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HYDROGEN IONS

THEIR DETERMINATION AND IMPORTANCE IN PURE AND INDUSTRIAL CHEMISTRY

BY

HUBERT T. S. BRITTON

D.Sc. LONDON AND BRISTOL, D.I.C., F.I.C.

PROFESSOR OF CHEMISTRY, WASHINGTON SINGER LABORATORIES, UNIVERSITY COLLEGE OF THE SOUTH-WEST OF ENGLAND, EXETER

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TO

E. B.

EDITORIAL PREFACE

In these days of intensive and extensive research, every worker in science or its applications knows how rapidly the contents of text-books and encyclopædias become out of date; and those who wish to see new work published know the difficulties which abnormal taxation and high labour costs offer to the realisation of their desire. The one obvious solution of the problem is the publication of monographs that would focus attention upon recent work, or upon new aspects of old work, and upon their theoretical implications. Such books are usually written by experts for other experts in related fields of science, or for the well-educated layman whose thirst for new knowledge has not been quenched by the more sensuous outpourings of the ephemeral press.

It is interesting at times to speculate upon what aspects of our civilisation the future historian will select as the most characteristic of our time. Scientific discoveries and their application to human welfare, we may be sure, will find a place; and to these many will add the growth of our sense of "values." The value of new work in science varies greatly: the golden grain is always accompanied by chaff, and there is no precious ore without country rock. Owing to the difficulty of assessing the value of work at the time of its production, we find that our scientific periodicals stand in danger of being swamped by the mass of second- and third-rate material that is thought to be worth publishing, but which posterity will decree would have been better left in manuscript form. It is the first duty of the monograph writer to estimate the value, either actual or potential, of recent work upon the subject of which he writes: he must pick out the plums to save others from the indigestion that follows eating the whole pie. Further, in addition to being

accurate, his work must be presented in a form that is both assimilable and attractive; in other words, he must show that lucid exposition can be achieved by the use of few words, if they are rightly chosen, and that attractive presentation is attained rather by clear thinking than by superficial display.

The present series of monographs has been designed with these objects and ideals in view. The task which the authors have been set is no easy one; so that should performance occasionally fall short of intention, the critical reader is asked to echo the words of Goethe that "higher aims, even if unfulfilled, are in themselves more valuable than lower aims quite attained."

E. HOWARD TRIPP.

AUTHOR'S PREFACE

HYDROGEN-ION concentrations have long been recognised as an essential factor in many biochemical processes, and it is undoubtedly on account of this recognition that considerable additions have been made in recent years to our knowledge of biochemical principles. In other branches of chemistry, hydrogen-ion concentrations are only just beginning to be regarded as being of fundamental importance, and the use of the hydrogen electrode and the other associated methods are being increasingly applied, not only to measure very small changes in acidity and alkalinity, but as valuable indicators of the extents to which reactions have proceeded and as a means of controlling these reactions with an exactitude hitherto impossible. This also applies to various manufacturing processes.

In writing this book the author has endeavoured: firstly, to provide a practical discussion of the various electrometric and colorimetric methods of determining the concentration of hydrogen ions; secondly, to show the fundamental importance of hydrogen-ion concentrations in general chemistry, including volumetric and gravimetric analytical procedures; and, finally, to indicate the important rôles played by hydrogen-ion concentrations in numerous industrial chemical processes, and how the various methods of measuring hydrogen-ion concentrations have been employed for the purpose of control. In order to elucidate the importance of hydrogen-ion concentrations in manufacturing processes to the general reader, brief outlines of the processes have been included wherever they were considered necessary.

Methods of very limited application of determining concentrations of hydrogen ions, such as those depending on the rate of

catalytic decompositions, and conductivity measurements have been excluded, in view of the marked superiority of the methods described in the book.

As is well known, much controversy is taking place as to the mode of ionisation of strong electrolytes. Unfortunately, the degree of ionisation, if considered in terms of the *concentration* of ions, leads to one standard with which electrode potentials are compared, whereas, if considered in terms of the *activity* of ions it leads to a slightly different standard. In view of there being no really satisfactory theory of solutions incorporating their many properties, the author has deemed it advisable to adhere to the more usual ion-concentration theory in the interpretation of electrode potentials. Discussions of the theories of G. N. Lewis and Debye and Hückel have been considered to be outside the scope of this book, and they should be sought in treatises on physical chemistry or in the original literature. Whatever may be the true interpretations of the potentials of the hydrogen electrode, and of the other electrodes which have been standardised against it, one thing is certain that the voltages constitute a remarkable and delicate means of registering and controlling acidity and alkalinity.

The author gratefully acknowledges his indebtedness to Mr. A. G. Pollard, B.Sc., A.R.C.S., D.I.C., Lecturer in Agricultural Chemistry in the Imperial College of Science and Technology (Royal College of Science), London, for writing the greater portion of the chapter on the " Fertility of Soils "; a subject on which he and his students have been actively carrying out research for the past few years. The author's best thanks are also due to the Editor of *The Industrial Chemist*, for kind permission to reproduce much material and for the use of the appropriate blocks of the diagrams, which first appeared in the author's articles in that invaluable journal; to the Chemical Society for kind permission to reproduce several of the diagrams which were published in the author's original papers in the Society's Journal; and to Messrs. A. Gallenkamp & Co., Ltd., London, Messrs. Cambridge Instrument Co., Ltd., London, Messrs. The British

Drug Houses, Ltd., London, and Messrs. La Motte Chemical Products Co., Baltimore, U.S.A., for the loan of blocks.

In conclusion the author wishes to record his warmest appreciation of the willing and unfailing help accorded him by Mr. F. W. Clifford, F.L.A., Librarian to the Chemical Society, and his able colleagues in the task of searching the extensive literature; and to thank Dr. E. Howard Tripp, Editor of the series of Industrial Monographs, and Dr. W. L. German, M.Sc., University College, Exeter, for their assistance in the reading of the proofs and for valuable criticisms; and Messrs. Chapman & Hall Ltd., for undertaking the publication of the book, and for the great care they have taken in its production.

H. T. S. BRITTON.

UNIVERSITY COLLEGE OF THE SOUTH-WEST OF ENGLAND,
EXETER, *June*, 1929.

PREFACE TO SECOND EDITION

IT is extremely gratifying that a Second Edition of " Hydrogen Ions " should be required so soon after the publication of the First Edition.

Every effort has been made to subject the book to a thorough revision and to bring the matter up-to-date in all of its many ramifications. In view of the increasing acceptance of the Debye-Hückel-Lewis Theory of Electrolytes, a chapter has been inserted in this edition which aims at providing an adequate discussion of the theory, inasmuch as it relates to the several factors involved in the study of the activity of hydrogen ions. In this regard, I am greatly indebted to my colleague, Dr. R. A. Robinson, for his kindness in writing the chapter. I might add that Dr. Robinson, during his tenure of a Commonwealth Research Fellowship, had the unique opportunity of collaborating with an eminent American authority in this particular field.

Finally, I wish to take this opportunity of expressing my sincere appreciation of the willing and valuable assistance in proof-reading given by Drs. Patricia Jackson, W. L. German, H. Henstock, R. A. Robinson, W. E. Battrick, F. H. Meek, and O. B. Westcott, all of University College, Exeter, and Dr. E. H. Tripp, who is editing the Series of Monographs of which the present book is the third volume.

H. T. S. BRITTON.

UNIVERSITY COLLEGE OF THE SOUTH-WEST OF ENGLAND,
EXETER, *December*, 1931.

PREFACE TO THIRD EDITION

OWING to the incidence of the War, the publication of a new edition of " Hydrogen Ions " has been somewhat delayed. The years which have intervened since the Second Edition appeared have been marked by a considerable increase in the original literature on *p*H, not only in regard to chemistry, but in regard to its many industrial applications. Nevertheless, the author has made every effort to bring the treatise up to date, and this has necessitated the incorporation of several new chapters. The whole text has been revised and substantial additions have been made throughout. In consequence of the much increased size, it has been deemed desirable to publish the work in the form of two volumes. The first volume deals mainly with the theory and methods of determining hydrogen-ion concentration, or activity, and the second, chiefly with the part played by hydrogen ions in chemistry and in its numerous technical processes.

As much of the fundamental work on hydrogen ions was carried out before the activity theory of electrolytes had gained wide acceptance, and as the electrometric determinations of *p*H are usually made with cells in which *liquid junctions* exist and to which the modern theory is not strictly applicable, the theoretical interpretation of the E.M.F. of such cells, given in the earlier editions, has been retained. To some, this procedure might appear unjustifiable, but the fact must not be lost sight of that the activity theory can only be rigidly applied to cells *without transport, i.e., without a liquid junction*, which type of cell is scarcely ever used for ordinary *p*H determinations. Whatever may be the true meaning of the *p*H value, there is no doubt that *p*H values will remain an invaluable means of accurately assessing the extent of the acidity or alkalinity of a solution.

A chapter was inserted in the Second Edition on the inter-

pretation of E.M.F. in the light of modern theory. This chapter has now been largely rewritten in an endeavour to throw more forcibly into relief the impact which modern theory is making on the computation and interpretation of *p*H values. Wherever advantageous, reference is made to modern theory throughout the text. Another chapter presents briefly the concept of acids and bases as enunciated by the late Professor Lowry and subsequently by Professor Brønsted.

Brief reference was made in the foregoing editions to the calculations, made by Professor Bjerrum, of the distances between ionising carboxyl groups of a dicarboxylic acid, from its two dissociation constants. Other workers have pursued this interesting line of attack and their observations now form the subject-matter of a separate chapter.

A serious omission from the earlier editions was that of oxidation-reduction systems, in spite of the fact that their potentials, or intensities of oxidation or reduction, were largely influenced by the concentration of hydrogen ions. This has been rectified by the inclusion of a chapter of 29 pages, in which Redox potentials, the symbol *r*H and the use of Redox Indicators are discussed. Redox systems encountered in industrial processes are described in the appropriate places.

It has also been considered of fundamental importance to describe advances which have been made in inorganic and analytical chemistry.

The appendix to Volume I will, it is hoped, prove useful and time-saving. It is an abridged version of a table published recently by Professor Giribaldo, Doctor en Quimica, of the University of Montevideo, in his monograph, " Expresion de la Reaccion y Calculos Potenciometricos en la Determinacion del *p*H," to whom grateful acknowledgement is made.

It is the author's pleasant duty to express his sincere appreciation of the valuable assistance given, and helpful criticisms made, by Miss Agnes Shore, B.Sc., A.I.C., of the Physiology Department of the London School of Medicine for Women (University of London), who very kindly helped in preparing

the manuscript for publication and also read the whole work in proof form. Finally, the author wishes to place on record his great indebtedness to his wife for the assistance which she has always so unstintingly given.

H. T. S. BRITTON.

DEPARTMENT OF CHEMISTRY,
WASHINGTON SINGER LABORATORIES,
UNIVERSITY COLLEGE OF THE SOUTH-WEST OF ENGLAND.

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VOLUME ONE

CHAPTER I

THEORY OF ELECTROMETRIC METHODS FOR THE DETERMINATION OF HYDROGEN-ION CONCENTRATION

THE increasing recognition of the rôle played by small variations of acidity or alkalinity in reactions, many of which are of technical importance, necessitates an increased attention being directed to those methods by which these factors may be accurately measured and controlled. The considerable effect which very minute changes may have on a reaction render such terms as " slightly acid " or " slightly alkaline " vague and without real meaning. Thus the concentration or " activity " of hydrogen ions is of fundamental importance in processes which involve the proteins, such as the manufacture of artificial milk foods, leather tanning, the manufacture of glue and gelatin, wool and silk industries, bread-making, and many of the fermentation processes connected with brewing. Although the enzymes, which enter into the fermentation reactions, are usually active to differing extents over wide ranges of acidity, it generally happens that maximum yields can only be obtained by restricting the acidity to relatively narrow limits.

The productivity of soils often depends upon the hydrogen-ion concentration which their constituents impart to the " soil solutions "—solutions which are too acid or, in exceptional cases, too alkaline, being poisonous to most plants, whilst too alkaline solutions may render any phosphate which the soil may contain inaccessible to the plant. From a knowledge of the hydrogen-ion concentration, many of the defects of soils can be remedied by the judicious application of lime and suitable fertilisers. By the careful adjustment of hydrogen-ion concentrations, water can be softened, cane and beet-sugar juices can be purified, metallic hydroxides and certain insoluble salts can be separated, certain metallic salts can be prepared, sludges can be precipitated, colloidal emulsions can be broken down, colloidal suspensions of clay can be flocculated, electro-plating can be efficiently carried out, pure metals electrolytically deposited and many operations which depend upon interfacial forces made satisfactory.

The first chapters deal with the potentiometric methods of determining the concentration or activity of hydrogen-ions, and

more especially the use of the hydrogen electrode, for it is with the voltages produced between this electrode, when immersed in different solutions, and some standard electrode, that the quinhydrone electrode, now often used, the oxygen electrode, various metal-metallic oxide electrodes, the glass electrode, and the colorimetric changes of indicators have been calibrated. Although the expression " hydrogen-ion concentration " has gained an almost universal usage, it is extremely doubtful what exactly is the true significance of the potential difference set up between a hydrogen electrode and a solution. This, however, does not detract from the usefulness of the electrode in studying and controlling reactions. When reactions are carried out in very dilute solutions, there is little doubt that the electromotive force measurements do furnish a satisfactory approximate measure of the concentration of hydrogen-ions.

Theory of Solutions.

Before describing the electrometric methods, it will be an advantage if we review the modern theory of solutions, for it constitutes the basis upon which E.M.F. data are interpreted in terms of ion-concentrations and sometimes of so-called " activities." Substances on dissolution in water affect to differing extents both the boiling- and freezing-points and vapour pressures of the solutions. The amounts by which these physical properties are changed can in the case of very dilute solutions of non-electrolytes be shown to be due to the osmotic pressures exerted by the solutes when considered in regard to their molecular concentrations. Now van't Hoff showed that for very dilute solutions of non-electrolytes the Laws of Boyle, Charles and Avogadro which govern the behaviour of perfect or ideal gases hold almost quantitatively if the osmotic pressure exerted by the solute molecules be substituted for the ordinary gas pressure. These three laws may be incorporated in the expression

$$PV = xRT,$$

in which P is the osmotic pressure instead of gaseous pressure, V the volume occupied by the solution containing x gram-molecules of solute, T the temperature in degrees on the Absolute scale of temperature and R the gas constant. The value assumed by R is the same for gases and dilute solutions under analogous conditions when the various factors are measured in the same units. For use in electrometric calculations we shall evaluate it in terms of the centimetre, gram and second or C.G.S. units. According to Berthelot in 1904, 1 g.-mol. of a perfect gas occupied in the

latitude of 45°, at 0° C. and at a pressure of one atmosphere (*i.e.*, at a pressure equal to that exerted on 1 sq. cm. by a vertical column of mercury of 76 cm.), a volume of 22,412 ± 2 c.c. The acceleration due to gravity in that year and latitude was 980·665 cm. per second, and therefore 76 cm. of mercury pressure, the specific gravity of mercury being 13·5945, corresponded in C.G.S. units to a force pressing downwards on 1 sq. cm. equal to

$$76 \times 13{\cdot}5945 \times 980{\cdot}665 \text{ dynes}$$
$$= 1{,}013{,}276 \text{ dynes.}$$

If this value, together with the volume occupied by 1 g.-mol. of gas at 273° A., be substituted in the above expression, we find that

$$R = \frac{P \times V}{x \times T} = \frac{1013276 \times 22412}{1 \times 273}$$
$$= 8{\cdot}315 \times 10^7 \text{ C.G.S. units or ergs per } 1° \text{ Absolute}$$
$$= 8{\cdot}315 \text{ joules per } 1° \text{ Absolute } (10^7 \text{ ergs} = 1 \text{ joule}).$$

It happens, however, that the unit of work, *the joule*, involved in this calculation is not quite equal to the amount of work which has been accepted as the practical unit of work, and known as the *international joule*. The relationship between the absolute value of the joule and the international value is that 1 absolute joule is equal to 0·99966 international joule. It will be seen from text-books on physics that electrical work is the product of the quantity of electricity and the E.M.F. which causes the transference of the electricity; in other words, it is equal to E volts × C ampères × t seconds, C × t being the quantity of electricity expressed in ampère-seconds or coulombs. The unit of electrical work is thus seen to be that done when a current of 1 ampère flows for 1 second by means of an E.M.F. equal to 1 volt. Such a unit of electrical work is the joule. As both the ampère and volt are now referred to the international standard, it will be necessary in our calculations to convert R into international joules. Hence

$$R = 8{\cdot}315 \text{ absolute joules per } 1° \text{ Absolute}$$
$$= 8{\cdot}313 \text{ international joules per } 1° \text{ Absolute.}$$

Van't Hoff found when dilute solutions of electrolytes, *i.e.*, solutes which give the solution the power to conduct the electric current, are considered, that the perfect gas laws are no longer applicable. The solutions are more osmotically active than solutions of the same concentrations of non-electrolytes. He, however, introduced a factor, i, now usually referred to as the van't Hoff factor, to indicate the increased osmotic pressure of

the electrolyte when compared with the osmotic pressure which would have been established if the solution had contained the same number of molecules of a non-electrolyte, *i.e.*,

$$i = \frac{\text{Osmotic pressure exerted by the Electrolyte in solution}}{\text{Osmotic pressure caused by a non-electrolyte at the same concentration.}}$$

Hence, for solutions of electrolytes

$$PV = ixRT.$$

The van't Hoff factor, i, thus gives the extent of the divergence of the osmotic pressure, and the properties colligative with osmotic pressure, *viz.*, boiling-point elevation, freezing-point depression and diminution in vapour pressure, of dilute solutions of electrolytes from those required to satisfy the perfect gas laws.

Arrhenius in 1885 introduced his well-known theory of Electrolytic Dissociation in order to correlate this anomalous behaviour with respect to the gas laws of solutions of electrolytes, with their equivalent conductivities. There was then available, chiefly due to the efforts of Kohlrausch, a considerable number of data regarding the conduction of electricity through solutions. If Ohm's Law be applied to a solution so that the electricity which passes through a cube of 1 cm. side from one face perpendicularly to the opposite face when the potential difference between the two faces is 1 volt, then the current, C ampères, is equal to

$$\frac{1 \text{ volt}}{\text{specific resistance (in ohms)}}.$$

This value is the *Specific Conductivity*, and may be conveniently expressed in terms of $\frac{1}{\text{ohm}}$, or reciprocal ohm, r.o., or sometimes, mho. The *Equivalent Conductivity* is the specific conductivity divided by the number of equivalents of solute dissolved in 1 c.c. of solution. It is thus the specific conductivity of a hypothetical solution which contains 1 gram-equivalent of the electrolyte in 1 c.c. Kohlrausch had in 1876 been able to show by applying Hittorf's Migration Numbers, which refer to the fraction of electricity carried by each type of ion, *viz.*, cation and anion, of the total amount passed through a solution, that the equivalent conductivities of dilute solutions were made up of the sum of the equivalent conductivities, or mobilities, of the cations and anions into which the electrolyte had dissociated. Knowing from Faraday's Laws of Electrolysis that the quantity of electricity required to liberate from the solution 1 gram-equivalent of ions at each pole is 96,500 coulombs (*i.e.*, 1 Faraday, or 1 F.), and

that this is effected, as indicated by Hittorf's work, by the transference of 1 gram-equivalent of ions, cations and anions together, through the solution towards the appropriate electrodes, it is possible to calculate the amount of electricity which is carried by each of the two kinds of ions, and therefore to calculate what the conductivity of a solution should be when it contains different amounts of ions. To account for the increase in equivalent conductivity which occurs with the dilution of a solution of an electrolyte, Arrhenius introduced the conception of *Electrolytic Dissociation*, the degree of which is a function of the concentration and which increases with increasing dilution but only becomes unity when the solution is infinitely dilute. Thus, consider the ionisation which accompanies the dissolution of sodium chloride. In an infinitely dilute solution electrolytic dissociation is considered to take place completely thus :

$$NaCl \rightarrow Na^{\cdot} + Cl'$$

when the equivalent conductivity, Λ_∞, becomes equal to the sum of the ionic conductivities, $l_{Na^{\cdot}}$ and $l_{Cl'}$, the conductivities of $Na^{\cdot}$ and Cl' ions, *i.e.*,

$$\Lambda_\infty = l_{Na^{\cdot}} + l_{Cl'}.$$

These *ionic conductivities*, l, are often referred to as the *ionic mobilities*.

At any other concentration ionisation is incomplete and of the gram-equivalent of sodium chloride dissolved α gram-equivalent has been converted into ions, which unlike the undissociated molecules of salt, permit electricity to pass through the solution. Hence we see that the equivalent conductivity, Λ, at any other concentration, is equal to $\alpha\ (l_{Na^{\cdot}} + l_{Cl'})$, and therefore that the degree of electrolytic dissociation at any particular concentration can be calculated from

$$\alpha = \frac{\Lambda}{\Lambda_\infty}.$$

Hence one gram-equivalent of sodium chloride produces $(1 - \alpha)$ gram-equivalents of undissociated NaCl molecules and α gram-equivalent each of sodium- and chloride-ions, all of which Arrhenius considered to be capable of exerting osmotic pressure. Instead of having 1 gram-equivalent of solute molecules, there arises $(1 - \alpha) + \alpha + \alpha = 1 + \alpha$ gram-equivalents of molecules and ions. If this is the true explanation of the variations in equivalent conductivity with dilution, then it is evident that $1 + \alpha$ is equal to van't Hoff's factor referred to above. In a

similar way calcium chloride and lanthanum chloride on ionising thus

$$CaCl_2 \rightleftharpoons Ca^{\cdot\cdot} + 2\ Cl'\ ;\quad LaCl_3 \rightleftharpoons La^{\cdot\cdot\cdot} + 3\ Cl'$$

produce respectively $1 + 2\alpha$ and $1 + 3\alpha$ osmotically active ions and molecules. Arrhenius showed in numerous instances that the degree of electrolytic dissociation as calculated from conductivity data gave figures which compare fairly well with the van't Hoff factor obtained from measurements of any of the thermodynamically related properties of solutions, *viz.*, osmotic pressure, elevation of boiling-point, lowering of the freezing-point and vapour pressure. Despite the lack of agreement in some few cases, it was formerly considered that the relationship between conductivity and those properties which may be shown to be thermodynamical consequences of the application of the perfect gas laws to dilute solutions had been firmly established.

In arriving at the relationship, $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$, it was tacitly assumed that at any given temperature, the mobilities of the ions constituting an electrolyte remain constant, irrespective of the possible effect which an increase in concentration might have in diminishing them, either through the greater number of ions per unit volume or by any variation in the viscosity of the solution which might result from this increased concentration. Table 1 illustrates the magnitude of the variations which occur in the Hittorf Migration, or Transport, Number of the cations of the electrolytes in aqueous solution ranging from $N/100$ to $N/5$ at 25°. The ionic mobility, l, is obtained by multiplying the transport number by the appropriate equivalent conductivity at infinite dilution.

TABLE 1

TRANSPORT NUMBERS OF CATIONS OF ELECTROLYTES IN AQUEOUS SOLUTIONS OF VARIOUS CONCENTRATIONS AT 25°

Electrolyte.	Equivalent Concentration.				
	0·01 *N*	0·02 *N*	0·05 *N*	0·1 *N*	0·2 *N*
HCl	0·8251	0·8266	0·8292	0·8314	0·8337
NaCl	0·3918	0·3902	0·3876	0·3854	0·3821
KCl	0·4902	0·4901	0·4899	0·4898	0·4894
KNO_3	0·5084	0·5087	0·5093	0·5103	0·5120
$CaCl_2$	0·4264	0·4220	0·4140	0·4060	0·3953
$LaCl_3$	0·4265	0·4576	0·4482	0·4375	0·4233

Longsworth, *J.A.C.S.*, 1932, **54**, 2741 ; 1935, **57**, 1185.

Other fundamental functions which are based on thermodynamical principles involving the validity of the application of the perfect gas laws to solutions are (*a*) that reactions in dilute solutions should obey the Law of Mass Action, (*b*) Nernst's interpretation of the E.M.F. of "concentration cells" and the potential difference which exists between a metal and the solution containing the metal ions. Wilhelm Ostwald applied the Law of Mass Action to the dissociation of weak acids and bases in solutions of varying dilution, and found that the values of the degree of electrolytic dissociation, calculated from conductivity measurements, on substitution in the mass law expression gave rise to dissociation or affinity constants which were almost constant. In these cases the empirical conductivity data and the thermodynamically established mass law are apparently in accord. This, however, is not so with the strong acids and bases and electrolytes in general.

TABLE 2

CALCULATION OF DISSOCIATION CONSTANT AT 25° C.

$$K = \frac{\alpha^2 C}{1-\alpha}, \text{ taking } \alpha = \frac{\Lambda_c}{\Lambda_0},$$

of a (i) *Weak acid, e.g.*, Acetic acid.
(ii) *Moderately Strong Acid, e.g.*, Monochloroacetic acid.
(iii) *Strong Acid, e.g.*, Hydrochloric acid.

Acetic Acid (*a*).		Monochloroacetic Acid (*b*).		Hydrochloric Acid (*c*).	
Conc.	K	Conc.	K	Conc.	K
0·00002801	$1·760 \times 10^{-5}$	0·0001101	$1·353 \times 10^{-3}$	0·0000284	$1·16 \times 10^{-2}$
0·0001532	$1·767 \times 10^{-5}$	0·001323	$1·436 \times 10^{-3}$	0·0005915	$6·00 \times 10^{-2}$
0·002414	$1·789 \times 10^{-5}$	0·007462	$1·501 \times 10^{-3}$	0·001577	$10·59 \times 10^{-2}$
0·05000	$1·808 \times 10^{-5}$	0·02018	$1·543 \times 10^{-3}$	0·002994	$15·23 \times 10^{-2}$

(*a*) MacInnes and Shedlovsky, *J.A.C.S.*, 1932, **54**, 1429.
(*b*) Shedlovsky, Brown and MacInnes, *Trans. Amer. Electrochem. Soc.*, 1934, **66**, 165.
(*c*) Shedlovsky, *J.A.C.S.*, 1932, **54**, 1411.

Table 2 reveals that, even in the case of acetic acid, there is a tendency for the dissociation constant, as computed from conductivity measurements, to increase as the concentration of the acid increases. With hydrochloric acid, K is by no means constant. As far as strong electrolytes are concerned, the Arrhenius Theory is far from satisfactory, and attempts have been made in recent years, with much success, to replace it by one which is based on theoretical and mathematical principles. G. N. Lewis and Debye and Hückel assume that electrolytes

are *completely ionised in solutions at all concentrations*, and acting on the premise that the perfect gas laws must apply to the thermodynamically interdependent properties of solutions of electrolytes, including electrode potentials and the applicability of the Law of Mass Action, introduce the concept of "*activity*" *of ions* in the place of "*concentrations.*" The ratio of *the activity of an ion* to *its concentration* is denoted by the activity coefficient. Substituting activities in calculations relating to the various properties of solution thus ensures the obedience of solutions to the perfect gas laws, whereas the activity coefficients may be considered as giving a measure of the divergence of the behaviour of solutions from the gas laws when regarded in terms of "*ion concentrations.*"

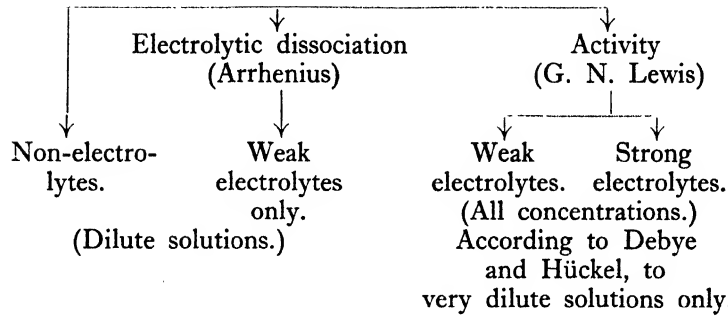
In their mathematical derivation, Debye and Hückel made use of such approximations that their equations can hardly apply quantitatively to solutions, other than those which are exceedingly dilute. As the validity of the perfect gas laws is assumed in the derivation of the expression connecting the difference in potential between an electrode and a solution containing related ions with their activities, G. N. Lewis and his followers confine their measurement to cells "without transport," and so avoid recourse to the Arrhenius Ionic Theory in order to calculate the diffusion potential which may exist in the cells, involving liquid junction and "transport of ions," commonly employed in *p*H measurement. Despite attempts which have recently been made by MacInnes to interpret "liquid junction potentials" mathematically on the activity theory, it cannot yet be considered that the activity theory has obtained much success in regard to "cells with transport." This question will be discussed in a later chapter.

It may be pointed out that the perfect gas laws hold in an approximate way for dilute solutions only. They cannot hold for concentrated solutions, for they do not involve such factors as cohesion and hydration of molecules and ions, whose effect then becomes pronounced. The foregoing considerations may be summarised thus :—

Perfect gas
$(PV = xRT)$
(or $PV = ixRT$, for those gases which undergo Thermal dissociation)
↓
Dilute solutions
$(PV = ixRT$, where P is osmotic pressure)

Thermodynamical deductions :—

(*a*) Mass law to be applicable.
(*b*) Laws relating to freezing-point, boiling-point, vapour pressures to hold.
(*c*) E.M.F. expression for "concentration cells," and electrode potentials.



Theory of Electromotive Force Measurements.

As already stated, the calculations of ion-concentrations or ion-activities from the potential differences which are set up between an electrode and a solution are based upon the assumption that the perfect gas laws apply to dilute solutions. Although such an assumption may not be entirely justifiable, it does provide a basis upon which a fairly plausible explanation of electrode potentials can be obtained. As regards controlling and, if need be, measuring variations in acidity and alkalinity, the E.M.F. data of the hydrogen electrode are, indeed, themselves sufficient, without any further effort being made to calculate hydrogen-ion concentrations or *p*H values. Nevertheless, these calculations yield useful results, and especially is this true when the E.M.F's produced by other electrodes which function in a manner parallel to the hydrogen electrode in the presence of hydrogen and hydroxyl-ions, and the colour changes of indicators are considered.

We shall now consider the E.M.F. established between a metal which dips into a solution, containing a salt which is ionised giving cations of the metal. Suppose the valency exercised by the metal in forming salts is n, and therefore each ion of the metal carries n positive charges, or, in other words, each gram-ion is composed of n gram-equivalents which for their electrical deposition from solution will necessitate a quantity of n Faradays, *i.e.*, $n \times 96{,}500$ coulombs. We shall assume that at the surface of the metal there exists a tendency for it to dissolve in the solution

as atoms, and that some of these atoms are converted into metallic-ions of the same kind as those already present in the solution in the form of a salt. The metal, therefore, may be regarded as possessing an *electrolytic solution pressure* at its interface as postulated by Nernst. There will consequently be established an equilibrium between the cations in solution and the tendency of the electrode to produce similar ions. Suppose that x gram-ions are contained in v litres of solution, and that the concentration of the ions is c gram-ions per litre, whence $c = x/v$. Let the volume occupied by x gram-ions liberated from, and present at the surface of, the electrode be V, and the concentration of ions so formed be $C = \frac{x}{V}$. The potential difference between the electrode and the solution is E volts, which might be considered as the *Intensity Factor* of the electrical work which would be entailed in driving x gram-ions of metal from the electrode into the solution, or *vice versa* by the application of the electric current. The quantity of electricity required by x gram-ions of n-valent ions will be xnF, where F represents 1 Faraday (96,500 coulombs), and therefore the electrical work to be performed will be equal to xnF $\times$ E (volt)

$$= xn \times 96{,}500 \times \text{E volt-coulombs, or joules,}$$
$$= xn \times 96{,}500 \times \text{E} \times 10^7 \text{ ergs.}$$

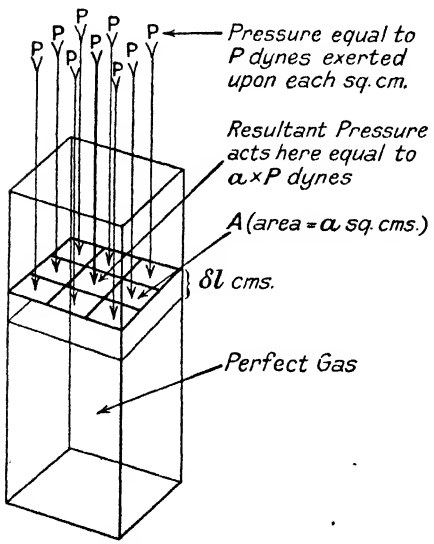


FIG. 1.—Isothermal Compression of a Perfect Gas.

This work should be carried out in such a way that there is no change in temperature of the solution. This transference of ions might also have been considered as having taken place by virtue of their osmotic pressure, and in this connexion we shall now consider how this might have been done had the ions been in the form of gas molecules. Such an analogy is valid if the perfect gas laws apply equally well to ions in dilute solutions. In Fig. 1 is represented a hollow rectangular prism containing a volume

of perfect gas and above which moves a gas-tight, frictionless and weightless cover. To this cover, whose area is a sq. cm., a pressure of P dynes is applied, which thereby causes the cover to move inwards δl cm. This means that a force of P dynes plays upon each square centimetre of the cover, equivalent to a total force of $a \times P$ dynes acting perpendicularly upon the cover at its centre of gravity. The work done in compressing the gas by the movement of the point of application of this force through δl cm. is

$$a \times P \times \delta l \text{ ergs.}$$

Such work results in the generation of heat by the gas, but if the compression be carried out at a sufficiently slow rate this heat will be radiated to the surroundings without appreciably changing the temperature of the gas. It will be seen that $a \times \delta l$ c.c. is the decrease in volume of the gas, namely δv, and therefore the work done is equal to

$$P \times \delta v \text{ ergs.}$$

To find the amount of work to be done to compress the gas from volume V litres down to v litres, it is necessary to integrate between the limits $V \times 1000$ c.c. and $v \times 1000$ c.c. Hence

$$\text{Work} = \int_{v \times 1000}^{V \times 1000} P dv,$$

and as $PV = xRT$, i being unity,

$$\text{Work} = xRT \int_{v \times 1000}^{V \times 1000} \frac{1}{v} dv$$

$$= xRT \log_e \frac{V \times 1000}{v \times 1000}$$

$$= xRT \log_e \frac{V}{v}.$$

Knowing that $C = \frac{x}{V}$ and $c = \frac{x}{v}$,

$$\therefore \text{Work} = xRT \log_e \frac{c}{C}.$$

Also $PV = pv$, and

$$\therefore \text{Work} = xRT \log_e \frac{p}{P} = xRT \log_e \frac{c}{C}.$$

Thus we see that the work involved in compressing x gram-

ions from volume V at the electrode to volume v in the solution is equal to

$$x\mathrm{RT}\log_e\frac{\mathrm{V}}{v} = x\mathrm{RT}\log_e\frac{p}{P} = x\mathrm{RT}\log_e\frac{c}{\mathrm{C}}.$$

The pressures included in the latter expression are seen to be p the osmotic pressure of the ions in the solution, and P the electrolytic solution pressure of the ions at the metal surface. We have seen earlier in this chapter that in order to express this osmotic work in terms of the same units, *viz.*, joules, as the electrical work, it is only necessary to put $\mathrm{R} = 8{\cdot}313$ joules per degree Absolute. Hence, by equating the two expressions giving the amounts of electrical work and osmotic work which are necessary to transfer x gram-ions from metal to solution, we get

$$\begin{aligned} xn\mathrm{FE}\ (\text{joules}) &= x\mathrm{RT}\log_e\frac{\mathrm{V}}{v} = x\mathrm{RT}\log_e\frac{c}{\mathrm{C}} \\ &= x\mathrm{RT}\log_e\frac{p}{P}\ (\text{joules}), \end{aligned}$$

and therefore

$$\mathrm{E\ volts} = \frac{\mathrm{RT}}{n\mathrm{F}}\log_e\frac{\mathrm{V}}{v} = \frac{\mathrm{RT}}{n\mathrm{F}}\log_e\frac{c}{\mathrm{C}} = \frac{\mathrm{RT}}{n\mathrm{F}}\log_e\frac{p}{P}.$$

The relation between the E.M.F. of a single metallic electrode and a solution is given by

$$\begin{aligned} \mathrm{E} &= \frac{\mathrm{RT}}{n\mathrm{F}}\log_e\frac{c}{\mathrm{C}} \\ &= -\frac{\mathrm{RT}}{n\mathrm{F}}\log_e\mathrm{C} + \frac{\mathrm{RT}}{n\mathrm{F}}\log_e c. \end{aligned}$$

The expression $-\frac{\mathrm{RT}}{n\mathrm{F}}\log_e\mathrm{C}$ includes the hypothetical concentration of metal-ions which have been assumed to exist at the surface of the metal and to have originated from the metal. There is no method available to measure this concentration. It is feasible that at a given temperature each metal has its own particular solubility in water, which in the case of those metals that do not react directly with water is extremely small. Of the atoms that dissolve, or, better, tend to dissolve, a definite proportion becomes electrically charged in the form of ions and thus determines the E.M.F. of the electrode. When, however, the metal is allowed to dip into a solution already containing those ions, such ions might have some repressing effect on the ions arising from the electrode surface, or *vice versa*. These effects can, in fact, only be tendencies, for an electrostatic condition is very probably set

up at the surface between layers of opposite charges (the Helmholtz Double Layer) which prevents metal dissolution from actually taking place. Taking for granted that the E.M.F. of a single electrode can be measured when immersed in a solution containing a known concentration of ions, we find that at any given temperature we can calculate exactly the concentration C. We also see that when the concentration of ions dissociated from the salt is equal to one gram-ion per litre, *i.e.*, $c = 1$, then the last term becomes zero and thus E then becomes equal to $-\frac{RT}{nF}\log_e C$. The value of this term for each particular metal is a constant, and is known as the *Normal Electrode Potential*, or sometimes as the *Electrolytic Potential.* We see from the foregoing that it is the E.M.F. given by any particular metal when immersed in, and in equilibrium with, a solution containing 1 gram-ion of its ions per litre. It varies with temperature as shown by electrode formula. It is usually denoted by either ε or "E.P." The expression connecting the E.M.F. with the concentration of ions in the solution may now be written

$$E = \varepsilon + \frac{RT}{nF}\log_e c = \varepsilon + 2{\cdot}3026\,\frac{RT}{nF}\log_{10} c,$$

and further simplified by inserting the values $R = 8{\cdot}313$, and $F = 96{,}500$, whence it is found that

$$E = \varepsilon + 0{\cdot}0001984\frac{T}{n}\log c.$$

At 18° C. (T = 291° A.)

$$E = \varepsilon + \frac{0{\cdot}0577}{n}\log c$$

and at 25° C. (T = 298° A.)

$$E = \varepsilon + \frac{0{\cdot}0591}{n}\log c.$$

In Table 3 are given the values of $R \times T \times 2{\cdot}303/F$ for temperatures 15° to 25° C.

TABLE 3

Temp. °C.	15	16	17	18	19	20	21	22	23	24	25
$\frac{RT\times 2{\cdot}303}{F}$	0·0571	0·0573	0·0575	0·0577	0·0579	0·0581	0·0583	0·0585	0·0587	0·0589	0·0591

With metals which attain equilibrium with positively charged ions, *viz.*, cations, the quantity of electricity required to deposit

1 gram-equivalent at the cathode, or to dissolve from the anode, is 1 Faraday, but with non-metals, like iodine which enters into equilibrium with negatively charged ions, anions, we must not forget that on electrolysing, these ions travel against the current, and are discharged at the electrode at which the current enters the solution. The Faraday of electricity associated with 1 gram-equivalent of anions must, therefore, be regarded as negative, and therefore the electrical work involved in driving x gram anions which are n-valent into solution will be equal to $-xn\mathrm{EF}$ joules. Hence

$$-xn\mathrm{EF} = x\mathrm{RT}\log_e \frac{c}{\mathrm{C}},$$

and therefore

$$\mathrm{E} = +\frac{\mathrm{RT}}{n\mathrm{F}}\log_e \mathrm{C} - \frac{\mathrm{RT}}{n\mathrm{F}}\log_e c$$

$$= \varepsilon - \frac{\mathrm{RT}}{n\mathrm{F}}\log_e c.$$

Alternate Method of Obtaining Electrode Potential Formulæ using van't Hoff Reaction Isotherm.

In view of the successful application, first by Biilmann, of the quinhydrone electrode for the determination of hydrogen-ion concentrations, we shall now consider how oxidation-reduction equilibria may sometimes be made use of by immersing an electrode of platinum in a solution, where such an equilibrium prevails in order that it might function as a hydrogen electrode and be readily responsive to changes in the concentration of hydrions. Incidentally, we shall see that the above formula can be arrived at in a somewhat different manner. It will be seen from text-books on physical chemistry that not only is the law of mass action a thermodynamic consequence of the application of the perfect gas laws to dilute solutions, but so also is the co-called van't Hoff reaction isotherm, which links up the affinity of, or maximum work which can be done by, a reaction if carried out in a manner in which there is no change in temperature of the solution during the process. This is generally true when a reaction is allowed to do electrical work at some given temperature. If we consider the general reaction

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D},$$

then, by applying the law of mass action we find that

$$\frac{[\mathrm{C}]_\epsilon^c \times [\mathrm{D}]_\epsilon^d}{[\mathrm{A}]_\epsilon^a \times [\mathrm{B}]_\epsilon^b} = \mathrm{K},$$

where the square brackets with suffix ϵ represent the concentra-

tions at equilibrium of the reactants and K, the mass law constant, or affinity constant. The maximum work, which the reaction is capable of doing in proceeding from left to right at a given temperature, is given by

$$\text{Work} = \text{RT} \log_e \frac{[\text{C}]_e^c \times [\text{D}]_e^d}{[\text{A}]_e^a \times [\text{B}]_e^b} - \text{RT} \log_e \frac{[\text{C}]^c \times [\text{D}]^d}{[\text{A}]^a \times [\text{B}]^b}$$

$$= \text{RT} \log_e \text{K} - \text{RT} \log_e \frac{[\text{C}]^c \times [\text{D}]^d}{[\text{A}]^a \times [\text{B}]^b}.$$

[C] and [D] represent the respective concentrations of C and D produced by the reaction, and [A] and [B] the respective concentrations of A and B at the beginning. We know that when 1 Faraday of electricity is passed through an electrolyte there is liberated at the cathode 1 gram-equivalent of metal, *i.e.*, 1 gram-equivalent of metal-ions give up their charge and become uncharged metal. The following equations may therefore be regarded as representing typical reactions taking place at the electrodes :—

$$\begin{aligned}
\text{H}^{\cdot} &\dashrightarrow \text{H} + 1\text{F} \times \text{E}_{\text{H}\cdot} \\
\text{Ag}^{\cdot} &\dashrightarrow \text{Ag} + 1\text{F} \times \text{E}_{\text{Ag}\cdot} \\
\text{Cu}^{\cdot} &\dashrightarrow \text{Cu} + 1\text{F} \times \text{E}_{\text{Cu}\cdot} \\
\text{Cu}^{\cdot\cdot} &\dashrightarrow \text{Cu} + 2\text{F} \times \text{E}_{\text{Cu}\cdot\cdot} \\
\text{Au}^{\cdot\cdot\cdot} &\dashrightarrow \text{Au} + 3\text{F} \times \text{E}_{\text{Au}\cdot\cdot\cdot}
\end{aligned}$$

The following reaction is an example of the change which takes place with an anion-forming element :—

$$\text{I} \dashrightarrow \text{I}' + 1\text{FE}_{\text{I}}.$$

In the above equations the E.M.F's at which these reactions take place are given by E, and thus we see that the products, nFE, give the amount of work necessary to convert one gram-ion of the various cations into the non-ionic state, whereas the reverse is the case of anions. These equations refer to simple processes of reduction, there being decreases in positive valency or an increase in negative valency. Looked at from another standpoint, these equations represent the natural tendency of cations to assume the un-ionised state, and for anion-forming elements to acquire the form of negative ions, and in so doing liberate energy equal to nFE, which may take the form of maximum work. As is well known, reduction and oxidation processes may occur entirely between ions. Thus the reducing action of stannous chloride on ferric chloride is shown by the equation

$$2\text{FeCl}_3 + \text{SnCl}_2 \rightleftharpoons 2\text{FeCl}_2 + \text{SnCl}_4$$

or, ionically,

$$2\text{Fe}^{\cdot\cdot\cdot} + \text{Sn}^{\cdot\cdot} \rightleftharpoons 2\text{Fe}^{\cdot\cdot} + \text{Sn}^{\cdot\cdot\cdot\cdot}.$$

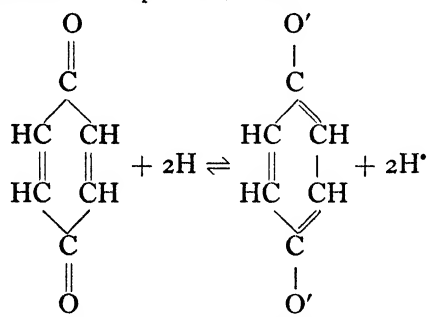
This reaction is seen to be the outcome of two opposing reactions, *viz.*,

$$2Fe^{\cdots\cdot} \rightarrow 2Fe^{\cdot\cdot} + 2F \times E_{Fe^{\cdots\cdot}\rightarrow Fe^{\cdot\cdot}}$$

and

$$Sn^{\cdot\cdot\cdot\cdot} \rightarrow Sn^{\cdot\cdot} + 2F \times E_{Sn^{\cdot\cdot\cdot\cdot}\rightarrow Sn^{\cdot\cdot}}$$

Each of the reduction reactions could have been effected by passing a current at a suitable E.M.F. The amount of electricity required to reduce the valency of a gram-ion by one unit is found to be 1 Faraday, and this accounts for the 2 Faradays shown in the above equations. Organic compounds may often be reduced by means of the electric current, and consequently it is reasonable to assume the quantity of electricity involved is that normally required to discharge the hydrogen ions as atoms which ultimately enter into combination to form the reduced compound. Quinhydrone is a molecular compound comprising one molecule of quinone and one of hydroquinone. When dissolved in water an equilibrium is set up between the hydrogen ions it contains and the constituent compounds, thus :—



Quinone (Q). Anion of Hydroquinone (Q″).

We are now in a position to apply the van't Hoff isotherm to the various reactions, and by equating the maximum work given by this expression to the electrical work involved, we arrive at the formulæ connecting (*a*) the E.M.F. of simple metallic or non-metallic electrodes and the respective ion concentrations of the solutions, and (*b*) the E.M.F. of platinum electrodes, immersed in solutions in which equilibria prevail between ions in different stages of oxidation and reduction.

Case I

Type of Electrode.—*Metals and Non-metals immersed in Salt Solutions containing their respective ions* :—

(*a*) Metal-ions of valency *n* reduced to metal ;

(*b*) Non-metals reduced to non-metal-ions of valency *n*.

Reactions:

$$(a)\ M^{\cdots n} \rightarrow M + nF \times E_M$$
$$(b)\ A \rightarrow A^{\prime\prime\prime\cdots n} + nF \times E_A$$

For reaction (*a*)

$$\text{Work} = nFE_M = RT \log_e \frac{[M]_\epsilon}{[M^{\cdots n}]_\epsilon} - RT \log_e \frac{[M]}{[M^{\cdots n}]}.$$

The concentrations denoted by $[M]_\epsilon$ and $[M^{\cdots n}]_\epsilon$ are those which are attained when equilibrium is reached; [M], the concentration of metal which is in solution in the atomic state and $[M^{\cdots n}]$, the concentration of metal-ions. Now the concentrations of atomic metal in solution, $[M]_\epsilon$ and [M], are due to the solubility of the metal in the salt solution, at temperature T, which concentration in all probability is scarcely affected by different concentrations of its ions that may be in the salt solution in which the metal is placed. Hence $[M]_\epsilon = [M]$ and therefore

$$\text{Work} = nFE_M = - RT \log_e [M^{\cdots n}]_\epsilon + RT \log_e [M^{\cdots n}]$$

and

$$E_M = - \frac{RT}{nF} \log_e [M^{\cdots n}]_\epsilon + \frac{RT}{nF} \log_e [M^{\cdots n}]$$

$$= \varepsilon_M + \frac{RT}{nF} \log_e [M^{\cdots n}].$$

Similarly for a non-metallic electrode A in equilibrium with ions $A^{\prime\prime\prime\cdots n}$; reaction (*b*),

$$E_A = \varepsilon_A - \frac{RT}{nF} \log_e [A^{\prime\prime\prime\cdots n}].$$

It will be observed that these expressions are identical with those obtained in the preceding paragraph, and the characteristic constants, ε_M and ε_A, have the same significance, being the normal electrode or electrolytic potentials.

Application to the Hydrogen Electrode.

Consider the reaction: $H^\cdot \dashrightarrow H + 1FE_H$.

$$\text{Work} = 1FE_H = RT \log_e \frac{[H]_\epsilon}{[H^\cdot]_\epsilon} - RT \log_e \frac{[H]}{[H^\cdot]}$$

and

$$\therefore E_H = \frac{RT}{F} \log_e \frac{[H]_\epsilon}{[H^\cdot]_\epsilon} - \frac{RT}{F} \log_e \frac{[H]}{[H^\cdot]},$$

where $[H]_\epsilon$ and [H] refer to the solubilities of atomic hydrogen under equilibrium and experimental conditions respectively at

temperature T. Provided that the gaseous pressures of hydrogen maintained above the solution (actually acting through the medium of an inert metal covered with a finely divided adsorbent, *e.g.*, Pt black) are equal in the two instances (*e.g.*, equal to one atmosphere pressure), then $[H]_e = [H]$, whence

$$E_H = -\frac{RT}{F}\log_e [H^\bullet]_e + \frac{RT}{F}\log_e [H^\bullet]$$

$$= \varepsilon_H + \frac{RT}{F}\log_e [H^\bullet],$$

for which, when the pressure of gaseous hydrogen is 1 atmosphere, and $[H^\bullet] = 1$ g.-mol. of hydrogen ions per litre $\varepsilon_H = 0$ and

$$\therefore E_H = \frac{RT}{F}\log_e [H^\bullet].$$

Hydrogen Electrode at Pressure, π.

It is sometimes necessary to employ a hydrogen electrode with a gaseous pressure of π atmospheres, but as the arbitrary standard electrode involves hydrogen gas at atmospheric pressure, we must derive an expression for the potential of the hydrogen electrode at pressure π, *viz.*, $E_{H_{2\pi}}$. Under these conditions, in the expression :

$$E_{H_{2\pi}} = \frac{RT}{F}\log_e \frac{[H]_e}{[H^\bullet]_e} - \frac{RT}{F}\log_e \frac{[H]}{[H^\bullet]}$$

$[H]_e$ = solubility of atomic hydrogen under hydrogen gas pressure = 1 atmosphere at temperature T.

and $[H]$ = solubility under π atmospheres at temperature T. The amount of molecular hydrogen, $[H_2]$, which dissolves in the electrolyte medium in which the electrode is immersed, will be determined by Henry's Law and therefore $[H_2] = \lambda\pi$; also, through the catalytic agency of the electrode, an extremely small quantity of the dissolved H_2 molecules may be assumed to dissociate into atomic hydrogen, thus

$$H_2 \rightleftharpoons 2H$$

whence $[H]^2/[H_2] = k$, and

consequently $[H] = \sqrt{k \cdot \lambda \cdot \pi}$.

Hence $[H]_e = \sqrt{k \cdot \lambda \cdot 1}$ and $[H] = \sqrt{k \cdot \lambda \cdot \pi}$.

Substituting in the foregoing expression and simplifying, we obtain

$$E_{H_2\pi} = -\frac{RT}{F}\log_e [H^\cdot] + \frac{RT}{F}\log_e \frac{[H^\cdot]}{\sqrt{\pi}}$$

$$= \varepsilon_{H_2\pi=1} + \frac{RT}{F}\log_e \frac{[H^\cdot]}{\sqrt{\pi}}$$

As $\varepsilon_{H_2\pi=1} = 0$, (*i.e.*, N . H = 0, see page 24).

$$\therefore E_{H_2\pi} = \frac{RT}{F}\log_e \frac{[H^\cdot]}{\sqrt{\pi}}$$

Converting from Napierian to Briggsian logarithms, and putting $-\log_{10}[H^\cdot] = p\text{H}$ and $-\log_{10}\pi = r\text{H}$, we obtain

$$E_{H_2\pi} = \frac{2{\cdot}3026 \times RT}{2 \times F}\{r\text{H} - 2p\text{H}\}$$

Case II (*a*)

Type of Electrode.—*Platinum dipping in a solution containing ions with different valencies.*

Reactions :

(*a*) Cations $M^{\bullet\bullet}{}^{..m}$ (*m* positive charges) and $M^{\bullet\bullet}{}^{..n}$ (*n* positive charges), *m* being *greater* than *n*.

$$M^{\bullet\bullet}{}^{..m} \rightarrow M^{\bullet\bullet}{}^{..n} + (m-n)FE_M.$$

(*b*) Anions $A''{}^{..m}$ (*m* negative charges) and $A''{}^{..n}$ (*n* negative charges), *m* being *less* than *n*.

$$A''{}^{..m} \rightarrow A''{}^{..n} + (n-m)FE_A.$$

Each of the processes (*a*) and (*b*) represent reductions, with, in the first reaction, a *diminution in positive valency*, (= (*m* − *n*) equivalents), and in the second, an *increase in negative valency* (= (*n* − *m*) equivalents). Examples of the first class are ferric-ferrous, and stannic-stannous ions equilibria, and of the second equilibria involving ferricyanide and ferrocyanide ions. For reduction of *cations* (*a*)

$$\text{Work} = (m-n)FE = RT\log_e \frac{[M^{\bullet\bullet}{}^{..n}]_e}{[M^{\bullet\bullet}{}^{..m}]_e} - RT\log_e \frac{[M^{\bullet\bullet}{}^{..n}]}{[M^{\bullet\bullet}{}^{..m}]},$$

whence

$$E_{\text{Cations}} = \frac{RT}{(m-n)F}\log_e \frac{[M^{\bullet\bullet}{}^{..n}]_e}{[M^{\bullet\bullet}{}^{..m}]_e} - \frac{RT}{(m-n)}\log_e \frac{[M^{\bullet\bullet}{}^{..n}]}{[M^{\bullet\bullet}{}^{..m}]},$$

and for *anions* (*b*)

$$\text{Work} = (n - m)\text{FE} = \text{RT} \log_e \frac{[\text{A}''..^n]_\epsilon}{[\text{A}''..^m]_\epsilon} - \text{RT} \log_e \frac{[\text{A}''..^n]}{[\text{A}''..^m]}.$$

$$\text{E}_{\text{Anions}} = \frac{\text{RT}}{(n - m)\text{F}} \log_e \frac{[\text{A}''..^n]_\epsilon}{[\text{A}''..^m]_\epsilon} - \frac{\text{RT}}{(n - m)\text{F}} \log_e \frac{[\text{A}''..^n]}{[\text{A}''..^m]}.$$

Both the above expressions involve a term corresponding to concentrations of the ions when in a state of equilibrium. These terms of constant value are characteristic of each particular reduction process which may be considered, being then of constant value. If reactions be considered for which there are available equal concentrations (*a*) of $[\text{M}^{\bullet\bullet}..^n]$ and $[\text{M}^{\bullet\bullet}..^m]$and (*b*) of $[\text{A}''..^n]$ and $[\text{A}''..^m]$, then the last terms in the respective formulæ become equal to zero and therefore the E.M.F. between the platinum electrode and the solution becomes equal to the first term in each case. Thus, it is seen that the first term corresponds to the E.M.F. set up when the reductions have proceeded half-way. Such E.M.F's are constant at a given temperature for a given reaction, and are known as the *Normal Reduction Potentials*. Naturally they constitute a valuable index of the power of the oxidising or reducing action of any particular reagent. These equations may therefore be re-written

$$\text{E} = \varepsilon_{\text{oxidised ions} \rightarrow \text{reduced ions}} - \frac{\text{RT}}{n\text{F}} \log_e \frac{[\text{reduced ions}]}{[\text{oxidised ions}]}.$$

One of the chief difficulties encountered in using the hydrogen electrode is the readiness with which the hydrogen in presence of platinum black may be utilised in reducing any reducible substances that may be present in the solution. It is probable that in the hydrogen electrode some of the hydrogen is present in the atomic state, for its behaviour then appears to be comparable with that of so-called nascent hydrogen. If the solution contains ferric ions, for example, reduction ensues immediately and the electrodes are rendered useless. The withdrawal of the atomic hydrogen from a hydrogen electrode may be represented thus :

$$\text{Fe}^{\bullet\bullet\bullet} + \text{H} \rightleftharpoons \text{Fe}^{\bullet\bullet} + \text{H}^{\bullet}.$$

Applying the van't Hoff isotherm to the reaction having the higher normal reduction potential, we find that the potential assumed by the hydrogen electrode when all its hydrogen has been utilised in the catalytic reduction of the $\text{Fe}^{\bullet\bullet\bullet}$ ions will be governed by the ratio of the concentrations of ferric- to ferrous-ions. The

electrode will consequently function as a platinum electrode, whose potential is given by

$$E = \frac{RT}{F} \log_e \frac{[Fe^{\cdot\cdot}]_\epsilon}{[Fe^{\cdot\cdot\cdot}]_\epsilon} - \frac{RT}{F} \log_e \frac{[Fe^{\cdot\cdot}]}{[Fe^{\cdot\cdot\cdot}]}.$$

Thus the potential of a hydrogen electrode in a solution in which it is effecting reduction of ions of the nature of ferric will not be influenced by the concentration of hydrogen-ions in the solution.

Case II (*b*)

Type of Electrode.—*Platinum electrode dipping into solutions containing oxidation-reduction systems which involve hydrogen ions.*

Examples of such systems are illustrated by the following equations :—

$$\begin{aligned} MnO_4' &+ 8H^{\cdot} \rightarrow Mn^{\cdot\cdot} + 4H_2O + 5FE_{MnO_4'} \\ CrO_4'' &+ 8H^{\cdot} \rightarrow Cr^{\cdot\cdot\cdot} + 4H_2O + 3FE_{CrO_4''} \\ BrO_3' &+ 6H^{\cdot} \rightarrow Br' + 3H_2O + 6FE_{BrO_3'} \end{aligned}$$

Each of these reductions involves hydrogen ions, and the charges carried by the latter must be considered in conjunction with the charges carried by the oxidised ions, when finding the total loss of positive charges resulting from reductions. Thus in the case of bromate ions undergoing reduction to bromide ions the diminution in positive charges is $(-1 + 6) - (-1) = 6$. In other words, 6 Faradays of electricity represent the loss when 1 gram-equivalent of bromate ions is reduced to 1 gram-equivalent of bromide ions. Taking this process as a typical example of the class of oxidising agents, we get

$$\text{Work} = 6FE_{BrO_3'} = RT \log_e \frac{[Br']_\epsilon}{[BrO_3']_\epsilon [H^{\cdot}]_\epsilon^6} - RT \log_e \frac{[Br']}{[BrO_3'][H^{\cdot}]^6}$$

$$= RT \log_e K - RT \log_e \frac{[Br']}{[BrO_3'][H^{\cdot}]^6}$$

and therefore

$$E_{BrO_3'} = \frac{RT}{6F} \log_e K - \frac{RT}{6F} \log_e \frac{[Br']}{[BrO_3'][H^{\cdot}]^6}$$

The term $\frac{RT}{6F} \log_e K$ is the Normal Oxidation-Reduction Potential, ε, of the process. It is the potential set up at an inert electrode when the concentrations of the oxidised and reduced forms are equal, *i.e.*, when $[BrO_3'] = [Br']$, and also the hydrogen ion concentration, $[H^{\cdot}]$, is 1 g.-mol. per litre. In

such circumstances, the second term becomes zero. Hence

$$E_{BrO_3' \rightarrow Br'} = \varepsilon_{BrO_3' \rightarrow Br'} - \frac{RT}{6F} \log_e \frac{[Br']}{[BrO_3'][H^\cdot]^6},$$

which shows what considerable effects may be introduced by varying the hydrogen ion concentration on $E_{BrO_3' \rightarrow Br'}$ and therefore on the oxidising intensity of the bromate ion.

Case II (*c*)

Type of Electrode.—*Platinum electrode dipping into solution containing quinhydrone.*

We shall now discuss the equilibrium between quinone and hydroquinone in which, due to the solubility of quinhydrone, the ratio of oxidised to reduced portions is kept equal to unity, and as a result the variation in the potential difference between a platinum electrode and a solution containing quinhydrone is over a certain range purely a function of hydrogen-ion concentations.

Of the two constituent reactions given on page 16 the one having the higher Normal Reduction Potential is

$$\text{Quinone (Q)} \rightleftharpoons \text{Anion of Hydroquinone (Q'')} + 2FE_Q.$$

Hence the potential of a platinum electrode immersed in a solution in which an equilibrium prevails between Q and Q''-ions will be given by

$$E_{Quin.} = \frac{RT}{2F} \log_e \frac{[Q'']_e}{[Q]_e} - \frac{RT}{2F} \log_e \frac{[Q'']}{[Q]}.$$

Thus the reduction potential of quinone is determined directly by the ratio of the dibasic anions of hydroquinone to the quinone present. This concentration of anions is, however, dependent not only upon the total concentration of hydroquinone, *i.e.*, in the undissociated and ionised condition, but upon the hydrogen-ion concentration of the solution. As each of the hydroxyl groups of hydroquinone, H_2Q, are capable of ionisation, which we may represent thus,

$$H_2Q \rightleftharpoons H^\cdot + HQ'$$

for which $$K_1 = \frac{[H^\cdot][HQ']}{[H_2Q]},$$

and $$HQ' \rightleftharpoons H^\cdot + Q''$$

whence $$K_2 = \frac{[H^\cdot][Q'']}{[HQ']}$$

we see that the *total concentration of hydroquinone*, [hydroquinone]

$$= [H_2Q]_{(\text{undissociated})} + [HQ'] + [Q'']$$

$$= \frac{[H^\cdot]^2[Q'']}{K_1 . K_2} + \frac{[H^\cdot][Q'']}{K_2} + [Q''].$$

Hence

$$[Q''] = \frac{K_1 . K_2}{[H^\cdot]^2 + K_1[H^\cdot] + K_1 . K_2} \times [\text{hydroquinone}],$$

and therefore

$$E_{\text{Quin.}} = \varepsilon_Q - \frac{RT}{2F} \log_e \frac{[\text{hydroquinone}]}{[\text{quinone}]} \times \frac{K_1 . K_2}{[H^\cdot]^2 + K_1[H^\cdot] + K_1K_2}$$

i.e.,

$$E_{\text{Quin.}} = \varepsilon_Q - \frac{RT}{2F} \log_e K_1K_2 + \frac{RT}{2F} \log_e \frac{[\text{quinone}]}{[\text{hydroquinone}]} + \frac{RT}{2F} \log_e ([H^\cdot]^2 + K_1[H^\cdot] + K_1K_2).$$

The first two terms are constants and the third term becomes equal to zero in the case of quinhydrone, for the quinone and hydroquinone are present in an equimolecular ratio. K_1 and K_2 are of the order of 10^{-10} and 10^{-12} respectively and therefore in a solution whose *p*H is smaller than 8, $K_1[H^\cdot]$ and $K_1 . K_2$ are of negligible magnitude.

Consequently

$$E_{\text{Quin.}} = \text{a constant } (\lambda) + \frac{RT}{2F} \log_e [H^\cdot]^2,$$

i.e.,

$$E_{\text{Quin.}} = \lambda + \frac{RT}{F} \log_e [H^\cdot].$$

The value of λ can be determined by comparison with the hydrogen electrode, thus giving to a platinum electrode an E.M.F. which varies with the hydrogen-ions present and whose concentrations can be calculated.

Single Electrode Potentials.

Hitherto we have tacitly assumed that the potential differences between individual electrodes and any solutions in which they may be immersed could be measured. This, however, is very probably not the case. We can only measure the potential difference between two electrodes dipping in the same solution, or else, in different solutions which are connected with one another by means of a suitable junction. There is also a distinct possibility of potential differences being established at the points

of contact of the different solutions present in the cell. It is extremely likely that these can be eliminated almost entirely by inserting a saturated solution of potassium chloride between the two electrode solutions. If it were only possible to know the potential difference between one particular electrode and a solution, then cells could be made up involving this electrode, or as it is sometimes called half-element, and an unknown electrode, and from the observed voltage the E.M.F. of the unknown electrode could readily be found. Thus if a cell were composed such that the more positive electrode was at a potential of E_1 volts and the other electrode at E_2 volts, then the E.M.F. which could be measured between the two electrodes would be equal to $E_1 - E_2$ volts; *i.e.*, the observed E.M.F. of cell

$$= E_1 - E_2 \text{ volts.}$$

Until the absolute potential of a half-element can be determined, it has been found convenient to assign to one particular electrode system an arbitrary potential, thus rendering it possible to calculate the relative potential differences between any other electrodes and solutions, and to compare the electromotive behaviour of the different electrodes. The usual convention is equivalent to saying that the normal electrode potential of hydrogen is zero. Hence the equation connecting the E.M.F. of a hydrogen electrode and the concentration of hydrogen ions of the solution becomes at 18° to 20° C.

$$E = 0 + 0{\cdot}058 \log [H^{\cdot}].$$

Electrode of Arbitrary Zero Potential.

Though at different times no less than three electrodes have been taken as being of zero potential, the so-called *Normal Hydrogen Electrode* is now generally regarded as the zero potential standard. This arbitrary zero electrode is the ordinary hydrogen electrode in equilibrium with hydrogen gas at one atmosphere pressure, *i.e.*, 760 mm. of hydrogen alone, and a hypothetical solution containing 1 g.-mol. of hydrogen ions per litre. This electrode, furthermore, is also taken as of zero potential at all temperatures. At the time this convention was made hydrogen-ion concentrations were calculated from conductivity measurements, and consequently it was not a difficult matter to prepare a solution whose hydrogen-ion concentration could be regarded as *one*-Molar, as required by the normal hydrogen electrode. Nowadays, some little confusion has arisen through the introduction by G. N. Lewis of the activity theory, and, therefore, instead of using the degree of dissociation for the purpose of

calculation, the exponents of that theory regard as their standard, the hydrogen electrode, supplied with hydrogen gas at 1 atmosphere pressure, and immersed in an acid solution, usually hydrochloric acid, the mean ionic activity of which is unity. We shall in this book assume the correctness of conductivity data as leading to the true concentration of hydrogen ions. Though this view may be unjustifiable, it seems both more convenient and satisfactory in view of the fact that the majority of buffer solutions of known *p*H have been calibrated on this basis. (Chapter XVI.) Chapter XIV has, however, been included in the present edition dealing with the newer theories in regard to their importance in the interpretation of E.M.F's.

CHAPTER II

STANDARD HALF-ELEMENTS

Calomel Electrodes.

ALTHOUGH the normal hydrogen electrode provides a very convenient arbitrary zero of potential, it is by no means a suitable practical standard. Perhaps the most suitable standard half-elements are those of potassium chloride solutions of definite concentration which are saturated with pure mercurous chloride, calomel, and which have attained equilibrium with mercury. The concentrations of potassium chloride solution which are used are 0·1N, 1·0N, 3·5N and saturated, and the resulting electrodes are respectively known as decinormal, normal, 3·5 normal and saturated calomel electrodes. The origin of the potential differences which are set up between the mercury and the various solutions lies in the fact that the mercurous chloride is sufficiently soluble to furnish the solution with mercurous-ions. Hence we see from Chapter I that the E.M.F. thus established is given by

$$E = \epsilon_{Hg_2^{\cdot\cdot} \rightarrow 2Hg} + \frac{0{\cdot}058}{2} \log [Hg_2^{\cdot\cdot}] .$$

at 18° to 20° C. The common ion, *viz.*, chloride, in the potassium chloride solution depresses the solubility of the calomel, with the result that with increasing concentrations of potassium chloride the mercurous-ion concentration becomes diminished and so reduces the value, E, the electrode potential. This will be understood from a consideration of the solubility product of the calomel, $L = [Hg_2^{\cdot\cdot}] \times [Cl']^2$, for when [Cl′] is made large by virtue of a greater concentration of potassium chloride, $[Hg_2^{\cdot\cdot}]$ must become correspondingly lower to maintain the constancy of the solubility product. These half-elements, once set up, give rise to stable P.D's, which are only slightly affected by temperature. Their precise potentials are ascertained by measuring the fall in potential between a calomel electrode and a hydrogen electrode immersed in a solution of known hydrogen-ion concentration when connected together by means of a saturated solution of potassium chloride. It is, of course, unnecessary to prepare the particular hydrogen electrode which is assumed to have zero potential, for it is an easy matter to calculate from the observed

E.M.F. the exact potential difference which would have been created had it been used. In a cell composed of these electrodes, the calomel electrode would be the positive electrode and the hydrogen the negative. If E_{cal} represents the potential of the calomel electrode and E_{H_2} the potential of the hydrogen electrode used, then the observed E.M.F., which drives the current from the calomel to the hydrogen electrode through the wire which joins them, is equal to

$$E_{cal} - E_{H_2} \text{ volts,}$$

and as $E_{H_2} = 0{\cdot}058 \log [H^{\cdot}]$ at 18° to 20° C,

of which $[H^{\cdot}]$ is known from conductivity data, we can calculate the value of E_{H_2} and so find the extent by which this hydrogen electrode differs from the normal hydrogen electrode. As a rule the hydrion concentration will be less than 1-Molar, and therefore the E.M.F due to the hydrogen electrode will be more negative than the normal hydrogen electrode. Thus, when the concentration of hydrogen-ions is decimolar, then the expression $0{\cdot}058 \log [H^{\cdot}]$ becomes equal to $-0{\cdot}058$ volt with respect to the arbitrary zero; when $[H^{\cdot}]$ is equal to 10^{-2} gram-ions per litre $E_{H_2} = -0{\cdot}116$ volt, and so on. If we take x as being the actual number of volts by which the potential of the hydrogen electrode employed differs from the arbitrary zero electrode, then we see that if the concentration of hydrogen-ions be greater than 1-Molar x is positive, and becomes negative if less than 1-Molar. Hence in the first instance, the observed

$$\begin{aligned} \text{E.M.F.} &= E_{cal} - E_{H_2}, \\ &= E_{cal} - x \text{ volt,} \end{aligned}$$

and in the second case, the observed

$$\begin{aligned} \text{E.M.F.} &= E_{cal} - (-x) \\ &= E_{cal} + x \text{ volt.} \end{aligned}$$

In this way we obtain the P.D. of the calomel half-element referred to the normal hydrogen electrode. That the potential of the calomel electrode merely gives the voltage it is above the arbitrary zero will be evident from Fig. 2.

The "Potential Commission" of the Bunsen Gesellschaft decided in 1911 that the most satisfactory value of the potential of the normal calomel electrode was $+0{\cdot}283$ volt, and $+0{\cdot}337$ volt for the decinormal calomel electrode. Of these, the latter suffers so very little change in voltage with temperature that Auerbach suggested that it could safely be taken as 0·3370 volt between 20° and 30° C. Discrepancies of two or three millivolts may arise from uncertainties of the exact degree of the ionisation

of the various hydrochloric acid solutions which have been used in the hydrogen electrodes against which the calomel electrodes have been compared. Every care must be taken when using either of these two standard electrodes to protect them from any variation in the concentration of their potassium chloride, and this is especially apt to occur through possible diffusion of the saturated potassium chloride solution employed as junction liquid. To obviate such alterations Michaelis introduced the saturated calomel electrode. The great drawback to this electrode as a standard lies in the fact that the influence which temperature has on the solubility of potassium chloride causes it to undergo greater changes in P.D. than either the normal or tenth normal electrodes. It is therefore necessary when using

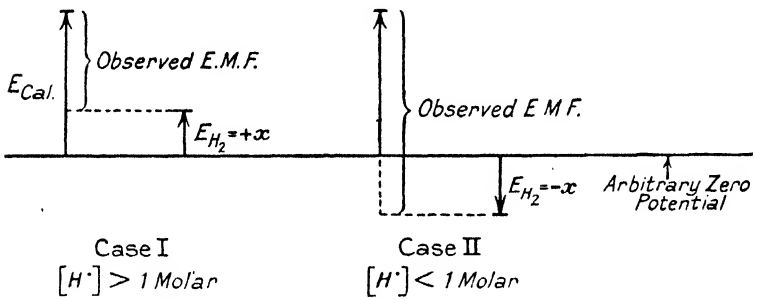


FIG. 2.

this electrode to standardise it against the more constant decinormal calomel electrode.

Table 4, which gives the potentials of Decinormal, Normal and Saturated Calomel Electrodes at various temperatures, was compiled from the data obtained by many workers including Sørensen (*Ergebn. Physiol.*, 1912, **12**, 393), Sørensen and Linderstrøm-Lang (*Compt. rend. Lab. Carlsberg*, 1924, 15) and Britton and Welford (*J. Chem. Soc.*, 1937, 1846).

It should be emphasised that the potentials recorded in Table 4 are referred to the Normal Hydrogen Electrode as zero for which the original hydrogen-ion concentration was calculated from the conductance ratio at *each particular temperature*, and *at one atmosphere pressure of hydrogen.*

As stated on page 63, it may be necessary, when using the hydrogen electrode in conjunction with a calomel electrode, to introduce a correction for the fact that the hydrogen supplied to the electrode is not always at atmospheric pressure. This

TABLE 4

POTENTIALS OF CALOMEL ELECTRODES

Temp. ° C.	Decinormal.	Normal.	Saturated.
12·5	—	0·287	—
15	—	—	0·2525
18	0·3380	0·2864	0·2509
20	0·3378	—	0·2488
25	0·3371	0·2846	0·2458
30	0·3370	—	—
34	0·337	0·284	—
38	—	—	0·2350
40	0·3359	—	—
50	0·3344	—	—
53	0·333	0·278	—
60	0·3321	—	—
63	0·331	0·275	—
75	0·330	0·270	—
91	0·324	0·263	—

variation in pressure is caused by changes in the pressure of the surrounding atmosphere and also by the pressure of water vapour, which, as the hydrogen is bubbled through the aqueous solution in the electrode vessel, may be assumed equal to the saturated vapour-pressure of water at the given temperature. Strictly speaking, correction should be made for the vapour pressure of the solution being investigated, but at ordinary temperature any errors arising therefrom have a negligible effect on the potential of the hydrogen electrode. At room-temperature the deviations due to the two causes are almost negligible, but as the saturated vapour pressure of water becomes considerable as the temperature is raised, it is essential that the correction should be made at elevated temperatures. The following expression gives the potential of the hydrogen electrode when surrounded with hydrogen at a pressure equal to P mm. of mercury.

$$E_{H_2} = 0{\cdot}000{,}198{,}4\ T \log \frac{[H^+]}{\sqrt{\frac{P}{760}}}, \quad (cf.\ \text{page } 18)$$

P is thus equal to the barometric pressure *less* a pressure equal to the saturated vapour pressure of water at temperature T.

Britton and Welford measured the E.M.F's of the cell:

$$\overset{+}{Hg} \mid Hg_2Cl_2, \text{N-KCl} \mid \begin{matrix}\text{Sat.}\\ \text{KCl}\end{matrix} \mid 0{\cdot}08\ \text{N-HCl} \mid \overset{-}{H_2}^{Pt}$$

at a series of temperatures.

Hence E.M.F.

$$= E_{\text{N-Calomel}} - E_{H_2}$$

$$= E_{\text{N-Calomel}} - 0{\cdot}000{,}198{,}4\,T \log \frac{[H^{\cdot}]}{\sqrt{\frac{P}{760}}}$$

$$= E_{\text{N-Calomel}} - 0{\cdot}000{,}198{,}4\,T \log [H^{\cdot}] + 0{\cdot}000{,}198{,}4\,T \log \sqrt{\frac{P}{760}};$$

the $[H^{\cdot}]$ of 0·08 N-HCl being calculated from the conductivity data of hydrochloric acid solutions of Noyes (*J. Amer. Chem. Soc.*, 1908, **30**, 335). The last term, $0{\cdot}000{,}198{,}4T \log \sqrt{\frac{P}{760}}$, is the correction to be applied for pressure. If this correction is not made, then we obtain a value for $E_{\text{N-Calomel}}$ which includes this error, thus:

$$E_{\text{N-Calomel (uncorrected)}} = E_{\text{N-Calomel (corrected)}} + 0{\cdot}000{,}198{,}4T \log \sqrt{\frac{P}{760}}.$$

It therefore follows that by using $E_{\text{N-Calomel (uncorrected)}}$, instead of $E_{\text{N-Calomel (corrected)}}$, we automatically correct for water-vapour pressure, and consequently the E.M.F. of a cell:—

$$\overset{-}{Pt}H_2 \,|\, H^{\cdot} \,|\, \begin{matrix}\text{Sat.}\\ \text{KCl}\end{matrix} \,|\, \text{N-KCl . } Hg_2Cl_2 \,|\, \overset{+}{Hg}$$

$$= E_{\text{N-Calomel (uncorrected)}} - 0{\cdot}000{,}198{,}4\ T \log [H^{\cdot}].$$

Table 5 gives the potentials obtained by Britton and Welford of N-Calomel electrode.

TABLE 5

$E_{\text{(uncorrected)}}$ AND $E_{\text{(corrected)}}$ OF N-CALOMEL ELECTRODE

Temp. °C.	E.M.F. of $\overset{-}{H_2}\,|\,\overset{+}{N}$-cal.	$\alpha_{0{\cdot}08\text{N-HCl}}$	0·0001984T × log $[H^{\cdot}]$.	$E_{\text{N-cal.}}$ (Uncorrected).	Sat.v.p. of Water, mm.	0·0001984T × log $\sqrt{\frac{P}{760}}$	$E_{\text{N-cal.}}$ (Corrected).
12·5	0·351	0·934	− 0·064	+ 0·287	10·8	0·00017	+ 0·287
25	0·352	0·929	− 0·067	+ 0·285	23·8	0·00041	+ 0·285
34	0·352	0·925	− 0·069	+ 0·283	39·8	0·00071	+ 0·284
53	0·349	0·917	− 0·073	+ 0·276	107·2	0·00213	+ 0·278
63	0·347	0·913	− 0·076	+ 0·271	171·5	0·00370	+ 0·275
75	0·342	0·908	− 0·079	+ 0·263	289·3	0·00718	+ 0·270
91	0·325	0·901	− 0·082	+ 0·243	546·3	0·01990	+ 0·263

Fales and Mudge (*J. Amer. Chem. Soc.*, 1920, **42**, 2454) have determined the E.M.F. of the cell at 25°:

$$\overset{+}{\mathrm{Hg}} \,|\, \mathrm{Hg_2Cl_2},\ x\mathrm{N\text{-}KCl} \,\|\, \begin{matrix}\text{Sat.}\\ \mathrm{KCl}\end{matrix} \,|\, 0{\cdot}1\mathrm{M.\text{-}HCl} \,|\, \overset{-}{\mathrm{H_2}}{}^{\mathrm{Pt}}$$

for different values of x. Their results are given in Table 6, together with values of $E_{x\text{N-calomel}}$. These values were calculated on the basis that the *p*H of 0·1M.-HCl is 1·076, and therefore $E_{H_2} = \cdot 0591 \log 10^{-1\cdot076} = -0{\cdot}0636$ volt.

TABLE 6

POTENTIALS OF $E_{x\text{N-calomel}}$ AT 25°

Conc. KCl x . N.	E.M.F. of Cell.	Barometric Pressure, mm. Hg.	E.M.F. of Cell (Corrected).	$E_{x\text{N-calomel}}$
0·1	0·4016	759	0·4020	+ 0·3384
0·5	0·3642	761	0·3646	+ 0·3010
1·0	0·3479	760	0·3483	+ 0·2847
2·0	0·3321	760	0·3325	+ 0·2690
3·0	0·3209	760	0·3213	+ 0·2577
Saturated	0·3099	761	0·3103	+ 0·2467

A cell which is useful in testing calomel electrodes is:

$$\overset{+}{\mathrm{Hg}} \,|\, \mathrm{Hg_2Cl_2}\,.\,\mathrm{N\text{-}KCl} \,\|\, \mathrm{Sat.\ KCl}\,.\,\mathrm{Hg_2Cl_2} \,|\, \overset{-}{\mathrm{Hg}},$$

the E.M.F. of which at 25° is 0·0387 volt (Fales and Mudge, *loc. cit.*; Ewing, *J. Amer. Chem. Soc.*, 1925, **47**, 301).

Samuelson (*J. Amer. Chem. Soc.*, 1935, **57**, 2711) gives + 0·2446 + 0·0002 ($t - 25°$) volt as the potential of the saturated calomel electrode.

Preparation of Calomel Electrodes.

In making calomel electrodes care must be taken to use pure materials and also to be certain that the solid phase, the calomel, has entered into complete equilibrium with the potassium chloride solution which must be saturated with calomel, and in this regard an electrode should not be used until it has acquired a steady and correct potential. It is well known that the initial solubility of a difficultly soluble substance is in some way connected with the fineness of its particles, and also with its condition, whether it has just been precipitated and not allowed to dry or else has been prepared for some time and dried. Thus Hulett (*Z. physikal. Chem.*, 1901, **37**, 384) has found that the solubility of barium sulphate when in the form of fine particles

of average diameter of 0·00004 cm. is almost twice that of coarser particles whose average diameter is 0·0018 cm. The fact that the smaller particles dissolve more rapidly and also appear to have a higher solubility, no doubt due to a false equilibrium being created, can be traced to the relatively much greater total surface which they have compared with their mass, with the result that a greater solvent action can take place through the increased interfacial tension effects which come into play. As the effect of the surface tension of a liquid is to make the exposed surface, *e.g.*, the surface in contact with that of a particle smaller, we see why such forces when acting upon the surface of a particle will tend to cause the particle to dissolve, and, furthermore, why those particles which are allowed to separate from a supersaturated solution under conditions which permit surface tension to become effective, result in larger grains. Once a substance, especially a sparingly soluble one, has formed a slightly supersaturated solution, thereby corresponding to a state of false equilibrium, it is often a difficult matter to destroy such a state of affairs. Hence the importance of precipitating the calomel very slowly, by adding the hydrochloric acid drop by drop and stirring well. It is probable that the best conditions for preparing calomel for electrodes are obtained in the electrolytic preparation.

There is no doubt that ageing tends to reduce the rate at which dissolution can proceed, while on the other hand, a freshly formed precipitate when placed in an aqueous solution rapidly attains equilibrium with it, and may even supersaturate the solution. Such factors would have their effect on the E.M.F. of a calomel electrode on account of the changes in the mercurous-ion concentration. The necessity of using pure materials will be understood when it is remembered that mercury may often contain base metals, and calomel may contain traces of soluble mercuric chloride which, if not eliminated, would create a further equilibrium between the mercury and the mercuric-ions so introduced into the electrode.

Unless pure mercury is available it will be necessary to subject the commercial product to a treatment with nitric acid of density 1·1 to 1·2 by allowing it to drop down through a column of the acid for about six hours in order to remove any soluble material, then to oxidise any zinc remaining in the mercury by means of air, or by shaking with a dilute solution of potassium permanganate, and finally to distil *in vacuo* at low temperature. The last process may often safely be omitted, when the zinc and lead oxides which will rise to the surface have been removed, and the remaining mercury dropped through a length of nitric acid and

then forced through a U-capillary tube, 1 mm. in bore, from which it will emerge in a sufficiently pure state.

Calomel of the purity demanded by the British Pharmacopœia is satisfactory, but in case it is desired to prepare it, the following note is given. Some pure mercury is partly dissolved in pure diluted nitric acid, and then hydrochloric acid (s.g. 1·1) is added drop by drop to the solution, in which free mercury is present, with thorough shaking. Decant the clear liquid from the precipitated calomel, wash the calomel-mercury mixture thoroughly with several changes of water and finally a few times with potassium chloride solution of the concentration to be employed subsequently in the electrode. It may also be prepared by electrolysing a normal solution of hydrochloric acid between a platinum cathode and pure mercury, kept well stirred by paddles, as anode (*vide* Lipscomb and Hulett, *J. Amer. Chem. Soc.*, 1916, **38**, 21, and Ewing, *ibid.*, 1925, **47**, 301). A 4-volt accumulator should be used. The calomel so obtained is of a more uniform grain and is mixed with mercury. Before use it must be washed with water and repeatedly with the potassium chloride solution. Unless potassium chloride of A.R. quality can be obtained, the commercial product should be purified by recrystallisation.

Ewing uses a two-compartment cell, which consists of two vessels, connected with one another by means of filter paper impregnated with potassium chloride solution and reinforced with collodion. In the vessel containing mercury, which serves as the anode, a saturated solution of potassium chloride is placed. A copper cathode and a solution of cupric chloride are placed in the other vessel. An anode C.D. of 1·3 amps./dm.^{2} at 35–40 volts is applied for 20–30 minutes. The anode vessel is fitted with a stirrer which scrapes the surface of the mercury and removes the calomel as it is formed.

Although much has been written as to the possible effects which the manner of preparing the mercury-calomel paste may have on the potential of the particular electrode, it is probable that appreciable differences will not be caused if the paste is composed of an intimate mixture of finely divided mercury and calomel particles. Errors are only likely to be introduced by the presence of coarse calomel particles, on account of the sluggishness with which they attain equilibrium with the solution, and the poor contact with the mercury which may result. The paste may be made by grinding, but not excessively, calomel with mercury in a mortar using a little of the potassium chloride solution; after washing several times by decantation the paste is thoroughly shaken with more potassium chloride solution and

then poured into the electrode vessel. Some workers advocate merely shaking the calomel with mercury in the potassium chloride solution without resorting to grinding. There is probably no great efficacy in either method—the important point is to ensure as far as possible that true equilibrium is reached between the solid and liquid phases.

Various forms of vessel are used for calomel electrodes, though as far as accuracy and efficiency are concerned it is immaterial which shape is actually chosen. The author generally uses the simple form represented in Fig. 25, which is a wide-necked, two to four ounce bottle, tightly fitted with a rubber bung through which three glass tubes are passed. Into the closed end of the middle one, which *dips below the level of the mercury layer*, is sealed a piece of platinum wire in order to make contact with the mercury. External contact with the platinum wire is made by placing a little mercury in the tube, in which is inserted a copper wire having its end amalgamated. The copper lead may, of course, be brought into direct contact with the platinum wire by soldering the two wires together before sealing the platinum into the tube. Above the mercury which is sufficient to cover completely the protruding end of the platinum wire, a paste of calomel and mercury is placed, and above this is the solution of potassium chloride of the desired concentration, either 0·1 M, 1·0 M, 3·5 M, or saturated, which must be saturated with calomel. The tube bent at an obtuse angle is fitted tightly with a rubber bung. Its lower end is not allowed to dip into the solution. The tube is used to blow solution into, or out of, the connecting tube which dips into the liquid. After the connecting tube, whose outer end is tapered off somewhat, has been dipping into the saturated potassium chloride solution in the junction vessel there is every possibility that the solution in the tube may thereby have become contaminated, and this is guarded against by flushing out the tube with fresh liquid from the electrode vessel after each experiment. Needless to say, all bungs and tubes should fit perfectly in order to make the vessel air-tight, so that no solution actually leaves the connecting tube during determinations. Some little interchange of solution is inevitable at the point where the tube dips into the junction liquid, but any evil effects which might produce an alteration in the concentration of the solution in the electrode vessel can be avoided by taking these precautions. Other forms of calomel electrode vessels are given in Fig. 3. Their special advantage lies in the fact that being small they necessitate the use of less of the components; in the first type, contact is made with the mercury through a platinum wire which is sealed into the bottom of the

vessel, and in the second form, by means of a tube, containing mercury and a platinum wire sealed into its closed end, which passes through a rubber bung fitting tightly into the mouth of the vessel. The tap in the connecting arm is an advantage in that it can be employed to reduce the size of the orifice, and so tend to make diffusion more difficult. Closing the tap, while the electrode is not being used, prevents evaporation of the electrode solution, though in the case of saturated potassium chloride solution this is immaterial. The side-tubes shown in both forms are closed with rubber tubing and clips. Yet another modification is to be seen in Fig. 39, in which a tap is inserted in the connecting tube and also a funnel into which saturated potassium chloride solution is placed which may be run into the outer portion of the arm and

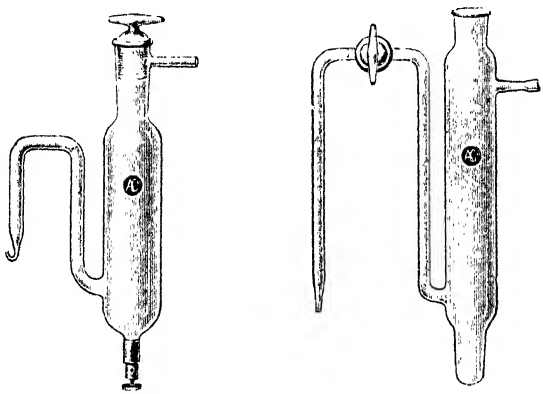


FIG. 3.—Forms of Calomel Electrode Vessels.

so serve as junction liquid. Although very convenient for electrometric titration great care must be taken, if accurate E.M.F's are also aimed at, to prevent any possible leaking into the electrode. Such a form is very suitable when using the saturated potassium chloride-calomel electrode.

The voltages of half-elements, including some that are occasionally used as being of known potential, are given in the table on page 36, which was taken from Ostwald-Luther-Drucker, *Physiko-Chemische Messungen*, 4th Edition, 1925. Other forms of electrode vessel have been described with a view to minimising the risk of diffusion, sometimes by attentuating the connecting arm and sometimes by introducing several U-bends. To guard against possible diffusion the author keeps the level in the electrode vessel slightly higher than that in the vessel containing

TABLE 7

POTENTIALS (VOLTS) OF HALF-ELEMENTS

Electrode.	E_h at 18° C.	E_h at 25° C.
H_2 | N-H•	0·000	0·000
Hg | HgCl . 0·1 N-KCl	+ 0·336	+ 0·336
Hg | HgCl . 1·0 N-KCl	+ 0·284	+ 0·283
Hg | HgCl . 3·5 N-KCl	+ 0·252	+ 0·250
Hg | HgCl . 0·1 N-HCl	+ 0·335	+ 0·335
Ag | AgCl . 0·1 N-KCl	+ 0·292	+ 0·290
Ag | AgCl . 0·1 N-HCl	+ 0·291	+ 0·289
H_2 | 0·1 N-HCl	− 0·063	− 0·064
H_2 | 0·1 N-H_2SO_4	—	− 0·073
Hg | Hg_2SO_4 . 0·1 N-H_2SO_4	—	+ 0·682
H_2 | 0·1 N-NaOH	− 0·759	− 0·761
Hg | HgO . 0·1 N-NaOH	—	+ 0·165

the saturated potassium chloride. This tends to cause the liquid to flow out of the electrode tube and so militates against any diffusion taking place. For further information regarding the reproducibility of calomel electrodes the reader is referred to Veibel (*J. Chem. Soc.*, 1923, **123**, 2206).

Standard Quinhydrone Electrode.

Veibel (*loc. cit.*) has shown that an electrode comprising a piece of bright platinum foil immersed in a solution containing quinhydrone and 0·01 Normal with respect to hydrochloric acid and 0·09 Normal with respect to potassium chloride has, at 18° C., an E.M.F. of + 0·7040 ± 0·0002 volt above the hydrogen electrode in equilibrium *with the same electrolyte*, and 0·2485 ± 0·0002 volt above the potential of the decinormal calomel electrode. It is readily reproduced. Black and Barton (*Ind. Eng. Chem., Anal. Edn.*, 1939, **11**, 261) have found that in two days the potential of the electrode falls by 0·6 mv., in 10 days by 5 mv., and in 18 days by 12 mv., no matter whether Pyrex or soft glass is used in the electrode vessel. As the 0·1 N-calomel electrode is more positive than the normal hydrogen electrode by + 0·337 volt, we find that the E.M.F. of this special quinhydrone electrode is + 0·586 volt when referred to the arbitrary zero potential. It can conveniently be set up in a calomel electrode vessel of the form shown in Fig. 3 (*b*), fitted with a rubber stopper through which is passed a tube containing mercury in contact with a platinum wire sealed into the bottom end, and to the other end of the wire is fused a strip of bright platinum foil.

Schomaker and Brown (*Ind. Eng. Chem., Anal. Edn.*, 1937, **9**, 34) find that the electrode

Pt | solution of potassium quadroxalate + quinhydrone

serves as a useful reference electrode. The solution is prepared by saturating water with $KHC_2O_4,H_2C_2O_4,2H_2O$ at 0° C. The E.M.F. of the cell

$$\overset{+}{Pt} \left| \begin{array}{l} \text{Solution of potassium} \\ \text{quadroxalate + quinhydrone} \end{array} \right| \begin{array}{l} \text{sat.} \\ \text{KCl} \end{array} \left| \begin{array}{l} \text{KCl (sat.)} \\ \end{array} \right| Hg_2Cl_2 \mid \overset{-}{Hg}$$

is given in Table 8.

TABLE 8

Temp. ° C.	E.M.F.	$E_{Sat.\ cal.}$	$E_{Pt\text{-}Quin.}$
0	0·36566	0·24625	+ 0·61191
25	0·35236	0·2446	+ 0·59595
35	0·34743	0·2380	+ 0·5854

Donnan-Allmand Standard Electrode.

An electrode, sometimes used, is one in which mercury is placed in either N- or N/10-solution of sodium hydroxide or a N-potassium hydroxide solution kept saturated with mercuric oxide by means of an excess of fairly coarse-grained mercuric oxide. This oxide may be prepared by heating either mercuric or mercurous nitrate gently in a porcelain basin, with constant stirring, occasional cooling and gentle grinding until all the oxides of nitrogen have been driven off. The product obtained, which is light reddish-brown, contains very little of the extremely small particles, and consequently permits of the rapid attainment of equilibrium as shown by the constancy of the E.M.F. Donnan and Allmand (*J. Chem. Soc.*, 1911, **99**, 845) found that if the correctness of the *Planck liquid potential formula* be assumed, these electrodes are more positive than the normal hydrogen electrode, as shown by the following expressions :—

E.M.F. of Hg | HgO . N-KOH $= + 0{\cdot}1100 - 0{\cdot}00011\,(t - 25°)$
E.M.F. of Hg | HgO . N-NaOH $= + 0{\cdot}1135 - 0{\cdot}00011\,(t - 25°)$
E.M.F. of Hg | HgO . N/10-NaOH $= + 0{\cdot}1690 + 0{\cdot}00007\,(t - 25°)$

(These values are based on the potential of the N-calomel electrode being + 0·283 volt at 18°.)

Samuelson and Brown (*J. Amer. Chem. Soc.*, 1935, **57**, 2711) have modified the Hg | HgO. alkali. electrode by replacing the NaOH or KOH by saturated solutions of either barium or

calcium hydroxide. The electrodes were standardised against the saturated calomel electrode at various temperatures thus :

$$\overset{+}{Hg} \mid Hg_2Cl_2, \text{sat. KCl} \,\Big|\, \begin{matrix}\text{sat.}\\ \text{KCl}\end{matrix} \,\Big|\, \text{sat. } Ba(OH)_2, HgO \mid \overset{-}{Hg}$$

$$\overset{+}{Hg} \mid Hg_2Cl_2, \text{sat. KCl} \,\Big|\, \begin{matrix}\text{sat.}\\ \text{KCl}\end{matrix} \,\Big|\, \text{sat. } Ca(OH)_2, HgO \mid \overset{-}{Hg}$$

The E.M.F. of the baryta cell is

$$E_{t°C} = 0{\cdot}1462 + 0{\cdot}0006\,(t° - 25°)$$

and that of the lime-water cell is

$$E_{t°C} = 0{\cdot}1923 + 0{\cdot}0001\,(t° - 25°).$$

Taking + 0·2446 as the potential of the Saturated Calomel Electrode at 25°, it follows that the potential of Hg | HgO, sat. $Ba(OH)_2$ is + 0·0984 volt, and that of Hg | HgO, sat. $Ca(OH)_2$ is + 0·0523 volt. At other temperatures, the potentials are for

Hg | HgO, $Ba(OH)_2$: + 0·0794 at 0° ; + 0·0902 at 15° ; + 0·1066 at 35° C.

Hg | HgO, $Ca(OH)_2$: + 0·0497 at 0° ; + 0·0512 at 15° ; + 0·0533 at 35° C.

The electrode adjusts its potential to changes in temperature within half an hour.

Silver-silver Chloride Electrode.

Instead of using precipitated silver chloride in conjunction with silver electrodes, the silver chloride may be deposited as an adherent layer on a silver-plated platinum wire. Harned (*J. Amer. Chem. Soc.*, 1929, **51**, 416) chloridises reduced silver oxide paste by anodic treatment, whereas MacInnes and Beattie (*ibid.*, 1920, **42**, 1117) and Brown (*ibid.*, 1934, **56**, 646) and Carmody (*ibid.*, 1929, **51**, 2901 ; 1932, **54**, 188) electrolyse the silver electrodes in alkali chloride or hydrochloric acid solutions, the silver electrodes being the anodes.

When platinum wires are silver-plated, it appears to be important that the $KAg(CN)_2$ bath should not contain any excess of free KCN. This can be removed by the cautious addition of silver nitrate solution until a faint cloudiness is produced, which should be allowed to settle and the solution decanted.

Brown seals a platinum wire into Jena thermometer glass so that 1 cm. length is left exposed. Silver is deposited by the electrolysis of a solution containing 10 grams of recrystallised $KAg(CN)_2$ per litre for 2–6 hours with 2–0·5 milliamps. Six

electrodes are prepared together and they serve as cathodes which are separated from the anode (platinum) by means of an alundum disc, 9 mm. internal diameter and 2 mm. thick. After rinsing, the electrodes are immersed in distilled water.

Chloridising is carried out by making the silvered electrodes cathodes in 0·1 N-hydrochloric acid for ½ hour at C.D. = 2 milliamps/cm². These electrodes are purplish brown, are unaffected by sunlight and retain their potentials in alkali chloride solutions for long periods. The use of lower C.D's gives electrodes which may be spotted with grey patches and give somewhat erratic potentials in silver nitrate solutions. Other methods of preparing silver-silver chloride electrodes have been described. (See, for example, Guntelberg, *Z. physikal Chem.*, 1926, **123**, 199; Noyes and Ellis, *J. Amer. Chem. Soc.*, 1917, **39**, 2532.)

According to Scatchard (*J. Amer. Chem. Soc.*, 1925, **47**, 641) the E.M.F. of

$$\overset{+}{\mathrm{Ag}}\,|\,\mathrm{AgCl},\ 0{\cdot}1\ \text{N-KCl}\,|\,\text{sat. KCl},\ \mathrm{Hg_2Cl_2}\,|\,\overset{-}{\mathrm{Hg}}$$

is 0·0453 volt at 25°, and the E.M.F. of

$$\overset{+}{\mathrm{Hg}}\,|\,\mathrm{Hg_2Cl_2},\ 0{\cdot}1\ \text{N-KCl}\,|\,0{\cdot}1\ \text{N-KCl},\ \mathrm{AgCl}\,|\,\overset{-}{\mathrm{Ag}}$$

is 0·0466 volt at 25°. This shows that the potential, E_h, of

Ag | AgCl, 0·1 N-KCl is + 0·291 volt at 25°.

CHAPTER III

THE HYDROGEN ELECTRODE AND *p*H

In order to make a hydrogen electrode advantage is taken of the large adsorptive powers for hydrogen of finely-divided platinum, palladium or iridium when electrolytically deposited on the bright surfaces of any one of these metals or on gold, and of the tendency possessed by these finely divided metals to promote catalytically the change from the molecular condition of hydrogen to the atomic and thence to the ionic state. Care must be taken to prepare electrodes in which this catalytic behaviour is not too great, otherwise they will respond to the slightest disturbing condition, such as traces of reducible substances, even though these may only be reduced with difficulty, instead of rapidly establishing equilibrium with the hydrogen ions in the solution. In practice, it is often more convenient to use the hydrogen electrode in solutions exposed to the air. This will necessitate the use of electrodes which are either indifferent to possible traces of dissolved oxygen or else will rapidly reduce them and almost immediately attain equilibrium with the hydrions. The simplest form of electrode is that described by Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847). It comprises a rectangular piece of platinised platinum foil connected by a platinum wire to a glass tube containing mercury. This tube is enclosed in another tube having an inlet for hydrogen and a bulb to surround the platinum foil. This bulb is perforated usually at the bottom and in front of, and behind, the foil, such that when the electrode is immersed in a solution and the hydrogen is passing, the foil is about half immersed (Fig. 31). The commercial hydrogen now supplied under pressure in cylinders is usually sufficiently pure for routine work, without any further purification, and by the careful adjustment of its flow, it can be employed for the dual purpose of maintaining the platinum black in a saturated condition and also in keeping the solution, being tested, thoroughly mixed.

The chief processes worked industrially for the manufacture of hydrogen are by electrolysis and by separation from " water gas." The only impurities likely to be encountered in electrolytically prepared hydrogen are traces of air and carbon dioxide which may be removed by passing the gas through bubblers containing

potassium hydroxide and alkaline pyrogallol solutions respectively. Moser (*Z. anorg. Chem.*, 1920, **110**, 125) states that iron carbonyl can often be detected in hydrogen prepared from " water gas," but if it is present in the hydrogen manufactured in this country the amount is so minute that it is without any deleterious effects on the hydrogen electrode.

If a hydrogen electrode is to be used in a solution containing no reducible substances, then it does not very much matter what form the platinum electrode takes, whether it be foil or whether it be wire, or how the adsorptive covering has been deposited, which may be either of platinum, palladium or iridium black. The speed with which the electrode attains a state of equilibrium with the solution will depend upon the nature of the deposit. Too heavy a deposit will make the electrode very sluggish, though it must be conceded that such an electrode will attain equilibrium if allowed sufficient time. When reducible substances are present the author found that the hydrogen soon becomes removed from the coating on wire electrodes, whereas when larger electrodes are used, and provided they are covered with the right kind of black, they sometimes do not respond to such influences.

Though it is undoubtedly upon the nature of the " black " coating that the efficiency of the electrode depends, the author, in common with many other workers, has failed to determine just those conditions which lead to the best deposits. It is in some way connected in the first place with the quality of the surface, platinum or gold, upon which the black layer is deposited. Those surfaces should be as highly polished as possible—this was often done by removing the old platinum black layer with the finest moistened emery powder, then laying the electrode on a plane glass surface and rubbing with the rounded end of a glass rod. The reducing property of hydrogen in presence of colloidal platinum is inherently connected with the relative magnitude of the surface of the colloidal particles ; if the particles be exceedingly minute then the surface becomes very great and this is reflected in an enhanced catalytic activity. A coating of such particles would be unsuitable on electrodes for use in solutions in contact with air or in solutions containing reducible substances. Suitable deposits can, however, be obtained, which are sufficiently catalytically active to produce sensitive and accurate hydrogen electrodes, but which will effect reduction only after some time has elapsed, as the author was able to demonstrate in an extreme case in which the hydrogen did not immediately reduce free chromic acid.

The catalytic reducing power of an electrode is often a question

of the *p*H of the liquid. Thus, although it was only in comparatively few cases that the author was able to prepare electrodes which, if they caused reduction at all, the rate at which it took place was so small that the hydrogen-ion concentrations of free chromic acid solutions could be measured before the error became perceptible; most of the good hydrogen electrodes prepared gave potentials corresponding to the true *p*H in dilute solutions of chromates when their *p*H values were greater than about 4 (*cf. J. Chem. Soc.*, 1926, 125).

It may be an advantage to discuss the behaviour of hydrogen electrodes when giving rise to reduction, as this may often occur, especially in oxygenated biological fluids. The behaviour of such hydrogen electrodes in free chromic acid solution may be taken as typical. With the majority of electrodes no constant E.M.F. could be obtained, and the precise value at any moment appeared to depend on both the rate of passage of hydrogen through the electrode vessel and whether the electrode was partly or totally immersed in the solution. Rapid passing of hydrogen effected rapid reduction, as indicated by the E.M.F. becoming less negative and even becoming positive, so much so that with a very plentiful supply of gas, the potential became of the same magnitude as that produced when a bright platinum electrode was substituted for the hydrogen electrode. This reducing action was more pronounced when the hydrogen electrode was partly immersed.

Certain electrodes, saturated with hydrogen previous to immersion in chromic acid solutions, gave on complete immersion initial E.M.F's indicating hydrion concentrations equal to those calculated from conductivity data. These E.M.F's fell slowly and the fall became much more rapid when the solution was agitated or the hydrogen turned on. On stopping the hydrogen supply and allowing the solution to become quite still once again, the potential in some cases gradually rose to a true constant value. The hydrogen electrode has been used in the presence of other reducible ions. F. L. Brown (*J. Amer. Chem. Soc.*, 1923, **45**, 297) measured hydrion concentrations in presence of ferric ions. He saturated several platinised platinum wire electrodes with hydrogen in vessels of the Hildebrand type and observed the E.M.F's immediately the electrodes were immersed. By using several electrodes he was able to measure accurately the initial E.M.F. before the reduction had commenced.

Previous saturation of hydrogen electrodes before immersion in the solution being investigated often renders *p*H measurements possible which otherwise would be extremely difficult, and this is especially the case with biological liquids, *e.g.*, blood.

The position of the electrode with respect to the solution is a question of some importance. The catalytic activity of the hydrogen in the electrode is much more pronounced when the electrode is only partly immersed. In this connexion, reference may be made to the work of J. Eggert (*Z. Elektrochem.*, 1914, **20**, 370; 1915, **21**, 349). He investigated the velocity of adsorption of hydrogen by platinised platinum and solutions of metallic salts at 17° C. He found that the reduction of ferric iron attained a maximum velocity when the platinum which served as catalyst was brought into contact with the hydrogen atmosphere above the solution. His results show that the maximum velocity of adsorption is proportional to the surface of the platinum and the time during which it is in contact with the gas space, but is independent of the number of times per minute the electrode was raised into the gas space and lowered into the solution. Under uniform conditions, the initial velocity of adsorption of hydrogen is constant and independent of the nature of the solutes. As the reaction approaches completion, a decrease in the velocity occurs. Eggert interpreted the constancy of the initial velocity, which varied with the nature of the platinum black, as being due entirely to the occlusion process, and the second velocity which gradually fell off, to the activation of the gas by the platinum. Hydrogen is capable of distributing itself in platinised platinum and can exert a chemical influence in places other than the point of occlusion. He found, moreover, that electrolytically deposited platinum and palladium have practically the same activating power.

Lockwood (*J. Soc. Chem. Ind.*, 1935, **54**, 295 T) states that with electrodes of the Hildebrand type steady potentials were observed only while the hydrogen was flowing. They, however, indicated greater hydrogen-ion concentrations than were actually the case. He attributes this discrepancy to part of the electrode being exposed to the hydrogen gas. His design of hydrogen electrode vessel (Fig. 7) ensures complete immersion of the platinised platinum wire electrode. Lockwood's observation is only part of the truth. Provided a suitable covering of platinum black is deposited on the electrode, it is immaterial whether the hydrogen is flowing or not at the time of making the measurement, or whether part of the electrode is exposed to the hydrogen, or whether the electrode is completely immersed. As a safeguard, it is advisable to turn off the gas and to allow the electrode to become completely immersed in the solution before making a reading. Steady and reproducible results are obtained within two minutes. The electrode system, introduced by Bollen (*Ind. Eng. Chem., Anal. Edn.*, 1931, **3**, 203), and illustrated in Fig. 8,

employs duplicate platinum wire spiral electrodes which are kept completely immersed. The solution and the electrodes are kept saturated with hydrogen by passing the gas through a T-tube which also forms part of the mechanical stirrer. The flow of the hydrogen through the electrode vessel is regulated by means of the syphon arrangement. Bollen states that anything from 6 to 10 minutes are required to obtain steady potentials with bubbling hydrogen electrodes, whereas equilibrium is reached within two minutes when the hydrogen is not led directly to the electrode. This is especially true of solutions containing free carbon dioxide.

According to Lorch (*Ind. Eng. Chem., Anal. Edn.*, 1934, **6**, 164; see also Hammett and Lorch, *J. Amer. Chem. Soc.*, 1933, **55**, 70) the catalysts used in hydrogen electrodes gradually lose their activity when exposed to pure hydrogen, which decay is accelerated enormously by increase in temperature. He believes that deviations from the hydrogen equilibrium potentials are caused by polarisation of the hydrogen electrode by substances which are able to oxidise activated hydrogen or to reduce hydrogen-ions.

It is a good practice to use two hydrogen electrodes in the same solution. In general, if both electrodes attain the same potential it can be safely assumed that this potential corresponds with equilibrium conditions. The electrodes should, however, not have been prepared in an absolutely identical manner, or it might conceivably happen that the effect of polarising impurities in the solution might be the same on the two electrodes, and, in consequence, the same but erroneous potentials be registered. Lorch points out that the only certainty that the electrodes are indicating true equilibrium potentials is to use hydrogen electrodes having widely different catalytic activities. He varies the catalytic activity by exposing the electrodes to hydrogen for a few days. Lorch recommends (*a*) platinum black for use in decidedly acid or basic solutions and in strongly buffered neutral solutions, and also for the maximum resistance to catalytic poisons, (*b*) bright thin deposits of either platinum or iridium for use in unbuffered, neutral or slightly acid solutions (it may be desirable to plate these deposits from an alkaline bath in order to minimise the absorption of hydrogen-ions by the metal (*cf.* Beans and Hammett, *J. Amer. Chem. Soc.*, 1925, **47**, 1215)), (*c*) bright thin deposit of iridium for use in slightly basic, unbuffered solutions.

Platinum black is electrodeposited from a 2 per cent. solution of platinic chloride, containing a trace (0·02 per cent.) of lead

acetate, with a current density of 60 milliamps./cm.^{2} for 1–2 minutes with gentle stirring. The electrode is allowed to stand in water for a few hours before use. As basis metal, the author prefers platinum foil which has been highly polished. There is no great need to regulate the C.D. carefully, for if a voltage is applied to give a vigorous evolution of gas, satisfactory deposits are usually obtained. The surface of the platinum is only just covered. The current may be reversed, preferably every half-minute, and under these conditions, platinisation should not take more than five minutes (*vide* Britton, *J. Chem. Soc.*, 1924, **125**, 1573; 1925, **127**, 2111). Any traces of chlorine left in the electrode can be removed by placing it in a dilute solution of sulphuric acid as cathode and electrolysing for half an hour. Although the presence of lead in the "black" layer is not absolutely necessary, it assists in providing a better covering, one which is adherent, and which has diminished reducing catalytic activity. The reason why electrodes containing traces of lead are more satisfactory seems to be linked up with the greater size of the platinum black particles.

Lorch produces electro-deposits of bright platinum by electrolysing a 2 per cent. platinous chloride solution in N-HCl with a C.D. equal to 1 milliamp./cm.^{2} for 10–30 minutes, the electrolyte being kept still. The platinous chloride is prepared by heating chloro-platinic acid on a sand-bath for one hour at 300° C. An alkaline bath may also be used, which consists of a 0·5 per cent. solution of Na_2PtCl_6 and NaOH. The C.D. is 10 milliamps./cm.^{2} or more, and according to Lorch the thickness of the deposit should be from 2 to 6 times the amount required to cover the electrode metal. Bright iridium, which should be deposited on a gold base, is obtained from 0·1–0·5 per cent. solution of $IrCl_4$ with a C.D. of 0·1 to 1 milliamp./cm.^{2} by electrolysis for 3–4 hours. Stirring is unnecessary.

Limitations of the Hydrogen Electrode.

Because of the reducing action the hydrogen electrode has a limited use, though with some hydrogen electrodes these limitations are not so great as with others; their success or failure being an inherent characteristic of the particular coating of the platinum black. This failure can often be traced to either reduction, or adsorption from solution of some gaseous product, such as ammonia or carbon dioxide. As a rule, it cannot be used in presence of oxidising agents, such as nitrates, chlorates, permanganates, ferric salts, and substances which are capable of still further reduction, such as sulphur dioxide, sulphides and

sulphur. When used in presence of chromates care must be taken to guard against erroneous data. It cannot be used in presence of some organic compounds, especially those which are unsaturated, and certain amines and alkaloids. The electrode behaves anomalously in presence of cyanides and of lead, cadmium, and univalent thallium salts. Salt solutions of metals more "noble" than hydrogen, namely, those metals whose normal electrode potentials are positive, *e.g.*, copper, silver, gold, render the electrode useless. Sometimes the hydrogen electrode functions satisfactorily, even though reducible substances may be present. Thus, as already stated, the author was able to prepare electrodes which responded to changes in hydrogen-ion concentration in dilute chromic acid solutions, but, as a rule, this is not the case. Sometimes its application is restricted to a range of hydrogen-ion concentrations, as was found by the author (*J. Chem. Soc.*, 1927, **147**) in the titration of an alkaline solution of tungstic acid, for when the hydrogen-ion concentration had become 10^{-4} reduction could be seen to be taking place. The presence of nitrates and chromates when in weakly acid or alkaline solutions is very often without any disturbing effect on the electrode.

It is sometimes stated that the hydrogen electrode is sluggish and only attains equilibrium after some time has elapsed. This depends entirely upon the electrode itself—some, once having attained a state of equilibrium, for which 10 minutes are usually ample, are immediately and accurately responsive to both small and large changes in hydrion concentration. Some become sluggish when being subjected to large and sudden changes. The author recommends in all cases that before a hydrogen electrode E.M.F. be taken as true, the same voltage within a millivolt should be given by at least one other electrode immersed in the same solution. It should also be mentioned, that, whereas a really satisfactory electrode gives identical results in both still and agitated solutions, in general less reliable values are given when the solutions are being agitated, the latter tending to give E.M.F's which are a few millivolts too low. It is, of course, immaterial what form, whether foil or wire, of platinum electrode is used in solutions which do not interfere with it, but for solutions containing reducible substances, wire electrodes will often be found unserviceable on account of the ease with which the hydrogen is discharged.

Much confusion has arisen over the precise conditions which are necessary for the preparation of really fool-proof electrodes. Although the author has used hydrogen electrodes extensively, he

has endeavoured to be quite sure that each electrode was behaving satisfactorily, by using at least two good electrodes. Even by so doing, electrodes were obtained, which though they worked satisfactorily in solutions of moderate acidity or alkalinity, were not all that could be desired in solutions in the region of neutrality, and especially so if those solutions were unbuffered. It seems certain that in the hands of inexperienced and unsuspecting workers, E.M.F's given by hydrogen electrodes often do not correspond to the true equilibrium conditions, and consequently erroneous *p*H values are calculated. Many have been the explanations of, and excuses for, the unsatisfactory functioning of hydrogen electrodes, with the consequence that many are the methods which have been advocated for the preparation of satisfactory electrodes. Probably the conditions which are most conducive to the production of good electrodes involve the deposition of a very thin layer of fairly coarse particles of platinum black upon a highly polished platinum surface. Many workers have preferred to deposit the " black " upon gold surfaces, and they have usually attributed the sluggishness of the electrodes in which they used platinum as basis metal, to the possible diffusion of hydrogen through the black coating into the metal. It is well known that, whereas metallic platinum has the power to adsorb hydrogen, gold does not adsorb hydrogen. The sluggishness experienced with platinised platinum electrodes was therefore held to be due to the slower rate at which equilibrium was attained with the hydrogen which had passed beyond the " black " layer. Though this may have had some effect it seems more likely to have been more a question of the metallic surface, and the superior surface of gold would account for certain workers' preference for gold as the supporting medium. It is interesting to recall that Böttger (*Z. physikal. Chem.*, 1897, **24**, 251), who was the first to carry out electrometric titrations with the hydrogen electrode, found platinised platinum unsuitable for the purpose, and on the advice of Wilhelm Ostwald resorted to gold electrodes coated with palladium black. Incidentally, Andrews (*J. Biol. Chem.*, 1924, **50**, 479) found that palladium black on platinum gave less reliable electrodes than platinised platinum. Gold, plated with palladium black, is also preferred by W. D. Treadwell and Weiss (*Helv. Chim. Acta*, 1920, **2**, 433). They state that for titration work the ordinary platinum electrode required too much time to come to equilibrium. Some workers have employed gold-plated platinum electrodes covered with platinum or palladium black. The gold plating is best carried out from a potassium cyanide solution of auric oxide which has been freshly precipi-

tated from gold chloride solution with a small quantity of ammonium hydroxide and washed.

Another method of preparing platinised platinum electrodes, in which an attempt was made to reduce the possibility of the slow diffusion of hydrogen into the metal, was to deposit on a glass surface, *e.g.*, a sealed glass tube, a continuous film of metallic platinum by carefully heating after a solution of platinic chloride and some organic reducing body had been uniformly applied. Thus Westhaver (*Z. physikal. Chem.*, 1905, **51**, 90) formed an iridium film on glass with the aid of an alcohol flame and a mixture prepared by dissolving 0·3 gram iridium chloride, which had been moistened with concentrated hydrochloric acid, in 1 c.c. of absolute alcohol saturated with boric acid, and then adding 1 c.c. Venetian turpentine and 2 c.c. of lavender oil. In order to burn platinum films on to the glass, solutions of platinic chloride have been used containing glycerin and also essence of camomile (Gooch and Burdick, *Amer. J. Science*, 1912, **34**, 107; Meillère, *J. pharm. chim.*, 1921, **21**, 311).

Calculation of Hydrogen-Ion Concentration and the Meaning of *p*H.

It was shown in an earlier paragraph that the E.M.F. of the hydrogen electrode with respect to a solution containing hydrogen ions was equal to 0·058 log [H·] at 18° to 20° C. Now the observed E.M.F. of a cell is the difference between the E.M.F's of the two electrodes, *i.e.*, E.M.F. observed

$$= E_{\text{N-calomel}} - E_{\text{hydrogen}}$$

$$= 0{\cdot}283 \quad - 0{\cdot}058 \log [H^{\cdot}]$$

Whence $$\log [H^{\cdot}] = \frac{0{\cdot}283 \quad - \text{observed E.M.F.}}{0{\cdot}058},$$

which for solutions containing less than 1 g.-mol. of hydrogen ions per litre will be negative, and equal to $-x$ (say). Hence $[H^{\cdot}] = 10^{-x}$; x is the negative power of concentration to the base 10, and is spoken of as the *p*H value. It is therefore equal to

$$-\log [H^{\cdot}] \text{ or } \log \frac{1}{[H^{\cdot}]};$$

hence $$p\text{H} = \frac{\text{observed E.M.F.} - \text{E.M.F. of calomel}}{0{\cdot}058}.$$

To put it more clearly: *p*H = 1 corresponds to a concentration of 10^{-1} gram-hydrogen-ions per litre, or M/10,

$$p\text{H} = 2, \text{ or } \frac{\text{M}}{100}, \; p\text{H} = 10, \text{ or } 10^{-10}\text{M},$$

or M/10,000,000,000. To suggest that one is able to measure such an infinitesimally small concentration of hydrogen ions appears to be ridiculous. The *p*H scale, however, does supply a useful and delicate scale of acidity and alkalinity, and it often happens that the adjustment of hydrogen-ion concentration to within narrow limits of this scale is the factor on which the success of a reaction may depend. Thus, for example, magnesium hydroxide cannot be precipitated until the hydrogen-ion concentration has been depressed to $10^{-10\cdot5}$, or *p*H 10·5 (*J. Chem. Soc.*, 1925, **127**, 2115).

Moreover, whatever may be the interpretation which eventually will be placed upon the voltages of the hydrogen electrode, the *p*H hydrogen-ion concentration scale will probably remain an exceedingly convenient one, for it is one which permits of the correlation of true acidity, or alkalinity, as indicated by the colorimetric changes of indicators, and by other electrodes—all of which, in the first place have to be standardised against the hydrogen electrode. Failing such a scheme, the acidity and alkalinity as obtained by either indicator or electrometric methods would have to be calculated in terms of potentials of hydrogen electrode. In a narrow sense, it may be held that this is all that is accomplished by the *p*H scale. Actually, it does considerably more, for as will be seen in later chapters the hydrogen-ion concentration concept provides an excellent means of studying the ionisation and neutralisation of weak acids and bases. As mentioned before, it is in regard to the behaviour of strong electrolytes that the ion-concentration idea is far from satisfactory, and should the concept of ion-activity gain general acceptance, then the above *p*H scale will be superseded by a *p*H scale of hydrogen-ion activity; values on which will differ slightly in magnitude from those on the present scale.

It now remains to show the relationship which these hydrogen-ion concentrations bear to acidity and alkalinity. Water dissociates electrolytically to an extremely small extent into hydrogen and hydroxyl ions. The product, K_w, of these concentrations, [H·] and [OH′], for any particular temperature is a fixed quantity, and is termed the *ionic product of water*. At 18° C., $K_w = 10^{-14\cdot13}$, and consequently, when pure water dissociates, $H_2O \rightleftharpoons H^{\cdot} + OH'$, into equal quantities of hydrogen and hydroxyl ions [H·] = [OH′], and therefore $[H^{\cdot}]^2 = 10^{-14\cdot13}$, or $[H^{\cdot}] = 10^{-7\cdot1}$. This means that at 18° C. exact neutrality corresponds to a hydrion concentration of $10^{-7\cdot1}$ or *p*H 7·1. The hydroxyl-ion concentration of a solution of *p*H 10 (say), i.e. $[H^{\cdot}] = 10^{-10}$, is therefore $[OH'] = 10^{-14\cdot2}/10^{-10} = 10^{-4\cdot2}$. Solutions are acid up to *p*H 7·1, and are alkaline, above.

Fig. 4 explains the origin of the E.M.F. of the cell in a somewhat clearer way. The positive potentials of the various calomel electrodes are shown above the arbitrary zero potential, *viz.*, E of $H_2|H^+$ (1 g.-mol. per litre) = 0, and the varying negative potentials of the hydrogen electrode in solutions containing less than 1 g.-mol. of hydrogen ions per litre, below. The concentrations of ions corresponding to the various voltages of the

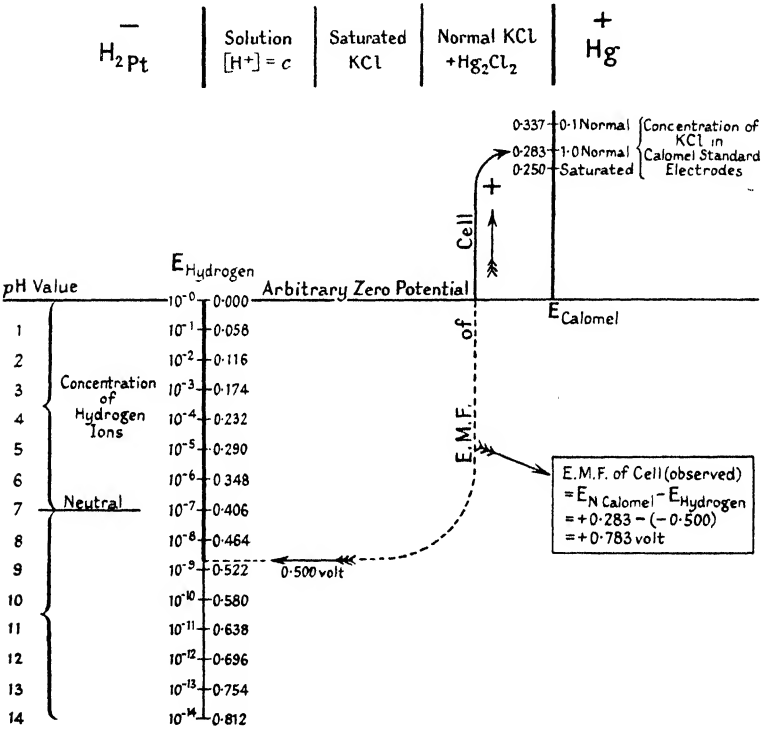


FIG. 4.—Variation in E.M.F. of Hydrogen-Calomel Cell with Hydrogen-ion Concentration at 18° to 20° C.

hydrogen electrode alone were calculated from $E_h = 0{\cdot}058 \log [H^+]$. Thus the arrows showing a P.D. of 0·783 volt (say) between the N-calomel electrode and hydrogen electrode immersed in a solution whose hydrion concentration is $10^{-8{\cdot}62} = 2{\cdot}4 \times 10^{-9}$ or pH = 8·62, indicate that − 0·500 volt was due to the hydrogen electrode from which these concentrations were found.

Ionic Product of Water.

In the foregoing calculations, we had occasion to consider the *ionic product of water*, and as this constant is of fundamental importance in the quantitative study of acidity and alkalinity we shall now give it some discussion. It is the outcome of the application of the law of mass action to the electrolytic dissociation of pure water; thus, the equation $H_2O \rightleftharpoons H^{\cdot} + OH'$ represents the main course of the dissociation of water—there is also an infinitesimally small concentration of oxygen ions, O'', but as we shall see in a later chapter, the further dissociation of the hydroxyl ions necessary to produce them is so small as to be without any practical significance here—and therefore on the grounds of the mass law

$$\frac{[H^{\cdot}] \times [OH']}{[H_2O]} = K,$$

whence $$K_w = K \times [H_2O] = [H^{\cdot}][OH'],$$

for the concentration of undissociated water can, in comparison with the extremely small portion which undergoes ionisation, be regarded as constant. Hence the constant, K_w, known as the ionic product of water, is equal to the true dissociation constant of water multiplied by the concentration of water in a litre, *viz.*, 1000/18 g. mols.

Values of K_w have been found in a variety of ways, the more important being those based on conductivity and electromotive force measurements. Kohlrausch and Heydweiller found the specific conductivity of pure water to be $0{\cdot}0384 \times 10^{-6}$ r.o's at 18° C. In pure water the concentrations of hydrogen ions and of hydroxyl ions are equal, and therefore

$$0{\cdot}0384 \times 10^{-6} = n(l_{H^{\cdot}} + l_{OH'}).$$

Knowing that the ionic mobility of the hydrogen ion, $l_{H^{\cdot}} = 314$, and that of the hydroxyl ion, $l_{OH'}$, is 174, the number of each ion, n, in 1 c.c. of water is given by

$$0{\cdot}0384 \times 10^{-6} = n(314 + 174),$$

whence $$n = 7{\cdot}86 \times 10^{-9}.$$

Hence the number of $H^{\cdot}$ ions in 1 litre, *i.e.*, $[H^{\cdot}]$, also the number of OH' ions, $[OH']$, is

$$1000 \times 7{\cdot}86 \times 10^{-9} = 7{\cdot}86 \times 10^{-6},$$

and therefore

$$K_w = (7{\cdot}86 \times 10^{-6})^2 = 0{\cdot}62 \times 10^{-14} = 10^{-14{\cdot}21}.$$

The ionisation of water, though very small, is affected by temperature changes to a marked extent. The reason for this

can be seen from calculations based on the van't Hoff isochore. It has been found experimentally that the neutralisation of strong acids by strong bases, *e.g.*, HCl, HNO_3, KOH and NaOH, at 20° C., results in the production of 13,700 calories when gram-equivalents of the acid and alkali are employed. In such cases the heat evolved happens to be numerically equal to the heat of ionisation of water, though opposite in sign, and it can therefore be substituted for U in the van't Hoff isochore, in order to calculate the variation in K_w which would be expected to occur for temperatures in the region of 20° C. (*i.e.*, 293° A.).

Hence

$$\frac{d \log_{10} K}{dT} = -\frac{U}{2{\cdot}303 \times R \times T^2} = -\frac{13700}{2{\cdot}303 \times 1{\cdot}988 \times (293)^2}$$
$$= -0{\cdot}0349,$$

where the factor 2·303 is introduced to convert the expression from hyperbolic to common logarithms and 1·988 is R in calories per degree. The negative value of the expression, — 0·0349, indicates that the formation of water from its ions has an increasing tendency not to reach completion, *i.e.*, to form undissociated water molecules, with rise in temperature. In other words, increased electrolytic dissociation into hydrogen and hydroxyl ions occurs with rise in temperature. Hence, we should expect K_w to increase in magnitude with rise in temperature. The calculation would suggest that the negative index would become more positive by 0·0349 per degree. The average of practical values obtained from 16° to 26° C. show that the actual increment per degree is 0·0340. This will be seen from the table on page 53, which gives the values of K_w and pK_w, *i.e.*, the negative exponent of K_w to the base 10, for temperatures from 16° to 40° C. They are taken from Michaelis' *Die Wasserstoffionen-Konzentration*, 1922, p. 23.

These figures show that temperature has an appreciable effect on K_w and therefore upon the hydrogen-ion concentrations corresponding to true neutrality at different temperatures. Thus at neutrality $[H^\cdot] = [OH']$, and therefore $[H^\cdot]^2 = K_w$ or

$$[H^\cdot] = \sqrt{K_w} = \sqrt{10^{-pK_w}} = 10^{-\frac{pK_w}{2}}.$$

Hence from Table 9 we see that $[H^\cdot]$ at neutrality at 16° C. is $10^{-7{\cdot}10}$ and becomes $10^{-6{\cdot}71}$ at 40° C. These negative indices are usually referred to as the *p*H value in the case of hydrogen-ion concentrations. In other words, the hydrogen-ion concentration at neutrality has a *p*H value of $\frac{1}{2}\ pK_w$. Some experimental

TABLE 9

Temperature °C.	$K_w \times 10^{14}$.	pK_w.
16	0·63	14·20
17	0·68	14·17
18	0·74	14·13
19	0·79	14·10
20	0·86	14·07
21	0·93	14·03
22	1·01	14·00
23	1·10	13·96
24	1·19	13·93
25	1·27	13·90
26	1·38	13·86
27	1·50	13·83
28	1·62	13·79
29	1·76	13·76
30	1·89	13·73
31	2·04	13·69
32	2·19	13·66
33	2·35	13·63
34	2·51	13·60
35	2·71	13·57
36	2·92	13·54
37	3·13	13·51
38	3·35	13·48
39	3·59	13·45
40	3·80	13·42

values of pK_w at more removed temperatures show that at 0° C. $pK_w = 14{\cdot}94$, and at 100° C. $pK_w = 12{\cdot}24$. For a fuller discussion of the many methods by which K_w has been found the student is referred to Lewis's *Text-Book of Physical Chemistry*.

Actual Number of Hydrogen Ions in Water.

Although in the measurement of acidity we do not concern ourselves with the actual number of hydrogen ions present, but merely with their concentration *expressed in terms of gram-ions or gram-molecules*, it is not without interest to consider for a moment the numbers of ions which produce the changes in acidity. One gram-molecule of any gas contains $6{\cdot}06 \times 10^{23}$ molecules. This value is the so-called Avogadro number, and is the direct result of Avogadro's hypothesis. The precise value given is probably accurate within 0·1 per cent. and is based on Millikan's determination of the electronic charge. Now we see from the previous paragraph that at ordinary temperatures, $K_w = 10^{-14}$ (approx.), and as in pure water the concentration of hydrogen ions, [H·], is equal to that of hydroxyl ions, [OH′], and consequently each is equal to 10^{-7} g.-mol. of ions per litre. Such a concentration of ions appears therefore to be composed of $10^{-7} \times 6{\cdot}06 \times 10^{23}$

$= 6{\cdot}06 \times 10^{16}$ hydrogen or hydroxyl ions, as the case may be, and these are contained in 1 litre of water. But 1 litre of water contains 1000/18 g.-mols. of water, each of which comprises $6{\cdot}06 \times 10^{23}$ molecules, and therefore the actual number of molecules of water in 1 litre

$$= \frac{1000}{18} \times 6{\cdot}06 \times 10^{23}$$

$$= 337 \times 10^{23} \text{ molecules of } H_2O.$$

From these $6{\cdot}06 \times 10^{16}$ hydrogen ions and $6{\cdot}06 \times 10^{16}$ hydroxyl ions are formed. Hence out of 337×10^{23} water molecules $6{\cdot}06 \times 10^{16}$ are electrolytically dissociated, and therefore of 556 million water molecules only one is ionised.

Nature of the Hydrogen Ion in Solution.

The precise nature of the hydrogen ion as it exists in aqueous solution is uncertain. If it were simply a positively charged hydrogen atom, then it would consist merely of the positive nucleus: in other words, a single proton. Whilst there is no doubt that the positive charge on a single hydrogen ion is the same as that of a proton, it is extremely unlikely that the hydrogen ion, as it exists in solution, is the same as a proton. There is every reason to believe that in aqueous solution the hydrogen ion is appreciably hydrated, but as to how great an extent there is, as yet, no definite knowledge. Yet several workers represent the hydrogen ion as $H_3O^{\cdot}$, as if it were hydrated by a single molecule of water only, instead of by x molecules, where x is unknown but is most probably much greater than one. It might be considered that Volmer's (*Liebig Annalen*, 1924, **440**, 200) X-ray study of the crystals of ammonium perchlorate and perchloric acid monohydrate, in which he showed that the crystals exhibited complete crystallographic agreement, provided evidence of the $H_3O^{\cdot}$ ion, the crystals being $NH_3.H^{\cdot}\ ClO'_4$ and $H_2O.H^{\cdot}\ ClO'_4$, *i.e.*, NH_4ClO_4 and H_3OClO_4. These conclusions apply to the crystalline state. It is quite another matter to assume that they are true of perchloric acid in solution. In this book, we shall represent the hydrogen ion in the conventional way, $H^{\cdot}$, it being tacitly assumed that $H^{\cdot}$ actually stands for $H^{\cdot}.xH_2O$.

*p*H Values.

We have seen that the potential of a hydrogen electrode, referred to the normal hydrogen electrode as being of zero potential, may be expressed by the following formula :—

$$E_{H_2} = 0{\cdot}0001984\ T \log [H^{\cdot}]$$

and therefore,

$$p\mathrm{H} = -\log [\mathrm{H}^{\cdot}] = \log \frac{1}{[\mathrm{H}^{\cdot}]} = \frac{-\mathrm{E}_{\mathrm{H}_2}}{0{\cdot}0001984\mathrm{T}},$$

consequently at 18° to 20° C.

$$p\mathrm{H} = -\frac{\mathrm{E}_{\mathrm{H}_2}}{0{\cdot}058}.$$

In view of the fact that for any particular temperature the product of the concentrations of hydrogen ions and of hydroxyl ions in any aqueous solution is of constant value, namely, K_w, we find that if the hydrogen-ion concentration be known then the hydroxyl-ion concentration can be easily calculated. Moreover, we are provided with a scheme by which the gradual transition of the reaction of a solution from acidity to alkalinity can be quantitatively mapped out in terms of decreasing hydrogen-ion concentrations, *i.e.*, increasing *p*H values, or in terms of increasing hydroxyl-ion concentrations, *i.e.*, decreasing *p*OH values. If we take the ionic product of water, K_w, to be equal to 10^{-14} at ordinary temperatures, we find that the hydroxyl-ion concentration of a solution containing 1 g.-mol. of hydrogen ions per litre, *i.e.*, 1M-H$^{\cdot}$ or 1N-H$^{\cdot}$, is equal to $\mathrm{K}_w/1 = 10^{-14}$ g.-mols. of hydroxyl ion per litre. Similarly, a solution decinormal with respect to hydrogen ions contains 10^{-13} g.-mols. of hydroxyl ions per litre, and, on the other hand, a solution decinormal with respect to hydroxyl ions will contain 10^{-13} g.-mols. of hydrogen ions. If we represent the negative exponent to the base 10 of hydroxyl-ion concentrations by the symbol *p*OH, and the negative index of the ionic product by $p\mathrm{K}_w$, then

$$p\mathrm{K}_w = p\mathrm{H} + p\mathrm{OH}.$$

As stated on page 49, true neutrality occurs when

$$p\mathrm{H} = p\mathrm{OH} = \tfrac{1}{2}\, p\mathrm{K}_w = 7,$$

and therefore *p*H 0 to *p*H 7 or *p*OH 14 to *p*OH 7, represents the range of diminishing acidity, and *p*H 7 to *p*H 14, or *p*OH 7 to *p*OH 0, corresponds to the range of increasing alkalinity at ordinary temperatures. In general, however, the different degrees of acidity are from *p*H 0 to $p\mathrm{H} = \frac{1}{2}\, p\mathrm{K}_w$, or, $p\mathrm{OH} = p\mathrm{K}_w$ to $p\mathrm{H} = \frac{1}{2}\, p\mathrm{K}_w$; and alkalinity, from $p\mathrm{H} = \frac{1}{2}\, p\mathrm{K}_w$ to $p\mathrm{H} = 14$, or, $p\mathrm{OH} = \frac{1}{2}\, p\mathrm{K}_w$ to $p\mathrm{OH} = 0$. Of course, in concentrated acid solutions the concentration of hydrogen ions will be greater than 1 molar, whence *p*H becomes negative, say $-x$, and therefore $p\mathrm{OH} = 14 + x$ at ordinary temperatures, and similarly for alkaline solutions containing greater concentrations of hydroxyl ions than 1M, $p\mathrm{OH} = -x$, whence $p\mathrm{H} = 14 + x$.

In Table 10 there is set out these hydrogen- and hydroxyl-ion concentrations, their respective *p*H or *p*OH values, and the

TABLE 10

VARIATIONS IN E.M.F. OF HYDROGEN AND QUINHYDRONE ELECTRODES WITH *p*H

	[H·].	[OH'].	*p*H.	*p*OH.	E.M.F. of Hydrogen Electrode against			E.M.F. of Quinhydrone Electrode against	
					Arb. Zero (N-Hyd.).	N-Calomel.	Sat. Cal.	Arb. Zero (N-Hyd.).	N-Calomel.
Acidity	1 (10°)	10^{-14}	0	14	0·000	−0·283	−0·250	+0·704	+0·421
	10^{-1}	10^{-13}	1	13	−0·058	−0·341	−0·308	+0·646	+0·363
	10^{-2}	10^{-12}	2	12	−0·116	−0·399	−0·366	+0·588	+0·305
	10^{-3}	10^{-11}	3	11	−0·174	−0·457	−0·424	+0·530	+0·247
	10^{-4}	10^{-10}	4	10	−0·232	−0·515	−0·482	+0·472	+0·189
	10^{-5}	10^{-9}	5	9	−0·290	−0·573	−0·540	+0·414	+0·131
	10^{-6}	10^{-8}	6	8	−0·348	−0·631	−0·598	+0·356	+0·073
Neutrality	10^{-7}	10^{-7}	7	7	−0·406	−0·689	−0·656	+0·298	+0·015
Alkalinity	10^{-8}	10^{-6}	8	6	−0·464	−0·747	−0·714	+0·240	−0·043
	10^{-9}	10^{-5}	9	5	−0·522	−0·805	−0·772	+0·180	−0·101
	10^{-10}	10^{-4}	10	4	−0·580	−0·863	−0·830		
	10^{-11}	10^{-3}	11	3	−0·638	−0·921	−0·888		
	10^{-12}	10^{-2}	12	2	−0·696	−0·979	−0·946		
	10^{-13}	10^{-1}	13	1	−0·754	−1·037	−1·004		
	10^{-14}	1 (10°)	14	0	−0·812	−1·095	−1·062		

E.M.F's of hydrogen and quinhydrone electrodes, to which they give rise, both referred to the normal hydrogen electrode as arbitrary zero, and also to the normal calomel electrode. The voltages of the hydrogen electrode are also compared with that of the saturated calomel electrode. These figures were calculated for temperatures 18° to 20° C. from the formulæ

$$E_{H_2} = 0{\cdot}058 \log [H^{\cdot}]$$

and

$$E_{observed} = E_{calomel} - E_{H_2},$$

denoting the E.M.F. produced when the hydrogen electrode is incorporated in a cell, the other pole of which is a standard calomel. It will be seen that with each increasing *p*H unit, the E.M.F. of both the hydrogen and the quinhydrone (see later) electrodes become more negative or smaller by 58 millivolts, as will be understood from the formula.

It should always be remembered that the *p*H notation is merely

TABLE II

HYDROGEN-ION CONCENTRATIONS CORRESPONDING TO
*p*H $n{\cdot}00$—*p*H $(n+1){\cdot}00$

*p*H.	[H·].	*p*H.	[H·].	*p*H.	[H·].
$n{\cdot}00$	$1{\cdot}00 \times 10^{-n}$	$n{\cdot}34$	$0{\cdot}46 \times 10^{-n}$	$n{\cdot}68$	$0{\cdot}21 \times 10^{-n}$
$n{\cdot}01$	$0{\cdot}98 \times 10^{-n}$	$n{\cdot}35$	$0{\cdot}45 \times 10^{-n}$	$n{\cdot}69$	$0{\cdot}20 \times 10^{-n}$
$n{\cdot}02$	$0{\cdot}96 \times 10^{-n}$	$n{\cdot}36$	$0{\cdot}44 \times 10^{-n}$	$n{\cdot}70$	$0{\cdot}20 \times 10^{-n}$
$n{\cdot}03$	$0{\cdot}93 \times 10^{-n}$	$n{\cdot}37$	$0{\cdot}43 \times 10^{-n}$	$n{\cdot}71$	$0{\cdot}20 \times 10^{-n}$
$n{\cdot}04$	$0{\cdot}91 \times 10^{-n}$	$n{\cdot}38$	$0{\cdot}42 \times 10^{-n}$	$n{\cdot}72$	$0{\cdot}19 \times 10^{-n}$
$n{\cdot}05$	$0{\cdot}89 \times 10^{-n}$	$n{\cdot}39$	$0{\cdot}41 \times 10^{-n}$	$n{\cdot}73$	$0{\cdot}18 \times 10^{-n}$
$n{\cdot}06$	$0{\cdot}87 \times 10^{-n}$	$n{\cdot}40$	$0{\cdot}40 \times 10^{-n}$	$n{\cdot}74$	$0{\cdot}18 \times 10^{-n}$
$n{\cdot}07$	$0{\cdot}85 \times 10^{-n}$	$n{\cdot}41$	$0{\cdot}39 \times 10^{-n}$	$n{\cdot}75$	$0{\cdot}18 \times 10^{-n}$
$n{\cdot}08$	$0{\cdot}83 \times 10^{-n}$	$n{\cdot}42$	$0{\cdot}38 \times 10^{-n}$	$n{\cdot}76$	$0{\cdot}17 \times 10^{-n}$
$n{\cdot}09$	$0{\cdot}81 \times 10^{-n}$	$n{\cdot}43$	$0{\cdot}37 \times 10^{-n}$	$n{\cdot}77$	$0{\cdot}17 \times 10^{-n}$
$n{\cdot}10$	$0{\cdot}80 \times 10^{-n}$	$n{\cdot}44$	$0{\cdot}36 \times 10^{-n}$	$n{\cdot}78$	$0{\cdot}17 \times 10^{-n}$
$n{\cdot}11$	$0{\cdot}78 \times 10^{-n}$	$n{\cdot}45$	$0{\cdot}35 \times 10^{-n}$	$n{\cdot}79$	$0{\cdot}16 \times 10^{-n}$
$n{\cdot}12$	$0{\cdot}76 \times 10^{-n}$	$n{\cdot}46$	$0{\cdot}35 \times 10^{-n}$	$n{\cdot}80$	$0{\cdot}16 \times 10^{-n}$
$n{\cdot}13$	$0{\cdot}74 \times 10^{-n}$	$n{\cdot}47$	$0{\cdot}34 \times 10^{-n}$	$n{\cdot}81$	$0{\cdot}15 \times 10^{-n}$
$n{\cdot}14$	$0{\cdot}73 \times 10^{-n}$	$n{\cdot}48$	$0{\cdot}33 \times 10^{-n}$	$n{\cdot}82$	$0{\cdot}15 \times 10^{-n}$
$n{\cdot}15$	$0{\cdot}71 \times 10^{-n}$	$n{\cdot}49$	$0{\cdot}32 \times 10^{-n}$	$n{\cdot}83$	$0{\cdot}15 \times 10^{-n}$
$n{\cdot}16$	$0{\cdot}69 \times 10^{-n}$	$n{\cdot}50$	$0{\cdot}32 \times 10^{-n}$	$n{\cdot}84$	$0{\cdot}14 \times 10^{-n}$
$n{\cdot}17$	$0{\cdot}68 \times 10^{-n}$	$n{\cdot}51$	$0{\cdot}31 \times 10^{-n}$	$n{\cdot}85$	$0{\cdot}14 \times 10^{-n}$
$n{\cdot}18$	$0{\cdot}66 \times 10^{-n}$	$n{\cdot}52$	$0{\cdot}30 \times 10^{-n}$	$n{\cdot}86$	$0{\cdot}14 \times 10^{-n}$
$n{\cdot}19$	$0{\cdot}65 \times 10^{-n}$	$n{\cdot}53$	$0{\cdot}30 \times 10^{-n}$	$n{\cdot}87$	$0{\cdot}13 \times 10^{-n}$
$n{\cdot}20$	$0{\cdot}63 \times 10^{-n}$	$n{\cdot}54$	$0{\cdot}29 \times 10^{-n}$	$n{\cdot}88$	$0{\cdot}13 \times 10^{-n}$
$n{\cdot}21$	$0{\cdot}62 \times 10^{-n}$	$n{\cdot}55$	$0{\cdot}28 \times 10^{-n}$	$n{\cdot}89$	$0{\cdot}13 \times 10^{-n}$
$n{\cdot}22$	$0{\cdot}60 \times 10^{-n}$	$n{\cdot}56$	$0{\cdot}28 \times 10^{-n}$	$n{\cdot}90$	$0{\cdot}13 \times 10^{-n}$
$n{\cdot}23$	$0{\cdot}59 \times 10^{-n}$	$n{\cdot}57$	$0{\cdot}27 \times 10^{-n}$	$n{\cdot}91$	$0{\cdot}12 \times 10^{-n}$
$n{\cdot}24$	$0{\cdot}58 \times 10^{-n}$	$n{\cdot}58$	$0{\cdot}26 \times 10^{-n}$	$n{\cdot}92$	$0{\cdot}12 \times 10^{-n}$
$n{\cdot}25$	$0{\cdot}56 \times 10^{-n}$	$n{\cdot}59$	$0{\cdot}26 \times 10^{-n}$	$n{\cdot}93$	$0{\cdot}12 \times 10^{-n}$
$n{\cdot}26$	$0{\cdot}55 \times 10^{-n}$	$n{\cdot}60$	$0{\cdot}25 \times 10^{-n}$	$n{\cdot}94$	$0{\cdot}12 \times 10^{-n}$
$n{\cdot}27$	$0{\cdot}54 \times 10^{-n}$	$n{\cdot}61$	$0{\cdot}25 \times 10^{-n}$	$n{\cdot}95$	$0{\cdot}11 \times 10^{-n}$
$n{\cdot}28$	$0{\cdot}53 \times 10^{-n}$	$n{\cdot}62$	$0{\cdot}24 \times 10^{-n}$	$n{\cdot}96$	$0{\cdot}11 \times 10^{-n}$
$n{\cdot}29$	$0{\cdot}51 \times 10^{-n}$	$n{\cdot}63$	$0{\cdot}23 \times 10^{-n}$	$n{\cdot}97$	$0{\cdot}11 \times 10^{-n}$
$n{\cdot}30$	$0{\cdot}50 \times 10^{-n}$	$n{\cdot}64$	$0{\cdot}23 \times 10^{-n}$	$n{\cdot}98$	$0{\cdot}11 \times 10^{-n}$
$n{\cdot}31$	$0{\cdot}49 \times 10^{-n}$	$n{\cdot}65$	$0{\cdot}22 \times 10^{-n}$	$n{\cdot}99$	$0{\cdot}10 \times 10^{-n}$
$n{\cdot}32$	$0{\cdot}48 \times 10^{-n}$	$n{\cdot}66$	$0{\cdot}22 \times 10^{-n}$	$(n+1){\cdot}00$	$0{\cdot}10 \times 10^{-n}$
$n{\cdot}33$	$0{\cdot}47 \times 10^{-n}$	$n{\cdot}67$	$0{\cdot}21 \times 10^{-n}$		

a convenient method of representing hydrogen-ion concentrations, which are related to one another by the equation

$$[H^{\cdot}] = 10^{-p\mathrm{H}}.$$

Very often the *p*H scale of acidity is compared with a thermometric scale of temperature. The analogy is superficial, for each unit of increase in the *p*H value corresponds to a diminution in hydrogen-ion concentration by one-tenth of the concentration indicated by the preceding *p*H value—in other words, the *p*H scale represents the hydrion concentrations given by the terms of a geometrical progression whose first term is 1 and the ratio,

$\frac{1}{10}$. Moreover, this is true of the successive tenth and hundredth divisions of each individual *p*H unit. In Table 11 are given the hydrogen-ion concentrations corresponding to *p*H values, *n*·00 to *n* + 1·00, where *n* is any *p*H integer (see also the Appendix).

These data are plotted in Fig. 5. They show that each succeeding tenth division of a *p*H unit represents differing and increasingly smaller decreases in the concentration of hydrogen ions. Thus, it happens that an increase of 0·5 *p*H unit from *p*H *n*·0 to *p*H *n*·5 refers to a fall in hydrion concentration of 68 per

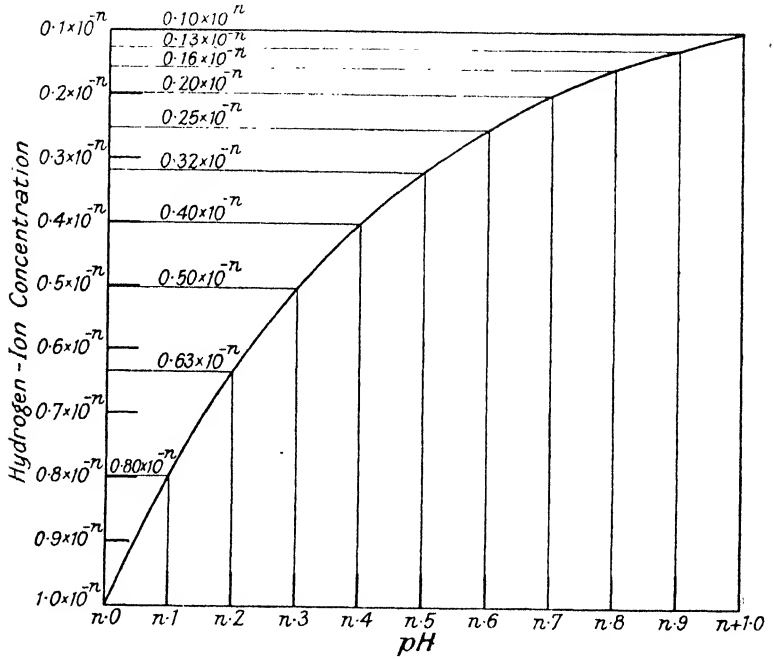


FIG. 5.—Relationship between *p*H and Hydrogen-Ion Concentration.

cent. of the concentration indicated by *p*H *n*, whereas the increase of a further 0·5 *p*H unit from *p*H *n*·5 to *p*H *n* + 1·0 brings about a diminution of less than a third of that amount, namely, 22 per cent.

Table 12 gives examples of the hydrogen- and hydroxyl-ion concentrations, together with their *p*H and *p*OH values of certain acids and bases at different dilutions at 18° C. The *p*OH values and hydroxyl-ion concentrations were derived from $pK_w = 14{\cdot}13$ (Table 3).

TABLE 12

HYDROGEN-ION CONCENTRATIONS AND *p*H VALUES OF ACIDS AND BASES

Electrolyte.	[H·].	*p*H.	[OH'].	*p*OH.
N-HCl	$8{\cdot}0 \times 10^{-1}$	0·10	$9{\cdot}3 \times 10^{-15}$	14·03
0·1 N-HCl	$8{\cdot}5 \times 10^{-2}$	1·07	$8{\cdot}7 \times 10^{-14}$	13·06
0·01 N-HCl	$9{\cdot}6 \times 10^{-3}$	2·02	$7{\cdot}8 \times 10^{-13}$	12·11
0·001 N-HCl	$9{\cdot}8 \times 10^{-4}$	3·01	$7{\cdot}6 \times 10^{-12}$	11·12
0·0001 N-HCl	$9{\cdot}8 \times 10^{-5}$	4·01	$7{\cdot}6 \times 10^{-11}$	10·12
N-CH_3COOH	$4{\cdot}3 \times 10^{-3}$	2·37	$1{\cdot}7 \times 10^{-12}$	11·76
0·1 N-CH_3COOH	$1{\cdot}3 \times 10^{-3}$	2·87	$5{\cdot}5 \times 10^{-12}$	11·26
0·01 N-CH_3COOH	$4{\cdot}3 \times 10^{-4}$	3·37	$1{\cdot}7 \times 10^{-11}$	10·76
0·001 N-CH_3COOH	$1{\cdot}3 \times 10^{-4}$	3·87	$5{\cdot}5 \times 10^{-11}$	10·26
0·1 N-H_2SO_4	$5{\cdot}9 \times 10^{-2}$	1·23	$1{\cdot}3 \times 10^{-13}$	12·90
N-NaOH	$8{\cdot}9 \times 10^{-15}$	14·05	$8{\cdot}3 \times 10^{-1}$	0·08
0·1 N-NaOH	$8{\cdot}5 \times 10^{-14}$	13·07	$8{\cdot}7 \times 10^{-2}$	1·06
0·01 N-NaOH	$7{\cdot}6 \times 10^{-13}$	12·12	$9{\cdot}8 \times 10^{-3}$	2·01
0·001 N-NaOH	$7{\cdot}4 \times 10^{-12}$	11·13	$1{\cdot}0 \times 10^{-3}$	3·00
N-NH_4OH	$1{\cdot}7 \times 10^{-12}$	11·77	$4{\cdot}4 \times 10^{-3}$	2·36
0·1 N-NH_4OH	$5{\cdot}4 \times 10^{-12}$	11·27	$1{\cdot}4 \times 10^{-3}$	2·86
0·01 N-NH_4OH	$1{\cdot}7 \times 10^{-11}$	10·77	$4{\cdot}4 \times 10^{-4}$	3·36
0·001 N-NH_4OH	$5{\cdot}4 \times 10^{-11}$	10·27	$1{\cdot}4 \times 10^{-4}$	3·86

Corrections to be Applied to Hydrogen Electrode E.M.F. Measurements for Aqueous Vapour Pressure and Variations in Atmospheric Pressure.

In our discussions on page 10 of the mathematical interpretations which are placed upon the potentials existing between a metal and a solution, we postulated the existence of an electrolytic solution pressure acting at the electrode surface tending to cause atoms to pass into solution in the form of ions. This pressure was believed to be counteracted by the osmotic pressure of the same ions which were already in solution through the dissociation of a salt. Thus, if P be the electrolytic solution pressure and p the osmotic pressure of the cations, then

$$E = \frac{RT}{F} \log_e \frac{p}{P}.$$

In the case of a metal electrode, this electrolytic solution pressure is an intrinsic property of the metal, whereas with gas electrodes it is also dependent upon the pressure of the gas surrounding the adsorbing electrode. Thus at the interface of hydrogen gas and platinum black, an equilibrium is set up between the molecules of hydrogen and the molecules of gas adsorbed by the ' black,' and these in turn enter into equilibrium with atoms which are supposed to exist therein, a proportion of which auto-

matically becomes ionised through the catalysing action of the finely divided platinum. This series of equilibria may be represented schematically :—

H_2	$\rightleftharpoons$	H_2	$\rightleftharpoons$	$2H$	$\rightleftharpoons$	$2H^{\cdot}$
Gas phase.		Platinum black.		Atoms in ' black.'		Ions at ' black '-liquid interface.

If these equilibria are all interdependent, then the pressure of the hydrogen surrounding the electrode may be expected to have some influence upon the electromotive activity of the hydrogen electrode. For ordinary routine work, errors from this source will generally be of negligible dimensions, but as such errors are produced, they must be taken into account in the case of hydrogen electrode measurements of a high degree of precision and therefore will here be considered. If hydrogen be passed through the electrode vessel very slowly, then the pressure inside the vessel will be equal to that of the atmosphere, with the exception that the gas after bubbling slowly through an aqueous solution into the gas space will have become saturated, or very nearly so, with water vapour. The pressure of hydrogen in contact with the electrode will be partial and will be equal to the atmospheric pressure, as indicated by the barometer, less that of water vapour required to saturate air at the temperature at which the experiment is being performed.

In order to evaluate the correction involved in working at hydrogen pressures other than 1 atmosphere (760 mm. mercury pressure), we shall consider the E.M.F. of a cell in which two hydrogen electrodes dip into the same solution ; the pressures of the hydrogen surrounding the two electrodes being π_1 and π_2 atmospheres, giving rise to the respective electrolytic solution pressures P_1 and P_2, and therefore to the individual electrode potentials E_1 and E_2 respectively, with regard to the solution. Now, we see from the above expression that if $P_1 > P_2$, then $E_2 > E_1$, and conversely, if $P_1 < P_2$, then $E_2 < E_1$. The E.M.F. of the cell comprises the difference $E_2 - E_1$ in the first instance, and $E_1 - E_2$ in the second.

Hence, if $E_2 > E_1$

$$\begin{aligned} \text{E.M.F.}_{(\text{observed})} &= E_2 - E_1 \\ &= \frac{RT}{F} \log_e \frac{p}{P_2} - \frac{RT}{F} \log_e \frac{p}{P_1} \\ &= \frac{RT}{F} \log_e \frac{P_1}{P_2}. \end{aligned}$$

Now $$\frac{[H^{\cdot}]}{[H]} = k_1,$$

and $H_2 \underset{\text{(in black)}}{\rightleftharpoons} 2H$ $$\therefore \frac{[H]^2}{[H_2]_{(\text{black})}} = k_2,$$

and $$H_2 \underset{\text{gas}}{\rightleftharpoons} \underset{\text{(in black)}}{H_2}, \qquad \therefore \frac{[H_2]_{\text{black}}}{[H_2]_{\text{gas}}} = k_3,$$

we find that $$[H^{\cdot}]^2 = k_1^2 k_2 k_3 [H_2]_{\text{gas}}.$$

$$i.e., \; [H^{\cdot}] = \sqrt{\lambda}.\sqrt{[H_2]_{\text{gas}}}, \text{ or } P = \sqrt{K} \cdot \sqrt{\pi}.$$

As each of the above quantities expressed in square brackets refer to pressures of hydrogen in either the molecular, atomic or ionic state, we find that the electrolytic solution pressure, *i.e.*, P, is proportional to the square root of the pressure of the hydrogen gas in the electrode vessel $= \pi$. Hence the observed

$$\text{E.M.F.} = E_2 - E_1 = \frac{RT}{F} \log_e \frac{P_1}{P_2}$$

$$= \frac{RT}{F} \log_e \frac{\sqrt{K} \cdot \sqrt{\pi_1}}{\sqrt{K} \cdot \sqrt{\pi_2}} = \frac{RT}{2F} \log_e \frac{\pi_1}{\pi_2},$$

and therefore if E_1 be produced by a hydrogen electrode with hydrogen pressure equal to 1 atmosphere, and E_2 the potential set up by another hydrogen electrode, whose hydrogen pressure is π atmospheres, both immersed in the same solution, then the difference in potential between these two electrodes gives the correction which should be applied to measurements performed with a hydrogen electrode not served with hydrogen at exactly one atmosphere pressure. The correction is thus

$$E_{\text{pressure}} = \frac{RT}{2F} \log_e \frac{1}{\pi}$$

$$= \frac{0{\cdot}0001984T}{2} \log_{10} \frac{1}{\pi}$$

$$= 0{\cdot}0000992T \log \frac{1}{\pi}.$$

When π is less than 1, then E is positive; and negative when π is greater than one atmosphere. We may therefore write

$$E_{\text{pressure}} = E_{\text{uncorrected}} - E_{\text{corrected}},$$

and therefore $$E_{\text{uncorrected}} = E_{\text{corrected}} + E_{\text{pressure}}.$$

Hence the P.D's between a hydrogen electrode at pressure π and a standard calomel electrode are equal to

$$\begin{aligned}\text{E.M.F.}_{\text{cell}} &= E_{\text{calomel}} - E_{\text{H, uncorrected}} \\ &= E_{\text{calomel}} - (E_{\text{H, corrected}} + E_{\text{pressure}}) \\ &= E_{\text{calomel}} - E_{\text{H, corrected}} - E_{\text{pressure}} \\ &= E_{\text{calomel}} - 0{\cdot}0001984T \log [H^{\cdot}] - 0{\cdot}0000992T \log \frac{1}{\pi},\end{aligned}$$

whence

$$pH = \frac{\text{E.M.F.}_{\text{cell}} - E_{\text{calomel}} + 0{\cdot}0000992T \log \frac{1}{\pi}}{0{\cdot}0001984T}.$$

The standard atmospheric pressure is that which is produced by a column of mercury 760 mm. in height at 0° C. acting downwards on a square centimetre. On account of the expansion which mercury undergoes with temperature, it is evident that this column will increase in height, and consequently a pressure equal to 760 mm. mercury at 0° C. will be produced by a column slightly higher at a higher temperature. Strictly speaking, therefore, all barometric heights should be corrected for expansion in order to make them comparable. In hydrogen electrode measurements the error involved in omitting this correction is usually much less than 1 millivolt. Another point to remember is that this so-called unit atmospheric pressure refers only to the latitude 45° where the 1 gram weight is equal to a force of 980·6 dynes, thus defining the unit atmosphere in absolute units as $76 \times 13{\cdot}596 \times 980{\cdot}6 = 1{,}013{,}300$ dynes per sq. cm.

The pressure correction when pressures are expressed in terms of barometric heights becomes

$$E_{\text{pressure}} = 0{\cdot}0000992T \log \frac{760}{x}.$$

Table 13 gives the magnitude of this correction for a series of temperatures ranging from 10° to 40° C. corresponding to barometric readings of 760, 740 and 780 mm. taken at the respective temperatures, from which were deducted the appropriate tensions of saturated water vapour.

The effect of hydrogen pressures up to 1½ atmospheres has been investigated by Lewis and Randall (*J. Amer. Chem. Soc.*, 1914, **36**, 1969), Loomis and Acree (*ibid.*, 1916, **38**, 2391) and Ellis (*ibid.*, p. 737), whilst Hainsworth, Rowley and MacInnes (*ibid.*, 1924, **46**, 1437) have worked with pressures up to, and over, 1000 atmospheres.

TABLE 13

TYPICAL PRESSURE CORRECTIONS OF HYDROGEN ELECTRODE POTENTIALS

Temperature °C.		10	15	18	20	25	30	35	40
Vapour Pressure.		9·2	12·8	15·5	17·5	23·8	31·8	42·2	55·3
Error volt for B.H.	(*a*) 760	0·0001	0·0002	0·0003	0·0003	0·0006	0·0006	0·0008	0·0010
	(*b*) 740	0·0004	0·0005	0·0006	0·0006	0·0008	0·0009	0·0011	0·0014
	(*c*) 780	−0·0002	−0·0001	−0·0001	0·0000	0·0002	0·0002	0·0004	0·0006

These figures show that for ordinary practical purposes no appreciable error is likely to be made by neglecting to make the pressure correction.

The potential given by

$$E_{\text{pressure}} = \frac{RT}{2F} \log_e \frac{1}{\pi}$$

thus gives the difference between that of the hydrogen electrode at a gaseous pressure, π atmospheres, and that with hydrogen at one atmosphere pressure, when both are immersed in the same solution, the hydrogen-ion concentration of which is $[H^\cdot]$. The potential of the latter electrode when referred to that of the arbitrary standard, *i.e.*, when $\pi = 1$ and $[H^\cdot] = 1$, is equal to $\frac{RT}{F} \log_e [H^\cdot]$, whence it follows that the hydrogen electrode at pressure, π, and in equilibrium with hydrogen-ions of concentration, $[H^\cdot]$, when referred to Normal Hydrogen Electrode (N . H = 0), must have a potential, E_π, given by

$$\begin{aligned} E_\pi &= \frac{RT}{F} \log_e [H^\cdot] + \frac{RT}{2F} \log_e \frac{1}{\pi} \\ &= \frac{RT}{F} \log_e \frac{[H^\cdot]}{\sqrt{\pi}} \\ &= \frac{2{\cdot}3026RT}{2F} \{ - \log_{10} \pi + 2 \log_{10} [H^\cdot] \} \\ &= \frac{2{\cdot}3026RT}{2F} \{ r\mathrm{H} - 2p\mathrm{H} \}, \end{aligned}$$

rH being $- \log_{10} \pi$ or $\log_{10} \frac{1}{\pi}$. (Compare p. 19)

Glasstone's Modified Hydrogen Electrode.

Glasstone (*Analyst*, 1925, **50**, 327) suggested a method for the approximate determination of hydrogen-ion concentration, especially in solutions containing oxidising agents that incapacitate the ordinary hydrogen electrode. It can only be applied to solutions more acid than *p*H 3 and more alkaline than *p*H 11, but may be used for solutions of intermediate *p*H *if these solutions are well-buffered.* We have seen that the potential of a hydrogen electrode in equilibrium with a solution containing hydrions of concentration [H·] is given at 20° C. by

$$E = 0{\cdot}058 \log [H^{\cdot}].$$

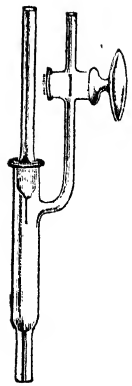
If the electrode process were strictly reversible, then this potential would also be that of the cathode which potential on passing an electric current through a solution would have to be reached before the evolution of hydrogen gas at atmospheric pressure could commence. Caspari (*Z. physikal. Chem.*, 1899, **30**, 89) found, however, that the cathodic potential at which evolution began depended upon the nature of the electrode itself. Usually, more negative potentials have to be applied, and the differences between them and the calculated values are known as "overvoltages." It happens, however, that when a platinised platinum cathode is used in acid solutions the "overvoltage" is almost zero, and it is this property that Glasstone has used. Two electrodes of platinum are used, the one to serve as anode, being a short piece of bright wire, and the other as cathode, either a small piece of platinised foil or wire about 1 cm. long. These electrodes are placed in the liquid under examination, and a gradually increasing polarising current applied from a battery of accumulators connected across a variable resistance until bubbles of hydrogen gas are just seen to be evolved at the cathode. When the potential has been adjusted such that the rate of evolution is not more than one bubble per minute, the cathode potential is measured against a saturated calomel electrode. The end of the connecting tube of the standard electrode was packed with cotton wool, and in order to overcome any errors due to the resistance of the solution he placed the tip of the standard electrode as close as possible to the polarised cathode during the measurement of the difference in potential between these two poles.

This polarised hydrogen electrode appeared to come to equilibrium with solutions containing large proportions of ethyl alcohol. It was inapplicable for the electrometric titration of acid by an alkali, due to the fact that the rate of removal of

hydrogen ions from the vicinity of the platinised platinum electrode was greater than their rate of replacement, with the result that the catholyte showed an enhanced *p*H.

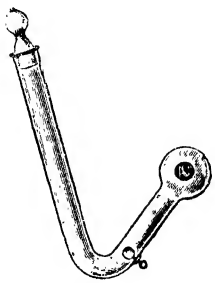
Hydrogen Electrode Vessels.

Considerably more attention has been given to the form of electrode vessel than to the more important, but more exasperating, problem of the electrode itself. Different ideas regarding the factors which various workers believe to determine the accurate functioning of the hydrogen electrode underlie many of the vessel designs, some of which are illustrated in Fig. 6. There is probably no greater accuracy to be obtained from electrodes contained in these vessels than from the simple electrode described on page 143, provided that a satisfactory sorptive coating has been deposited upon the electrode. Two disadvantages of the Hildebrand form, however, are that it is extravagant in regard to the supply of pure hydrogen, and that unless the ' black ' coating is satisfactory the oxygen dissolved through exposure of the solution to the air may lead to erroneous E.M.F's. Oxygen is often present in solutions to be examined, especially biological fluids, *e.g.*, blood, so that this difficulty may also arise in closed vessels, and the oxygen therefore will probably be reduced by the electrode hydrogen. The exclusion of air may readily be effected as in the Bunker form (*J. Biol. Chem.*, 1920, **41**, 11), which is an adaptation of the Hildebrand bubbling electrode. Some workers, *e.g.*, Michaelis, Walpole, and Monier-Williams, saturate the platinised platinum wire electrode with hydrogen and then allow the end to impinge upon the surface of the solution being tested, thereby setting up a localised equilibrium with the immediate film of liquid. Walpole's vessel (*Biochem. J.*, 1913, **7**, 410; 1914, **8**, 131) comprises a tube, passing through the closed upper end of which is a platinum wire electrode sealed into glass, fitted with a side tube which can be used either to pass hydrogen into the electrode chamber, or to suck up liquid, by means of the syringe, through the tube at the bottom from a solution into which it dips. The Monier-Williams vessel is similar (*The Analyst*, 1921, **46**, 315). A platinum wire is fixed into the left-hand compartment and the liquid sucked up into the vessel through the right-hand tube, and then hydrogen passed into the vessel until the level of the solution is that of the end of the electrode wire. Moloney (*J. Physical Chem.*, 1921, **25**, 758) uses an electrode of the bubbling type. By means of a loop of glass rod placed around the electrode wire, and attached to the glass tube into which the electrode is sealed, Moloney obtains a drop of the test-liquid

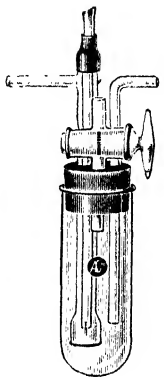


Walpole.

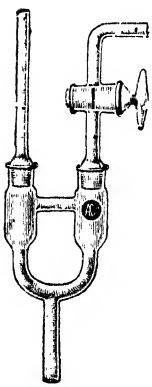
Walpole Filler.



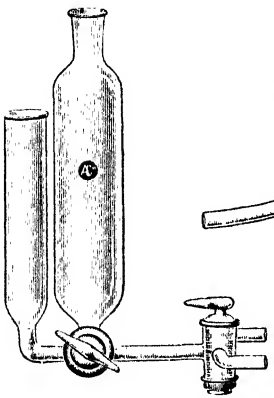
Bailey.



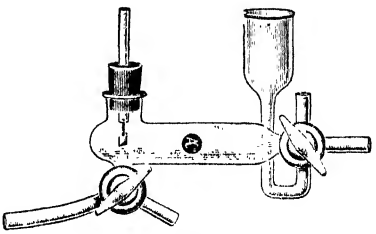
Bunker (modified).



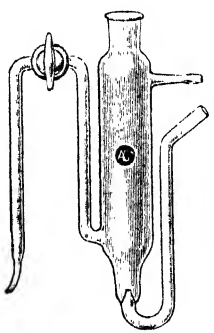
Monier-Williams.



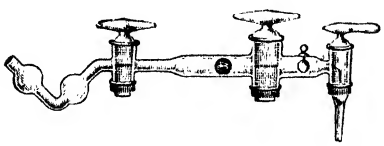
Clark Connecting Vessel.



Clark Electrode.



Gas Electrode.



McClendon.

FIG. 6.—Some Types of Hydrogen Electrode Vessels.

which, whilst being stationary, is small enough to ensure the rapid attainment of equilibrium. It should be emphasised that in the case of electrodes which depend upon localised equilibrium, the liquid should be perfectly still whilst reading the potentiometer. With certain platinum black layers the oscillation of the E.M.F. produced can be observed as each bubble of gas leaves the vicinity of the electrode. McClendon's electrode (*J. Biol. Chem.*, 1916, **24**, 519) is a convenient form for blood work and prevents the loss of carbon dioxide. It has a platinised gold electrode. The Bailey electrode vessel (*J. Amer. Chem. Soc.*, 1920, **42**, 45) has become very popular—probably on account of its simplicity (see Fig. 6). It contains platinised gold foil as the electrode, and readings are taken while the electrode is completely immersed. To use it, sufficient liquid is placed in the open arm to fill it completely, so that on tilting the tube, the liquid flows backwards into the bulb and a little remains in the open arm. Hydrogen is then led in through a narrow tube dipping into the solution. This is allowed to raise the solution into the open arm, and after adding more solution, if necessary, to drive out any air, the ground glass stopper is inserted and the tube shaken vigorously for two minutes. Afterwards, the solution is allowed to cover the foil and is then connected in the usual way to a calomel electrode. Shaking undoubtedly facilitates equilibrium, and this, together with the fact that repeated exposure of the electrode to the hydrogen gas, followed by immersion in the liquid (see p. 43), assists the catalytic reducing action of the hydrogen in the platinum "black" are the principles upon which the electrode vessels of Hasselbalch (*Biochem. Zeitsch.*, 1913, **49**, 451) and Clark (*J. Biol. Chem.*, 1915, **23**, 475) have been based. The Clark vessel shown in Fig. 6 is mounted on a cam, driven by a small motor, so as to give a continuous rocking motion. Hydrogen is led in at the right and connexion with the "salt bridge" is effected by opening the tap shown on the left. This is connected by means of a rubber tube to the connecting vessel shown, the larger chamber containing a saturated potassium chloride solution which can pass into the smaller vessel into which is dipped the end of a calomel electrode. (For picture of complete apparatus, see Fig. 161, Vol. II.) The gas electrode vessel, given in Fig. 6, is useful for solutions from which air must be excluded. The usual electrode is fixed into a rubber bung and gas is passed in through the tube at the bottom, thence through the solution and emerges through the right-hand tube. To this tube is connected a bubbler to prevent access of air, the tube just dipping below the surface of the liquid, *e.g.*, mercury, in

order that it may have no appreciable effect upon the pressure of hydrogen in the electrode vessel.

Fig. 7 refers to three recent electrode vessels, due to Lindsey (*Analyst*, 1932, **57**, 573), Lockwood (see page 43) and Frediani

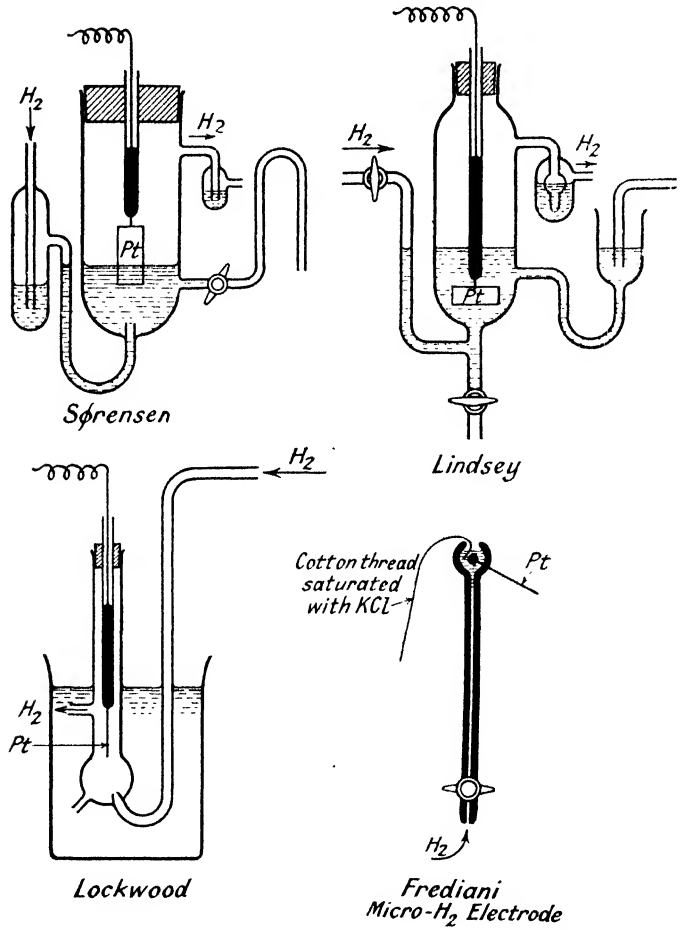


FIG. 7.—Further Types of Hydrogen Electrode Vessels.

(*Ind. Eng. Chem., Anal. Edn.*, 1939, **11**, 53). Lindsey's vessel is a modification of Sørensen's original vessel, also shown in Fig. 7. The hydrogen outlet traps are placed at right angles to the plane of the paper and not in the same plane as indicated.

Frediani's electrode is of interest in that it was designed for

use with very small volumes of solution. The electrode consists of a piece of No. 20 platinum wire, flattened at one end in the form of a thin disc, 1·5 mm. in radius and platinised. The test solution is placed in the cup, the maximum capacity of

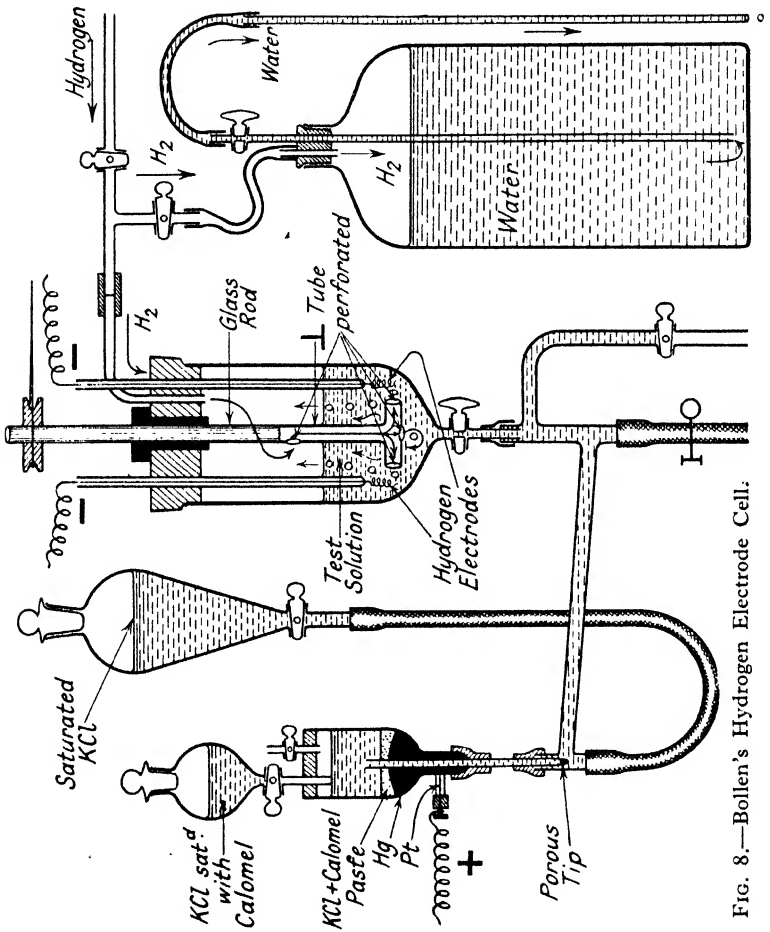


FIG. 8.—Bollen's Hydrogen Electrode Cell.

which is 0·1 c.c., and contact with the solution and the reference calomel electrode is made with a "No. 50" cotton thread, saturated with a saturated solution of KCl. If the tap is closed when the solution is introduced into the cup, the entrapped hydrogen in the capillary prevents the liquid from dropping out of the cell. A slight pressure of hydrogen through the cock

makes it possible for small bubbles of hydrogen to pass through the cup and so keep the electrode supplied.

Pd_2H Electrode.

Palladium black is a very poor substitute for platinum black in hydrogen electrodes, both as regards catalytic activity and adsorptive capacity. Nylén (*Z. Elektrochem.*, 1937, **43**, 921) has found that palladium electrodes, charged with hydrogen so as to correspond with Pd_2H, give constant, reproducible potentials and can therefore be used to measure *p*H. Three processes are available for charging palladium electrodes with hydrogen, *viz.*: (i) saturation with hydrogen at 6·8 mm. pressure at 20° C., (ii) cathodic polarisation, (iii) treatment with a reducing agent. A solution of N-formic acid is an excellent reducing agent for the purpose, and immersion of a palladinised electrode in such a solution for two minutes is sufficient to produce a good working electrode. The palladium black is deposited electrolytically on either platinum wire or foil. The wire should be 7–8 mm. in length and 0·3–0·4 mm. in diameter. The use of a larger electrode, particularly platinum foil, yields an electrode which retains its potential for longer periods.

Palladinising is effected by cathodic deposition for four minutes from a 1–2 per cent. palladous chloride solution containing about N-hydrochloric acid, using an E.M.F. of 4 volts. Before electrolysis, the platinum electrode is thoroughly cleaned with chromic acid, and then with water, and when palladinised, the electrodes are washed and dried in air. The completely dry electrodes are immersed in approximately normal formic acid; after a few seconds, a vigorous evolution of hydrogen and carbon dioxide occurs and, after two minutes, the electrodes are removed and placed in distilled water for three minutes, when the electrodes are ready for use.

The electrode may also be used for electrometric titration, but when vigorous stirring is employed, the effect of the air may become considerable. It can be largely overcome by using a platinum foil electrode (10 mm. × 5 mm.) which has been palladinised in dilute sulphuric acid, there being a weak evolution of gas.

The electrode is slowly poisoned by prussic acid, hydrogen sulphide, sulphite and tervalent arsenic, so much so that it is sometimes possible to extrapolate the potential set up at the time of inserting the electrode in the solution. Ammonia is without poisoning action on the electrode.

Calibration of the electrode is made by immersion in a buffer

solution of known *p*H. The P.D. between the electrode and a standard electrode is measured. If it remains constant, or nearly so, over a period of 10 minutes, the electrode may be used for the determination of the *p*H of a solution, which can be calculated from the E.M.F. of the cell by means of the expression

$$p\mathrm{H} = p\mathrm{H}_{\text{buffer solution}} - \frac{\text{E.M.F.}}{0{\cdot}0001984\mathrm{T}}.$$

CHAPTER IV

THE QUINHYDRONE ELECTRODE

BIILMANN (*Ann. Chim. Phys.*, 1921, **15**, 109) was the first to show that the oxidation-reduction reaction which takes place between hydroquinone and quinone can be made use of for the measurement of hydrogen-ion concentrations, merely by dissolving some quinhydrone in the solution under investigation and observing the potential established between the solution and some unattackable metal, such as gold or platinum. We have seen on page 23 that the potential of the quinhydrone electrode,

$$E_{quin.} = \lambda + \frac{RT}{F} \log_e [H^+],$$

when the ratio of the concentrations of hydroquinone to quinone is maintained constant.

Quinhydrone consists of fine dark bronze-green needles and is only sparingly soluble in water. It is an equimolecular compound of quinone and hydroquinone, which compound dissociates on dissolution in water, thus

$$\underset{\text{Quinhydrone.}}{(C_6H_4)_2O_2(OH)_2} \rightleftharpoons \underset{\text{Quinone.}}{(C_6H_4)O_2} + \underset{\text{Hydroquinone.}}{C_6H_4(OH)_2}$$

At 25° C. this dissociation proceeds to the extent of 93 per cent.

The solubility of quinhydrone in distilled water is given in Table 14 (Coons, *Ind. Eng. Chem., Anal. Edn.*, 1931, **3**, 402).

TABLE 14

Temp. ° C. .	0·3	6·0	8·4	10·0	15·0	20·1
Grams/100 c.c.	0·116	0·122	0·156	0·154	0·245	0·320
Temp ° C.	21·0	30·2	30·9	40·5	50·0	
Grams/100 c.c. . . .	0·321	0·530	0·542	0·754	1·035	

Preparation of Quinhydrone.

Three methods are available for the preparation of quinhydrone, *viz.*: (1) combination of quinone and hydroquinone;

(2) partial oxidation of hydroquinone, and (3) partial reduction of quinone. Valeur (*Ann. Chim. Phys.*, 1900, **21**, (7), 546) prepared it by the first method. He poured a solution of 20 grams of hydroquinone in 40 c.c. of 95 per cent. alcohol into a solution containing 10 grams of quinone in 300 c.c. of 95 per cent. alcohol and then set aside for 24 hours. The precipitated crystals were washed with a little alcohol and dried between filter papers, the last traces of alcohol being removed by standing over sulphuric acid in a desiccator. Yield 17·5 grams. When heated rapidly in a capillary tube the melting-point is found to be 172° C.

Biilmann (*Trans. Faraday Soc.*, 1923, **19**, 57) prepared it by the second method by dissolving 100 grams of iron alum, *i.e.*, ferric ammonium sulphate, in 300 c.c. of water at 65° C., pouring into a solution of 25 grams of hydroquinone in 300 c.c. of water, cooling in ice and separating the crystals by suction. In this way, a yield of 15 grams may be obtained, and after washing four or five times with water, the quinhydrone should contain only a trace of iron, which, according to Biilmann, does not affect the E.M.F. of the electrode. In this reaction sulphuric acid is liberated, which not only keeps hydrolysed ferric hydroxide in solution, but the acid reaction minimises the risk of oxidation of the quinhydrone, such as would occur in solutions of *p*H higher than about 7. In spite of Biilmann's remarks concerning the presence of a trace of iron, every effort should be made to make the filtration and washing thorough, for the author has found that it is an easy matter to prepare unsatisfactory material. In several instances the presence of iron has been found to be at the root of the trouble.

After drying the quinhydrone between filter papers in air for a couple of days, it should be placed in a well-stoppered bottle to prevent any possible oxidation. If drying by heat is resorted to there is a risk, if the temperature becomes too high, of some of the more volatile component, quinone, vaporising, though the extent to which occurs is negligible, when the material is dried for the minimum time in an ordinary steam-oven.

The platinum electrodes should be highly polished and clean. Cleaning should be carried out by treatment with a hot mixture of chromic acid and concentrated sulphuric acid, washing with distilled water and heating to a red heat in an alcohol flame or in a benzine blow lamp, but not in a gas flame.

Great care should be taken to avoid any cracks in the glass where the platinum wire is sealed into the tube, otherwise mercury may seep through and make contact with the solution. This is a frequent source of trouble with the quinhydrone electrode and may

often be caused during heat treatment. Morgan, Lammert, and Campbell (*J. Amer. Chem. Soc.*, 1931, **53**, 454) have traced errors of almost 0·1 volt to this cause, and urge that Biilmann's treatment in an alcohol flame should be discontinued. The use of sealing-in glass and carefully annealing are recommended. The existence of leaks is ascertained by subjecting the electrode to boiling in water. Faulty electrodes will break into pieces. Cleaning is effected by immersion in cold chromic acid cleaning mixture, raising to 125° C. and slowly cooling (see also Lammert, Morgan, and Campbell, *ibid.*, 597).

Use of Quinhydrone Electrode: Advantages and Disadvantages.

In order to determine the concentration of hydrogen ions with quinhydrone, all that is necessary is to dissolve a little in the solution, place in it a piece of bright platinum or gold to serve as one pole of the cell and then connect up the solution through a saturated potassium chloride solution bridge to a standard electrode and measure the potential difference between the two electrodes. The potential at the surface of the noble metal electrode is produced almost momentarily. It is stated, however, that this is not so when an electrode has been immersed in one solution and then transferred to another solution of considerably different *p*H, a much longer time often being necessary if a small error is to be avoided. There is sometimes a tendency for the E.M.F.'s to lag behind when the electrode is being used for titration work and the hydrogen-ion concentration is undergoing a sharp change. As Biilmann and Jensen (*Bull. Soc. chim.*, 1927, **41** (4), 151) have shown, the solution need not be saturated with respect to quinhydrone to give reproducible potentials, and they found by using one-tenth of the amount required for saturation, *viz.*, 0·035 gram at 25 °C. per 100 c.c., that the error was within a millivolt at 18° C. It is advisable to have sufficient quinhydrone to make the solution 0·005 M. (0·11 gram per 100 c.c.). Coons (*Ind. Eng. Chem., Anal. Edn.*, 1931, **3**, 402) states that the minimum amount of quinhydrone for *p*H determinations is 0·007 gram per 100 c.c.; a point of importance is using quinhydrone for continuous *p*H recording. It is immaterial whether the solution in the electrode vessel has access to the air. The area of the unattackable electrode should be as large as possible, since the larger it is, the larger the current that can be drawn from the cell without appreciably disturbing the equilibrium when determining the null point on the potentiometer. The platinum electrode is fused on to platinum wire which is fused

into the closed end of a glass tube containing mercury to provide a contact for an amalgamated copper wire.

By comparison of the potentials of the quinhydrone electrode in solutions of definite *p*H with those set up by the hydrogen electrode, the potential of each electrode being measured against the same standard half-element, it is found that those of the quinhydrone electrode at 18° C. are more positive than those of the hydrogen electrode by 0·7044 volt. This will be seen from Table 10 in which the voltages are given for both the hydrogen and quinhydrone electrodes when compared with that of the normal calomel electrode. Hence it follows that when [H·] becomes equal to 1 molar, the last term, *viz.*, $\frac{RT}{F} \log_e [H\cdot]$ becomes zero, in the expression given above and then

$$E_{quin.} = \lambda = 0{\cdot}7044 \text{ volt.}$$

Hence, *provided the ratio of quinone to hydroquinone in the solution remains equimolecular*,

$$E_{quin.} = +\ 0{\cdot}7044 + 0{\cdot}0001984T \log [H\cdot]$$

at a temperature T° Absolute.

As mentioned before, the value 0·7044 volt is the reduction potential of quinone in a solution containing 1 g.-mol. of hydrogen ions. It varies with temperature and has a fairly large negative temperature coefficient. The precise value for any temperature between 0° and 37° C. can be calculated from the formula

$$\lambda_t = 0{\cdot}7175 - 0{\cdot}00074t \text{ volt,}$$

where λt is the voltage at 0° C. and t is temperature in degrees Centigrade, (Biilmann and Krarup, *J. Chem. Soc.*, 1924, **125**, 1954); Biilmann and Jensen, (*Bull. Soc. chim.*, 1927, **41**, 151), however, substitute 0·7177 for 0·7175. Thus, at 18° to 20° C.

$$E_{quin.} = 0{\cdot}704 + 0{\cdot}058 \log [H\cdot].$$

Compared with the potentials of the standard calomel electrodes, the potential of the quinhydrone electrode in acid solutions is positive, but becomes equal to, and subsequently negative to the calomel standards when the hydrion concentrations fall below definite *p*H's. This may be seen from the last column of Table 10 where the potentials against the calomel electrodes diminish with increasing *p*H, become equal to that of the normal calomel electrode at a *p*H value between 7 and 8, and thereafter become negative. This will also be seen to be true when the electrode is used in conjunction with the saturated calomel electrode from the electrometric titration data of La Mer and Parsons (*J. Biol. Chem.*, 1923, **57**, 622) given in Table 15.

TABLE 15

ELECTROMETRIC TITRATIONS AT 25° C. OF 20 C.C. 0·200 M.-ACETIC ACID WITH 0·204 N-NaOH

c.c. NaOH.	E.M.F. against Saturated Calomel of		*p*H (Hyd. El.).	*p*H (Quin. El.).	E.M.F. Quin. E. −Hyd. El.	*p*H Error of Quin. El.
	Hydrogen E.	Quinhydrone E.				
0·00	− 0·406	+ 0·294	2·86	2·68	0·700	− 0·18
2·00	− 0·466	+ 0·233	3·71	3·71	0·699	0·00
4·00	− 0·486	+ 0·214	4·05	4·04	0·700	− 0·01
6·00	− 0·499	+ 0·201	4·27	4·26	0·700	− 0·01
8·00	− 0·510	+ 0·189	4·45	4·45	0·699	0·00
10·00	− 0·520	+ 0·179	4·63	4·62	0·699	0·00
12·00	− 0·531	+ 0·168	4·80	4·80	0·699	0·00
14·00	− 0·543	+ 0·156	5·02	5·02	0·699	0·00
16·00	− 0·558	+ 0·140	5·26	5·26	0·699	0·00
17·00	− 0·569	+ 0·130	5·45	5·45	0·699	0·00
18·00	− 0·582	+ 0·114	5·70	5·72	0·696	+ 0·02
18·50	− 0·595	+ 0·103	5·89	5·90	0·698	+ 0·01
19·00	− 0·616	+ 0·084	6·25	6·22	0·701	− 0·03
19·40	− 0·670	+ 0·044	7·16	6·91	0·714	− 0·25
19·50	− 0·737	+ 0·029	8·30	7·16	0·766	− 1·24
19·80	− 0·892	− 0·048	10·90	8·47	0·844	− 2·43
20·00	− 0·909	− 0·071	11·20	8·85	0·838	− 2·35
20·50	− 0·925	− 0·102	11·50	9·36	0·803	− 2·14
21·00	− 0·934	− 0·119	11·63	9·66	0·815	− 1·97
21·50	− 0·940	− 0·132	11·71	9·86	0·808	− 1·85
22·00	− 0·945	− 0·145	11·85	10·10	0·800	− 1·75
22·50	− 0·948	− 0·156	11·88	10·29	0·792	− 1·59

The measured potential difference between a quinhydrone and a standard calomel electrode is given by

$$\text{E.M.F.}_{(\text{observed})} = E_{\text{quin.}} - E_{\text{standard}}$$
$$= 0{\cdot}704 + 0{\cdot}058 \log [H^{\cdot}] - E_{\text{standard}}$$

and, therefore, at 18° to 20° C.,

$$p\text{H} = \frac{0{\cdot}704 - E_{\text{standard}} - E_{\text{observed}}}{0{\cdot}058}.$$

If the standard electrode is Veibel's quinhydrone electrode, page 36, then at 18° C. the above expression reduces to the following :—

$$p\text{H} = -2{\cdot}04 + \frac{E_{\text{observed}}}{0{\cdot}0577}.$$

The chief advantages of the quinhydrone electrode are that

(*a*) it attains equilibrium rapidly ;

(*b*) it may often be used in solutions containing certain oxidising agents and salts of metals more noble than hydrogen, for which the hydrogen electrode is inapplicable ;

(*c*) it is not as readily incapacitated as the hydrogen electrode.

Its disadvantages are that

(*a*) it cannot be used in solutions of $p\mathrm{H} > 8$;
(*b*) there is a possibility of side reactions taking place which may alter the molecular ratio of quinone to hydroquinone;
(*c*) it has appreciable "protein-errors";
(*d*) it has "salt-errors," though often extremely small.

It is inadvisable to use the quinhydrone electrode for the measurement of the *p*H of solutions more dilute than 0·001 M. Errors of 5 to 30 millivolts may arise through the high resistance of the solution, the escape of carbon dioxide, and the acid properties of the quinhydrone. There is also a greater tendency for the electrode to become polarised.

Although the quinhydrone electrode is limited chiefly to the acid side of neutrality, the fact that it can give steady and reproducible potentials in the presence of oxidising agents opens up a field of usefulness not covered by the hydrogen electrode. Needless to say, the experimenter must always be on the look out for unsteady E.M.F's through side-reactions taking place which may materially affect the constancy of the 1 : 1 ratio. Except for the great convenience in using the compound, quinhydrone, there is no reason why other ratios of quinone to hydroquinone might not be used, and, indeed, both the hydro-quinhydrone and the quino-quinhydrone electrodes have been used: in the former electrode the solution was saturated with both hydroquinone and quinhydrone, and in the latter with quinone and quinhydrone. Alteration of the ratios merely introduces another term of constant value into the expression connecting the E.M.F. with hydrogen-ion concentration. Thus at 18° to 20° C., the potentials of these electrodes may be expressed by the following formulæ:—

$$E_{\text{hydro-quinhydrone}} = 0{\cdot}618 + 0{\cdot}058 \log [H^{\cdot}]$$
$$E_{\text{quino-quinhydrone}} = 0{\cdot}756 + 0{\cdot}058 \log [H^{\cdot}].$$

The constants in these two expressions vary with temperature. According to the data of Schreiner (*Z. physikal. Chem.*, 1925, **117**, 57) referring to the quino-quinhydrone electrode, the value of the constant is given by $\lambda_t = 0{\cdot}7716 - 0{\cdot}000842t$, where t is any temperature lying between 0° and 25° C. In the case of the hydro-quinhydrone electrode he gives 0·6177 volt at 18° and values between 12° and 25° C. may be obtained from $\lambda_t = 0{\cdot}6216 - 0{\cdot}000650\,(t - 12)$. These electrodes have no advantages over

the ordinary quinhydrone electrode. Side-reactions are probable only with strong oxidising and reducing agents such as ferric and titanous salts, and also with more concentrated solutions of nitric and chromic acids.

In addition to those solutions in which the hydrogen electrode can be used, the quinhydrone electrode can be used in solutions of copper salts, unsaturated acids, dilute nitric acid, nitrates and alkaloids. It may also be safely used in many biological and natural solutions where the hydrogen electrode would cause reduction. Biilmann has shown that it may be used in presence of nitric, acrylic, crotonic, fumaric, maleic, and phenylpropionic acids.

Strictly speaking, the reason for this increased applicability of the quinhydrone electrode over that of the hydrogen electrode is to be found in the magnitude of the reduction potential of quinone; but Biilmann, by means of calculations similar to those carried out on page 61 for hydrogen electrodes at different pressures of hydrogen gas, has shown that, in effect, the quinhydrone electrode might be considered as a hydrogen electrode having an extremely small pressure of hydrogen gas and consequently possessing very small reducing action. Though the figures so obtained can have no real physical meaning, they may perhaps lead to a better appreciation of the cause of the utility of the quinhydrone electrode.

If the reaction between quinone and hydroquinone be regarded in a purely chemical sense, then it may be represented thus:—

$$H_2 + C_6H_4O_2 \rightleftharpoons C_6H_4O_2H_2,$$

whence by the law of mass action

$$[H_2] = K \cdot \frac{[\text{hydroquinone}]}{[\text{quinone}]}$$

or

$$\pi = K' \cdot \frac{[\text{hydroquinone}]}{[\text{quinone}]},$$

where π is regarded as the hypothetical pressure of hydrogen gas. Now we have seen that the E.M.F. of a cell, composed of two hydrogen electrodes at different hydrogen pressures, is given by

$$E_{\text{pressure}} = 0{\cdot}0000992 \log \frac{1}{\pi},$$

and as the potential of the quinhydrone electrode is 0·704 volt above that of the normal hydrogen electrode, we see that the E.M.F. of a cell constituted of these two electrodes in the same solution will be 0·704, or $E_{\text{pressure}} = 0{\cdot}704$.

In this way, Biilmann has calculated that the quinhydrone electrode corresponds to a hydrogen electrode having a hydrogen pressure of $10^{-24\cdot4}$ atmosphere at 18° C., and $10^{-23\cdot6}$ atmosphere at 25° C. Such fictitious pressures can have no real significance, though as Biilmann points out they may " serve " as very useful characteristics of the reducing powers of the electrode substances. A pressure of $10^{-24\cdot4}$ atmospheres corresponds to 1 molecule of gas in about 90 litres, so that in the amount of a solution undergoing examination there would not be one single molecule of hydrogen. Incidentally, the *p*H is 24·4 at 18° and 23·6 at 25°.

The great drawback to the quinhydrone electrode is that it cannot be used in solutions of above *p*H 8. This is because hydroquinone behaves as a dibasic acid and above *p*H 8 begins to have an effect upon the hydrogen-ion concentration of the solution. In the case of a solution containing no buffers, (see later) this effect may be great at the comparatively low *p*H values, though with a buffered solution the error, thereby introduced, may not become considerable until much higher *p*H values are reached. Sheppard (*Trans. Amer. Electrochem. Soc.*, 1921, **39**, 429) found that K_1 of hydroquinone is $1\cdot75 \times 10^{-10}$, *i.e.*, $pK_1 = 9\cdot8$; and the second dissociation constant, K_2 to be 4×10^{-12}, $pK_2 = 11\cdot4$. Generally, the concentration of hydroquinone is about 0·01 M., and consequently, if pure water were being examined we should be concerned with the hydrogen-ions produced by the dissociation of the water,

$$H_2O \rightleftharpoons H^{\cdot} + OH',$$

and those liberated by the first stage of dissociation of hydroquinone, H_2Q,

$$H_2Q \rightleftharpoons H^{\cdot} + HQ'.$$

By the principle of the electro-neutrality of solutions, we find that

$$[H^{\cdot}] = [OH'] + [HQ'],$$

the concentration of ions arising from the second stage of dissociation here being considered negligible. As

$$K_w = [H^{\cdot}][OH'] \text{ and } K_1 = \frac{[H^{\cdot}][HQ']}{[H_2Q]}$$

we get

$$[H^{\cdot}]^2 = K_w + K_1[H_2Q].$$

Very often K_w is negligible compared with the other term, *i.e.*, when K_1 is fairly great. In the case of hydroquinone, its effect is scarcely perceptible. It is found from this expression that pure water, *p*H 7·0, when tested with the quinhydrone electrode, would show a *p*H of 5·9 with a concentration of 0·01 M.-hydroquinone, and *p*H 6·5 with a 0·001 M.-solution. Appreciable errors

may thus be obtained in unbuffered solutions whose *p*H values are about 6. If the solution contains buffering agents, then no great error might be expected to occur until about *p*H 8, for as will be shown later only 1 per cent. of the first stage of neutralisation of hydroquinone can occur before

$$p\text{H } 9{\cdot}8 - 2{\cdot}0 = p\text{H } 7{\cdot}8.$$

This functioning of hydroquinone as an acid leads to another error, that of disturbing the molecular ratio of quinone to hydroquinone, for the concentration of undissociated hydroquinone becomes reduced. Biilmann calculates that at *p*H 8, the ratio becomes 1·01 : 1, voltage error = 0·0001 volt; at *p*H 9, the ratio is 1·10 : 1 with a resulting error of 0·001 volt.

The last column of Table 15 shows that the *p*H values, calculated from the data given by the quinhydrone electrode, began

TABLE 16

COMPARATIVE *p*H VALUES OF BUFFER SOLUTIONS OBTAINED BY KOLTHOFF

Buffer Solution.	*p*H Hydrogen Electrode.	*p*H Quinhydrone Electrode.	Error of Quinhydrone Electrode.
0·05 M.-KH_2PO_4 and 0·05 M.-borax mixtures	6·20	6·17	− 0·03
	6·27	6·27	0·00
	7·04	7·00	− 0·04
	8·30	8·33	+ 0·03
KH_2PO_4—NaOH mixtures. Clark	7·20	7·25	+ 0·05
	7·60	7·62	+ 0·02
Boric—NaOH mixtures. Clark	8·20	8·20	0·00
	8·80	8·80	0·00
	9·20	9·24	+ 0·04
	9·60	9·49	− 0·11

to be erroneous at *p*H 6. This corresponded to the final part of neutralisation of acetic acid when the buffering capacity had almost disappeared. When the solutions contain buffers, then the quinhydrone electrode potentials may be expected to give fairly accurate *p*H values up to about 9. This will be seen from the values of Kolthoff (*Z. physiol. Chem.*, 1925, **144**, 259) given in Table 16.

Colloidal material, and especially certain proteins, give rise to errors, though Linderstrøm-Lang (*Comp. rend. Lab. Carlsberg*, 1925, **16** (3), 1), by comparison with the *p*H values calculated from hydrogen electrode potentials, has found that it is possible to apply suitable corrections to the quinhydrone *p*H values.

Such corrections are, however, not always possible. The extent of these errors is indicated in Table 17 :—

TABLE 17

COMPARATIVE *p*H VALUES OF PROTEIN SOLUTIONS OBTAINED BY KOLTHOFF

Solution.	*p*H Hydrogen Electrode.	*p*H Quinhydrone Electrode.	Error of Quinhydrone Electrode.
Blood serum with NaCl	6·04	5·94	— 0·10
	6·06	5·88	— 0·18
Blood serum with NaCl and Na_2HPO_4	6·85	6·71	— 0·14
	7·04	6·89	— 0·15
	7·18	7·00	— 0·18
Casein—NaOH solution	6·59	6·51	— 0·08
	7·03	6·94	— 0·09
	7·19	7·10	— 0·09
	7·42	7·29	— 0·13
	7·69	7·45	— 0·24

When quinhydrone is mixed with casein, suspended in water, the casein is coloured red, and this occurs more quickly on warming. Adsorption of quinone occurs. Proteins are permanently reddened by quinone. Amino-compounds, *e.g.*, triethanolamine, hydroxylamine hydrochloride, hexamine, methyldiphenylamine, *p*-toluidine, naphthylamine, morpholine, also give the coloration. To reduce any such adsorption to a minimum, in measuring the *p*H of rennet casein, Cooper and Hand (*J. Soc. Chem. Ind.*, 1936, 341 T) recommend the following procedure. Allow 10 grams of casein, 40/60 mesh, to swell in 30 c.c. of water for 15–30 minutes, and then immediately before making the measurement introduce 0·5 gram of quinhydrone.

In the presence of precipitates there is a tendency for the quinol and quinone to become adsorbed, and this tendency may be appreciable in the presence of inorganic bases which, owing to possible chemical reaction, may adsorb the quinol preferentially. If thorough mechanical stirring is adopted, this risk will usually be negligible.

The potential of the quinhydrone electrode may be slightly affected by the concentrations of neutral salts—the errors are generally negligible. Sørensen has shown that when the total concentration of salt is 0·2 M. the error is about 0·01 *p*H, and in the case of a decinormal hydrochloric acid solution which was 4-normal with respect to NaCl the error had only become 0·2 *p*H.

It should be borne in mind that the behaviour of the quinhydrone electrode is always standardised against that of the hydrogen electrode, and that all the foregoing errors correspond with divergences from it produced by the quinhydrone electrode. These electrodes should from time to time be tested in buffer solutions of known *p*H. In acid solutions the quinhydrone electrode gives almost immediately steady voltages which remain constant over prolonged periods. In alkaline solutions oxidation of the hydroquinone occurs more readily, as shown by a darkening in the colour of the solution. Its rate increases with increasing *p*H, though it is decreased somewhat in well-buffered solutions. Much of this oxidation is caused by the action of air, and it may be diminished and sometimes eliminated by using an enclosed electrode vessel and passing through it some inert gas, *e.g.*, nitrogen. For fuller information regarding the use of the electrode for titration purposes the reader is referred to a paper by Rabinowitsch and Kargin (*Z. Elektrochemie*, 1927, **33**, 11).

To measure the *p*H of semi-plastic solids or viscous solutions Sanders (*Ind. Eng. Chem., Anal. Edn.*, 1938, **10**, 274) wets the electrode wire with the test liquid and then dips it into quinhydrone crystals, or else dips the wire into a saturated solution of quinhydrone in acetone, and by drying allows a layer of quinhydrone crystals to form on the surface before dipping into the test liquid.

The quinhydrone electrode may be used for the continuous recording of *p*H by means of self-recording potentiometers, provided that the amount of quinhydrone in the solution passing through the electrode vessel is maintained greater than 7 mg. per 100 c.c. Two methods of maintaining such a concentration have been described by Coons (*Ind. Eng. Chem., Anal. Edn.*, 1931, **3**, 402; 1932, **4**, 175). One method is to allow the water at 20°. to flow over pellets of quinhydrone 1 gram in weight, placed in a tube, at a rate not greater than 100 c.c. per minute This just ensures the dissolution of the minimum amount of 7 mg. per 100 c.c. The other method is to dissolve 30 grams of quinhydrone in 1 litre of either methyl alcohol, ethyl alcohol or acetone, and to drop the solution at the rate of 18 drops per minute into the electrode compartment through which water is passing at the rate of 80–100 c.c. per minute. The electrode is a semicircular piece of platinum. Cleaning is effected by boiling the electrode in a 5–10 per cent. sodium bisulphite solution. A preliminary treatment with acid may be necessary. (See also Parker, *Ind. Eng. Chem.*, 1927, **19**, 660; Parker and Greer, *Trans. Amer. Electrochem. Soc.*, 1926, **49**, 9).

Martin (*J. Soc. Chem. Ind.*, 1937, **56**, 179T) has shown that it is possible to carry out titrations with the quinhydrone electrode without a potentiometer. Instead, the two electrodes of the titration cell are connected together through a sensitive galvanometer and a one megohm resistance. The deflexions of the galvanometer are plotted against the amount of alkali added. Satisfactory titration curves can thus be obtained in which end-points are clearly indicated.

CHAPTER V

THE OXYGEN AND AIR ELECTRODES

THE oxygen and air electrodes, like that of hydrogen, depend upon the adsorption of gas by platinum black, and, as an instrument of control in technical processes, the Hildebrand type of gas electrode described on page 40 is quite satisfactory, oxygen or simply air being passed through instead of hydrogen.

Although the oxygen electrode (or air electrode) is, in general, readily responsive to changes in hydrogen-ion concentration, and may be used for the control of graded precipitation from solutions, such as those of copper sulphate containing ferric salts (for which the hydrogen electrode is unsuited), by treatment with alkalis (*vide* Tilley and Ralston, *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 79; Britton, *J. Chem. Soc.*, 1925, **127**, 2148), and of boiler-feed water (Arthur and Keeler, *Power*, 1922, **55**, 768), the fact that it is irreversible does not allow of the direct calculation of the hydrogen-ion concentrations. The E.M.F's which it registers over known ranges of *p*H can, however, be calibrated with a fair degree of accuracy in terms of *p*H or hydrogen-ion concentration (*cf.* Britton, *loc. cit.*, 1924, **125**, 1574). The cause of its irreversibility lies in the tendency of the gas to combine with the platinum to form a series of oxides or perhaps of " solid solutions."

The theory of the oxygen electrode rests on the fact that to a large extent, though not completely, the oxygen electrode enters into equilibrium with the hydroxyl-ions, and, consequently, the hydrogen-ions, thus $O'' + H_2O \rightleftharpoons 2OH'$. If the reactions which prevail at the platinum black surfaces could be correctly expressed by the following scheme,

$\frac{1}{2}O_2$	$\rightleftharpoons$	O	$\rightleftharpoons$	$O'' + 2FE_{O_2}$
Gas phase.		In Pt black.		At interface of Pt and solution.

then we see from page 14 that the potential between the electrode and the solution can be expressed by the following equations :—

$$E_{O_2} = \frac{RT}{2F} \log_e \frac{P}{p} = \frac{RT}{2F} \log_e \frac{C}{c}$$

$$= \varepsilon_{O_2} - \frac{0{\cdot}058}{2} \log [O'']$$

at 18° to 20° C.

The normal electrode potential of oxygen is + 0·41 volt, and therefore it might be expected that

$$E_{O_2} = 0{\cdot}41 - \frac{0{\cdot}058}{2} \log [O'']$$

and as an equilibrium must be set up between the oxygen ions and hydroxyl ions,

$$O'' + H_2O \rightleftharpoons 2OH'$$

$$\therefore \frac{[OH']^2}{[O'']} = K,$$

whence $$E_{O_2} = 0{\cdot}41 - \frac{0{\cdot}058}{2} \log \frac{[OH']^2}{K}$$

$$= 0{\cdot}41 + 0{\cdot}029 \log K - 0{\cdot}058 \log [OH'].$$

But the equilibrium between the hydroxyl ions and the hydrogen ions is given by

$$[H^\cdot][OH'] = K_w,$$

whence by substitution, we find that if the oxygen electrode were reversible,

$$E_{O_2} = 0{\cdot}41 + 0{\cdot}029 \log K - 0{\cdot}058 \log K_w + 0{\cdot}058 \log [H^\cdot]$$

$$E_{O_2} = \lambda + 0{\cdot}058 \log [H^\cdot]$$

$$= \lambda - 0{\cdot}058\, p\mathrm{H}.$$

This expression might also have been obtained from a consideration of a series of equilibria as follows :—

$$H_2O \rightleftharpoons H^\cdot + OH', \text{ and } OH' \rightleftharpoons O'' + H^\cdot$$

and $$\therefore [O''] = \frac{K_w \,.\, k}{[H^\cdot]}.$$

The E.M.F. of a hydrogen electrode immersed in the same solution as an oxygen electrode would be

$$E_{H_2} = 0{\cdot}058 \log [H^\cdot],$$

and consequently the potential difference between the oxygen and hydrogen electrodes constituting such a cell would be equal to

$$\text{E.M.F.} = E_{O_2} - E_{H_2} = \lambda \text{ volts},$$

the oxygen electrode being positive.

In a similar manner, if we consider the E.M.F. of cell composed of a hydrogen electrode immersed in a solution of concentration [H$^\cdot$] and a standard electrode, say, the normal calomel electrode, and also the E.M.F. of a combination of an oxygen electrode in a solution of the same concentration of hydrions and a normal calomel, then we find that

E.M.F. of O_2 | — | N-calomel — E.M.F. of H_2 | — | N-calomel

$= \lambda$ volt.

It follows, that if the oxygen electrode behaved in a reversible manner, we should expect it to indicate potentials which would be always more positive by a constant value, λ, the theoretical potential of the oxygen-hydrogen cell, or the co-called *Knall-Gas Kette*, than that of a hydrogen electrode in the same solution. This quantity will be referred to later in connexion with efforts which have been made to study both the behaviour of the oxygen electrode and possible methods for calibrating its potentials for the purpose of calculating hydrogen-ion concentrations.

Nernst and Wartenberg (*Z. physikal. Chem.*, 1906, **56**, 534) found, by extrapolation from the results obtained in their classical researches on the dissociation of steam at high temperatures, that the potential difference of the oxygen-hydrogen cell at the ordinary temperature could be calculated from the expression E.M.F. $= 1{\cdot}232 - 0{\cdot}00085\ (t^\circ - 17)$, and therefore the E.M.F. at 20° should be 1·229 volts. Similar values have been obtained by indirect methods based on the potential of the $Ag \mid Ag_2O$. NaOH electrode and the dissociation pressure of silver oxide (*vide* Britton, *J. Chem. Soc.*, 1925, **127**, 2960). Thus, if the oxygen in the platinum black, or even on the bare surface of bright platinum, behaved in a strictly reversible way as is the case with hydrogen we should expect the potentials of the oxygen electrode to be 1·229 volts more positive than those of a hydrogen electrode when immersed in the same solution at 20° C. Actual measurements of the E.M.F. of an oxygen-hydrogen cell show that true equilibrium values are never attained. Though the E.M.F's are variable, the final values usually lie between 1·08 and 1·14 volt. Hence, it was thought that, even if the difference between the voltage of the oxygen electrode and the hydrogen electrode did not become equal to 1·229 volt, it might at least acquire some definite and characteristic value and thereby would permit of the calibration of each individual oxygen electrode for the determination of *p*H values. Provided that the oxygen electrode is subjected to no sudden variations in hydrogen-ion concentration, it may be reasonably expected that its voltages will be parallel to those of a hydrogen electrode in equilibrium with the same solution. This is usually true, but if the solution contains either oxidising or reducing agents, it will be found that they often exert some influence on the electromotive force such that the relationship between the oxygen and hydrogen electrodes becomes altered, for then the concentration of oxygen ions will be dependent both upon the concentration of hydrogen ions and that of the oxidising or reducing agents. The effects of these agents become more pronounced within certain ranges of *p*H.

Although the oxygen electrode when placed in a solution does not actually attain a constant E.M.F., it is found that in general a value is shown after oxygen has been passed for about 15 minutes which varies only slightly with time—a matter of a few millivolts. As was first pointed out by Furman (*J. Amer. Chem. Soc.*, 1922, **44**, 12), this does not detract from its use in electrometric titrations for the variations in potential due to variations in hydrogen-ion concentration overpower the " drift " due to the oxygen electrode itself. He has demonstrated its use for the accurate electrometric titrations of acids and alkalis in solutions of coloured oxidising agents, *e.g.*, potassium chromate, potassium permanganate, and potassium ferricyanide, in whose presence the hydrogen electrode would, of course, be useless, and whose colour may prevent titration with the usual indicators. Bright platinum-oxygen and air electrodes have been used for the determination of the " acid number " of acids and fats with alcoholic potassium hydroxide (Kremann and Schöpfer, *Die Seife*, 1922, **8**, 35), and for the titration of alkaloids, quinine, cocaine, cinchonidine and strychnine, by Popoff and McHenry (*J. Amer. Pharm. Assoc.*, 1925, **14**, 473). The oxygen electrode has been employed for the control of the hydrogen-ion concentration of boiler feed-water, which through the dissolved oxygen would interfere with the hydrogen electrode especially when the solutions were flowing through the electrode chamber. Thus Arthur and Keeler (*loc. cit.*) used it in connexion with the purification of boiler feed-water in conjunction with a decinormal calomel electrode, and, moreover, found that the dissolved oxygen was sufficient to maintain the electrode in a saturated state. They were able to obtain by means of an automatic recording potentiometer, a satisfactory record of the reaction of the water, and by a system of relays and contacts they found that a motor-operated valve could be made to control automatically the additions of alkali when necessary.

It is probable that the oxygen electrode is applicable to most of the solutions in which the hydrogen electrode is useless, though the author has found that in sulphite solutions both electrodes fail.

Air, free from carbon dioxide, may be used to saturate the platinum with oxygen (*vide* Furman, *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 79). The electrode so prepared should, on theoretical grounds, be 0·008 volt less positive than the oxygen electrode under atmospheric pressure. Actually, such a difference is often masked by the anomalous behaviour of the oxygen in the electrode.

It may be an advantage to summarise here some of the author's

observations regarding the oxygen electrode (*J. Chem. Soc.*, 1924, **125**, 1572; 1925, **127**, 1896, 2148, 2964). Figs. 9 and 10 refer to the oxygen electrode titrations of chromic, malonic, tartaric and oxalic acids with approximately decinormal sodium hydroxide, the comparison electrode being the normal calomel. Each of these titrations were also performed with the hydrogen electrode (see pages 192 and 196) and therefore the E.M.F's of the oxygen-hydrogen cell could be extrapolated from the curves given by the two different electrodes. It might be thought that any

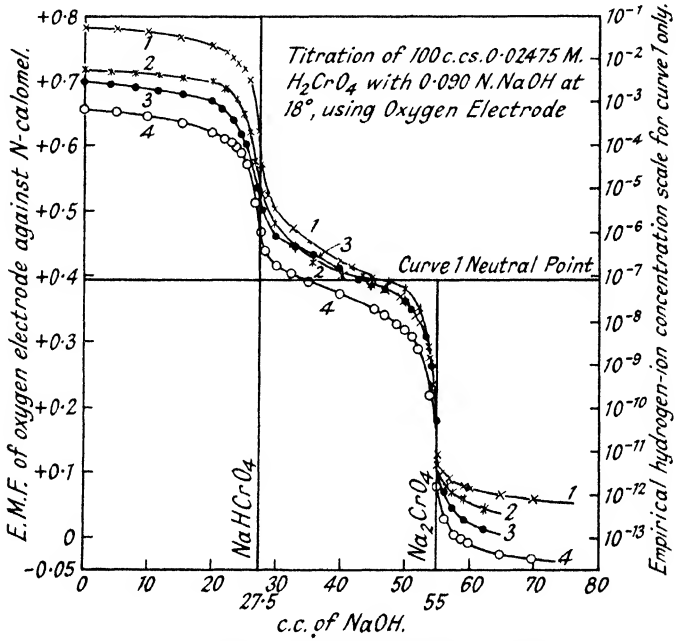


FIG. 9.—Oxygen Electrode Titration Curves.

particular oxygen electrode when placed in the same solution on different occasions would assume, or at any rate tend to approach, the same potential, so that once an electrode had been standardised against a hydrogen electrode some approximate idea of the hydrogen-ion concentration of a solution could be calculated from its E.M.F. set up in another solution at some subsequent time. This, however, is not the case, for the difference between the oxygen and hydrogen electrode potentials varies appreciably on keeping, even though the electrodes are kept immersed in distilled water when not in use. Thus in Fig. 9, curves 1 and 2 were given simultaneously by two different electrodes in the same

solution on one day, but on the next day the curves obtained with the respective electrodes were 4 and 3. The curves given in Fig. 10 were obtained with the same electrodes on three successive days, that of malonic acid on the first, tartaric acid on the second, and oxalic acid on the last. It is surprising that the initial voltages were so different seeing that the *p*H values of the malonic and tartaric acids were *p*H 2·28 and *p*H 2·29

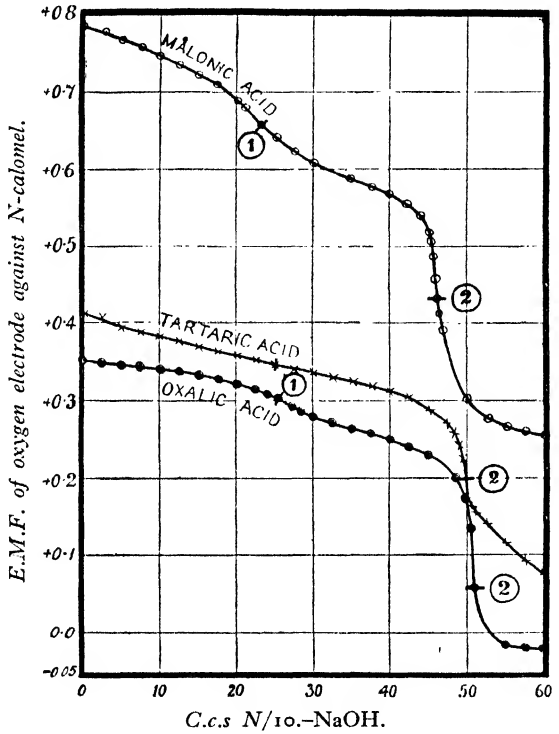


FIG. 10.—Oxygen Electrode Titration Curves.

respectively, while that of oxalic acid was *p*H 1·65, and consequently it might have been expected that the potential of the oxygen electrode in the oxalic acid would have been considerably more positive. These curves show, then, that oxygen-electrodes on ageing lose much of their value as indicator electrodes. Though they are capable of indicating end-points, the sudden falls in potential differences which occur in the vicinity of these points become less in extent, and thereby render it more difficult to locate the point of inflexion at the true end-point with accuracy.

It was stated above that oxidising agents affect the potentials of the oxygen electrode, and also that there is a lag in the potentials of the oxygen electrode when it is being subjected to a rapid change in hydrogen-ion concentration. This will be seen

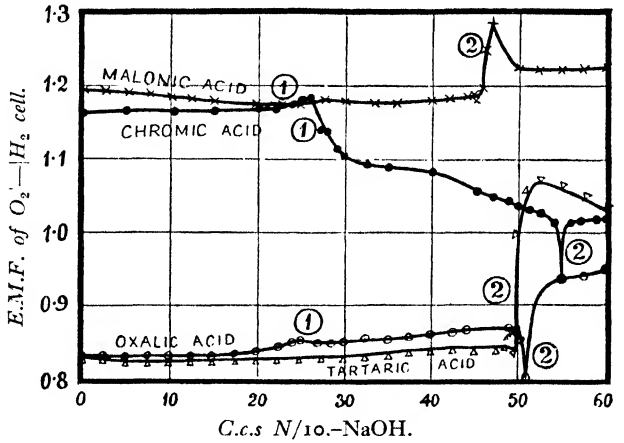


FIG. 11.—Comparison of Oxygen Electrode and Hydrogen Electrode Titration Curves on the Basis of the Oxygen-Hydrogen Cell.

from Fig. 11 in which the extrapolated E.M.F's of the oxygen-hydrogen cell corresponding to the different stages of the titration of the four acids are given. The curves show that the variations in the extrapolated E.M.F's at the beginnings and endings of the different titrations, given in Table 18, were not incorporated

TABLE 18

Acid.	E.M.F. of Oxygen-Hydrogen Cell at		
	Beginning.	End.	Difference.
Malonic	1·195	1·228	+ 0·033
Tartaric	0·828	1·034	+ 0·206
Oxalic	0·830	0·950	+ 0·120
Chromic	1·162	1·027	— 0·135

proportionally in the oxygen electrode voltages throughout the whole courses of the titrations, but were chiefly introduced in the final stages of the neutralisations. It was thought that these differences were due simply to a lag in the E.M.F's of the oxygen electrodes caused by the considerable change in hydrion concen-

tration, and could be overcome by allowing time before taking further readings. When the change was considerable, it was sometimes found that time produced some little effect, but in general, the extrapolated E.M.F's never fell to the initial values. This change which takes place as the titrated solution attains alkalinity seems to be connected both with the age of the electrodes and with the oxidising nature of the acids. The curve showing the change which took place in the titration of chromic

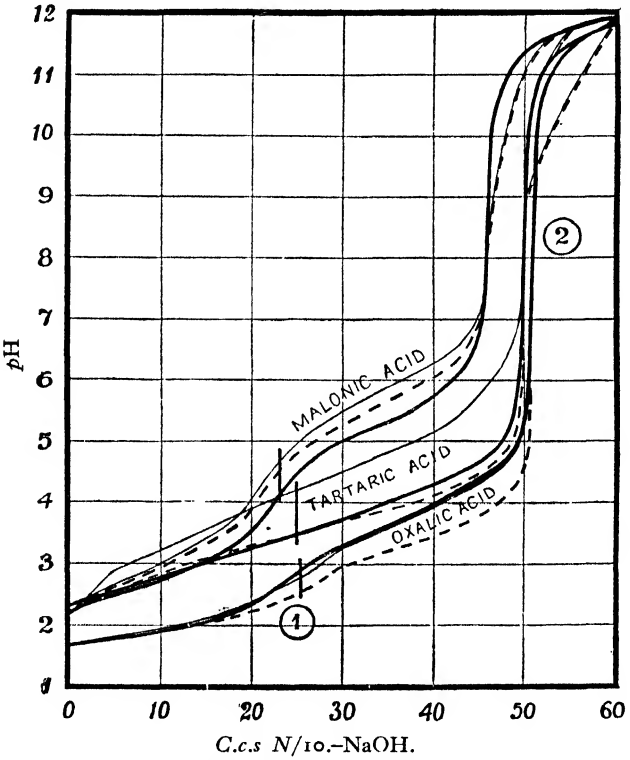


FIG. 12.—Adjusted Oxygen Electrode Curves.

acid is given in Fig. 11, the actual titration curve being No. 1 in Fig. 9. Although there was no change in the extrapolated E.M.F. during the first half of the neutralisation, there was a somewhat irregular falling-off during the second stage, and when the solution had become alkaline it was found that the E.M.F. was less than the initial value. This occurred in every one of the many titrations undertaken. The hydrogen-ion concentration prevailing during the second half of the titration lay between

10^{-6} and 10^{-7}, and it seems that it was here and later in the alkaline solution that the oxidising nature of the chromic acid came into play. No irregularities occurred with the non-oxidising acids and especially with malonic acid, the second part of the neutralisation of which was not far removed from *p*H 7.

Calibration of the Oxygen Electrode in Titrations.

The erratic behaviour of the oxygen electrode while being subjected to rapid changes in hydrion concentration, such as have been shown (Fig. 10) to take place at the end-points of titrations, renders it almost impossible to affix a satisfactory hydrogen-ion concentration scale to the measured voltages. It is possible, however, to get an approximate idea of the changes in *p*H over the greater range of the titration, for which purpose the following two schemes of calibration have been examined.

First, knowing the *p*H's of solutions at two remote stages of a titration and the corresponding voltages given by the oxygen electrode, one assumes that the intermediate *p*H's are proportional to the observed E.M.F's. Such a scale is affixed to one of the chromic acid curves, Fig. 9, and permits of *p*H values being read off to within 0·5 *p*H unit, except from that portion of the curve around the end-point. In Fig. 12 are given the hydrogen electrode titration curves (heavy lines) of the three organic acid solutions which were studied with the oxygen electrode, together with the approximate *p*H curves calibrated from the oxygen electrode data. The thin unbroken lines referring to *p*H values were arrived at on the basis suggested above. Except in the case of the oxalic acid curve, the agreement with hydrogen electrode curves is unsatisfactory—the great errors indicated by the tartaric acid being due to a lag of 0·206 volt introduced at the end-point being divided proportionally over the whole range of voltages covered by the titration. Hence it appears that when the extrapolated E.M.F's of the oxygen-hydrogen cell for the initial and final stages of an oxygen electrode titration are widely different, a simple proportional *p*H scale may be very far from satisfactory.

The second method of calibration was based on the fact, illustrated by Fig. 11, that the oxygen electrode voltages are more positive than the corresponding hydrogen electrode voltages by approximately a fixed amount when working over a range of hydrion concentration which does not involve sudden changes, and that the appreciable variations occur only when a very sharp change in hydrion is encountered. Thus in any one of the present titrations, if the *p*H's at the beginning and at the end are known, the E.M.F's given by the hydrogen electrode, compared with the

normal calomel electrode, can be calculated, and thus the E.M.F. of the corresponding oxygen-hydrogen cells can be extrapolated. The difference between the initial and the final values may then be assumed to have been introduced at that stage of the titration where the addition of a few drops of alkali caused a considerable change in the observed E.M.F. This difference is then added to, or subtracted from, as the case may be, those readings which were taken after the marked change had taken place. For the titration readings which have thus been adjusted, the hydrogen-ion concentration scale may be found by proportion, or by what amounts to the same thing, from the formula :

Observed E.M.F. — Initial extrapolated E.M.F. of oxygen-hydrogen cell (λ)

$$= \text{E.M.F. of corresponding N-calomel} - \text{hydrogen cell}$$
$$= E_{cal} - E_{H_2} = 0{\cdot}283 + 0{\cdot}0577 p\text{H at } 18^\circ \text{ C.}$$

For example, suppose that all that was known of the tartaric acid titration was the initial *p*H, 2·29, and the *p*H when 60 c.c. of alkali had been added, *viz.*, 11·75. The oxygen electrode compared with the normal calomel gave + 0·413 and + 0·073 volt respectively, and from the known *p*H's it is calculated that the E.M.F. of the hydrogen electrode against the normal calomel would have been — 0·415 volt at the beginning and — 0·961 volt when 60 c.c. of alkali had been added. Hence the extrapolated E.M.F. of the oxygen-hydrogen cell increased from + 0·413 — (— 0·415) = 0·828 volt to + 0·073 — (— 0·961) = 1·034 volt in the course of the titration, a difference of 0·206 volt. This is a considerable quantity to be divided proportionally over the whole titration as was done in the first method of calibration, and consequently produced a very unsatisfactory hydrion scale. But, as Fig 11 shows, the greater part of this difference was introduced at the end-point. Therefore, if the difference 0·206 volt be added to each of the voltages observed after the end-point had been passed and then either a proportional scale be affixed or calculated from $E = 0{\cdot}828 + 0{\cdot}283 + 0{\cdot}0577\ p\text{H}$, a more satisfactory calibration is obtained, save for that part of the curve corresponding to the stage when the solutions have just become alkaline. The curves obtained by this procedure are given by dotted lines in Fig. 12. The tartaric acid curve thereby becomes nearly coincident with the one obtained by the hydrogen electrode, and the malonic acid curve lies closer to the true curve. The position of the oxalic curve, however, is less satisfactory.

The first method of calibration was adopted in connexion with some precipitation studies with sodium hydroxide from acid

solutions of salts of either reducible metals, or metals more noble than hydrogen, where the hydrogen electrode is inapplicable (Britton, *J. Chem. Soc.*, 1925, **127**, 2148). The initial *p*H's were calculated from the concentrations of acids in which the salts had been dissolved. Salt solutions of the metals: mercuric, cadmium, lead, silver, cupric, uranium, and ferric-iron were studied, and in all cases the electrode furnished an excellent method of detecting when changes in *p*H occurred. The approximate *p*H scales which were assigned to the observed voltages were of reasonable accuracy, with the exception of that referring to the precipitation of silver oxide, for which the extrapolated values of λ at the beginning and the end differed by 0·17 volt. The error was introduced in the E.M.F's registered during the precipitation with the consequence that the precipitation *p*H appeared to be about 6, instead of between *p*H 9 and 10.

CHAPTER VI

METAL-METALLIC OXIDE ELECTRODES

The Mercury-Mercuric Oxide Electrode.

EFFORTS have been made recently to utilise oxidisable metals as electrodes to indicate changes in *p*H. The behaviour of these electrodes is due to the presence or formation of insoluble hydroxides. An electrode occasionally used for the measurement of hydroxyl-ion concentration is that of mercury immersed in a solution containing a suspension of mercuric oxide. The E.M.F. of a mercury electrode in contact with a solution containing mercuric-ions is

$$E = \varepsilon_{Hg}^{\cdot\cdot} + \frac{0{\cdot}058}{2} \log [Hg^{\cdot\cdot}],$$

but in a solution in which mercuric oxide is almost insoluble, $[Hg^{\cdot\cdot}]$ is determined by the solubility product

$$S = [Hg^{\cdot\cdot}]\ [OH']^2,$$

and therefore $$[Hg^{\cdot\cdot}] = \frac{S}{[OH']^2} = \frac{S}{K_w^2} \times [H^{\cdot}]^2,$$

whence $$E = \varepsilon_{Hg}^{\cdot\cdot} + \frac{0{\cdot}058}{2} \log \frac{S}{K_w^2} + \frac{0{\cdot}058}{2} \log [H^{\cdot}]^2$$

$$= \text{a constant} + 0{\cdot}058 \log [H^{\cdot}] \text{ at } 18^\circ \text{ to } 20^\circ \text{ C.}$$

$$= E' - 0{\cdot}058\ p\text{H}.$$

This equation is independent of the valency of the metal, and thus it appears on theoretical grounds that a metal electrode, dipping into a solution in which some of its oxide is placed so as to saturate the solution with the hydroxide, should set up potentials depending upon the concentration of hydrogen ions and some constant function, involving both the electromotive activity of the metal and the solubility product of its hydroxide. Its potential should therefore alter by 58 millivolts for a change in hydrogen-ion concentration indicated by one *p*H unit. The above linear relationship must be regarded as the ideal case, however, for experimental complications arise due to the solubility of the oxide, its dependence upon the size of grain, and a certain sluggishness with which the oxide enters into equilibrium when encoun-

tering changes in hydrogen-ion concentration. These factors affect the constancy of E′, but as these fluctuations are often themselves functions of the *p*H attained in the solution, it is possible in the case of certain metals to construct a calibration curve connecting true *p*H values and observed potentials.

These metal-metallic oxide electrodes are, in effect, oxygen electrodes in which the precise pressure of oxygen is determined by the tendency of the oxide to dissociate into free oxygen and the metal at the particular temperature. Thus, G. N. Lewis (*J. Amer. Chem. Soc.*, 1906, **28**, 158) calculated from the observed pressures of oxygen of silver oxide at high temperatures that the pressure of oxygen which originates from silver oxide at 25° C. is equal to 5×10^{-4} atmospheres.

If we assume for the present that the oxygen electrode is reversible, then the difference in potential which exists between two oxygen electrodes having different oxygen pressures immersed in a solution, whose oxygen ions exert an osmotic pressure of *p* atmospheres, could be accounted for on the grounds that the oxygen ions at the surfaces of the two electrodes would have different electrolytic solution pressures. These solution pressures of oxygen ions would bear a similar relationship to the pressures of the gaseous oxygen surrounding the platinum electrodes, as was the case with the hydrogen electrode as shown on page 60. Hence, the electrode reaction : $O_2 \rightleftharpoons 2O''$, could be expressed as

$$\frac{[\text{electrolytic solution pressure of O}'' \text{ ions}]^2}{[\text{gaseous pressure of O}_2 \text{ molecules}]} = \frac{P^2}{\pi} = K,$$

and therefore the potential of a single oxygen electrode, at pressure π, would be

$$E_{O_2} = \frac{RT}{2F} \cdot \log_e \frac{P}{p} = \frac{RT}{2F} \cdot \log_e \frac{\sqrt{K \times \pi}}{p}.$$

(*N.B.*—This expression is the reciprocal of that given for the hydrogen electrode, because oxygen forms anions—see p. 14.)

If the pressure at one oxygen electrode were equal to one atmosphere, and that at the other were π atmospheres, then the E.M.F. of the cell would be

$$\begin{aligned} \text{E.M.F.} &= E_{1 \text{ atmos.}} - E_{\pi \text{ atmos.}} \\ &= \frac{RT}{2F} \log_e \frac{\sqrt{K \times 1}}{p} - \frac{RT}{2F} \log \frac{\sqrt{K \times \pi}}{p} \\ &= \frac{RT}{4F} \log_e \frac{1}{\pi} = \frac{0{\cdot}058}{4} \log \frac{1}{\pi} \text{ at } 18^\circ \text{ to } 20^\circ \text{ C.} \end{aligned}$$

If therefore a metal-metallic oxide electrode be substituted for the oxygen electrode of pressure π such that π is the dissociation pressure of the oxide, then the electrode process could be represented, for example, as

$$2Ag_2O \rightleftharpoons 4Ag + O_2$$
$$2HgO \rightleftharpoons 2Hg + O_2$$

in the case of the $Ag \mid Ag_2O$ and $Hg \mid HgO$ electrodes respectively. According to G. N. Lewis's computation the dissociation pressure, of silver oxide is 5×10^{-4} atmospheres at 25° C., and therefore the potential of a silver-silver oxide electrode in any solution at 25° C. will be

$$\frac{0{\cdot}0591}{4} \log \frac{1}{5 \times 10^{-4}} = 0{\cdot}049 \text{ volt}$$

less positive than the hypothetical reversible oxygen electrode at 1 atmos. pressure. Despite some unknown disturbing influences on the potential of the $Ag \mid Ag_2O$ electrode, the author found that by using *freshly* precipitated oxide in sodium hydroxide solutions *p*H 11·4 the potentials which were readily attained were 1·167 volts more positive than those of hydrogen electrode in the same solution at 20° C. If we add 0·049 volt, which is true for 20° C. as well as for 25°, to 1·167 volt, we obtain 1·216 volt as that of the oxygen-hydrogen cell,—a value a few millivolts lower than the extrapolated value of Nernst and Wartenberg, *viz.*, 1·226 volts.

The mercury-mercuric oxide electrode has been used for the determination of the concentration of hydrogen ions and also for following *p*H changes in alkaline solutions. According to Allmand (*Z. Elektrochemie*, 1910, **16**, 263; see p. 37) it is always 0·925 volt more positive at 18° C. than the corresponding normal hydrogen electrode, and thus the potential of the mercury-mercuric oxide electrode,

$$E_{Hg \mid HgO} = 0{\cdot}925 + 0{\cdot}058 \log [H^{\cdot}].$$

By comparing this formula with that evaluated on page 95, we see that the constant, 0·925, might have been calculated from

$$\varepsilon_{Hg^{\cdot\cdot}} + \frac{0{\cdot}058}{2} \log \frac{S}{K_w{}^2},$$

to which it is equal. Of the quantities involved, ε, the normal potential of divalent mercury is equal to + 0·86 volt, $K = 10^{-14{\cdot}13}$ at 18° C., and $S = [Hg^{\cdot\cdot}][OH']^2$. The value of the solubility product may be calculated from the potential of

the Hg | HgO electrode when immersed in solutions of known pH from

$$E = \varepsilon_{Hg}^{\cdot\cdot} + \frac{0{\cdot}058}{2} \log \frac{S}{K_w^2} + 0{\cdot}058 \log [H^{\cdot}].$$

If we take Donnan and Allmand's values of E in 0·1 N-NaOH, (pH = 13·07,) E = 0·169 volt, and in 1·0 N-NaOH, (pH = 14·05), E = 0·114 volt, we find that $S = 1 \times 10^{-26}$ (approx.) = $[Hg^{\cdot\cdot}][OH']^2$ in each case. By knowing that the mercury-mercuric oxide electrode establishes a potential, 1·232 − 0·925 = 0·307 volt less than that of the hypothetical reversible oxygen-electrode in the same solution, Allmand calculated that the electrode exerted an oxygen pressure of 6×10^{-22} atmosphere, which is thus the dissociation pressure of mercuric oxide at 18° C. Hence we conclude that this particular electrode behaves reversibly as an oxygen electrode and may be used to calculate the pH of alkaline solutions. Its nature imposes upon it certain limitations. It can only be used in alkaline solutions, for the oxide dissolves in acids. Another disadvantage arises from the tendency of reduction of mercuric ions to mercurous ions at the expense of the mercury, thus

$$Hg + Hg^{\cdot\cdot} \rightleftharpoons Hg_2^{\cdot\cdot}$$

with the formation of black mercurous oxide, though this does not occur in the more alkaline solutions as it is known that the Donnan-Allmand standard electrodes remain at constant potential for long periods of time. This is because the concentration of mercurous ions is, at such pH's, vanishingly small. Pinkhof (*Diss., Amsterdam*, 1919) has shown that chloride ions interfere with the electrode by accelerating reduction to form calomel. If chloride-ions are not present the electrode can be used above pH 8; below which both reduction and solution occur. If the concentration of chloride ions is 10^{-2} gram ions per litre, then the electrode can only be used above pH 9, if $[Cl'] = 10^{-1}$, above pH 10, and if [Cl'] = 1 Molar, above pH 11. Pinkhof showed that electrometric titrations can be performed with the electrode, but on account of the alkaline range of utility, he found it necessary to employ fairly concentrated solutions and to titrate solutions to which excesses of concentrated alkali had been added in order to get the inflection within the range of pH. In this way he was able to estimate magnesium in the presence of calcium by titration with N-HNO_3. Phosphates, pyrophosphates, borates, and alkaloids could also be estimated.

Many other metal-metallic oxides have been investigated. From what has been written, it is probable that silver-silver

oxide is useless, so also is copper-cupric oxide, for, as found by the author (*J. Chem. Soc.*, 1925, **127**, 2796), reduction readily takes place. Certain metals are so readily oxidisable that they become covered with an oxide film as soon as the *p*H of the salt solutions in which they may be immersed is increased, and then they function, often irregularly, as hydrogen electrodes. This applies to aluminium, zinc, cadmium, and antimony. Heyrovský (*J. Chem. Soc.*, 1920, **117**, 35) proved that the action taking place at the surface of an aluminium electrode was due to the formation of a skin of aluminium hydroxide, which, owing to its extremely small solubility product, *viz.*, 10^{-33}, resisted to a very great extent the action of acids, so that the potential of the electrode was determined directly by the hydroxyl-ion concentration, and only by the aluminium-ion concentration to the extent permitted by the solubility product equilibrium.

The Antimony-Antimonous Oxide Electrode.

The potential which is set up at an antimony electrode is a function of the hydrogen-ion concentration of the solution, whether antimonous oxide is, or is not, suspended in the solution. A very small amount of oxide is always present on the metal surface which ensures the electrode operating as $Sb \mid Sb_2O_3 . H^{\cdot}$, but, owing to the relative insolubility of the oxide in aqueous solutions, even 0·1 N-HCl and 0·1 N-NaOH, the electrode is not completely reversible. It serves as an excellent indicator in potentiometric titrations of acids and bases and in precipitation reactions, so much so that a fairly satisfactory *p*H scale can be attached to the titration graph from a consideration of the potentials given at the ends of the titration, if the *p*H values then prevailing happen to be known. Because of the solvent action of hydroxy acids on antimony oxide, the variations in potential of the antimony electrode in the presence of tartaric and citric acids do not follow closely the change in *p*H.

The presence of oxidising agents in the solution also causes some disturbance, evidently through the tendency to convert the Sb_2O_3 into Sb_2O_5. Inflexions in titration curves are clearly indicated, but the interpretation of the potentials in terms of *p*H values becomes difficult. This is particularly true above *p*H 7.

The potential set up at the $Sb \mid Sb_2O_3$ electrode, besides depending on the hydrogen-ion concentration of the solution, is determined to a small extent by (*a*) the nature of the metallic antimony, (*b*) the condition of the antimonous oxide, whether it is formed on the surface of the electrode or whether it is sus-

pended in the solution, (*c*) the passage, including the rate, of oxygen or air through the solution, and (*d*) the agitation of the solution in immediate contact with the electrode.

Several workers have paid considerable attention to the preparation of the antimony electrode itself in the hope of obtaining a form which would give results that were more reproducible than those given by cast antimony electrodes. Despite the elaborate methods which have been adopted, the electrodes appear to possess no special advantages over freshly polished cast antimony electrodes.

Various electrolytic methods have been tried. Roberts and Fenwick (*J. Amer. Chem. Soc.*, 1928, **50**, 3125) used antimony crystals which were obtained by electro-deposition at high C.D. from a hydrofluoric acid solution of antimony trioxide. Perley (*Ind. Eng. Chem., Anal. Edn.*, 1939, **11**, 317) employs a similar method, but subsequently melts the crystals and casts the metal into circular rods, around which a hard rubber covering is moulded so as to leave only the bottom end exposed. This end serves as the electrode and is kept highly polished. Pure Sb_2O_3 is dissolved in hydrofluoric acid to give a 12 per cent. solution of SbF_3 which is electrolysed using a platinum cathode, 1 cm. × 1 cm., and a platinum anode of 20 sq. cm. surface, which are immersed in the solution together with an excess of Sb_2O_3 in an extraction thimble compartment. A current of 5 ampères produced excellent crystals of antimony. The area of the antimony electrode to be exposed to the test-solution depends on the galvanometer available, large surfaces being necessary with low sensitivity instruments. For *p*H measurements polished surfaces should be used, which must be etched by immersion in a solution at *p*H 7–9 for an hour or two before use. Fischbeck and Eimer (*Z. Elektrochem.*, 1938, **44**, 845) electro-deposit a fine silver-white crystalline coating of antimony on nickel, nickel-alloys or noble metals from a bath composed of 50 grams of saturated antimony trichloride solution and 100 grams of 2N-HCl containing 2 grams of tartaric acid at 85°–90°. The deposit is polished with fine glass-paper and then cathodically polarised in 2N-HCl between two antimony rod anodes for 40 minutes, after which it is washed with water and then treated with boiling water for five minutes. It is thoroughly dried and, except the end, is covered with nitrocellulose varnish. These electrodes do not appear to be serviceable for more than a single determination. Shukov and Awsejewitch (*Z. Elektrochem.*, 1929, **35**, 349) claim to have prepared satisfactory electrodes by deposition on a mercury

coated platinum wire, 1 cm. long, from a 25 per cent. $SbCl_3$ solution in acetone with a current of 0·6–2·2 milliamps. for 30 minutes. Perley also used methyl alcohol and acetonitrile as solvents and obtained good electrodes. The potentials of amalgamated platinum-antimony electrodes, although fairly reproducible, differed from those set up at cast antimony electrodes. The electroplated electrode only held its potential at *p*H 10·8 for 5–8 hours when in contact with air, probably on account of the dissolution of the antimony.

Böttger and Szebellédy (*Z. Elektrochem.*, 1932, **38**, 737) deposit a greyish black, adherent layer of antimony on the electrode, by placing the polished antimony in a 10 per cent. $SbCl_3$ solution in 2N-HCl, the electrode having twisted around it 8–10 cm. of thin flower iron wire in the form of a spiral, which on dissolution causes a deposit of finely divided antimony to be formed on the electrode surface. It is washed with water, wiped with a filter paper and kept in distilled water overnight. The disadvantage of this electrode is that its life is not long. They showed that a low melting-point antimony alloy with bismuth and cadmium (Hahn, *Z. angew. Chem.*, 1930, **43**, 712) could be used as an electrode, so also could "explosive antimony" deposited on platinum by the method of Cohen and Ringer (*Z. physikal. Chem.*, 1904, **47**, 1). They also found that boiling an antimony electrode for 10 minutes in 10 per cent. H_2SO_4, followed by immersion in 2N-HNO_3 for 3 hours, washing with water and leaving overnight in distilled water, produced a suitable oxide layer.

Perley observed that it was not essential that the solution undergoing test should contain dissolved oxygen; in fact, the antimony electrode gave satisfactory results between *p*H 4 and 11 when the solution was saturated with nitrogen. The potential of the electrode depends on the equilibrium set up at the electrode-solution interface, and in consequence a small agitation of the solution has almost the same disturbing influence as a vigorous agitation. When the solution is saturated with air, Perley finds that below 15° very little differences are caused by a moving solution, and by substituting oxygen for air the differences are still smaller. He also observed that when an antimony electrode is used in a solution of *p*H 10, the Na content of which is greater than 1 M., white crystals are slowly formed on the antimony surface. These interfere with the normal functioning of the electrode and must be removed. In still solutions the potentials obtained are more in accord with the ordinary Nernst equation. Wulff, Kordatzki and Ehrenberg

(*Z. Elektrochem.*, 1935, **41**, 542), on the other hand, consider that the potentials are greatly influenced by the movement of the electrolyte. (See also Fischbeck and Eimer.) Using an antimony stick as electrode, they found that saturating the solution with Sb_2O_3 had no effect on the potential. The formation of Sb_2O_5 increased the potential by about 10 mv. By leading oxygen through the solution more positive potentials were obtained than when air was used. With oxygen the potentials assumed constant values for any given *p*H within the range *p*H 2–12. To prevent the unnecessary deposition of oxide on the

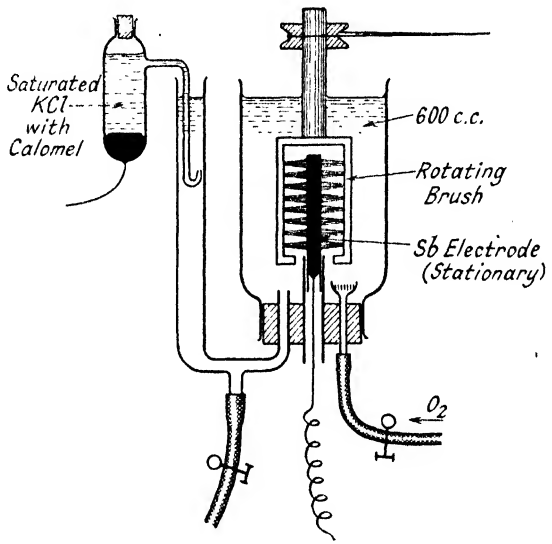


FIG. 13.—The Antimony Electrode of Wulff, Kordatzki and Ehrenberg.

electrode, they surrounded the stationary electrode with a mechanically operated brush. Their apparatus is illustrated in Fig. 13. The results were constant within 2 or 3 mv. (extreme variation 7 mv.) over a period ranging from 2 minutes to 2 hours.

The antimony electrode may also be used for the measurement of *p*H values. Calibration, however, is necessary by means of buffer solutions of known *p*H values. These buffer solutions must not contain hydroxy acids.

Britton and Robinson (*J. Chem. Soc.*, 1931, 458) investigated the antimony electrode with the dual object of ascertaining its scope as a titrimetric indicator and the extent to which the E.M.F's may be accurately converted into *p*H values.

Massive metal electrodes, that had been coated with the trioxide by treatment with warm 50 per cent. nitric acid, were found to enter rapidly into almost stable equilibrium and to be capable of leading to correct *p*H values. Their use on subsequent days, however, gave erratic results. Of the many forms investigated, Britton and Robinson concluded that electrodes prepared by cleaning cast antimony bars with emery paper immediately before use in conjunction with purified antimonous oxide suspended in the solution were the most satisfactory. The oxide was prepared by the method described by Schuhmann (*J. Amer. Chem. Soc.*, 1924, **46**, 52), by precipitating basic antimonous chloride from a hydrochloric acid solution, redissolving it in acid, and precipitating the oxide by stirring the solution into a boiling sodium carbonate solution. King (*Ind. Eng. Chem., Anal. Edn.*, 1933, **5**, 323) used stick antimony, but found that after a time the electrode became heavily coated with oxide and then became sluggish. It could be regenerated by re-polishing with emery powder and allowing to stand in water for three days in order to oxidise slightly. Thorough mechanical stirring is essential for the maintenance of the equilibrium on which the electrode potential depends.

As already stated several factors may influence the potential of the antimony electrode, but it is the opinion of the author that if the method adopted to measure the *p*H of the solution is exactly the same as that employed in calibrating the electrode in standard buffer solutions, reasonable accuracy can be obtained.

Instead of using a series of separate buffer solutions for calibrating the electrodes, it was considered better to adopt a slightly modified form of the Prideaux-Ward universal buffer mixture (see p. 313), which, on gradual neutralisation with sodium hydroxide, would subject the electrode to continuous changes of hydrogen-ion concentration ranging from *p*H 2–12. Moreover, the behaviour of the electrode could also be tested when it was immersed in the buffer solution which had been previously neutralised to some desired stage. In this way, it would be possible to ascertain whether the potential of the electrode could be considered as an indication of the true *p*H values, not only during a titration, but also in the case of any single measurement.

Whilst the antimony-antimonous oxide electrode on immersion in an acid solution did not give a steady reading until about five minutes had elapsed, it was found that throughout the buffer titration steady E.M.F's were set up in less than three minutes. It should be stated here that, although apparently stable E.M.F's were produced after five minutes, these values showed a very

small variation of about 4 millivolts per hour in solutions of *p*H 2–12. Nevertheless, the potentials throughout the complete neutralisation of the universal buffer mixture were reproducible to within 1 millivolt, the titration having been performed at least a dozen times with the same electrode.

The E.M.F's of the cell: Sb | Sb_2O_3 solution | sat. KCl | N-Calomel are given in Tables 19 and 20 for *p*H values ranging from *p*H 1·8–11·94, and are also plotted in Fig. 14.

The fifth column gives the E.M.F. of the cell Sb| Sb_2O_3, solution |H_2, and if the antimony electrode behaved reversibly as

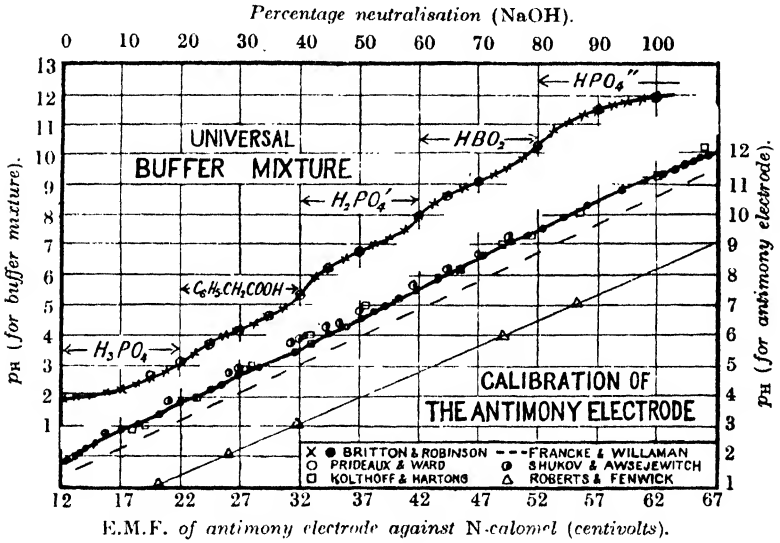


FIG. 14.

regards hydrogen ions this E.M.F. would have had the same value whatever the *p*H of the solution. The data show that there was a steady increase from 0·263 to 0·302 volt, *i.e.*, the antimony electrode gave potentials that were more positive than the hydrogen potentials by amounts varying within this range. This shows that in the expression, $E = E' - 0{\cdot}057\ p\text{H}$ at 14° C., which would have represented the potentials of the antimony electrode if it had behaved strictly as a hydrogen electrode,

the slope $$\frac{dE}{dp\text{H}} = -0{\cdot}057 \text{ at } 14^\circ \text{ C.}$$

did not remain absolutely constant but became less as the *p*H was raised. Fig. 14, however, shows that the potential of the

TABLES 19 AND 20

TITRATION OF 100 C.C. OF THE UNIVERSAL BUFFER MIXTURE WITH 0·2N-NaOH AT 14° USING (1) THE ANTIMONY ELECTRODE AGAINST THE N.-CALOMEL, (2) THE HYDROGEN ELECTRODE AGAINST THE N.-CALOMEL

TABLE 19

C.c.	*p*H.	$E_{Sb.}$ (− *ve*)	E_{H_2} (− *ve*)	Diff.
0	1·81	0·124	0·387	0·263
2·5	1·91	0·127	0·393	0·266
5	1·98	0·131	0·397	0·266
7·5	2·10	0·135	0·404	0·269
10	2·21	0·141	0·410	0·269
12·5	2·38	0·147	0·420	0·273
15	2·55	0·156	0·429	0·273
17·5	2·84	0·167	0·446	0·279
20	3·05	0·184	0·458	0·274
22·5	3·38	0·203	0·477	0·274
25	3·75	0·221	0·498	0·277
27·5	3·92	0·233	0·507	0·274
30	4·22	0·244	0·525	0·281
32·5	4·33	0·255	0·531	0·276
35	4·65	0·268	0·549	0·281
37·5	4·92	0·286	0·564	0·278
40	5·43	0·316	0·594	0·278
42·5	6·02	0·343	0·627	0·284
45	6·33	0·359	0·645	0·286
47·5	6·59	0·371	0·660	0·289
50	6·79	0·382	0·671	0·289

TABLE 20

C.c.	*p*H.	$E_{Sb.}$ (− *ve*)	E_{H_2} (− *ve*)	Diff.
52·5	6·99	0·393	0·682	0·289
55	7·24	0·404	0·697	0·293
57·5	7·51	0·418	0·712	0·294
60	7·95	0·435	0·737	0·302
62·5	8·35	0·456	0·760	0·304
65	8·68	0·473	0·779	0·306
67·5	8·90	0·487	0·791	0·304
70	9·10	0·497	0·803	0·306
72·5	9·36	0·510	0·818	0·308
75	9·58	0·524	0·830	0·306
77·5	9·93	0·539	0·850	0·311
80	10·33	0·559	0·873	0·310
82·5	10·81	0·589	0·900	0·311
85	11·12	0·610	0·918	0·308
87·5	11·35	0·624	0·930	0·306
90	11·47	0·634	0·938	0·304
92·5	11·64	0·643	0·947	0·304
95	11·75	0·650	0·954	0·304
97·5	11·84	0·656	0·959	0·303
100	11·94	0·663	0·965	0·302

antimony electrode bears almost a rectilinear relationship with *p*H. The calibration values are also seen to be in good agreement with those of Kolthoff and Hartong (*Rec. trav. chim.*, 1925, **44**, 113), and Shukov and Awsejewitch, but not with those of Francke and Willaman (*Ind. Eng. Chem.*, 1928, **20**, 87), and Roberts and Fenwick. Similar observations have been made by Sava and Hemedes (*Philipine Agr.*, 1928, **17**, 337), Harrison and Vridhachalam (*Mem. Dept. Agr., India*, 1929, **10**, 157), Tomiyama (*J. Biochem., Japan*, 1933, **18**, 285), King (*loc. cit.*), Parks and Beard (*J. Amer. Chem. Soc.*, 1932, **54**, 856), Mehta and Jatkar (*J. Indian Inst. Sc.*, 1935, A, **18**, (12) 85), Bravo (*Chim. Ind.*, Milan, 1935, **17**, 521) and Fischbeck and Eimer (*loc. cit.*).

Britton and Robinson carried out a series of titrations with the antimony electrode and found that not only were the curves correct as regards inflexions but that the *p*H values read off from the calibration curve were, in the case of acetic, malonic, maleic, fumaric, boric, hydrocyanic, and phosphoric acids, of a reasonably high degree of accuracy. Other acids, *viz.*, chromic, sulphurous,

permanganic, hydrazoic, telluric, selenious, selenic, hydrocyanic, maleic and fumaric, to which the hydrogen electrode is normally inapplicable, may be either completely or partly titrated as far as inflexions are concerned in the presence of antimony electrodes. The *p*H values are, however, usually inaccurate. Technically pure cast antimony was quite suitable for use as electrodes, but impurities, *e.g.*, bismuth, lead, and tin, caused the calibration curve to be displaced a few millivolts.

Fenwick and Gilman (*J. Biol. Chem.*, 1929, **84**, 605) have used the antimony-antimonous oxide electrode, as modified by Roberts and Fenwick, to determine the dissociation constants of anæsthetics. The antimony electrode has been used to follow the precipitation reactions of aluminium, iron and magnesium salts with alkali (Treadwell and Bernasconi, *Helv. Chim. Acta*, 1930, **13**, 500; Elder, *Trans. Amer. Electrochem. Soc.*, 1930, **57**, 383; Malvea and Withrow, *J. Amer. Chem. Soc.*, 1930, **54**, 2243; Kanning and Kratli, *Ind. Eng. Chem., Anal. Edn.*, 1933, **5**, 381)

Temperature has a little effect on the potentials of the antimony electrode, but as the electrode must be calibrated, and used, under the same rigorously controlled conditions, if it is to be used for accurate *p*H determinations, the influence of temperature will be included in the calibration data.

A modification of the antimony electrode has been described by Ball, Schmidt and Bergstresser (*Ind. Eng. Chem., Anal. Edn.*, 1934, **6**, 60). Instead of the usual Sb_2O_3 coating, Sb_2S_3 is used. It appears to be useful over the range *p*H 2·2–10, in which it will give *p*H values accurate to within 0·05 *p*H and the difference between individual electrodes in the same solution is not more than 2–3 mv. More alkaline solutions, however, remove the sulphide layer. The electrodes are prepared by suspending cast antimony electrodes in hot 0·3N-HNO_3 for one hour and then saturating the solution with hydrogen sulphide.

Tungsten-Manganic Oxide Electrode.

As previously stated, Baylis showed that tungsten wire behaved as a metal-metallic oxide electrode so that it could be used for investigating changes in hydrogen-ion concentration of river water. This work has been followed up by Parker (*J. Ind. Eng. Chem.*, 1925, **17**, 737), who also took advantage of the observation of Thompson and Crocker (*Trans. Amer. Electrochem. Soc.*, 1915, **27**, 167) that manganese dioxide will act as an oxygen electrode. Working with different metals and oxides not in immediate contact, it was found that very often the electrode ceased to function, but when the oxide was brought into intimate contact with

the electrode metal this difficulty was overcome. Table 21 gives the results obtained when such electrodes were placed in buffer solutions of different *p*H values. The E.M.F's are referred to the potentials of the hydrogen electrode when in equilibrium with the various solutions.

TABLE 21

E.M.F'S OF METAL | OXIDE. BUFFER SOLUTION | H_2 (PARKER)

Electrode.	Buffer Solution.			
	Phthalate *p*H = 3·92.	Phosphate *p*H = 6·35.	Borate, NaCl *p*H = 8·25.	Borate *p*H = 9·07.
W—Co_2O_3	0·387	0·480	0·501	0·508
W—MnO_2	0·448	0·448	0·512	0·516
W—Mn_2O_3	0·402	0·486	0·501	0·502
W—Mn_2O_3, treated	0·450	0·462	0·466	0·464
W, bare	0·371	0·410	0·457	0·453
W, treated	0·355	0·410	0·435	0·433
Pt—Mn_2O_3	0·981	1·016	1·015	1·016
Pt, platinised	0·928	0·940	0·945	0·940
Pt, platinised—Co_2O_3	0·918	0·952	0·952	0·954
Au, platinised—Mn_2O_3	0·965	0·976	0·971	0·967
Pt, platinised—Mn_2O_3	0·968	0·974	0·970	0·969

The table shows that the only two electrodes to give a really satisfactory relationship to the hydrogen electrode potentials throughout the *p*H range from 4 to 9 were platinised gold and platinised platinum electrodes both in contact with manganese sesquioxide. Many of the different electrodes gave constant values in alkaline solutions and could therefore be used in solutions of *p*H greater than 8. Though tungsten cannot be regarded as an unattackable metal and therefore to behave as does platinised platinum or gold, Parker found that, when tungsten electrodes were placed in a strongly alkaline buffer solution, their potentials drifted for several days but ultimately approached a definite value. Electrodes treated in this way may, as shown in Table 21, be used in solutions down to *p*H 4. The effect of this alkali treatment lasts for two or more weeks, during which time, Parker states, the electrodes can be used in flowing solutions in conjunction with a self-recording potentiometer. One advantage of the tungsten-manganic oxide electrode appears to rest in its resistance to "poisoning." As may be expected from Table 21, the E.M.F's of these electrodes are not linear functions of *p*H, and in order to ascertain *p*H values it is necessary to calibrate the potentials of

the electrode in solutions of known *p*H values. These electrodes do not function in solutions below *p*H 4. They have been patented by the Leeds and Northrup Co. (Parker and Dannerth, *J. Ind. Eng. Chem.*, 1925, **17**, 637; U.S.P. 1,513,558/1924), and have been used in the sugar and other industries (see Chapter XXXVI). As the electrodes require 20–30 minutes in which to attain equilibrium, they are placed in position sometime before being incorporated in the potentiometer circuit.

It appears that manganic oxide in contact with a platinised electrode tends to supply it with oxygen, thus

$$4Mn(OH)_3 \rightleftharpoons 4Mn(OH)_2 + O_2 + 2H_2O,$$

so that the pressure of oxygen,

$$[O_2] = \frac{K[Mn(OH)_3]^4}{[Mn(OH)_2]^4},$$

and therefore if the ratio of the extremely low concentrations of the two dissolved hydroxides remained constant, we see that the electrode would function as an oxygen electrode under a constant pressure of oxygen gas. The concentration of manganous hydroxide will be kept extremely small on account of the ease with which it becomes oxidised to the hydroxide of higher valency, but as this oxidation process is a question of the prevailing *p*H and also as the higher oxide becomes soluble at a *p*H value below 4, it is seen that the electrode is useless in the more acid solutions. It is therefore in neutral and alkaline solutions where the electrode may be expected to function best. Taking the tungsten-manganese oxide electrode as 0·46 volt more positive than the corresponding hydrogen electrode, we see that it will be 0·77 volt less than that of the hypothetical oxygen electrode in equilibrium with the same solution, whence it follows that the effective oxygen pressure in the electrode is 10^{-53} atmospheres. This explanation is comparable with that applied to the quinhydrone electrode. The disregard of the fact that the tungsten electrode is attackable is not justifiable, especially as gold- and platinum-manganic oxide electrodes are each about 0·5 volt more positive than the tungsten-manganic oxide electrode. There must be therefore an involved series of equilibria established between any oxides of tungsten, formed at the electrode surface, and those of manganese. This type of electrode, in spite of being in its preliminary stages of development, has already been found of service in water purification, treatment of boiler feed-water, sugar refining, and sewage disposal.

The Tungsten Electrode.

Baylis (U.S.P. 1,727,094, 1929) has patented the use, as an electrode, of the tungsten filament of an electric lamp, but Holven (*Ind. Eng. Chem.*, 1929, **21**, 965) has found that bare tungsten wire electrodes are only capable of yielding accurate *p*H measurements of sugar liquors for a day after being coated with an oxide film by immersion in a solution of normal sodium phosphate for two days, followed by a further two days' immersion in sugar solution. Britton and Dodd (*J Chem. Soc.*, 1931, 829) have investigated the possibilities of bare tungsten, in filament and rod form, over a *p*H range of 2–12. Calibration was effected by means of a series of titrations of the modified universal buffer mixture (p. 313). The formation of the oxide film by anodic oxidation in very dilute sodium hydroxide solution led to unsatisfactory electrodes, but simple immersion in the buffer mixture at *p*H 12 in presence of air caused sensitive, but invisible, films to be formed. As titration indicators, tungsten electrodes are very suitable, though, as Holven found, they do not retain their calibration for periods longer than a day. If the solution, whose *p*H value is to be determined, does not contain any oxidising or reducing substances the *p*H value can be accurately estimated by reading off from a calibration curve obtained immediately before making the determination. Fig. 15 gives typical calibration curves and shows the effect of ageing over a period of nine days.

The lower curves in the two sets refer to the E.M.F's established in solutions of varying *p*H values after immersion of the electrodes for four hours, whilst the upper ones correspond to the E.M.F's indicated after nine days of continuous use. Over the whole *p*H range there was a tendency for the electrodes to assume more positive values on ageing, as will be seen from Fig. 15. The intermediate curves were obtained at various times within this period. The magnitude of these variations was greater in the case of the filament than in the case of the rod electrode. Thus at *p*H 2, *p*H 6, and *p*H 12 the filament became respectively 32, 36, and 38 millivolts more positive, and the corresponding positive changes of the rod electrode were 28, 18, and 13 millivolts respectively. Nevertheless, it was found that these electrodes could be used in the titration of acetic, boric, phosphoric, maleic and hydrazoic acids, and, by referring the voltages observed to a calibration curve obtained prior to each titration, the *p*H values prevailing at any stage of the various neutralisations could be estimated with considerable accuracy. Though the tungsten electrode could be used to indicate the successive stages in the

neutralisation of such acids as hydrocyanic and sulphurous acids, the *p*H values so estimated were inaccurate, evidently due to some reaction between the acids and the electrode in interfering with the usual electrodic reaction.

If the reaction occurring at the electrode interface were similar to that of a reversible metal-metallic oxide electrode, then the

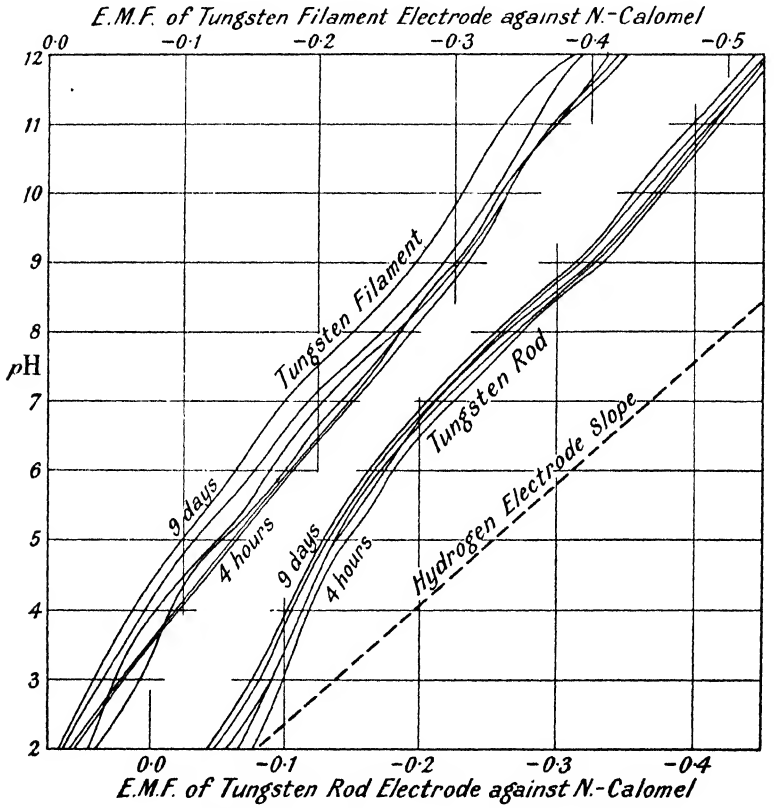


FIG. 15.—Typical Calibration Curves of Tungsten Electrodes (Britton and Dodd).

potentials of the tungsten electrode should show a constant difference with respect to those of the hydrogen electrode in the same solutions. In other words, the extrapolated E.M.F. of the cell $\overset{+}{W}|\text{solution}|\overset{-}{H_2}$ should be the same whatever the *p*H value of the solution. This is not the case, for the difference is much greater with solutions of high *p*H, *e.g.*, at *p*H 2 the

potential of the thin rod was 0·322 volt, at *p*H 6 it was 0·446 volt, and at *p*H 12 it was 0·510 volt more positive than that of the hydrogen electrode. The broken line in Fig. 15 gives the theoretical slope of the calibration curves if the potential of the tungsten electrode had been simply a function of the concentration of hydrogen ions.

The Tellurium Electrode.

Tomicek and Poupe (*Coll. Czech. Chem. Comm.*, 1936, **8**, 520) have found that pure tellurium rods are reliable *p*H indicators over the range *p*H 2–12. They affirm that in some cases it is a more suitable *p*H indicator than the antimony electrode. It appears to be unaffected by strong oxidising agents and organic anions. Rods 7–9 mm. in diameter are employed.

Germanium-Germanic Oxide Electrode.

Nichols and Cooper (*Ind. Eng. Chem., Anal. Edn.*, 1935, **7**, 350, 353) have shown that in a qualitative sense the potential of the $Ge|GeO_2$ electrode is a function of *p*H, but up to the present the electrode has not been prepared in such a way as to give reproducible results. It can, however, be used as a *p*H indicator electrode in potentiometric titrations, in which case the presence of GeO_2 in the solution is unnecessary.

Bismuth Electrode.

This electrode appears to be of very limited application. According to Mehta and Jatkar (*J. Indian Inst. Sci.*, 1935, A, **18**, 109), bismuth electrodes which show interference colours, due to oxide film, may be used within the range *p*H 5·0–7·4.

CHAPTER VII

THE GLASS ELECTRODE

Haber's Glass Electrode.

As the result of an idea thrown out by Nernst (*Z. physikal. Chem.*, 1892, **9**, 137) regarding the potential difference which should exist at the boundary between a mixed crystal and its saturated solution, Haber conceived the idea that potentials should exist at glass-aqueous solution interfaces. Freundlich and Rona (*Berlin Akad. Ber.*, 1920, 397) confirmed Haber and Klemensiewicz's observations (*Z. physikal. Chem.*, 1909, **47**, 385), whilst both Hughes (*J. Amer. Chem. Soc.*, 1922, **44**, 2860; *J. Chem. Soc.*, 1928, 491) and von Steiger (*Z. Elektrochemie*, 1924, **30**, 259) amplified the manipulative details and compared glass electrode potential data with those given by the hydrogen electrode in the same solutions. The problem of obtaining suitable glass, as regards the functioning of the electrode as if it were one of hydrogen and also as regards its electrical resistance, has been investigated by Horowitz (*Z. Physik*, 1923, **15**, 369), Schiller (*Ann. Physik*, 1924, **74**, 105), and recently by Hughes (*loc. cit.*), and MacInnes and Dole.

Theory of Glass Electrode.

Much of the theory underlying the potential of a glass electrode is a matter of conjecture, for the potential depends upon the composition and nature of the glass, inasmuch as these factors seem to determine with which type of ion present in a solution it will enter into equilibrium. Table 22 gives the analyses of various glasses studied by Hughes.

It will be observed that the glasses which conducted electricity well had both high sodium oxide and calcium oxide contents, but that in the two glasses from which satisfactory electrodes could be made there was a comparatively small percentage of alumina, much less than 2 per cent. It appears therefore that the less alumina a glass contains the better it will be for glass electrode work; also that a high soda content enhances the conductivity, whereas potash seems to decrease it. Hughes states that the glass represented by the first set of analyses had such a high conductivity that electrostatic shielding of the cell was unnecessary,

TABLE 22

PERCENTAGE COMPOSITIONS OF GLASSES SUITABLE AND UNSUITABLE FOR GLASS ELECTRODES

Constituent.	Suitable.		Unsuitable.			
SiO_2	71·83	69·75	70·62	67·56	66·88	72·19
Al_2O_3	0·44	1·04	3·23	6·53	4·60	8·96
TiO_2	—	—	Trace	Trace	Trace	—
Fe_2O_3	0·04	0·05	0·11	0·13	0·08	—
MnO	—	0·21	Trace	0·17	Trace	—
CaO	8·36	11·26	7·58	6·54	6·76	0·08
MgO	Trace	Trace	0·25	—	0·81	—
Na_2O	18·83	16·54	15·48	15·82	15·48	18·79
K_2O	—	0·66	2·62	3·34	5·56	—
SO_3	0·22	0·34	—	—	—	—
Sb_2O_3	—	0·22	—	—	—	—
Conductivity	Excellent	Very good	Good	Poor	Very poor	Good
Change in voltage per 1 *p*H, compared with hydrogen electrode E.M.F. (*p*H 0–10)	95-98%	95 (?) %	92%	88%	—	24–27%

and in addition, the electrode potential was scarcely influenced by large variations in sodium-ion concentration, provided that the *p*H was less than 9. If boric oxide be present in a glass, then it may function, as was found by Horowitz and Schiller (*loc. cit.*), as both a sodium and a hydrogen electrode. Hence in borosilicate glasses the sodium content partly determines the potential of the resulting glass electrodes, whereas soda-lime glasses containing no boric oxide or relatively small quantities, (less than 2 per cent.), assume potentials which, within the range *p*H 0 to *p*H 10, are almost a linear function of the *p*H of the solutions in which the electrodes are immersed. This will be evident from the last line in Table 22.

Glass electrodes give a linear relationship between E.M.F. and *p*H from *p*H 2·0 to 8·5, the slope at 22° being 0·0585 in accord with the Nernst equation. At *p*H 8·5 the slope begins to decrease slightly until at about *p*H 13 it becomes zero and thereafter acquires a negative value. Dole (*J. Amer. Chem. Soc.*, 1931, **53**, 260), MacInnes and Belcher (*ibid.*, 3315), Powney and Jordan (*J. Soc. Chem. Ind.*, 1937, **56**, 133T) and Jordan (*Trans. Faraday Soc.*, 1938, **34**, 1305) observed appreciable deviations at about *p*H 10, owing to the glass electrode then functioning not

only as a hydrogen electrode, but also as a sodium electrode ; the divergence from the linearity of the E.M.F./*p*H graph being greater the greater the sodium-ion concentration of the solution. To use the glass electrode for the determination of the *p*H of alkaline solutions it is imperative that the electrode should be calibrated by means of buffer solutions having approximately the same sodium-ion concentration as that of the solution undergoing test. Employing lithia, instead of soda, in the glass, (Li_2O, 10 per cent. ; CaO, 10 per cent. ; SiO_2, 80 per cent.) Sokolov and Passinski (*Z. physikal. Chem.*, 1923, A, **160**, 360) found that in the presence of NaOH, *p*H values can be determined up to 12·5 and in the presence of KOH, RbOH and CsOH, up to 13·5. Lorch (*Ind. Eng. Chem., Anal. Edn.*, 1934, **6**, 165) found that anions were without effect.

Britton and Welford (*J. Chem. Soc.*, 1940, 764) have observed that the glass electrode is especially suited to titrations at elevated temperatures ; in fact, it then appears to be much more sensitive to *p*H changes than at ordinary temperatures. This is, no doubt, due to the diminution in the specific resistance with increase in temperature. Thus Kahler and de Eds (*J. Amer. Chem. Soc.*, 1931, **53**, 2998) found that the specific resistance of one glass was 1200 megohms at 5° but fell to 12 megohms at 55° C. Incidentally the specific resistance changes with time, especially if the electrode is dry. Over a period of 10 days MacInnes and Belcher (*ibid.*, p. 3315) found that the resistance of glass electrodes kept in moist air increased by 34 per cent., whereas, the increase was 230 per cent. in dry air.

The question of glass suitable for glass electrode work has been carried an important step further by MacInnes and Dole (*J. Amer. Chem. Soc.*, 1930, **52**, 29). They have prepared a number of samples of glass and have measured the resistance and electromotive behaviour of very thin glass membranes made from them. In making these glasses *no alumina was used.* Mixes were made of weighed amounts of dry silica and the various carbonates. After thorough grinding, they were inserted, a few grams at a time, in an electric furnace, melted, and then held for an hour or so at 1200°–1400° until all gas bubbles had escaped from the melts and they had acquired a homogeneous appearance. The glass was first allowed to cool slowly and was finally quenched in a stream of cold water. This caused the glass to crack into small pieces, some of which were suitable for making electrode diaphragms.

Fig. 16 represents the form of electrode used by MacInnes and Dole. The glass membrane, which is sufficiently thin to

give interference colours, is attached to the end of a tube of ordinary soft glass. To prepare the diaphragm, a piece of the specially prepared glass, about 50 mg., is first melted into the end of a pyrex tube of about 4 mm. diameter, then heated to a low red heat and blown into the form of a bubble with walls thin enough to show interference colours. The end of the electrode supporting tube of soft glass is then heated somewhat below red heat and brought into contact with the bubble wall. In this way, it is possible to seal the diaphragms completely and firmly on to the soft glass tube. Though such diaphragms are, of course, easily broken by sudden jars, MacInnes and Dole state that they are able to support columns of 9 cm. of mercury for several weeks. Harrison (*J. Chem. Soc.*, 1930, 1528), however, experienced considerable difficulty in preparing this type of electrode and, even when apparently satisfactorily made the electrode was sometimes found to contain very fine holes. The properties of these diaphragms as electrodes are recorded in Table 23.

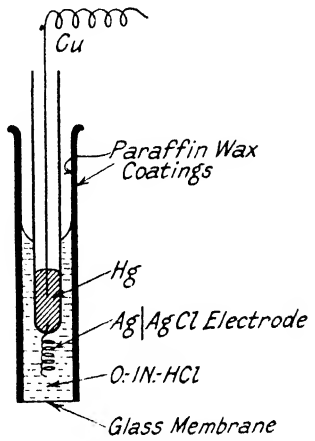


FIG. 16.—MacInnes and Dole's Glass Electrode.

From this table, it will be observed that those glasses whose resistances were so high as to render them unsuitable for use as glass electrodes, also had high asymmetry E.M.F's (see later) and yielded very variable potentials when immersed in 0·1 N-NaOH. Glass No. 6 was found to be the most serviceable. Incidentally, it corresponds nearly in composition to Morey's lowest temperature melt in the system :— $CaO - SiO_2 - Na_2O$ (*J. Soc. Glass Tech.*, 1925, **9**, 232). As shown in the Table 23, there is a very low potential due to the membrane alone, the resistance is low and the error in alkaline solution is the smallest observed. (This glass can be secured from the Corning Glass Co., Corning, N.Y., as No. 015.) Glass No. 7 was definitely too soft. Unfortunately, all glasses suitable for *p*H measurements are very soft, and when used in unbuffered solutions for any length of time may dissolve to an appreciable extent. It is for these reasons that MacInnes and Dole recommend the use of the special glass in the diaphragm only and not in the electrode as a whole. Lithium, magnesium

TABLE 23

PROPERTIES OF GLASSES AS ELECTRODES

(*MacInnes and Dole*)

No.	Glass.	Percentage Composition.				Asymmetry E.M.F. (millivolts).		Resistance (Megohms)	Variation of E.M.F. in 0·1 N-NaOH.
		SiO_2	CaO	Li_2O	Na_2O	1st day.	2nd day.		
1	Pyrex . . .	—	—	—	—	—	—	Very high	—
2	Potassium . .	72	6	0	22*	− 52	—	High	RI
3	Jena thermometer	—	—	—	—	− 47	− 43	400	RI
4	Soft commercial.	—	—	—	—	− 28	− 6	72	I
5	Soda lime . .	72	8	0	20	+ 4	+ 6	47	SI
6	Best soda lime .	72	6	0	22	− 4	+ 1	12	− 32 C
7	Soda lime . .	72	4	0	24	− 3	—	5	I
8	Soda lime . .	70	6	0	24	− 8	− 2	8	− 32 VSI
9	Soda lime . .	74	6	0	20	− 15	− 4	20	SI
10	Soda lime . .	74	4	0	22	− 3	0	5	SI
11	Soda lime . .	70	8	0	22	− 2	− 1	20	SI
12	Lithium . . .	72	6	22	0	0	+ 1	2	RI
13	Sodium lithium .	72	6	2	20	—	—	600	RI
14	Sodium lithium .	72	6	4	18	—	—	700 (?)	RI
15	Potassium lithium	72	6	4	18	—	—	3000	RI
16	Magnesium . .	64·5	10†	—	25·5	12	− 8	45	RI

and potassium glasses were generally unsuitable. Glass No. 6 gave potentials that were in strict accord with $E = \lambda + \frac{R'T}{F} \log[H^+]$ up to *p*H 9·5, after which the E.M.F. became a function not only of the *p*H but also the salt content of the solution.

According to Lengyel and Blum (*Trans. Faraday Soc.*, 1934, **30**, 461) soda glass, used in glass electrode work, is soluble in water to the extent of 5·6 mg. Na_2O per square decimetre of surface, compared with 0·2 mg. for ordinary borosilicate glass. Glasses containing larger proportions of Na_2O respond to both sodium and hydrogen ions, but this response is uniform throughout the whole *p*H range, so that the E.M.F./*p*H curve is parallel to that given by the usual electrode glass. Lengyel and Blum consider that the action of the glass electrode depends only upon the composition of the glass and not on its solubility in water or its electrical resistance.

In developing a tentative explanation of those glass electrodes which respond to changes in hydrogen-ion concentration in a

* K_2O, † MgO. RI = rapidly increasing, I = increasing, SI = slowly increasing, C = constant, VSI = very slowly increasing.

manner analogous to that of the hydrogen electrode, we shall regard the soft soda glass as being a solid solution of soda and silica more or less in a state of chemical combination and an excess of silica, such that when a thin bulb of glass is immersed in an aqueous solution a certain amount of water will be attracted into the glass phase, through adsorptive processes, and tend to combine with the free silica, thereby imparting to it acidic properties. Such a cause may be attributed to the fact that a considerable amount of water is adsorbed by glass in contact with acids, as observed by Frazer, Patrick and Smith (*J. Physical Chem.*, 1927, **31**, 897). Hughes considers that his " results are best explained on the view that the hydrogen-ion concentration in the glass phase is held relatively constant by the buffer action of the glass," which " action *prevents* ionic exchange between the glass phase and the solution from altering the hydrogen-ion concentration in the glass, which is thus maintained relatively constant in spite of the exchange of ions with the solution." The author's hydrogen electrode titration curves of silicic acid (pp. 223 and 277, Vol. II., *J. Chem. Soc.*, 1927, 425) show that alkalis, *e.g.*, NaOH and the hydroxides of the alkaline earths, enter into perceptible combination with silicic acid over an extensive *p*H range above *p*H 6. Whilst the curve corresponding to the action of sodium hydroxide upon silicic acid does not permit of the calculation of satisfactory dissociation constants, K_1 and K_2, of the hypothetical metasilicic acid, the curve resolves itself into two sections in which pronounced buffer actions on the hydrogen-ion concentration are produced. The first stage refers to the neutralisation reaction :

$$H_2SiO_3 + NaOH \rightarrow NaHSiO_3 + H_2O,$$

during which the hydrogen-ion concentration is confined mainly within the range *p*H 9–10·4, thereafter further addition of alkali produces a fairly rapid diminution in hydrogen-ion concentration. It will be remembered that solid sodium silicates only become readily soluble in water when their soda contents have become sufficiently great, so much so that glasses containing a great excess of silica possess no solubility in water, except when the water has been rendered strongly alkaline. Through the action of the soda on the silica in the surface layers, silicates with higher sodium contents become formed and solution thereupon results. Hence it may be assumed that, except in solutions above *p*H 10, the glass electrode will have maintained at its surface, through the adsorbed water which tends to dissolve the glass, a constant concentration of hydrogen ions of about *p*H 9. This low, but

definite concentration of hydrogen ions will produce a pressure at the glass surface, comparable with the electrolytic solution pressure in the case of ordinary reversible electrodes, which in tending to oppose the osmotic pressure of hydrogen ions already in the solution, will establish a difference in potential between it and the solution. As glass might be considered as a solution of extremely high viscosity, ions will only be able to travel through it with great difficulty, especially as the resistance of the thinnest glass membrane is of the order of 50 megohms. The diffusion of water molecules into the membrane will facilitate the motion of ions through the glass film, and as hydrogen ions and hydroxyl ions travel much more rapidly than any other ions in aqueous solutions it is probable that they will do so through the glass-water solution, and consequently it follows that these ions alone will carry the electricity across the diaphragm. If two solutions having different concentrations of hydrogen ions are separated by such a wall, then there should exist a difference in potential between them urging the movement of hydrogen ions through the glass in one particular direction.

We shall now consider this potential difference. Suppose we have the system :—

	Solution I	Glass	Solution II
Concentration :	$[H^{\cdot}]_I$ pH_I	$[H^{\cdot}]_G$ A B	$[H^{\cdot}]_{II}$ pH_{II}
Osmotic pressure :	p_I	P	p_{II}
		E_I	E_{II}

The components of the glass are such that, through their buffer action, they tend to maintain a constant pressure, P, of hydrogen ions in the glass. We have, therefore, in effect two solutions in equilibrium with the same hydrogen electrode. Its potential, E_I, with respect to Solution I, will be equal to

$$E_I = \frac{RT}{F} \log_e \frac{p_I}{P} = \frac{RT}{F} \log_e \frac{[H^{\cdot}]_I}{[H^{\cdot}]_G}$$

whereas its potential, E_{II}, with regard to Solution II, will be

$$E_{II} = \frac{RT}{F} \log_e \frac{p_{II}}{P} = \frac{RT}{F} \log_e \frac{[H^{\cdot}]_{II}}{[H^{\cdot}]_G}.$$

Hence $E_I - E_{II}$ is the difference in potential between Solution I

and Solution II, and therefore the E.M.F. tending to force hydrogen ions across the glass barrier,

$$\text{E.M.F.} = \frac{RT}{F}\log_e\frac{[H^\cdot]_I}{[H^\cdot]_G} - \frac{RT}{F}\log_e\frac{[H^\cdot]_{II}}{[H^\cdot]_G}$$

$$= \frac{RT}{F}\log_e\frac{[H^\cdot]_I}{[H^\cdot]_{II}}$$

$$= 0{\cdot}0001984T\log\frac{[H^\cdot]_I}{[H^\cdot]_{II}}$$

$$= 0{\cdot}0001984T\ (pH_{II} - pH_I)$$
$$= 0{\cdot}058(pH_{II} - pH_I) \text{ at } 18^\circ \text{ to } 20^\circ \text{ C.}$$

It will be observed that this potential difference does not involve the postulated concentration of hydrogen ions in the glass. Moreover, the change in the potential difference between two solutions having different hydrogen-ion concentrations should be 58 millivolts for each *p*H unit difference. Table 22 shows that these variations in E.M.F. are approximately true of the satisfactory glass electrodes—over the *p*H range 0–10. Above *p*H 10 the solvent action of the alkali upon the glass becomes apparent in that it disturbs the buffer action within the glass and so alters its hydrogen-ion "osmotic" pressure.

Other theories have been advanced to account for the behaviour of the glass electrode. Schiller (*Ann. Physik.*, 1924, **74**, 105), Lengyel (*Z. physikal. Chem.*, 1931, **154**, 371) and Haugaard (*ibid.*, 1932, **160**, 279) postulate a differential adsorption of ions at the glass-liquid interface, which, in causing a separation of charges, leads to a kind of condenser. This theory appears improbable, for ions can migrate through glass and, moreover, the potential of the glass electrode is independent of anions, which in all probability, would influence adsorption. Dole (*J. Amer. Chem. Soc.*, 1931, **53**, 4260; 1932, **54**, 3095; *J. Chem. Phys.*, 1934, **2**, 862) has approached the problem with the aid of statistical mechanics. He assumes that the potential of the glass electrode is due to certain ions, $H^\cdot$ and $Na^\cdot$, being able to pass from energy levels in the glass across the potential barrier to other levels in the solution and thus establish a distribution potential. In this way he attempted to explain the effect of sodium ions.

In order to measure the potential difference between the two solutions, Kerridge employed two saturated calomel electrodes with the tip of one dipping into one solution and that of the other

in the second solution. The cell thus made is

Hg	Saturated KCl Hg_2Cl_2	Solution I	Glass + water	Solution II	Saturated KCl Hg_2Cl_2	Hg

and as the contact potentials introduced where the saturated calomel electrodes are connected with the solutions are very small and act in opposition to one another, it follows that the observed E.M.F. of the cell will be produced by the fall in potential between Solution I and Solution II. In the Hughes' type of glass electrode the cell is set up in the following way :—

Hg	Saturated KCl Hg_2Cl_2	Solution I	Glass + water	Solution II (N-HCl) . Hg_2Cl_2	Hg,

there being no attempt made to eliminate extraneous potentials, but the potentials introduced are of constant value, namely, that of the saturated calomel electrode and that established between mercury and a N-HCl solution saturated with calomel. The contact potential between the saturated calomel electrode and the solution will be negligibly small. In the Kerridge cell, therefore, the E.M.F. $= 0{\cdot}0001984T \log \frac{[H^{\bullet}]_I}{[H^{\bullet}]_{II}}$, but in the Hughes' cell, the E.M.F. observed is the direct outcome of the potential difference between the saturated KCl and N-HCl calomel electrodes together with the E.M.F. given by the Kerridge cell. Let the constant difference in potential between the two different calomel half-elements used in the Hughes' arrangement be a volt, then the observed E.M.F. of the cell will be given by

$$\text{E.M.F.} = a + 0{\cdot}0001984T \log \frac{[H^{\bullet}]_I}{[H^{\bullet}]_{II}},$$

but as $[H^{\bullet}]_{II}$ refers to the hydrion concentration of N-HCl solution saturated with calomel, (Solution II), we see that this will be constant in value, and

$$\therefore \text{E.M.F.} = b + 0{\cdot}0001984T \log [H^{\bullet}]_I,$$

where b is a constant involving a and the $[H^{\bullet}]_{II}$ term. Hence on theoretical grounds, whereas it is only necessary to know the pH of one of the solutions present in the Kerridge cell in order to calculate the pH of the other solution, with the Hughes' arrangement the constant b must first be evaluated. This can be done by placing in the cell a solution of known pH and observing the E.M.F. established. Actually, on account of the possibility of the erratic behaviour of the glass electrode, *e.g.*, through slug-

gishness in the attainment of equilibrium with the solution being tested, the observed E.M.F's may not always be represented by the foregoing expressions. Moreover, there is always a so-called *asymmetry* E.M.F. between the two sides of the glass membrane itself, irrespective of the solutions in contact with them. In our considerations, we have assumed that the " osmotic " pressure of the hydrogen ions was the same on both sides. In good glass electrodes this asymmetry E.M.F. is fairly low and assumes a steady value within a few hours of the electrodes being placed in contact with solutions. Though the quality of the glass is of some importance in this connexion, much depends upon the blowing and thickness of the glass membrane, for different glass electrodes can be prepared from the same glass which give quite different asymmetry E.M.F's. This E.M.F., through its failure to acquire an absolutely constant value, probably explains why the E.M.F. of a glass cell corresponding to a given change in *p*H of the solution in contact with a glass diaphragm varies from cell to cell, and from day to day in the same cell. Hence, it is necessary to standardise the glass cell at least once each day. In the Kerridge form, this is done by inserting a buffer solution of known *p*H in the vessel in which the solution of unknown *p*H is ordinarily placed. Hence by knowing the *p*H values of Solution I and Solution II, and the E.M.F. of the cell, the extent by which the formula given above may be expected to be in error for any particular day may be calculated; suppose it to be equal to E_a, then

$$E_a = \text{E.M.F.}_{(\text{observed})} - \text{E.M.F.}_{(\text{calculated})}$$

and therefore

$$\text{E.M.F.}_{(\text{observed})} = 0{\cdot}0001984T \log \frac{[H^{\cdot}]_I}{[H^{\cdot}]_{II}} + E_a$$

$$= E_a + 0{\cdot}058\,(pH_{II} - pH_I) \text{ at } 18^\circ \text{ to } 20^\circ \text{ C.}$$

For standardisation, Kerridge recommends a M/20-solution of potassium hydrogen phthalate, which has a *p*H of 3·97 at 18° C. The change in *p*H with temperature is very small. Such a solution will remain at *p*H 3·97 for at least a fortnight if kept in a waxed bottle.

Hughes, on the other hand, considers it better to check the measurement of the *p*H of the solution under examination by measuring the E.M.F's produced by two standard buffer solutions, one being of slightly lower *p*H and the other of slightly higher *p*H than the unknown solution—and then to interpolate the required *p*H from the two voltages. In this way, errors will probably be eliminated entirely.

Attention has already been directed to the glass most suitable for electrode purposes. Soft soda-lime glass such as that ordinarily found in soft glass tubing will often be found quite satisfactory. Thus Kerridge (*J. Sci. Inst.*, 1926, **3**, 404) used most frequently a cheap German soft soda glass which was considered inferior from the glass-blower's point of view. The glass membrane should be as thin as possible, preferably between 0·025 and 0·030 mm. in its thinnest part and should never exceed 0·1 mm. The thinner the membrane the more likely is the electrode to function as a hydrogen electrode, and the more easily will the E.M.F's of the cell be measured, through the smaller resistance of the glass wall. Needless to mention the electrode must be as thin as is consistent with mechanical strength. The bulb must be as free from strain as possible and in order to minimise asymmetry E.M.F's caused by strain the glass membrane must be blown as rapidly as possible and no attempt made to work the glass. Devitrification of the membrane renders it useless, as the glass, in becoming crystalline, loses its electrode function which seems to be inherent in its being a supercooled liquid. The E.M.F. of the glass electrode depends upon its previous treatment. Thus if it has been cleaned by immersion in chromic acid, it will often be found necessary to place the electrode in water for a period of about two days before it can be used, as a potential will have been produced at the glass surface which, however, rapidly disappears on treatment with water. This is generally true of electrodes which are being used in either strongly acid or alkaline solutions, but in the case of the latter solutions the electrode potentials may never again become normal. This is in accord with the fact that the glass electrode behaves abnormally in alkaline solutions through possible attack. It is advisable, therefore, not to resort to strong acids or alkalis for cleaning, but to employ gently running water. Between use, the electrode should be kept in a buffer whose *p*H lies in the region in which the electrode is subsequently to be used, otherwise in distilled water.

Fig. 17 is a diagram of the Kerridge type of electrode, which is particularly convenient for work when only small quantities, *e.g.*, 0·5 c.c., of solution are available. Because of the extremely high resistance of the glass cell, only extremely small currents can be produced and therefore every care must be taken to mount the cell on insulating material such as glass, (H, Fig. 17) paraffin or orca. This type of electrode may now be obtained commercially, and Fig. 22 gives a picture of a complete outfit, including a zinc-lined box, which effectively shields the glass

cell from external electrostatic fields, a suitable potentiometer and a Lindemann electrometer, required for the measurement of *p*H, as manufactured by the Cambridge Instrument Co., Ltd., London. In the Kerridge cell, the glass membrane is in the form of a small bulb which has been sucked back into a larger and thicker bulb, G, from the side of which two tubes project, enabling it to be readily cleaned and filled with a buffer solution, B, whose *p*H is accurately known. This arrangement of the glass membrane has the dual advantage that it affords protection of the exceedingly thin membrane, and that

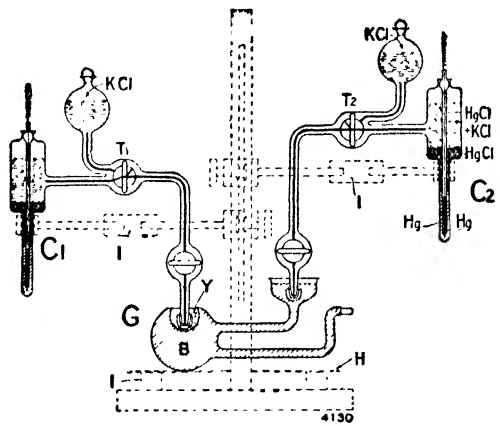


FIG. 17.—Glass Cell (Kerridge Type)

T_1, T_2 = Two-way Taps.
I = Insulators.
B = Buffer solution of known *p*H.
G = Glass vessel containing membrane.
Y = Solution of unknown *p*H.
C_1 and C_2 = Saturated Calomel Electrodes.

its formation by suction seems to leave less strain in the glass. The buffer solution advocated by Kerridge comprises a solution of potassium phosphates of about *p*H 7. It seems preferable to use N-HCl solution, which being of *p*H lower than that of the solutions usually tested avoids the reversal of the polarity of the electrodes of the glass cell when the *p*H of the unknown solution is raised above that of the buffer solution. This particularly applies when the electrode is used for titration work. Though the form illustrated is not suitable for this kind of test, Kerridge has described a modified form which is suitable (*loc. cit.*). Moreover, the glass electrode functions more satisfactorily when there exists an appreciable difference in hydrogen-

ion concentration on the two sides of the glass diaphragm. If the solution is likely to be oxidised by exposure to the air, or suffer loss of carbon dioxide, it may be covered with a thin layer of liquid paraffin. In any case, the paraffin will serve to lessen electrical leakage across the external surface of the electrode. The two saturated calomel electrodes, mounted on earthed metal stands provided with adjustments for altering the levels of the electrodes, are connected with the solutions in the glass electrode, but in order to prevent diffusion of the potassium chloride solution small ground caps are loosely fitted over the ends

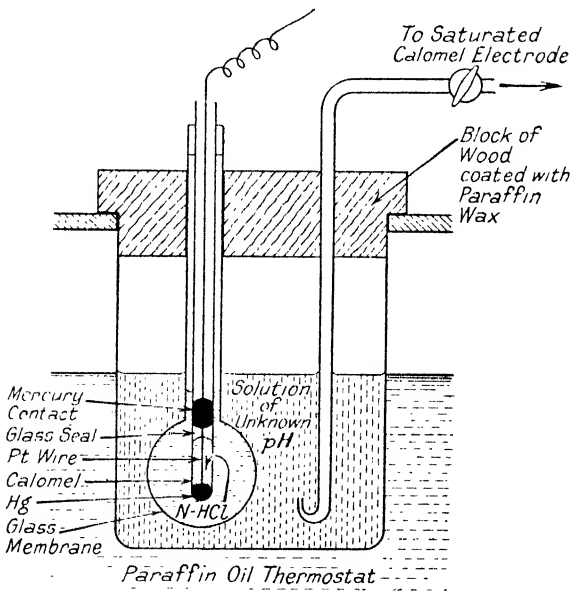


FIG. 18.—Hughes' Type of Glass Electrode.

of the connecting arms, and the two taps, which are ungreased in the middle race, are turned off while the E.M.F. of the cell is being measured. The added resistance introduced by these precautions is negligible compared with that of the glass electrode.

The Hughes' form is shown in Fig. 18. This type is convenient for titration purposes, and, moreover, has one advantage over the previously described pattern, in that less violent stirring is required than is the case when a solution has to attain equilibrium with a membrane in a cavity. It is a modification of the original Haber electrode (*loc. cit.*, see also Horowitz, *loc. cit.*, and Hughes, *J. Amer. Chem. Soc.*, 1922, **44**, 2860), in which a glass bulb, with

walls 0·06 mm. thick, containing potassium chloride solution into which dipped a platinum wire to serve as one electrode, was immersed in the solution under test and this was connected to a calomel electrode. In the Hughes' improved form, the platinum-wire contact is substituted by a perforated glass tube, shown in the diagram, at the rounded bottom of which is placed a little mercury covered with calomel, which thereby maintains the N-hydrochloric acid solution, instead of KCl, contained in the bulb in a saturated state. Contact is made with the mercury by means of a platinum wire fused into a glass seal which is connected with a little mercury in the upper part of the tube, into which an amalgamated copper wire dips. In order to avoid electrical leakage the cell is placed in a paraffin-oil thermostat, the neck of the bulb is held in a block of wood, coated with paraffin wax, cut to fit the beaker as a cover, and the rim of the beaker is supported by the paraffin-wax-coated wooden thermostat cover.

The glass electrode system of MacInnes and Dole is

$$Hg|Hg_2Cl_2 \text{ . KCl (satd.)}|\text{Test solution}|\text{Glass membrane}|\text{0·1 N-HCl . AgCl}|Ag,$$

the glass-silver portion of which is illustrated in Fig. 16. Above the membrane is a solution of decinormal hydrochloric acid in which dips a silver-silver chloride electrode prepared in the manner described on page 38.

If the glass surfaces are reversible with respect to hydrogen ions on both sides of the membrane, then the above combination may be considered, as far as its E.M.F. is concerned, as the sum of the two cells acting in opposition to one another:

$$\overset{+}{Hg}|Hg_2Cl_2 \text{ . KCl (satd.)}|\text{Test solution}|\overset{-}{H_2} \quad \text{(I)}$$

and

$$\overset{-}{H_2}|\text{0·1 N-HCl . AgCl}|\overset{+}{Ag} \quad \text{(II)}.$$

At 25° the E.M.F. of cell I is 0·2458 − 0·059 log [H$^+$] (see p. 29), and that of cell II is + 0·3524 volt (*cf.* MacInnes and Dole, *loc. cit.*, and Scatchard, *J. Amer. Chem. Soc.*, 1925, **47**, 641), Hence the E.M.F. of the glass electrode combination

$$= E_{\text{cell I}} - E_{\text{cell II}}$$
$$= -0{\cdot}1066 - 0{\cdot}059 \log [H^+]$$
$$= -0{\cdot}1066 + 0{\cdot}059\, p\text{H}.$$

The fact that the glass interfaces cannot be regarded as being of the same potentials as hydrogen electrodes served with hydrogen at atmospheric pressure does not affect the E.M.F. of the complete cell, provided that the hypothetical hydrogen pressure on the two sides of the glass electrode remain constant.

MacInnes and Dole found that all suitable glass electrodes gave E.M.F's in agreement with this equation in solutions of *p*H 8, but in 0·1 N-NaOH, *p*H 12·75, large variations were always observed. In a series of experiments in which the potential of the glass electrode system, using their best glass (p. 114), was measured directly against the hydrogen electrode, *i.e.*,

H_2|Test solution|Glass membrane|0·1 N-HCl . AgCl|Ag,

they found that with solutions of *p*H 7·72–10·47, the E.M.F's ranged from 0·354–0·358, being in good agreement with the

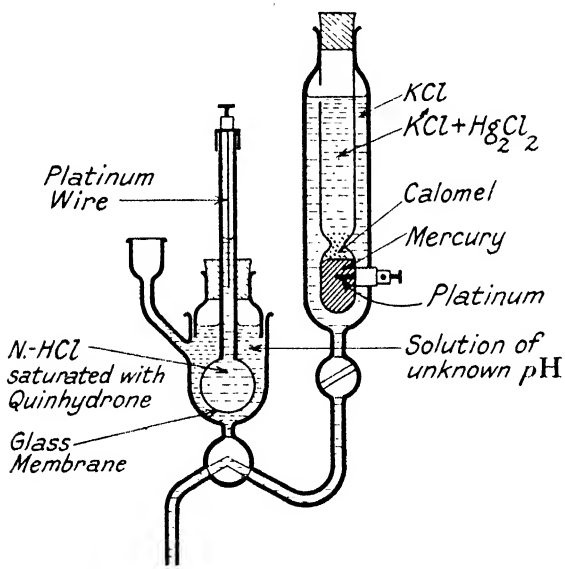


FIG. 19.—Morton's Glass Electrode Cell.

E.M.F. of cell II. In a solution at *p*H 11·64 the potential was 0·369 volt.

Corning No. 015 glass has been used by Robertson (*Ind. Eng. Chem. Anal. Ed.*, 1931, **3**, 5), who was able to prepare diaphragms of 2 to 3 megohms resistance which was sufficiently low to permit the use of a sensitive galvanometer in the ordinary potentiometer circuit. The accuracy of the method is described as fair. Instead of attaching a glass diaphragm to the end of a glass tube, Robertson blows a bulb at the end of a tube of the special glass. The tube has a diameter of 1 cm. and a length of about 8 cm. The bulb, which has a capacity of 8–10 c.c., is blown from 100–151 mg. of glass, the average thickness of the wall being 0·03 mm., though it may vary from 0·015–0·05 mm. Morton (*J. Scient.*

Instruments, 1930, **7**, 187) and Harrison (*J. Chem. Soc.*, 1930, 1528) also used bulbs. According to Harrison, their resistance may be less than 100 megohms. The glass is prepared from a mixture of 60 per cent. SiO_2, 30 per cent. Na_2CO_3 and 10 per cent. $CaCO_3$. The arrangement of Morton's glass electrode system is shown in Fig. 19 and E.M.F. measurements are made by means of the ballistic galvanometer (see p. 156). Harrison uses a special electrometer valve potentiometric method (see p. 169).

The measurement of the E.M.F. of glass cells presents a certain amount of difficulty on account of the very high resistance of the glass membrane. Hence, the current produced will be too small to permit the use of a capillary electrometer or a sensitive

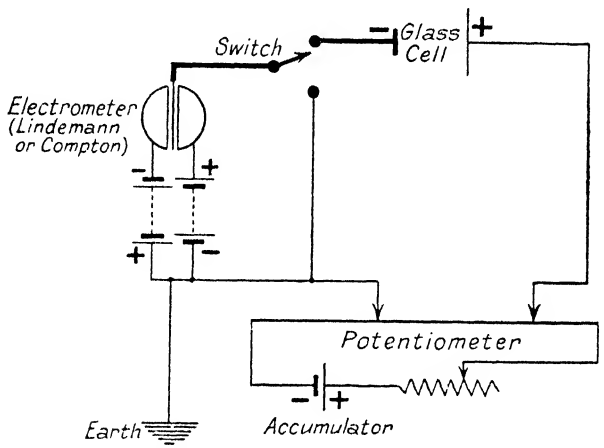


FIG. 20.—Simple Circuit for the Measurement of the E.M.F. of Glass Cell.

galvanometer in connexion with the potentiometric method of measuring potential differences described in Chapter VIII. Instead, resort must be made to the quadrant electrometer as a null-point instrument. Compton, Dolazalek and Lindemann electrometers have been used by various workers, but without doubt the Lindemann (*Phil. Mag.*, 1924, **67**, 578) is the most convenient and easy to manipulate; it possesses sufficient sensitivity for this work, and is compact and portable. It is contained in the box, placed under the microscope in Fig. 22.

Besides being compact and robust, the Lindemann electrometer, as supplied by the Cambridge Instrument Co., has a stable zero and does not require levelling. It consists of a needle supported centrally at the mid-point of a quartz fibre, so that it can

rotate between four cross-connected plates. The quartz fibre is fixed at both ends under tension so that the centre of rotation of the needle is fixed, and the movement of the needle is controlled by the torsion of the fibre; the rotation can therefore be determined by observing the movement of one end of the needle through a microscope. A total magnification of 250 diameters, obtained, say, by using a microscope with 160 mm. tube length, 16 mm. objective, and 10 mm. eyepiece, enables deflections corresponding to less than one millivolt to be observed. An objective of focus smaller than 16 mm. should not be used, as the needle could not then be sharply focussed.

The simple potentiometric system, using a quadrant electrometer as the null-point indicator, is given in Fig. 20. No electrical leakage must be allowed to occur between the glass cell and the electrometer, *i.e.*, along the wires indicated by heavy lines.

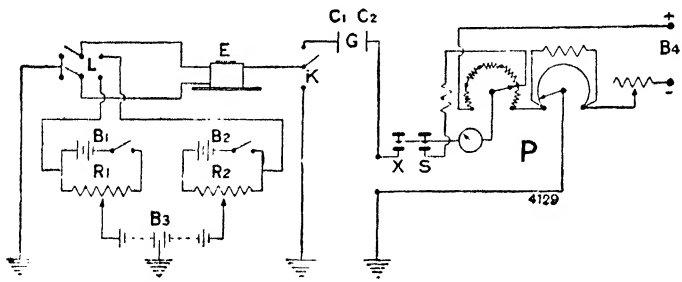


FIG. 21.—Arrangement of Wiring of Potentiometer System using Lindemann Electrometer.

E = Lindemann Electrometer. P = Potentiometer.
B_1, B_2 = 4-volt Batteries. R_1 and R_2 = 300-ohm Potentiometers.
B_3 = 66-volt Dry Battery. B_4 = Accumulator.

These wires should be as short as possible and thoroughly insulated. The switch should be constructed of orca or ebonite insulation and placed on a block of clean paraffin wax. Fig. 21 shows the wiring of the potentiometer circuit using the Lindemann electrometer, employed in the Cambridge glass electrode outfit (Fig. 22). It differs but slightly from that described by Kerridge. In the Cambridge apparatus the glass cell is enclosed in a light metal box having apertures in the top and bottom, closed with microscope cover slides. The leads from the two sets of plates pass through quartz tubes to terminals at one end, while the lead from the needle is similarly carried to a terminal at the other end. An earthing terminal enables the effect of stray electrostatic fields to be eliminated. A moisture absorption chamber, containing phosphorus pentoxide, prevents humid con-

PLATE I

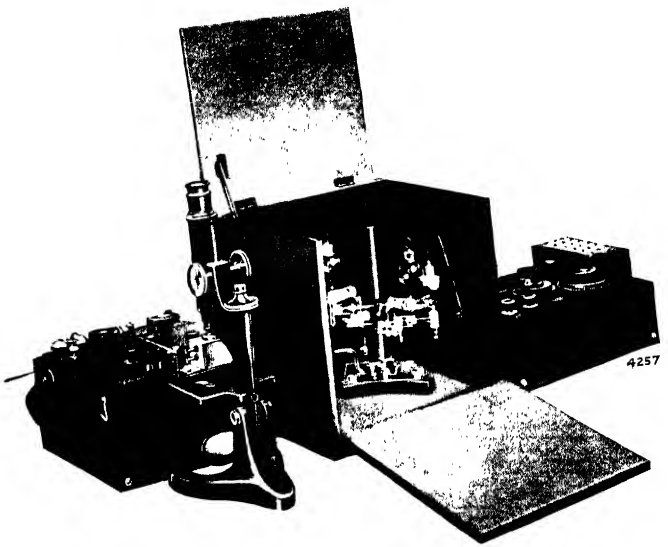


FIG. 22.—Cambridge Glass Electrode Apparatus, showing Lindemann Electrometer, Glass Electrode (Kerridge Type), and Potentiometer.

(*Block lent by* Cambridge Instrument Co., Ltd.)

[*To face page* 128.

ditions from affecting the silica insulation. The electrometer plates are charged by means of a high-tension battery, the needle being connected in the electrode circuit. The charge required is about + 30 and − 30 volts on the two pairs of plates respectively. In order to ensure that the electrical and mechanical zeros of the electrometer coincide, it is necessary to adjust, to within 0·5 volt, the charges on each pair of plates for the particular instrument in use. For this purpose, a potentiometric system is put in series with the high-tension battery. The arrangement of the wiring is shown in Fig. 21. The mid-point of a 66-volt dry battery B_3 is earthed and the positive and negative terminals are connected to the movable contacts of two small 300-ohm potentiometers, R_1, R_2, across each of which is a potential difference of 4 volts. A two-way double-pole switch L enables the electrometer plates to be earthed or charged, and a two-way single-pole switch K is provided for earthing or charging the needle. The two small potentiometers and the switches are mounted together in a separate box, to the front of which the electrometer can be directly attached, terminals being fitted on the box for connecting up the high-tension battery, electrometer and electrodes. The potential difference between the two poles of the glass cell is measured by means of a potentiometer (P, Fig. 21); that shown at the right of the picture, Fig. 22, is the Cambridge portable potentiometer (see Fig. 30).

For details regarding the use of the Dolazalek and Compton electrometers reference must be made to Kerridge's paper.

It should be stated that though the glass electrode functions best over the *p*H range 0 — 9, it may be employed by using two suitable buffer solutions of known *p*H for the determination of higher *p*H values quite satisfactorily by interpolating from data given by the buffer solutions. Once the fundamental needs of adjustment, insulation, shielding and standardisation have been satisfied, only a few minutes are required to make a determination. The electrode has already been applied successfully to biological problems, and there is every reason to believe that it will receive more general recognition, especially in regard to its use in those solutions which cannot be studied by either the hydrogen or quinhydrone electrodes and which are too coloured to be dealt with colorimetrically.

Recent Forms of Glass Electrode.

MacInnes and Belcher (*Ind. Eng. Chem., Anal. Edn.*, 1933, **5**, 199) have described an electrode (Fig. 23) in which the glass electrode, *ab*, takes the form of a spiral of Corning 015 glass

tubing, which has 14 turns of about 2·5 cm. in diameter. The tubing is 92 cm. in length, with an external diameter of 5 mm. and walls of about 0·6 mm. The spiral is joined at *a* to Corning seal glass.

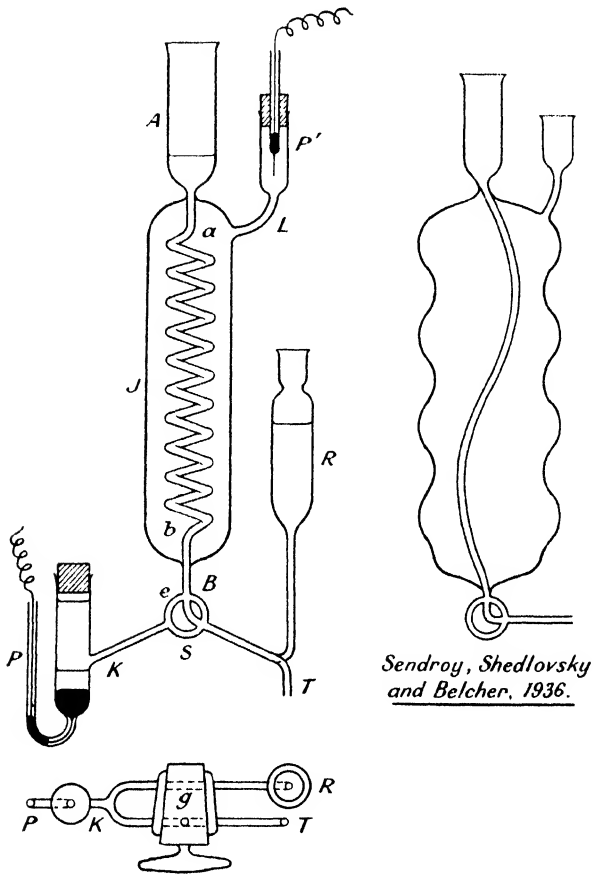


FIG. 23.—Durable Glass Electrode. (MacInnes and Belcher, 1933.)

The resistance of the glass walls is about 25 megohms, but the extra thickness of the walls is compensated for by the considerable area of exposed glass. The asymmetry E.M.F., initially, is high—about 100 mv., but after keeping the spiral filled with distilled water, it decreases slowly, and after about a month it assumes a constant value. Thompson (*Bur. Standards J. Research*, 1932, **9**, 833) also has shown that comparatively thick

glass can be used if corresponding large areas are employed as electrode.

The rest of MacInnes and Belcher's electrode system is made of Jena thermometer glass. P′ and J are filled with 0·1 N-HCl and at P′ a Ag|AgCl electrode is inserted. The test-solution (about 7 c.c.) is poured in at A and allowed to fill the spiral. K is a reference calomel electrode. The liquid junction between the test-solution in the spiral and the calomel electrode K is made in the following way. With the stop-cock, S, closed, the test-solution is placed in the upper reservoir, A. Then the stop-cock is turned so as to connect the tube, B, with the reject tube, T, but it is turned in a clockwise direction before the level of the solution has passed the point *a*. Rotating the stop-cock further in the same direction connects the tubes K and T and also allows the saturated KCl solution to flow from the reservoir, R, through the extra bore, *g*, in the rear of the stop-cock, and thence through the reject tube, T. A further turn (clockwise) of S through 120° forms the liquid junction at the point *e* between the test-solution and the saturated potassium chloride solution, the latter already being connected with the calomel electrode, preferably the saturated calomel electrode.

The other diagram in Fig. 23 represents a form of the foregoing apparatus, adapted by Sendroy, Shedlovsky and Belcher (*J. Biol. Chem.*, 1936, **115**, 529) for use at elevated temperatures. In order to prevent fracture of the glass on heating, the thin glass electrode tube is bent and the outer vessel is blown in the form of a series of bulbs.

Schwabe's (*Z. Elektrochem.*, 1936, **42**, 147; 1937, **43**, 874) glass cell is illustrated in Fig. 24. He asserts that, if the glass electrode, which is in the form of a spherical bulb, is immersed in the test-solution which is kept moving exceedingly slowly by means of drops falling from the dropper into a receptacle just above the electrode bulb and over-flowing into the solution surrounding the electrode, constant E.M.F's are obtained and the *p*H values indicated are more accurate than when absolutely still solutions are used. By turning the dropper, the test-solution may be made to pass the electrode at rates varying from 20 c.c. to 500 c.c. per hour. Moreover, the potentials remain constant over long periods, in one case 30 hours. The electrodes are immersed in concentrated chromic acid solution for a day and then kept in distilled water for about a fortnight before use. The asymmetry E.M.F. is about 2 mv. The sintered glass diaphragm fitted in the reject tube also helps to regulate the flow of test-solution past the electrode.

Fig. 25 illustrates electrodes, designed in such a way as to make use of the thinnest possible glass membranes, which are protected from fracture by surrounding them with the more robust parts of the apparatus. Nichols and Schempf's (*Ind. Eng. Chem., Anal. Edn.*, 1938, **10**, 286) glass electrode is constructed from Corning 015 glass tubing, 9 mm. in diameter, by the stages

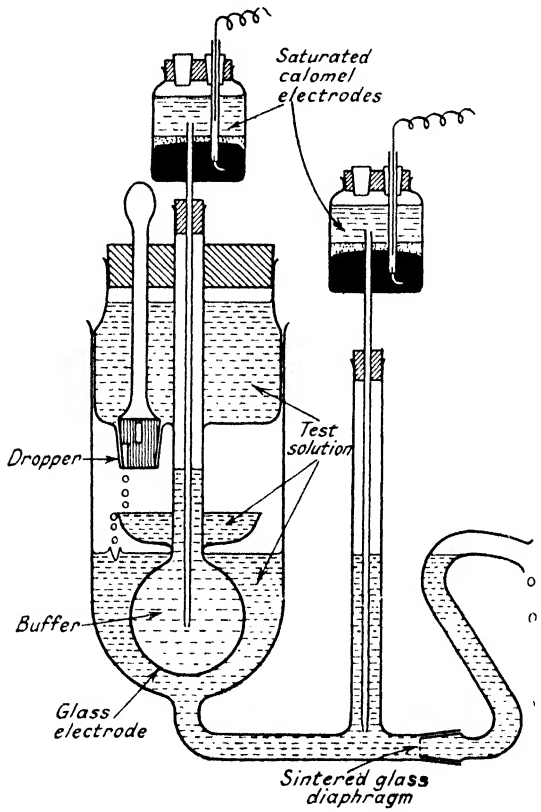


FIG. 24.—Schwabe's Dropping Glass Cell, 1936–7.

shown on the right of Fig. 25. The part which forms the glass membrane is originally prepared by drawing 9-mm. tubing to thinner tubing of 2–3 mm. diameter and then at one end blowing a bulb of 12 mm. diameter. After breaking off the major part of the bulb, the remaining portion is incorporated in the apparatus, as shown, and subsequently further expanded.

Mouquin and Garman (*Ind. Eng. Chem., Anal. Edn.*, 1937, **9**, 287) claim by the scheme, shown in Fig. 25, to be able to pre-

pare membranes of resistance of 10^4–10^5 ohms, instead of 10^7 ohms, the order of magnitude of the resistance of ordinary glass elec-

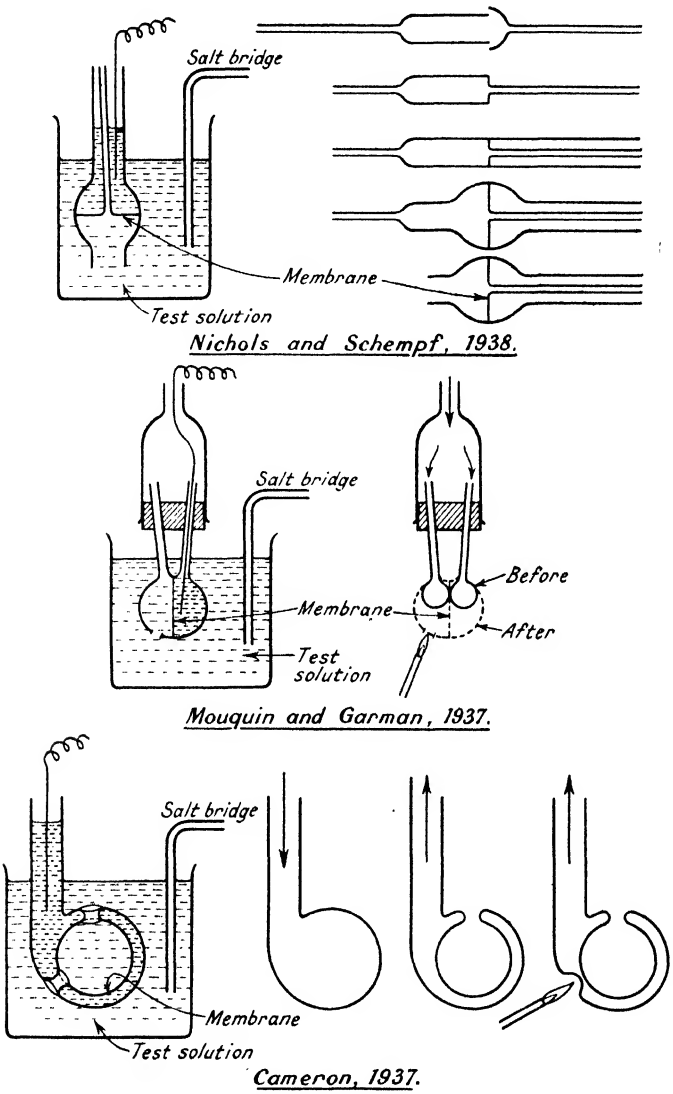


FIG. 25.—Low Resistance Glass Electrodes and their Method of Construction.

trodes. The electrodes are blown from Corning 015 tubing of 5- or 10-mm. bore. At the end of two tubes, bulbs are blown,

which subsequently are allowed to touch, and then blowing is continued until the glass contained at the position where the bulbs originally touched forms the partition between the two hemispheres. The test-solution in the beaker is admitted to one hemisphere through a hole.

Cameron's apparatus (*ibid.*, 1937, **9**, 436) consists of two concentric spherical bulbs, the inner one, constituting the electrode membrane, having been formed by sucking back the glass heated at a point in the original thick-walled bulb. In order to permit ready access of the test-solution to the glass membrane a second hole is made, as shown, by causing the external and internal bulbs to fuse together by playing a fine gas jet at the point. Corning 015 glass tubing of 1-cm. bore is used and the resistance of the membrane is 1–10 megohms.

CHAPTER VIII

THE MEASUREMENT OF ELECTROMOTIVE FORCE

HITHERTO we have considered the seats of potential difference in a cell, and have, moreover, seen that it is not possible to measure directly the potential of an electrode with respect to the solution in which it may be immersed. If we assume that the difference of potential, which originates from the contact of the two electrode solutions through the migration of ions across the boundary, can be nullified by interposing a saturated solution of potassium chloride between the two solutions, then the E.M.F. of a cell will be the result of the difference of the two electrode potentials, and if one electrode is of a constant and known value the potential of the other electrode can readily be obtained, once the E.M.F. of the cell has been ascertained. We shall now direct our attention to the methods for the determination of potential differences, but shall, in the first place, deal with the fundamental principles on which these methods are based.

Suppose we have a circuit which includes a cell whose internal resistance is r ohms, and a voltmeter whose resistance is R ohms. The voltmeter registers a potential difference of E_v volts, which simply corresponds to the fall in potential across the terminals of the voltmeter. But Ohm's law states that the fall in potential, if measured in volts, produced when a current, measured in ampères, passes through a conductor whose resistance is measured in ohms, is equal to the product of the current and the resistance, in other words,

$$\text{current (ampères)} = \frac{\text{potential difference (volts)}}{\text{resistance (ohms)}},$$

and therefore the E.M.F. shown by the voltmeter, E_v, $= C \times R$, C being the current sent out by the cell. If, however, the E.M.F. of the whole circuit, E, be considered, when sufficient time has been allowed for the current in any part of the system to become constant, *i.e.*, through the external circuit and through the cell itself, we find that

$$C = \frac{E}{R + r},$$

$$E = CR + Cr.$$

Now this value, E, is derived from the chemical processes involved in the cell, and it is the quantity which it is desired to measure. Hence, as C is the uniform current circulating throughout the closed system, we see that

$$E = E_v + Cr$$

and consequently the voltmeter reading is too low by the amount Cr. Unless these quantities are known the actual E.M.F. of the cell cannot be ascertained. If no current be drawn from the cell, *i.e.*, $C = 0$, then $E = E_v$, so that in order to measure E directly, it will be necessary to adopt a method which does not necessitate the performance of electrical work by the cell. This is effected in the Poggendorf compensation method, using the potentiometer.

It might be an advantage here to point out the relationship between the potential difference between the two electrodes of a cell and the E.M.F. of the cell. In " open circuit," *i.e.*, when the two poles are not connected by means of a conducting wire, these are equal and opposed to one another, for the current tends to pass from the negative pole through the cell-liquid to the positive pole and is urged by the chemical action, *i.e.*, the E.M.F. of the cell, but this transference of electricity is prevented by the difference in potential between that of the positive electrode and that of the negative electrode, *i.e.*, P.D. In a " closed circuit " this P.D. becomes smaller than the E.M.F. on account of its forcing the current round the external circuit. The current, C, on attaining a constant value is equal to $\frac{\text{P.D.}}{\text{R}}$ in the external circuit whose resistance is R, whereas this current, C, is equal to $\frac{\text{E.M.F.} - \text{P.D.}}{r}$ when passing through the cell, resistance $= r$. Hence

$$C = \frac{\text{P.D.}}{\text{R}} = \frac{\text{E.M.F.} - \text{P.D.}}{r},$$

and therefore

$$\text{E.M.F.} = r \times \frac{\text{P.D.}}{\text{R}} + \text{P.D.},$$

whence

$$\text{E.M.F.} = rC + \text{P.D.}$$

It will be observed that this equation is identical with the one obtained in the previous paragraph by a somewhat different method.

Poggendorf's Method for the Measurement of E.M.F's.

By this method the electromotive force of a cell is measured by what is equivalent to an " open circuit " method in that no electricity is allowed to flow from the cell while this is undergoing test. If we consider the fall in potential produced when a current of electricity is sent along a wire of uniform cross-section and resistance, we find from Ohm's law that the amount of loss in potential suffered by the current is proportional to the length of wire through which it has passed. Hence if a *constant current* is allowed to pass through such a wire, it is possible to calculate the actual potential difference between two points, once the potential difference between any other two points on the wire has been ascertained. Thus if d_1 be the distance between two points on the wire corresponding to the unknown P.D.$_1$, and d_2 the distance to P.D.$_2$,

$$\frac{\text{P.D.}_1}{\text{P.D.}_2} = \frac{d_1}{d_2},$$

and therefore if either P.D.$_1$ or P.D.$_2$ is known, then the other potential difference becomes calculable. If we connect up a cell,

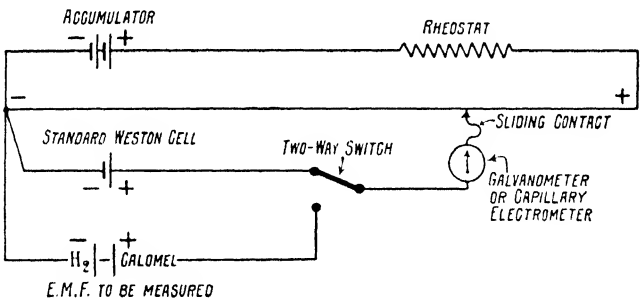


FIG. 26.—Poggendorf's Method for the Measurement of E.M.F's.

whose E.M.F. it is desired to measure, " in series " with some current indicator, across this connect a wire " in parallel " so that the cell-circuit makes contact with it at two points d cm. apart, and the fall in potential both in the wire and in the cell takes place in the same direction, then it is possible to find some length of wire between the points of contact along which the fall in potential is equal to that acting across the poles of the cell, and as a result it will not be possible for any current to leave the cell as shown by the indicator. Briefly this is the principle of Poggendorf's method.

Fig. 26 gives the arrangement of the circuit. The wire, against whose uniform potential gradients other potential differences are balanced, is known as the potentiometer. In the simple metre bridge potentiometer (Fig. 27) this wire is a metre long, but there is no reason why it should not be any other convenient length. In order that there should be a suitable fall in potential along the wire it should have a resistance of about 10 ohms per metre, but as high resistance is associated with the thinness of the wire care must be exercised not to choose a potential wire which is too fine or it may become severely damaged or even severed by the sliding contact. If the wire is to be sufficiently durable for general use, it should not be thinner than 36 S.W.G. and preferably about 32 S.W.G. Wires used for this purpose

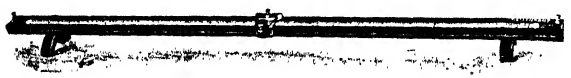


FIG. 27.—Metre Bridge Potentiometer with Precision Adjustments (Messrs. Gallenkamp).

are usually made of either manganin (84 per cent. Cu, 4 per cent. Ni, 12 per cent. Mn), German silver (60 per cent. Cu, 15 per cent. Ni, 25 per cent. Zn), Eureka (Constantan ; 60 per cent. Cu, 40 per cent. Ni), or platinoid (German silver + tungsten), and sometimes platinum or iridio-platinum. The following table, No. 24, gives the resistances of wires, of different diameters—Standard Wire Gauge—made of some of these alloys :—

TABLE 24

RESISTANCE OF WIRE SUITABLE FOR POTENTIOMETERS (OHMS PER METRE)

S.W.G.	Diameter mm.	Manganin.	Constantan (Eureka).	Platinoid.	German Silver.
30	0·315	5·45	6·10	5·25	2·90
32	0·274	7·18	8·04	8·72	3·83
34	0·234	9·90	11·08	9·77	5·27
36	0·193	14·5	12·90	13·99	7·74

The resistance of German silver wire is somewhat too low for use in potentiometers.

The current passed through this potentiometer wire should be constant and such that the potential difference between the two ends is about 1·1 volts. For this, a current will be required

equal to E/R = 1·1/10 (the resistance of the wire being taken as 10 ohms) = 0·11 ampère. If an ordinary accumulator be used as the source of current, and as its resistance is usually negligible, we find that to supply 0·11 ampère of current the resistance of the complete circuit will have to be 2/0·11 ohms = 18 ohms. Hence an additional resistance of about 8 ohms must be introduced into the accumulator circuit. This is accomplished by including in the circuit either a rheostat (Fig. 26) or simply a suitable length of one of the high resistance wires referred to in Table 24. The required length may be conveniently obtained by allowing one end to pass through a clip connected to the copper wire. The use of comparatively low resistance potentiometers necessitates the flowing of a fairly large current along the wire. As it often is necessary to make a series of E.M.F. measurements at a time, it is an advantage to standardise the potentiometer once for all. This procedure is, however, justifiable only when it is known that the current is being maintained constant. Using low capacity accumulators there is a tendency for their E.M.F's to vary appreciably over protracted periods, and consequently for the currents to change. This can be obviated to a considerable extent by using large capacity accumulators, say of 60 ampère-hours. There is, however, a risk that currents of this magnitude, in passing through the unknown P.D. circuit whilst the sliding contact is placed at a point on the potentiometer wire such that the two opposing P.D's are not balanced, may disturb the equilibrium prevailing in the cell. Errors from this cause, however, will, in general, be negligibly small, except when the potentiometric system has been kept out of balance for some time. When it is desired to obtain measurements of a higher degree of precision a series of high resistance coils should be substituted for the single wire, as these will permit only extremely small currents to leave the accumulator, though more sensitive galvanometers will have to be employed.

To use the potentiometer to measure E.M.F's it is necessary to set up the apparatus as shown in Fig. 26, in which it will be seen that the negative poles of both the standard Weston cell and the experimental cell are placed in opposition to that of the accumulator. Of course the polarity of all the cells might have been reversed. To standardise the potentiometer the two-way switch is put in the position shown and the sliding contact moved along the wire until no current passes through the indicator—galvanometer or capillary electrometer—shown by no deflection of the former instrument and no movement of the mercury meniscus in the latter. It should be emphasised that contact

with the potentiometer wire should be momentary in order that the only minimum of current might be drawn from the cell. In finding the balance point, it is better to work on both sides of the point and to move the contact inwards until the exact point is found. To minimise experimental error it is an advantage to have as long a stretch of wire corresponding to the E.M.F. of the Weston cell as possible. This is done by placing the sliding contact in the desired position and adjusting the rheostat in the accumulator circuit. It is now possible to calculate by simple proportion the exact potential gradient in any other length of wire as the E.M.F. of the standard Weston cell is accurately known for any given temperature. Thus at 20° C. the E.M.F. is 1·01830 volts. Hence, if the determinations are being carried out at 20° C. and the potentiometer is a little longer than a metre, it will facilitate calculation of unknown E.M.F's if the potential gradient in 101·83 cm. of wire is made equal to 1·0183 volts, the E.M.F. of the standard Weston cell. Then 1 cm. of wire will correspond to 0·01 volt and 1 mm. to 0·001 volt. Slide wire potentiometers are constructed with vernier scales affixed to the sliding contact which permit of measurements being made accurately to one-tenth of mm., and therefore under the above conditions to 0·0001 volt. The potentiometer illustrated in Fig. 21 sold by Messrs. Gallenkamp has such a provision. To measure the E.M.F. of the experimental cell its circuit must be closed by throwing over the two-way switch and the position of the sliding contact found which causes no current as indicated by the null-point instrument. Its E.M.F. can then be read off directly from the bridge reading, or if the potentiometer has not been standardised in this particular manner, then

$$\frac{\text{E.M.F. of experimental cell}}{\text{E.M.F. of Weston cell}} = \frac{d_e}{d_w}$$

where d_e = length of wire whose potential gradient is equal to the E.M.F. of the experimental cell, and

d_w = length of wire whose potential gradient is equal to the known E.M.F. of the Weston cell.

As before mentioned, this relationship presupposes that the potentiometer wire is of uniform gauge, and consequently before using a potentiometer for precision work, the wire should be calibrated. This may be done by means of resistance boxes arranged to form a Wheatstone's bridge, or by the method of Strouhal and Barus. (For details, see Ostwald-Luther, *Physiko-Chemische Messungen*, 4th edition, 1925, pp. 434–40.) Care must always be taken to see that the sliding contact is kept in a satisfactory state and does

not become corroded, which may be prevented by covering it with a very thin film of pure vaseline.

It is often more convenient to use a potentiometer in which the complete circuit is enclosed in a box, and in which the slide wire is replaced by a series of accurately constructed resistance coils made to correspond to P.D's of, say, from 0 to 1·7 volts and a slide wire wound on a revolving drum which is subdivided so that the smallest divisions may be made to correspond to 0·0001

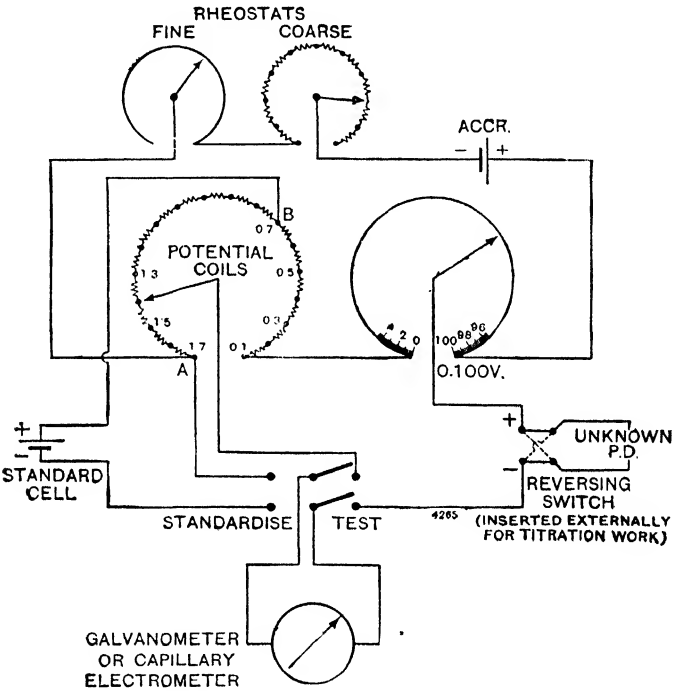


FIG. 29.—Schematic Diagram of a Circuit of the Cambridge Potentiometer.

or 0·0002 volt. Fig. 28 is a picture of the Cambridge potentiometer, and Fig. 29 a simple schematic diagram of its circuit, which the author has found to be admirably suited to hydrogen-ion work. All its moving parts, with the exception of the handles of the controlling switches, are inside the case, thus eliminating corrosion and other deteriorating effects. It has a selective switch and terminals which enable three different experimental cells to be connected to the potentiometer at the same time. The remaining terminals connect to the galvanometer or capillary

electrometer, the standard Weston cell and the accumulator respectively. Thermo-electric effects are reduced to a minimum by having the resistances made of manganin, hard-soldered to copper. To standardise the instrument, it is necessary to depress the standardising key provided, thereby throwing the standard cell into circuit with the null-point indicator and at the same time breaking the experimental cell circuit, and to adjust the rheostats (coarse and fine) until the flowing of no current is indicated. Then the figures given on the two potentiometer dials refer to volts, and consequently by rotating these dials until the null-point is obtained on depressing the tapping-key, the standardising key and the rheostats may be adjusted at any time, thus enabling the potentiometer to give accurate readings.

The Cambridge Instrument Co. produces an excellent portable potentiometer, which can be standardised without a standard cell. It is specially adaptable to hydrogen-ion concentration determinations and is capable of giving voltages correct to 1 millivolt, which happens to be the limit of accuracy to be expected from the hydrogen electrode, unless extreme precautions be taken, and, moreover, a sufficiently delicate electrode be employed. It contains a galvanometer of the unipivot type, which is used both in connexion with the standardisation of the instrument and as the null-point indicator. Fig. 30 is a picture of the Cambridge instrument. The instrument also contains an adjustable resistance to standardise the battery circuit with the galvanometer, a five-range switch to give steps of 200 millivolts and a fine adjustable resistance. The electrodes are connected to the right-hand terminals of the instrument, a dry cell being connected to the left-hand terminals. With the standardising key depressed, the rheostat is adjusted until the pointer of the galvanometer is directly over the red mark on the scale. The "X" key is then lightly depressed and the range-switch set to give the minimum deflection, while the circular graduated dial is at zero. To obtain the final reading, the latter is rotated until the pointer comes to zero. The reading of the circular dial is then added to the number of millivolts indicated by the range-switch, this total giving the E.M.F. of the electrodes.

We shall now direct our attention to the several components included in the potentiometric system.

The Experimental Cell Combination.

Fig. 31 represents the simplest cell arrangement involving the hydrogen and calomel electrodes, and contact with each electrode is made by means of amalgamated copper wire dipping into

PLATE II

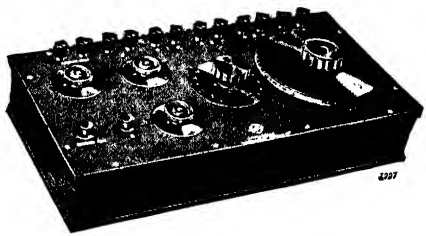


FIG. 28.—Cambridge Slide Wire Potentiometer.
(Cambridge Instrument Co., Ltd.)

[*See page* 141.

FIG. 30.—Cambridge Portable Potentiometer.

[*To face page* 142.

mercury. As stated on page 24, the potential difference at the junction of the liquids in the two electrodes can, for all practical purposes, be eliminated by inserting a saturated solution of potassium chloride between them. The narrow glass cylinder is filled with this solution to the level of the liquid in the beaker. The two electrode solutions are connected through the " salt-bridge," a

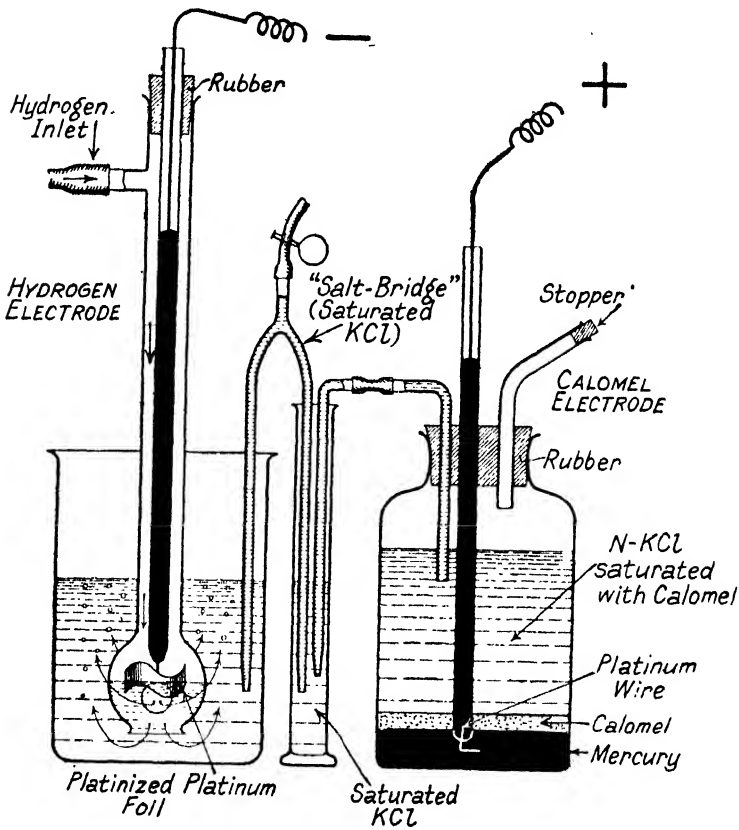


FIG. 31.—Hydrogen Electrode Titration Apparatus.

narrow inverted U-tube, containing saturated KCl solution. This " salt-bridge " tube should not be made of capillary tubing, as this would create a new source of potential. It is filled by suction with saturated potassium chloride solution by inserting both ends in a beaker containing the solution. If the hydrogen electrode should be contained in a closed vessel, then this " salt-bridge " is dispensed with, and the connecting arm of the hydrogen electrode simply

dipped into the vessel of saturated potassium chloride solution. A difficulty which sometimes arises is perhaps worthy of note. It may occur that a bubble of air settles over the orifice of one of the connecting tubes, which thereby breaks the circuit, but often evades observation. In carrying out an electrometric titration care has to be taken to keep the level of the solution in the cylinder the same as that in the beaker. This is omitted by some workers, who either insert filter paper impregnated with KCl, or glass wool, in the two ends of the U-tube to prevent diffusion, or fill the tube with agar containing saturated KCl solution. La Mer and Baker (*J. Amer. Chem. Soc.*, 1922, **44**, 1954) have used ground

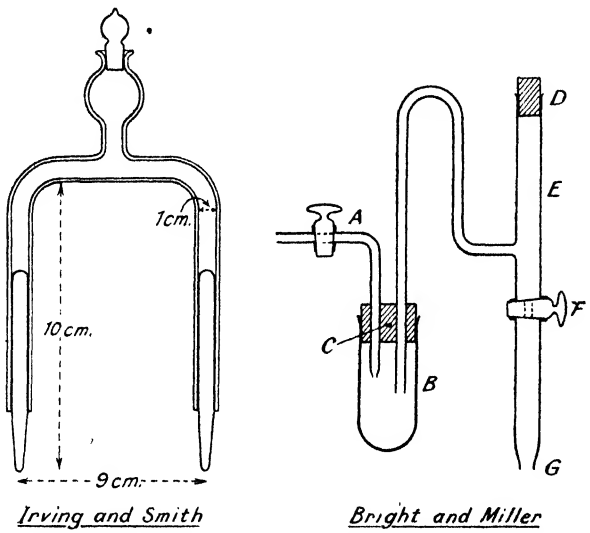


FIG. 32.—Salt Bridges.

glass plugged into the ends of the " salt-bridge " and have found that strictly reproducible potentials are obtained, whilst Irving and Smith (*Ind. Eng. Chem., Anal. Edn.*, 1934, **6**, 480) have shown that ground glass yields potentials identical with those given by using agar-agar in the " salt-bridge " in buffer solutions, soils and culture media. The form of " salt-bridge " devised by Irving and Smith is shown in Fig. 32, together with that described by Bright and Miller (*ibid.*, 1937, **9**, 346). The former make use of two Pyrex glass rods ground into the tapered ends of the bridge, contact being made through the films of saturated KCl solution between the plugs and the tubes. The latter workers make use of the liquid film in the ground glass tap.

The Irving and Smith form of " salt-bridge " is made of heavy walled Pyrex glass tubing of about 1 cm. in diameter. The reservoir bulb has a capacity of about 25 c.c. The bridge is filled to the level of the ground glass stopper with saturated KCl solution and the plugs are loosened momentarily to ensure a film of KCl solution in the ground glass joints, which are then seated firmly. Before use the tips are washed thoroughly with distilled water and dried with filter paper.

The tube A shown in the Bright and Miller form is part of the standard half-element. To prepare the bridge the reservoir, constructed from a Pyrex boiling tube, is filled with saturated KCl solution and forced on to the rubber bung C, thereby filling the apparatus to E, any excess being drawn off through F. The vertical tube is filled by upward suction, tap F being open. F is closed while the plug D is fitted into the tube. Contact with the solution undergoing test is made by inserting G. It is necessary to keep the bridge air-tight when the taps A and F are open, otherwise siphoning will occur.

Bollen (*Ind. Eng. Chem., Anal. Edn.*, 1931, **3**, 203) describes an effective diaphragm to minimise diffusion from the calomel electrode. Its position in the cell-combination is shown in Fig. 8. It consists of a sintered mixture of equal parts of " 100 mesh " Pyrex glass and Alundum in one end of a Pyrex tube. A tube of appropriate size is sealed at one end and enough of the Pyrex-Alundum mixture is introduced to give a column of about 3 cm. when well tamped down. The end is then placed in the flame of the blow-pipe, the mixture is gently tamped with a glass rod and heated to incipient redness. This eliminates air bubbles. After withdrawing the glass rod, heating is continued to, and maintained for 5 minutes at, 950°. After slowly cooling, the end of the tube is cut off so that a plug, 5–7 mm. long, remains in the tube. The exposed end is ground smooth with carborundum dust and water on a glass plate, washed, dried and finally fire-polished. Plugs of varying porosity may be prepared by altering the size of the Pyrex and Alundum particles, and the time and the intensity of heating.

The junction liquid may also be inserted in one half of the tube leading from the calomel cell, through a funnel and a three-way tap fitted in the tube. Such a device is shown in Fig. 25, and thus permits the end of the calomel connecting arm to dip into the solution. This arrangement is more suitable with the saturated calomel electrode and is particularly useful for rapid electrometric titrations.

The Standard Cell.

Two standard cells are available, namely (*a*) the standard Weston cell, and (*b*) the Clark cell. Schematically, they may be represented thus :

Standard Weston :

+ Hg	Hg_2SO_4 (paste)	Solution saturated with both Hg_2SO_4 and $CdSO_4$: $3CdSO_4 . 8H_2O$ (crystals)	—	12·5 per cent. Cd amalgam.

Standard Clark :

+ Hg	Hg_2SO_4 (paste)	Solution saturated with both Hg_2SO_4 and $ZnSO_4$: $ZnSO_4 . 7H_2O$ (crystals)	—	10 per cent. Zn amalgam.

In terms of international units, the standard Weston cell has an E.M.F. of 1·01830 volts at 20° C., and according to Wolff (1908) its E.M.F. at any other temperature, $t°$, between 0° to 40° C. may be found from

$$E_t = E_{20} - 0{\cdot}0000406(t - 20) - 9{\cdot}5 \times 10^{-7}(t - 20)^2.$$

The E.M.F's at different temperatures are given in Table 25 :—

TABLE 25

E.M.F. OF STANDARD WESTON CELL AT VARIOUS TEMPERATURES

Temp. °C.	0°.	10°.	15°.
E.M.F.	1·01866.	1·01860.	1·01848.
Temp. °C.	20°.	25°.	30°.
E.M.F.	1·01830.	1·01807.	1·01781.

The Clark cell might be considered obsolescent, and unlike the Weston cell it has a large temperature coefficient, as shown by the following formula which gives its E.M.F. between 10° and 25° C. :—

$$E_t = E_{15} - 0{\cdot}00119(t - 15) - 0{\cdot}000007\,(t - 15)^2,$$

the E.M.F. at 15° C. (E_{15}) being 1·4326 international volts.

The small temperature coefficient of the Weston standard cell was found by Smith (1910) to be due to the positive electrode increasing by 0·00031 volt per degree rise in temperature at 20°,

whereas the negative pole undergoes a diminution of 0·00035 volt. For this reason, it is advisable to protect the cell from local heating by enclosing it in a suitable container. Fig. 33 shows a convenient method of mounting the cell, which is enclosed in a brass cylindrical box. Sometimes two Weston cells are mounted side by side in order that one may be compared with the other. It is an advantage to have a hole in the ebonite top through which a thermometer may be inserted. These cells are now supplied with, if so desired, a certificate of the exact E.M.F., issued by some public testing institute, *e.g.*, by the National Physical Laboratory in England, or by the Bureau of Standards in the U.S.A., or by the Physik.-Techn. Reichsanstalt in Germany.

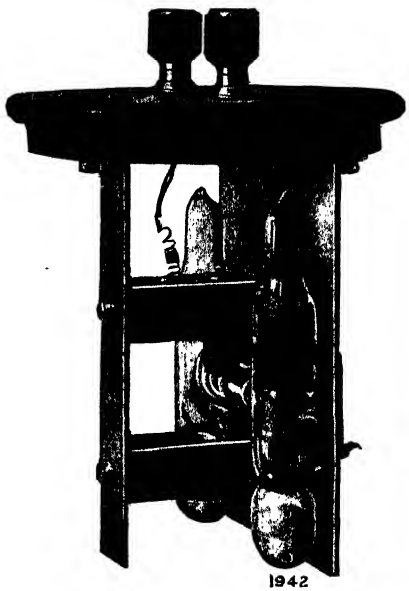


FIG. 33.—Internal View of "Cambridge" Weston Standard Cell.

In laboratories where many E.M.F. determinations have to be made, it is advisable to retain the standard cell which has been checked against a cell of accurately known E.M.F. as a standard, and to prepare a working cell. These may be readily prepared in the following way. An H-shaped vessel, similar to that illustrated in Fig. 34, is procured, and in the closed ends are carefully fused two short pieces of platinum wire. Into one limb is placed a little pure mercury and into the other a little cadmium amalgam. This amalgam should contain 12·5 per cent. (by weight) of pure cadmium (it must be free from zinc). It is prepared by mixing the two metals, warming on a water-bath and stirring the resulting liquid amalgam until it has become thoroughly homogeneous. Should any cadmium oxide be formed it must be removed, and this may be effected by passing the molten amalgam through a test-tube, the end of which has been drawn out into a long capillary. It is then poured into the bottom of one side of the H-tube, and to prevent fracturing the glass tube by the hot amalgam the tube should be kept in suitably hot water. On removing from water the amalgam solidifies. This amalgam is covered with a

thin layer of finely-powdered crystals of cadmium sulphate and then with large crystals to keep the cadmium sulphate solution saturated. A saturated solution of cadmium sulphate is prepared from the crystals, $3CdSO_4$, $8H_2O$, and if heating is resorted to it should be as gentle as possible and on no account should the temperature be allowed to rise above 75° C., for at this temperature the stable solid phase is $CdSO_4$, H_2O, and this will influence the concentration of the liquid phase. Moreover, hydrolysis of salts, such as would occur at elevated temperatures, is known to have an effect upon the amount of cadmium sulphate required to saturate a solution at any given temperature. The paste of mercurous

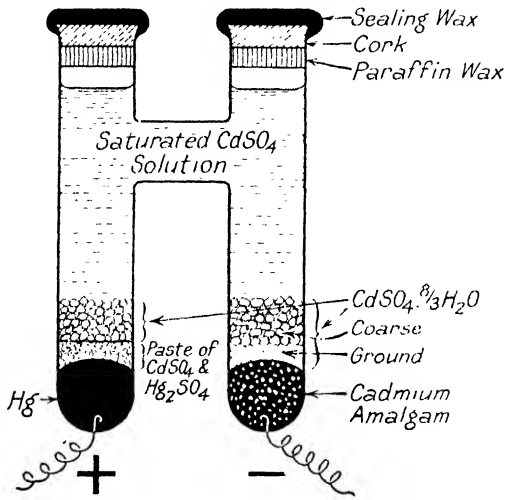


FIG. 34.—Weston Standard Cell.

sulphate is made by rubbing the pure salt with mercury and a little of the cadmium sulphate solution together in a mortar, filtering through a funnel, plugged with cotton wool, to remove any mercuric sulphate, and repeating the process two or three times with fresh quantities of mercury and cadmium sulphate solution. This paste is placed on top of the mercury, covered with crystals of cadmium sulphate, and the vessel nearly filled with the saturated cadmium sulphate solution. The vessel is sealed in the manner indicated in Fig. 34. The E.M.F. of the cell should be tested from time to time by comparison with a standardised Weston cell. Some kind of support will be necessary, *e.g.*, a large cork having two holes in which the two limbs fit.

Null-Point Indicators.

Quadrant electrometers are never used in conjunction with the hydrogen- or hydrogen-functioning electrodes, except in the case of the glass electrode. The capillary electrometer, Fig. 35, being the modified form of Ostwald and Luther, may be used, or suitable types of moving coil galvanometers which are rapidly coming into favour.

Capillary Electrometer.

This instrument, which in the first place was due to Lippmann (1873), depends upon the fact that there exists a difference in potential between a metal and a solution, which affects the surface energies of the two substances at the interface. If, therefore, it happens that the metal is a liquid, *e.g.*, mercury, then we see that its surface tension at the interface must be governed by the potential difference prevailing across the interface. Thus the potential difference between mercury and dilute sulphuric acid (1 part in 6 of water) is 0·93 volt. Hence, if an external positive potential be applied to the mercury, its surface tension will decrease such that if the mercury-acid interface occurs inside a capillary tube, this diminished surface tension will result in the mercury meniscus rising up the tube. On the other hand, if a current is made to flow across the interface from the acid to the mercury the potential of the mercury will become less positive, and this, in increasing the surface tension of the mercury, will cause the level of the mercury to become lower in the capillary. In the electrometer shown in Fig. 35 this interface is arranged to be about mid-way up the capillary tube, and the dilute sulphuric acid which lies upon it connects it to the mercury in the bulb on the right. Platinum wire contacts are sealed through the apparatus in the positions indicated. On joining these two contacts with a copper wire the mercury-acid interface acquires its normal contact potential and the meniscus almost immediately assumes its original condition. The movement of the mercury level on momentarily passing a current through the electrometer can be seen through a microscope fitted directly in front, Fig. 36, and illuminated, if necessary, by a suitable electric lamp placed immediately behind. With satisfactory magnification the minutest movement can be detected. Observation is facilitated by including a vertical scale in the eyepiece. It must be borne in mind that the current passed through the electrometer must, at most, be only for a few moments, and instantaneous when large currents are indicated. The reason is that electrolysis

will ensue, and should the current flow across from the mercury across the interface to the acid solution, it is possible the mercurous sulphate may be deposited on the wall of the capillary and so tend to clog it. Hence, it is necessary to short-circuit the

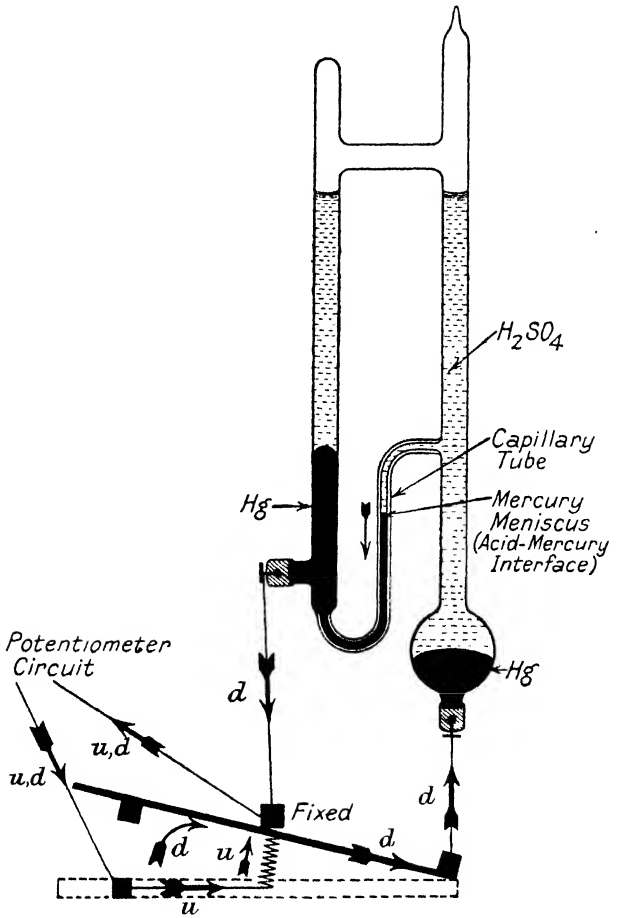


FIG. 35.—Capillary Electrometer showing Short-circuiting.

electrometer and to allow the current to pass only for the very brief periods when making a reading. This is accomplished by means of a tapping key, which is diagramatically explained in Fig. 35. The letter *u* indicates the direction of the current from and to the potentiometer when the tapping key remains up, the position shown, and *d* the direction when the key is

depressed. In the former case, the current passes through the spring and back to the potentiometer, and in the latter, after passing through the spring it is conducted through the key arm into the electrometer and from thence to the potentiometer. For the reason stated above, it is preferable to search for the null-point with the current flowing in this direction, though, of course, contact will have occasionally to be made such that the current flows through the electrometer in the reverse direction; in fact, very often the only way to find the null-point is to make contact on each side of the balance-point and to work inwards until the point which gives no movement of the meniscus is found. This electrometer has the advantage that it is dead-beat, and on short-circuiting the meniscus passes back immediately to the zero level. The form shown in Fig. 36 is especially serviceable in that, should the capillary have become impaired through the deposition of mercurous sulphate, it can easily be cleaned by inverting the electrometer, allowing the mercury to flow through the capillary, and exposing a new meniscus to the acid.

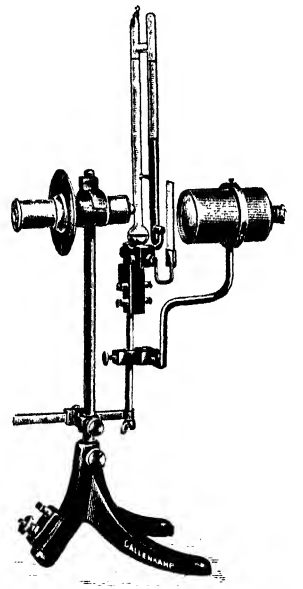


FIG. 36.—Complete Capillary Electrometer Outfit.

Galvanometers.

Galvanometers are becoming more popular in electrometric determinations, though in order to get the necessary sensitivity the D'Arsonval moving-coil pattern must be chosen. With such a type, it is more usual to have a mirror attached to the moving coil, which moves between the poles of a strong permanent magnet, and to observe the movement of a reflected spot of light upon a distant scale. This is a disadvantage, which, coupled with the fact that such a galvanometer often requires some time to respond completely to slight currents, probably explains why the capillary electrode is still preferred by many workers. In recent years, more attention has been directed to the production of more satisfactory galvanometers. Thus the unipivot type of moving coil galvanometer included in the Cambridge portable

potentiometer (Fig. 30) is extremely useful and satisfactory in every way, so also for routine work are the self-contained Daylight Reflecting Moving-coil Galvanometers, manufactured by Messrs. Tinsley Ltd. and Cambridge Instrument Co. of London. Most scientific instrument makers have now available galvanometers suitable for hydrogen-ion work, and when a galvanometer is to be purchased some points to be remembered are that (i) it must be responsive to momentary currents, for contact should not be made with the potentiometer wire for more than about ten seconds at a time; (ii) it should have sufficient sensitivity, but not too much, for the work it is intended; and in this connexion it is advisable to calculate the minimum currents to which it must respond—these will be smaller in testing experimental cells of high resistance; and (iii) it should be possible to damp its vibration rapidly. For great precision, a much more sensitive galvanometer must be used than the one described above.

CHAPTER IX

MODIFIED POTENTIOMETRIC AND OTHER METHODS

THE simple method of determining potential differences by means of the potentiometer may be modified in the following ways :—

(*a*) By using two precision decade resistance boxes ;
(*b*) By placing a voltmeter across a resistance between the ends of which the fall in potential is made equal to that of the unknown potential difference, and
(*c*) By using a thermionic valve.

These methods will now be discussed.

Decade Resistance Box Method.

This method has the advantage, if two accurate decade resistance boxes are available, that the current drawn from the accumulator can be made as small as desired which will assist the accumulator to maintain a constant current, and will prevent large currents from being extracted from the cell under test that otherwise would destroy the cell equilibria. The circuit is arranged in the usual potentiometer system, as given in Fig. 37, in which the two resistances, placed in series, take the place of the potential wire, and the side circuits are connected across one of the boxes only. To establish a constant current in the accumulator circuit, resistance is introduced equal to some definite number of ohms, say 100, 1000 or 10,000 ohms, by removing plugs from either of the boxes. Then the resistance plugs are taken from Box I required to balance the side circuit,

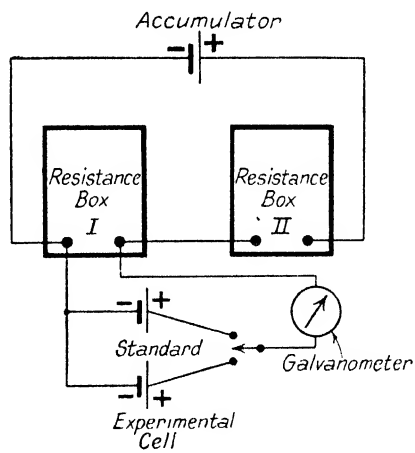


FIG. 37.—Potentiometric System, using Two Precision Resistance Boxes.

as shown by the galvanometer, and whatever plugs are taken from one box are placed in the corresponding sockets in Box II so as to keep the constant resistance in the accumulator circuit. Thus, if x ohms resistance were required to be used in Box I, and it was arranged to keep a total resistance of 1000 ohms from Boxes I and II together, then

$$\text{E.M.F. of experimental cell} = \frac{x}{1000} \times \text{P.D. across } 1000\ \Omega.$$

The P.D. between the ends of the 1000 ohms resistance must be found in the usual manner with the standard Weston cell.

This method is essentially the same as that using the Ostwald "Decade" Rheostat, by which the accumulator is connected across 1000 ohms and the side circuit connected across the resistances required to give balance by means of two wander plugs. (For further details, see Ostwald-Luther, "Physiko-Chemische Messungen," 4th edition, 1925, p. 463). Needless to add, in employing a resistance-box method every care must be taken to see that all plugs are fitting exactly.

Potentiometer-Voltmeter Method.

In this method, full dependence is put upon the voltmeter with which the potential measurements are made. Instead of using a potentiometer wire, the accumulator is connected across a suitable rheostat, and the side circuit connected from one end to the sliding contact, in parallel with which is a voltmeter. When the sliding contact has been moved to the position which indicates that no current is passing through the galvanometer, the potential difference corresponding to that of the test-cell is read off from the voltmeter. Such a method was used in conjunction with hydrogen-electrode measurements by Sand and Law (*J. Soc. Chem. Ind.*, 1911, **30**, 3872) and later by Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847). Figs. 38 and 39 are of the electrometric titration apparatus manufactured by Messrs. A. Gallenkamp & Co., of London. The principle underlying the method of measuring the E.M.F's is that described above, but in order to get an exact balance of potential two rheostats are employed, one for coarse adjustment and the other for fine adjustment. It will be observed (Fig. 39) that the accumulator (in this set a dry battery is provided) is connected across the two resistances R and R_1, and the potential difference of the cell under test is made equal to the fall in potential along a portion of these rheostats between the two points of contact by moving the sliding contacts RC and RC_1 until no deflection is obtained

in the galvanometer. When this state of affairs is established, the P.D. is observed on the voltmeter. In using this compact piece of apparatus, it is unnecessary to keep the battery switch, BS, closed except when taking a measurement. Kling and Lassieur (*Comp. rend.*, 1922, **174**, 165) have described a similar circuit in which they use a millivoltmeter and also two movable

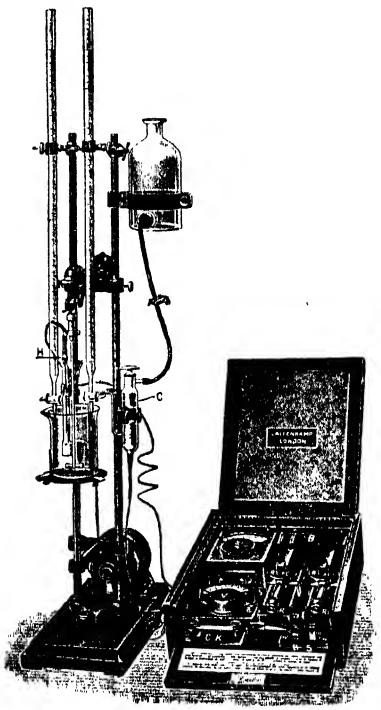


FIG. 38.—Electrometric Titration Apparatus (Messrs. Gallenkamp).

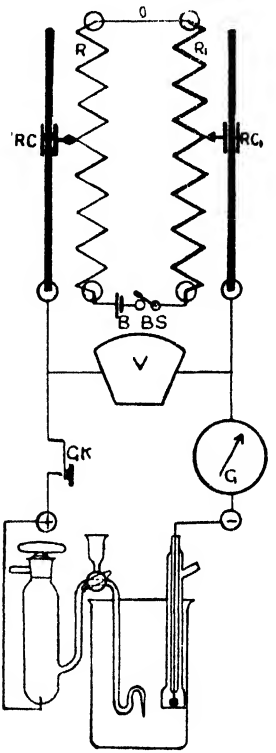


FIG. 39.—Circuit Diagram of Electrometric Titration Apparatus (Messrs. Gallenkamp).

contacts, one moving along a rheostat of 195 ohms, whereas the other is used for fine adjustment and moves upon a resistance of 5 ohms.

This method is convenient for titration work and has the distinct advantage that neither is a standard cell, nor are accurate resistances required. One difficulty encountered, however, apart from the fact that the voltmeter will require periodical checking,

is that a voltmeter which covers the whole range of E.M.F's met with in titration work usually reads only to 1 centivolt, and consequently reading to a millivolt will be approximate.

Ballistic Galvanometer Method.

The ballistic galvanometer has been found of use in the determination of the E.M.F's of cells that have a high internal resistance, and as a consequence are capable of yielding only the smallest currents. Beans and Oakes (*J. Amer. Chem. Soc.*, 1920, **42**, 2116) showed that it was particularly serviceable in the case of cells in which water was the electrolyte, and Morton (*J. Scientific Instruments*, 1930, **7**, 187), Britton and Robinson (*Trans. Faraday*

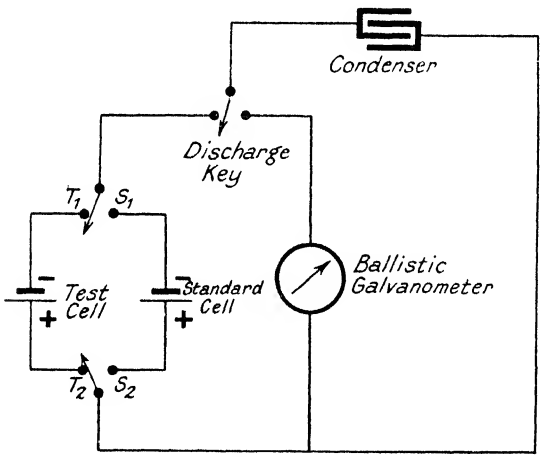


FIG. 40.—Ballistic Galvanometer Circuit.

Soc., 1932, **28**, 531) and Bennewitz and Kellner (*Z. anal. Chem.*, 1935, **102**, 1) have used it to measure the P.D. of glass electrode systems. The circuit is shown in Fig. 40. The ballistic galvanometer is an instrument which, on suddenly discharging through it a quantity of electricity, gives a deflection or " kick," the magnitude of which is proportional to the quantity of electricity passed. This sudden discharge through the galvanometer actually takes place from a condenser, which has previously been charged by a cell for a given time. The diagram shows that it is possible to do this from either the standard cell, by closing the switches S_1 and S_2, or the test-cell, using switches T_1 and T_2. During the charging process the galvanometer is out of circuit.

As the capacity, C, of a condenser is equal to $\frac{Q}{E}$, where Q is the quantity of electricity received and E the difference in potential applied to its plates, *i.e.*, the potential difference of the two electrodes of the charging cell, we see that if a cell gives a current, i, for a time t, $Q = i \times t$, and therefore $C = \frac{i \times t}{E}$. On discharging through the ballistic galvanometer a deflection, d, is produced. Hence $Q = i \times t = E \times C = K \times d$, K being the galvanometer constant, and therefore cells of E.M.F's, E_1 and E_2, giving currents i_1 and i_2 for time t, and subsequently deflections, d_1 and d_2, from condenser charges of Q_1 and Q_2 respectively may be compared thus:

$$\frac{Q_1}{Q_2} = \frac{i_1 \times t}{i_2 \times t} = \frac{E_1 . C}{E_2 . C} = \frac{d_1}{d_2}.$$

Consequently, if the two cells be the Standard Weston and the test-cell, then one E.M.F. will be known and the other becomes calculable.

The time required for charging the condenser will depend on its capacity and also on the sensitivity of the galvanometer. For glass electrode work, Morton recommends a mica condenser, variable in steps of 0·1, 0·3, and 0·5 microfarad, and high sensitivity moving-coil galvanometer whose approximate characteristics are: coil resistance, 2800 Ω; ballistic period (undamped), twenty-two seconds; external critical damping resistance, 70,000 Ω; factor of merit, 100; ballistic sensitivity, 3430 mm. per microcoulomb at 1 metre.

Efficient earthing of both the calomel electrode, and the plate of the condenser to which it is connected, is essential. It is advisable to insulate the glass electrode and its connexion to the condenser. This insulation should be as thorough as possible.

Owing to the high resistance of the glass electrode, very little advantage is gained by using a variable condenser. This will be understood from the equation

$$i \times t = CE(1 - e^{\frac{t}{RC}}),$$

which gives the charge received by a condenser in time t from a cell, of E.M.F. = E and of resistance R. Substituting 1 volt for E, and putting R equal to 100 megohms, it is found that the charge acquired in 30 seconds by a condenser of 1 microfarad capacity is 0·258 microcoulomb, whereas condensers of 1·5 and 0·5 microfarad capacity receive 0·270 and 0·224 microcoulombs respectively.

It might be argued that this method is particularly susceptible to the introduction of errors resulting from the withdrawal of current from the test-cell and the consequent polarisation effects produced therein. Beans and Oakes, however, have found that the E.M.F's found by this method are the same, within $\pm$ 0·0005 volt, as the voltages recorded by the potentiometer. They point out that if a condenser of 1 microfarad is used and the E.M.F. of the cell is 1 volt, then 10 ^{11} equivalent of ion will be discharged, which amount they say is still less than the amount which ordinarily would be discharged during the adjustment of an instrument when a potentiometer is used.

The accuracy of determining the potentials of hydrogen electrodes has been investigated by Davis and Davidson (*J. Amer. Chem. Soc.*, 1928, **50**, 2053). Errors may arise from (*a*) difficulty in accurately reading the galvanometer-throw, (*b*) the condenser, (*c*) the formula used for the calculation of the E.M.F. They may cause a total error of as much as $\pm$ 4 millivolts.

Calibration of the glass cell is necessary and this may be carried out by means of simple buffer mixtures for limited ranges, or with one of the Universal Buffer Mixtures for more extended ranges. Curves are constructed connecting *p*H values with deflections of the ballistic galvanometer. Unlike the calibration curves obtained on two successive occasions by using a thermionic valve method of measuring the potentials of the glass cells (when the E.M.F.-*p*H curves are parallel owing to a uniform change in the asymmetry E.M.F.), the ballistic galvanometer calibration curves change in slope and intersect at deflections corresponding to about *p*H 6. This is illustrated in Fig. 41, which was taken from a paper by Britton and Robinson (*loc. cit.*). The curves refer to two glass electrodes A and B, each of which was calibrated on successive days. Both are rectilinear over the range *p*H 2·5–10·0. Calibrations A_2 and B_2 were carried considerably beyond *p*H 10 and both show a deviation from linearity. The daily variation of the calibration curves do not show a trend in any particular direction.

Morton (*J. Chem. Soc.*, 1934, 256) points out that under certain conditions the instrument used for measuring the potential may be responsible for the distortion of the E.M.F.-*p*H calibration graph. Occasionally the input-impedance of the potential-measuring device (*e.g.*, the insulation resistance of the condenser used in a ballistic system, or the grid-filament impedance of a valve potentiometer in which valves of the ordinary type are used) may be as low as 10,000 megohms ; the error in the determination, for an electrode having a resistance of 100 megohms, is then of the

order of 1 per cent. and the slope is altered by a corresponding amount. This accounts for the different slopes shown in Fig. 41. Using the exponential theorem, Morton (*ibid.*, 1932, 2469) showed

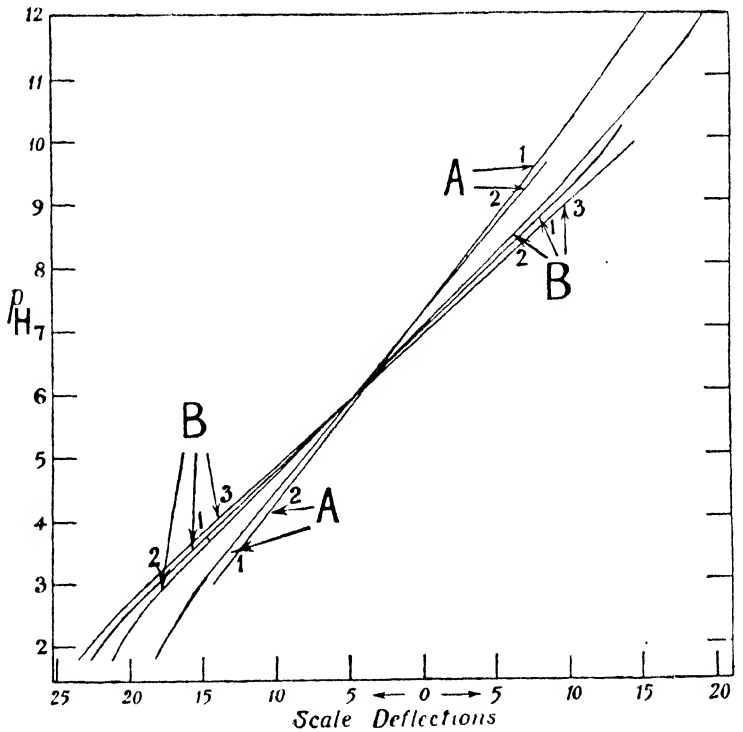


FIG. 41.—Condenser-Ballistic Galvanometer Calibration Curves of Glass Electrodes.

that if a condenser of sufficiently large capacity be used, the average charging current for time t is $i = E/R$ and the accumulated charge is thus

$$Q = E \times t/R = r \times t\,(K \pm 0{\cdot}0001984\,.\,T\,.\,pH/R(R + r),$$

where R is the resistance of the glass membrane, r the insulation resistance of the condenser and K a constant. Hence the slope of the calibration graphs in Fig. 41 may be represented by

$$\frac{\delta d}{\delta pH} = 0{\cdot}0001984\ T\ .\ t\ .\ s./\left(\frac{R^2}{r} + 1\right),$$

where d is the observed deflection and s the ballistic sensitivity of the galvanometer. As the denominator contains R^2, it appears

that changes in the resistance of the glass membrane will lead to appreciable changes in slope. Morton has shown that changes in the resistance of the glass electrode occur with changes in temperature, particularly at 18°, and suggests, therefore, that careful temperature control is necessary when using the ballistic galvanometer-condenser system.

Fig. 41 shows that the calibration graphs tend to oscillate about a point corresponding almost with zero deflection. Hence this point refers to the stage when the E.M.F. of the glass cell is approximately zero, and is therefore not affected by changes in the resistance of the glass electrode.

The ballistic galvanometer has been used as a null-point instrument in the determination of the E.M.F's of cells that have a high internal resistance (Jones and Kaplan, *J. Amer. Chem. Soc.*, 1928, **50**, 1853; Dole, *ibid.*, 1931, **53**, 620). Instead of placing the test-cell in the potentiometer circuit, a suitable condenser is inserted in series with a ballistic galvanometer and the sliding contact. The test-cell is connected in parallel with the condenser, which is charged for definite periods by the cell, the plates of the condenser acquiring the P.D. of the test-cell, and then discharged through the galvanometer with the contact fixed in suitable positions. This process is repeated until the galvanometer gives no deflection. This method necessitates the use of a sensitive galvanometer, and to bring the galvanometer back quickly to its zero reading a shunt of resistance equal to that of the critical damping resistance of the galvanometer and a tapping key should be used. Dole has demonstrated the use of this method in determining glass electrode potentials.

Thermionic Valve Method.

As mentioned before in this chapter, in making E.M.F. measurements of cells, of which one electrode is that of hydrogen, every precaution must be taken not to draw any more current from the experimental cell than is absolutely unavoidable, on account of the risk of upsetting the equilibrium existing between that electrode and the solution in which it is immersed. It is, moreover, essential that the sliding contact should complete the test-cell circuit with the potentiometer only for those short periods when observations are being made. By means of the thermionic valve, it is possible to make observations without extracting from the cell any appreciable amount of current, and for this reason it is possible to perform electrometric titrations with the hydrogen electrode whilst leaving the titration cell in circuit. Goode (*J. Amer. Chem. Soc.*, 1922, **44**, 26) first applied the valve to

electrometric titrations with the hydrogen electrode. In the ordinary triode valve the plate or anode is maintained at some high positive potential, the grid is given a negative potential, and the filament made incandescent by means of a suitable low potential. In so doing, it emits a stream of electrons, which, though repelled by the grid, are attracted to the positive plate. Thus a current of negative electricity is generated in the anode circuit away from the anode, or, conversely and, incidentally, according to the more usual convention, a current of positive electricity flows from the plate through the valve to the positive filament-lead into the anode circuit. Goode pointed out that this *plate or anode current* might be considered as the sum of a constant current, which depends upon the valve and its applied

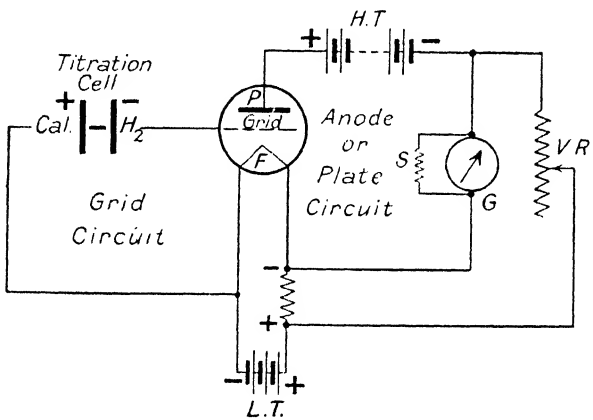


FIG. 42.—Goode's Thermionic Valve Electrometric Titration Circuit.

potentials only, and the remaining portion which, besides being dependent upon the negative grid potential, is a linear function of the potential applied to the grid. Hence, when no potential is applied to the grid, the plate current depends entirely upon the valve, and if some equal opposing current can be introduced into the anode circuit, it should be possible to neutralise the current set up by the valve alone, so that when some negative potential is applied to the grid, the current, generated in the plate circuit, will be a linear function of that potential. This, Goode accomplished with the circuit represented in Fig. 42. The hydrogen electrode, being the negative pole of the titration cell, was connected to the grid and the calomel electrode to the negative filament lead. A shunted (S) moving-coil galvanometer, G, detected currents in the anode circuit, and the anode current due

to the valve with no cell in the grid circuit was opposed by an equal current passing through the galvanometer, produced by a potential difference between the two ends of a small resistance placed in the positive filament lead, and regulated by means of a large variable resistance, VR. Thus, having once adjusted the galvanometer circuit such that no current flows through it when there is no applied grid potential, the current registered by the galvanometer when the titration cell is introduced into the grid circuit will bear some simple proportional relationship to its E.M.F. The galvanometer may, therefore, be calibrated in terms of the applied voltages, or simply in terms of *p*H. Hence, if an electrometric titration be performed, a curve will be obtained between the amounts of reactant added and galvanometer readings which will be similar in form to that obtained by direct titration. Later, Goode (*J. Amer. Chem. Soc.*, 1925, **47**, 2483) described a circuit by which the original plate current was amplified about 25 times, by two stages of valve amplification using resistances, and thereby he was able to read off the *p*H values from a milliammeter after suitable calibration. Treadwell (*Helv. Chim. Acta*, 1925, **8**, 89) used a similar arrangement for electrometric titration, with the exception that he placed an additional potential of 1·6 volts in the grid lead between the negative electrode of titration cell and the grid.

Morton (*Pharm. J.*, 1927, **118**, 761) has modified Goode's procedure, and has shown that not only is it possible to measure the voltages set up by a titration cell, but to also locate the end-points more accurately than is possible from the ordinary titration curve. This is done by means of a differential curve which is obtained by plotting the amount of reactant added against the increase in the deflection of the galvanometer for each increment of titrant. This is obtained by balancing out the component of the normal anode current as described above, then including the titration cell in the grid-filament circuit and again causing the galvanometer in the anode circuit to remain undeflected. Afterwards small amounts of reactant are added, each galvanometer deflection observed, and the potential dividers adjusted after each addition so as to give no galvanometer deflection. The galvanometer readings thus obtained are proportional to $\frac{dE}{dx}$, where E is the E.M.F. of the titration cell when x c.c. of reactant have been added. Fig. 43 gives the arrangement of Morton's circuit. The method is to place the switch in position 1 and then to balance out the anode current by adjusting R_2. Throw switch over to position 2, thereby including titration cell in the grid-filament

circuit and now adjust R_1 until the galvanometer again remains undeflected. An increment of reagent is added, the galvanometer reading noted, and again balanced out, and so on. Fig. 45 gives a curve obtained by this method in which it will be seen that the end-points, corresponding to points of inflection (*cf.* Fig. 56) were marked by maximum galvanometer readings. The ordinary titration curve can be drawn from observations of the millivoltmeter, MV. Morton (see also Crocker and Matthews, *Theoretical and Experimental Physical Chemistry*, London, 1927, p. 412) showed

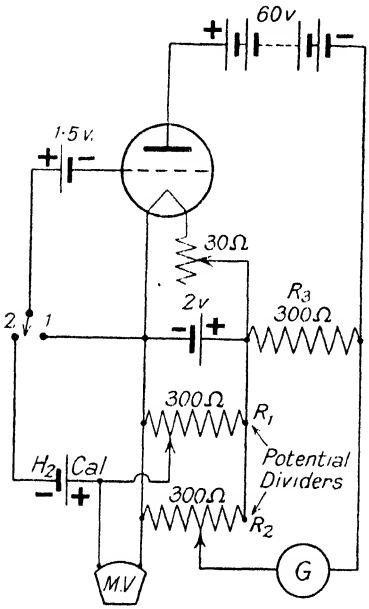


FIG. 43.—Morton's Differential Method of Electrometric Titration.

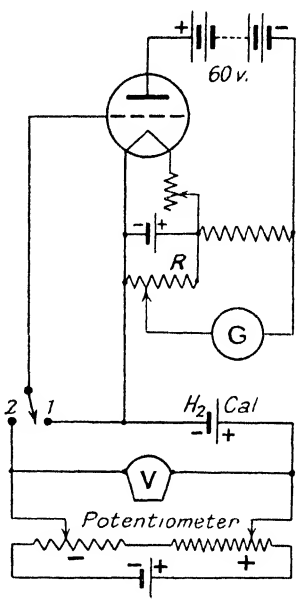


FIG. 44.—Galvanometer in Anode Circuit to Balance Potentiometer.

that the valve-galvanometer circuit could be used for ascertaining the point of balance of a potentiometric system when connected across from the grid to the negative-lead to the filament, in such a way that the negative potential is joined to the grid (Fig. 44). The anode current produced when the switch is in position 1 is balanced out as above by adjustment of R, and when the switch is moved to position 2 the sliding potentiometer contacts are adjusted until the galvanometer remains undeflected. The potentiometer is then balanced, and the potential may be read off from the potentiometer as usual or with the circuit shown in

Fig. 43 from the voltmeter. (See also Buytendijk and Brinkman, *Proc. K. Akad. Wetensch.*, Amsterdam, 1926, **29**, 816.)

As emphasised before, it is essential in the measurement of a reversible E.M.F. that no current should be taken from the cell. This necessitates the use of a fairly great negative potential in the grid circuit, though it must not be made high, for then it is possible that a small grid current will be set up in the opposite direction. As will be seen from Fig. 46, the introduction of increasingly negative grid potential causes the current in the plate circuit to be considerably diminished, but this difficulty may be

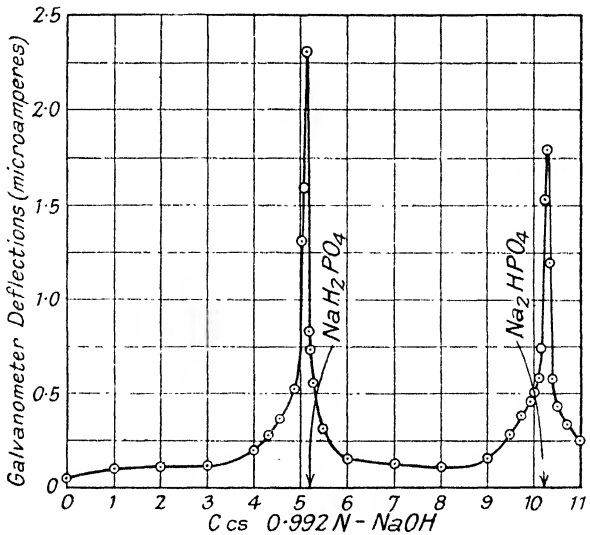


FIG. 45.—Differential Titration Curve of 5 c.c. 1·022 M.-H_3PO_4 with 0·992 N-NaOH.

surmounted by using a highly sensitive galvanometer. Before the currents passing through the plate circuit are calibrated, it is, of course, imperative that the filament current should be kept constant. Usually, this is a matter of no great difficulty, though Williams and Whitenach (*J. Physical Chem.*, 1927, **31**, 519) advocate the insertion of a rheostat and an ammeter in the filament circuit to ensure constancy.

The foregoing methods, together with that of Schwarzenbach (*Helv. Chim. Acta*, 1930, **13**, 865), involve the passage of small grid-currents through the cell while undergoing test. It is just possible that these currents might cause sufficient polarisation to make the methods incapable of giving accuracy beyond ± 1 milli-

volt. To eliminate such grid-currents Voegtlin, de Eds and Kahler (*Amer. J. Physiol.*, 1929, **91**, 225; U.S. Pub. Health Reports, 1930, **45**, 2223), Müller (*Z. Elektrochem.*, 1930, **36**, 923), Fosbinder (*J. Physical Chem.*, 1930, **34**, 1299) and Dubois (*J. Biol. Chem.*, 1930, **88**, 729), work at the floating grid potential by introducing high resistances.

According to Stadie (*J. Biol. Chem.*, 1929, **83**, 477), both deflection and null-methods require current indicators in the plate circuit with high sensitivity ($0{\cdot}3 \times 10^{-6}$ ampères), to measure 0·001 volt in the grid circuit. They should also be of considerable range, since the plate current may vary from 0·5 to 1·5 milliampères. Such conditions cannot be satisfied by one instrument,

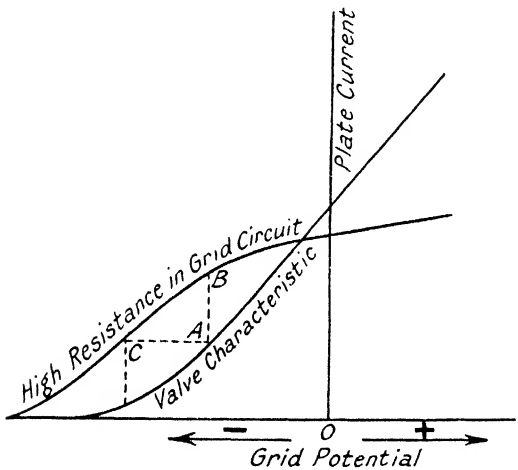


FIG. 46.—Thermionic Valve Characteristic Curves.

and consequently the following procedures have been adopted to overcome the difficulty: (1) Use of shunt with high sensitivity galvanometer (Elder and Wright, *Proc. Nat. Acad. Sci.*, 1928, **14**, 936); (2) Diminution of plate voltage (Pope and Gowlett, *J. Scientific Instruments*, 1927, **4**, 380); (3) Increasing negative grid potential (Williams and Whitenach, *loc. cit.*). Each of these schemes involves loss of amplification. (4) Multiple stage amplification and use of milliammeter (Goode, *loc. cit.*; Partridge, *J. Amer. Chem. Soc.*, 1929, **51**, 1).

To overcome difficulties inherent in these methods, Stadie (*loc. cit.*) has devised a balanced Wheatstone Bridge circuit (Fig. 47). The four resistance arms comprise the two internal filament-to-plate resistances of the screened grid valves and the

other two are external variable resistances of the plate circuits. A high sensitivity galvanometer is used as a null-point instrument.

Stadie employed this method to measure the potential difference of glass electrode systems whose feature is high resistance and very low current. He used a grid bias of a potential, represented by A (say) in Fig. 46, when the test-cell was excluded from the grid circuit, which gave a suitable current in the plate circuit. Then the glass cell, together with a potentiometer, reading zero, was included in the circuit by opening the key. If the solutions on both sides of the glass electrode diaphragm are at the same *p*H, then there will be no P.D. across the membrane

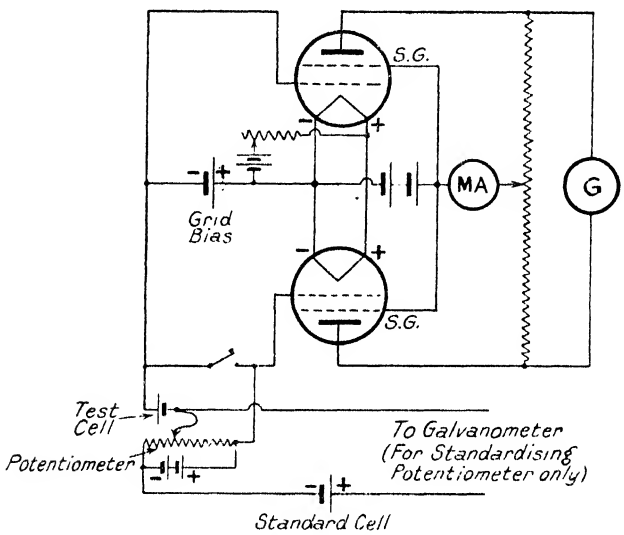


FIG. 47.—Stadie's Balanced Thermionic Valve Wheatstone Bridge Circuit.

(except possibly an asymmetry E.M.F.), though when inserted in the grid circuit the glass resistance will cause an increase in the plate current, indicated by A B.

Adjustment of the grid potential by means of the potentiometer will restore the original current in the plate circuit, as shown by the galvanometer. In order to facilitate the maintenance in the plate circuit of some definite working current Stadie uses a second valve whose plate current is so arranged as to be equal and opposite to the initial anode current, which thus makes it possible to use a galvanometer as a null-point instrument. The additional negative potential, E, in the grid circuit is AC (Fig. 46). Now if a liquid of different *p*H is inserted in one compartment

of the glass cell, which thereby sets up a further E.M.F. of e volts, then a potential equal to E + e must be introduced into the grid circuit from the potentiometer to bring the plate current back to its initial value. From these two P.D's the E.M.F. of the glass cell, e, can be found. Stadie employed low filament currents and low plate voltages. Harrison (*J. Chem. Soc.*, 1930, 1530) points out, however, that the resistance of the grid-filament circuits of ordinary radio valves may be of the same order as that of glass electrodes, and consequently much current may be extracted from the test-cell; a difficulty which apparently he has experienced.

Similar circuits, which involve balanced valves in two arms of a Wheatstone's Bridge, have been described by Williams (*Phil. Mag.*, 1928, **6**, 324), Müller (*Z. Elektrochem.*, 1932, **38**, 425), Müller and Durichen (*ibid.*, 1935, **41**, 559; 1936, **42**, 730) and by McFarlane (*J. Sci. Instr.*, 1933, **10**, 142, 208). Müller originally employed two tetrodes, but later used two indirectly heated pentodes. Fig. 48 gives McFarlane's circuit in which two Mullard valves (PM.1HL) are used. These valves have been matched by the makers and pass approximately the same anode current at an anode voltage of 85 and a grid voltage of − 0·25.

McFarlane's circuit may be used either as a null-point indicator or as a *p*H-meter. When used for the latter purpose the potential applied to the grid is subdivided so that only a portion is actually employed to charge the grid. This makes it possible to convert the galvanometer scale into one of *p*H covering the range 1–12·5. The whole apparatus and glass cell are enclosed in earthed metal boxes. The connexion from the glass electrode is insulated in sulphur, placed inside a copper tube.

Gilbert and Cobb (*Ind. Eng. Chem., Anal. Edn.*, 1933, **5**, 69) point out that the use of two apparently identical valves in the arms of a Wheatstone's Bridge not only presents difficulty through slight differences in initial resistances, but these difficulties increase with time as the two valves do not age equally. They, therefore, substitute a variable resistance and a small potential for one of the valves which causes a current just as if it were produced by passing through a valve. Using their modified circuit, they claim that the same accuracy can be obtained as when two valves are used.

Harrison has devised a system of valve amplification for the measurement of potential differences of cells, and especially of the glass cell. In principle it is essentially the same as that of Stadie, but the method is devoid of many of its difficulties. This

has been made possible by using a new type of valve, known as the *Electrometer Triode.* It is manufactured by Philips Lamps, Ltd., though others of similar design are on the market. The essential feature of this valve is that when the grid potential

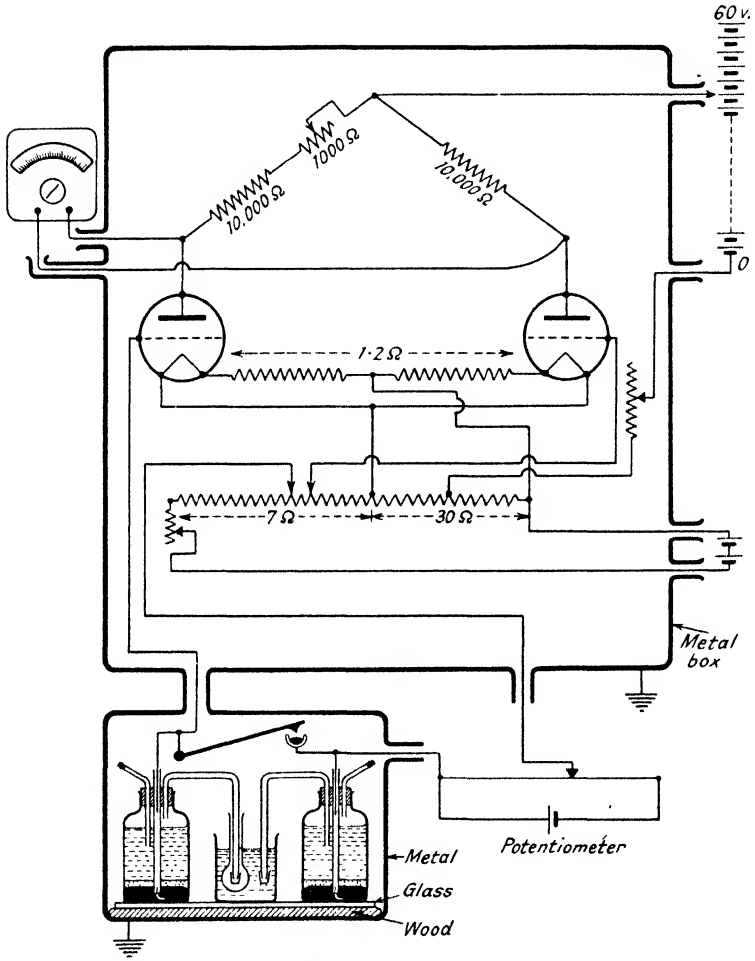


FIG. 48.—McFarlane's Compensated Valve-Voltmeter

is — 2 volts the grid current is less than 10^{-14} ampères. Hence, however great may be the resistance in the grid circuit there will be no variation in the plate or anode circuit current due to the introduction of the resistance, as we have seen to be the

case with ordinary valves and shown in Fig. 46. This renders the electrometer valve of especial value in the measurement of P.D's across high resistances such as exist in glass cells. As regards the construction of the valve, it will be seen from Fig. 49 that the grid is placed outside the path of the electrons from the filament to the plate. The characteristic curve of this valve when the grid is negative is similar to that of the ordinary valve, but the slope is only about 0·03 milliamp. per volt. The amplification, however, according to Harrison, is sufficient for the purpose. The filament current is 0·7 ampère and the voltage is 2. The anode voltage is low, *viz.*, 4–9. In a private communication Mr. C. Morton states that in the most successful valve circuit he has used the test-cell and potentiometer are placed

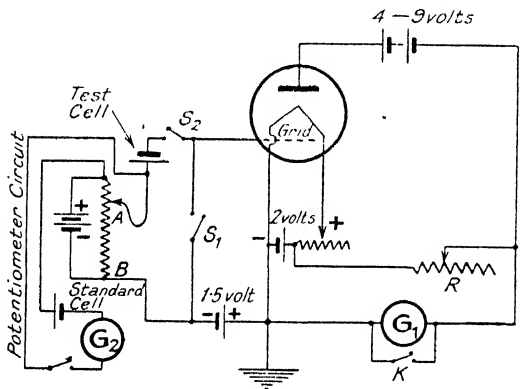


FIG. 49.—Harrison's Electrometer Triode Valve Circuit.

in the grid circuit and the galvanometer is placed in the secondary circuit of a transformer the primary coil of which is in the plate circuit. Screening is necessary and balancing is carried out as in Harrison's method. By using the galvanometer in this manner, it is unaffected by any gradual drift that may occur in the plate circuit, and there is thus no instability of the zero. Fig. 49 gives the circuit used by Harrison. The test-cell and potentiometer can be short-circuited from the grid circuit by means of the switches S_1 and S_2. The anode current, of the order of 200 microamps., passes through the galvanometer, G_1, together with a compensating current drawn from the filament accumulator, the variable resistance, R, being used for adjustment. The short-circuiting key, K, must be closed when the instrument is turned on, otherwise the compensating current which begins to flow instantaneously through the plate circuit will be immedi-

ately balanced by the plate current. This sudden onrush of current might damage the galvanometer. The lag in the production of the actual plate current is caused by the filament having an exceptionally large heat capacity, so much so that it requires more than ten seconds to attain its final temperature.

To use the apparatus for the determination of the E.M.F. of the test-cell, the switch, S_1, is closed and the galvanometer needle, G_1, is accurately noted. On introducing the test-cell and the potentiometer, set to zero, by opening the switch, S_1, and closing S_2, the extra E.M.F. due to the test-cell applied to the grid causes a variation in the anode current which will be indicated by the movement of the galvanometer needle, G_1. This variation in the grid potential is then counteracted by means of a measurable potential applied by means of the potentiometer. When the correct potential difference has been applied the needle of G_1 will be restored to its original position. This P.D. will, of course, be equal and opposite to the potential of the test-cell. The position of the galvanometer needle can be checked against the initial position by closing the switch, S_1, and opening S_2 (see also Elder, *J. Amer. Chem. Soc.*, 1929, **51**, 3266; Morton, *Trans. Faraday Soc.*, 1928, **24**, 14; Greville and Maclagan, *ibid.*, 1931, **26**, 210; Fosbinder, *J. Physical Chem.*, 1930, **34**, 1294; Rosebury, *Ind. Eng. Chem., Anal. Edn.*, 1932, **4**, 398).

Amplified Ballistic Method of Measuring the E.M.F. of the Glass Cell.

Morton (*J. Chem. Soc.*, 1931, 2977) has introduced a method in which a condenser is discharged through the grid of a valve and the amplified current is detected by means of a ballistic galvanometer. By connecting the glass cell in opposition to a potentiometer in the condenser circuit, so that the condenser is charged by the combined cell system, the condenser on discharge through the valve, or valves, will indicate the presence of a difference in E.M.F. between that of the glass cell and the opposing E.M.F. from the potentiometer by a " kick " of the galvanometer. When the potentiometer has been adjusted such that the E.M.F. impressed on the circuit is exactly equal and opposite to that of the glass cell, no deflection will be given by the galvanometer. The sensitivity of the method, which may be increased to any desired degree by the standard methods of audio-frequency amplification, is such that an E.M.F. of 0·01 mv. operating through a resistance of 1000 megohms may be detected.

Hemingway and Arnow (*Ind. Eng. Chem., Anal. Edn.*, 1933, **5**, 278) have designed an amplified ballistic circuit by which the

E.M.F. of a glass cell can be determined with an accuracy of less than 0·5 mv. in less than a minute. The circuit diagram is given in Fig. 50. The condenser, C_1 (a paper condenser, 0·1 microfarad), is charged to a potential difference equal to the difference, $\pi_G - \pi_P$; π_G being the E.M.F. of the glass cell and π_P the E.M.F. introduced by the potentiometer, for a short period of time, say half a minute. On depressing the key, K, the condenser discharges through R, the discharge being amplified by the valve system and indicated by the galvanometer.

The American valves, UX240 and UX222, are suitable. The galvanometer is of the moving-coil type, the sensitivity of which is 0·003 ampères per millimetre, or if the enclosed lamp and scale type of galvanometer is used, its sensitivity should be

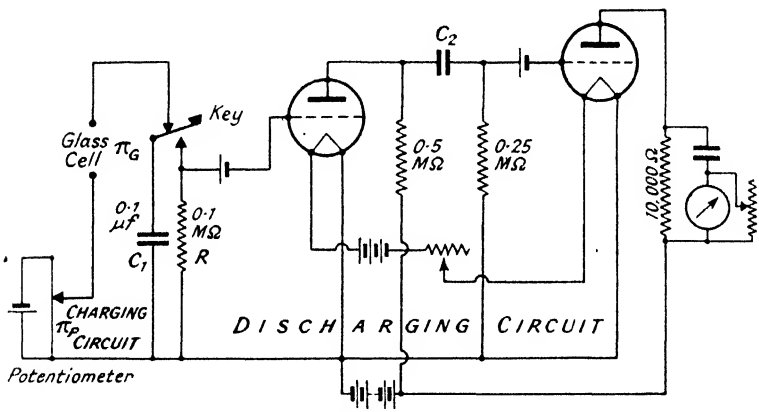


FIG. 50.—Hemingway and Arnow's Amplified Ballistic Circuit.

0·025 ampères per millimetre. By using a low grid resistance, $R_1 = 0{\cdot}1$ megohm, there is no need for shielding, or for the use of an extra condenser in the discharging circuit (*vide* Morton, *loc. cit.*). A by-pass condenser, C_2 (paper condenser, 2 microfarads), however, is necessary to prevent the ballistic throw becoming of an oscillatory nature, thus making adjustment difficult. If the condenser has stood for some time without being discharged, a charge will have accumulated—the so-called absorbed charge—and this will on discharge produce a false throw, which should, of course, be ignored.

Hemingway and Arnow state that a single stage of amplification increased the throw six times, whereas two stages gave a sixtyfold increase. Their glass electrode was a bulb, 1–2 cm. in diameter, blown from Corning H 015 glass tubing of 5 mm. bore.

Subsequently, Hemingway (*ibid.*, 1935, **7**, 203) improved on the foregoing circuit by using three A.C. valves, which also have higher amplification. He also introduced a temperature-correction device, involving variations in resistance, by which the potentiometer may be converted into a *p*H-meter for any temperature.

Insulation.

All leads from the grid of the first valve to the glass electrode should be thoroughly insulated. Sulphur coverings, which are enclosed in earthed copper tubes, have been used. Bromley (*Analyst*, 1935, **60**, 533) suggests that grid leads should be taken through glass tubes filled with " halowax " and jacketed with earthed copper wire spirals.

McFarlane states that the ebonite used as the bases of valves may not constitute sufficiently good insulation between the legs of the valves. Valves to be used for glass electrode work should therefore have their bases removed. Contacts with the appropriate terminals should be made directly and the valves mounted on rubber bungs. Bromley, however, mounts the valve in three sockets supported in " halowax," but detaches the anode leg-socket, which is air-insulated. When air-insulation is not possible, chloronaphthalene wax is used. The glass body of the valve, the stem of the glass electrode and the electrode wire inserted therein should all be waxed.

Any switches used in the grid circuit should be insulated by mounting on sulphur blocks, or they may be moulded and carved out of an insulating wax, such as chloronaphthalene, and, wherever possible, connexions should be made by means of little pools of mercury contained in drill-holes in the wax. Terminals should be carefully insulated and the potentiometer should be mounted on a block of sulphur or " halowax."

It is advisable to enclose the valve circuit and the glass cell in an earthed copper box, but needless to say, the apparatus including the glass cell should be mounted on good insulating material, such as sulphur. The air surrounding both the cell and the valve should be kept as dry as possible by means of a desiccating agent, *e.g.*, silica gel.

CHAPTER X

THE PRINCIPLES OF VOLUMETRIC ANALYSIS

The Importance of Electrometric Titration.

VARIATIONS in hydrogen-ion concentration, or maybe " hydrogen-ion activity," underlie many analytical procedures. This has become apparent from the results of the enhanced attention which has been devoted in recent years to the neutralisation reactions of acids, bases, and ampholytes, which include many protein bodies and alkaloids. Besides leading to a clearer understanding of the principles of analysis, they have, moreover, led to the discovery of new methods for the estimation of acids and bases which are too weak to be titrated volumetrically in the usual way with the aid of indicators.

In this chapter the aim will be to give a survey of the subject in so far as it concerns volumetric analytical practice, and in so doing, to emphasise the practical bearing and significance of the physico-chemical affinity constants of acids and bases. The importance of these constants is apt to be regarded as being merely theoretical, instead of providing, as they do, a measure of the reactivity, and in this respect they may be truly said to supply the only real information relating to the strengths of acids and bases.

Practical Significance of the Dissociation Constants of Acids and Bases.

It is feared that much of the failure to appreciate the full practical meaning of dissociation constants lies in the apparent complexity of the constants themselves, it being difficult to grasp the real significance of constants of such small magnitudes as, say, 10^{-5} or 10^{-13}. The development of the idea of representing varying degrees of acidity and alkalinity in terms of concentrations of hydrogen ions, or more simply in terms of *p*H, has supplied a means by which dissociation constants, however small they may be, become intelligible, so much so that it is an easy matter to find what variations in *p*H any particular acid or base will set up whilst undergoing neutralisation.

The equilibrium constants governing the ionisation of an acid, $HR \rightleftharpoons H^{\cdot} + R'$, or a base, $BOH \rightleftharpoons B^{\cdot} + OH'$,

may be expressed as

$$K_a = \frac{[H^{\cdot}][R']}{[HR]}, \text{ and } K_b = \frac{[B^{\cdot}][OH']}{[BOH]}$$

respectively, where the quantities enclosed in square brackets represent the concentrations of ions or of undissociated acid or base denoted. If the acid or base be dissociated to the extent of a fraction, α, of the concentration, C, present, then the concentrations of each of the various ions will be αC, and the concentrations of undissociated acid or base will be $C - \alpha C$, or $(1 - \alpha)C$, and therefore K_a or K_b will be equal to

$$\frac{\alpha C \times \alpha C}{(1 - \alpha)C} = \frac{\alpha^2 C}{1 - \alpha}.$$

This expression is approximately satisfied by acids and bases which have constants of 10^{-3} and less, when considered in accordance with the Arrhenius Theory. See, however, Chapters I and XIV. The extents to which dissociation proceeds in solutions of concentration, say M/100, of either the free acids or bases whose constants decrease from 10^{-3}, have been calculated and are given below :—

TABLE 26

SHOWING VARIATION IN THE VALUES OF α FOR M/100 SOLUTIONS OF ACIDS AND BASES WITH DIMINISHING K_a OR K_b

K_a or K_b	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}
α	0·270	0·095	0·031	0·010	0·003	0·001

It will be seen that when K_a or K_b has become as low as 10^{-6} the value of α becomes equal to 1 per cent. When, however, the free acid or base is partially neutralised by a strong base, *e.g.*, NaOH, or a strong acid, *e.g.*, HCl, as the case may be, the value of α rapidly becomes diminished through the formation of salts and the consequent introduction of appreciable concentrations of common ions, anions in the former case and of cations in the latter. Thus, consider the reactions (1) $HR + NaOH = NaR + H_2O$ and (2) $BOH + HCl = BCl + H_2O$, which, when they take place in dilute solutions, will produce (1) NaR and (2) BCl, which, for all practical purposes, may be considered to ionise completely to give equivalent concentrations of R' and $B^{\cdot}$ respectively. The

relatively large concentrations of ions so produced drive back the ionisation of the free acid or base, and they may become so large as to prevent the ionisation of the acid or base altogether, or more accurately stated, to reduce the ionisation to within almost infinitesimal limits. Hence, the expression

$$K_a = \frac{[H^{\cdot}][R']}{[HR]}$$

might *then* be rewritten

$$K_a = [H^{\cdot}] \times \frac{[\text{salt}]}{[\text{acid}]}$$

in order to represent the variation in hydrogen-ion concentration throughout a neutralisation reaction in which the concentration of R'-ions from the salt formed is sufficient to depress to within negligible limits the dissociation of the unneutralised acid. If x is the number of c.c. of strong alkali required for neutralisation, and y the number of c.c. of alkali actually added, then the hydrogen-ion concentration may be calculated from

$$K_a = [H^{\cdot}] \times \frac{y}{x - y}$$

and similarly from

$$K_b = [OH'] \times \frac{y}{x - y}$$

for bases. This approximate expression holds during a large part of the neutralisation of weak acids and bases, the dissociation constants of which are not greater than 10^{-4}. Fig. 51 gives a graphical representation of the variation in *p*H during the neutralisation of acids and bases having different constants. The hydrogen-ion concentrations were calculated from these expressions for the curves corresponding to $K_a = 10^{-4}$ to 10^{-10} and K_b 10^{-4} to 10^{-10}, except for the beginning of the neutralisation reactions before the concentrations of the suppressing ions had grown sufficiently large to have their maximum effect on α. Here α had to be taken into account, and in order to arrive at specific values of hydrogen-ion concentration the initial concentration of acid or base was taken as centimolar. The shaded portions show the divergence from the curve so found and the curve corresponding to the above expression. For acids of K_a greater than 10^{-4} the magnitude of α is too great to be without effect and the curves vary with the dilution. Thus, two curves are given which show the courses of neutralisation of M/10 and M/100 acid solutions of $K_a = 10^{-3}$. The two bottom curves refer to the neutralisation of M/100 and M/10-HCl solutions

with NaOH. The curves of acids having constants greater than 10^{-4} lie in the lower section of the diagram. If a temperature, namely, 22° C., be taken such that K_w, the ionic product of water, is exactly 10^{-14}, then the neutralisation curves of the bases, of which $K_b = 10^{-x}$, with hydrochloric acid, will be coincident

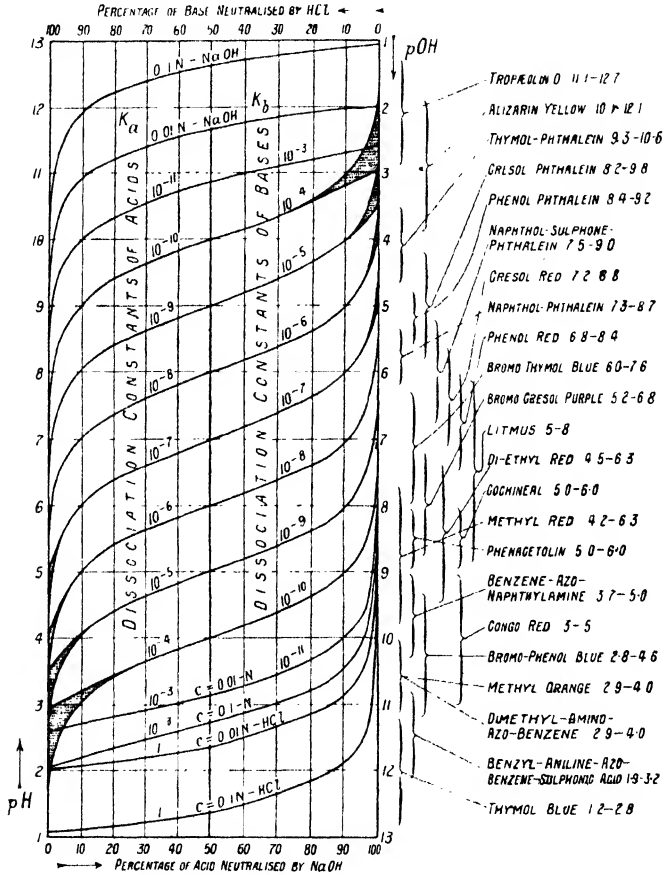


FIG. 51.—Variation in *p*H during Neutralisation of Acids and Bases.

with those of acids $K_a = 10^{-(14-x)}$, *when the amount of neutralisation is plotted in the reverse order as shown by the abscissa at the top of the diagram.* During the second half of the neutralisation of weak acids, of $K_a = 10^{-10}$ and less, the hydrolysis of the salt formed becomes considerable and this will increase the *p*H above that calculated from the simple formula. The neutralisation

curves of such extremely weak acids depend upon the concentrations employed and lie in the extreme alkaline part of the diagram. The opposite is true of extremely weak bases. In the case of a very weak acid, the fact that alkaline solutions are produced when alkali is added shows that not all the acid could have combined to form a neutral salt. The amount unreacted upon can, however, be ascertained from the *p*H and the degree of ionisation of the alkali in such a dilution. The dissociation constant of the acid can then be calculated, being equal to

$$\frac{[H^{\cdot}][x-y]}{[HR]-[x-y]},$$

where [HR] is the original concentration of acid, x is the concentration of alkali added and y the concentration of alkali found from the *p*H to have remained uncombined.

The dissociation constants of extremely weak bases can be found in a similar manner. *The evaluation of these constants is of fundamental importance in connexion with the method of estimating weak acids or bases*, to be described later.

Hence, we see that the neutralisation curve of an acid, HR, with NaOH depends upon K_a, not only in regard to its position upon the *p*H scale, but also in regard to the shape which it will assume. For moderately strong acids, having affinity constants greater than about 10^{-4}, the hydrogen ions and the anions liberated from the unneutralised acid acquire such relatively large concentrations, depending upon the dilution of the solution, that they invalidate the simple expression,

$$K_a = [H^{\cdot}] \times \frac{[\text{salt}]}{[\text{acid}]}$$

which we have found to hold for weak acids in which the unneutralised portions yield negligibly small hydrogen-ion concentrations. For these strong acids, we must include the concentrations of anions, $[R_u']$, dissociated from the unneutralised acid, and of the undissociated acid which remains, thus:

$$K_a = [H^{\cdot}] \times \frac{[\text{salt}] + [R_u']}{[\text{acid}] - [R_u']} = \frac{[H^{\cdot}][R']}{[HR]}.$$

Towards the end of the neutralisation of a weak acid, the salt formed from the alkali begins to hydrolyse, while in the case of an extremely weak acid considerable hydrolysis occurs throughout the whole course of the neutralisation, and therefore

$$K_a = [H^{\cdot}] \times \frac{[\text{salt}] - [OH']}{[\text{acid}] + [OH']} = \frac{[H^{\cdot}] \cdot [R']}{[HR]}.$$

Similar considerations are necessary with regard to the neutralisation of bases of differing strengths.

We shall now consider certain important *p*H values which are established at various stages of neutralisation of an acid. As

$$K_a = [H^\cdot] \times \frac{[R']}{[HR]},$$

therefore

$$pH = pK_a + \log \frac{[R']}{[HR]},$$

so that, *for moderately strong acids mixed with their respective salts of strong bases,*

$$pH = pK_a + \log \frac{[\text{salt}] + [R_a']}{[\text{acid}] - [R_a']},$$

for weak acids in presence of their respective salts of strong bases,

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]},$$

for extremely weak acid solutions containing their respective salts of strong bases,

$$pH = pK_a + \log \frac{[\text{salt}] - [OH']}{[\text{acid}] + [OH']}$$

When $[R'] = [HR]$,

we see that $K_a = [H^\cdot]$,

and $pK_a = pH$.

In connexion with the partly neutralised strong acids, this *p*H value is of little importance as it varies with concentration, but in the case of weak and extremely weak acids it marks the point at which the acids become half neutralised. For weak acids [salt] is then equal to [acid], and thus it follows that this *p*H is independent of concentration. In the case of very weak acids, [salt], *i.e.*, the concentration of neutral, or unhydrolysed, salt, does not become equal to [acid] when one half of an equivalent of sodium hydroxide has been added. Nevertheless, pK_a denotes the *p*H value when one-half of an equivalent of alkali has actually reacted, and as we shall see later this almost fixed *p*H is of fundamental importance in the titration of such extremely weak acids. Therefore, this particular *p*H fixes the positions of the actual neutralisation curves of all acids, except those which are appreciably dissociated, and whose ionisations are not depressed sufficiently by the anions

arising from their salts. Moreover, their actual neutralisation curves, unlike the observed titration curves, are fixed, because

$$pH = pK_a + \log \frac{[\text{unhydrolysed salt}]}{[\text{undissociated acid}]}.$$

Table 27 gives the variations of pH from pK_a for different percentages of [salt] and [acid], and in effect represents the titration curve of a weak acid.

TABLE 27

pH VALUES DURING NEUTRALISATION OF WEAK ACID, HR, WHOSE CONSTANT IS K_a

Per cent. Neutralisated (*i.e.*, per cent. Salt Formed).	pH.	Increment in pH per 5 per cent. Neutralisation.	Solutions.
0·01	$pK_a - 4·00$		Unbuffered
0·1	$pK_a - 3·00$		,,
1·0	$pK_a - 2·00$	+ 2·72	,,
2·5	$pK_a - 1·59$		,,
5	$pK_a - 1·28$		,,
10	$pK_a - 0·95$	+ 0·33	Buffered
15	$pK_a - 0·75$	+ 0·20	,,
20	$pK_a - 0·60$	+ 0·15	,,
25	$pK_a - 0·48$	+ 0·12	,,
30	$pK_a - 0·37$	+ 0·11	,,
35	$pK_a - 0·27$	+ 0·10	,,
40	$pK_a - 0·17$	+ 0·10	,,
45	$pK_a - 0·09$	+ 0·08	,,
50	$pK_a \mp 0·00$	+ 0·09	,,
55	$pK_a + 0·09$	+ 0·09	,,
60	$pK_a + 0·17$	+ 0·08	,,
65	$pK_a + 0·27$	+ 0·10	,,
70	$pK_a + 0·37$	+ 0·10	,,
75	$pK_a + 0·48$	+ 0·11	,,
80	$pK_a + 0·60$	+ 0·12	,,
85	$pK_a + 0·75$	+ 0·15	,,
90	$pK_a + 0·95$	+ 0·20	,,
95	$pK_a + 1·28$	+ 0·33	,,
97·5	$pK_a + 1·59$		Unbuffered
99·0	$pK_a + 2·00$	+ 2·72	,,
99·9	$pK_a + 3·00$		,,
99·99	$pK_a + 4·00$		,,

It will be observed from Table 27 that there should be well-defined ranges of pH values within which weak and extremely weak acids are neutralised. This is the case, and as the mass law holds throughout these neutralisation reactions, the neutralisation pH range can be stated accurately if the constant, K_a, be known. Thus, if we consider the beginning of titration to occur when 0·01 per cent. of the acid has been reacted upon, the pH would

be $p\mathrm{K}_a - 4$, and to end when 99·99 per cent. has been neutralised, the final pH would be $p\mathrm{K}_a + 4$, and the total pH range would be

$$(p\mathrm{K}_a + 4) - (p\mathrm{K}_a - 4) = 8\ p\mathrm{H}\ \text{units.}$$

Such limits are extensive, and, moreover, unnecessarily wide. Both at the beginning and at the end of a neutralisation very rapid changes in pH are produced with only very slight additions of alkali—there being 2 pH units change produced by an addition from 0·01 per cent. to 1 per cent. of alkali at the two extreme ends. If, however, we regard the neutralisation process to begin effectively when 1 per cent. of alkali has been added and has formed the salt, and to finish at 99 per cent., we find that the

$$\textit{Initial}\ p\mathrm{H} = p\mathrm{K}_a - 2,$$

and the

$$\textit{Final}\ p\mathrm{H} = p\mathrm{K}_a + 2,$$

and therefore, the *range of pH values required for neutralisation* to be

$$(p\mathrm{K}_a + 2) - (p\mathrm{K}_a - 2) = 4\ p\mathrm{H}\ \text{units} = p\mathrm{K}_a \mp 2.$$

This relationship is of practical importance and will be considered later.

Similar relationships hold for weak and very weak bases throughout their courses of neutralisation with a strong acid such as hydrochloric acid. Thus

$$\mathrm{K}_b = \frac{[\mathrm{B}^{\cdot}][\mathrm{OH}']}{[\mathrm{BOH}]}$$

holds for the dissociation of a base BOH as represented

$$\mathrm{BOH} \rightleftharpoons \mathrm{B}^{\cdot} + \mathrm{OH}'.$$

Hence, we may write

$$\mathrm{K}_b = [\mathrm{OH}'] \times \frac{[\mathrm{B}^{\cdot}]}{[\mathrm{BOH}]} = [\mathrm{OH}'] \times \frac{[\text{unhydrolysed salt}]}{[\text{undissociated base}]},$$

and therefore

$$p\mathrm{OH} = p\mathrm{K}_b + \log \frac{[\text{salt}]}{[\text{base}]}.$$

At the mid-point of neutralisation $\dfrac{[\text{salt}]}{[\text{base}]} = 1$, consequently

$$p\mathrm{OH} = p\mathrm{K}_b,$$

and as

$$\mathrm{K}_w = [\mathrm{H}^{\cdot}] \,.\, [\mathrm{OH}'],$$

i.e.,

$$p\mathrm{H} + p\mathrm{OH} = p\mathrm{K}_w,$$

therefore, the pH corresponding to pK_b is given by

$$pH = pK_w - pK_b.$$

As the initial pOH (*i.e.*, at 1 per cent. neutralisation) of the titration of a base is given by $pK_b - 2$, and the final pOH by $pK_b + 2$ (*i.e.*, 99 per cent. neutralisation), we see that in terms of hydrogen-ion concentration the

$$\textit{Initial } pH = pK_w - pK_b + 2,$$

the

$$\textit{Final } pH = pK_w - pK_b - 2,$$

and the

$$\textit{Titration Range} = pK_w - pK_b \pm 2.$$

Buffer Action.

Though this subject will receive further treatment in Chapter XVI, we shall accord it a preliminary treatment here. On referring to the third column of Table 27 it will be observed that the pH increment corresponding to each 5 per cent of neutralisation of the acid, HR, is of the order of 0·1 pH unit over the range extending from about 20 per cent. to about 80 per cent. of neutralisation—in fact the pH is approximately a linear function of the amount of alkali added. Thus we see that alkali when added to a solution containing a weak acid partly neutralised within these limits will not, unless it is added in excess, exert any great influence on the concentration of hydrogen ions of the solution, *i.e.*, it will cause only a very little change in the " reaction " or pH value of the solution. On the other hand, very small additions of alkali will produce considerable pH changes if the solution contains either free acid or almost completely neutralised acid. Similar remarks apply to the addition of strong acids to such solutions, and also to the variations in hydrogen-ion concentration which may be set up in solutions of weak bases neutralised to differing extents. Moreover, we know that if a little free NaOH or HCl be added to distilled water, pH *ca.* 7, there will result a very large and sudden increase or decrease in pH as the case may be.

As far back as 1900, Fernbach and Hubert (*Comp. rend.*, 1900, **131**, 293), in the course of some work on the diastatic activity of malt, observed that partly neutralised solutions of phosphoric acid (see Fig. 55) tended to resist changes in hydrogen-ion concentration, and they compared this resistance to that exerted by " *un tampon.*" Sørensen, later, used this term, which was translated into German as *Puffer*, and subsequently into English as " buffer." Hence this " buffer action " is pronounced in the case of solutions of weak acids or bases which have been neutralised to extents varying from 20 to 80 per cent. It attains to a maximum, as

shown by Table 27, in an acid or base solution which has been half-neutralised. The figures given in column 3 constitute a measure of this action, for they indicate the change in *p*H produced by the additions of equal amounts of alkali. Actually, they are a measure of the slope of the neutralisation curve at the various points, for they are the tangents of the angles made by the tangents drawn to the curve and the abscissa, *i.e.*, they are equal to $\frac{dp\mathrm{H}}{dx}$, dx being a small increment of alkali (or acid) added. It is sometimes more convenient to speak of the Buffer-Capacity of a solution, and for this purpose to know the amount of an acid or alkali of some definite concentration which must be added to produce a change in hydrogen-ion concentration represented by 1 *p*H unit. In a more restricted sense, this so-called "buffer-capacity" is given by $\frac{dx}{dp\mathrm{H}}$, and then it refers to the reciprocal of the tangent (*i.e.*, cotangent) of the angle of the slope of the curve at the point corresponding to the composition of the particular "buffer-solution." Unless the concentration of the buffering agents is large compared with that of the acid or alkali to be added, the buffer-capacity may undergo appreciable changes in value as the reagent is added. It is only, therefore, in the case of solutions of high buffer concentration, that such a function has any real meaning. It very often happens in biological operations that enzymes or bacteria require a definite small *p*H range for their optimum action or growth, and yet they cause substances to be developed, which if there were no buffering agents present in the solution would produce an unsuitable reaction. As will be shown later, controlled hydrogen-ion concentrations are of fundamental importance in analytical processes. Such control is often effected by the inclusion of buffering agents in the solutions; in fact, many of the methods, which were developed quite empirically, depend solely upon the efficiency of the buffer action of the reagents.

Detection of Volumetric Titration End-Points.

It will be understood from the foregoing discussion that it is an easy matter to stipulate when the titration of a weak acid or base will be complete for all practical purposes (*viz.*, 99 per cent.), and therefore to choose an indicator which will turn colour at that particular *p*H, or better, a little after that stage has been reached. The table of indicators affixed to Fig. 51 show the *p*H's at which they may each be used. Now, methyl orange is often used as an

indicator in the titration of strong acids, but it will be seen from two curves at the base of the diagram that if the solution be as dilute as N/100 the methyl orange will begin to change colour, on account of *p*H 2·9 being attained, some time before neutralisation has ended—and, indeed, it will hardly be complete when the colour has been completely changed. Centimolar solutions of strong acids represent the limit of concentration which can be used with methyl orange. Methyl red would appear to be more satisfactory, but, as may be seen from the neutralisation curve of carbonic acid, Fig. 126 its end-point will be affected by any carbon dioxide which may be present in the solution. The following tables, 28, 29, 30, 31, 32 and 33, give the dissociation :—

TABLE 28

MONOBASIC ACIDS

Name.	Formula.	K_a.	pK_a.
Hydrochloric acid	HCl	—	—
Nitric acid	HNO_3	—	—
Picric acid	$C_6H_2(NO_2)_3OH$	—	—
Trichloracetic acid	$CCl_3 . COOH$	3×10^{-1}	—
Dichloracetic acid	$CHCl_2 . COOH$	5×10^{-2}	—
Monochloracetic acid	$CH_2Cl . COOH$	$1{\cdot}6 \times 10^{-3}$	—
Salicylic acid	$C_6H_4(OH)COOH$	1×10^{-3}	3
Nitrous acid	HNO_2	5×10^{-4}	3·3
Formic acid	$H . COOH$	2×10^{-4}	3·7
Glycollic acid	$CH_2OH . COOH$	$1{\cdot}5 \times 10^{-4}$	3·8
Lactic acid	$CH_3 . CHOH . COOH$	$1{\cdot}4 \times 10^{-4}$	3·8
Benzoic acid	$C_6H_5 . COOH$	7×10^{-5}	4·2
Phenylacetic acid	$C_6H_5CH_2COOH$	$5{\cdot}4 \times 10^{-5}$	4·3
Acetic acid	$CH_3 . COOH$	$1{\cdot}8 \times 10^{-5}$	4·7
Hydrazoic acid	HN_3	$1{\cdot}5 \times 10^{-5}$	4·8
Propionic acid	$C_2H_5 . COOH$	$1{\cdot}4 \times 10^{-5}$	4·8
Uric acid	$C_5H_4N_4O_3$	$1{\cdot}5 \times 10^{-6}$	5·8
o-Nitro-phenol	$C_6H_4(NO_2)OH$	$5{\cdot}6 \times 10^{-8}$	7·3
p-Nitro-phenol	$C_6H_4(NO_2)OH$	$5{\cdot}6 \times 10^{-8}$	7·3
Hypochlorous acid	HClO	4×10^{-8}	7·4
m-Nitro-phenol	$C_6H_4(NO_2)OH$	$3{\cdot}9 \times 10^{-9}$	8·4
Hydrocyanic acid	HCN	1×10^{-9}	9
Boric acid	$HBO_2 . H_2O$	6×10^{-10}	9·2
p-Chlorophenol	$C_6H_4 . Cl . OH$	6×10^{-10}	9·2
Arsenious acid	H_3AsO_3	$5{\cdot}5 \times 10^{-10}$	9·26
Phenol	$C_6H_5 . OH$	1×10^{-10}	10
Hydrogen peroxide	H_2O_2	1×10^{-12}	12
Dextrose	$C_6H_7O(OH)_5$	$5{\cdot}8 \times 10^{-13}$	12·2
Cane sugar, sucrose	$C_{12}H_{22}O_{11}$	1×10^{-13}	13
Mannitol	$C_6H_8(OH)_6$	3×10^{-14}	13·5
Glycerol	$C_3H_5(OH)_3$	7×10^{-15}	14·2
Glycol	$C_2H_4(OH)_2$	6×10^{-15}	14·2

TABLE 29

DIBASIC ACIDS

Name		K_{a_1}.	pK_{a_1}.	K_{a_2}.	pK_{a_2}.	$\frac{K_{a_1}}{K_{a_2}}$.
Oxalic acid	$(COOH)_2$	1×10^{-2}	—	$1{\cdot}3 \times 10^{-4}$	3·9	*ca.* 1,000
Chromic acid	H_2CrO_4	—	—	$4{\cdot}4 \times 10^{-7}$	6·4	*ca.* 10^6
Sulphurous acid	H_2SO_3	$1{\cdot}7 \times 10^{-2}$	—	5×10^{-8}	5·3	3,400
Dibromsuccinic acid	$C_2H_2Br_2(COOH)_2$	$3{\cdot}4 \times 10^{-2}$	—	$1{\cdot}6 \times 10^{-3}$	—	21
Monobrom-succinic acid	$C_2H_3Br(COOH)_2$	$2{\cdot}8 \times 10^{-3}$	2·6	$3{\cdot}9 \times 10^{-5}$	4·4	72
Succinic acid	$(CH_2)_2(COOH)_2$	$9{\cdot}2 \times 10^{-5}$	4·0	$5{\cdot}3 \times 10^{-6}$	5·3	17
Tartaric acid	$C_2H_2(OH)_2 \cdot (COOH)_2$	$1{\cdot}3 \times 10^{-3}$	2·9	$9{\cdot}7 \times 10^{-5}$	4·0	13
Maleic acid	$C_2H_2 \cdot (COOH)_2$	$1{\cdot}3 \times 10^{-2}$	2·9	$3{\cdot}0 \times 10^{-7}$	6·5	$4{\cdot}3 \times 10^4$
Fumaric acid	$C_2H_2 \cdot (COOH)_2$	1×10^{-3}	3·0	$2{\cdot}5 \times 10^{-5}$	4·6	40
o-Phthalic acid	$C_6H_4 \cdot (COOH)_2$	$1{\cdot}2 \times 10^{-3}$	2·9	$8{\cdot}0 \times 10^{-6}$	5·1	150
m-Phthalic acid	$C_6H_4 \cdot (COOH)_2$	$2{\cdot}9 \times 10^{-4}$	3·5	$2{\cdot}4 \times 10^{-5}$	4·6	12
Carbonic acid	H_2CO_3	3×10^{-7}	6·5	6×10^{-11}	10·2	5,000
Hydrosulphuric acid	H_2S	9×10^{-8}	7·0	$1{\cdot}2 \times 10^{-15}$	14·9	$7{\cdot}5 \times 10^7$
Malonic acid	$CH_2 \cdot (COOH)_2$	$2{\cdot}0 \times 10^{-3}$	2·7	$4{\cdot}4 \times 10^{-6}$	5·4	460
Glutaric acid	$(CH_2)_3 \cdot (COOH)_2$	$4{\cdot}7 \times 10^{-5}$	4·3	$2{\cdot}9 \times 10^{-6}$	5·5	16
Suberic acid	$(CH_2)_6 \cdot (COOH)_2$	$3{\cdot}0 \times 10^{-5}$	4·5	$1{\cdot}9 \times 10^{-6}$	5·7	16
Azelaic acid	$(CH_2)_7 \cdot (COOH)_2$	$2{\cdot}5 \times 10^{-5}$	4·6	$2{\cdot}4 \times 10^{-6}$	5·6	10
Sebacic acid	$(CH_2)_8 \cdot (COOH)_2$	$2{\cdot}4 \times 10^{-5}$	4·6	$2{\cdot}5 \times 10^{-6}$	5·6	10

TABLE 30

TRIBASIC ACIDS

Name.	K_{a_1}.	pK_{a_1}.	K_{a_2}.	pK_{a_2}.	K_{a_3}.	pK_{a_3}.
Phosphoric acid	$9{\cdot}4 \times 10^{-3}$	—	$1{\cdot}4 \times 10^{-7}$	6·9	$2{\cdot}7 \times 10^{-12}$	11·6
Arsenic	$5{\cdot}6 \times 10^{-3}$	2·25	$1{\cdot}7 \times 10^{-7}$	6·77	$3{\cdot}0 \times 10^{-12}$	11·53
Citric acid	$1{\cdot}0 \times 10^{-3}$	3·0	$2{\cdot}5 \times 10^{-5}$	4·6	$1{\cdot}5 \times 10^{-6}$	5·8

TABLE 31

MONO-ACIDIC BASES

Name.	K_b.	pK_b.
Ammonia	$1{\cdot}8 \times 10^{-5}$	4·7
Hydrazine	2×10^{-6}	5·7
Phenylhydrazine	$1{\cdot}6 \times 10^{-9}$ (40°)	8·8
Methylamine	5×10^{-4}	3·3
Dimethylamine	$5{\cdot}5 \times 10^{-4}$	3·3
Trimethylamine	7×10^{-5}	4·2
Ethylamine	$5{\cdot}6 \times 10^{-4}$	3·3
Diethylamine	$1{\cdot}3 \times 10^{-3}$	2·9
Triethylamine	$6{\cdot}4 \times 10^{-4}$	3·2
Aniline	$3{\cdot}5 \times 10^{-10}$	9·5
o-Nitro-aniline	1×10^{-14}	14
m-Nitro-aniline	$3{\cdot}6 \times 10^{-12}$	11·4
p-Nitro-aniline	1×10^{-12}	12
m-Bromoaniline	$3{\cdot}8 \times 10^{-11}$	10·4
p-Bromoaniline	1×10^{-10}	10
m-Chloroaniline	$3{\cdot}4 \times 10^{-11}$	10·5
p-Chloroaniline	$1{\cdot}5 \times 10^{-10}$	9·8
Acetamide	3×10^{-15}	14·5
Pyridine	$1{\cdot}2 \times 10^{-9}$	8·9
Piperidine	$1{\cdot}6 \times 10^{-3}$	2·8
Quinoline	$3{\cdot}2 \times 10^{-10}$	9·5
Isoquinoline	$1{\cdot}1 \times 10^{-9}$	9
Conine	8×10^{-4}	3·1
Atropine	$4{\cdot}5 \times 10^{-5}$	4·4
Cocaine	$2{\cdot}6 \times 10^{-6}$	5·6
Narcotine	$1{\cdot}5 \times 10^{-8}$	7·8
Codeine	9×10^{-7}	6·1
Aconitine	$1{\cdot}3 \times 10^{-6}$	5·9

TABLE 32

DIACIDIC BASES

Name.	K_{b_1}.	pK_{b_1}.	K_{b_2}.	pK_{b_2}.	$\frac{K_{b_1}}{K_{b_2}}$.
Piperazine	9×10^{-5}	4·1	$5{\cdot}7 \times 10^{-9}$	8·3	$1{\cdot}6 \times 10^{4}$
Novocain	$7{\cdot}1 \times 10^{-6}$	5·2	$1{\cdot}8 \times 10^{-12}$	11·8	4×10^{6}
Nicotine	7×10^{-7}	6·2	$1{\cdot}4 \times 10^{-11}$	10·9	5×10^{4}
Quinine	$1{\cdot}1 \times 10^{-6}$	6	2×10^{-10}	9·7	$5{\cdot}5 \times 10^{3}$
Cinchonidine	$1{\cdot}6 \times 10^{-6}$	5·8	$9{\cdot}3 \times 10^{-11}$	10	$1{\cdot}7 \times 10^{4}$
Cinchonine	$1{\cdot}4 \times 10^{-6}$	5·9	$1{\cdot}2 \times 10^{-10}$	9·9	$1{\cdot}2 \times 10^{4}$
Strychnine	1×10^{-6}	6	$2{\cdot}2 \times 10^{-12}$	11·7	$4{\cdot}5 \times 10^{5}$
Brucine	$9{\cdot}2 \times 10^{-7}$	6	2×10^{-12}	11·7	$4{\cdot}6 \times 10^{5}$
Pilocarpine	7×10^{-8}	7·2	$2{\cdot}7 \times 10^{-13}$	12·6	$2{\cdot}6 \times 10^{5}$

TABLE 33

AMPHOLYTES

	K_a.	pK_a.	K_b.	pK_b.
Morphine*	$1{\cdot}4 \times 10^{-10}$	9·85	$7{\cdot}5 \times 10^{-7}$	6·13
Apomorphine*	$1{\cdot}2 \times 10^{-9}$	8·92	1×10^{-7}	7
Narcein	5×10^{-10}	9·3	2×10^{-11}	10·7
Ecgonine	8×10^{-12}	11·1	6×10^{-12}	11·2
α-Alanine	$1{\cdot}9 \times 10^{-10}$	9·7	$5{\cdot}1 \times 10^{-12}$	11·3
Glycine	$1{\cdot}8 \times 10^{-10}$	9·7	$2{\cdot}7 \times 10^{-12}$	11·6
Leucine	$1{\cdot}8 \times 10^{-10}$	9·7	$2{\cdot}3 \times 10^{-12}$	11·6
Phenyl-alanine	$2{\cdot}5 \times 10^{-9}$	8·6	$1{\cdot}3 \times 10^{-12}$	11·9
Valine	2×10^{-10}	9·7	2×10^{-12}	11·7
m-Aminobenzoic acid	$1{\cdot}6 \times 10^{-5}$	4·8	$1{\cdot}2 \times 10^{-12}$	11·9

AMINO-DICARBOXYLIC ACIDS

	K_{a_1}.	pK_{a_1}.	K_{a_2}.	pK_{a_2}.	K_b.	pK_b.
Glutamic acid	$6{\cdot}2 \times 10^{-5}$	4·2	$1{\cdot}6 \times 10^{-10}$	9·8	$1{\cdot}3 \times 10^{-12}$	11·9
Aspartic acid	$1{\cdot}5 \times 10^{-4}$	3·8	$1{\cdot}4 \times 10^{-10}$	9·9	$1{\cdot}2 \times 10^{-12}$	11·9
Tyrosine*	4×10^{-10}	9·4	4×10^{-11}	10·4	$2{\cdot}6 \times 10^{-12}$	11·6

* One K_a refers to the dissociation of a phenolic group.

DIAMINO-CARBOXYLIC ACIDS

	K_a.	pK_a.	K_{b_1}.	pK_{b_1}.	K_{b_2}.	pK_{b_2}.
Histidine	$2{\cdot}2 \times 10^{-9}$	8·7	$5{\cdot}7 \times 10^{-9}$	8·2	5×10^{-13}	12·3
Arginine	$>1{\cdot}1 \times 10^{-14}$	14	$<1 \times 10^{-7}$	7	$2{\cdot}2 \times 10^{-12}$	11·7
Lysine	$1{\cdot}2 \times 10^{-12}$	12	$<1 \times 10^{-7}$	7	$1{\cdot}1 \times 10^{-12}$	12

constants of various typical acids, bases and ampholytes, and also the value of *p*K, which, as shown above, is the *p*H prevailing when a weak acid, and the *p*OH when a weak base, has been half-neutralised, and in the case of polybasic acids or polyacidic bases, the *p*H or *p*OH, at the mid-point of each stage of neutralisation. In the case of extremely weak acids and bases, the stage of half-neutralisation does not occur when the alkali or acid added is the quantity theoretically required, on account of the hydrolysis of the salt formed, but occurs when more reagent, sufficient to counteract that hydrolysis, has been added.

The approximate end-point pH's in the neutralisation of weak acids with a strong base are given by

$$p\mathrm{H} = p\mathrm{K}_a + 2,$$

and the titration end-points of weak bases with strong acids by

$$p\mathrm{H} = p\mathrm{K}_w - p\mathrm{K}_b - 2.$$

They may, however, be judged with sufficient accuracy from Fig. 51. Thus, the neutralisation curve of acetic acid, Table 15, $p\mathrm{K}_a = 4{\cdot}7$, will be just below that corresponding to $\mathrm{K}_a = 10^{-5}$, and, consequently, for its volumetric estimation an indicator will be required which turns colour above pH 6, such as Cresol Red or Phenolphthalein.

It might be surprising to some to find substances such as hydrogen peroxide, sugars and glycerol included in the table of monobasic acids. Though their dissociation constants can be measured electrometrically, they are so very small that the buffered neutralisation curves of these extremely weak acids occur at high pH values, owing to the considerable hydrolysis of the salts which they form, and, in consequence, the ends of their neutralisation are not indicated by inflexions. This is illustrated by the titration curve of dextrose given in Fig. 56.

Di- and Tribasic Acids.

Tables 29 and 30 refer to dibasic and tribasic acids, and, needless to say that, in order to ascertain what indicator should be used for the complete titration of the acid, it is only necessary to consider the magnitude of the final dissociation constant. Thus, $p\mathrm{K}_{a_2}$ for chromic acid is 6·4, and the neutralisation curve for the second half will lie almost midway between the 10^{-6} and 10^{-7} curves, the pH at complete neutralisation being about 9, and, consequently, if phenolphthalein be used it will begin to redden slightly before the true end-point is reached. A more satisfactory indicator would be thymolphthalein.

It is often possible to titrate certain polybasic acids and polyacidic bases to an intermediate end-point corresponding to the formation of, in the former case, an acid salt, and in the latter, a basic salt. This possibility will be studied in a subsequent paragraph. It will be observed from Table 30 that the last dissociation constant of phosphoric acid is so excessively small that its neutralisation is not complete until pH 13·6 is reached, the final branch of the neutralisation curve merging into the alkali curve without giving an inflexion.

Bases and Alkaloids.

Tables 31 and 32 give the affinity constants of mono- and di-acidic bases respectively. It will be noticed that the alkaloids appear in these tables; the results were taken from an important paper by Kolthoff (*Biochemische Z.*, 1925, **162**, 289), which gives the constants for many other alkaloids, including their solubilities and solubility products.

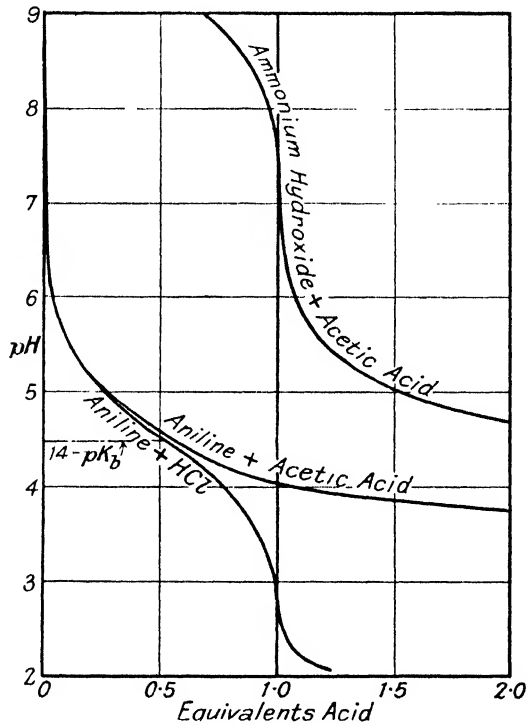


FIG. 52.—Titration of Weak Bases.

One of the most accurate methods for the estimation of alkaloids is by titration, though it is here that the problem of indicators becomes of fundamental importance. Thus MacGill (*J. Amer. Chem. Soc.*, 1922, **44**, 2156) has shown that the indicators used in the titration of morphine, atropine and quinine give results which are not nearly as accurate as could be obtained with more appropriate indicators. In the case of morphine the average error using methyl red was 1·4 per cent., whereas bromophenol blue gave an average error of 0·5 per cent., and in

some titrations it was as low as 0·1 per cent. Kolthoff recommends that the indicator to be used with all mono-acidic bases having K_b equal to or greater than 5×10^{-7} should be methyl red. This will be obvious from Fig. 51, for all curves lying above that of K_b, $10^{-6.3}$, show that neutralisation becomes complete above or at *p*H 5, the change-point of methyl-red. For weaker bases indicators changing at a lower *p*H, such as methyl orange or bromophenol blue, will be necessary. Aniline and the substituted aniline derivatives have very small constants, so much so that it appears from Fig. 52, that the *p*H inflexion on complete neutralisation with acid will be so very small as to render the accurate location of the end-point by means of indicators a matter of extreme difficulty. Another matter which militates against the use of indicators with aniline is the tendency which it has to darken and thus to obscure the colour change. As stated by Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847), the location of the end-point can best be made electrometrically (see Fig. 52). The remarks concerning the variation in *p*H during the neutralisation of dibasic acids also hold for diacidic bases, but, as shown in the last column of Table 32, K_{b_2} is often so very small compared with K_{b_1} that a sharp *p*H inflexion occurs with the neutralisation of the first stage, which, by reason of the magnitude of K_{b_1} (pK_{b_1} being usually about 6) permits of its titration to methyl red, before the second and considerably weaker stage enters into the reaction. Rasmussen and Schou (*Pharm. Zentralhalle*, 1924, **65**, 729) advocate methyl red with strychnine, brucine, morphine, codeine, nicotine, and atropine; methyl orange buffered to *p*H 4·2 for narcotine and *p*-nitrophenol buffered to *p*H 6·2 for quinine. These end-points are in accord with Fig. 51 and the data given in the tables.

The basic dissociation constants of the alkaloids also supply information which may be of importance in connexion with their separation. Thus, for example, consider a mixture of the salts of two alkaloids, both soluble in an organic solvent, but having dissociation constants widely different from one another. On treatment with an alkali, the salt whose alkaloid has the greater dissociation constant will first be reacted upon and will dissolve in the organic solvent before the second salt becomes decomposed. The difficulty arises, however, of knowing when to stop adding alkali in order to prevent the liberation of the second base. From a knowledge of the basic constants, it may be possible to employ a solution buffered within a small *p*H range, instead of the free alkali, and thereby to prevent the second base from being extracted (see Evers, *Yearbook of Pharmacy*, 1922). Again, it is possible that

use will be made of the solubility products of the alkaloids, coupled with their dissociation constants, to separate them from their salt solutions by means of fractional precipitation with alkali, or better with suitably buffered solutions. The work of Mauz (*Physik-Chem. Untersuchungen über Alkaloide*, Dissertation, Stuttgart, 1904, cited by Kolthoff, *loc. cit.*), has indicated the possibility of such methods.

Titration of Solutions for either Mixed Acids or Mixed Bases.

Hitherto, we have confined our attention to the titration of single acids and bases, though if the solution contains two acids or two bases, whose dissociation constants are sufficiently different, the stronger acid or base will be neutralised before the reaction with the weaker component can begin. Hence the final pH of the effective titration range of the first acid, which is $p\mathrm{K}_{a_1} + 2$ must be less than the initial pH of the titration range of the second acid, *viz.*, $p\mathrm{K}_{a_2} - 2$,

i.e.,
$$p\mathrm{K}_{a_2} - 2 > p\mathrm{K}_{a_1} + 2,$$
$$p\mathrm{K}_{a_2} - p\mathrm{K}_{a_1} > 4,$$

and therefore K_{a_1}, the dissociation constant of the first acid, must be greater than 10,000 times K_{a_2}, the dissociation constant of the second acid. Similar remarks apply to mixtures of bases.

When the constants are closer together, the end-points will not be sharp through some of the weaker acid having begun to be neutralised before the stronger acid had been completely neutralised. When the first constant is not more than, say, 10 to 100 times the second, the titration curve may fail to show even a slight inflexion corresponding to the addition of reagent equivalent to the first component.

Electrometric Titration of Acids and Bases.

We shall now consider various typical electrometric pH neutralisation curves. In Fig. 53 curves of solutions of three weak monobasic acids having different concentrations are given. These curves were drawn from data obtained with the quinhydrone electrode by Auerbach and Smolczyk (*Z. physikal. Chem.*, 1924, **110**, 83). The slightly different forms assumed by the first halves of the curves illustrate the effect of the acid concentration. The end-points were located by finding the points of inflexion of the upward curves. These can often be judged from the graph, but may be obtained with greater precision by calculating the tangent of the angle of slope of the curve until the

point is found at which the tangent becomes of maximum value. This is the same as calculating $\frac{\delta E}{\delta x}$, where δE is the increase in voltage produced by adding a small increment, δx, of alkali, say 0·1 c.c. (*cf.* Hostetter and Roberts, *J. Amer. Chem. Soc.*, 1919, **41**, 1337).

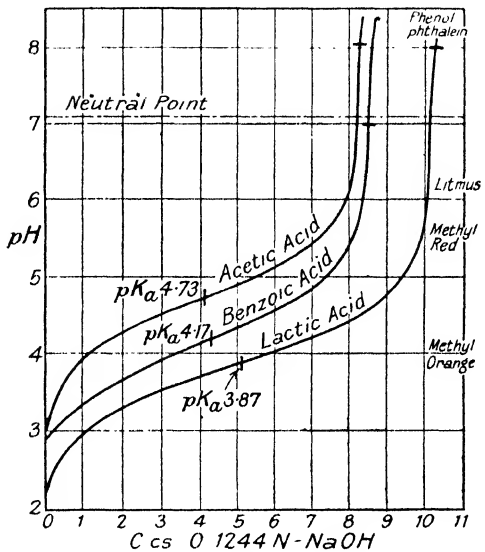


FIG. 53.—Quinhydrone Electrode Titration Curves of Monobasic Acids: 10 c.c. 1277 N-Lactic Acid; 50 c.c. 0·02114 N-Benzoic Acid; 10 c.c. 0·1025 N-Acetic Acid.

Fenwick (*Ind. Eng. Chem., Anal. Edn.*, 1932, **4**, 144) has shown that the end-point may be calculated from a titration curve, by assuming that in the vicinity of the end-point the curve is that of a cubic equation:

$$aV^3 + bV^2 + cV + d = E$$

where V is the volume of the titrant and E the E.M.F. Then at the end-point,

$$\frac{d^2E}{dV^2} = 6aV + 2b = 0.$$

By taking four values of V, equidistant from one another in the region of the end-point, the constants a and b may be calculated, from which V, the titre to give the end-point may be found.

The neutralisation of the weak bases, ammonia and aniline, is represented in Fig. 52. As might have been predicted, it is pos-

sible to titrate ammonium hydroxide with acetic acid to an equivalence-point, which occurs sharply at approximately *p*H 7·5, in contrast with, for instance, the titration of hydrochloric acid, in which case the actual end-point might be extended over a fairly wide *p*H range without introducing any great error. For such a titration an electrometric method must be employed. It might be possible, however, to perform such a titration by titrating to a definite colour of an indicator corresponding to some predetermined *p*H value, indicated by comparison with the colour obtained by adding a suitable quantity of indicator to a buffer solution adjusted to that *p*H. Of the other curves, one

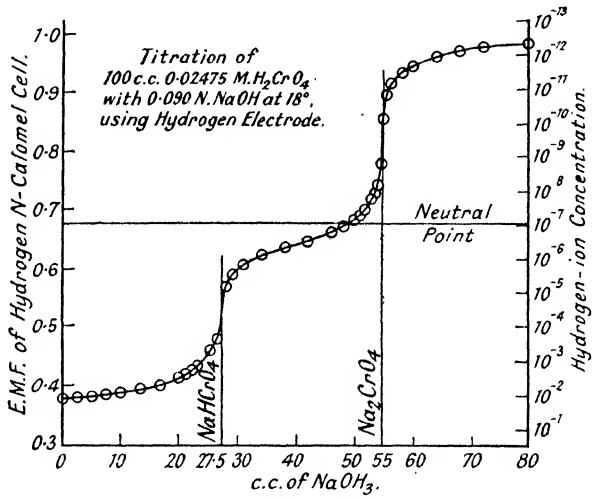


FIG. 54.—Hydrogen Electrode Titration of Chromic Acid (Britton, *J. Chem. Soc.*, 1924, 125, 1572).

shows that the magnitude of the decrease in *p*H which accompanies the formation of aniline hydrochloride is great enough to permit of the electrometric titration of aniline, whilst the other curve illustrates that, owing to the large amount of hydrolysis of aniline acetate, much acetic acid fails to combine and so makes such a titration impossible. This might have been foreseen from a consideration of the basic and acidic constants.

Electrometric titration curves of polybasic acids are given in Figs. 54 and 55. Perhaps the simplest curve is that of chromic acid (Fig. 54). On account of the failure to measure the extremely slight ionisation of the hydrochromate ion, $HCrO_4'$, it being much too small to have any influence upon the physical properties of free chromic acid solutions, *e.g.*, the conductivity in different

dilutions and the depression of the freezing-point, the erroneous idea of the existence of dichromic acid was introduced by Ostwald (see Britton, *J. Chem. Soc.*, 1924, **125**, 1572). The curve shows that the first stage of chromic acid neutralisation is solely that of a strong monobasic acid, *viz.*, $H_2CrO_4 \rightleftharpoons H^{\cdot} + HCrO_4'$, whose dissociation constant is approximately one million times the second. The second branch corresponds entirely to that of the neutralisation of a weak monobasic acid. The two dissociation constants may therefore be calculated in the simple manner adopted for monobasic acids. The inflexion of the curve pro-

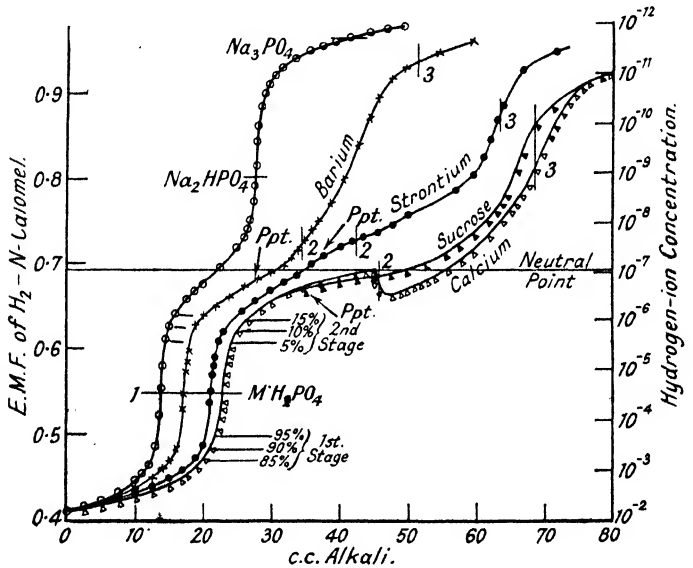


FIG. 55.—Hydrogen Electrode Titration Curves of Phosphoric Acid (Britton, *J. Chem. Soc.*, 1927, 614).

duced at the end of the first half of the neutralisation shows that it is possible to titrate chromic acid to about *p*H 4·5 with methyl orange. A similar curve is given of phosphoric acid, Fig. 55. Each of the three stages of neutralisation is quite distinct from the others. Thus the first corresponds to the neutralisation of a strong acid, $H_3PO_4 \rightleftharpoons H^{\cdot} + H_2PO_4'$, the second to that of a weak acid, $H_2PO_4' \rightleftharpoons H^{\cdot} + HPO_4''$, and the last, whose curve is indistinguishable, on account of the excessive weakness of the acid and the resulting considerable hydrolysis, from the curve representing an excess of sodium hydroxide, to the neutralisation of an extremely weak acid, $HPO_4'' \rightleftharpoons H^{\cdot} + PO_4'''$

TABLE 34

TITRATION OF 100 C.C. OF 0·01277 M.-H_3PO_4 WITH 0·0919 N-NaOH AT 20°, WITH HYDROGEN ELECTRODE N-CALOMEL ELECTRODE COMBINATION (NaH_2PO_4 = 13·9 C.C. ; Na_2HPO_4 = 27·8 C.C.).

NaOH (c.c.).	*E.M.F.*	*p*H.	$[H_2PO_4'] \times 10^2$.	$[H_3PO_4] \times 10^3$.	$K_1 \times 10^3$.
0·0	0·408	2·14	7·24	5·53	9·55
2·55	0·416	2·28	7·54	4·92	8·13
5·0	0·423	2·40	8·36	3·80	8·71
7·5	0·433	2·57	9·10	2·78	8·91
10·0	0·447	2·81	9·90	1·71	9·12
11·0	0·455	2·94	10·26	1·24	9·55
12·0	0·464	3·10	10·64	0·76	11·22
13·0	0·486	3·48	10·90	0·36	10·00
13·5	0·521	4·10	11·00	0·26	3·31
				Mean	9·4

NaOH (c.c.).	*E.M.F.*	*p*H.	C.c. NaH_2PO_4.	C.c. Na_2HPO_4.	$K_2 \times 10^7$.
14·5	0·610	5·60	13·3	0·6	1·12
15·0	0·625	5·86	12·8	1·1	1·18
16·0	0·640	6·11	11·8	2·1	1·38
17·5	0·657	6·40	10·3	3·6	1·38
20·0	0·675	6·71	7·8	6·1	1·51
22·5	0·695	7·06	5·3	8·6	1·41
25·0	0·719	7·47	2·8	11·1	1·35
26·0	0·731	7·67	1·8	12·1	1·44
27·0	0·751	8·01	0·8	13·1	1·35
27·5	0·773	8·39	0·3	13·6	1·82
				Mean	1·4

NaOH (c.c.).	*E.M.F.*	*p*H.	$[PO_4'''] \times 10^2$.	$[HPO_4''] \times 10^3$.	$K_3 \times 10^{13}$.
29·0	0·883	10·28	0·66	9·24	3·72
30·0	0·909	10·72	1·02	8·80	2·24
31·0	0·921	10·92	1·42	8·33	2·04
32·0	0·928	11·05	1·80	7·87	2·04
34·0	0·940	11·26	2·43	7·10	1·91
36·0	0·949	11·40	3·03	6·36	1·91
38·0	0·954	11·49	3·70	5·55	2·19
40·0	0·959	11·57	4·29	4·83	2·40
42·5	0·964	11·66	4·91	4·05	2·63
45·0	0·968	11·72	5·65	3·16	3·39
47·5	0·973	11·81	5·81	2·85	3·16
50·0	0·975	11·85	6·52	1·99	4·57
				Mean	2·7

The other curves show that when phosphoric acid is treated with either calcium, strontium or barium hydroxides, the first stage of the reaction is the formation of the soluble salt, *e.g.*, $Ca(H_2PO_4)_2$, but thereafter insoluble phosphates are formed. These will be referred to in Chapters XXVI, XXXVI, XXXIX and XLII. The titration curve of phosphoric acid may, therefore, be regarded as being composed of the curves of three separate mono-basic acids of widely different strengths. The complete data of the phosphoric acid-sodium hydroxide curve are given in Table 34. They are of interest in that they show how the different methods of calculation of the dissociation constants of monobasic acids described on page 177 have been applied.

The polybasic acids, which we have so far considered, have had widely differing dissociation constants governing their several stages of ionisation such that their titration curves were divided into well-defined sections similar to the neutralisation curves of weak monobasic acids. These curves are by no means typical of the neutralisation of polybasic acids, for as we shall see, the dissociation constants of successive stages of ionisation are often not so widely different that the neutralisation of the hydrogen ions arising from the first step is completed before those from the second stage begin to enter into reaction. Fig. 56 gives the titration curves of four typical dibasic acids, and was taken from the author's paper, *J. Chem. Soc.*, 1925, **127**, 1896. Both oxalic and malonic acids give inflexions when one equivalent of alkali have been added, but it will be observed that they are drawn out over a period corresponding to the addition of a fair amount of alkali. No inflexions were produced in the tartaric or succinic acid curves.

Before proceeding to discuss the construction of these curves, we shall consider the methods by which the dissociation constants of dibasic acids can be found. We shall ignore for the moment the fact that the second hydrogen ion often comes into play long before half the stoicheiometrical amount of alkali has been added, and calculate the constants in the manner adopted for phosphoric acid (Table 34).

The complete data of the neutralisation of tartaric acid are given in Table 35. The figures in the fifth column show the extent of the dissociation of the unneutralised acid as calculated from the observed E.M.F's of the hydrogen electrode compared with that of the normal calomel electrode. They show that as the titration proceeded the degree of ionisation diminished at first, and later appeared to increase. Though the value of K_1 remained at $1{\cdot}3 \times 10^{-3}$ for the first three readings, it also appeared to

increase for the subsequent additions of alkali. The assumption that the alkali, after 25 c.c. had been added, reacted only with the hydrogen ions from the second stage, is shown by the variable values found for K_2. They, too, increased to about 9×10^{-5}. The falling-off of the values of K_2 towards the end of the titration is probably to be accounted for by the fact that the solution was

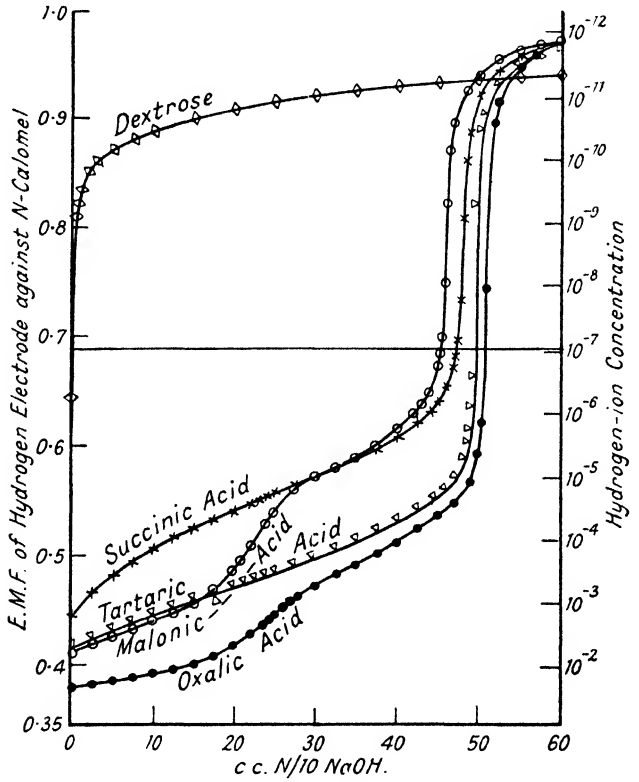


FIG. 56.—Hydrogen Electrode Titration Curves of Dibasic Acids and of Dextrose :—100 c.c. of (i) 0·0255 M.-Oxalic acid, (ii) 0·0250 M.-Tartaric acid, (iii) 0·0240 M.-Succinic acid, (iv) 0·0230 M.-Malonic acid, and 140 c.c. of 0·3572 M.-Dextrose.

then undergoing a rapid change in *p*H, thus causing very small inaccuracies in reading the voltages to lead to comparatively large errors in K_2. Hence, Table 35 shows that no constancy in the values of K_1 and K_2 is obtained, except perhaps for those values calculated from voltages indicated at the beginning and towards the end of the titration.

TABLE 35

TITRATION OF 100 C.C. OF 0·0250 M.-TARTARIC ACID WITH 0·100 N-NaOH at 18°

C.c. of NaOH.	E.M.F. against N-calomel Volt.	*p*H.	Conc. of Free Tartaric Acid $\times 10^3$.	*a*.	$[H_2T]$ $\times 10^3$.	$[HT']$ $\times 10^3$.	K_1 $\times 10^3$.
0	0·415	2·29	25·0	0·206	19·9	—	1·34
2·5	0·423	2·43	22·0	0·170	18·3	6·18	1·27
5·0	0·430	2·55	19·0	0·149	16·2	7·60	1·33
7·5	0·437	2·67	16·3	0·132	14·1	9·29	1·41
10·0	0·444	2·79	13·6	0·119	12·0	10·7	1·45
12·5	0·450	2·89	11·1	0·115	9·8	13·4	1·61
15·0	0·457	3·02	8·70	0·111	7·7	14·0	1·75
17·5	0·463	3·12	6·38	0·119	5·6	15·7	2·11
20·0	0·470	3·24	4·17	0·138	3·6	17·2	2·76
21·25	0·473	3·29	3·09	0·164	—	—	—
22·5	0·477	3·36	2·04	0·213	—	—	—
23·75	0·480	3·41	1·01	0·382	—	—	—
25·0	0·4835	3·474	—	—	—	—	—
					Na_2T.	NaHT.	$K_2 \times 10^5$.
27·5	0·490	3·59	—	—	2·5	22·5	2·87
30·0	0·496	3·69	—	—	5·0	20·0	5·08
32·5	0·506	3·87	—	—	7·5	17·5	5·85
35·0	0·514	4·00	—	—	10·0	15·0	6·62
37·5	0·523	4·16	—	—	12·5	12·5	6·92
40·0	0·529	4·26	—	—	15·0	10·0	8·19
42·55	0·540	4·45	—	—	17·55	7·45	8·30
45·0	0·551	4·64	—	—	20·0	5·0	9·08
46·25	0·559	4·78	—	—	21·25	3·75	9·35
47·5	0·571	4·99	—	—	22·5	2·5	9·19
48·5	0·587	5·27	—	—	23·5	1·5	8·43
49·0	0·604	5·56	—	—	24·0	1·0	6·56
49·25	0·616	5·77	—	—	24·25	0·75	5·48
49·5	0·637	6·14	—	—	24·5	0·5	3·59
49·75	0·664	6·60	—	—	24·75	0·25	2·47
50·0	0·822	9·34	—	—	—	—	—
50·5	0·884	10·42	—	—	—	—	—
51·0	0·901	10·71	—	—	—	—	—
52·5	0·928	11·18	—	—	—	—	—
55·0	0·945	11·48	—	—	—	—	—
57·5	0·956	11·66	—	—	—	—	—
60·0	0·961	11·75	—	—	—	—	—

Calculation of the Dissociation Constants of Dibasic Acids from Titration Curves.

The following equations are based on the mass law and apply to solutions which are so dilute that the sodium salts may be taken as completely dissociated.

Let c = the total concentration of acid, a = total concentration

of added alkali, and h = hydrogen-ion concentration. A dibasic acid, H_2R, dissociates thus :

$$\text{(i) } H_2R \rightleftharpoons H^{\cdot} + HR', \quad \text{(ii) } HR' \rightleftharpoons H^{\cdot} + R'',$$

such that $K_1 = h[HR']/[H_2R]$ and $K_2 = h[R'']/[HR']$. Then $[H_2R] + [HR'] + [R''] = c$ and in the case of the neutralisation of the majority of dibasic acids, excepting those which are extremely weak, and also the ion-concentrations prevailing towards the end of the neutralisation of fairly weak acids,

$$a + h = [HR'] + 2[R''] \text{ (Case I.)}$$

In the case of extremely weak acids and during the final stage of neutralisation of fairly weak acids, hydrolysis comes into play and the hydroxyl-ion concentrations so introduced must be taken into account, then

$$a + h = [HR'] + 2[R''] + \overline{oh} \qquad \text{(Case II. : } \overline{oh} = [OH]).$$

Case I

By eliminating the three unknown concentrations $[H_2R]$, $[HR']$ and $[R'']$ from the first four equations, we obtain the equation

$$\frac{a + h}{h + 2K_2} = \frac{cK_1}{h^2 + hK_1 + K_1K_2}$$

and $\therefore$

$$K_1 = h^2(a + h)/\{K_2(2c - a - h) - (ah + h^2 - hc)\} \quad . \quad (1)$$

$$K_2 = \{h^2(a + h) + K_1(ah + h^2 - hc)\}/K_1(2c - a - h) \; . \; (2)$$

Putting

$$a_nh_n + h_n^2 - h_nc_n = A_n, \quad 2c_n - a_n - h_n = B_n,$$

and

$$h_n^2(a_n + h_n) = D_n,$$

then $K_1 = D_n/(K_2B_n - A_n)$ and $K_2 = (D_n + K_1A_n)/K_1B_n$.

Hence, by taking any two points on the titration curve whose parameters are respectively A_1, B_1, D_1, and A_2, B_2, D_2, the values of K_1 and K_2 can be found.

Thus

$$K_1 = (B_1D_2 - B_2D_1)/(A_1B_2 - A_2B_1) \quad . \quad . \quad (3)$$

$$K_2 = (A_1D_2 - A_2D_1)/(B_1D_2 - B_2D_1) \quad . \quad \therefore \quad (4)$$

Many of the values of K_2 for dibasic acids have hitherto been obtained from determinations of the hydrogen-ion concentrations of solutions of the acid salts and calculated by means of a formula, worked out by Noyes (*Z. physikal. Chem.*, 1893, **11**, 495), identical with (2), for when $a = c$, as is the case with an acid salt, NaHR, the equation becomes

$$K_2 = h^2(c + K_1 + h)/K_1(c - h) \quad . \quad . \quad (5)$$

Case II

Elimination of the three unknowns $[H_2R]$, $[HR']$ and $[R'']$ from the first three fundamental equations and the equation involving $\overline{oh}$, we obtain the expression

$$\frac{a + h - \overline{oh}}{h + 2\overline{K_2}} = \frac{cK_1}{h^2 + hK_1 + K_1K_2'}$$

from which it follows that

$$K_1 = h^2(a + h - \overline{oh})/\{K_2(2c - a - h + \overline{oh}) - (ah + h^2 - hc - h \,.\, \overline{oh})\}$$

and

$$K_2 = \{h^2(a + h - \overline{oh}) + K_1(ah + h^2 - hc - h \,.\, oh)\}/K_1(2c - a - h + \overline{oh}).$$

In Table 36 the values of K_1 and K_2 as calculated from the titration data of tartaric acid, Table 35, by means of the formulæ derived on page 198, are compared with the values given in Table 35, which were obtained from the data corresponding to

TABLE 36

CALCULATION OF K_1 AND K_2 FROM TITRATION CURVE. DISSOCIATION CONSTANTS OF TARTARIC ACID

C.c. of NaOH.	$K_1 \times 10^3$.		$K_2 \times 10^5$.	
	Formula.	Table.	Formula.	Table.
5 / 45	1·22	1·33	9·56	9·08
10 / 40	1·24	1·45	9·30	8·19
15 / 35	1·30	1·75	8·56	6·62
20 / 30	1·22	2·76	10·61	5·08
0 / 25	1·28	1·34	9·68	—
5 / 30	1·21	1·33	10·65	5·08
0 / 15	1·29	1·34 / 1·75	9·16	—
20 / 30	1·29	—	9·64	—
0 / 5	1·35	1·33 / 1·27	[− 1·24]	—
40 / 50	[0·91]	—	9·65	8·19 / 9·08
Mean	1·27	—	9·65	—

the same positions on the curve. The values of K_1 and K_2 calculated from the formulæ are much more satisfactory than those based on the assumption that the second hydrogen ion does not react until the first equivalent of alkali has been added, provided that the pairs of points employed for the calculation are not taken at either of the ends of the titration curve. The last two sets of values gave absurd results of the particular constant which at that stage of the neutralisation was not then being involved. These values are given in square brackets. That the second dissociation came into play during the neutralisation of the first 15 c.c. of NaOH (= 0·6 equivalent) will be evident from the satisfactory values of K_2 calculated from the two points 0 and 15 c.cs. by the two methods of calculation.

Hydrogen-Ion Concentration at Half-Neutralisation of a Dibasic Acid.

If it happens that the two stages of ionisation of a dibasic acid, H_2R, are similar to those of weak monobasic acids, then for

$$H_2R \rightleftharpoons H^{\cdot} + HR'$$

$$K_1 = \frac{[H^{\cdot}][HR']}{[H_2R]} = [H^{\cdot}] \times \frac{[\text{acid salt}]}{[\text{acid}]}$$

and for

$$HR' \rightleftharpoons H^{\cdot} + R'$$

$$K_2 = \frac{[H^{\cdot}][R']}{[HR']} = [H^{\cdot}] \frac{[\text{neutral salt}]}{[\text{acid salt}]}.$$

Now suppose that when 1 equivalent of NaOH had been added a fraction of an equivalent, β, of the hydrogen ions arising from the first stage of ionisation failed to react, then β equivalent of NaOH must have reacted with the hydrogen ions produced by the subsequent ionisation of HR′ ions. If c is the original concentration of H_2R, then the NaHR formed will be $(1 - \beta)c$ and the concentration of Na_2R will be βc. The concentration of undissociated acid, $[H_2R]$, will be βc. Substituting these values in the above expressions, we get

$$K_1 = [H^{\cdot}] \times \frac{(1 - \beta)c}{\beta c},$$

and

$$K_2 = [H^{\cdot}] \times \frac{\beta c}{(1 - \beta)c},$$

whence by multiplication, we find that

$$K_1 \times K_2 = [H^{\cdot}]^2,$$

or

$$pH = \frac{pK_1 + pK_2}{2}.$$

Thus, provided that both stages of a dibasic acid are weak, the *p*H at the mid-point of its neutralisation is equal to the mean of the exponents, pK_1 and pK_2. These for weak monobasic acids are equal to the *p*H of the hydrogen-ion concentrations prevailing at their half-neutralisation, and, in fact, they are true for the respective stages of a dibasic acid, for, as a general rule, up to the point corresponding to the addition of the first half an equivalent of alkali the hydrogen-ion concentration is uninfluenced by K_2, and later during the addition of the final half equivalent K_1 becomes ineffective.

The identity, $K_1K_2 = [H^\cdot]^2$, may also be derived from Noyes' formula, connecting K_1 and K_2 with the hydrogen-ion concentration of solutions of acid salts, NaHR, and proved on page 198. As $K_2 = h^2(c + K_1 + h)/K_1(c - h)$ we find that the condition for

$$K_1 . K_2 = h^2$$

is that

$$\frac{c + K_1 + h}{c - h}$$

must be equal to unity. This can only be true when both K_1 and h are negligibly small compared with the concentration, c. Such conditions hold when the first stage of dissociation is governed by a constant not greater than 10^{-3}. This will be seen from Table 37, in which pH_M corresponds to the hydrogen-ion concentration at the mid-point of neutralisation of each of the four acids given in Fig. 56. The figures in the last column are the values assumed by

$$\frac{c + K_1 + h}{c - h} = \frac{K_1 . K_2}{[H^\cdot]^2_M}$$

for the various acids. With the exception of oxalic acid, in which

TABLE 37

RELATIONSHIP BETWEEN THE HYDROGEN-ION CONCENTRATION AT HALF-NEUTRALISATION AND THE DISSOCIATION CONSTANTS OF DIBASIC ACIDS

Acid.	pH_M.	pK_1.	pK_2.	$\frac{pK_1 + pK_2}{2}$.	$\frac{K_1 . K_2}{[H^\cdot]^2_M}$.
Oxalic	2·88	0·77	3·86	2·32	13·0
Tartaric	3·47	2·90	4·02	3·46	1·09
Succinic	4·73	4·04	5·28	4·66	1·42
Malonic	4·11	2·70	5·36	4·03	1·45

case the first stage is that of a fairly strong acid, the value of this expression is approximately 1, so much so that $p\mathrm{H_M}$ and

$$\frac{p\mathrm{K_1} + p\mathrm{K_2}}{2}$$

are in fair accord.

By an approximate mathematical analysis, Auerbach and Smolczyk have shown how the character of the titration curves is determined by the ratio of their dissociation constants. Thus when $\mathrm{K_1}$ is greater than $16\mathrm{K_2}$ the curve will have an inflexion in the middle, whereas when $\mathrm{K_1} = 16\mathrm{K_2}$ the curve will be a straight line, and when $\mathrm{K_1}$ is less than $16\mathrm{K_2}$ the curve will be similar to that of a monobasic acid. The curves of oxalic and malonic acids, the second dissociation constants of which are considerably less than $1/16\mathrm{K_1}$, *viz.*, 1/1269 and 1/476 respectively, have each large inflexions (Fig. 56), whereas in that of succinic acid ($\mathrm{K_1} = 17\mathrm{K_2}$) and of tartaric acid ($\mathrm{K_1} = 13\mathrm{K_2}$) no inflexions are discernible.

It is striking that the first two members—oxalic acid and malonic acid—of the saturated dibasic acid series,

$$\mathrm{HO_2C} \cdot [\mathrm{CH_2}]_n \cdot \mathrm{CO_2H},$$

should exhibit such a great difference in their two dissociation constants, in each case the first constant being several hundred times the second, as compared with the next number, succinic acid, the first constant of which is only seventeen times the second. The dissociation constants found by Chandler (*J. Amer. Chem. Soc.*, 1908, **30**, 713) for the remaining members of the series up to sebacic acid, $n = 8$, reveal the remarkable fact that the values of $\mathrm{K_2}$ from malonic acid upwards are all approximately equal and of the order 10^{-6}, and that there is only a small diminution in $\mathrm{K_1}$ of the ascending acids of the series, but they are all of the order given by succinic acid, *viz.*, 10^{-5}. Hence the titration curves of these acids will be similar to that of succinic acid, and, in fact, almost coincident with it.

The neutralisation curves of polybasic acids or polyacidic bases are composed essentially of the curves corresponding to each separate stage of ionisation. Provided the acid or base is not too strong, we have seen that the mid-point of each integral curve will pass through a $p\mathrm{H}$ equal to $p\mathrm{K}_a$ or, in the case of bases, equal to $p\mathrm{K}_w - p\mathrm{K}_b$. In Figs. 57 and 58 the theoretical neutralisation curves of the first and second stages of some dibasic acids have been inserted as broken lines. Whereas in the chromic acid curve the two stages of neutralisation are distinct from one another, the theoretical lines being coincident with

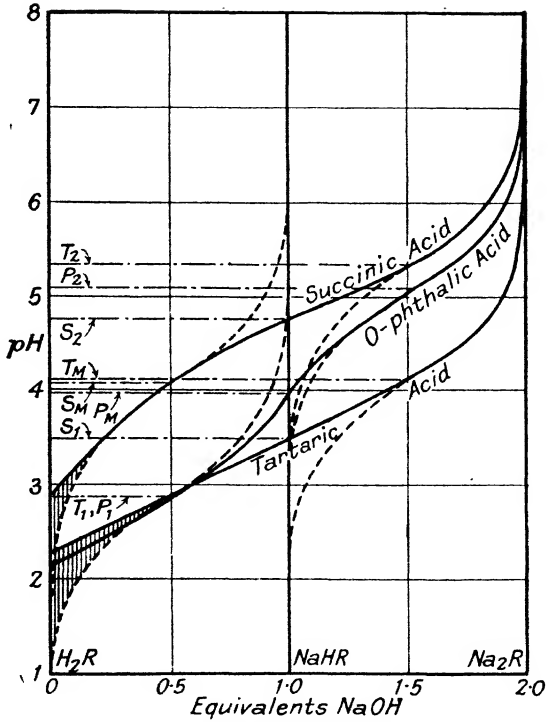


FIG. 57.—Analysis of Titration Curves.

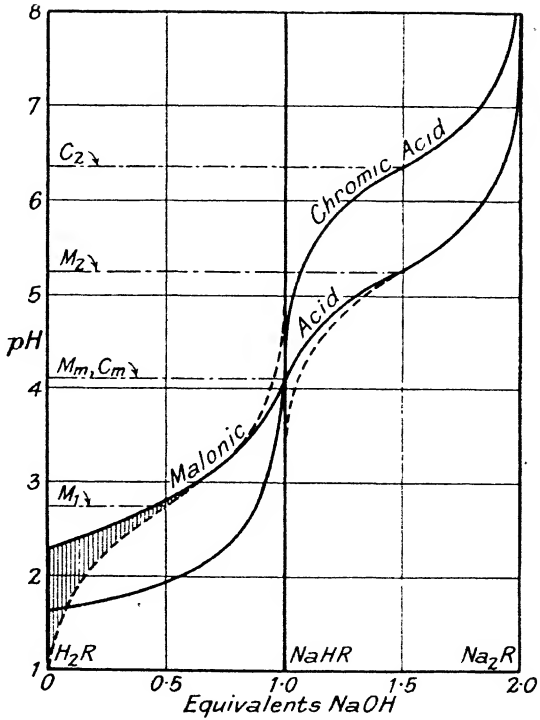


FIG. 58.—Analysis of Titration Curves.

the two branches, we find that if the first stage of malonic acid were uninfluenced towards the end of its neutralisation by the second dissociation, the reaction would be completed at about *p*H 4·8, and the second hydrogen ion would come into action at about *p*H 3·3 and the *p*H change would follow the broken line to approximately the mid-point of the second half of the curve. Such a state of affairs would, of course, be impossible, and consequently we see from the actual curve that neither of these *p*H values is attained, but that the hydrogen-ion concentrations indicated refer to intermediate *p*H values indicated by the two theoretical curves. The actual curve is tangential to the two monobasic branches. The proximity of the two constants, compared with those of chromic acid, leads to a less well-defined inflexion. In Fig. 57, the inflexion is seen to be less for orthophthalic acid, of which $K_1 = 150\ K_2$. We also see from the positions where the observed curve becomes tangential to the constituent curves why ionisation of the second stage becomes involved early during the addition of the first half of alkali and why hydrogen ions arising from the first stage are not completely used up until considerably more than one equivalent of alkali has been added. This effect is greater with tartaric and succinic acids, whose respective constants are much closer together, $pK_2 - pK_1$ being slightly greater than 1. It therefore becomes evident why the *p*H curves corresponding to the middle stages of their neutralisation should be rectilinear and give no evidence of inflexions, as mentioned above. A glance of the three constants of citric acid given in Table 30 will reveal that no very pronounced inflexions can occur in its *p*H curve. As the difference between pK_2 and pK_1 is 1·6, a very small inflexion will be produced on the addition of the first equivalent of alkali, whereas $pK_3 - pK_2$ being 1·2 the inflexion at the end of the second stage will be imperceptible. It is for this reason that citric acid and its salts are often included in buffer solutions.

Potentiometric Estimation of Acids and Bases which are too weak to be estimated volumetrically.

Harris (*Proc. Roy. Soc.*, 1923, B, **95**, 440; *J. Chem. Soc.*, 1923, **123**, 3294) has recently developed a method for the estimation of very weak acids and bases, similar to that previously employed by Tague (*J. Amer. Chem. Soc.*, 1920, **42**, 180) in connexion with work on certain ampholytes of importance in the chemistry of flour. Incidentally, it is the same in principle as that employed for the calculation of the dissociation constants of weak acids (and bases), which on treatment with alkali (or acid) give rise to salts

which are considerably hydrolysed (*cf.* p. 178). It was shown that for an acid whose degree of dissociation α is negligibly small $K_a = [H^+] \times \frac{[salt]}{[acid]}$, and similarly for a base $K_b = [OH^-] \times \frac{[salt]}{[base]}$. In the case of moderately weak acids and bases the salt formed, *i.e.*, [salt], was equivalent to the titrant added, but for extremely weak acids and bases this is far from being the case. The " salt " concentration can be calculated from the amount of titrant added and the hydroxyl-ion concentration, for the latter concentration is set up solely by the amount of titrant which has failed to react. Hence by knowing the degree of dissociation of the titrant when in the concentration indicated by the *p*H, it is an easy matter to calculate how many c.cs. of titrant had actually failed to react, which when subtracted from the amount of titrant actually added, gives the amount which has combined with the acid or base. The amount of titrant which has failed to react, alkali or acid, may, of course, be ascertained directly by merely adding it to water, until the *p*H, produced in the actual titration, is attained, and finding by simple proportion the amount required for the particular volume of the titrated solution. Harris, however, realised that for an acid or base of which its affinity constant was known, neutralisation, within experimental error, must take place between two definite *p*H's. These could be calculated by taking the radio of [salt] [acid], (or [base]), at the beginning of a titration as 1/99, and at the end 99/1 respectively.

Thus, as shown on page 180, the limits of *p*H prevailing during the neutralisation of a weak acid by a strong alkali are $pK_a \mp 2$, and similarly the *p*H limits between which weak bases are neutralised by strong acids are $14 - pK_b \pm 2$. For glycine, $K_a = 1{\cdot}8 \times 10^{-10}$, and, therefore, when the acid is 1 per cent. neutralised the *p*H is 7·75, and when 99 per cent. neutralised it is 11·75. The basic dissociation constant K_b of glycine is $2{\cdot}7 \times 10^{-12}$, and, therefore, the *p*H at beginning of neutralisation with hydrochloric acid is 4·43 and 0·43 at the end (actually 99 per cent. neutralised). It is, therefore, only necessary to titrate between these limits, and by ascertaining the amount of free reactant the amount neutralised by the acid or base is known. Fig. 59 gives the *p*H curves, constructed from the data of Tague and Harris, which represent potentiometric titrations of glycine when treated with alkali, and also when treated with an acid, from which the true neutralisation curves were obtained by deducting the amounts of titrant which had failed to react, which gave rise to the *p*H from the various additions of titrant.

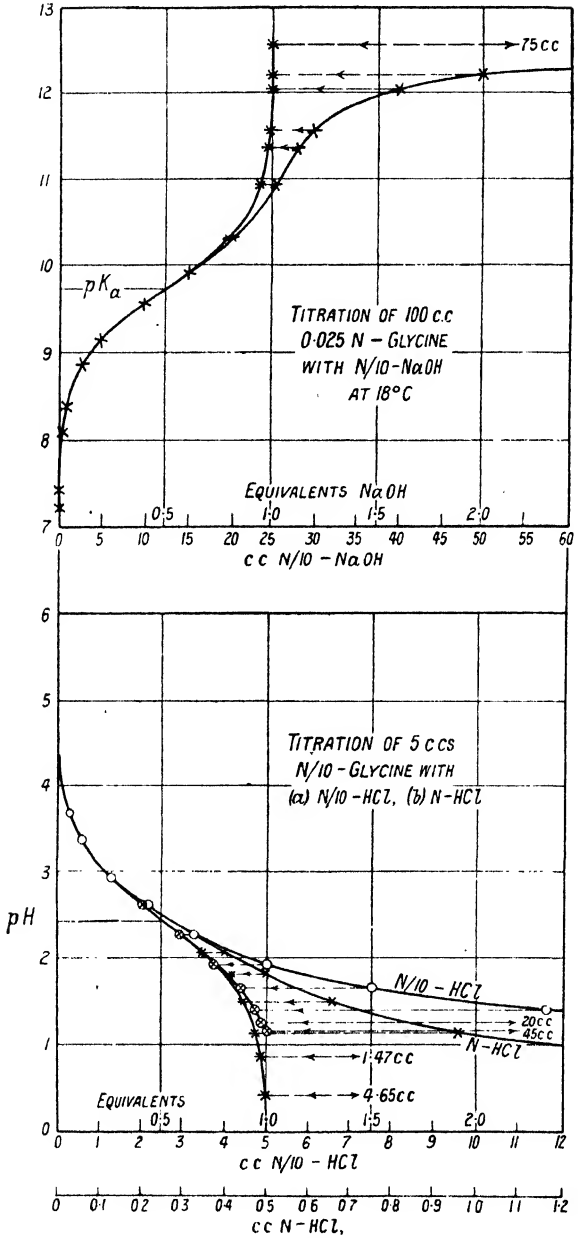


FIG. 59.—Potentiometric Titrations of Glycine with Sodium Hydroxide and Hydrochloric Acid.

Titration of Glutamic Acid.

Harris (*J. Chem. Soc.*, 1923, **123**, 3299) has titrated glutamic acid hydrochloride by means of the quinhydrone electrode. As will be seen from Table 33 this acid is an ampholyte and contains two carboxyl groups and one amino-group. Moreover, the values of the affinity constants of the two acid groups are widely different, *viz.*, $6{\cdot}2 \times 10^{-5}$ and $1{\cdot}6 \times 10^{-10}$, and thus the *p*H

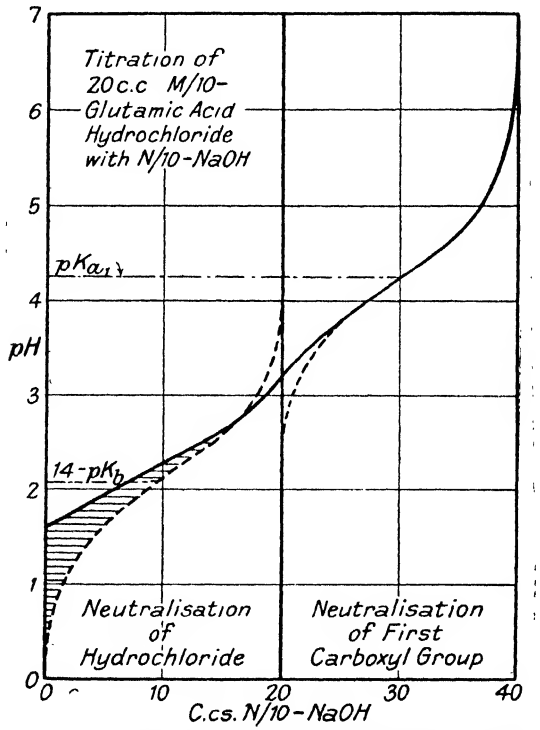


FIG. 60.—Titration of Glutamic Acid Hydrochloride.

ranges of neutralisation of the two stages will be quite distinct. The weaker group will enter into reaction between *p*H 7·8 and 11·8, and the stronger between *p*H 2·21 and 6·21. The dissociation constant of the basic group being $1{\cdot}3 \times 10^{-12}$ will cause its neutralisation to take place between *p*OH 9·9 and 13·9, or as $K_w = 10^{-14}$ between *p*H 4·1 and 0·1. It appears therefore that the neutralisation of the stronger acid group and the basic group will take place within the *p*H range covered by the quinhydrone electrode. Furthermore, the *p*H of a solution of glutamic acid

will be determined by some kind of compensation of the stronger acid group and the basic group. The continuous curve in Fig. 60 represents the *p*H change undergone when 20 c.c. of a decimolar solution of glutamic acid hydrochloride were titrated with decinormal alkali. In order to estimate the glutamic acid, we see from the foregoing, that it will be necessary to find the exact amount of sodium hydroxide which reacts only with the unhydrolysed hydrochloride in the first place, and with the stronger carboxyl group in the second. These two reactions take place between *p*H 0·1 and *p*H 6·21. Owing to the considerable hydrolysis of the glutamic acid hydrochloride, resort must be made to the procedure, adopted in the case of glycine, to find the amount of hydrochloric acid, in terms of c.c. of N/10-HCl for each particular volume of solution corresponding to the hydrolysed acid and indicated by the *p*H after each addition of alkali. In this way, the "ideal curve of neutralisation of the glutamic acid hydrochloride," shown in Fig. 60 as a broken line, can be constructed. The curve shows that 40 c.c. of NaOH were required. The so-called "ideal curve" is actually that of the amino-group, which on neutralisation with N/10-HCl would have followed the course from the 20 c.c. abscissa to the left. The broken lines in the middle of the curve refer to the base and acid in the absence of one or the other. The very small inflexion of the actual curve illustrates the effect of the two constants.

Hydrolysis.

We shall now consider the mathematical relationships involved in the hydrolysis of salt solutions and in the ionisation of ampholytes.

It is well known that very few salts when dissolved in water produce solutions which are neutral in reaction. Some of the base, in the case of a salt formed from a strong base and a weak acid, breaks away and imparts to the solution an alkaline reaction, whereas an acidic reaction is established by a salt composed of a strong acid and a weak base. If both the acid and the base from which the salt was formed happen to be soluble in water, then it becomes possible to calculate the hydrolysis constant of such hydrolytic reactions and the *p*H values of the resulting solutions.

(*a*) **Hydrolysis of a Salt of a Strong Base and a Weak Acid** (*e.g.*, Sodium acetate).

Consider the reaction

$$BR + H_2O \rightleftharpoons HR + BOH.$$

If the salt, BR, be in dilute solution, we may assume that that

portion of it which has not suffered hydrolysis will be almost completely ionised into B$^{\bullet}$ and R′ ions. For the purpose of calculation we shall regard it as complete. The base, BOH, is a strong one, so that its ionisation will also be taken as complete. The acid, HR, is a weak one and its dissociation, $HR \rightleftharpoons H^{\bullet} + R'$, is so very small, that in conjunction with the relatively large concentration of hydroxyl ions resulting from hydrolysis, will cause the hydrogen ions produced by the acid to have no measurable effect upon the reaction of the solution. The hydrolytic action might therefore be re-written

$$R' + H_2O \rightleftharpoons HR + OH',$$

the cations, B$^{\bullet}$, through the assumed complete ionisation of BR, taking no part. On applying the mass law, we find that

$$K_{\text{hydrolysis}} = \frac{[HR][OH']}{[R']}.$$

Multiplying numerator and denominator by [H$^{\bullet}$], and knowing that

$$K_w = [H^{\bullet}][OH'],$$

and

$$K_a = [H^{\bullet}][R']/[HR],$$

we obtain

$$K_{\text{hydrolysis}} = \frac{[HR]}{[H^{\bullet}][R']} \times [H^{\bullet}][OH'],$$

i.e.,

$$K_{\text{hydrolysis}} = \frac{K_w}{K_a}.$$

We are now in a position to obtain an approximate expression connecting the *p*H of a solution of BR, K_w and the dissociation constant of HR, *viz.*, K_a. We may assume if *the amount of hydrolysis be very small* that the concentration, *c*, of the salt, BR, = [R′], and as [HR] = [OH′], then

$$\frac{[HR][OH']}{[R']} = \frac{[OH']^2}{c} = \frac{K_w}{K_a},$$

$$\therefore [OH'] = \sqrt{\frac{K_w}{K_a} \times c},$$

whence

$$pOH = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_a - \tfrac{1}{2}\log c$$

and therefore

$$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a + \tfrac{1}{2}\log c.$$

The degree of hydrolysis of such a salt is equal to $[OH']/c$, and the percentage hydrolysis is given by $[OH'] \times 100/c$.

(*b*) **Hydrolysis of a Salt of a Weak Base and a Strong Acid** (*e.g.*, Ammonium chloride).—In this case HR is strong and BOH weak, and the hydrolytic reaction will be

$$B^{\bullet} + H_2O \rightleftharpoons BOH + H^{\bullet},$$

the R′ ions taking no part in the reaction, as both the salt and strong acid are strongly ionised, and are here assumed to be ionised completely. As above

$$K_{hydrolysis} = \frac{[BOH][H^{\cdot}]}{[B^{\cdot}]} = \frac{[BOH]}{[B^{\cdot}][OH']} \times [H^{\cdot}][OH'] = \frac{K_w}{K_b},$$

where K_b is the affinity constant of the base, BOH. Also

$$\frac{K_w}{K_b} = \frac{[H^{\cdot}]^2}{c},$$

for $[H^{\cdot}] = [BOH]$ and $c = [B^{\cdot}]$. Therefore

$$[H^{\cdot}] = \sqrt{\frac{K_w}{K_b}} \times c.$$

and consequently,

$$pH = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_b - \tfrac{1}{2}\log c.$$

The percentage degree of hydrolysis

$$= [H^{\cdot}] \times 100/c.$$

(*c*) **Hydrolysis of a Salt of a Weak Base and a Weak Acid** (*e.g.*, Ammonium acetate).—Here both the ions, B$^{\cdot}$ and R′, constituting the salt BR, which is taken as completely dissociated, are free to enter into combination with the few hydrogen and hydroxyl ions dissociated from the water to form undissociated base, BOH, and the undissociated acid, HR, by virtue of their weakness. The reaction is therefore

$$B^{\cdot} + R' + H_2O \rightleftharpoons BOH + HR$$

and

$$K_{hydrolysis} = \frac{[BOH][HR]}{[B^{\cdot}][R']} = \frac{[BOH]}{[B^{\cdot}][OH']} \times \frac{[HR]}{[H^{\cdot}][R']} \times [H^{\cdot}][OH'] = \frac{K_w}{K_b \,.\, K_a}$$

Now $[BOH] = [HR]$,

and $[B^{\cdot}] = [R'] = c$, the concentration of the salt.

Hence

$$\frac{K_w}{K_b \,.\, K_a} = \frac{[BOH][HR]}{[B^{\cdot}][R']} = \frac{[HR]^2}{c^2},$$

but

$$K_a = \frac{[H^{\cdot}][R']}{[HR]} = \frac{[H^{\cdot}] \,.\, c}{[HR]},$$

therefore $$\frac{[HR]^2}{c^2} = \frac{[H^\cdot]^2}{K_a^2} = \frac{K_w}{K_b \cdot K_a},$$

$$\therefore [H^\cdot] = \sqrt{\frac{K_w \cdot K_a}{K_b}},$$

and, finally, $$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a - \tfrac{1}{2}pK_b.$$

The percentage degree of hydrolysis is $[HR] \times 100/c$, which may be evaluated from the foregoing expressions.

We observe from the above theoretical considerations that in the cases (*a*) and (*b*) the *p*H of the salt solutions is linked up with the concentration of the salt dissolved, but that in the last case (*c*) the *p*H is independent of the salt concentration. These *p*H values represent the true end-points of the neutralisation of (*a*) the acid, (*b*) the base, more accurately than do the *p*H values calculated by the approximate method given earlier in this chapter. The formulæ lead to *p*H values which are in good agreement with those practically determined.

*p*H Value of Solutions of Ampholytes.

Ampholytes are those substances which have the power of reacting either as an acid or a base. As a rule their basic and acidic functions are weak and can only be brought effectively into action by means of strong acids and bases respectively. Examples are to be found amongst the carbon compounds such as glycine and the proteins, and the inorganic compounds, e.g., hydrated alumina Amphoteric bodies like the proteins and certain inorganic hydroxides do not always pass into true solution, and their behaviour is thereby rendered more difficult to study through their colloidal nature. In those cases, it is probable that the reactivity and the *p*H imparted to the aqueous medium are the result of interfacial equilibria of ionic micelles. The isoelectric point of an ampholyte corresponds to a state of affairs when the ampholyte is at its minimum chemical activity, and it therefore exists in solution, or in pseudo-solution, in its maximum undissociated condition. This causes colloidal bodies, *e.g.*, gelatin, to acquire their minimum solubility, and inter-related with it are such physical properties as changes in the viscosity of their hydrosols, and the swelling of their gels, which then acquire minimum values. The main factor which determines the isoelectric point of an ampholyte is the *p*H of the mother-liquor with which it enters into equilibrium. At *p*H values below that of the isoelectric point the colloidal particles bear positive charges, for under the influence of an electric field they migrate towards the cathode, whereas at *p*H

values above that of the isoelectric point the particles assume a negative charge and move in the opposite direction. At the isoelectric point they behave as if they were without an electric charge, for they remain stationary when a current is passed through the solution. Actually, the particles are in a state of electrical neutrality. Expressed in purely chemical terms, this means that in acid solutions having a hydrogen-ion concentration greater than that indicated by the isoelectric point *p*H the colloidal particles are basic in nature, whereas at smaller hydrion concentrations they behave as if they were acids and react with alkalis. Thus an ampholyte will be in the isoelectric condition when no part of it is in combination with any acid or alkali. In the case of an ampholyte which is a distinct chemical individual, *e.g.*, glycine, it is customary to refer to this condition merely in terms of the hydrogen-ion concentration which it establishes in its solution, and to confine the term, isoelectric point, to the complex colloidal amphoteric bodies.

We shall now evaluate the *p*H value of a solution of a simple ampholyte in terms of the affinity constants of the acid and basic groups. We see from Fig. 59 that the amino-group in glycine reacts with acid below *p*H 6, whereas above this *p*H glycine reacts with alkali, apparently through interaction with the carboxyl group. Because of the great difference between the two *p*H ranges within which these groups enter into reaction, it follows that at *p*H about 6 the amount of combination with either of these groups will be immeasurably small. This, however, is not true for such ampholytes as *m*-aminobenzoic acid and aspartic acid. The values given in Table 33 show that *m*-aminobenzoic acid reacts as an acid between *p*H 2·8 and *p*H 6·8, and as a base between *p*H 0·1 and *p*H 4·1. These two ranges overlap and consequently whilst only the basic function is reacted upon from *p*H 0·1, the acid function comes into play at *p*H 2·8 before the neutralisation of the basic group is complete. The titration curve is similar to that of glutamic acid, Fig. 60. The behaviour of aspartic acid is similar. It is evident, then, that the *p*H of a solution of an ampholyte will be dependent upon the affinity constants of the basic and acidic groups, for their magnitude will determine whether any interaction will take place between these groups and so set up a state of partial mutual neutralisation. There are two ways of regarding the behaviour of ampholytes: (i) to assume that a molecule may behave either as if it were a base alone or as an acid, *i.e.*, once the $-NH_2$ group has entered into reaction the -COOH becomes incapacitated and vice versa; (ii) to assume that the carboxyl- and the amino-groups of a molecule

of an ampholyte have interacted to form an " inner salt," which may be decomposed either by an acid or an alkali. In the latter case, one part of the molecule behaves as an anion, *i.e.*, negatively charged, and the other part as a cation, positively charged. A doubly ionised molecule is a so-called " hybrid ion " or a " Zwitterion." This is *Bjerrum's Theory* (*Z. physikal. Chem.*, 1923, **104**, 147); the mathematical consequences of which will be dealt with subsequently.

Bjerrum was led to this view on account of the great disparity of the dissociation constants of the acidic group and basic group in an ampholyte, *e.g.*, glycine, and those of derivatives in which the basic or acidic group was absent as the case may be. Thus in glycine $K_a = 1{\cdot}8 \times 10^{-10}$, whereas for acetic acid $K_a = 1{\cdot}8 \times 10^{-5}$. Similarly K_b for methylamine is 5×10^{-4}, but the K_b for the basic group in glycine is $2{\cdot}7 \times 10^{-12}$. If Bjerrum's theory is correct, then, as we shall see later, what we have been calling the constant of the basic group is actually that of the acidic group, and vice versa.

Hence we see that the dissociation constants of the acidic and basic groups, when considered from the standpoint of the one theory, refer to the basic and acidic groups respectively, when considered in terms of the other theory, and expressed as on page 186.

We shall now consider the *p*H value of a solution of an ampholyte in terms of the first concept. Thus glycine may react in accordance with either the dissociation,

$$\begin{array}{l}\mathrm{COOH} \\ | \\ \mathrm{CH_2NH_2}\end{array} + \mathrm{H_2O} \rightleftharpoons \begin{array}{l}\mathrm{COOH} \\ | \\ \mathrm{CH_2NH_3^+}\end{array} + \mathrm{OH^-}$$

or the dissociation,

$$\begin{array}{l}\mathrm{COOH} \\ | \\ \mathrm{CH_2NH_2}\end{array} \rightleftharpoons \mathrm{H^+} + \begin{array}{l}\mathrm{COO^-} \\ | \\ \mathrm{CH_2NH_2}.\end{array}$$

Let [A] represent the concentration of undissociated ampholyte in either of the two modes of ionisation, [A$^\cdot$], the concentration of basic ions (cations), and [A′], the concentration of anions. Hence in the general case

$$\mathrm{A} + \mathrm{H_2O} \rightleftharpoons \mathrm{A^\cdot} + \mathrm{OH'}$$

and

$$\mathrm{A} \rightleftharpoons \mathrm{H^\cdot} + \mathrm{A'}.$$

For the basic dissociation,

$$K_b = \frac{[\mathrm{A^\cdot}][\mathrm{OH'}]}{[\mathrm{A}]},$$

and for the acidic dissociation,

$$K_a = \frac{[H^\cdot][A']}{[A]}.$$

Because of the electrical neutrality of the solution, we can write

$$[A^\cdot] + [H^\cdot] = [OH'] + [A'].$$

By substituting $\frac{K_w}{[H^\cdot]}$ for $[OH']$,

$$\frac{K_b \cdot [A][H^\cdot]}{K_w} \text{ for } [A^\cdot],$$

and $$\frac{K_a \cdot [A]}{[H^\cdot]} \text{ for } [A']$$

in the above equation, and solving for $[H^\cdot]$, we obtain the following relationship :—

$$[H^\cdot] = \sqrt{\frac{K_a \cdot [A] + K_w}{\frac{K_b}{K_w} \cdot [A] + 1}}.$$

This expression gives the hydrogen-ion concentration of an ampholyte in terms of the several constants and the unknown concentration, [A]. If, as we have seen, the *p*H titration ranges of the acidic and basic groups are sufficiently well apart, as is the case with glycine, then the concentration of the undissociated ampholyte will be equal to the concentration of the ampholyte, *c*, so that $[A] = c$. In the other cases referred to on page 212 there will be appreciable concentrations of $A^\cdot$ and A', and then the equality

$$c = [A] + [A^\cdot] + [A']$$

must be taken into consideration. For such ampholytes Kolthoff (" Indicators," Kolthoff, translated by Furman, New York, 1926, p. 44) has shown that if as a first approximation [A] is assumed equal to *c*, an approximate estimate of $[H^\cdot]$ may be obtained which, when substituted in the equation,

$$[A^\cdot] + [H^\cdot] = [OH'] + [A']$$

will give an equation which, when solved for $[A^\cdot]$ and $[A']$ in conjunction with

$$[A^\cdot] + [A'] = -c - [A],$$

will lead to a more satisfactory value for [A]. By substituting this new value of [A] in the original equation, a value of $[H^\cdot]$ will be obtained which may be regarded as accurate. The following

Table 38 gives the results of Kolthoff's computations for aspartic acid, and were taken from his book :—

TABLE 38

CALCULATION OF *p*H VALUES OF ASPARTIC ACID

c.	*p*H.	*p*H Calculated *without* Correction.	*p*H Calculated *with* Correction.
1	2·95	2·95	2·95
10^{-1}	2·97	2·97	2·95
10^{-2}	3·11	3·08	2·97
10^{-3}	3·52	3·44	3·52
10^{-4}	4·17	3·91	4·17

If the values of K_a and K_b happen to be much greater than K_w, and not smaller than about 10^{-11}, and the concentration of undissociated ampholyte molecules, [A], large, then we can write

$$[H^{\cdot}] = \sqrt{\frac{K_a \cdot [A] + K_w}{\frac{K_b}{K_w} \cdot [A] + 1}} = \sqrt{\frac{K_a \cdot K_w}{K_b}}.$$

This expression is usually given for calculating the isoelectric point of proteins and of similar amphoteric substances. It should be mentioned, however, that the acid and basic functions of these bodies cannot be satisfactorily represented in terms of dissociation constants (*cf.* Harris, *Proc. Roy. Soc.*, 1925, **97**, B, 379).

Leonar Michaelis (" Hydrogen-Ion Concentrations," translated by Perlzweig, 1927) obtains the expression in a somewhat different way. Substituting the values for [A˙] and [A′] given on page 214, in

$$c = [A] + [A^{\cdot}] + [A']$$

we get

$$\frac{c}{[A]} = 1 + \frac{K_a}{[H^{\cdot}]} + \frac{K_b}{K_w} \cdot [H^{\cdot}].$$

Differentiating, we obtain

$$\frac{d\left(\frac{1}{[A]}\right)}{d[H^{\cdot}]} = -\frac{K_a}{[H^{\cdot}]^2} + \frac{K_b}{K_w},$$

so that $\frac{1}{[A]}$ is at a minimum, when [A] is at a maximum, and this occurs when

$$-\frac{K_a}{[H^{\cdot}]^2} + \frac{K_b}{K_w} = 0.$$

Hence at the isoelectric point

$$[H^{\cdot}] = \sqrt{\frac{K_a K_w}{K_b}}.$$

It remains for us to discuss the ionisation of ampholytes on the basis of Bjerrum's " Zwitterion " Theory, according to which an ampholyte may dissociate in any of the ways shown by the following equations :—

$$NH_2 . R . COOH + H_2O \rightleftharpoons HO . NH_3 . R . COOH$$
$$\rightleftharpoons \overset{+}{N}H_3 . R . \overset{-}{C}OO + H_2O$$
$$\rightleftharpoons \overset{+}{N}H_3 . R . COOH + OH'$$
$$\rightleftharpoons HO . NH_3 . R . \overset{-}{C}OO + H^{\cdot}.$$

According to this scheme, we see that on solution there occurs a combination of the ampholyte with water molecules, molecule for molecule, and immediately followed by *either*, an internal neutralisation of the acid and basic groups, forming an electrically neutral and undissociable " inner " salt, which therefore will be without effect on the conductivity of the solution and is known as the " Zwitterion " or " hybrid-ion," *viz.*, $\overset{+}{N}H_3 . R . \overset{-}{C}OO$, or the formation of simple cations, $\overset{+}{N}H_3 . R . COOH$, or, of simple anions, $HO . NH_3 . R . \overset{-}{C}OO$. On account of these equilibria it is unlikely that any undissociated ampholyte would remain as such in a solution, the solution being constituted of ions or " Zwitterions."

The acidic nature of the cations may be represented by the following reaction :—

$$\overset{+}{N}H_3 . R . COOH \rightleftharpoons \overset{+}{N}H_3 . R . \overset{-}{C}OO + H^{\cdot}$$

and the basic nature of the anions by

$$HO . NH_3 . R . \overset{-}{C}OO \rightleftharpoons OH' + \overset{+}{N}H_3 . R . \overset{-}{C}OO.$$

If we denote the " Zwitterion " by Z, the cations by $A^{\cdot}$, and the anions by A', these equations may be rewritten

$$A^{\cdot} \rightleftharpoons Z + H^{\cdot}$$
$$A' \rightleftharpoons OH' + Z.$$

Hence, the acid ionisation will be governed by

$$\frac{[Z][H^{\cdot}]}{[A^{\cdot}]} = k_a$$

and the dissociation of the base, producing OH′ ions, by

$$\frac{[OH'][Z]}{[A']} = k_b.$$

Bjerrum regards k_a and k_b as the *True Dissociation Constants* of the acidic and basic groups, whereas the constants K_a and K_b, previously discussed, are merely their *Apparent Constants.*

The concentration of the "Zwitterion," [Z], of which the ampholyte in solution is chiefly composed, save for those concentrations which have entered into combination by virtue of either the acidic or basic groups, *viz.*, [A˙] and [A′], is clearly equal to the concentration of undissociated ampholyte when considered in terms of the first theory, *i.e.*, [Z] = [A]. If we multiply K_a by k_b we find that

$$K_a \cdot k_b = \frac{[H^{\cdot}][A']}{[A]} \cdot \frac{[OH'][Z]}{[A']}$$

and therefore, Bjerrum's basic constant,

$$k_b = \frac{K_w}{K_a}.$$

Similarly Bjerrum's acidic constant,

$$k_a = \frac{K_w}{K_b}.$$

If Bjerrum's constants are compared with those derived on page 209 for the hydrolysis of salts, it will be observed that k_a is also the hydrolysis-constant of a salt formed from a weak base, whose dissociation constant is K_b, and a strong acid, and that k_b is the hydrolysis-constant of a salt obtained from a strong base and a weak acid having a constant, K_a. In other words, Bjerrum's constant, k_a, refers to the hydrolytic action by means of hydrogen ions from the carboxyl-end of the "Zwitterion." Thus the action of hydrochloric acid might be represented thus:

$$\overset{-}{O}OC \cdot R \cdot \overset{+}{N}H_3 + H^{\cdot} + Cl' \rightleftharpoons HOOC \cdot R \cdot \overset{+}{N}H_3 + Cl',$$

whereas, according to the first theory, such a reaction is essentially that of the neutralisation of a base, thus:

$$HOOC \cdot R \cdot NH_2 + H^{\cdot} + Cl' \rightleftharpoons HOOC \cdot R \cdot \overset{+}{N}H_3 + Cl'$$

and is consequently controlled by K_b. Likewise k_b refers to the hydrolysis of the "Zwitterion" to form the anion carrying the free base thus:

$$\overset{-}{O}OC \cdot R \cdot \overset{+}{N}H_3 + Na^{\cdot} + OH' \rightleftharpoons Na^{\cdot} + \overset{-}{O}OC \cdot R \cdot HNOH$$

and K_a to the analogous reaction:

$$NH_2 . R . COOH + Na^{\cdot} + OH' \rightleftharpoons Na^{\cdot} + \bar{O}OC . R . NH_2.$$

For these reasons the " Zwitterion " theory provides a satisfactory explanation of the mode of dissociation of ampholytes and accounts, as equally well as the previously described theory, for the titration curves obtained.

If Bjerrum's concept be the true one, then it appears that instead of amino-acids containing very weak acidic and basic groups they must contain groups which have comparatively strong acidic and basic properties which cause the basic and acidic groups to interact with one another to form stable " Zwitterions." Thus we have seen that the ordinary constants of glycine are

$$K_a = 10^{-9.7} \text{ and } K_b = 10^{-11.6},$$

whereas by taking $K_w = 10^{-14}$ it follows that Bjerrum's corresponding constants are

$$k_b = 10^{-4.3} \text{ and } k_a = 10^{-2.4} \text{ respectively.}$$

The lower curve in Fig. 59, showing the action of hydrochloric acid, would therefore correspond to the hydrolysing action of the " Zwitterion " by the acid in liberating the ampholyte acid, of which $k_a = 10^{-2.4}$ and the upper curve corresponds to the opening-up of the " Zwitterion " by the sodium hydroxide and setting free the ampholyte base, $k = 10^{-4.3}$. If this is actually the case, then we see that Bjerrum's constants are indeed the true constants and the generally accepted constants apparent only. The theory appears to bring the strengths of acidic groups and basic groups contained in certain ampholytes into line with non-ampholyte acids and bases belonging to the different classes of derivatives.

The " Zwitterion " principle can be made a little clearer if the ionised inner salt or Zwitterion is compared with a salt such as ammonium acetate. The *p*H curve obtained on adding sodium hydroxide to ammonium acetate shows buffering and corresponds to the displacement of ammonium hydroxide, thus

$$NH_4OOC.CH_3 + NaOH \rightarrow NH_4OH + NaOOC.CH_3$$

and the hydrogen-ion concentration is governed by K_{NH_4OH}. In like manner, the addition of an alkali to a Zwitterion is considered by Bjerrum to result in the displacement of the base and the *p*H values set up to be determined by the dissociation constant of the displaced base. Thus on Bjerrum's theory the reaction with alkali involves the basic part of the ampholyte, and the alkali does not combine with the carboxyl group, as suggested by the classical theory. Similarly the reaction of an acid with an ampholyte liberates the ampholytic acid, and it does not combine with the free base considered to be present on the older theory.

Effect of Non-Aqueous Liquids on the Dissociation of Weak Bases.

Though comparatively little work has been done on the hydrogen-ion concentrations produced by acids and bases when neutralised in solutions comprising mixtures of water and organic liquids, *e.g.*, alcohol and acetone, volumetric estimations are often performed in such media. These solvents may have pronounced effects on the colour changes of indicators and also on the dissociation constants of the weak acids. Hence the *p*H values corresponding to the equivalence-points will depend on the proportion of organic liquid in the solution. Pring (*Trans. Faraday Soc.*, 1924, **19**, 705) has investigated the effect of acetone on the dissociation constants of a series of weak organic bases. The neutral point varies with the composition of the solution. Thus Pring found that pK_w of a solution of 50 per cent., by volume, of each acetone and water was 15·5, and 19·7 for a 90 per cent.

TABLE 39

DEPRESSING EFFECT OF ACETONE ON THE DISSOCIATION OF SOME WEAK ORGANIC BASES

Solvent.	pK_b in		
	Water.	50 Per Cent. Acetone. 50 Per Cent. Water.	90 Per Cent. Acetone. 10 Per Cent. Water.
Aniline	9·5	11·5	16·3
Methylaniline	9·3	11·5	16·0
Dimethylaniline	9·0	11·5	16·1
p-Nitroso-dimethylaniline . .	10·0	11·7	18·7
Glycine	11·5	12·5	—

acetone—10 per cent. water solution, compared with $pK_w = 14·1$ for pure water. Hence, the neutral points occur at *p*H 7·75, 9·85 and 7·05 respectively. The depressing effect of the non-aqueous solvent on the ionisation of some weak bases is shown in Table 39 in which is quoted some of the values obtained by Pring. The large increases in pK_b show that in every case the dissociation constants were diminished many-fold. Similar observations have been made by Richardson (*Proc. Roy. Soc.*, 1934, B, **115**, 170) in the case of weak acids in 90 per cent. acetone-water solutions.

Further information relating to the use of indicators in volumetric analysis will be found on pages 384 to 393.

CHAPTER XI

THE STANDARDISATION OF VOLUMETRIC SOLUTIONS

In addition to the usual methods of standardising volumetric solutions by means of sodium carbonate, oxalic acid, constant-boiling hydrochloric acid solution, and silver nitrate, the following reagents, mercuric oxide, borax and sulphamic acid, may also be used.

Mercuric Oxide Method.

Rosenthaler and Abelmann (*Pharm. J.*, 1913, **91**, 144) and Incze (*Z. anal. Chem.*, 1917, **56**, 177; 1918, **57**, 176) have shown that mercuric oxide dissolves in concentrated solutions of potassium iodide to liberate an exactly equivalent amount of alkali, which can be titrated by acids with methyl orange, methyl red, or phenolphthalein. This depends upon the reaction:

$$HgO + 4KI + H_2O \rightarrow K_2HgI_4 + 2KOH,$$

the accuracy of which is shown by the high *p*H of the solution so produced and the glass electrode titration curve given in Fig. 61. Owing to smaller stability of the complex anions, $HgBr_4''$ and $HgCl_4''$, considerably greater concentrations of alkali bromide or chloride are necessary to dissolve the mercuric oxide. Nevertheless, when dissolution occurs an equivalent amount of alkali is set free, which corresponds exactly with equations comparable with the one for potassium iodide.

The first section of the NaCl curve reveals that only a small portion of the NaOH was liberated in the solution, evidently owing to some alkali having entered into equilibrium with the $HgCl_4''$ anions, probably thus:

$$2NaOH + HgCl_4'' \rightleftharpoons Hg[(OH)_2Cl_2]'' + 2NaCl.$$

On the progressive addition of HCl, the free alkali is neutralised and the complex anion, $HgCl_4''$, re-formed, for it happens that the amount of HCl required to bring the solution to the change-point of methyl orange is exactly 2 equivalents. A similar explanation would also account for the slopes of the KI and KBr curves in the vicinity of the end-point. In each titration the end-point was correctly indicated by means of methyl orange, though, as the curves show, phenolphthalein gave titres that were too low.

If KI is used, only a little more than is indicated by the equation is necessary. On dissolving 0·4 gram of HgO in 10 c.c. of KI solutions, containing amounts of KI ranging from 2 to 10 grams, it was found on titration with 0·1 N-HCl that phenolphthalein yielded results which were on the average 2·5 per cent. too low, whereas methyl orange gave accurate results.

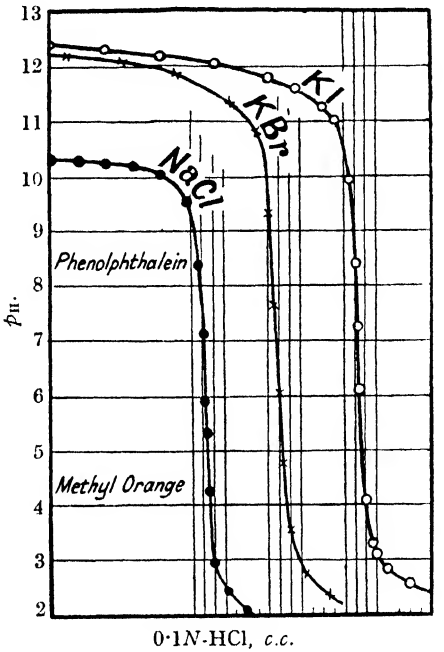


FIG. 61.—End-points in Glass Electrode Titrations of (i) 100 c.c. 0·1 M.-KI + 0·4348 gm. HgO
(ii) 100 c.c. 1·5 M.-KBr + 0·4348 gm. HgO
(iii) 100 c.c. saturated NaCl + 0·2709 gm. HgO
each with 0·1 N-HCl.
(Britton and Wilson, *J. Chem. Soc.*, 1933, 9.)

HgO also dissolves in KCN aq. with quantitative liberation of KOH: $HgO + 4KCN + H_2O \rightarrow 2KOH + K_2Hg(CN)_4$. The validity of this reaction has been proved by glass electrode titrations with HCl, but, owing to the excess of KCN present, and the fact that the replacement reaction of HCN by HCl takes place between *p*H 11·3 and 7·3, the inflexion produced on the neutralisation of the liberated alkali is not sufficiently well-defined to permit of its accurate estimation by glass electrode titration.

Borax Method.

Borax in solution gives a solution of half-neutralised boric acid and has therefore a pH = pK = 9·2. On adding hydrochloric acid all the boric acid is liberated soon after pH 7·2, when the solution immediately becomes acidic. This change is indicated by a sudden inflexion in the HCl-pH curve, the mid-point being indicated by methyl red. When using 0·1 M.-HCl, Hurley (*Ind. Eng. Chem., Anal. Edn.*, 1936, **8**, 220; 1937, **9**, 237) has found that the precise equivalence point is obtained by matching with a colour standard, prepared by adding 5 drops of methyl red to 70 c.c. of a solution containing 1 gram of NaCl and 2·2 grams of boric acid in 500 c.c. of water.

The difficulty appears to be in obtaining borax with a definite water content. He prepares $Na_2B_4O_7,10H_2O_7$ by crystallisation below 55° C. from a solution of 15 grams of borax per 50 c.c. of water. The crystals are dried by washing twice with alcohol, followed by two washings with ether; each washing being followed by suction. The remaining ether is removed either by drying in open air—under ordinary conditions the crystals may be left exposed to the air for a week—or by Menzel's method, which consists of spreading the crystals on a watch-glass and placing in a desiccator over a solution saturated with respect to both sugar and salt. Dry re-crystallised borax may be stored in tightly stoppered bottles for as long as a year without suffering loss in water of hydration greater than 0·1 per cent.

Sulphamic Acid Method.

Hoffmann and Bielsalski (*Ber.*, 1912, **45**, 1394) first suggested that sulphamic acid might serve as an acidimetric standard. The acid is a stable, crystalline solid (m.pt. 205° C.) and in aqueous solution it is largely ionised. Cupery (*Ind. Eng. Chem.*, 1938, **30**, 627), Butler, Smith and Audrieth (*Ind. Eng. Chem., Anal. Edn.*, 1938, **10**, 690), have carried out glass electrode titrations of sulphamic acid with sodium and barium hydroxide and found that its strength is comparable with that of sulphuric acid. Although many indicators are suitable, bromothymol blue is to be preferred, for its colour change occurs almost exactly at the equivalence point from yellow at pH 6·4 to blue at pH 7. Sulphamic acid can now be procured commercially and provides an excellent standard.

CHAPTER XII

ABNORMAL ACIDS

A NUMBER of oxides, such as silica, tungsten and molybdenum trioxides, vanadium pentoxide, possess definite acidic properties and form normal salts, yet they exhibit abnormal changes in *p*H during neutralisation. Thus the existence of sodium tungstate, Na_2WO_4, would seem to indicate that tungstic acid is a dibasic acid comparable with sulphuric acid and chromic acid. This, however, is not the case, as will be shown in this chapter.

Silicic Acid.

Although the reaction of silicic acid with alkalis has received some study in recent years by measurements of the hydrogen-ion concentrations of solutions of silicic acid in sodium hydroxide (Bogue, *J. Amer. Chem. Soc.*, 1920, **42**, 2575 ; Joseph and Oakley, *J. Chem. Soc.*, 1925, **127**, 2814 ; Harman, *J. Physical Chem.*, 1926, **30**, 1100 ; Hägg, *Z. anorg. Chem.*, 1926, **155**, 20), there still remains much uncertainty as to the actual manner in which the acid ionises, and, moreover, the results hitherto recorded do not give a complete account of the variation in hydrogen-ion concentration throughout the course of neutralisation at 18°. Hägg states that, if silicic acid is not colloidal, K_1 of metasilicic acid is of the order of 10^{-9} and K_2 about 10^{-13}. The curve given in Fig. 146 on page 277, Vol. II, shows the change in hydrogen-ion concentration when 100 c.c. of a solution 0·0929 N with respect to NaOH and 0·0224 M. with respect to SiO_2, were titrated at 18° with 0·0973 N-hydrochloric acid. The ratios of Na_2O to SiO_2 present in the solution at the different stages of neutralisation are indicated on the curve. Two inflexions occurred in that portion corresponding to the addition of 2 equivalents of sodium hydroxide to 1 molecule of silicic acid, and the point corresponding to half-neutralisation of metasilicic acid, *i.e.*, $Na_2O,2SiO_2$, lies just at the beginning of the second inflexion at *p*H 10·4. As other workers have shown, the ionisation of silicic acid cannot be represented satisfactorily in terms of two dissociation constants ; moreover, the titration curve is not typical of a dibasic acid inasmuch as when K_1 and K_2 are widely different the point corresponding to half-neutralisation should lie somewhere about the middle of

the second inflexion—in Fig. 146 it should be near the point corresponding to *p*H 11. The curve, however, shows that silicic acid enters into some kind of combination with sodium hydroxide, and it gives some idea of the hydrogen-ion concentrations that are thereby set up. It also shows that the hydrogen-ion concentration imparted by silicic acid to a solution is much too small to have any effect on the methyl orange end-point, and hence the reason why the alkali present in a silicate solution may be titrated by using such an indicator.

Tungstic and Molybdic Acids.

As tungsten and molybdenum appear in the same group of the periodic classification as sulphur and chromium, it might be expected that the acids corresponding to the sexavalent oxides would bear some similarity to one another.

Anhydrous tungstic oxide is insoluble in water, whilst the solubility of molybdic acid is extremely small. Crystalline hydrated forms of these two oxides can be prepared which are fairly soluble in water. Thus Dr. Bevan in the author's laboratory has prepared $MoO_3,2H_2O$ and a hydrated tungstic oxide, the composition of which agreed closely with $4WO_3,9H_2O$, although it is quite possible that it was essentially $WO_3,2H_2O$, the extra $1/4$ H_2O per WO_3 being adsorbed. The *p*H values, measured with the glass electrode, of their solutions were quite low, as shown in Table 40.

TABLE 40

*p*H VALUES OF SOLUTIONS OF MOLYBDIC AND TUNGSTIC ACIDS

MoO_3 g.-mols./litre . .	0·2	0·1	0·05	0·025	0·0125
*p*H	1·53	1·69	1·93	2·12	2·33
α	0·29	0·40	0·48	0·60	0·75
WO_3 g.-mols./litre . .	0·104	0·052	0·026	0·013	0·0065
*p*H	1·61	1·76	1·99	2·26	2·53
α	0·47	0·67	0·79	0·84	0·92

The degree of ionisation, α, was calculated on the assumption that the acids, $H_2[O(MoO_3)_4]$ and $H_2[O(WO_4)_4]$, were present in the respective solutions. Direct glass electro-titrations with sodium hydroxide gave curves similar to those of the back-titrations in Fig. 62. The incidence of the first inflexion, *viz.*, with 0·5 equivalent of NaOH per molecule of MoO_3 (WO_3), confirms that such polyacids actually do exist in solution. Bevan has also shown that the reaction which occurs when the next 1·5 equivalents of alkali are added, *i.e.*, the amount required to

convert $Na_2[O(MoO_3)_4]$ into Na_2MoO_4 is governed by the ionic equilibrium :

$$O(MoO_3)_4'' + 3H_2O \rightleftharpoons 4MoO_4'' + 6H^{\cdot}$$

the dissociation constant being approximately 10^{-37}. There is good reason to believe that a similar reaction is involved in the formation of sodium tungstate from sodium tetratungstate. It should be mentioned, however, that the latter process does not take place spontaneously, for immediately 0·5 equivalent of alkali is added to an aqueous solution of tungstic acid the solution

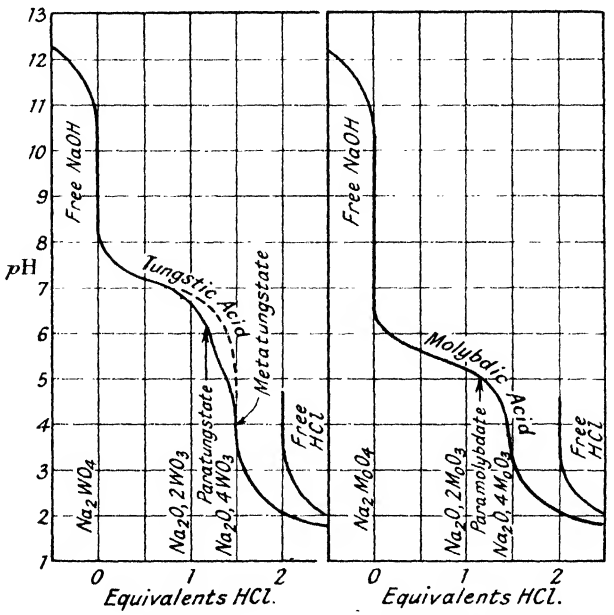


FIG. 62.—Titration of Alkaline Solutions of Tungstate and Molybdate.

becomes quite alkaline, the inflexion extending upwards on further addition of sodium hydroxide to beyond *p*H 10 and the solution continuing to be appreciably alkaline despite the fact that the requisite amount of alkali to form the normal tungstate may not have been added. Boiling, however, or long standing after each addition of alkali causes the change in *p*H suggested by Fig. 62, which gives the back-titration curves of alkaline tungstate and molybdate solutions with hydrochloric acid. The curves were obtained by Britton and German (*J. Chem. Soc.*, 1930, 1249). The broken line refers to the *p*H values immediately set up,

whereas the continuous line indicates the *p*H values after equilibrium had been reached. This point is important in connexion with the volumetric method of estimating tungstic oxide using phenolphthalein, for unless the titration is carried out at 100° erroneous results will be obtained.

Vanadic Acid.

Vanadic acid behaves in an entirely anomalous way. This has been demonstrated by the work of Britton and Robinson (*J. Chem. Soc.*, 1930, 1261; 1932, 1955) and of Britton and Welford (*ibid.*, 1940, 764).

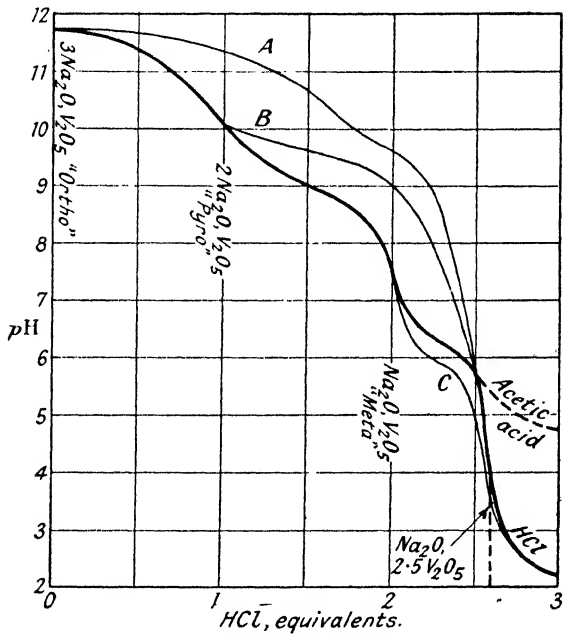


FIG. 63.—Glass Electrode Titrations of Sodium Vanadate Solutions. (Britton and Robinson.)

Fig. 63 illustrates the *p*H change, as measured by the glass electrode (both the hydrogen and quinhydrone electrodes being unsuitable owing to reduction) of solutions of vanadium pentoxide in sodium hydroxide. The heavy curve represents the effect of adding increasing amounts of hydrochloric acid at 18°, boiling until the yellow solutions had become colourless—a few minutes—and cooling to 18° again before making the *p*H determination. It should be emphasised, however, that solutions to

which two or more equivalents of acid had been added, *i.e.*, when the solute had become that of the so-called sodium metavanadate, $NaVO_3$ or Na_2O,V_2O_5, no amount of boiling yielded colourless solutions. They continued to remain yellow. As shown by Britton and Welford, an exactly similar undulating curve can be obtained at 90° by carrying out the titration with alkali with the glass electrode or by carrying out a direct titration of a solution of vanadium pentoxide, which, owing to the very sparing solubility of V_2O_5 in water, was very dilute.

The curve and inflexions corresponding with the formation of sodium pyrovanadate, $2Na_2O,V_2O_5$ or possibly $Na_4V_2O_7$, and of sodium metavanadate, Na_2O,V_2O_5 or $NaVO_3$, suggest that in these respects vanadic acid is comparable with phosphoric acid, and that the vanadates formed by the combination of 1 molecule of V_2O_5 with 2 molecules of Na_2O and 1 molecule of Na_2O might, indeed, be Na_2HVO_4 and NaH_2VO_4 respectively. Hence the salt formed with 3 molecules of Na_2O and 1 molecule of V_2O_5 might be regarded as the normal sodium orthovanadate, Na_3VO_4. The two sections of the curve corresponding to the reaction of 1 to 3 molecules of Na_2O with 1 molecule of V_2O_5 suggest that the stages of ionisation involved are

$$H_2VO_4' \rightleftharpoons H^{\cdot} + HVO_4''$$

and

$$HVO_4'' \rightleftharpoons H^{\cdot} + VO_4''',$$

K_{a_2} being *ca.* 10^{-9} and K_{a_3} about $10^{-11.5}$. This view, however, is not confirmed by measurements made on solutions of different concentrations when variable values of the constants are obtained.

An abnormal inflexion appears when the solute has become $Na_2O,2{\cdot}5V_2O_5$; thereafter the solution becomes strongly acidic and, unless a relatively high concentration of alkali vanadate has been used, no precipitate of vanadium pentoxide is obtained. Instead, the V_2O_5 remains in solution as the salt of strong poly-vanadic acid, $Na_2O,2{\cdot}5V_2O_5$. The direct glass electro-titration of an aqueous solution of vanadic acid confirms that it functions as a very strong acid, which in its simplest form might be regarded as $H_2O(V_2O_5)_{2.5}$. In the presence of sufficient amounts of strong acids, such as hydrochloric and sulphuric, vanadium pentoxide assumes weak basic properties and then is retained in solution (*vide* Britton and Welford, *J. Chem. Soc.*, 1940, 895).

Aqueous solutions of vanadic acid on neutralisation with alkali give a well-defined inflexion when sufficient alkali is added to form $Na_2O,2{\cdot}5V_2O_5$. If the titration is carried out at 18° this inflexion extends up into the extreme alkaline range, but, if either considerable time is allowed or else the solution is boiled,

the *p*H value falls to a value indicated by the heavy curve in Fig. 63. Until this has occurred the solution continues to remain yellow. Curves A and B represent the *p*H values immediately set up when acid is added to cold solutions of alkali vanadates, $3Na_2O,V_2O_5$ and $2Na_2O,V_2O_5$ respectively; both solutions having previously been boiled and cooled and were therefore colourless. Unlike the solutions represented by the heavy curve, these solutions became yellow immediately on the addition of a little hydrochloric acid and remained so throughout the back-titrations. The *p*H values were unsteady and fell somewhat on allowing the solutions to stand for some time. There appears to be no doubt that the yellow colour is to be attributed to the existence in the solutions of the yellow alkali polyvanadate, $Na_2O,2{\cdot}5V_2O_5$, or the free polyvanadic acid, $H_2O,2{\cdot}5V_2O_5$.

The broken curve in Fig. 63 illustrates the final section of the back-titration curve with acetic acid. Owing to the weakness of acetic acid compared with that of polyvanadic acid, it is seen that acetic acid does not readily set up *p*H 4 at which the heavy curve indicates that the 1 : 2·5 polyvanadate is formed, unless, of course, relatively large amounts of acetic acid are added.

The titration curves with acetic acid are of interest in considering the crystallisation of polyvanadates from solutions of the metavanadates acidified with acetic acid under different conditions. A large number of alkali-metal polyvanadates have been described, but the existence of so many separate compounds is very doubtful. It is remarkable, however, that Lachartre (*Bull. Soc. chim.*, 1924, **35**, 321) isolated the ammonium 2 : 3-vanadate by the action of 4 per cent. acetic acid on the 1 : 1-vanadate, whereas 10 per cent. acetic acid yielded the 1 : 3-salt. Similarly, Ditte (*Compt. rend.*, 1887, **104**, 1061) obtained the sodium 2 : 3-vanadate from the 1 : 1-vanadate acidified with small quantities of acetic acid, and Rammelsberg (*Wied. Ann.*, 1883, **20**, 934) found that a large excess of acetic acid was required to form the 2 : 5-salt. Similar principles explain the observation of Friedheim and Michaelis (*Z. anorg. Chem.*, 1893, **5**, 441), that, according to the amount of sodium dihydrogen phosphate added to a solution of sodium 1 : 1-vanadate, the 4 : 7- or the 5 : 8-compound can be crystallised.

As vanadium pentoxide is so very sparingly soluble in water direct titration of the resulting very dilute solution with alkali is a matter of some difficulty. However, such a solution has been prepared by Britton and Welford and titrated with the glass electrode at a series of temperatures ranging from 15° to 90°. The curves, which refer to the titration of 50 c.c. of 0·00193 *M*-V_2O_5 solution with 0·01158 *N*-NaOH, are given in

Fig. 64. In order to make the curves directly comparable with one another at the various temperatures, they are plotted in such a way that the appropriate ordinates are so adjusted that they extend over the same ranges of acidity and alkalinity. This would not have been the case if all the curves had been plotted

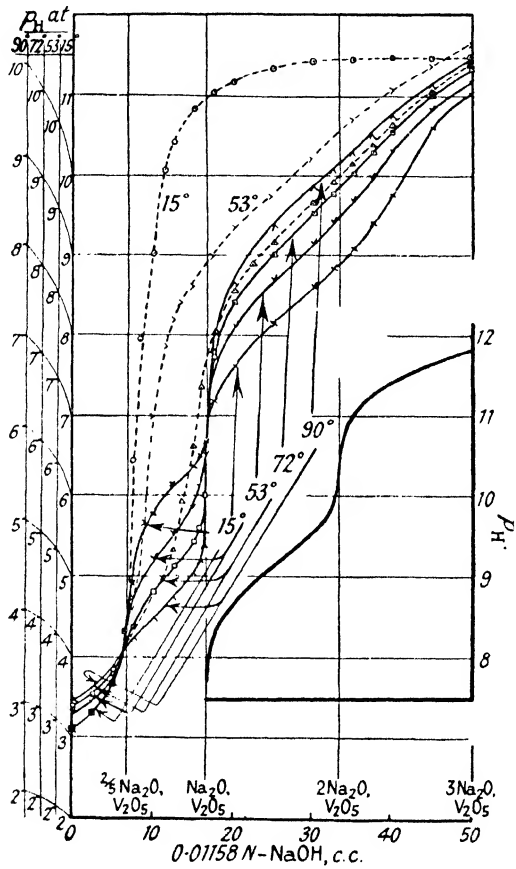


FIG. 64.—Glass Electrode Titrations of 50 c.c. of 0·00193 M-V_2O_5 with 0·01158 N-NaOH at 15°, 53°, 72° and 90° C.

with respect to the same pH ordinate, because, owing to the considerable increase in K_w with temperature (page 53), the pH range covering the variations from say $[H^{\cdot}] = 1$ to $[OH'] = 1$ is much greater at 0° than at 100°: at 0° such a range would be indicated by 14·9 pH units with neutrality at pH 7·45, whereas at

100° it is represented by 12·2 *p*H units with neutrality at *p*H 6·10. The horizontal scale lines in Fig. 64 refer to 15°, and the positions of the ordinates at higher temperatures were ascertained from the appropriate values of K_w.

The continuous curves represent the *p*H values which were reached at the respective temperatures only after prolonged standing, or almost instanteously after boiling and then cooling. The broken lines indicate the *p*H values obtained immediately after each addition of alkali and stirring. The initial branches reveal that the acid, $H_2[O(V_2O_5)_{2\cdot5}]$, exists in solution of vanadium pentoxide, for well-defined inflexions occur on the addition of 0·4 mol. Na_2O per mol. of V_2O_5 dissolved. Calculation from the *p*H values of the aqueous solutions show that the polyvanadic acid is strong: its degree of ionisation at 5° C. is 58 per cent. and 71 per cent. at 89°. The immediate titrations, illustrated by the discontinuous lines at 15° and 53° give some idea of the difficulty with which alkali reacts with the complex polyvanadate anion.

A somewhat surprising property of solutions containing Na_2O and V_2O_5 in equimolar proportions (*i.e.*, corresponding with NaH_2VO_4) is that, after they have been rendered colourless, either by ageing or by boiling, they react immediately with alkali to give *p*H values that remain unchanged after subjection to boiling or ageing. For instance, the *p*H curve, inset in Fig. 64, represents a glass electrode titration of 100 c.c. of

0·01 *M*-NaH_2VO_4 with alkali at 18°.

Niobic and Tantalic Acids.

Both niobium and tantalum pentoxides are very insoluble in water. On the other hand, when fused with potassium or sodium hydroxide they form salts, which are soluble in water. Crystallisation from such solutions yields complex niobates and tantalates, *e.g.*, $K_8Nb_6O_{19},16H_2O$, $Na_7Ta_5O_{16}$. Britton and Robinson (*J. Chem. Soc.*, 1932, 2265; 1933, 419) have carried out hydrogen electrode titrations of solutions of alkali niobates and tantalates with hydrochloric acid and also with acetic acid, oxalic acid and various hydroxy acids.

Strong and moderately strong acids precipitate the pentoxides readily, acetic acid precipitates tantala but not niobia, whilst oxalic, lactic, tartaric, and malic acids retain both these oxides in solution. Russ (*Z. anorg. Chem.*, 1902, **31**, 42) found that, in contrast with the slight solubility of tantala, niobia is appreciably soluble in oxalic acid solutions; he attributed this to the different behaviours of the oxalo-acids formed.

Fig. 65 illustrates the variation in *p*H as hydrochloric acid was gradually added to potassium niobate and tantalate solutions. Immediately hydrochloric acid was added to the niobate solution a milkiness was produced, but actual coagulation did not occur until about one-half of the theoretical quantity had been added. Precipitation was complete when the total quantity of acid was added.

The fact that the tantalum curve indicates that higher *p*H values prevailed than was the case in the niobate titration

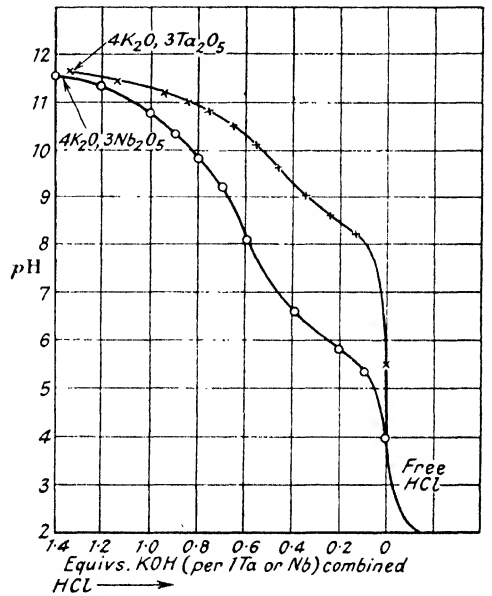


FIG. 65.—Hydrogen Electrode Titrations of Potassium Tantalate and Niobate with Hydrochloric Acid.

shows that the acidic nature of tantalic acid is less pronounced than that of niobic acid. Furthermore, tantalum pentoxide separated as a flocculent white precipitate as soon as a little hydrochloric acid was introduced. This was at *p*H 11·6, whereas niobium pentoxide does not begin to precipitate appreciably until *p*H 8 is reached. When approximately decinormal solutions of the following acids: monochloroacetic, formic, lactic, acetic, oxalic, tartaric, malic and citric, were used, the variations in *p*H were the same as those which would have been set up if hydrochloric acid had been employed as far as the decomposition of the alkali niobate or tantalate is concerned.

The comparatively strong acids, formic and monochloroacetic, caused almost immediate precipitation, but the weaker acids, acetic and phenylacetic, whilst precipitating the tantalic acid from the alkaline solutions, did not cause niobic acid to precipitate until slightly more than the stoicheiometrical amount of acid had been added when the *p*H had fallen to *ca.* *p*H 5. Until then the solution remained perfectly clear.

This difference in the *p*H range required for the precipitation of tantala, *viz.*, above *p*H 8, and that for niobia, below about *p*H 5, when effected by weak acids, is evidently the explanation of the method investigated by Weiss and Landecker (*Z. anorg. Chem.*, 1909, **64**, 65), Foote and Langley (*Chem. News*, 1911, **103**, 103), Hauser and Lewite (*Z. angew. Chem.*, 1912, **25**, 100), in which tantala is precipitated from alkaline solution by passing carbon dioxide, whereas niobia remains in solution. (See, however, Schoeller, "The Analytical Chemistry of Tantalum and Niobium," London, 1937, p. 4). A difficulty sometimes encountered in the separation of gelatinous precipitates such as hydrated niobia and tantala is the so-called loss in individuality of one or both of the hydroxides which occurs when they are present in solution together. This has been found by the author in certain separation processes that have been introduced for the separation of alumina from beryllia. The result is that although a reagent may not precipitate beryllia from a solution in the absence of aluminium, it does so in its presence. Schoeller finds that this is the case of niobia in the presence of tantala when an alkaline solution of the two earths is treated with carbon dioxide.

Neither oxalic acid nor the hydroxy acids caused any precipitation from the niobate or tantalate solutions even when they had become distinctly acid in reaction. Calculation also showed that the presence of Nb_2O_5 and Ta_2O_5 in the oxalic acid solutions affected the second stage of ionisation of the added excess of oxalic acid, inasmuch as the second dissociation constant was lowered, the precise extents depending on the relative amounts of earth-oxide present. No effect was observed on the primary stage of ionisation. This was also confirmed by hydrogen electrode titrations of oxalic acid solutions of niobia.

A *p*H titration of an oxalic acid solution of Ta_2O_5 was made, but, probably owing to the relatively small solubility of that oxide in the acid, the amount dissolved was such as to have no perceptible effect on the *p*H values set up throughout the whole neutralisation. To dissolve 0·3 gram of Ta_2O_5, a solution containing no less than 9 grams of $(CO_2H)_2,2H_2O$ was necessary. The solution titrated contained 0·015 gram of Ta_2O_5 and 0·45 gram

of $(CO_2H)_2,2H_2O$, *i.e.*, 52·6 molecules of acid to 1 molecule of Ta_2O_5. Addition of NaOH did not cause precipitation.

Similar observations were made with tartaric and malic acid solutions, but the effect of K_2 was not so marked. Lactic acid, however, whilst yielding clear solutions when added to alkali niobate and tantalate, appeared to be uninfluenced by the presence of the oxides as far as its dissociation constant was concerned.

Russ claims to have isolated alkali complex oxalo-niobates of the general formula :

$$3R_2O,Nb_2O_5,6C_2O_3,xH_2O$$

R being Na, K, NH_4, and from an application of the empirical basicity rule of Ostwald he concluded that in solution the complex salt was hexabasic. As the complexity of the salt is now shown to be intimately connected with some reaction between Nb_2O_5 and hydrogen ions originating from the second stage of ionisation of oxalic acid, it is reasonable to consider its formation as the result of interaction shown by the equation :

$$6KHC_2O_4 + Nb_2O_5 \rightarrow 6K^{\cdot} + \left[\begin{matrix}Nb_2 & O_2 \\ & (C_2O_4)_6\end{matrix}\right]'''''' + 3H_2O.$$

Such an interaction between the HC_2O_4' and niobia would also account for the effect which the earth has on the second stage of ionisation of oxalic acid. The progressive addition of a strong acid causes the niobia gradually to be released from the complex anion, and although its precipitation does not actually ensue there is no doubt that the solution becomes increasingly colloidal and therefore unstable.

Note on Schoeller and Powell's Method of Separating Tantalum from Niobium (*op. cit.*) *Analyst*, 1925, **50**, 485 ; 1932, **57**, 750.

This method depends on the difference in the stability of ammonium oxalate solutions of tantalum and niobium pentoxides, which are obtained by treating a mixture of the oxides with a boiling solution of ammonium oxalate. As stated above, niobic acid is much more readily soluble in oxalic acid and its salts than tantalic acid. Neither of the oxides is precipitated, however, with alkali or ammonia. If, however, a solution of tannin is carefully run into the boiling solution, a yellow coloration results if the amount is sufficient to affect the tantala only, but if greater amounts are inserted when the tannin becomes associated with the niobia, the colour changes through orange to red, depending on the relative amounts of tannin and niobia present. Fractional precipitation is carried out from solutions to which varying

amounts of tannin have been added, the amounts being regulated by the colorations which they produce. Thus in the yellow solutions tantala is most susceptible to precipitation, and its flocculation is effected by adding 30–50 c.c. of saturated ammonium chloride solution to the boiling solution, and in addition it is sometimes necessary to add small amounts of ammonium hydroxide. The Ta_2O_5-tannin complex precipitate is yellow.

The niobia left in solution is precipitated by adding enough tannin to produce a red coloration, and then adding a small excess of ammonia. The Nb_2O_5-tannin precipitate is red.

The method of precipitation is thus seen to be one of the mutual coagulation of tannin and the colloidal oxide, which is facilitated by the added ammonium chloride. Whereas the Ta_2O_5-tannin precipitate, owing to the relatively greater instability of the oxalo-tantalic acid complex, can be obtained from a solution buffered by ammonium oxalate at about *p*H 5, the Nb_2O_5-tannin precipitate does not separate until the solution has been rendered ammoniacal. The *p*H then set up corresponds to a state of maximum instability of the oxalo-niobic acid complex. An attempt was made by Britton and Robinson to ascertain the *p*H ranges within which the two oxides become precipitable, but it was found that the *p*H was largely dependent upon the amounts of tannin employed.

Basic Molybdates and Tungstates.

Claims have been made that the three alkali molybdates (the normal molybdate, Na_2MoO_4; the paramolybdate, $Na_2O,2{\cdot}33MoO_3$; and the metamolybdate, $Na_2O,4MoO_3$) react with solutions of salts of the heavy metals and thereby precipitate by simple double decomposition the corresponding molybdates (see, for example, Abegg's *Handbuch der anorganischen Chemie*, 1921, IV, (I), (ii), pp. 577, 578, 636). Britton and German (*J. Chem. Soc.*, 1931, 1429) have followed the reactions of the three sodium molybdates with very dilute solutions of salts of typical metals with the quinhydrone electrode. Their results are illustrated in Table 41, which gives the *p*H at which precipitates began to form, together with their composition.

Although the *p*H of sodium molybdate solutions is slightly above 7, a perusal of Fig. 65 on page 231 shows that the smallest reaction with an acid causes the *p*H to fall to about *p*H 6·5, whilst further reaction produces buffer action between *p*H 6 and 5. When sodium molybdate is allowed to react with beryllium salt solutions no precipitates are formed despite the fact that alkali causes precipitation at *p*H 5·69. This is to be attri-

TABLE 41

Solution.	Na_2MoO_4		$Na_2O,2{\cdot}33MoO_3$		$Na_2O,4MoO_3$		NaOH
	*p*H	Ppt.	*p*H	Ppt.	*p*H	Ppt.	*p*H.
$ZrCl_4$	1·75	?	1·74	$\{ZrO_2, 0{\cdot}86\ MoO_3\}$	1·75	?	1·86
$ThCl_4$	3·02	$\{ThO_2, 2{\cdot}07\ MoO_3\}$	3·00	$\{ThO_2, 2{\cdot}21\ MoO_3\}$	2·97	$\{ThO_2, 2{\cdot}82\ MoO_3\}$	3·51
$Al_2(SO_4)_3$	4·39	$\{Al_2O_3, 2{\cdot}61\ MoO_3\}$	No ppt.		No ppt.		4·14
$CuSO_4$	5·28	$\{CuO, 0{\cdot}70\ MoO_3\}$	,,	,,	,,	,,	5·20
$Cr_2(SO_4)_3$	4·54	$\{Cr_2O_3, 2{\cdot}80\ MoO_3\}$	,,	,,	,,	,,	5·34
$BeSO_4$	No ppt.		,,	,,	,,	,,	5·69
$NiSO_4$	,,	,,	,,	,,	,,	,,	6·66
$MgSO_4$	,,	,,	,,	,,	,,	,,	10·50

buted to the peculiar property of beryllium of forming " soluble basic salts," thus permitting the alkali molybdate to be decomposed partly and consequently to set up a *p*H lower than *p*H 5·69. The failure to reach the hydroxide precipitation *p*H values of nickel and magnesium also explains the absence of precipitation. Similar remarks apply to the reactions of the paramolybdate and metamolybdate with salt solutions of aluminium, copper, chromium, beryllium, nickel and magnesium in failing to effect precipitation.

Table 41 shows that the three reactants yielded precipitates with solutions of thorium chloride at *p*H 3·00, instead of at the hydroxide precipitation *p*H of 3·5. Thorium molybdate, $Th(MoO_4)_2$, is a comparatively insoluble salt, and from the compositions shown in Table 41, it is clear that the precipitation of much normal molybdate, in conjunction with some polymolybdate, was responsible for the low *p*H. In the case of the precipitate obtained from chromium sulphate solution with sodium molybdate analysis indicated that it contained Cr_2O_3 to MoO_3 in the ratio of 1 : 2·8. Here the low *p*H at which precipitation occurred would suggest that the precipitate was a mixture of $Cr_2(MoO_4)_3$ and a small amount of basic chromium molybdate. The buffering between *p*H 5·2 and 6·5, when an excess of sodium molybdate was added, confirms the precipitation of some basic molybdate.

The compositions of the precipitates obtained by using sodium paramolybdate and sodium metamolybdate indicate that they are not the respective compounds of the heavy metals.

As Britton and German (*J. Chem. Soc.*, 1931, 703) have also shown, similar reactions occur with sodium tungstate, paratungstate and metatungstate. Using either of the polytungstates there is a tendency for the precipitates to contain relatively higher proportions of tungstic oxide to the oxide of the heavy metal. These amounts, however, are not large enough to show that double decomposition takes place. It is possible that the higher contents of tungstic oxide are to be attributed to the greater instability of polytungstic acid, $H_2O(WO_3)_4$, at low *p*H values and especially in solutions from which precipitates separate. This would tend to cause co-precipitation of tungstic oxide and the heavy metal tungstate, or maybe, basic tungstate. For obvious reasons, precipitation does not occur with either of the three reactants from nickel and magnesium salt solutions.

Vanadates and Basic Vanadates.

It was shown on page 228 that in solutions which have been boiled there is good reason to believe that the three vanadates, *viz.*, sodium orthovanadate, $3Na_2O,V_2O_5$ or Na_3VO_4, the so-called sodium pyrovanadate, $2Na_2O,V_2O_5$ or $Na_4V_2O_7$ or Na_2HVO_4, and the so-called metavanadate, Na_2O,V_2O_5 or $NaVO_3$ or NaH_2VO_4, are formed. The *p*H of sodium orthovanadate solutions is somewhat higher than 12, that of the pyrovanadate solution in the region of *p*H 10, and *p*H 7·5 in the case of alkali metavanadate solutions. It would therefore appear that sodium orthovanadate should precipitate a basic vanadate from magnesium salt solutions, whereas neither the pyrovanadate nor the metavanadate are able to set up *p*H values as high as *p*H 10·5, and consequently they should be unable to cause precipitation of basic vanadates. If, however, the three sodium vanadates were salts of three distinct vanadic acids, then it is possible that the corresponding insoluble vanadates might be obtained, at least in the case of certain metals. In reacting with solutions of salts of metals which do not form such insoluble vanadates, precipitation is governed by the ability to reach the appropriate " hydroxide *p*H," whereas insoluble normal vanadates precipitate at lower *p*H values.

Fig. 66 refers to a series of glass electrode titrations carried out by Britton and Robinson (*J. Chem. Soc.*, 1933, 512) of typical metallic salt solutions given in Table 42 with 0·1 N-solutions of the three sodium vanadates (*i.e.*, 0·1 N with respect to Na). Precipitation began at *p*H values that were approximately those at which the corresponding metallic hydroxides would normally separate. The ratios V_2O_5/(Metal oxide) at this stage

are lower than those (in parentheses) which would have been found if the respective vanadates had been precipitated. The V_2O_5 contents of the precipitates obtained in the pyro- and meta-vanadate titrations of the acid solution of mercurous nitrate were,

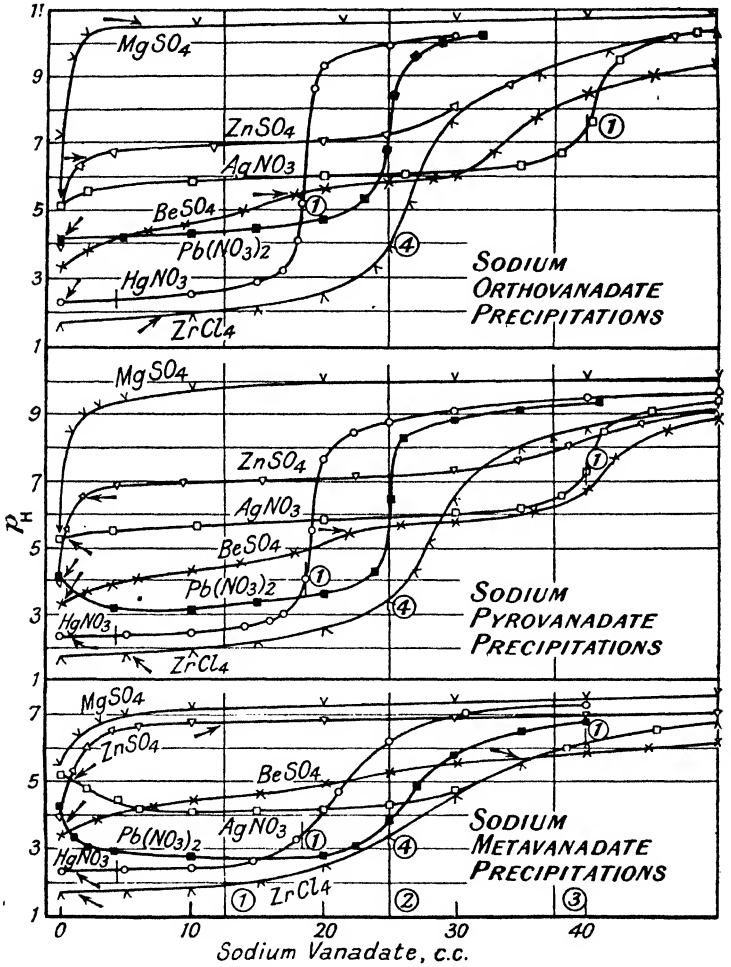


FIG. 66.—Precipitation of Vanadates.

however, slightly higher, probably owing to the action of the excess HNO_3 on the precipitant. The ratios in the Mg and Be titrations correspond to precipitates formed by twice the stoicheiometrical amount of titrant, and those for the remaining tirtations

were obtained from analyses of the precipitates when exactly theoretical amounts had been added.

The " hydroxide *p*H " was not reached in the pyro- and meta-vanadate titrations of $MgSO_4$; hence no precipitates were produced. In all other reactions, the respective " hydroxide *p*H " was exceeded and precipitation took place, the points at which it began being marked by arrows in Fig. 66. As a rule, it began very soon after the first few drops of alkali vanadate had been added, but in the Be titrations it was considerably delayed owing to the peculiar property of this metal of forming " soluble basic salts." It was also delayed in those titrations in which the particular alkali vanadate was only just able to establish the *p*H conditions for basic precipitation: *e.g.*, in the reaction of Na_3VO_4 with $MgSO_4$ the requisite *p*H was not reached until 0·56 equivalent had been added, whilst in the titration of $ZnSO_4$ with $NaVO_3$ 0·96 equivalent was necessary. In both these reactions, excess of the precipitants did not greatly raise the *p*H of the mother-liquors, and in consequence, precipitation was partial, the extents depending on the actual amounts employed. Comparison of the sections of the curves corresponding to excess of the three sodium vanadates with the vanadic acid curve in Fig. 63 on page 226, shows that the *p*H values set up tend to approach the values given by solutions of the respective vanadates. The *p*H values due to excess of the precipitants, together with any V_2O_5 remaining in solution, appear, however, to be higher than would have been the case if the solutions had been kept or boiled.

TABLE 42

TITRATION OF 100 C.C. OF METALLIC SALT SOLUTIONS BY 0·1N-SODIUM VANADATES: *p*H AND OXIDE RATIO AT PRECIPITATION

Salt.		$3Na_2O,V_2O_5$.	$2Na_2O,V_2O_5$.	Na_2O,V_2O_5.	Hydroxide pptn. *p*H.
0·0125 M.-$MgSO_4$	*p*H	10·50	no ppt.	no ppt.	10·49
	V_2O_5/MgO	0·105 (0·333)	—	—	
0·0125 M.-$ZnSO_4$	*p*H	6·63	6·72	6·74	6·80
	V_2O_5/ZnO	0·235 (0·333)	0·226 (0·5)	0·272 (1·0)	
0·0125 M.-$BeSO_4$	*p*H	5·50	5·54	5·75	5·69
	V_2O_5/BeO	0·052 (0·333)	0·100 (0·5)	0·175 (1·0)	
0·00625 M.-$ZrCl_4$	*p*H	1·85	1·79	1·70	1·86
	V_2O_5/ZrO_2	0·471 (0·667)	0·649 (1·0)	0·610 (2·0)	
0·0143 M.-$HgNO_3$ + 0·0042 M.-HNO_3	*p*H	2·5	2·5	2·5	2·5–3·0
	V_2O_5/Hg_2O	0·273 (0·333)	0·588 (0·5)	1·111 (1·0)	

Except in the Mg titrations and those of $ZnSO_4$ with ortho- and pyro-vanadate, the mother-liquors were yellow and were more intense in those reactions where precipitation occurred at

a low *p*H. Hence some of the added vanadate must have remained in solution in the form of yellow alkali polyvanadates, and, as judged from the colour produced in the more acid solutions, their composition must have approached that of the stable complex, *viz.*, $Na_2O,2{\cdot}5V_2O_5$. The colourless mother-liquors during the titrations in which precipitation occurred in the alkaline zone are due to the inability of the low concentration of $H^{\cdot}$ ions to decompose the alkali vanadates; H_3BO_3, for instance, does not cause colourless alkali vanadates to become yellow, but KH_2PO_4 readily does so. A pale yellow coloration accompanied the precipitate from $ZnSO_4$ solution with $NaVO_3$; this was due to the fact that a " basic metavanadate " was separating and some sodium polyvanadate consequently was being formed in the solution.

If the view be accepted that 1 equivalent of the H_2SO_4 in combination with $Be(OH)_2$ is loosely bound, and that this acid reacts with the alkali vanadates so as to convert them into the stable salt $Na_2O,2{\cdot}5V_2O_5$ (see Figs. 63 and 64), calculation shows that this amount of acid (12·5 c.c. of N/10) would require 14·4 c.c. of Na_3VO_4, 15·6 c.c. of $Na_4V_2O_7$, and 20·8 c.c. of $NaVO_3$; *i.e.*, these amounts of titrant would set up a *p*H of 4 and therefore more alkali vanadate would be necessary before *p*H 5·7 [the precipitation *p*H of $Be(OH)_2$] could be reached. Precipitation actually occurred when 18, 22, and 35 c.c. of the respective alkali vanadate had been added.

Fig. 66 also gives curves representing the *p*H changes during the precipitation of definite vanadates from silver nitrate and lead nitrate solutions. In each titration, precipitation occurred below the respective " hydroxide *p*H." For the Ag titrations 100 c.c. of 0·01 M.-$AgNO_3$ were titrated with 0·025 N- solutions of the three sodium vanadates. Ag_3VO_4 was precipitated between *p*H 5·8 and 6·5, $Ag_4V_2O_7$ at *p*H 5·5–6·0 and $AgVO_3$ at *p*H 4·25–4·75. Carrière and Guite (*Compt. rend.*, 1937, **204**, 1339; *Ann. chim. anal.*, 1938, **20**, 181) find that silver nitrate precipitates $AgVO_3$ from vanadate solutions adjusted to *p*H 4·0–4·6 with acetic acid.

The Pb curves refer to the reactions of 0·1 N-alkali vanadate with 100 c.c. of 0·0125 M.-$Pb(NO_3)_2$. $Pb_3(VO_4)_2$ was precipitated at *p*H 4·2, $Pb_2V_2O_7$ at *p*H 4–3·2, $Pb(VO_3)_2$ at *p*H 3·8–2·8. Carrière and Guite have shown that lead acetate precipitates $Pb_3(VO_4)_2$ quantitatively from acetic solutions of alkali- or ammonium vanadates between *p*H 4·3 and 5.

Methods of estimating vanadic acid as $AgVO_3$ and Ag_3VO_4 have been described by Browning and Palmer (*Amer. J. Science*, 1910, **30**, 220) and Moser and Brandl (*Monatsh.*, 1929, **51**, 169)

respectively. The first method consists of rendering a nitric acid solution of vanadium pentoxide alkaline with ammonia, boiling until the solution becomes faintly yellow, thereby indicating that the solution contains NH_4VO_3, and precipitating then with silver nitrate. Britton and Robinson confirmed the quantitative precipitation of $AgVO_3$. Moser and Brandl's method aims at producing orthovanadate-ions by means of sodium acetate and a little concentrated ammonia solution before adding silver nitrate and completing precipitation as Ag_3VO_4 by boiling for half an hour. Whilst most of the vanadate is precipitated as Ag_3VO_4 Britton and Robinson found that low results were invariably obtained through the precipitation of some $Ag_4V_2O_7$.

CHAPTER XIII

THEORY OF THE IONISATION OF DIBASIC AND POLYBASIC ACIDS

THE views relating to the acidity of dicarboxylic acids held at the present time appear to be those which were first enunciated by Ostwald (*Z. physikal. Chem.*, 1892, **9**, 553) and are based on the electrostatic charges carried by the various ions and the influence that may be exerted by virtue of the proximity of the carboxyl groups. He considered that in the ionisation of a dicarboxylic acid the negative charge carried by the anion, arising from the first dissociation, exerted a force of repulsion on the negative charge carried by the other ionised carboxyl group and that the nearer one carboxyl group was to the other the greater would be this repulsive force, which would therefore tend to prevent the ionisation proceeding to the second stage. The examples which Ostwald gave were those of fumaric and maleic acids, the relative magnitudes of their two dissociation constants thus giving excellent support to van't Hoff theory accounting for their structure.

Let us consider the ionisation of an unsymmetrical dibasic acid, such as, for example, a carboxylic benzene sulphonic acid or even salicylic acid, in which both the phenol and the carboxyl groups are able to ionise. Such an acid may be represented thus : HRR^0H.

Clearly its first stage of ionisation may take place in either or both of two ways, *viz.* :—

(i) $$HRR^0H \rightleftharpoons H^{\cdot} + {}'RR^0H,$$

(ii) $$HRR^0H \rightleftharpoons H^{\cdot} + HRR^{0\prime}$$

whence $$K_{(i)} = \frac{[H^{\cdot}][{}'RR^0H]}{[HRR^0H]}$$

and $$K_{(ii)} = \frac{[H^{\cdot}][HRR^{0\prime}]}{[HRR^0H]}$$

are the mass law expressions which govern the respective ionisation processes. It thus happens that in the experimental determination of the apparent dissociation constant, K_1, of

the first stage of ionisation, both equilibria (i) and (ii) may be involved.

$$\text{Hence} \quad K_1 = \frac{[H^+]([{}'RR^0H] + [HRR^{0'}])}{[HRR^0H]}$$

$$= K_{(i)} + K_{(ii)}.$$

It follows therefrom that the second stage of ionisation will involve the two equilibria (iii) and (iv)—

(iii) $\quad {}'RR^0H \rightleftharpoons H^+ + {}'RR^{0'}$

(iv) $\quad HRR^{0'} \rightleftharpoons H^+ + {}'RR^{0'}$

for which respectively

$$K_{(iii)} = \frac{[H^+][{}'RR^{0'}]}{[{}'RR^0H]},$$

and

$$K_{(iv)} = \frac{[H^+][{}'RR^{0'}]}{[HRR^{0'}]}.$$

But the second dissociation constant, K_2, as determined experimentally, includes both processes (iii) and (iv)—

i.e.,

$$K_2 = \frac{[H^+][{}'RR^{0'}]}{[{}'RR^0H] + [HRR^{0'}]}$$

Consequently,

$$K_2 = \frac{K_{(iii)} \cdot K_{(iv)}}{K_{(iii)} + K_{(iv)}}$$

If, however, the dibasic acid is symmetrical, *e.g.*,

$$HOOC \cdot (CH_2)_x \cdot COOH,$$

and it is assumed that each mode of ionisation, (i), (ii), (iii) and (iv), is an independent process, or in other words, is uninfluenced by either of the other three processes, and that under these very particular circumstances each process has the same dissociation constant, K, then

$$K_{(i)} = K_{(ii)} = K_{(iii)} = K_{(iv)} = K,$$

and therefore

$$K_1 = 2K,$$

and

$$K_2 = \frac{K^2}{2K} = \frac{1}{2}K.$$

Hence

$$\frac{K_1}{K_2} = 4, \text{ or } K_1 = 4K_2.$$

This expression can only refer to rather hypothetical conditions, for, as stated above, the ionisation of one carboxyl group of a dibasic acid will diminish the ionisation of the second carboxyl group through the electrostatic attraction between the

negatively charged carboxyl end and the hydrogen ion originating from the second carboxyl group. Hence it follows for a symmetrical-carboxylic acid for which $K_{(i)} = K_{(ii)}$ and $K_{(iii)} = K_{(iv)}$, the constants referring to the more ionised first stage must be greater than those governing the second stage of ionisation,

i.e., $$K_{(i)} = K_{(ii)} > K_{(iii)} = K_{(iv)},$$

and therefore $$\frac{K_1}{K_2} > 4.$$

Hence $\frac{K_1}{K_2} - 4$ is a measure of the electrostatic effects involved in the ionisation of a symmetrical dibasic acid. Bjerrum expresses this in terms of logarithms, thus $\log_{10} K_1 - \log_{10} K_2 - \log 4 = n$, whence $pK_2 - pK_1 - 0{\cdot}60 = n$.

The foregoing proof is due to Adams (*J. Amer. Chem. Soc.*, 1916, **38**, 1503). Wegscheider (*Monatsh.*, 1895, **16**, 1895) arrived at the hypothetical relationship, $K_1/K_2 = 4$, on statistical grounds ; it being considered that (*a*) the probability of ionisation of a hydrogen ion from a dibasic acid should be twice that of a similar acid molecule having one ionisable hydrogen atom only, (*b*) the probability of a hydrogen ion recombining with a divalent anion should be twice as great as with a singly charged anion.

Following Bjerrum (*Z. physikal. Chem.*, 1923, **106**, 219), we shall consider a method by which n, referred to above, can be computed. A negatively charged molecule, such as an anion of a dissociated acid, will attract hydrogen ions. They will tend to arrange themselves in the form of a spherical atmosphere with the negative ion as its centre. The relationship between the concentration of hydrogen ions in this atmosphere, C_r, compared with the average concentration of hydrogen ions in the solution, C, can, by applying Boltzmann's Law, be represented by

$$C_r = C \times e^{-\frac{N.A}{R.T}},$$

in which A is the electrical work necessary to bring a hydrogen ion from an infinite distance into the presence of hydrogen ions at concentration, C_r, at a distance, r, from the negatively charged ion. N is the Avogadro Number. As a first approximation,

$$A = \frac{(+\varepsilon)(-\varepsilon)}{D \cdot r},$$

ε being equal to $4{\cdot}774 \cdot 10^{-10}$ e.s.u., the charge on an electron, and D, the dielectric constant of the medium. Therefore

$$C_r = C \times e^{\frac{N.\varepsilon^2}{RTDr}}.$$

If, now, we consider the distance between the negatively charged end of a symmetrical dibasic acid and the carboxyl group at the other end from which a hydrogen ion is just proceeding, to be r, we can ascertain the influence which these electrostatic influences should have on the dissociation constants, K_1 and K_2.

Thus if r is so great that the electrostatic effects are nullified, and if we represent the second dissociation constant under these very special conditions by K_2^*, then $\frac{K_1}{K_2^*} = 4$

and
$$K_2^* = \frac{[H^\cdot]_r \cdot \times [{}'RR^{\circ\prime}]}{[HRR^{\circ\prime}]}$$
$$= \frac{[H^\cdot] \times e^{\frac{N\varepsilon^2}{RTDr}} \times [{}'RR^{\circ\prime}]}{[HRR^{\circ\prime}]}$$
$$= K_2 \cdot e^{\frac{N\varepsilon^2}{RTDr}},$$

$[H^\cdot]_r$ being C_r, and $[H^\cdot] = C$.
Eliminating K_2 from these two equalities, it follows that

$$\frac{K_1}{K_2} = 4 \cdot e^{\frac{N\varepsilon^2}{RTDr}}$$

and

$$n = pK_2 - pK_1 - 0{\cdot}60 = \frac{N\varepsilon^2}{2{\cdot}303RTDr}.$$

Taking N, the Avogadro Number, as $6{\cdot}06 \times 10^{23}$, D for water as 80, $R = 8{\cdot}35 \times 10^7$ and $T = 298°$ Abs., it follows that for a dibasic acid in aqueous solution at 25° C.—

$$n = pK_2 - pK_1 - 0{\cdot}60 = \frac{3{\cdot}08 \times 10^{-8}}{r},$$

which expression provides a method of calculating the distance, r, between the two carboxyl groups of a symmetrical dibasic acid. Bjerrum showed that the values so obtained were of the same order of magnitude as those which might be expected from the dimensions of the carbon atom, as indicated by X-ray measurements on the diamond, multiplied by the number of carbon atoms in the chain terminating with the carboxyl groups.

Gane and Ingold (*J. Chem. Soc.*, 1928, 1594; 1931, 2153; Ingold, *ibid.*, 2179) point out that Bjerrum's computation is necessarily approximate, for it does not take into consideration effects due to the solvent and the possibility of electromeric effects being propagated through the dibasic acid molecule in

consequence of one of the carboxyl groups undergoing dissociation. By employing the Clausius-Mosotti equation and the Debye expression connecting the average moment of a molecule with its polarisability, Ingold arrived at the expression

$$\frac{K_1}{K_2} = 4e^{\frac{N\epsilon}{RT}\psi}.$$

Comparison with the Bjerrum equation shows that in that equation the potential, ψ, of an ion at a distance, r, from an ionised carboxyl group is equal to $-\frac{\epsilon}{Dr}$. Instead, Ingold has derived further rather complicated expressions connecting ψ not only with r and ϵ, but with the dielectric constant of the solvent. In order to calculate r, it is therefore necessary to find ψ directly from K_1 and K_2 and then to compute r from Ingold's equations (*J. Chem. Soc.*, 1931, 2179). Jones and Soper (*ibid.*, 1934, 1836; 1936, 133) state that the effects which Ingold considered as being due to the compressibility of the solvent and to anisotropy become of minor importance when r is equal to, or greater than, 4×10^{-8} cm. (4Å.U.). For aqueous solutions at 25° they show that

$$\psi_{25°} = 6{\cdot}112 \times \frac{10^{-12}}{r} + \frac{1{\cdot}368 \times 10^{-41}}{r^5}$$

r being $\geqslant 4 \times 10^{-8}$ cm.

A proof of Ingold's main equation is that of Maxwell and Partington (*Trans. Faraday Soc.*, 1937, **33**, 670), and, for the purpose, we shall consider a typical dibasic acid, namely, ortho-phthalic acid, in conjunction with benzoic acid.

In the first place, consider the difference between the work which is necessary to remove the hydrogen ion from benzoic acid, thus

$$C_6H_5COOH \rightarrow C_6H_5COO' + H^{\cdot},$$

and the work entailed in removing the hydrogen ion from the singly charged ortho-phthalate-anion,

$$C_6H_4\begin{matrix}COO'\\COOH\end{matrix} \rightarrow C_6H_4\begin{matrix}COO'\\COO'\end{matrix} + H^{\cdot}$$

For the moment let us assume that the difference between the two amounts of work is due solely to the electrical work required to dislodge the hydrogen ion from the latter owing to the fact that the anion is already negatively charged and thereby exerts an attractive force which has to be overcome. Suppose the potential due to this charge at the point occupied by the dissociating

hydrogen ion is ψ, and knowing that the maximum work, A_T, and the equilibrium constant, K, involved is

$$A_T = RT \log_e K,$$

it follows that

$$A_{T\ (\text{Benzoic acid})} - A_{T\ (\text{Phthalate anion})}$$
$$= RT \log_e K_{\text{Benzoic acid}} - RT \log_e 2K_{2\text{Phthalic acid}}$$
$$= N \cdot \varepsilon \cdot \psi.$$

$N \cdot \varepsilon$ being the quantity of electricity associated with one gram-molecule of hydrogen ions and therefore $N \cdot \varepsilon \cdot \psi$ = electrical work. In the above expression, $2K_{2\text{Phthalic acid}}$, is used instead of K_2 because the measured value of K_2 is only one-half of the value for a single carboxyl anion, in which case the hydrogen ion can return to one position only. Hence

$$\log_e \frac{K_{\text{Benzoic acid}}}{2K_{2\text{Phthalic acid}}} = \frac{N \cdot \varepsilon \cdot \psi}{RT}$$

i.e.,

$$K_{\text{Benzoic acid}} = 2K_{2\text{Phthalic acid}} \cdot e^{\frac{N\varepsilon\psi}{RT}}.$$

It is thus seen that the factor $e^{\frac{N\varepsilon\psi}{RT}}$ corrects the statistical relationship

$$K_{\text{Benzoic acid}} = 2K_{2\text{ Phthalic acid}}$$

for the influence of the negative charge on the hydrophthalate ion.

If a further statistical relationship be assumed that

$$K_{1\text{ Phthalic acid}} = 2K_{\text{Benzoic acid}},$$

for the dissociation of a single hydrogen ion from phthalic acid can take place from either of the two carboxyl groups, whereas it is confined to only one in benzoic acid, it follows that for phthalic acid

$$\frac{K_1}{K_2} = 4 \cdot e^{\frac{N\varepsilon\psi}{RT}},$$

which is precisely the fundamental relationship of Ingold.

It will be seen that the essential difference between this derivation and that of Bjerrum and Ingold lies in the fact that they considered the electrical work to be the difference between that entailed in removing a hydrogen ion from a dibasic acid and that required to remove the hydrogen ion from a singly charged anion, whereas Maxwell and Partington considered the electrical work as being equal to the difference in the work of removing a hydrogen ion from the corresponding monobasic acid and from the singly charged anion of the dibasic acid. Where the carboxyl

groups are a considerable distance apart there is little to choose between the two assumptions, but when the carboxyl groups are close together and the ability of the first carboxyl group to ionise is greatly enhanced by the close proximity of the second carboxyl group the assumption of Maxwell and Partington appears to be preferable. There is no doubt that the nearer two carboxyl groups are together the more will they influence one another in promoting ionisation. This is seen in the great increase in K_1 of phthalic acid ($1{\cdot}05 \times 10^{-3}$) compared with that of benzoic acid ($6{\cdot}8 \times 10^{-5}$). Influences which cause such pronounced changes are probably: (i) electrical effects transmitted through the atom chain (electromeric effects), (ii) external interaction between carboxyl groups, *e.g.*, interaction between dipoles, (iii) solvation effects.

Table 43 gives the results of such calculations and is based on the work of Gane and Ingold (*J. Chem. Soc.*, 1928, 1594, 2267; 1928, 1691; 1931, 2153), German, Vogel and Jeffery (*Phil. Mag.*, 1936, (7), **22**, 790), German and Vogel (*J. Amer. Chem. Soc.*, 1936, **58**, 1546; *J. Chem. Soc.*, 1937, 1108), Jones and Soper (*J. Chem. Soc.*, 1934, 1836; 1936, 133) and Ashton and Partington (*Trans. Faraday Soc.*, 1934, **30**, 598). The column headed B. gives the values of r in Ångstrom units (1 Å $= 10^{-8}$ cm.) obtained by using Bjerrum's formula, whereas the column I. records values obtained by the method of Ingold (*J. Chem. Soc.*, 1931, 2179; Gane and Ingold, *ibid.*, 1931, 2153). For the values marked with an asterisk, slightly smaller values of K_1 and K_2 than those recorded in Table 43 were used, the actual values used being those obtained by extrapolation to $\mu = 0$ (see page 267). The effect on the values of r is almost negligible.

The values obtained by Bjerrum's method are seen to be smaller than those given by Ingold's method, but whichever method is used the values of r lead to the same general conclusions. Thus in the oxalic acid series, $HOOC.(CH_2)_x.COOH$, as x increases from 0 in oxalic acid to 7 in azaleic acid, r increases correspondingly. On the contrary, the increase in r (B) in passing from oxalic acid to malonic acid is extremely small, but from succinic acid onwards there is a progressive increase. The relatively small changes shown by the lower members is attributed to the transmission of polar effects (electromeric effects) internally from one carboxyl group to the other through the methylene chain. In succinic acid these influences are considered to become so damped that the effect is subsidiary to the external electrical field between the ionising carboxyl groups. Gane and Ingold postulate that the methylene groups are oriented in a zig-zag manner.

TABLE 43

RELATIONSHIP BETWEEN DISSOCIATION CONSTANTS OF DIBASIC ACIDS AND DISTANCE BETWEEN CARBOXYL GROUPS

	K_1.	K_2.	$r \times 10^8$ cm. B.	I.
Oxalic	$5{\cdot}90 \cdot 10^{-2}$	$6{\cdot}4 \cdot 10^{-5}$	—	3·37*
Malonic	$1{\cdot}43 \cdot 10^{-3}$	$2{\cdot}20 \cdot 10^{-6}$	1·39	3·47
Succinic	$6{\cdot}37 \cdot 10^{-5}$	$2{\cdot}54 \cdot 10^{-6}$	3·89	5·13
	$6{\cdot}89 \cdot 10^{-5}$	$2{\cdot}47 \cdot 10^{-6}$	—	4·98 (S)
Glutaric	$4{\cdot}46 \cdot 10^{-5}$	$3{\cdot}77 \cdot 10^{-6}$	6·60	7·15*
Adipic	$3{\cdot}90 \cdot 10^{-5}$	$5{\cdot}29 \cdot 10^{-6}$	11·5	8·22*
Pimelic	$3{\cdot}33 \cdot 10^{-5}$	$4{\cdot}87 \cdot 10^{-6}$	13·2	9·43*
Suberic	$3{\cdot}07 \cdot 10^{-5}$	$4{\cdot}71 \cdot 10^{-6}$	14·5	11·07*
Azaleic	$2{\cdot}82 \cdot 10^{-5}$	$4{\cdot}64 \cdot 10^{-6}$	16·8	12·03*
Methyl malonic	$1{\cdot}08 \cdot 10^{-3}$	$3{\cdot}43 \cdot 10^{-6}$	1·64	3·51*
Ethyl ,,	$1{\cdot}27 \cdot 10^{-3}$	$2{\cdot}81 \cdot 10^{-6}$	1·50	3·44*
n-Propyl ,,	$1{\cdot}07 \cdot 10^{-3}$	$2{\cdot}08 \cdot 10^{-6}$	1·47	3·42*
iso-Propyl ,,	$1{\cdot}17 \cdot 10^{-3}$	$1{\cdot}59 \cdot 10^{-6}$	1·37	3·38*
Dimethyl ,,	$8{\cdot}27 \cdot 10^{-4}$	$1{\cdot}53 \cdot 10^{-6}$	1·45	3·40*
Diethyl ,,	$6{\cdot}27 \cdot 10^{-3}$	$5{\cdot}90 \cdot 10^{-8}$	0·71	2·75*
Di-*n*-propyl ,,	$8{\cdot}67 \cdot 10^{-3}$	$3{\cdot}42 \cdot 10^{-8}$	0·64	2·67*
β-methyl glutaric	$5{\cdot}77 \cdot 10^{-5}$	$6{\cdot}28 \cdot 10^{-7}$	2·27	4·06*
β-*n*-propyl ,,	$4{\cdot}97 \cdot 10^{-5}$	$4{\cdot}32 \cdot 10^{-7}$	2·12	3·97*
ββ-dimethyl ,,	$2{\cdot}03 \cdot 10^{-4}$	$5{\cdot}51 \cdot 10^{-7}$	1·57	3·58*
ββ-diethyl ,,	$3{\cdot}40 \cdot 10^{-4}$	$7{\cdot}85 \cdot 10^{-8}$	1·02	3·12*
ββ-*n*-propyl ,,	$2{\cdot}03 \cdot 10^{-4}$	$5{\cdot}42 \cdot 10^{-8}$	1·01	3·12*
Cyclic | : | *Diacetic Acids* of—				
cyclo-*Pentane*	$1{\cdot}60 \cdot 10^{-4}$	$17{\cdot}0 \cdot 10^{-8}$	1·30	3·38
3-Methylcyclopentane	$1{\cdot}61 \cdot 10^{-4}$	$18{\cdot}2 \cdot 10^{-8}$	1·32	3·40
cyclo-*Hexane*	$3{\cdot}27 \cdot 10^{-4}$	$8{\cdot}26 \cdot 10^{-8}$	1·03	3·12
2-methyl cyclo-Hexane	$2{\cdot}96 \cdot 10^{-4}$	$13{\cdot}00 \cdot 10^{-8}$	1·16	3·25
3 ,, ,, ,,	$3{\cdot}23 \cdot 10^{-4}$	$8{\cdot}34 \cdot 10^{-8}$	1·04	3·15
4 ,, ,, ,,	$3{\cdot}23 \cdot 10^{-4}$	$8{\cdot}02 \cdot 10^{-8}$	1·03	3·13
Maleic	$1{\cdot}20 \cdot 10^{-2}$	$5{\cdot}95 \cdot 10^{-7}$	1·19	2·90
Fumaric	$9{\cdot}57 \cdot 10^{-4}$	$4{\cdot}13 \cdot 10^{-5}$	4·05	5·25
Citraconic	$5{\cdot}14 \cdot 10^{-3}$	$7{\cdot}15 \cdot 10^{-7}$	0·95	3·05
Mesaconic	$8{\cdot}22 \cdot 10^{-4}$	$1{\cdot}78 \cdot 10^{-5}$	2·99	4·48
cis-Caronic	$4{\cdot}59 \cdot 10^{-3}$	$4{\cdot}94 \cdot 10^{-9}$	—	2·59 (S)
trans-Caronic	$1{\cdot}52 \cdot 10^{-4}$	$4{\cdot}78 \cdot 10^{-6}$	—	4·85 (S)
Bromomaleic	$3{\cdot}58 \cdot 10^{-2}$	$2{\cdot}40 \cdot 10^{-5}$	1·21	3·27
Bromofumaric	$3{\cdot}47 \cdot 10^{-2}$	$2{\cdot}70 \cdot 10^{-4}$	2·06	3·93
Chloromaleic	$1{\cdot}90 \cdot 10^{-2}$	$1{\cdot}37 \cdot 10^{-4}$	2·01	3·90
Chlorofumaric	$1{\cdot}67 \cdot 10^{-2}$	$1{\cdot}54 \cdot 10^{-4}$	2·16	3·82

In considering r for the substituted dibasic acids, malonic and glutaric, it is seen that the introduction of one or more alkyl groups causes a diminution in the distance between the carboxyl groups. Gane and Ingold made similar observations

with substituted succinic acids. It would appear that substitution leads to a bending of the zig-zag chain so as to bring the carboxyl groups closer together.

The values of r for the cyclic diacetic acids compare with that of oxalic acid, although alkyl substitution reduces the distance slightly.

Table 43 also supplies confirmation of the geometrical isomerism of maleic and fumaric acids and of their monomethyl analogues, citraconic and mesaconic acids. The closer proximity of the carboxyl groups in maleic and citraconic acids than in their respective analogues, fumaric and mesaconic, is reflected in the smaller values of r. Substitution of hydrogen atoms by chlorine and bromine in both maleic and fumaric acids appears to lengthen the distance between the carboxyl groups in the substituted maleic acids and to reduce it in the substituted fumaric acids. These effects may possibly be caused either by solvation or by internal effects propagated through the molecule from one carboxyl group to the other.

Gane and Ingold have endeavoured to interpret the values of r in terms of the precise spatial orientation of the methylene groups within dibasic acid molecules.

Regarding the ionisation of dibasic acids, see also Kirkwood and Westheimer (*J. Chem. Phys.*, 1938, **6**, 506, 513).

Maxwell and Partington (*loc. cit.*) have extended the foregoing considerations to polybasic acids and have determined the dissociation constants of a series of substituted benzene acids. Their results are given in Table 44. The total ionic strengths of the solutions investigated were each 0·03. (See p. 267.)

TABLE 44

DISSOCIATION CONSTANTS OF SUBSTITUTED BENZENE ACIDS

Acid.	K_1	K_2	K_3	K_4	K_5	K_6
Benzoic	$6{\cdot}8 \cdot 10^{-5}$					
Phthalic (1 : 2)	$1{\cdot}05 \cdot 10^{-3}$	$5{\cdot}2 \cdot 10^{-6}$				
Isophthalic (1 : 3)	$3{\cdot}3 \cdot 10^{-4}$	$3{\cdot}5 \cdot 10^{-5}$				
Hemimellitic (1 : 2 : 3)	$1{\cdot}6 \cdot 10^{-3}$	$6{\cdot}3 \cdot 10^{-5}$	$1{\cdot}35 \cdot 10^{-6}$			
Trimellitic (1 : 3 : 4)	$3{\cdot}0 \cdot 10^{-3}$	$1{\cdot}45 \cdot 10^{-4}$	$6{\cdot}3 \cdot 10^{-6}$			
Trimesic (1 : 3 : 5)	$7{\cdot}5 \cdot 10^{-4}$	$1{\cdot}3 \cdot 10^{-4}$	$2{\cdot}0 \cdot 10^{-5}$			
Mellophanic (1 : 2 : 3 : 4)	$8{\cdot}8 \cdot 10^{-3}$	$5{\cdot}6 \cdot 10^{-4}$	$1{\cdot}9 \cdot 10^{-5}$	$6{\cdot}1 \cdot 10^{-7}$		
Prehnitic (1 : 2 : 3 : 5)	$4{\cdot}2 \cdot 10^{-3}$	$3{\cdot}1 \cdot 10^{-4}$	$3{\cdot}6 \cdot 10^{-5}$	$1{\cdot}55 \cdot 10^{-6}$		
Pyromellitic (1 : 2 : 4 : 5)	$1{\cdot}2 \cdot 10^{-2}$	$1{\cdot}3 \cdot 10^{-3}$	$3{\cdot}2 \cdot 10^{-5}$	$2{\cdot}35 \cdot 10^{-6}$		
Benzenepenta-carboxylic	$1{\cdot}6 \cdot 10^{-2}$	$1{\cdot}85 \cdot 10^{-3}$	$1{\cdot}1 \cdot 10^{-4}$	$5{\cdot}6 \cdot 10^{-6}$	$3{\cdot}5 \cdot 10^{-7}$	
Mellitic (hexacarb-oxylic)	$4{\cdot}0 \cdot 10^{-2}$	$6{\cdot}4 \cdot 10^{-3}$	$4{\cdot}9 \cdot 10^{-4}$	$1{\cdot}65 \cdot 10^{-5}$	$1{\cdot}3 \cdot 10^{-6}$	$1{\cdot}1 \cdot 10^{-7}$

General Statistical Treatment of the Dissociation Constants of Polybasic Acids.

Following the method used by Maxwell and Partington, if we assume that, under the same conditions, a carboxyl group always ionises and re-forms at a rate which is independent of the molecule or ion to which it is attached and is not affected by the presence of either undissociated or dissociated carboxyls in the latter, then the *relative theoretical values* of the *dissociation constants* may be calculated in the following manner.

Suppose an n-basic acid, H_nR, has ionised through $(n - a)$ successive stages, thus

$$H_nR \rightarrow (n - a)H^{\cdot} + H_aR^{(n-a)'}.$$

If the acid is an n-carboxylic acid, it follows that in the anion, $H_aR^{(n-a)'}$, a carboxyl groups remain undissociated, $(n - a)$ groups having already ionised. Now consider the ionisation of the anion, $H_aR^{(n-a)'}$ to the next stage, thus

$$H_aR^{(n-a)'} \rightleftharpoons H^{\cdot} + H_{a-1}R^{(n-a+1)'},$$

for which v_1 = the rate of dissociation of a single carboxyl group and v_2 = the rate of recombination of a single pair of ions shown by the lower arrow. Then as the anion, $H_aR^{(n-a)'}$, contains a un-ionised carboxyl groups, the number of carboxyl groups per litre which may dissociate is $[H_aR^{(n-a)'}] \times N_0 \times a$, where $[H_aR^{(n-a)'}]$ represents the concentration in gram-molecules per litre, and N_0, the Avogadro Number. Hence the rate of dissociation of these carboxyl groups is

$$v_1 \,.\, a \,.\, [H_aR^{(n-a)'}] \,.\, N_0.$$

Regarding the back-reaction, *viz.*, the re-formation of the anion, $H_aR^{(n-a)'}$ by the combination of $H^{\cdot}$ with $H_{a-1}\ R^{(n-a+1)'}$, the number of ionised carboxyl groups is $(n - a + 1)$ per each individual anion, and therefore for a concentration,

$$[H_{a-1}R^{(n-a+1)'}],$$

the actual number of ionised carboxyl groups with which $N_0[H^{\cdot}]$ hydrogen ions may combine is

$$(n - a + 1) \,.\, [H_{a-1}R^{(n-a+1)'}] \,.\, N_0.$$

Hence the rate of recombination of the hydrogen ions with anions is

$$v_2 \,.\, N_0[H^{\cdot}] \,.\, (n - a + 1)[H_{a-1}R^{(n-a+1)'}]N_0.$$

Applying the condition of equilibrium as enunciated by Guldberg and Waage, it follows that

$$v_1 \,.\, a \,.\, [H_aR^{(n-a)'}] \,.\, N_0 = v_2 \,.\, N_0[H^{\cdot}] \,.\, (n - a + 1)[H_{a-1}R^{(n-a+1)'}]N_0$$

and therefore

$$K_{n-a+1} = \frac{[H^{\cdot}][H_{(a-1)}R^{(n-a+1)'}]}{[H_aR^{(n-a)'}]} = \frac{a}{n-a+1} \times \frac{v_1}{v_2 \cdot N_0} = \frac{a}{n-a+1} \times K_{(Carboxyl)}.$$

The equality $\frac{v_1}{v_2 \cdot N_0} = K_{(Carboxyl)}$ follows from a consideration of the ionisation of a monobasic acid (or monocarboxylic acid), $HR \rightleftharpoons H^{\cdot} + R'$. On the present statistical hypothesis,

$$v_1 \cdot [HR] \cdot N_0 = v_2 \cdot [H^{\cdot}] \cdot N_0 \cdot [R'] \cdot N_0 \quad .$$

whence $$\frac{[H^{\cdot}][R']}{[HR]} = \frac{v_1}{v_2 \cdot N^0} = K_{HR} = K_{(Carboxyl)}$$

It follows from the above expression, which is of general application, that for a dibasic acid, H_2R, $K_1/K_2 = 4$; for a tribasic acid, H_3R, $K_1 : K_2 : K_3 = 3 : 1 : \frac{1}{3}$; for a tetrabasic acid, H_4R, $K_1 : K_2 : K_3 : K_4 = 4 : \frac{3}{2} : \frac{2}{3} : \frac{1}{4}$; etc. Thus for a dibasic acid, H_2R, $n = 2$ and by putting $a = 2$, we get

$$K_{2-2+1} = K_1 = \frac{2}{2-2+1} \cdot K_{(Carboxyl)}$$

and by putting $a = 1$, we get

$$K_{2-1+1} = K_2 = \frac{1}{2-1+1} \cdot K_{(Carboxyl)}$$

and therefore $\frac{K_1}{K_2} = 4$ (see page 242).

We are now in a position to consider the data given in Table 44. If we regard benzoic acid as the monobasic acid to which the various benzene substituted carboxylic acids should be referred, it is necessary to assume that $K_{(Carboxyl)} = K_{Benzoic\ acid}$, whence

$$K_{n-a+1} = \frac{a}{n-a+1} \times K_{Benzoic}.$$

Calculation on purely statistical grounds shows that the ratio of the primary dissociation constants of the substituted carboxylic acids to that of benzoic acid : K_1 (mellitic) : K_1 (benz. pentacarboxylic) : K_1 (mellophanic) : K_1 (prehnitic : K_1 (pyromellitic) : K_1 (hemimellitic) : K_1 (trimellitic) : K_1 (trimesic) : K_1 (phthalic) : K_1 (isophthalic) : K (bensoic) should be equal to 6 : 5 : 4 : 4 : 4 : 3 : 3 : 3 : 2 : 1, whereas Table 44 gives 590 : 240 : 130 : 62 : 180 :

24 : 45 : 11 : 15 : 5 : 1. Maxwell and Partington also compare the dissociation constant of benzoic acid with the final constants of the various acids. On statistical grounds $K_{Benzoic} : K_2$ (isophthalic) : K_2 (phthalic) : K_3 (trimesic) : K_3 (trimellic) : K_3 (h. mellitic) : K_4 (pyromellitic) : K_4 (prehnitic) : K_4 (mellophanic) : K_5 (benz. penta.) : K_6 (mellitic) should be 6 : 3 : 3 : 2 : 2 : 2 : 1·5 : 1·5 : 1·5 : 1·2 : 1, as compared with 620 : 320 : 47 : 180 : 57 : 12 : 21 : 14 : 5·5 : 3 : 1 actually found.

It must not be forgotten that the statistical computations pay no regard to the influence which the charges, already borne by the anions, may have on the ionisation of further carboxyl groups. The differences between the statistical and observed values are largely caused by influence of un-ionised carboxyl groups in promoting the ionisation of another carboxyl group, and *vice-versâ* by the inhibiting effect of ionised carboxyl groups. The effect of the proximity of the carboxyl group is seen in Table 44. Thus in the case of *iso*-phthalic and trimesic acids the carboxyls are in the *meta*-position with respect to each other, and consequently the statistical relationships would be expected to apply more nearly than in other acids which have at least one group *ortho* with respect to another. It appears that an ionised group in the *meta*-position has but little inhibiting effect on the dissociation of another carboxyl group.

CHAPTER XIV

THE ACTIVITY THEORY OF SOLUTIONS

THE classical Ionisation Theory of Arrhenius, despite its simplicity, supplies a remarkable explanation of the abnormal osmotic pressure and its colligative properties of aqueous solutions of electrolytes, when considered from the standpoint of van't Hoff's Theory of Solutions. The theory gained general acceptance, because, in many instances, it was able approximately to account for the values of i, the so-called van't Hoff 'activity' factor in the expression, $PV = ixRT$ (see Chapter I). This will be understood from Table 45, which gives data comparing "i", as calculated from freezing-point determinations, with "i", computed from conductivity data, assuming that $\alpha = \Lambda_v/\Lambda_\infty$ at comparable concentrations (Arrhenius, *Z. physikal. Chem.*, 1887, **1**, 631).

TABLE 45

Electrolyte.	α.	$i_{\text{F.P.}}$	$i_{\text{Conductivity}}$
NaOH	0·88	1·91	1·88
KOH	0·93	1·79	1·93
NH_4OH	0·01	1·00	1·01
$Ba(OH)_2$	0·84	2·69	2·68
HCl	0·90	1·98	1·90
HNO_3	0·92	1·94	1·92
H_2SO_4	0·60	2·06	2·20
CH_3COOH	0·01	1·03	1·01
$H_2C_2O_4$	0·25	1·25	1·50
KCl	0·86	1·82	1·86
K_2SO_4	0·67	2·11	2·33
$BaCl_2$	0·77	2·63	2·54

In a few cases, the differences between the values of i are obviously too great to be attributed to experimental error. Hence, it must be concluded that the Arrhenius Theory can, at best, be only an approximation to the truth. Yet, on further consideration, it cannot be comprehensive and apply to solutions of electrolytes in non-aqueous solvents as well, for it does not incorporate such an important factor as the dielectric constant of the solvent, which has a considerable effect on the inter-ionic

forces. Neither does it deal with properties such as the size of ions and the problem of the solvation of ions.

From the standpoint of thermodynamics, it can be shown that, if the Perfect Gas Laws be assumed to apply to electrolytes in solution, the Law of Mass Action must govern all ionisations, whether of strong acids and bases, salts or weak acids and bases. In actual fact, the Arrhenius Theory applies fairly satisfactorily to the dissociation of weak electrolytes, *viz.*, weak acids and bases, water, complex ions and solubility products, but it fails utterly with strong electrolytes. Even in regard to weak electrolytes, a more rigid application could be desired, although it must be admitted that the divergence from constancy of the dissociation constant for solutions of widely varying concentration is usually very small. On the contrary, the Arrhenius Theory signally fails in regard to the ionisation of strong electrolytes. Table 46 illustrates the extent to which the Law of Mass Action applies to the ionisation of a " weak," " moderately strong," and " strong acids," the degree of ionisation, α, being assumed equal to Λ_c/Λ_o as postulated by Arrhenius.

TABLE 46

VALUES OF $K = \frac{\alpha^2 c}{1 - \alpha}$

HCl.*		$CH_2ClCOOH$.†		CH_3COOH.‡	
C.	K.	C.	K × 10^3.	C.	K × 10^5.
0·0000284	0·0116	0·000110	1·353	0·0000280	1·760
0·000177	0·0336	0·000590	1·409	0·000153	1·767
0·001577	0·1059	0·000132	1·436	0·001028	1·781
0·002994	0·1523	0·00746	1·501	0·005912	1·798
		0·02018	1·543	0·05230	1·811

* Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1411.

† Shedlovsky, Brown and MacInnes, *Trans. Amer. Electrochem. Soc.*, 1934, **66**, 165.

‡ MacInnes and Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1429.

It will be observed that K_{HCl} shows no constancy, but that K for monochloracetic acid and K for acetic acid retain the respective orders of magnitude 1×10^{-3} and 2×10^{-5} with increasing concentration. There is, however, a distinct tendency for both constants to increase, it being more pronounced in the case of the moderately strong acid, monochloroacetic, than for the weaker acid, acetic.

Another important influence on the ionisation of acids and

bases, that is not accounted for by the Arrhenius Theory, is the effect produced by neutral salts, which yield no ions in common with the acids or bases.

As the theory does not take into account the dielectric constant of the solvent, it cannot be regarded as comprehensive and of general application and thus to include solutions of electrolytes in non-aqueous media as well, although as Walden has shown, it holds qualitatively for solutions in different media, when considered separately. When it is remembered that ions are charged positively or negatively, it will be realised how important a part is played by the dielectric nature of the solvent medium in determining the magnitude of the electrostatic forces of attraction and of repulsion which exist between oppositely and similarly charged ions respectively. The extent of these forces will be governed by the Inverse Square Law, *viz.*, $F = \frac{\varepsilon_+ \cdot \varepsilon_-}{D \cdot d^2}$, ε_+ being the charge on the cation and ε_- the charge on the anion, D the dielectric constant, and d the distance between the ions. Instead of assuming partial dissociation of an electrolyte, as did Arrhenius, we may equally well assume complete ionisation of electrolytes in solutions at all concentrations as was first done by Sutherland (*Phil. Mag.*, 1902, **3**, 161 ; 1906, **12**, 1 ; also Milner, *ibid.*, 1912, **23**, 551 ; 1913, **25**, 745, and Debye and Hückel, *Physikal. Z.*, 1923, **21**, 185).

In the latter case, however, the force of attraction between some oppositely charged ions will conceivably be so great that they are drawn so closely together that such pairs may, in effect, be considered as undissociated. This state of affairs is more likely to be set up in the more concentrated solutions. Incidentally, it is obvious that ions of neutral salts will have some effect on the apparent dissociation of weak electrolytes on account of these inter-ionic forces.

In view of these forces which exist between ions, and that in consequence the movements of the ions throughout the volume of a solution are largely determined by these attractive and repulsive inter-ionic forces, it will be realised that a solution of ions bears little resemblance to a volume of gas made up of molecules between which only slight forces, if any, come into play ; none in the case of a perfect gas. It seems scarcely feasible, therefore, to attempt to apply the Perfect Gas Laws to solutions of electrolytes. Yet, even the application of the Arrhenius Theory to solutions of weak electrolytes suggests that the Gas Laws can be applied with some degree of success.

Because of the departure of ions in solution from the random

distribution, supposed to exist in the case of the molecules of a perfect gas, Milner applied the *Clausius Virial Equation*, $p \times v = 2/3$ (Kinetic Energy) $- 1/3$ (Virial), in which the *virial* $= \phi(f \,.\, r)$, f being the force existing between a pair of molecules at a distance, r. The term $1/3$ (virial) thus indicates the difference between the values of $p \times v$ at any given temperature a real gas and perfect gas, for which $p \,.\, v = 2/3$ (K.E.). He derived an expression with which the van't Hoff factor, i, of dilute solutions of electrolytes could be calculated.

Another characteristic property of electrolytes in different solvents, which is brought out by Walden's work on non-aqueous solutions of electrolytes, is that the speed of ions is closely related to the viscosity of the solvent, so much so that the ionic mobility, l, of a given ion multiplied by the viscosity of the solvent, η, is approximately a constant (Walden's Rule).

TABLE 47

VALUES OF $l \times \eta$

Ion.	Water.	Methyl Alcohol.	Ethyl Alcohol.	Acetone.
$Li^{\cdot}$	0·358	0·217	0·192	0·224
Cl'	0·682	0·290	0·232	0·332
$N(C_2H_5)^{\cdot}_4$	0·295	0·295	0·295	0·294
$Picrate'$	0·269	0·273	0·263	0·266

The table shows that Walden's Rule is valid for the large ions, tetraethyl ammonium cation and the picrate anion but fails for the smaller ions, $Li^{\cdot}$ and Cl', particularly in aqueous solution. The explanation is most probably to be found in the fact that, owing to the relatively larger specific surfaces of the small ions, they are heavily hydrated. This belief is supported by considerations based on Stokes' Law, which connects the terminal velocity of a small sphere of radius, r, with its velocity when moving in a liquid of viscosity, η, under a constant force, Force,

viz. $$\text{Velocity} = \frac{\text{Force}}{6\pi\eta r}.$$

If this law is applicable to particles so small as ions, then the velocity of an ion, moving under a potential gradient of 1 volt per 1 cm.

$$= \frac{\text{Ionic Mobility}}{1 \text{ Faraday}} = \frac{l}{\text{F}} \text{ cm. per sec.}$$

Substituting in the above expression, Force $= 1{\cdot}57 \times 10^{-12}$

dynes (the force acting on a univalent ion under unit potential gradient), and $F = 96{,}500 \times 10^7$, we find that

$$\eta \times l = \frac{8 \times 10^{-9}}{r}.$$

Thus, if the radius of the ion remains constant in different solvents, then $\eta \times l =$ constant. Calculations based on this equation give r for $Li^{\cdot} = 2{\cdot}26 \times 10^{-8}$ cm., $1{\cdot}74 \times 10^{-8}$ cm. for $Na^{\cdot}$, $1{\cdot}17 \times 10^{-8}$ cm. for $K^{\cdot}$, $1{\cdot}12 \times 10^{-8}$ cm. for $Rb^{\cdot}$ and $1{\cdot}11 \times 10^{-8}$ cm. for $Cs^{\cdot}$. Although these dimensions are of the same order of magnitude as those derived from the atomic volumes of the respective elements and from X-ray measurements of the crystal lattices of salts containing these elements, they differ in the important respect that the two latter methods show that the atoms increase in radius from Li to Cs, whereas for the ions in solution the reverse is the case. It seems certain, therefore, that in solution, we are calculating the apparent radii of the ions, which include the layers of solvent tightly adhering to the ions themselves, the effective depth of the layer being greatest in the case of the smallest ion, as would be expected and which has been proved experimentally by Washburn and others.

Kohlrausch observed that the fall in equivalent conductivity of an electrolyte in a solution of increasing dilution often follows the relationship, $\Lambda_0 - \Lambda_c = k\sqrt{c}$, in which k is a constant for a particular electrolyte, but which is also connected with the dielectric constant of the solvent and the valencies of the ions involved.

The Activity Theory of G. N. Lewis.

The fundamental principle underlying the Lewis Activity Theory is that the Perfect Gas Laws must, of necessity, apply to solutions of electrolytes, and consequently that the colligative properties, osmotic pressure, lowering of vapour pressure, elevation of the boiling-point, depression of freezing-point, and above all, the Law of Mass Action must be applicable to ionisation processes, and reactions involving ions. The Perfect Gas Laws must also be applied more rigidly to the interpretation of electrode potentials, which interpretation therefore precludes the use of α, the Arrhenius degree of ionisation in calculating ion-concentrations.

The failure of the Arrhenius Theory to give ion-concentrations, which in the case of strong electrolytes do not satisfy the Law of Mass Action when applied to ionisation equilibria, was attributed to the inability of Λ_c/Λ_0 to give the true degree of dissociation.

Hence, instead of considering concentrations, Lewis contends that a function of each particular concentration should be employed in the Mass Law Equation. This function is similar to the concept of "Active Masses" introduced by Guldberg and Waage, when they enunciated the Law of Mass Action. This function is called the "activity," denoted by a. The relationship between *activity* and *concentration* is

$$\frac{\text{activity}}{\text{concentration}} = \text{activity coefficient.}$$

If the concentration is expressed as a *molarity*, *i.e.*, c g.-mols. or gram ions *per litre*, then

$$\frac{a}{c} = f, \quad \therefore a = f \times c,$$

whereas if the concentration is expressed as a *molality*, *i.e.* m g.-mols. or gram ions *per 1000 grams* of water, then

$$\frac{a}{m} = \gamma, \quad \therefore a = \gamma \times m.$$

The advantage of using molalities is that they are independent of volume changes caused by changes of temperature.

By using activities in the place of concentrations the Perfect Gas Laws are made to apply to solutions of electrolytes. Since the activity coefficient may be computed from one or more of the colligative properties, it follows that the activity coefficient simply indicates the extent by which an actual concentration deviates from the requirements of the Gas Laws. Lewis, however, defines the activity of a substance in terms of free energy. Thus if its free energy in one state is F_1, when its activity is a_1, and in another state it is F_2, when its activity has become a_2, then in passing from one state to the other, the change in free energy,

$$-\Delta F = F_1 - F_2 = RT \ln \frac{a_1}{a_2}$$

$$= RT \ln \frac{\gamma_1 \cdot m_1}{\gamma_2 \cdot m_2}.$$

If the activity coefficients, γ_1 and γ_2, should each be unity, then the Perfect Gas Laws apply, and

$$-\Delta F = F_1 - F_2 = RT \ln \frac{m_1}{m_2}.$$

Suppose now that F is the free energy of the substance, when its activity is a, and that F^0 represents the free energy

when the substance is in a standard state, *viz.*, when its activity, $a = 1$, then

$$-\Delta F = F - F^0 = RT \ln \frac{a}{1}.$$

This expression is the original definition of activity given by Lewis, and shows the change in free energy which results when a substance at activity a passes to a state when its activity is unity.

Proof of the Law of Mass Action in Terms of Activities.

Consider the equilibrium:

$$xA + yB \rightleftharpoons pC + qD.$$

Equilibrium will be established when the total free energy of the system has become zero, *i.e.*, when $-\Delta F = 0$. The free energy of each reactant is:—

for x mols. of A,

$$-\Delta F_A = xF_A - xF_A^0 = xRT \ln a_A;$$

for y mols. of B,

$$-\Delta F_B = yF_B - yF_B^0 = yRT \ln a_B;$$

for p mols. of C,

$$-\Delta F_C = pF_C - pF_C^0 = pRT \ln a_C;$$

for q mols. of D,

$$-\Delta F_D = qF_D - qF_D^0 = qRT \ln a_D.$$

The *total free energy of the reaction system* is

$$(-\Delta F_A - \Delta F_B) - (-\Delta F_C - \Delta F_D),$$

whence

$$(xF_A + yF_B - pF_C - qF_D) - (xF_A^0 + yF_B^0 - pF_C^0 - qF_D^0)$$
$$= -RT \ln \frac{a_C^p \times a_D^q}{a_A^x \times a_B^y}$$

But $-\Delta F = xF_A + yF_B - pF_C - qF_D$
$= 0$ (the system being at equilibrium).

The second term, involving F^0 terms, which refer to the free energies possessed by the reactants at unit activity at temperature, T, is a constant, and therefore

$$\frac{a_C^p \times a_D^q}{a_A^x \times a_B^y} = k.$$

Mean Ionic Activity.

No method has yet been evolved by which the activity of a single ion may be experimentally determined. This has necessitated the introduction of the term, *mean ionic activity of an*

electrolyte, which is the geometric mean of the activities of the two ions of an electrolyte at a given concentration. Lewis tacitly assumes that strong electrolytes are completely dissociated at all concentrations. Consider $HCl \rightleftharpoons H^{\cdot} + Cl'$, $a_{H^{\cdot}} = a_+$ and $a_{Cl'} = a_-$. The mean ionic activity of hydrochloric acid,

$$a_{\pm} = \sqrt{a_+ \cdot a_-}.$$

Similarly the mean ionic activity of

$$BaCl_2,\ a_{\pm BaCl_2} = (a_+ \cdot a_-^2)^{\frac{1}{3}}$$

and that of

$$La_2(SO_4)_3,\ a_{\pm La_2(SO_4)_3} = (a_+^2 \cdot a^3_-)^{\frac{1}{5}}.$$

Expressing in terms of concentrations and activity coefficients:

$$\begin{aligned} a_{\pm HCl} &= (\gamma_{H^{\cdot}}[H^{\cdot}] \cdot \gamma_{Cl'}[Cl'])^{\frac{1}{2}} \\ &= (\gamma_{H^{\cdot}} \cdot \gamma_{Cl'})^{\frac{1}{2}} \cdot m_{HCl} \\ &= (f_{H^{\cdot}} \cdot f_{Cl'})^{\frac{1}{2}} \cdot C_{HCl}. \end{aligned}$$

(HCl being assumed to be completely ionised and therefore $[H^{\cdot}] = [Cl'] = [HCl]$.)

The term $(\gamma_{H^{\cdot}} \cdot \gamma_{Cl'})^{\frac{1}{2}} = \gamma_{\pm}$ is the *mean ionic activity coefficient* of hydrochloric acid at *molality*, m_{HCl}, and $(f_{H^{\cdot}} \cdot f_{Cl'})^{\frac{1}{2}} = f_{\pm}$, is the *mean ionic activity coefficient at molarity*, c_{HCl}.

Similarly $a_{\pm La_2(SO_4)_3} = (\gamma^2_{La^{\cdots}} \times \gamma^3_{SO_4''})^{\frac{1}{5}} \cdot m_{La_2(SO_4)_3}$
$= (f^2_{La^{\cdots}} \times f^3_{SO_4''})^{\frac{1}{5}} \cdot c_{La_2(SO_4)_3}$

whence $\gamma_{\pm La_2(SO_4)_3} = (\gamma^2_{La^{\cdots}} \times \gamma^3_{SO_4''^3})^{\frac{1}{5}}$

and $f_{\pm La_2(SO_4)_3} = (f^2_{La^{\cdots}} \times f^3_{SO_4''^3})^{\frac{1}{5}}$.

It is considered that at infinite dilution the Gas Laws apply to ions as if they were independent osmotically active entities and therefore the activity of an ion becomes equal to its concentration. In other words, the mean ionic activity coefficient *at infinite dilution* is equal to unity, *i.e.*,

$$\frac{a_{\pm}}{m} = \gamma_{\pm} = 1 \text{ and } \frac{a_{\pm}}{c} = f_{\pm} = 1.$$

This is a point of fundamental importance in the computation of activities from E.M.F. data.

Section I. Cells without Transport.

E.M.F. Method of determining Mean Ionic Activities and Mean Ionic Activity Coefficients.

In view of the difficulty of interpreting liquid junction potentials in cells *with transport*, activities and activity coefficients are determined experimentally from the E.M.F's of cells *without*

transport. As an example we shall consider such a cell and, incidentally, one which is extremely important in activity determinations, as it involves the arbitrary zero standard hydrogen electrode. The cell is

$$\underset{E_1}{^{Pt}H_2} \mid \underset{I}{HCl(m_1),AgCl} \mid \underset{E_2}{Ag} \mid \underset{E_3}{AgCl,HCl(m_2)} \mid \underset{E_4}{H_2{}^{Pt}}$$
$$\text{II}$$

The sources of potential differences are indicated by E_1, E_2, E_3 and E_4. The cell is really two cells, *viz.*, I and II, connected in opposition to one another. Suppose that the concentration of hydrochloric acid is so arranged that the E.M.F. of cell II is greater than that of cell I, and therefore

$$\text{E.M.F.} = \text{E.M.F. of Cell II} - \text{E.M.F. of Cell I},$$

and as the silver electrodes are more positive than those of hydrogen, whence

$$\text{E.M.F.} = (E_3 - E_4) - (E_2 - E_1).$$

Assuming, for the moment, that the classical theory of Arrhenius is applicable, then

$$\begin{aligned}\text{E.M.F.} &= \left(\varepsilon_{Ag} + \frac{RT}{F} \ln [Ag^{\cdot}]_{II} - \frac{RT}{F} \ln [H^{\cdot}]_{II}\right) \\ &\quad - \left(\varepsilon_{Ag} + \frac{RT}{F} \ln [Ag^{\cdot}]_{I} - \frac{RT}{F} \ln [H^{\cdot}]_{I}\right) \\ &= \frac{RT}{F} \ln \frac{[Ag^{\cdot}]_{II} \cdot [H^{\cdot}]_{I}}{[Ag^{\cdot}]_{I} \cdot [H^{\cdot}]_{II}}\end{aligned}$$

Assuming $[Ag^{\cdot}]$ in HCl in I and II is governed by the solubility product principle, then

$$[Ag^{\cdot}]_I \cdot [Cl']_I = [Ag^{\cdot}]_{II} \cdot [Cl']_{II} = L,$$

and

$$\therefore \text{E.M.F.} = \frac{RT}{F} \ln \frac{[H^{\cdot}]_I \cdot [Cl']_I}{[H^{\cdot}]_{II} \cdot [Cl']_{II}}.$$

If now we substitute *ion-activities* for *ion-concentrations*, then

$$\begin{aligned}\text{E.M.F.} &= \frac{RT}{F} \ln \frac{a_{H^{\cdot}_I} \cdot a_{Cl'_I}}{a_{H^{\cdot}_{II}} \cdot a_{Cl'_{II}}} \\ &= \frac{2RT}{F} \ln \frac{a_{\pm HCl_I}}{a_{\pm HCl_{II}}}, \\ &= \frac{2RT}{F} \ln \frac{\gamma_{\pm HCl_I} \cdot m_{HCl_I}}{\gamma_{\pm HCl_{II}} \cdot m_{HCl_{II}}}, \\ &= \frac{2RT}{F} \ln \frac{f_{\pm HCl_I} \cdot c_{HCl_I}}{f_{\pm HCl_{II}} \cdot c_{HCl_{II}}}.\end{aligned}$$

We shall assume that the hydrochloric acid in cell I is in the standard state, *i.e.*, $a_{\pm} = 1$ and its E.M.F. $= E_0$. Let E be the E.M.F. of cell II, which is measured independently for different molalities, m, of hydrochloric acid. The E.M.F. of the combined cell, I and II,

$$= E - E_0 = \frac{2RT}{F} \ln \frac{1}{\gamma_{\pm HCl} \cdot m_{HCl}}$$

whence $$E_0 - \left(E + \frac{2RT}{F} \ln m_{HCl}\right) = \frac{2RT}{F} \ln \gamma_{\pm HCl}.$$

This expression thus gives the E.M.F. of the cell:

$$\overset{+}{Ag} \mid AgCl \,.\, HCl(m) \mid \overset{-}{H_2}^{Pt}$$

in terms of E_0, the molality, m_{HCl}, of the hydrochloric acid used, and its mean ionic activity coefficient, $\gamma_{\pm HCl}$. Clearly, if E_0 can be ascertained, then $\gamma_{\pm HCl}$ can be calculated directly from E_0 and m_{HCl}.

The value of E_0 can be obtained by graphical extrapolation by plotting

$$E + \frac{2RT}{F} \ln m_{HCl} \text{ against } m_{HCl}$$

or $\sqrt{m_{HCl}}$, and finding the intercept at m_{HCl} (or $\sqrt{m_{HCl}}$) $= 0$, $\frac{2RT}{F} \ln \gamma_{\pm}$ then being zero. Unfortunately, the extrapolation depends largely on values of E, obtained with exceedingly dilute solutions of hydrochloric acid, in which solutions the hydrogen electrode tends to give erratic results. To avoid errors in extrapolation due to this cause, Brown and MacInnes (*J. Amer. Chem. Soc.*, 1935, **57**, 1356) incorporated in the above expression the Debye–Hückel equation for the activity of an ion and so were able to plot two variables which on theoretical grounds gave a straight line.

Table 48 records the E.M.F's at 25° of the cell

$$\overset{+}{Ag} \mid AgCl \,.\, HCl(m) \mid \overset{-}{H_2}^{Pt}$$

as determined by Carmody (*ibid.*, 1932, **54**, 188). The third column gives the calculated values of $E + \frac{2RT}{F} \ln m_{HCl}$, which he plotted, together with similar data obtained by other investigators, against $\sqrt{m_{HCl}}$. By using $\sqrt{m_{HCl}}$, instead of m_{HCl}, he obtained a straight line which made extrapolation easier. (Strictly speaking, the mathematical relationship is not rectilinear, except possibly over the narrow range of m_{HCl} employed.)

TABLE 48

E.M.F. OF CELL: $\overset{+}{Ag} \mid AgCl \cdot HCl(m) \mid \overset{-}{H_2}^{Pt}$ AT 25° C.

$m_{HCl.}$	E.	$E + 0{\cdot}1183 \log m_{HCl.}$
0·1165	0·3449	0·2344
0·1083	0·3483	0·2341
0·1056	0·3496	0·2341
0·09425	0·3552	0·2338
0·04572	0·3901	0·2316
0·009582	0·4660	0·2272
0·004965	0·4987	0·2261
0·002799	0·5271	0·2251
0·001910	0·5462	0·2245
0·001129	0·5727	0·2241
0·0007280	0·5950	0·2238
0·0005518	0·6090	0·2236
0·0003288	0·6353	0·2233

Prentiss and Scatchard (*Chem. Rev.*, 1933, **13**, 139) have analysed the data obtained for this particular cell by various workers and conclude that $E_0 = 0{\cdot}2225 \pm 0{\cdot}0001$ volt. Brown and MacInnes' modified extrapolation method applied to the experimental data of Harned and Ehlers (*J. Amer. Chem. Soc.*, 1932, **54**, 1380) and of Roberts (*ibid.*, p. 3877) also gives 0·2225 volt.

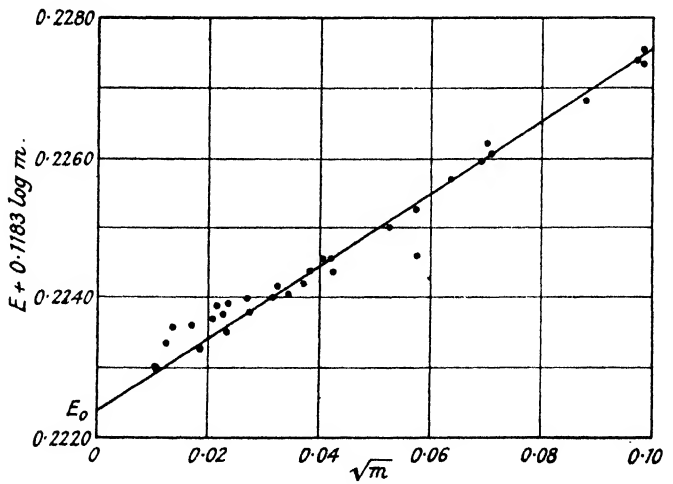


FIG. 67.—Carmody's Extrapolation of E_0 of Cell:

$\overset{+}{Ag} \mid AgCl \cdot HCl(m) \mid \overset{-}{H_2}^{Pt}$ at 25°.

From the data of Linhart, Noyes and Ellis, Nonhebel and Carmody.

Once E_0 is known, it is an easy matter to calculate $\gamma_\pm$ for each molality of hydrochloric used by means of the above equation.

TABLE 49

MEAN IONIC ACTIVITY COEFFICIENTS AT 25°.

m.	$\gamma_\pm$					
	HCl.	NaOH.	NaCl.	KCl.	H_2SO_4.	HBr.
0·005	0·930	—	0·928	0·927	0·643	0·930
0·01	0·906	0·899	0·903	0·902	0·545	0·906
0·02	0·878	0·860	0·872	0·869	0·455	0·879
0·05	0·833	0·805	0·821	0·817	0·341	0·838
0·10	0·798	0·759	0·778	0·770	0·266	0·805
0·20	0·768	0·719	0·732	0·719	0·210	0·782
0·50	0·769	0·681	0·680	0·652	0·155	0·790
1·00	0·811	0·667	0·656	0·607	0·131	0·871
1·50	0·898	0·671	0·655	0·587	—	—
2·00	1·011	0·685	0·670	0·578	0·125	—
3·00	1·31	—	0·719	0·574	0·142	—
4·00	1·74	—	0·791	—	0·172	—

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NaOH . Harned, *ibid.*, 1925, **47**, 677; Harned and Hecker, 1933, **55**, 4838.

NaCl . Harned and Nims, *ibid.*, 1932, **54**, 423; Brown and MacInnes, *ibid.*, 1935, **57**, 1356.

KCl . . Shedlovsky and MacInnes, *ibid.*, 1937, **59**, 503.

H_2SO_4 . Harned and Hamer, *ibid.*, 1935, **57**, 27; Shrawder and Cowperthwaite, *ibid.*, 1934, **56**, 2340.

HBr . . Harned, Keston and Donelson, *ibid.*, 1936, **58**, 989.

Table 49 gives the mean ionic activity coefficients at 25° of a number of uni-univalent electrolytes, HCl, NaOH, NaCl, KCl and HBr, and one uni-divalent electrolyte, H_2SO_4, over a wide range of molalities. It will be observed that in the more dilute solutions $\gamma_\pm$ of the uni-univalent electrolytes are almost identical, being 0·93 for 0·005 m solutions. That of sulphuric acid is much smaller, 0·64. At the same molality $\gamma_\pm$ for $CaCl_2$ is 0·789, and for $ZnCl_2$ it is 0·767, these two salts being examples of di-univalent electrolytes and it might, therefore, have been expected that they should have been comparable with sulphuric acid. The effect of the valency of the ions is clearly seen in the case of $ZnSO_4$ and $CdSO_4$, for which at $m = 0{\cdot}005$, $\gamma_\pm$ is 0·477 and 0·476 respectively. It can be generally concluded from these data that in dilute solutions the mean ionic activity coefficient

is dependent chiefly on the valency of the ions concerned. It will also be noticed that, with the increasing molality of certain electrolytes $\gamma_{\pm}$ passes through a minimum and then increases, *e.g.*, HCl, NaCl, HBr. On the other hand, $\gamma_{\pm}$ of sulphuric acid progressively decreases.

Arbitrary Hydrogen Standard Electrode.

Under ideal conditions, the electrode arbitrarily chosen as being of zero potential should be the hydrogen electrode, under hydrogen gaseous pressure of 1 atmosphere, and in equilibrium with hydrogen ions at unit activity. Such an electrode should be the standard for each particular temperature. As no method has yet been devised to determine the activities of single ions, the arbitrary standard is H_2(1 atmos.) | HCl, $a_{\pm} = 1$, $a_{\pm HCl}$ being substituted for $a_{H^{\cdot}}$. This is a disadvantage, for obviously the activity of the anion, Cl′, must have some effect on that of the H·-ion, and so be included in $a_{\pm HCl}$. Any other anion, *e.g.*, Br′, would presumably have a different effect. However, the presence of HCl in the arbitrary standard hydrogen electrode appears to be tacitly assumed. It thus happens that the cell

$$\overset{+}{\text{Ag}} \mid \text{AgCl} \,.\, \text{HCl}\ a_{\pm} = 1 \mid \overset{-}{\text{H}_2}^{\text{Pt}}$$

contains the arbitrary standard electrode, against which the electrode Ag | AgCl,HCl $a_{\pm} = 1$ is compared. It therefore follows that the potential of the latter is + 0·2225 volt with respect to the hydrogen standard.

Standard Potential, E_0, of Electrode, Ag | AgCl,. Cl′.

This refers to the electrode when in equilibrium with Cl′-ions at unit activity, but as this is not known with certainty $a_{Cl'}$ is assumed to be equal to $a_{\pm HCl}$.

Its potential is therefore + 0·2225 volt.

Calculation of Potential of Ag | AgCl,0·1 N-KCl.

The potential of this electrode is

$$E_{Ag} = \varepsilon_{Ag} + \frac{RT}{F} \ln a_{Ag^{\cdot}}$$

But as the KCl solution is saturated with AgCl, it follows that $a_{Ag^{\cdot}} \times a_{Cl'}$ = activity solubility product = L, and therefore

$$E_{Ag} = \varepsilon_{Ag} + \frac{RT}{F} \ln L - \frac{RT}{F} \ln a_{\pm KCl} \,.$$

The terms $\varepsilon_{Ag} + \frac{RT}{F} \ln L = E_0$ of $Ag \mid AgCl,Cl' = + 0{\cdot}2225$;

also 0·1N-KCl = 0·1006 *m*KCl and $\gamma_{\pm KCl} = \gamma_{Cl'} = 0{\cdot}770$.

Hence, the potential of $Ag \mid AgCl$, 0·1 N-KCl at 25° is

$$= E_{Ag} = 0{\cdot}2225 - 0{\cdot}0591 \log 0{\cdot}1006 \times 0{\cdot}77$$
$$= + 0{\cdot}2882 \text{ volt.}$$

Standard Potential, E_0, of $Hg \mid Hg_2Cl_2$, Cl'.

Randall and Young (*J. Amer. Chem. Soc.*, 1928, **50**, 989) found that at 25° the E.M.F. of the cell:

$$\overset{+}{Hg} \mid Hg_2Cl_2 \,.\, HCl \,.\, AgCl \mid Ag$$

is 0·0456 volt over a wide range of concentration of hydrochloric acid solutions. By assuming that both electrodes are therefore in equilibrium with an electrolyte at $a_{\pm} = 1$, and taking 0·2225 volt as the potential of the silver electrode, it follows that E_0 of $Hg \mid Hg_2Cl_2,Cl'$ is 0·0456 volt more positive, *viz.* = + 0·2681 volt.

Calculation of Potentials of Normal and Decinormal Calomel Electrodes.

The potential of the mercury electrode in equilibrium with KCl solution is

$$E_{Hg_2^{\cdot\cdot}} = E_{0Hg \mid Hg_2Cl_2,Cl'} - \frac{RT}{F} \ln a_{\pm KCl}$$
$$= E_{0Hg \mid Hg_2Cl_2,Cl'} - \frac{RT}{F} \ln \gamma_{\pm KCl} \cdot m_{KCl}$$

To obtain the potential of the N-Calomel Electrode, we take $\gamma_{\pm KCl} = 0{\cdot}607$ and $m = 1{\cdot}0327$, and therefore

$$E_{N\text{-calomel}} = + 0{\cdot}2801 \text{ volt at } 25°.$$

Similarly, for 0·1 N-KCl, $\gamma_{\pm KCl} = 0{\cdot}770$ and $m = 0{\cdot}1006$, whence

$$E_{0{\cdot}1\text{ N-calomel}} = + 0{\cdot}3338 \text{ volt at } 25°.$$

Standard Potential, E_0 of $^{Pt}H_2 \mid H_2O$ (liq.), OH'.

The potential of the hydrogen electrode is given by $E_{H_2} = 0 + \frac{RT}{F} \ln a_{H\cdot}$, and as the activity ionic product of water, $k_w = a_{H\cdot} \times a_{OH'} = 1{\cdot}0083 \times 10^{-14}$ at 25°,

$$E_{H_2} = \frac{RT}{F} \ln \frac{k_w}{a_{OH'}} = 0{\cdot}0591 \log \frac{1{\cdot}0083 \times 10^{-14}}{a_{OH'}}.$$

Hence, when $a_{OH'} = 1$, we have E_0, the potential of

$$Pt_{H_2} \mid H_2O \text{ (liq.)}, OH', = - 0{\cdot}8279 \text{ volt.}$$

Standard Potential, E_0, of Hg | HgO, OH'.

Kobayshi and Wang (*J. Sci. Hiroshima Univ.*, 1934, **5A**, 71) find that the E.M.F. of the cell:

$$\overset{+}{\mathrm{Hg}} \mid \mathrm{HgO} \,.\, \mathrm{NaOH}(m) \mid \overset{-}{\mathrm{H_2}}^{\mathrm{Pt}} \text{ at } 25^\circ$$

is + 0·9255 volt with NaOH from 0·05 *m* to 0·5 *m*. Both electrodes may therefore be regarded as being at unit activity.

Hence $+ 0{\cdot}9255 = E_{0\ \mathrm{Hg}\mid\mathrm{HgO},\ \mathrm{OH'}} - E_{0\ \mathrm{H_2}\mid\mathrm{H_2O},\ \mathrm{OH'}}$

$= E_{0\ \mathrm{Hg}\mid\mathrm{HgO},\ \mathrm{OH'}} - (- 0{\cdot}8279)$

and therefore $E_{0\ \mathrm{Hg}\mid\mathrm{HgO},\ \mathrm{OH'}} = + 0{\cdot}0976$ volt.

Calculation of Potential of Donnan-Allmand Electrode viz., Hg | HgO, 0·1 N-NaOH, at 25°.

The potential of this electrode is given by

$$E = E_{0\ \mathrm{Hg}\mid\mathrm{HgO},\ \mathrm{OH'}} - 0{\cdot}0591 \log a_{\pm\mathrm{NaOH}}.$$

For 0·1 N-NaOH, $f_{\pm\mathrm{NaOH}} = 0{\cdot}75$, and therefore

$$E = + 0{\cdot}0976 + 0{\cdot}0664$$
$$= + 0{\cdot}1640 \text{ volt.}$$

Mixed Electrolytes.

The Ionic Strength.

Lewis and Randall (*J. Amer. Chem. Soc.*, 1921, **43**, 1112) point out that when considering the mean ionic activity coefficient of an electrolyte in a solution containing other electrolytes, due attention should be given to the concentration and valency of (and, therefore, the number of charges carried by) all the ions in the solution. In other words, the mean ionic activity coefficient of a particular electrolyte should be considered in regard to the total electrical state of the solution. As a measure of this state, Lewis and Randall introduced the term " Ionic Strength," usually denoted by μ. Assuming each electrolyte to be completely ionised, $\mu = \frac{1}{2}\Sigma$ (molality of each ion $\times$ the square of its valency) *e.g.*, (1) μ of a solution, 0·5 *m* with respect to HCl and 0·06 *m* with respect to $BaCl_2$

$= \frac{1}{2}(0{\cdot}5 \times 1^2 + 0{\cdot}5 \times 1^2 + 0{\cdot}06 \times 2^2 + 0{\cdot}12 \times 1^2)$
$= 0{\cdot}68.$

(2) μ of a solution, 0·02 *m* with respect to H_2SO_4 and 0·3 *m* with respect to $La_2(SO_4)_3$

$= \frac{1}{2}(0{\cdot}04 \times 1^2 + 0{\cdot}02 \times 2^2 + 0{\cdot}6 \times 3^2 + 0{\cdot}9 \times 2^2)$
$= 4{\cdot}56.$

They find that, as a general rule, in dilute solutions the mean ionic activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength.

Action of Neutral Salts.

As early as 1915, Harned (*J. Amer. Chem. Soc.*, 1915, **37**, 2640; 1916, **38**, 1986), noticed that the addition of simple salts, such as the alkali chlorides, to hydrochloric acid concentration cells resulted in changes in the cell potentials which could not be attributed entirely to the change in chloride ion concentration effected by the added salt; in other words the deviations from the Gas Laws to which even dilute solutions are subject, are also modified by the presence of neutral salts and these modifications can be expressed in terms of the activity coefficients of the ions to which the cell is reversible. Thus measurements of the E.M.F's of cells of the type:

$$^{Pt}H_2|HCl(0{\cdot}1m),AgCl|Ag|AgCl\,.\,HCl(m_1)\,.\,MCl(m_2)|H_2{}^{Pt}$$

give the mean activity coefficient, γ_{HCl}, of hydrochloric acid in the alkali chloride (MCl) solution with respect to the activity coefficient in 0·1*m*-HCl solution, from the equation:

$$E = 0{\cdot}05915 \log \frac{\gamma_{H'} \cdot \gamma_{Cl'} \cdot m_1(m_1 + m_2)}{\gamma_{H'_{0\cdot1}} \cdot \gamma_{Cl'_{0\cdot1}} \cdot (0{\cdot}1)^2}$$

$$= 0{\cdot}1183 \log \frac{\gamma_{\pm HCl}\sqrt{m_1(m_1 + m_2)}}{\gamma_{\pm HCl_{0\cdot1}}(0{\cdot}1)},$$

where $\gamma_{H'}$, $\gamma_{Cl'}$, γ_{HCl} refer to the salt solution and $\gamma_{H_{0\cdot1}}$, $\gamma_{Cl_{0\cdot1}}$, $\gamma_{\pm HCl_{0\cdot1}}$ refer to the salt-free solution of hydrochloric acid and E is the E.M.F. of the complete cell at 25°. Measurements of this type have been made on hydrochloric, hydrobromic, hydriodic and sulphuric acids, and a remarkable similarity is to be found in the salt effects on these acids. Fig. 68 illustrates the variation of the mean activity coefficients of 0·1 N hydrochloric and sulphuric acids respectively on addition of varying amounts of different neutral salts. The general effect in the case of the halide acids is that with increasing salt concentration the activity coefficient first diminishes, passes through a minimum at about $\mu = 0{\cdot}5$ and then increases somewhat rapidly.

This treatment has been extended to salt effects on hydroxides by means of cells of the type:

$$H_2|MOH,\quad MX(\text{or } M_2SO_4)|M_xHg|MOH|H_2,$$

where M = alkali metal and X = halide. From the E.M.F. of

a cell of this type can be calculated the variation in the mean activity coefficient, γ_{MOH}, of the alkali hydroxide on the addition of increasing amounts of the corresponding halide or sulphate. The general effect is similar to the salt effect on acids ; the first addition of salt results in a diminution of the activity coefficient of the hydroxide. In the case of the effect of the corresponding chlorides on sodium, potassium, and lithium hydroxides and of potassium sulphate on potassium hydroxide a minimum value is obtained, followed by a very slight increase in the activity coefficient on further addition of salt, while in the case of the salt

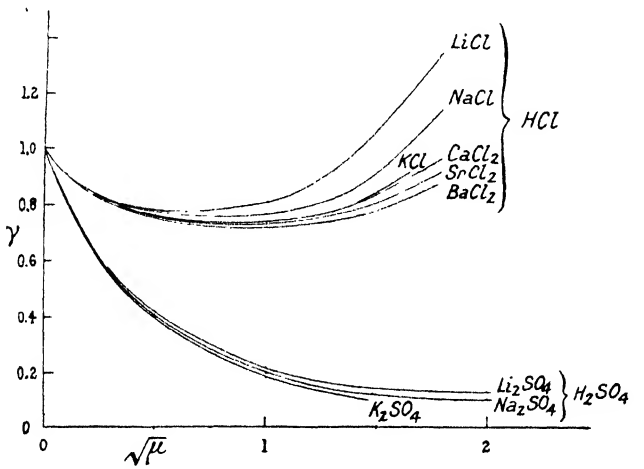


FIG. 68.—Effect of Neutral Salts on Mean Activity Coefficients on (*a*) 0·1*N* HCl, (*b*) 0·1*N* H_2SO_4.

effects of sodium and lithium sulphates on the corresponding hydroxides, no minimum is observed, the activity coefficient decreasing slowly with increasing salt concentration.

In the case of the salt effects on the hydroxides the order of magnitude of the effects is the reverse of those on a strong acid. Thus in the case of hydrochloric acid at any given total ionic concentration

$$\gamma_{HCl(LiCl)} > \gamma_{HCl(NaCl)} > \gamma_{HCl(KCl)}$$

whilst in the case of the alkali hydroxides,

$$\gamma_{KOH(KCl} > \gamma_{NaOH(NaCl)} > \gamma_{LiOH(LiCl)}$$

where the bracketed suffixes refer to the salt present in the solution.

In view of this reversal of the specific salt effect, it is of interest to consider the activity coefficients, γ_{MCl}, of alkali chlorides

in aqueous solution. These have been measured from the E.M.F's set up by cells of the type:

$$Ag|AgCl MCl(0{\cdot}01m)M_xHg|MCl(m)AgCl|Ag$$

where M = alkali metal. The activity coefficients, γ_{MCl}, vary with concentration in a manner similar to the change in γ_{HCl} caused by addition of these salts to hydrochloric acid; a minimum is observed in all cases, the curve being very flat in the case of potassium chloride, but the specific salt effects are apparent in the wider separation of the three curves, the order of the curves being the same as in the case of the salt effects on hydrochloric acid, *i.e.*, $\gamma_{LiCl} > \gamma_{NaCl} > \gamma_{KCl}$.

Harned and his collaborators (*J. Amer. Chem. Soc.*, 1925, **47**, 930; 1926, **48**, 126; 1930, **52**, 3892; *J. Phys. Chem.*, 1926, **30**, 1060) have shown that the mean activity coefficient of water in salt solutions, $\gamma_{H_2O} = \sqrt{\gamma_{H^+} \cdot \gamma_{OH^-}}$, is also subject to neutral salt effects of a magnitude comparable with the salt effects on acids and bases, the curve of $\sqrt{\gamma_{H^+} \cdot \gamma_{OH^-}}$ against salt concentration showing the characteristic minimum at about $\mu = 0{\cdot}5$, the specific salt effects being in the order

$$\gamma_{H_2O(KCl)} > \gamma_{H_2O(NaCl)} > \gamma_{H_2O(LiCl)},$$

which is the same order as that which holds for the salt effects on the hydroxides. Fig. 69 shows the effect of neutral salts on the ionic product of water at 25°.

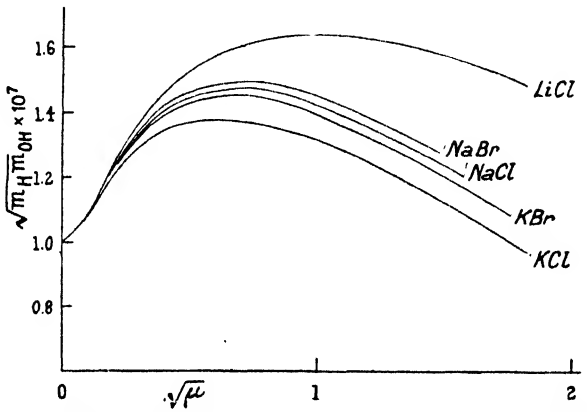


FIG. 69.—Effect of Neutral Salts on the Ionic Product of Water.

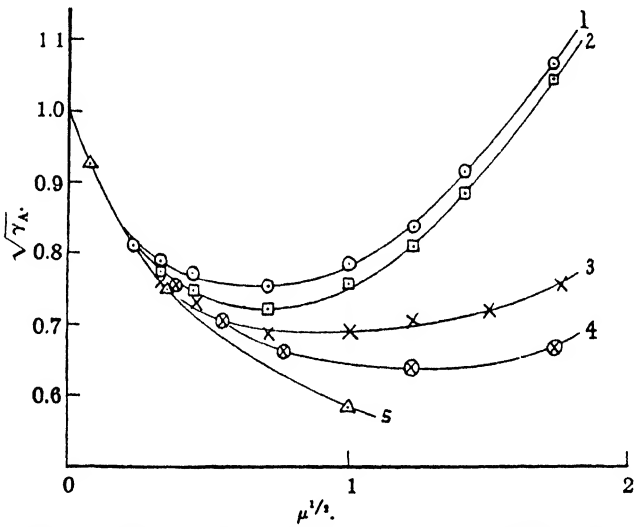
Neutral salt effects on weak acids and bases were studied by Harned and Robinson (*J. Amer. Chem. Soc.*, 1928, **50**, 3157), using a cell of the type:

$$^{Pt}H_2|HA, \underset{I}{MCl(m_1)}, AgCl|Ag|AgCl, \underset{II}{MCl(m_3)}HCl(m_2)|H_2{}^{Pt}$$

where M = Li, Na, K, or ½ Ba, HA = weak acid (*e.g.*, acetic acid). The E.M.F. of the combined cell is given by

$$E = 0{\cdot}05915 \log \frac{\gamma_{H\cdot_I} \cdot \gamma_{Cl'_I} \cdot m_{II\cdot} \cdot m_1}{\gamma_{H\cdot_{II}} \cdot \gamma_{Cl'_{II}} \cdot m_2(m_2 + m_3)}$$

They concluded that the mean activity coefficient, $\sqrt{\gamma_{H\cdot}\gamma_{Cl'}}$, in the weak acid-salt solution could be computed from previous data on hydrochloric acid-salt solutions with the single assumption that this mean activity coefficient was not changed by the presence of the undissociated molecules of the weak acid, which is probably



1, KCl; 2, NaCl; 3, LiCl; 4, $BaCl_2$; 5, Debye and Hückel theory.

FIG. 70.—Influence of Neutral Salts on the Mean Activity Coefficient of Acetic Acid.

correct at low acid concentrations in view of the small effect of un-ionised molecules on the dielectric constant of water. As a consequence, all the quantities in the above equation are known with the exception of m_H, which can therefore be calculated and substituted in the Mass Action Law:

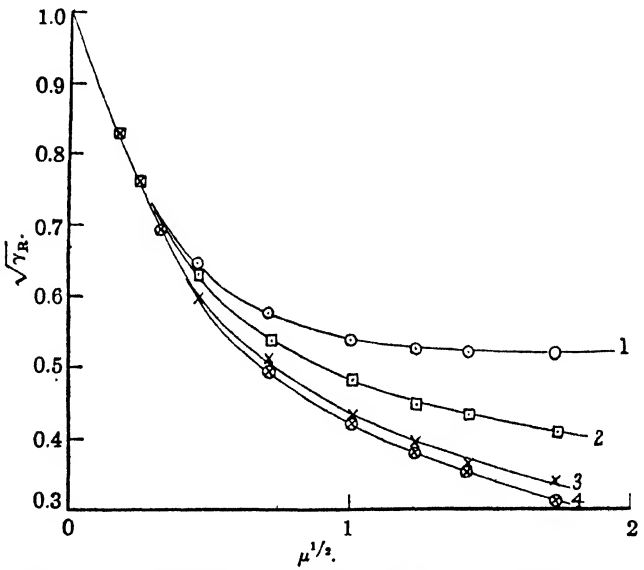
$$K = \frac{\gamma_{H\cdot}\gamma_{A'}}{\gamma_{HA}} \cdot \frac{m^2_H}{M - m_{H\cdot}}$$

where M is the stoicheiometric concentration of the weak acid and $\sqrt{\frac{\gamma_{H\cdot}\gamma_{A'}}{\gamma_{HA}}}$ is the mean activity coefficient of the weak acid. Fig. 70 illustrates the variation of the mean activity coefficient of 0·2M

acetic acid in solutions of sodium, potassium, lithium, and barium chlorides. The curves are very similar to the curves illustrating the salt effect on hydrochloric acid ; indeed, in the case of sodium chloride the two curves almost coincide ; a closer examination, however, reveals the fact that the specific salt effects are reversed in the case of acetic acid, the activity coefficients at any given ionic strength being

$$\gamma_{HAc(KCl)} > \gamma_{HAc(NaCl)} > \gamma_{HAc(LiCl)}$$

which is the same as the order found for salt effects on the hydroxide and on water.



1, NH_4OH; 2, CH_3NH_2OH; 3, $(CH_3)_2NH_2OH$; 4, $(CH_3)_3NHOH$.

FIG. 71.—Effect of Sodium Chloride on the Activity Coefficient of Weak Bases.

Using a slightly modified method, Harned and Robinson have measured the activity coefficients, $\sqrt{\frac{\gamma_{B^+}\gamma_{HO'}}{\gamma_{BOH}}}$, and the hydroxyl-ion concentration of several weak bases in salt solution. Fig. 71 shows the activity coefficients of ammonia, mono-, di- and trimethylamine in sodium chloride solution. The variation in activity coefficient of these amines on addition of sodium chloride resembles the behaviour of sodium hydroxide on addition of the same salt.

Güntelberg and Schiödt (*Z. physikal. Chem.*, 1928, **135**, 393), have come to very similar conclusions regarding the effect of

sodium and potassium chlorides on the mean activity coefficient of the hydrogen and bicarbonate ions. Harned and Hickey (*J. Amer. Chem. Soc.*, 1937, **59**, 1284, 2303) have also studied the effect of neutral salts on the ionisation of weak acids.

The problem of the neutral salt effect on weak electrolytes has been approached from a somewhat different angle by Morton (*J. Chem. Soc.*, 1928, 1401 ; *Trans. Faraday Soc.*, 1928, **24**, 14), who has investigated partially neutralised salt solutions of aspartic, acetic, cacodylic, phthalic, glycerylphosphoric, and pyrophosphoric acids and arginine. The hydrogen ion activity of a salt solution of a half-neutralised weak monobasic acid, H_A, is given by :

$$pa_H = pK + \log \frac{\gamma_{A'}}{\gamma_{HA}}$$

where $\gamma_{A'}$, γ_{HA}, are the activity coefficients of the anion and the undissociated molecule respectively. It is assumed that γ_{HA} will not depart much from unity and $\gamma_{A'}$ is expressed by means of the Debye-Hückel limiting equation, as

$$-\log \gamma_{A'} = A\sqrt{\mu} - B\mu.$$

(see page 285). The equation then becomes

$$pa_H = pK - A\sqrt{\mu} + B\mu.$$

Dissociation Constants of Weak Acids.

Unlike strong electrolytes, weak acids and bases are not considered to be completely ionised from the standpoint of the activity theory. A weak acid, HA, ionises thus

$$HA \rightleftharpoons H^{\cdot} + A'$$

and its thermodynamic dissociation constant,

$$k = \frac{a_{H^{\cdot}} \times a_{A'}}{a_{HA}} = \frac{\gamma_{H^{\cdot}} m_{H^{\cdot}} \times \gamma_{A'} m_{A'}}{\gamma_{HA} \cdot m_{HA}}.$$

The problem of determining these constants by means of cells without transport has been largely solved by Harned and Ehlers (*J. Amer. Chem. Soc.*, 1932, **54**, 1350), though not without making certain fundamental assumptions.

Consider the cell :

$$\overset{+}{Ag}|AgCl,NaCl(m_3),NaA(m_2),HA(m_1)|\underset{1\ atm.}{\bar{H}_2}$$

Following the derivation, given on page 268, it can be easily shown that its E.M.F.,

$$E = E_0 - \frac{RT}{F} \ln a_{H^{\cdot}} \times a_{Cl'},$$

E_0 being the E.M.F. of the reference cell

$$\overset{+}{\mathrm{Ag}}|\mathrm{AgCl}\,.\,\mathrm{HCl}\,a_{\pm} = 1|\underset{1\text{ atm.}}{\mathrm{H_2}}\,.$$

Combining the dissociation constant expression with this equation, it follows that

$$E = E_0 - \frac{RT}{F}\ln\frac{m_{HA}\cdot m_{Cl'}}{m_{A'}} - \frac{RT}{F}\ln\frac{\gamma_{Cl'}\cdot\gamma_{HA}}{\gamma_{A'}} - \frac{RT}{F}\ln k$$

and therefore

$$E - E_0 + \frac{RT}{F}\ln\frac{m_{HA}\cdot m_{Cl'}}{m_{A'}} = -\frac{RT}{F}\ln\frac{\gamma_{Cl'}\cdot\gamma_{HA}}{\gamma_{A'}} - \frac{RT}{F}\ln k.$$

The right-hand side of this equation may be put equal to $-\frac{RT}{F}\ln k'$, where $k' = k$ at infinite dilution, the various activity coefficients then becoming unity. The left-hand side can be evaluated for different molalities of HA, NaA and NaCl, since E is the observed E.M.F. and E_0 is known. The value of $m_{HA} = m_1 - m_{H'}$, $m_{H'}$ being the molality of hydrogen ions; $m_{Cl'} = m_3$, and $m_{A'} = m_2 + m_{H'}$. The difficulty arises, however, in computing $m_{H'}$, and it is here that Harned and Ehlers have been compelled to make use of the dissociation constant of the acid, which they set out to determine. It should, in fairness to them, be stated that an approximate value only is needed, which they say will give a sufficiently accurate value of $m_{H'}$. The different values of the left-hand side of the equation are now plotted against the ionic strength, μ, of the mixture in the cell. Extrapolation to $\mu = 0$ gives an intercept $= -\frac{RT}{F}\ln k$, for the first term will have then become equal to zero. The thermodynamic constant, k, therefore can be calculated. Table 50 gives some of Harned and Ehlers' data, obtained by using sodium acetate and acetic acid, from which $k_{\text{Acetic acid}}$ at 25° and $\mu = 0$ was extrapolated.

TABLE 50

$CH_3COOH.$ m_1.	NaAc. m_2.	NaCl. m_3.	μ.	E.M.F.	$k' \times 10^5$.
0·004779	0·004599	0·004896	0·00951	0·63959	1·752
0·012035	0·011582	0·012426	0·02403	0·61583	1·747
0·021006	0·020216	0·21516	0·04175	0·60154	1·743
0·04922	0·04737	0·05042	0·09781	0·57977	1·734
0·08101	0·07796	0·08297	0·16095	0·56712	1·724
0·09056	0·08716	0·09276	0·17994	0·56423	1·726

$\therefore k_{HAc} = 1{\cdot}754 \times 10^{-5}$ at $\mu = 0$.

Table 51 gives the thermodynamic dissociation constants at various temperatures of a number of weak acids, ampholytes and water, which have been similarly determined from cells without liquid junctions.

TABLE 51

THERMODYNAMIC DISSOCIATION CONSTANTS

Compound.		$k_{\times}$	0° C.	10° C.	20° C.	25° C.	30° C.	40° C.	50° C.	60° C.
Formic acid	(1)	10^4	1·638	1·728	1·765	1·772	1·768	1·716	1·650	1·551
Acetic acid	(2)	10^5	1·657	1·729	1·753	1·754	1·750	1·703	1·633	1·542
Monochloroacetic acid	(3)	10^3	1·528	1·491	—	1·378	—	1·229	—	—
Propionic acid	(4)	10^5	1·274	1·326	1·338	1·336	1·326	1·284	1·229	1·160
n-Butyric acid	(5)	10^5	1·563	1·576	1·542	1·515	1·484	1·395	1·302	1·199
H_3PO_4: 1st Stage	(6)	10^3	8·983	8·519	7·896	7·537	7·152	6·330	5·475	—
H_2PO_4'	(7)	10^8	—	—	6·056	6·226	6·349	6·471	6·439	—
HSO_4'	(8)	10^3	14·8	13·9	12·7	12·0	11·3	9·73	7·94	5·96
Boric acid	(9)	10^{10}	—	4·17	5·25	5·80	6·35	7·39	8·33	—
Glycollic acid	(10)	10^4	1·334	1·413	1·463	1·475	1·481	1·480	1·449	—
Lactic acid	(11)	10^4	1·290	1·346	1·372	1·374	1·367	1·332	1·267	—
Glycine-*acid*	(12)	10^3	—	3·94	4·31	4·47	4·59	4·81	—	—
Glycine-*base*	(12)	10^5	—	4·68	5·57	6·07	6·52	7·43	—	—
dl-Alanine 1st	(13)	10^3	—	—	7·30	6·54	6·68	6·76	—	—
dl-Alanine 2nd	(13)	10^{10}	—	—	0·986	1·31	2·27	3·19	—	—
Water	(14)	10^{14}	0·115	0·293	0·681	1·008	1·471	2·916	5·476	9·614

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Dissociation Constants of Dibasic Acids.

Jones and Soper (*J. Chem. Soc.*, 1934, 1836; 1936, 133) have made use of the combined cell:

$$\underset{\text{I}}{H_2|HCl,C = 0{\cdot}001\,N,AgCl|Ag|AgCl.0{\cdot}001\,N\text{-}NaCl}\,.\,\underset{\text{II}}{Na_2X,H_2X|H_2}$$

The

$$\text{E.M.F.} = \frac{RT}{F}\ln\frac{a_{H^+_{II}}\cdot a_{Cl'_{II}}}{a_{H^+_{I}}\cdot a_{Cl'_{I}}}$$

$$= E_{0{\cdot}001} - E,$$

$E_{0{\cdot}001}$ being the E.M.F. of the reference cell containing 0·001 N-HCl, and E, the E.M.F. of the cell II, in which the dibasic acid, H_2X, and its normal salt, Na_2X, are introduced in different ratios and concentrations.

Table 52 gives the values of $E_{0\cdot001}$ for temperatures ranging from 25° to 75° C. The potentials are not corrected for the saturated vapour pressure of water at the different temperatures, but refer to a total gaseous pressure of 760 mm. of mercury.

$$E_{0\cdot001} - E = \frac{RT}{F} \ln \frac{f_{H^\cdot} \cdot [H^\cdot]_{II} \cdot f_{Cl'} \cdot [NaCl]}{f^2_{\pm 0\cdot001}[HCl]^2_I}$$

$$= \frac{RT}{F} \ln \frac{f^2_{\pm II} \cdot [H^\cdot] \times 10^{-3}}{f^2_{\pm 0\cdot001} \times 10^{-6}},$$

NaCl and HCl being each 0·001 N.

$$\therefore E_{0\cdot001} - E = 2\frac{RT}{F} \ln \frac{f_{\pm II}}{f_{\pm 0\cdot001}} + 3\frac{RT}{F} + \frac{RT}{F} \ln [H^\cdot].$$

$$\text{Hence} \quad -\log [H^\cdot] = \frac{E - E_{0\cdot001}}{0\cdot0001983T} + 3\cdot00 + 2 \log \frac{f_{\pm II}}{f_{\pm 0\cdot001}}.$$

The mean ionic activity coefficient $f_\pm$ of 0·001 N-HCl is taken as 0·965, and an approximate value of $f_{\pm II}$ is computed from the Debye-Hückel Activity equation,

$$-\log f = \frac{Az^2\sqrt{\mu}}{1 + aB\sqrt{\mu}}, \qquad \text{(see p. 285)}$$

for each ionic strength μ, A being equal to 0·504 at 25°, 0·548 at 50°, 0·620 at 74°, and B, 0·328 at 25°, 0·338 at 50°, 0·348 at 74°. a is the mean effective diameter of the ions and is taken as 4 Å. It thus becomes possible to calculate the concentration of hydrogen ions in each mixture.

As $\quad H_2X \rightleftharpoons H^\cdot + HX'$

$$\therefore \quad k_1 = \frac{[H^\cdot][HX'] \cdot f^2_\pm}{[H_2X]}$$

and $\quad HX' \rightleftharpoons H^\cdot + X''$

$$\therefore \quad k_2 = \frac{[H^\cdot][X''] \cdot f_{X''}}{[HX']},$$

in which $f_{X''}$ is the activity coefficient of the divalent ion and is calculated from the Debye-Hückel Equation for each particular μ.

The chief merit of this method is that it permits the determination of hydrogen-ion concentrations using cells without transport. The classical constants are first calculated (see page 198) and these are corrected by multiplying by the appropriate activity coefficients. Such a method is only applicable to exceedingly dilute solutions, in which the hydrogen electrode does not function at its best unless extreme care is taken to guarantee the reproducibility of the E.M.F's observed.

TABLE 52

E.M.F. OF CELL :

$$\overset{+}{Ag}\,|\,AgCl\,.\,N/1000\ HCl\,|\,\overset{-}{H_2}^{Pt}\ \left(1\ \text{atmos.} - \text{vap. press. of water}\right)$$

Temp .	25·0°	35·0°	46·8°	57·0°	64·8°	74·8°
E.M.F. .	0·5793	0·5847	0·5897	0·5920	0·5931	0·5929

Dissociation of Water.

From the standpoint of thermodynamics, the ionisation of $H_2O \rightleftharpoons H^{\cdot} + OH'$ is governed by the Law of Mass Action, thus

$$k = \frac{a_{H^{\cdot}} \times a_{OH'}}{a_{H_2O}},$$

k being the "thermodynamic dissociation constant." Also

$$k = \frac{\gamma_{H^{\cdot}} \cdot m_{H^{\cdot}} \times \gamma_{OH'} \cdot m_{OH'}}{\gamma_{H_2O} \cdot m_{H_2O}} = \frac{\gamma_{H^{\cdot}} \cdot \gamma_{OH'}}{\gamma_{H_2O}} \cdot \frac{m_{H^{\cdot}} \cdot m_{OH'}}{m_{H_2O}}$$

$$= \frac{\gamma_{H^{\cdot}} \cdot \gamma_{OH'}}{\gamma_{H_2O}} \times \frac{K_w}{m_{H_2O}},$$

and

$$k_w = \frac{\gamma_{H^{\cdot}} \cdot \gamma_{OH'}}{\gamma_{H_2O}} \times m_{H^{\cdot}} \cdot m_{OH'} = \frac{\gamma_{H^{\cdot}} \cdot \gamma_{OH'}}{\gamma_{H_2O}} \times K_w.$$

Hence we have the relationship between the "*thermodynamic ionic activity product of water*," k_w, and the "*classical ionic product of water*," K_w. It is thus seen that only at infinite dilution, when $\gamma_{H^{\cdot}} \cdot \gamma_{OH'}/\gamma_{H_2O}$ is equal to unity, that k_w and K_w are equal. As γ_{H_2O} is most probably unity, it follows that k_w is approximately equal to $a_{H^{\cdot}} \times a_{OH'}$ or $\gamma_{H^{\cdot}} \cdot \gamma_{OH'} \cdot K_w$.

The determination of k_w from the E.M.F's of cells of the type :

$$\overset{+}{Ag}|AgCl\,.\,KCl(m_2),KOH(m_1)|\overset{-}{H_2}^{Pt}$$

has been made by Roberts (*J. Amer. Chem. Soc.*, 1930, **52**, 3877) and by Harned *et al.* (*ibid.*, 1932, **54**, 3112; 1933, **55**, 2194, 2206, 4496; 1935, **57**, 1873; 1937, **59**, 1280, 2032, 2304).

The principle of the method will now be described. As before the E.M.F. of the above cell,

$$E = E_0 - \frac{RT}{F} \ln a_{H^{\cdot}} \cdot a_{Cl'};$$

E_0 being the E.M.F. of the reference cell $\overset{+}{Ag}|AgCl\,.\,HCl\ a_{\pm}=1|\overset{-}{H_2}^{Pt}$

Substituting

$$a_{H^+} = k_w \cdot \frac{\gamma_{H_2O}}{\gamma_{OH^-} \times m_{OH^-}},$$

in the previous expression and re-arranging, we get

$$E - E_0 + \frac{RT}{F} \ln \frac{m_{Cl^-}}{m_{OH^-}} = -\frac{RT}{F} \ln k_w - \frac{RT}{F} \ln \frac{\gamma_{H^+} \cdot \gamma_{Cl^-} \cdot \gamma_{H_2O}}{\gamma_{H^+} \cdot \gamma_{OH^-}}$$

$$= -\frac{RT}{F} \ln k_w'$$

where $$k_w' = k_w \times \frac{\gamma_{H^+} \cdot \gamma_{Cl^-} \cdot \gamma_{H_2O}}{\gamma_{H^+} \cdot \gamma_{OH^-}}.$$

At infinite dilution, *i.e.*, when $\mu = 0$, the activity coefficients become unity, and then $k_w' = k_w$. Plotting

$$E - E_0 + \frac{RT}{F} \ln \frac{m_{Cl^-}}{m_{OH^-}}$$

against μ of the mixture present in the cell solution, and extrapolating to $\mu = 0$, therefore gives an intercept equal to

$$-\frac{RT}{F} \ln k_w,$$

from which k_w can be readily obtained. Using such a method Harned and Hamer (*J. Amer. Chem. Soc.*, 1933, **55**, 2194) obtained

$$k_w = 1{\cdot}0083 \times 10^{-14} \text{ at } 25^\circ \text{ and } \mu = 0.$$

Section II. Cells with Transport

A serious difficulty in considering cells with liquid junctions is the problem of interpreting, and calculating, the liquid junction potential on the basis of the activity theory. It is very probable that the interposition of a saturated solution of potassium chloride, owing to the mobilities of the potassium and chloride ions being almost the same, between the two electrodes of a cell reduces the junction potential very considerably. When the solutions which are thus separated do not contain hydrogen or hydroxyl ions in large concentrations, it is highly probable that potassium chloride reduces the junction potential to the order of a millivolt or so, but it is by no means certain that this is true of fairly acid or alkaline solutions. As *p*H measurements are generally made by using cells with transport, any errors caused by the existence of any junction potential are included in the calculation of the *p*H values.

This does not militate against the practical value of the *p*H results so obtained.

If we consider a concentration cell such as

$$\overset{+}{\underset{\text{I}}{\text{Ag}}}|\text{AgNO}_3(c_1)|\underset{\text{E}_\text{D}}{\quad}|\text{AgNO}_3(c_2)|\overset{-}{\underset{\text{II}}{\text{Ag}}},$$

it can be shown that as the result of the unequal mobilities of the cation and the anion, both ions will diffuse from the more concentrated solution to the less concentrated at different rates. The result will be, depending on whether the cation or the anion is the faster ion, a difference in potential between the two solutions at their junction. If the cation is the faster ion, then the less concentrated solution will be positive with respect to the more concentrated solution and *vice versa.*

Nernst (*Z. physikal. Chem.*, 1888, **2**, 613) showed that this diffusion potential could be evaluated in the case of simple concentration cells. Thus in the above cell, let $c_1 > c_2$, and let δx faradays of electricity, $\delta x \times \text{F}$, pass from right to left. $\delta x \times \eta_{\text{Cation}}$ equivalents of cations would therefore travel from right to left and $\delta x \times \eta_{\text{Anion}}$ equivalents of anions in the opposite direction. The osmotic work involved is

$$\delta x \times \eta_{\text{Cation}} \times \text{RT} \ln \frac{a_{+\text{II}}}{a_{+\text{I}}} + \delta x \times \eta_{\text{Anion}} \times \text{RT} \ln \frac{a_{-\text{I}}}{a_{-\text{II}}}$$

and the electrical work is $\delta x \times \text{F} \times \text{E}_\text{D}$, whence

$$\text{E}_\text{D} = \eta_{\text{Cation}} \times \frac{\text{RT}}{\text{F}} \ln \frac{a_{+\text{II}}}{a_{-\text{I}}} + \eta_{\text{Anion}} \times \frac{\text{RT}}{\text{F}} \ln \frac{a_{-\text{I}}}{a_{+\text{II}}}.$$

η_{Cation} = transport number of the cation,

η_{Anion} = transport number of the anion,

$a_{+\text{I}}$ and $a_{+\text{II}}$, the respective activities of the cations ($\text{Ag}^{\cdot}$) in electrodes I and II,

$a_{-\text{I}}$ and $a_{-\text{II}}$, the respective activities of the anions (NO_3') in electrodes I and II.

It has recently been shown that the transport numbers of ions depend, to some extent, on the concentrations of the electrolytes to which they belong. Hence the transport number of an ion may be expected to vary as the ion passes from one concentration to another. Another serious difficulty is that the expression involves the activities of single ions, and it will be remembered that no method has yet been devised by which single ion activities may be experimentally determined.

If it be assumed that

$$(a_\pm)_\text{I} = (a_{+\text{I}} \cdot a_{-\text{I}})^{\frac{1}{2}} \text{ and } (a_\pm)_\text{II} = (a_{+\text{II}} \cdot a_{-\text{II}})^{\frac{1}{2}},$$

and that the transport numbers are sufficiently constant, then it

can be proved that the E.M.F. of the complete concentration cell, *i.e.*, including the liquid junction potential, is given by

$$E = 2\eta_{Anion} \cdot \frac{RT}{F} \ln \frac{(a_{\pm})_I}{(a_{\pm})_{II}}.$$

By substituting mean ionic activities for single ion activities and by introducing a function, involving the variation in transport number with concentration, Brown and MacInnes (*J. Amer. Chem. Soc.*, 1935, **57**, 1356; see also Shedlovsky and MacInnes, *ibid.*, 1936, **58**, 1970; 1937, **59**, 503; MacInnes and Brown, *Chem. Reviews*, 1936, **18**, 335), have used concentration cells, with liquid junction, to determine the mean activity coefficients of sodium, potassium, calcium and hydrogen chlorides and silver nitrate solutions.

Instead of the E.M.F. of the cell being given by

$$E = 2\eta_{Anion} \cdot \frac{RT}{F} \ln \frac{(a_{\pm})_I}{(a_{\pm})_{II}},$$

they use the expression

$$E = 2\frac{R'T}{F}\int_{c_{II}}^{c_I} \eta_{Anion} \cdot d \ln a,$$

in which $\eta_{Anion} = \eta_1 + \Delta\eta$, where η_1 is the value at some reference concentration, c_1. Suppose this concentration is c_2 in the above cell and that c_1 is any concentration, c. Hence

$$E = 2\frac{RT}{F}\int_{c_1}^{c} \eta_{Anion} \cdot d \ln a,$$

$$\therefore dE = 2\frac{RT}{F}(\eta_1 + \Delta\eta)(d \ln c + d \ln f),$$

$$\therefore \ln\frac{f}{f_1} = \Delta \ln f = \frac{EF}{2\eta_1 RT} - \ln\frac{c}{c_1} - \frac{1}{\eta_1}\int_{c_1}^{c} \Delta\eta d \ln c$$

$$- \frac{1}{\eta_1}\int_{c_1}^{c} \Delta\eta d(\Delta \ln f).$$

The term $\Delta \ln f = \ln f - \ln f_1$, when f_1 is the mean activity coefficient in the reference solution, and therefore may be considered constant. The third term on the right-hand side of the equation can be evaluated graphically from the observed variation in transport number with concentration, whilst $\Delta \ln f$ in the fourth term can be converted into actual activity coefficients by using the Debye-Hückel activity equation,

$$-\log f = \frac{\alpha\sqrt{c}}{1 + \beta\sqrt{c}},$$

where α is a universal constant and β an adjustable constant, incorporating the size of ions.

Since $$\Delta \ln f = \ln f - \ln f_1 = \ln f + A,$$

then $$\Delta \ln f + \alpha\sqrt{c} = A + \beta(A - \Delta \ln f)\sqrt{c}.$$

For dilute solutions a plot of $\Delta \ln f + \alpha\sqrt{c}$ against $(A - \Delta \ln f)\sqrt{c}$ should give a straight line with an intercept equal to A, and a slope, β. A is obtained by successive approximation.

Standard Reference Electrode for use in interpreting the E.M.F's of cells *with transport* in terms of "ion-activities."

In dealing with cells *with transport* the potential of the calomel electrode used is generally based on ion-concentrations as determined by applying the Arrhenius Theory to conductance measurements. As shown on pages 265 to 267 the potentials of the reference electrodes may be calculated on the basis of the activity theory. On the other hand, Guggenheim and Schindler (*J. Physical Chem.*, 1934, **38**, 536) have measured the potentials at 25° of the hydrogen electrode in solutions of acetic acid and sodium acetate against the Decinormal Calomel electrode, 3·5 N-KCl being interposed between the electrodes. The small junction potentials on each side of the 3·5 N-KCl were calculated by means of Henderson's formula using 0·490 as the transport number of the potassium ion (Longsworth, *J. Amer. Chem. Soc.*, 1930, **52**, 1897; MacInnes and Dole, *ibid.*, 1931, **53**, 1357). Bjerrum and Unmack (*Kgl. Danske Videnskab. Selskab. Math. fys. Medd.*, 1929, **9**, No. 1) carried out similar E.M.F. measurements, but used 0·497 as the transport number of the potassium ion. Bjerrum and Unmack concluded that the potential of $Hg|Hg_2Cl_2.10\cdot1N\text{-}KCl$ is + 0·3360 volt at 25°, whereas Guggenheim and Schindler prefer 0·3337 volt at 25° C. Part of the discrepancy between these two values is to be attributed to the different values of the transport number taken, but the main cause appears to be more dilute solutions of hydrochloric acid used by Bjerrum and Unmack where, as Guggenheim and Schindler state, the experimental uncertainty is likely to be great. Instead, the latter take Harned and Ehlers' value of k of acetic acid, $1\cdot75 \times 10^{-5}$ at 25° C., as correct, assume that $f_{HAc} = 1$ and then ascertain which potential must be assigned to the Decinormal Calomel electrode to give satisfactory values of $f_{Ac'}$ for the various ionic strengths. A rough estimate of the small junction potential, introduced by using 3·5 N-KCl as junction liquid, may be made

by the Bjerrum method. In this method, the E.M.F. of the cell, in which 1·75 N-KCl is used instead of 3·5 N-KCl, is measured. The difference between the two E.M.F's is considered to be equal to the junction potential set up when 3·5 N-KCl is used. Bjerrum and Unmack now, however, recommend this procedure only when calculation of the junction potential cannot conveniently be made.

Table 53 gives the data upon which Guggenheim and Schindler base the value of + 0·3337 vole for the N/10-calomel electrode at 25°.

TABLE 53

E.M.F. OF CELL AT 25°

$$\overset{+}{Hg}|Hg_2Cl_2 \,.\, 0{\cdot}1M\text{-}KCl|3{\cdot}5N\text{-}KCl|\text{Solution S}|\overset{-}{H_2}$$

Solution S.	E.M.F.	pH.	E_D (calc.).	μ.	$f_{Ac'}$.
0·01 N-NaAc + 0·01 N-HAc. . .	0·6139	4·80	0·00148	0·01	0·90
0·01 N-NaAc + 0·01 N-HAc + 0·09 N-KCl	0·60975	4·67	0·0000	0·10	0·81
0·10 N-NaAc + 0·10 N-HAc . .	0·6101	4·66	0·00060	0·10	0·80

The E.M.F. of the cell $= E_{N/10\ calomel} - E_{H_2} + E_D$, E_D being the calculated junction potential. Hence

$$\text{E.M.F.} = E_{N/10\ Calomel} - 0{\cdot}059151 \log a_{H} + E_D$$

$$= E_{N/10\ calomel} - 0{\cdot}059151 \log k_{HAc} - 0{\cdot}059151 \log \frac{[HAc]}{[Ac']}$$

$$- 0{\cdot}059151 \log \frac{f_{HAc}}{f_{Ac'}} + E_D$$

and as $[HAc] = [Ac']$, $k = 1{\cdot}75 \times 10^{-5}$, f_{HAc} is assumed $= 1$, then

$$\text{E.M.F.} = E_{N/10\ calomel} - 0{\cdot}059151 \log 1{\cdot}75 \times 10^{-5} + 0{\cdot}059151 \log f_{Ac'} + E_D.$$

It is thus seen that by putting $f_{Ac'}$ equal to the values given in the last column, $E_{N/10\ calomel} = 0{\cdot}3337$ volt (*cf.* p. 266) Guggenheim and Schindler justify the choice of $f_{Ac'} = 0{\cdot}90$ for $\mu = 0{\cdot}01$, as it is the value of $f_{\pm}$ for any typical uni-univalent electrolyte at $\mu = 0{\cdot}01$, whilst $f_{Ac'} = 0{\cdot}80$ to $0{\cdot}81$ at $\mu = 0{\cdot}10$ falls within the range of $f_{\pm}$ of typical uni-univalent electrolytes at $\mu = 0{\cdot}10$ (see p. 264).

Table 54 gives the potentials of the Decinormal Calomel electrode at various temperatures. They are based on calcula-

tions made by Guggenheim and Schindler using Bjerrum and Unmack's data.

TABLE 54

POTENTIAL OF $Hg|Hg_2Cl_2$. 0·1 N-KCl AT VARIOUS TEMPERATURES

Temp.	0°	18°	25°	37°
$E_{0\cdot1\ N\text{-calomel}}$ . .	0·3342	0·3342	0·3337	0·3327

The adoption of 0·3337 volt at 25°, instead of Sörensen's value of 0·3376 volt, leads to *p*H values which are 0·065 *p*H unit higher than those generally obtained by using 0·3376 volt.

According to Guggenheim and Schindler, the E.M.F. at 25° C. of the cells :

(i) $Hg|Hg_2Cl_2$. 0·1 N-KCl|3·5 N-KCl|0·01 N-HCl|H_2
0·09 N-KCl
= 0·45830 volt (0·45840 B. & U.)

(ii) $Hg|Hg_2Cl_2$. 0·1 N-KCl|3·5 N-KCl|0·10 N-HCl|H_2
= 0·40080 volt (0·40090 B. & U.)

The observed

$$\text{E.M.F.} = E_{N/10\ \text{calomel}} + E_D - 0{\cdot}059151 \log a_{H^\cdot}$$
$$= E_{N/10\ \text{calomel}} + E_D - 0{\cdot}059151 \log [H^\cdot] - 0{\cdot}059151 \log f_{H^\cdot}$$

Here $[H^\cdot] = [HCl]$, 0·01 (cell i), 0·1 (cell ii)

E_D for cell (i) = 0·0004 volt ; for cell (ii) = 0·00364 volt.

By putting $E_{N/10\ \text{calomel}} = 0{\cdot}3337$,
we get

$f_{H^\cdot} = 0{\cdot}795$ in 0·01 N-HCl + 0·09 N-KCl

and $f_{H^\cdot} = 0{\cdot}85$ in 0·10 N-HCl.

Setting $f_{Cl'}$ in both solutions equal to 0·76 (this being $f_\pm$ for 0·1 N-KCl), we get $f_{H^\cdot} = 0{\cdot}80$ for the first solution and $f_{H^\cdot} = 0{\cdot}84$ for the second solution.

The Debye-Hückel Theory.

A more concrete meaning can be ascribed to the concept of " activity coefficient " in the light of the Debye-Hückel theory

(Debye and Hückel, *Physikal. Z.*, 1923, **24**, 185, 305 ; see Noyes, *J. Amer. Chem. Soc.*, 1924, **46**, 1080). These investigators adopt the hypothesis that most strong electrolytes are completely dissociated in solution and the deviations from the behaviour of perfect gases is interpreted in terms of the interionic forces originating in the opposite charges on the ions. As a consequence of these forces, any positive ion in a solution exerts a repulsive force on all the other positive ions and an attractive force on all the negative ions, according to the Inverse Square Law, and *vice versa* in the case of a negative ion ; these forces tend to orient the ions in a condition of symmetry in such a way that the positive ions are each surrounded by negative ions, in other words, there is a tendency for the ions to arrange themselves in a cubic lattice like a crystal of sylvine, but the Brownian Motion of the ions opposes this trend towards a perfectly symmetrical orientation of the ions. Because of this translational energy the ions tend to become distributed through the solution in a state of complete randomness. Therefore, as a result of these two opposing forces, it can only be said that, taken over a time interval, there will be an excess of positive ions in the neighbourhood of a negative ion and of negative ions in the vicinity of a positive ion, in other words each ion will be surrounded by an " atmosphere " of oppositely charged ions, the density of which will depend on the charges on the ions, the temperature, the dielectric constant of the solution and, particularly, on the concentration of the ion.

By making use of Poisson's Equation and the Boltzmann Principle of the equipartition of energy, Debye and Hückel derived expressions for (*a*) the activity coefficient of an ion and (*b*) the variation in equivalent conductivity of an electrolyte with dilution. These expressions show the dependence of ion-activity and electrical conductance on such factors as temperature and the dielectric constant of the solvent. Moreover, the conductivity equation is similar to that known as the Kohlrausch Square Root Law, in fact the theory places Kohlrausch's empirical law on a theoretical basis. Unfortunately, the expressions obtained by Debye and Hückel are not of general application, owing to a number of approximations made in their derivation. They refer, therefore, only to very dilute solutions ; usually not more concentrated than 0·01 M. Even if these approximations were reduced in magnitude, as indeed some investigators have done, it is extremely improbable that such a comparatively simple theory could hold for concentrated solutions, for other difficulties undoubtedly arise on account of the solvation of ions, the effects of which would then become pronounced. Nevertheless, the theory has

supplied the necessary background for the G. N. Lewis Activity Theory, including the concept of Ionic Strength.

According to the Debye-Hückel theory the activity coefficient of single ion of valency z is given by the expression :

$$-\log f = \frac{\varepsilon^3 \cdot z^2}{2{\cdot}303(DkT)^{\frac{3}{2}}} \times \frac{\sqrt{\frac{2\pi N\mu}{1000}}}{1 + a\sqrt{\frac{8\pi N\varepsilon^2\mu}{1000DkT}}}$$

in which ε = unit ionic charge = $4{\cdot}774 \times 10^{-10}$ e.s.u.
N = Avogadro's Number = $6{\cdot}064 \times 10^{23}$
μ = Total Ionic Strength = $\frac{1}{2}\Sigma cz^2$
D = Dielectric constant of solvent
k = Boltzmann's constant

$$= \frac{R}{N} = \frac{8{\cdot}315 \times 10^7}{6{\cdot}064 \times 10^{23}}$$

T = Absolute temperature
a = Sum of ionic radii of two oppositely charged ions, *i.e.*, the so-called distance of "closest approach."

On simplification, this expression becomes

$$-\log f = \frac{z^2 A\sqrt{\mu}}{1 + \beta \cdot a \cdot \sqrt{\mu}}.$$

When water is the solvent, A = 0·4863 at 0° C., 0·4992 at 18°, 0·5056 at 25° and 0·5186 at 38°, and $\beta = 3{\cdot}243 \times 10^7$ at 0° C., $3{\cdot}272 \times 10^7$ at 18°, $3{\cdot}286 \times 10^7$ at 25° and $3{\cdot}314 \times 10^7$ at 38°. a varies from ion to ion, but in general it is of the order of 2–3 Ångström units, *i.e.*, $2 - 3 \times 10^{-8}$ cm. It will thus be seen that for very dilute solutions, when μ is exceedingly small, the term $\beta \cdot a \cdot \sqrt{\mu}$ becomes negligible when compared with unity, and the expression thus assumes its limiting form, *viz.*,

$$-\log f = z^2 \cdot A\sqrt{\mu}.$$

Hückel in 1925 extended the theory so as to apply to higher concentrations, in which it is postulated that the dielectric constant of the solution is different from that of the solvent. It was assumed that the dielectric constant of a solution is a linear function of its concentration ; an assumption which probably is not valid. The expression thus becomes

$$-\log f = \frac{z^2 \cdot A \cdot \sqrt{\mu}}{1 + \beta \cdot a \cdot \sqrt{\mu}} - C\mu,$$

C being a constant, dependent on the nature of all the ions in the solution. Fig. 72 illustrates the theoretical values for the activity coefficient of a univalent ion in aqueous solution at 25°. Curve I represents the limiting equation taking A = 0·5, while Curves II and III show the changes caused by introducing (1) the $\beta . a$ term and (2) the B and C terms respectively.

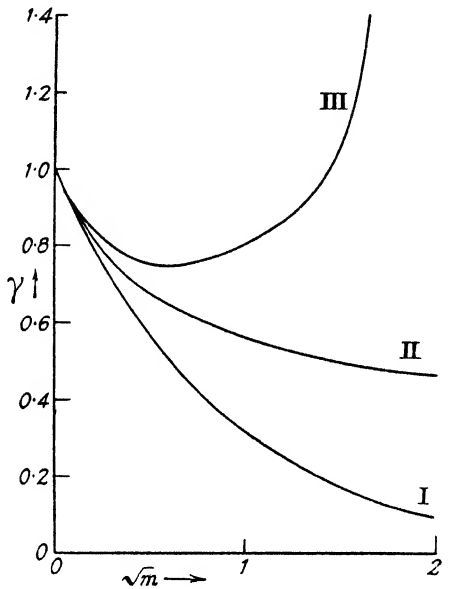


FIG. 72.—Theoretical Values of the Activity Coefficient of a Univalent ion in Aqueous Solution.

Hitherto, we have been concerned with the activity coefficient of a single ion, but as this cannot be determined experimentally, it will be an advantage to consider the mean ionic activity coefficient of an electrolyte in terms of the Debye-Hückel theory.

The mean ionic activity coefficient, $f_{\pm}$, of electrolyte, having cations of valency, z_+, and anions of valency, z_-, is given by

$$f_{\pm} = (f_+^{z_-} . f_-^{z_+})^{\frac{1}{z_- + z_+}}$$

(see p. 259).

Hence

$$- \log f_{\pm} = - (z_- . \log f_+ + z_+ . \log f_-) \times \frac{1}{z_- + z_+}.$$

Substituting the values for $-\log f$ for the cations and anions in this equation, we obtain

$$-\log f_{\pm} = \left\{ z_- \cdot \left(\frac{z_+^2 \mathrm{A}\sqrt{\mu}}{1+\beta \cdot a \cdot \sqrt{\mu}} - \mathrm{C}\mu \right) + z_+ \left(\frac{z_-^2 \mathrm{A}\sqrt{\mu}}{1+\beta . a . \sqrt{\mu}} - \mathrm{C}\mu \right) \right\} \times \frac{1}{z_- + z_+} = \frac{z_+ \cdot z_- \cdot \mathrm{A} \cdot \sqrt{\mu}}{1+\beta \cdot a \cdot \sqrt{\mu}} - \mathrm{C}\mu,$$

the limiting form of which, is

$$-\log f_{\pm} = z_+ \cdot z_- \cdot \mathrm{A} \cdot \sqrt{\mu},$$

the latter expression applying only to very dilute solutions.

Strictly speaking, in giving Hückel's modified equation in regard to more concentrated solutions a further term should have been added to the right-hand side—a term which, in the case of dilute solutions, is exceedingly small and has a negligible effect on f.

The complete expression is

$$-\log f_{\pm} = \frac{z_+ \cdot z_- \cdot \mathrm{A}\sqrt{\mu}}{1+\beta \cdot a \cdot \sqrt{\mu}} - \mathrm{C}\mu + \log \left(\frac{d - 0{\cdot}001 \times \mathrm{M} \times c + 0{\cdot}001 \times \mathrm{M}_s \times n \times c}{d_0} \right)$$

where d = density of the solution
d_0 = density of the solvent
M = molecular weight of solute
M_s = molecular weight of solvent, and
n = number of ions into which one molecule of solute dissociates.

If the concentrations are expressed in terms of molality, m, then the expression becomes

$$-\log \gamma_{\pm} = \frac{z_+ \cdot z_- \cdot \mathrm{A}\sqrt{\mu}}{1+\beta \cdot a \cdot \sqrt{\mu}} - \mathrm{C}\mu + \log (1 + 0{\cdot}001 \times \mathrm{M}_s \times n \times m).$$

These expressions have been tested experimentally for solutions, the concentrations of which are greater than 0·1 g.-mol. per litre. In order to make them fit the data, however, it has frequently been necessary to adjust "a" to a suitable value. Such values of "a" are usually devoid of any physical significance.

It should be mentioned that, although the activity coefficient, f, expression as derived by Debye and Hückel refers to concentrations in terms of gram-molecules per litre, no great error will be involved if f is assumed equal to γ when applied to low molalities, m, *i.e.*, to very dilute solutions.

Thermodynamic Dissociation Constants of Acids.

1. Monobasic Acids.

The thermodynamic dissociation constant of the acid, HA, $HA \rightleftharpoons H^{\cdot} + A'$,

$$k = \frac{a_{H^{\cdot}} \times a_{A'}}{a_{HA}}.$$

If the potentials of hydrogen electrodes can only be correctly interpreted in terms of hydrogen-ion activities, then it follows that pH values refer to $-\log_{10} a_{H^{\cdot}}$. Taking logarithms, to base 10, of the above equation, we obtain

$$-\log k = -\log a_{H^{\cdot}} - \log \frac{a_{A'}}{a_{HA}}$$

and therefore $$p\mathrm{H} = pk + \log \frac{a_{A'}}{a_{HA}}.$$

Assuming that the activity coefficient f_{HA} of the molecules of undissociated HA is unity, then

$$p\mathrm{H} = pk + \log \frac{f_{A'} \cdot [A']}{f_{HA} \cdot [HA]}$$

$$= pk + \log \frac{[A']}{[HA]} + \log f_{A'}.$$

Although the activity-coefficient, $f_{A'}$, of a single ion cannot be determined experimentally, it can be calculated by means of the Debye-Hückel limiting equation,

$$-\log f = A \cdot z^2 \cdot \sqrt{\mu}$$

which holds for solutions of very low ionic strength. For a monobasic acid, z, the valency of the anion is 1, and at 25°, $A = 0{\cdot}505$.

Hence the modified Henderson-Hasselbalch equation at 25° becomes

$$p\mathrm{H} = pk + \log \frac{[A']}{[HA]} - 0{\cdot}505\sqrt{\mu}.$$

It would appear from the activity theory that the dissociation constants, K, which have formerly been determined electrometrically, do not refer wholly to concentrations, *viz.*,

$$\mathrm{K} = \frac{[H^{\cdot}] \cdot [A']}{[HA]},$$

for instead of determining hydrogen-ion concentration, [H·], the activity of the hydrogen ions, $a_{H^{\cdot}}$, has been found, and $a_{H^{\cdot}}$ has

been employed in the equation in conjunction with the two concentrations, [A′] and [HA]. The result is that

$$K = \frac{a_{H^\cdot} \times [A']}{[HA]}$$

and thus K might be described as an "*imperfect constant.*"

Hence $$k = \frac{a_{H^\cdot} \cdot a_{A'}}{a_{HA}}$$

$$= \frac{a_{H^\cdot} \cdot [A'] \cdot f_{A'}}{[HA]} \text{ in very dilute solution,}$$

$$= K \times f_{A'}$$

$$\therefore \quad -\log k = -\log K - \log f_{A'}$$

i.e., $$pk = pK + 0{\cdot}505\sqrt{\mu} \text{ at } 25°.$$

Calculation of the Ionic Strength of HA during neutralisation with NaOH.

The ions present at any point of the titration are $Na^\cdot$, $H^\cdot$ and A'. Let the total concentration of the acid (free and neutralised) be c and the concentration of the added alkali be b. Let $\omega = b + [H^\cdot]$; for the purpose of calculation, $[H^\cdot]$ is assumed to be equal to the observed $a_{H^\cdot}$.

$$c = [HA] + [H^\cdot]$$

and $$\mu = \tfrac{1}{2}\{[H^\cdot] \times 1^2 + [Na^\cdot] \times 1^2 + [A'] \times 1^2\},$$

$$= \tfrac{1}{2}\{[H^\cdot] + b + [H^\cdot] + b\},$$

$$= [H^\cdot] + b = \omega.$$

Another way of computing μ is in terms of b, c and $[H^\cdot]$ is the following :—

$$\mu = \tfrac{1}{2}\{[H^\cdot] + [Na^\cdot] + [A']\},$$

$$= \tfrac{1}{2}\left\{[H^\cdot] + b + \frac{[A']}{[HA] + [A']} \times c\right\}$$

$$= \tfrac{1}{2}\left\{[H^\cdot] + b + \frac{1}{1 + \frac{[H^\cdot]}{K}} \times c\right\}.$$

2. Dibasic Acids.

For a dibasic acid, H_2A, we have

$$H_2A \rightleftharpoons H^\cdot + HA',$$

$$k_1 = \frac{a_{H^\cdot} \cdot a_{HA'}}{a_{H_2A}} = \text{and } K_1 = \frac{a_{H^\cdot} \cdot [HA']}{[H_2A]},$$

and $$\therefore pk_1 = pK_1 - \log f_{HA'}$$

$$= pK_1 + 0{\cdot}505\sqrt{\mu} \text{ at } 25°.$$

Also $$HA' \rightleftharpoons H^{\cdot} + A'',$$

$$k_2 = \frac{a_{H^{\cdot}} \cdot a_{A''}}{a_{HA'}} = \frac{a_{H^{\cdot}} \cdot [A''] \cdot f_{A''}}{[HA'] \cdot f_{HA'}} \text{ and } K_2 = \frac{a_{H^{\cdot}} \cdot [A'']}{[HA']}$$

$$\therefore \quad pk_2 = pK_2 - \log \frac{f_{A''}}{f_{HA'}}$$

$$= pK_2 + 0{\cdot}505 \times 2^2 \times \sqrt{\mu} - 0{\cdot}505\sqrt{\mu} \text{ at } 25^\circ \text{ C.}$$

$$= pK_2 + 1{\cdot}515\sqrt{\mu}.$$

Calculation of the Ionic Strength of H_2A during Neutralisation with NaOH.

During neutralisation the acid may be present as H_2A, HA' and A'', whence

$$c = [H_2A] + [HA'] + [A''].$$

Let b be the concentration of added NaOH, and ω the sum of the concentrations of added NaOH and hydrogen ions.

Then

$$\mu = \tfrac{1}{2}\{[H^{\cdot}] + [Na^{\cdot}] + [HA'] + 2^2 \cdot [A']\}$$

$$[HA'] = \frac{c}{\frac{[H^{\cdot}]}{K_1} + 1 + \frac{K_2}{[H^{\cdot}]}} \text{ and } [A''] = \frac{c}{\frac{[H^{\cdot}]}{K_2} + 1 + \frac{[H^{\cdot}]^2}{K_1 \cdot K_2}}$$

$$\therefore \mu = \tfrac{1}{2}\left\{[H^{\cdot}] + b + c\left(\frac{1}{\frac{[H^{\cdot}]}{K_1} + 1 + \frac{K_2}{[H^{\cdot}]}} + \frac{4}{\frac{[H^{\cdot}]}{K_2} + 1 + \frac{[H^{\cdot}]^2}{K_1 \cdot K_2}}\right)\right\}.$$

This expression may be resolved in terms of ω, by making use of

$$\omega = [Na^{\cdot}] + [H^{\cdot}] = [HA'] + 2[A'']$$

whence $$\mu = \omega \times \left\{\frac{[H^{\cdot}] + 3K_2}{[H^{\cdot}] + 2K_2}\right\}.$$

3. Tribasic Acids.

For $$H_3A \rightleftharpoons H^{\cdot} + H_2A',$$

$$pk_1 = pK_1 - \log f_{H_2A'} = pK_1 + 0{\cdot}505\sqrt{\mu} \text{ at } 25^\circ,$$

$$H_2A' \rightleftharpoons H^{\cdot} + HA'',$$

$$pk_2 = pK_2 - \log \frac{f_{HA''}}{f_{HA'}} = pK_2 + (2^2 - 1^2) \times 0{\cdot}505\sqrt{\mu}$$

$$= pK_2 + 1{\cdot}515\sqrt{\mu} \text{ at } 25^\circ,$$

and for $$HA'' \rightleftharpoons H^{\cdot} + A'''$$

$$pk_3 = pK_3 - \log \frac{f_{A'''}}{f_{HA''}} = pK_3 + (3^2 - 2^2) \times 0{\cdot}505\sqrt{\mu}$$

$$= pK_3 + 2{\cdot}525\sqrt{\mu}, \text{ at } 25^\circ.$$

Calculation of Ionic Strength of H_3A during Neutralisation with NaOH.

$c = [H_3A] + [H_2A'] + [HA''] + [A''']$

$b = [Na^\cdot]$, and $\omega = [Na^\cdot] + [H^\cdot]$

$$\mu = \tfrac{1}{2}\{[H^\cdot] + [Na^\cdot] + [H_2A'] + [HA''] \times 2^2 + [A'''] \times 3^2\}$$

$$= \tfrac{1}{2}\left\{[H^\cdot] + b + c\left(\frac{[H^\cdot]}{K_1} + 1 + \frac{1}{\frac{K_2}{[H^\cdot]} + \frac{K_2 \cdot K_3}{[H^\cdot]^2}}\right.\right.$$

$$\left.\left. + \frac{4}{\frac{[H^\cdot]^2}{K_1K_2} + \frac{[H^\cdot]}{K_2} + 1 + \frac{K_3}{[H^\cdot]}} + \frac{9}{\frac{[H^\cdot]^3}{K_1K_2K_3} + \frac{[H^\cdot]^2}{K_2K_3} + \frac{[H^\cdot]}{K_3} + 1}\right)\right\}.$$

In terms of ω,

$$\mu = \omega \frac{\left\{\frac{K_1}{[H^\cdot]} + \frac{3K_1K_2}{[H^\cdot]^2} + \frac{6K_1K_2K_3}{[H^\cdot]^3}\right\}}{\left\{\frac{K_1}{[H^\cdot]} + \frac{2K_1K_2}{[H^\cdot]^2} + \frac{3K_1K_2K_3}{[H^\cdot]^3}\right\}}.$$

Note : μ for a dibasic acid, H_2A

$$= \omega \frac{[H^\cdot] + 3K_2}{[H^\cdot] + 2K_2}.$$

Multiplying numerator and denominator by $\frac{K_1}{[H^\cdot]^2}$, we get

$$\mu = \omega \frac{\left\{\frac{K_1}{[H^\cdot]} + \frac{3K_1K_2}{[H^\cdot]^2}\right\}}{\left\{\frac{K_1}{[H^\cdot]} + \frac{2K_1K_2}{[H^\cdot]^2}\right\}},$$

in which the numerator and denominator contains the first two terms of the expression giving μ for H_3A. Söderbäck (*Arkiv. Kemi, Mineral Geol.*, 1933, **11A**, 1) has derived the following general expression for μ of the n-basic acid, H_nA during neutralisation with NaOH :

$$\mu = \omega \frac{\left\{\frac{K_1}{[H^\cdot]} + \frac{3K_1K_2}{[H^\cdot]^2} + \frac{6K_1K_2K_3}{[H^\cdot]^3} + \ldots + \frac{n+n^2}{2} \cdot \frac{K_1K_2K_3 \ldots K_n}{[H^\cdot]^n}\right\}}{\left\{\frac{K_1}{[H^\cdot]} + \frac{2K_1K_2}{[H^\cdot]^2} + \frac{3K_1K_2K_3}{[H^\cdot]^3} + \ldots + n \cdot \frac{K_1K_2K_3 \ldots K_n}{[H^\cdot]^n}\right\}}$$

in which $[H^\cdot]$ is assumed equal to $a_{H^\cdot}$, as determined experimentally.

Table 54A furnishes an example of the effect which the ionic strength, μ, has on the imperfect constants of a dibasic acid.

They were computed by German, Vogel and Jeffery (*Phil. Mag.*, 1936, (7), **22**, 790) from a quinhydrone titration at 25° of 100 c.c. of 0·01 N-fumaric acid with 0·0103 N-NaOH. K_1 and K_2 were calculated with the aid of the equations on page 198 and μ as shown on page 289. The concentrations used in this titration are, however, probably too high for the limiting activity expression, $-\log f = 0{\cdot}505z^2\sqrt{\mu}$ to apply rigidly.

TABLE 54A

K_1, K_2 AND k_1, k_2 OF FUMARIC ACID

Pairs of Points used. NaOH.	*p*H.	$\mu \times 10^3$.	$K_1 \times 10^3$.	$k_1 \times 10^3$.	$K_2 \times 10^5$.	$k_2 \times 10^4$.
15·0 c.c.	2·996	2·45	1·019	0·963		
65·0 ,,	4·137	5·28			5·28	4·10
22·5 ,,	3·139	2·71	1·019	0·959		
72·5 ,,	4·345	5·65			5·29	4·07
30·0 ,,	3·287	3·04	1·022	0·959		
80·0 ,,	4·766	5·98			5·98	4·16

Calculation of the Thermodynamic Constants of an n-basic acid from its Titration Curve with a Monoacid Base, e.g., NaOH.

Maxwell and Partington (*Trans. Faraday Soc.*, 1935, **31**, 924) have extended the equation which Morton (*ibid.*, 1928, **24**, 14) derived for a tribasic acid to that for the titration of an *n*-basic acid, thus:

$$\frac{k_1!\,.\,a_{H^\cdot}^{n-1}/f_1 + 2k_2!\,.\,a_{H^\cdot}^{n-2}/f_2 + 3k_3!\,.\,a_{H^\cdot}^{n-3}/f_3 + \ldots + nk_n!/f_n}{a_{H^\cdot}^{n} + k_1!\,.\,a_{H^\cdot}^{n-1}/f_1 + k_2!\,.\,a_{H^\cdot}^{n-2}/f_2 + k_3!\,.\,a_{H^\cdot}^{n-3}/f_3 + \ldots + k_n!/f_n} = \frac{\omega}{C}$$

where C = total concentration of acid and its salts
ω = concentration of $Na^\cdot$ ions + $[H^\cdot]$ − $[OH']$,
f_1, f_2, etc., the activity coefficients of the acid anions,
k_1, k_2, etc., the thermodynamic dissociation constants,
and $k_n!$ = product of constants, k_1, k_2, $k_3 \ldots k_n$.

Conclusion.

Sørensen (*Compt. rend. Lab. Carlsberg*, 1909, **8**, 1) originally defined *p*H as $-\log_{10}[H^\cdot]$. More recently, there has been a tendency to regard it as a similar function of activity.

The first definition is not quite true and the second cannot be substantiated thermodynamically without the introduction of several vital assumptions, particularly in regard to the determination of the activity of a single ion. No method has yet been devised by which this can be done, although it must be admitted

that the assumptions made in making such computations seem to be justifiable, especially in regard to extremely dilute solutions. The chief justification lies in the theoretical calculations of activity coefficients of single ions in solutions of known ionic strength. Another objection is that *p*H measurements are made with cells which involve liquid junctions. Despite the efforts of MacInnes, the attempts made on the basis of the activity theory have signally failed to interpret the junction potentials of cells involving complex solutions often used for *p*H determinations. Moreover, since 1909 the majority of the buffer solutions have been calibrated in terms of Sørensen's original definition, which indirectly involves the classical theory of Arrhenius, for it was on the basis of his theory that what was then considered to be hydrogen ion concentrations were computed and the arbitrary standard electrode, the Normal Hydrogen Electrode, was actually defined. It was by comparison with this standard that the various " standard " or " reference " electrodes were standardised.

Since the introduction of the *p*H concept, however, the activity theory has been developed, particularly in connexion with cells without transport, and the theory has received considerable support from the Debye-Hückel theory. Many of the solutions, of which the *p*H is required, are much too concentrated for the Debye-Hückel theory to apply. The activity theory has brought another arbitrary standard hydrogen electrode, involving, as it does, the potential of the hydrogen electrode (1 atmosphere pressure) in equilibrium with a solution containing hydrogen ions, the activity of which is unity ; and this is despite the fact that the activity of a single ion cannot be determined without making a fundamental assumption, *viz.*, that the activity of a single ion is the same as the mean ionic activity of the electrolyte concerned. Apparently the influence of the activity of the associated anion on that of the hydrogen ion is considered either to be nil or else to be negligibly small. This can hardly be the case, for as Guggenheim and Schindler (p. 281) have shown that in order to account for the potential of the hydrogen electrode in 0·1N-HCl it is necessary to assume one value for the activity of the hydrogen ion and a different value for that of the chloride ion. It is significant that this was in an attempt to interpret the E.M.F. of a cell *with transport* in terms of ion-activities. The activity theory thus furnishes us with another arbitrary standard, with which reference electrodes have been compared.

Much confusion therefore arises over the precise potential to be attributed to a particular reference half-element. Fortunately the two arbitrary zero standards do not differ greatly, but never-

theless they differ sufficiently to give a difference of about 0·07 *p*H unit in the calculated *p*H values. Furthermore, it must be remembered that (*a*) almost all colorimetric determinations of *p*H are made by using buffer solutions, which were calibrated in terms of the original definition of the arbitrary zero standard, (*b*) the usual electrometric measurements are carried out with cells *with transport*, and (*c*) interpretations of the practical significance of *p*H in the many branches of chemistry have been based on data so obtained.

The position in regard to which arbitrary standard electrode should be adopted for ordinary routine *p*H determinations thus seems clear. It appears to be desirable that the original standard zero should be retained, and, to avoid any doubts as to whether the concentration or activity of the hydrogen ions is actually involved, *p*H should be defined in terms of the method by which it is determined, *viz.*,

$$p\mathrm{H} = \frac{\text{E.M.F.} - \text{E}}{2{\cdot}3026 \cdot \mathrm{RT/F}'}$$

where E.M.F. is that observed of the cell employed, and E the potential of the standard electrode used, the electrode having been standardised in accordance with the original Normal Hydrogen Electrode as zero, in which the conductance ratio, Λ_c/Λ_0 was used to compute the supposed concentration of hydrogen ions.

CHAPTER XV

THE LOWRY-BRØNSTED THEORY OF ACIDS AND BASES

A SOMEWHAT different conception of acids and bases has been gaining acceptance in recent years. Its main object seems to be to link up the ionisation of an electrolyte more intimately with the solvent itself than is the case with the theories of Arrhenius and Debye and Hückel. The theory was first introduced in 1923 by Lowry (*Chem. & Ind.*, 1923, **42**, 43 ; see also *Trans. Faraday Soc.*, 1930, **26**, 45) and a few months later again by Brønsted (*Rec. trav. chim.*, 1923, **42**, 718 ; *J. Physical Chem.*, 1926, **30**, 777 ; *Ber.*, 1928, **61**, 2049 ; *Chem. Reviews*, 1928, **5**, 232).

They define an acid as being any substance which has a tendency to lose a proton, whereas a base is any substance which has a tendency to take up a proton. If we represent a proton as a positively charged hydrogen atom, thus $H^{\cdot}$, (see p. 54), we see that the relationship which is considered to exist between an acid, A, and a base, B, is given by the scheme : $A \rightleftharpoons B + H^{\cdot}$. There is no restriction as to the charge on an acid or base, except that there is a unit difference of charge between the related acid and base, the charge on the acid being one positive charge more than on the corresponding base. The following examples illustrate the relationship between so-called acids and bases.

Acids.		Bases.	Protons.
H_2O	$\rightleftharpoons$	OH'	$+ H^{\cdot}$
HCl	$\rightleftharpoons$	Cl'	$+ H^{\cdot}$
CH_3COOH	$\rightleftharpoons$	CH_3COO'	$+ H^{\cdot}$
H_3PO_4	$\rightleftharpoons$	H_2PO_4'	$+ H^{\cdot}$
H_2PO_4'	$\rightleftharpoons$	HPO_4''	$+ H^{\cdot}$
HPO_4''	$\rightleftharpoons$	PO_4'''	$+ H^{\cdot}$
$H_3O^{\cdot}$	$\rightleftharpoons$	H_2O	$+ H^{\cdot}$
$NH_4^{\cdot}$	$\rightleftharpoons$	NH_3	$+ H^{\cdot}$
$CH_3NH_3^{\cdot}$	$\rightleftharpoons$	CH_3NH_2	$+ H^{\cdot}$
$C_2H_2(NH_3^{\cdot})_2$	$\rightleftharpoons$	$C_2H_2(NH_2)(NH_3^{\cdot})$	$+ H^{\cdot}$
$C_2H_2(NH_2)(NH_3^{\cdot})$	$\rightleftharpoons$	$C_2H_2(NH_2)_2$	$+ H^{\cdot}$

It will thus be seen that the terms *acid* and *base* are purely relative in respect of any particular system, the *acid* being, in fact, the *oxidised form* of the *base*.

Assuming that these equilibria, which involve the splitting-off of a proton, are governed by the Law of Mass Action, it follows for

$$A \rightleftharpoons B + H^{\cdot}$$

that

$$K_A = \frac{c_B}{c_A} \times a_{H^{\cdot}},$$

where K_A is the equilibrium constant of the acid-base system, c_B being the concentration of the base at equilibrium, c_A that of the acid, and $a_{H^{\cdot}}$ the activity of the proton. Considered from the standpoint of the base, *i.e.*, in accord with the lower arrow, we get

$$K_B = \frac{c_A}{c_B \times a_{H}},$$

K_B being the equilibrium constant of the base. The constant K_A thus supplies a direct measure of the ability of the *acid* to lose a proton, whereas K_B gives a measure of the ability of the base to gain a proton. In practice, these constants can have little more than theoretical interest, for there is no method available by which the activity of a proton, $a_{H^{\cdot}}$, can be measured or evaluated ; in fact the term $a_{H^{\cdot}}$ appears to be indefinable.

We shall now apply this theory to ionic reactions, the ionic product of water and the dissociation of acids in aqueous and non-aqueous solvents.

Consider the reaction between acetic acid and ammonium hydroxide :

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO' + NH_4^{\cdot}$$

i.e.

$$A_I + B_{II} \rightleftharpoons B_I + A_{II},$$

A_I and B_I, and B_{II} and A_{II} being the related acid-base and base-acid systems respectively. We obtain

$$K = \frac{[B_I]}{[A_I]} \times \frac{[A_{II}]}{[B_{II}]}.$$

By multiplying numerator and denominator by $a_{H^{\cdot}}$, it follows that the equilibrium constant

$$K = K_{A_I} \times K_{B_{II}}$$

$$= \frac{K_{A_I}}{K_{A_{II}}}$$

Water is an amphoteric substance. Representing it as a *base*, we have

$$H_2O + H^{\cdot} \rightleftharpoons H_3O^{\cdot},$$

therefore $$K_B = \frac{[H_3O^{\cdot}]}{[H_2O] \cdot a_{H^{\cdot}}};$$

by putting

$$K_B \times [H_2O] = K'_B = K_B \times \frac{1000}{18},$$

then $$K'_B = \frac{[H_3O^{\cdot}]}{a_{H^{\cdot}}}.$$

Representing water as an *acid*, we have

$$H_2O \rightleftharpoons OH' + H^{\cdot},$$

whence $$K_A = \frac{[OH']}{[H_2O]} \cdot a_{H^{\cdot}};$$

and therefore $$K_A' = [OH'] \cdot a_{H^{\cdot}}.$$

Hence the ionic product, K_w, of water

$$= [H_3O^{\cdot}] \times [OH']$$
$$= K_B' \times K_A'$$

The relationship between the activity dissociation constant, k_A, of an acid and K_A, as defined by the Lowry–Brønsted Theory, is

$$k_A = K_A \times \frac{f_B}{f_A},$$

where f_B and f_A are the activity coefficients of the related base and acid, *if it can be assumed that the activity of the proton, $a_{H^{\cdot}}$ is the same as that of a hydrogen ion.* This will be made clear by referring to the ionisation of acetic acid,

$$CH_3COOH \rightleftharpoons CH_3COO' + H^{\cdot}.$$

$$k_A = \frac{a_{H^{\cdot}} \times a_{CH_3COO'}}{a_{CH_3COOH}} = a_{H^{\cdot}} \cdot \frac{[CH_3COO']}{[CH_3COOH]} \times \frac{f_{CH_3COO'}}{f_{CH_3COOH}} = K_A \times \frac{f_B}{f_A}.$$

We shall now consider the ionisation of an acid in aqueous solution along the lines of the Lowry–Brønsted Theory. In this case, we must take into account the two equilibrium systems :

$$A \rightleftharpoons B + H^{\cdot}$$

and $$H^{\cdot} + H_2O \rightleftharpoons H_3O^{\cdot},$$

i.e., $$A + H_2O \rightleftharpoons B + H_3O^{\cdot}.$$

Thus the ionisation of acetic acid in aqueous solution is the result of the processes:

$$CH_3COOH \rightleftharpoons CH_3COO' + H^{\cdot}$$

and

$$H^{\cdot} + H_2O \rightleftharpoons H_3O^{\cdot},$$

therefore

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO' + H_3O^{\cdot}.$$

The dissociation constant of acetic acid, considered in terms of the classical theory, is therefore

$$K_{HAc} = \frac{[CH_3COO'][H_3O^{\cdot}]}{[CH_3COOH]}$$

$$= \frac{[CH_3COO'][H_3O^{\cdot}] \cdot a_{H^{\cdot}}}{[CH_3COOH] \cdot a_{H^{\cdot}}}$$

$$= \frac{[CH_3COO']}{[CH_3COOH]} \cdot a_{H^{\cdot}} \times K'_{B(Water)}$$

$$= K_A \cdot K'_{B(Water)}.$$

In a similar way, the ionisation of an acid in a non-aqueous solvent, Sv, is supposed to take place by virtue of the reactions:

$$A \rightleftharpoons B + H^{\cdot}$$

and

$$H^{\cdot} + Sv \rightleftharpoons SvH^{\cdot},$$

whence

$$A + Sv \rightleftharpoons B + SvH^{\cdot}.$$

For example, the reactions involved in the dissociation of acetic acid in ethyl alcohol are represented as

$$CH_3COOH \rightleftharpoons CH_3COO' + H^{\cdot}$$

$$H^{\cdot} + C_2H_5OH \rightleftharpoons C_2H_5OH.H^{\cdot}$$

and therefore

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COO' + C_2H_5OH \cdot H^{\cdot},$$

for which

$$K_{HAc(C_2H_5OH)} = \frac{[CH_3COO'][C_2H_5OH \cdot H^{\cdot}]}{[CH_3COOH]}$$

$$= \frac{[CH_3COO']}{[CH_3COOH]} \cdot a_{H^{\cdot}} \times K'_{B(C_2H_5OH)}$$

$$= K_A \cdot K'_{B(C_2H_5OH)}$$

where

$$K'_{B(C_2H_5OH)} = K_{B(C_2H_5OH)} \times [C_2H_5OH].$$

It would appear therefrom that

$$\frac{K_{HAc(H_2O)}}{K_{HAc(C_2H_5OH)}} = \frac{K_A \cdot K'_{B(H_2O)}}{K_A \cdot K'_{B(C_2H_5OH)}}$$

$$= \frac{K'_{B(H_2O)}}{K'_{B(C_2H_5OH)}},$$

and therefore that the ratio of the classical dissociation constants of a given acid in water and alcohol (or any other solvent) is independent of the acid itself, but depends solely on the ratio of the basic constants K′ for water and alcohol (or other solvent). If this were actually the case, then the classical dissociation constants of any acids in water and in alcohol (say) should bear the same ratio to one another at any given temperature. Experimental work seems to prove that this is approximately the case, thus demonstrating the rôle of the solvent in the mechanism of ionisation.

CHAPTER XVI

SOLUTIONS OF KNOWN HYDROGEN-ION CONCENTRATION

Standard Buffer Solutions.

SOLUTIONS which have definite hydrogen-ion concentrations, and which are buffered, are required in the colorimetric methods for the determination of *p*H values. They are of service in bacteriological culture work and are of importance in analytical practice. Such solutions constitute the basis of the greater part of colorimetric work, and for this reason several investigators have made very careful measurements of the hydrogen-ion concentrations by the standard electrical methods. These standard buffer solutions thus provide a means by which the hydrogen-ion concentrations of unknown solutions are compared indirectly with the electromotive force data of the hydrogen electrode. In the following tables are quoted data of solutions whose *p*H values extend from 0·6–12·0. The data are based upon those obtained by Walpole (*Biochem. J.*, 1914, **105**, 2501, 2521), Sørensen (*Biochem. Z.*, 1909, **21**, 131 ; **22**, 352 ; *Ergebn. Physiol.*, 1912, **12**, 393), Clark and Lubs (*J. Bacteriol.*, 1917, **2**, 1, 109, 191), McIlvaine (*J. Biol. Chem.*, 1921, **49**, 183), Palitzsch (*Biochem. Z.*, 1915, **70**, 333), Ringer (cited by Kolthoff, " Indicators "), Kolthoff (*J. Biol. Chem.*, 1925, **63**, 135), Michaelis (*ibid.*, 1930, **87**, 33), Britton and Welford (*J. Chem. Soc.*, 1937, 1848), German and Vogel (*Analyst*, 1937, **62**, 271), Thiel, Schulz and Coch (*Z. Elektrochem.*, 1934, **40**, 150), and King and Delory (*Enzymologia*, 1940, **8**, 278). Table 88 (*a*) gives details of the " Universal Buffer Mixture " of Prideaux and Ward (*J. Chem. Soc.*, 1924, **125**, 426), and in Table 88 (*b*) more detailed *p*H data are recorded corresponding to the titration of the Universal Buffer Mixture as determined by Britton and Robinson (*J. Chem. Soc.*, 1931, 458). Details of a new Universal Buffer Mixture introduced by Britton and Robinson (*ibid.*, p. 1456) are also included. This mixture was slightly modified by Britton and Welford (*ibid.*, 1937, 1848) and standardised at temperatures ranging from 12·5° to 91° C.

TABLE 55

*p*H RANGE: 0·65–5·20 (WALPOLE)

50 *c.c N-Sodium Acetate* + *x c.c. N-HCl made up to* 250 *c.c.*

*p*H	0·65	0·75	0·91	1·09	1·24	1·42	1·71
HCl (*x*)	100	90	80	70	65	60	55
*p*H	1·85	1·99	2·32	2·64	2·72	3·09	—
HCl (*x*)	53·5	52·5	51·0	50·0	49·75	48·5	—
*p*H	3·29	3·49	3·61	3·79	3·95	4·19	—
HCl (*x*)	47·5	46·25	45·0	42·5	40·0	35·0	—
*p*H	4·39	4·58	4·76	4·95	5·20	—	—
HCl (*x*)	30·0	25·0	20·0	15·0	10·0	—	—

TABLE 56

*p*H RANGE: 1·00–2·20 (CLARK AND LUBS)

50 *c.c.* 0·2 *M.-KCl* + *x c.c.* 0·2 *N-HCl made up to* 200 *c.c.*

*p*H	1·0	1·2	1·4	1·6	1·8	2·0	2·2
HCl (*x*)	97·0	64·5	41·5	26·3	16·6	10·6	6·7

TABLE 57

*p*H RANGE: 1·04–3·68 (SØRENSEN)

10 *c.c. Mixtures of x c.c. of* 0·1 *M.-Glycine* (0·1 *M.-NaCl*), *and y c.c. of* 0·1 *M.-HCl*

*p*H	1·04	1·15	1·25	1·42	1·645	1·93
Glycine (*x*)	0·0	1·0	2·0	3·0	4·0	5·0
HCl (*y*)	10·0	9·0	8·0	7·0	6·0	5·0
*p*H.	2·28	2·61	2·92	3·34	3·68	—
Glycine (*x*)	6·0	7·0	8·0	9·0	9·5	—
HCl (*y*)	4·0	3·0	2·0	1·0	0·5	—

TABLE 58

*p*H RANGE: 1·04–4·96 (SØRENSEN)

10 *c.c. Mixtures of x c.c. of* 0·1 *M.-Disodium Hydrogen Citrate and y c.c. of* 0·1 *M.-HCl*

*p*H	1·04	1·17	1·42	1·925	2·27	2·97
Citrate (*x*)	0·0	1·0	2·0	3·0	3·33	4·0
HCl (*y*)	10·0	9·0	8·0	7·0	6·67	6·0
*p*H	3·36	3·53	3·69	3·95	4·16	4·45
Citrate (*x*)	4·5	4·75	5·0	5·5	6·0	7·0
HCl (*y*)	5·5	5·25	5·0	4·5	4·0	3·0
*p*H	4·65	4·83	4·89	4·96	—	—
Citrate (*x*)	8·0	9·0	9·5	10·0	—	—
HCl (*y*)	2·0	1·0	0·5	0	—	—

TABLE 59

*p*H RANGE: 1·20–2·00 AT 25° (GERMAN AND VOGEL)

100 *c.c. containing x c.c.* 0·2 *M.-p-Toluenesulphonic Acid Monohydrate* (38·024 *gm. per litre*) *and y c.c.* 0·2 *M.-Sodium p-toluenesulphonate* (38·82 *gm. per litre*)

*p*H.	1·20	1·30	1·40	1·50	1·60	1·70	1·80	1·90	2·00
x	42·0	31·6	28·4	18·9	15·35	12·6	10·6	8·7	6·9
y	8·0	18·4	25·2	31·1	34·65	37·4	39·4	41·3	43·1

TABLE 60

*p*H RANGE: 1·40–2·20 AT 25° (GERMAN AND VOGEL)

100 *c.c. containing x c.c.* 0·1 *M.-p-Toluenesulphonic Acid Monohydrate* (19·012 *gm. per litre*) *and y c.c.* 0·1 *M.-Sodium p-Toluenesulphonate* (19·41 *gm. per litre*)

*p*H.	1·40	1·50	1·60	1·70	1·80	1·90	2·00	2·10	2·20
x	48·9	37·2	27·4	19·0	16·6	13·2	10·0	7·6	4·4
y	1·1	12·8	22·6	31·0	33·4	36·8	40·0	42·4	45·6

TABLE 61

*p*H RANGE: 1·5–11·0 AT 18° (THIEL, SCHULZ AND COCH)

100 *c.c. Mixtures of two of the following Solutions:*

A. 0·05 M.-Oxalic acid + 0·20 M.-Boric acid
B. 0·20 M.-Boric acid + 0·05 M.-Succinic acid + 0·05 M.-Na_2SO_4
C. 0·05 M.-$Na_2B_4O_7,12H_2O$ (Borax)
D. 0·05 M.-$NaHCO_3$

*p*H	1·5	2·0	2·5	—	—	—	—
x c.c. A	84·1	34·3	10·0	—	—	—	—
(100 − *x*) c.c. B	15·9	65·7	90·0	—	—	—	—

*p*H	3·0	3·5	4·0	4·5	5·0	5·5	6·0
x c.c. B	98·0	89·85	79·2	69·1	60·85	55·2	51·75
(100 − *x*) c.c. C	2·0	10·15	20·8	30·9	39·15	44·8	48·25

*p*H	6·5	7·0	7·5	8·0	8·5	9·0	—
x c.c. B	49·78	47·6	43·4	35·9	24·4	8·3	—
(100 − *x*) c.c. C	50·22	52·4	56·6	64·1	75·6	91·7	—

*p*H	9·5	10·0	10·5	11·0	—	—	—
x c.c. C	54·6	25·3	11·0	3·0	—	—	—
(100 − *x*) c.c. D	45·4	74·7	89·0	97·0	—	—	—

TABLE 62

*p*H RANGE: 2·2–3·8 (CLARK AND LUBS)

50 *c.c.* 0·1 *M.-Potassium Biphthalate* + *x c.c.* 0·1 *N-HCl made up to* 100 *c.c.*

*p*H	2·2	2·4	2·6	2·8	—
HCl (*x*)	46·70	39·60	32·95	26·42	—
*p*H	3·0	3·2	3·4	3·6	3·8
HCl (*x*)	20·32	14·70	9·90	5·97	2·63

TABLE 63

*p*H RANGE: 2·12–6·46 AT 12·5° 2·14–6·86 AT 91° etc.

(BRITTON AND WELFORD)

100 *c.c.* 0·2 *N-Citric Acid neutralised with x c.c.* 0·2 *N.NaOH at various Temperatures*

x.	*p*H values at						
	12·5°.	25°.	34°.	53°.	63°.	75°.	91°.
0	2·12	2·13	2·13	2·14	2·14	2·14	2·14
5	2·43	2·43	2·43	2·44	2·44	2·44	2·44
10	2·70	2·70	2·70	2·70	2·70	2·70	2·70
15	2·93	2·93	2·93	2·93	2·93	2·93	2·93
20	3·15	3·15	3·15	3·15	3·15	3·15	3·15
25	3·37	3·37	3·37	3·37	3·37	3·37	3·37
30	3·59	3·59	3·60	3·60	3·60	3·60	3·60
35	3·82	3·83	3·83	3·83	3·83	3·83	3·83
40	4·04	4·05	4·05	4·05	4·05	4·06	4·06
45	4·27	4·27	4·27	4·27	4·27	4·28	4·28
50	4·44	4·44	4·45	4·46	4·46	4·47	4·47
55	4·64	4·64	4·64	4·65	4·65	4·67	4·69
60	4·82	4·85	4·87	4·87	4·87	4·88	4·92
65	5·00	5·05	5·05	5·07	5·08	5·13	5·18
70	5·21	5·25	5·28	5·32	5·34	5·36	5·42
75	5·43	5·47	5·48	5·54	5·56	5·61	5·68
80	5·65	5·67	5·69	5·75	5·78	5·83	5·90
85	5·85	5·89	5·90	5·96	6·00	6·06	6·13
90	6·11	6·14	6·16	6·24	6·25	6·33	6·40
95	6·46	6·50	6·52	6·61	6·67	6·71	6·84

TABLE 64

*p*H RANGE: 2·30–3·30 AT 25° (GERMAN AND VOGEL)

100 *c.c. containing x c.c.* 0·01 *M.-p-Toluenesulphonic Acid Monohydrate* (1·9012 *gm. per litre*) *and y c.c.* 0·01 *M.-Sodium p-Toluenesulphonate* (1·941 *gm. per litre*)

*p*H	2·30	2·40	2·50	2·60	2·70	2·80
x	50·0	44·2	35·8	27·6	21·2	18·5
y	0·0	5·8	14·2	22·4	28·8	31·5

*p*H	2·90	3·00	3·10	3·20	3·30
x	12·4	10·0	8·0	6·2	5·0
y	37·6	40·0	42·0	43·8	45·0

TABLE 65

*p*H RANGE: 2·2–8·0 (MCILVAINE)

20 *c.c. Mixtures of x c.c. of* 0·2 *M.-*Na_2HPO_4 *and y c.c. of* 0·1 *M.-Citric Acid*

*p*H			2·2	2·4	2·6	2·8	
Na_2HPO_4 (*x*)			0·40	1·24	2·18	3·17	
Citric acid (*y*)			19·60	18·76	17·82	16·83	
*p*H	3·0	3·2	3·4	3·6	3·8		
Na_2HPO_4 (*x*)	4·11	4·94	5·70	6·44	7·10		
Citric acid (*y*)	15·89	15·06	14·30	13·56	12·90		
*p*H	4·0	4·2	4·4	4·6	4·8		
Na_2HPO_4 (*x*)	7·71	8·28	8·82	9·35	9·86		
Citric acid (*y*)	12·29	11·72	11·18	10·65	10·14		
*p*H	5·0	5·2	5·4	5·6	5·8		
Na_2HPO_4 (*x*)	10·30	10·72	11·15	11·60	12·09		
Citric acid (*y*)	9·70	9·28	8·85	8·40	7·91		
*p*H	6·0	6·2	6·4	6·6	6·8		
Na_2HPO_4 (*x*)	12·63	13·22	13·85	14·55	15·45		
Citric acid (*y*)	7·37	6·78	6·15	5·45	4·55		
*p*H	7·0	7·2	7·4	7·6	7·8	8·0	
Na_2HPO_4 (*x*)	16·47	17·39	18·17	18·73	19·15	19·45	
Citric acid (*y*)	3·53	2·61	1·83	1·27	0·85	0·55	

TABLE 66

*p*H RANGE: 2·90–4·10 AT 25° (GERMAN AND VOGEL)

100 *c.c. containing x c.c.* 0·01 *M.-Furoic Acid* (1·1203 *gm. per litre*) *and y c.c.* 0·01 *M.-Sodium Furoate* (1·3402 *gm. per litre*)

*p*H	2·90	3·00	3·10	3·20	3·30	3·40	3·50
x	45·2	39·6	34·0	28·4	24·8	21·4	18·0
y	4·8	10·4	16·0	21·6	25·2	28·6	32·0

*p*H	3·60	3·70	3·80	3·90	4·00	4·10
x	14·8	12·3	10·1	8·4	6·7	5·4
y	35·2	37·7	39·9	41·6	43·3	44·6

TABLE 67

*p*H RANGE: 3·0–5·8 (KOLTHOFF)

10 *c.c. Mixtures of x c.c.* 0·05 *M.-Succinic Acid and y c.c.* 0·05 *M.-Borax*

*p*H	3·0	3·2	3·4	3·6	3·8
Succinic acid (*x*)	9·86	9·65	9·40	9·05	8·63
Borax (*y*)	0·14	0·35	0·60	0·95	1·37
*p*H	4·0	4·2	4·4	4·6	4·8
Succinic acid (*x*)	8·22	7·78	7·38	7·00	6·65
Borax (*y*)	1·78	2·22	2·62	3·00	3·35
*p*H	5·0	5·2	5·4	5·6	5·8
Succinic acid (*x*)	6·32	6·05	5·79	5·57	5·40
Borax (*y*)	3·68	3·95	4·21	4·43	4·60

TABLE 68

*p*H RANGE: 3·40–5·20 AT 25° (GERMAN AND VOGEL)

100 *c.c. containing x c.c.* 0·01 *M.-Phenylacetic Acid* (1·3606 *gm. per litre*) *and y c.c.* 0·01 *M.-Sodium Phenylacetate* (1·5806 *gm. per litre*)

*p*H	3·40	3·50	3·60	3·70	3·80	3·90	4·00
x	48·7	46·6	44·4	42·2	39·9	37·2	34·4
y	1·3	3·4	5·6	7·8	10·1	12·8	15·6
*p*H	4·10	4·20	4·30	4·40	4·50	4·60	
x	30·8	28·0	25·1	22·0	19·4	16·9	
y	19·2	22·0	24·9	28·0	30·6	33·1	
*p*H	4·70	4·80	4·90	5·00	5·10	5·20	
x	14·4	12·1	10·2	8·6	7·2	5·7	
y	35·6	37·9	39·8	41·4	42·8	44·3	

TABLE 69

*p*H RANGE: 3·72–5·57 (WALPOLE)

10 *c.c. Mixtures of x c.c.* 0·2 *N-Acetic Acid and y c.c.* 0·2 *N-Sodium Acetate*

*p*H	3·72	4·05	4·27	4·45	4·63
Acetic acid (*x*)	9·0	8·0	7·0	6·0	5·0
Sodium acetate (*y*)	1·0	2·0	3·0	4·0	5·0
*p*H	4·80	4·99	5·23	5·37	5·57
Acetic acid (*x*)	4·0	3·0	2·0	1·5	1·0
Sodium acetate (*y*)	6·0	7·0	8·0	8·5	9·0

TABLE 70

*p*H RANGE: 4·0–6·2 (CLARK AND LUBS)

50 *c.c.* 0·1 *M.-Potassium Biphthalate* + *x c.c.* 0·1 *N-NaOH made up to* 100 *c.c.*

*p*H	4·0	4·2	4·4	4·6	4·8
NaOH (*x*)	0·40	3·70	7·50	12·15	17·70
*p*H	5·0	5·2	5·4	5·6	5·8
NaOH (*x*)	23·85	29·95	35·45	39·85	43·00
*p*H	6·0	6·2	—	—	—
NaOH (*x*)	45·45	47·00	—	—	—

TABLE 71

*p*H RANGE: 4·80–6·20 AT 25° (GERMAN AND VOGEL)

100 *c.c. containing x c.c.* 0·01 *M.-Sodium Hydrogen Succinate* (0·5903 *gm. Succinic Acid* + 0·8102 *gm. Sodium Succinate per litre*) *and y c.c.* 0·01 *M.-Sodium Succinate* (1·6203 *gm. per litre*)

*p*H	4·80	4·90	5·00	5·10	5·20	5·30	5·40	5·50
x	48·8	46·9	44·4	40·4	36·2	32·6	28·6	24·7
y	1·2	3·1	5·6	9·6	13·8	17·4	21·4	25·3
*p*H	5·60	5·70	5·80	5·90	6·00	6·10	6·20	
x	21·0	17·6	14·7	12·0	9·9	7·8	5·6	
y	29·0	32·4	35·3	38·0	40·1	42·2	44·4	

TABLE 72

*p*H RANGE: 4·96–6·33 (SØRENSEN)

10 *c.c. Mixtures of x c.c.* 0·1 *M.-Disodium Hydrogen Citrate and y c.c.* 0·1 *N-NaOH*

*p*H at 18° C.	4·96	5·02	5·11	5·31	5·57	5·97	6·33
Citrate (*x*)	10·0	9·5	9·0	8·0	7·0	6·0	5·5
NaOH (*y*)	0·0	0·5	1·0	2·0	3·0	4·0	4·5
*p*H at 10° C.*	4·93	4·99	5·08	5·27	5·53	5·97	6·30
*p*H at 40° C.*	5·05	5·10	5·19	5·39	5·64	6·04	6·41
*p*H at 70° C.*	5·14	5·20	5·29	5·49	5·75	6·15	6·51

* Walbum, *C.R. Soc. Biol.*, 1920, **83**, 707.

TABLE 73

*p*H RANGE: 5·8–8·0 (CLARK AND LUBS)

50 *c.c.* 0·1 *M.-KH_2PO_4* + *x c.c.* 0·1 *M.-NaOH made up to* 100 *c.c.*

*p*H	5·8	6·0	6·2	6·4	6·6	6·8
NaOH	3·66	5·64	8·55	12·60	17·74	23·60
*p*H	7·0	7·2	7·4	7·6	7·8	8·0
NaOH	29·54	34·90	39·34	42·74	45·17	46·85

TABLE 74

*p*H RANGE: 5·8–9·2 (KOLTHOFF)

10 *c.c. Mixtures of x c.c.* 0·1 *M.-*KH_2PO_4 *and y c.c.* 0·05 *M.-Borax*

*p*H	5·8	6·0	6·2	6·4	6·6	6·8
Phosphate (*x*)	9·21	8·77	8·30	7·78	7·22	6·67
Borax (*y*)	0·79	1·23	1·70	2·22	2·78	3·33
*p*H	—	7·0	7·2	7·4	7·6	7·8
Phosphate (*x*)	—	6·23	5·81	5·50	5·17	4·92
Borax (*y*)	—	3·77	4·19	4·50	5·83	5·08
*p*H	—	8·0	8·2	8·4	8·6	8·8
Phosphate (*x*)	—	4·65	4·30	3·87	3·40	2·76
Borax (*y*)	—	5·35	5·70	6·13	6·60	7·24
*p*H	—	9·0	9·2	—	—	—
Phosphate (*x*)	—	1·75	0·50	—	—	—
Borax (*y*)	—	8·25	9·50	—	—	—

TABLE 75

*p*H RANGE: 5·86–12·27 AT 12·5° C.
5·86–10·74 AT 91° C.

(BRITTON AND WELFORD)

100 *c.c.* 0·2 *N.-*KH_2PO_4 *neutralised with x c.c.* 0·2 *N.-NaOH at various Temperatures*

x.	*p*H values at						
	12·5°.	25°.	34°.	53°.	63°.	75°.	91°.
5	5·86	5·86	5·86	5·86	5·86	5·86	5·86
10	6·21	6·21	6·21	6·20	6·20	6·20	6·20
15	6·45	6·44	6·42	6·42	6·42	6·42	6·40
20	6·64	6·64	6·62	6·62	6·62	6·62	6·61
25	6·82	6·81	6·80	6·80	6·80	6·80	6·79
30	6·99	6·98	6·98	6·98	6·98	6·98	6·97
35	7·17	7·17	7·16	7·16	7·15	7·15	7·15
40	7·41	7·40	7·39	7·38	7·38	7·38	7·38
45	7·75	7·75	7·74	7·74	7·74	7·74	7·74
50	9·23	9·26	9·24	9·16	9·10	9·00	8·94
55	10·84	10·74	10·61	10·37	10·23	10·07	9·84
60	11·19	11·06	10·93	10·68	10·53	10·36	10·11
65	11·43	11·27	11·13	10·88	10·71	10·53	10·29
70	11·58	11·45	11·28	10·99	10·83	10·66	10·39
75	11·74	11·56	11·41	11·10	10·92	10·75	10·49
80	11·87	11·68	11·51	11·18	11·01	10·84	10·55
85	11·98	11·78	11·61	11·26	11·09	10·89	10·63
90	12·10	11·87	11·69	11·33	11·15	10·95	10·67
95	12·20	11·98	11·76	11·38	11·20	11·00	10·71
100	12·27	12·02	11·82	11·44	11·24	11·04	10·74

TABLE 76

*p*H RANGE: 5·91–8·04 (SØRENSEN)

10 *c.c. Mixtures of x c.c. M./15-NaH_2PO_4 and y c.c. M./15-Na_2HPO_4*

*p*H	5·91	6·24	6·47	6·64	6·81
NaH_2PO_4 (*x*)	9·0	8·0	7·0	6·0	5·0
Na_2HPO_4 (*y*)	1·0	2·0	3·0	4·0	5·0

*p*H	6·98	7·17	7·38	7·73	8·04
NaH_2PO_4 (*x*)	4·0	3·0	2·0	1·0	0·5
Na_2HPO_4 (*y*)	6·0	7·0	8·0	9·0	9·5

TABLE 77

*p*H RANGE: 6·80–9·60 (MICHAELIS)

Temperature 25° *C.*

10 *c.c. Mixtures of x c.c. of* 0·1 *M.-Sodium Diethylbarbiturate (Veronal-sodium) and y c.c. of* 0·1 *M.-HCl*

*p*H	6·80	7·00	7·20	7·40	7·60
Na Salt (*x*)	5·22	5·36	5·54	5·81	6·15
HCl (*y*)	4·78	4·64	4·46	4·19	3·85

*p*H	7·80	8·00	8·20	8·40	8·60
Na Salt (*x*)	6·62	7·16	7·69	8·23	8·71
HCl (*y*)	3·38	2·84	2·31	1·77	1·29

*p*H	8·80	9·00	9·20	9·40	9·60
Na Salt (*x*)	9·08	9·36	9·52	9·74	9·85
HCl (*y*)	0·92	0·64	0·48	0·26	0·15

TABLE 78

*p*H RANGE: 6·8–9·6

(BRITTON AND ROBINSON)

100 *c.c.* 0·04 *M.-Sodium Diethylbarbiturate* + *x c.c.* 0·2 *N-HCl*

Temperature 18° *C.*

pH	6·8	7·0	7·2	7·4	7·6	7·8	8·0	—
x	18·4	17·8	16·7	15·3	13·4	11·5	9·4	—

*p*H	8·2	8·4	8·6	8·8	9·0	9·2	9·4	9·6
x	7·2	5·2	3·8	2·52	1·65	1·13	0·70	0·35

TABLE 79

*p*H RANGE: 6·77–9·24 (PALITZSCH)

10 c.c. Mixtures of x c.c. 0·2 M.-Boric Acid and y c.c. 0·05 M.-Borax

*p*H	6·77	7·09	7·36	7·60	7·78	7·94
Boric acid (*x*)	9·7	9·4	9·0	8·5	8·0	7·5
Borax (*y*)	0·3	0·6	1·0	1·5	2·0	2·5
*p*H	8·08	8·20	8·41	8·60	8·69	8·84
Boric acid (*x*)	7·0	6·5	5·5	4·5	4·0	3·0
Borax (*y*)	3·0	3·5	4·5	5·5	6·0	7·0
*p*H	8·98	9·11	9·24	—	—	—
Boric acid (*x*)	2·0	1·0	0·0	—	—	—
Borax (*y*)	8·0	9·0	10·0	—	—	—

TABLE 80

*p*H RANGE: 7·43–10·52 AT 12·5° C.
7·37–9·80 AT 91° C.

(BRITTON AND WELFORD)

100 c.c. 0·2 N-Boric Acid neutralised with x c.c. 0·2 N-NaOH at various Temperatures

x.	*p*H values at						
	12·5°.	25°.	34°.	53°.	63°.	75°.	91°.
5	7·43	7·47	7·46	7·44	7·38	7·37	7·37
10	7·89	7·89	7·86	7·81	7·75	7·74	7·73
15	8·19	8·15	8·12	8·05	8·00	7·98	7·94
20	8·41	8·38	8·32	8·27	8·19	8·14	8·11
25	8·61	8·55	8·48	8·42	8·36	8·31	8·26
30	8·75	8·69	8·65	8·55	8·47	8·45	8·37
35	8·91	8·85	8·77	8·67	8·61	8·56	8·49
40	9·04	8·97	8·89	8·77	8·71	8·66	8·58
45	9·16	9·08	8·99	8·89	8·81	8·76	8·68
50	9·27	9·18	9·10	8·97	8·91	8·86	8·76
55	9·38	9·29	9·20	9·09	8·99	8·96	8·86
60	9·48	9·37	9·31	9·18	9·10	9·04	8·94
65	9·59	9·48	9·39	9·28	9·20	9·15	9·04
70	9·68	9·59	9·50	9·39	9·31	9·23	9·15
75	9·77	9·68	9·59	9·49	9·41	9·34	9·25
80	9·91	9·81	9·72	9·62	9·54	9·47	9·36
85	10·06	9·95	9·89	9·78	9·68	9·60	9·49
90	10·21	10·14	10·03	9·91	9·83	9·75	9·64
95	10·52	10·40	10·32	10·16	10·07	9·93	9·80

Table 81

*p*H Range: 7·48–10·7 at 22°.
*p*H Range: 7·45–10·4 at 37°.

(King and Delory)

To 25 c.c. 0·1 M.-Sodium Diethylbarbiturate add x c.c. 0·1 N-HCl, then 25 c.c. 0·05 M-Na_2CO_3, and make up to 100 c.c.

x . . .	50	40	30	25
*p*H at 22° C. .	7·48	7·96	8·44	9·00
*p*H at 37° C. .	7·45	7·87	8·34	8·83

x . . .	20	12·5	7·5	2·5
*p*H at 22° C. .	9·44	9·95	10·3	10·7
*p*H at 37° C. .	9·27	9·79	10·1	10·4

Table 82

*p*H Range: 7·62–9·24 (Sørensen)

10 *c.c. Mixtures of x c.c. 0·05 M.-Borax and y c.c. 0·1 N-HCl*

*p*H at 18° C. .	7·62	7·94	8·14	8·29	8·51	—	—
Borax (*x*) . .	5·25	5·5	5·75	6·0	6·5	—	—
HCl (*y*) . .	4·75	4·5	4·25	4·0	3·5	—	—
*p*H at 10° C.* .	7·64	7·96	8·17	8·32	8·54	—	—
*p*H at 40° C.* .	7·55	7·86	8·06	8·19	8·40	—	—
*p*H at 70° C.* .	7·47	7·76	7·95	8·08	8·26	—	—

*p*H at 18° C. .	8·68	8·80	8·91	9·01	9·09	9·17	9·24
Borax (*x*) . .	7·0	7·5	8·0	8·5	9·0	9·5	10·0
HCl (*y*) . .	3·0	2·5	2·0	1·5	1·0	0·5	0·0
*p*H at 10° C.* .	8·72	8·84	8·96	9·06	9·14	9·22	9·30
*p*H at 40° C.* .	8·56	8·67	8·77	8·86	8·94	9·01	9·08
*p*H at 70° C.* .	8·40	8·50	8·59	8·67	8·74	8·80	8·86

* Walbum.

Table 83

*p*H Range: 7·81–10·0 (Clark and Lubs)

50 *c.c. 0·1 M.-Boric Acid* (0·1 *M.-KCl*) + *x c.c. 0·1 N-NaOH made up to 100 c.c.*

*p*H . .	7·8	8·0	8·2	8·4	8·6	8·8
NaOH (*x*) .	2·61	3·97	5·90	8·50	12·00	16·30

*p*H . .	9·0	9·2	9·4	9·6	9·8	10·0
NaOH (*x*) .	21·30	26·70	32·00	36·85	40·80	43·90

TABLE 84

*p*H RANGE: 8·24–10·14 (SØRENSEN)

10 *c.c. Mixtures of x c.c.* 0·1 *M.-Glycine* (0·1 *N-NaCl*) *and y c.c.* 0·1 *N-NaOH*

*p*H at 18° C.	.	8·24	8·58	8·93	9·36	9·71	10·14
Glycine (*x*).	.	9·75	9·5	9·0	8·0	7·0	6·0
NaOH (*y*) .	.	0·25	0·5	1·0	2·0	3·0	4·0
*p*H at 10° C.*	.	—	8·75	9·10	9·54	9·90	10·34
*p*H at 40° C.*	.	—	8·12	8·45	8·85	9·18	9·58
*p*H at 70° C.*	.	—	7·48	7·79	8·16	8·45	8·82

* Walbum.

TABLE 85

*p*H RANGE: 9·24–9·97 (SØRENSEN)

10 *c.c. Mixtures of x c.c.* 0·05 *M.-Borax and y c.c.* 0·1 *N-NaOH*

*p*H.	.	9·24	9·36	9·50	9·68	9·97
Borax (*x*)	.	10·0	9·0	8·0	7·0	6·0
NaOH (*y*)	.	0·0	1·0	2·0	3·0	4·0
*p*H at 10° C.*	.	9·30	9·42	9·57	9·76	10·06
*p*H at 40° C.*	.	9·08	9·18	9·30	9·44	9·67

* Walbum.

TABLE 86

*p*H RANGE: 10·17–11·36 (KOLTHOFF)

50 *c.c.* 0·1 *M.-*Na_2CO_3 + *x c.c.* 0·1 *N-HCl made up to* 100 *c.c.*

*p*H .	10·17	10·35	10·55	10·86	11·04	11·36
HCl (*x*)	20·0	15·0	10·0	5·0	3·0	0·0

TABLE 87

*p*H RANGE: 10·97–12·06 (RINGER)

Add x c.c. 0·1 *N-NaOH to* 50 *c.c.* 0·15 *M.-*Na_2HPO_4

*p*H . . .	10·97	11·29	11·77	12·06
NaOH (*x*) . .	15·0	25·0	50·0	75·0

* Walbum.

TABLE 88 (*a*)

UNIVERSAL BUFFER MIXTURE (PRIDEAUX AND WARD)

*p*H RANGE: 2·0–11·94

100 *c.c. of a solution of mixed acids, being*

0·04 *M.-*H_3PO_4,
0·04 *N-Phenylacetic acid, and*
0·04 *N-Boric acid* (HBO_2, H_2O),

neutralised with x c.c. of 0·2 *N-NaOH, and made up to* 200 *c.c.*

*Interpolation Formula :—p*H = 0·773 + 0·1185 *x when x lies between* 15 *and* 90 *c.c.*

*p*H	1·99	2·13	2·65	3·10	3·73
Per cent. neutralised	0	5·0	15·0	20·0	25·0
*p*H (calculated from formula)	—	—	2·55	3·14	3·74
*p*H	4·21	4·80	5·43	6·30	6·84
Per cent. neutralised	30·0	35·0	40·0	45·0	50·0
*p*H (calculated from formula)	4·33	4·91	5·51	6·11	6·70
*p*H	—	7·91	8·62	9·11	—
Per cent. neutralised	55·0	60·0	65·0	70·0	75·0
*p*H (calculated from formula)	7·28	7·88	8·48	9·07	9·66
*p*H	10·21	—	11·41	—	11·94
Per cent. neutralised	80·0	8·50	90·0	95·0	100·0
*p*H (calculated from formula)	10·25	10·85	11·45	—	—

N.B.—A similar mixture may also be prepared by substituting either potassium or sodium primary phosphate for the phosphoric acid, so as to make the buffer solution 0·04 Molar with respect to KH_2PO_4 or NaH_2PO_4. Such a solution on dilution from 100 c.c. to 200 c.c. will correspond in composition to that of the previous buffer solution neutralised to the extent of 20 per cent. Its *p*H will therefore be 3·10, and on being neutralised will follow an approximate linear relationship in *p*H until 90 per cent. of theoretical amount of alkali has been added. In the case of the modified buffer solution this will correspond to the addition of 70 c.c. of 0·2 N-NaOH to 100 c.c. of the buffer solution and made up to 200 c.c. The interpolation formula will thus become

$$p\mathrm{H} = 3{\cdot}10 + 0{\cdot}1185x.$$

Prideaux and Ward's universal buffer mixture is simply a selection of acids whose dissociation constants differ from one another, when taken in turn, by a small ratio such that on neutralisation with alkali the *p*H-alkali curve is approximately rectilinear. We saw on page 202 that if K_1 of a dibasic acid is not greater than 16 times K_2 no inflexion in the *p*H curve is obtained

TABLE 88 (*b*)

TITRATION OF 100 *c.c.* OF UNIVERSAL BUFFER MIXTURE OF PRIDEAUX AND WARD WITH 0·2 N-NaOH (BRITTON AND ROBINSON)

*p*H RANGE: 1·81–11·94.

100 *c.c. of previous solution neutralised with* 0·2 *N-NaOH*

*p*H	1·81	1·91	1·98	2·10	2·21	2·38	2·55	2·84
c.c. NaOH	0	2·5	5·0	7·5	10·0	12·5	15·0	17·5
*p*H	3·05	3·38	3·75	3·92	4·22	4·33	4·65	4·92
c.c. NaOH	20·0	22·5	25·0	27·5	30·0	32·5	35·0	37·5
*p*H	5·43	6·02	6·33	6·59	6·79	6·99	7·24	7·51
c.c. NaOH	40·0	42·5	45·0	47·5	50·0	52·5	55·0	57·5
*p*H	7·95	8·35	8·68	8·90	9·10	9·36	9·58	9·93
c.c. NaOH	60·0	62·5	65·0	67·5	70·0	72·5	75·0	77·5
*p*H	10·33	10·81	11·12	11·33	11·47	11·64	11·75	11·84
c.c. NaOH	80·0	82·5	85·0	87·5	90·0	92·5	95·0	97·5
*p*H	11·94	—	—	—	—	—	—	—
c.c. NaOH	100	—	—	—	—	—	—	—

TABLE 88 (*c*)

TITRATION OF 100 c.c. OF MODIFIED UNIVERSAL BUFFER MIXTURE WITH 0·2 N-NaOH (BRITTON AND ROBINSON)

TEMPERATURE 18° C. *p*H RANGE 1·81–11·98

100 *c.c. of a solution of mixed acids, being*

0·04 M.-H_3PO_4
0·04 N.-Acetic acid, and
0·04 N.-Boric acid (HBO_2, H_2O)

*p*H	1·81	1·89	1·98	2·09	2·21	2·36	2·56
c.c. NaOH	0	2·5	5·0	7·5	10·0	12·5	15·0
*p*H	2·87	3·29	3·78	4·10	4·35	4·56	4·78
c.c. NaOH	17·5	20·0	22·5	25·0	27·5	30·0	32·5
*p*H	5·02	5·33	5·72	6·09	6·37	6·59	6·80
c.c. NaOH	35·0	37·5	40·0	42·5	45·0	47·5	50·0
*p*H	7·00	7·24	7·54	7·96	8·36	8·69	8·95
c.c. NaOH	52·5	55·0	57·5	60·0	62·5	65·0	67·5
*p*H	9·15	9·37	9·62	9·91	10·38	10·88	11·20
c.c. NaOH	70·0	72·5	75·0	77·5	80·0	82·5	85·0
*p*H	11·40	11·58	11·70	11·82	11·92	11·98	—
c.c. NaOH	87·5	90·0	92·5	95·0	97·5	100·0	—

(See also Prideaux, *Proc. Roy. Soc.* 1916, **92**, A 463).

and the curve is perfectly straight. Greater ratios of $K_1 : K_2$ will lead to inflexions, though as may be seen from Fig. 58 the inflexion is not considerable in the case of *o*-phthalic acid of which $K_1 = 150$ times K_2. The universal buffer mixture, being made up of equivalent proportions of phenylacetic acid and boric acid and

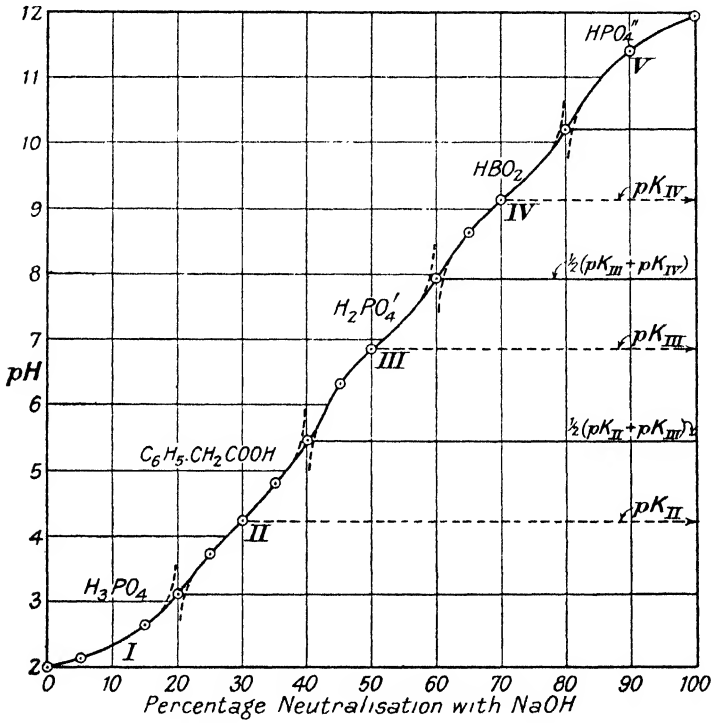


FIG. 73.—Percentage Neutralisation with NaOH. Prideaux and Ward's Universal Buffer Mixture.

an equimolecular proportion of phosphoric acid, may be regarded as a pentabasic acid whose constants, given as exponents, are successively

$pK_1 = 2{\cdot}0$ (H_3PO_4, 1st stage), $pK_2 = 4{\cdot}3$ (phenylacetic acid), $pK_3 = 6{\cdot}9$ (H_3PO_4, 2nd stage), $pK_4 = 9{\cdot}2$ (HBO_2),

and $pK_5 = 11{\cdot}6$ (H_3PO_4, 3rd stage).

Prideaux and Ward's intention appears to have been to prepare a mixture whose buffer action towards NaOH could be represented as a rectilinear *p*H curve. If each succeeding pair of constants bore to one another the ideal relationship for this condition to

hold, the first constant should not be greater than 16 times the second. As the logarithm of 16 is 1·2, it follows that this should be the maximum increment in the increasing *p*K values. The differences between the exponents of the several constants given above are 2·3, 2·6, 2·3 and 2·4, and as these are each greater than 1·2, the appearance of the many small inflexions are thus explained (Fig. 73). This has been made clearer in the figure by showing

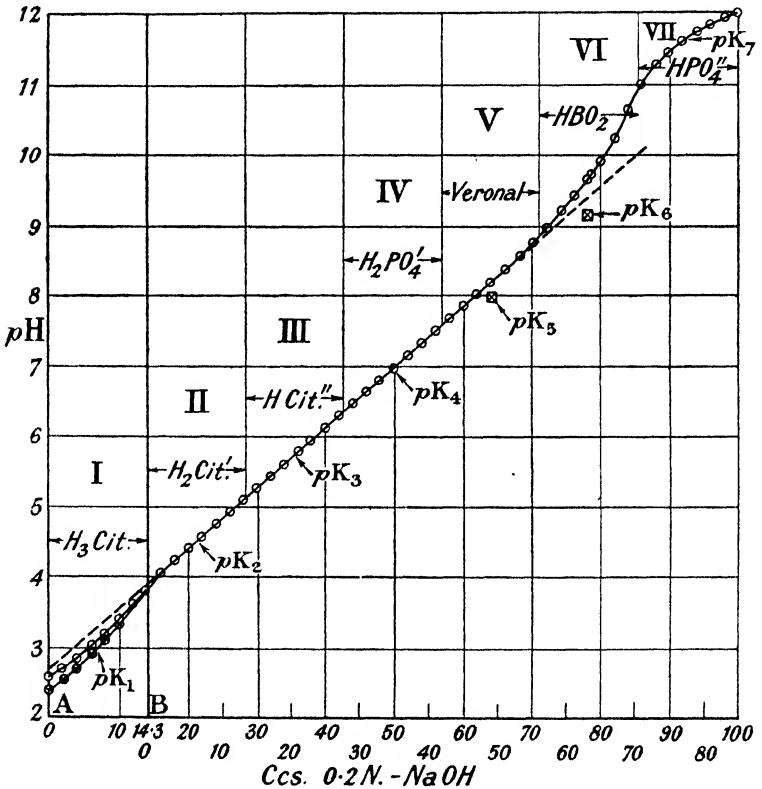


FIG. 74.—The Britton-Robinson Universal Buffer Mixture.

the separate monobasic acid titration curves, partly as broken lines. The curve of the buffer mixture is tangential to the separate constituent curves and incorporates just those sections which exhibit the more uniform buffer action. The horizontal lines drawn from the curve to the right-hand ordinate illustrate the approximate relationship, which we found on page 190, to exist between the exponents of the various constants of a mixture of acids at

the apparent beginning and ending of the neutralisation of each individual acid. The numerous data obtained by Britton and Robinson (Table 89 (*a*), Fig. 74) during the titration of this mixture reveal the undulating form of the curve. As a consequence, the interpolation formula of Prideaux and Ward can only yield very rough estimates of the *p*H values, with the exception of a few cases. Table 88 refers to a similar mixture in which phenylacetic acid is replaced by acetic acid.

TABLE 89 (*a*)

UNIVERSAL BUFFER MIXTURE (BRITTON AND ROBINSON)

*p*H RANGE 2·4–12·0 (18° C.)

100 *c.c. of a solution of HCl, KH_2PO_4, citric acid, boric acid and veronal (barbitone) (0·02857 M with respect to each constituent) titrated with x c.c. of 0·2 N-NaOH*

Interpolation Formula : $p\mathrm{H} = 2{\cdot}676 + 0{\cdot}0853\ x$.

D = Diluted to 200 c.c.
T = Direct Titration
C = Calculated from Formula.

*p*H (D)	2·58	2·72	2·86	3·03	3·21	3·43	—
*p*H (T)	2·40	2·55	2·73	2·92	3·12	3·35	—
*p*H (C)	2·68	2·85	3·02	3·19	3·36	3·53	—
NaOH, *x*	0	2	4	6	8	10	—
*p*H (D)	3·66	3·87	4·09	4·26	4·42	—	—
*p*H (T)	3·57	3·80	4·02	4·21	4·40	—	—
*p*H (C)	3·70	3·87	4·04	4·21	4·38	—	—
NaOH, *x*	12	14	16	18	20	—	—
*p*H (D and T)	4·57	4·75	4·91	5·08	5·25	5·40	—
*p*H (C)	4·55	4·72	4·89	5·06	5·23	5·40	—
NaOH, *x*	22	24	26	28	30	32	—
*p*H (D and T)	5·57	5·70	5·91	6·10	6·28	6·45	6·62
*p*H (C)	5·57	5·74	5·91	6·09	6·26	6·43	6·60
NaOH, *x*	34	36	38	40	42	44	46
*p*H (D and T)	6·79	6·94	7·12	7·30	7·47	7·66	7·82
*p*H (C)	6·77	6·94	7·11	7·28	7·45	7·62	7·79
NaOH, *x*	48	50	52	54	56	58	60
*p*H (D and T)	7·98	8·17	8·35	8·55	8·76	8·97	9·20
*p*H (C)	7·96	8·13	8·30	8·47	8·65	8·82	8·99
NaOH, *x*	62	64	66	68	70	72	74
*p*H (D + T)	9·41	9·65	9·88	10·21	10·63	11·00	—
NaOH, *x*	76	78	80	82	84	86	—
*p*H (D + T)	11·23	11·44	11·60	11·75	11·85	11·94	12·02
NaOH, *x*	88	90	92	94	96	98	100

The Universal Buffer Mixture (Tables 89 (*a*) and 89 (*b*) of Britton and Robinson gives an exact linear relationship between *p*H and the volume of sodium hydroxide within the range *p*H 4·0–8·4, so that the *p*H values can then be accurately calculated by means of an interpolation formula. Fig. 74 shows that the process of neutralisation involves the successive neutralisation of seven stages. The acids concerned are citric, phosphoric, boric and diethylbarbituric acid, the latter being liberated from veronal-sodium by means of an equivalent of hydrochloric acid. With respect to replaceable hydrogen the mixture is 0·2 N, so that each of the acid stages, being in equimolecular proportions, is $\frac{1}{7}$ of 0·2 N.

The order of neutralisation will be that of increasing *p*K values, *viz.*, $pK_{H_3Cit} = 3{\cdot}0$, $pK_{H_2Cit'} = 4{\cdot}6$, $pK_{HCit''} = 5{\cdot}8$, $pK_{H_2PO_4'} = 6{\cdot}9$, $pK_{Veronal} = 7{\cdot}96$, $pK_{HBO_2} = 9{\cdot}2$, $pK_{HPO_4''} = 11{\cdot}6$. The successive increases in the *p*K values are 1·6, 1·2, 1·1, 1·04, 1·24 and 2·4 respectively, and thus it appears why, with the exception of the initial and final portions of neutralisation, the *p*H curve is a straight line. The advantage of using the primary potassium phosphate and hydrochloric acid lies in the fact that the former can be obtained in a pure crystalline form. If a buffer solution is required for *p*H 3·8 upwards the hydrochloric acid is omitted in which case all the constituents are solids and the solution can thus be prepared by weighing. The *p*H values for the mixture containing hydrochloric acid are given in Table 89 (*a*), whilst those for the latter mixture are recorded in Table 89 (*b*).

TABLE 89 (*b*)

UNIVERSAL BUFFER MIXTURE (BRITTON AND ROBINSON)

*p*H RANGE 3·8–12·0

100 *c.c. of a solution of* KH_2PO_4, *Citric Acid, Boric Acid and Veronal, neutralised with x c.c.* 0·2 *N-NaOH*

Interpolation Formula : $pH = 3{\cdot}896 + 0{\cdot}0853\ x'$

*p*H (D and T) .	3·84*	—*	11·41	11·54	11·66	11·79	11·87	11·94
NaOH, *x* . .	0	—	75·7	77·7	79·7	81·7	83·7	85·7

* *Note.*—The intermediate *p*H values are the same as those given in Table 89(*a*), where $x' = x - 14{\cdot}3$.

As diethylbarbituric acid can now be procured commercially, there is no need to use its sodium salt (veronal, barbitone) and an equivalent amount of hydrochloric acid in preparing this Universal Buffer Mixture. Instead, Britton and Welford (*J. Chem. Soc.*, 1937, 1848; see also Johnson and Lindsey, *Analyst*, 1939, **64**, 490) prepare the Universal Buffer Mixture by making

the solution 0·02857 M. with respect to each of the four constituents : diethylbarbituric acid, citric acid, potassium dihydrogen phosphate and boric acid. Britton and Welford standardised this mixture by titrating 100 c.c. of the solution with 0·2 N-NaOH at a series of temperatures ranging from 12·5° to 91° C. Fig. 75

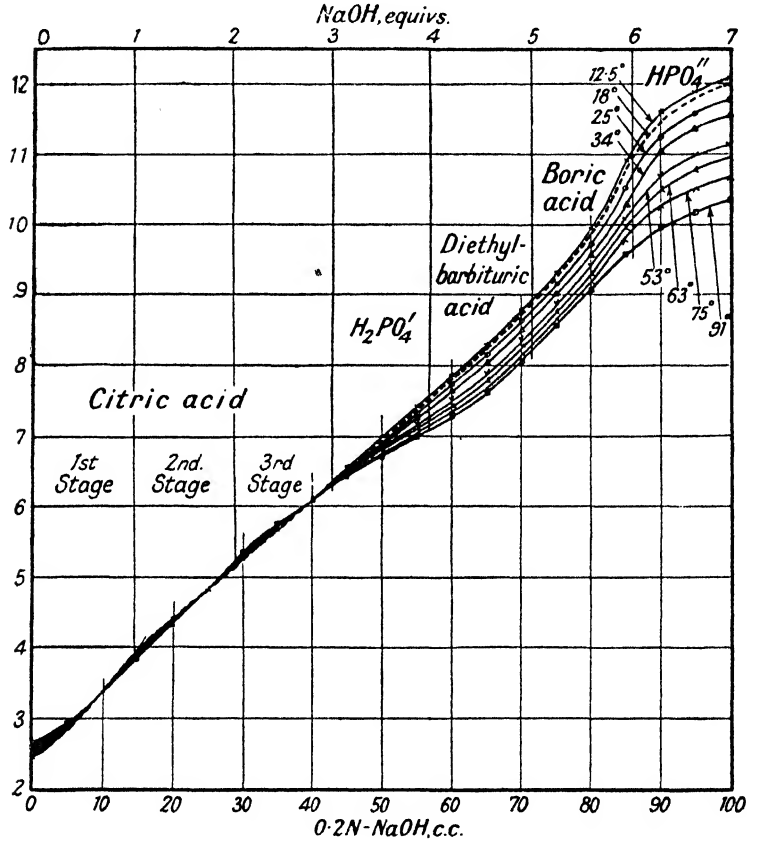


FIG. 75.—Calibration of the Britton-Robinson Universal Buffer Solution at Elevated Temperatures (Britton and Welford, *J. Chem. Soc.*, 1937, 1848).

shows that above 25° the *p*H–NaOH curve gradually departs from the rectilinear relationship at *p*H values just above 6 as the temperature is raised. Nevertheless, this Universal Buffer Mixture is the only one so far described which can be used at elevated temperatures, the difficulty with the previously described mixtures being the volatility of phenylacetic and acetic acids.

TABLE 90

100 *c.c. Universal Buffer Mixture, 0·02857 M with respect to Diethylbarbituric Acid, Citric Acid, KH_2PO_4, and Boric Acid, neutralised with x c.c. 0·2 N-NaOH at various temperatures.*

(BRITTON AND WELFORD)

x.	*p*H values at						
	12·5°.	25°.	34°.	53°.	63°.	75°.	91°.
0	2·38	2·42	2·47	2·53	2·55	2·59	2·64
5	2·86	2·90	2·92	2·94	2·94	2·96	2·96
10	3·36	3·36	3·36	3·35	3·35	3·35	3·35
15	3·94	3·92	3·89	3·85	3·84	3·83	3·82
20	4·42	4·40	4·37	4·35	4·34	4·33	4·33
25	4·83	4·82	4·80	4·80	4·80	4·80	4·80
30	5·25	5·27	5·28	5·28	5·30	5·31	5·33
35	5·65	5·68	5·70	5·73	5·74	5·76	5·75
40	6·10	6·10	6·10	6·10	6·10	6·10	6·10
45	6·55	6·51	6·49	6·47	6·46	6·45	6·44
50	6·96	6·90	6·85	6·80	6·77	6·73	6·71
55	7·38	7·30	7·24	7·15	7·09	7·02	6·98
60	7·82	7·71	7·61	7·48	7·42	7·33	7·27
65	8·27	8·14	8·01	7·87	7·76	7·67	7·59
70	8·77	8·63	8·48	8·35	8·25	8·16	8·07
75	9·30	9·15	9·01	8·87	8·77	8·67	8·58
80	9·90	9·71	9·55	9·40	9·30	9·16	9·06
85	10·90	10·50	10·27	10·06	9·93	9·77	9·57
90	11·60	11·25	11·02	10·68	10·48	10·24	9·95
95	11·91	11·58	11·36	10·98	10·77	10·51	10·17
100	12·10	11·79	11·56	11·14	10·97	10·69	10·34

If satisfactory standards are to be prepared every care must be taken to use pure materials, and in this respect the following notes may be of assistance.

Sodium Hydroxide.

Perhaps the most important solution, and incidentally the most troublesome to prepare, is that of sodium hydroxide, in that it should be free from carbonate. For ordinary purposes, however, absolute freedom is unnecessary, and the method adopted by Sørensen might be employed. A good sample of sodium hydroxide, *e.g.*, one prepared from sodium, which preferably has been purified with alcohol, is dissolved in water; about 100 grams of alkali to 120 c.c. water. This solution is placed in a tall stoppered cylinder and the impurities, mainly carbonate, allowed to settle out by leaving the cylinder standing for a couple of days. After

decantation of the clear liquid and filtration through glass wool, the solution which is about 17 N, is diluted to the required concentration. The diluted alkali solution should be tested for any carbonate by carefully adding hydrochloric acid to a portion until the pink colour produced by phenolphthalein is just on the point of disappearing. This will cause any carbonate to be converted into bicarbonate, whose presence may be detected by adding a neutral solution of barium chloride. If the colour fades, then bicarbonate may be taken as present.

The sodium hydroxide solution may be standardised against either hydrochloric acid, or a solution of benzoic acid, prepared from the pure crystals, or as suggested by Dodge (*J. Ind. Eng. Chem.*, 1915, **7**, 29) against a solution of carefully purified potassium hydrogen phthalate (see p. 321).

Other methods are available for the preparation of carbon dioxide-free sodium hydroxide. One is to cover some cooled boiled-out water with a layer of ether and to introduce into the mixture freshly cut pellets of sodium. These will float on the surface of the water and so interact. The ethereal layer will prevent the ingress of carbon dioxide. Afterwards the ether is expelled by boiling. Another method is to suspend some bright sodium in a nickel or silver gauze cage above a beaker placed inside a bell-jar and to lead in steam. A concentrated alkali solution will result. Much care is necessary to suck out the hydrogen that is liberated, not to allow any appreciable pressure to be set up within the bell-jar and to avoid too rapid an attack of the steam metal which may result from the sudden fall of a little condensed water on to the sodium. This method has been known to end in disaster.

The most satisfactory method is to prepare sodium amalgam electrolytically and to run it into CO_2-free water. This may be carried out in a separating funnel. Redistilled mercury is placed in the bottom, above which is a saturated solution of pure sodium chloride. Electrolysis is effected by means of two or three 2-volt accumulators placed in series. The mercury is made the cathode by connecting the negative pole to it by a wire dipping into a mercury contact placed in a closed glass tube, passing through the end of which is a platinum wire whose other end is completely immersed in the mercury in the funnel. The anode is a platinum wire. As the electrolysis proceeds shaking may be necessary to prevent the crystallisation of the amalgam. When sufficient amalgam is formed, the current is stopped, and the amalgam cautiously dropped into water by opening the tap and placing the end of the tube below the level of the water.

Hydrochloric Acid.

The preparation of a solution of hydrochloric acid presents no difficulty. It may be standardised against sodium carbonate, or may be standardised by preparation from a " constant-boiling " solution of hydrochloric acid (*cf.* Hulett and Bonner, *J. Amer. Chem. Soc.*, 1909, **31**, 390). Under an atmospheric pressure of 760 mm. of mercury this solution boils at 108·5° C., and at 15° C. contains 20·242 per cent. HCl by weight. To prepare a decinormal solution it is necessary to take 18·017 grams of the acid and make up to 1 litre.

Potassium Biphthalate. (Potassium hydrogen phthalate.)

This compound, which is used in some of Clark and Lubs' standard buffer solutions, may be prepared by Dodge's method (*loc. cit.*). Between 10 and 20 grams of orthophthalic acid, or a proportionally greater amount of phthalic anhydride, are dissolved in 100 c.c. of a concentrated potassium hydroxide solution (about 15 per cent.) and the *p*H of the resulting solution adjusted to that corresponding to a faint pink colour of phenolphthalein by the addition of just the necessary amount of acid or alkali. Boil and filter while hot. Set to crystallise and recrystallise twice from distilled water. The temperature at which crystallisation is allowed to take place must be above 20° C., for according to Dodge at lower temperatures a more acid phthalate separates out. The salt is rendered anhydrous by drying to constant weight at 110° to 115° C. It may be obtained commercially in a pure state.

Phosphoric Acid and Alkali Metal Phosphates.

Primary and secondary orthophosphates appear in the standard mixtures, though in the opinion of the author it is more convenient to prepare suitable solutions of them by the partial neutralisation of phosphoric acid. Unless one is very fortunate, there is every likelihood that the primary and secondary products of commerce will be somewhat indefinite in composition, in regard to both the phosphate and water contents. The reason for this will be apparent from the results of D'Ans and Schreiner (*Z. physikal. Chem.*, 1910, **75**, 95) and of Parker (*J. Physical Chem.*, 1914, **8**, 653) of the appropriate Ternary Systems, *viz.*,

$$NaOH—H_3PO_4—H_2O,$$

and

$$KOH—H_3PO_4—H_2O.$$

According to Sørensen, the primary potassium phosphate,

KH_2PO_4, should be free from sulphate and chloride and when dried at 100° C. under 20 to 30 mm. pressure should not lose 0·1 per cent. of its weight, while on ignition the loss should be 13·23 per cent. The primary sodium salt which crystallises above 10° is NaH_2PO_4,H_2O and if crystallised out below 10° C., NaH_2PO_4, $2H_2O$. On drying at 100°, it yields the anhydrous salt. This salt may replace the potassium salt in the buffer mixtures without introducing any error.

Sørensen used a Kahlbaum preparation of disodium hydrogen phosphate corresponding to Na_2HPO_4, $2H_2O$, which when dried at 100° under 20 to 30 mm. pressure lost 25·28 ± 0·1 per cent.; and 13·23 ± 0·1 on ignition. It may be as well to point out here that the hydration of this salt is dependent upon the temperature at which it is crystallised. It crystallises with 12 molecules of water below 36·5° C.; above this temperature and below 48° C. with 7; between 48° and 95° with 2; while above 95°, in the anhydrous state. It is essential, therefore, that no calculations should ever be based upon any particular composition, unless it has been definitely ascertained.

Boric Acid and Borax.

Boric acid should be purified by recrystallisation, spread into thin layers and placed in a desiccator over fused calcium chloride until perfectly dry. It has the formula HBO_2, H_2O.

Borax, $Na_2B_4O_7$, $10H_2O$, after the necessary recrystallisation should be dried to constant weight over deliquescent sodium bromide. One great advantage which attends the use of this salt lies in the fact that it can be accurately weighed. If, however, solutions of boric acid and sodium hydroxide whose concentrations are accurately known are available, solutions of borax can be readily prepared, for the composition of the solute is that of half-neutralised boric acid, HBO_2,H_2O. (See also Chapter XI.)

Sodium Carbonate.

This salt can easily be obtained by gently heating either sodium bicarbonate or sodium oxalate to constant weight. The salt should not be allowed to fuse and the temperature not to exceed 360° C.

Citric Acid. $H_3C_6H_5O_7,H_2O$.

The water of crystallisation may be found by drying to constant weight at 70° and 20 to 30 mm. Loss in weight should be 8·58 ± 0·1 per cent.

Succinic Acid. $(CH_2.COOH)_2$.

This acid contains no water of crystallisation and care must be taken not to form the anhydride by heating to too high a temperature. Solutions must be freshly made, for like those of tartaric and citric acids, it has a distinct tendency to become contaminated by mould formation, though to a great extent this may be prevented by adding a few drops of thymol solution without influencing the *p*H. M.p. 185–185·5° C.

Glycine, Glycocoll, Amino-acetic Acid. $CH_2.NH_2.COOH$.

This compound appears in one of the Sørensen buffer solutions, but these particular solutions are rapidly becoming discontinued. Sørensen states that the solution obtained by dissolving 2 grams in 20 c.c. of water should be clear and free from chloride and sulphate. Not more than 5 mgms. of ash should result from the ignition of 5 grams of glycine, and the nitrogen content found by the Kjeldahl method should be 18·68 ± 0·1 per cent.

Phenylacetic Acid. $C_6H_5.CH_2COOH$.

Melting-point is 76° C.

Sodium diethylbarbiturate. $(C_2H_5)_2C\begin{<}{CO\,.\,HN}{CO\,.\,NaN}\!>CO$.

Kolthoff (Gebrauch der Farben-Indikatoren, Berlin, 1923) found by means of indicators that the dissociation constant of diethylbarbituric acid was $3{\cdot}7 \times 10^{-8}$. Using the hydrogen electrode Britton and Robinson (*J. Chem. Soc.*, 1931, 1456) obtained $10^{-7{\cdot}95}$. The commercial products, veronal-sodium, barbitone-sodium, save for possible traces of water that can be driven off at 100°, are of suitable purity. To make a M/10-solution 10·30 grams are dissolved in CO_2-free water and made up to 500 c.c.

***p*-Toluenesulphonic Acid.** $C_6H_4CH_3.SO_2OH$, H_2O.

This acid may be obtained commercially, or prepared by the method of Meyer (*Liebig Ann.*, 1923, **443**, 331 ; *cf.* Gattermann, McCartney, "Lab. Methods of Org. Chem.," 1932, *p.* 183). M.pt. 105°–6° in a sealed tube. It may be purified by crystallising from an aqueous solution, saturated with gaseous hydrogen

chloride, and then dried over stick caustic potash or fused calcium chloride. It is somewhat deliquescent.

Furoic Acid. M.pt. 132°.

For most practical purposes, re-crystallisation of the commercial product from hot water and then from chloroform affords sufficient purification.

CHAPTER XVII

COLORIMETRIC METHODS FOR THE DETERMINATION OF HYDROGEN-ION CONCENTRATIONS

IN order to obtain a working hypothesis of the principles underlying the estimation of *p*H values by observing the various colours and intensities of colour produced by indicators, we shall first of all briefly refer to some of the theories which have been advanced to account for the colour and the constitution of indicators in solutions of acid or alkaline reaction.

Theory of Indicators.

As the result of extensive studies on the changes of colour which many indicators undergo, Wilhelm Ostwald concluded that colour is inherently connected with the presence of ions, and that the colour of a solution is the resultant of mixing two colours: (*a*) the colour produced by a coloured or colourless un-ionised compound and (*b*) that produced by the differently coloured ions into which the compound may have dissociated. Thus, he considered indicators to be either weak acids or bases which may have one colour in the undissociated condition, and whose anions, in the case of acids, and cations, in the case of bases, have a different colour. If we denote an indicator which is a weak acid by HIn, and a weak base indicator by InOH, then we may represent their colour changes in terms of the equilibria

$$\underset{\text{(undissociated, coloured)}}{HIn} \rightleftharpoons \underset{\text{(differently coloured anions)}}{H^{\cdot} + In'}$$

and

$$\underset{\text{(undissociated, coloured)}}{InOH} \rightleftharpoons \underset{\text{(differently coloured cations).}}{In^{\cdot} + OH'}$$

In some cases, the indicator is colourless in one of its forms. Such equilibria would be governed by the law of mass action throughout the neutralisation of the indicators, and therefore

$$\frac{[H^{\cdot}][In']}{[HIn]} = K_{HIn}$$

and

$$\frac{[In^{\cdot}][OH']}{[InOH]} = K_{InOH}$$

might be expected to give some quantitative measure of the colour changes undergone by the respective types of indicators. Hence the colour-change of a weak acid indicator at varying *p*H values may be expressed by

$$pH = pK_{HIn} + \log \frac{[In']}{[HIn]}$$

$$= pK_{HIn} + \log \frac{[In' \text{ colour}]}{[HIn \text{ colour}]}$$

and of a weak base indicator by

$$pOH = pK_{InOH} + \log \frac{[In^{\cdot}]}{[InOH]^{\cdot}}$$

We have seen from the neutralisation curves of monobasic acids and of monoacid bases (Fig. 52), that though these reactions normally set up a change in hydrogen-ion concentration corresponding to 4 *p*H units, a variation of 1 *p*H unit occurs during the neutralisation from 1 to 10 per cent. and another change of 1 *p*H unit is introduced during the last phase, from 90 to 99 per cent. Hence, there occurs a colour change indicated by 2 *p*H units during neutralisation from 10 to 90 per cent., and, moreover, it will be observed that this gradual change is almost a linear function of the degree of neutralisation. In the case of the weak acids or the weak bases which constitute the various indicators, it is found in general that the colour due to the ionised form is not discernible until 10 per cent. of the indicator has been converted into the salt form, and that the colour of the undissociated acid or base does not become completely masked to the eye until the indicator has undergone 90 per cent. neutralisation. Hence the *p*H range within which an indicator suffers a gradual change in colour is known as the *Transition Interval*, which, on theoretical grounds, should be given by the following expressions :—

(*a*) Acidic Indicator : HIn.

$$\text{Initial } pH = pK_{HIn} + \log \frac{10}{90}$$

$$= pK_{HIn} - 1 \text{ (approx.)}.$$

$$\text{Final } pH = pH_{HIn} + \log \frac{90}{10}$$

$$= pK_{HIn} + 1 \text{ (approx.)}.$$

$$\therefore \text{ Transition interval} = \text{final } pH - \text{initial } pH$$

$$= 2\ pH \text{ units (approx.)} = pK_{HIn} \mp 1.$$

(*b*) **Basic Indicator : InOH.**

Similarly initial pOH $= p\mathrm{K}_{\mathrm{InOH}} - 1$ (approx.)

and final pOH $= p\mathrm{K}_{\mathrm{InOH}} + 1$ (approx.).

$\therefore$ Transition interval = final pOH − initial pOH

= 2 pH units (approx.)

$= p\mathrm{K}_{\mathrm{InOH}} \mp 1.$

Hence, the initial pH $= p\mathrm{K}_w - p\mathrm{K}_{\mathrm{InOH}} + 1$

and, the final pH $= p\mathrm{K}_w - p\mathrm{K}_{\mathrm{InOH}} - 1.$

We should therefore expect the colour change of an acidic indicator to begin at a pH value 1 unit below that of $p\mathrm{K}_{\mathrm{HIn}}$ and to end at a pH value 1 unit above, and that of a basic indicator to begin at a pH value 1 unit higher than $p\mathrm{K}_w - p\mathrm{K}_{\mathrm{InOH}}$ and to finish at a value 1 unit below $p\mathrm{K}_w - p\mathrm{K}_{\mathrm{InOH}}$.

Table 91, which gives a selected list of indicators suitable for use over the whole pH range from 0 — 14, shows that the transition interval for most indicators extends over about 2 pH units. The actual transition intervals are influenced by other factors such as (1) the sparing solubility of the indicator in one of its forms, (2) a difference in the intensity of the two coloured forms, (3) dichromatism of certain types of indicators, and (4) possible effects of the concentration of the indicator used.

The dissociation constants of a few indicators have been determined on the assumption that the colour changes are produced by the neutralisation of a monobasic acid. Two methods have been employed. One which is more suitable for one-coloured indicators, though it has been used for two-coloured indicators, involves the measurement of the proportion of indicator in the coloured form in a solution of known pH by means of a colorimeter or a spectrophotometer. The constant calculated from a series of such data by Rosenstein (*J. Amer. Chem. Soc.*, 1912, **34**, 1117; 1913, **35**, 1883) for phenolphthalein in solutions ranging from pH 8·96–9·95 reveals that the colour-change takes place in accord with the assumption that the intensity of the colour constitutes a measure of the extent of neutralisation of the indicator in producing red indicator-anions. Moreover, the amounts of neutralisation so found were in good agreement with those calculated from the concentrations of the reactants. The second method, which is more appropriate for two-coloured indicators, necessitates the measurement of the hydrogen-ion concentration of a solution of an indicator whose colour has been found to have been half-changed, *i.e.*, when the solution contains the

TABLE 91

SELECTED INDICATORS

*p*H Range.	Common Name.	Chemical Name.	Colour Change.	Used By :
0·0–1·3	Picric acid	Trinitrophenol	Colourless—yellow	M. and G.
0·0–2·0	Crystal violet	Hexamethyl-*p*-rosaniline	Green—blue	—
0·0–2·0	Malachite green	Tetramethyl di-*p*-aminotriphenyl-carbinol	Yellow—green	—
0·1–3·2	Methyl violet	Mixture	Yellow—violet	S.
0·5–2·5	Metacresol purple	*m*-Cresol sulphone phthalein	Red—yellow (*also* *p*H 7·6–9·2 yellow—purple)	C.
1·2–2·3	Metanil yellow	*m*-Sulphobenzene-azo-di-phenylamine	Red—yellow	S.
1·2–2·8	Xylenol blue	*p*-Xylenol sulphonephthalein	Red—yellow (*also* *p*H 8·0–9·6 yellow—blue)	C. and L.
1·2–2·8	Thymol blue	Thymol sulphonephthalein	Red—yellow (*also* *p*H 8·0–9·6 yellow—blue)	C. and L.
1·3–3·2	Tropæolin OO	Phenylaminoazobenzene-sulphonic acid	Pink—yellow	S.
1·5–5·0	Benzopurpurin	Ditolyldisazobi-β-naphthylamine-β-sulphonic acid	Blue—violet—orange	S.
1·7–4·4	β-Dinitrophenol	2 : 6 Dinitrophenol	Colourless—yellow	M. and G.
2·0–4·7	α-Dinitrophenol	2 : 4 Dinitrophenol	Colourless—yellow	M. and G.
2·9–4·0	Methyl yellow	Dimethylanilinoazobenzene	Red—yellow	S.
3·0–4·6	Bromophenol blue	Tetrabromophenol-sulphonephthalein	Yellow—blue	C. and L.
3·0–5·0	Congo red	Diphenyldisazobinaphthionic acid	Blue—red	—
3·1–4·4	Methyl orange	*p*-Benzenesulphonic acid-azo-dimethyl-aniline	Red—yellow	S.
3·2–4·8	Bromochlorophenol blue	Dibromodichlorophenol-sulphonephthalein	Yellow—blue	C.
3·5–4·5	Ethyl orange	*p*-Benzenesulphonic acid-azo-diethylaniline	Pink—yellow	—
3·5–5·7	—	*p*-Benzenesulphonic acid-azo-α-naphthyl-amine	Red—orange	S.

3·7–5·2	Sodium alizarine sulphonate	Sodium alizarine sulphonate	Yellow—violet (*also* *p*H 10·0–12·0		
3·9–5·9	ϵ-Dinitrophenol	2 : 3 Dinitrophenol	Colourless—yellow		—
3·9–6·3	4-Nitrocatechol	—	Straw—lemon / Red at *p*H 10·6	(3)	—
4·0–5·6	Bromocresol green	Tetrabromo-*m*-cresol sulphonephthalein	Yellow—blue		C.
4·0–6·0	γ-Dinitrophenol	2 : 5 Dinitrophenol	Colourless—yellow		M. and G.
4·0–7·0	Chrysoïdin	Benzene-azo-*m*-phenylenediamine	Orange—yellow		—
4·2–6·3	Methyl red	*o*-Carboxybenzene-azo-dimethylaniline	Red—yellow		S. : C. & L.
4·3–6·3	δ-Dinitrophenol	3 : 4 Dinitrophenol	Colourless—yellow		—
4·4–6·2	Ethyl red	*o*-Carboxybenzene-azo-diethylaniline	Red—yellow		—
4·4–6·6	Lacmoid	—	Red—blue		S.
4·6–6·6	Propyl red	*o*-Carboxybenzene-azo-di-*n*-propyl-aniline	Red—yellow		—
4·8–6·2	Cochineal	—	Yellow—lilac		—
5·0–5·6	Benzoyl auramine G	—	Violet-grey–yellow	(2)	—
5·0–7·0	Chlorophenol red	Dichlorophenol sulphonephthalein	Yellow—red		C.
5·0–7·0	*p*-Nitrophenol	*p*-Nitrophenol	Colourless—yellow		S.
5·0–8·0	Litmus, Azolitmin	—	Red—blue		S.
5·2–6·8	Bromocresol purple	Dibromo-*o*-cresol sulphonephthalein	Yellow—purple		C. and L.
5·4–7·0	Bromophenol red	Dibromophenol sulphonephthalein	Yellow—red		C.
6·0–7·6	Bromothymol blue	Dibromothymol sulphonephthalein	Yellow—blue		C. and L.
6·4–6·8	Nitrazine yellow	2, 4-dinitrobenzene-azo-1-naphthol-3-6-disulphonic acid	Yellow—blue	(1)	—
6·5–8·5	*m*-Nitrophenol	*m*-Nitrophenol	Colourless—yellow		M. and G.
6·8–8·0	Aurine	*p*-Rosolic acid	Brown—red		S.
6·8–8·0	Neutral red	Dimethyldiaminotoluphenazine	Red—yellow		S.
6·8–8·4	Phenol red	Phenolsulphonephthalein	Yellow—red		C. and L.
7·0–8·0	Quinoline blue	Cyanine	Colourless—violet		—
7·2–8·8	Cresol red	*o*-Cresol sulphonephthalein	Yellow—red		C. and L.
7·3–8·7	—	α-Naphtholphthalein	Red—blue		—
7·6–8·9	Tropæolin OOO	*p*-Sulphobenzene-azo-α-naphthol	Brownish-yellow—red		S.
7·6–9·2	Meta cresol purple	—	Yellow—purple		C.
7·8–9·2	Turmeric	—	Yellow—orange		—

TABLE 91 (*continued*)

*p*H Range.	Common Name.	Chemical Name.	Colour Change.	Used By :
8·0–9·6	Xylenol blue	*p*-Xylenol sulphonephthalein	Yellow—blue (*also* *p*H 1·2–2·8 red—yellow)	C. and L.
8·0–9·6	Thymol blue	Thymol sulphonephthalein	Yellow—blue (*also* *p*H 1·2–2·8 red—yellow)	C. and L.
8·2–9·8	Cresolphthalein	*o*-Cresolphthalein	Colourless—red	C. and L.
8·3–10·5	Phenolphthalein	Phenolphthalein	Colourless—red	S. : C. & L.
9·3–10·5	Thymolphthalein	Thymolphthalein	Colourless—blue	S.
10·0–12·0	Alizarine yellow GG (Salicyl yellow)	*p*-Nitrobenzene-azo-salicylic acid	Colourless—yellow	M. and G.
10·0–12·0	Sodium alizarine sulphonate	Sodium alizarine sulphonate	Brownish-red—yellow	S.
10·5–11·5	Azo blue	Ditolyldisazobi-α-naphthol-4-sulphonic acid	Violet—pink	—
10·8–12·8	Nitramine	Picrylmethylnitramine	Colourless—orange brown	S.
11·0–13·0	Tropæolin O	*p*-Sulphobenzene-azo-resorcin	Yellow—orange brown	S.
11·5–14·0	Orange G.	Benzene-azo-β-naphthol γ-Disulphonic acid	Yellow—pink	—

C. . . . . Clark.
C. and L. . . . Clark and Lubs.
M. and G. . . . Michaelis and Gyemant.
S. . . . . Sørensen.

(1) Wenker (*Ind. Eng. Chem., Anal. Edn.*, 1935, **7**, 40).
(2) Scanlan and Reid (*ibid.*, p. 125).
(3) Cooper and Tulane (*ibid.*, 1936, **8**, 210).

indicator in equal concentrations in its acid form and in its alkaline form. The half-way colour may be ascertained by having two tubes of the same size and shape such that one contains a certain amount of the indicator completely in the acid form and the other the same amount of indicator but completely in the alkaline form. If one tube is then placed on the top of the other and illuminated at the bottom, the tint on looking down through the two tubes will correspond to the half-way tint for the particular concentration of indicator used. If now, a tube of double length and the same cross-section is taken and filled with a solution containing twice the amount of indicator used in the separate solutions and whose colour has been adjusted by the addition of buffer agents such that the tint, when the liquid has been similarly illuminated, is identical with the half-way colour, it is only necessary to determine the hydrogen-ion concentration of the solution to find the dissociation constant of the indicator. Then if this half-way colour change is produced at the half-neutralisation of the indicator, considered either as a monovalent acid (or base) it follows that

$$p\mathrm{H} = p\mathrm{K}_{\mathrm{HIn}} \text{ (or } p\mathrm{OH} = p\mathrm{K}_{\mathrm{InOH}}\text{)}.$$

A selection of indicator constants is given in Table 92, together with the predicted useful ranges of these indicators and the ranges for which they have been found to be available. The colour changes of azo-indicators such as methyl orange and methyl red

TABLE 92

DEPENDENCE OF TRANSITION INTERVAL ON DISSOCIATION CONSTANT OF INDICATOR

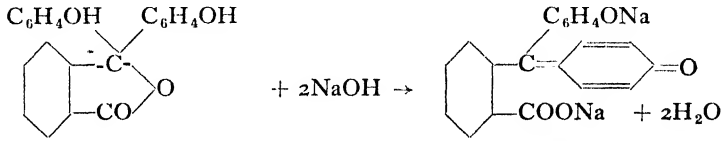
Indicator.	pK.	Transition Interval, pH.	
		Theoretical.	Practical.
Thymol blue (acid range)	1·7	0·7–2·7	1·8–2·8
Thymol blue (alk. range)	8·9	7·9–9·9	8·0–9·6
Methyl orange	3·7	2·7–4·7	3·0–4·6
Bromophenol blue	4·1	3·1–5·1	3·1–4·4
Methyl red	5·1	4·1–6·1	4·2–6·3
Ethyl red	5·4	4·4–6·4	4·4–6·2
Propyl red	5·4	4·4–6·4	4·6–6·6
Bromocresol purple	6·3	5·3–7·3	5·2–6·8
Bromothymol blue	7·1	6·1–8·1	6·0–7·6
Cresol red	8·1	7·1–9·1	7·2–8·8
Phenol red	7·8	6·8–8·8	6·8–8·4
α-Naphtholphthalein	8·4	7·4–9·4	7·3–8·7
Thymolphthalein	9·2	8·2–10·2	9·3–10·5
Phenolphthalein	9·7	8·7–10·7	8·3–10·5

are really due to the indicators behaving as bases (see p. 327), but in the values given they are treated as if they were acids. The sulphonephthalein indicators of Clark and Lubs are dibasic, but, as suggested by Clark, the colour changes are functions of the weak stages of ionisation, namely, the neutralisation of the phenolic groups, and not of the comparatively strong sulphonic acid group ionisations. Kolthoff has, moreover, shown that their behaviour may be satisfactorily considered in terms of the simple equation given above.

The Ostwald theory of the colour changes of indicators, being due to ionisation, is inadequate. It does not, for instance, explain why the solid salt of phenolphthalein is red. It is hardly fitting in a book of this type to enter into a lengthy discussion of the elaborate theories of colour and constitution of organic compounds. There is no doubt that many colour changes can be attributed to changes in constitution. Thus if ionisation were the sole cause of the change in colour, it is difficult to understand why certain indicators, *e.g.*, tropæolin OOO, and hæmatein, require time for the colour change instead of this occurring instantaneously instead of requiring time. It may be that the conception of Wolfgang Ostwald, that the colour change of an indicator is traceable to it being a colloid in solution and therefore that the colour assumed by a solution is connected with the size of the dispersed particles, provides an explanation for such time reactions. The mechanism of the change brought about by hydrogen and hydroxyl ions might therefore be due to reactions with a colloidal electrolyte with the consequent changes in the magnitude of the micellar ions. Baly accounts for the colour of solutions on a purely physical theory based upon his extensive observations of absorption spectra. Such a theory gains support when it is remembered that colour is essentially an optical property and that as light is electromagnetic in nature, absorption involves a change in energy dependent upon the dissolved molecules.

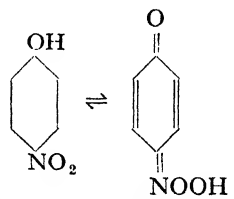
The theory that colour change is one of tautomeric change affords plausible explanations of the ultimate substances which are formed possessing colour, in that they contain chromophoric quinone groups. As Kolthoff states, however ("Indicators," p. 239), the chromophoric theory gives "no explanation of the change, but calls attention to a phenomenon that accompanies the colour change. The colour change is accompanied by a change in constitution, but this is not the cause of the colour change." Simply, because the two changes take place simultaneously, it is not logical to conclude that a change in constitution is the cause of a change in colour, any more than it is to

suggest that a change in colour is the cause of the change in constitution. In the case of phenolphthalein, the researches of Friedländer, Bernsthen, Hantzsch and pupils, show that the colourless compound contains a lactone ring whereas the red salt formed by the interaction of alkalis has the chromophoric quinoid group, thus :



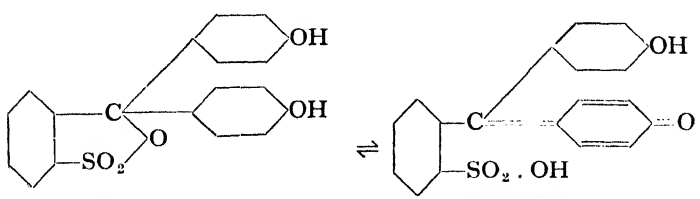
Lactone ring (colourless). Quinone group (red).

The colour of an indicator solution may be governed by the equilibrium existing between tautomers. Thus the normal form of *p*-nitro-phenol is a true nitro-body which exists in solution in tautomeric equilibrium with nitrolic acid. Whereas the former form is colourless, the latter is yellow. The equilibrium may be represented



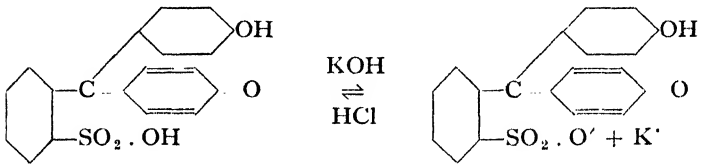
Colourless. Yellow.

The colours of the sulphonephthaleins have been attributed by Lubs and Acree to the opening of a lactoid ring and the resulting formation of a quinoid group, to be followed by the ionisation of the sulphonic acid and phenolic groups through neutralisation with a strong base. As an example, we shall consider the stages in the production of colour by phenol sulphonephthalein, *i.e.*, phenol red. In acid solutions it is supposed to be present in an equilibrium between its two tautomers,

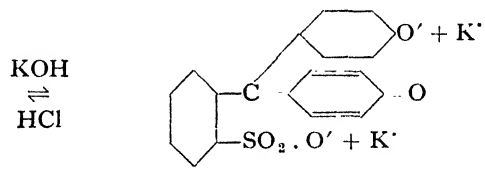


Colourless (lactoid ring). Pale yellow (quinoid group).

though, owing to the strongly acidic nature of the sulphonic acid group, it is believed that the quinoidal body must predominate. On the addition of an alkali, the sulphonic acid group will be the first to be reacted upon but the ionisation of the salt thus formed is considered to have very little effect upon the colour. When, however, more alkali is added the phenolic group enters into reaction and it is the ionisation thus brought about which, it is believed, is responsible for the transformation from the yellow to the characteristic deep red colour of the indicator. These two stages are therefore,

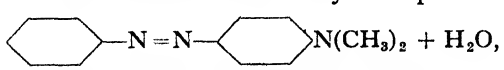


Pale yellow. Pale yellow.

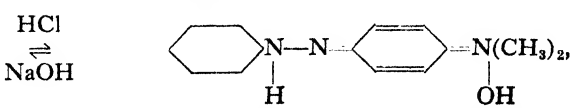


Deep red.

We shall now direct our attention to the explanation afforded by the chromophoric theory of the behaviour of indicators containing the azo-group, *e.g.*, methyl orange and methyl red. In alkaline solution they possess the azo linkage, but on making the solution acid a benzene group undergoes transformation of the quinoid type. Methyl yellow, dimethylaminoazobenzene, is the simplest type of an azo indicator. Its yellow form, which is present in alkaline solution, is a very feeble base, and then contains the azo grouping, but on rendering the solution acidic it assumes the property of being a strong base, due to an intramolecular change in forming a quinoid group, and at the same time the solution becomes red. This transformation may be represented thus :

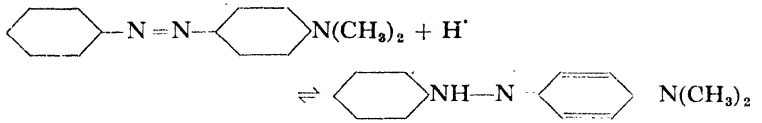


Azo linkage : yellow : in alk. solution.



Quinoid group : red : in acid solution.

or ionically, as



The behaviour of dimethylaminoazobenzene towards an acid is thus seen to be that of a base. On the other hand, the hydrogen-ion concentration of a solution giving a half-way tint corresponds to *p*H 3·2, and therefore, if it were an acid, its dissociation constant would be $10^{-3\cdot2}$, corresponding to that of a fairly strong acid. Actually, this is the hydrolysis constant of its salt with a strong acid with alkali, and therefore its basic constant $= K_w/10^{-3\cdot2} = 10^{-11}$.

The various colours of the indicators of this class, such as those of methyl orange and methyl red, can be accounted for by similar changes in structure, but the actual processes of colour change can only be placed on a quantitative footing in terms of electrolytic dissociation, as we have just seen to be the case with dimethylaminoazobenzene. This will be seen more forcibly from a study of the colour change of methyl orange. In its solid form, it is the sodium salt of dimethylaminoazobenzene-sulphonic acid which on dissolution in water imparts to it a yellow colour, due, we may reasonably imagine, to the organic anion, whilst on the addition of acid the red form is developed. Salm (*Z. physikal. Chem.*, 1907, **57**, 471) found that the *p*H of the solution at 18° C. required to give half-way colour is 3·3, and therefore if we regard the transition from the red form to the yellow form by reacting with an alkali, methyl orange would appear to be a fairly strong monobasic acid whose constant is $10^{-3\cdot3}$. It is of interest that Tizard's results (*J. Chem. Soc.*, 1910, **97**, 2477) obtained by the first method described on page 327, led to an apparent acidic constant of $10^{-3\cdot4}$ at 25° C. As before, this constant is merely the hydrolysis constant of the weak indicator base — strong acid salt. It is likely that the change is most satisfactorily represented on the basis of the "Zwitter" ion theory, whence the yellow anion is

$$(CH_3)_2N \cdot R \cdot SO_2O'$$

in which R is $C_6H_4 \cdot N = N \cdot C_6H_4$, and the red form, the "Zwitter" ion

$$^{+}H(CH_3)_2N \cdot R \cdot SO_2O'$$

and therefore the change in colour is given by

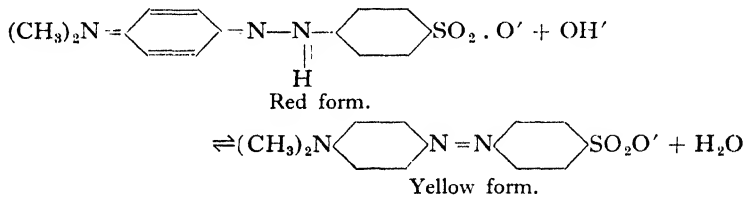
$$\underset{\text{Red.}}{^{+}H(CH_3)_2N \cdot R \cdot SO_2O'} + OH' \rightleftharpoons \underset{\text{Yellow.}}{(CH_3)_2N \cdot R \cdot SO_2O'} + H_2O$$

Using the symbols adopted on page 216, we find that

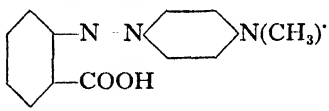
$$\frac{[Z][OH']}{[A']} = k_b = \frac{[Red][OH']}{[Yellow]}.$$

Hence at 18° $pk_b = pK_w - pK_a$,
$= 14{\cdot}1 - 3{\cdot}3$
$= 10{\cdot}8.$

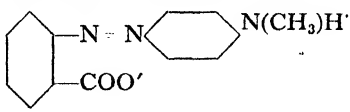
A more recent value was obtained at 18° by Kolthoff (*Rec. trav. chim.*, 1925, **44**, 68) of $pk_b = 10{\cdot}7$ and Thiel and Dassler (*Ber.*, 1923, **56**, 1667) of 10·5 at 25° C. Whereas these considerations give no reasons why the ampholytic or " Zwitter " ion should be different in colour from the anion, a possible clue is to be found in the tautomeric rearrangements within the ions, thus :



The acidic dissociation, *i.e.*, the reaction of the ampholytic ion with hydrogen ions forming cations containing the free sulphonic acid, are without effect upon the colour of the solution. This is also true for methyl red, which is



and in solution forms the " Zwitter " ion



The acid dissociation has the constant, $k_a = 2{\cdot}5 \times 10^{-3}$ or $pk_a = 2{\cdot}60$. The *p*H at half-neutralisation is therefore $pK_w - pk_a = 11{\cdot}5$. This mode of ionisation, however, is unimportant as it has no effect on the colour change, for as in the previous two examples, this is connected entirely with the basic neutralisation. Again the " Zwitter " ion is red and the anion yellow, and the value of $pk_b = 9{\cdot}15$ and therefore the *p*H at half-way colour change is $14{\cdot}14 - 9{\cdot}15 = 5{\cdot}0$ at 18° C.

It will be concluded from the foregoing discussion that, whatever may be the true cause of the colour changes of indicators, the

application of the ionisation theory and the law of mass action has led to a remarkably useful working hypothesis. This will be appreciated in connexion with the methods to be described for the approximate measurement of hydrogen-ion concentrations without the aid of standard buffer solutions, as in the methods of Michaelis, Gillespie, and McCrae.

Approximate Colorimetric Methods of Determining *p*H.

Two types of methods of finding the approximate *p*H value of a solution are available.

One type is based on the theoretical principle that the ionisation of an indicator acid, considered as a monobasic acid, constitutes a measure of the degree of change undergone in the colour. Hence if the extent of neutralisation is known and the resulting colour observed, it is possible to calculate from a knowledge of the apparent dissociation constant of the indicator the hydrogen-ion concentration which produces any particular shade of colour. Thus, we have seen that

$$p\mathrm{H} = p\mathrm{K} + \log \frac{[\mathrm{In}']}{[\mathrm{HIn}]}$$

and if x be the percentage of neutralisation of HIn, then

$$p\mathrm{H} = p\mathrm{K} + \log \frac{x}{100 - x}.$$

The second type involves the matching of the colour, obtained when a definite quantity of indicator is added to a definite volume of liquid undergoing test, with that of one of a series of standard buffer solutions differing by about 0·2 *p*H unit (being of the same volume), and each containing the same amount of indicator solution. These colours must be matched by viewing through the same thickness or depth of solution. Of the two kinds of methods it is probable that the results obtained by the latter will be the more accurate. The difficulties attendant on colorimetric methods are such that the limit of accuracy attainable probably does not extend much beyond 0·05 *p*H unit, unless special precautions are taken in regard to the ionic strengths of the solutions used and possible errors introduced by the indicator itself (see page 371).

In all these methods the validity of Beer's law is assumed; namely, that when light is transmitted through two solutions, of different depth or thickness and having different concentrations of the solute which produces the particular colour and causes the two solutions to appear identical, then provided the conditions of illumination are the same, the product of the concentration of

one solution and the distance through which the light passed, is equal to the product of the concentration of the other solution and the distance travelled through it by the light. Hence if c_1 and d_1 be the respective concentration and depth of one solution, and c_2 and d_2 of another, then

$$c_1 \times d_1 = c_2 \times d_2.$$

In colorimetric work, it is usual to keep the distances through which the light passes in the various solutions the same, *i.e.*, $d_1 = d_2$, and therefore it is essential that the indicator concentrations of liquids in the comparison tubes shall be the same. In the case of two coloured indicators a difficulty arises on account of the possible differences in the transmission coefficients of the various light radiations which pass through a solution. For this reason, it is a matter of some importance to employ suitable illumination. Clark points out that all the sulphone-phthalein indicators may be used in electric light. Bromothymol blue and thymol blue require light which is strong in blue radiations. It is in this regard that the absorption spectra of indicator solutions may be of assistance, of which descriptions for certain indicators will be found in Prideaux' useful book, "The Theory and Use of Indicators," London, 1917.

Colorimetric Methods without Standard Buffer Solutions.

These methods are based on the assumption that the colour changes of the various indicators employed are quantitatively proportional to the amounts of the neutralisation undergone by the indicator if considered as a monobasic acid. Consequently, if the apparent dissociation constant of the indicator be known and some satisfactory means can be devised to compare quantitatively the colour intensities, then the *p*H of a solution giving any particular colour can be readily calculated. Thus we have seen that when x is the actual amount of neutralisation,

$$\begin{aligned} p\mathrm{H} &= p\mathrm{K}_{\mathrm{HIn}} + \log \frac{x}{1 - x} \\ &= p\mathrm{K}_{\mathrm{HIn}} + \log \frac{\text{colour of alkaline form}}{\text{colour of acid form}}. \end{aligned}$$

In the case of one-colour indicators, colourless when in the acid form and coloured in the alkaline form, the extent to which the indicator has been reacted upon will be given by the depth of colour. Thus, if a definite amount of such an indicator in a solution produced a depth, or intensity of colour, equal to a fraction, ϕ, of that which would have been produced had that

concentration of indicator been converted entirely into the alkaline form, then

$$pH = pK_{HIn} + \log \frac{\phi}{1 - \phi}.$$

Methods based on these principles are the following :—

(1) *Wedge methods of Bjerrum and McCrae.*
(2) *Colorimeter method of Gillespie.*
(3) *"Drop Ratio" Comparator method of Gillespie, and*
(4) *Colour Intensity method of Michaelis.*

These individual methods will now be discussed.

Wedge Methods.

This method appears to have first been adopted by Bjerrum ("Die Theorie der alkalimetrischen und azidimetrischen Titrierungen," Stuttgart, 1914, also in Ahren's *Sammlung*, Vol. 21) for the determination of indicator constants of two-colour indicators. He used a rectangular box having glass sides. It was about 30 cm. in length, 10 cm. high and 2 cm. thick, and was divided into two wedge-shaped compartments by a piece of glass inserted diagonally. One compartment was filled with a solution containing the indicator completely transformed into the acid form, and the other with the same amount of indicator completely converted into the alkaline form. A narrow cell, 2 cm. wide, having narrow glass apertures in the two opposite ends was moved along on the top of this vessel. In it was placed a buffer solution of known *p*H and having the same concentration of indicator as that of the solutions used in the lower vessels. The cell was moved until a position was found such that the colour of the solution in the upper cell was the same as that produced by light passing through the two sections of the wedges immediately below. This was made possible by a slit arrangement attached to the small test-cell. Then, by measuring the width of the two solutions respectively coloured by the acid- and alkaline-forms of the indicator, it was known what proportion of the indicator in the test-cell had been converted into the alkaline form. It was possible, moreover, to adjust the *p*H of the test solution until the indicator colour agreed with that shown when light passed through equal widths of the two liquids in wedges, and so obtain the value of pK_{HIn}. It is, of course, possible to calculate pK_{HIn} from the *p*H of buffer solutions, placed in the movable cell which give colour-matches with those produced at other positions of the double wedge cell other than that at the mid-point. Once the pK_{HIn} of the indicator is known, the test solution is placed in the movable cell, the correct amount of

indicator added, and the position on the double wedge cell is found which gives a complete matching of colour.

The principle of this method will be understood from Fig. 76, which is a plan of a two-wedge cell arrangement. On looking through a section of liquid in the wedge cells, the observed colour will be composed of the light transmitted through a portion of solution tinted by the alkaline form of the indicator and a portion coloured by the acid form of the indicator. Thus, in the figure the colour in the test-cell is represented as matching the colour produced by the thickness of liquid, 60 per cent. of which corresponds to the acid form of the indicator and 40 per cent. to the alkaline form. Hence the colour produced by the same concen-

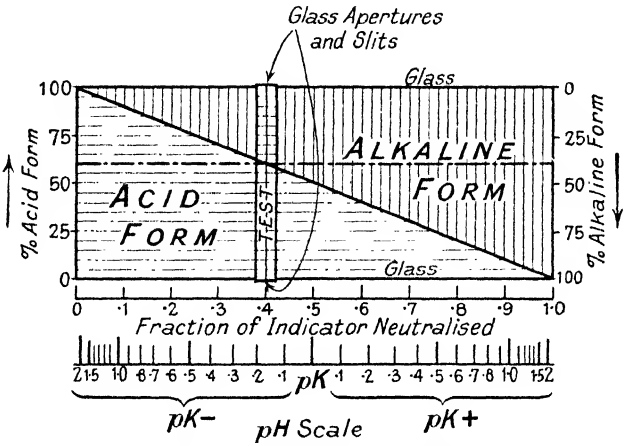


FIG. 76.—Principle of Colorimetric Determination of *p*H Values.

tration of indicator in the unknown solution shows that the indicator has suffered 40 per cent. neutralisation and therefore, if pK_{HIn} be known, the *p*H can be readily calculated as described on page 337. Scales may be affixed to such a colorimeter showing (*a*) the fraction of neutralisation of the indicator represented by each different shade of colour when viewed through the slits on the opposite sides of the apparatus, and (*b*) the *p*H value referring to the various colours in terms of pK_{HIn}. Such scales are shown in Fig. 76. The *p*H scale shows clearly that determinations are more likely to be accurate round about half-neutralisation, for a difference of 0·1 *p*H unit corresponds to a much greater variation in neutralisation than when $pH = pK_{HIn} \pm 1{\cdot}0$. Whenever possible, indicators should be chosen in order that the *p*H of the solution under test should lie within $pK_{HIn} \mp 0{\cdot}7$. In

Table 93 are given the actual amounts of neutralisation corresponding to changes of 0·1 *p*H unit of those indicators which can be treated as weak monobasic acids. The values are indicated for half-neutralisation, *i.e.*, when $pH = pK_{HIn}$ of certain indicators which may be employed in this method (*cf.* Table 93).

A modified form of this apparatus has been introduced by McCrae (*The Analyst*, 1926, **51**, 287). It is shown in Fig. 77. The two triangular glass cells which are placed together to form a divided rectangular cell are covered with metal provided with lateral slots. The triangular cells have an internal dimension of 15 cm. along the long side forming the right angle, and 3·5 cm.

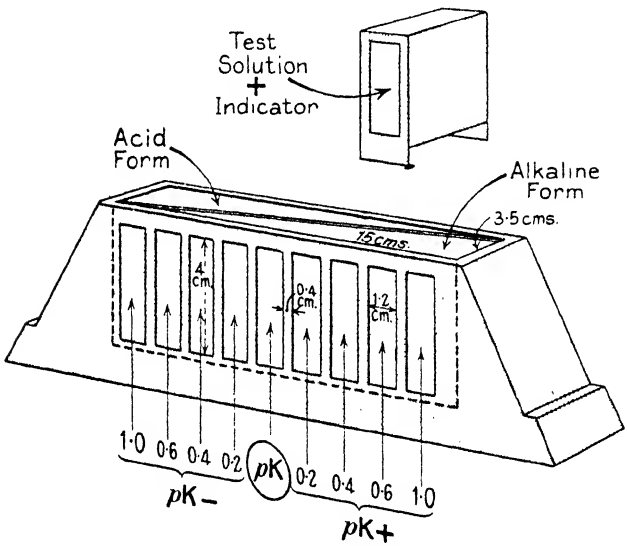


FIG. 77.—McCrae's Modification of the Wedge Colorimeter.

along the other side, the hypotenuse thus being about 15·4 cm. The depth of the cell is 4·7 cm. and the capacity at 125 c.c. A sliding holder, carrying a rectangular glass cell, internal dimensions 3·5 cm. × 1·4 cm. × 4·7 cm., moves along the top of the combined cells. The capacity is about 2·4 c.c. There are nine slots, 4 cm. high and 1·2 cm. wide which are separated from one another by 0·4 cm. Looking through the middle slot a colour is seen which is that of the half-way change of the indicator, and therefore $pH = pK_{HIn}$. The colours seen through the slots on each side refer to *p*H values which increase or decrease by amounts of 0·2 *p*H unit, with the exception of the two end slots which correspond to differences of 0·4 *p*H. The reason for this will be appar-

ent from the scales on Fig. 76 or from Table 93. To ascertain the *p*H value of a solution using McCrae's apparatus, about 300 c.c. of the solution are treated with sufficient of the appropriate indicator to impart a good strong colour, and are then poured into each of the two triangular cells and also into the small rectangular cell. The full acid colour is developed in one of the triangular cells by the addition of a few drops of hydrochloric acid, and the full alkaline colour in the other by means of a little sodium hydroxide. Uniformity of these colours is ensured by stirring, after which the cover is placed over the triangular cells and the metal carrier with the small rectangular cell placed on top. This is moved along until the tint of the solution, as viewed against a white background, matches the colour through a slot immediately below. If the solution available is insufficient for the above procedure, then distilled water may be substituted in the cells and coloured with the amount of indicator to give the same concentrations in the solution undergoing examination and in the solutions in the lower vessels. Thus if 250 c.c. of water used in the triangular cells required 1 c.c. of indicator solution, and 25 c.c. of unknown solution were available then this volume would require $\frac{1}{10}$ c.c. of indicator solution.

Gillespie's Colorimetric Methods.

(1) Colorimeter Method.

The colorimeter devised by Gillespie (*J. Bact.*, 1921, **6**, 399) is shown in Fig. 78. The tubes A and B are fixed such that their bottoms are on a level with one another. The outer vessels, which are identical, are also fixed at the same level and are equally illuminated from the bottom. The inner vessel in vessel I is movable upwards and downwards, and has a pointer which travels along a scale showing the percentage amount of indicator neutralised to give a particular colour. If the solution to be tested is both clear and colourless no solutions are placed in A and B. The test solution, with a suitable quantity of a suitable indicator, is placed in vessel II, such that the end of tube B is immersed. Water, having the same indicator concentration, is poured into the two compartments of vessel I, and that in the inner vessel rendered sufficiently acidic to generate the full acid colour, whilst that in the outer vessel is treated with alkali to produce the full alkaline colour. By observing the two colours produced in I and II from above, the vessels being suitably enclosed, it is possible to find a position of the movable cell at which the resulting colours will appear the same. Then by measuring the lengths

of the columns of the acid and alkaline liquids, the amount of neutralisation undergone by the indicator in the test-cell II is known, whence the *p*H can be calculated. In the diagram, the pointer represents 60 per cent. of indicator in the acid form and 40 per cent. in alkaline form.

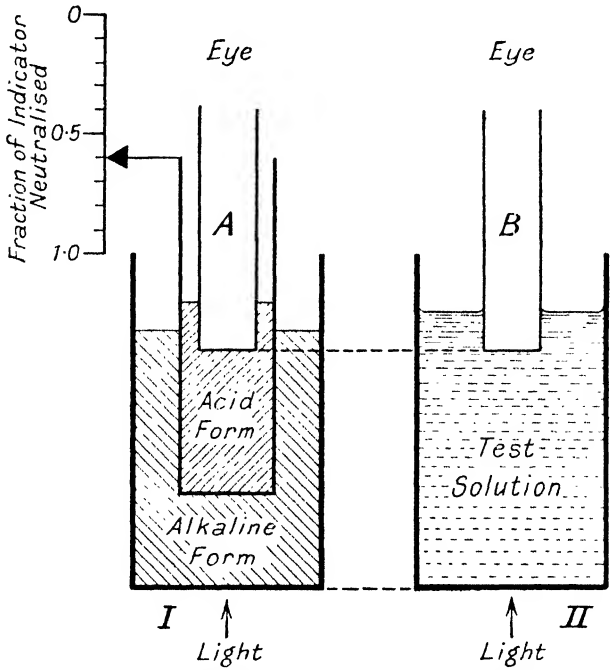


FIG. 78.—Diagram of Gillespie's Colorimeter.

Should the solutions be either turbid or coloured, then the tube A is filled with the test solution without the indicator to a height equal to that between the bottom of the tube and the base of the apparatus, whereas the same quantity of distilled water is inserted in B. The determination is then carried out as above described. In this way, compensation for colour or turbidity is obtained.

(2) "**Drop-Ratio**" **Method.**

This method which Gillespie (*J. Amer. Chem. Soc.*, 1920, **42**, 742) proposed is especially useful for rapid approximate determinations. The colours corresponding to different *p*H stages in the colour change of an indicator are obtained by having a series of

two identical glass test-tubes, one placed immediately behind the other and containing the same volume of water. They may be conveniently inserted in a test-tube rack. To each pair of tubes 10 drops of an indicator solution of suitable concentration are added, so that if one tube receives one drop then the other must receive nine drops. The acid colour is developed in one tube by the addition of a suitable acid or acid salt, and the alkaline form in the other. The colour observed when viewed directly through the two tubes will be the result of so much in the alkaline form and so much in the acid form. Hence, a solution matching such a colour, provided that 10 drops of indicator solution had been added to it, would have a *p*H value given by

$$pH = pK_{HIn} + \log \frac{\text{drops of alkaline form}}{\text{drops of acid form}}.$$

Gillespie calls the ratio in the last term, the "drop ratio" and therefore $pH = pK_{HIn} + \log$ "drop ratio."

The "drop ratios" which correspond to the different amounts of neutralisation are given in Table 93. This method of measuring the volume of a solution is far from satisfactory for accurate

TABLE 93

RELATIONSHIP BETWEEN NEUTRALISATION OF AN INDICATOR, GILLESPIE'S "DROP RATIO" AND *p*H

Per cent. neutralised	9·1	11·2	13·7	16·6	20·0
*p*H = *p*K −	1·0	0·9	0·8	0·7	0·6
"Drop Ratio"	1/9	—	1½ / 8½	—	2/8
Per cent. neutralised	24·0	28·5	33·4	38·7	44·3
*p*H = *p*K −	0·5	0·4	0·3	0·2	0·1
"Drop Ratio"	—	3/7	—	4/6	—
Half neutralised	50	Bromo-phenol blue.	Methyl red.	Bromo-cresol purple.	Bromo-thymol blue.	Phenol red.	Cresol red.	Thymol blue.
*p*H =	*p*K$_{HIn}$ =	4·1	5·0	6·3	7·1	7·7	8·1	8·8
"Drop Ratio"	5/5	—	—	—	—	—	—	—
Per cent. neutralised	55·8	61·3	66·7	71·6	76·0
*p*H = *p*K +	0·1	0·2	0·3	0·4	0·5
"Drop Ratio"	—	6/4	—	7/3	—
Per cent. neutralised	80·0	83·4	86·3	88·8	90·9
*p*H = *p*K +	0·6	0·7	0·8	0·9	1·0
"Drop Ratio"	8/2	—	8½ / 1½	—	9/1

comparisons. The table shows the different drop ratios for the variations of 0·2 pH from that of $p\mathrm{K_{HIn}}$. Moreover, the rough nature of the method was allowed for by Gillespie, for when an acid indicator is neutralised to the extent of 13·7 per cent., the ratio $\frac{\text{alkaline form}}{\text{acid form}} = \frac{13{\cdot}7}{86{\cdot}3}$, whereas the nearest drop ratio is $\frac{1\frac{1}{2}}{8\frac{1}{2}}$. Similarly the drop ratio for 28·5 per cent. is $\frac{3}{7}$, and for 38·7 per cent. $\frac{4}{6}$. It would also be more satisfactory to employ a microburette to measure out the indicator as was done by Hastings, Sendroy and Robson (*vide infra*), and in comparing the colour of the unknown solution to view it through a tube of the same diameter filled with water, so that any error introduced by the different thicknesses of liquid may be eliminated. Rectangular glass cells of equal size, instead of the test-tubes, would probably facilitate colour matching in that each pair of cells could be placed close together. The tubes used by Gillespie were 15 cm. long and 1·5 cm. in diameter, and the solutions were about 5 to 6 c.c. in volume.

Gillespie found that the following indicators could be employed: bromophenol blue, methyl red, bromocresol purple, bromothymol blue, phenol red, cresol red and thymol blue. His values of $p\mathrm{K_{HIn}}$ are given in Table 93. With the exception of the solutions of bromocresol purple and phenol red, whose concentrations should be 0·012 per cent. and 0·004 per cent. respectively, Gillespie recommends that the concentration of the indicator solution should be 0·008 per cent. The acid colour should be developed by adding 1 c.c. of N/20 solution of HCl to 10 c.c. of solution when using bromophenol blue, and 1 drop only when using either methyl red, bromocresol purple, bromothymol blue or phenol red, but in the case of cresol red and thymol blue 1 drop of a 2 per cent. solution of KH_2PO_4 should be added in order to prevent the appearance of the further colours arising from the acid ranges of these two indicators. Hatfield (*J. Amer. Chem. Soc.*, 1923, **45**, 930) advocates, on the grounds of the enhanced stability of indicator colours, extending over a period of from 1 to 2 months, the use of weak acids or bases for the development of the acid or alkaline colours. Thus he adds a N-acetic acid solution with bromophenol blue and methyl red, and a 7-gram per litre KH_2PO_4 solution with bromo cresol purple, bromothymol blue, phenol red, cresol red and thymol blue to the solutions to produce the respective acid colours. The alkaline colours of bromophenol blue, methyl red, bromocresol purple and bromothymol blue are obtained in a solution containing 18 grams $Na_2HPO_4,12H_2O$ per litre, and those of bromocresol

purple, bromothymol blue, phenol red, cresol red and thymol blue with a 1-gram per litre Na_2CO_3 solution.

If it is desired to make *p*H measurements by either of the two methods of Gillespie with a one-coloured indicator, say colourless in the acid condition, then the vessels, in which the indicator is put and transformed to give the acid colour, may either be eliminated altogether or merely filled with distilled water. The latter procedure applies more particularly to the colorimeter method, for it is scarcely necessary in the tube method.

Gillespie's "drop-ratio" method has been elaborated by Hastings, Sendroy and Robson (*J. Biol. Chem.*, 1925, **65**, 381). Instead of measuring the indicator solution as drops, it is carefully measured out with a microburette. The method will be obvious from the data given in Tables 93 (*a*) to 93 (*d*). It will be seen that exactly 2·5 c.c. of indicator-solution are divided between each pair of alkali and acid tubes in varying amounts and the solution in each tube is made up to 25 c.c. with the respective alkali and acid solutions. For the determination of *p*H

TABLE 93 (*a*)

BI-COLOUR STANDARDS PREPARED FROM 0·016 PER CENT. BROMOCRESOL GREEN, 0·002 N-HCl AND 0·001 N-NaOH

$pK_{Indicator} = 4{\cdot}72$ *at* 20° *and* 38°

*p*H at 20° and 38°.	Alkali Tube.		Acid Tube.	
	Indicator. c.c.	NaOH. c.c.	Indicator. c.c.	HCl. c.c.
4·00	0·40	24·60	2·10	22·90
4·10	0·49	24·51	2·01	22·99
4·20	0·58	24·42	1·92	23·08
4·30	0·69	24·31	1·81	23·19
4·40	0·81	24·19	1·69	23·31
4·50	0·94	24·06	1·56	23·44
4·60	1·08	23·92	1·42	23·58
4·70	1·23	23·77	1·27	23·73
4·80	1·38	23·62	1·12	23·88
4·90	1·51	23·49	0·99	24·01
5·00	1·64	23·36	0·86	24·14
5·10	1·77	23·23	0·73	24·27
5·20	1·88	23·12	0·62	24·38
5·30	1·98	23·02	0·52	24·48
5·40	2·07	22·93	0·43	24·57
5·50	2·14	22·86	0·36	24·64
5·60	2·21	22·79	0·29	24·71
5·70	2·26	22·74	0·24	24·76
5·80	2·31	22·69	0·19	24·81

TABLE 93 (*b*)

BI-COLOUR STANDARDS PREPARED FROM 0·01 PER CENT. CHLOROPHENOL RED, 0·01 N-HCl AND 0·01 N-NaOH

$pK_{Indicator} = 6{\cdot}02$ *at* 20°; 5·93 *at* 38°

*p*H.		Alkali Tube.		Acid Tube.	
20°	38°	Indicator. c.c.	NaOH. c.c.	Indicator. c.c.	HCl. c.c.
5·09	5·00	0·26	24·74	2·24	22·76
5·19	5·10	0·32	24·68	2·18	22·82
5·29	5·20	0·39	24·61	2·11	22·89
5·39	5·30	0·48	24·52	2·02	22·98
5·49	5·40	0·57	24·43	1·93	23·07
5·59	5·50	0·68	24·32	1·82	23·18
5·69	5·60	0·80	24·20	1·70	23·30
5·79	5·70	0·93	24·07	1·57	23·43
5·89	5·80	1·07	23·93	1·43	23·57
5·99	5·90	1·20	23·80	1·30	23·70
6·09	6·00	1·35	23·65	1·15	23·85
6·19	6·10	1·50	23·50	1·00	24·00
6·29	6·20	1·63	23·37	0·87	24·13
6·39	6·30	1·75	23·25	0·75	24·25

TABLE 93 (*c*)

BI-COLOUR STANDARDS PREPARED FROM 0·008 PER CENT. BROMOCRESOL PURPLE, 0·002 N-HCl AND 0·01 N-NaOH

$pK_{Indicator} = 6{\cdot}19$ *at* 20°; 6·09 *at* 38°

*p*H.		Alkali Tube.		Acid Tube.	
20°	38°	Indicator. c.c.	NaOH. c.c.	Indicator. c.c.	HCl. c.c.
5·70	5·60	0·61	24·39	1·89	23·11
5·80	5·70	0·72	24·28	1·78	23·22
5·90	5·80	0·85	24·15	1·65	23·35
6·00	5·90	0·99	24·01	1·51	23·49
6·1	6·00	1·12	23·88	1·38	23·62
6·2	6·10	1·26	23·74	1·24	23·76
6·3	6·20	1·40	23·60	1·10	23·90
6·4	6·30	1·55	23·45	0·95	24·05
6·5	6·40	1·68	23·32	0·82	24·18
6·6	6·50	1·80	23·20	0·70	24·30
6·7	6·60	1·91	23·09	0·59	24·41
6·8	6·70	2·01	22·99	0·49	24·51
6·9	6·80	2·09	22·91	0·41	24·59
7·00	6·90	2·16	22·84	0·34	24·66

TABLE 93 (*d*)

BI-COLOUR STANDARDS PREPARED FROM 0·0075 PER CENT. PHENOL RED, 0·001 N-HCl, AND 0·01 N-NaOH

$pK_{Indicator} = 7{\cdot}78$ *at* 20°; 7·65 *at* 38°

*p*H.		Alkali Tube.		Acid Tube.	
20°	38°	Indicator. c.c.	NaOH. c.c.	Indicator. c.c.	HCl. c.c.
6·83	6·70	0·25	24·75	2·25	22·75
6·93	6·80	0·31	24·69	2·19	22·81
7·03	6·90	0·38	24·62	2·12	22·88
7·13	7·00	0·46	24·54	2·04	22·96
7·23	7·10	0·55	24·45	1·95	23·05
7·33	7·20	0·65	24·35	1·85	23·15
7·43	7·30	0·77	24·23	1·73	23·27
7·53	7·40	0·90	24·10	1·60	23·40
7·63	7·50	1·04	23·96	1·46	23·54
7·73	7·60	1·18	23·82	1·32	23·68
7·83	7·70	1·32	23·68	1·18	23·82
7·93	7·80	1·46	23·54	1·04	23·96
8·03	7·90	1·60	23·40	0·90	24·10
8·13	8·00	1·73	23·27	0·77	24·23
8·23	8·10	1·85	23·15	0·65	24·35
8·33	8·20	1·95	23·05	0·55	24·45

2·5 c.c. of indicator are inserted in a tube and then made up to 25 c.c. with the solution to be tested. The colour obtained is matched with one of the colours seen through pairs of alkali and acid tubes. The *p*H corresponding to the colour produced by the indicator-solutions in any pair of alkali and acid tubes may be calculated from the " drop-ratio " expression, or else may be read off from the tables.

The indicator solutions may be prepared by grinding 0·1 gram of indicator with alkali solution (5·7 c.c. of 0·05 N-NaOH for phenol red; 4·1 c.c. for bromocresol purple; 5·2 c.c. for chlorophenol red and 3·2 c.c. for bromocresol green) in an agate mortar, and then making up to the desired concentration with water.

Michaelis' Method with One-Coloured Indicators.

Many one-coloured indicators behave as if they were weak monobasic acids the anions alone of which are coloured. Owing to their weakness, the ionisation of the free indicator acids is so slight that the indicators are colourless in acid solutions. On reaction with an alkali a strongly ionised salt, NaIn, is formed which leads to the production of colour. Michaelis and Gyemant (*Biochem. Zeitsch.*, 1920, **109**, 165) have shown that the intensity of this

colour, compared with that obtained when the indicator is fully transformed into the indicator salt, NaIn, *i.e.*, in alkaline solutions, constitutes a measure of the degree of neutralisation, so that if the $p\mathrm{K}_{\mathrm{HIn}}$ be known, the $p\mathrm{H}$ value can easily be calculated. Instead, however, of making comparisons of different intensities of colour, they adopt a somewhat indirect method by which the same relations are obtained. Thus they add to a measured amount of the solution (5 to 10 c.c.), whose $p\mathrm{H}$ value is to be found, sufficient indicator solution, the volume of which is accurately measured (0·2 c.c. to 1·0 c.c.), to impart to the solution a pale but definite coloration. This colour is now reproduced by adding to an excess of N/100-NaOH solution just that quantity of indicator to give the colour when made up to the volume of the test solution. It is necessary that the volume of indicator should be accurately known, and it should therefore be measured out from a burette, reading to 0·01 c.c. The accuracy can be somewhat increased by using for the latter purpose an indicator solution, diluted 10 or 20 times. Thus, if T c.c. of indicator solution were used in the test solution and A c.c. of indicator solution of the same concentration were required to match the colour of the alkali solution with that produced in the test solution, then of the T c.c. an amount equivalent to A c.c. must have been in the alkaline or anion form, and therefore the amount of neutralisation, x, undergone by the indicator in the test solution was $\frac{\mathrm{A}}{\mathrm{T}}$. Hence

$$p\mathrm{H} = p\mathrm{K}_{\mathrm{HIn}} + \log \frac{x}{1 - x}.$$

This equation was found to hold quantitatively for the α-, β- and γ-dinitrophenols and *para*- and *meta*-nitrophenols. Michaelis and Gyemant's values of $p\mathrm{K}_{\mathrm{HIn}}$ for temperatures ranging from 5° to 50° C. are given in Table 94.

TABLE 94

$p\mathrm{K}_{\mathrm{HIn}}$ OF MICHAELIS' INDICATORS

Temperature.	α-Dinitro Phenol.	β-Dinitro Phenol.	γ-Dinitro Phenol.	*p*-Nitro Phenol.	*m*-Nitro Phenol.
5° C. . .	4·13	3·76	5·21	7·33	8·43
10° C. . .	4·11	3·74	5·18	7·27	8·39
15° C. . .	4·08	3·71	5·15	7·22	8·35
20° C. . .	4·05	3·68	5·14	7·16	8·31
30° C. . .	3·99	3·62	5·09	7·04	8·22
40° C. . .	3·93	3·56	5·04	6·93	8·15
50° C. . .	3·88	3·51	4·99	6·81	8·07

In order to make *p*H measurements over almost the complete *p*H range, Michaelis and Gyemant studied the colour changes of phenolphthalein and alizarine yellow, GG (salicyl yellow; *m*-nitrobenzeneazosalicylic acid). They found, although the varying colour intensities were not strictly parallel with their extents of neutralisation as monobasic acids on account of their polyacidic nature and the closeness of their dissociation constants, that it was possible to calibrate the degrees of dissociation, x, found as with the nitrophenols, against *p*H values. Their data are recorded in Tables 95 and 96.

TABLE 95

CALIBRATION OF PHENOLPHTHALEIN. TEMPERATURE 18° C.
TEMPERATURE CORRECTION 0·011 + ($t°$ − 18)

x.	*p*H.	x.	*p*H.	x.	*p*H.
0·01	8·45	0·16	9·1	0·55	9·8
0·014	8·5	0·21	9·2	0·60	9·9
0·030	8·6	0·27	9·3	0·65	10·0
0·047	8·7	0·34	9·4	0·70	10·1
0·069	8·8	0·40	9·5	0·75	10·2
0·090	8·9	0·45	9·6	0·80	10·3
0·120	9·0	0·50	9·7	0·845	10·4
—	—	—	—	0·873	10·5

TABLE 96

CALIBRATION OF SALICYL YELLOW

Temp. 20° C.

x.	*p*H.	x.	*p*H.	x	*p*H.
0·13	10·0	0·36	10·8	0·75	11·6
0·16	10·2	0·46	11·0	0·83	11·8
0·22	10·4	0·56	11·2	0·88	12·0
0·29	10·6	0·66	11·4	—	—

The following table, Table 97, gives the ranges for which the Michaelis' indicators are applicable, and the suitable concentrations of the indicator solutions :—

TABLE 97

PARTICULARS OF THE MICHAELIS' INDICATORS

Indicator.	*p*H Range.	Solution.
2 : 4 Dinitrophenol (α) . .	2·0–4·7	Saturated aqueous.
2 : 6 Dinitrophenol (β) . .	1·7–4·4	0·05% ,,
2 : 5 Dinitrophenol (γ) . .	4·0–6·0	Saturated ,,
p-Nitrophenol	4·7–7·9	0·1% ,,
m-Nitrophenol	6·3–9·0	0·3% ,,
Phenolphthalein	8·5–10·5	0·04%, 70% water, 30% alcohol.
Salicyl yellow	10·0–12·0	Diluted saturated alcoholic.

The *p*H ranges given in Table 97 appear to be somewhat too wide for accurate work, and Kolthoff ("Indicators," p. 161) has found that the useful ranges of the indicators are less extensive. Thus, he suggests that with the α-, β-, and γ-dinitrophenols *p*H measurements should be made within the respective ranges : *p*H 2·6–4·4, 2·4–4·0, and 4·0–5·8 ; with *p*-nitrophenol from *p*H 5·6–7·6 ; with *m*-nitrophenol, *p*H 6·6–8·6 ; with phenolphthalein from *p*H 8·2 to *p*H 10·0 ; and with salicyl yellow the same range as that advocated by Michaelis. Kolthoff prepares the indicator solutions of slightly different concentrations. They are the following : α-dinitrophenol, 0·1 per cent. dilute alcoholic solution ; β-dinitrophenol, 0·1 per cent. dilute alcoholic solution ; γ-dinitrophenol, 0·1 per cent. dilute alcoholic solution ; *p*-nitrophenol, 0·3 per cent. aqueous solution ; *m*-nitrophenol, 0·3 per cent. aqueous solution ; phenolphthalein, 0·1 per cent. in 50 per cent. alcohol ; salicyl yellow, 0·1 per cent. alcoholic solution for the range *p*H 10 to 11, and 0·025 per cent. in 25 per cent. alcohol for the determination of *p*H values from 11 to 12.

This method can be made more rapid when a large number of *p*H determinations are to be made. Michaelis and Gyemant point out that it is an easy matter to prepare a series of solutions containing increasing amounts of the various indicators in the coloured or so-called alkaline forms, such that the intensity of colour in one tube corresponds to a known *p*H under certain definite conditions of working, whilst that of the solution in the next tube to a *p*H value which is 0·2 *p*H higher, and so on. The concentrations of a series of these standard coloured solutions can easily be calculated for those indicators which behave as a monobasic acid. The solutions given in Table 98 used by Michaelis and Gyemant constitute suitable standards. To 6 c.c. of solution under test 1 c.c. of the indicator solution is added and the colour

TABLE 98

MICHAELIS AND GYEMANT'S INDICATOR STANDARDS

α-Dinitrophenol

Diluted Indicator, c.c. .	0·51	0·78	1·20	1·74	2·5
*p*H	2·8	3·0	3·2	3·4	3·6
Diluted Indicator, c.c. .	3·4	4·6	5·7	6·7	—
*p*H	3·8	4·0	4·2	4·4	—

γ-Dinitrophenol

Diluted Indicator, c.c. .	0·74	1·1	1·65	2·4	3·4
*p*H	4·0	4·2	4·4	4·6	4·8
Diluted Indicator, c.c. .	4·5	5·5	6·6	—	—
*p*H	5·0	5·2	5·4	—	—

p-Nitrophenol

Diluted Indicator, c.c. .	0·16	0·25	0·4	0·63	0·94
*p*H	5·4	5·6	5·8	6·0	6·2
Diluted Indicator, c.c. .	1·4	2·0	3·0	4·05	—
*p*H	6·4	6·6	6·8	7·0	—

m-Nitrophenol

Diluted Indicator, c.c. .	0·27	0·43	0·66	1·0	1·5
*p*H	6·8	7·0	7·2	7·4	7·6
Diluted Indicator, c.c. .	2·3	3·0	4·2	5·2	—
*p*H	7·8	8·0	8·2	8·4	—

produced matched with that of one of the standards. These may be prepared by running the calculated volumes of the various indicator solutions which have been diluted ten times into the test-tubes of standard size, and then making up the volume in each tube to 7 c.c. (the final volume employed of the test solution) with centinormal sodium hydroxide solution. The tubes are sealed with corks, carefully coated with paraffin wax to prevent the passage of cork-acids into the solutions, and when not in use should be stored in the dark.

These solutions are stated to retain their correct depths of colour for some months, but certain investigators have found that the colours in the more alkaline solutions undergo change. The

best results are to be obtained by using freshly prepared standards of comparison. To overcome this difficulty Kolthoff ("Indicators," p. 164) has prepared a series of solutions, having comparable colours, from potassium chromate and potassium bichromate the colours of which are permanent for upwards of a year. His solutions are prepared from 0·1 per cent. solutions of either K_2CrO_4 or $K_2Cr_2O_7$ and diluting to 10 c.c. The *p*H data corresponding to the various shades of colour are based on experiment. The data are given in Table 99 and were taken from Kolthoff's book. (See also *Pharm. Week.*, 1923, **60.**)

TABLE 99

KOLTHOFF'S CHROMATE IMITATION COLOUR STANDARDS FOR THE MICHAELIS INDICATORS. TEMP. 15° C.

C.c. 0·1 % K_2CrO_4 in 10 c.c. . . .	0·3	0·45	0·7	1·1	1·5	1·8	2·3	3·1	3·7	4·0
Colour similar to that produced at *p*H by:										
(*a*) 0·2 c.c., 0·1 % *α-Dinitrophenol* per 10 c.c.	3·0	3·2	3·4	3·6	3·8	4·0	4·2	4·4	4·6	—
(*b*) 0·2 c.c., 0·3 % *p-Nitrophenol* per 10 c.c.	(5·6)	5·7	5·8	5·9	6·1	6·2	6·5	6·8	7·1	7·2
(*c*) 0·1 c.c. ditto .	—	—	—	—	—	7·1	7·4	7·6	—	—

C.c. 0·1 % $K_2Cr_2O_7$ in 10 c.c. . .	0·23	0·35	0·55	0·72	1·1	1·55	1·8	2·2	3·0
Colour similar to that produced at *p*H by:									
(*a*) 0·2 c.c., 0·1 % *γ-Dinitrophenol* per 10 c.c.	4·0	4·1	4·3	4·5	4·7	4·9	5·1	5·3	5·5
(*b*) 0·4 c.c., 0·3 % *m-Nitrophenol* per 10 c.c. . . .	7·0	7·2	7·5	7·7	7·9	8·1	8·3	8·5	—
(*c*) 0·2 c.c., 0·05 % *Salicyl yellow* per 10 c.c. . . .	—	—	—	(9·8)	10·2	10·5	10·6	10·8	11·3
(*d*) 0·2 c.c., 0·025 % *Salicyl yellow* per 10 c.c. . . .	—	—	10·2	10·4	10·8	—	—	—	—

Michaelis, Gyemant and Krüger (*Biochem. Zeitsch.*, 1920, **109**, 165; 1921, **119**, 307) have investigated the errors which may be introduced into the determination of hydrogen-ion concentrations through the presence of neutral salts. For neutral

salt concentrations up to 0·5 N, the error involved in the use of *p*-nitrophenol is negligible, but for the other indicators the *p*H values are approximately 0·1 *p*H unit too high when the concentration is 0·15 N; and for 0·5 N salt concentration with either α-dinitrophenol, *m*-nitrophenol or phenolphthalein, the *p*H values are 0·2 *p*H too high, with β-dinitrophenol, 0·3 *p*H too high, and with γ-dinitrophenol the *p*H values are about 0·1 *p*H unit too high.

Alcohol has a very marked effect on the dissociation of electrolytes and especially of indicators. Michaelis and Mizutani (*Biochem. Zeitsch.*, 1924, **147**, 7) have determined the variations in the dissociation constants of the Michaelis indicators caused by the varying alcohol contents of solutions. It is, of course, not possible to attach any real meaning to *p*H values of aqueous alcoholic solutions, but their determination may occasionally furnish a convenient method of control. As it was not possible to obtain alcohol-water solutions of known hydrogen-ion concentration, they standardised their hydrogen electrode measurements of these solutions against those given by the electrode in aqueous solutions of known *p*H values. The variations in pK_{HIn} of the nitrophenol indicators are given in Table 100.

Table 100 shows that the increasing alcohol contents depressed the ionisation of the indicators. The *p*H values of alcoholic solutions may be determined with the aid of the indicators given in Table 100 and the appropriate pK_{HIn} values by the Michaelis method, with the modification that the colour is developed in the comparison solutions, which must have the same alcohol content as the solution under examination, by means of N/100-NaOH

TABLE 100

VALUES OF pK_{HIn} OF THE MICHAELIS INDICATORS IN AQUEOUS ALCOHOLIC SOLUTIONS

	pK_{HIn} at Alcohol Contents (Per Cent. Volume).									
	0%.	10%.	20%.	30%.	40%.	50%.	60%.	70%.	80%.	90%.
m-Nitrophenol	8·37	8·56	8·75	8·97	9·15	9·40	9·64	9·92	10·24	10·73
p-Nitrophenol .	7·15	7·17	7·28	7·38	7·63	7·85	8·11	8·34	8·59	8·90
γ-Dinitrophenol	5·15	5·20	5·23	5·39	5·45	5·58	5·70	5·95	6·08	9·4
α-Dinitrophenol	4·00	4·00	4·00	4·00	4·00	4·15	—	—	—	—

for alcohol contents up to 70 per cent., and by N/10-NaOH for contents from 70 per cent. to 100 per cent. The method may

also be used for work with phenolphthalein, using the data of Michaelis and Mizutani given in Table 101.

TABLE 101

RELATION BETWEEN *p*H AND THE DEGREE OF NEUTRALISATION, *x*, OF PHENOLPHTHALEIN IN ALCOHOLIC SOLUTIONS

	*p*H Values for Alcohol Contents (Percentage by Volume).										
	0%.	10%.	20%.	30%.	40%.	50%.	60%.	70%.	80%.	90%.	95%.
0·01	8·5	8·7	8·9	9·2	9·5	9·8	10·2	10·6	10·8	11·1	11·3
0·02	8·6	8·8	9·0	9·3	9·7	10·0	10·4	10·7	11·0	11·2	11·5
0·04	8·8	8·9	9·2	9·5	9·9	10·2	10·6	10·9	11·2	11·4	11·7
0·06	8·9	9·0	9·4	9·7	10·0	10·3	10·7	11·0	11·3	11·6	11·8
0·08	8·98	9·1	9·5	9·8	10·1	10·4	10·8	11·1	11·4	11·7	11·9
0·1	9·04	9·2	9·6	9·8	10·2	10·5	10·9	11·2	11·5	11·8	12·0
0·2	9·22	9·4	9·8	10·1	10·5	10·8	11·1	11·5	11·9	12·1	12·3
0·3	9·38	9·6	9·9	10·2	10·6	10·9	11·3	11·7	12·1	12·3	12·4
0·4	9·54	9·7	10·1	10·4	10·8	11·1	11·4	11·8	12·2	12·4	12·6
0·5	9·70	9 9	10·2	10·5	10·9	11·2	11·5	12·0	12·4	12·6	12·7

Colorimetric Method using Standard Buffer Solutions.

In Chapter XVI buffer mixtures are described whose *p*H values have been accurately determined. If therefore we select a series of these solutions, covering the *p*H range in which lie the *p*H values of the solutions requiring examination, such that the buffer solutions differ successively in *p*H by about 0·2, and place 10 c.c. (say) of each in test-tubes of colourless glass and having the same dimensions, and then carefully add a small equal quantity of a suitable indicator for the particular *p*H range to each solution, we obtain a series of different colours corresponding to the different *p*H values. Hence, if we take the same volume, 10 c.c., of the test solution and add to it a volume of the indicator solution equal to that used in the buffer solutions, we obtain a colour which we may be able to match exactly with one of the coloured standard buffer solutions. If a complete match is found, then the test solution and the corresponding buffer solution will have the same *p*H value. If, however, a complete match has not been obtained but the colour of the test solution falls between those of two successive standards, then it is known that the desired *p*H value must lie between the *p*H values of the two standards. Hence, by choosing standards with *p*H values sufficiently close to one another the unknown *p*H value can be ascertained with a precision of 0·1 or 0·05 *p*H unit. It must be

emphasised here that the indicator concentrations must be the same for all the solutions, and that the colours of the different solutions must be examined through the same thicknesses of the liquids. As we have seen the indicator concentration has an important bearing on the depth of colour of a one-coloured indicator. With a two-coloured indicator, the colour produced is the result of the ratio of indicator in the acid- and alkaline-forms, which remains constant at any given *p*H, and consequently the amount of indicator used is not then of such vital importance, though it will be appreciated that the difference in intensities of colour will render comparison difficult.

Selection of Indicator.

As a rule the most satisfactory range to employ an indicator for the determination of *p*H lies round about $pH = pK_{HIn}$, for it is in this region that the colours undergo their maximum change which facilitates colorimetric determinations of *p*H. This, however, only holds for those indicators whose acid and alkaline colours are of about the same intensity. If one form should happen to produce a deeper coloration than the other, then this will tend to cause the more useful *p*H range to be displaced towards the end where the deeper colour begins to assert itself. In the case of the sulphone-phthaleins the various alkaline colours are much more intense than the yellow acid forms, and this leads to more pronounced changes in colour occurring during the first halves of the neutralisation. Saunders (*Proc. Camb. Phil. Soc.*, 1923 **1**, 31) found that for bromocresol purple the best range was from *p*H 5·8 to *p*H 6·4, *p*K = 6·3 ; bromothymol blue, *p*H 6·4–7·2, *p*K = 7·1 ; phenol red, *p*H 7·1–7·9, *p*K = 7·7 ; cresol red, *p*H 7·65–8·45, *p*K = 8·1 ; and for thymol blue, *p*H 8·4–9·2, *p*K = 8·8. He claims that measurements can be made within these ranges having an accuracy of 0·01–0·02 *p*H unit. This must be regarded as exceptional accuracy for colorimetric estimations. Indicators having wide transition intervals usually exhibit a very gradual change in colour, tending to make colour-matching difficult and the accuracy poor, *e.g.*, litmus. The choice of indicators should be guided by considerations of this kind rather than by the desire to use the minimum number of indicators to span the entire *p*H range.

The chart given in Fig. 79 which was taken from a paper by Davis and Salisbury (*Ind. Eng. Chem., Anal. Edn.*, 1929, **1**, 2) will be of considerable use in the choice of suitable indicators. The ordinates of the parabolæ and ellipses correspond to the various depths of colour, and where they overlap an estimate of

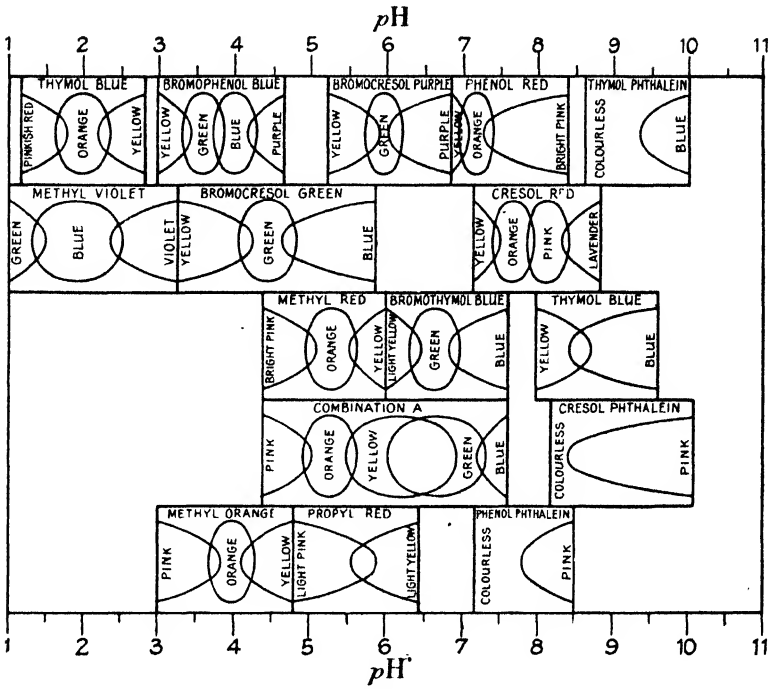


FIG. 79.—Davis and Salisbury's Indicator Colour Chart.

the amount of colour blending can be made. The colours represented correspond to those obtained on adding 4 drops of each indicator to 10 c.c. of buffer solutions. The concentrations of indicator solutions used are given in Tables 102 and 103.

TABLE 102

Indicator.	Conc. per cent.	Solvent.
Methyl violet . .	0·10	Aq. + 1 per cent. alcohol.
Methyl orange . .	0·02	Aq.
Bromocresol green	0·02	Aq.
Methyl red . . .	0·02	Aq. + 60 per cent. alcohol.
Propyl red . . .	0·02	Aq. + 60 ,, ,,
Phenolphthalein .	1·00	Aq. + 95 ,, ,,
Thymolphthalein .	0·20	Aq. + 95 ,, ,,

In selecting an indicator for any given determinations, the most appropriate indicator for the purpose should be used. This may be done by means of either preliminary tests with several indicators or a mixed indicator. If the former method of orienta-

tion be used, a few drops of the various indicators available are added to different portions of the test solution. The indicator to employ is the one in which neither the full acid nor the full alkaline colour is developed. This preliminary selection of an indicator may be carried out on a " spotting tile." An approximate idea of the unknown *p*H value may be obtained by adding a few drops of a mixed indicator, of which there are several now on the market. (See however page 374.)

" Universal " or Mixed Indicators.

It may be as well to include a few notes on the preparation of mixed indicators.

Bogen (*J. Amer. Med. Assoc.*, 1927, **89**, 199) introduced the following mixed indicator, whose colours range from red to blue in the order of the spectrum for *p*H values varying from *p*H 2 to *p*H 10. In 500 c.c. of absolute alcohol, 0·1 gram of phenolphthalein, 0·2 gram of methyl red, 0·3 gram of dimethyl-aminoazobenzene, 0·4 gram of bromothymol blue, and 0·5 gram of thymol blue are dissolved and then just sufficient sodium hydroxide is added to produce a yellow colour. Amounts of from 1 drop to 1 c.c. may be used. At *p*H 2 its colour is red; at *p*H 4, orange; at *p*H 6, yellow; at *p*H 8, green; and at *p*H 10, blue.

Van Urk's Universal Indicator (*Pharm. Weekblad*, 1928, **65**, 1246; see also, *ibid.*, 1929, **66**, 157) gives spectrum colours within the range, *p*H 3–11·5. It contains 0·1 gram of methyl orange, 0·04 gram of methyl-red, 0·4 gram of bromothymol blue, 0·32 gram of α-naphtholphthalein, 0·5 gram of phenolphthalein and 1·6 gram of cresolphthalein in 100 c.c., having first been dissolved to 70 per cent. alcohol and then diluted to 100 c.c. with water.

McCrumb (*Ind. Eng. Chem., Anal. Edn.*, 1931, **15**, 233) prepares a solution in 60 per cent. alcohol and 40 per cent. water containing 0·02 per cent. of methyl red, 0·04 per cent. of bromothymol blue, 0·04 per cent. of thymol blue and 0·02 per cent. of phenolphthalein. 0·25 c.c. of mixed indicator solution is added to 5 c.c. of solution to be tested. The colours are: at *p*H 3·0, red; *p*H 4·0, orange-red; *p*H 5·0, orange; *p*H 6·0, yellow; *p*H 7·0, yellow-green; *p*H 8·0, green-blue; *p*H 10·0, violet; *p*H 11·0, red-violet.

Fairbrother's (*Industrial Chemist*, 1928, **4**, 96) mixed indicator covering a *p*H range from 3 to 11 is prepared by dissolving 0·04 gram of methyl orange, 0·02 gram of methyl red, 0·12 gram of α-naphthol-phthalein, and 0·08 gram of phenolphthalein in 100 c.c. of 70 per cent. alcohol. The following colours are

obtained with increasing *p*H red, orange, yellow, green, blue, violet, reddish violet.

In using Universal Indicators, it should be remembered that the various indicators present may themselves materially alter the *p*H of the solution undergoing test. In testing unbuffered solutions or dilute solutions containing buffer systems, the principle of *isohydry* (see p. 371) should be applied. A series of indicator solutions, adjusted to different *p*H values, should be used and the indicator solution found which suffers little or no change in colour when added to the solution being tested. The *p*H of the solution is approximately that of the particular " adjusted " indicator solution used. As McCrumb states, errors as much as 3 or 4 *p*H units may result from the use of a Universal Indicator previously neutralised to some particular *p*H, *e.g.*, 7·0.

. . . . . .

For the colorimetric determination the most suitable indicator should be chosen from Table 91. There is a tendency nowadays to use those of Clark and Lubs and Cohen on account of their brilliant colour changes.

Preparation of Indicator Solutions.

(1) *Clark and Lubs' Indicators.*—In regard to the sulphonephthaleins it is essential that the purest products should be used, for with impure samples difficulty may sometimes be experienced in getting them into aqueous solution. It is probably for this reason that several workers have resorted to the use of alcohol. Clark and Lubs prefer aqueous solutions which they prepare in the following manner: 0·1 gram of the dry powder is ground in an agate mortar with the stoicheiometrical amount of N/20-NaOH, Table 103, to form the sodium salt, and the solution thus formed

TABLE 103

CLARK AND LUBS' INDICATORS

Indicator.	Mol. Wt.	C.c. N/20-NaOH to 0·1 gm. solid.	Concentration, per Cent.
Thymol blue	466	4·3	0·04
Bromophenol blue	669	3·0	0·04
Methyl red	269	7·4	0·02
Bromocresol purple. . . .	540	3·7	0·04
Bromothymol blue	624	3·2	0·04
Phenol red	354	5·7	0·02
Cresol red	382	5·3	0·02
Cresol-phthalein.	—	—	0·02

is diluted with water to 25 c.c. This gives a 0·4 per cent. solution which is put aside as a stock solution, and which they dilute to either 0·04 per cent. or 0·02 per cent. for use. For ordinary purposes, about 5 drops of indicator should be added to 10 c.c. of solution.

Kolthoff, however, prefers to prepare the sulphone-phthalein indicators by dissolving 0·1 gram in 20 c.c. of warm alcohol and then diluting to 100 c.c. with water.

(2) For the majority of the ordinary indicators, the solution should contain about 0·1 per cent. of the indicator. Soluble indicators, *e.g.*, methyl orange, methyl violet, Congo red, benzo-purpurin, litmus (1 per cent. solution), salicyl yellow, tropæolin O and tropæolin OOO, are simply dissolved in water. Many of the indicators have first to be dissolved in alcohol and the solutions then diluted with the requisite volume of water. 100 c.c. of each of the following indicator solutions should contain approximately: 0·1 gram of dimethylaminoazobenzene and 90 c.c. of alcohol, 0·2 gram of methyl red and 60 c.c. of alcohol, 0·1 gram of neutral red and 60 c.c. of alcohol, 0·1 gram of α-naphthol-phthalein and 50 c.c. of alcohol, 0·1–1·0 gram of phenol-phthalein and 60 c.c. of alcohol, 0·1 gram of thymol-phthalein in 100 per cent. alcohol, 0·2 gram of alizarine and 90 c.c. of alcohol, 0·5 gram of rosolic acid and 50 c.c. of alcohol, and 0·1 gram nitramine and 60 c.c. of alcohol. Of these solutions volumes varying from 1 to 10 drops, which should be measured out from a graduated pipette and preferably not from a bottle, should be added to each 10 c.c. of the test solution.

Indicator Colour Matching.

The matching of the colour of a test solution, to which the correct amount of indicator solution has been added, with that produced in a buffer solution of known *p*H, may be carried out directly, merely by arranging the coloured buffer solutions in the alternate holes of a test-tube stand in the order of *p*H, and then to move the solution undergoing examination from hole to hole until the position is found such that its colour is seen to fall between those of two consecutive buffer solutions. Suitable illumination is necessary and the comparison is facilitated if a white background is placed behind the test-tube stand. It is often an advantage to have the tubes inclined at a small angle to the vertical so that the solutions may be viewed through a greater depth of liquid. As mentioned above, it is imperative that the concentrations of the indicator in all the solutions should be

the same, and moreover, that the same thickness of the various solutions should be compared.

Dichromatism of the Sulphone-phthaleins.

A difficulty encountered in matching the colours of certain of the sulphone-phthalein indicators is that of " dichromatism." In other words, a solution when viewed through one thickness appears to have one colour whereas when the same solution is seen through another it may appear to have a different colour. Dichromatism is also exhibited by solutions containing different amounts of an indicator. This is the case with bromophenol blue and bromocresol purple. So far we have regarded the colours of solutions as if they were separate entities. Strictly speaking, we should consider the colour of each solution in terms of its absorption spectrum and of the changes in the intensities of the light radiations which the solution transmits. It is the relative intensities of the transmitted waves which determine the colour sensation, or the colour which the solution will appear to have. The extent of the absorption of light waves is determined, not only by the wave-lengths, but by the width of the solution layer and the concentration of the solution. These factors will also determine the proportion of light transmitted through the solution. The intensities of the colour radiations after travelling through a liquid will be a function of the intensities of the respective radiations before entering the liquid. It is well known that the intensities of the many colour radiations which make up ordinary solar " white " light are very different from one another. They differ also from those emitted by hot bodies, *e.g.*, an electric filament, an electric arc or an incandescent gas burner. Hence the solar and artificial " white " lights are quite different from one another, as is exemplified by the appearance of the colours of articles when examined under their illumination. Ordinary daylight is rich in blue, whereas the light emitted by an electric carbon filament may be compared with light corresponding to the red end of the spectrum and relatively weak in blue radiations. The attempt to imitate daylight in modern electric lamps is effected by absorbing some of the red by means of a blue bulb. It happens that the absorption spectrum of bromophenol blue in its alkaline form has a large band in the yellow and the green, with the consequence that the transmitted light is made up almost entirely of red and blue light. Hence, such a solution would appear blue in daylight on account of its greater intensity of blue, whilst in the light from an electric carbon filament lamp with its preponderance of red it will appear red.

The cause of the different colours seen through different thicknesses of solution has been very neatly explained by Clark ("Determination of Hydrogen Ions," 1923, p. 65). For simplicity, consider that the colour of a bromophenol blue solution seen by transmitted light is composed of red and blue, and that the intensities of these two kinds of radiations in the incident light are I_r and I_b respectively. Suppose that a_r and a_b are their respective "transmission coefficients" through the solution, *i.e.*, the ratios of the intensities of the incident beam and that of light transmitted through unit thickness. Hence the intensity of the transmitted red light through unit thickness will be $I_r \times a_r$, and that of blue will be $I_b \times a_b$. After traversing a thickness, x, the intensities become

$$I_r \times a_r^x \text{ and } I \times a_b^x.$$

Although the actual values of these two expressions have not been determined, their importance will be understood by assuming that the intensity of the incident blue is 100, and of the red 30, and that $a_b = 0{\cdot}5$ and $a_r = 0{\cdot}8$. When $x = 1$, $I_b \times a_b^x = 50$ and $I_r a^r = 24$, and therefore the blue colour will predominate. If, however, $x = 10$, $I_b \times a_b^x = 0{\cdot}01$ and $I_r \times a_r^x = 0{\cdot}30$, and thus the solution will appear red. Hence a solution may appear blue through a thin layer, but may appear red when viewed through thicker layers. The effect of varying the intensities of the incident radiations will also be to alter the colours of the solutions. Thus if we interchange the numerical values taken in the above calculations, *i.e.*, let $I_r = 100$ and $I_b = 30$, then we find that for unit thickness, $x = 1$,

$$I_r \times a_r^x = 80 \text{ and } I_b \times a_b^x = 15,$$

and consequently the solution will now appear red, instead of blue as in the previous case.

Kolthoff calls attention to the different effect which buffer solutions may have on the "transmission-coefficients" compared with that of the solution undergoing examination, and so may cause the colours corresponding to the same *p*H value of different solutions to be in no way similar. He found that the dichromatism of bromophenol blue and other sulphone-phthaleins could be entirely eliminated by the use of alcohol or acetone. Due to this, the transition colours of bromophenol blue from yellow to blue in alcohol or dilute alcoholic solutions are quite different from those exhibited by aqueous solutions.

The Walpole Comparator.

Should the test solution be either slightly coloured or turbid, then the direct method of matching its colour obtained by the

PLATE III

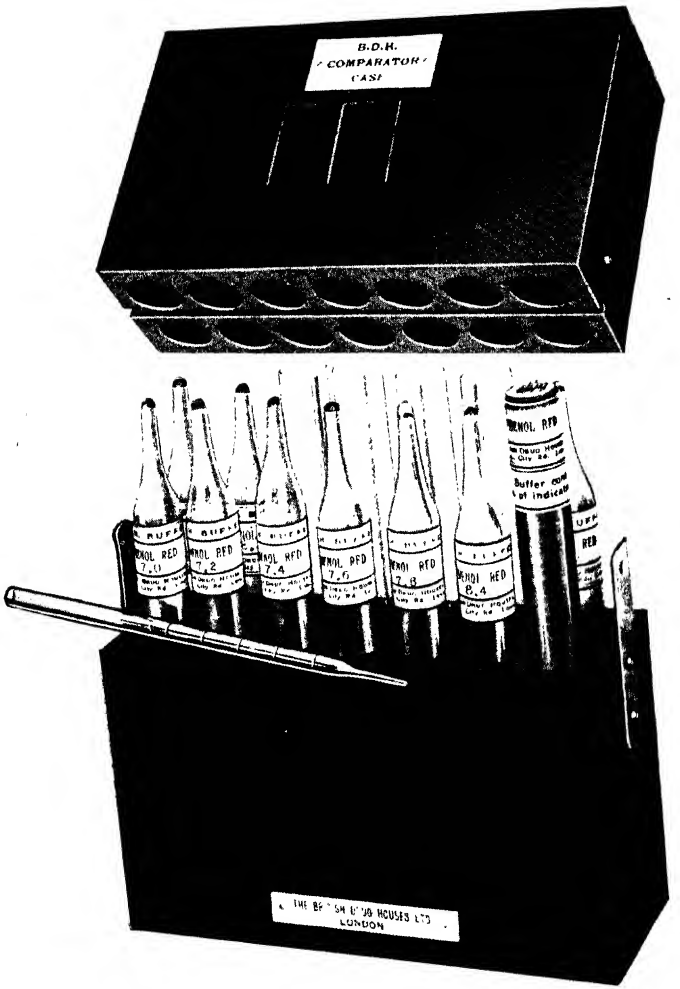


FIG. 81.—The B.D.H. Comparator Case.

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addition of indicator with that of a clear standard buffer solution will no longer be applicable. If the colour effects which give rise to the resulting colour are additive, then the colour seen by transmitted light through equal, superimposed, thicknesses of a clear buffer solution with added indicator and having the same *p*H as the test solution and of the test solution without indicator, should be the same as that observed when the same light passes through the same thickness of pure water and then through an equal thickness of the test solution having the same concentration of indicator as the standard buffer solution. This is the principle of the Walpole comparator and the so-called block comparator. Fig. 80 represents a section of Walpole's apparatus (*Biochem. Jour.*, 1910, **24**, 40). The interior is painted black. The various liquids are placed in the four plane bottom cells to the same depth in each. Light is made to pass up through these liquids, either by means of a reflector or reflecting surface or by some suitable direct illumination placed underneath the apparatus. The cell containing a standard buffer and indicator is replaced by others until a perfect match is obtained. A modified form of this apparatus has been designed by Biehler (*Zeitsch. physiolog. Chem.*, 1910, **110**, 298). In this type of comparator the two pairs of solutions are viewed through the same depth of liquid. In the block comparator of Hurwitz, Meyer and Ostenberg test-tubes are filled with various liquids and the colours observed through pairs, one placed behind the other (*Proc. Soc. Exp. Biol. and Med.*, 1915, **13**, 24). Equal widths of liquid are examined by comparing the colours seen through the central sections of each pair of tubes. Figs. 80 and 81 refer to this type of comparator. The tubes are placed in blackened holes bored into a block of wood, and the colours observed through each of the three pairs of tubes through

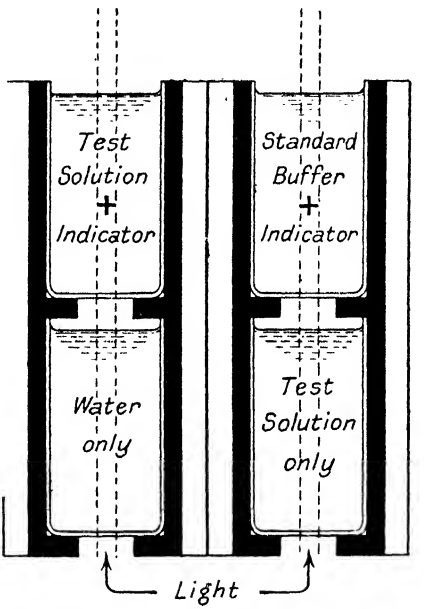

FIG. 80—Walpole Comparator.

the rectangular slots provided. In A (Fig. 82) and C samples of the solution undergoing examination are placed, while in D and F are inserted standard buffer solutions containing indicator and differing by about 0·2 *p*H. Another portion of the test solution is placed in B together with the same concentration of indicator as in D and F, *viz.*, a definite volume of each 10 c.c., and the colour of this is modified by the tube of distilled water in E. The standard coloured buffer solutions in D and F are changed until a pair is found giving colours between which the colour of the unknown solution, when viewed in the direction of the arrow, is found to lie.

The determination of hydrogen-ion concentrations by this device is rendered very much more rapid if a permanent series of buffer standards containing measured amounts of suitable indicators are available for *p*H intervals of about 0·2 *p*H. These may be prepared in glass tubes which are not attacked and by using only those indicators which give colours that remain unchanged over long periods. Such solutions should be preserved in sealed tubes and kept out of the light except when in use. If sealing is effected with corks, the corks must be carefully coated with a paraffin wax to prevent the passage of any of the acids contained in cork into the buffer solutions. Convenient ranges of these coloured standards are now procurable commercially and are guaranteed for a year. Table 104 gives those indicators which are suitable for the purpose. Nevertheless, the standards should be continually checked, and preferably *p*H measurements should be made using two sets of colour standards prepared from different indicators.

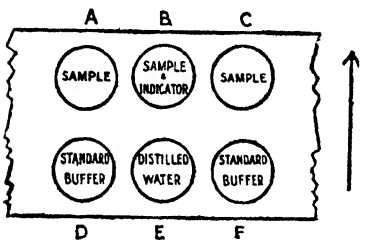

FIG. 82.—Arrangement of Tubes in the Comparator.

An improved comparator, known as the " Roulette Comparator," is made by the La Motte Chemical Products Co. of Baltimore, U.S.A., with which *p*H measurements can be made rapidly and under excellent conditions of illumination. A picture of the apparatus is given in Fig. 83. It comprises a stationary base and a metal band, inside which a wooden drum revolves on ball bearings. Illumination is provided by a 40-watt Mazda lamp fixed in the centre of the base. A piece of " Dalite " glass is placed in the back of the block between the three test-tubes and the colour standards, and a piece of etched glass is placed on the outside of the block directly over the three slots. To operate the comparator

TABLE 104

INDICATORS SUITABLE FOR USE IN COMPARATORS AS PERMANENT COLOUR STANDARDS

	*p*H Range.	
Metacresol purple	0·5–2·5	red—yellow
	7·6–9·2	yellow—violet
Thymol blue	1·2–2·8	red—yellow
	8·0–9·6	yellow—blue
Bromophenol blue	3·0–4·6	yellow—violet
Methyl orange	3·1–4·4	red—yellow
Ethyl orange	3·5–4·5	red—orange
Benzene-azo-α-naphthylamine	3·5–5·7	red—orange
Bromocresol green	4·0–5·6	yellow—blue
Chlorophenol red	5·0–7·0	yellow—violet red
Bromocresol purple	5·2–6·8	yellow—violet
Bromothymol blue	6·0–7·6	yellow—blue
Neutral red	6·8–8·0	red—yellow
Phenol red	6·8–8·4	yellow—red
Cresol red	7·2–8·8	yellow—violet red

a series of tubes of colour standards, covering the *p*H range of the solutions to be tested, is placed in *p*H order in the alternative holes of the revolving drum. Tubes of the same bore, filled with distilled water, are inserted in the vacant holes. Suppose the required *p*H range is *p*H 5–9. Sets of standard buffer solutions coloured with chlorophenol red, *p*H 5·2–6·8; bromothymol blue, *p*H 6·0–7·6; and phenol red, *p*H 6·8–8·4 might therefore be used. If the *p*H of the solution being tested lies within the range of bromothymol blue, fill three of the test-tubes to the mark, 10 c.c., and place them in the three holes in the block. After adding the requisite amount of bromothymol blue to the middle tube, and shaking, no indicator being added to the test-solution in the other two tubes as they serve merely to compensate for any colour which the solution undergoing test may have, the light is switched on and the drum revolved until the bromothymol blue standards are directly behind the test sample containing the indicator. Looking towards the electric bulb through the three slots in the block, slowly revolve the drum until the colour seen through the central test-tube exactly matches that of one of the tubes on either side of it, or else lies between them. The *p*H value can then be read off directly from the labelled colour standards.

Micro-Colorimetric Methods.

Occasionally the amounts of the samples to be tested are so small as not to permit of the application of the foregoing methods. Micro-methods have been introduced, of which two will now be discussed: (*a*) spotting, and (*b*) using the capillator.

(*a*) **Spotting.**—Felton (*J. Biol. Chem.*, 1921, **46**, 299) places a drop of the liquid on a porcelain or " opal " glass plate and mixes with it an equal drop of a suitable indicator. The colour is compared with those given by the same treatment of buffer solutions of known *p*H values. The drops must be accurately measured. (*Cf.* Myers, Schmitz, and Booker, *J. Biol. Chem.*, 1923, **57**, 209, and Brown, *Chem. Abs.*, 1924, **18**, 1135.)

(*b*) **Using Capillator.**—The capillator, as supplied by Messrs. The British Drug Houses, Ltd., and illustrated in Fig. 84, was designed by Ellis, Brit. Patent 235,458, 1924. It consists of a series of capillary tubes filled with buffer solutions containing an indicator. These tubes are mounted, three together, on a white card, and form a series of coloured strips, each strip being marked with its exact *p*H value. Each card illustrates the complete colour change of the indicator.

A slot is provided in the card, so that, by holding it up, colour comparisons may be made by transmitted light, whereas by viewing against the white background of the card comparisons may be made by reflected light. The whole series of colours being visible all the time, the actual colour-matching can be carried out very quickly.

A determination of *p*H is carried out by using a capillary tube as a pipette and measuring by this means equal quantities of the liquid and indicator, mixing the two in a small watch glass and then drawing the mixed liquids back into the capillary tube. The colour of the mixed liquids is then matched against the capillator standards.

Imitation Indicator Colour Standards.

There have been recently several attempts to prepare solutions of different colours which match exactly the colours established by certain indicators in buffer solutions of different *p*H values. In order that the solutions might be stable, and therefore their colours, attention has been directed to inorganic salt solutions. Actually, to secure an inorganic salt solution of exactly the same colour as that of indicator dye solution is almost impossible, but it must be conceded that very many satisfactory imitations have been prepared, and which may be of appreciable use as colour standards. Taub (*J. Amer. Pharm. Assoc.*, 1927, **16**, 116) has prepared 73 such solutions of mixtures of salts of copper, iron and cobalt, which may be substituted for indicator colour standards corresponding to *p*H values varying from *p*H 1·2 to *p*H 9·0. Kolthoff (*Pharm. Weekblad*, 1922, **59**, 104) found that the colours obtained by mixing a solution containing 45·05 grams of $FeCl_3$,

PLATE IV

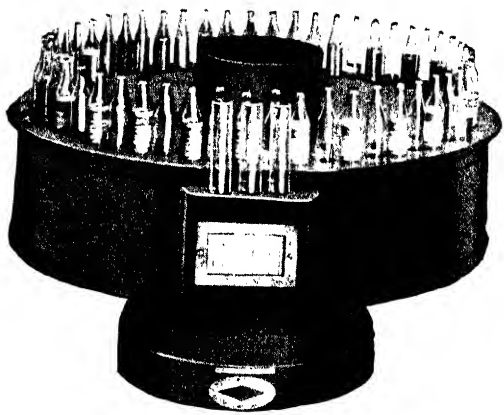

FIG. 83.—La Motte Roulette Comparator.

[*See page* 364

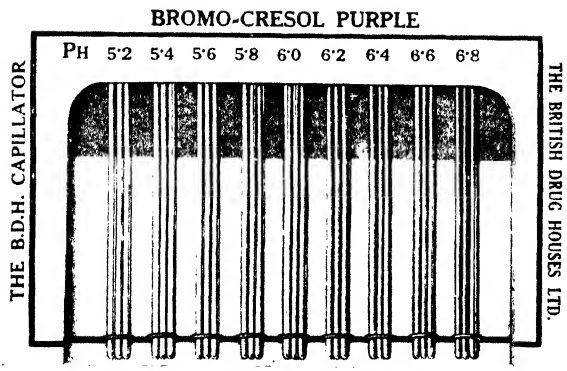

FIG. 84.—The B.D.H. Capillator.

[*To face page* 366.

$6H_2O$ in 1 litre of 1 per cent. hydrochloric acid with another solution made up of 72·8 grams of $Co(NO_3)_2,6H_2O$ per litre of 1 per cent. hydrochloric acid solution in various proportions closely resemble those given by adding 0·2 c.c. of a 0·05 per cent. indicator solution to a buffer solution (10 c.c.) at the *p*H shown in Table 105, in the case of neutral red, methyl orange and methyl red, and 0·2 c.c. of a 0·1 per cent. tropæolin OO solution.

TABLE 105

KOLTHOFF'S IMITATION COLOUR STANDARDS

Solution; To 10 c.c. $Co(NO_3)_2$ add c.c. of $FeCl_3$.	*p*H Values corresponding to			
	Neutral Red.	Methyl Red.	Methyl Orange.	Tropæolin OO.
0	—	5·2	3·1	2·0
1	7·0	—	3·2	—
3	7·1	5·3	3·5	2·1
5	7·2	5·5	3·7	2·2
7·5	7·4	5·6	3·9	2·3
10	7·6	5·6	4·0	2·3
15	7·8	5·7	4·2	2·4
20	7·9	5·8	4·3	2·5
30	—	5·8	4·5	2·5

The search for really satisfactory inorganic colour standards will necessitate increased attention being given to the absorption spectra and the transmittancies of light of varying wave-lengths through salt solutions. This may eventually show the way by which absorption spectra of solutions of mixtures of inorganic salts may be obtained that compare favourably with those given by some particular indicator solution at a definite *p*H value. Work of the type recently done by Mellon and Martin (*J. Physical Chem.*, 1927, **31**, 161) on the spectral transmission curves of aqueous solutions of ordinary indicators and of inorganic salts may prove to be extremely useful. It is possible that a series of coloured glasses might serve as standards. Such coloured glass standards are incorporated in certain comparators now on the market.

Spectrophotometric Method.

Brode (*J. Amer. Chem. Soc.*, 1924, **46**, 581) has found that, with few exceptions, *e.g.*, methyl violet, the change in the hydrogen-ion concentration of a solution containing an indicator (*e.g.*, phthalein- and azo-dyes) does not shift the absorption bands as regards wave-length, but merely changes the intensity of absorp-

tion. He found that by comparing the intensities of absorption at a wave-length within the absorption bands by a solution of unknown *p*H with those in a standard buffer containing the same indicator, the *p*H value could be calculated. For this purpose the most suitable indicators covering the *p*H range 1 to 10 are thymol blue (*p*H 1·0 to 3·5 and 7·5 to 10·0) and a mixture of methyl red and bromothymol blue, the latter covering the blank range of the former. Holmes (*J. Amer. Chem. Soc.*, 1934, **46**, 627) made similar observations with one- and two-colour

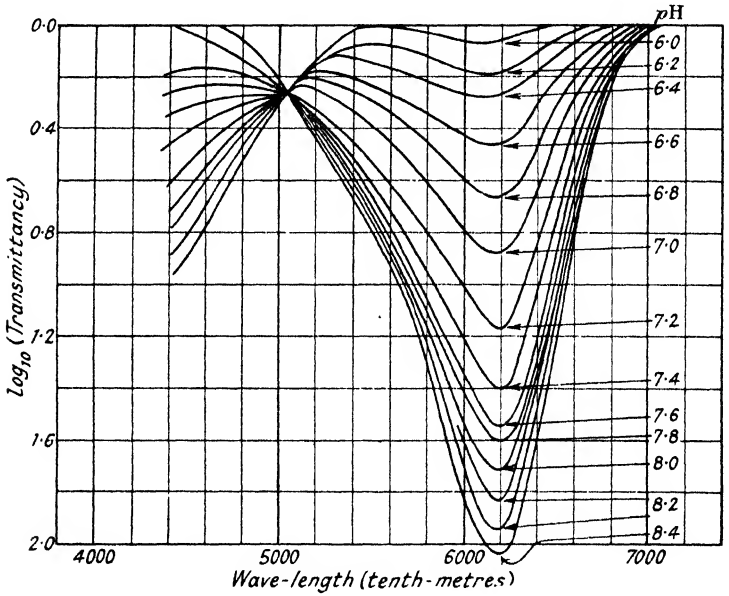

FIG. 85.—Variation in the Intensity of the Orange Absorption Band of Bromothymol Blue with *p*H (Brode, *J. Amer. Chem. Soc.*, 1924, **46**, 591).

indicators. With two-colour indicators, however, he showed that the ratios of the absorption intensities at two wave-lengths, selected at, or near, the respective maxima of two absorption bands, varied with the *p*H value of the solution. Thus for phenol-sulphone-phthalein he measured with the spectrophotometer the intensities of the absorption at 460 $\mu\mu$ and 560 $\mu\mu$ respectively. By constructing a calibration curve connecting the ratio of such intensities with *p*H values, he was able to read off unknown *p*H values once the value of the ratio had been found. Holmes and Snyder (*J. Amer. Chem. Soc.*, 1925, **47**, 221, 226) studied the

dissociation curves of thymol blue in alkaline solution and of bromocresol green by this method and found them to conform with the theoretical formula between 10 per cent. and 90 per cent. neutralisation. So also did thymol blue up to the point of half-neutralisation, but thereafter the dissociation of the indicator appeared to be retarded. They used the method for standardising α-naphthol 2-sulphonate indophenol as an indicator for use in the Gillespie "drop-ratio" method, $p\mathrm{K}_{\mathrm{HIn}} = 8{\cdot}63$, *p*H range 7·6–9·6 (*J. Amer. Chem. Soc.*, 1925, **47**, 2232). Vlès (*Comp. rend.*, 1925, **180**, 584) endeavoured to avoid the tedious empirical calibration which the method involves, and derived an expression based on the absorption constants of the two tautomeric forms, the absorption ratio of the test solution, and the ionic dissociation of the indicator, by which if the *p*H values were not extremely small, he was able to calculate *p*H values correct to the first decimal place. Crystal violet and methyl red were anomalous.

Fig. 85 illustrates the variation in the intensity of the orange absorption band of bromothymol blue when subjected to the different *p*H values indicated. It will be seen that as the *p*H is increased from 6·0 to 8·4 the absorption increases (*i.e.*, the transmittancy decreases, and that these changes reach their "peak" values at the same wave-length, *viz.*, 617 μμ. Brode made similar observations with other indicators, the maximum absorption always occurring at the wave-lengths given in Table 106.

TABLE 106

WAVE-LENGTHS OF ABSORPTION BANDS

Indicator.	λ(μμ).	Indicator.	λ(μμ).
Thymol blue (acid)	544	Cresol red	572
Bromophenol blue	592	Phenol red	558
Methyl red	530	Thymol blue (alk.)	596
Bromocresol purple	591	Neutral red	533
Bromothymol blue	617	Phenol-phthalein	553
		Thymol-phthalein	598

The effect of a change in *p*H on the absorption at the wave-lengths corresponding to the peaks of the characteristic bands is shown in Fig. 86. The arrows refer to the *p*H values at which the logarithm of the transmittancies is unity. These points are seen to represent the mean extinction coefficients between the highest and lowest values given by the various indicators over their effective *p*H ranges. Hence the *p*H's should provide a measure of $p\mathrm{K}_{\mathrm{HIn}}$ of the indicators, and this Brode proved experimentally to be the case.

Lothian (*Trans. Faraday Soc.*, 1937, **33**, 1239) makes use of

Brode's principle for the determination of *p*H by means of the Hilger Spekker Photoelectric Absorptiometer. The method consists of the measurement of the absorption of an indicator solution of the light transmitted by a filter extending over a small band of wave-lengths covered by the absorption band of the indicator being used. The instrument incorporates a photoelectric cell of the rectifier type and a galvanometer. The photoelectric cell, in

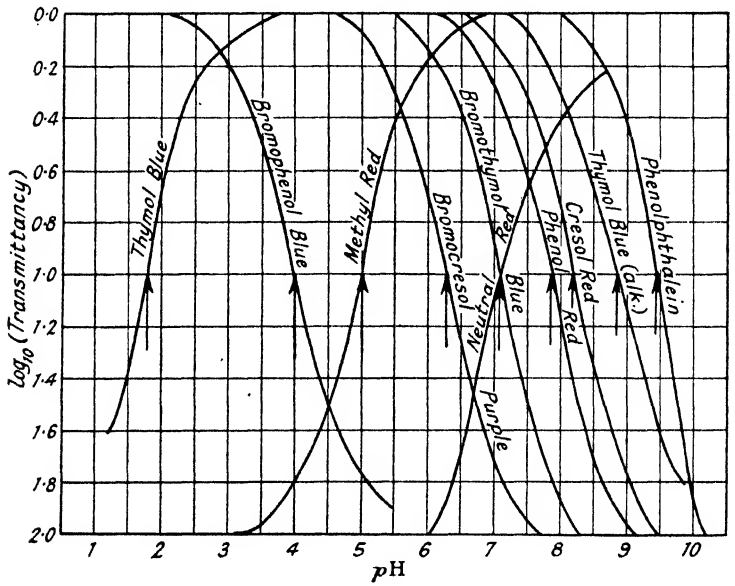

FIG. 86.—Relation between the Extinction Coefficient, at the Peak of the Absorption Bands of Indicators, and *p*H (Brode, *J. Amer. Chem. Soc.*, 1924, **46**, 592).

conjunction with three stages of amplification, has also been used by Müller and Partridge (*Ind. Eng. Chem., Anal. Edn.*, 1931, **3**, 169) for the photometric colorimetric determination of *p*H. Greater precision is obtained than is secured visually.

Highly Coloured and Turbid Solutions.

Apart from the more satisfactory electrometric methods for the determination of *p*H values of those solutions which are either so turbid or so highly coloured as to interfere seriously with the colorimetric methods just described, two modifications of the colorimetric method seem to have been attempted. One, which is available for solutions which are highly buffered, is to dilute

the turbid solution with distilled water until the colour or turbidity has become suitably diminished. That dilution can have very little effect, if any, on the hydrogen-ion concentration of well-buffered solutions will be apparent from Chapter X. The assumption is taken for granted by biochemists in their investigations of body fluids such as blood and urine, by bacteriologists and by soil-chemists with the so-called " soil solutions."

The second method, which is due to Sørensen, is to add to the standard buffer solutions amounts of a dye which exactly reproduce the colour of the test solution and then to proceed in the usual way with indicators.

Isohydric Method of determining *p*H. Extremely Dilute and Weakly Buffered Solutions.

In order to ascertain precise *p*H data of very dilute or weakly buffered solutions particular attention must be given to the indicator solutions, to ensure that they themselves do not contribute to the hydrogen-ion concentration of the solution undergoing test. For this purpose, indicator solutions should be so chosen that they are isohydric with the test solution, *i.e.*, the hydrogen-ion concentration of the indicator solution and the test-solution should be the same. Hence, if the adjusted indicator solution and the test-solution have the same *p*H, no change in *p*H will occur on mixing, and consequently the colour will remain unchanged. Acree and Fawcett (*Ind. Eng. Chem., Anal. Edit.*, 1930, **2**, 78) have devised a method by which this state of affairs can approximately be obtained. In the first instance the suitable indicator is found in the usual way. Then to another portion some indicator solution, that has been buffered at $pH = pK_{ind.}$, is added and the resulting colour compared with buffer-colour *p*H standards until a match is obtained. To another portion of test solution indicator solution buffered to the " approximate *p*H " thus observed is added and the resulting colour compared once more with the standards. The *p*H value indicated by these standards is regarded as the correct value.

In view of the importance of the isohydric technique, which may be used with solutions more dilute than 0·0001 M. and which are usually outside the scope of accurate electrometric *p*H methods, the isohydric method will now be described in more detail. After having ascertained which indicator will respond to the *p*H of the solution, from 0·2 to 10 c.c. of the test-solution are added to 0·2 c.c. of the indicator solution which has previously been adjusted to the mid-point of its useful range. By comparing the colour thus obtained with the Buffer Colour *p*H

Standards (0·001 M. or 0·05 M.), in the preparation of which the same volumes of indicator solution and buffer solution were employed, an *approximate* pH *value* of the unknown solution will be obtained, which will be either *below*, *at* or *above* $p\text{H} = p\text{K}_{\text{Indicator}}$. If the *true* pH of the unknown solution is below $p\text{H} = p\text{K}_{\text{Ind.}}$, the *approximate* pH will be lower than $p\text{K}_{\text{Ind.}}$; if the same, *true* $p\text{H} = p\text{K}_{\text{Ind.}}$ and if higher, then the colour of the unknown solution will indicate an *approximate* pH higher than $p\text{K}_{\text{Ind.}}$. When the *true* pH is lower than $p\text{K}_{\text{Ind.}}$ the *approximate* pH so obtained will be higher than the *true* pH, and similarly, when the *approximate* pH is higher than $p\text{K}_{\text{Ind.}}$, the *true* pH will be a little higher still. Experience makes it possible to estimate the true pH values, which are responsible for these alterations in the colour of the indicator. Such experimental estimates of the true pH values we shall refer to as "*estimated* pH *values*." It now remains to prepare an indicator solution adjusted to the "*estimated* pH," to add 0·2 c.c. to the same volume of unknown solution previously employed, and to match the colour against the buffer colour standards. Generally there will be an exact, or nearly exact, agreement between the indicator adjusted to the "*estimated* pH" and the buffer colour standard corresponding to the same pH. When this state of affairs is reached the "*true* pH of the unknown solution will have been found.

Acree and Fawcett state that correct pH values may be determined by the isohydric method by using solutions of indicators which have been adjusted (salt errors being omitted)—

(*a*) at their mid-point pH for use with the usual buffers up to about 50-fold dilutions,

(*b*) at their lowest, mid-point and highest useful pH values for buffered solutions diluted about 50- to 1000-fold,

(*c*) in 0·2 pH steps over their useful ranges for very dilute buffer solutions and waters.

The application of the method by using indicator solutions, adjusted as in (*b*), is illustrated in Table 107, in which some of Acree and Fawcett's data are recorded.

Stene (*Ind. Eng. Chem., Anal. Edn.*, 1936, **8**, 398) has suggested a slightly different method of determining pH which is also based on the isohydric principle. If identical volumes of an indicator solution, previously neutralised to a pH in the neighbourhood of the acid (or alkaline) border of its useful range, are added to (*a*) a small volume and (*b*) a large volume of a solution of unknown pH, but which pH is known to lie within the range of the indicator, the pH of the small volume (*a*) will be lower (or higher) than that of the larger volume (*b*). If the

TABLE 107

Solution.	*p*H of Indicator adjusted to						"*True* *p*H."
	Lowest Point.	"*Approx.* *p*H."	Mid-point.	"*Approx.* *p*H."	Highest Point.	"*Approx.* *p*H."	
	Bromocresol Purple						
5000 dilution of 0·05 M.-Phthalate buffer (*p*H 4·21) . . .	5·0	5·25	5·8	5·6	6·6	6·1	5·4
	Phenol Red or Cresol Red						
10,000 dilution of 0·05 M.-Phosphate buffer (*p*H 7·82) . . .	7·0	7·2	7·4	7·4	7·8	7·65	7·4
	Bromocresol Purple						
Water saturated with Air and CO_2 (*p*H 5·75)	5·2	5·45	5·8	5·75	6·6	6·0	5·75
	Bromothymol Blue						
Water (CO_2 free) (*p*H 7·00)	6·2	6·4	7·0	7·05	7·6	7·5	7·05

*p*H of the indicator solution should happen to be the same as the unknown *p*H, then no change in *p*H occurs in (*a*) or (*b*) and the colours remain the same. Stene therefore adopts the following method. Take two Nessler cylinders of the same size, and run into each equal volumes of specially prepared indicator solution, and then unequal volumes of the test solution, say 20 c.c. into one cylinder and 100 c.c. into the other. Now titrate each solution with equal volumes of 0·001 N- or 0·0001 N-alkali (or acid) until the solutions in both tubes are seen to have the same colour when looking down the axis of each tube. In so doing, the indicator in the two tubes will have been adjusted such that the *p*H corresponding to the indicator and that of the unknown solution will be the same. When this colour has been found the *p*H can be ascertained by comparison with colour standards obtained with buffer solutions of known *p*H.

With unbuffered or feebly buffered solutions, the so-called universal indicators may lead to considerable errors in *p*H. One way to minimise these errors is to prepare a series of universal indicator solutions which are adjusted at intervals of one *p*H unit from *p*H 3 to 11, and also a series of buffer colour standards corresponding to 0·2 *p*H steps over the entire range. Then, by making use of the *principle of isohydry*, test the unknown solution by dividing it into a number of equal volumes and adding to each the same number of drops of universal indicator, one portion

being treated with indicator adjusted to *p*H 3, another portion with *p*H 4 indicator, and so on. Then by appropriately comparing the separate solutions with colour standards corresponding respectively with *p*H 3, *p*H 4, etc., it can be ascertained which adjusted indicator underwent the least colour change. The *p*H of the unknown solution will be in the vicinity of the *p*H of that particular indicator. A fairly good estimate of the *p*H can then be made by comparing the actual colour with 0·2 *p*H interval colour standards. Table 108 gives an idea of the magnitude of the errors which may result from the use of universal indicators. They were measured by McCrumb (*Ind. Eng. Chem., Anal. Edn.*, 1931, **15**, 233) by means of a universal indicator (see p. 358) adjusted at *p*H 5·25, 7·45 and 9·10.

TABLE 108

ERRORS CAUSED BY UNIVERSAL INDICATORS

Solution.	*p*H.	*p*H as determined by Universal Indicator adjusted to *p*H –		
		5·25	7·45	9·10
Distilled water	6·8	5·6	7·0	8·8
Drinking water	7·5	6·6	7·4	8·6
Natural water	6·8	6·4	7·0	7·4
Boiler-feed water	10·2	10·0	10·0	10·0
,, ,, ,,	9·6	8·0	8·8	9·4
Paper extract	4·2	4·4	4·6	4·8
,, ,,	5·9	6·0	6·6	8·0
Soil extract	6·4	5·8	6·4	7·4
,, ,,	8·0	7·6	8·0	8·4
Laundry rinses	5·5	5·4	5·6	6·0
Pan liquors (sugar)	7·3	7·2	7·6	8·2

CHAPTER XVIII

ERRORS IN INDICATOR METHODS. THE USE OF INDICATORS IN TITRATIONS

APART from the ordinary manipulative errors, there are a number of errors which are inherent in the various indicators themselves. They are (1) errors introduced by the dissociation of the indicator as either an acid or a base in supplying hydrogen ions to the test solution, the "acid error"; (2) errors due to the action of neutral salts which may be present in a solution upon the colour and the incidence of the colour change, the "salt error"; (3) errors through the interaction of an indicator with ampholytic bodies such as the proteins, the "protein error"; (4) errors due to effect of temperature upon the indicator dissociation; and (5) errors caused by the presence of alcohol.

The "Acid Error."

As indicators function either as weak acids or bases, it is obvious that in the minute concentrations used in test-solutions they can have no appreciable effect upon the hydrogen-ion concentration of those solutions which are well buffered. If, however, the solution contains no buffering agents, then, according as the dissociation constant of the indicator is sufficiently great to enable it to affect the hydrogen-ion concentration of the solution, will there be introduced a difference between the observed and actual *p*H values. It is quite an easy matter to get some idea of the magnitude of the error from a knowledge of the dissociation constant of the indicator, the value of K_w, and the indicator concentration imparted to the solution. The error may become considerable when the *p*H of an unbuffered solution, *e.g.*, a very dilute alkali solution, is greater than pK_{HIn}. Thus a solution of alkali of about *p*H 10 may appear to have a value somewhere about *p*H 8–9 when examined with phenolphthalein. The use of two indicators of widely different constants will indicate the existence of such an error. (See page 371.)

The "Salt Error."

The fact that organic substances can sometimes be forced out of an aqueous solution by the addition of common salt suggests that

a neutral salt has some effect on the organic compound even when the amount of added salt is inadequate to cause its separation from the solution. In the case of indicators, it should be understood that many have very limited solubility in aqueous solutions, so that the presence therein of salts may have relatively large effects on their behaviour. In some cases, neutral salts cause a variation in the colour changes and also in the *p*H values at which these changes normally occur. It is probable that the salt influences the ionic equilibria involved in the functioning of an indicator and that it has different effects on the two so-called acid and alkaline forms, which are here considered to be responsible for the colour produced by the indicator. The ions of neutral salts also affect the electrical environment of the indicator by altering the ionic strength of the solution. As suggested by Kolthoff, neutral salts may have some effect on the optical absorption of the two forms of the indicator.

Numerous investigators have measured the salt errors of the various indicators, and in so doing have compared their colours with those produced by the indicators in standard buffer solutions, which themselves often contain free salts and thereby may give rise to additional errors. The phthalate buffer solutions of Clark and Lubs cause certain indicators to precipitate, *e.g.*, methyl violet. With the majority of the common synthetic indicators the apparent error due to neutral salts does not exceed 0·2 *p*H unit. As a general rule, it is more satisfactory for a worker first to standardise the behaviour of his indicators under the conditions prevailing in his solutions against the hydrogen electrode, and so get some estimate of the errors which may be introduced. Very often, the "salt error" of an indicator is studied in regard to its behaviour in the presence of alkali metal salts. In actual practice, the salts encountered are often very different. Unless a worker bases his colorimetric measurements directly on electrometric data gained from a preliminary examination of the type of solutions with which he has to deal, he should always take precautions to ensure that neutral salts present in the solutions undergoing test do not introduce errors in the *p*H values determined colorimetrically. It is to avoid the introduction of such errors that the use of two indicators has been recommended. Numerous researches have been directed to the evaluation of the salt errors of particular indicators by Sørensen, Palitzsch, Szyskovski, Kolthoff, Saunders, McClendon, and others. In the opinion of the author, it would be of little value to attempt to summarise their conclusions, but in order to give some idea of the magnitude of the salt errors of the common

indicators, Tables 109 and 110 are inserted. These were taken from Kolthoff (*Rec. trav. Chim.*, 1922, **41**, 54; 1925, **44**, 275), and Saunders (*Proc. Camb. Phil. Soc.*, 1923, **1**, 31). The positive sign shows that the salt-error should be added to the observed *p*H value, found by means of a particular indicator, whereas a negative sign shows that the salt-error must be subtracted.

TABLE 109

SALT ERRORS OF INDICATORS

Indicator and Salt.	Neutral Salt Concentration.				
	1·0 N.	0·5 N.	0·25 N.	0·2 N.	0·1 N.
Tropæolin OO—KCl .	+ 0·23	+ 0·06	— 0·01	—	— 0·05
Thymol blue, *p*H 1·2–2·8 KCl.	+ 0·05	— 0·04	—	— 0·06	— 0·06
Methyl orange—KCl .	+ 0·23	+ 0·02	— 0·08	—	— 0·08
Methyl yellow—KCl .	—	—	—	—	— 0·08
Bromophenol blue—KCl	— 0·35	— 0·35	— 0·15	—	— 0·05
" " —NaCl	— 0·35	— 0·27	—	—	— 0·15
Congo red—NaCl . .	— 0·9	— 0·55	—	— 0·25	0
Bromocresol purple—NaCl.	—	— 0·25 (0·6 N)	—	—	—
Bromothymol blue—NaCl.	—	— 0·19 (0·6 N)	—	—	—
Methyl red—NaCl . .	—	+ 0·1	—	—	—
p-Nitro-phenol—NaCl .	—	— 0·05	—	—	—
Azolitmin—NaCl . .	—	— 0·55	—	—	—
Phenol red—NaCl . .	—	— 0·15	—	—	—
Neutral red—NaCl . .	—	+ 0·12 (0·6 N)	—	—	—
Cresol red—NaCl . .	—	— 0·20	—	—	—
Brilliant yellow—NaCl .	—	0·0	—	—	—
Phenol-phthalein—NaCl	—	— 0·17	—	—	—
Thymol blue, *p*H 8·0–9·6 NaCl.	—	— 0·17	—	—	—
Nitramin—KCl . . .	— 0·16	— 0·10	— 0·10	—	— 0·06
Tropæolin O—NaCl .	+ 0·62	+ 0·53	+ 0·44	—	+ 0·38

The "salt errors" of Congo red, tropæolin O, azolitmin (litmus) and of bromophenol blue in the higher concentrations of neutral salts given in Table 109 show that these indicators are unsatisfactory for *p*H determinations. The errors of the remaining indicators listed in Table 109 reveal that in normal circumstances they may be expected to behave satisfactorily, for their errors are seen to be negligible for ordinary solutions. Their salt errors only become large with increasing salt concentration. (See for example McCrumb and Kenny, *J. Soc. Chem. Ind.*, 1930, **49**, 426T). The errors given in Table 110 are remarkable in that they

show that *p*H values, determined colorimetrically on the assumption that the salts included in Clark's buffer solutions do not influence the colours of the several indicators, are, however, affected by very small concentrations of electrolytes. Certain indicators, particularly chlorophenol red, bromocresol green and phenol red, give large errors in the presence of very small salt concentrations, whilst α-naphtholphthalein, cresol red, neutral red, methyl red, methyl orange, bromothymol blue and bromocresol purple in causing small errors appear to be most serviceable for such solutions.

TABLE 110

SALT ERRORS OF INDICATORS WHEN USED WITH SOLUTIONS OF LOW ELECTROLYTE CONCENTRATIONS IN COMPARISON WITH THE MORE CONCENTRATED BUFFER SOLUTIONS OF CLARK AND LUBS.

Total Electrolyte Concentration.	Thymol Blue. (acid)	Phenol-phthalein.	α-Naph-tholphtha-lein.	Phenol Red.	Cresol Red.	Neutral Red.	Bromo-thymol Blue.
0·001 N	+ 0·25	+ 0·25	+ 0·18	+ 0·35	+ 0·17	− 0·09	+ 0·19
0·005 N	+ 0·19	+ 0·19	+ 0·14	+ 0·28	+ 0·15	− 0·04	+ 0·17
0·01 N	+ 0·13	+ 0·14	+ 0·10	+ 0·22	+ 0·12	0·00	+ 0·15
0·02 N	+ 0·05	+ 0·06	0·00	+ 0·15	+ 0·09	0·00	+ 0·12
0·03 N	—	—	—	+ 0·09	+ 0·07	0·00	—

	Chloro-phenol Red.	Bromo-cresol Purple.	Bromo-cresol Green.	Methyl Red.	Alizarine.	Methyl Orange.	Bromo-phenol Blue.
0·001 N	+ 0·47	+ 0·13	+ 0·45	+ 0·17	+ 0·25	− 0·15	+ 0·25
0·005 N	+ 0·3	+ 0·10	+ 0·24	+ 0·10	+ 0·18	− 0·07	+ 0·20
0·01 N	+ 0·21	+ 0·09	+ 0·16	+ 0·06	+ 0·12	− 0·06	+ 0·17
0·02 N	+ 0·15	+ 0·08	+ 0·10	+ 0·03	+ 0·10	− 0·04	+ 0·15
0·03 N	+ 0·09	+ 0·07	+ 0·07	0·00	+ 0·06	− 0·02	—

An approximate computation of the magnitude of salt errors may be made on the basis of the Debye-Hückel theory relating to the influence of ionic strength, μ, on the activity of ions. This theory, however, holds only for extremely dilute solutions, so that it cannot be expected to give any idea of the errors involved in using indicators in the presence of neutral salts in the concentrations frequently encountered.

If we consider the indicator to function as a monobasic acid, HIn, one colour corresponding to HIn and the other to In ions, then if the colour imparted to two solutions, I and II, is the same, it follows that

$$\frac{[\mathrm{In}']_{\mathrm{I}}}{[\mathrm{HIn}]_{\mathrm{I}}} = \frac{[\mathrm{In}']_{\mathrm{II}}}{[\mathrm{HIn}]_{\mathrm{II}}},$$

As $$\frac{a_{H^+_I} \cdot a_{In'_I}}{a_{HIn_I}} = \frac{a_{H^+_{II}} \cdot a_{In'_{II}}}{a_{HIn_{II}}} = K$$

therefore $$\frac{a_{H^+_I}}{a_{H^+_{II}}} = \frac{a_{HIn_I}}{a_{In'_I}} \cdot \frac{a_{In'_{II}}}{a_{HIn_{II}}}$$

whence

$$\begin{aligned} pa_{H_I} - pa_{H_{II}} &= pH_I - pH_{II} \\ &= \log \frac{a_{In'_I}}{a_{HIn_I}} - \log \frac{a_{In'_{II}}}{a_{HIn_{II}}} \\ &= \log \frac{f_{In'_I}[In']_I}{f_{HIn_I}[HIn]_I} - \log \frac{f_{In'_{II}}[In']_{II}}{f_{HIn_{II}}[HIn]_{II}} \\ &= \log \frac{f_{In'_I}}{f_{HIn_I}} - \log \frac{f_{In'_{II}}}{f_{HIn_{II}}}. \end{aligned}$$

If we assume that the activity coefficients of the undissociated indicator acid in the two solutions are both equal to unity, then

$$pH_I - pH_{II} = \log f_{In'_I} - \log f_{In'_{II}}.$$

The Debye-Hückel expression for the activity coefficient of an individual ion in very dilute solution is

$$-\log f = z^2 A\sqrt{\mu},$$

z being the valency, A being equal 0·505 at 25° and 0·487 at 0° C. Hence for a univalent ion, In′, $\log f_{In'} = -0{\cdot}505\sqrt{\mu}$, and therefore

$$pH_I - pH_{II} = -0{\cdot}505(\sqrt{\mu_I} - \sqrt{\mu_{II}}).$$

In the case of some indicators, *e.g.*, the sulphonephthaleins, colour changes accompany the second stage of ionisation. Thus representing the indicator as H_2In, the equilibria are

$$H_2In \rightleftharpoons H^+ + HIn'$$

and

$$HIn' \rightleftharpoons H^+ + In''.$$

Identical colours in solutions I and II will be produced when

$$\frac{[In'']_I}{[HIn']_I} = \frac{[In'']_{II}}{[HIn']_{II}}$$

and therefore

$$pH_I - pH_{II} = \log \frac{f_{In''_I}}{f_{HIn'_I}} - \log \frac{f_{In''_{II}}}{f_{HIn'_{II}}}.$$

As before, the activity coefficient of a univalent ion, *viz.*, HIn′, is given by $-\log f_{HIn'} = +0{\cdot}505\sqrt{\mu}$, but for a divalent ion, In″, $z = 2$, $-\log f_{In''} = 0{\cdot}505 \times 4 \times \sqrt{\mu}$

$$= 2{\cdot}020\sqrt{\mu}.$$

Hence

$$pH_I - pH_{II} = (-2{\cdot}020 + 0{\cdot}505)\sqrt{\mu_I} - (-2{\cdot}020 + 0{\cdot}505)\sqrt{\mu_{II}}$$
$$= -1{\cdot}515(\sqrt{\mu_I} - \sqrt{\mu_{II}}).$$

In a similar way, identical colours produced by a tribasic indicator acid, H_3 In, are given when

$$pH_I - pH_{II} = -2{\cdot}525(\sqrt{\mu_I} - \sqrt{\mu_{II}}).$$

If, in all these cases, pH_{II} represents the pH value of a buffer mixture, the pH of which had been determined electrometrically, then the difference $pH_I - pH_{II}$ represents the "salt error," involved in estimating the pH of solution, I, by comparison with buffer mixture, II.

Similar calculations can be made for indicators which function as bases as far as their colour changes are concerned. For a monoacid base, InOH,

$$pH_I - pH_{II} = +0{\cdot}505(\sqrt{\mu_I} - \sqrt{\mu_{II}});$$

the second stage of ionisation of a diacid base, $In(OH)_2$,

viz., $$InOH^{\cdot} \rightleftharpoons In^{\cdot\cdot} + OH'$$

$$pH_I - pH_{II} = +1{\cdot}515(\sqrt{\mu_I} - \sqrt{\mu_{II}}),$$

and for the third stage of a triacid base, $In(OH)_3$,

viz., $$In(OH)^{\cdot\cdot} \rightleftharpoons In^{\cdot\cdot\cdot} + OH'$$

$$pH_I - pH_{II} = +2{\cdot}525(\sqrt{\mu_I} - \sqrt{\mu_{II}}).$$

The positive signs show the salt errors occur in the opposite direction in the case of a basic indicator. Another point brought out by these considerations is that the salt error is larger when multivalent indicator ions are involved.

TABLE III

SALT ERRORS AND IONIC STRENGTH

μ	Thymol Blue (acid range).	Tropæolin OO.	Methyl Orange.	Bromophenol Blue.	Bromocresol Green.	Methyl Red.	Chlorophenol Red.	p-Nitrophenol.	Bromothymol Blue.	Phenol Red.	Neutral Red.	Phenolphthalein.	Thymol Blue (alk. range).
0·0025	—	—	− 0·04	+ 0·15	+ 0·21	0·00	—	+ 0·06	+ 0·14	+ 0·14	− 0·07	—	—
0·005	—	—	− 0·04	+ 0·14	+ 0·18	0·00	+ 0·15	+ 0·05	+ 0·12	+ 0·12	− 0·06	+ 0·18	+ 0·16
0·01	0·00	0·00	− 0·02	+ 0·14	+ 0·16	0·00	+ 0·18	+ 0·03	+ 0·11	+ 0·11	− 0·05	+ 0·12	+ 0·12
0·02	0·00	0·00	0·00	+ 0·13	+ 0·14	0·00	+ 0·12	+ 0·02	+ 0·07	+ 0·07	− 0·04	+ 0·10	+ 0·09
0·05	0·00	0·00	0·00	+ 0·10	+ 0·05	0·00	+ 0·05	+ 0·01	+ 0·04	+ 0·04	− 0·02	+ 0·05	+ 0·05
0·1	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
0·5 (KCl)	0·00	0·00	0·00	− 0·10	− 0·12	0·00	− 0·16	− 0·18	− 0·20	− 0·20	+ 0·07	− 0·26	− 0·12
0·5 (NaCl)	0·00	0·00	0·00	− 0·18	− 0·16	0·00	− 0·19	− 0·19	− 0·28	− 0·29	− 0·12	− 0·21	− 0·19

Table 111, taken from Kolthoff's ("Säure-Basen-Indicatoren," 4th Edition, Berlin, 1932, page 348), shows the errors introduced by various ionic strengths in colorimetric comparisons with buffer solutions, the ionic strength of which is 0·1.

Variation of Indicator Constant with Ionic Strength of the Solution.

Instead of considering the change in colour of an indicator in terms of the expression given on page 338, it may be regarded in terms of activities and their dependence on the ionic strength of the solution. Thus by regarding the indicator as an acid, $HIn \rightleftharpoons H^{\cdot} + In'$, we see from Chapter XIV that

$$pa_{H^{\cdot}} = pk + \log \frac{[In']}{[HIn]} + \log \frac{\gamma_{In'}}{\gamma_{HIn}}.$$

Table 112 gives the values of pk in solutions of different ionic strength, together with the values extrapolated for zero ionic

TABLE 112

VALUES OF INDICATOR pk'S AT 20°

Indicator.	pk at Ionic Strength of :—				
	0	0·01	0·05	0·1	0·5
m-Cresol purple	1·5 ?	—	—	1·51	—
Thymol blue	1·65	—	1·65	1·65	1·65
Bromophenol blue	4·10	4·06	4·00	3·85	3·75
Bromocresol green	4·90	4·80	4·70	4·66	4·46
Chlorophenol red	6·25	6·15	6·05	6·00	5·9
Bromocresol purple	6·40	6·28	6·21	6·12	5·9
Bromothymol blue	7·30	7·19	7·13	7·10	6·85
Phenol red	8·00	7·92	7·84	7·81	7·65
o-Cresol red	8·46 (38)	—	8·30	8·25	—
m-Cresol purple	—	—	—	8·32 (38)	—
Thymol blue	9·20	9·01	8·95	8·90	—
Methyl orange	3·46	3·46	3·46	3·46	3·46
Dimethylaminoazobenzene	3·25	—	—	3·34	3·40
Methyl red	5·00	—	—	5·00	5·00
α-Dinitrophenol	4·10	—	3·95	3·90	3·80
β-Dinitrophenol	3·70	—	—	3·50	—
γ-Dinitrophenol	5·20	—	5·12	5·10	5·00
p-Nitrophenol	7·00–7·15	—	—	—	—
m-Nitrophenol	8·35	—	8·30	8·25	8·15
Quinaldine red	2·63	2·80	—	2·90	3·10
Pinachrom	7·34	—	—	7·34	—

strength. The table was taken from Kolthoff (*J. Physical Chem.*, 1930, **34**, 1466) and as a rule the salts investigated were sodium and potassium chlorides.

This table shows that with the exception of a few indicators the variations introduced in *pk* by the presence of neutral salts are very small.

The "Protein Error."

This error is only likely to arise with physiological liquids and certain technical solutions such as those obtained in the leather, cereal and brewing industries. Proteins and their decomposition products, besides being colloidal, are amphoteric. They may, therefore, interact with acidic and basic indicators and in consequence the indicators may become partially adsorbed, and thus affect the colour. This is especially true of indicators which are colloidal. Thus, Congo red, which might be regarded as a colloidal electrolyte, is useless for solutions containing proteins. Azo-dye indicators are generally useless, though the protein error of methyl red is often very small. This was observed by Palitzsch (*Comp. rend. Lab. Carlsberg*, 1911, **10**, 162) when the *p*H values of the various protein solutions were about *p*H 5, but in more acid solutions, *ca.* *p*H 4, the indicator colours corresponded with values *ca.* *p*H 5. Similar observations have been made by Kent-Jones (see p. 326, Vol. II) in connexion with the hydrogen-ion concentrations of aqueous extracts of flour. Good agreement between the electrometric and colorimetric *p*H values was obtained above *p*H 5·5, but between this value and *p*H 5·0 discrepancies just became apparent, the indicator always indicating a higher *p*H value. At *p*H 5·0 errors as high as 0·15 were found by the colorimetric method, whilst below, the error became more and more marked, depending upon both the nature of the protein and its concentration. Hence colorimetric methods in solutions of proteins are of doubtful worth, and electrometric methods should be employed (*vide* McCrumb and Kenny, *J. Soc. Chem., Ind.*, 1930, **49**, 428T).

Hartley (*Trans. Faraday Soc.*, 1934, **30**, 444) has made some interesting observations on the colorimetric determination of the *p*H of solutions which contain proteins and salts that dissociate to give large ions, *e.g.*, cetyltrimethyl ammonium iodide and sodium cetylsulphonate. Large ions originating from such salts and from proteins may adsorb ions of opposite sign, especially when the ions carry more than a single charge. If the adsorbed ions happen to be those of the indicator in one of its coloured forms, then the colour imparted to the solution will not be

entirely that corresponding to its true *p*H. It is obvious, therefore, that for use with proteins indicators should be so selected that their colour changes involve only ions which bear the same charge as the protein ions or other heavy ions.

The Temperature Effect.

An increase in temperature has a marked effect on electrolytic dissociation. It is well known that water, acids and bases, and therefore indicators, undergo enhanced ionisation. In other words, K_w, the ionic product of water, and the constants of acids and bases, *viz.*, K_a and K_b, become larger, so that pK_w, pK_a and pK_b assume lower values. The chief effect of this is to diminish (*a*) the *p*H scale, (*b*) the *p*H corresponding to neutrality, and (*c*) the limiting *p*H values of the various indicator transition ranges. Thus at 18° C., $pK_w = 14{\cdot}2$; at 70°, 12·75; and at 100°, 12·2, and the hydrogen-ion concentration at neutrality at the respective temperatures are given by *p*H 7·1, *p*H 6·4, and *p*H 6·1.

TABLE 113

EFFECT OF TEMPERATURE ON *p*H RANGES AND DISSOCIATION CONSTANTS OF INDICATORS

Indicator.	*p*H Ranges at :—		pK_{HIn} at 18° $-pK_{HIn}$ at 70°.
	18° C.	100° C.	
Methyl violet	0·1–3·2	0·5–1·7	—
Thymol blue	1·2–2·8	1·2–2·6	0·4
Tropæolin OO	1·3–3·3	0·8–2·2	0·45
Methyl yellow	2·9–4·0	2·3–3·5	0·18
Methyl orange	3·1–4·4	2·5–3·7	0·3
Methyl red	4·2–6·3	4·0–6·0	0·2
p-Nitro-phenol	5·0–7·0	5·0–6·5	0·5
Phenol red	6·8–8·4	7·3–8·3	0·3
Cresol red	7·2–8·8	7·6–8·8	—
Phenolphthalein	8·3–10·0	8·1–9·0	0·9 to 0·4
Thymol blue	8·0–9·6	8·2–9·2	0·0
Thymol-phthalein	9·3–10·5	8·7–9·5	—
Nitramine	11·0–12·5	9·0–10·5	1·45

It is necessary therefore to employ buffer solutions whose hydrogen-ion concentrations are accurately known at the temperature at which the determinations are to be made, and if the measurements are to be carried out without the aid of reference solutions, then the constant of the indicator at the desired temperature must be known.

Effect of Alcohol.

Very little systematic work seems to have been done on the effect which alcohol may have on the behaviour of indicators, in spite of the fact that volumetric estimations are sometimes made in alcoholic solutions. It has a very pronounced effect on the sensitivity on certain indicators. Thus if an aqueous solution containing phenolphthalein be rendered sufficiently alkaline to produce a slight reddening of the indicator, it will be found on the addition of alcohol that the colour becomes paler and paler and eventually disappears. Here the alcohol makes the phenolphthalein more resistant to colour change, *i.e.*, it reduces its sensitivity, and considerably more alkali must be added to restore to the solution its original faint red coloration. If the colour is due to the existence of indicator-anions, In′, in the solution through the formation of the sodium salt, then it will be inferred that the alcohol represses the ionisation of the phenolphthalein, *i.e.*, increases $p\mathrm{K}_{\mathrm{HIn}}$, so that much of the added alkali fails to interact and thus the free alkali raises the *p*H of the alcohol-water solution before the colour change becomes apparent. Kolthoff (*Rec. trav. chim.*, 1923, **42**, 251) has investigated, in a preliminary way, the effect of alcohol on many indicators in a complete range of alcohol-water mixtures. He found that nitramine, bromophenol blue, thymol blue (acid range) and curcumine became more susceptible to colour change in the presence of alcohol, whereas thymolphthalein, phenolphthalein, thymol blue (alkaline range), tropæolin O, tropæolin OO, methyl orange and methyl yellow do not undergo a change in colour until considerably more reagent has been added than in aqueous solutions. For the majority of indicators tested, the error involved in *p*H value determinations through the amount of alcohol being less than 10 per cent. by volume is usually about 0·1 *p*H, though the error for greater volumes becomes considerable.

The Use of Indicators in Titrations.

We saw in Chapter X that, in general, there corresponds to the equivalence- or end-point of a neutralisation reaction some definite *p*H value, and that a very small excess of the titrant may, or may not, cause a considerable *p*H change. The indicator should be so chosen that the *p*H corresponding to its most marked colour change is, or only a little above, that at which the true end-point is reached.

First Perceptible Appearance of Colour of a One-Colour Indicator—its Dependence on the Concentration and Solubility.

In carrying out a titration with a one-colour indicator, HIn, such as phenolphthalein, or paranitrophenol, the beginning of the colour change, *i.e.*, of the appearance of colour, is a matter of some importance. In the case of a one-colour indicator, it is reasonable to suppose that when the colour just becomes visible, there must be formed in the solution a small proportion of In′ ions, whose concentration is the minimum requisite for the visible production of colour. This limiting concentration will be independent of the concentration of the indicator, and will be characteristic of the indicator itself. Let this concentration be denoted by $[In']_v$, and suppose that the hydrogen-ion concentration corresponding to the visible beginning of the colour change of an indicator whose concentration is $[HIn]_a$ is $[H^\cdot]_a$, and that for the indicator in concentration, $[HIn]_b$ to be $[H^\cdot]_b$. Then

$$[H^\cdot]_a = \frac{[HIn]_a}{[In']_v} \times K_{HIn},$$

and

$$[H^\cdot]_b = \frac{[HIn]_b}{[In']_v} \times K_{HIn}.$$

Hence

$$pH_a = pK_{HIn} + \log \frac{[In']_v}{[HIn]_a},$$

and

$$pH_b = pK_{HIn} + \log \frac{[In']_v}{[HIn]_b},$$

and therefore

$$pH_a - pH_b = \log \frac{[HIn]_b}{[HIn]_a}.$$

Thus, we see that the first visible appearance of colour of a one-colour indicator is directly connected with the concentration of indicator. If $[HIn]_b$ were equal to 10 times $[HIn]_a$, then would $pH_a - pH_b = 1$, and consequently the appearance of colour in the solution having the greater concentration of indicator would occur at a lower pH value, in the special case 1 pH unit below.

We have seen on page 326 that the pH range within which an indicator changes colour is determined by the magnitude of its constant, either as an acid or a base. The ranges of certain indicators are curtailed through the relatively small solubilities of one or the other forms, namely, the acid form of an acid indicator, and the alkaline form of a basic indicator. It will be understood from the above considerations, that saturated solutions of two similar indicators, having the same dissociation constants, but having

different solubilities, S_a and S_b, will on treatment with alkali become coloured at different pH values, which will be related to one another by

$$p\mathrm{H}_a - p\mathrm{H}_b = \log \frac{S_b}{S_a}.$$

provided that the two indicators require the same limiting $[\mathrm{In}']_r$ before their respective colours become perceptible.

Titration Exponent.

In performing titrations the worker is concerned with the pH value at which the more or less abrupt colour change takes place, and not with the pH range governing the whole transition. Bjerrum refers to these pH values as the indicator "titration-exponents," and denotes them by p_T. Some generalisations have been made by Noyes (*J. Amer. Chem. Soc.*, 1910, **32**, 825) on the incidence of these changes. If a one-colour indicator be used in the minimum amount, then the colour first becomes perceptible only after the indicator, HIn, has been neutralised to the extent of 25 per cent. As

$$p\mathrm{H} = p\mathrm{K}_{\mathrm{HIn}} + \log \frac{[\mathrm{In}']}{[\mathrm{HIn}]}$$

$$\therefore\ p_T = p\mathrm{K}_{\mathrm{HIn}} + \log \frac{25}{100 - 25}$$

$$i.e.,\ p_T = p\mathrm{K}_{\mathrm{HIn}} - 0{\cdot}5 \text{ (approx.)}.$$

In the case of phenolphthalein, $p\mathrm{K}_{\mathrm{HIn}} = 9{\cdot}7$, and therefore the first observable colour would be expected at pH 9·2. It should not be forgotten, however, that the actual value of p_T is largely determined by the concentration of indicator employed, so much so that if the solution had been saturated with phenolphthalein it would have begun to redden at pH 8·4. On the contrary, the very small solubility of thymolphthalein fixes its titration exponent at pH 9·5.

The location of the titration exponent of a two-colour indicator is a question of greater difficulty, created by the fact that usually one of the two colours is considerably more intense than the other, and also that the eye may be more sensitive to one than to the other. Hence in following the change in colour of an indicator during a titration, if it should happen that the first colour is more intense than the second, the first variation in colour produced by the formation of some of the second coloured form will be somewhat more delayed than would have been the case if the two colours had been either equally intense, or the second the more intense. Conversely, if the titration is carried out in the reverse

direction the greater depth of the one colour will cause the visible change to appear at an earlier stage in the neutralisation of the indicator. Noyes found that as a rule from 5 to 20 per cent. of the indicator must be neutralised when carrying out a titration in one way, whereas when performing the titration in the opposite way the decomposition of the indicator salt must proceed to somewhere between 5 and 20 per cent., *i.e.*, corresponding to neutralisation of the indicator ranging from 95 to 80 per cent. respectively. Due, however, to the greater intensity of the red form of methyl orange, he found that in the titration of an acid with an alkali the colour-change appeared between 20 and 30 per cent. neutralisation of the indicator. Titrating in the opposite way the change in colour became evident when between 5 and 20 per cent. of the indicator had been reacted upon.

One point of importance in the use of indicators in titrations is that their colour-changes may often be made sharper, if these changes can be confined to as little a range of *p*H as possible. A step towards this end may be made by using the smallest possible amounts of indicator solution. The indicators should preferably be synthetic, as those derived from vegetable sources, in some cases comprise mixtures of acids and yield variations in colour extending over a wide *p*H range, *e.g.*, litmus, *p*H 4·8–8·0. Table 114 gives the titration exponents and concentrations of commonly used indicators. It is taken from Kolthoff's ("Indicators," page 109).

Roller (*J. Amer. Chem. Soc.*, 1932, **54**, 3485) has made a mathematical study of the errors caused by using indicators which do not change colour precisely at the stoicheiometric end-point in acid-base titrations. Errors due to variations in the sensitivity of the indicator are also included. These errors become apparent when a titration is carried to some pre-arranged tint of an indicator in a suitably buffered solution. When the colour obtained in the solution undergoing titration is matched, by means of the unaided eye, with that of the external standard, errors as great as $\pm$ 0·3 *p*H unit may be made.

The percentage error, E, in an acid-base titration is given by

$$E = \pm 200\sqrt{\mathrm{K}} \,.\, \sinh \Delta,$$

where Δ is the known error of the indicator at the end-point, and K is a function of the dissociation constants and concentrations (for details, the original paper must be consulted).

In the titration of a weak acid with a strong base, K reduces substantially to $\sqrt{\frac{\mathrm{K}_w}{\mathrm{C} \,.\, \mathrm{K}_a}}$; C being the concentration of the salt

TABLE 114

INDICATOR "TITRATION EXPONENTS"

Indicator.	p_T.	Colour.	Add to 100 c.c. Solution.	
			No. of c.c.	Conc. Indicator.
				Per Cent.
Thymol blue . . .	2·6	Yellowish-rose	1·0	1
Tropæolin OO . . .	2·8	Yellowish-orange	1·0	1
Bromothymol blue . .	4	Purplish-green	0·5–1·0	1
Methyl yellow . . .	4·(2)	Yellowish-orange	0·2–0·5	1
Methyl orange . . .	4·(3)	Orange	0·2–0·5	1
Methyl red	5	Yellowish-red	0·2–0·5	2
Bromocresol purple .	6	Purplish-green	0·5–1·0	1
Bromothymol blue . .	6·8	Green	0·5–1·0	1
Phenol red	7·5·	Rose-red	0·5–1·0	1
Neutral red	7	Orange-red	0·2–0·8	1
Cresol red	8	Red	0·5–1·0	1
Thymol blue . . .	8·8	Blue-violet	0·5–1·0	1
Phenolphthalein . .	8	Pale-rose	0·8–1·0	1
,, . .	9	Pale-rose	0·3–0·4	1
Thymolphthalein . .	10	Pale-blue	0·5–1·0	1
Nitramine	11·6	Orange-brown	0·5–1·0	1

formed at the end-point; K_a, the dissociation constant of the weak acid, and $\Delta = 2{\cdot}30\ \delta p\mathrm{H}$, in which $\delta p\mathrm{H}$ is the deviation in pH as shown by the indicator from that at which the true end-point occurs, together with any pH error inherent in the use of the indicator. When Δ is small, then $\sinh \Delta = \Delta$.

"Achromatic Indicator Mixtures."

As we have seen, the colour-changes of indicators take place more or less continuously over a fairly wide pH range, and even though an indicator may seem to undergo a visible abrupt change in colour at its so-called titration exponent, that change is often not sufficiently distinct to enable titrations to be made exactly to that pH. For this reason several workers have employed mixtures of (*a*) two suitable indicators, (*b*) an indicator and a suitable dye. The principle underlying these mixed indicators appears to be to obtain a colour which is exactly the complementary colour of that formed by the indicator alone at its transition point. Hence the colour produced at the end-point by such a mixture would appear grey, or, if the solution is sufficiently dilute, colourless. On either side of the transition point the indicator colours would not be complementary to that of the

added dye and consequently colours would be observed. Thus Hallstrom (*Berichte*, 1905, **38**, 2288) used a mixture of ethyl orange and indigo; on the alkaline side of the ethyl orange range the yellow is converted into a green by the blue dye, on the acid side the indicator red is changed into violet, whilst at the end-point the orange of the indicator is complementary to the blue of the dye and so imparts to the solution either a grey or colourless appearance. Hickman and Linstead (*J. Chem. Soc.*, 1922, **121**, 2502) mixed xylene cyanole FF with methyl orange which gave the change, violet—grey or colourless—green on passing from low to high *p*H. Similar mixtures of methyl orange and indigo carmine have been studied by Kirschnik (*Chem. Ztg.*, 1907, **31**, 960), Luther (*ibid.*, p. 1172) and Moerk (*Amer. J. Pharm.*, 1921, **93**, 675). Acid blue and acid green were used with methyl orange by Salle (*J. Infect. Diseases*, 1926, **38**, 293), methylene blue and methyl red by Cohn (*J. Gen. Physiol.*, 1922, **6**, 697), and various blue and blue-green dyes were tested by Johnson and Green (*Ind. Eng. Chem., Anal. Edn.*, 1930, **2**, 2) in conjunction with methyl red and sodium alizarin sulphonate.

Their most sensitive combinations are given in Table 115. The methyl red solutions were alcoholic and those of sodium alizarin sulphonate were aqueous. The transition grey colour is produced at approximately *p*H 5·0–5·4.

TABLE 115

INDICATOR MIXTURES

Methyl red, 0·125 per cent. Methylene blue, 0·0825 per cent.	Sodium alizarin sulphonate, 0·5 per cent. Indigo carmine, 0·125 per cent.
Methyl red, 0·75 per cent. Guinea green, 0·0625 per cent.	Sodium alizarin sulphonate, 0·5 per cent. Guinea green, 0·0629 per cent.

Indicator mixtures, which give a grey tint at the transition point of the indicator, have been called by Smith (*Quart. J. Pharm.*, 1930, **3**, 499) " achromatic " indicators. He divides the majority of available indicators into five groups in accordance with their colour changes from the acid to the alkaline side of their range: (1) Red to blue; (2) Red to yellow, or *vice versa*; (3) Yellow to blue; (4) Colourless to red; (5) Colourless to yellow. In the first group are all the less sensitive indicators, Congo red, litmus and lacmoid. The second group contains some very sensitive indicators, *viz.*, thymol blue (acid range), methyl yellow, methyl orange, methyl red, neutral red, phenol red and cresol red. All

of these indicators become highly sensitive "achromatic" indicators by adding the appropriate quantity of a suitable blue or greenish-blue dye, *e.g.*, methylene blue, acid green, or bromocresol green (*p*H being > 5). The use of a second indicator to provide the complementary colour to that of the transition-point of the main indicator has the added advantage that it has also a range of colour change, which may possibly serve as an indicator of the approaching desired end-point. *Cf.*, Lizius (*Analyst*, 1921, **46**, 355); Scholtz (*Z. Elektrochem.*, 1904, **10**, 549); Simpson (*Ind. Eng. Chem.*, 1924, **16**, 709); Cohen (*J. Amer. Chem. Soc.*, 1922, **44**, 1851); Kolthoff (*Biochem. Z.*, 1927, **189**, 26). Kolthoff describes a series of twenty-five mixtures whose transition-points range from *p*H 3·2 to 10·8. The purity of the grey that occurs at the transition-point is, of course, dependent on the actual amount of complementary colouring substance used. Smith found that with mixtures of phenol red and bromocresol green in ratios varying from 3 : 1 to 3 : 1·5 the colour changed from green, passing through the intermediate greyish hue, to a brilliant violet. The intermediate stage occurred within 0·1 *p*H unit, and the actual *p*H value varied slightly with the ratio, being from *p*H 7·15 to *p*H 7·35. The purest grey was secured with 3 : 1·5 mixture. Such an end-point can easily be detected, even in artificial light.

Bromophenol blue, bromocresol green, bromothymol blue and thymol blue (alkaline range) find a place in the third class in that they change from yellow to blue. At their change-point they are green and therefore require a suitable red dye to produce a neutral or grey colour, in which the total change would be from orange, through grey, to purple. Kolthoff essayed to use neutral red to give the colour to complement the green at the transition-point of bromothymol blue. According to Smith the colour so obtained is dirty orange. He recommends 0·09 per cent. of bromothymol blue and 0·08 per cent. of alizarin red (B.D.H.). At *p*H 6·8 the colour changes from orange-red to orange-grey, pure grey at *p*H 6·9, blue-grey at *p*H 7·0 to a clear purple-blue. Besides having an end-point at *p*H 7, this mixture changes from yellow to orange-red between *p*H 4–6 and so gives warning in the case of titrations with alkali of the approaching end-point. Another mixture giving a grey transition colour at *p*H 4·5 contains 0·4 per cent. of bromocresol green and 0·09 per cent. of neutral red.

Phenolphthalein and cresolphthalein alone belong to the fourth group. Their change is from colourless to redness of increasing intensity, but not of hue. The complementary

colour, green, is required, but in order to produce the grey it is clear that just that intensity of the correct green must be used to neutralise the red developed at some particular *p*H. With this type of indicator it would appear that the transition-point could be adjusted to any desired *p*H. Smith was able to prepare a satisfactory green to match the red of phenolphthalein by using a 2 : 1 mixture of methyl red and methylene blue, which incidentally forms a satisfactory achromatic indicator at *p*H 5·4. His observations for the achromatic phenolphthalein mixtures are given in Table 116.

TABLE 116

"ACHROMATIC" PHENOLPHTHALEIN MIXTURES

Composition of Mixture.			*p*H at Transition Point.
Methyl Red.	Methylene Blue.	Phenolphthalein.	
2	1	100	8·25
2	1	30	8·55
2	1	15	8·80
2	1	7·5	9·00
2	1	3·0	9·40
2	1	1·9	9·80

As an example of mixed achromatic indicators with two end-points, Smith gives the following :—

Bromocresol Green	0·02 gram.
Neutral Red	0·0045 ,,
p-Nitrophenol	0·95 ,,
Phenolphthalein	0·60 ,,
Alcohol	100 c.c.

This indicator changes from orange, through grey at *p*H 4·5 to blue, changing slowly to green and then again through grey at *p*H 8·5 to red. These two transition-points render the mixture particularly serviceable in the titration of phosphoric acid (see Fig. 56).

Smith was unable to prepare useful mixtures from the nitrophenols (group 5).

Pierre, Tully and Ashburn (*Ind. Eng. Chem., Anal. Edn.*, 1938, **10**, 72) and Horat (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 264) have described some achromatic indicator mixtures. Those of the former workers are given in Table 117.

TABLE 117

Achromatic Indicator Mixture.	*p*H.	Colour Change.
*M.O. 0·02% + B.C.G. 0·1%	4·3	Orange—yellow—green
M.O. 0·1% + I.C. 0·25%	4·1	Violet—grey—green
M.O. 0·1% + An.B. 0·1%	4·3	,, ,, ,,
M.O. 0·05% + Ac.B. 0·1%	4·2	,, ,, ,,
M.O. 0·1% + Ac.G. 0·1%	3·6	,, ,, ,,
M.O. 0·1% + X.C. 0·28%	3·8	,, ,, ,,
M.O. 0·2% + M.B. 0·05%	3·9	,, ,, ,,
E.O. 0·2% + X.C.FF. 0·28%	4·2	,, ,, ,,
E.O. 0·2% + M.G. 0·1%	4·3	Blue—grey—green
E.O. 0·02% + B.C.G. 0·1%	4·5	Orange—yellow—green
M.R. 0·13% + M.B. 0·083%	5·2	Violet—grey—green
*A.R.S. 0·5% + M.B. 0·063%	4·3	Green—grey—wine
B.P.B. 0·1% + M.B. 0·03%	3·5	Green—grey—blue

M.O. = Methyl orange.
I.C. = Indigo carmine.
Ac.B. = Acid blue.
X.C. = Xylene cyanole.
E.O. = Ethyl orange.
M.R. = Methyl red.
B.P.B. = Bromophenol blue.
B.C.G. = Bromocresol green.
An.B. = Aniline blue.
Ac.G. = Acid green.
M.B. = Methylene blue.
M.G. = Methyl green.
A.R.S. = Alizarin red S.

The indicator mixtures marked with an asterisk were found satisfactory in the titration of phosphoric acid, especially as the transition colour appears at *p*H 4·3, the first end-point *p*H. Precipitates may interfere with achromatic indicators owing to adsorption of the dye.

Detection of End-Points by (*a*) Spectroscope, (*b*) Photo-electric Cell.

The location of the end-points of titrations of coloured solutions to which indicators are added has been investigated by Bruère (*Bull. Soc. Chim. biol.*, 1928, **10**, 283) by following the variation in the absorption spectra with the spectroscope. The indicators belonged to the phthalein and sulphonephthalein groups, and it was found that accurate results could be obtained.

An automatic method of titration based on the variation in the intensity of light transmitted through a solution containing indicator in the vicinity of the colour-change has recently been described by Müller and Partridge (*J. Ind. Eng. Chem.*, 1928, **20**, 423). Light passes through the titration cell on to a photo-electric cell, and the variation in the intensity of light during the titration is sufficient to actuate the photoelectric cell. The current so generated is amplified by passing through a valve, when it is made to operate a relay which controls the volume of

titrant run in from a burette. The method is stated to be capable of much greater precision than the visual detection of the indicator colour-change, and this claim is substantiated by the *plate current —colour-change* curves. The whole procedure is entirely automatic and rapid which should make it of importance in routine analysis.

Titration Error of Indicators.

The fact that an indicator behaves either as an acid or a base is often overlooked as regards the error which this factor may introduce into a volumetric estimation. The following figures show that the errors involved may indeed be quite considerable. Two drops (= 0·1 c.c.) of a 1 per cent. solution of phenolphthalein requires 0·06 c.c. of N/10-alkali; 0·1 c.c. of 1 per cent. methyl orange, 0·03 c.c. N/10-titrant; 0·1 c.c. of 1 per cent. methyl red, 0·03 c.c. N/10-titrant.

CHAPTER XIX

INDICATOR PAPERS AND THEIR USE FOR THE APPROXIMATE DETERMINATION OF *p*H

LITMUS papers have long been used to detect whether a solution is acid or alkaline. The question whether litmus and other indicator papers could be used for the approximate determination of *p*H has been considered by Hemple (*Compt. rend. Lab. Carlsberg*, 1917, **13**, 1), Haas (*J. Biol. Chem.*, 1919, **38**, 49) and Kolthoff (*Pharm. Weekblad*, 1921, **58**, 962; see also "Säure-Basen-Indicatoren," p. 374, Berlin, 1932), whilst Behrens (*Z. anal. Chem.*, 1928, **73**, 129) and Kolthoff (*op. cit.*, p. 379; *Biochem. Z.*, 1927, **189**, 26) have shown that a series of papers, impregnated with "*achromatic*" indicators (see page 388) so as to give their transition shades, usually grey, at definite *p*H values, could be used with advantage.

Difficulties arise in the use of papers through (*a*) the possibility of an indicator being adsorbed to differing extents in either its acid or alkaline form, (*b*) differences in adsorption of the solute responsible for the *p*H value of the test-solution, and (*c*) the fact that the paper itself contains buffering agents such as basic aluminium sulphate and the sizing agent, present as abietate, etc. These, however, can largely be removed by treatment with hydrochloric acid and then with ammonia solution. Afterwards thorough washing with distilled water is necessary, followed by drying. A hard filter paper or the special papers now available for "spot analysis" are probably the most satisfactory. Good notepaper may also be used.

Hemple found that lackmoid papers could be used to determine *p*H values between *p*H 3·8 and 6·0 with an accuracy of 0·2–0·5 *p*H unit. She prepared a series of lackmoid papers, buffered at definite *p*H values, which served as colour standards. The colour produced when a drop of the solution under investigation was placed on a lackmoid paper was then compared with the colour standards and the *p*H thus estimated.

It would appear that in the case of unbuffered or poorly buffered solutions the principle of isohydry (see p. 371) could be advantageously employed. Thus a drop of the test-solution may be applied to each of the indicator-papers, adjusted to different

*p*H values, until the particular paper is found which gives no change in colour. The *p*H of the solution would then be that corresponding to the particular indicator paper.

Haas adopts a similar method to that of Hemple, with the exception that before comparing the colours he dries the indicator paper strips over soda-lime. The standard colour strips may be preserved by coating with good paraffin. Besides lackmoid paper he also used methyl orange paper for *p*H 2·4–3·8; bromophenol blue paper, *p*H 3·4–4·6; alizarin paper, *p*H 4·0–6·0; azolitmin paper, *p*H 6·2–8·0, and neutral red paper, *p*H 7·0–9·0. The accuracy was 0·2–0·4 *p*H unit. A more extensive investigation of the problem was made by Kolthoff, who found Schleicher and Schüll's filter paper for capillary analysis very suitable. He also found that no advantage could be obtained by drying the indicator paper to which the test-solution had been added. Furthermore, he prefers to dip the end of the indicator paper in the solution and allow the solution to rise up the paper by capillarity. He agrees that the accuracy obtained with indicator papers is about 0·2 *p*H unit. Table 118 summarises his conclusions, together with the concentrations of the indicator-solutions in which the papers were originally immersed.

TABLE 118

INDICATOR PAPERS SUITABLE FOR APPROXIMATE *p*H MEASUREMENTS (KOLTHOFF)

Paper.	Concentration of Indicator Solution.	*p*H Range.
Congo Red (Hard Paper)	0·1%	2·5 – 4·0
Methyl orange	0·2%	2·6 – 4·0
Alizarin (Hard Paper)	0·1%	4·6 – 5·8
Blue Lackmoid	0·1%	4·6 – 6·0
Brilliant Yellow	0·2%	6·8 – 8·5
Red Litmus	—	6·6 – 8·0
Blue Litmus	—	6·0 – 8·0
Azolitmin	1%	5·5 – 8·0
Phenol Red	0·1%	7·0 – 8·2
Cresol Red	0·1%	7·6 – 9·0
α-Naphtholphthalein (Capillary Paper)	0·2%	8·2 – 9·5
Turmeric	0·1%	7·0 – 9·0
Thymolphthalein	0·1%	10·0–11·0

Litmus papers may be prepared in the following way. Boil the litmus cakes with alcohol, dry and extract with cold distilled water. Acidify the violet extract with sulphuric acid, or else render the extract alkaline with sodium hydroxide, so as to give

the desired colours and then immerse the prepared papers in the resulting solutions.

In preparing Congo Red papers the purified dyestuff should be used. To purify the crude Congo Red, Horst (*Z. angew. Chem.*, 1925, **38**, 947) dissolves 1 gram in 30–35 c.c. of hot water, allows the solution to stand for a short time in order to allow any insoluble matter and any sparingly soluble calcium or magnesium salts that may be present to separate; filters through glass-wool, warms the filtrate and adds sodium chloride to salt out the dyestuff. The Congo red is then washed with a hot solution of salt (10 per cent.). The acid of the dye is precipitated by stirring a solution with hydrochloric acid. After decanting the liquid, the acid is dried by pressing between filter papers. It is then dissolved in a hot solution of ammonia to form a 0·1 per cent solution, in which the filter paper strips are soaked.

Achromatic Indicator Papers.

Papers, incorporating mixed indicators, together with suitable dyestuffs to provide colours which are complementary to the colours set up at various *p*H values, have been described by Behrens (*loc. cit.*). The papers are prepared by soaking filter paper (Schleicher and Schüll, No. 602, Hard) several times in the solutions described in Table 119, drying, cutting into strips and keeping in a desiccator. These papers require, of course, no comparison colour standards and are suitable only for solutions which are well buffered.

Kolthoff (*op. cit.*, p. 379) gives the following details for making papers with transition colours at *p*H 8·0, 9·3 and 9·7.

*p*H 8·0 : 50 c.c. cresol red (0·1 per cent. solution in alcohol), 10 c.c. brilliant green and 40 c.c. water. At *p*H 8·0 the colour is bluish grey, below *p*H 8·0 green and above *p*H 8·0 lilac.

*p*H 9·3 : Hard filter paper is soaked in 70 per cent. alcohol solution of phenolphthalein (0·3 per cent.) and α-naphtholphthalein (0·1 per cent.). The paper is pale rose in colour, at *p*H 9·2 it is pale green and at *p*H 9·4 it gives a rose circle surrounded by a green zone. At *p*H 9·6 it is appreciably violet surrounded by a green ring, and at *p*H 9·8 it is deep purple.

*p*H 9·7 : This paper is prepared from a solution containing 0·1 per cent phenolphthalein and 0·1 per cent. α-naphtholphthalein. At *p*H 9·4 it is coloured pure green, at *p*H 9·6 pale rose-violet with a green ring, and at *p*H 9·8 a reddish-violet.

TABLE 119

BEHRENS' ACHROMATIC INDICATOR PAPERS

Solutions used :

Bordeaux Red (0·1 per cent., water) ; Brilliant Green (0·1 per cent., water) ; Methylene Blue (0·1 per cent., water) ; Metanil Yellow (0·1 per cent., alcohol) ; Methyl orange (0·05 per cent. in 50 per cent. alcohol-water) ; Bromphenol Blue (0·1 per cent., alcohol) ; Bromocresol Green (0·1 per cent., alcohol) ; Bromocresol purple (3·1 per cent., alcohol) ; Methyl Red (0·1 per cent., alcohol) ; Phenol Red. (0·1 per cent., alcohol).

Transition Colour given at *p*H	Composition of Solution. c.c.	Colour at *p*H below Indicator *p*H.	Colour at *p*H above Indicator *p*H.
1·5	M.Y. 40 ; B.G. 5 ; M.B. 10 ; conc. HCl 5 ; Alcohol, 10 ; H_2O 5.	lilac	green
2·0	M.Y. 40 ; B.R. 20 ; M.B. 20 ; conc. HCl 5 ; Alcohol 10 ; H_2O 5.	lilac	bluish green
2·5	M.O. 75 ; B.G. 18 ; M.B. 12.	violet	bluish green
3·0	M.O. 75 ; M.B. 12.	lilac	green
3·5	M.O. 75 ; B.R. 4·5 ; M.B. 12.	red	yellow-green
4·0	B.P.B. 50 ; M.Y. 20 ; H_2O 30.	yellow-green	violet
4·5	B.C.G. 50 ; B.R. 17·5 ; H_2O 32·5.	yellow-rose	blue
5·0	B.C.G. 50 ; B.R. 30 ; M.Y. 15.	yellow-rose	green-blue
5·5	B.C.P. 50 ; B.R. 14 ; M.B. 4·5 ; H_2O 32.	dirty yellow	violet
6·0	B.C.P. 50 ; B.R. 2 ; M.Y. 6 ; H_2O 54.	dirty yellow	lilac
6·5	M.R. 50 ; B.R. 8 ; M.B. 15 ; H_2O 27 ; + 1 drop NaOH solution.	red	green
7·0	P.R. 50 ; M.B. 7·5 ; H_2O 42.	yellow-green	red
7·5	P.R. 50 ; B.G. 30 ; H_2O 20.	green	lilac

CHAPTER XX

NOTES ON THE PREPARATION OF SOME INDICATORS

MOST of the indicators can now be procured commercially. No attempt will therefore be made here to deal with their preparation in anything like an exhaustive manner. Nevertheless, it is thought that it might be of service to some readers if a few practical details of the methods of preparation of certain indicators and, especially, of some of the newer ones be included.

Methyl Orange.

Method I.—Dimethylaniline is allowed to react on diazobenzene sulphonic acid in a hydrochloric acid solution.

Method II.—From aniline and dimethylaniline. Approximately equimolecular quantities of these compounds are added to an equal weight of concentrated hydrochloric acid solution and the resulting mixture dissolved in about 15 times its weight of water. Diazotise by slowly adding $NaNO_2$, in an amount equal to one-third of the weight of HCl used, and an amount of NaOH equal to one-half of the $NaNO_2$, both dissolved in about 5 times their total weight of water. Dissolve the precipitate in HCl, reprecipitate with NaOH, wash and crystallise from hot alcohol. Sulphonate by dissolving in an excess of concentrated H_2SO_4. Pour into water and dissolve in alkali. Recrystallise from hot water.

Methyl Red.

Diazotise a well-stirred solution, composed of 20 grams of anthranilic acid, 60 c.c. of concentrated HCl and 600 c.c. of water, with a solution of 10 grams of $NaNO_2$ in 50 c.c. of water. Stand for half an hour, if no HNO_2 remains, transfer to a solution of 19 grams of dimethylaniline in 20 c.c. of concentrated HCl and 20 c.c. of water. Stir for half an hour and then add 200 grams of sodium acetate. Raise carefully to 40° C. and maintain there for three hours. Stand for 24 hours at room temperature. Filter. Wash. To purify, dissolve in 100 c.c. of a 5 per cent. NaOH solution at 70° C. Carefully add a boiling solution of hydrochloric acid (90 c.c. concentrated HCl + 270 c.c. of water). On

cooling, the hydrochloride of methyl red separates out as steely blue crystals. Wash with 100 c.c. of 10 per cent. HCl. Dry.

Yield: 28 grams.

To prepare water-soluble methyl red, dissolve the above crystals in 100 c.c. of 5 per cent. NaOH solution. Cool and salt out with 5 grams of NaCl. Wash. Dry below 40° C.

Yield: 28 grams.

See also ("Organic Syntheses," Vol. II. Edited by J. B. Conant, p. 47. Chapman & Hall, 1922).

Neutral Red.

Dissolve 1 g.-mol. of *m*-toluylene diamine in 2½ litres of water at 30° C. Add paste of 1 g.-mol. of nitrosodimethylaniline hydrochloride and 500 c.c. of water. Stir for 1 hour. Stand 18 hours. Add 7 litres of water, boil and blow air through for half an hour and then add 1 g.-mol. HCl. Salt out. Purify by making 5 per cent. solution in water, and precipitating with 10 per cent. HCl.

Phenolphthalein.

Heat at 120° for several hours a mixture of phenol, phthalic anhydride and concentrated H_2SO_4 in the respective proportion by weight of 10 : 5 : 4. Wash with water, dissolve in dilute alkali. Reprecipitate with acid, wash, and dry. Purify by crystallisation from alcohol, after treatment with charcoal, and diluting with little water. White crystals. Melting-point, 250° C.

α-Naphtholphthalein.

Grind 28 grams of α-naphthol to a fine powder and mix in a mortar with 15·2 grams of phthalic anhydride. Place in an enamelled iron digester with 3 c.c. of concentrated H_2SO_4, then heat on water-bath with constant stirring at 60° C. for 4 hours, taking care that the temperature does not rise above 65° C. Wash by decantation with water until acid free. Treat with 4 litres of ½ per cent. NaOH solution at 70° C. Filter off the blue by-product. Cool. Neutralise about a half of the alkali with HCl, and the remainder by passing carbon dioxide. Brown solid remains. To purify, dissolve in NaOH and reprecipitate as above. Yield: 7 grams.

Thymolphthalein.

Heat a mixture of equivalent weights of thymol and phthalic acid to about 150° C. When action ceases, cool, wash with dilute

HCl, then with water and afterwards with petroleum spirit. Recrystallise from ether-alcohol. Melting-point: 253° C.

Sulphonephthaleins.

To prepare sulphonephthalein indicators of the type of phenol red, a very convenient starting material is *o*-sulphobenzoic anhydride. It may be prepared from dithiosalicylic acid which is now on the market, or from anthranilic acid by the sulphydrate Sandmeyer reaction. The potassium salt of ortho-sulphobenzoic acid may be prepared as follows: stir 300 c.c. of 65° Tw. nitric acid in a 5-litre vessel with 1·2 litres of water. Heat to about 70° C. on a steam-bath and slowly add 153 grams of dithiosalicylic acid (frothing!). Add 40 c.c. of nitric acid, evaporate to small bulk, and then with stirring to dryness in an enamelled iron dish on a steam-bath. Dissolve in 250 c.c. of hot water and filter. Treat filtrate whilst boiling with 90 grams of KCl. Cool and dry the potassium salt, which separates, in a steam oven. The amount so obtained is about 171 grams, and this is now converted into the anhydride by the action of thionyl chloride (137 c.c.) under a reflux condenser on a steam-bath for 3 hours. After distilling off the excess of thionyl chloride under reduced pressure, the anhydride is extracted by refluxing with 300 c.c. of dry benzene. Filter and set to crystallise. Dry crystals in a steam oven. Re-extract residue with mother-liquor. Yield: 98 grams.

Phenol Red.

Melt 22·4 grams of phenol and add 20 grams of finely divided *o*-sulphobenzoic anhydride, with stirring, at 120° C. in an oil-bath. Heat for 2 hours at 120° to 125° C. and then for 8 hours at 135° to 140° C. Cool. Boil with water to extract any uncombined phenol. Dissolve residue in 11 c.c. of 30 per cent. NaOH at 60°, cool, precipitate with 12 c.c. of concentrated HCl, filter and wash. Yield: 20 grams.

Ortho-Cresol Red.

Heat 6·5 grams of *o*-cresol at 120° to 125° C., add 5 grams of *o*-sulphobenzoic anhydride, continue heating with stirring for 2 hours and finally at 135° to 140° C. for 8 hours. Extract cooled mass with *ca.* 50 c.c. of dilute NaOH, acidify with *ca.* 50 c.c. of HCl and boil to drive off excess of cresol. Dissolve solid in dilute NaOH at 60° to 70° C. Filter. Cool, pour into dilute HCl with agitation. Filter off precipitated *o*-cresol red, wash and dry. Yield: 7 grams.

Bromocresol Purple.

Dissolve 5 grams *o*-cresol red in 50 c.c. of glacial acetic acid. Heat to boiling under reflux, then add 2 c.c. of bromine in 20 c.c. of glacial acetic acid and gently boil for 1 hour. Cool. Filter off the bromocresol purple, wash with a little acetic acid and dry. Yield : 4 grams.

Thymol Blue.

Heat and stir a mixture of 38 grams of thymol and 25 grams of *o*-sulphobenzoic anhydride in a salt-bath at 105° C. for 12 hours. Cool, add 50 c.c. of water and heat on a water-bath. Pour the tarry liquid thus formed into 400 c.c. of water and add 12 grams of sodium carbonate. Extract oily matter with benzene. Dilute clear solution to 700 c.c., filter, precipitate with dilute HCl. Purify by redissolving in NaOH and reprecipitating with acid. Yield : 18 grams.

Bromothymol Blue.

Dissolve 5 grams of thymol blue in 30 c.c. of glacial acetic acid. Raise to boiling, add 2 c.c. of bromine in 10 c.c. of acetic acid and boil gently for half an hour. Evaporate to dryness on a water-bath and recrystallise from alcohol. Yield : 6 grams.

Bromophenol Blue.

Shake up 18 grams of phenol red with 90 c.c. of glacial acetic acid and after adding a solution of 10 c.c. of bromine in 40 c.c. of glacial acetic acid, heat on a steam-bath for 1½ hours. Cool. Filter off bromophenol blue crystals, wash with dilute acetic acid and dry. Yield : 27 grams.

For further information see Prideaux, ("The Theory and Use of Indicators." London, Constable. Lubs and Clark, *J. Wash. Acad. Science*, 1915, **5**, 609. Fairbrother, *Industrial Chemist*, 1929).

APPENDIX

*p*H Values at 18°, 25° and 38° corresponding to Hydrogen Electrode Potentials, E_{H_2} Volt

$$E_{H_2} = -\frac{RT}{2{\cdot}303F} \cdot pH$$

This Table may also be used to calculate *p*H values from the Potential of the Quinhydrone Electrode, $E_{Quin.}$ From pages 22, 75 and 76 it is seen that

$$E_{Quin.} = \lambda - \frac{RT}{2{\cdot}303F} pH$$

whence

$$E_{Quin.} - \lambda = -\frac{RT}{2{\cdot}303F} pH,$$

λ at 18° C. = 0·7044 volt,
λ at 25° C. = 0·6992 volt,
λ at 38° C. = 0·6896 volt.

Volt. −ve	18°	25°	38°	Volt. −ve	18°	25°	38°
0·001	0·02	0·02	0·02	0·027	0·47	0·46	0·44
0·002	0·04	0·03	0·03	0·028	0·49	0·47	0·45
0·003	0·05	0·05	0·05	0·029	0·50	0·49	0·47
0·004	0·07	0·07	0·07	0·030	0·52	0·51	0·49
0·005	0·09	0·09	0·08	0·031	0·54	0·52	0·50
0·006	0·10	0·10	0·10	0·032	0·55	0·54	0·52
0·007	0·12	0·12	0·11	0·033	0·57	0·56	0·54
0·008	0·14	0·14	0·13	0·034	0·59	0·58	0·55
0·009	0·16	0·15	0·15	0·035	0·61	0·59	0·57
0·010	0·17	0·17	0·16	0·036	0·62	0·61	0·58
0·011	0·19	0·19	0·18	0·037	0·64	0·63	0·60
0·012	0·21	0·20	0·19	0·038	0·66	0·64	0·62
0·013	0·23	0·22	0·21	0·039	0·68	0·66	0·63
0·014	0·24	0·24	0·23	0·040	0·69	0·68	0·65
0·015	0·26	0·25	0·24	0·041	0·71	0·69	0·67
0·016	0·28	0·27	0·26	0·042	0·73	0·71	0·68
0·017	0·29	0·29	0·28	0·043	0·75	0·73	0·70
0·018	0·31	0·30	0·29	0·044	0·76	0·74	0·71
0·019	0·33	0·32	0·31	0·045	0·78	0·76	0·73
0·020	0·35	0·34	0·32	0·046	0·80	0·78	0·75
0·021	0·36	0·36	0·34	0·047	0·81	0·80	0·76
0·022	0·38	0·37	0·36	0·048	0·83	0·81	0·78
0·023	0·40	0·39	0·37	0·049	0·85	0·83	0·79
0·024	0·42	0·41	0·39	0·050	0·87	0·85	0·81
0·025	0·43	0·42	0·41	0·051	0·88	0·86	0·83
0·026	0·45	0·44	0·42	0·052	0·90	0·88	0·84

Volt. —ve	18°	25°	38°	Volt. —ve	18°	25°	38°
0·053	0·92	0·90	0·86	0·109	1·89	1·84	1·77
0·054	0·94	0·91	0·88	0·110	1·91	1·86	1·78
0·055	0·95	0·93	0·89	0·111	1·92	1·88	1·80
0·056	0·97	0·95	0·91	0·112	1·94	1·89	1·82
0·057	0·99	0·96	0·92	0·113	1·96	1·91	1·83
0·058	1·01	0·98	0·94	0·114	1·97	1·93	1·85
0·059	1·02	1·00	0·96	0·115	1·99	1·95	1·86
0·060	1·04	1·02	0·97	0·116	2·01	1·96	1·88
0·061	1·06	1·03	0·99	0·117	2·03	1·98	1·90
0·062	1·07	1·05	1·01	0·118	2·04	2·00	1·91
0·063	1·09	1·07	1·02	0·119	2·06	2·01	1·93
0·064	1·11	1·08	1·04	0·120	2·08	2·03	1·95
0·065	1·13	1·10	1·05	0·121	2·10	2·05	1·96
0·066	1·14	1·12	1·07	0·122	2·11	2·06	1·98
0·067	1·16	1·13	1·09	0·123	2·13	2·08	1·99
0·068	1·18	1·15	1·10	0·124	2·15	2·10	2·01
0·069	1·20	1·17	1·12	0·125	2·17	2·11	2·03
0·070	1·21	1·18	1·14	0·126	2·18	2·13	2·04
0·071	1·23	1·20	1·15	0·127	2·20	2·15	2·06
0·072	1·25	1·22	1·17	0·128	2·20	2·17	2·07
0·073	1·26	1·24	1·18	0·129	2·23	2·18	2·09
0·074	1·28	1·25	1·20	0·130	2·25	2·20	2·11
0·075	1·30	1·27	1·22	0·131	2·27	2·22	2·12
0·076	1·32	1·29	1·23	0·132	2·29	2·23	2·14
0·077	1·33	1·30	1·25	0·133	2·30	2·25	2·16
0·078	1·35	1·32	1·26	0·134	2·32	2·27	2·17
0·079	1·37	1·34	1·28	0·135	2·34	2·28	2·19
0·080	1·39	1·35	1·30	0·136	2·36	2·30	2·20
0·081	1·40	1·37	1·31	0·137	2·37	2·32	2·22
0·082	1·42	1·39	1·33	0·138	2·39	2·33	2·24
0·083	1·44	1·40	1·35	0·139	2·41	2·35	2·25
0·084	1·46	1·42	1·36	0·140	2·43	2·37	2·27
0·085	1·47	1·44	1·38	0·141	2·44	2·39	2·29
0·086	1·49	1·46	1·39	0·142	2·46	2·40	2·30
0·087	1·51	1·47	1·41	0·143	2·48	2·42	2·32
0·088	1·52	1·49	1·43	0·144	2·49	2·44	2·33
0·089	1·54	1·51	1·44	0·145	2·51	2·45	2·35
0·090	1·56	1·52	1·46	0·146	2·53	2·47	2·37
0·091	1·58	1·54	1·48	0·147	2·55	2·49	2·38
0·092	1·59	1·56	1·49	0·148	2·56	2·50	2·40
0·093	1·61	1·57	1·51	0·149	2·58	2·52	2·42
0·094	1·63	1·59	1·52	0·150	2·60	2·54	2·43
0·095	1·65	1·61	1·54	0·151	2·62	2·55	2·45
0·096	1·66	1·62	1·56	0·152	2·63	2·57	2·46
0·097	1·68	1·64	1·57	0·153	2·65	2·59	2·48
0·098	1·70	1·66	1·59	0·154	2·67	2·61	2·50
0·099	1·72	1·68	1·61	0·155	2·69	2·62	2·51
0·100	1·73	1·69	1·62	0·156	2·70	2·64	2·53
0·101	1·75	1·71	1·64	0·157	2·72	2·66	2·55
0·102	1·77	1·73	1·65	0·158	2·74	2·67	2·56
0·103	1·78	1·74	1·67	0·159	2·75	2·69	2·58
0·104	1·80	1·76	1·69	0·160	2·77	2·71	2·59
0·105	1·82	1·78	1·70	0·161	2·79	2·72	2·61
0·106	1·84	1·79	1·72	0·162	2·81	2·74	2·63
0·107	1·85	1·81	1·73	0·163	2·82	2·76	2·64
0·108	1·87	1·83	1·75	0·164	2·84	2·77	2·66

Volt. —ve	18°	25°	38°	Volt. —ve	18°	25°	38°
0·165	2·86	2·79	2·67	0·221	3·83	3·74	3·58
0·166	2·88	2·81	2·69	0·222	3·85	3·76	3·60
0·167	2·89	2·83	2·71	0·223	3·86	3·77	3·61
0·168	2·91	2·84	2·72	0·224	3·88	3·79	3·63
0·169	2·93	2·86	2·74	0·225	3·90	3·81	3·65
0·170	2·94	2·88	2·76	0·226	3·91	3·82	3·66
0·171	2·96	2·89	2·77	0·227	3·93	3·84	3·68
0·172	2·98	2·91	2·79	0·228	3·95	3·86	3·70
0·173	3·00	2·93	2·80	0·229	3·97	3·87	3·71
0·174	3·01	2·94	2·82	0·230	3·98	3·89	3·73
0·175	3·03	2·96	2·84	0·231	4·00	3·91	3·74
0·176	3·05	2·98	2·85	0·232	4·02	3·92	3·76
0·177	3·07	2·99	2·87	0·233	4·04	3·94	3·78
0·178	3·08	3·01	2·89	0·234	4·05	3·96	3·79
0·179	3·10	3·03	2·90	0·235	4·07	3·98	3·81
0·180	3·12	3·05	2·92	0·236	4·09	3·99	3·83
0·181	3·14	3·06	2·93	0·237	4·11	4·01	3·84
0·182	3·15	3·08	2·95	0·238	4·12	4·03	3·86
0·183	3·17	3·10	2·97	0·239	4·14	4·04	3·87
0·184	3·19	3·11	2·98	0·240	4·16	4·06	3·89
0·185	3·20	3·13	3·00	0·241	4·17	4·08	3·91
0·186	3·22	3·15	3·02	0·242	4·19	4·09	3·92
0·187	3·24	3·16	3·03	0·243	4·21	4·11	3·94
0·188	3·26	3·18	3·05	0·244	4·23	4·13	3·96
0·189	3·27	3·20	3·06	0·245	4·24	4·14	3·97
0·190	3·29	3·21	3·08	0·246	4·26	4·16	3·99
0·191	3·31	3·23	3·10	0·247	4·28	4·18	4·00
0·192	3·33	3·25	3·11	0·248	4·30	4·20	4·02
0·193	3·34	3·27	3·13	0·249	4·31	4·21	4·04
0·194	3·36	3·28	3·14	0·250	4·33	4·23	4·05
0·195	3·38	3·30	3·16	0·251	4·35	4·25	4·07
0·196	3·40	3·32	3·18	0·252	4·37	4·26	4·08
0·197	3·41	3·33	3·19	0·253	4·38	4·28	4·10
0·198	3·43	3·35	3·21	0·254	4·40	4·30	4·12
0·199	3·45	3·37	3·23	0·255	4·42	4·31	4·13
0·200	3·46	3·38	3·24	0·256	4·43	4·33	4·15
0·201	3·48	3·40	3·26	0·257	4·45	4·35	4·17
0·202	3·50	3·42	3·27	0·258	4·47	4·36	4·18
0·203	3·52	3·43	3·29	0·259	4·49	4·38	4·20
0·204	3·53	3·45	3·31	0·260	4·50	4·40	4·21
0·205	3·55	3·47	3·32	0·261	4·52	4·42	4·23
0·206	3·57	3·48	3·34	0·262	4·54	4·43	4·25
0·207	3·59	3·50	3·36	0·263	4·56	4·45	4·26
0·208	3·60	3·52	3·37	0·264	4·57	4·47	4·28
0·209	3·62	3·54	3·39	0·265	4·59	4·48	4·30
0·210	3·64	3·55	3·40	0·266	4·61	4·50	4·31
0·211	3·66	3·57	3·42	0·267	4·62	4·52	4·33
0·212	3·67	3·59	3·44	0·268	4·64	4·53	4·34
0·213	3·69	3·60	3·45	0·269	4·66	4·55	4·36
0·214	3·71	3·62	3·47	0·270	4·68	4·57	4·38
0·215	3·72	3·64	3·49	0·271	4·69	4·58	4·39
0·216	3·74	3·65	3·50	0·272	4·71	4·60	4·41
0·217	3·76	3·67	3·52	0·273	4·73	4·62	4·43
0·218	3·78	3·69	3·53	0·274	4·75	4·64	4·44
0·219	3·79	3·70	3·55	0·275	4·76	4·65	4·46
0·220	3·81	3·72	3·57	0·276	4·78	4·67	4·47

Volt. — ve	18°	25°	38°	Volt. — ve	18°	25°	38°
0·277	4·80	4·69	4·49	0·333	5·77	5·63	5·40
0·278	4·82	4·70	4·51	0·334	5·79	5·65	5·41
0·279	4·83	4·72	4·52	0·335	5·80	5·67	5·43
0·280	4·85	4·74	4·54	0·336	5·82	5·68	5·45
0·281	4·87	4·75	4·55	0·337	5·84	5·70	5·46
0·282	4·88	4·77	4·57	0·338	5·85	5·72	5·48
0·283	4·90	4·79	4·59	0·339	5·87	5·73	5·50
0·284	4·92	4·80	4·60	0·340	5·89	5·75	5·51
0·285	4·94	4·82	4·62	0·341	5·91	5·77	5·53
0·286	4·95	4·84	4·64	0·342	5·92	5·79	5·54
0·287	4·97	4·86	4·65	0·343	5·94	5·80	5·56
0·288	4·99	4·87	4·67	0·344	5·96	5·82	5·58
0·289	5·01	4·89	4·68	0·345	5·98	5·84	5·59
0·290	5·02	4·91	4·70	0·346	5·99	5·85	5·61
0·291	5·04	4·92	4·72	0·347	6·01	5·87	5·62
0·292	5·06	4·94	4·73	0·348	6·03	5·89	5·64
0·293	5·08	4·96	4·75	0·349	6·05	5·90	5·66
0·294	5·09	4·97	4·77	0·350	6·06	5·92	5·67
0·295	5·11	4·99	4·78	0·351	6·08	5·94	5·69
0·296	5·13	5·01	4·80	0·352	6·10	5·95	5·71
0·297	5·14	5·02	4·81	0·353	6·11	5·97	5·72
0·298	5·16	5·04	4·83	0·354	6·13	5·99	5·74
0·299	5·18	5·06	4·85	0·355	6·15	6·00	5·75
0·300	5·20	5·07	4·86	0·356	6·17	6·02	5·77
0·301	5·21	5·09	4·88	0·357	6·18	6·04	5·79
0·302	5·23	5·11	4·90	0·358	6·20	6·06	5·80
0·303	5·25	5·13	4·91	0·359	6·22	6·07	5·82
0·304	5·27	5·14	4·93	0·360	6·24	6·09	5·84
0·305	5·28	5·16	4·94	0·361	6·25	6·11	5·85
0·306	5·30	5·18	4·96	0·362	6·27	6·12	5·87
0·307	5·32	5·19	4·98	0·363	6·29	6·14	5·88
0·308	5·34	5·21	4·99	0·364	6·30	6·16	5·90
0·309	5·35	5·23	5·01	0·365	6·32	6·17	5·92
0·310	5·37	5·24	5·02	0·366	6·34	6·19	5·93
0·311	5·39	5·26	5·04	0·367	6·36	6·21	5·95
0·312	5·40	5·28	5·06	0·368	6·37	6·23	5·97
0·313	5·42	5·29	5·07	0·369	6·39	6·24	5·98
0·314	5·44	5·31	5·09	0·370	6·41	6·26	6·00
0·315	5·46	5·33	5·11	0·371	6·43	6·28	6·01
0·316	5·47	5·35	5·12	0·372	6·44	6·29	6·03
0·317	5·49	5·36	5·14	0·373	6·46	6·31	6·05
0·318	5·51	5·38	5·15	0·374	6·48	6·33	6·06
0·319	5·53	5·40	5·17	0·375	6·50	6·34	6·08
0·320	5·54	5·41	5·19	0·376	6·51	6·36	6·09
0·321	5·56	5·43	5·20	0·377	6·53	6·68	6·11
0·322	5·58	5·45	5·22	0·378	6·55	6·39	6·13
0·323	5·59	5·46	5·24	0·379	6·56	6·41	6·14
0·324	5·61	5·48	5·25	0·380	6·58	6·43	6·16
0·325	5·63	5·50	5·27	0·381	6·60	6·45	6·18
0·326	5·65	5·51	5·28	0·382	6·62	6·46	6·19
0·327	5·66	5·53	5·30	0·383	6·63	6·48	6·21
0·328	5·68	5·55	5·32	0·384	6·65	6·50	6·22
0·329	5·70	5·57	5·33	0·385	6·67	6·51	6·24
0·330	5·72	5·58	5·35	0·386	6·69	6·53	6·26
0·331	5·73	5·60	5·37	0·387	6·70	6·55	6·27
0·332	5·75	5·62	5·38	0·388	6·72	6·56	6·29

Volt. —ve	18°	25°	38°	Volt. —ve	18°	25°	38°
0·389	6·74	6·58	6·31	0·445	7·71	7·53	7·21
0·390	6·76	6·60	6·32	0·446	7·73	7·54	7·23
0·391	6·77	6·61	6·34	0·447	7·74	7·56	7·25
0·392	6·79	6·63	6·35	0·448	7·76	7·58	7·26
0·393	6·81	6·65	6·37	0·449	7·78	7·60	7·28
0·394	6·82	6·66	6·39	0·450	7·79	7·61	7·29
0·395	6·84	6·68	6·40	0·451	7·81	7·63	7·31
0·396	6·86	6·70	6·42	0·452	7·83	7·65	7·33
0·397	6·88	6·72	6·44	0·453	7·85	7·66	7·34
0·398	6·89	6·73	6·45	0·454	7·86	7·68	7·36
0·399	6·91	6·75	6·47	0·455	7·88	7·70	7·38
0·400	6·93	6·77	6·48	0·456	7·90	7·71	7·39
0·401	6·95	6·78	6·50	0·457	7·92	7·73	7·41
0·402	6·96	6·80	6·52	0·458	7·93	7·75	7·42
0·403	6·98	6·82	6·53	0·459	7·95	7·76	7·44
0·404	7·00	6·83	6·55	0·460	7·97	7·78	7·46
0·405	7·01	6·85	6·56	0·461	7·99	7·80	7·47
0·406	7·03	6·87	6·58	0·462	8·00	7·82	7·49
0·407	7·05	6·88	6·60	0·463	8·02	7·83	7·50
0·408	7·07	6·90	6·61	0·464	8·04	7·85	7·52
0·409	7·08	6·92	6·63	0·465	8·05	7·87	7·54
0·410	7·10	6·94	6·65	0·466	8·07	7·88	7·55
0·411	7·12	6·95	6·66	0·467	8·09	7·90	7·57
0·412	7·14	6·97	6·68	0·468	8·11	7·92	7·59
0·413	7·15	6·99	6·69	0·469	8·12	7·93	7·60
0·414	7·17	7·00	6·71	0·470	8·14	7·95	7·62
0·415	7·19	7·02	6·73	0·471	8·16	7·97	7·63
0·416	7·21	7·04	6·74	0·472	8·18	7·98	7·65
0·417	7·22	7·05	6·76	0·473	8·19	8·00	7·67
0·418	7·24	7·07	6·78	0·474	8·21	8·02	7·68
0·419	7·26	7·09	6·79	0·475	8·23	8·04	7·70
0·420	7·27	7·10	6·81	0·476	8·24	8·05	7·72
0·421	7·29	7·12	6·82	0·477	8·26	8·07	7·73
0·422	7·31	7·14	6·84	0·478	8·28	8·09	7·75
0·423	7·33	7·16	6·86	0·479	8·30	8·10	7·76
0·424	7·34	7·17	6·87	0·480	8·31	8·12	7·78
0·425	7·36	7·19	6·89	0·481	8·33	8·14	7·80
0·426	7·38	7·21	6·91	0·482	8·35	8·15	7·81
0·427	7·40	7·22	6·92	0·483	8·37	8·17	7·83
0·428	7·41	7·24	6·94	0·484	8·38	8·19	7·85
0·429	7·43	7·26	6·95	0·485	8·40	8·20	7·86
0·430	7·45	7·27	6·97	0·486	8·42	8·22	7·88
0·431	7·47	7·29	6·99	0·487	8·44	8·24	7·89
0·432	7·48	7·31	7·00	0·488	8·45	8·25	7·91
0·433	7·50	7·32	7·02	0·489	8·47	8·27	7·93
0·434	7·52	7·34	7·03	0·490	8·49	8·29	7·94
0·435	7·53	7·36	7·05	0·491	8·50	8·31	7·96
0·436	7·55	7·38	7·07	0·492	8·52	8·32	7·97
0·437	7·57	7·39	7·08	0·493	8·54	8·34	7·99
0·438	7·59	7·41	7·10	0·494	8·56	8·36	8·01
0·439	7·60	7·43	7·12	0·495	8·57	8·37	8·02
0·440	7·62	7·44	7·13	0·496	8·59	8·39	8·04
0·441	7·64	7·46	7·15	0·497	8·61	8·41	8·06
0·442	7·66	7·48	7·16	0·498	8·63	8·42	8·07
0·443	7·67	7·49	7·18	0·499	8·64	8·44	8·09
0·444	7·69	7·51	7·20	0·500	8·66	8·46	8·10

Volt. -ve	18°	25°	38°	Volt. -ve	18°	25°	38°
0·501	8·68	8·47	8·12	0·557	9·65	9·42	9·03
0·502	8·70	8·49	8·14	0·558	9·67	9·44	9·04
0·503	8·71	8·51	8·15	0·559	9·68	9·46	9·06
0·504	8·73	8·53	8·17	0·560	9·70	9·47	9·08
0·505	8·75	8·54	8·19	0·561	9·72	9·49	9·09
0·506	8·76	8·56	8·20	0·562	9·73	9·51	9·11
0·507	8·78	8·58	8·22	0·563	9·75	9·52	9·13
0·508	8·80	8·59	8·23	0·564	9·77	9·54	9·14
0·509	8·82	8·61	8·25	0·565	9·79	9·56	9·16
0·510	8·83	8·63	8·27	0·566	9·80	9·57	9·17
0·511	8·85	8·64	8·28	0·567	9·82	9·59	9·19
0·512	8·87	8·66	8·30	0·568	9·84	9·61	9·21
0·513	8·89	8·68	8·32	0·569	9·86	9·63	9·22
0·514	8·90	8·69	8·33	0·570	9·87	9·64	9·24
0·515	8·92	8·71	8·35	0·571	9·89	9·66	9·26
0·516	8·94	8·73	8·36	0·572	9·91	9·69	9·27
0·517	8·95	8·75	8·38	0·573	9·92	9·71	9·29
0·518	8·97	8·76	8·40	0·574	9·94	9·68	9·30
0·519	8·99	8·78	8·41	0·575	9·96	9·73	9·32
0·520	9·01	8·80	8·43	0·576	9·98	9·74	9·34
0·521	9·02	8·81	8·44	0·577	9·99	9·76	9·35
0·522	9·04	8·83	8·46	0·578	10·01	9·78	9·37
0·523	9·06	8·85	8·48	0·579	10·03	9·79	9·38
0·524	9·08	8·86	8·49	0·580	10·05	9·81	9·40
0·525	9·09	8·88	8·51	0·581	10·06	9·83	9·42
0·526	9·11	8·90	8·53	0·582	10·08	9·84	9·43
0·527	9·13	8·91	8·54	0·583	10·10	9·86	9·45
0·528	9·15	8·93	8·56	0·584	10·12	9·88	9·47
0·529	9·16	8·95	8·57	0·585	10·13	9·90	9·48
0·530	9·18	8·97	8·59	0·586	10·15	9·91	9·50
0·531	9·20	8·98	8·61	0·587	10·17	9·93	9·51
0·532	9·21	9·00	8·62	0·588	10·18	9·95	9·53
0·533	9·23	9·02	8·64	0·589	10·20	9·96	9·55
0·534	9·25	9·03	8·66	0·590	10·22	9·98	9·56
0·535	9·27	9·05	8·67	0·591	10·24	10·00	9·58
0·536	9·28	9·07	8·69	0·592	10·25	10·01	9·60
0·537	9·30	9·08	8·70	0·593	10·27	10·03	9·61
0·538	9·32	9·10	8·72	0·594	10·29	10·05	9·63
0·539	9·34	9·12	8·74	0·595	10·30	10·06	9·64
0·540	9·35	9·13	8·75	0·596	10·32	10·08	9·66
0·541	9·37	9·15	8·77	0·597	10·34	10·10	9·68
0·542	9·39	9·17	8·79	0·598	10·36	10·12	9·69
0·543	9·41	9·19	8·80	0·599	10·37	10·13	9·71
0·544	9·42	9·20	8·82	0·600	10·39	10·15	9·73
0·545	9·44	9·22	8·83	0·601	10·41	10·17	9·74
0·546	9·46	9·24	8·85	0·602	10·43	10·18	9·76
0·547	9·47	9·25	8·87	0·603	10·44	10·20	9·77
0·548	9·49	9·27	8·88	0·604	10·46	10·22	9·79
0·549	9·51	9·29	8·90	0·605	10·48	10·23	9·81
0·550	9·53	9·30	8·91	0·606	10·50	10·25	9·82
0·551	9·54	9·32	8·93	0·607	10·51	10·27	9·84
0·552	9·56	9·34	8·95	0·608	10·53	10·28	9·85
0·553	9·58	9·35	8·96	0·609	10·55	10·30	9·87
0·554	9·60	9·37	8·98	0·610	10·57	10·32	9·89
0·555	9·61	9·39	9·00	0·611	10·58	10·34	9·90
0·556	9·63	9·41	9·01	0·612	10·60	10·35	9·92

Volt. −ve	18°	25°	38°	Volt. −ve	18°	25°	38°
0·613	10·62	10·37	9·94	0·669	11·59	11·32	10·84
0·614	10·63	10·39	9·95	0·670	11·60	11·33	10·86
0·615	10·65	10·40	9·97	0·671	11·62	11·35	10·88
0·616	10·67	10·42	9·98	0·672	11·64	11·37	10·89
0·617	10·69	10·44	10·00	0·673	11·66	11·38	10·91
0·618	10·70	10·45	10·02	0·674	11·67	11·40	10·92
0·619	10·72	10·47	10·03	0·675	11·69	11·42	10·94
0·620	10·74	10·49	10·05	0·676	11·71	11·43	10·96
0·621	10·76	10·50	10·07	0·677	11·73	11·45	10·97
0·622	10·77	10·52	10·08	0·678	11·74	11·47	10·99
0·623	10·79	10·54	10·10	0·679	11·76	11·49	11·01
0·624	10·81	10·56	10·11	0·680	11·78	11·50	11·02
0·625	10·83	10·57	10·13	0·681	11·80	11·52	11·04
0·626	10·84	10·59	10·15	0·682	11·81	11·54	11·05
0·627	10·86	10·61	10·16	0·683	11·83	11·55	11·07
0·628	10·88	10·62	10·18	0·684	11·85	11·57	11·09
0·629	10·89	10·64	10·20	0·685	11·86	11·59	11·10
0·630	10·91	10·66	10·21	0·686	11·88	11·60	11·12
0·631	10·93	10·67	10·23	0·687	11·90	11·62	11·14
0·632	10·95	10·69	10·24	0·688	11·92	11·64	11·15
0·633	10·96	10·71	10·26	0·689	11·93	11·65	11·17
0·634	10·98	10·72	10·28	0·690	11·95	11·67	11·18
0·635	11·00	10·74	10·29	0·691	11·97	11·69	11·20
0·636	11·02	10·76	10·31	0·692	11·99	11·71	11·22
0·637	11·03	10·78	10·32	0·693	12·00	11·72	11·23
0·638	11·05	10·79	10·34	0·694	12·02	11·74	11·25
0·639	11·07	10·81	10·36	0·695	12·04	11·76	11·27
0·640	11·09	10·83	10·37	0·696	12·06	11·77	11·28
0·641	11·10	10·84	10·39	0·697	12·07	11·79	11·30
0·642	11·12	10·86	10·41	0·698	12·09	11·81	11·31
0·643	11·14	10·88	10·42	0·699	12·11	11·82	11·33
0·644	11·15	10·89	10·44	0·700	12·12	11·84	11·35
0·645	11·17	10·91	10·45	0·701	12·14	11·86	11·36
0·646	11·19	10·93	10·47	0·702	12·16	11·87	11·38
0·647	11·21	10·94	10·49	0·703	12·18	11·89	11·39
0·648	11·22	10·96	10·50	0·704	12·19	11·91	11·41
0·649	11·24	10·98	10·52	0·705	12·21	11·93	11·43
0·650	11·26	11·00	10·54	0·706	12·23	11·94	11·44
0·651	11·28	11·01	10·55	0·707	12·25	11·96	11·46
0·652	11·29	11·03	10·57	0·708	12·26	11·98	11·48
0·653	11·31	11·05	10·58	0·709	12·28	11·99	11·49
0·654	11·33	11·06	10·60	0·710	12·30	12·01	11·51
0·655	11·35	11·08	10·62	0·711	12·32	12·03	11·52
0·656	11·36	11·10	10·63	0·712	12·33	12·04	11·54
0·657	11·38	11·11	10·65	0·713	12·35	12·06	11·56
0·658	11·40	11·13	10·67	0·714	12·37	12·08	11·57
0·659	11·41	11·15	10·68	0·715	12·38	12·09	11·59
0·660	11·43	11·16	10·70	0·716	12·40	12·11	11·61
0·661	11·45	11·18	10·71	0·717	12·42	12·13	11·62
0·662	11·47	11·20	10·73	0·718	12·44	12·15	11·64
0·663	11·48	11·22	10·75	0·719	12·45	12·16	11·65
0·664	11·50	11·23	10·76	0·720	12·47	12·18	11·67
0·665	11·52	11·25	10·78	0·721	12·49	12·20	11·69
0·666	11·54	11·27	10·80	0·722	12·51	12·21	11·70
0·667	11·55	11·28	10·81	0·723	12·52	12·23	11·72
0·668	11·57	11·30	10·83	0·724	12·54	12·25	11·74

Volt. —ve	18°	25°	38°	Volt. —ve	18°	25°	38°
0·725	12·56	12·26	11·75	0·761	13·18	12·87	12·33
0·726	12·57	12·28	11·77	0·762	13·20	12·89	12·35
0·727	12·59	12·30	11·78	0·763	13·22	12·91	12·37
0·728	12·61	12·31	11·80	0·764	13·23	12·92	12·38
0·729	12·63	12·33	11·82	0·765	13·25	12·94	12·40
0·730	12·64	12·35	11·83	0·766	13·27	12·96	12·42
0·731	12·66	12·37	11·85	0·767	13·28	12·97	12·43
0·732	12·68	12·38	11·86	0·768	13·30	12·99	12·45
0·733	12·70	12·40	11·88	0·769	13·32	13·01	12·46
0·734	12·71	12·42	11·90	0·770	13·34	13·02	12·48
0·735	12·73	12·43	11·91	0·771	13·35	13·04	12·50
0·736	12·75	12·45	11·93	0·772	13·37	13·06	12·51
0·737	12·77	12·47	11·95	0·773	13·39	13·08	12·53
0·738	12·78	12·48	11·96	0·774	13·41	13·09	12·55
0·739	12·80	12·50	11·98	0·775	13·42	13·11	12·56
0·740	12·82	12·52	11·99	0·776	13·44	13·13	12·58
0·741	12·83	12·53	12·01	0·777	13·46	13·14	12·59
0·742	12·85	12·55	12·03	0·778	13·48	13·16	12·61
0·743	12·87	12·57	12·04	0·779	13·49	13·18	12·63
0·744	12·89	12·59	12·06	0·780	13·51	13·19	12·64
0·745	12·90	12·60	12·08	0·781	13·53	13·21	12·66
0·746	12·92	12·62	12·09	0·782	13·54	13·23	12·68
0·747	12·94	12·64	12·11	0·783	13·56	13·24	12·69
0·748	12·96	12·65	12·12	0·784	13·58	13·26	12·71
0·749	12·97	12·67	12·14	0·785	13·60	13·28	12·72
0·750	12·99	12·69	12·16	0·786	13·61	13·30	12·74
0·751	13·01	12·70	12·17	0·787	13·63	13·31	12·76
0·752	13·02	12·72	12·19	0·788	13·64	13·33	12·77
0·753	13·04	12·74	12·21	0·789	13·67	13·35	12·79
0·754	13·06	12·75	12·22	0·790	13·68	13·36	12·80
0·755	13·08	12·77	12·24	0·791	13·70	13·38	12·82
0·756	13·09	12·79	12·25	0·792	13·72	13·40	12·84
0·757	13·11	12·81	12·27	0·793	13·74	13·41	12·85
0·758	13·13	12·82	12·29	0·794	13·75	13·43	12·87
0·759	13·14	12·84	12·30	0·795	13·77	13·45	12·89
0·760	13·16	12·86	12·32	0·796	13·79	13·46	12·90

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