal 0.02 mv.

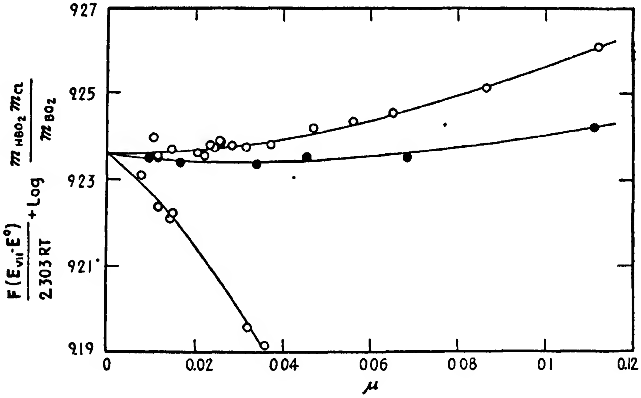

Fig. (15-4-2). Evaluation of the ionization constant of boric acid at 25° according to equation (15-4-2). The ratio, m_{HBO_2}/m_{BO_2}, is 1 in the upper curve, 1.18 in the center curve, and 2.69 in the lower curve.

K_h, of the acid anion. A sufficiently accurate value of m_{OH} is given by $m_{OH} \simeq K_h m_2/m_1$, and a suitable value of K_h is obtained from the ratio of K_w, and a rough estimate of K_A.

Returning to equation (15-4-2), it will be seen that the last term on the right contains the logarithm of the ratio of two activity coefficients of the same valence type, and the logarithm of the activity coefficient of a neutral molecule. Since both of these quantities vary little with the ionic strength at high dilution, a plot of the left hand member of equation (15-4-2) against μ permits the determination of $(-\log K_A)$. Figure (15-4-1) illustrates the extrapolation by which the ionization constant of acetic acid[40] is evaluated at 25°.

The tendency of boron to form complex polybasic ions, even in relatively dilute solutions, results in a peculiar plot for the extrapolation function for boric acid. The determination of the first ionization constant of boric acid (H_3BO_3) at 25° is illustrated in Figure (15-4-2). Variation in the ratio, m_1/m_2, has a much more pronounced effect upon the position and shape of the curves than would be observed for acetic acid. The upper curves in Figure (15-4-2) become horizontal at $\mu \simeq 0.01$. This makes extrapolation unnecessary below that concentration. Furthermore, equation (15-4-2) may be rearranged so that E^0 may be determined if K_A is known. The combination of these circumstances, and the stability of iodides in alkaline solutions, has made it possible to determine the standard potential of the silver-silver iodide electrode[41] with much greater ease in borax buffers than by cells containing dilute hydriodic acid solutions. The use of buffer solutions has been found advantageous in determining other standard potentials[42,43] [See Chapter (12), Section (2)].

For polybasic acids, the extrapolation function is complicated by stepwise dissociation, and the presence of polyvalent ions, but this is of little practical importance if the ratios of the constants of the several dissociation processes are greater than 10^3 or 10^4. The second ionization constant of phosphoric acid will be used to illustrate the calculations.[44] The cell used is

$$H_2 \mid MH_2PO_4(m_1),\ M_2HPO_4(m_2),\ MCl(m_3) \mid AgCl\text{-}Ag \qquad \text{VIII}$$

and its electromotive force is represented by equation (15-1-4). The second ionization constant of phosphoric acid is given by

$$K_{2A} = \frac{\gamma_H \gamma_{HPO_4}}{\gamma_{H_2PO_4}} \frac{m_H m_{HPO_4}}{m_{H_2PO_4}} \qquad (15\text{-}4\text{-}6)$$

The elimination of $\gamma_H m_H$ between these two expressions leads to

$$\frac{(E_{VIII} - E^0)F}{2.303\,RT} + \log \frac{m_{Cl} m_{H_2PO_4}}{m_{HPO_4}} = -\log K_{2A} - \log \frac{\gamma_{Cl} \gamma_{H_2PO_4}}{\gamma_{HPO_4}} \qquad (15\text{-}4\text{-}7)$$

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[40] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **54**, 1350 (1932). *Ibid.*, **55**, 652 (1933).

[41] B. B. Owen, *J. Am. Chem. Soc.*, **57**, 1526 (1935); R. K. Gould and W. C. Vosburgh, *Ibid.*, **62**, 1817 (1940).

[42] B. B. Owen and L. Foering, *J. Am. Chem. Soc.*, **58**, 1575 (1936).

[43] R. G. Bates and W. C. Vosburgh, *Ibid.*, **59**, 1188 (1937).

[44] L. F. Nims, *J. Am. Chem. Soc.*, **55**, 1946 (1933).

The last term on the right contains the activity coefficients of two univalent ions in the numerator, and of a bivalent ion in the denominator. Application of the Debye-Hückel equation to this term allows its replacement by $-\ 2\mathcal{S}_{(f)}\sqrt{\mu d_0} \pm \beta\mu$ at high dilution, so that equation (15-4-7) may be written

$$\frac{(\mathrm{E_{VIII}} - \mathrm{E^0})\mathrm{F}}{2.303RT} + \log\frac{m_{\mathrm{Cl}}m_{\mathrm{H_2PO_4}}}{m_{\mathrm{HPO_4}}} + 2\mathcal{S}_{(f)}\sqrt{\mu d_0} = -\log K_{2\mathrm{A}} \pm \beta\mu \quad (15\text{-}4\text{-}8)$$

The determination of $(-\log K_{2\mathrm{A}})$ by equation (15-4-8) is illustrated in Figure (15-4-3).[44] In the phosphate buffer solutions, the value of m_{H} is of the order 10^{-7}, which is so small relative to m_1 and m_2 that it was disregarded in computing $m_{\mathrm{H_2PO_4}}$ and $m_{\mathrm{HPO_4}}$. In general, it will be found that both m_{H} and m_{OH} may be neglected if $m_1/m_2 \simeq 1$, and K is between 10^{-5} and 10^{-9}.

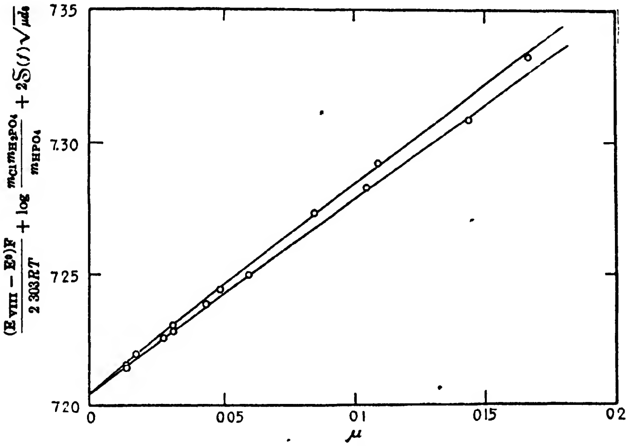

Fig. (15-4-3). Evaluation of the second ionization constant of phosphoric acid at 25° according to equation (15-4-8). Lower curve, sodium salts, $m_1 = m_2$. Upper curve, monosodium phosphate and dipotassium phosphate, $4\ m_1 = 3m_2$.

The electrometric determination of the ionization constants of weak bases is analogous in principle to those just described, but some substitute for the silver-silver chloride electrode must be used in ammoniacal and other basic solutions in which silver chloride is quite soluble. The sodium amalgam electrode is known[45] to give results comparable with those of the silver-silver chloride electrode in a system where both can be used. The use of thallium amalgam has been suggested.[46] The silver-silver

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[45] H. S. Harned and B. B. Owen, *J. Am. Chem. Soc.*, **52**, 5091 (1930).

[46] E. J. Roberts, *J. Am. Chem. Soc.*, **56**, 878 (1934).

iodide electrode is a convenient one for this purpose, and will be used to illustrate the method. The electromotive force of the cell,

$$H_2 \mid BOH(m_1),\ BI(m_2) \mid AgI\text{-}Ag \qquad \text{IX}$$

can be expressed by equation (15-1-4), if the substitution of I for Cl is taken into account. The product, $\gamma_H m_H$, can be eliminated by combination with the expressions

$$K_w = \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} m_H m_{OH} \qquad (15\text{-}4\text{-}9)$$

and

$$K_B = \frac{\gamma_B \gamma_{OH}}{\gamma_{BOH}} \frac{m_B m_{OH}}{m_{BOH}} \qquad (15\text{-}4\text{-}10)$$

The resulting extrapolation function becomes

$$\frac{(E_{IX} - E^0)F}{2.303\,RT} + \log K_w + \log \frac{m_B m_I}{m_{BOH}} - \mathfrak{S}_{(f)}\sqrt{\mu d_0} = \log K_B \pm \beta\mu \qquad (15\text{-}4\text{-}11)$$

upon substitution of $-\mathfrak{S}_{(f)}\sqrt{\mu d_0} \pm \beta\mu$ for $\log \gamma_B\gamma_I/\gamma_{BOH}$. Making use of some preliminary measurements[47] on ammonia-ammonium iodide solutions at 25°, it was found that a plot of the left hand member of equation (15-4-11) against μ was linear up to $\mu \simeq 0.1$. The value of K_B obtained by extrapolation, 1.75×10^{-5}, is of the expected order of magnitude. More reliable values of K_B have been derived for the basic ionization of amino-acids, and will be discussed in the next section.

The familiar methods of determining ionization constants by visual colorimetry, either directly, when the weak electrolyte or its ion is colored, or indirectly, by the use of colored indicators and standard buffer solutions, are quite inferior in accuracy to the modern conductometric and electrometric methods. If, however, the subjective visual matching of light intensities is replaced by the completely objective photoelectric technique[48] now available, the most important source of error is eliminated. The resulting "photoelectric colorimetry" is capable of very high accuracy indeed. The first application of the photoelectric method to the precise determination of an ionization constant is the investigation of picric acid by von Halban and Ebert.[49] The apparatus and experimental technique are described by von Halban and Siedentopf.[50] The method is very

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[47] B. B. Owen, *J. Am. Chem. Soc.*, **56**, 2785 (1934).

[48] E. Meyer and H. Rosenberg, *Vierteljahres schr. Astron. Ges.*, **48**, 3 (1913).

[49] H. v. Halban and L. Ebert, *Z. physik.,Chem.*, **112**, 359 (1924).

[50] H. v. Halban and K. Siedentopf, *Z. physik. Chem.*, **100**, 208 (1922); *Ibid.*, **103**, 71 (1922).

simple in principle, and makes use of the laws of Lambert and Beers in the integrated form,

$$\log \frac{I_0}{I} = \mathfrak{E}cx \tag{15-4-11a}$$

Here, I_0 and I represent the intensity of the light before and after traversing x centimeters of the solution, and $\mathfrak{E}$ is a constant characteristic of the solution, the temperature, and the wave length of the light. We will conform to the usage of von Halban, and refer to $\mathfrak{E}$ as the extinction coefficient. The quantity, $\mathfrak{E}c = (1/x) \log (I_0/I)$, will be designated the extinction.

The conditions underlying equation (15-4-11a) have been examined by von Halban,[51] and found to be fulfilled in his experiments. It is assumed that the absorption of light by the acid anion is independent of the nature of the cations present. This introduces an element of uncertainty, but the effect of varying the nature of added neutral salts is very small in dilute solutions, and the hydrogen ion concentrations involved are so small that the specific effects of this ion are presumably negligible.

Von Halban and Kortüm[52] determined the degree of ionization of α-dinitrophenol (1, 2, 4) by comparing the extinctions of solutions of this acid with those of its alkali salts at the same ionic strength. Since the extinction is $\mathfrak{E}c\alpha$ in the acid solution and $\mathfrak{E}c$ in the salt solution at a given stoichiometric concentration c, the degree of ionization, α, is the ratio of these quantities. In an unbuffered acid solution, the expression for the ionization of a weak acid, HR, is

$$K_{\mathrm{A}} = \frac{y_{\mathrm{H}}y_{\mathrm{R}}}{y_{\mathrm{HR}}}\frac{c_{\mathrm{H}}c_{\mathrm{R}}}{c_{\mathrm{HR}}} = \frac{y_{\mathrm{H}}y_{\mathrm{R}}}{y_{\mathrm{HR}}}\frac{c\alpha^2}{1-\alpha} \tag{15-4-12}$$

If we write $k_{\mathrm{A}} \equiv c\alpha^2/(1 - \alpha)$, and represent the activity coefficients by the limiting law, this equation becomes

$$\log K_{\mathrm{A}} = -2\mathfrak{S}_{(f)}\sqrt{\mu d_0} + \log k_{\mathrm{A}} \tag{15-4-13}$$

The experimental values of $\log k_{\mathrm{A}}$ in solutions of α-dinitrophenol, in pure water, and in various salt solutions[53,54] are plotted against $\sqrt{\mu d_0}$ in the upper portion of Figure (15-4-4), and the straight line is drawn with the theoretical slope 1.013. In the lower part of Fig. (15-4-4), values of log

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[51] H. v. Halban and L. Ebert, *Z. physik. Chem.*, **112**, 321 (1924); H. v. Halban and J. Eisenbrand, *Ibid.*, **122**, 337 (1926); **146**, 294 (1930); H. v. Halban and G. Kortüm, *Ibid.*, **A170**, 212, 351 (1934); H. v. Halban and M. Seiler, *Ibid.*, **A181**, 70 (1937); G. Kortüm, *Ibid.*, **B33**, 243 (1936).

[52] H. v. Halban and G. Kortüm, *Z. physik. Chem.*, **A170**, 351 (1934).

[53] H. v. Halban and G. Kortüm, *Z. physik. Chem.*, **A170**, 351 (1934).

[54] H. v. Halban, G. Kortüm and M. Seiler, *Ibid.*, **A173**, 449 (1935).

$k_A - 1.013\sqrt{\mu d_0}$ are plotted against the concentration of undissociated acid, c_u, and the nearly horizontal straight line through these points is drawn to correspond to $\log K_A = \bar{5}.9103$. Although the data for the weak acid alone (upper curve) could be more closely represented by a slope some 20% higher than the theoretical, the results in salt solutions seem satisfactorily expressed by the theoretical value up to $\mu = 0.0004$, or higher. In view of the discussion concerning Figs. (7-6-1) and (7-6-2), we might expect some evidence of a discontinuity at $\mu \simeq 0.0002$, where the data for the pure acid meet the data for the acid in salt solutions, because the concentration of the undissociated molecules varies continuously below

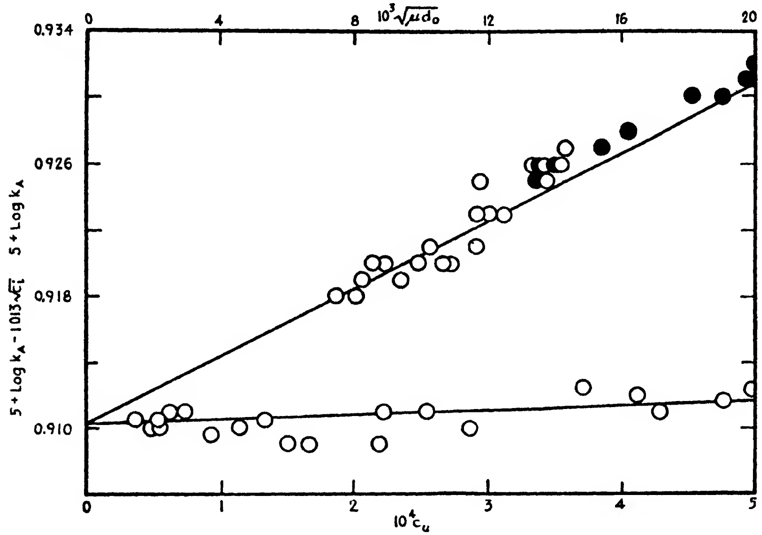

Fig. (15-4-4). Evaluation of the ionization constant of α-dinitrophenol in water at 25°. ○, Weak acid alone; ●, Neutral salts present.

this point, but is practically constant above it. In Fig. (7-6-1), the medium effect of the neutral molecules is already appreciable at $\mu \simeq 0.0002$, and increases so rapidly that the data at higher concentrations cannot be used for extrapolation unless this effect is formally provided for, as in Figure (7-6-2). In Figure (15-4-4), however, the conditions are quite different. The medium effect is practically constant from $\mu = 0.0002$ upwards, so the results in the more concentrated range of the plot may furnish a more reliable test of the limiting law than those in the more dilute range. Therefore, it seems justifiable to employ data up to $\mu = 0.0004$ in determining the limiting slope, and to consider the data satisfactorily represented by the theoretical slope within the experimental uncertainty.

The average deviation of the points from the curves is about 1/4 per cent, and only five or six points deviate as much as 1/2 per cent. These deviations are of the same order as those encountered in electrometric determinations of ionization constants from cells without liquid junctions (0.05 mv. average, with 0.1 mv. maximum).[55] It should be remarked, however, that the colorimetric method is often applicable at concentrations outside the range which can be investigated by the use of cells.

(5) DETERMINATION OF THE IONIZATION CONSTANTS OF AMPHOLYTES

The determination of the ionization of the most important ampholyte, water, by cells without liquid junctions, has been discussed in Section (1). The other ampholytes which have been investigated by this method have all been aliphatic amino acids. The electrically neutral molecules of these compounds in solution have been shown[56–59] to be mainly zwitterions (amphions), bearing a positive and negative charge. Indicating such molecules by $Z^{\pm}$, the acidic and basic dissociation of a simple amino-acid may be represented by,

$$ZH^+ \rightleftharpoons Z^{\pm} + H^+ \tag{15-5-1}$$

and

$$ZOH^- \rightleftharpoons Z^{\pm} + OH^- \tag{15-5-2}$$

and the corresponding ionization constants by [60,61]

$$K_A = \frac{\gamma_Z \gamma_H}{\gamma_{ZH}} \frac{m_Z m_H}{m_{ZH}} \tag{15-5-3}$$

and

$$K_B = \frac{\gamma_Z \gamma_{OH}}{\gamma_{ZOH}} \frac{m_Z m_{OH}}{m_{ZOH}} \tag{15-5-4}$$

The most convenient determination of acidic ionization is performed with cells containing approximately equal concentrations of amino-acid and its hydrochloride. The electromotive force of the cell,

$$H_2 \mid Z^{\pm}(m_1),\ HZCl(m_2) \mid AgCl\text{-}Ag \qquad \text{X}$$

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[55] In comparing the two methods, H. v. Halban and G. Kortüm [*Z. physik. Chem*, **A170**, 351 (1934)] unintentionally include the effects of impurities in sample, and neglect the medium effect in their estimate of the accuracy of the electrometric method, but omit these factors in estimating the accuracy of their photoelectric determination.

[56] E. Q. Adams, *J. Am. Chem. Soc.*, **38**, 1503 (1916).

[57] N. Bjerrum, *Z. physik. Chem.*, **104**, 147 (1923).

[58] J. T. Edsall and M. H. Blanchard, *J. Am. Chem. Soc.*, **55**, 2337 (1933).

[59] J. Wyman Jr. and T. L. McMeekin, *Ibid.*, **55**, 908, 915 (1933).

[60] N. Bjerrum, *Z. physik. Chem.*, **104**, 147 (1923).

[61] H. S. Harned and B. B. Owen, *J. Am. Chem. Soc.*, **52**, 5091 (1930).

is given by equation (15-1-4), and elimination of $\gamma_{H}m_{H}$ by (15-5-3) leads to

$$\frac{(E_{x} - E^{0})F}{2.3\,RT} + \log\frac{m_{Cl}\,m_{ZH}}{m_{Z}} + \log\frac{\gamma_{Cl}\gamma_{ZH}}{\gamma_{Z}} = -\log K_{A} \qquad (15\text{-}5\text{-}5)$$

The last term of the left side may be replaced by $-2\mathcal{S}_{(f)}\sqrt{\mu d_0} \pm \beta\mu$, and the unknown linear term transposed to give an extrapolation function,

$$\frac{(E_{x} - E^{0})F}{2.3\,RT} + \log\frac{m_{Cl}m_{ZH}}{m_{Z}} - 2\mathcal{S}_{(f)}\sqrt{\mu d_0} = -\log K_{A} \pm \beta\mu \qquad (15\text{-}5\text{-}6)$$

very similar to that used for phosphoric acid. Since $m_{Cl} = m_2$, $m_{Z} = m_1 + m_{H}$, and $m_{ZH} = m_2 - m_{H}$, the concentration term may be evaluated by successive approximations from a preliminary value of K_A, obtained by neglecting m_H altogether. Convergence of successive approximations is rather slow for the amino acids investigated to date, because their values of K_A are of the order 10^{-3} to 10^{-2}. It is perhaps more satisfactory to rewrite equation (15-1-4) as

$$-\log m_{H} = \frac{(E_{x} - E^{0})F}{2.3\,RT} + \log m_{Cl} + \log \gamma_{H}\gamma_{Cl} \qquad (15\text{-}5\text{-}7)$$

and estimate m_H with the help of the approximation, $\log \gamma_{H}\gamma_{Cl} \simeq -2\mathcal{S}_{(f)}\sqrt{\mu d_0}$.

Figure (15-5-1) illustrates the use of equation (15-5-6) in evaluating K_A for dl-alanine.[62] At each temperature, the lower curve is the plot of the the left-hand member of (15-5-6) against μ. The upper, almost horizontal, curves represent an alternative function, obtained by replacing $-2\mathcal{S}_{(f)}\sqrt{\mu d_0}$ in equation (15-5-6) by known values of $\log \gamma_{H}\gamma_{Cl}$ in pure aqueous solutions at the ionic strength and temperatures in question. Since both extrapolation functions must give the same value of $(-\log K_A)$, their difference in slopes is of some practical advantage in accurately locating the common intercept.

The basic ionization constants of ampholytes can be determined by cells of the type,

$$H_2 \mid Z^{\pm}(m_1),\ MZOH(m_2),\ MCl(m_3) \mid AgCl\text{-}Ag \qquad XI$$

in which the concentrations of the constituents are usually made equal. MZOH represents a convenient alkali (Na, or K) salt of the ampholyte, and MCl the corresponding chloride. Strictly speaking, the symbol, MZOH, indicates a hydrated form of the salt. Hydration affects the interpretation of K_B, but not its numerical evaluation.

Eliminating $\gamma_{H}m_{H}$ and $\gamma_{OH}m_{OH}$ between equations (15-1-4), (15-5-4), and the expression for the ionization of water, we obtain

$$\frac{(E_{XI} - E^{0})F}{2.3\,RT} + \log\frac{m_{Cl}m_{Z}}{m_{ZOH}} + \log K_{w} = \log K_{B} - \log\frac{\gamma_{Cl}\,\gamma_{Z}\,a_{H_2O}}{\gamma_{ZOH}} \qquad (15\text{-}5\text{-}8)$$

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[62] L. F. Nims and P. K. Smith, *J. Biol. Chem.*, **101**, 401 (1933).

The last term on the right involves only neutral molecules and the ratio of two similar ionic activity coefficients. It is therefore linear in μ at high

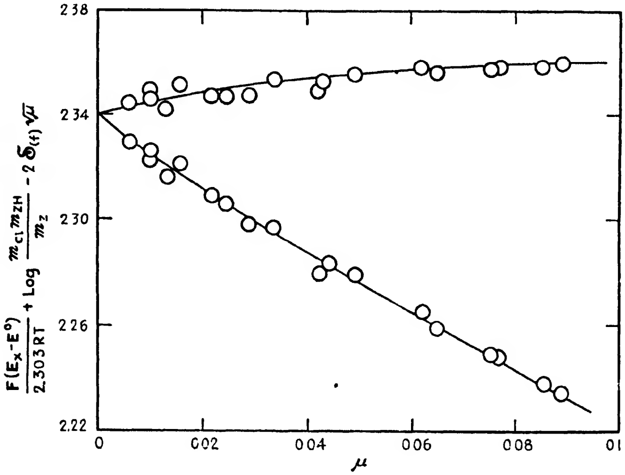

Fig. (15-5-1). Evaluation of the acidic ionization constant of dl-alanine at 25° according to equation (15-5-6) In the upper curve, $-2\mathfrak{S}_{(f)}\sqrt{\mu d_0}$ has been replaced by experimental values of log $\gamma_H\gamma_{Cl}$ in pure sodium chloride solutions [Table (14-2-1A)].

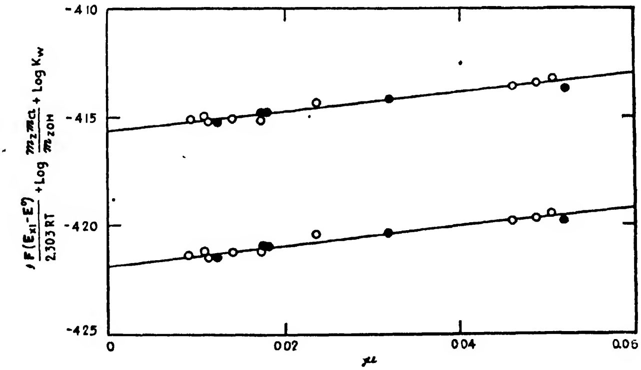

Fig. (15-5-2). Evaluation of the basic ionization constant of glycine at 25 and 35° (upper curve) according to equation (15-5-8).

dilution. Fig. (15-5-2) illustrates the use of this extrapolation function to evaluate the basic ionization constant of glycine.[68]

If log K_B has been evaluated, the quantity $\gamma_{Cl}\gamma_Z a_{H_2O}/\gamma_{ZOH}$ in a salt

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[68] B. B. Owen, *J. Am. Chem. Soc.*, **56**, 24 (1934).

solution may be evaluated by equation (15-5-8) since the left side may be computed from experimental data. Similarly, $\gamma_{\mathrm{Cl}}\gamma_{\mathrm{ZH}}/\gamma_{\mathrm{Z}}$ may be estimated in a salt solution by equation (15-5-5).

Cells of the type

$$\text{Ag-AgCl} \mid \text{KCl}(m_2) \mid \text{KCl}(m_2), \text{ glycine } (m_3) \mid \text{AgCl-Ag}$$

have been employed by Roberts and Kirkwood[64] to determine both the activity coefficients of potassium chloride $y_\pm$ and glycine y_3 in aqueous solutions containing both these substances at molal concentrations m_2 and m_3, respectively. From the cell measurements $y_\pm/y_\pm^0$ is determined where $y_\pm^0$ is the activity coefficient of potassium chloride in the absence of glycine. From the equation

$$2\left(\frac{\partial \ln y_\pm}{\partial m_3}\right)_{T,P,m_2} = \left(\frac{\partial \ln y_3}{\partial m_2}\right)_{T,P,m_3} \tag{15-5-9}$$

which follows from the conditions of integrability of equation (1-2-7), y_3 may be computed. The values of these quantitities at 25° as determined by Roberts and Kirkwood are given by the empirical equations

$$\log \frac{y_\pm}{y_\pm^0} = -0.08942m_3 + 0.1226m_2^{1/2}/m_3 + 0.01074m_3^2 - 0.0628m_2m_3 \tag{15-5-10}$$

and

$$\log y_3 = -0.1789m_2 - 0.06278m_2^2 + 0.1635m_2^{3/2} \tag{15-5-11}$$

(6) The Calculation of Ionization Constants and the Derived Thermodynamic Functions, ΔH_i^0, ΔS_i^0, and $\Delta C_{p_i}^0$

Ionization constants, obtained by the methods described in the preceding sections are compiled in Tables (15-6-1A), (15-6-2A) and (15-6-3A). Table (15-6-1A) contains the observed ionization constants in water at various temperatures. Table (15-6-2A) contains the ionization constants of water, formic, acetic, propionic acids and glycine in dioxane-water mixtures at 5° intervals from 0° to 50°. In Table (15-6-3A), values of the acid and base constants of some amino-acids in water from 1 to 50° are recorded. In all cases, the references to the original sources are to be found in these tables.

The change in ionization constant with dielectric constant is large. For aliphatic acids and water, it amounts to a decrease in K of five powers of ten for a change in D from 80 (pure water) to 10 (82% dioxane-water). Since determinations have been made in only five solvent mixtures in water and dioxane [Table (15-6-2A)], these results cannot be interpolated accurately from a single graph. Harned and Fallon[65] have suggested a method

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[64] R. M. Roberts and J. G. Kirkwood, *J. Am. Chem. Soc.*, **63**, 1373 (1941).

[65] H. S. Harned and L. D. Fallon, *J. Am. Chem. Soc.*, **61**, 2377 (1939).

of interpolation, based upon the fact that log K varies nearly linearly with the mol fraction of water, or dioxane. This is shown by Fig. (15-6-1) in which $\log K - \log K_{(N_2=0)}$ at 25° is plotted against the mol fraction of dioxane, N_2. The experimental values for water, acetic, and propionic acids indicate a maximum deviation from linearity of the order of 0.05 or

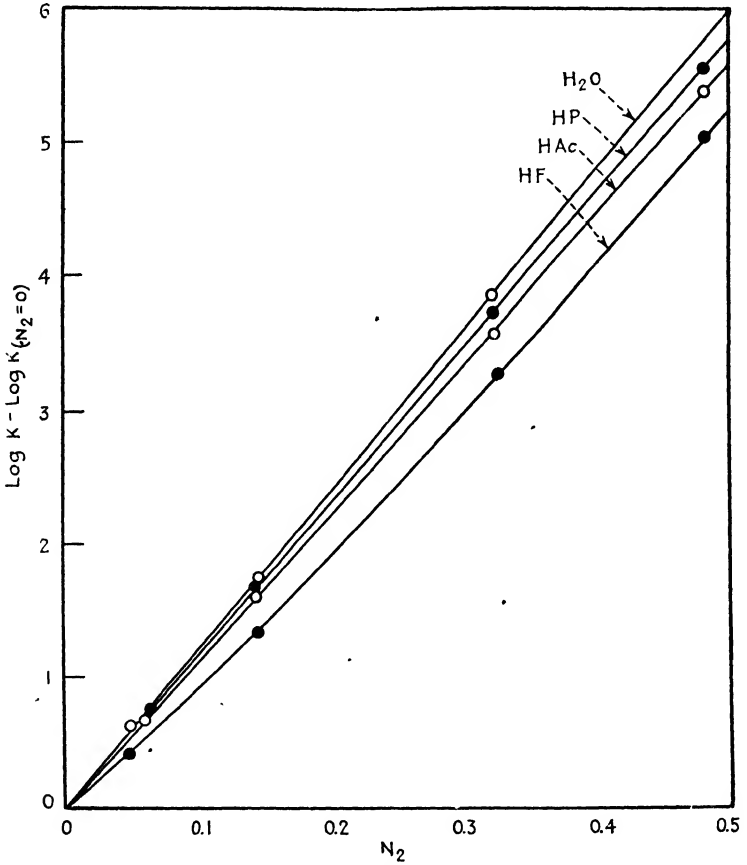

Fig. (15-6-1). Logarithm of ionization constants as a function of mol fraction of dioxane ($t = 25°$). HP, propionic; HAc, acetic; HF, formic acid.

about 1 per cent in log K. A plot of these deviations from the simple linear relationship may be employed for accurate interpolation. The graph for formic acid possesses the greater curvature.

As in the study of the ionization of water [Section (3)], many empirical equations have been employed for representing the ionization constants of weak electrolytes as a function of T, and for computing the thermochemical functions. The same difficulties in drawing conclusions from the observed results concerning the behavior of $\Delta C^0_{p_i}$ occur as those found with water. The data in Table (15-6-1) illustrate this point thoroughly. Here, observed values of ($-$ log K_A) for formic acid are given in the second column. The other columns contain the deviations of these values computed by the five equations given at the bottom of the table. The constants of these equations were obtained by the method of least squares. We note that the first three of these equations have the same form as equations (15-3-3), (15-3-6), and (15-3-7), used for the calculation of the ionization constant of water [Table (15-3-1)]. The calculated and observed values show mean deviations of only 0.0007 in log K, and are the same for all three equations. We arrive at the same conclusion found for the ionization of water, that from these results we cannot decide how $\Delta C^0_{p_i}$ varies with temperature. We have shown that existing evidence indicates that the ionization constant of water passes through a maximum in the neighborhood of 250°C, which is far from the region of temperature (0 to 60°) through which it is known accurately. The maxima for formic and other aliphatic acids occur at about room temperature. In the neighborhood of the maxima, it has been found that a quadratic equation in T is also satisfactory for the calculation of log K. This is illustrated by the values of the deviations in

TABLE (15-6-1). IONIZATION CONSTANT OF FORMIC ACID*

$\Delta = [-\log K_A]_{\text{calc}} - [-\log K_A]_{\text{obs}}$.

$\Delta \times 10^4$

t	$-\log K_A$	(1)	(2)	(3)	(4)	(5)
0	3.7857	−5	−5	−6	−22	−32
5	3.7719	+6	+5	+7	+6	−5
10	3.7625	+5	+4	+6	+14	+3
15	3.7572	−7	−8	−5	+6	−4
20	3.7533	−2	−3	−2	+6	+2
25	3.7515	+5	+6	+4	+11	+5
30	3.7525	+13	+15	+10	+11	−11
35	3.7577	0	+3	−3	−6	−4
40	3.7655	−15	−13	−18	−25	−18
45	3.7734	−11	−9	−13	−21	−8
50	3.7825	+3	+5	0	−5	+15
55	3 7940	+11	+11	+11	+13	+39
60	3.8094	−2	−6	+1	+12	+49
Δ (total)		85	83	86	158	195
Δ (mean)		6.5	6.4	6.6	12	15

$$(1)\ \log K_A = 30.9965 - \frac{2013.5}{T} - 0.0075841T - 10.4000 \log T \tag{15-6-1}$$

$$(2)\ \log K_A = 56.7186 - \frac{2684.1}{T} - 20.8000 \log T \tag{15-6-2}$$

$$(3)\ \log K_A = -\frac{1342.85}{T} + 5.2744 - 0.0151682T \tag{15-6-3}$$

$$(4)\ \log K_A = -8.0502 + 0\ 028803T - 4.826 \times 10^{-5}T^2 \tag{15-6-4}$$

$$(5)\ \log K_A = -8.1868 + 0.02978T - 5 \times 10^{-5}T^2 \tag{15-6-5}$$

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* H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

the last two columns of Table (15-6-1). The first of these calculations was made with equation (15-6-4) in which all three constants were obtained by least squares. The last column contains deviations of observed values from those calculated by equation (15-6-5) in which the coefficient of the term in T^2 was taken to be 5×10^{-5}, and the other constants determined by least squares. The agreement is not so exact as with the first three equations, since the mean deviations (0.0012 and 0.0015 in log K, respectively) are about twice as great. This indicates definitely that for the computation of the most accurate results, equations (15-6-1) to (15-6-3) are better than the quadratic equations.

The ionization constants of a number of weak electrolytes [Table (15-6-1A)] exhibit maxima between 0 and 60°. Harned and Embree[66] suggested that this is a property of all weak electrolytes. They also showed that as a first approximation the equation

$$\log K - \log K_\theta = -p(t - \theta)^2 \qquad (15\text{-}6\text{-}6)$$

represents the results closely (± 0.002 in log K) provided that it is applied in the neighborhood of the temperature, θ, at which the ionization constant is a maximum, or K_θ. Thus, the ionization constant is given in terms of two empirical constants, θ and K_θ, and a universal constant, p, which was found to be 5×10^{-5}. Expanded and rearranged, equation (15-6-6) becomes

$$\log K = [\log K_\theta - p\theta^2] + 2p\theta t - pt^2 \qquad (15\text{-}6\text{-}7)$$

This equation is the same as equation (15-6-5), and its applicability to formic acid has been illustrated in the last column of Table (15-6-1). Although this equation does not represent the best data as accurately as the other equations we have discussed, it yields a good approximation, and can be applied readily without resorting to least squares. Thus, upon rearranging,

$$\log K + pt^2 = [\log K_\theta - p\theta^2] + 2p\theta t \qquad (15\text{-}6\text{-}8)$$

is obtained. The left side of this equation is determined from the data, and then plotted against t. A straight line should be obtained with a slope, $2p\theta$, and an intercept at $t = 0$, $[\log K_\theta - p\theta^2]$. Since p is known both θ and K_θ may be evaluated. Such graphs are given in Fig. (15-6-2), in which pt^2 plus the mantissa of log K for formic, acetic, propionic, and chloroacetic acids are plotted against t. From 0 to 45° the points fall on straight lines within the estimated accuracy of the observed ionization constants. Deviations occur from 50 to 60°.[67]

All of these equations have been employed at various times. Recently, systematic computations of the thermodynamic quantities from the ioniza-

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[66] H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.*, **56**, 1050 (1934).

[67] J. L. Magee, T. Ri and H. Eyring, *J. Chem. Phys.*, **9**, 419 (1941).

tion constants in Tables (15-6-1A), (15-6-2A), and (15-6-3A) have been made by Harned and Owen[68] by means of equation (15-6-6), and by Everett and Wynne-Jones[69] who employed equation (15-3-6). The latter equation represents the experimental results more accurately than the quadratic form, and is therefore somewhat more reliable for the computation of the thermodynamic properties.

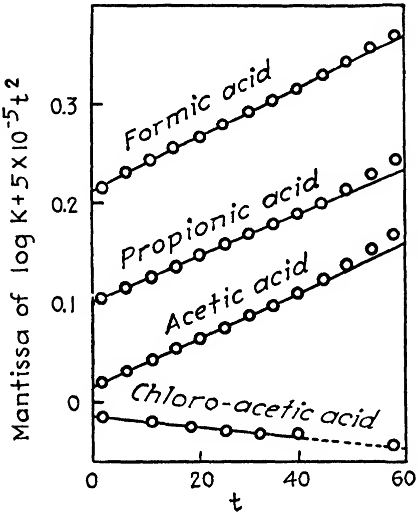

Fig. (15-6-2)
Graphs of the left side of equation (15-6-8) for acetic, propionic, formic, and chloro-acetic acids.

For this purpose, we have employed equation (15-3-7) in the form,[70]

$$\log K = -\frac{A^*}{T} - C^*T + D^* \tag{15-6-9}$$

Whence

$$\Delta F_i^0 = A' - D'T + C'T^2 \tag{15-6-10}$$

$$\Delta H_i^0 = A' - C'T^2 \tag{15-6-11}$$

$$\Delta C_{p_i}^0 = -2C'T \tag{15-6-12}$$

$$\Delta S_i^0 = D' - 2C'T \tag{15-6-13}$$

$$T_\theta = \sqrt{\frac{A^*}{C^*}} \tag{15-6-14}$$

$$\log K_\theta = D^* - 2\sqrt{C^*A^*} \tag{15-6-15}$$

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[68] H. S. Harned and B. B. Owen, *Chem. Rev.*, **25**, 31 (1939).

[69] D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939); **37**, 373 (1941); J. F. J. Dippy and H. O. Jenkins, *Ibid.*, **37**, 366 (1941).

[70] H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940). We are greatly indebted to Dr. Robert A. Robinson for most of the following calculations.

where A', C', and D' equal 2.3026 R times A^*, C^* and D^*, respectively. Our choice of this method of treatment depends on the fact that all the experimental electromotive forces can be expressed within the estimated accuracy over the temperature ranges involved by a quadratic equation in T. Possibly, when more accurate results are obtained, or temperature ranges greater than 60° are investigated, the quadratic equation for **E** may be proved to be inadequate, but so far no further extension has been found necessary. As typical of the equations used in determining K by extrapolation, we may select equation (15-4-2) which, at $\mu = 0$, becomes

$$\frac{(\mathbf{E}_{\text{VII}} - \mathbf{E}^0)\mathbf{F}}{2.303\,RT} + \log \frac{m_{\text{Cl}} m_{\text{HR}}}{m_{\text{R}}} = -\,[\log K_{\text{A}}]_{\mu=0} \qquad (15\text{-}6\text{-}16)$$

Since both $\mathbf{E}^0$ and $\mathbf{E}_{\text{VII}}$ are quadratic in T, and the term containing the molalities is independent of the temperature, equations (15-6-9) and (15-6-10) for log K and ΔF_i^0 result. Equations (15-6-11) to (15-6-15) for the other thermodynamic quantities immediately follow.

The constants, A^*, C^*, D^*, A', C' and D' of equations (15-6-9) to (15-6-13) are recorded in Table (15-6-4A). Values of the temperatures of the maxima, T_θ, and ($-$log K_θ) are also included. In Table (15-6-2), ΔF_i^0, ΔH_i^0, $\Delta C_{p_i}^0$, and ΔS_i^0 at 25°, calculated by equations (15-6-9) to (15-6-13), are compiled. These results agree well with those obtained by Everett and Wynne-Jones by use of equations (15-3-4), (15-3-5) and (15-3-6). The most notable exception is $\Delta C_{p_i}^0$ for water for which Everett and Wynne-Jones obtained -51 cal. compared with -46.5.

The most accurate results have been obtained with the aliphatic acids and water in aqueous solution, and in water-dioxane mixtures of higher dielectric constant ($D > 30$). In mixtures of high dioxane content, the greatest uncertainty resides in the determination of $\mathbf{E}^0$ [Chapter (11), Section (3)], and the error in the ionization constant increases progressively as the dielectric constant decreases. In 70 percent dioxane, the result is fairly reliable, but in the 82% mixtures, the values are approximate.

There is a discrepancy of 1 or 2 percent between the independently determined constants of dl-alanine that appear in Table (15-6-1A) and those in Table (15-6-3A). Whenever the absolute magnitude of K_{A} or K_{B} is required, the data in Table (15-6-1A) are preferable, because the results in Table (15-6-3A) were obtained with very limited amounts of material, and without the complete exclusion of air from the cell. On the other hand, the thermochemical quantities derived from the data in Table (15-6-3A) may be the more accurate because of the longer temperature range.

The determinations of ionization constants by cells with liquid junctions, or from electrometric titration curves, are very numerous.[71] Table

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[71] *The International Critical Tables*, Vol. VI, pp. 259–304, McGraw-Hill Book Co., New York (1929).

TABLE (15-6-2). ΔF_i^0, ΔH_i^0, $\Delta C_{p_i}^0$, AND ΔS_i^0 AT 25° IN CALORIES

	ΔF_i^0	ΔH_i^0	$\Delta C_{p_i}^0$	ΔS_i^0
Acids				
Water	19089	13519	−46.5	−18.7
Formic	5117	−23	−41.7	−17.6
Acetic	6486	−92	−36.5	−22.1
Propionic	6647	−163	−38.3	−22.8
Butyric	6574	−693	−36.4	−24.4
Chloroacetic	3901	−1158	−40.0	−17.0
Lactic	5267	−99	−40.7	−18.0
Glycolic	5225	175	−38.8	−16.9
Sulphuric (2)	2721	−5200	−50.0	−26.5
Oxalic (2)	5846	−1577	−57.8	−24.9
Malonic (2)	7767	−1157	−60.0	−29.9
Phosphoric (1)	2896	−1773	−50.7	−15.7
(2)	9829	822	−45.1	−30.2
Boric	12596	3328	−45.0	−31.1
Amino-Acids				
Glycine A	3205	1156	−32.2	−6.9
B	5753	2713	−21.9	−10.2
dl-Alanine A	3191	714	−34.2	−8.3
	3203	773	−37.3	−8.2
B	5627	2787	−44.8	−9.5
	5631	2539	−29.9	−10.4
dl-α-Amino-*n*-Butyric A	3123	298	−34.1	−9.5
B	5681	2824	−29.9	−9.6
dl-α-Amino-*n*-Valeric A	3161	487	−34.2	−9.0
B	5714	2685	−38.7	−10.1
dl-Norleucine A	3183	528	−33.1	−8.9
B	4314	2593	−32.3	−5.8
dl-α-amino-isobutyric A	3215	492	−38 0	−9.1
B	5170	1988	−31.5	−10.7
Valine A	3118	59	−37.8	−10.3
B	5835	2872	−32.7	−9.9
dl-Leucine A	3176	382	−36.8	−9.4
B	5796	2705	−32.5	−10.4
dl-isoleucine A	3163	264	−38.1	−9.7
B	5786	2772	−28.6	−10.1
Water and Acids in Dioxane- and Methanol-Water Mixtures				
Water in X per cent Dioxane $X = 20$	19940	13515	−50.4	−21.5
$= 45$	21470	13190	−54.0	−27.8
$= 70$	24353	12662	−49.4	−39.2
Formic Acid in X per cent Dioxane $X = 20$	5701	359	−43.4	−17.92
$= 45$	6944	1067	−48.1	−19.72
$= 70$	9569	1474	−46.2	−27.16
$= 82$	12002	2509	−109.1	−31.84
Acetic Acid in X per cent Dioxane $X = 20$	7217	−52	−44.0	−24.4
$= 45$	8602	−442	−51.1	−30.3
$= 70$	11348	−610	−51.7	−40.1
$= 82$	13827	−1338	−124.5	−50.8
Propionic Acid in X per cent Dioxane $X = 20$	7455	−48	−42.0	−25.5
$= 45$	8937	−206	−46.8	−30.7
$= 70$	11746	−201	−47.6	−40.1
$= 82$	14203	−1064	−120.1	−51.2

TABLE (15-6-2).—*Continued*

		ΔF_i^0	ΔH_i^0	$\Delta C_{p_i}^0$	ΔS_i^0
Acetic Acid in X per cent Methanol	$X = 10$	6690	30	−43.3	−22.3
	$= 20$	6929	168	−47.1	−22.7
Glycine K_A in X per cent Dioxane	$X = 0$	3205	1156	−32 2	−6.9
	$= 20$	3586	1183	−34.1	−8.1
	$= 45$	4233	993	−32.4	−10.9
	$= 70$	5412	829	−30.9	−15.4
Glycine K_B in X per cent Dioxane	$X = 0$	5753	2713	−21.9	−10.2
	$= 20$	6428	2869	−27.4	−11.9
	$= 45$	7511	3342	−19.5	−14.0
	$= 70$	8968	3763	......	−17.5

(15-6-3) gives some values obtained from cells with liquid junctions, which seem representative of the best results of modern technique and extrapolations based upon the interionic attraction theory. The corresponding values from cells without liquid junction were interpolated to 18°. In the examples illustrated in Table (15-6-3), the two methods yield results within 1.5% on the average, which is unusually satisfactory. Discrepancies of ten times this magnitude are very common, and are probably due to uncertainties in corrections for liquid junction potentials rather than to gross experimental errors. This emphasizes the advantage of employing cells without liquid junctions, or combinations of cells by which the junction potential may be eliminated. [Chapter (10), Section (7)]

TABLE (15-6-3). COMPARISON OF IONIZATION CONSTANTS DERIVED FROM CELLS WITH, AND WITHOUT LIQUID JUNCTIONS AND FROM CONDUCTANCE

Acid	18°		25°	
	With L J.*	Without L J.	Without L J	Conductance
Formic	1.79×10^{-4}	1.76×10^{-4}	1.772×10^{-4}	1.830×10^{-4}
Acetic	1.73×10^{-5}	$1\ 75 \times 10^{-5}$	1.754×10^{-5}	1.758×10^{-5}
Propionic	1.32×10^{-5}	$1\ 34 \times 10^{-5}$	$1\ 336 \times 10^{-5}$	1.347×10^{-5}
n-Butyric	1.53×10^{-5}	$1\ 56 \times 10^{-5}$	$1\ 515 \times 10^{-5}$	1.512×10^{-5}
Chloroacetic	1.49×10^{-3}	1.44×10^{-3}	$1\ 379 \times 10^{-3}$	1.400×10^{-3}
α-Lactic	1.38×10^{-4}	1.37×10^{-4}	1.374×10^{-4}	$1\ 391 \times 10^{-4}$
Glycolic	1.46×10^{-4}	1.455×10^{-5}	1.475×10^{-4}	

* E. Larsson and B. Adell, *Z. physik. Chem.*, **A156**, 352, 381 (1931); *Ibid.*, **A157**, 342 (1931).

Comparisons of ionization constants at 25° derived from cells without liquid junctions and from conductance [Table (7-6-1)] are shown in the last two columns of Table (15-6-3). The agreement is particularly good for acetic and butyric acids, and unsatisfactory for formic acid.*

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* The discrepancy for formic acid is puzzling because the same sample of acid was used in both determinations.

It is very difficult to estimate the accuracy of the thermal data. All the difficulties, encountered in evaluating quantities such as $\bar{L}_2$ and $\bar{J}_2$ of strong electrolytes [Chapters (11), (12) and (13)] by differentiation, occur in determining ΔH_i^0 and $\Delta C_{p_i}^0$ of the ionization reactions. In the most favorable cases (water and aliphatic acids in water), ΔH_i^0 at 25° is probably known to within 50 cal. For the least reliable results (acid and base constants of the amino acids) the error may be as great as 250 cal. Thus, for the acid ionization of glycine, Sturtevant[72] obtains 906 cal. by calorimetric measurements which is 250 cal. lower than the value recorded in Table (15-6-1). The values of $\Delta C_{p_i}^0$ in the middle range of temperature (15 to 35°) may be known to within ±1 cal. for the most accurate results. On the other hand, errors of the order of ±7 cal., or greater probably occur in the most unfavorable cases. Further considerations of these uncertainties are to be found in the contributions of Walde,[73] Pitzer,[74] Everett and Wynne-Jones,[75] and Harned and Owen.[76]

A general discussion of the thermodynamics of ionization equilibria, and proposed theories of the variation of ionization constants with temperature, will be given [Section (10)] after the theoretical treatment of the unbuffered cell with liquid junction and the discussion of medium and salt effects [Sections (7) and (8)].

(7) MEDIUM EFFECTS. THE UNBUFFERED CELL WITHOUT LIQUID JUNCTION

In Chapter (11), Section (3), the effect of changes in composition of water-organic solvent mixtures upon the standard potential of the cell

$$H_2 \mid HCl(m), \text{ Solvent } (X), \text{ Water } (Y) \mid AgCl\text{-}Ag$$

were considered. It was shown that the Born equation (3-10-13) predicts the order of magnitude of the effect, but cannot be relied upon for accurate calculations. A more general treatment of the subject of medium effects upon the properties of both strong and weak electrolytes remains to be undertaken.

In discussing the influence of the solvent medium upon the numerical value of the activity coefficient, or ionization constant of an ionized solute, it will be convenient to distinguish between a primary and a secondary medium effect. In a solution of an electrolyte in the presence of neutral (non-aqueous) molecules, the total medium effect is defined as the logarithm of the ratio of the activity coefficient of the electrolyte in the presence of the neutral molecules to that in pure water at the same con-

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[72] J. M. Sturtevant, *J. Am. Chem. Soc.*, **62**, 1879 (1940).

[73] A. W. Walde, *J. Phys. Chem.*, **39**, 477 (1935).

[74] K. S. Pitzer, *J. Am. Chem. Soc.*, **59**, 2365 (1937).

[75] D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939).

[76] H. S. Harned and B. B. Owen, *Chem. Rev.*, **25**, 31 (1939).

centration of electrolyte. Both of the activity coefficients in this ratio are referred to unity at infinite dilution in pure water. The primary medium effect is the limit to which the total effect converges as the electrolyte concentration approaches zero. The secondary medium effect is always given by the difference between the total and primary effects.

To make use of these terms without confusion, we must be able to identify the reference state of any activity coefficient. Throughout this section, all activity coefficients in any medium are understood to be referred to unity at infinite dilution in pure water unless written with an asterisk (*viz.*, γ^*), in which case they are referred to infinite dilution in the medium in which the solute is dissolved. When this medium is pure water, a superscript zero will be used (*viz.*, γ^0). A subscript zero indicates that the concentration of electrolyte is zero. Thus for all concentrations, we may write

$$\log \gamma = \log \gamma_0 + \log \gamma^* \tag{15-7-1}$$

or, adding $-\log \gamma^0$ to both sides

$$\log \frac{\gamma}{\gamma^0} = \log \gamma_0 + \log \frac{\gamma^*}{\gamma^0} \tag{15-7-2}$$

is obtained. The three terms of this last equation give the definitional relationship between the total, primary and secondary medium effects,[77] respectively. The primary medium effect is the one with which equations (3-10-12) and (3-10-13) are concerned.

The values of $(-\log K_A)$ in water-organic solvent mixtures, given in Table (15-6-2A), were obtained from the cells

$$H_2 \mid HR(m_1),\ NaR(m_2),\ NaCl(m_3),\ \text{Solvent } (X),\ H_2O\ (Y) \mid AgCl\text{-}Ag$$

by employing equation (15-4-2). There are two simple equivalent ways of expressing the electromotive force of such a cell, namely

$$\frac{\mathbf{F}(\mathbf{E} - \mathbf{E}^0)}{2.3\,RT} = -\log m_{\mathrm{H}} m_{\mathrm{Cl}} - \log \gamma_{\mathrm{H}} \gamma_{\mathrm{Cl}} \tag{15-7-3}$$

and

$$\frac{\mathbf{F}(\mathbf{E} - \mathbf{E}^{0*})}{2.3\,RT} = -\log m_{\mathrm{H}} m_{\mathrm{Cl}} - \log \gamma^*_{\mathrm{H}} \gamma^*_{\mathrm{Cl}} \tag{15-7-4}$$

In the first expression, $-\mathbf{E}^0$ is the standard potential of the silver-silver chloride electrode in pure water. In the second expression, $-\mathbf{E}^{0*}$ is the standard potential in the mixed solvent. Combination of these two equations, and comparison with equation (15-7-1), shows that the primary

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[77] B. B. Owen, *J. Am. Chem. Soc.*, **54**, 1758 (1932).

medium effect of the solvent upon the hydrogen and chloride ions is given directly by the two standard potentials. Thus

$$\log \gamma_{0\mathrm{HCl}} = \frac{1}{2} \log \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}}{\gamma^*_{\mathrm{H}}\gamma^*_{\mathrm{Cl}}} = \frac{\mathrm{F}(\mathrm{E}^0 - \mathrm{E}^{0*})}{4.6\,RT} \qquad (15\text{-}7\text{-}5)$$

The primary medium effect of the organic solvent upon the activity coefficient or ionization constant of acetic acid can be determined by extrapolation of the data for the above cell in accordance with equation (15-4-2). Employing equation (15-7-4), we obtain a quantity, K^*_{A}, whose value is a function of the medium, because γ^* is always unity at infinite dilution. If we write,

$$\gamma^2_{\mathrm{A}} = \frac{\gamma_{\mathrm{H}}\,\gamma_{\mathrm{R}}}{\gamma_{\mathrm{HR}}} \quad \text{and} \quad k_{\mathrm{A}} = \frac{m_{\mathrm{H}}\,m_{\mathrm{R}}}{m_{\mathrm{HR}}} \qquad (15\text{-}7\text{-}6)$$

the thermodynamic ionization constant in pure water, K_{A}, is related to the properties of the acid in the mixed solvent by the definitional equation,

$$K_A = \gamma^2_A k_A = \gamma^2_{0A}\gamma^{*2}_A k_A \doteq \gamma^2_{0A} K^*_A \qquad (15\text{-}7\text{-}7)$$

Accordingly,

$$\log \gamma_{0A} = \frac{1}{2} \log \frac{K_A}{K^*_A} \qquad (15\text{-}7\text{-}8)$$

Table (15-7-1) contains the values of E^{0*} obtained for the methanol-water and dioxane-water mixtures, and the corresponding values of $\log \gamma_{0\mathrm{HCl}}$ and $\log \gamma_{0A}$. It will be noticed that the medium effect of acetic acid upon hydrochloric acid is greater than that of methanol or dioxane, and that the effects of the latter upon acetic acid are greater than upon hydrochloric acid. The medium effect of acetic acid molecules upon ionized acetic acid has not yet been determined experimentally.

If equation (15-7-3) be employed for extrapolation instead of equation (15-7-4), the situation would be similar to that encountered with cells containing unbuffered solutions of weak acids. Equation (15-7-3) can be written

$$\frac{\mathrm{F}(\mathrm{E} - \mathrm{E}^0)}{2.3RT} + \log \frac{m_{\mathrm{HR}}}{m_{\mathrm{R}}} m_{\mathrm{Cl}} = -\log K_A + 2 \log \gamma_A - 2 \log \gamma_{\mathrm{HCl}} \qquad (15\text{-}7\text{-}9)$$

Extrapolation of the left-hand member to zero ionic strength yields $(-\log K_A + 2 \log \gamma_{0A} - 2 \log \gamma_{0\mathrm{HCl}})$, so that knowing K_A, we obtain the difference between the primary medium effects of the solvent upon the weak acid and upon hydrochloric acid. From this, it is clear that $\log \gamma_{0A}$ cannot be obtained from the above cell unless either $\log \gamma_{0\mathrm{HCl}}$ or E^{0*} is known [Equation (15-7-5)].

We are now in a position to consider unbuffered cells of the type,

$$\mathrm{H_2} \mid \mathrm{HR}(m_1),\ \mathrm{NaCl}(m_2) \mid \mathrm{AgCl\text{-}Ag}$$

first used to determine ionization constants,[78] and the activity coefficients[79] of weak electrolytes in salt solutions. In such cells the weak acid concentration was maintained constant at some particular value of m_1, while the salt concentration, m_2, was varied. If the electromotive force expression for this cell is rearranged, and $2 \log \overset{0}{\gamma}_{\mathrm{HCl}}$ added to both sides of the equation, we obtain

TABLE (15-7-1). PRIMARY MEDIUM EFFECTS AT 25° IN ORGANIC SOLVENT-WATER MIXTURES

X = Weight Per Cent Organic Solvent

Solvent	X	E^{0*a}	Log γ_0HCl	Log γ_{0A}[b] Formic Acid	Log γ_{0A}[b] Acetic Acid	Log γ_{0A}[b] Propionic Acid
Water	0	0.22239	0.0	0.0	0.0	0.0
Methanol	10	.21535	.0595	......	.0741	......
	20	.20881	.1148	......	.1614	......
Dioxane	20	.20303	.1636	.2143	.2678	.2961
	45	.16352	.4976	.6200	.7755	.8392
	70	.06395	1.3392	1.6318	1.7823	1.869
	82	−.0415	2.230	2.52	2.69	2.77
Acetic Acid	10	.21050	.1005	......	......	......
	20	.19682	.2161	......	......	......
	30	.18091	.3506	......	......	......
	40	.16211	.5095	......	......	......
	50	.13945	.7010	......	......	......
	60	.11150	.9373	......	......	......

[a] Table (11-3-2); Acetic acid, B. B. Owen, *J. Am. Chem. Soc.*, **54**, 1758 (1932).
[b] From data in Table (15-6-2A).

$$\frac{\mathrm{F}(\mathrm{E} - \mathrm{E}^0)}{2.3RT} + \log m_2 + 2 \log \overset{0}{\gamma}_{\mathrm{HCl}} = -\log m_{\mathrm{H}} - 2 \log \frac{\gamma_{\mathrm{HCl}}}{\overset{0}{\gamma}_{\mathrm{HCl}}} \qquad (15\text{-}7\text{-}10)$$

The right-hand member contains the total medium effect of the weak acid upon the chloride and hydrogen ions. This quantity is ordinarily unknown. Consequently, it is useful to define an apparent hydrogen ion concentration, m'_{H}, by

$$\log m'_{\mathrm{H}} = \log m_{\mathrm{H}} + 2 \log \frac{\gamma_{\mathrm{HCl}}}{\overset{0}{\gamma}_{\mathrm{HCl}}} \qquad (15\text{-}7\text{-}11)$$

which can be calculated directly from the left-hand member of equation (15-7-10). The corresponding apparent activity coefficient of the weak

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[78] H. S. Harned and B. B. Owen, *J. Am. Chem. Soc.*, **52**, 5079 (1930); H. S. Harned and G. M. Murphy, *Ibid.*, **53**, 8 (1931).

[79] H. S. Harned and R. A. Robinson, *Ibid.*, **50**, 3157 (1928).

acid, γ'_A, is defined in terms of the thermodynamic ionization constant by the equation

$$K_A = \frac{\gamma'_H \gamma'_R}{\gamma'_{HR}} \frac{m'^2_H}{m_1 - m'_H} = \gamma'^2_A k'_A \qquad (15\text{-}7\text{-}12)$$

analogous to the expression,

$$K_A = \frac{\gamma_H \gamma_R}{\gamma_{HR}} \frac{m^2_H}{m_1 - m_H} = \gamma^2_A k_A \qquad (15\text{-}7\text{-}13)$$

which relates the real activity coefficient with the real hydrogen ion concentration. In both of these expressions all activity coefficients are referred to unity at infinite dilution in pure water.

Combining equations (15-7-11) to (15-7-13), we find that

$$\log \gamma'_A = \log \gamma_A - 2 \log \frac{\gamma_{HCl}}{\gamma^0_{HCl}} + \frac{1}{2} \log \frac{m_1 - m'_H}{m_1 - m_H} \qquad (15\text{-}7\text{-}14)$$

which shows that log γ'_A is expressed in terms of real activity coefficients, and indeed must simulate the properties of a real activity coefficient when the term containing m'_H is small. If the concentration, m_1, of the weak acid is kept constant while the ionic strength is altered by variations in salt concentration, m_2, we can obtain a series of values of m'_H and k'_A in a $(m_1 - m_H)$ molal solution of unionized weak electrolyte in water. So long as m_H is much smaller than m_1, the composition of the solvent is very nearly constant, and the primary medium effect, and, as a first approximation, the total medium effect may be considered independent of the salt concentration. It is therefore practicable to obtain

$$k_{0A} = \lim_{\mu \to 0} [k'_A] \qquad (15\text{-}7\text{-}15)$$

by extrapolation. The logarithm of the corresponding quantity,

$$\gamma'_{0A} = \lim_{\mu \to 0} [\gamma'_A] \qquad (15\text{-}7\text{-}16)$$

is of the nature of a primary medium effect, since it would equal

$$\log \gamma_{0A} - 2 \log \gamma_{0HCl}$$

by equation (15-7-14), if the concentration term is eliminated by the extrapolation.

The extrapolation of log k'_A is performed by means of the equations,

$$\log k'_A - 2\mathfrak{S}_{(f)}\sqrt{\mu' d_0} = \log k'_{0A} \pm 2\beta\mu' \qquad (15\text{-}7\text{-}17)$$

or

$$\log k'_A - \frac{2\mathfrak{S}_{(f)}\sqrt{\mu' d_0}}{1 + A'\sqrt{\mu' d_0}} = \log k'_{0A} \pm 2\beta\mu' \qquad (15\text{-}7\text{-}18)$$

in which μ' ($= m_2 + m'_H$) is used for $\mu (= m_2 + m_H)$ as a very close approximation. The use of the numerical value of $\mathcal{S}_{(f)}$ for pure water neglects the secondary medium effect of the weak acid, but this approximation is unavoidable because the influence of HR molecules upon the dielectric constant of the solvent is generally unknown. The extrapolation is illustrated in Fig. (15-7-1), in which log k'_{0A} is determined for acetic acid[80] for six values of m_1 by equation (15-7-17). A recent investigation[81] shows that it is necessary to use equation (15-7-18) if higher values of μ' are included.

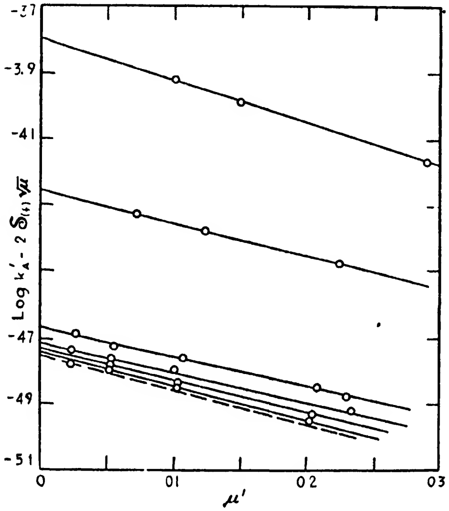

Fig. (15-7-1)
Evaluation of k'_{0A} for acetic acid at 25° for various values of m_1. Reading down, m_1 equals 10.2, 5.41, 1.0, 0.52, 0.2, and 0.1. The dashed line represents the hypothetical limiting curve when $m_1 = 0$.

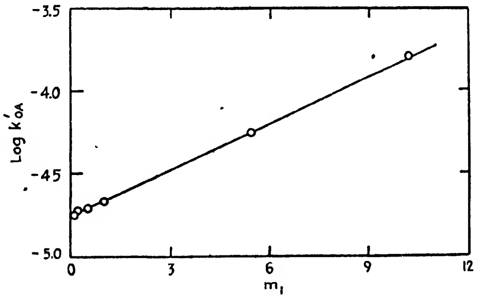

Fig. (15-7-2). Evaluation of log K_A for acetic acid at 25°.

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[80] H. S. Harned and B. B. Owen, *J. Am. Chem. Soc.*, **52**, 5079 (1930).
[81] H. S. Harned and F. C. Hickey, *J. Am. Chem. Soc.*, **59**, 1284 (1937).

From the nature of γ'_{0A}, it is clear that it must become unity when $m_1 = 0$, for under this condition the medium is pure water. According to equation (15-7-12), extrapolation of k'_{0A} to $m_1 = 0$ must yield K_A. This second extrapolation is shown in Fig. (15-7-2). The fact that this extrapolation is linear within the experimental error is without theoretical significance, because it is impossible at present to evaluate the effects of the several approximations involved in the calculations. It is known that $\log \gamma_{0HCl}$ is not linear[82] when similarly plotted, but the behavior of $\log \gamma_{0A}$ is unknown.[83]

(8) THE ACTIVITY COEFFICIENTS OF WEAK ACIDS IN SALT SOLUTIONS

It was shown in Section (2) that the function, $\log(\gamma_H\gamma_{OH}/a_{H_2O})$, for water in salt solutions could be derived from the electromotive forces of suitable cells without liquid junctions. The electromotive force method is also applicable to the estimation of analogous functions for other weak electrolytes. Similar results may be obtained by the optical method described in Section (4). In this section, we shall illustrate the calculation of the function, $\log \gamma_H\gamma_R/\gamma_{HR}$, for acetic acid from electromotive force data, and for α-dinitrophenol from optical data. The electromotive force method will be considered first because it is based upon the results just discussed in Section (7).

The nearly parallel nature of the lines for low concentrations in Fig. (15-7-1) suggests that the broken line drawn from the intercept, $\log K_A$, would represent the properties of infinitely dilute acetic acid in sodium chloride solutions. In such solutions, the medium effect of the weak acid is zero. This illustrates a very important restriction upon the information which may be derived from the unbuffered cell without liquid junction. Without extra-thermodynamical information, this cell gives k_A, or $m_H^2/(m_1 - m_H)$, in salt solutions at zero concentration of weak acid ($m_1 = 0$). It does not measure this quantity in a solution containing a finite amount of the weak electrolyte. On the other hand, the method points the way toward such knowledge because it shows that, in order to solve the problem, the medium effect of the weak acid, or the effect of change of m_1 upon k_A, must be known. As these studies are extended, and the general laws of the effects of change of solvent composition become known, it will be possible to obtain m_H in acid-salt solutions of various compositions. The important determination of m_H in buffered solutions will also be possible.

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[82] B. B. Owen, *J. Am. Chem. Soc.*, **54**, 1758 (1932).

[83] In the original paper by H. S. Harned and B. B. Owen [*J. Am. Chem. Soc.*, **52**, 5079 (1932)] the third equality in equation (17) is invalid as it neglects the medium effect of acetic acid upon the real γ_A. The third sentence on p. 5081 of this paper is incorrect as it refers γ_A to "a given solvent" rather than to pure water. These mistakes were corrected by H. S. Harned and B. B. Owen, [*Chem. Rev.*, **25**, 31 (1939)] whose recent treatment has been followed in the text.

When the medium effect of the weak acid is zero ($m_1 = 0$), we drop the primes in equation (15-7-15), or (15-7-16). If we refer to equation (15-7-11), it follows that the slope of the broken line can be identified with 2β in an equation such as,

$$2 \log \gamma_A = \log K_A - \log k_A = \frac{-2\mathfrak{S}_{(f)}\sqrt{\mu d_0}}{1 + A'\sqrt{\mu d_0}} + 2\beta\mu \qquad (15\text{-}8\text{-}1)$$

This may be used to evaluate the ionization, or activity coefficient, γ_A, of the weak acid in salt solutions.

In Table (15-8-1), we have recorded values of k_A at 25° in some salt solutions obtained by Harned and Hickey.[84] These are plotted in Fig. (15-8-1), and we note the similarity to the plots of $m_H m_{OH}$ in halide solutions shown in Fig. (15-2-2). In concentrated solutions, the order of the salt effect is the same as that found for water, and agrees with the first, but less accurate, results of this kind found by Harned and Robinson,[85] who also obtained the same order for the weak hydroxide, monomethylamine. In alkali halide solutions, the greatest ionization occurs in the solution containing the cation of smallest radius, and the remarks in Section (2) concerning specific salt effects on the ionization of water also apply to weak acids and hydroxides. In general, the ionization of weak electrolytes in concentrated solutions depends to a large extent on the fields of the ions.

TABLE (15-8-1). THE IONIZATION OF ACETIC ACID AT INFINITE DILUTION IN SALT SOLUTIONS AT 25°

$k_A \times 10^5$

μ	LiCl	NaCl	KCl	$BaCl_2$
0.	1.754	1.754	1.754	1.754
.02	2.290	2.292	2.302	2.292
.03	2.401	2.401	2.415	2.404
.06	2.630	2.622	2.650	2.635
.11	2.874	2.850	2.891	2.885
.21	3.167	3.101	3.151	3.190
.51	3.546	3.315	3.340	3.609
1.01	3.670	3.158	3.071	3.799
2.01	3.432	2.475	2.182	3.680
3.01	.....	1.824	.....	.....

Harned and Hickey have determined k_A for acetic acid in sodium chloride solutions by this method from 0 to 40°. They found the temperature variation could be expressed by the relation,

$$\log k_A = \log k_\vartheta - 5 \times 10^{-5}(t - \vartheta)^2 \qquad (15\text{-}8\text{-}2)$$

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[84] H. S. Harned and F. C. Hickey, *J. Am. Chem. Soc.*, **59**, 1284 (1937); **59**, 2303 (1937). The ionization of lactic acid in sodium chloride solutions from 0 to 37.5° has been determined by F. C. Hickey, *Ibid.*, **62**, 2916 (1940).

[85] H. S. Harned and R. A. Robinson, *J. Am. Chem. Soc.*, **50**, 3157 (1928).

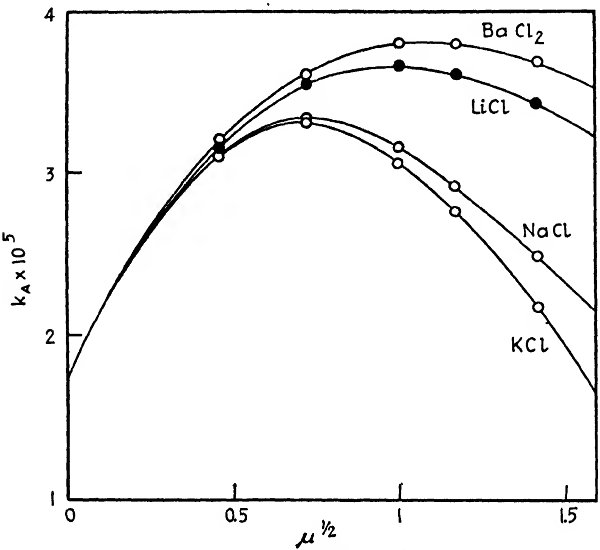

Fig. (15-8-1). The ionization of acetic acid at infinite dilution in chloride solutions at 25°.

TABLE (15-8-2). PARAMETERS OF EQUATION (15-8-2) FOR ACETIC ACID AT INFINITE DILUTION IN SODIUM CHLORIDE SOLUTIONS

μ	$-\log k_\vartheta$	ϑ	Δ ave.
0.00	4.7544	22.6	0.0009
.02	4.6388	25.1	.0007
.03	4.6189	25.6	.0007
.06	4.5798	26.4	.0007
.11	4.5432	27.6	.0009
.21	4.5061	29.2	.0011
.51	4.4752	32.5	.0009
1.01	4.4957	35.7	.0012
2 01	4.5875	45.0	.0029
3.01	4.7132	50.9	.0038

similar to equation (15-6-6). This leads to the interesting conclusion that log γ_A varies linearly with temperature, for by combining equations (15-8-1) and (15-8-2) with (15-6-6), we obtain

$$\log \gamma_A = (1/2) \log (K_\theta/k_\vartheta) + 2.5 \times 10^{-5}(\vartheta^2 - \theta^2) - 5 \times 10^{-5}(\vartheta - \theta)t \qquad (15\text{-}8\text{-}3)$$

Values of log k_ϑ and ϑ are given in Table (15-8-2). The average deviations between observed values of log k_A and those calculated by equation (15-8-2) are indicated by $\Delta_{\text{ave.}}$.

The behavior of the activity coefficients of several weak electrolytes in sodium chloride solutions is illustrated in Fig. (15-8-2), where they are compared with the activity coefficient of the strong electrolyte, hydrochloric acid, in the same salt solutions. The results for α-dinitrophenol are due to von Halban and Kortüm.[86] Although the points for this acid differ from those of the other weak electrolytes by lying above the curve for hydrochloric acid, the difference is small. A close similarity in the behavior of 1-1 type weak acids in salt solutions appears to be quite general. The activity coefficient functions of twenty-four such acids, studied by Larsson and Adell[87] with the cells containing liquid junctions, would almost exactly fall within the upper and lower limits set by the points for α-dinitrophenol and water in Fig. (15-8-2). Judging from these results, it may be said that the activity coefficients of the normal fatty acids are practically indistinguishable, and that the introduction of a methyl, phenyl or hydroxyl group into the acid anion is without significant effect unless it occupies the α-position to the carboxyl group. Further discussion of constitutional effects are given by Larsson and Adell, and Güntelberg and Schiödt.[88]

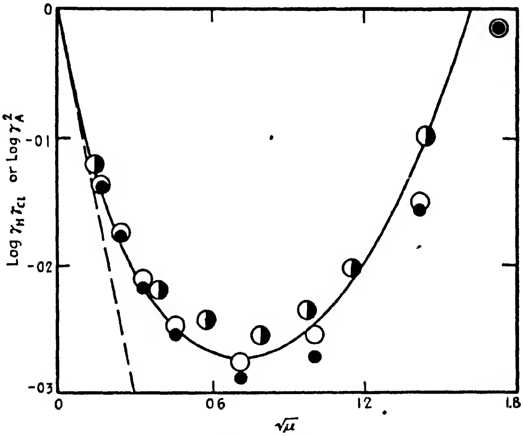

Fig. (15-8-2). Comparison of activity coefficients of electrolytes at infinite dilution in sodium chloride solutions at 25°. Smooth curve, log $\gamma_H\gamma_{Cl}$; ●, log $\gamma_H\gamma_{OH}/a_{H_2O}$; ○, log $\gamma_H\gamma_{Ac}/\gamma_{HAc}$; ◑, log $\gamma_H\gamma_{D_n}/\gamma_{HD_n}$ (Dn = α-dinitrophenol ion)

The presence of the term, γ_{HR}, in the activity coefficient function, γ_A, of weak acids is of considerable importance in determining the order of the salt effects at high ionic strengths [Fig. (12-10-3)]. For α-dinitrophenol in sodium and potassium chloride solutions, the curves actually cross at

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[86] H. v. Halban and G. Kortüm, *Z. physik. Chem.*, **A170**, 351 (1934).

[87] E. Larsson and B. Adell, *Z. physik. Chem.*, **A157**, 342 (1931); *Ibid.*, **A156**, 381 (1931).

[88] E. Güntelberg and E. Schiödt, *Z. physik. Chem.*, **135**, 393 (1928).

about 2*M*, so that the order at high concentrations is the reverse of that at low concentrations. This may be a very unusual phenomenon, because in dilute solutions the order of the salt effects upon α-dinitrophenol follows the order for the relatively non-deformable hydrogen halides. Furthermore, von Halban, Kortüm and Seiler[89] have shown, from solubility

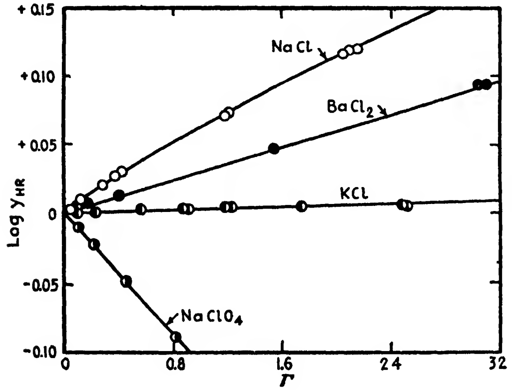

Fig. (15-8-3). The activity coefficient of undissociated α-dinitrophenol in aqueous salt solutions at 25°C.

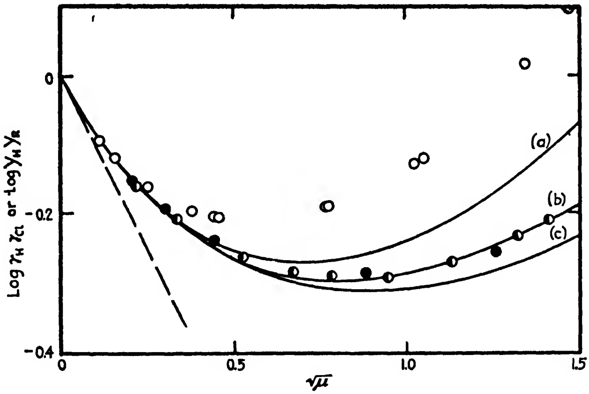

Fig. (15-8-4). The activity coefficient of ionized α-dinitrophenol in aqueous salt solutions at 25°. ○, NaCl; ◐, KCl; ●, $BaCl_2$. The curves represent the activity coefficient of hydrochloric acid in the same salt solutions; (a) NaCl; (b) KCl; (c) $BaCl_2$

measurements, that the variation of y_{HR} for this acid is quite large. Plots of their values of log y_{HR} against Γ in several salt solutions are reproduced in Fig. (15-8-3). The difference in magnitudes of the salt effects of sodium and potassium chlorides upon y_{HR} is so great that if these results are used

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[89] H. v. Halban, G. Kortüm and M. Seiler, *Z. physik. Chem.*, **A173**, 449 (1935).

to eliminate y_{HR} from the function, $y_H y_R / y_{HR}$, which exhibited a reversal in order of salt effect at about $2M$, it is found that there is no indication of a reversal in salt effect upon $y_H y_R$ at any concentration. In Fig. (15-8-4), the behavior of log $y_H y_R$ for α-dinitrophenol in sodium, potassium, and barium chloride solutions is compared with that of log $\gamma_H \gamma_{Cl}$ in the same salt solutions. It will be noticed that the order of the curves is the same for the two acids, and that curves for the weak acid are higher than the corresponding curves for hydrochloric acid. No explanation of these interesting anomalies has yet been offered.

Cells without liquid junction have been employed by Batchelder and Schmidt[90] to determine the dissociation of alanine, aspartic acid, arginine and ornithine in potassium, sodium and barium chloride solutions.

(9) HYDROLYSIS OF ORGANIC ACID ANIONS IN SALT SOLUTIONS

By combination of the activity coefficient functions, $\gamma_H \gamma_R / \gamma_{HR}$ and $\gamma_H \gamma_{OH} / a_{H_2O}$, the influence of salts upon the hydrolysis of the anion, R^- (at infinite dilution of HR), may be investigated. The relationships for the hydrolytic reaction,

$$R^- + H_2O \rightleftharpoons HR + OH^-$$

are

$$K_h = \frac{K_w}{K_A} = \frac{\gamma_{HR}\,\gamma_{OH}}{a_{H_2O}\,\gamma_R}\,\frac{m_{HR}\,m_{OH}}{m_R} = \frac{\gamma_w^2\,k_w}{\gamma_A^2\,k_A} = \gamma_h^2\,k_h \qquad (15\text{-}9\text{-}1)$$

Since the four quantities, γ_w, k_w, γ_A, and k_A, are separately known in some salt solutions, γ_h and k_h may be evaluated in these solutions.

Table (15-9-1) contains values of k_h for the hydrolysis of the acetate ion in sodium chloride solution from 0 to 40°, and in potassium, lithium, and barium chloride solutions at 25°, obtained by Harned and Hickey. At a given ionic strength, barium chloride produces the greatest salt effect at 25°, and the other salt effects decrease in the order lithium, sodium and potassium chloride.

Values of the activity coefficient function, log γ_h, for sodium chloride at 25° are plotted in Fig. (15-9-1) as circles, the radii of which represent an uncertainty of 0.1 percent in γ_h. This figure illustrates two interesting points. The total variation of γ_h with salt concentration is very small, being less than 2 percent. This nearly ideal behavior of the hydrolysis reaction is maintained also at 30 and 40°, but tends to disappear at lower temperatures. The second point of interest is the form taken by the plot in dilute solutions. Since γ_h is $\gamma_{HAc}\gamma_{OH}/a_{H_2O}\gamma_{Ac}$ by equation (15-9-1), a plot of log γ_h against $\sqrt{\mu}$ must approach the intercept, log $\gamma_h = 0$, with

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[90] A. C. Batchelder and C. L. A. Schmidt, *J. Phys. Chem.*, **44**, 880 (1940); **44**, 893 (1940).

zero slope. It is clear from the figure that this condition is not fulfilled at the lowest experimental concentration, 0.02*M*. To illustrate the extreme dilutions which might be required before the plot shows definite signs of becoming horizontal, the curve is drawn for the ratio of two hypothetical univalent ions conforming to the Debye-Hückel equation.

TABLE (15-9-1). HYDROLYSIS FUNCTION, $k_h = k_w/k_A$, FOR THE ACETATE ION AT INFINITE DILUTION IN CHLORIDE SOLUTIONS

$k_h \times 10^{10}$

μ	NaCl						KCl	LiCl	BaCl$_2$
	0°	10°	20°	25°	30°	40°	25°	25°	25°
0.0	0.684	1.688	3.88	5.74	8.40	17.11	5.74	5.74	5.74
.02	.697	1.706	3.92	5.79	8.45	17.29	5.77	5.81	5.83
.03	.704	1.701	3.92	5.79	8.45	17.29	5.74	5.83	5.85
.06	.706	1.714	3.93	5.79	8.44	17.31	5.69	5.93	5.96
.11	.708	1.720	3.95	5.82	8.50	17.39	5.65	6.08	6.05
.21	.719	1.741	3.98	5.84	8.54	17.36	5.61	6.27	6.29
.51	.738	1.770	4.03	5.91	8.57	17.44	5.65	6.53	6.81
1.01	.761	1.820	4.09	5.96	8.65	17.68	5.57	6.87	7.43
2.01	.801	1.864	4.11	5.93	8.54	17.48	5.85	7.13	8.28
3.01	.818	1.858	4.02	5.74	8.27	17.05	....	....	9.02

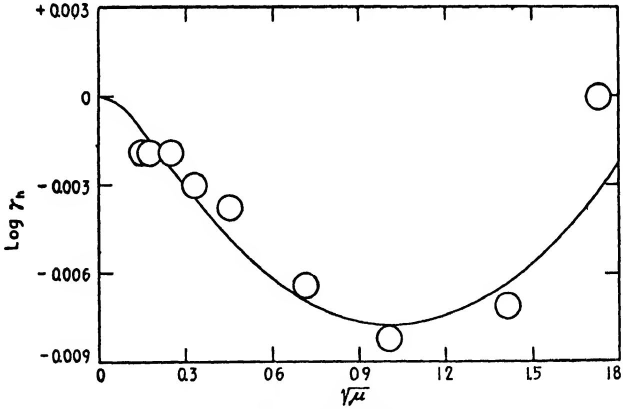

Fig. (15-9-1). Variation of log γ_h for hydrolysis of acetate ion at infinite dilution in sodium chloride solutions at 25°.

The $\mathring{a}$-values were taken as 4.0 and 4.5, and a linear term, 0.005μ, was selected to give approximate agreement with the data at high ionic strengths. The numerical values of these parameters are too arbitrary to be significant, but they demonstrate the essential conformity of the data with theory, and their difference, 0.5 Å., calls attention to the very small magnitude of the effect which has been measured experimentally.

(10) THEORETICAL CONSIDERATIONS

The ionization constant data of weak electrolytes given in the preceding sections has been the subject of a number of recent discussions.[91] None of these yield an exact, or a complete solution of any of the numerous questions raised. In such a complicated situation, a further analysis of the experimental data in relation to the important variables and proposed theories will lead to interesting conclusions and problems.

In Fig. (15-10-1), (−log *K*) on the *m*-scale at 25° for water, formic, acetic, and propionic acids in dioxane-water mixtures is plotted against 1/*D*. As pointed out by Harned[92], these plots are not linear and, therefore, Born's equation [Equation (3-10-13)] is not valid. If the logarithm of the ionization constant on the *c*-scale or *N*-scale be plotted, the result is similar. This departure from the result required by the Born equation

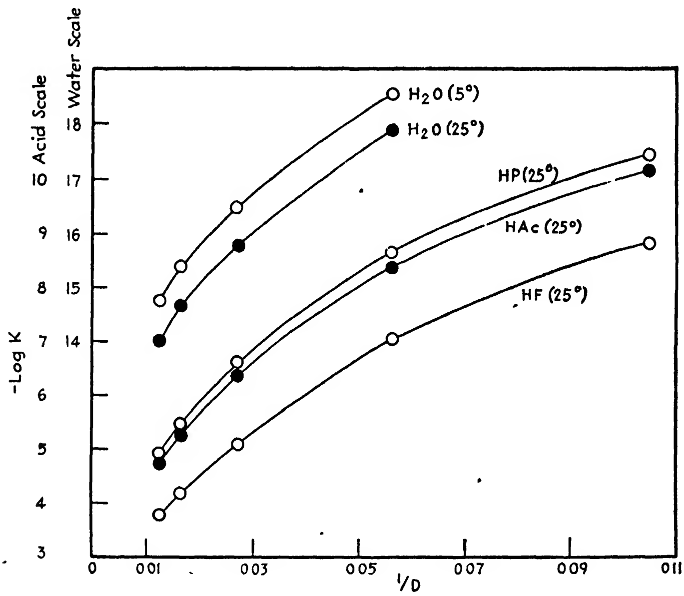

Fig. (15-10-1). Ionization constants as a function of dielectric constant in dioxane-water mixtures. HP, propionic acid; HAC, acetic acid; HF, formic acid.

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[91] H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.*, **56**, 1050 (1934); K. S. Pitzer, *Ibid.*, **59**, 2365 (1937); R. W. Gurney, *J. Chem. Phys.*, **6**, 499 (1938); E. C. Baughan, *Ibid.*, **7**, 951 (1939); D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939); D. H. Everett and C. A. Coulson, *Ibid.*, **36**, 633 (1940); J. F. J. Dippy, *Chem. Rev.*, **25**, 131 (1940); H. S. Harned and B. B. Owen, *Chem. Rev.*, **25**, 31 (1939); H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

[92] H. S. Harned, *J. Phys. Chem.*, **43**, 275 (1939).

is not unexpected, since a similar result was noted for the standard potentials of the hydrogen-silver chloride cell [Chapter (11), Section (3)]. Further, similar results are obtained at all temperatures between 0 and 50°.

Gurney[93] has suggested a theory for the temperature variation of ionization constants which has been developed in a more suitable manner for calculation of these results by Baughan.[94] In the first place, consider two types of ionization reactions,

$$RNH_3^+ + H_2O \rightleftharpoons RNH_2 + H_3O^+ \qquad \text{I}$$

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+ \qquad \text{II}$$

Reactions of Type I involve a proton shift, but not the creation of a new field. They are isoelectric. Type II reactions involve both a proton shift, and the creation of a new field. A third type represented by

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{--} + H_3O^+ \qquad \text{III}$$

involves the creation of a new field, and additional work of separating a positively charged proton from a negative ion.

According to Born's equation, the electrical contribution to the standard free energy change of process II is given by

$$\Delta F^0(\text{El}) = \frac{N\epsilon^2}{2D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \qquad (15\text{-}10\text{-}1)$$

If the total free energy, ΔF^0, is separated into a chemical, $\Delta F^0_{(D=\infty)}$, and an electrical part, $\Delta F^0(\text{El})$, then

$$\Delta F^0 = \Delta F^0_{(D=\infty)} + \Delta F^0(\text{El}) \qquad (15\text{-}10\text{-}2)$$

$$= -RT \ln K = -RT \ln K_{(D=\infty)} + \frac{N\epsilon^2}{2D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \qquad (15\text{-}10\text{-}3)$$

or

$$-\ln K = -\ln K_{(D=\infty)} + \frac{N\epsilon^2}{2DRT}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \qquad (15\text{-}10\text{-}4)$$

Upon substitution in equation (1-10-12), or

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H^0}{RT^2} \quad \text{and} \quad \frac{\partial \ln K_{(D=\infty)}}{\partial T} = \frac{\Delta H^0_{(D=\infty)}}{RT^2} \qquad (15\text{-}10\text{-}5)$$

and differentiating, we obtain

$$\Delta H^0 = \Delta H^0_{(D=\infty)} + C\left[\frac{1}{D}\left(1 + T\frac{\partial \ln D}{\partial T}\right)\right] \qquad (15\text{-}10\text{-}6)$$

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[93] R. W. Gurney, *J. Chem. Phys.*, **6**, 499 (1938).

[94] E. C. Baughan, *J. Chem. Phys.*, **7**, 951 (1939).

where

$$C = \frac{N\epsilon^2}{2}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{15-10-7}$$

Equation (15-10-6) is the one employed by Baughan for representing reactions of types II and III.

The validity of equation (15-10-6) rests upon two factors. It presupposes the exactness of the Born equation from 0 to 60°, which, for aqueous solutions, involves a change in D from 88 to 67. The second factor involves an assumption regarding the variation of $\Delta H^0_{(D=\infty)}$ with temperature. From the recent measurements of Everett and Wynne-Jones[95] of the ionization of the ammonium ion, and of Pedersen[96] who determined the ionization constants of the anilinium and o-chloroanilinium ion, it appears that, for these isoelectric dissociations corresponding to Type I, log K varies with temperature according to the relation,

$$\log K = A - \frac{B}{T} \tag{15-10-8}$$

in which A and B are constants. If this is true, then ΔH^0_i is constant, and $\Delta C^0_{p_i}$ is 0. More recent studies[97] reveal, however, that the mono-, di-, and tri-methyl ammonium ion dissociations are accompanied by changes in heat capacities of 7, 20, and 41 cals., respectively. Following Gurney, Baughan assumes that $\Delta H^0_{(D=\infty)}$ is independent of T for isoelectric reactions. In spite of the doubtful nature of this assumption, and the inexactness of Born's equation, Baughan succeeded in obtaining some results which lead to the right order of magnitude of the ionic radii. A few further computations will show that the situation is too complicated to be explained by this simplified treatment.

According to equation (15-10-6), if ΔH^0 be plotted against $\frac{1}{D}\left(1 + T\frac{\partial \ln D}{\partial T}\right)$, a straight line should be obtained with a slope, C, and an intercept, $\Delta H^0_{(D=\infty)}$. Such a plot is shown in Fig. (15-10-2) for water and acetic acid in aqueous solutions. Values of ΔH^0 were computed by equation (15-6-7), using the parameters in Table (15-6-4A). The plots are nearly straight lines, but each shows distinct curvatures. The deviations are greater than the estimated experimental errors. Similar results are obtained for water, formic, acetic and propionic acids in dioxane-water mixtures. From values of C, estimated roughly from the slopes of the curves, values of a mean radius, r, defined by the equation,

$$\frac{2}{r} = \frac{1}{r_+} + \frac{1}{r_-} \tag{15-10-8a}$$

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[95] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.* (*London*), **169A,** 190 (1938).

[96] K. Pedersen, *K. Danske Vidensk. Selsk. Skr.*, **14,** 9 (1937); **15,** 3 (1937).

[97] D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **35,** 1380 (1939).

have been determined, and recorded in Table (15-10-1). Similar results for these and other acids in water have been obtained by Baughan, who found values of r between 0.65 and 0.85.

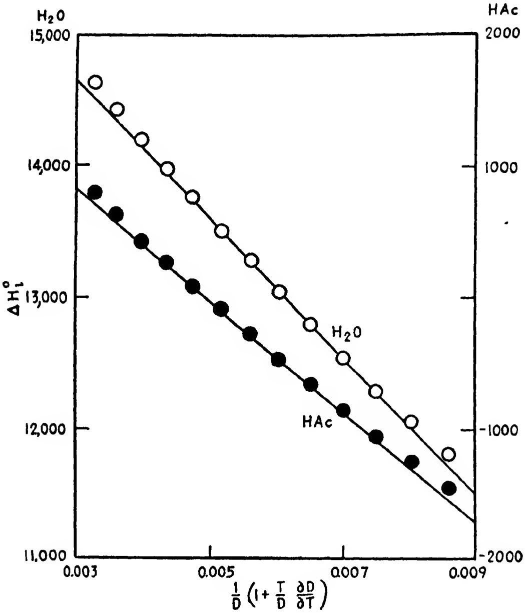

Fig. (15-10-2). Plot of ΔH_i° according to equation (15-10-6) for water, ○, and acetic acid, ●.

Table (15-10-1). Values of Mean Ionic Radii Derived by Means of Equation (15-10-7)*

Solvent is Water-Dioxane Mixtures. X = Per Cent Dioxane; r (Å) by equation (15-10-8)

X	H_2O	HCOOH	CH_3COOH	C_2H_5COOH
0	0.61	0.68	0.77	0.74
20	.86	1.00	.99	1.04
45	1.51	1.70	1.60	1.75
70	3.62	3.88	3.47	3.76
82	....	2.38	2.09	2.17

* H. S. Harned and T. R. Dedell, *J. Am. Chem. Soc.*, **63**, 3308 (1941).

Although the values of r are of the right order of magnitude, no convincing conclusions can be obtained from them. In water, they seem to be too small, and in 70% dioxane-water mixtures they are too large. Indeed, their variation with change in solvent will be difficult to explain.

It is interesting to note that by combining equations (15-10-4) and (15-10-6), the equation

$$\log K = A - \frac{B}{T} - \frac{C'}{DT} \tag{15-10-9}$$

is obtained where A, B, and C' are constants. This equation, different in form from the empirical equations discussed in Sections (3) and (6), fits the data fairly well.*

That a simplified electrostatic theory is inadequate in aqueous solutions becomes apparent from consideration of the heat capacities of the reactions. Examination of the values of $\Delta C^0_{p_i}$ in Table (15-6-2) leads to the following rough classification corresponding to the type reactions. Thus,

$HA + H_2O \rightleftharpoons A^- + H_3O^+$ $\qquad \Delta C^0_{p_i} \cong -(36 \rightarrow 41)$

${}^+NH_3RCO_2H + H_2O \rightleftharpoons {}^+NH_3RCO_2^- + H_3O^+$ $\qquad \Delta C^0_{p_i} \cong -36$ (Mean)

$NH_2RCO_2^- + H_2O \rightleftharpoons {}^+NH_3RCO_2^- + OH^-$ $\qquad \Delta C^0_{p_i} \cong -32$ (Mean)

The heat capacities of the acid dissociations of ampholytes vary from -32 to -38, whereas those of the basic dissociation range from -29 to -39 if the anomalous result of -22 for the basic dissociation of glycine be omitted. It is important to note that although these reactions are of quite different electrical types, $\Delta C^0_{p_i}$ is roughly the same for all of them. These results may be stated in a more significant way by comparison with a common reference reaction. Thus, we have chosen

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ $\qquad \Delta C^0_{p_i} \cong -47$

although other reactions such as the ionization of acetic acid would be suitable. Subtracting the above three reactions in turn from the water reaction, and including the first of them, we obtain

(a) $HA + H_2O \rightleftharpoons A^- + H_3O^+$ $\qquad \Delta C^0_{p_i} \cong -(36 \rightarrow 41)$

(b) $A^- + H_2O \rightleftharpoons HA + OH^-$ $\qquad \Delta C^0_{p_i} \cong -(6 \rightarrow 11)$

(c) ${}^+NH_3RCO_2^- + H_2O \rightleftharpoons {}^+NH_3RCO_2H + OH^-$ $\qquad \Delta C^0_{p_i} \cong -11$

(d) ${}^+NH_3RCO_2^- + H_2O \rightleftharpoons NH_2RCO_2^- + H_3O^+$ $\qquad \Delta C^0_{p_i} \cong -16$

The isoelectric reactions (b) are accompanied by appreciable changes in $\Delta C^0_{p_i}$ which is contrary to the assumption that $\Delta H_{(D\to\infty)}$ is independent of the temperature, and to the result expressed by equation (15-10-8).

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* V. K. LaMer and F. Brescia [*J. Am. Chem. Soc.*, **62**, 617 (1940)] on the basis of the preceding theory have obtained an expression for the empirical constant, p, in equation (15-6-6) of Harned and Embree. J. L. Magee, T. Ri and H. Eyring [*J. Chem. Phys.*, **9**, 419 (1941)] have extended the ideas of Gurney and Baughan to include a more detailed discussion of the mechanism of the ionization process and the influence of temperature and change of solvent media on ionization constants.

In Fig. (15-10-3), a plot of $\Delta C^0_{p_i}$ against the number of carbon atoms of the first four acids of the aliphatic series is shown. There is a definite decrease in $(-\Delta C^0_{p_i})$ with increasing complexity of the acids. This would not be the case if $\Delta C^0_{p_i}$ were zero for isoelectric reactions. If we subtract (c) from (d), we obtain another isoelectric reaction,

(e) $^+NH_3RCO_2H + OH^- \rightleftharpoons NH_2RCO_2^- + H_3O^+ \qquad \Delta C^0_{p_i} \cong -5$

in which $\Delta C^0_{p_i}$ is indeed low. Considering the errors involved, this value may be nearly zero.

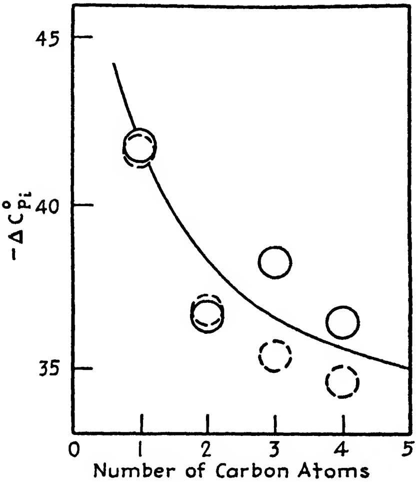

Fig. (15-10-3)
The heat capacity of ionization reactions as a function of the number of carbon atoms in aliphatic acids. Broken circles, Everett and Wynne-Jones, Equation (15-3-6). Circles, Table (15-6-1), Equation (15-6-9).; diameter of circles equals 1 cal.

Two general conclusions result from these considerations. (1) Values of $(-\Delta C^0_{p_i})$ for isoelectric reactions are considerably smaller than for other types. This indicates that the Coulombic forces are responsible for a considerable part of the effect. (2) It is also clear that the chemical type, as well as the electrical type, of these reactions, is important. This factor adds greatly to the complexity of the phenomena.

In view of the inadequacy of the Born expression for the interpretation of ionization equilibria and the thermodynamic properties of the ions, attempts have been recently made to compute these properties in terms of the orientation of water molecules around the ions. Bernal and Fowler,[98] from considerations of the structure of liquid water and its orientation around ions, have computed heats of solutions of ions in water. Eley and Evans[99] have extended this theory to the computation of the entropy of ions derived from the investigations of Latimer.[100] Everett and Coulson[101]

[98] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

[99] D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).

[100] W. M. Latimer, K. S. Pitzer and C. M. Shansky, *J. Chem. Phys.*, **7**, 108 (1939).

[101] D. H. Everett and C. A. Coulson, *Trans. Faraday Soc.*, **36**, 633 (1940).

have attempted to employ this procedure for the computation of ionic heat capacities, and the estimation of the heat capacity changes of the ionization of a weak acid. After summing the orientation effect of the water molecules in the immediate neighborhood of the ions, and the Born electrostatic effect outside the tetrahedral shell of the water molecules, they obtain values of $(-\Delta C^0_{p_i})$ which are less than those observed, even though values of the ionic radii of 1 Å. are employed. They suggest that other effects, particularly that due to the "free volume" of the water molecules, may explain the discrepancy.*

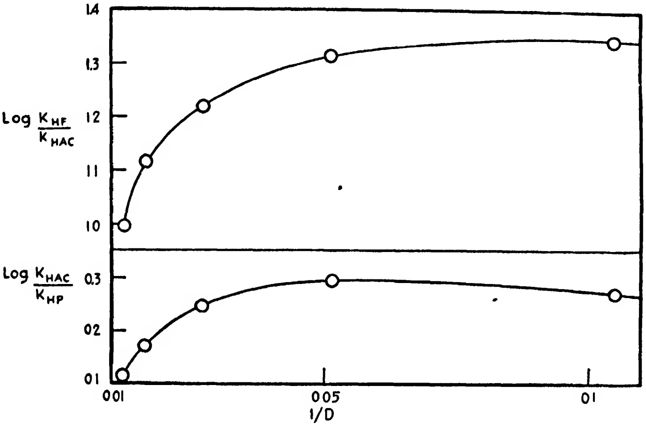

Fig. (15–11–1). Variations of the logarithms of ionization constant ratios as a function of dielectric constant in dioxane-water mixtures at 25°. HF, formic acid; HAc, acetic acid; HP, propionic acid.

(11) Additional Observations

These recent investigations of ionization constants as a function of the medium, and of the temperature, show that considerable care must be taken in attempting to develop a theory of the relation of ionization constants to the constitution of the weak electrolytes. Wynne-Jones[102] showed the ratio of the ionization constants of two weak electrolytes to be a function of the dielectric constant of the medium. His results (obtained in media of high dielectric constant) indicated that the logarithm of this ratio varied linearly with $1/D$. The more recent and more extended results do not

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* Extensive investigations of relative strengths of acids in butyl alcohol have been made by L. A. Wooten and L. P. Hammett [*J. Am. Chem. Soc.*, **57**, 2289 (1935)] by the electrometric method, and R. B. Mason and M. Kilpatrick [*Ibid.*, **59**, 572 (1937)] who employed a photoelectric colorimeter. These studies have been extended to other solvents by L. J. Minnick and M. Kilpatrick [*J. Phys. Chem.*, **43**, 259 (1939)] and J. H. Elliott and M. Kilpatrick [*Ibid.*, **45**, 454 (1941); **45**, 466 (1941); **45**, 472 (1941); **45**, 485 (1941)].

[102] W. F. K. Wynne-Jones, *Proc. Roy. Soc.*, **140**, 440 (1933).

confirm a linear variation. In Fig. (15-11-1), the logarithm of the ratios of the ionization constants of formic to acetic acids (upper curve), and acetic to propionic acids (lower curve) have been plotted against $1/D$. The plots possess greater curvature as $1/D$ decreases, and their extrapolation to $0(D = \infty)$ without an exact theoretical function is without significance.

It is also apparent from Fig. (15-11-2), in which $(-\log K_A)$ for acetic and butyric acids is plotted against the temperature, that the ratio of the ionization constants of two weak electrolytes changes considerably with

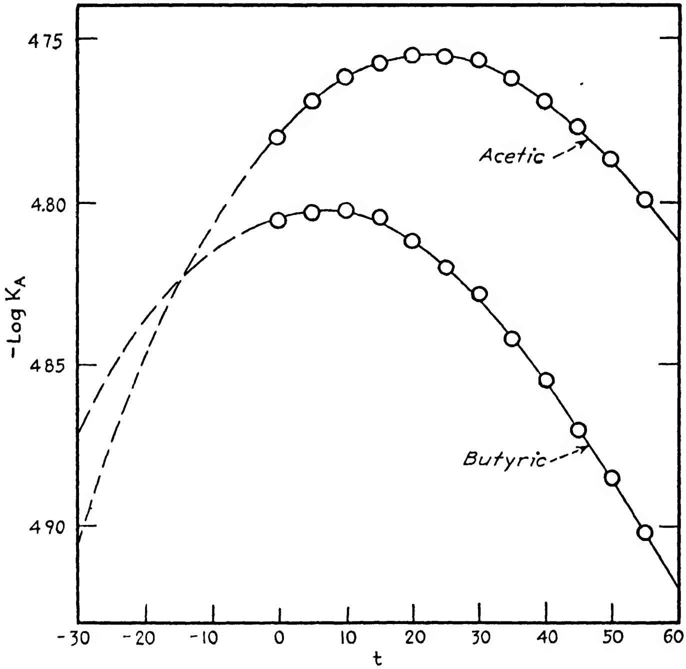

Fig. (15-11-2). Variation of ionization constants of acetic and butyric acids with temperature.

temperature. Indeed, if the curves be extended below 0°, they cross at −15°. Above this temperature, acetic acid is more highly dissociated than butyric acid whereas below this temperature butyric acid is the stronger.

The ionization constant has usually been employed as a measure of the strength of an electrolyte, and the ratio of ionization constants as a measure of the relative strengths. The preceding observations show that the relative "strength" is a function of the nature of the medium and the temperature, and is by no means a fixed quantity. To adequately understand acid and base equilibria, it will be necessary to take into account the effects of these and other variables, such as pressure and salt concentration.

Appendix A

TABLE (6-2-1A). THE EQUIVALENT CONDUCTANCES OF ELECTROLYTES IN AQUEOUS SOLUTIONS AT 25°

	$c^* = 0$	0.0005	0 001	0.005	0 01	0.02	0 05	0.1	Reference
HCl	426 16	422 74	421 36	415 80	412 00	407 24	399 09	391 32	1, 19
LiCl	115 03	113 15	112 40	109 40	107 32	104 65	100 11	95 86	1, 2, 3
NaCl	126 45	124 50	123 74	120 65	118 51	115 76	111 06	106 74	4, 20
KCl	149.86	147.81	146 95	143.55	141 27	138 34	133 37	128 96	1, 20
NH_4Cl	149 7	..	. .	.	141.28	138 33	133 29	128.75	5
KBr	151 9		..	146 09	143 43	140.48	135 68	131.39	6, 7
NaI	126 94	125 36	124 25	121 25	119 24	116 70	112 79	108 78	8
KI	150 38	.		144 37	142 18	139 45	134 97	131 11	7
KNO_3	144 96	142 77	141 84	138 48	132 82	132 41	126 31	120 40	1
$KHCO_3$	118 00	116 10	115 34	112 24	110 08	107 22	.		9
NaO_2CCH_3	91 0	89.2	88 5	85 72	83 76	81 24	76 92	72 80	10
$NaO_2C(CH_3)_2CH_3$	82 70	81 04	80 31	77 58	75 76	73 39	69.32	65 27	11
NaOH	247.8	245 6	244 7	240 8	238 0				18
$AgNO_3$	133 36	131 36	130 51	127 20	124 76	121.41	115.24	109.14	1
$MgCl_2$	129 40	125 61	124.11	118 31	114 55	110 04	103 08	97.10	12
$CaCl_2$	135 84	131 93	130 36	124 25	120 36	115 65	108 47	102 46	12
$SrCl_2$	135 80	131 90	130 33	124 24	120 29	115 54	108 25	102 19	12
$BaCl_2$	139.98	135 96	134 34	128 02	123.94	119 09	111 48	105.19	12
Na_2SO_4	129 9	125 74	124 15	117.15	112 44	106.78	97.75	89.98	7
$CuSO_4$	133 6	121 6	115 26	94 07	83 12	72 20	59 05	50 58	13
$ZnSO_4$	132 8	121 4	115 53	95 49	84 91	74 24	61 20	52.64	13
$LaCl_3$	145 8	139 6	137.0	127 5	121 8	115 3	106 2	99.1	6, 14
$K_3Fe(CN)_6$	174 5	166.4	163 1	150 7	.....	. .	. .	......	15
$K_4Fe(CN)_6$	184 5	.. ..	167.24	146 09	134.83	122 82	107.70	97.87	16, 17

* Concentrations expressed in equivalents per liter.

(1) T. Shedlovsky, *J. Am Chem Soc*, **54,** 1411 (1932)
(2) D. A. MacInnes, T Shedlovsky and L G Longsworth, *Ibid*, **54,** 2758 (1932).
(3) K. A Krieger and M. Kilpatrick, *Ibid*, **59,** 1878 (1937)
(4) T. Shedlovsky, A S Brown, and D A MacInnes, *Trans Electrochem Soc*, **66,** 165 (1934).
(5) L G Longsworth, *J Am Chem Soc*, **57,** 1185 (1935)
(6) G Jones and C F Bickford, *Ibid*, **56,** 602 (1934)
(7) Unpublished measurements of T Shedlovsky and L G. Longsworth quoted by MacInnes in "Principles of Electrochemistry," Reinhold Publishing Corp, New York (1939), p 339.
(8) P A Lasselle and J G Aston, *J Am Chem Soc*, **55,** 3067 (1933).
(9) T Shedlovsky and D A MacInnes, *Ibid*, **57,** 1705 (1935)
(10) D. A MacInnes and T Shedlovsky, *Ibid*, **54,** 1429 (1932)
(11) D. Belcher, *Ibid*, **60,** 2744 (1938)
(12) T Shedlovsky and A S Brown, *Ibid*, **56,** 1066 (1934)
(13) B B. Owen and R W Gurry, *Ibid*, **60,** 3074 (1938). These values have been corrected for presence of $M(OH)^+$ and HSO_4^- ions
(14) L. G. Longsworth and D. A MacInnes, *Ibid*, **60,** 3070 (1938).
(15) G S. Hartley and G W Donaldson, *Trans Faraday Soc*, **33,** 457 (1937)
(16) G Jones and F C. Jelen, *J Am Chem Soc*, **58,** 2561 (1936)
(17) E. Swift Jr, *Ibid*, **60,** 728 (1938)
(18) V. Sivertz, R E Reitmeier, and H V Tartar, *Ibid*, **62,** 1379 (1940)
(19) Values up to c equal to 12 and at 10° intervals between 5 and 65° are given by B. B. Owen and F. H. Sweeton, *Ibid*, **63,** 2811 (1941).
(20) Values from 15° to 45° are given by H. E. Gunning and A. R. Gordon, *J. Chem. Phys.*, **10,** 126 (1942).

TABLE (6-6-1A). CATION TRANSFERENCE NUMBERS IN AQUEOUS SOLUTIONS AT 25° BY THE MOVING BOUNDARY METHOD

Electrolyte	Ref.	Λ^0	$\mathfrak{S}_{(T_+)}$*	T_+^0	Concentration (equivalents/liter)				
					.01	02	.05	.10	.20
HCl...	a	426.17	+0.04507	.8209	.8251	.8266	.8292	.8314	.8337
$NaC_2H_3O_2$	b	90.99	+ .03336	.5507	.5537	.5550	.5573	.5594	.5610
$KC_2H_3O_2$	f	114.40	+ .07467	.6427	.6498	.6523	.6569	.6609	.....
KNO_3	b	144.96	+ .00297	.5072	.5084	.5087	.5093	.5103	.5120
NH_4Cl	b	149.94	− .00363	.4909	.4907	.4906	4905	.4907	.4911
KCl	a	149.86	− .00376	.4906	.4902	.4901	.4899	.4898	.4894
KI	b	150 29	− .00430	.4892	.4884	.4883	.4882	.4883	.4887
KBr	b	151.63	− .00596	.4849	.4833	.4832	.4831	.4833	.4841
$AgNO_3$	c	133.36	− .01604	.4643	.4648	.4652	.4664	.4682	.....
NaCl	a	126.43	− .04910	3963	.3918	.3902	.3876	.3854	.3821
LiCl.	a	115.03	− .08514	.3364	.3289	3261	.3211	.3168	.3112
$CaCl_2$	b	135.84	− .26174	.4380	.4264	.4220	.4140	.4060	.3953
Na_2SO_4	b	129.9	+ .0632	.386	.3848	.3836	.3829	.3828	.3828
K_2SO_4	d	153.3	+ .1482	.479	.4829	.4848	.4870	.4890	4910
$LaCl_3$	e	145.9	− .5491	.477	.4625	.4576	.4482	.4375	.4233

References to sources of data: (a) L. G. Longsworth, *J. Am. Chem. Soc.*, **54**, 2741 (1932); (b) L. G. Longsworth, *Ibid.*, **57**, 1185 (1935); (c) D. A. MacInnes and I. A. Cowperthwaite quoted by D. A. MacInnes and L. G. Longsworth, *Chem. Rev.*, **11**, 171 (1932); (d) G. S. Hartley and G. W. Donaldson, *Trans. Faraday Soc.*, **33**, 457 (1937); (e) L. G. Longsworth and D. A. MacInnes, *J. Am. Chem. Soc.*, **60**, 3070 (1938); (f) D. J. LeRoy and A. R. Gordon, *J. Chem. Phys*, **6**, 398 (1938).

* These values of $\mathfrak{S}_{(T_+)}$, calculated by equation (6-6-4a), require that the concentration be expressed in moles per liter. If the data are plotted against the square root of the equivalent concentration, the limiting slopes become −0.18508, +0.0447, +0.1048 and −0.3170 for the last four salts in the table.

TABLE (8-2-1A). ϕ_L, RELATIVE APPARENT MOLAL HEAT CONTENTS IN DILUTE AQUEOUS SOLUTIONS AT 25°

Part I

$\sqrt{m}$	Ref	.01	.02	.04	.06	.08	.10	.15	.20	.25	.30	Δ^*
HCl	(1)	4.8	9.6	19 2	29	38	48	71	93	114	134	0
LiCl	(2)	4.3	8 4	16.6	25	33	40	60	78	96	114	81
LiBr	(3, 16)	4.2	8.2	16 2	24	32	39	59	76	93	110	7
NaCl	(4)	4.5	8.5	17.0	25	33	40	55	67	77	83	2
NaBr	(5, 9)	4.2	8.4	16 4	24	31	38	52	62	69	73	2
$NaNO_3$	(7)	4 3	8.5	16 5	23	29	34	43	44	40	31^a	4.5
$NaClO_3$	(7)	4.2	8.4	17.0	24	30	35	43	49	48	43^a	1
$NaBrO_3$	(7)	4 3	8.5	16.7	24	30	34	39	38	34	26^a	1
$NaIO_3$	(7)	4.0	7.5	14 0	19	21	21	16	0	−24	-57^a	2
NaOH	(8)	4.8	9.5	19 0	28	36	44	62	77	90	99	0
KF	(6)	4.7	9 2	18 3	27	36	45	66	83	99	113	6
KCl	(9, 10, 12)	4.5	8.5	16 0	24	31	38	54	65	72	77	2
KBr	(5, 9)	4.2	8.2	15.6	23	29	36	47	55	61	64	2
KNO_3	(12)	4.1	8.0	15 1	20	23	24	22	12	−6	-29^b	4
$KClO_3$	(13)	4.2	8 2	15.5	21	26	29	28	19	4	-19^a	3
$KClO_4$	(13)	4.3	8.0	13.0	16	16	14	−3	−28	−59	-109^a	3
RbF	(12)	4	8	14	20	26	31	44	57	69	80^c	4
CsCl	(16)	4	8	15	21	27	32	43	49	51	51^d	2.5
NH_4Cl	(11)	4.4	8 6	17	25	33	39	53	66	78	88^e	7
Li_2SO_4	(15)	24	47	91	135	177	218	307	377	438	488	3
Na_2SO_4	(15)	23	44	84	119	150	175	216	237	243	237	2
K_2SO_4	(15)	22	42	81	116	146	171	214	238	249	250	2
Rb_2SO_4	(15)	21	41	79	114	143	166	200	215	226	219	2
Cs_2SO_4	(15)	20	39	71	99	121	139	160	161	152	137	3
$MgCl_2$	(14)	24	47	89	129	167	202	280	350	415	471	0
$MgBr_2$	(14)	23	45	86	124	161	196	271	334	389	437	0
$Mg(NO_3)_2$	(15)	23	44	81	119	155	187	254	304	344	376	5
$CaCl_2$	(14)	24	47	88	127	165	199	275	340	398	445	1
$CaBr_2$	(14)	23	44	83	120	154	186	252	308	355	394	1
$Ca(NO_3)_2$	(15)	22	43	79	111	136	158	200	222	230	224	5
$SrCl_2$	(14)	23	46	86	124	161	195	270	332	381	420	1
$SrBr_2$	(14)	23	44	82	120	152	182	244	293	333	366	1
$Sr(NO_3)_2$	(15)	21	40	72	99	122	140	166	169	159	135	5
$BaCl_2$	(14)	23	46	86	124	160	194	268	329	375	412	2
$BaBr_2$	(14)	22	43	81	117	150	180	240	287	325	356	1
$Ba(NO_3)_2$	(15)	19	36	59	70	72	66	20	−46	−128	−223	5
$MgSO_4$	(15)	44	118	154	369	463	542	685	784	842		−25
$CaSO_4$	(12)	47	125	283	415	523	611	700^f				−25
$ZnSO_4$	(17)	51	127	273	396	501	581	731	826	896	953	−25
$CdSO_4$	(17)	70	180	386	554	693	807	1018	1150	1246	1324	−40
$CuSO_4$	(17)	62	159	345	501	618	713	885	1012	1109	1183	−35

* Approximate increase involved in new extrapolation.

[a] At $\sqrt{m} = 0.3162$.

[b] At $\sqrt{m} = 0.35$, $\phi_L = -55$.

[c] At $\sqrt{m} = 0.35, 0.40, 0.45,$ and 0.50, $\phi_L = 91, 101, 111,$ and 120, respectively.

[d] At $\sqrt{m} = 0.35,$ and 0.40, $\phi_L = 49,$ and 44, respectively.

[e] At $\sqrt{m} = 0.4, 0.5, 0.6, 0.72, 0.88,$ and 1, $\phi_L = 101, 111, 127, 136, 142,$ and 143, respectively.

[f] At $\sqrt{m} = 0.125$.

(1) J M. Sturtevant, *J. Am. Chem. Soc.*, **62**, 584 (1940); Corrections, *Ibid* , **62**, 3265 (1940).

(2) E Lange and F. Dürr, *Z physik. Chem* , **121**, 361 (1926).

(3) E Lange and E. Schwartz, *Ibid.*, **133**, 129 (1928).

(4) A. L. Robinson, *J. Am. Chem. Soc* , **54**, 1311 (1932).

(5) H. Hammerschmid and A. L Robinson, *Ibid*, **54,** 3120 (1932).
(6) E. Lange and A. Eichler, *Z physik Chem.*, **129,** 285 (1927).
(7) E. Lange and A L Robinson, *Ibid*, **148A,** 97 (1930).
(8) J. M. Sturtevant, *J. Am Chem Soc.*, **62,** 2276 (1940).
(9) J. Wüst and E Lange, *Z physik Chem.*, **116,** 161 (1925).
(10) E Lange and P. A Leighton, *Z. Elektrochem.*, **34,** 566 (1928).
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(12) E. Lange and J Monheim, *Ibid*, **150A,** 349 (1930).
(13) M. Andauer and E. Lange, *Ibid*, **165A,** 89 (1933).
(14) E. Lange and H. Streeck, *Ibid*, **152A,** 1 (1931)
(15) E. Lange and H Streeck, *Ibid.*, **157A,** 1 (1931).
(16) E. Lange and J Messner, *Z Elektrochem*, **33,** 431 (1927)
(17) E Lange, J. Monheim, and A L. Robinson, *J. Am. Chem. Soc*, **55,** 4733 (1933).

TABLE (8-2-1A).* ϕ_L, RELATIVE APPARENT MOLAL HEAT CONTENTS IN WATER AT 25°
Part II

m	HCl	LiCl	LiBr	NaCl	NaBr	NaOH	KF	KCl	KBr
0.1	140	119	117	83	73	102	117	78	64
.2	191	162	156	90	72	117	143	81	70
.3	229	194	185	84	63	121	155	76	46
.4	261	220	210	72	53	119	163	63	29
.5	290	242	232	58	41	114	169	48	9
.6	317	263	252	42	27	108	174	33	−13
.7	342	283	271	26	13	101	179	18	−35
.8	368	300	289	9	−3	94	183	3	−58
.9	391	318	306	−7	−20	86	186	−12	−81
1.0	414	334	322	−23	−37	78	190	−26	−104
1.2	460	365	352	−57	−72	61	198	−55	−148
1.5	526	410	394	−105	−124	38	209	−99	−212
1.7	569	438	421	−136	−160	25	215	−128	−251
2.0	633	479	460	−177	−212	8	223	−169	−306
2.5	739	547	524	−224	−294	−10	234	−236	−394
3.0	847	615	588	−304	−364	−17	246	−300	−480
3.5	954[a]	683	652	−355	−424	−12	260	−355	−559
4.0	...	758	716	−395	−482	3	279	−405	−631
4.5	...	838	780	−427	−533	36[a]	305	−448	−697
5.0	...	921	849	−453	−578	..	334	−472[c]	−760
5.5	...	1007	920	−470	−617	...	368	...	−819
6.0	...	1098	994	−483[b]	−648	..	404	...	−839[d]

[*] Sources of data are indicated in Part I of this table.
[a] Extrapolated.
[b] For sat. soln., $m = 6.12$.
[c] For sat. soln., $m = 4.82$.
[d] For sat. soln., $m = 5.68$.

TABLE (8-2-2A).* $\bar{L}_2$, RELATIVE PARTIAL MOLAL HEAT CONTENTS IN DILUTE AQUEOUS SOLUTIONS AT 25°

Part I

$\sqrt{m}$	01	02	04	.06	.08	.10	.15	.20	.25	.30
HCl	7.2	14.3	28.6	43	57	71	105	136	165	193
LiCl	6.4	12.5	24 7	37	49	60	89	115	141	165
LiBr	6.3	12.2	24.0	35	47	59	86	111	136	159
NaCl	6.5	12.5	24.0	35	46	57	77	92	100	104
NaBr	6.3	12.2	24 2	35	45	54	70	79	83	82
$NaNO_3$	6.0	11.5	22 5	31	40	46	51	40	27	13[a]
$NaClO_3$	6.6	12 9	24.4	34	41	47	55	55	45	27[a]
$NaBrO_3$	6.5	12 7	24.2	33	39	43	42	33	22	8[a]
$NaIO_3$	5.8	11.0	19.8	24	24	20	0	−41	−88	−143[a]
NaOH	7.1	14.0	28 0	42	54	65	89	104	117	125
KF	7.0	13.8	27.4	41	54	66	94	117	136	151
KCl	6.5	12.5	24.0	36	46	55	71	82	88	91
KBr	6.1	12.1	23.0	33	41	48	62	69	71	68
KNO_3	5.7	11.0	20 3	26	29	28	12	−17	−57	−103[b]
$KClO_3$	6.7	12.3	21.7	28	32	32	20	−6	−37	−77[a]
$KClO_4$	6.2	11.3	16.6	17	13	4	−34	−86	−148	−228[a]
NH_4Cl	6.7	13	25	37	47	56	75	91	105	121[a]
Li_2SO_4	35	69	135	200	260	317	424	508	578	620
Na_2SO_4	33	64	122	170	206	229	261	264	241	287
K_2SO_4	32	62	119	164	200	226	262	272	266	233
Rb_2SO_4	31	61	115	162	195	216	233	233	225	201
Cs_2SO_4	29	57	102	136	161	176	172	152	124	87
$MgCl_2$	36	70	130	187	240	287	388	484	567	626
$MgBr_2$	34	67	125	181	233	278	372	453	519	564
$Mg(NO_3)_2$	32	62	121	175	224	264	339	393	437	465
$CaCl_2$	35	68	127	185	237	282	378	463	530	576
$CaBr_2$	34	65	120	172	219	260	340	410	462	498
$Ca(NO_3)_2$	31	62	114	152	183	212	245	250	234	191
$SrCl_2$	34	66	125	180	232	277	372	443	492	528
$SrBr_2$	33	64	119	170	216	254	324	383	423	452
$Sr(NO_3)_2$	30	58	102	137	159	180	185	161	116	46
$BaCl_2$	34	66	124	180	231	275	369	435	480	513
$BaBr_2$	33	64	118	169	214	251	317	372	412	439
$Ba(NO_3)_2$	27	51	75	80	68	37	−65	−195	−352	−528
$MgSO_4$	79	191	380	525	631	715	865	937	951	...
$CaSO_4$	80	208	418	588	712	802	882[c]	...	...	...
$ZnSO_4$	86	202	415	595	698	765	893	989	1064	1120
$CdSO_4$	119	290	567	785	939	1071	1266	1380	1467	1542
$CuSO_4$	106	256	518	711	826	930	1115	1242	1321	1375

* Sources of data are indicated in Table (8-2-1A).

[a] At $\sqrt{m} = 0.3162$.

[b] At $\sqrt{m} = 0.35$, $\bar{L}_2 = -149$.

[c] At $\sqrt{m} = 0.125$.

TABLE (8-2-2A).* L_2, RELATIVE PARTIAL MOLAL HEAT CONTENTS IN WATER AT 25°
Part II

m	HCl	LiCl	LiBr	NaCl	NaBr	NaOH	KF	KCl	KBr
0.1	202	173	166	102	78	127	155.	91	70
.2	273	234	223	90	58	133	179	72	39
.3	332	279	267	62	31	122	190	44	1
.4	383	318	305	28	2	105	197	12	−42
.5	430	352	339	−10	−30	89	203	−21	−89
.6	475	384	371	−48	−66	69	209	−55	−136
.7	518	313	400	−85	−100	51	215	−85	−180
.8	560	440	424	−120	−136	33	220	−115	−224
.9	604	467	448	−156	−173	13	226	−146	−268
1.0	645	491	471	−188	−206	−4	231	−176	−309
1.2	728	540	515	−252	−280	−37	240	−233	−390
1.5	853	614	580	−343	−382	−70	254	−316	−507
1.7	934	665	625	−398	−448	−81	262	−370	−579
2.0	1055	744	696	−466	−538	−86	274	−446	−678
2.5	1269	885	821	−556	−654	−73	291	−558	−823
3.0	1484	1044	960	−626	−751	−24	318	−648	−956
3.5	1690[a]	1205	1097	−671	−832	57	376	−721	−1076
4.0	....	1375	1237	−688	−897	180	456	−782	−1181
4.5	....	1524	1386	−683	−945	....	546	−828	−1269
5.0	....	1743	1544	−656	−981	....	643	−853[c]	−1345
5.5	....	1947	1700	−620	−1001	....	754	....	−1392
6.0	....	2163	1865	−570[b]	−992	....	884	....	−1412[d]

* Sources of data are indicated in Table (8-2-1A).

[a] Extrapolated.

[b] For sat. soln., $m = 6.12$.

[c] For sat. soln., $m = 4.82$.

[d] For sat. soln., $m = 5.68$.

TABLE (9-5-1A).* VALUES OF $-\text{Log}\ \gamma_{\pm}$ AT THE FREEZING POINTS OF AQUEOUS SOLUTIONS (1)

	Ref	$m =$ 0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.5	0.7	1.0
LiCl	(4)	0.0343	0.0463	0.0605	0.0830	0.1017	0.1192	0.1262	0.1281	0.1220	0.1055
LiBr	(4)	.0298	0400	.0525	.0720	.0877	.1008	.1041	.0996	.0875	.0621
$LiNO_3$	(2)	.0304	.0412	.0543	.0760	.0947	.1125	.1204	.1246	.1220	.1122
$LiClO_3$	(5)	.0302	.0406	.0537	0745	.0915	.1070	.1131	.1141	.1080	.0923
$LiClO_4$	(5)	.0290	.0386	.0506	.0692	.0835	0940	.0948	0856	.0697	.0396
LiO_2CH	(6)	.0311	.0424	.0573	0826	.1057	.1312	.1465	.1637	.1729	.1802
LiO_2CCH_3	(6)	.0309	.0421	.0564	.0799	.1000	.1201	.1298	.1373	.1370	.1296
NaCl	(4)	.0306	.0416	.0557	.0804	1039	.1309	.1476	.1690	.1824	.1948
NaBr	(4)	0282	.0377	.0503	.0721	.0928	.1161	.1300	.1465	.1554	.1622
$NaNO_3$	(2)	.0311	.0428	0584	.0870	1165	1543	.1812	2214	.2525	.2907
$NaClO_3$	(5)	.0316	.0433	.0588	.0865	.1139	1482	.1718	.2066	.2330	.2644
$NaClO_4$	(5)	0321	.0439	.0588	0857	1116	.1429	.1640	.1936	.2151	.2393
NaO_2CH	(6)	.0308	.0416	.0557	0794	1012	.1262	.1415	.1606	.1720	.1829
NaO_2CCH_3	(6)	.0306	.0412	0544	0754	.0928	.1089	.1160	.1199	.1172	.1074
KCl	(4)	.0317	.0434	.0587	0857	.1121	.1430	.1632	.1903	.2093	.2302
KBr	(4)	.0313	.0428	.0578	.0839	.1091	.1392	.1590	.1855	.2038	.2236
KNO_3	(2)	.0329	.0461	.0645	.1001	.1391	.1923	.2336	.2979	.3502	.4158
$KClO_3$	(5)	.0301	.0418	.0583	.0913	.1277	.1771	....	....	....	.....
$KClO_4$	(5)	.0347	0492	.0697	..	..	...	....	...	....	....
KO_2CH	(6)	.0302	.0406	.0543	.0774	.0989	.1221	.1356	.1509	1589	.1648
KO_2CCH_3	(6)	.0306	.0411	.0544	.0750	.0915	.1061	.1113	.1107	.1034	.0867
NH_4Cl	(3)	.0405	0555	.0732	.1025	1298	.1616	.1818	.2081	.2249	.2423
NH_4Br	(3)	.0451	0605	.0786	.1082	1351	.1657	.1849	.2097	.2260	.2427
NH_4I	(3)	.0375	.0509	.0674	.0947	.1193	.1479	.1659	.1897	.2052	.2218
NH_4NO_3	(3)	.0401	.0547	0736	.1064	.1390	.1806	.2101	.2542	.2884	.3306
$(NH_4)_2SO_4$	(3)	.1308	.1749	.2294	3194	.4023	.4994	.5633	.6514	.7141	.7836

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* Results for CsCl and the iodides of Li, Na, K, and Cs are available up to about 0.1 *N*. See J. Lange, *Z. physik. Chem.*, **177A**, 193 (1936).

(1) Calculated by equation (9-5-25), the term

$$-\frac{1000}{\nu M_1}\int_0^m \frac{dX}{m}$$

being neglected.

(2) G. Scatchard, P. T. Jones and S. S Prentiss, *J. Am Chem Soc* , 54, 2690 (1932).

(3) G. Scatchard and S. S. Prentiss, *Ibid* , 54, 2696 (1932). For tetrasubstituted ammonium chlorides and iodides, see J. Lange, *Z. physik. Chem.*, 168A, 147 (1934)

(4) G. Scatchard and S S. Prentiss, *J Am Chem. Soc* , 55, 4355 (1933).

(5) G. Scatchard, S. S. Prentiss and P T Jones, *Ibid.*, 56, 805 (1934).

(6) G. Scatchard and S. S. Prentiss, *Ibid.*, 56, 807 (1934).

TABLE (11-1-1A). DIELECTRIC CONSTANTS AND VISCOSITIES OF DIOXANE-WATER MIXTURES. CONSTANTS OF EQUATIONS (5-3-4) AND (5-3-5)

Wt. % dioxane	t°	D_0	$100\eta_0$	α^*	β^*
20	15	64.01	1.689	0.3258	35.73
20	25	60.79	1.292	.3345	47.17
20	35	57.73	1.017	.3439	60.42
20	45	54.83	0.8243	.3542	75.29
45	15	40.70	2.453	.6425	30.85
45	25	38.48	1.837	.6642	41.66
45	35	36.37	1.430	.6878	54.14
45	45	34.39	1.142	.7131	68.62
70	15	18.72	2.483	2.060	44.94
70	25	17.69	1.918	2.131	58 85
70	35	16.72	1.522	2.207	75.03
70	45	15.80	1.232	2.290	93.83
82	15	10.01	2.106	5.268	72.46
82	25	9.53	1.671	5.389	92.02
82	35	9.06	1.356	5.532	114.39
82	45	8.62	1.117	5.683	140.12

TABLE (11-3-1A). LIMITING SLOPES FOR ACTIVITY COEFFICIENTS IN DIOXANE-WATER MIXTURES. DIELECTRIC CONSTANTS
X = Weight Percent of Dioxane

t	$X = 20$		$X = 45$	
	D	$\mathcal{S}_{(f)}$	D	$\mathcal{S}_{(f)}$
0	69.16	0.6989	44.28	1.364
5	67.39	.7072	43.05	1.385
10	65.68	.7156	41.86	1.406
15	64.01	.7245	40.70	1.429
20	62.38	.7339	39.57	1.453
25	60.79	.7437	38.48	1.477
30	59.94	.7540	37.41	1.503
35	57.73	.7648	36.37	1.530
40	56.26	.7760	35.37	1.557
45	54.83	.7877	34.39	1.586
50	53.43	.7999	33.43	1.616

t	$X = 70$		$X = 82$	
	D	$\mathcal{S}_{(f)}$	D	$\mathcal{S}_{(f)}$
0	20.37	4.373	....	.....
5	19.81	4.437	10 52	11.47
10	19.25	4.510	10.27	11.58
15	18.72	4.581	10.01	11.72
20	18.20	4.657	9.77	11.85
25	17.69	4.738	9.53	11.98
30	17.20	4.820	9.29	12.16
35	16.72	4.907	9 06	12.30
40	16 26	4.995	8.84	12.46
45	15.80	5.092	8.62	12.64
50	15.37	5.185	....	.....

Table (11-3-2A). Densities of Pure Solvents, and of Solutions of Hydrochloric Acid in Dioxane-Water Mixtures. Parameters of Equations Designated. (c May Be Obtained from m by, $c/m = d_0 - Am$, with an Accuracy of 0.1%.) Δ = Percentage Difference between Calculated and Observed Values. Δ_1 Refers to Equation for d; Δ_2 Refers to Equation for c/m. X = Weight Percent of Dioxane[*]

$X = 20$

$d = d_0 + am - bm^3 + em \log m$; Valid to 3 M

t	d_0	a	b	e	Δ_1	A	Δ_2
0	1.0271	0.0133	0 00032	0.008	0.02	0.02159	0.16
5	1.0245	.0142	.00035	.007	.02	.02116	.12
10	1.0219	.0149	.00025	.004	.02	.02077	.09
15	1.0193	.0154	.00005	.000	.02	.02038	.05
20	1 0167	.0160	00013	..	.02	.02013	.03
25	1.0141	.0161	00013	. .	.01	.01989	.02
30	1.0115	.0167	.00019	. . .	.02	.01965	.01
35	1.0090	.0168	.00020	....	.01	01954	.01
40	1.0063	.0168	00018	....	.02	01933	.01
45	1.0038	.0166	00015	. . .	02	.01922	.02
50	1.0014	.0164	00014	....	.01	01933	.02

$X = 45$

$d = d_0 + am - bm^3$; Valid to 3 M

t	d_0	a	b	Δ_1	A	Δ_2
0	1.0484	......	....	....	(0.02267)[a]	0.07
5	1.0450	0.0143	0.00005	0.01	.02223	.05
10	1.0419	.0145	.00008	.01	.02209	.05
15	1.0386	.0144	.00002	01	.02171	.07
20	1.0353	.0147	.00004	.01	.02148	.06
25	1 0319	.0150	.00010	.01	.02138	.04
30	1.0282	.0153	.00011	.01	02109	.03
35	1.0246	.0156	.00012	.01	.02072	.02
40	1.0210	.0157	.00012	.01	.02052	.01
45	1.0175	.0160	.00013	.01	.02021	.02
50	1.0139	.0163	.00016	.01[a]	.01995	.01

[a] Extrapolated.

$X = 70$

$d = d_0 + am + em \log m$; Valid to 1.5 M

t	d_0	a	e	Δ_1	A	Δ_2
0	1.0619	......	......	....	(0.02559)[a]	....
5	1.0570	0.0123	0.0085	0.03	.02489	0.13
10	1.0522	.0128	.0080	.03	.02420	.12
15	1.0474	.0135	.0060	.02	.02352	.11
20	1.0426	.0142	.0040	.02	.02275	.07
25	1.0378	.0150	.0020	.02	.02200	.05
30	1.0332	.0155	.0015	.01	.02128	.05
35	1.0285	.0159	.0000	.01	.02077	.02
40	1.0239	.0165	.....	.01	.01998	.02
45	1.0194	.0167	.....	.01	.01968	.02
50	1.0148	.0169	.....	.01	.01926	.02

[a] Extrapolated.

[*] H. S. Harned and C. Calmon, *J. Am. Chem. Soc.*, **60**, 334 (1938).

TABLE (11-3-2A)—*Concluded*

$X = 82$

$d = d_0 + am$; Valid to 0.6 M

t	d_0	a	Δ_1	A	Δ_2
5	1.0540	0.0152	0.01	0.0224	0.01
10	1.0488	.0159	.02	.0220	.02
15	1.0436	.0165	.02	.0212	.02
20	1.0387	.0165	.01	.0210	.01
25	1.0338	.0166	.01	.0210	.01
30	1.0288	.0165	.01	.0206	.01
35	1.0236	.0173	.01	.0198	.01
40	1.0183	.0178	.01	.0198	.02
45	1.0130	.0183	.03	.0178	.05

TABLE (11-3-3A). STANDARD POTENTIALS OF THE CELL, H_2 | HCl (m), SOLVENT (X), H_2O (Y) | AgCl-Ag

X and Y are weight percentages

Dioxane-Water Mixtures

$X = 0$; $E^0 = 0.22237 - 639.64 \times 10^{-6}(t - 25) - 3.181 \times 10^{-6}(t - 25)^2$
$X = 20$; $E^{0*} = 0.20303 - 760.5 \times 10^{-6}(t - 25) - 3.70 \times 10^{-6}(t - 25)^2$
$X = 45$; $E^{0*} = 0\ 16352 - 1135 \times 10^{-6}(t - 25) - 3.70 \times 10^{-6}(t - 25)^2$
$X = 70$; $E^{0*} = 0.06395 - 1767 \times 10^{-6}(t - 25) - 3.70 \times 10^{-6}(t - 25)^2$
$X = 82$; $E^{0*} = 0.0413 - 2370 \times 10^{-6}(t - 25) - 8.80 \times 10^{-6}(t - 25)^2$

These have a range of validity from 0 to 50° inclusive.

Methanol-Water Mixtures

$X = 10$; $E^{0*} = 0.21818 - 555.63 \times 10^{-6}(t - 20) - 4.128 \times 10^{-6}(t - 20)^2$
$X = 20$; $E^{0*} = 0.21151 - 529.10 \times 10^{-6}(t - 20) - 4.706 \times 10^{-6}(t - 20)^2$

These have a range of validity from 0 to 40° inclusive.

Ethyl Alcohol-Water Mixtures(a)

$X = 10$; $E^{0*} = 0.21900 - 5.03 \times 10^{-4}(t - 20) - 3.82 \times 10^{-6}(t - 20)^2$
$X = 20$; $E^{0*} = 0.21025 - 4.19 \times 10^{-4}(t - 20) - 6\ 00 \times 10^{-6}(t - 20)^2$

Isopropyl Alcohol-Water Mixtures(b)

$X = 5$; $E^{0*} = 0.22110 - 5.7425 \times 10^{-4}(t - 20) - 3.8357 \times 10^{-6}(t - 20)^2$
$X = 10$; $E^{0*} = 0.21666 - 5.3324 \times 10^{-4}(t - 20) - 4.7405 \times 10^{-6}(t - 20)^2$
$X = 20$; $E^{0*} = 0.20905 - 4.9001 \times 10^{-4}(t - 20) - 6.8362 \times 10^{-6}(t - 20)^2$

Glycerol-Water Mixtures(c)

$X = 50$; $E^{0*} = 0.18392 - 7.45 \times 10^{-4}(t - 25) - 3 \times 10^{-6}(t - 25)^2$; Valid from 0 to 90° inclusive.

(a) A. Patterson and W. A. Felsing, *J. Am. Chem. Soc.*, **64**, 1478 (1942). Revised.
(b) R. L. Moore and W. A. Felsing, *Ibid.*, **69**, 1076 (1947).
(c) H. S. Harned and F. H. M. Nestler, *Ibid.*, **68**, 665 (1946)

TABLE (11-4-1A). MEAN ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN WATER†

m	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
0.0001	(0.9890)	(0.9886)	(0.9890)	(0.9890)	(0.9892)	(0.9891)	(0.9890)	(0.9886)	(0.9885)	(0.9883)	(0.9879)	(0.9879)	(0.9879)
.0002	(.9848)	(.9847)	(.9846)	(.9844)	(.9844)	(.9842)	(.9835)	(.9838)	(.9833)	(.9835)	(.9831)	(.9833)	(.9831)
.0005	(.9756)	(.9756)	(.9756)	(.9757)	(.9759)	(.9752)	(.9747)	(.9745)	(.9741)	(.9741)	(.9738)	(.9735)	(.9734)
.001	(.9668)	(.9662)	(.9666)	(.9661)	(.9661)	(.9656)	(.9650)	(.9647)	(.9643)	(.9644)	(.9639)	(.9636)	(.9632)
.002	.9541	.9539	.9544	.9530	.9527	.9521	.9515	.9513	.9505	.9504	.9500	.9497	.9491
.005	.9303	.9300	.9300	.9297	.9294	.9285	.9275	.9268	.9265	.9261	.9250	.9240	.9235
.01	.9065	.9056	.9055	.9055	.9052	.9048	.9034	.9025	.9016	.9008	.9000	.8990	.8987
.02	.8774	.8768	.8773	.8770	.8768	.8755	.8741	.8731	.8715	.8704	.8690	.8680	.8666
.05	.8346	.8344	.8338	.8329	.8317	.8304	.8285	.8265	.8246	.8232	.8211	.8195	.8168
.1	.8027	.8023	.8016	.8000	.7985	.7964	.7940	.7918	.7891	.7872	.7850	.7829	.7813
.2	.7756	.7756	.7740	.7717	.7694	.7667	.7630	.7604	.7569	.7538	.7508	.7474	.7437
.5	.7761	.7730	.7694	.7658	.7616	.7571	.7526	.7477	.7432	.7387	.7344	.7292	.7237
1.	.8419	.8363	.8295	.8229	.8162	.8090	.8018	.7942	.7865	.7790	.7697	.7628	.7541
1.5	.9452	.9365	.9270	.9154	.9065	.8962	.8849	.8740	.8601	.8517	.8404	.8276	.8178
2.	1.078	1.068	1.053	1.039	1.024	1.009	.9929	.9755	.9602	.9481	.9327	.9186	.9072
3.	1.452	1.427	1.401	1.373	1.345	1.316		...	...	...		...	...
4.	2.006	1.960	1.911	1.862	1.812	1.762				...		...	...

† From observed electromotive forces. Results at concentrations less than $M = 0.002$ were obtained from plots used for extrapolation. These values are based on the data of H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 2179 (1933). N. J. Anderson [Dissertation, University of Chicago (1934)] has made a very careful study of the hydrogen silver-silver chloride cell containing hydrochloric acid at concentrations between 0.00002 and 0.003 M. Corrections were made for the solubility of silver chloride and other effects. At 25°, the activity coefficient was found to be 0.9751, 0.9653 and 0.9523 at 0.0005, 0.001 and 0.002 M, respectively. These values agree remarkably well with the extrapolated results in the table. We are grateful to Professor T. F. Young for bringing this matter to our attention.

TABLE (11-6-1A). MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN DIOXANE-WATER MIXTURES[a]

X = weight percent of dioxane

X = 20

m	0°	10°	20°	25°	30°	40°	50°
0.005	0.902	0.900	0.898	0.896	0.895	0.892	0.889
.007	.889	.886	.883	.880	.880	.876	.871
.01	.872	.869	.865	.862	.861	.857	.851
.02	.835	.830	.825	.821	.820	.814	.808
.03	.811	.805	.800	.796	.795	.788	.781
.05	.780	.774	.768	.763	.762	.755	.748
.07	.759	.753	.746	.740	.740	.732	.725
.1	.736	.729	.722	.720	.716	.708	.701
.2	.696	.688	.681	.676	.673	.665	.656
.3	.682	.675	.667	.661	.658	.649	.639
.5	.684	.675	.666	.660	.656	.646	.633
.7	.649	.690	.679	.672	.667	.655	.641
1.	.736	.725	.712	.704	.698	.683	.666
1.5	.830	.815	.797	.786	.777	.755	.732
2.	.959	.938	.913	.898	.885	.855	.823
3.	1.337	1.293	1.245	1.219	1.195	1.141	1.085

X = 45

m	0°	10°	20°	25°	30°	40°	50°
0.003	0.849	0.846	0.844	0.842	0.839	0.834	0.828
.005	.824	.817	.811	.808	.803	.795	.786
.007	.802	.793	.786	.782	.777	.767	.757
.01	.776	.766	.758	.753	.747	.737	.725
.02	.720	.707	.697	.692	.686	.673	.660
.03	.683	.671	.661	.654	.649	.635	.622
.05	.637	.624	.613	.607	.600	.586	.573
.07	.605	.593	.583	.577	.570	.557	.545
.1	.579	.566	.553	.547	.540	.525	.512
.2	.529	.514	.503	.496	.488	.474	.459
.3	.511	.496	.484	.476	.466	.453	.438
.5	.503	.487	.473	.465	.456	.440	.423
.7	.513	.495	.480	.471	.461	.443	.424
1.	.547	.526	.508	.497	.485	.463	.442
1.5	.640	.612	.585	.570	.555	.524	.496
2.	.773	.733	.695	.676	.655	.614	.575
3.	1.191	1.112	1.037	1.001	.962	.887	.818

X = 70

m	0°	10°	20°	25°	30°	40°	50°
0.001	0.719	0.713	0.705	0.700	0.696	0.686	0.675
.0015	.672	.665	.656	.651	.647	.636	.624
.002	.641	.633	.623	.618	.613	.601	.589
.003	.589	.582	.573	.568	.563	.552	.540
.005	.530	.521	.510	.505	.499	.487	.473
.007	.488	.479	.468	.462	.457	.444	.431
.01	.446	.436	.425	.418	.413	.401	.388
.02	.369	.359	.348	.342	.336	.324	.312
.03	.328	.318	.308	.303	.297	.286	.275
.05	.283	.274	.264	.258	.253	.243	.232
07	.259	.249	.239	.234	.229	.219	.208
.1	.236	.226	.217	.212	.207	.197	.188
.2	.204	.194	.185	.180	.175	.165	.156
.3	.193	.182	.173	.168	.163	.154	.144
.5	.191	.179	.169	.163	.158	.147	.137
.7	.200	.187	.175	.168	.162	.150	.139
1.0	.227	.211	.195	.187	.179	.165	.151
1.5	.303	.277	.252	.240	.228	.207	.187

Table (11-6-1A)—*Concluded*

$X = 82$

m	5°	15°	25°	35°	45°
0.001	0.4242	0.4129	0.3979	0.3795	0.3592
.0015	.3725	.3627	.3488	.3318	.3129
.002	.3369	.3277	.3147	.2990	.2810
.003	.2862	.2781	.2682	.2553	.2378
.005	.2319	.2267	.2181	.2062	.1916
.007	.2019	.1977	.1900	.1791	.1654
.01	.1744	.1707	.1629	.1529	.1412
.015	.1472	.1440	.1371	.1282	.1176
.02	.1311	.1274	.1213	.1131	.1035
.03	.1112	.1076	.1020	.0946	.0869
.05	.0912	.0876	.0826	.0766	.0698
.07	.0780	.0756	.0713	.0659	.0596
.1	.0701	.0675	.0634	.0582	.0525
.15	.0627	.0597	.0560	.0513	0460
.2	.0589	.0560	.0521	.0476	.0425
.3	.0563	.0532	.0490	.0443	.0392
.5	.0595	.0554	.0504	.0445	.0386

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[a] For bibliography, see reference 22, Chapter (11).

TABLE (11-6-2A). MEAN ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN ORGANIC SOLVENTS, AND IN ORGANIC SOLVENT-WATER MIXTURES.
N_2 = MOL FRACTION OF ORGANIC SOLVENT

I. Methanol

m	N_2 = 0.0588[a]			N_2 = 0 1233[a]		
	0°	25°	40°	0°	25°	40°
0.001	0.964	0.962	0.961	0 961	0.959	0.957
.002	.951	.948	.946	.946	.943	.941
.005	.926	.922	.919	.919	.915	.912
.01	.901	.897	.893	.893	.888	.884
.02	.872	.866	.861	.862	.856	.850
.05	.825	.819	.812	.814	.806	.798
.1	.790	.780	.772	.771	.762	.751
.2	.762	.747	.736	.741	.727	.715
.5	.754	.737	.718	.726	.708	.693
1.	.809	.783	.756	.772	.747	.722
1.5	.898	.861	.827	.855	.814	.781
2.	1.020	.966	.917	.965	.911	.860

N_2 = 1[b]

m	25°	m	25°	m	25°
0.00236	0.826	0.01444	0.658	0.0733	0.470
.002683	.817	.01722	.638	.0751	.468
.002980	.809	.01986	.621	.0947	.443
.003161	.804	.02363	.601	.1155	.423
.00494	.766	.02549	.592	.4802	.325
.00542	.758	.04261	.532	.5574	.322
.00711	.732	.04356	.530	.....	....
.00986	.699	.05312	.507	.....	....

II. Ethanol

N_2 = 0 0417[c]		N_2 = 0 0891[c]		N_2 = 0.5[d,e]		N_2 = 1[d,e]	
m	25°	m	25°	m	25°	m	25°
0.00631	0.914	0.00470	0.915	0.005	0.815	0.005	0.728
.00758	.907	.00787	.894	.01	.757	.01	.632
.01088	.891	.01015	.883	.02	.676	.02	.544
.01987	.864	.01983	.850	.05	.586	.0249	.514
.04210	.824	.04150	.809	.1	.521	.0423	.445
.05100	.814	.05166	.794	.2	.471	.05	.426
.07085	.795	.07123	.775	.5	.432	.1	.352
.0800	.788	.0816	.770	1.	.449	.1242	.327
.0885	.783	.0924	.761	1.5	.510	.1782	.300
.1091	.773	.1042	.751	2.	.582	.2	.286
.1990	.744	.3038	.699	2.5	.697	.4437	.218
.2999	.731	.4751	.698	....	....	1.	.177
.5050	.730	.7309	.709	....	....	1.050	.168
.7014	.743	1.0216	.741	....	....	1.481	.159
.9946	.776	1.549	.819	....	....	3.62	.150
1.499	.856	2.079	.930	....	....	....	....
1.994	.954	....	....	....	....	....	....

TABLE (11-6-2A)—*Concluded*

III. Isopropanol[e]

$N_2 = 0.0323$

m	25°	m	25°	m	25°
0.001862	0.948	0.03558	0.830	0.2990	0.726
.004019	.927	.04855	.813	.4451	.723
.006356	.911	.06685	.795	.6993	.737
.008616	.899	.07947	.785	.8863	.757
.00892	.898	.1119	.766	1.	.770
.02089	.858	.1921	.740	.....	.....

IV. Glycerol[d]

m	$N_2 = 0.01$	$N_2 = 0.05$
	25°	25°
0.002	0.951	.....
.005	.924	0.898
.01	.902	.885
.02	.873	.858
.05	.826	.810
.1	.798	.775
.2	.764	.744
.28	.756	.738
.38	.753	.738
.5	.755	.737
.7	.772	.760
1.	.810	.801
1.5	.901	.901
2.	1.019	1.030
2.5	1.161	1.190
3.	1.345	1.385
4.	1.792	1.914

[a] H. S. Harned and H. C. Thomas, *J. Am. Chem. Soc.*, **58**, 761 (1936).
[b] G. Nonhebel and H. Hartley, *Phil. Mag.*, [6] **50**, 298, 729 (1923).
[c] H. S. Harned and C. Calmon, *J. Am. Chem. Soc.*, **61**, 1491 (1939).
[d] H. S. Harned and M. H. Fleysher, *Ibid.*, **47**, 82 (1925).
[e] W. W. Lucasse, *Z. physik. Chem.*, **121**, 254 (1926).

TABLE (11-7-1A). LIMITING SLOPES, $\mathcal{S}_{(L)}$, FOR L_2 IN DIOXANE-WATER MIXTURES

X = weight percent of dioxane

t	$X = 0$	$X = 20$	$X = 45$	$X = 70$	$X = 82$
0	433	945	2480	7480	.....
10	537	1147	2930	8940	14630
20	654	1364	3440	10570	17610
25	717	1485	3720	11470	19210
30	785	1605	4010	12410	20910
40	931	1872	4640	14450	24520
50	1090	2173	5340	16730	.....

TABLE (11-7-2A). PARAMETERS OF EQUATIONS, $L_2 = \alpha + \beta T^2$; $J_2 = 2\beta T$, AND $\bar{L}_2$ AND $\bar{J}_2$ AT 25°. VALID FROM 0 TO 50°[a]

X = weight percent of dioxane

$X = 20$

m	$-\alpha$	β	$\bar{L}_2$ (25°)	$\bar{J}_2$ (25°)
0.005	77	0.00208	108	1.2
.007	77	.00254	149	1.5
.01	72	.00277	169	1.7
.02	77	.00346	235	2.1
.03	87	.00393	262	2.3
.05	87	.00438	302	2.6
.07	96	.00485	335	2.9
.1	144	.00554	348	3.3
.2	298	.00808	420	4.8
.3	435	.01015	467	6.1
.5	682	.01384	548	8.3
.7	871	.01684	625	10.0
1.	1156	.02123	731	13.8
1.5	1517	.02723	903	16.2
2.	1753	.03207	1097	19.1
3.	2013	.03946	1494	23.5

$X = 45$

m	$-\alpha$	β	$\bar{L}_2$ (25°)	$\bar{J}_2$ (25°)
0.003	640	0.00923	180	5.5
.005	619	.01061	324	6.3
.007	630	.01154	395	6.9
.01	609	.01223	478	7.3
.02	651	.01408	600	8.4
.03	669	.01500	664	8.9
.05	703	.01638	753	9.8
.07	735	.01730	802	10.2
.1	754	.01823	866	10.9
.2	839	.02077	1007	12.4
.3	934	.02284	1096	13.6
.5	1179	.02723	1241	16.2
.7	1430	.03138	1359	18.7
1.	1704	.03646	1536	21.7
1.5	1999	.04292	1815	25.6
2.	2169	.04799	2095	28.6
3.	2285	.05561	2657	33.1

$X = 70$

m	$-\alpha$	β	$\bar{L}_2$ (25°)	$\bar{J}_2$ (25°)
0.001	701	0.0129	446	7.7
.0015	862	.0157	533	9.4
.002	994	.0180	606	10.7
.003	1121	.0196	621	11.7
.005	1233	.0228	793	13.6
.007	1266	.0242	884	14.4
.01	1270	.0254	987	15.1
.02	1299	.0282	1207	16.8
.03	1348	.0295	1273	17.6
.05	1389	.0316	1419	18.8
.07	1397	.0328	1518	19.6
.1	1413	.0341	1617	20.3
.2	1417	.0371	1880	22.1
.3	1477	.0397	2051	23.7
.5	1558	.0438	2334	26.1
.7	1635	.0475	2586	28.3
1.0	1697	.0519	2915	30.9
1.5	1700	.0579	3445	34.5

TABLE (11-7-2A)—*Concluded*

$X = 82$

m	$-\alpha$	β	$\bar{L}_2$ (25°)	$\bar{J}_2$ (25°)
0.001	5190	0.0752	1493	44.8
.0015	5710	.0824	1612	49.1
.002	6550	.0930	1714	55.4
.003	7800	.1082	1815	64.5
.005	9240	.1258	1939	75 0
.007	10100	.1364	2021	81.3
.01	10500	.1418	2101	84.5
.015	10860	.1468	2185	87.5
.02	11000	.1488	2223	88 7
.03	11120	.1510	2298	90.0
.05	11240	.1538	2427	91.7
.07	11360	.1560	2503	93.0
.1	11480	.1589	2640	94.7
.15	11630	.1624	2802	96 8
.2	11860	.1666	2945	99.3
.3	12200	.1742	3280	103.9
.5	12830	.1880	3876	112.1

[a] For bibliography, see reference 22, Chapter (11).

Table (11-9-1A). Cation Transference Numbers, T_+, of Hydrochloric Acid in Water and Dioxane-Water Mixtures[a]

X = weight percent of dioxane

m	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
0.0	.....	0.842	0.837	0.831	0.826	0 821	0.816	0.811	0.806	0.801	0.796
.005	.....	.844	.840	.834	.829	824	.819	.814	.809	.804	.799
.01	....	.845	.841	.835	830	.825	.821	.816	.811	.806	.801
.02	.....	.846	.842	.836	.832	.827	.822	.818	.813	.808	.803
.05	.....	.848	.844	.838	.834	.830	.825	.821	.816	.811	.806
.1	.....	.850	.846	.840	.837	.832	.828	.823	.819	.814	.810
.2	.....	.851	.847	.843	.839	.835	.830	.827	.823	.818	.814
.5	.....	.854	.850	.846	.842	.838	.834	.831	.827	.822	.819
1.0	.....	.855	.852	.848	.844	.841	.837	.833	.829	.824	.821
1.5	.....	.857	.853	.849	.845	.842	.839	.835	.830	.825	.822
2.0	.....	.857	.853	.849	.846	.843	.839	.835	.831	.826	.822
3.0	.....	.858	.854	.850	.846	843	.840	.836	.832	.827	.823
						20					
0.0	0.856	.851	.846	.841	.836	.831	.825	.821	.816	.810	.805
.005	.861	.855	.850	.845	.840	.835	829	.825	.820	.814	.809
.01	.862	.857	851	.846	.841	.836	.831	.827	.821	.816	.811
.02	.865	.859	.853	.848	.843	838	.833	.829	.824	.818	.813
.05	.867	.861	.856	.851	.846	.841	837	.832	.827	.822	.816
.1	.868	.862	.857	.852	.848	.843	.839	.834	.829	.823	.818
.2	.869	.863	.858	.853	.849	.844	.840	.835	.830	.825	.820
.5	.867	.862	.857	.852	.847	.843	.838	.833	.829	.823	.818
1.0	.864	.860	.854	.849	.844	.840	.836	.831	.826	.821	.816
1.5	.862	.857	.852	.847	.842	.838	.834	.829	.824	.819	.814
2.0	.860	.855	.850	.845	841	.836	.832	.828	.823	.818	.813
3.0	.856	.852	.847	.842	.838	.833	.829	.825	.820	.816	.811
						45					
0.0	.828	.824	.820	.816	.811	.806	.801	.796	.791	.787	.783
.005	.833	.829	.825	.821	.816	.811	.807	.801	.797	.793	.788
.01	.835	.830	.827	.823	.818	.813	.809	.804	.799	.795	.790
.02	.838	.833	.829	.825	.820	.816	.811	.807	.802	.798	.793
.05	.842	.837	.833	.829	.824	.820	.816	.812	.807	.803	.798
.1	.845	.840	836	.831	.827	.823	.819	.816	.811	.807	.803
.2	.849	.844	.840	.834	.830	.826	823	.820	.816	.812	.807
.5	.851	.846	.842	.836	.833	.829	.826	.822	.819	.815	.811
1.0	.851	.846	.841	.836	.832	.828	.825	.822	.819	.815	.811
1.5	.850	.845	.840	.835	.832	.828	.824	.821	.818	.814	.810
2.0	.849	.844	.839	.835	.831	.827	.824	.820	.817	.813	.809
3.0	.847	.843	.838	.833	.830	.825	.822	.817	.814	.810	.807
						70					
0.0	.....	.772	.768	.764	.760	.755	.750	.746	.742	.738	.734
.005	.....	.781	.778	.774	.770	.766	.761	.757	.753	.750	.747
.01	.....	.783	.780	.777	.773	.769	.764	.760	.756	.753	.751
.02	.....	.786	.783	.779	.776	.772	.767	.763	.760	.757	.755
.05	.....	.788	.785	.782	.778	.774	.770	.766	.763	.760	.758
.1	.....	.789	.786	.783	.780	.775	.771	.768	.765	.762	.759
.2	.....	.789	.786	.784	.780	.776	.771	.768	.765	.762	.759
.5	.....	.789	.786	.783	.779	.774	.770	.766	.764	.760	.757
1.0	.....	.788	.785	.782	.777	.772	.768	.764	.762	.758	.754
1.5	.....	.788	.784	.781	.776	.771	.766	.763	.760	.757	.752

[a] H. S. Harned and E. C. Dreby, *J. Am. Chem. Soc.*, **61**, 3113 (1939).

TABLE (11-9-1A)—*Concluded*

$X = 82$

m	5°	10°	15°	20°	25°	30°	35°	40°	45°
0.0	0.677	0.675	0.673	0.672	0 670	0 668	0.667	0.665	0 663
.05	.742	.735	.730	.726	.722	.717	.712	.708	.702
.1	.767	.764	762	.759	.756	.754	.752	.750	.747
.2	.755	.751	.747	.744	.740	.738	.735	.732	.729
.3	.718	.715	.711	.708	.705	.702	.699	.696	.693
.5	.660	.657	.654	.651	.648	.645	.642	.639	.637

Theoretical Limiting Slopes, $\mathfrak{S}_{(T)}\sqrt{d_0}$, of the Equation, $T_+ = \mathfrak{S}_{(T)}\sqrt{d_0}\ \sqrt{m}$

	H_2O	20%	45%	70%
15°	0.04278	0.04906	0.06773	0.1629
25°	.04509	.05195	.07186	.1642
35°	.04714	.05507	.07492	.1664

TABLE (12-1-1A). FUNCTION FOR CONVERTING m TO c FOR 1-1 ELECTROLYTES IN WATER

$c/m = d_0 - Am + Bm^2$; $d_0 = 0.9970$

Accuracy ≃ ± 0.05%

I. 25°; Valid to 4 M[a]

		Cl	Br	I	NO_3
Li	A	0.0182	0.0247	0.0358	0.0289
	B	0	.0002	.0009	.0004
Na	A	.0183	.0245	.0356	.0288
	B	0	0	.0008	0
K	A	.0284	.0345	.0458	.0392
	B	.0003	.0005	.0014	.0007
Rb	A	.0331	.0395	.0508	.0439
	B	.0004	.0008	.0016	.0008
Cs	A	.0400	.0470	.0580	.0503
	B	.0008	.0015	.0021	0

II. $B = 0$ for all Substances Except Sodium Bromide

t	d_0	NaBr[b]		HCl[c]	HBr[d]	KCl[e]	NaCl[f]
		A	B	A	A	A	A
0	0.9999	0.0212	−0.0003	0.0171	0.0228	0.0263	0.0160
5	1.0000	.0222	− .0001	.0174	.0232	.0265	.0166
10	.9997	.0231	− .0000	.0176	.0236	.0266	.0171
15	.9991	.0237	.0000	.0178	.0239	.0267	.0176
20	.9982	.0244	.0001	.01805	.0241	.0270	.0180
25	.9970	.0248	.0002	.0182	.0243	.0272	.0183
30	.9957	.0252	.0002	.0182	.0244	.0273	.0186
35	.9940	.0255	.0003	.01825	.0245	.0274	.0188
40	.9922	.0257	.0004	.01825	.0245	.0276	.0189
45	.9901	.....	.....	.01815	.0245	.....	.....
50	.9879	.....	.....	.01815	.0245	.....	.....
55	.9855	.....	.....	.01805	.0244	.....	.....
60	.9832	.....	.....	.01805	.0244	.....	.....

[a] Dr. R. A. Robinson, Private communication.

[b] H. S. Harned and C. C. Crawford, *J. Am. Chem. Soc.*, **59**, 1903 (1937).

[c] H. S. Harned and R. W. Ehlers, *Ibid.*, **59**, 2179 (1933).

[d] H. S. Harned, A. S. Keston and J. G. Donelson, *Ibid.*, **58**, 989 (1936).

[e] H. S. Harned and M. A. Cook, *Ibid.*, **59**, 1290 (1937).

[f] H. S. Harned and M. A. Cook, *Ibid.*, **61**, 495 (1939).

TABLE (12-1-2A). MEAN ACTIVITY COEFFICIENT OF SODIUM CHLORIDE FROM 0 TO 100°[d]

m	0°	0°[a]	5°	10°	15°	20°	25°[b]	25°[c]	30°	35°	40°	50°	60°	70°	80°	90°	100°[e]
0.1	0.781	0.781	0.781	0.781	0.780	0.779	0.778	0.778	0.777	0.776	0.774	0.770	0.766	0.762	0.757	0.752	0.746
.2	.731	.731	.733	.734	.734	.733	.732	.732	.731	.7295	.728	(.725)	.721	.717	.711	.705	.698
.5	.671	.673	.675	.677	.678	.679	.679	.678	.679	(.679)	(.678)	(.675)	(.671)	.667	.660	.653	.644
1.	.6375	.635	.6435	.649	.652	.654	.656	.654	.657	(.657)	.657	(.656)	(.654)	.648	.641	.632	.622
1.5	.626	. .	.6355	.6425	.648	.652	.6555	.658	.658	(.660)	(.661)	(.662)	(.659)	(.655)	.646	.638	.629
2.	.630		.6425	.652	.659	.665	.670	.670	.674	(.676)	(.678)	(.678)	(.676)	.672	.663	.651	.641
2.5	.641	.	.659	.667	.677	.684	.691		.695	(.697)	(.698)	(.699)	(.696)	(.692)	.685	.674	.659
3.0	.660	.	.677	.691	.702	.7115	.719	.718	.724	.7255	(.728)	(.728)	(.726)	(.721)	(.712)	.700	.687
3.5	.687[e]	. .	.706	.721	.735	.744	.752		.756	(.759)	.761	(.762)	(.760)	(.758)	.742	.730	.716
4.	.717		.7395	.757	.772	.783	.791		.797	.800	(.802)	(.802)	(.799)	(.791)	.777	.763	.746

[a] From freezing point. G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **55**, 4855 (1933).

[b] H. S. Harned and L. F. Nims, *Ibid.*, **54**, 423 (1932).

[c] H. S. Harned, *Ibid.*, **51**, 416 (1929).

[d] R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1222 (1939).

[e] Values from 60 to 100° are based on the boiling point data of R. P. Smith and D. S. Hirtle, *J. Am. Chem. Soc.*, **61**, 1123 (1939). Values in parenthesis were obtained from graphs in Figs. (12-1-1) and (12-1-2).

TABLE (12-1-3A). RELATIVE PARTIAL MOLAL HEAT CONTENT OF SODIUM CHLORIDE[a]

m	0°	10°	20°	25°	30°	40°	60°	70°	80°	90°	100°
0.5	− 330	− 185	− 90	− 45	15	170	300	400	500	600	700
1.	− 630	− 440	−250	−180	−100	30	310	430	550	670	760
1.5	− 860	− 680	−430	−330	−260	− 60	240	420	580	720	800
2.	−1120	− 840	−560	−450	−330	−130	280	450	650	820	1020
2.5	−1300	−1070	−710	−560	−380	−140	290	480	700	890	1040
3.	−1650	−1190	−770	−580	−400	−150	300	500	730	910	1040
3.5	−1800	−1230	−800	−590	−420	−170	310	520	820	960	1120
4.	−1850	−1380	−850	−620	−440	−150	360	590	890	1100	1300

[a] R. P. Smith and D. S. Hirtle, *J. Am. Chem. Soc.*, **61**, 1123 (1939). Combined calorimetric, electromotive force, and boiling point data.

TABLE (12-2-1A). MEAN ACTIVITY COEFFICIENT OF HYDROBROMIC ACID IN AQUEOUS SOLUTION[a]

$\bar{L}_2$ and $\bar{J}_2$ at 25°

m	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°	$\bar{L}_2$	$\bar{J}_2$
0.001	0.967	0.967	0.967	0.966	0.966	0.966	0 966	0.965	0.964	0 964	0.964	0.963	0.963	22	0.4
.005	.932	.932	.932	.930	.930	.930	.929	.928	.928	.927	.926	.924	.924	47	.8
.01	.910	.910	.909	.908	.907	.906	906	.905	.904	.904	.902	.900	.898	64	1.
.02	.883	.883	.883	.882	.879	.879	.879	.878	.877	.875	.873	.871	.869	85	1.5
.05	.843	.843	.843	.842	.838	.838	.837	.834	.833	831	.830	827	.826	124	2 2
.1	.812	.812	.811	.808	.807	.805	.804	.802	.800	.797	.795	791	.788	163	2.9
.2	.793	.791	.790	.787	.785	.782	.780	.777	.774	.772	.769	.765	.758	222	3.9
.5	.806	.803	.800	.797	.793	.790	.784	.781	.776	.772	.767	.764	.760	338	5.6
1.	.900	.894	.889	.888	.877	.871	.864	.856	.850	.844	.838	.831	823	500	7.7

[a] H. S. Harned, A. S. Keston and J. G. Donelson, *J. Am. Chem. Soc.*, **58**, 989 (1936).

TABLE (12-2-2A). MEAN ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTION[a]

m	0°	5°	10°	15°	20°	25°	30°	35°	40°
0.1	0.768	0.769	0.769	0.769	0.770	0.769	0.768	0.767	0.765
.2	.717	.718	.718	.719	.718	.719	.718	.717	.715
.3	.683	.685	.687	.687	.688	.688	.687	.685	.682
.5	.642	.646	.648	.650	.651	.651	.651	.648	.646
.7	.613	.619	.623	.624	.627	.628	.629	.627	.626
1.	.588	.595	.598	.601	.604	.606	.604	.604	.603
1.5	.563	.570	.576	.579	.582	.585	.585	.585	.585
2.	.547	.554	.562	.568	.573	.576	.578	.579	.578
2.5	.540	.549	.556	.562	.568	.572	.574	.575	.575
3.	.539	.549	.556	.562	.567	.571	.573	.574	.573
3.5	.540	.550	.558	.565	.571	.574	.577	.578	.578
4.	....	....	.563	.569	.574	.579	.582	.584	.585

[a] H. S. Harned and M. A. Cook, *J. Am. Chem. Soc.*, **59**, 1290 (1937).

TABLE (12-2-3A). RELATIVE PARTIAL MOLAL HEAT CONTENT AND HEAT CAPACITY OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTION

$\bar{L}_2 = \bar{L}_2(0°) + \alpha t + \beta t^2$; $\bar{J}_2 = \alpha + 2\beta t$.[a] Valid from 0 to 40°

m	$\bar{L}_2(0°)$	α	β
0.05	(34)	2.0	0.014
.1	− 15	3.5	.025
.2	− 80	5.1	.030
.3	− 190	7.5	.034
.5	− 280	9.4	.037
.7	− 430	12.0	.040
1.0	− 570	14.4	.045
1.5	− 760	18 4	.049
2.0	− 920	22.2	.055
2.5	−1000	23 0	.060
3.0	−1025	25.4	.066
3.5	−1200	27.7	.072
4.0	−1270	29.6	.079

[a] H. S. Harned and M. A. Cook, *J. Am. Chem. Soc.*, **59**, 1290 (1937).

TABLE (12-2-4A). MEAN ACTIVITY COEFFICIENT OF SODIUM BROMIDE IN AQUEOUS SOLUTION[a]

m	0°	5°	10°	15°	20°	25°	30°	35°	40°
0.1	(0.784)	(0.784)	(0.784)	(0.783)	(0.783)	(0.782)	(0.781)	(0.779)	(0.777)
.2	.738	.739	.741	.740	.741	.740	.739	.737	.734
.3	.713	.716	.718	.720	.718	.718	.717	.715	.712
.5	.685	.689	.693	.693	.695	.695	.694	.692	.689
.7	.670	.675	.681	.684	.683	.687	.686	.685	.685
1.	.659	.667	.675	.680	.684	.686	.687	.686	.686
1.5	.664	.673	.686	.693	.699	.703	.706	.708	.707
2.	.679	.693	.708	.719	.727	.734	.739	.741	.743
2.5	.708	.727	.745	.738	.769	.773	.784	.789	.791
3.	.745	.766	.787	.802	.815	.826	.834	.839	.842
3.5	.787	.811	.834	.852	.866	.878	.887	.893	.896
4.	.832	.858	.885	.905	.921	.934	.945	.951	.954

[a] H. S. Harned and C. C. Crawford, *J. Am. Chem. Soc.*, **59**, 1903 (1937).

The boiling point elevations of aqueous solutions of potassium bromide to 5*M* from 60 to 100° have been measured by G. C. Johnson and R. P. Smith, *J. Am. Chem. Soc.*, **63**, 1351 (1941).

Table (12-2-5A). Relative Partial Molal Heat Content and Heat Capacity of Sodium Bromide in Aqueous Solution[a]

$\overline{L}_2 = \overline{L}_2(0°) + \alpha t + \beta t^2$; $\overline{J}_2 = \alpha + 2\beta t$. Valid from 0 to 40°

m	$\overline{L}_2(0°)$	α	β
0.1	− 23	4.6	0.015
.2	− 140	8.2	.023
.3	− 210	11.8	.027
.5	− 400	15.5	.036
.7	− 580	21.8	.044
1.	− 830	23.5	.049
1.5	−1140	27.4	.055
2.	−1390	30.6	.061
2.5	−1600	33.6	.066
3.	−1790	37.0	.073
3.5	−1940	41.4	.079
4.	−2020	43.2	.086

[a] H. S. Harned and C. C. Crawford, *J. Am. Chem. Soc.*, **59**, 1903 (1937).

Table (12-2-6A). Mean Activity Coefficient of Sodium Hydroxide in Aqueous Solution[a]

m	0°	5°	10°	15°	20°	25°	30°	35°
0.05	0.820	0.821	0.820	0.820	0.819	0.818	0.818	0.816
.1	.767	.768	.768	.767	.766	.766	.765	.764
.25	.713	.715	.716	.717	.714	.713	.712	.712
.5	.684	.688	.690	.692	.693	.693	.693	.694
1.	.660	.668	.672	.676	.678	.679	.680	.678
1.5	.661	.669	.673	.681	.682	.683	.685	.683
2.	.674	.682	.689	.694	.696	.698	.700	.698
2.5	.696	.708	.717	.724	.727	.729	.730	.726
3.	.736	.751	.762	.769	.774	.774	.775	.772
3.5	.792	.801	.816	.822	.825	.826	.827	.822
4.	.857	.874	.882	.887	.889	.888	.888	.882

[a] 0.05 to 1.5*M*, H. S. Harned and J. C. Hecker, *J. Am. Chem. Soc.*, **55**, 4838 (1933); See also G. Åkerlöf and G. Kegeles, *Ibid.*, **62**, 620 (1940) and Table (B-5-2).

TABLE (12-2-7A). MEAN ACTIVITY COEFFICIENT OF POTASSIUM HYDROXIDE IN AQUEOUS SOLUTION[a]

m	0°	5°	10°	15°	20°	25°	30°	35°
0.05	(0.829)	(0.828)	(0.828)	(0 827)	(0 825)	(0.824)	(0.823)	(0.822)
.1	.795	.796	798	798	.798	.798	.796	.793
.15	.778	.778	.778	.777	.776	.774	773	.771
.25	.758	.757	.759	.758	.757	.757	.753	.751
.35	.738	.740	.740	.739	.739	.739	.736	.733
.5	.737	.736	.735	.734	.732	.728	.725	.725
.75	.742	.742	.743	.743	.741	740	740	.736
1.	.755	.756	.758	.757	.756	.756	.755	.752
1.5	.809	.812	.815	.815	.814	.814	.812	.809
2.	.889	.886	.890	.890	.889	.888	.884	.879
2.5	.974	978	1 981	.982	.980	.974	.972	.965
3.	1 088	1.091	1 094	1 093	1 087	1 081	1.072	1.065
3.5	1.219	1 229	1 231	1 229	1 219	1.215	1.199	1.195
4.	1.391	1.395	1.389	1 381	1 361	1.352	1.334	1.314

[a] H. S. Harned and M. A. Cook, *J. Am. Chem Soc.*, **59**, 496 (1937).

TABLE (12-2-8A).[a] RELATIVE PARTIAL MOLAL HEAT CONTENT AND HEAT CAPACITY OF SODIUM HYDROXIDE IN AQUEOUS SOLUTION[b]

$$\bar{L}_2 = \bar{L}_2(0°) + at; \ \bar{J}_2 = a$$

m	$-\bar{L}_2(0°)$	a
0.05	7	6
.1	70	9.5
.25	200	15
.5	400	20
1.	680	27
1.5	820	30.5
2.	940	35

[a] H. S. Harned and J. C. Hecker, *J. Am. Chem. Soc.*, **55**, 4838 (1933).

[b] Extensive tables of $\bar{L}_2$ and $\bar{J}_2$ from 0 to 70°, and to 17*M* sodium hydroxide are given by G. Åkerlöf and G. Kegeles, *J. Am. Chem. Soc.*, **62**, 620 (1940).

TABLE (12-2-9A). RELATIVE PARTIAL MOLAL HEAT CONTENT AND HEAT CAPACITY OF POTASSIUM HYDROXIDE IN AQUEOUS SOLUTION[a]

$$\bar{L}_2 = \bar{L}_2(0°) + at + \beta t^2; \ \bar{J}_2 = a + 2\beta t. \quad \text{Valid from 0 to 40°}$$

m	$\bar{L}_2(0°)$	a	β
0.05	37	2.4	0.017
.1	41	3.6	.029
.15	30	4.7	.030
.25	− 1	6.4	.032
.35	− 35	8 2	.034
.5	− 95	10.4	.036
.75	−180	13.6	.040
1.0	−270	16.2	.043
1.5	−335	20.6	.050
2.0	−381	24.6	.057
2.5	−390	28.2	.063
3.0	−356	31.5	.070
3.5	−335	34.5	.078
4.0	−226	37.4	.081

[a] H. S. Harned and M. A. Cook, *J. Am. Chem. Soc.*, **59**, 496 (1937).

TABLE (12-3-1A). MEAN ACTIVITY

m	LiCl	NaCl	KCl	RbCl	CsCl
0.1	0.792	0.778	0.769	0.764	0.755
.2	.761	.734	.717	.709	.693
.3	.748	.710	.687	.675	.653
.5	.742	.682	.650	.634	.604
.7	.754	.668	.626	.607	.573
1.	.781	.658	.605	.583	.543
1.5	.841	.659	.585	.559	.514
2.	.931	.671	.575	.547	.495
2.5	1.043	.692	.572	.540	.485
3.	1.174	.720	.573	.538	.480
3.5	....	.753	.576	.539	.476
4.	....	.792	.582	.541	.474
4.5	....	....	.590	.544	.474
5.	....	....	....	.547	.476

m	LiBr	NaBr	KBr	RbBr	CsBr
0.1	0.794	0.781	0.771	0.763	0.754
.2	.764	.739	.721	.706	.692
.3	.757	.717	.692	.674	.652
.5	.755	.695	.657	.634	.603
.7	.770	.687	.637	.606	.570
1.	.811	.687	.617	.579	.537
1.5	.899	.704	.601	.552	.504
2.	1.016	.732	.596	.537	.486
2.5	1.166	.770	.596	.527	.474
3.	1.352	.817	.600	.521	.468
3.5	....	.871	.606	.518	.462
4.	....	.938	.615	.517	.460
4.5	....	....	....	.517	.459
5.	....	....	....	.518	.460

m	LiI	NaI	KI	RbI	CsI
0.1	0.811	0.788	0.776	0.762	0.753
.2	.800	.752	.731	.705	.691
.3	.799	.737	.704	.673	.651
.5	.819	.726	.675	.631	.599
.7	.848	.729	.659	.602	.566
1.	.907	.739	.646	.575	.532
1.5	1.029	.772	.639	.548	.495
2.	1.196	.824	.641	.533	.470
2.5	1.423	.889	.649	.525	.450
3.	1.739	.967	.657	.519	.434
3.5	....	1.060	.667	.518	....
4.	....	....	.678	.517	....
4.5	....	....	.692	.519	....
5.	....	....	....	.520	....

TABLE (12-3-1A)—*Continued*

m	$LiNO_3$	$NaNO_3$	KNO_3	$RbNO_3$	$CsNO_3$
0.1	0.788	0.758	0.733	0.730	0.729
.2	.751	.702	.659	.656	.651
.3	.737	.664	.607	.603	.598
.5	.728	.615	.542	.534	.526
.7	.731	.583	.494	.484	.475
1.	.746	.548	.441	.429	.419
1.5	.783	.509	.378	.365	.354
2.	.840	.481	.327	.319	....
2.5	.903	.457	.293	.284	....
3.	.973	.438	.266	.256	....
3.5	1.052	.423	.244	.235	....
4.	....	.410	....	.216	....
4.5	....	.398	....	.200	....
5.	....	.388	....	....	....
5.5	....	.380	....	....	....
6.	....	.373	....	....	....

m	LiAc[a]	NaAc	KAc	RbAc	CsAc
0.1	0.782	0.791	0.796	0.797	0.798
.2	.740	.755	.767	.771	.773
.3	.718	.741	.752	.759	.763
.5	.698	.740	.751	.760	.765
.7	.691	.741	.755	.769	.777
1.	.690	.757	.779	.795	.802
1.5	.709	.799	.839	.859	.868
2.	.734	.854	.910	.940	.952
2.5	.769	.920	.993	1.034	1.046
3.	.807	.993	1.086	1.139	1.153
3.5	.847	1.070	1.187	1.255	1.277
4.	.893	....	....	....	....

m	NaF	KF	NaCNS	KCNS	HI
0.1	0.764	0.774	0.787	0.769	0.818
.2	.708	.727	.750	.716	.807
.3	.675	.701	.731	.685	.811
.5	.631	.672	.715	.646	.839
.7	.602	.657	.710	.623	.883
1.	.572	.649	.712	.600	.965
1.5	....	.649	.725	.574	1.139
2.	....	.663	.751	.558	1.367
2.5	....	.684	.784	.548	1.656
3.	....	.713	.820	.542	2.025
3.5	....	.748	.860	.537	....
4.	....	.790	.911	.533	....
4.5	....	....	....	.531	....
5.	....	....	....	.529	....

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[a] Ac represents acetate radical.

TABLE (12-3-1A)—*Continued*

m	$CsNO_3$	$Li\bar{S}$*	$Na\bar{S}$	$K\bar{S}$	$TlNO_3$	$TlClO_4$	TlAc	$AgNO_3$
0.1	0.729	0.773	0.764	0.760	0.701	0.730	0.748	0.731
0.2	0.651	0.729	0.708	0.701	0.605	0.652	0.684	.654
0.3	0.598	0.698	0.672	0.662	0.544	0.599	0.643	.603
0.5	0.526	0.664	0.624	0.607	....	0.527	0.588	.534
0.7	0.475	0.642	0.592	0.562	....	....	0.552	.483
1.0	0.419	0.621	0.551	0.509	....	....	0.513	.428
1.5	0.354	0.595	0.502	0.438	...	...	0.472	.362
2.0	...	0.574	0.460	0.387	..	..	0.444	.315
2.5	....	0.565	0.428	0.349	....	..	0.422	.280
3.0	....	0.563	0.403	0.318	...	...	0.405	.252
3.5	....	0.566	0.385	0.294	...	....	0.390	.229
4.0	....	0.573	0.368	....	....	....	0.377	.210
4.5	....	0.584	....	....	....	....	0.365	.194
5.0	....	....	....	....	....	....	0.354	.181
5.5	....	....	....	....	....	....	0.345	.169
6.0	....	....	....	....	....	....	0.336	.159
8.0	....	....	....	....	....	....	....	.129
10.0	....	....	....	....	....	....	....	.110
13.0	....	....	....	....	....	....	....	.0908

* $\bar{S}$ = p-toluenesulfonate radical.

Bibliography: R. A. Robinson and D. A. Sinclair, *J. Am. Chem. Soc.*, **56**, 1830 (1934); R. A. Robinson, *Ibid.*, **57**, 1161 (1935); **57**, 1165 (1935); **59**, 84 (1937); R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1217 (1939); R. A. Robinson, *J. Am. Chem. Soc.*, **62**, 3131 (1940); *Ibid.*, **63**, 628 (1941); H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **37**, 302 (1941); R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

TABLE (12-3-1A)*—*Concluded*

m	$NaClO_3$(1)	$KClO_3$(2)	$NaBrO_3$(3)	$KBrO_3$(3)	$LiClO_4$(4)	$NaClO_4$(4)	NaH_2PO_4(5)	KH_2PO_4(5)
0.1	0.772	0.749	0.758	0.745	0.812	0.775	0.744	0.731
.2	0.720	0.681	0.696	0.674	0.794	0.729	0.675	0.653
.3	0.688	0.635	0.657	0.625	0.792	0.701	0.629	0.602
.5	0.645	0.568	0.605	0.552	0.808	0.668	0.563	0.529
.7	0.617	0.518	0.569		0.834	0.648	0.517	0.477
1.0	0.589		0.528		0.887	0.629	0.468	0.421
1.4	0.563		0.489		0.979	0.616	0.420	0.369
2.0	0.538		0.450		1.158	0.609	0.371	
2.5	0.525		0.426		1.350	0.609	0.343	
3.0	0.515				1.582	0.611	0.320	
3.5	0.508				1.866	0.617	0.305	
4.0					2.18	0.626	0.293	
5.0						0.649	0.276	
6.0						0.677	0.265	

(1) J. H. Jones, *J. Am. Chem. Soc.*, **65**, 1353 (1943); (2) J. H. Jones, *Ibid.*, **66**, 1672 (1944); (3) J. H. Jones, *Ibid.*, **69**, 1066 (1947); (4) J. H. Jones, *J. Phys. Chem.*, **51**, 516 (1947); (5) J. M. Stokes, *Trans. Faraday Soc*, **41**, 685 (1945) See summary of osmotic and activity coefficients by R. A. Robinson and R. H. Stokes, Trans. Faraday Soc., **45**, 612(1949).

* For results at very high concentrations, see Table (B-5-2).

TABLE (12-6-1A). CONSTANTS AND $f_\pm$ (STANDARD) OF GUGGENHEIM'S EQUATION, (12-6-3), $\log f_\pm = \log f_\pm(\lambda = 0) + \lambda c$. VALUES OF $\gamma_{0\,1}$

	λ	$\gamma_{0\,1}$	m	$f_\pm(\lambda = 0)$
HCl	+.240	0.801	0.001	0.966
LiCl	+.195	.793	.005	.927
NaCl	+.130	.781	01	.901
KCl	+.072	.771	.02	.867
$LiClO_3$	+.243	.802	.03	.844
$NaClO_3$	+.035	.764	.04	.825
$KClO_3$	−.143	.734	.05	.810
$LiClO_4$	+.330	.818	.06	.797
$NaClO_4$	+.065	.770	.07	.786
$KClO_4$	−.435	..	.08	.776
$LiNO_3$	+.226	.799	.09	.767
$NaNO_3$	+.000	.758	.1	.758
KNO_3	−.206	.723	....	....
$CsNO_3$	+.00	(.758)	....	....
$NaIO_3$	−.35	.700	....	....
KIO_3	− 35	.700	....	....
LiOOCH	+.122	780	...	....
NaOOCH	+.148	.785	....	....
KOOCH	+.165	.787	....	....
$LiOOC\cdot CH_3$	+ 183	.791	...	....
$NaOOC\cdot CH_3$	+.252	.804	....	....
$KOOC\cdot CH_3$	+.252	.804	....	....

TABLE (12-10-1A). SALTING COEFFICIENTS
k_m (25°) [Equation (12-10-5)]

	He (1)	A (1)	H_2 (2)	O_2 (2)	N_2O (2)	CO_2 (2)	C_2H_4 (2)	$CH_3COOC_2H_5$ (3)	$C_6H_{12}O_6$ (4)	$CS\left\langle{NHC_6H_5 \atop NH_2}\right.$ (5)	C_2H_5OH (6)
HCl	....	....	.020	.022	.016	.006	....	...	...	..	....
LiCl	−.015	.037	.066	...	.081	....	...	.088	077	....	.181
NaCl	.053	.058	.094	.132	101	....	093	166	139	.140	220
NaBr	....	....	....	....	.089	....	.077	.119	.109	. .	....
NaI	....	....	....	....	. .	...	.. .	.024	.041	029	...
$NaNO_3$	.050	.058	.080	. .	072	(I_2) 053	050	.074	.	.019	....
Na_2SO_4	....	....	....	...	.110	(I_2) .100	098	. .	.159	.133	...
KCl	.055	.061	.078	..	.085	059	062	143	.118	.118	.245
KBr	....	....	....	....	.063	.045	049	105	090	.055	...
KI	....	...	....	....	.058	.032	...	037	034	057	....
KNO_3	....	....	.061	....	.047	.025	030	.060	....	.013	....
NH_4NO_3	....	....	....	....	.007	..	...	027	. .	−.057	...
$BaCl_2$	....	.070	....	....	.073	.060	.067	080	....	.074	.069
$SrCl_2$	....	.033	....	....	...	....	.	..	..	....	.064
$CaCl_2$	....	.018	.065	.. .	064	....	058	...	....	....	.062
$Ca(NO_3)_2$	....	....	....	..	041	.. .	.028	022	....	....	.062
$MgCl_2$	....	.012	...	..	..	....	055	....	.060	... .	.060
$MgSO_4$	...	...	057	...	.070	...	064	.127	.105	080	...
$AlCl_3$	....	.021	.028	....	..	..	.044	...	043	.063	...
$Al_2(SO_4)_3$	....	....	....	....	.045	....	.043	. ..	.076	....	....
LiI	−.038	....	....	....	....	....	. .	....	....	....	....
$HClO_4$	−.048	−.022	....	....	....	....	....	....	...	....	....

(1) G. Åkerlöf, *J. Am. Chem. Soc.*, **57**, 1196 (1935); (2) M. Randall and C. F. Failey, *Chem. Rev.*, **4**, 271 (1927); **4**, 285 (1927); (3) S. Glasstone and A. Pound, *J. Chem. Soc.*, **127**, 2660 (1925); S. Glasstone, A. Dimond and D. W. Pound, *Ibid.*, **128**, 2935 (1926); (4) G. Åkerlöf, *J. Am. Chem. Soc.*, **51**, 984 (1929); (5) W. Biltz, *Z. physik. Chem.*, **43**, 41 (1903); V. Rothmund, *Ibid.*, **33**, 401 (1900); (6) W. Herz and F. Hiebenthal, *Z. anorg. Chem.*, **177**, 363 (1929).

TABLE (12-10-2A). SALTING COEFFICIENTS FOR SOME WEAK ACIDS. k_m (25°) [Equation (12-10-5)]

	(a)	(b)	(c)	(d)	(e)	(f)
NaCl	0.191	0.232	0.180	0.196	0.066	0.088
KCl	.152	....	....	.140	.033	.026
$NaNO_3$	.064	.089	....	− .078	....	....
LiCl	....	....	....	....	.075	....
NaAc	....	....	....	....	− .014	....
$NaOOC \cdot CH_2Cl$	....	....	....	....	....	− .016
$BaCl_2$	.100	.134	.105	....	....	.056
$Ba(NO_3)_2$	.030	.040	.004	....	....	....
KBr	....	....	....	....	.014	.008
KNO_3	.025	....	....	− .006	− .020	− .043
KSCN	....	....	....	....	.010	....
$C_{12}H_{22}O_{11}$	....	....	....	....	.025	....

(f) Chloro-acetic.

TABLE (13-1-1A). MEAN ACTIVITY COEFFICIENT OF BARIUM CHLORIDE[a]

m	0°	15°	25°	35°	45°
0.01	0.725	0.727	0.723	0.720	0.710
.05	.555	.565	.559	.554	.536
.1	.483	.498	.492	.492	.487
.2	.422	.442	.436	.436	.431
.3	.394	.416	.411	.411	.405
.5	.371	.395	.390	.390	.382
.7	.365	.390	.384	.384	.376
1.	.377	.395	.389	.389	.381
1.5	.410	.410	.425	.417	.409

[a] E. A. Tippetts and R. F. Newton, *J. Am. Chem. Soc.*, **56**, 1675 (1934).

TABLE (13-1-2A). MEAN ACTIVITY COEFFICIENTS OF 2-1 SALTS AT 25°. SEE TABLE (B-5-3)

m	$MnCl_2$[c]	$CoCl_2$[c]	$NiCl_2$[c]	$CuCl_2$[c]	$FeCl_2$[f]	$MgCl_2$[a]	$CaCl_2$[b,e]	$SrCl_2$[b]	$BaCl_2$[b]	$MgBr_2$[a]	MgI_2[a]	$BaBr_2$[d]	$Cd(NO_3)_2$[g]	$Ca(NO_3)_2$[d]	$Cu(NO_3)_2$[g]	K_2CrO_4[g]
0.1	(0.522)	(0.526)	(0.526)	(0.501)	(0.525)	(0.565)	(0.531)	(0.514)	(0.492)	(0.582)	(0.599)	(0.513)	(0.517)	(0.480)	(0.513)	(0.455)
.2	.474	.482	.483	.447	.480	.520	.482	.463	.438	.546	.577	.465	.469	.421	.464	.379
.3	.454	.466	.468	.423	.463	.507	.462	.440	.411	.547	.585	.446	.448	.391	.443	.338
.4	.446	.463	.465	.409	.459	.508	.456	.430	.398	.560	.607	.438	.437	.373	.434	.311
.5	.446	.465	.468	.405	.460	.514	.457	.425	.390	.579	.637	.437	.433	.360	.432	.292
.6	.448	.473	.476	.403	.467	.527	.462	.426	.386	.604	.676	.439	.431	.351	.434	.276
.7	.455	.483	.489	.403	.475	.542	.469	.430	.384	.635	.723	.444	.432	.344	.438	.263
.8	.463	.496	.504	.405	.486	.563	.479	.436	.385	.671	.782	.452	.435	.339	.445	.253
.9	.474	.514	.522	.408	.501	.587	.493	.444	.388	.714	.851	.463	.438	.336	.453	.244
1.	.486[e]	.538	.542	.411	.519	.613	.509	.455	.392	.764	.929	.473	.443	.334	.463	.236
1.2	.516	.578	.595	.419	.558	.680	.550	.480	.402	.885	1.112	.500	.455	.332	.485	.224
1.4	.554	.635	.660	.430	.607	.764	.599	.510	.416	1.032	1.353	.534	.469	.333	.513	.214
1.6	.596	.706	.737	.442	.668	.867	.657	.546	.431	1.214	1.651	.572	.487	.335	.541	.207
1.8	.637	.785	.826	.454	.739	.986	.726	.587	.450	1.440		.616	.507	.339	.577	.201
2.	.682	.884	.938	.466	.817	1.143	.807	.636				.666	.528	.343	.614	.197

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[a] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **36**, 733 (1940).

[b] R. A. Robinson, *Ibid.*, **36**, 735 (1940).

[c] R. A. Robinson and R. H Stokes, *Ibid.*, **36**, 1137 (1940).

[d] R. A. Robinson, *Ibid.*, **36**, 1135 (1940)

[e] T. Shedlovsky and D. A. MacInnes [*J. Am. Chem. Soc.*, **59**, 503 (1937)] have obtained values of $\gamma_{\pm}$ at 25°, and concentrations below 0.1 M from cells with liquid junctions.

[f] R. H. Stokes and R. A. Robinson, *Trans. Faraday Soc.*, **37**, 419 (1941).

[g] R. A. Robinson, Private communication.

TABLE (13-3-1A). STANDARD POTENTIALS:

Cd-Cd_xHg | $CdCl_2(m)$ | AgCl-Ag; $E^0(CdCl_2)$
Cd-Cd_xHg | $CdBr_2(m)$ | AgBr-Ag; $E^0(CdBr_2)$
Cd-Cd_xHg | Cd^{++} (a = 1) ; π^0

t	$E^0(CdCl_2)$	$E^0(CdBr_2)$	π^{0a}	π^{0b}
0	0.5815	......	0.3452	......
5	.5804	0.4250	.3465	0.3452
10	.5790	.4248	.3477	.3468
15	.5776	.4243	.3491	.3483
20	.5758	.4236	.3503	.3499
25	.5730	.4227	.3515	.3514
30	.5716	.4215	.3526	.3528
35	.5696	.4201	.3539	.3541
40	.5673	.4185	.3553	.3554

[a] H. S. Harned and M. E. Fitzgerald, *J. Am. Chem. Soc.*, **58**, 2624 (1936).
[b] R. G. Bates, *Ibid.*, **61**, 308 (1939).

TABLE (13-3-2A). STANDARD POTENTIALS:

Zn-Zn_xHg | $ZnCl_2$ (m) | AgCl-Ag; $E^0(ZnCl_2)$
Zn-Zn_xHg | ZnI_2 (m) | AgI-Ag; $E^0(ZnI_2)$
Zn-Zn_xHg | Zn^{++} (a = 1); π^0

t	$E^0(ZnCl_2)^a$	$E^0(ZnI_2)^b$	π^{0b}	π^{0a}
5	......	0.6176	0.7646	......
10	0.9962	.6161	.7642	0.7639
15	.9919	.6145	.7637	.7635
20	.9885	.6126	.7632	.7630
25	.9848	.6105	.7627	.7625
30	.9810	.6083	.7622	.7619
35	.9770	.6059	.7617	.7614
40	.9728	.6038	.7612	.7608

Zn-Zn_xHg | $ZnBr_2$ (m) | AgBr-Ag; t = 25°; $E^0(ZnBr_2)$ = 0.8339; π^0 = 0.7628[c]

[a] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **36**, 740 (1940).
[b] R. G. Bates, *J. Am. Chem. Soc.*, **60**, 2983 (1938).
[c] H. N. Parton and J. W. Mitchell, *Trans. Faraday Soc.*, **35**, 758 (1939).

TABLE (13-3-3A). MEAN ACTIVITY COEFFICIENTS OF ZINC AND CADMIUM HALIDES, AND OF LEAD CHLORIDE

I. $\gamma_\pm$ at 25°

m	$PbCl_2$[a]	$ZnCl_2$[b]	$ZnBr_2$[c]	ZnI_2[d]	$CdCl_2$[e]	$CdBr_2$[f]	CdI_2[g]
0.0005	0.902	....	....	. ..	0.880	0.855	....
.001	.859	....	....	. .	819	.787	....
.002	.803	....	....	0 851	743	699	....
.003	....	....	....	.833	....	..	....
.005	.704	0.789	. ..	.799	.623	.570	0.490
.007	....	....	...,	.772	....	.520	.441
.01	.612	.731	.	.746	.524	.468	.379
.02	.497	.667	0.685	.690	456	.370	.281
.05	....	.628	.605	621	304	.259	.167
.1	....	.575	.555	578	.228	.189	.108
.2	....	.459	.517	564	.163[h]	.132	.0685
.5	....	.394	.490	624	.1001	.0789	.0382
.7	....	.367	.485	.701	0825	.0651	.0310
1.	....	.337	.492	....	.0664	.0533	.0254
1.5	....	.306 (1.49M)	.500	.	.0523	.0425	....
2.	....	.282 (2.83M)	.516	.	.0439	....	.0183

[a] W. R. Carmody, *J. Am. Chem. Soc*, **51**, 2905 (1929).
[b] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **36**, 740 (1940).
[c] H. N. Parton and J. W. Mitchell, *Ibid.*, **35**, 758 (1939).
[d] R. G. Bates, *J. Am. Chem. Soc.*, **60**, 2983 (1938).
[e] H. S. Harned and M. E. Fitzgerald, *Ibid.*, **58**, 2624 (1936).
[f] R. G. Bates, *Ibid.*, **61**, 308 (1939).
[g] R. G. Bates and W. C. Vosburgh, *Ibid.*, **59**, 1583 (1937).
[h] R. A. Robinson, *Trans. Faraday Soc.*, **36**, 1135 (1940).

TABLE (13-3-3A)—*Continued*

II. $\gamma_\pm$ at Various Temperatures

m	$ZnCl_2$				ZnI_2			
	10°	20°	30°	40°	5°	15°	30°	40°
0.005	0.794	0.791	0.787	0.783	0.808	0.802	0.797	0.793
.007	....	....	....	....	.782	.775	.770	.765
.008	....	....	....	....	.772	.765	.759	.754
.01	.737	.733	.728	.723	.757	.750	.744	.738
.02	.673	.669	.663	.657	.701	.694	.687	.680
.03	.635	.631	.625	.617	.671	.664	.655	.648
.05	.587	.582	.575	.566	.634	.627	.617	.609
.07	.556	.551	.543	.532	.611	.604	.594	.585
.1	.525	.520	.510	.497	.592	.585	.574	.564
.2	.476	.465	.452	.434	.581	.572	.559	.546
.5	.453	.439	.419	.393	.650	.638	.614	.593
.7	.433	.409	.379	.347	.740	.723	.687	.656
.8	.415	.384	.349	.313	.787	.766	.724	.687
1.0	.394	.357	.318	.280	....	....	....	....

m	$CdCl_2$		$CdBr_2$			
	0°	40°	5°	15°	30°	40°
0.0005	0.885	0.872	0.850	0.854	0.855	0.853
.001	.834	.811	.777	.784	.787	.784
.002	.746	.739	.688	.696	.699	.696
.005	.659	.607	.553	.564	.571	.569
.007	....	....	.504	.514	.521	.518
.01	.545	.505	.453	.463	.468	.465
.02	.444	.408	.358	.366	.370	.367
.03	....	....	.309	.317	.320	.317
.05	.318	.292	.250	.257	.259	.256
.07	....	....	.215	.221	.223	.221
.1	.237	.218	.182	.187	.189	.186
.2	....	....	.127	.130	.132	.129
.5	....	....	.0753	.0779	.0787	.0772
.7	....	....	.0619	.0643	.0650	.0638
1.	....	....	.0505	.0526	.0532	.0522
1.2	....	....	.0449	.0467	.0473	.0465
1.5	....	....	.0400	.0418	.0424	.0417
1.8	....	....	.0359	.0376	.0383	.0376

TABLE (13-3-3A)—*Concluded*

II. $\gamma_{\pm}$ at Various Temperatures

m	CdI$_2$†					
	5°	15°	20°	25°	30°	40°
0.002	0.566	0.596	0.607	0 615	0 622	0.629
.005	.445	.472	.483	.492	.499	.506
.007	.391	.417	428	.436	.443	.440
.01	.338	.364	374	.382	.389	.397
.02	.243	.265	.274	.281	.287	.294
.05	.141	.156	162	.167	.171	.177
.07	.113	.126	.131	.135	.139	.143
.1	.0891	0989	.103	107	.110	.113
.2	.0562	.0625	.0652	0675	.0694	.0718
.5	.0307	0342	.0356	.0369	.0379	.0393
.7	.0254	.0282	.0294	.0304	0312	.0323
1.	.0210	.0233	.0242	0250	.0257	.0265
1.5	.0173	.0191	.0198	0205	.0210	.0216
2.	.0155	.0171	0177	.0183	.0187	.0192

† R. G. Bates, *J. Am. Chem. Soc.*, **63**, 399 (1941).

TABLE (13-3-4A). $\bar{L}_2$ AND $\bar{J}_2$ OF $ZnCl_2$ AND ZnI_2 FROM ELECTROMOTIVE FORCE DATA. CONSTANTS OF EQUATIONS:

$$\bar{L}_2 = \alpha + \beta T^2; \text{ and } \bar{J}_2 = 2\beta T$$

Valid from 0 to 40°

1. $ZnCl_2$[a]

m	$-\alpha$	β	$\bar{L}_2(25°)$	$\bar{J}_2(25°)$
0.005	295	0.0060	237	4
.01	718	.0116	316	7
.02	1540	.0219	403	13
.03	2140	.0295	485	18
.05	3380	.0453	644	27
.07	4400	.0587	812	35
.1	5700	.0752	981	45
.2	9340	.1224	1530	73
.3	12110	.1639	2450	98
.5	11760	.1773	3990	106
.7	11430	.1846	4970	110
1.	10290	.1846	6110	110

[a] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **36**, 740 (1940).

2. ZnI_2[b]

m	$-\alpha$	$\beta \times 10^4$	$\bar{L}_2(25°)$	$\bar{J}_2(25°)$
0.005	739	106	204	6
.007	848	125	259	7
.008	895	134	294	8
.01	1152	166	324	10
.02	1719	240	413	15
.03	2095	291	488	18
.05	2623	360	576	22
.07	3009	411	640	25
.1	3381	461	720	28
.2	4291	586	917	35
.5	6852	932	1432	56
.7	8740	1200	1922	72
.8	9405	1301	2160	78

[b] R. G. Bates, *J. Am. Chem. Soc.*, **60**, 2983 (1938).

TABLE (13-3-5A). RELATIVE PARTIAL MOLAL HEAT CONTENT OF CADMIUM HALIDE SOLUTIONS†

m	$CdCl_2$		$CdBr_2$		CdI_2	
	15°	25°	15°	25°	15°	25°
0.0001	47	67	−4	6	−287	−157
.0005	112	157	−74	−7	−819	−564
.001	162	232	−134	−23	−1148	−828
.005	362	634	−343	−108	−2155	−1587
.01	472	759	−414	−131	−2622	−1941
.05	702	993	−540	−127	−3700	−2789
.1	778	1134	−591	−70	−4074	−3108
.2	860	1323	−639	−9	......	......
.4	. .	....	−686	−5	......	......

† A. L. Robinson and W. E. Wallace, *Chem. Rev.*, **30**, 195 (1942).

TABLE (13-7-1A). ACTIVITY COEFFICIENTS OF TRIVALENT METAL CHLORIDES AT 25°†

m	Activity Coefficients								
	$AlCl_3$	$ScCl_3$	YCl_3	$LaCl_3$	$CeCl_3$	$PrCl_3$	$NdCl_3$	$SmCl_3$	$EuCl_3$
0.05	0.409	0.395	0.392	0.392	0.392	0.390	0.389	0.385	0.389
0.1	0.360	0.342	0.336	0.336	0.331	0.333	0.332	0.331	0.335
0.2	0.308	0.297	0.293	0.292	0.292	0.292	0.291	0.290	0.294
0.3	0.323	0.302	0.288	0.281	0.279	0.278	0.279	0.280	0.283
0.5	0.354	0.319	0.297	0.285	0.282	0.280	0.282	0.284	0.288
0.7	0.415	0.363	0.328	0.305	0.306	0.301	0.308	0.306	0.313
1.0	0.578	0.474	0.412	0.366	0.366	0.362	0.368	0.373	0.383
1.2	0.750	0.582	0.494	0.426	0.423	0.423	0.431	0.442	0.453
1.4	1.002	0.724	0.606	0.503	0.502	0.500	0.514	0.526	0.543
1.6	1.374	0.913	0.750	0.600	0.598	0.597	0.617	0.643	0.666
1.8	1.946	1.165	0.946	0.724	0.732	0.722	0.753	0.795	0.830
2.0			1.216	0.883	0.906	0.883	0.928	0.997	1.076

† C. M. Mason, *J. Am. Chem. Soc.*, **60**, 1638 (1938); **63**, 220 (1942). Recalculated by R. A. Robinson to conform with the new isopiestic vapor pressure standards (See Appendix B, Section (5)) and referred by us to the value for $LaCl_3$ at 0.05*M* (See Table (13-7-1)).

TABLE (13-11-1A). MEAN ACTIVITY COEFFICIENT OF SULFURIC ACID IN AQUEOUS SOLUTIONS FROM ELECTROMOTIVE FORCES[a]

m	0°	10°	20°	25°	30°	40°	50°	60°
0.0005	0.912	0.901	0.890	0.885	0.880	0.869	0.859	0.848
.0007	.896	.880	.867	.857	.854	.841	.828	.814
.001	.876	.857	.839	.830	.823	.806	.790	.775
.002	.825	.796	.769	.757	.746	.722	.701	.680
.003	.788	.754	.723	.709	.695	.669	.645	.622
.005	.734	.693	.656	.639	.623	.593	.566	.533
.007	.691	.647	.608	.591	.574	.543	.515	.489
.01	.649	.603	.562	.544	.527	.495	.467	.441
.02	.554	.509	.470	.453	.437	.407	.380	.356
.03	.495	.453	.417	.401	.386	.358	.333	.311
.05	.426	.387	.354	.340	.326	.301	.279	.260
.07	.383	.346	.315	.301	.290	.266	.246	.228
.1	.341	.307	.278	.265	.254	.227	.214	.197
.2	.271	.243	.219	.209	.199	.161	.166	.153
.5	.202	.181	.162	.154	.147	.133	.122	.107
1.	.173	.153	.137	.130	.123	.111	.101	.0922
1.5	.167	.147	.131	.124	.117	.106	.0956	.0869
2.	.170	.149	.132	.124	.118	.105	.0949	.0859
3.	.201	.173	.151	.141	.132	.117	.104	.0926
4.	.254	.215	.184	.171	.159	.138	.121	.106
5.	.330	.275	.231	.212	.196	.168	.145	.126
6.	.427	.350	.289	.264	.242	.205	.174	.150
7.	.546	.440	.359	.326	.297	.247	.208	.177
8.	.686	.545	.439	.397	.358	.296	.246	.206
9.	.843	.662	.527	.470	.425	.346	.285	.237
10.	1.012	.785	.618	.553	.493	.398	.325	.268
11.	1.212	.930	.725	.643	.573	.458	.370	.302
12.	1.431	1.088	.840	.742	.656	.521	.418	.339
13.	1.676	1.261	.965	.851	.750	.590	.471	.379
14.	1.958	1.458	1.104	.967	.850	.664	.525	.420
15.	2.271	1.671	1.254	1.093	.957	.741	.583	.462
16.	2.612	1.907	1.420	1.234	1.076	.828	.647	.511
17.	3.015	2.176	1.604	1.387	1.204	.919	.712	.559
17.5	3.217	2.316	1.703	1.471	1.275	.972	.752	.589

[a] H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 27 (1935). (Regions of confirmed validity 0 to 4 *M* and 9 to 11 *M* inclusive.)

TABLE (13-13-1A). THE RELATIVE PARTIAL MOLAL HEAT CONTENT OF SULFURIC ACID.[a] CONSTANTS OF EQUATION:

$$\bar{L}_2 = \bar{L}_2(0°) + \alpha t + \beta t^2$$

m	$\bar{L}_2(0°)$	α	$\beta \times 10^2$	$\bar{L}_2(25°)$	$J_2(25)^{\bullet}$ (E.M.F.)	$J_2(25°)$ (Cal.)
0.0005	397	7.228	6.748	620	11	..
.001	858	7.678	6.706	1092	11	..
.002	1481	7.038	6.664	1699	10	..
.005	2503	6.948	6.676	2719	10	..
.01	3244	7.538	6.691	3474	11	6
.02	3729	7.328	6.713	3954	11	7
.05	4192	7.128	6.628	4411	10.	8
.1	4672	7.748	6.712	4908	11	9
.2	4903	8.008	6 798	5145	11	11
.5	5063	8 268	6.828	5313	12	15
1.	5310	10.168	7.118	5608	14	21
2.	5766	11.068	7.658	6091	15	27
3.	6607	11.528	7.488	6942	15	25
4.	7464	11.908	7.458	7809	15	21
6.	9059	12.578	7.638	9421	16	16
8.	10399	13.898	7.908	10795	18	13
10.	11474	16.768	8.518	11946	21	20
12.	12434	18.218	8.748	12944	23	24
14.	13402	16.168	8.308	13858	20	26
16.	14320	12.438	7 388	14677	16	28
17.5	14961	11.508	7.488	15296	15	29

[a] H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 27 (1935).

TABLE (13-14-1A). THE CATION TRANSFERENCE NUMBERS OF SULFURIC ACID[a] IN WATER

m	0°	10°	15°	25°	35°	45°	60°
0.0	(0.840)	(0.829)	(0.824)	(0.813)	(0.801)	(0.788)	(0.761)
.05	.839	.834	.830	.819	.807	.793	.770
.10	.838	.834	.829	.819	.807	.793	.770
.20	.837	.833	.829	.819	.806	.792	.770
.50	.834	.828	.824	.815	.801	.787	.764
1.00	.828	.822	.818	.808	.793	.779	.755
2.00	.816	.808	.803	.793	.779	.763	.737
3.00	.803	.793	.788	.776	.762	.747	.720
5.00	.772	.762	.756	.744	.730	.715	.689
8.00	.720	.708	.702	.690	.676	.663	.641
10.00	.682	.672	.666	.655	.642	.629	.610
12.00	.638	.629	.625	.616	.605	.595	.578
14.00	.591	.584	.580	.573	.564	.556	.543
17.00	.512	.508	.506	.502	.498	.494	.488
$\mathcal{S}_{(T)}\sqrt{d_0}$	.0331	.0362	.0370	.0375	.0363	.0331	.0250

[a] W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 662 (1935).

TABLE (14-2-1A). THE MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC AND HYDROBROMIC ACIDS IN HALIDE SOLUTIONS. ACID CONCENTRATION = 0.01M. SALT CONCENTRATION = m

Part I. Hydrochloric Acid

m	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
(1) Salt = KCl^a											
0 0	0.906	0.906	0.906	0.905	0.905	0.905	0.904	0.903	0.902	0.901	0.900
.01	.876	.875	.875	.874	.874	.874	.873	.871	.871	.869	.866
.02	.856	.855	.853	.853	.853	.852	.851	.850	.850	.847	.844
.03	.841	.841	.840	.839	.838	.837	.836	.834	.834	.831	.828
.05	.819	.819	.817	817	.816	.816	.814	.812	.812	.809	.806
.1	.786	.786	.786	.784	.783	.782	.780	.778	.777	.773	.769
.2	.753	.753	.752	.750	.749	.747	.746	.743	.742	.739	.734
.5	.712	.712	.711	.709	.708	.706	.704	.701	.699	.695	.690
1.	.731	.727	.728	.725	.723	.720	.716	.712	.709	.702	.697
1.5	.758	.757	.754	.750	.747	.743	.738	.732	.728	.722	.713
2.	.801	.749	.796	.791	.786	.781	.773	.767	.761	.753	.743
3.	.893	.890	.882	875	.868	.860	.851	.841	.831	.820	.808
3.5	.939	.933	.926	917	.908	.899	.888	876	.867	.853	.839
(2) Salt = NaCl^b											
0.01	0.877	0.876	0.876	0.875	0 874	0.874	0.873	0.872	0.871	0.870	0.869
.02	.856	.856	.856	.855	.855	.854	.853	.851	.850	.849	.847
.05	.821	.821	.821	.819	.819	818	.816	.814	.812	.810	.807
.1	.789	.789	.788	.786	.785	784	.781	.779	.777	.774	.771
.2	.758	.758	.757	754	753	.752	.749	.747	.745	.742	.739
.5	.738	.737	.736	.733	.732	.730	.727	.724	.721	.718	715
1.	.765	.764	.762	.759	.756	.754	.750	.746	.742	.738	.733
2.	.898	.896	.893	888	.883	.878	.871	864	.856	.847	.838
3.	1.103	1.099	1.094	1 086	1.077	1.068	1.056	1.043	1.029	1.014	.999
(3) Salt = LiCl^c											
0.01	.....	.....	.....	0.878	0.878	0.881	0.879	0.877	.....	.....	.....
.02	.....	.....	.....	.859	.859	.861	.859	.857	.....	.....	.....
.05	.....	.....	.....	.826	.826	.827	.824	.822	.....	.....	.....
.1	.....	.....	.....	.798	.797	.796	.793	.789	.....	.....	.....
.2	.....	.....	.....	.769	.767	.766	.762	.760	.....	.....	.....
.5	.....	.....	.....	.762	.759	.757	.753	.749	.....	.....	.....
1.	.....	.....	.....	.812	,806	.801	.793	.787	.....	.....	.....
1.5	.....	.....	.....	.896	.887	.879	.869	.858	.....	.....	.....
2.	.....	.....	.....	1.012	.999	.986	.972	.958	.....	.....	.....
3.	.....	.....	.....	1.334	1.308	1.284	1.257	1.232	.....	.....	.....
4.	.....	.....	.....	1.791	1.748	1.708	1.665	1.624	.....	.....	.....

(4) Salt = $BaCl_2{}^d$; μ = Ionic strength of solution

μ	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
0.01	0.906	0.906	0.905	0.905	0 905	0 905	0.903	0.903	0.902	0.901	0.900
.02	.876	.876	.875	.875	.875	.875	.873	.872	.871	.870	.869
.03	.855	.855	.855	.855	.855	.854	.853	.852	.851	.850	.848
.05	.829	.828	.827	.827	.827	.826	.825	.824	.823	.821	.820
.07	.808	.808	.808	.808	.808	.807	.805	.804	.802	.801	.799
.1	.788	.788	.787	.787	.787	.786	.784	.783	.781	.779	.777
.2	.747	.748	.748	.747	.747	.746	.744	.741	.739	.736	.733
.5	.710	.709	.709	.708	.707	.705	.702	.698	.694	.690	.686
.7	.704	.704	.703	.702	.700	.698	.694	.691	.686	.682	.677
1.	.707	.706	.705	.704	.702	.699	.693	.690	.685	.680	.675
2.	.760	.758	.756	.752	.748	.743	.737	.731	.724	.716	.708
3.	.847	.844	.841	.836	.830	.823	.815	.805	.796	.785	.774

TABLE (14-2-1A)—*Continued*

Part II. Hydrobromic Acid

m	*0°*	*5°*	*10°*	*15°*	*20°*	*25°*	*30°*	*35°*	*40°*	*45°*	
(1) Salt = KBr[e]											
0.0	*0.910*	*0.910*	*0.909*	*0.908*	*0.907*	*0.906*	*0.906*	*0.905*	*0.904*	*0.903*	*0.902*
.01	*.881*	*.880*	*.879*	*.877*	*.876*	*.874*	*.874*	*.873*	*.871*	*.870*	*.868*
.02	*.861*	*.860*	*.858*	*.856*	*.855*	*.853*	*.852*	*.852*	*.849*	*.847*	*.846*
.03	*.845*	*.844*	*.843*	*.841*	*.834*	*.838*	*.837*	*.835*	*.833*	*.831*	*.829*
.05	.824	.824	.822	.821	.820	.818	.817	.814	.812	.811	.810
.1	.792	.792	.790	.787	.785	.783	.782	.778	.776	.773	.771
.2	.760	.759	.757	.754	.752	.750	.748	.744	.741	.738	.736
.5	.728	.728	.725	.722	.722	.717	.714	.710	.705	.701	.697
1.	.748	.745	.741	.737	.732	.728	.724	.718	.712	.706	.700
1.5	.777	.774	.770	.765	.760	.756	.751	.743	.736	.729	.722
2.	.840	.836	.831	.825	.818	.810	.803	.794	.785	.776	.767
3.	.974	.967	.958	.948	.937	.926	.916	.903	.890	.874	.864
(2) Salt = NaBr[e]											
0.01	0.884	0.883	0.882	0.880	0.879	0.878	0.878	0.878	0.875	0.876	0.874
.02	.866	.866	.865	.863	.861	.859	.858	.858	.854	.852	.850
.03	.850	.850	.848	.846	.844	.842	.841	.841	.837	.835	.833
.05	.829	.828	.827	.824	.822	.821	.820	.818	.815	.813	.811
.1	.801	.799	.797	.795	.793	.791	.789	.788	.783	.781	.779
.2	.780	.778	.775	.772	.769	.767	.765	.765	.759	.756	.753
.5	.774	.772	.768	.764	.761	.756	.752	.747	.739	.735	.730
1.	.833	.827	.821	.814	.808	.801	.795	.788	.778	.770	.762
1.5	.934	.926	.916	.906	.895	.884	.875	.865	.852	.840	.828
2.	1.050	1.038	1.026	1.009	.995	.981	.967	.954	.936	.921	.905
3.	1.362	1.337	1.311	1.284	1.258	1.233	1.208	1.184	1.156	1.131	1.106
(3) Salt = LiBr[f]											
0.0	0.911	0.910	0.910	0.909	0.908	0.907	0.905	0.904	0.902	0.901	0.899
.01	.885	.885	.884	.883	.882	.880	.878	.877	.874	.872	.870
.02	.866	.867	.866	.865	.864	.863	.861	.858	.856	.853	.850
.03	.854	.854	.853	.852	.851	.849	.847	.844	.841	.838	.835
.05	.834	.834	834	.833	.831	.829	.827	.824	.821	.817	.814
.07	.821	.821	.821	.820	.818	.816	.813	.811	.807	.804	.799
.1	.810	.809	.807	.807	.805	.802	.799	.796	.793	.789	.785
.2	.796	.794	.792	.789	.787	.783	.780	.776	.772	.767	.763
.3	.796	.793	.791	.788	.784	.780	.776	.772	.768	.763	.758
.4	.802	.799	.796	.792	.788	784	.780	.775	.770	.765	.760
.6	.824	.822	.818	.814	.809	.805	.800	.794	.789	.783	.777
1.	.911	.905	.898	.892	.885	.878	.870	.863	.856	.848	.840
1.5	1.061	1.050	1.039	1.028	1.017	1.006	.996	.985	.974	.964	.954
2.	1.255	1.241	1.227	1.213	1 197	1.160	1.168	1.152	1.137	1.121	1.105
3.	1.775	1.748	1.720	1.694	1.667	1.641	1.615	1.589	1.564	1.538	1.514

TABLE (14-2-1A)—*Concluded*

Part III. Hydrochloric Acid at 25°

Acid concentration = m_1; salt concentration = m_2

m_2	(m_1 = 0.01) $CsCl^g$	m_2	(m_1 = 0.05) $AlCl_3^h$	m_2	(m_1 = 0.01) $CeCl_3^i$	m_2	(m_1 = 0.01) $SrCl_2^j$
0.0	0.905	0.0	0.830	0.0	0.904	0.0	0.904
.01	.875	.005	.809	.005	.839	.025	.797
.03011	.836	.075	.799	.01	.805	.05	.761
.07	.795	.01	.789	.03	.745	.075	.743
.1	.773	.02	.763	.05	.717	.1	.731
.2	.730	.03	.750	.075	.699	.2	.706
.4	.685	.05	.728	.1	.689	.3	.711
.7	.656	.07	.714	.165	.662	.5	.739
1.	.644	.1	.708	.25	.655	75	.801
1.34	.638	.2	.716	.375	.664	1.	.888
1.5	.639	.4	.797	.5	.698	1.5	1.121
2.	.641	.6	.920	.75	.767	2.	1.460
3.	.672	1.	1.402	1.	.855	2.5	1.944
		2.	3.96				

[a] H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).
[b] H. S. Harned and G. E. Mannweiler, *Ibid*., **57**, 1873 (1935).
[c] H. S. Harned and H. R. Copson, *Ibid.*, **55**, 2296 (1933).
[d] H. S. Harned and C. G. Geary, *Ibid.*, **59**, 2032 (1937).
[e] H. S. Harned and W. J. Hamer, *Ibid.*, **55**, 4496 (1933).
[f] H. S. Harned and J. G. Donelson, *Ibid.*, **59**, 1280 (1937).
[g] H. S. Harned and O. E. Schupp Jr., *Ibid.*, **52**, 3892 (1930).
[h] H. S. Harned and C. M. Mason, *Ibid.*, **53**, 3377 (1931).
[i] C. M. Mason and D. B. Kellam, *J. Phys. Chem.*, **38**, 689 (1934).
[j] J. E. Vance, *J. Am. Chem. Soc.*, **55**, 2729 (1933).

TABLE (14-9-1A).[a] SMOOTHED VALUES OF LOG $\gamma_\pm$ FOR HYDROCHLORIC ACID IN CONCENTRATED AQUEOUS SOLUTIONS

m	0°	10°	20°	25°	30°	40°	50°
3	0.1544	0.1377	0.1205	0.1120	0.1028	0.0841	0.0650
4	.2955	.2732	.2503	.2389	.2269	.2025	.1775
5	.4427	.4145	.3857	.3714	.3564	.3260	.2951
6	.5922	.5581	.5233	.5059	.4879	.4516	.4146
7	.7413	.7011	.6603	.6400	.6190	.5765	.5335
8	.8877	.8415	.7948	.7714	.7475	.6990	.6500
9	1.0297	.9776	.9250	.8988	.8718	.8175	.7625
10	1.1661	1.1082	1.0498	1.0208	.9908	.9306	.8699
11	1.2962	1.2326	1.1684	1.1366	1.1036	1.0377	.9712
12	1.4196	1.3503	1.2803	1.2457	1.2097	1.1380	1.0657
13	1.5366	1.4613	1.3855	1.3479	1.3090	1.2314	1.1531
14	1.6476	1.5662	1.4841	1.4436	1.4016	1.3178	1.2334
15	1.7536	1.6656	1.5770	1.5333	1.4878	1.3975	1.3065
16	1.8559	1.7608	1.6650	1.6179	1.5687	1.4711	1.3730

[a] G. Åkerlöf and J. W. Teare, *J. Am. Chem. Soc.*, **59**, 1855 (1937). Extensive tables of L_2, J_2, etc. are also given in this contribution.

TABLE (15-2-1A). THE IONIC ACTIVITY FUNCTION OF WATER, $\gamma_H\gamma_{OH}/a_{H_2O}$, IN SALT SOLUTIONS

KCl[a]

μ	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
0.01	0.819	0.818	0.818	0.818	0.817	0.816	0.816	0.812	0.809	0.809	0.808
.02	.765	.762	.764	.762	.759	.760	.760	.754	.753	.751	.750
.03	.732	.729	.726	.727	.726	.726	.725	.720	.718	.715	.713
04	.707	.709	.706	.706	.704	.702	.700	.696	.694	.691	.687
.06	.672	.672	.669	.671	.669	.668	.667	.662	.661	.655	.655
.11	.621	.621	.622	.623	.619	.618	.617	.612	.611	.605	.602
.21	.574	.576	.576	.576	.572	.574	.573	.567	.565	.562	.558
.51	.534	.536	.537	.538	.535	.534	.534	.527	.524	.519	.514
1.01	.600	.596	.601	.599	.595	.592	.588	.580	.574	.563	.558
1.51	.698	.689	.696	.693	.677	.672	.665	.652	.643	.633	.620
2 01	.816	.815	.813	.807	.795	.787	.774	.761	.744	.728	.710
3.01	1.128	1.126	1 109	1.095	1.075	1 056	1.037	1.006	-.979	.948	.925
3.51	1.313	1.301	1.285	1.264	1.234	1.205	1.183	1.147	1.109	1.075	1.043

NaCl[b]

0.02	0.764	0.764	0.763	0.763	0.760	0.759	0.759	0.756	0.752	0.752	0.751
.03	.726	.728	.732	.728	.726	.725	.725	.720	.717	.715	.715
.06	.663	.665	.666	.665	.664	.664	.663	.658	.653	.650	.649
.11	.612	.613	.613	.611	.608	.607	.605	.600	.595	.591	.589
.21	.562	.562	.559	.559	.557	.556	.553	.549	.544	.540	.538
.51	.519	.519	.520	.518	.516	.514	.513	.508	.502	.498	.497
1.01	.542	.543	.542	.541	.537	.535	.531	.524	.517	.511	.507
2.01	.694	.698	.699	.696	.691	.696	.681	.667	.654	.640	.629
3.01	.975	.982	.985	.982	.972	.962	.998	.925	.898	.878	.855

LiCl[c]

μ	15°	20°	25°	30°	35°	μ	15°	20°	25°	30°	35°
0.02	0.758	0.758	0 759	0 759	0.758	0.35	0.466	0.464	0.462	0.459	0.456
.03	.717	.718	.719	.718	.717	.40	.456	.454	.452	.449	.447
.05	.664	.663	.665	.664	.662	.45	.449	.446	.443	.440	.440
.06	.645	.646	.645	.644	.642	.50	.442	.439	.437	.433	.431
.10	.591	.590	.589	.587	.584	1.01	.409	.405	.400	.395	.390
.11	.581	.580	.579	.575	.572	1.51	.408	.402	.397	.390	.383
.15	.546	.544	.543	.540	.536	2.01	.427	.418	.410	.401	.393
.20	.515	.513	.511	.508	.505	2 51	.459	.449	.438	.427	.416
.25	.493	.491	.489	.486	.483	3.01	.496	.483	.470	.456	.442
.30	.478	.476	.474	.471	.468	....	....	....	....	....	....

KBr[d]

μ	0°	5°	10°	15°	20°	25°	30°	35°	40°
0.02	0.778	0.775	0.774	0.771	0.769	0.766	0.764	0.764	0.761
.03	.744	.739	.739	.736	.734	.731	.729	.728	.725
.04	.719	.715	.713	.709	.710	.709	.706	.704	.701
.06	.685	.683	.680	.678	.676	.675	.672	.671	.668
.11	.635	.633	.628	.630	.628	.624	.621	.621	.617
.21	.583	.583	.582	.582	.581	.579	.576	.574	.570
.51	.540	.540	540	.540	.541	.536	.532	.529	.523
1.01	.601	.601	.600	.598	.595	.590	.584	.578	.570
1.51	.677	.677	.677	.672	.667	.661	.651	.642	.630
2.01	.798	.795	.795	.785	.776	.764	.752	.739	.721
3.01	1.062	1.053	1.045	1.029	1.009	.993	.971	.947	.921

TABLE (15-2-1A)—*Concluded*

NaBr[d]

μ	0°	5°	10°	15°	20°	25°	30°	35°	40°
0.02	0.777	0.773	0.773	0.771	0.769	0.767	0.765	0.765	0.761
.03	.745	.742	.741	.737	.735	.731	.728	.726	.723
.04	.715	.711	.711	.707	.705	.703	.701	.699	.695
.06	.678	.675	.674	.670	.668	.666	.662	.660	.655
.11	.624	.622	.621	.618	.615	.612	.608	.606	.601
.21	.571	.569	.570	.568	.566	.565	.563	.561	.558
.51	.524	.525	.528	.527	.526	.524	.520	.518	.513
1.01	.552	.551	.553	.551	.550	.547	.542	.539	.532
1.51	.648	.640	.638	.633	.626	.618	.609	.600	.592
2.01	.752	.746	.740	.730	.718	.706	.693	.679	.662
3.01	1.044	1.020	1.007	.983	.959	.931	.905	.878	.847

LiBr[e]

μ	0°	5°	10°	15°	20°	25°	30°	35°	40°
0.02	0.778	0.778	0.777	0.773	0.771	0.769	0.770	0.769	0.767
.03	.736	.736	.738	.735	.733	.731	.733	.731	.729
.04	.707	.708	.709	706	.704	.702	.704	.701	.698
.06	.659	.662	.663	.661	.660	.658	.659	.657	.653
.08	.624	.628	.630	.629	.628	.627	.628	.625	.622
.11	.590	.593	.594	.593	.592	.590	.591	.588	.584
.21	.525	.527	.528	.526	524	.522	.522	.518	.513
.31	.492	.493	.494	.491	489	.486	.484	.481	.476
.41	.469	.470	.469	.467	.464	.461	.460	.456	.451
.61	.442	.442	.441	.438	.435	.432	.430	.426	.421
1.01	.426	.426	.424	.420	.416	.412	.409	.404	.398
1 51	.442	.437	.436	.430	.425	.419	.415	.408	.400
2 01	.478	.472	.469	.462	.455	.449	.443	.434	.424
2.51	.553	.549	.544	.535	.527	.517	.509	.498	.486

$BaCl_2$[f]

μ	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
0.03	0.727	0.728	0.723	0.720	0.716	0.716	0.719	0.716	0.711	0.710	0.713
.05	.676	.677	.671	.668	665	.660	.665	.663	.658	.655	.658
.07	.637	.638	.637	.633	.629	626	.628	.624	.619	.616	.617
.1	.597	.598	.594	.593	.589	.587	.589	.584	.579	.574	.574
.2	.516	.517	.515	.514	.511	507	.507	.502	.495	.490	.488
.5	.426	.423	.421	.418	.416	.412	.410	.404	.397	.391	.385
.7	.391	.394	.392	.390	.386	.383	.381	.375	.368	.362	.358
1.	.364	.367	.364	.363	.361	.357	.354	.350	.343	.337	.333
2.	337	.341	.339	.337	.334	330	.326	.320	.313	.307	.301
3.	.339	.344	.344	.341	.337	.333	.328	.320	.310	.302	.292

Values in cesium chloride[g], strontium chloride[h], and sodium, potassium, and lithium sulfates[i] have been obtained at 25°.

[a] H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).
[b] H. S. Harned and G. E. Mannweiler, *Ibid.*, **57**, 1873 (1935).
[c] H. S. Harned and H. R. Copson, *Ibid.*, **55**, 2206 (1933).
[d] H. S. Harned and W. G. Hamer, *Ibid.*, **55**, 4496 (1933).
[e] H. S. Harned and J. G. Donelson, *Ibid.*, **59**, 1280 (1937).
[f] H. S. Harned and C. G. Geary, *Ibid.*, **59**, 2032 (1937).
[g] H. S. Harned and O. E. Schupp Jr., *Ibid.*, **52**, 3892 (1930).
[h] J. E. Vance, *Ibid.*, **55**, 2729 (1933).
[i] G. Åkerlöf, *Ibid.*, **48**, 1160 (1926).

TABLE (15-6-1A). OBSERVED IONIZATION CONSTANTS IN WATER. ALL VALUES ARE ON THE *m*-SCALE. SEE TABLE (B-10-1)

Acids		0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°	Ref.
Formic....	$K_A \times 10^4$	1.638	1.691	1.728	1.749	1.765	1.772	1.768	1.747	1.716	1.685	1.650	1.607	1.551	(1)
Acetic......	$K_A \times 10^5$	1.657	1.700	1.729	1.745	1.753	1.754	1.750	1.728	1.703	1.670	1.633	1.589	1.542	(2)
Propionic...	$K_A \times 10^5$	1.274	1.305	1.326	1.336	1.338	1.336	1.326	1.310	1.280	1.257	1.229	1.195	1.160	(3)
n-Butyric	$K_A \times 10^5$	1.563	1.574	1.576	1.569	1.542	1.515	1.484	1.439	1.395	1.347	1.302	1.252	1.199	(4)
Chloro-acetic....	$K_A \times 10^3$	1.528		1.488	1.440†		1.379	1.308‡		1.230					(5)
Lactic	$K_A \times 10^4$	1.287		1.361*			1.374		1.336**			1.270			(6)
Glycolic.	$K_A \times 10^4$	1.334		1.427*			1.475		1.471**			1.415			(7)
Sulfuric	$K_{2A} \times 10^2$		1.80		1.36		1.01		0.75		0.56		0.41		(7a)
Carbonic...	$K_{2A} \times 10^{11}$	2.36	2.77	3.24	3.71	4.20	4.69	5.13	5.62	6.03	6.38	6.73			(7b)
Oxalic	$K_{2A} \times 10^5$	5.91	5.82	5.70	5.55	5.40	5.18	4.92	4.67	4.41	4.09	3.83			(8)
Malonic ..	$K_{2A} \times 10^6$	2.140	2.165	2.152	2.124	2.076	2.014	1.948	1.863	1.768	1.670	1.575	1.469	1.362	(8a)
Phosphoric....	$K_{1A} \times 10^3$	8.968		8.394*			7.516		6.531**			5.495			(9)
	$K_{2A} \times 10^8$					6.056	6.226	6.349	6.430	6.471	6.475	6.439			(10)
Boric....	$K_A \times 10^{10}$		3.63	4.17	4.72	5.26	5.79	6.34	6.86	7.38		8.32			(11)
Amino-Acids															
Glycine..	$K_A \times 10^3$			3.94		4.31	4.47	4.50		4.81					(12)
	$K_B \times 10^5$			4.68	5.12	5.57	6.04	6.52	6.98	7.43	7.87				(12)
Alanine	$K_A \times 10^3$					4.47	4.57	4.66	4.71	4.74	4.76				(13)
	$K_B \times 10^5$					6.90	7.47	8.08	8.61	9.10	9.60				(13)

* At 12.5°; † At 18°; ‡ At 32°; ** At 37.5°.

(1) H. S. Harned and N. D Embree, *J. Am. Chem. Soc*, 56, 1042 (1934).
(2) H. S. Harned and R W. Ehlers, *Ibid*, 55, 652 (1933).
(3) H. S. Harned and R. W Ehlers, *Ibid*, 55, 2379 (1933).
(4) H. S. Harned and R. O Sutherland, *Ibid*, 56, 2039 (1934).
(5) D D. Wright, *Ibid*, 56, 314 (1934).
(6) L. F. Nims and P. K. Smith, *J. Biol Chem.*, 113, 145 (1936).
(7) L. F. Nims, *J. Am. Chem. Soc.*, 58, 987 (1936).
(7a) Private communication from Professor T. F. Young based on the Dissertations of I. M Klotz and C. R. Singleterry, University of Chicago (1940).
(7b) H. S. Harned and S. R. Scholes, Jr, *J Am Chem Soc*, 63, 1706 (1941).
(8) H. S. Harned and L. D. Fallon, *Ibid.*, 61, 3111 (1939).
(8a) W. J. Hamer, J. O. Burton and S. F. Acree, *Bur. Standard J. Research*, 24, 292 (1940).
(9) L. F. Nims, *J. Am. Chem. Soc.*, 56, 1110 (1934).
(10) L. F. Nims, *Ibid.*, 55, 1946 (1933).
(11) B. B. Owen, *Ibid.*, 56, 1695 (1934); 56, 2785 (1934).
(12) B. B Owen, *Ibid.*, 56, 24 (1934).
(13) L. F. Nims and P. K. Smith, *J. Biol. Chem*, 101, 401 (1933).

H. V. Tartar and H. H. Garretson [*J. Am. Chem. Soc.*, 63, 808 (1941)] have determined the ionization constants of sulphurous acid at 25° from cells without liquid junctions. K_{1A} and K_{2A} are found to be 1.72×10^{-2} and 6.24×10^{-8}, respectively.

TABLE (15-6-2A). IONIZATION CONSTANTS IN DIOXANE-WATER AND METHANOL-WATER MIXTURES. ALL VALUES ARE ON THE m-SCALE. SEE TABLE (B-10-2).

X = Weight Percent of Organic Solvent

X		0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
Water in Dioxane-Water Mixtures (1)												
0 (6)	$K_w \times 10^{14}$	0.1139	.1846	.2920	.4505	.6809	1.008	1.469	2.089	2.919	4.018	5.474
20	$K_w \times 10^{15}$	.2702	.4375	.6918	1.067	1.622	2.399	3.477	4.922	6.947	9.531	12.87
45	$K_w \times 10^{16}$	.2114	.3409	.5349	8188	1.234	1.809	2.594	3.655	5.077	6.914	9.277
70	$K_w \times 10^{18}$	.1789	.2819	.4348	.6511	.9654	1.395	1.974	2.743	3.779	5.064	6.719
Formic Acid in Dioxane-Water Mixtures (2)												
0 (7)	$K_A \times 10^{4}$	1.638	1.691	1.728	1.749	1.765	1.772	1.768	1.747	1.716	1.685	1.650
20	$K_A \times 10^{5}$	6.412	6.548	6.625	6 656	6.651	6.605	6.519	6.394	6.243	6.077	5.876
45	$K_A \times 10^{6}$	8.702	8.702	8.614	8.488	8.318	8.099	7.834	7.537	7.212	6.867	6.510
70	$K_A \times 10^{8}$	11.077	10.876	10.641	10.347	10.005	9.634	9.213	8.778	8.310	7.842	7.359
82	$K_A \times 10^{9}$	.	1.883	1.836	1.774	1.690	1.588	1.472	1.339	1.208	1.079	. . .
Acetic Acid in Dioxane-Water Mixtures (3)												
0 (7)	$K_A \times 10^{5}$	1.657	1.700	1.729	1.745	1.753	1.754	1.750	1.728	1.703	1.670	1.633
20	$K_A \times 10^{6}$	4.75	4.87	4.98	5.05	5.09	5.11	5.08	5.03	4.95	4.86	4.73
45	$K_A \times 10^{7}$	4.78	4.89	4.96	4.96	4.96	4.93	4 86	4.75	4.61	4.44	4.28
70	$K_A \times 10^{9}$	4.75	4.83	4.89	4.83	4.83	4.78	4.69	4.56	4.42	4.22	4.05
82	$K_A \times 10^{11}$	. . . .	7.41	7.50	7.55	7.55	7.24	6.92	6.61	6.09	5.49	. . .
Propionic Acid in Dioxane-Water Mixtures (4)												
0 (7)	$K_A \times 10^{5}$	1.274	1.305	1.326	1.336	1.338	1.336	1.326	1.310	1.280	1.257	1.229
20	$K_A \times 10^{6}$	3.175	3.267	3.337	3.385	3.412	3.417	3.403	3.370	3.319	3.252	3.172
45	$K_A \times 10^{7}$	2.641	2.713	2.764	2.796	2.808	2.801	2.776	2.734	2.677	2.607	2.526
70	$K_A \times 10^{9}$	2.299	2.364	2.410	2.439	2.450	2.444	2.422	2.386	2.336	2.274	2.202
82	$K_A \times 10^{11}$	. . .	3.797	3.917	3.966	3.946	3.860	3.716	3.524	3.293	3.035	. . .
Acetic Acid in Methanol-Water Mixtures (5)												
10	$K_A \times 10^{5}$	1.138		1.200	..	1.242	1.247	1.237	. .	1.214	.....	. . .
20	$K_A \times 10^{6}$	7.38	. .	7.94	. .	8.24	8.34	8.30	. ...	8.19	.. .	.....
Glycine in Dioxane-Water Mixtures (8)												
20	$K_A \times 10^{3}$	1.832	1.953	2.067	2.169	2.257	2.352	2.428	2.481	2.533	2.573	2.591
45	$K_A \times 10^{4}$	6.339	6.707	7.034	7.348	7.626	7.847	8.091	8.232	8.350	8.457	8.484
70	$K_A \times 10^{5}$	8.933	9.350	9.759	10.01	10.43	10.84	10.98	11.15	11.26	11.36	11.39
20	$K_B \times 10^{5}$	1.179	1.317	1.473	1.618	1.781	1.937	2.088	2.241	2.407	2.548	2.690
45	$K_B \times 10^{6}$	1.789	2.024	2.272	2.541	2.840	3 120	3.408	3.707	4.015	4.342	4.680
70	$K_B \times 10^{7}$	1.47	1.68	1.91	2.13	2.39	2.66	2.94	3.24	3.60	3.96	4.34

(1) H. S. Harned and L. D. Fallon, *J. Am. Chem. Soc.*, 61, 2374 (1939).

(2) H. S. Harned and R S. Done, *Ibid.*, 63, 2579 (1941).

(3) H. S. Harned and G. L. Kazanjian, *Ibid.*, 58, 1912 (1936); H. S. Harned and L. D. Fallon, *Ibid.*, 61, 2377 (1939). Revised by H. S. Harned, *J. Phys. Chem.*, 43, 275 (1938).

(4) H. S. Harned and T. R. Dedell, *Ibid.*, 63, 3308 (1941).

(5) H. S. Harned and N. D. Embree, *Ibid.*, 57, 1669 (1935).

(6) Table (15-1-1).

(7) Table (15-6-1A).

(8) H. S. Harned and C. M. Birdsall, *J. Am. Chem. Soc.*, 65, 54 (1943) for values of K_A; *Ibid.*, 65, 1117 (1943) for values of K_B.

Table (15-6-3A). Observed Ionization Constants of Amino-Acids[a] in Water. All Values Are on the *m*-Scale

	1°	12.5°	25°	37.5°	50°
dl-Alanine, $K_A \times 10^3$	3.75	4.14	4.49	4.68	4.66
$K_B \times 10^5$	4.83	6.10	7.40	8.73	9.86
dl-α-Amino-n-butyric acid, $K_A \times 10^3$	4.63	4.90	5.18	5.15	5.05
$K_B \times 10^5$	4.25	5.50	6.81	8.22	9.38
dl-α-Amino-n-valeric acid, $K_A \times 10^3$	4.21	4.57	4.81	4.91	4.86
$K_B \times 10^5$	4.04	5.18	6.47	7.64	8.63
dl-Norleucine, $K_A \times 10^3$	4.04	4.41	4.62	4.74	4.70
$K_B \times 10^4$	4.41	5.62	6.87	8.05	9.16
α-Aminoisobutyric acid, $K_A \times 10^3$	3.81	4.17	4.40	4.46	4.41
$K_B \times 10^4$	1.14	1.38	1.61	1.84	1.99
dl-Valine, $K_A \times 10^3$	4.79	5.05	5.18	5.11	4.90
$K_B \times 10^5$	3.24	4.21	5.27	6.28	7.28
dl-Leucine, $K_A \times 10^3$	4.14	4.49	4.70	4.71	4.65
$K_B \times 10^5$	3.57	4.52	5.60	6.71	7.59
dl-Isoleucine, $K_A \times 10^3$	4.32	4.59	4.81	4.82	4.66
$K_B \times 10^5$	3.61	4.57	5.77	6.79	7.85

[a] P. K. Smith, A. C. Taylor and E. R. B. Smith, *J. Biol. Chem.*, **122**, 109 (1937).

TABLE (15-6-4A). CONSTANTS OF EQUATIONS (15-6-9) TO (15-6-15) FOR IONIZATION CONSTANTS, ΔF_i^0, ΔH_i^0, $\Delta C_{p_i}^0$, ΔS_i^0, $-\log K_\theta$, and T_θ. SEE TABLE (B-10-3).

$$\log K = -\frac{A^*}{T} + D^* - C^*T \qquad A' = 2\ 3026\ RA^*$$

$$D' = 2.3026\ RD^*$$

$$C' = 2.3026\ RC^*$$

$$\Delta \overset{o}{F_i} = A' - D'T + C'T^2$$

$$\Delta \overset{o}{H_i} = A' - C'T^2$$

$$\Delta \overset{o}{C}_{p_i} = -2C'T$$

$$\Delta \overset{o}{S_i} = D' - 2C'T$$

$$T_\theta = \sqrt{\frac{A^*}{C^*}};\ \log K_\theta = D^* - 2\sqrt{C^*A^*}$$

Part I. Aqueous Solutions

Acids	A^*	D^*	C^*	A'	D'	C'	T_θ	$-\log K_\theta$
Formic	1342.85	5 2743	0.015168	6143 59	24.1301	0.069395	297.5	3.7519
Acetic	1170 48	3 1649	013399	5354 99	14 4795	.061301	295 6	4 7555
Propionic	1213 26	3 3860	014055	5550.71	15 4911	064302	293.8	4.8729
n-Butyric	1033 39	2 6215	013334	4727 90	11 9935	061004	278 4	4.8026
Chloroacetic	1049 05	5 0273	.014654	4799.45	23 0001	067043	267.6	2 8143
Lactic	1304 72	4 9639	014926	5969 15	22 7100	068287	295 7	3.8620
Glycolic ...	1303 26	4.7845	014236	5962 47	21 8893	065130	302 6	3 8302
Carbonic (2)	2902.39	6 4980	.02379	13278 55	29.7286	.10884	349.3	10.121
Oxalic	1539.31	7 1966	021200	7042 40	32 9247	096991	269 5	4 2285
Malonic	1703 31	6 5810	022014	7792 71	30 1083	100715	278.2	5 6659
Phosphoric (1)	1264 51	7 6601	.018590	5785 18	35 0452	085050	260.8	2 0368
(2)	1648.88	3 2542	016534	7543 69	14 8880	075644	315.8	7.1885
Boric	2193 55	3 0395	.016499	10035.58	13 9058	075484	364 6	8.9923
Amino-Acids								
Glycine A	1300.53	5 5277	.011792	5949.98	25.2894	053949	332 1	2 3045
B	1307.30	2 5629	008038	5980 95	11 7254	.036773	403.3	3 9202
dl-Alanine A	(1383 06)	(6 3639)	(013661)	(6327 55)	(29 1151)	(062502)	(318 2)	(2 3297)
	1271.17	5 6650	.012548	5815 65	25 9176	057408	318 3	2.3226
B	2069 10	7.7123	01643	9466 22	35 2841	075159	354 9	3 9481
	(1529.44)	(4.2704)	(010966)	(6997.25)	(19 5373)	(050168)	(373 5)	(3 9201)
dl-α-Amino-*n*-Butyric A	1174 74	5 3735	012487	5374 48	24.5840	.057129	299.8	2.2866
B	1591 68	4 4429	010965	7282 0	20 3264	.05017	381 0	3.9126
dl-α-Amino-*n*-Valeric A	1222 02	5 5238	.012553	5590 79	25 2716	.05743	312 0	2 3094
B	1852.42	6 2544	014191	8474.9	28.6141	.064923	361.3	3.9999
dl-Norleucine A	1193.30	5 2850	.012130	5459.40	24 179	055495	313.7	2.3242
B	1619.10	5 7984	.011842	7407.45	26 5279	.054178	369 8	2 9591
dl-α-Amino-isobutyric A	1344.95	6 3053	.013924	6153.20	28 8470	.063703	310 8	2.3497
B	1460 04	4 5471	.011540	6679.41	20 8032	.052796	355.7	3.6624
dl-Valine A	1245.31	6 0251	.013868	5697.34	27.5650	.063447	299.6	2 2863
B	1694.53	4.9842	.012004	7752.54	22.8029	.054919	375.7	4.0360
dl-Leucine A	1283.60	6.0027	.013505	5872.52	27.4026	.061786	308.3	2.3244
B	1651.61	4.8479	.011933	7556 18	22.1793	.054594	372.0	4.0310
dl-Isoleucine A	1298.09	6.1967	.013959	5938.81	28.3502	.063863	205.0	2.3169
B	1537.47	4.0396	.010482	7033.99	18.4813	.047956	383.0	3.9893

TABLE (15-6-4A)—*Concluded*

Part II. Water and Acids in Dioxane- and Methanol-Water Mixtures. X = Weight Percent of Organic Solvent. See Table (B-10-3)

X	A^*	D^*	C^*	A'	D'	C'	T_θ	$-\log K_\theta$
Water in Dioxane-Water Mixtures								
0	4470.99	6.0875	0.01706	20454.96	27.8506	0.078050	511.9	11.3796
20	4596.78	6.3108	.0184867	21030.45	28.8722	.084577	498.7	12.1260
45	4641.08	5.7231	.019784	21233.13	26.1834	.090513	484.3	13.4414
70	4377.47	2.2289	.018116	20027.10	10.1973	.082882	491.6	15.5815
Formic Acid in Dioxane-Water Mixtures								
20	1339.04	5.0628	.015983	6126.17	23.1626	.072917	289.8	4.1766
45	1333.79	4.6393	.017634	6102.16	21.2248	.080676	275.0	5.0602
70	1181.65	1.9920	.016922	5406.09	9.1135	.077419	264.2	6.9513
82	3006.85	13.2110	.040005	13755.07	60.4408	.18302	274.1	8.7232
Acetic Acid in Dioxane-Water Mixtures								
20	1423.45	4.2934	.016136	6512.34	19.6425	.073822	297.0	5.2917
45	1568.31	4.5387	.018736	7175.08	20.7650	.085718	289.3	6.3027
70	1549.12	2.5194	.018933	7087.29	11.5264	.086619	286.0	8.3119
82	3763.40	16.0925	.045641	17217.71	73.6238	.208809	287.2	10.1194
Propionic Acid in Dioxane-Water Mixtures								
20	1356.57	3.67038	.015384	6206.67	16.7930	.070385	297.0	5.4662
45	1480.12	3.52870	.017163	6771.94	16.1447	.078525	293.7	6.5516
70	1508.10	1.65390	.017466	6879.96	7.5670	.079914	293.8	8.6112
82	3680.11	15.05723	.044030	16837.48	68.8908	.20145	289.1	10.4015
Acetic Acid in Methanol-Water Mixtures								
10	1417.19	4.5806	.015874	6483.70	20.9564	.072624	298.8	4.9055
20	1572.21	5.3447	.017279	7192.92	24.4522	.079052	301.7	5.0796
K_A of Glycine in Dioxane-Water Mixtures								
0	1300.53	5.5277	.011792	5949.98	25.2894	.053949	332.1	2.3043
20	1368.94	5.6875	.012493	6263.16	26.0216	.057161	331.0	2.5806
45	1273.49	4.7113	.011887	5826.47	21.5553	.054386	327.3	3.0702
70	1187.30	3.3894	.011322	5432.12	15.5073	.051801	323.8	3.9435
K_B of Glycine in Dioxane-Water Mixtures								
0	1307.30	2.5629	.008038	5980.95	11.7254	.036673	403.3	3.9203
20	1519.89	3.3800	.010046	6953.78	15.4642	.045964	389.0	4.4350
45	1364.90	1.1999	.007139	6244.69	5.4898	.032663	437.2	5.0433
70	895.27	−3.328	.000818	4096.02	−15.227	.003743	..	.....

Appendix B

Table of Contents

(B-1) The Dielectric Constant of Water. Recalculation of Theoretical Limiting Slopes and Functions Involving the Dielectric Constant of Water. Revision of Tables (5-1-1), (5-2-1), (5-2-5) and (5-3-1). Tabulation of Theoretical Limiting Slopes for Partial Molal Volumes, Expansibilities and Compressibilities. The Function $g(x)$.

In the preparation of this treatise, calculations of theoretical limiting slopes, etc., which involve the dielectric constant of water, D, were based upon the measurements of Wyman[1] as expressed by equation (5-1-1):

$$D = 78.54\,[1 - 4.6 \times 10^{-3}\,(t - 25) + 8.8 \times 10^{-6}\,(t - 25)^2] \qquad (5\text{-}5\text{-}1)$$

As this work was nearing completion, Wyman and Ingalls[2] corrected Wyman's results for the thermal expansion of the resonator used in the measurements, and proposed the revised equation

$$D = 78.54\,[1 - 4.579 \times 10^{-3}\,(t - 25) + 11.9 \times 10^{-6}\,(t - 25)^2 + 28 \times 10^{-9}\,(t - 25)^3] \qquad (\text{B-1-1})$$

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[1] J. Wyman, Jr., *Phys. Rev.*, **35**, 623 (1930).

[2] J. Wyman, Jr. and E. N. Ingalls, *J. Am. Chem. Soc.*, **60**, 1182 (1938).

as representing the corrected results. Values of D given by these two equations differ by less than $\frac{1}{4}$ per cent between 0 and 50°, and by a maximum of 1 per cent at 100°. This difference is of the same order of magnitude as the difference between Wyman's values and those of Drake, Pierce, and Dow[3] as expressed by the equation[*]

$$D = 78.57\,[1 - 4.61 \times 10^{-3}\,(t - 25) + 15.5 \times 10^{-6}\,(t - 25)^2] \qquad \text{(B-1-2)}$$

Therefore, it seemed probable that the uncertainty in the absolute value of the dielectric constant was at least as great as the differences derived from the above equations, and that a recalculation of all limiting slopes would be without real significance. Although no new measurements have appeared which might alter our opinion regarding the uncertainty in the absolute values, equation (B-1-1) seems to be generally preferred by physical chemists. This preference and the revision of the fundamental physical constants, N, ϵ, k, etc., by Birge[4] have led us to recalculate all the theoretical limiting slopes on the basis of equation (B-1-1) and the revised constants in Table (B-1-1).

TABLE (B-1-1). FUNDAMENTAL PHYSICAL CONSTANTS RECOMMENDED BY BIRGE[*]

Symbol	Constant	Value
ϵ	Electronic charge	$4.8025_1 \times 10^{-10}$ abs. e.s.u.
F	Faraday constant	$96{,}501._2$ int-coul· g-equiv $^{-1}$
	“ “	$23{,}060_5$ cal_{15}· volt^{-1} g-equiv.$^{-1}$
	“ “	2.89247×10^{14} abs. e.s.u. g-equiv.$^{-}$
	Ideal gas volume (0°C, norm. atm.)	$22{,}414.6$ cm.^{3} atm. mole^{-1}
T_0	Ice point (absolute scale) 0°C (1 atm.)	273.16°K
R	Gas constant	8.31436×10^7 erg. deg.$^{-1}$ mole^{-1}
	“ “	1.98646_7 cal_{15}· deg.$^{-1}$ mole^{-1}
N	Avogadro number (chemical scale)	$6.0228_3 \times 10^{23}$ mole^{-1}
k	Gas constant per molecule	$1.38047_4 \times 10^{-16}$ erg. deg.$^{-1}$
	Normal atmosphere	1.013246×10^6 dyne. cm.$^{-2}$ atm.$^{-1}$
	Liter	$1{,}000.028$ cm.^{3}
cal_{15}	Gram calorie	4.1855 abs-joule
	“ “	4.1847 int-joule

[*] R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

Those slopes which involve the dielectric constant, but not its derivatives, are changed by about $\frac{1}{2}$ per cent, which does not cause any im-

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[3] F. H. Drake, G. W. Pierce and M. T. Dow, *Phys. Rev.*, **35**, 613 (1930).

[*] This equation is limited to the range 10 to 60°.

[4] R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941). Compare Tables (5-1-1) and (B-1-1).

portant change in the extrapolated properties such as E^0, log $\gamma_\pm$, Λ^0, K_u, etc. On the other hand, those slopes which involve the first or second derivatives of the dielectric constant, $\mathcal{S}_{(H)}$, $\mathcal{S}_{(C_p)}$, $\mathcal{S}_{(V)}$, etc., are changed considerably. Thus the recalculated values of $\mathcal{S}_{(C_p)}$ and $\mathcal{S}_{(V)}$ in Table (B-1-2) differ from those used in Chapter (8) by about 30 per cent. It should be emphasized that this large figure, 30 per cent, is not so much a measure of the "error" in the older values of the slopes as it is a demonstration of the sensitivity of the values of these slopes to uncertainties in the derivatives of D. The new values are just as sensitive to these uncertainties as are the older ones, and whether they are more or less in error can be decided only by an elaborate and precise redetermination of the dielectric constant of water as a function of temperature and pressure.

TABLE (B-1-2) THEORETICAL COEFFICIENTS FOR UNI-UNIVALENT* ELECTROLYES IN WATER

$t°$	$\mathcal{S}_{(f)}$	$A'/å$	$\mathcal{S}_{(V)}$	$-W_{(V)}/å$	$\mathcal{S}_{(H)}$	$-W_{(H)}/å$	h	$\mathcal{S}_{(C_p)}$	$\mathcal{S}_{(K)}$	$\mathcal{S}_{(E)}$	α^*	β^*
0	.4883	.3241	3.700	.1189	509.2	57.45	−.0222	6.520	00165	−.0050	.2195	29.61
5	.4921	.3249	3.684	.1186	543 4	58 25	+.0051	7.123	.00159	−.0015	.2212	35.07
10	.4960	.3258	3.685	.1190	580.4	59 56	0275	7.657	.00155	+.0016	.2230	40.77
15	.5002	.3267	3.701	.1199	620.2	61 30	0462	8 164	.00152	.0045	.2249	46.78
20	.5046	.3276	3.732	.1212	662 6	63 40	.0619	8.674	.00151	.0071	2268	53 24
25	.5091	3286	3.776	.1230	707 7	65 86	0752	9.194	00151	.0096	.2289	60.19
30	5139	.3297	3 833	1252	755 5	68 64	.0866	9 731	00151	0120	.2311	67 51
35	.5189	.3307	3 902	1279	806 2	71 70	0966	10 300	00153	.0143	2333	75 21
40	.5241	3318	3 982	1310	860 0	75.07	1054	10.922	.00155	0166	.2356	83.21
45	.5295	.3330	4.075	1345	917.1	78.78	1130	11.666	.00158	0189	2381	91 41
50	.5351	.3341	4.180	.1385	978.1	82.87	1196	12.365	.00162	.0212	.2406	99.72
55	.5410	3353	4.297	.1428	1043.2	87.33	.1255	13.208	.00167	0236	2432	108.37
60	.5470	3366	4.427	.1477	1112 8	92 24	1306	14.142	.00172	.0260	2460	117 41
65	.5534	.3379	4 569	.1530	1187 6	97 63	1350	15.185	.00179	.0285	.2488	126 79
70	.5599	.3392	4.725	.1589	1268.1	103 46	1389	16 354	.00186	.0312	2517	136.58
75	.5668	3406	4 895	.1655	1355 2	110 11	.1422	17.673	.00195	.0339	.2548	146.68
80	.5739	3420	5.079	.1722	1449 4	117.34	.1449	19.169	.00204	.0368	2580	157.03
85	.5813	.3435	5 279	.1797	1551.8	125.35	.1472	20 851	.00215	.0398	.2614	167.71
90	.5891	.3450	5.495	.1879					.00226		2649	178.61
95	5972	.3466	5.728	.1968					.00239		.2685	189 74
100	.6056	.3482	5.979	.2064					.00254		.2723	201.04
18	.5028	.3273	3.718	.1206	645.3	62.54	.0559	8.469	.00151	.0061	.2261	50.59
Factor	w'	w''	$w'\nu/2$	$w'w''\nu/2$	$w'\nu/2$	$w'w''\nu/2$	1	$w'\nu/2$	$w'\nu/2$	$w'\nu/2$	$w'Q$	w^*

* For electrolytes of higher valence types, multiply the figures in any column by the valence factor given at the bottom of the column.

The theoretical quantities which appear in Table (B-1-2) include several functions which have recently been estimated for the first time. Details of the calculations are given by Owen and Brinkley,[5] and the properties of water upon which they are based are given below. The temperature range for α^*, β^*, $\mathcal{S}_{(H)}$ and $\mathcal{S}_{(C_p)}$ has been extended considerably.

The coefficient of expansion of water, α, was derived from the Tilton

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[5] B. B. Owen and S. R. Brinkley, Jr., *Ann. N. Y. Acad. Sci.*, **51**, 753 (1949).

and Taylor[6] equation

$$d = 1 - \frac{(t - 3.9863)^2}{508929.2}\left(\frac{t + 288.9414}{t + 68.12963}\right) \qquad \text{(B-1-3)}$$

which represents the data of Chappuis[7] from 0 to 42°. From 45 to 85°, values of α were based upon measurements of White[8] and of Smith[9]. The first and second derivatives of D with respect to temperature were derived from Equation (B-1-1). Values of β and of its temperature and pressure derivatives were obtained from the Tait Equation (8-7-19) which for water is

$$\beta = \frac{0.1368}{B + P} \qquad \text{(B-1-4)}$$

The variation of B with temperature is given[10] by the expression

$$B = 2996.0 + 7.5554\,(t - 25) - 0.17814\,(t - 25)^2 + 0.000608\,(t - 25)^3 \qquad \text{(B-1-5)}$$

The several pressure derivatives of D were derived from the empirical equation of Owen and Brinkley[11]

$$\frac{1}{D}\left(\frac{\partial D}{\partial P}\right) = \frac{0.1754}{B + P} \qquad \text{(B-1-6)}$$

Just how well Equation (B-1-6) represents the dielectric constant of water at temperatures other than 20° is unknown, but since it is the *only* equation available for our purpose and has been thoroughly tested for other liquids, we have used it to estimate $\mathcal{S}_{(V)}$, $\mathcal{S}_{(K)}$, and $\mathcal{S}_{(E)}$ at all temperatures under consideration. In Section (4) we shall present experimental evidence which indicates that $\mathcal{S}_{(V)}$ is probably correct to two figures at room temperatures. The insensitivity of $\mathcal{S}_{(K)}$ to temperature, and the change in the sign of $\mathcal{S}_{(E)}$ at low temperatures are also indicated by experiment,[12, 13] but the concentration range is too high to test the numerical values of these theoretical slopes.

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[6] L. W. Tilton and J. K. Taylor, *J. Research Nat. Bur. Stand.*, **18**, 205 (1937).

[7] P. Chappuis, *Travaux et Memoires du Bureau International des Poids et Mesures*, **13**, D40 (1907).

[8] J. R. White, Dissertation, Yale University (1944).

[9] J. S. Smith, Dissertation Yale University (1943).

[10] B. B. Owen, *J. Chem. Ed.*, **21**, 59 (1944). B and P are expressed in bars.

[11] B. B. Owen and S. R. Brinkley, Jr., *Phys. Rev.*, (*2*) **64**, 32 (1943). For evaluation of the factor 0.1754, see B. B. Owen and S. R. Brinkley, Jr., *Ann. N. Y. Acad. Sci.*, **51**, 753 (1949).

[12] F. T. Gucker, Jr., *J. Am. Chem. Soc.*, **55**, 2709 (1933).

[13] R. E. Gibson and O. N. Loeffler, *Ibid.*, **63**, 443 (1941).

TABLE (B-1-3). THE FUNCTION $g(x)$. SUPPLEMENTARY VALUES TO TABLE (5-3-5)

x	$g(x)$	x	$g(x)$	x	$g(x)$
2.6	0.11721	3.2	0.10367	3.8	0.09272
2.8	.11236	3.4	.09977	4.0	.08952
3.0	.10786	3.6	.09612	4.2	.08656

(B-2) CONDUCTANCE AND TRANSFERENCE NUMBERS. EXTENSION OF TABLES (6-6-1), (6-6-2), AND (6-8-2)

In connection with testing the general validity of equation (6-2-2), Jörn Lange[14] made use of the theoretical limiting slope, $\mathcal{S}_{(\Lambda)}$, and demonstrated that the equation

$$\Lambda = \Lambda^0 - \mathcal{S}_{(\Lambda)}\sqrt{c} + Bc \qquad \text{(B-2-1)}$$

adequately represents the data for some 560 strong electrolytes in a variety of solvents and at concentrations up to 0.05 or 0.10 molar. He also made the interesting observation that (in our symbols) the parameter B can be expressed by

$$B = \frac{3.0 \times 10^8 \Lambda^0}{(DT)^2} - \zeta[z_+^2 z_-^2 - 1]\Lambda^0 \qquad \text{(B-2-2)}$$

The coefficient ζ is characteristic of the solvent, and is 0.19 for water.

Within the last decade, the conductances and transference numbers of several salts and hydrochloric acid have been carefully measured over temperature ranges of 40 to 60 degrees. These measurements are so numerous that they will not be tabulated as functions of both temperature and concentration, but the values at infinite dilution are given in Table (B-2-1). Values at concentrations up to 0.01 or 0.02 normal may be found in the original literature referred to in the table. These limiting values and those at 25° for the same electrolytes, and sodium iodide, which appear in Tables (6-2-1A) and (6-6-1A) are enough to permit the construction of a reasonably consistent set of "preferred" limiting mobilities of seven simple ions over a 50 degree temperature range. These preferred values and their variation with temperature can be represented by the cubic equation

$$\lambda^0 = \lambda^0_{(25°)} + a(t - 25) + b(t - 25)^2 + c(t - 25)^3 \qquad \text{(B-2-3)}$$

the parameters of which are recorded in Table (B-2-2).

Values of Λ^0 and of T^0_+, calculated by equation (B-2-3) and the parameters in Table (B-2-2), are compared in Table (B-2-1) with the observed values. The difference between calculated and observed values of Λ^0 is less than 0.02 per cent on the average, and exceeds 0.04 per cent only in the case

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[14] J. Lange, *Z. phys. Chem.*, **A188**, 284 (1941).

TABLE (B-2-1). COMPARISON OF CONSISTENT SET OF VALUES OF Λ^0 AND T^0_+ WITH THE EXPERIMENTAL VALUES* FROM WHICH THEY WERE DERIVED

		5°	15°	25°	35°	45°	55°	Source
HCl,	Λ^0	*297.53*	*362.16*	*426.20*	*489.11*	*550.34*	*609.38*	a
		297.57	362.07	426.24	489.15	550.30	609.47	b
				426.16				c
	T^0_+	*.8403*	*.8304*	*.8209*	*.8115*	*.8021*	*.7926*	a
		.842	.831	.821	.811	.801		k
				.8210				j
LiCl,	Λ^0	*70.28*	*91.62*	*114.99*	*140.17*	*166.94*	*195.15*	a
		70.30	91.60	114.99	140.18	166.92	195.14	d
				115.03				c
				114.95				e
	T^0_+	*.3240*	*.3296*	*.3360*	*.3422*	*.3476*	*.3523*	a
				.3368				l
NaCl,	Λ^0	*77.81*	*101.14*	*126.50*	*153.74*	*182.69*	*213.23*	a
		77.84		126.49			213.28	d
			101.18	126.45	153.75	182.65		f
				126.45				g
	T^0_+	*3894*	*.3927*	*.3964*	*.4002*	*.4039*	*.4072*	a
			.3929	3962	.4002	.4039		m
				.3963				l
KCl,	Λ^0	*94 23*	*121.03*	*149 85*	*180.41*	*212.43*	*245.67*	a
		94.26		149.88			245.69	h
			121.07	149.85	180.42	212.41		f
				149.86				g
	T^0_+	*.4959*	*.4925*	*.4905*	*.4889*	*.4873*	*.4855*	a
			.4928	.4905	.4889	.4872		n
				.4906				l
KBr,	Λ^0	*95.99*	*122 81*	*151 67*	*182 23*	*214.17*	*247.15*	a
		96.00		151.68			247.15	h
			122.81	151 64	182.24	214.17		f
				151.63				i
	T^0_+	*4868*	*4854*	*.4846*	*4840*	*4834*	*.4826*	a
				4847				o
KI,	Λ^0	*95.32*	*121.83*	*150 35*	*180.56*	*212.13*	*244.74*	a
		95.32	121.83	150.34	180.60	212.13	244.73	h
				150.38				j
	T^0_+	*.4902*	*.4893*	*.4889*	*4885*	*.4880*	*.4873*	a
				.4887				p

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[*] All values have been adjusted to the primary standard of G. Jones and B. C. Bradshaw, *J. Am. Chem Soc.*, **55**, 1780 (1933)

[a] Calculated from equation (B-2-3) and the parameters in Table (B-2-2).

[b] Data of B. B. Owen and F. H. Sweeton [*J Am. Chem. Soc.*, **63**, 2811 (1941)] re-extrapolated by equation (6 3-6).

[c] T. Shedlovsky, *J. Am. Chem. Soc* , **54**, 1411 (1932).

[d] F. W. Tober, Dissertation, Yale University (1948).

[e] K. A. Krieger and M. Kilpatrick, Jr , *J. Am. Chem. Soc.*, **59**, 1878 (1937)

[f] G. C. Benson and A. R. Gordon, *J. Chem. Phys.*, **13**, 473 (1945).

[g] T. Shedlovsky, A. S. Brown and D. A. MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

of the value for potassium bromide at 25° recorded in Table (6-2-1A). Therefore, Λ^0 for this salt, 151.9, was disregarded in constructing the set of preferred mobilities. Bearing in mind that the experimental values of T^0_+ for hydrochloric acid (Ref. *k*) are expressed to only three places, the agreement between the calculated and observed results of T^0_+ appears satisfactory. One value, 0.4837 (Ref. *p*), for potassium bromide was, however, rejected in favor of 0.4847 (Ref. *o*) in order to obtain maximum consistancy for the whole set.

One very interesting result of this study of ionic mobilities is the observation of a reversal in the order of the limiting mobilities of the chloride and iodide ions as the temperature is increased. Thus, at 5°, λ^0_{Cl} is 47.51 and less than λ^0_I, which is 48.60. At 55°, λ^0_{Cl} is 126.40 and greater than λ^0_I, which is 125.47.

TABLE (B-2-2). PARAMETERS OF EQUATION (B-2-3) EXPRESSING THE TEMPERATURE DEPENDENCE OF LIMITING IONIC MOBILITIES BETWEEN 5 AND 55°C.

Ion	$\lambda^0_{(25°)}$	a	$b \times 10^2$	$c \times 10^4$
H^+	349.85	4.81595	−1.03125	−0.7670
Li^+.	38.64	0.88986	+0.44075	−0.2042
Na^+	50.15	1.09160	0.47150	−0.1150
K^+	73.50	1.43262	0.40563	−0.3183
Cl^-.	76.35	1.54037	0.46500	−0.1285
Br^-	78.17	1.54370	0.44700	−0.2300
I^-	76.85	1.50893	0.43750	−0.2170

Fuoss and Shedlovsky[15] have recently pointed out that the determination of an ionization constant by employing one or the other of their functions,* $F(Z)$ and $S(Z)$, results in different values of K. If we denote these values by $K_{(F)}$ and $K_{(S)}$, the difference in their reciprocals can be calculated by the equation

$$K^{-1}_{(S)} - K^{-1}_{(F)} = (\mathcal{S}_{(\Lambda)}/\Lambda^0)^2 \tag{B-2-4}$$

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[15] R. M. Fuoss and T. Shedlovsky, *J. Am. Chem Soc.*, **71**, 1496 (1949)

* See Chapter (7), pages 186 to 190.

[h] H. Zeldes, Dissertation, Yale University (1947).

[i] G. Jones and C. F. Bickford, *J. Am. Chem Soc.*, **56**, 602 (1934).

[j] L. G. Longsworth, Private Communication, quoted by H. E. Gunning and A. R. Gordon, *J. Chem. Phys.*, **10**, 126 (1942).

[k] H. S. Harned and E. C. Dreby, *J. Am. Chem. Soc.*, **61**, 3113 (1939).

[l] L. G. Longsworth, *Ibid.*, **54**, 2741 (1932).

[m] R. W. Allgood and A. R. Gordon, *J. Chem. Phys.*, **10**, 124 (1942).

[n] R. W. Allgood, J. D. LeRoy and A. R. Gordon, *Ibid.*, **8**, 418 (1940).

[o] A. G. Keenan and A. R. Gordon, *Ibid.*, **11**, 172 (1943).

[p] L. G. Longsworth, *J. Am. Chem. Soc.*, **57**, 1185 (1935).

For most weak electrolytes ($K < 10^{-5}$) this difference is negligible, but for moderately strong electrolytes ($K > 10^{-3}$) it may be important. Thus, for zinc sulfate, the alternative extrapolations illustrated in Fig. (7-2-2) lead to $K_{(s)} = 0.0049$ and $K_{(r)} = 0.0052$, which differ by 6 per cent.

(B-3) Diffusion Coefficient of Potassium Chloride from 0 to 0.5*M* and Calcium Chloride from 0.002 to 0.005*M* in Aqueous Solutions

The recent development of a method for determining the differential diffusion coefficients of electrolytes by conductance measurements[16, 17] has yielded the first results of an accuracy sufficient to test the theory of Onsager and Fuoss.[18] The second column of Table (B-3-1) contains

Table (B-3-1). Observed and Calculated Differential Diffusion Coefficient of Potassium Chloride in Aqueous Solution at 25°

	$\mathfrak{D} \times 10^5$		
c	Observed	Theoretical$^{(a)}$	$\mathfrak{D}'_0 \times 10^5$
0.00000		(1.9958)	(1.996)
.00125	1.961	1.960	1.997
.00194	1.954	1.953	1.997
.00325	1.943	1.943	1.996
.00585	1.931	1.929	1.998
.00704	1.924	1.924	1.996
.00980	1.918	1.915	1.999
.01261	1.908	1.907	1.997
.02654	1.879	1.883	1.992
.03992	1.877	1.870	2.003
.04620	1.872	1.866	2.002
.05450	1.860	1.861	1.995
.06074	1.856	1.858	1.994
.1298	1.838	1.840	1.994
.3323	1.842	1.839	1.999
.5276	1.852	1.853	1.995
Average			1.997

(a) Values used in theoretical calculations according equations (B-3-1) (B-3-2) (B-3-3) (B-3-4): $T = 273.16$; $D = 78.54$; $\eta_0 = 8.949 \times 10^{-3}$; $\lambda_1^0 = 73.52$; $\lambda_2^0 = 76.34$; $\mathring{a} = 3.8$; $2B = 0.0213$; $\mathfrak{S}_{(f)} = 0.5092$; $d\ (25°) = 0.99707 + 0.04811\, c - 0.00232\, c^{3/2}$.

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[16] H. S. Harned and D. M. French, *Ann. N. Y. Acad. Sci.*, **46**, 267 (1945).

[17] H. S. Harned and R. L. Nuttall, *J. Am. Chem. Soc.*, **69**, 737 (1947); **71**, 1460 (1949); *Ann. N. Y. Acad. Sci* , **51**, 781 (1949).
See also H. S. Harned, *Chem. Rev.*, **40**, 461 (1947) for a comprehensive review of the quantitative aspects of electrolytic diffusion and L. G. Longsworth, [*Ann. N. Y. Acad. Sci.*, **46**, 211 (1945)] for a review of the experimental methods. These articles contain comprehensive bibliographies.

[18] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

the experimental values of the diffusion coefficient of potassium chloride at 25° at the molar concentrations listed in the first column.

With the newer values of the constants given in Table (B-1-1), the numerical quantities, 16.632, 1.074, 22.00, and 9.18 in equations (6-10-1) and (6-10-2) become 16.629, 1.0748, 22.148 and 9.304, respectively. Introducing these and the values of the required quantities at the bottom of the table, equations (6-10-1), (6-10-2), (6-10-4) and (6-10-5) become

$$\mathfrak{D} = 4.958 \times 10^{18}\left(\frac{\overline{\mathfrak{M}}}{c}\right)\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) \qquad \text{(B-3-1)}$$

$$\frac{\overline{\mathfrak{M}}}{c} \times 10^{20} = 40.253 - \frac{0.00573\sqrt{c}}{(1 + 1.249\sqrt{c})} + 18.96c\phi(1.249\sqrt{c}) \qquad \text{(B-3-2)}$$

$$\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{0.5873\sqrt{c}}{(1 + 1.249\sqrt{c})^2} + 0.0490c - c\psi(d) \qquad \text{(B-3-3)}$$

$$c\psi(d) = \frac{0.00959c - 0.00348c^{3/2}}{0.99707 + 0.00959c - 0.00232c^{3/2}}, \qquad \text{(B-3-4)}$$

All these equations were used to calculate the values in the third column of the table. The function, $\phi(1.249\sqrt{c})$, was obtained by interpolating the data in Table (5-3-2).

The observed and theoretical results show remarkable agreement throughout the entire concentration range. At concentrations below $0.05N$, there is little doubt of the validity of the calculation, but the agreement at higher concentrations is unexpected. This situation may be due to a fortunate choice of salt and temperature, since at 25° the relative viscosity of potassium chloride in water changes less than 0.3 per cent from 0 to $0.5N$.

These experimental results are the first which confirm accurately the validity of the limiting equation of Nernst for the diffusion coefficient of an electrolyte at infinite dilution. This conclusion is clearly established by the values in the last column of the table where the theoretical differences $(\mathfrak{D}_0 - \mathfrak{D})_{\text{theo}}$ are added to the observed values, $\mathfrak{D}_{\text{obs}}$, to give $\mathfrak{D}_0'$. The excellent agreement of $\mathfrak{D}_0'$ with the limiting value, $\mathfrak{D}_0$, particularly at concentrations below $0.01N$, affords complete confirmation of the limiting equation of Nernst for this 1-1 electrolyte.

The curves at 20, 25 and 30° in Fig. (B-3-1) illustrate the nature of the theoretical calculation. Curve A is obtained by the limiting equation (6-10-6), which, upon computing $\mathfrak{S}_{(\mathfrak{D})}$ at 25° by means of (6-10-7), becomes

$$\mathfrak{D} \times 10^5 = 1.9958 - 1.170\sqrt{c} \qquad \text{(B-3-5)}$$

Curve C represents the result obtained by omitting the theoretical electrophoretic contribution, and its equation is

$$\mathfrak{D} \times 10^5 = 1.9958\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) \qquad \text{(B-3-6)}$$

Curve B is derived from equations (B-3-1) to (B-3-4), so that the difference between Curve B and C represents the effect of the electrophoretic term. The results in Table (B-3-1) are represented by the circles and, judging from these, it appears that the electrophoretic term is required. The crosses designate values calculated by Gordon[19] from his diaphragm cell measurements and those of McBain and Dawson[20] and Hartley and Runnicles.[21] These measurements[22] have been revised by Gordon by using a cell calibration based on the conductometric results in Table (B-3-1) below 0.01*N*. At low concentrations the agreement is good, but as the concentration increases the diaphragm cell measurements are somewhat lower than those derived from conductance. The result of Cohen and Bruins[23] by the layer analysis method, and that of Lamm,[24] obtained by his scale method, are also shown on Fig. (B-3-1). Considering the wide variety of mechanisms used in these determinations, the agreement at the lower concentrations is satisfactory.

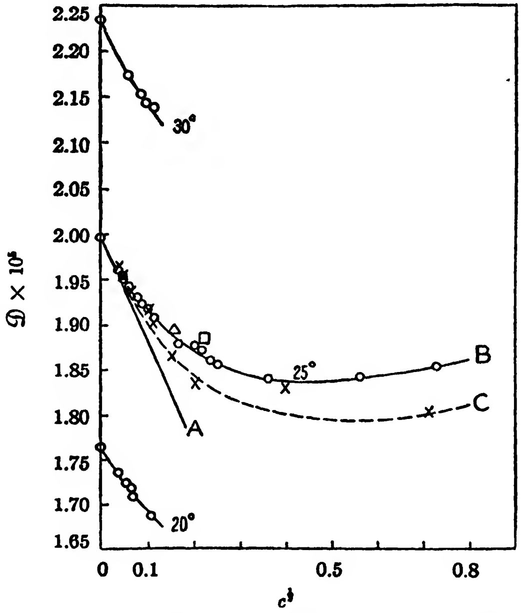

Fig. (B-3-1). Diffusion coefficient of potassium chloride in water ○, Conductometric; ×, diaphragm cell; △, Cohen and Bruins; □, Lamm

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[19] A. R. Gordon, *J. Phys. Chem.*, **5,** 522 (1937); *Ann. N. Y. Acad. Sci.*, **46,** 285 (1945).

[20] J. W. McBain and C. R Dawson, *Proc. Roy. Soc* , **A118,** 32 (1935).

[21] G. S. Hartley and D. F. Runnicles, *Ibid.*, **A168,** 401 (1938).

[22] H. S. Harned, *Chem Rev* , **40,** 461 (1947).

[23] E. Cohen and H R. Bruins, *Z. Physik. Chem.*, **103,** 337 (1923).

[24] O. Lamm, *Nova Acta Reg. Sci. Upsala, IV 10* (6) (1937).

The remarkable agreement of these results with the theoretical prediction does not prove the general validity of the theory for all types of electrolytes. Fig. (B-3-2) contains a plot of the results of Harned and Levy,[25] who measured the diffusion coefficient of calcium chloride in water at low concentrations at 25°. It is apparent that large deviations from the theory are to be observed at concentrations as low as 0.001*M*. This result may be compared to a similar deviation from theory which occurs with the transference number of the calcium ion, and which is illustrated by Fig. (6-6-2). These results are important since they lead us to suspect that the theory of Onsager and Fuoss, which is so successful in accounting for the diffusion coefficient of potassium chloride, is either wrong or incomplete for higher valence type electrolytes.

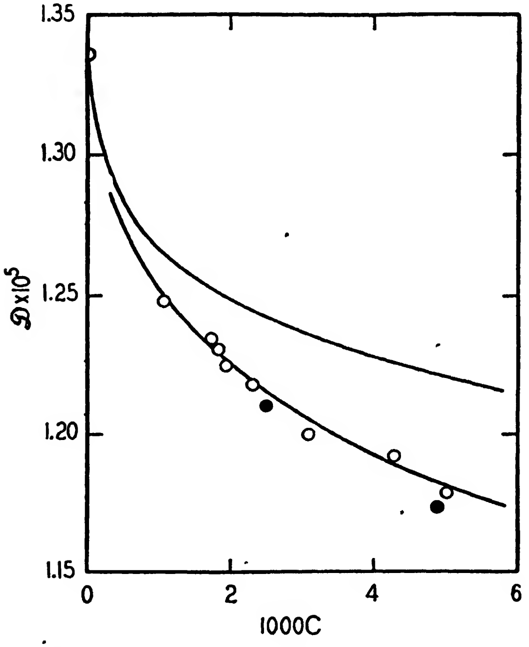

Fig. (B-3-2) Diffusion coefficient of calcium chloride in water at 25° Upper curve, theoretical; ○, conductometric; ●, diaphragm cell

(B-4) EXTRAPOLATION OF APPARENT MOLAL VOLUMES AND HEATS OF DILUTION. EXTENSION OF TABLE (9-5-1)

The uncertainties involved in the extrapolation of plots of apparent molal quantities against $c^{1/2}$ have been emphasized in Chapter (8), and

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[25] H. S. Harned and A. L. Levy, *J. Am. Chem. Soc.*, **71**, 2781 (1949).

the introduction of the $\mathring{a}$-parameter, without a term in the first power of c, was shown (p. 228–9) to be unsatisfactory. On the other hand, use of a term in c, without consideration of the $\mathring{a}$-parameter, appeared to result in satisfactory extrapolation of apparent molal volumes. It was shown (p. 254–5) that, for potassium chloride, sodium bromide and strontium chloride, plots of $[\phi_V - \frac{2}{3}\mathcal{S}_{(V)}c^{1/2}]$ against c were nearly linear, providing that 2/3 $\mathcal{S}_{(V)}$ be given the value 1.9 for 1-1 type salts and 1.9 $(3)^{3/2}$, or 9.9, for strontium chloride. Unfortunately, these numerical values for the limiting slope did not result in satisfactory extrapolations for other strong electrolytes of like valence types, and according to our calculations as given in Table (B-1-2), the theoretical value of 2/3 $\mathcal{S}_{(V)}$ at 25° should be about 2.5, rather than 1.9.

In a recent paper,[26] Owen and Brinkley demonstrated that the use of the $\mathring{a}$-parameter *and* a term in c results in a linear extrapolation* which appears to be consistent with the theoretical values for $\mathcal{S}_{(V)}$and $\mathcal{S}_{(H)}$. It was shown that the equations for ϕ_V and ϕ_H, corresponding† to equations (3-9-2) and (3-8-5) for $\bar{V}_2$ and $\bar{L}_2$, are

$$\phi_V - \phi_V^0 = \tfrac{2}{3}\,\mathcal{S}_{(V)}\,\Omega_{(V)}\,c^{1/2} + \tfrac{1}{2}K_{(V)}\,c \qquad \text{(B-4-1)}$$

and

$$\phi_H - \phi_H^0 = \tfrac{2}{3}\mathcal{S}_{(H)}\Omega_{(H)}c^{1/2} + \tfrac{1}{2}K_{(H)}c \qquad \text{(B-4-2)}$$

In these equations the entire effect of the $\mathring{a}$-parameter has been expressed in terms of the functions

$$\Omega_{(V)} = \left[\frac{1}{1+\kappa a}\,\frac{\partial \ln D}{\partial P} - \tfrac{1}{3}\beta\sigma\right]\left[\frac{\partial \ln D}{\partial P} - \tfrac{1}{3}\beta\right]^{-1} \qquad \text{(B-4-3)}$$

and

$$\Omega_{(H)} = \left[\frac{1}{1+\kappa a}\left(\frac{\partial \ln D}{\partial T} + \frac{1}{T}\right) + \tfrac{1}{3}\alpha\sigma\right]\left[\frac{\partial \ln D}{\partial T} + \frac{1}{T} + \tfrac{1}{3}\alpha\right]^{-1} \qquad \text{(B-4-4)}$$

Making use of equations (B-1-1) and (B-1-4) to (B-1-6) these become .

$$\Omega_{(V)} = \frac{1.3513}{1+\kappa a} - 0.3513\sigma \qquad \text{(B-4-5)}$$

at all temperatures, and

$$\Omega_{(H)} = \frac{1+h}{1+\kappa a} - h\sigma \qquad \text{(B-4-6)}$$

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[26] B B. Owen and S. R. Brinkley, Jr., *Ann N. Y. Acad. Sci.*, **51**, 753 (1949).

*The extrapolation functions take no account of the extended terms (p 39–41), and have been applied to ϕ_v and ϕ_H for 1-1 type electrolytes only. They should not be applied to higher valence types until the contribution of the extended terms has been thoroughly investigated. Furthermore, the derivatives $\partial\ln\mathring{a}/\partial T$ and $\partial\ln\mathring{a}/\partial P$, which are both unknown, are assumed to be zero.

† In changing the variable from Γ to the more convenient variable c, we have written $\mathcal{S}_{(V)}c^{1/2}$ for $\mathfrak{S}_{(V)}\Gamma^{1/2}$, and $K_{(V)}c$ for $\mathcal{K}_{(V)}\Gamma$, etc.

TABLE (B-4-1)*. THE FUNCTION σ

$$= \frac{3}{x^3}\left[1 + x - (1 + x)^{-1} - 2 \ln (1 + x)\right]$$

x	σ	x	σ	x	σ	x	σ
0.00	1.000000	0.50	0.537675	1.00	0.341117	2.00	0.176041
.01	.985178	.51	.532127	.02	.335718	.05	.171274
.02	.970704	.52	526668	04	.330451	.10	.166704
.03	.956568	.53	.521298	06	.325313	.15	.162321
.04	.942758	.54	.516014	.08	.320299	.20	.158114
0.05	0.929263	0.55	0.510813	1.10	0.315405	2.25	0.154074
.06	.916074	.56	505695	.12	310627	.30	.150191
.07	.903182	57	.500657	14	305962	35	.146458
.08	.890577	.58	.495699	.16	301405	.40	.142867
.09	.878250	59	.490817	.18	.296953	.45	.139410
0.10	0.866193	0.60	0.486010	1 20	0.292604	2.50	0.136082
.11	.854399	.61	.481278	22	.288353	.55	.132875
.12	.842859	62	.476617	24	.284198	.60	.129783
.13	.831565	.63	.472028	.26	.280136	65	.126801
.14	.820510	.64	.467507	.28	.276164	.70	.123924
0.15	0 809687	0.65	0.463055	1.30	0.272279	2.75	0.121147
.16	.799090	.66	.458669	.32	.268479	.80	.118464
.17	.788712	.67	.454348	34	.264761	.85	.115872
.18	.778547	.68	.450091	.36	.261123	.90	.113367
.19	.768589	.69	.445896	38	.257562	.95	.110945
0.20	0.758832	0.70	0.441763	1.40	0 254077	3.00	0.108601
.21	.749271	.71	.437689	.42	.250665	.05	.106333
.22	.739900	.72	433675	.44	.247323	.10	.104138
.23	.730714	.73	.429718	.46	.244051	.15	.102011
.24	.721707	.74	.425817	.48	.240846	.20	.099951
0.25	0.712876	0.75	0.421972	1 50	0.237705	3.25	0.097955
.26	.704216	.76	418182	52	.234628	.30	.096019
.27	.695721	.77	414444	.54	.231613	.35	.094142
.28	.687388	78	.410759	.56	228658	.40	.092320
.29	.679212	.79	.407125	.58	225761	.45	090553
0.30	0.671189	0.80	0.403542	1 60	0 222921	3 50	0.088837
.31	663316	81	.400008	.62	.220136	.55	.087170
.32	.655588	82	.396522	64	.217405	60	.085551
.33	.648002	.83	.393083	66	214727	.65	.083979
34	.640554	.84	.389692	68	.212099	.70	.082450
0.35	0.633241	0.85	0.386346	1.70	0.209521	3.75	0 080963
.36	626060	86	.383045	.72	.206992	.80	.079518
.37	.619007	.87	.379788	.74	.204510	.85	.078112
.38	.612078	.88	.376574	.76	202073	.90	.076743
.39	.605272	.89	.373403	.78	.199682	.95	.075412
0.40	0.598585	0.90	0.370273	1.80	0.197335	4.00	0.074115
.41	.592014	.91	.367185	.82	.195030	.05	.072853
.42	.585557	.92	.364137	.84	.192766	.10	.071623
.43	.579210	.93	.361128	.86	.190543	.15	.070425
.44	.572971	.94	.358158	.88	.188360	.20	.069257
0.45	0.566838	0.95	0.355226	1.90	0.186216	4.25	0.068119
.46	.560809	.96	.352332	92	.184109	.30	.067009
.47	.554880	.97	.349475	.94	.182039	.35	.065927
.48	.549049	.98	.346654	.96	.180005	.40	.064871
.49	543315	.99	.343868	.98	.178006	45	.063842
0.50	0.537675	1.00	0.341117	2.00	0.176041	4.50	0.062837

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* We are indebted to Dr. Stuart R. Brinkley, Jr., and Ruth F Brinkley for permission to publish this table.

where h is given at various temperatures in Table (B-1-2). The function σ, which is defined by equation (9-5-6), is given in Table (9-5-1). A more extensive tabulation, suitable for the extrapolations to be described below, is given in Table (B-4-1). The theoretical slopes $\mathcal{S}_{(V)}$ and $\mathcal{S}_{(H)}$ are given in Table (B-1-2).

In their final forms, suitable for extrapolation, equations (B-4-1) and (B-4-2) are rewritten

$$[\phi_V - \tfrac{2}{3}\mathcal{S}_{(V)}\Omega_{(V)}c^{1/2}] = \phi_V^0 + \tfrac{1}{2}K_{(V)}c \qquad \text{(B-4-7)}$$

and

$$[\phi_H - \phi_H' - \tfrac{2}{3}\mathcal{S}_{(H)}\Omega_{(H)}c^{1/2}] = \phi_H^0 - \phi_H' + \tfrac{1}{2}K_{(H)}c \qquad \text{(B-4-8)}$$

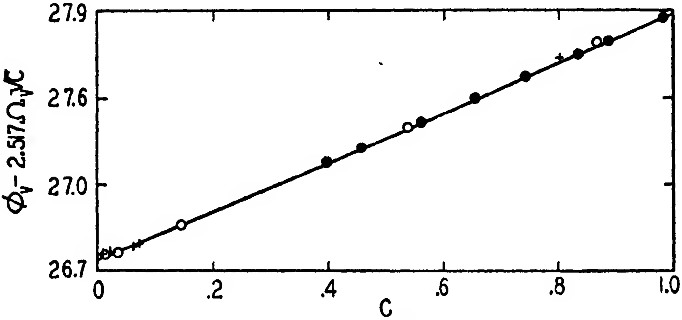

Fig. (B-4-1). Apparent molal volume of potassium chloride in water at 25° ●, ○, Data of Kruis; +, Geffcken and Price.

In the last equation ϕ_H' is the apparent molal heat content at some temporary reference concentration.

Plots of the left-hand members of these equations against c are shown in Figures (B-4-1) and (B-4-2). Both these plots appear to be linear within the experimental errors of the measurements. Fig. (B-4-1) is based upon the values of ϕ_V for potassium chloride at 25° obtained by Kruis,[27, 28] and by Geffcken and Price[29] Figure (B-4-2) is based upon heats of dilution of sodium chloride at 25° measured by Robinson.[30] The values of the $\mathring{a}$-parameter, 3.8 for potassium chloride and 4.0 for sodium chloride, are those given in Table (12-5-2). Note that they were derived independently from activity coefficients expressed in terms of equation (12-5-2).

[27] A. Kruis, *Z. physik. Chem.*, **B34**, 1 (1936).

[28] A. Kruis, *Ibid.*, **B34**, 13 (1936). Interpolation

[29] W Geffcken and D. Price, *Ibid.*, **B26**, 81 (1934).

[30] A. L. Robinson, *J. Am. Chem. Soc.*, **54**, 1311 (1932).

The equations derived from the slopes and intercepts obtained from the plots in Figs. (B-4-1) and (B-4-2) are

$$\phi_V = 26.742 + 2.517\,\Omega_{(V)}c^{1/2} + 0.85c; \qquad \mathring{a} = 3.8 \qquad \text{(B-4-9)}$$

for potassium chloride at 25°, and

$$\phi_H - \phi_H^0 = 471.8\,\Omega_{(H)}c^{1/2} + 217c; \qquad \mathring{a} = 4.0 \qquad \text{(B-4-10)}$$

for sodium chloride at 25°. As a final step in the illustrative treatment of these results, advantage may be taken of the fact that the constants 0.85 and 217 in equations (B-4-9) and (B-4-10) are the coefficients of c in equations (B-4-7) and (B-4-8). These are ½ the coefficients in the last term of the equations

$$\bar{V}_2 - \bar{V}_2^0 = \frac{\mathcal{S}_{(V)}\,c^{1/2}}{1 + A'c^{1/2}} + \frac{W_{(V)}\,c}{(1 + A'c^{1/2})^2} + K_{(V)}\,c \qquad \text{(B-4-11)}$$

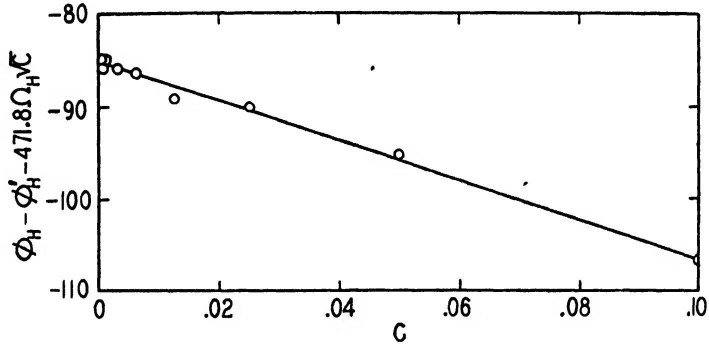

Fig. (B-4-2). Relative apparent molal heat content of sodium chloride in water at 25°. ○, Data of Robinson

and

$$\bar{L}_2 = \frac{\mathcal{S}_{(H)}\,c^{1/2}}{1 + A'c^{1/2}} + \frac{W_{(H)}\,c}{(1 + A'c^{1/2})^2} + K_{(H)}\,c \qquad \text{(B-4-12)}$$

which may be derived by introducing the expressions $\mathcal{S}_{(V)} = \mathfrak{S}_{(V)}(\sum \nu_j z_j^2)^{1/2}$, $W_{(V)} = \mathfrak{W}_{(V)} \sum \nu_j z_j^2$ and $K_{(V)} = \mathcal{K}_{(V)} \sum \nu_j z_j^2$ into equation (3-9-2), and $\mathcal{S}_{(H)} = \mathfrak{S}_{(H)}(\sum \nu_j z_j^2)^{1/2}$, $W_{(H)} = \mathfrak{W}_{(H)} \sum \nu_j z_j^2$ and $K_{(H)} = \mathcal{K}_{(H)} \sum \nu_j z_j^2$ into equation (3-8-5). Since values of the theoretical constants $W_{(V)}$ and $W_{(H)}$ are included in Table (B-1-2) along with the limiting slopes, the relative partial molal quantities $\bar{V}_2 - \bar{V}_2^0$ and $\bar{L}_2$ can be readily calculated.

(B-5) ACTIVITY COEFFICIENTS. NEW AND REVISED DATA FOR 1-1, 2-1 AND 1-2 ELECTROLYTES

Accurate values of the activity coefficients of sodium chloride, potassium chloride, potassium bromide and calcium chloride in dilute aqueous solutions from 15 to 45° have been determined by Gordon and his colleagues from transference numbers and electromotive forces of cells with liquid junction by the method of Brown and MacInnes described in Chapter (12), Section (1). The results may be computed by the equation

$$\log \gamma_{\pm} = -\frac{\mathcal{S}_{(f)}\sqrt{d_0}\,\sqrt{m}}{1 + A'\sqrt{m}} + Bm \qquad \text{(B-5-1)}$$

TABLE (B-5-1) PARAMETERS OF EQUATION (B-5-1) FOR THE COMPUTATION OF ACTIVITY COEFFICIENTS. VALIDITY RANGE = 0 TO $0.1M$.

	15°	25°	35°	45°
1. *Sodium Chloride*; $\mathring{a} = 4.12$*				
$\mathcal{S}_{(f)}\sqrt{d_0}$	0.4966	0.5049	0.5141	0.5254
A′	1.343	1.350	1.357	1.364
B	0.022	0.031	0.034	0.033
2. *Potassium Chloride*; $\mathring{a} = 3.97$†				
A′	1.300	1.307	1.314	1.321
B	-0.014_0	-0.007_5	-0.005_6	-0.004_0
3. *Calcium Chloride*; $\mathring{a} = 4.575$ Å‡				
$\mathcal{S}_{(f)}\sqrt{d_0}$	1.7321	1.7615	1.7925	
A′	2.588	2.600	2.613	
B	0.198	0.203	0.185	
4. *Potassium Bromide*§				
$t = 25°$; $\mathring{a} = 4.3$ Å.; $\mathcal{S}_{(f)}\sqrt{d_0} = 0.5049$; $A' = 1.420$ $B = -0.014$				

* G. J. Janz and A. R. Gordon, *J. Am. Chem. Soc.*, **65**, 218 (1943). Transference numbers by R. W. Allgood and A. R. Gordon, *J. Chem. Phys.*, **10**, 124 (1942).

† W. J. Hornibrook, G. J. Janz and A. R. Gordon, *J. Am. Chem. Soc.*, **64**, 513 (1942). Transference numbers by R. W. Allgood, D. J. LeRoy and A. R. Gordon, *J. Chem. Phys.*, **8**, 418 (1940).

‡ H. G. McLeod and A. R. Gordon, *J. Am. Chem. Soc.*, **68**, 58 (1946); Transference numbers by A. G. Keenan, H. G. McLeod and A. R. Gordon, *J. Chem. Phys.*, **13**, 466 (1945).

§ E. A. MacWilliam and A. R. Gordon, *J. Am. Chem. Soc.*, **65**, 984 (1943); Transference numbers by A. G. Keenan and A. R. Gordon, *J. Chem. Phys.*, **11**, 172 (1943).

The values of the parameters, *A′* and *B*, and references are listed in Table (B-5-1). This equation yields values of log $\gamma_{\pm}$ at $0.1M$ for the three 1-1 electrolytes which agree very closely with those obtained from cells without liquid junction, and which are listed in the Tables in Chapter (12) and Appendix A. The calcium chloride value at $0.1M$ is 0.518, which differs considerably from 0.531, given in Table (13-1-2A), but is consistent with the revised results given in Table (B-5-2). Butler and Gordon[31] have

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[31] J. P. Butler and A. R. Gordon, *J. Am. Chem. Soc.*, **70**, 2276 (1948).

TABLE (B-5-2). MEAN ACTIVITY COEFFICIENTS OF SOME 1-1 ELECTROLYTES, SULPHURIC ACID, CALCIUM CHLORIDE AND NITRATE AT 25° AND HIGH CONCENTRATIONS

m	NaCl	NaOH	LiCl	LiBr	$LiNO_3$	H_2SO_4	$CaCl_2$	$HClO_4$	$Ca(NO_3)_2$
0.1	0.778	0.766	0.790	0.796	0.788	0.2655	0.518	0.803	0.485
.2	.735	.727	.757	.766	.752	.2090	.472	.778	.426
.5	.681	.693	.739	.753	.726	.1557	.448	.769	.363
1.	.657	.679	.774	.803	.743	.1316	.500	.823	.336
1.5	.656	.683	.838	.896	.783			.923	.336
2.	.668	(0.700)	.921	1.015	.835	.1276	.792	1.055	.345
3.	.714	.774	1.156	1.341	.966	.1422	1.483	1.448	.380
4.	.783	.890	1.510	1.897	1.125	.1700	2.934	2.08	.435
5.	.874	1.060	2.02	2.74	1.310	.2081	5.89	3.11	.507
6.	.986	1.280	2.72	3.92	1.515	.2567	11.11	4.76	.592
7.		1.578	3.71	5.76	1.723	.3166	18.28	7.44	.690
8.		1.979	5.10	8.61	1.952	386	26.02	11.83	.801
9.		2.51	6.96	12.92	2.19	.467	34.20	19.11	.935
10.		3.18	9.40	19.92	2.44	.559	43.0	30.9	1.065
11.		4.04	12.55	31.0	2 69	.661		50.1	1.184
12.		5.11	16.41	46.3	2.95	.770		80.8	1.311
14.		7.91	26.2	104.7		1.017		205.	1.538
16.		11.38	37.9	198.0		1.300		500.	1.724
18.		15.15	49.9	331.		1.608			1.917
20.		19.0	62.4	485.		1.940			2.008
22.		22.7				2.300			
24.		26.1							
26.		29.0							
29.		33.2							
Ref.*	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)

* Comprehensive tables of osmotic and activity coefficients are given by R A. Robinson and R H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

(1) R. H. Stokes and B. J. Levien, *J. Am Chem. Soc.*, **68**, 333 (1946).

(2) R. H. Stokes, *Ibid.*, **67**, 1689 (1945). Referred to 0.700 at 2 M.

(3) R. A. Robinson, *Trans. Faraday Soc.*, **41**, 756 (1945).

(4) R. A. Robinson and H. J. McCoach, *J. Am. Chem. Soc.*, **69**, 2244 (1947).

(5) R. A. Robinson, *Ibid.*, **68**, 2402 (1946).

(6) R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948) (Review)

(7) R. H. Stokes, *Trans. Faraday Soc.*, **41**, 637 (1945).

(8) R. A. Robinson and O. J. Baker, *Trans. Roy. Soc., N. Z.*, **76**, 250 (1946).

(9) R. H. Stokes and R. A. Robinson, *J Am. Chem. Soc.*, **70**, 1871 (1948).

used this method to make the first accurate determination of an activity of a salt in dilute organic solvent-water mixtures. They determined $\gamma_\pm$ of sodium chloride in 50 mole per cent methanol-water mixtures.

Some of the values of mean activity coefficients at higher concentrations have received independent confirmation by Stokes[32] by a method depending

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[32] R. H. Stokes, *J. Am. Chem. Soc.*, **69**, 1291 (1947).

TABLE (B-5-3).* MEAN ACTIVITY COEFFICIENTS OF 2-1 AND 1-2 ELECTROLYTES AND THORIUM NITRATE AT 25°

m	$MgCl_2$	$MgBr_2$	MgI_2	$CaBr_2$	CaI_2	$SrCl_2$	$SrBr_2$	SrI_2	BaI_2	$Mg(NO_3)_2$	$Sr(NO_3)_2$	$Ba(NO_3)_2$	$Co(NO_3)_2$
0.1	0.529	0.550	0.580	0 532	0 560	0 511	0.526	0 553	0.542	0 523	0.478	0.428	0.518
.2	.489	.519	.558	.492	.531	.462	.483	.520	.509	.481	.410	.342	.471
.5	.481	.545	.614	491	.561	.430	.467	.536	.523	.470	.329		.445
.7	.506	.599	.698	.522	.614	.434	.484	.578	.562	.489	302		.455
1.	.570	.723	892	.597	.741	.461	.535	680	.649	.537	.275		.490
1.4	709	.975	1.291	.747	992	.524	643	885	.814	.632	253		.563
2.	1.053	1.614	2.43	1.121	1.640	.670	.906	1.407	1.221	.842	232		.726
3.	2.32	4.26	7.93	2.54		1.126							1.182
4.	5.54	12.2	29.0	6.28		1.977							1.972

m	$ZnCl_2$	$ZnBr_2$	ZnI_2	$Zn(ClO_4)_2$	$Zn(NO_3)_2$	$Mg(ClO_4)_2$	Na_2Fu†	Na_2Ma‡	Rb_2SO_4	Cs_2SO_4	K_2CrO_4	Na_2CrO_4	$Th(NO_3)_4$
0.1	0.515	0 547	0.581	0.581	0.531	0 590	0.465	0.430	0.451	0.456	0.456	0.464	0.279
.2	.462	.510	559	.564	.489	578	.402	.354	.374	382	.382	.394	.225
.5	.394	.511	.610	.629	473	.647	335	272	.279	.291	.292	.307	.189
.7	369	.528	683	720	.489	739	323	.250	.249	.262	.263	.280	.191
1.	.339	552	.800	.929	535	.946	319	.231	.219	.235	.235	.253	.207
1 4	.309	.567	.928	1.386	625	1.385	323	.219	196	.214	.214	.233	.246
2.	.289	.572	1.028	2.74	817	2.65	.343	.213			196	.222	.326
3.	287	.598	1.123	9.99	1.363	9.19		.220			190	.236	.486
4.	.307	.664	1.259	38 8	2.31							.285	.647

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* R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948) This contribution contains a complete bibliography of the original sources of these results.

† Na_2Fu = Sodium fumarate; ‡ Na_2Ma = Na_2 maleate; R. A. Robinson, P. K. Smith and E. R. B. Smith, *Trans. Faraday Soc.*, **38**, 63 (1942).

on equilibration through the vapor phase of a salt solution at 25° with water at a lower temperature. From accurate measurements of the difference in temperature, the temperature of the water is found, and its activity obtained from the standard vapor pressure data in "International Critical Tables." The results obtained for concentrated solutions of sodium and calcium chlorides, and sodium hydroxide indicate that the method is capable of high accuracy.

Since 1943, Robinson and Stokes have revised and considerably extended their isopiestic vapor pressure measurements of solutions of 2-1 and 1-2 electrolytes. They have also obtained results for a number of electrolytes at very high concentrations from which they have attempted to construct a self-consistent group of results using sulphuric acid and calcium chloride solutions as standards of reference. Table (B-5-2) contains the mean activity coefficients of these latter electrolytes, together with a number of 1-1 electrolytes whose activity coefficients were determined at high concentrations. By comparison with Table (12-3-1A), it is clear that this revision results in little change at concentrations below $2M$, but becomes approximately 1 per cent at $4M$.

Table (B-5-3) contains the new results for 2-1 and 1-2 electrolytes, which supplement those in Table (13-1-2A). For magnesium and strontium chloride and magnesium bromide and iodide, their new determinations differ widely from the earlier ones, and have been included. The activity coefficients of zinc chloride, bromide and iodide, which differ considerably from their values in Table (13-3-3A), have also been incorporated in the table. All the other results in the table are those of electrolytes not previously determined.

(B-6) Summary of Recent Contributions to Theories of Electrolytes

As stated in the critical survey at the end of Chapter (12), only slow progress is to be expected toward the elucidation and quantitative interpretation of the complicated interactions occurring in electrolytic solutions. A new point of view regarding the deviations from the limiting law of Debye and Hückel has been introduced by Frank,[33] which is based upon a model of Debye and Pauling,[34] originally intended to show that the limiting law for the chemical potential, or activity coefficient, was unaffected by changes in dielectric constant in the immediate neighborhood of the central ion.

The Debye and Pauling model presupposes a central rigid spherical ion of radius, $r = a$, and of charge, $z\epsilon$, located at the center of the ion. The

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[33] H. S. Frank, *J. Am. Chem. Soc.*, **63**, 1789 (1941); For further discussion of interactions of solutes with the water lattice, see: H. S. Frank, *J. Chem. Phys.*, **13**, 479, 493, (1945); H. S. Frank and M. W. Evans, *Ibid.*, **13**, 507 (1945).

[34] P. Debye and L. Pauling, *J. Am. Chem. Soc.*, **47**, 2129 (1925).

region within the ion and within a sphere of radius, $r = R > a$, is assumed to be a domain of continuous variation of the dielectric constant, while outside this region, from $r = R$ to $r = \infty$, the dielectric constant is assumed to be constant. From this model and suitable boundary conditions, a complicated equation for the potential of the ion is derived, which, upon expansion in a power series of the concentration, reduces to the limiting law plus terms involving first and higher powers of the concentration.

Frank derives the Debye and Pauling equation by an alternative method and obtains an expression for the free energy of the ion in its atmosphere rather than the potential. He then examines the consequences of the theory in the region of moderate concentrations by assuming series of values for the dielectric constant within the sphere of radius R, and a single constant value of the macroscopic dielectric constant of water (78.54 at 25^0) outside this sphere. As a result of these calculations, Frank finds that, when the local dielectric constant within the sphere of radius R does not exceed 25, and the ions can approach each other to a distance equal to the sum of the crystal radii, $(r_+ + r_-)$, the theory yields very large negative deviations from the Debye and Huckel limiting equation in disagreement with experimental results. These deviations decrease as the difference between R and a decreases. If the ions are hydrated and the hydrated ions are rigid impenetrable spheres, then dielectric saturation is reached within this layer of water molecules, and $R = a$. This condition, and the removal by hydration of the water molecules as solvent, leads to positive deviations from theory. If, however, the ions are hydrated and if they can penètrate the hydration shells of oppositely charged ions, the theory can be made to conform with experiment. This association-by-penetration-model will receive further attention in the next section.

In Chapter (12), Section (5)(a), we mentioned Huckel's[35] interpertation of the linear effect represented by Bc in equation (12-5-2) as being caused by a lowering of the macroscopic dielectric constant of the solvent upon addition of salt. This matter has been re-examined by Hasted, Ritson and Collie[36] in the light of their measurements of the dielectric constants and loss angles of concentrated electrolytic solutions at wave-lengths of 10, 3 and 1.25 cm. Unfortunately, their experimental procedure did not permit the evaluation of these quantities in dilute solutions. They found that from 0.5 to $2M$ the results may be represented by the equation

$$D = D_0 - (\delta_+ + \delta_-)c \qquad \text{(B-6-1)}$$

where D is the static dielectric constant, D_0 is the dielectric constant of water, and δ_+ and δ_- are positive constants characteristic of the cations and anions, respectively. Above $2M$, the linear relationship is no longer

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[35] E. Hückel, *Physik. Z.*, **26**, 93 (1925).

[36] J. B. Hasted, D. M. Ritson, and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948).

valid, and the results indicate that above this concentration $(\delta_+ + \delta_-)$ decreases with the concentration. Hasted, Ritson, and Collie compute minimum hydration values from their data by assuming that ions attract water molecules to form inner hydration sheaths which effectively remove them from contributing to the value of the dielectric constant. If n is the minimum number of water molecules in the inner layer and M_1 is the molecular weight of water, then

$$D = D_0 - \frac{nM_1 D_0}{1000} c = D_0 - (\delta_+ + \delta_-)c \qquad \text{(B-6-2)}$$

Outside this region, a relatively smaller lowering of the dielectric is caused by water molecules attracted to the ions For sodium chloride, where $(\delta_+ + \delta_-) = 11$, the authors assume, on theoretical grounds regarding the rotation of water molecules bound by attraction to the ions, that $\delta_+ = 8$ and $\delta_- = 3$. Further, for sodium chloride, they assume that the contribution to the fall in dielectric constant caused by the ions in the outer water layer is $\frac{1}{4}$ the contribution of the inner layer. Therefore, for the cation hydration number, n_+, of sodium chloride, they obtain

TABLE (B-6-1) THE CONSTANTS, δ_+, δ_-' AND SOME MINIMUM HYDRATION VALUES OF POSITIVE IONS

Ion	H^+	Li^+	Na^+	K^+	Rb^+	Mg^{++}	Ba^{++}	La^{+++}	Cl^-
δ_+, δ_-	17	11	8	8	7	24	22	35	3
n_+	10.5	6	4	4	3.5	15.5	14	23	

$$n_+ = (\delta_+ - 2) \frac{1000}{M_1 D_0} \qquad \text{(B-6-3)}$$

It is also assumed that this decrease of δ_+ by 2 units is common to all cations, so that equation (B-6-3) is considered to be general. We have recorded in Table (B-6-1) some values of δ_+, δ_-, and of n_+ computed by this equation.

Ritson and Hasted[37] developed a theory of dielectric saturation in the neighborhood of the ion on the basis of the reaction field theory of Onsager[38] and also on an extension of the theory of Kirkwood.[39] They obtained qualitative agreement with the observed values of the lowering of the dielectric constant. They also re-examined the theories of concentrated solutions and estimated the contributions of the van der Waals' co-volume effect, of Bjerrum's ion association, of varying dielectric constant, and of the solvent structure-breaking effect. They conclude that the situation requires a determined theoretical attack on ion-solvent interaction.

[37] D. M. Ritson and J. B. Hasted, *J. Chem. Phys.*, **16**, 11 (1948).

[38] L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

[39] J G. Kirkwood, *J. Chem. Phys.*, **4**, 592 (1936).

(B-7) Ionic Hydration, Activity Coefficients and Osmotic Coefficients

In Chapter (11), some theories proposed to account for the behaviors of the activity coefficients of electrolytes in concentrated solutions were considered in detail. Two of these extensions of the Debye and Hückel theory, those of Hückel and of Scatchard, depended largely on the computation of the effects produced upon the activity coefficient by ion-ion, ion-solvent, and molecule-molecule interactions in relation to change in dielectric constant produced by varying concentration of electrolyte. Another theory, developed by Van Rysselberghe, was based upon the estimation of a van der Waals' co-volume effect. At the end of this chapter, mention was made of a theory of ionic hydration proposed by Bjerrum[40] in 1920 before the advent of the Debye and Huckel theory. We shall now discuss a modernized version and expansion of Bjerrum's theory by Stokes and Robinson.[41]

In deriving the equations of this theory, we shall not use the method of Stokes and Robinson, who employed the Gibbs-Duhem equation, but shall follow closely a derivation by Harned[42] based directly upon the law of mass action. We shall assume that the equilibria in an aqueous solution of an electrolyte are represented by the reactions and equations

$$\begin{aligned} &(1)\ \mathrm{CA} \rightleftharpoons \mathrm{C}^+ + \mathrm{A}^- &&; K_1 = a_+ a_-/a_2 \\ &(2)\ \mathrm{C}^+ + h\,\mathrm{H_2O} \rightleftharpoons \mathrm{C}^+\cdot h\,\mathrm{H_2O}; &&K_2 = a_h/a_+a_w^h \\ &(3)\ \mathrm{A}^- + j\,\mathrm{H_2O} \rightleftharpoons \mathrm{A}^-\cdot j\,\mathrm{H_2O}\ ; &&K_3 = a_j/a_-a_w^j \end{aligned} \qquad \text{(B-7-1)}$$

where K_1, K_2 and K_3 are mass action constants; a_+, a_- are the activities of the non-hydrated ions; a_h, a_j, those of the hydrated ions; and a_w is the activity of water. Multiplication of the three mass action expressions yields

$$K_1K_2K_3 = \frac{a_h a_j}{a_2 a_w^n}; \qquad K_2K_3 = \frac{a_h a_j}{a_+ a_- a_w^n} \qquad \text{(B-7-2)}$$

where $n = (h + j)$. If the convention is adopted that $a_w = 1$ at infinite dilution of electrolyte, $K_2K_3 = 1$, and this expression becomes

$$a_+a_- = a_ha_j/a_w^n \qquad \text{(B-7-3)}$$

Upon introduction of the activity coefficients and molalities, and by conversion to logarithms

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[40] N. Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920).

[41] R. H. Stokes and R. A. Robinson, *J. Am. Chem. Soc.*, **70**, 1870 (1948); R. A. Robinson and R. H. Stokes, *Ann. N. Y. Acad. Sci.*, **51**, 593 (1949).

[42] H. S. Harned, in H. S. Taylor, "Treatise on Physical Chemistry," First Edition, Vol. 2, p. 776–8, D. Van Nostrand and Co., New York (1924).

$$\log \gamma_{\pm} m = \log \gamma'_{\pm} m' - \frac{n}{\nu} \log a_w \qquad \text{(B-7-4)}$$

is obtained. In this expression, $\gamma_{\pm}$ is the mean activity coefficient of the electrolyte, m its stoichiometric molality, $\gamma'_{\pm}$ *the activity coefficient of the* hydrated ions and m' their molality. If the electrolyte is assumed to be *completely dissociated at all concentrations* m' can be represented by

$$m' = \frac{55.51m}{55.51 - nm} = \frac{m}{1 - 0.018nm} \qquad \text{(B-7-5)}$$

As the concentration of the electrolyte tends toward zero, the mass action law requires that complete hydration of the ions is approached. Consequently, it is safe to assume that the Debye and Hückel equation (5-2-8) represents the activity coefficient of the hydrated ions or that

$$\log \gamma'_{\pm} = -\frac{\mathcal{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} - \log(1 + 0.018\,\nu m') \qquad \text{(B-7-6)}$$

If this result for $\log \gamma'_{\pm}$ is substituted in equation (B-7-4), m' eliminated by equation (B-7-5), and $A' \sqrt{c}$ expressed by equations (5-2-9) and (5-2-10), we obtain

$$\log \gamma_{\pm} = -\frac{\mathcal{S}_{(f)}\sqrt{c}}{1 + 0.3286\,\mathring{a}\sqrt{\Gamma/2}} - \frac{n}{\nu}\log a_w - \log(1 - 0.018(n - \nu)m) \qquad \text{(B-7-7)}$$

which is the "modernized" Bjerrum equation as employed by Stokes and Robinson, except that they replace c and $\Gamma/2$ by m and μ, respectively.

This equation contains two adjustable parameters, $\mathring{a}$ and n, and is capable of representing the activity coefficient with an accuracy equal to that of equation (12-5-2), and over a wider range of concentration. For practical purposes, it is not as easy to use as equations (12-5-2) and (12-5-3), since it is necessary to evaluate a_w from the experimental activity coefficients. Table (B-7-1) contains some of the values of $\mathring{a}$ and n listed in the more extended table of Stokes and Robinson.

In Chapter (12), Sections (5) and (8), we noted the possibility of obtaining a single-parameter equation for computing the activity coefficient over a considerable range of concentration. To this end, Stokes and Robinson introduce the relation

$$\mathring{a} = \left\{\left[\frac{3}{4\pi}(30n + V_{+})\right]^{1/3} + r_{-} - \Delta\right\} \qquad \text{(B-7-8)}$$

by which $\mathring{a}$ can be eliminated from equation (B-7-7). As a result, the hydration number, n, is the only parameter required. The justification of this equation rests on the conclusions of Bernal and Fowler[43] regarding

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[43] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

the apparent molal volumes of ions and water. It is assumed that the large anions, Cl^-, Br^-, I^-, are much less hydrated than the smaller cations, Li^+, Na^+ *etc., so that* r_- *is the crystallographic radius of the anion* It is also assumed that the water molecule occupies an effective volume of 30 cubic Angström units, and therefore, if V_+ is the apparent ionic volume of the cation, $\left[\frac{3}{4\pi}(30n + V_+)\right]^{1/3}$ is the effective "idealized" radius, r_1, of the hydrated cation. To estimate V_+, Stokes and Robinson computed the apparent molal volumes of some electrolytes at 1 M concentration from density data. These can be represented by the empirical equation, $V_{\text{app.}} = 6.47\,(r_+^3 + r_-^3)$ where r_+ and r_- are the crystallographic radii [Table (5-1-6)]. If each anion contributes $6.47\,r_-^3$ cubic Angstroms, the cation contribution is $V_+ = V_{\text{app.}} - 6.47\,\nu_- r_-^3/\nu_+$, where ν_-/ν_+ is the number of anions associated with one cation. From this relation, V_+ is calculated, and r_1 evaluated from V_+. It is found that $(r_1 + r_-)$ exceeds the values of å' derived by the two parameter equation (B-7-7), by 0.7 Å. for alkali halides, and 1.3 Å. for alkaline-earth halides. This quantity, Δ in equation (B-7-8), is interpreted as a penetration of the anion into the hydration shell of the cation,[44] or as a distortion of the ions in the field.

TABLE (B-7-1). CONSTANTS OF EQUATION (8-7-7), AND OF EQUATIONS (8-7-7) AND (8-7-8) COMBINED

Electrolyte	Equation (8-7-7)		Equations (8-7-7) and (8-7-8)		
	n	å	n	å	R
HCl	8.0	4.47	7.3	4.84	0.1–1
LiCl	7.1	4.32	6.5	4.66	.1–2
NaCl	3.5	3.97	3.5	3.97	.1–5
KCl	1.9	3.63	1.9	3.63	.1–4
RbCl	1.2	3.49	1.25	3.47	.1–2
$MgCl_2$	13.7	5.02	13 9	4.99	1–1
$CaCl_2$	12.0	4.73	11.9	4.75	.1–1.8
$SrCl_2$	10.7	4.61	10.8	4.60	1–1.8
$BaCl_2$	7.7	4.45	8 4	4.29	1–1

R—Molal concentration range of validity of the single-parameter equation (8-7-7) combined with (8-7-8)

In the fourth column of Table (B-7-1) are listed the values of n which yielded the most satisfactory agreement with the experimental data. The fifth column contains values of å computed by equation (B-7-8) and it is apparent that these agree closely with those in the third column. The agreement with the observed results is within ± 0.0015 in $\gamma_\pm$ over the concentration ranges listed in the last column, and is surprisingly good for calcium and strontium chlorides.

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[44] H. S. Frank, *J. Am. Chem. Soc.*, **63**, 1789 (1941).

Certain obvious criticisms of this theory have been recognized by Stokes and Robinson, who state that the parameter, n, is not to be interpreted as the number of water molecules in the layer around the ion but as a "number introduced to allow for the average effect of all ion-solvent interactions where these are large compared to kT". Like earlier hydration theories, the hydration numbers are so high that at high concentrations (e.g. $\sim 7\ M$ for hydrochloric acid) all the water will be combined with the ions and none will exist as solvent. Thus, equation (B-7-5) must be modified in the direction of a decreasing n with increasing concentration of electrolyte, a situation which would require the penetration of ions into the hydration shells of other ions. Indeed, the picture of just what is meant by the volume of free solvent becomes vague, and restricts this theory to the intermediate range of concentrations (up to 1 or 2 M) where the effect of penetration on the value of m' is less pronounced.

Stokes and Robinson have introduced a highly speculative idea to account quantitatively for the relation between concentration and water activity in very concentrated solutions. They found that calcium nitrate, which forms a saturated solution at 8.4 M at 25°, supersaturates easily, and upon further concentration forms semi-solid gels. This takes place with no apparent discontinuity, and the vapor pressure is a continuous function of the concentration. As a result, they picture a very concentrated solution of this and other electrolytes as containing some ions possessing partially filled hydration shells, some with monolayers of water, and others with two or more layers more weakly bound. The resemblance of this model to that of polylayer adsorption suggests the possibility of the application of a suitable modification of the Brunauer, Emmett, and Teller[45] adsorption isotherm, as well as its extension by Anderson.[46] The resulting equations give reasonable and accurate agreement with the vapor pressure data for a number of electrolytes in concentration ranges between 4 and 22 M.

(B-8) DISSOCIATION OF STRONG ELECTROLYTES AS DERIVED FROM RAMAN SPECTRUM

The problem of the dissociation of moderately strong and very strong electrolytes has been the subject of an excellent review by Redlich,[47] who emphasized particularly the unequivocal evidence for the presence of undissociated molecules which can be derived from Raman spectra. The presence of vibration spectra is a criterion which can be used to distinguish sharply between molecules and interacting ions. Redlich and Rosenfeld[48]

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[45] S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

[46] R. B. Anderson, *Ibid.*, **68**, 686 (1946).

[47] O. Redlich, *Chem. Rev.*, **39**, 333 (1946). Contains an extensive bibliography.

[48] O. Redlich and P. Rosenfeld, *Stizber. Acad. Wiss. Wien, Math.-Naturw. Klasse* (*Abt II b*) **145**, 87 (1936).

suggested that true ionic concentration can be determined by comparison of the spectrum of the solution with that of a completely dissociated electrolyte containing the same ion. It is known that the intensity of the Raman spectra of alkali nitrates is proportional to their concentrations[49, 50], which is evidence of their complete dissociation. Therefore, in order to find the concentration of the nitrate ions, αc, in nitric acid at a stoichiometrical concentration c, a sodium nitrate solution having Raman lines of equal intensity to the nitric acid solution is prepared. Since the reference nitrate solution of concentration, c_R, is completely dissociated, c_R equals αc.

TABLE (B-8-1). DEGREE OF DISSOCIATION OF NITRIC ACID IN THE NEIGHBORHOOD OF 25°

c	0.1	1	2	3	4	6	8	10	12	14
α	0.997	0.978	0.95	0.90	0.85	0.72	0.56	0.42	0.28	0.16

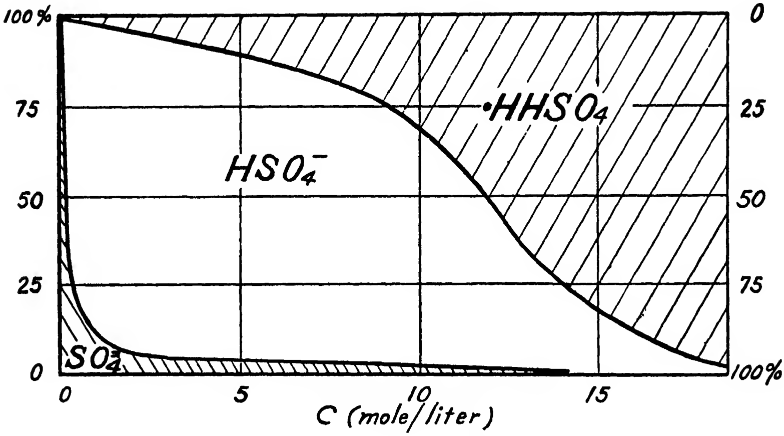

Fig. (B-8-1). Fractions of sulfuric acid present as undissociated acid, as bisulfate ion, and as sulfate ion, represented as vertical distances between adjacent lines.

Values of α determined in this manner are given in Table (B-8-1) from which the thermodynamic dissociation constant was estimated to be 21.4.

Young and Blatz[51] have utilized existing Raman spectrum measurements[52] to unravel the complex equilibria occurring in sulphuric acid solutions at all concentrations. The SO_4^{--} and HSO_4^- band intensities may be compared with those of $(NH_4)_2SO_4$ and $KHSO_4$ solutions, while the band

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[49] N. R. Rao, *Indian J. Phys.*, **15**, 185 (1941).

[50] O. Redlich and J. Bigeleisen, *J. Am. Chem. Soc.*, **65**, 1883 (1943); O. Redlich, E. K. Holt and J. Bigeleisen, *Ibid.*, **66**, 13 (1944).

[51] T. F. Young and L. A. Blatz, *Chem. Rev.*, **44**, 93 (1949).

[52] R. M. Bell and M. A. Jeppesen, *J. Chem. Phys.*, **2**, 711 (1934); *Ibid.*, **3**, 245

of H_2SO_4 is identified by its maximum at 50 mole per cent of H_2O and SO_3. The result of this analysis is clearly demonstrated by Fig. (B-8-1) in which the relative percentages of $HHSO_4$, HSO_4^- and SO_4^{--} in a solution of sulphuric acid are plotted against *c*. On the basis of the degrees of dissociation, a reasonable quantitative interpretation of the heats of dilution, surface tensions[53] and apparent molal volumes may be made.

The Raman spectra of iodic acid[54], trichloroacetic acid[55] and perchloric acid[56] prove that these substances are incompletely dissociated. Important progress is to be expected from this type of optical measurement with improved methods of measuring relative intensities.

(B-9) DISSOCIATION OF SOME MODERATELY STRONG ELECTROLYTES

Table (B-9-1) contains values of ionization constants of some moderately strong electrolytes, estimated by various methods, which are taken from the review of Redlich.[57] These results supplement the data contained in Table (6-3-2). The sources of this information, recorded by Redlich, are voluminous and have not been included.

TABLE (B-9-1). DISSOCIATION CONSTANTS OF SOME MODERATELY STRONG ELECTROLYTES

Substance	*K*	Substance	*K*
HIO_3	0.17	$PbBr^+$	0.07
CCl_3COOH	.22–0.23	PbI^+	035
Picric Acid	.16	H_2SO_3	.012–0.017
$CHCl_2COOH$	.14	$HSeO_4^-$	.01
$H_4P_2O_7$	.14	*o*-Nitrobenzoic acid	006
$PbCl^+$	.06–0.1		

(B-10) IONIZATION CONSTANTS AND IONIZATION OF WEAK ACIDS IN SALT SOLUTIONS

In Tables (B-10-1), (B-10-2), and (B-10-3) we have compiled accurate results on the ionization constants of weak electrolytes in water, in salt solutions, and in water-organic solvent mixtures, which have been determined in recent years by cells without liquid junctions, as described in

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(1935); J. Chedin, *Ann Chim* (*11*), **8**, 243 (1937); H. Gerding and W J. Nijveld, *Rec. trav. chim.*, **59**, 1206 (1940); H. Nisi, *Japan J. Phys*, **5**, 119 (1929); N. G. Pai, *Phil. Mag.*, **20**, 616 (1935); I. R. Rao, *Proc. Roy. Soc. London*, **A144**, 159 (1934); N. R Rao, *Indian J. Phys.*, **14**, 143 (1940).

[53] T. F. Young and S. R. Grinstead, *Ann. N Y. Acad. Sci.*, **51**, 765 (1949).

[54] N. R. Rao, *Indian J. Phys.*, **16**, 71 (1942).

[55] N. R. Rao, *Ibid.*, **17**, 332 (1943).

[56] O. Redlich, E. K. Holt and J. Begeleisen, *J. Am Chem. Soc.*, **66**, 13 (1944).

[57] O. Redlich, *Chem. Rev.*, **39**, 333 (1946).

TABLE (B-11-1) OBSERVED IONIZATION CONSTANTS IN WATER. ALL VALUES ARE ON THE *m*-SCALE

Acid	Solvent		0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	Ref.
Carbonic	Water	$K_{1A} \times 10^7$	2.64	3.04	3.44	3.81	4.16	4.45	4.71	4.90	5.04	5.13	5.19	1
	0.1*M* NaCl	"	4.48	5.16	5.84	6.49	7.11	7.66	8.14	8.54	8.85	9.06	9.16	2
	0.2*M* NaCl	"	5.15	5.93	6.70	7.44	8.14	8.78	9.33	9.79	10.15	10.39	10.51	2
	0.5*M* NaCl	"	6.23	7.14	8.04	8.90	9.70	10.41	11.03	11.53	11.92	12.19	12.32	2
	0.7*M* NaCl	"	6.62	7.56	8.47	9.34	10.15	10.81	11.51	12.03	12.45	12.75	12.93	2
	1.0*M* NaCl	"	7.02	7.98	8.92	9.80	10.63	11.37	12.02	12.58	13.03	13.37	13.58	2
Phosphoric	Water	$K_{2A} \times 10^8$	4.85	5.24	5.57	5.89	6.12	6.34	6.46	6.53	6.58	6.59	6.55	3
Phenolsulphonic	"	$K_{2A} \times 10^{10}$	4.45	5.20	6.03	6.92	7.85	8.85	9.89	10.94	12.00	13.09	14.16	4
Glycine	"	$K_{1A} \times 10^7$		3.82	3.99	4.17	4.32	4.46	4.57	4.66	4.73	4.77	4.79	5
Benzoic	"	$K_{1A} \times 10^5$					6.24	6.29	6.27	6.24				6
Citric	"	$K_{1A} \times 10^4$	6.03	6.31	6.69	6.92	7.21	7.45	7.66	7.78	7.96	7.99	8.04	7
	"	$K_{2A} \times 10^5$	1.45	1.54	1.60	1.65	1.70	1.73	1.76	1.77	1.78	1.76	1.75	7
	"	$K_{3A} \times 10^7$	4.05	4.11	4.14	4.13	4.09	4.02	3.99	3.78	3.69	3.45	3.28	7

[1] H. S Harned and R Davis, Jr., *J. Am. Chem Soc*, **65**, 2030 (1943)

[2] H. S. Harned and F T Bonner, *Ibid*, **67**, 1026 (1945)

[3] R. G. Bates and S. F. Acree, *J. Res Nat Bur Standards*, **30**, 129 (1943)

[4] R. G. Bates, G. L. Siegel and S. F. Acree, *Ibid*, **31**, 205 (1943)

[5] E. J. King, *J Am. Chem Soc*, **67**, 2178 (1945)

[6] H. N. Parton and A V Jones, Private Communication

[7] R. G. Bates and G. D Pinching, *J Am. Chem Soc.*, **71**, 1274 (1949)

TABLE (B-10-2) IONIZATION CONSTANTS OF WEAK ACIDS IN ORGANIC SOLVENT-WATER MIXTURES. ALL VALUES ARE ON THE *m*-SCALE

X = Weight Per Cent Organic Solvent

X		0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
Propionic Acid in Methyl Alcohol-Water Mixtures[2]												
0[1]	$K_A \times 10^5$	1.274	1.305	1.326	1.336	1.338	1.336	1.326	1.310	1.280	1.257	1.229
10	"	0.881		0.885		0.917	0.947	0.909		0.838		
20	"	0.603		0.608		0.586	0.578	0.553		0.525		
Propionic Acid in Ethyl Alcohol-Water Mixtures[2]												
10	$K_A \times 10^5$	0.870		0.900		0.900	0.900	0.906		0.902		
20	"	0.673		0.755		0.771	0.781	0.788		0.780		
Propionic Acid in Isopropyl Alcohol-Water Mixtures[3]												
5	$K_A \times 10^5$	1.015	1.038	1.052	1.061	1.060	1.053	1.044	1.032	1.012		
10	"	0.780	0.803	0.815	0.823	0.824	0.820	0.812	0.800	0.785		
20	"	0.431	0.448	0.459	0.466	0.466	0.466	0.462	0.454	0.444		
n-Butyric Acid in Isopropyl Alcohol-Water Mixtures[4]												
5	$K_A \times 10^5$	1.190	1.197	1.189	1.177	1.157	1.133	1.104	1.077	1.040		
10	"	0.922	0.929	0.925	0.916	0.907	0.888	0.861	0.839	0.813		
20	"	0.466	0.475	0.476	0.473	0.465	0.456	0.446	0.432	0.417		
Acetic Acid in Glycerol-Water Mixtures[5] (0 to 90°)												
50	$K_A \times 10^6$	4.78	4.96	5.10	5.22	5.32	5.35	5.38	5.37	5.33	5.27	5.18
		55°	60°	65°	70°	75°	80°	85°	90°			
50	"	5.07	4.95	4.81	4.65	4.47	4.31	4.14	3.93			

[1] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 2379 (1933)

[2] A. Patterson and W. A. Felsing, *Ibid.*, **64**, 1480 (1942)

[3] R. L. Moore and W. A. Felsing, *Ibid.*, **69**, 2420 (1947)

[4] W. A. Felsing and M. May, *Ibid.*, **70**, 2904 (1948).

[5] H. S. Harned and F. H. M. Nestler, *Ibid.*, **68**, 966 (1946)

Chapter (15). Table (B-10-3) contains the parameters of equations (15-6-9) to (15-6-15) which we have shown to be suitable for the calculation of the standard thermodynamic functions corresponding to the ionization reactions.[58]

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[58] H. O. Jenkins [*Trans. Faraday Soc.*, **40**, 19 (1944); **41**, 138 (1945)] has re-examined the empirical expressions [Equations (15-3-6), (15-3-7)] for the temperature variation of the ionization constant and has proposed a more complicated one with four empirical constants. The agreement of the calculated with the observed values shows no improvement over the simpler equation. These computations re-emphasize the difficulty in obtaining the desired thermodynamic functions by differentiation of empirical expressions for the free energy (see p. 516).

TABLE (B-10-3). CONSTANTS OF EQUATIONS (15-6-9) TO (15-6-15) FOR IONIZATION CONSTANTS, ΔF_i^0, ΔH_i^0, $\Delta C_{p_i}^0$, $-\log K_\theta$, AND T_θ

$$K = \frac{m_H m_{Ac}}{m_{HAc}} \frac{\gamma_H \gamma_{Ac}}{\gamma_{HAc}} = k \frac{\gamma_H \gamma_{Ac}}{\gamma_{HAc}}$$

$$\left.\begin{matrix}\log K \\ \log k\end{matrix}\right\} = -\frac{A^*}{T} + D^* - C^*T \qquad \begin{aligned} A' &= 2\ 3026\ RA^* \\ D' &= 2.3026\ RD^* \\ C' &= 2.3026\ RC^* \end{aligned}$$

$$\Delta F_i^0 = A' - D'T + C'T^2$$

$$\Delta H_i^0 = A' - C'T^2$$

$$\Delta C_{p_i}^0 = D' - 2C'T$$

$$T_\theta = \frac{A^*}{C^*}\ ; \log K_\theta = D^* - 2\sqrt{C^*A^*}$$

Part I Aqueous Solutions

		A^*	D^*	C^*	A'	D'	C'	T_θ	$-\log K_\theta$
Phosphoric acid	K_{2A}	1979 5	5.3541	0 019840	9055.0	24.491	0.090751	317	7.1795
Phenolsulphonic acid	K_{2A}	1961 2	1.1436	0.012139	8970.8	5.231	0.055525	402	8.3928
Benzoic acid	K_{1A}	1590.2	5.394	0.01765	7319.1	29 247	0.080733	301	4.2014
Citric acid	K_{1A}	1255.6	4.5635	0.011673	5143 3	20 874	0.053394	328	3 094
" "	K_{2A}	1585 2	5.4460	0.016399	7250 9	24.911	0.074012	311	5 751
" "	K_{3A}	1814.9	6 3664	0.022389	8301.6	29.121	0.102410	285	6.383

Part II. Carbonic Acid (K_{1A}), (k_{1A}) in Aqueous NaCl Solutions[1]

m_{NaCl}	A^*	D^*	C^*	m_{NaCl}	A^*	D^*	C^*
0.0	3404.71	14.8435	0.032786	0.5	3158.38	13 5235	0.029892
.1	3266.11	14.0256	.030811	7	2955.23	12.2139	.027721
.2	3228.50	13.8363	030401	1 0	2786.18	11.1187	.025885

Boric Acid in Aqueous NaCl Solutions[2]

.0	2291.9	3.6865	.017560	0 725	1695.2	0 0750	.010799
02	2221.1	3.2837	.016595	1 25	1496 2	−1.1962	.008662
.07	2136.4	2.7805	.015590	2.00	1264.9	−2.7439	.006053
36	1881.8	1.2322	.012782	3 00	984.7	−4.7340	.002626

Glycine (K_A) in Aqueous NaCl Solutions[3]

.0	1259.9	5.3980	.011817	1.25	1277.1	5.2559	.011412
.1	1278.0	5.5030	.011974	2.00	1213.1	4.6187	.010234
.3	1292.4	5.5727	.012067	3.00	1026.6	3.0809	007529
.725	1297.4	5.5234	.011931				

Propionic Acid in Isopropyl Alcohol-Water Mixtures

X				X			
0	1213.26	3.3860	.014055	10	1403.858	4.5143	.016406
5	1191.0865	3.1909	013995	20	1771.125	6.7087	.020457

TABLE (B-10-3)—Continued

n-Butyric Acid in Isopropyl Alcohol-Water Mixtures

m_{NaCl}	A^*	D^*	C^*	m_{NaCl}	A^*	D^*	C^*
0	1033.39	2.6215	.013334	10	1217.523	3.6903	015625
5	1048.516	2.6719	013753	20	1459.369	5.0187	018325

Acetic Acid in Glycerol-Water Mixture (0 to 90°)

m_{NaCl}	A^*	D^*	C^*	m_{NaCl}	A^*	D^*	C^*
50	1321.4256	3.4148	0.014268				

[1] H. S. Harned and F T. Bonner, *J Am. Chem Soc.*, **67**, 1026 (1945).
[2] B. B. Owen and E. J. King, *Ibid.*, **65**, 1612 (1943)
[3] E. J. King. *Ibid.*, **67**, 2178 (1945)

The first ionization of carbonic acid,

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

has been subjected to a comprehensive and consistent investigation by Harned and Davis,[59] and Harned and Bonner,[60] who measured the electromotive forces of the cell

$$\text{Pt-H}_2 \mid \text{NaHCO}_3(m_1),\ \text{NaCl}(m_2),\ \text{CO}_2(m_3) \mid \text{AgCl-Ag}$$

The general equation for the electromotive force of this cell is

$$\mathrm{E} = \mathrm{E}^0 - \frac{RT}{\mathrm{F}} \ln m_{\mathrm{H}} m_{\mathrm{Cl}} \gamma_{\mathrm{H}} \gamma_{\mathrm{Cl}} - \mathrm{E}_c \qquad \text{(B-10-1)}$$

where $\mathrm{E}_c = -RT/2\mathrm{F} \ln P_{\mathrm{H}_2}$. The term E_c is retained since the measurements were carried out with hydrogen-carbon dioxide gas mixtures which varied from 18 to 80 per cent carbon dioxide. The ionization constant may be defined by

$$K_{1\mathrm{A}} \equiv \frac{a_{\mathrm{H}} a_{\mathrm{HCO_3}}}{a_{\mathrm{H_2O}} a_{\mathrm{CO_2}}} = \frac{\gamma_{\mathrm{H}} \gamma_{\mathrm{HCO_3}} m_{\mathrm{H}} m_{\mathrm{HCO_3}}}{a_{\mathrm{H_2O}} \gamma_{\mathrm{CO_2}} m_{\mathrm{CO_2}}} = \frac{\gamma_{\mathrm{H}} \gamma_{\mathrm{HCO_3}}}{a_{\mathrm{H_2O}} \gamma_{\mathrm{CO_2}}} k_{1\mathrm{A}} \qquad \text{(B-10-2)}$$

As a reference state, the condition that $\gamma_{\mathrm{H}} = \gamma_{\mathrm{HCO_3}} = \gamma_{\mathrm{CO_2}} = a_{\mathrm{H_2O}} = 1$ in pure water was chosen, and therefore $K_{1\mathrm{A}}$ is an isothermal constant at all salt concentrations. By elimination of m_{H} between equations (B-10-1) and (B-10-2), we obtain

$$\begin{aligned}(\mathrm{E} + \mathrm{E}_c - \mathrm{E}^0) \frac{\mathrm{F}}{2.3026\,RT} + \log m_{\mathrm{CO_2}} + \log \frac{m_{\mathrm{Cl}}}{m_{\mathrm{HCO_3}}} &= \\ -\log K_{1\mathrm{A}} - \frac{\log \gamma_{\mathrm{H}} \gamma_{\mathrm{Cl}} a_{\mathrm{H_2O}} \gamma_{\mathrm{CO_2}}}{\gamma_{\mathrm{H}} \gamma_{\mathrm{HCO_3}}} &\equiv -\log K' \end{aligned} \qquad \text{(B-10-3)}$$

which defines the extrapolation function, $-\log K'$. Since the logarithmic term containing the activity coefficients is zero in pure water, $-\log K_{1\mathrm{A}}$

[59] H. S. Harned and R. Davis, Jr , *J. Am. Chem. Soc.*, **65**, 2030 (1943).
[60] H. S. Harned and F. T. Bonner, *Ibid.*, **67**, 1026 (1945).

may be obtained by extrapolating the right side of this equation to zero concentration of all solutes. An exact procedure requires two extrapolations, a first to zero ionic strength, and a second to zero concentration of carbon dioxide. The molality of the carbon dioxide may be obtained from Henry's law in the form

$$m_{CO_2} = S_0 P_{CO_2} \tag{B-10-4}$$

Harned and Davis, by using gas mixtures of a wide range of concentrations of carbon dioxide, showed that its presence in the solution produced no appreciable medium effect on $-\log K'$. The establishment of this fact eliminates the necessity of double extrapolation, and greatly simplifies subsequent experimental procedures.

The ionization, k_{1A}, in the salt solutions may be obtained by elimination of K_{1A} from equations (B-10-2) and (B-10-3) whereby

$$-\log k_{1A} = (\mathbf{E} - \mathbf{E}^0 + \mathbf{E}_c) \frac{\mathbf{F}}{2.3026\,RT} + \log \frac{m_{CO_2} m_{Cl}}{m_{HCO_3}} + \log \gamma_H \gamma_{Cl} \tag{B-10-5}$$

is obtained. All quantities on the right-hand side of this equation are known, since $\sqrt{\gamma_H \gamma_{Cl}}$, the activity coefficient of hydrochloric acid at zero concentration in sodium chloride solutions [Table (14-2-1A)], has been determined. The carbon dioxide molality may be calculated by means of

$$m_{CO_2} = S_{(s)} P_{CO_2} \tag{B-10-6}$$

if the Henry law constants for the salt solutions, determined by Harned and Davis, are employed. The observed values of K_{1A} and k_{1A} in sodium chloride solutions are given in Table (B-10-1), and the constants of equation (15-6-9) for computing their temperature variations are contained in Table (B-10-3).

By taking the logarithm of equation (B-10-2) and substituting the Debye and Huckel formula, with an additional linear term, for $\log \gamma_H \gamma_{HCO_3}$, we obtain

$$-\log k_{1A} = -\log K_{1A} - \frac{2\mathfrak{S}_{(f)}\sqrt{d_0 \mu}}{1 + A'\sqrt{\mu}} + B'\mu - \log \gamma_{CO_2} a_{H_2O} \tag{B-10-7}$$

It is found that from 0 to 1 M sodium chloride

$$\log \gamma_{CO_2} = \log \frac{S_0}{S_{(s)}} = \alpha\mu \tag{B-10-8}$$

where α is an isothermal constant. Further, the approximation

$$-\log a_{H_2O} = \beta m \tag{B-10-9}$$

represents the observed results within sufficiently narrow limits to permit us to reduce equation (B-10-7) to the simple form

$$-\log k_{1A} = -\log K_{1A} - \frac{2\mathbb{S}_{(f)}\sqrt{d_0\mu}}{1+\sqrt{\mu}} + B\mu \qquad \text{(B-10-10)}$$

by replacing A' by unity at all temperatures. The necessary quantities for the computation of k_{1A} from 0 to 50° and 0 to 1 M concentration are summarized in the following equations:

$$\log K_{1A} = -3404.71/T + 14.8435 - 0.032786T \qquad \text{(B-10-11)}$$

$$\mathbb{S}_{(f)}\sqrt{d_0} = 0.4883 + 0.75545 \times 10^{-3}t + 0.1743 \times 10^{-5}t^2 + 0.11665 \times 10^{-7}t^3 \qquad \text{(B-10-12)*}$$

$$B = 0.066 + 1.92 \times 10^{-3}t - 0.0176 \times 10^{-3}t^2 \qquad \text{(B-10-13)}$$

Harned and Bonner found that these equations represent the observed results with average deviations in $-\log k_{1A}$ of 0.001 from 0 to 10°, of 0.001 to 0.002 from 15 to 30°, and of 0.002 to 0.004 from 35 to 50°. The maximum deviation is 0.0063 at 50° and 1 M sodium chloride.

The values of α in equation (B-10-8), which permit the calculation of $\log \gamma_{CO_2}$ at all temperatures and concentrations under consideration, are given by the equation

$$\alpha = 0.1190 - 0.833 \times 10^{-3}t + 0.666 \times 10^{-5}t^2 \qquad \text{(B-10-14)}$$

The carbon dioxide concentration is given by

$$\log m_{CO_2} = \log S_0P_{CO_2} - \alpha\mu \qquad \text{(B-10-15)}$$

in which $\log S_0$ can be computed by the expression

$$-\log S_0 = -2385.73/T + 14.0184 - 0.015264\,T \qquad \text{(B-10-16)}$$

These investigations lead to the accurate evaluation of many important quantities involved in aqueous solutions of carbon dioxide. Besides the standard thermodynamic functions, ΔF_i^0, ΔH_i^0, $\Delta C_{p_i}^0$, and ΔS_i^0, the quantities, K_{1A}, k_{1A}, $\gamma_H\gamma_{HCO_3}/\gamma_{CO_2}a_{H_2O}$, $\gamma_H\gamma_{HCO_3}$, γ_{CO_2} and m_{CO_2} in the salt solutions, have been determined. However, it is important to note that this method does not yield any information regarding the ionization of the acid, H_2CO_3, but only that of $H_2O + CO_2$, or the sum of the reactions

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

and

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

Roughton,[61] by means of kinetic calorimetric measurements, has been able to estimate the heat contents of both these reactions and the velocity

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* G. Scatchard, *J. Am. Chem. Soc.*, **65**, 1249 (1943)

[61] F. J. W. Roughton, *J. Am. Chem. Soc.*, **63**, 2930 (1941)

constant of the second reaction. He employed the method of rapid mixing of solutions of sodium bicarbonate and hydrochloric acid. This mixture flowed at a known rate through an observation tube containing thermocouples at suitable distances. The temperature measurements showed conclusively that, with a strong acid, the reaction, $H^+ + HCO_3^- \rightarrow H_2CO_3$, was practically instantaneous, while the rate constant, k_0, of the slower reaction, $H_2CO_3 \rightarrow H_2O + CO_2$, was capable of measurement. Independent measurements[62] of the rate of formation of carbon dioxide in bicarbonate-cacodylate buffers ($P_H = 5.5$ to 7) yielded the velocity constant, k_1, of the rapid reaction, $H^+ + HCO_3^- \rightarrow H_2O + CO_2$. From the ratio, k_0/k_1, the ionization constant of H_2CO_3 was estimated to be of the order 2×10^{-4}.

The determination of the ionization of boric acid in sodium chloride solutions by Owen and King[63] was effected by means of buffered solutions in cells without liquid junctions. An interesting feature of this contribution consisted in their choice of a standard state which requires that the activity coefficients are unity at infinite dilution in each sodium chloride solution at concentration m. Thus, every salt solution is treated as an independent solvent. The mathematical procedure is analogous to that developed for organic solvent-water mixtures in Chapter (15), Section (7). Although this method has certain formal and logical advantages, it does not yield information which cannot be obtained by the earlier procedures, as exemplified by the treatment of the carbonic acid equilibrium described in this section.

The fruitfulness of the thermodynamic method for the determination of ionization constants, and the ionization of weak acids in a given solvent and in salt solutions from electromotive measurements of cells without liquid junctions, is further exemplified by its extension by Bates[64] to the overlapping dissociation of weak acids. He shows how the method can be employed to determine the product K_1K_2 for dibasic acids, and both the products K_1K_2 and K_2K_3 for tribasic acids. Bates and Pinching[65] have illustrated this method by a comprehensive study of the three ionization constants of citric acid. Their results are listed in Table (B-10-1), and the constants of the equations for computing the thermodynamic functions are incorporated in Table (B-10-3). At 18, 25, and 37°, their values of $-\log K_{2A}$ and $-\log K_{3A}$ agree closely with those determined by Bjerrum and Unmack[66] from cells with liquid junctions, but the results for $-\log K_{1A}$ by the two methods differ by approximately 0.06.

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[62] R. Brinkman, R. Margaria and F. J. W. Roughton, *Phil. Trans. Roy. Soc.*, **A332**, 65 (1933).

[63] B. B. Owen and E. J. King, *J. Am. Chem. Soc*, **65**, 1612 (1943).

[64] Bates, R. G., *J. Am. Chem. Soc.*, **70**, 1579 (1948).

[65] R. G. Bates and G. D. Pinching, *Ibid.*, **71**, 1274 (1949).

[66] N. Bjerrum and A. Unmack, *Kgl. Danske Videnskab, Selskab. Math.-fys.*, **Medd. 9**, No. 1 (1929).

(B-11) TRANSITION FROM SIMPLE IONS TO COMPLEX AGGREGATES AND POLYMER ELECTROLYTES

The scope of material in this treatise has been purposefully limited to the theories and properties of solutions containing ions of comparatively simple structures. In view of the large quantity of contemporary research upon long-chain, multiple-charge electrolytes and proteins, we thought it appropriate to discuss briefly results which illustrate the transition in properties of typical series of salt solutions containing ions of increasing complexity.

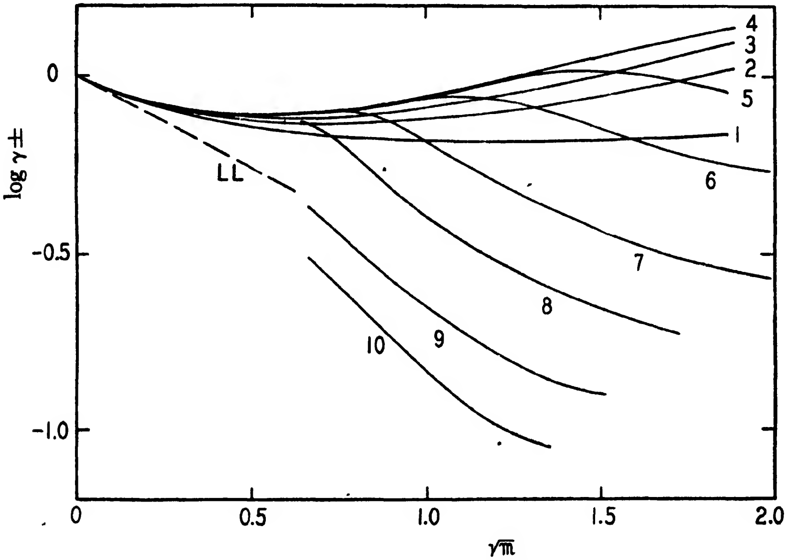

Fig. (B-11-1). Mean activity coefficients of sodium salts of monocarboxylic acid[8] in water at 25°. 1, Formate; 2, acetate; 3, propionate; 4, butyrate; 5, valerate; 6, caproate; 7, heptylate; 8, caprylate; 9, pelargonate; and 10, caprate.

Fig. (B-11-1) contains graphs of the mean activity coefficients of the sodium salts of the first ten normal aliphatic acids.[67] The activity coefficients of the first four members of the series show the characteristic behavior of simple 1-1 type strong electrolytes in water, as illustrated by Figs. (12-5-2), (12-5-3) and (12-9-1). Sodium valerate is the first to exhibit a deviation from normal behavior, since the plot of its activity coefficient is seen to cross that of sodium butyrate. Beginning with sodium caproate, the difference in behavior is very pronounced, and becomes in-

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[67] E. R. B. Smith and R. A. Robinson, *Trans. Faraday Soc.*, **38**, 70 (1942).

creasingly so as the number of carbon atoms in the salt increases. These results indicate the presence of micelle formation in all the solutions from the six- to ten-carbon atom salts. Extremely sharp bends occur with the salts containing nine and ten carbon atoms.

The abrupt transition from simple ions to micelles is very apparent in the variation of the equivalent conductivity with concentration. This is illustrated in Fig. (B-11-2) in which the appearance of characteristic breaks in the conductivity curves of the higher members of a series of alkylamine hydrochlorides[68, 69] indicate micelle formation. The break is very sharp for octadecylamine and hexadecylamine hydrochlorides, and becomes less pronounced with decreasing number of carbon atoms in the cation. The plot for octylamine hydrochloride is typical of normal 1-1 type strong electrolytes. The concentration at which this transition from the behavior of typical electrolytes to that of micelles takes place is very sensitive to the structure of the solute and the nature of the solvent medium. The complex behaviors of the above type of electrolytes in mixed solvents and in the presence of added electrolytes of simpler structures have been the subject of many recent investigations[70] by Kraus, Tartar, Ralston, and

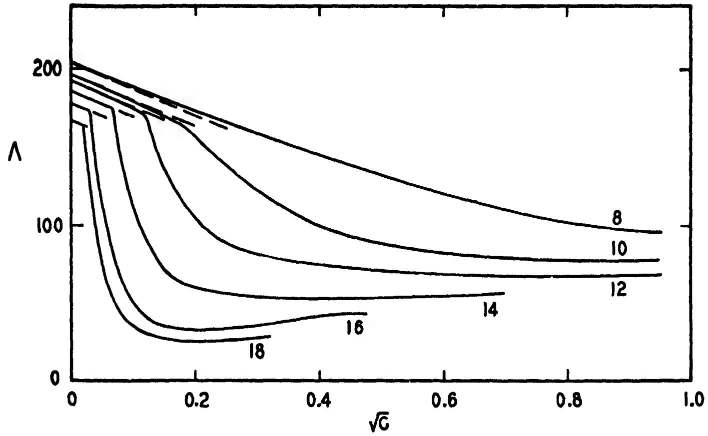

Fig. (B-11-2). Equivalent conductivities of alkylamine hydrochlorides in water at 25°. 8, Octyl-; 10, decyl-; 12, dodecyl-; 14, tetradecyl-; 16, hexadecyl-; and 18, octadecyl-amine hydrochloride.

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[68] A. W. Ralston and C. W. Hoerr, *J. Am. Chem. Soc.*, **64**, 772 (1942)

[69] A. W. Ralston, C. W. Hoerr and E. J. Hoffman, *Ibid.*, **64**, 97 (1942)

[70] For typical investigations of this kind, see P. F. Grieger and C. A. Kraus, *J. Am. Chem. Soc.*, **70**, 3803 (1948); A. B. Scott, H. V. Tartar and E. C. Lingafelter, *Ibid.*, **65**, 698 (1943); and A. W. Ralston and D. N. Eggenberger, *Ibid.*, **70**, 2918 (1948). A summary of some of this work is given by P. F. Grieger, *Ann. N. Y. Acad. Sci.*, **51**, 827 (1949).

their colleagues. An important theoretical interpretation of these effects has been proposed by Debye.[71]

Extensions of these methods of study, beyond the scope of this treatise, toward fields involving ions of increasing molecular size and complexity, approaching those of proteins, are summarized in a recent contribution by Fuoss.[72] He and his collaborators have described the properties of solutions of very long-chain electrolytes, of known structure and many charges, formed by polymerization. The conductance, viscosity and osmotic pressure of solutions of these substances exhibit many interesting and novel features.[73,74]

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[71] P. Debye, *Ann. N. Y. Acad. Sci.*, **51,** 575 (1949)

[72] R. M. Fuoss, *Science*, **108,** 545 (1948).

[73] R. M. Fuoss and U. P. Strauss, *Ann. N. Y. Acad. Sci.*, **51,** 836 (1949).

[74] U. P. Strauss and R. M. Fuoss, *J. Polymer Sci.*, **4,** 457 (1949).

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