BIRLA CENTRAL LIBRARY
PILANI (RAJASTHAN)
Call No. 541.3
I69P
Accession No 33948

Acc. No. 33948

ISSUE LABEL

Not later than the latest date stamped below.

PHYSICO CHEMICAL EXPERIMENTS

BY

ROBERT LIVINGSTON
Professor of Physical Chemistry, University of Minnesota

REVISED EDITION

THE MACMILLAN COMPANY
New York: 1948

Revised Edition, Copyright, 1948
By The Macmillan Company

All rights reserved — no part of this book may be reproduced in any form without permission in writing from the publisher, except by a reviewer who wishes to quote brief passages in connection with a review written for inclusion in magazine or newspaper.

Printed in the United States of America

First Edition, Copyright, 1939,
By The Macmillan Company

Reprinted November, 1948

PREFACE TO FIRST EDITION

This book has been prepared in the belief that the chief purpose of a laboratory course in physical chemistry is to illustrate the basic principles of the subject. Without the opportunity which such a course offers for practical experimentation and computation, the student is likely to find it difficult to correlate the abstract principles and equations of theoretical chemistry with the experimental observations upon which they are based. However, it must be recognized that this is not the sole purpose of the course. It is only in the physico chemical laboratory that the student has an opportunity to become familiar with many of the commoner types of apparatus and to achieve some competence in the simpler techniques. For this reason, the methods used in the several experiments were chosen, whenever it seemed consistent with the primary purpose of the experiments, to demonstrate the more important of the simple techniques and apparatus. The descriptions and directions for the use of the commoner apparatus have been placed in separate sections, in the hope that the student will realize that their utility is not limited to the immediate experiment.

As our college curricula are usually organized, the laboratory work in physical chemistry is one of the few courses, if not the only course, where the upper division student is required to compute and analyze data which are based upon his own experimental observations. For this reason, a fairly extensive account of computing methods and of the theory of errors and measurements has been introduced into the first part of this book. To emphasize further the importance of such considerations, the experiments presented here are, with few exceptions, quantitative in nature. In the author's opinion a student's report is not complete, unless it contains a quantitative discussion of the errors of the experiment.

This manual is intended neither as an encyclopedia of experimental methods nor as a textbook of theoretical chemistry. In the descriptions of laboratory methods, frequent references are made to such comprehensive works as Reilly and Rae, Physico Chemical Methods, and Daniels, Mathews, and Williams, Experimental Physical Chemistry, as well as to monographs and other specialized discussions. For the details of analytical procedures, students are referred to Kolthoff and Sandell, Textbook of Quantitative Inorganic Chemistry. Theoretical discussions of the principles related to the several experiments are not included in this manual, except in those few cases where the subject matter is not commonly treated in elementary texts. In the author's opinion, the discussions which usually appear in laboratory manuals of physical chemistry are too brief and disconnected to be of any real value, and have the disadvantage that the student is apt to substitute them for the more complete and comprehensive treatment contained in his theoretical text. While frequent references are made to MacDougall, Physical Chemistry, no difficulty should be experienced in using this manual with any other good modern text of physical chemistry. A list of abbreviations and of the symbols and notations used in this book are given in the appendix.

The procedures for the experiments are given in sufficient detail to permit of their performance by the average student without personal assistance or coaching. However, an effort has been made to avoid the "cook book" sort of directions. Some of the simpler experiments are presented as minor research problems; the purpose being indicated and the general method fully described, but the details of the procedure being left entirely to the discretion of the student. While certain required computations are indicated at the end of each experiment, the selection of the particular method of calculation is left to the student's initiative. The omission of detailed directions for preparing the reports is intentional, since the author believes that the student should assume full responsibility for this phase of the work.

The lists of apparatus which accompany each experiment were prepared upon the assumption that the student has access to an analytical balance and to the usual complement of laboratory glassware. In this connection, the author would like to express a strong prejudice against the common practice of having all of the equipment for each experiment assembled and prepared in advance for the student. While this procedure may save some time, and is practically necessary in the case of a few experiments which require complex apparatus, its general use seems ideally adapted to discourage any initiative or sense of responsibility which the student may possess.

The experiments are of varying length and difficulty; however, none of them require more skill than can be reasonably expected of an undergraduate student. A few, which are marked with an asterisk, can be performed most conveniently by two students working together. Wherever it seemed feasible, several substances have been listed as suitable for each experiment. In a number of cases, references are given to similar or to complementary experiments which appear in other manuals. In selecting the topics for the experiments, special emphasis has been placed upon the study of equilibria and to a lesser extent upon reaction kinetics. Since the experimental study of the quantitative aspects of crystal structure, photochemistry, and colloid chemistry requires rather complex apparatus and specialized techniques, relatively few experiments on these subjects are included. The additive and constitutive properties of matter are represented by only one (semi-quantitative) experiment; however, the student who is especially interested in this subject will find the outlines of some excellent experiments in Daniels, Mathews, and Williams, Experimental Physical Chemistry, Chapters III and XIII, and in Fajans and Wust, A Textbook of Practical Physical Chemistry, pp. 122–45.

Several of the experiments which appear in this manual were included because of their application to chemical engineering, organic chemistry, or biochemistry. The author believes that these applied subjects often furnish as sound examples of the fundamentals of physico chemical principles and methods as do the most abstract topics. It is worth remembering that relatively few of the students who are enrolled in the average elementary physical chemistry course are either destined to become or desirous of becoming professional physical chemists.

In conclusion the author would like to state that he will welcome any criticism and will be grateful to have his attention called to any errors which may have escaped him.

ROBERT LIVINGSTON

CHICAGO, ILL.
December, 1938.

PREFACE TO REVISED EDITION

Eight years of use of the first edition of this book have, in the author's opinion, justified its general plan and concept. Consequently, the preparation of the present edition has involved no major changes. In a number of places, notably the first chapter, the discussion of certain topics has been amplified. A few explanations, which students persistently found difficult, have been clarified. Two experiments have been added and one omitted. Experiment 16 has been dropped, not because it was unsatisfactory as a laboratory exercise, but because the apparatus as constructed in our shops was incapable of withstanding continued use.

It is apparent that this manual would be improved by the inclusion of a few experiments illustrating modern techniques; such as the use of radioactive tracers, applications of spectroscopy, etc. However, the expense of the required equipment and the difficulty of the techniques have to date prevented the development of practicable experiments of this type. Several experiments, which appeared promising in outline, proved to be failures in the student laboratory.

The author is indebted to Mr. W. C. Johnson of this department for a number of practical suggestions which materially aided the development of Experiment 42.

ROBERT LIVINGSTON

MINNEAPOLIS, MINN.

ACKNOWLEDGMENT

For permission to prepare this manual as a companion book to MacDougall, Physical Chemistry, I wish to express my gratitude to Dr. F. H. MacDougall, whose clear thinking and critical attitude have been an inspiration during the ten years that I have had the opportunity of working with him. At this time, I also wish to express my appreciation to Dr. E. D. Eastman, of the University of California, whose free and inspiring teaching first roused my interest in experimental physical chemistry. To acknowledge properly the assistance of all of those who have aided either directly or indirectly in the preparation of this manual would require a space comparable to the book itself. I would, however, particularly like to mention Dr. I. M. Kolthoff for his many valuable definite suggestions and Dr. G. Glockler for his interest and for his worthwhile criticism of certain parts of the book. I am indebted to Dr. W. D. Larson, of St. Thomas College, for suggesting the use of silver acetate in Experiment 32. Mr. W. Horwitz and Mr. C. Carr have been especially helpful in working out the details of new and modified experiments. Anyone familiar with the older literature will realize that I have borrowed ideas freely; chiefly from Daniels, Mathews, and Williams, Experimental Physical Chemistry; Fajans and Wust, A Textbook of Practical Physical Chemistry; Findlay, Practical Physical Chemistry, and Sherrill, Laboratory Experiments on Physico Chemical Principles. Finally I wish to mention my debt to Savetta L. Livingston, who prepared the line drawings, for her patience with details which were vexatious and, to her, at times incomprehensible.

ROBERT LIVINGSTON

TABLE OF CONTENTS

PAGE

I. MEASUREMENTS, ERRORS, AND COMPUTATIONS 1
Physical Measurements 2
Physical Laws and Measurements 3
Dimensions 4
Accuracy and Significant Figures 6
The Exponential Notation 7
Approximate Computations 9
Distribution of Errors 10
Best Value and Its Reliability 14
Application of Error Theory to Experimental Data 17
Application of Error Theory to Functions of a Single Variable 20
Application of Error Theory to Functions of Several Variables 22
Evaluation of the Constants of Empirical Equations 30
Graphical Methods of Computation 41
Graphical Differentiation and Integration 42
Graphical Evaluation of the Constants of an Empirical Equation 46
Empirical Equations Which Are Non-Linear in Respect to Their Constants 49
Report Writing 51

II. THE GASEOUS STATE
1. Determination of the Molecular Weight of a Vapor by the Dumas Method 53
   Use of the Barometer 55
2. Determination of the Molecular Weight of a Vapor by the Victor Meyer Method 57
3. Effusion of Gases. The Molecular Weight and Diameter 62

III. THE LIQUID STATE
4. The Vapor Pressure and the Heat of Vaporization of a Liquid* 67
   Correction of a Thermometer Reading for Exposed Stem 70
5. Surface Tension as a Function of Temperature 71

IV. THE SOLID STATE
6. Sublimation Pressure and Heat of Sublimation* 76
7. The Linear Rate of Crystallization of a Melt 80

V. THE STRUCTURE OF ATOMS
8. The Radioactive Decay Law 83
   Use of the Lind Electroscope 85

PAGE

VI. PHYSICAL PROPERTIES AND MOLECULAR CONSTITUTION

9. Absorption Spectra of Colored Solutions. Use of the Spectroscope 89

VII. SOLUTIONS

10. The Freezing Point of an Aqueous Solution and the Molecular Weight of the Solute 93
Use of a Differential Thermometer 95
Use of the Polarimeter 98
11.✓ Freezing Point Lowering and Molecular Weight (Beckmann Method) 103
Use of the Tablet Press 107
12.✓ Boiling Point Elevation and Molecular Weight 108
13. Viscosity of a Binary Solution 112
Use of the Westphal Balance 115
14.✓ Surface Tension of a Binary Solution (Drop Number Method) 118

VIII. THERMOCHEMISTRY

15. Heats of Ionic Reactions 122
16. Heats of Combustion. The Bomb Calorimeter 127

IX. EQUILIBRIUM

17. Chemical Equilibrium in a Liquid Phase 133

X. HETEROGENEOUS EQUILIBRIUM

18. Mutual Solubility of Two Liquids 135
19. Solubility Relations in a Three Component System 138
20. Steam Distillation 143
21. Distillation of Solutions of Two Completely Miscible Liquids 146
Use of the Abbé Refractometer 150
22. Fundamentals of Plate Still Fractionation 154
Use of the Sprengel Pycnometer 160
23. The Freezing Point Curve of a Binary Alloy 162
Preparation and Use of a Thermocouple 167

XI. CHEMICAL KINETICS

24. The Rate of Oxidation of Iodide Ion by Hydrogen Peroxide. A Clock Reaction 171
25. The Rate of a Homogeneous Catalyzed Reaction 175
26. The Temperature Coefficient of Reaction Velocity and the Heat of Activation 178
27. Catalysis and Inhibition of a Chain Reaction 182
28. The Rate of Evaporation of a Volatile Solute 185

PAGE

XII. ELECTRICAL CONDUCTANCE
29. The Determination of Transference Numbers 190
30. The Conductivity of Electrolytic Solutions. The Ionization Constant of Acetic Acid 193
31. Conductimetric Titrations 199

XIII. EQUILIBRIA INVOLVING IONS
32. The Solubility of Sparingly Soluble Salts in Presence of Electrolytes 202
33. Determination of an Indicator Constant and Some Properties of Buffered Solutions 205
Use of the Color Comparator 208
34. Determination of the Dissociation Constant of Triiodide Ion by Partition Measurements 210

XIV. ELECTROMOTIVE FORCE
35. Concentration Cells Involving Zinc Amalgams and Zinc Chloride Solutions* 212
Use of the Students' Potentiometer 216
36. Electromotive Force and the Equilibrium Constant* 222
37. Potentiometric Determination of the Activity of the Hydrogen Ion* 226
38. Potentiometric Titrations* 233
Acid-Base Titrations 234
Oxidation-Reduction Titrations 236
Precipitation Titrations 238

XV. ELECTROLYSIS AND POLARIZATION
39. Electrolysis and Polarization* 240

XVI. PHOTOCHEMISTRY
40. A Study of the First and Second Laws of Photochemistry 245

XVII. THE COLLOIDAL STATE
41. Adsorption from Solutions. Acetic Acid on Charcoal 248
42. Solubilization by a Soap of a Water-Insoluble Dye 251
Use of the Colorimeter 252

APPENDIX
Abbreviations and References 257
Notation 257
Atomic Weights and Numbers 259
Common Logarithms 260

INDEX 263

PHYSICO CHEMICAL EXPERIMENTS

MEASUREMENTS, ERRORS, AND COMPUTATIONS

Experimental physical chemistry is a laboratory science, not merely a collection of recipes and formulas, for obtaining specific results. The student of this subject should not be content with an effort to obtain certain expected results by blindly following detailed directions. He should endeavor to look beyond the immediate experiment, and when following specific directions try to see the reasons which prompted them. When he uses an Abbé refractometer he should understand the optical principles involved in its construction; or when he uses a "student potentiometer" he should have sufficient knowledge of the underlying principles to enable him to assemble a satisfactory substitute from ordinary resistance boxes. Such knowledge of the basic facts is necessary not only to satisfy what intellectual curiosity he may possess and to distinguish him from the proverbial bride with her first cook book; but also, to enable him to avoid faulty technique, to diagnose his own experimental difficulties, and when necessary to construct substitute apparatus. The scope and size of this book does not permit of a complete or even satisfactory discussion of the various fundamental principles involved in the construction and use of the apparatus. However, in most cases brief introductory discussions are included and references are given to more detailed and exact treatments.

A large part of the time required for the completion of an experiment in physical chemistry must be spent in the analysis and computation of the experimental data. It is therefore of utmost importance that the student have some general knowledge of the basic theory of physical measurements and laws, and that he acquire a good working knowledge of those numerical and graphic methods of mathematical approximation which are most commonly applied in the analysis of physical measurements. The discussion of these topics, which follows, is little more than an outline. The student is advised to consider it only as a study outline and to read and study as many of the special treatises on these subjects as he has time and opportunity for.

PHYSICAL MEASUREMENTS

A physical measurement consists of the comparison of some property of an object to the same property of some other object which is taken as a standard in respect to this property. Usually this comparison may be expressed numerically, as when we say the length of a wire is 98.4 cm., meaning that it is 0.984 "as long" as the standard meter. It is important to remember that every measurement involves three acts: the identification of the property being measured, the selection of a standard, and the comparison of the object and the standard in respect to the defined property. The first two acts determine the dimensions and units of the measured quantity; and the last, its magnitude and the accuracy with which the magnitude is known.

While magnitude is perhaps the most familiar characteristic of measurement, it should be apparent that a magnitude without dimensions (stated or implied) would be without significance and would have no logical relation to the process of measurement. For example, the statement that the length of an object was 1184.65 would be meaningless, so long as we did not know whether the unit of measurement was the millimeter or meter, the Ångstrom unit or light year. Furthermore, the unit must be appropriate to the property measured. If we were assured that the length of the object was 1184.65 grams, we would still have no idea as to how long it was, for we would be unable to conceive of any operation by which the length of an object could be compared to (or measured in terms of) a standard mass.

A consideration of the possible methods of comparison of the same property of two objects shows that it is impossible for the result of any measurement to be mathematically exact. All that a measurement, or more properly, a series of measurements, can ever demonstrate is that there is a certain probability that the true magnitude will lie within definite limits. For example, a series of weighings would never indicate that a weight was exactly 100 grams, but merely that the probability that the true weight fell within the limits 100.0001 to 99.9999 grams was equal to the probability that it fell beyond these limits, or that the probability was nineteen times greater that it fell within the limits 100.0003 to 99.9997 than beyond these. There are various ways of expressing the error of a measurement, and some of these are discussed in the following pages. Since the error of a physical measurement may vary from one part in ten million to several hundred per cent, it is obviously of great importance that the error of any measurement be determined and recorded. A measurement for which the error was entirely unknown would be quite meaningless; in other words, it would not be a measurement at all.

PHYSICAL LAWS AND MEASUREMENTS

It is a matter of common knowledge that the several properties of an object cannot be varied independently. If, at constant pressure, the temperature of a sample of gas is increased, its volume will increase. Or if the concentration of a solution is changed, corresponding changes will occur in its density, conductance, dielectric constant, and other properties. In some cases (for example, the relation between temperature and pressure of a sample of helium gas at constant volume) the change in one property is directly proportional to the change in the other. Although the relations between properties are frequently more complex, they are always of a type which can be represented by a mathematical function. In other words, every physical law can be expressed by an equation.

There are two general ways in which a suitable equation can be selected. Sometimes the experimental measurements are performed first, and the results of the measurements are arranged as a table or are represented graphically. The resulting table, or graph, is then compared to various functional tables, or graphs of functions, until some function is discovered which represents the data within the limits of experimental error. In practice, the selection of the appropriate equation is rendered less laborious by the use of standardized procedures, some of which are discussed later. If the analysis of the data is stopped at this point, the equation is known as an empirical one. Empirical equations are useful chiefly as interpolation formulas and to represent data in a brief compact way. It is possible in some cases to show that the empirical equation is in agreement with the predictions of some physical hypothesis. If the equation correctly predicts the results of further experiments, and the hypothesis is consistent with related theories, the equation is considered to be an expression of a physical law. Sometimes the process is reversed; first the hypothesis is suggested, then an equation derived from it, and finally experiments are performed which are designed to test the equation.

There is no general method for setting up the original hypothesis. The only things which seem to be necessary are a lively interest in the subject and (usually) a wide knowledge of related laws and facts. The type of reasoning used is largely intuitive; that is, guess work guided by analogy. The second step is the translation of a simple logical statement of the theory into an equation. Frequently, though not necessarily, this first equation is in differential form and must be integrated or otherwise transformed before it can be compared to the experimental data. If possible the experiments should be so planned that all independent variables except those occurring in the equation are kept constant. Temperature is frequently an extra variable, and it is for this reason that thermostats occupy such a prominent place in the physico chemical laboratory.

DIMENSIONS

When the law relating two or more physical properties is known it is often convenient to measure some property indirectly as a function of more readily measurable characteristics. For example, density, ρ, is equal to the ratio of the mass, m, to the volume, v,

$$\rho = m/v$$

and it is possible to determine the density of an object by comparing its mass and volume to standards of mass and volume, respectively. This makes it unnecessary to set up a separate standard of density. Furthermore, since all additive quantities must have identical dimensions (i.e., all equations are dimensionally homogeneous), density must have the dimensions of mass divided by volume.

$$\rho \equiv M/V \equiv M/L^3$$

To cite another example, surface tension, γ, is equal to half the force, f, necessary to maintain a film of unit width, L,

$$\gamma = f/2L$$

Surface tension, therefore, has the dimensions of force divided by length (dynes per cm.) or, since force equals mass × acceleration,

$$f = M\frac{d^2L}{dT^2}$$

the ultimate dimensions of surface tension are those of mass divided by time squared.

$$\gamma \equiv \frac{f}{L} \equiv \frac{M \cdot L/T^2}{L} \equiv \frac{M}{T^2}$$

A similar investigation of other physical quantities would reveal that all can be expressed in terms of three fundamental quantities, mass, length, and time, and a fourth property, temperature.

There is some difference in usage of dimensions. This arises from the fact that whenever an equation contains two factors which are not dimensionally defined by any independent relation, it is possible to assign either one an arbitrary dimension. In the case of the perfect gas law—

$$PV = nRT$$

the product nRT has the dimensions of energy. Since n is the ratio of the mass of the sample to the molecular weight expressed in the same units, it is dimensionless. It would be mathematically correct to assign the dimensions of energy to the gas constant, R, and treat temperature as a dimensionless quantity. However, it is conventional and has proven convenient to introduce temperature as an explicit dimension (with the symbol Θ), which results in R having the dimensions of energy divided by temperature

$$R \equiv \frac{ML^2}{\Theta T^2}$$

Coulomb's law, which relates the force, f, acting between charges, q_1 and q_2, separated by a distance, d, in a medium which has a dielectric constant, D, may be written

$$f = \left(\frac{k}{D}\right)\frac{q_1q_2}{d^2}$$

where k is a coefficient. In this case, the only dimensional information we have is that—

$$q_1q_2\left(\frac{k}{D}\right) \equiv \frac{ML^3}{T^2}$$

Even if we assume k to be dimensionless, there are still a number of ways which are both correct and possibly convenient, in which we can assign the dimensions. We may solve for the dimensions of charge by assuming that D is dimensionless or by assigning it the explicit dimension D, or else we may assign q the explicit dimension ϵ and solve for the dimension D. All three of these suggestions have been used as the basis of the dimensions of the electrostatic system of units. However, so long as we are consistent in our use of dimensions, it is not very important which conventions we adopt.

The foregoing discussion suggests one of the most important uses of dimensional analysis; testing for inconsistencies in equations which have been proposed to relate certain physical properties. If the suggested equation is not dimensionally homogeneous, it is certainly incorrect. Of course the converse is not true; an equation may be dimensionally correct but numerically have no relation to measured values. In applying this test, the student should remember that unnamed coefficients or constants are not necessarily dimensionless but may have any dimension necessary to balance the equation.

If a complex property, such as surface tension or viscosity, is determined by means of simultaneous measurements of mass, length and elapse of time, the measurement is said to be an absolute one. Since absolute measurements are usually experimentally difficult, it is customary to measure such properties by comparing them directly to some object for which the absolute value of the property is known (or assumed). Such determinations are known as relative measurements. They may also be performed by means of instruments whose scales have been calibrated with the aid of standard substances.

ACCURACY AND SIGNIFICANT FIGURES

The accuracy of a measurement may be indicated simply by the number of significant figures used in recording its magnitude. In this connection it is interesting to note that the very use of the decimal notation suggests that the quantity is not exactly known, since in this notation an infinite number of significant figures would be required to express the quantity exactly; on the other hand, a simple fraction is commonly used to represent a mathematically exact quantity. It is customary to retain enough significant figures that the uncertainty in the next to the last figure is not greater than unity. For example, if the result of a weighing were recorded as 2.4674 gm., this would indicate that it was quite improbable that the true weight was greater than 2.4679 or less than 2.4669 gm. If the average length of the side of a square were measured with an ordinary millimeter scale, the length would be accurate to the nearest millimeter, the estimated fractions of a millimeter being in doubt. This would be indicated by writing that the length was (say) 11.84 cm. It would be misleading to drop the last significant figure, and (unless the result was the average of a large number of separate measurements with a very accurately calibrated scale) it would not be justifiable to retain a fifth significant figure. If the area of this square were computed, it would be incorrect to retain all of the significant figures which the ordinary process of "long" multiplication would yield; for this number, 140.1856 cm.^{2}, would indicate that the area was known with an accuracy a thousand fold greater than that of the measured length. Since the relative accuracy with which we know the area is of the same order of magnitude as that with which we know the length, the area should be written as 140.2 cm.^{2}

THE EXPONENTIAL NOTATION

The number of significant figures is not related to the decimal place. The same number of significant figures would be required regardless of whether the area were expressed in square millimeters (14,020 mm.^{2}) or in square meters (0.01402 m.^{2}). There is some ambiguity in the figure which expresses the area in square millimeters, since it is not clear whether the last zero is to be regarded as significant or whether it is included only to give the correct decimal. This ambiguity can be avoided by the use of the exponential notation. This notation is especially convenient when very large or very small numbers must be dealt with. To write any (real) number in this notation, separate it into two factors, such that one is an integral power of 10 and the other is an ordinary decimal, usually lying between 1 and 10. The following cases will illustrate the method of changing a number from the decimal to the exponential notation:

$$\begin{aligned} 0.0001874 &= 1.874 \times 10^{-4} \\ 0.00000342 &= 3.42 \times 10^{-6} \\ 978{,}500 &= 9.785 \times 10^{5} \\ 18{,}000{,}000 &= 1.8 \times 10^{7} \end{aligned}$$

In changing the last number to the exponential notation it was assumed that none of the zeros of the decimal were significant figures. Had the number been known to contain four significant figures the exponential number would have been written 1.800×10^7. In the case of the area of the square which was discussed above, the values would be written: 1.402×10^2 cm.^{2}, 1.402×10^4 mm.^{2}, and 1.402×10^{-2} m^2.

Multiplying, dividing, and taking roots or powers of very large or very small numbers is greatly facilitated by the use of the exponential notation. These operations follow the same rules as are familiarly applied to algebraic quantities, as is illustrated by the following examples:

$$\begin{aligned}
(a \times 10^b)(c \times 10^d) &= ac \times 10^{b+d} \\
1.242 \times 10^3 \times 8.13 \times 10^7 &= 10.10 \times 10^{10} \\
&= 1.010 \times 10^{11} \\
3.212 \times 10^2 \times 4.411 \times 10^{-8} &= 1.417 \times 10^{-5} \\
\frac{a \times 10^b}{c \times 10^d} &= \frac{a}{c} \times 10^{b-d} \\
\frac{3.726 \times 10^3}{1.242 \times 10^{10}} &= 3.000 \times 10^{-7} \\
\frac{2.8336 \times 10^3}{8.822 \times 10^{-7}} &= 0.32120 \times 10^{10} \\
&= 3.2120 \times 10^9 \\
(a \times 10^b)^c &= a^c \times 10^{bc} \\
(2.13 \times 10^6)^2 &= 4.54 \times 10^{12}
\end{aligned}$$

In taking roots it is convenient to write the number so that the exponent is integral for the root as well as for the number. If we required the square root of 1.60×10^7, it would be convenient to rewrite the number as 16.0×10^6; then

$$(16.0 \times 10^6)^{1/2} = 4.0 \times 10^3$$

Likewise

$$\begin{aligned}
(6.4 \times 10^{-8})^{1/3} &= (64.0 \times 10^{-9})^{1/3} \\
&= 4.0 \times 10^{-3}
\end{aligned}$$

and

$$\begin{aligned}
(2.37 \times 10^{-7})^{2/3} &= (0.237 \times 10^{-6})^{2/3} \\
&= 0.383 \times 10^{-4} \\
&= 3.83 \times 10^{-5}
\end{aligned}$$

For addition and subtraction it is necessary to write all of the numbers which are to be added so that they have the same exponent. For example, if we desired to add 1.62×10^{-5}, 4.372×10^{-4}, and 7.23×10^{-8}, we would rewrite them as

$$\begin{array}{rll} & 0.162 & \times 10^{-4} \\ & 4.372 & \times 10^{-4} \\ & \underline{0.000723} & \underline{\times 10^{-4}} \\ \text{sum} & 4.535 & \times 10^{-4} \end{array}$$

APPROXIMATE COMPUTATIONS

All of the foregoing numerical examples have been treated as though the numbers represented measured quantities, since the same number of significant figures have been retained in the results as appeared in the original numbers. While these numbers, with the correct number of significant figures, can be obtained by first computing by any of the usual "exact" methods (as long multiplication or division) and then by rounding off the result to the desired number of significant figures, such a process is unnecessarily laborious and time consuming. The desired result may be obtained directly by means of a suitable "short" method of approximate computations. The student should realize that no one method of computation is suited to all problems. He should acquaint himself with several of the more generally useful methods and try to select that method which is best adapted to the problem at hand. The habitual use of the exact or long methods of computation not only wastes time and effort, but frequently leads the beginner to retain far too many significant figures in the resultant. Since an accuracy of 1% is sufficient for many physico chemical computations, the ordinary slide rule is well adapted to them. However, the student should remember that even this useful tool has its limitations. In many cases it will not yield results of sufficient accuracy; in no case can it be trusted to indicate the number of significant figures which should be retained. Its usefulness can be greatly extended by using it in combination with appropriate methods of approximate computation. The most generally applicable method of computation involves the use of common logarithms; a five or even four place table is sufficient for most physico chemical computations. Tables of powers, roots, reciprocals, and certain algebraic functions frequently prove very convenient. Graphical methods are of special interest and utility in the solution of a variety of problems. Routine computations are often facilitated by the use of simple graphs, networks of scales, or nomographs. It is assumed that the student is familiar with the use of the slide rule, common logarithms, and tables of functions. The more important graphical and a few of the analytical methods of approximate computation are discussed briefly in the later part of this chapter.

DISTRIBUTION OF ERRORS

Whenever a series of measurements of the same quantity are performed, it is found (unless the measuring instrument is not read with sufficient precision) that the results of the several measurements are not identical but are distributed about a mean value in an apparently random manner. It is also a matter of common experience, when the number of measurements is sufficiently great, that values which depart widely from the mean occur less frequently than those which are close to it, and that the individual values are symmetrically distributed about the mean. In a few types of measurements, for example the determination of tensile strength, the values are unsymmetrically distributed about the mean. The present discussion is limited to the common type of measurement which yields a symmetrical distribution of the individual measurements.

TABLE 1

Measured Values, S_i	Frequency of Occurrence, n_i		Relative Frequency of Occurrence, n_i/N	
	Series I 150 trials	Series IA 50 trials	Series I $N = 150$	Series IA $N = 50$
7.31	1	0	0.007	0
.32	3	1	.020	.02
.33	8	3	.053	.06
.34	18	6	.120	.12
.35	28	9	.187	.18
.36	34	11	.227	.22
.37	29	10	.193	.20
.38	17	6	.113	.12
.39	9	2	.060	.04
.40	2	1	.013	.02
.41	1	1	.007	.02

To illustrate this, let us assume that with micrometer calipers we have made 150 measurements of the diameter of a steel ball bearing. The individual values, S_i, vary between 7.31 and 7.41 mm.

Counting the number of times which each value occurs, we obtain the results listed in the first two columns of the table on page 10. The third column lists the number of times that the several values occurred in the first 50 of the 150 measurements. These data are also plotted in figure 1; the height of the rectangles indicating the number of times that a value was observed and their width corresponding to the interval (0.01 mm.) between recorded values. The rectangles corresponding to the 150 measurements are indicated in outline, those corresponding to the first 50 measurements are cross hatched.

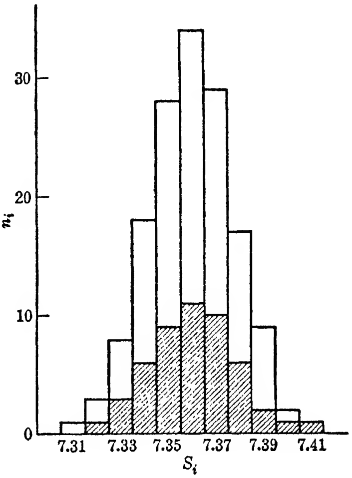

FIGURE 1

To reduce these data to a comparable basis, we can divide the frequency of occurrence, n_i, by the total number of measurements in the group, N. These values, which we shall call relative frequency, are given in columns 4 and 5 for the groups of 150 and 50, respectively. They are plotted in figure 2; the solid line representing the group of 150, the dotted line the first 50. When the data are treated in this way, the plots of the two groups of data are similar. The remaining differences are apparently due to erratic variations, which would be minimized if larger groups of measurements were compared. This view is supported by the fact that the irregularities appear greater in the plot which represents the smaller group.

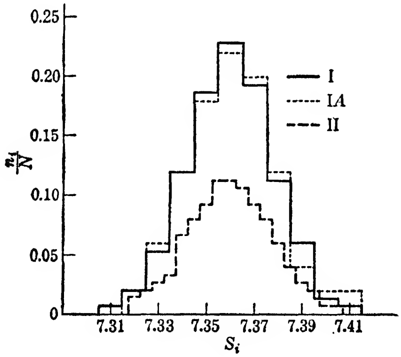

FIGURE 2

It is instructive to compare these groups of data with another set of 150 similar measurements, in which the micrometer setting was estimated to 5 units in the third decimal place. In this set, therefore, the interval between recorded values is reduced from 0.01 to 0.005 mm. These data are plotted as relative frequency, n_i/N, in figure 2, series II, and represented by a dash line. This quantity, n_i/N, for a given series of measurements, is directly proportional to the length of the interval, ΔS, between recorded values, S_i. Therefore, if we plot $n_i/N \cdot \Delta S$ against S_i, we obtain a figure (3) in which the plots of the three groups of measurements, I, I*A*, and II, are similar. If the number of measurements, N, is greatly increased and the interval, ΔS, is decreased to an infinitesimal, dS, the quantity $n_i/N \cdot \Delta S$ approaches a limit to which we shall assign the symbol, y.

$$y = \frac{1}{N}\frac{dn}{dS}$$

The values of y, corresponding to the particular experiment described above, are plotted as a dot-dash curve on figure 3.

The probability that any one, chosen at random, of the 150 measurements of series I has a value S_i (i.e., between $S_i - \frac{\Delta S}{2}$ and $S_i + \frac{\Delta S}{2}$) is equal to the ratio of the number of measurements observed with this value to the total number of measurements. More generally, the probability that a measurement chosen at random from a completed series of measurements will have the particular value S_i is

$$\frac{n_i}{N} = \frac{n_i}{N \cdot \Delta S}\Delta S$$

Correspondingly, the probability of the occurrence of a measurement with a value between S_i and $S_i + dS$, in a series similar to that represented by curve y of figure 3, is $y_i dS$.

$$\frac{(dn)_i}{N} = \frac{1}{N}\left(\frac{dn}{dS}\right)_i dS = y_i\, dS$$

It is perhaps worthy of emphasis, that (in the method of representing the distribution of measurements adopted here) the curve obtained by plotting y against S is merely the limit which the broken-line or staircase figure, obtained by plotting $(n_i/N\Delta S)$ against S_i, approaches as the number of measurements is increased greatly and the interval between recorded values is decreased to an infinitesimal, dS. It should be remembered, however, that the three broken-line figures and the curve (of figure 3) refer to measurements of one property of a given object by the same observer with the same instrument under unchanged conditions.

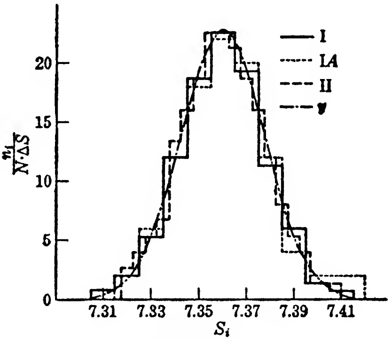

FIGURE 3

Since $y_i\ dS$ (not y_i) represents the probability of occurrence of a measurement between S_i and $S_i + dS$, the summation of ydS over all possible values of S is equal to unity, since this summation is the probability that any measurement chosen from the series at random will have some possible value.

$$\int_{-\infty}^{\infty} ydS = \sum_i \left(\frac{n_i}{N \cdot \Delta S}\right) \Delta S = 1$$

In other words, the area under any of the figures (of figure 3) is equal to unity. This is also true for a y vs S or $\frac{n_i}{N \cdot \Delta S}$ vs S_i figure corresponding to any set of measurements, regardless of the number of determinations, interval between values, or the precision of the measurements. On the other hand, the form of the curve (or of the broken-line figure) depends upon the precision of the measurements. For example, figure 4a, which corresponds to a relatively precise set of measurements, is tall and narrow, while figure 4b, which represents a crude set of measurements, is low and broad. In these figures r, rather than S, is plotted as abscissa. This quantity, r_i, which is called the residual, is the

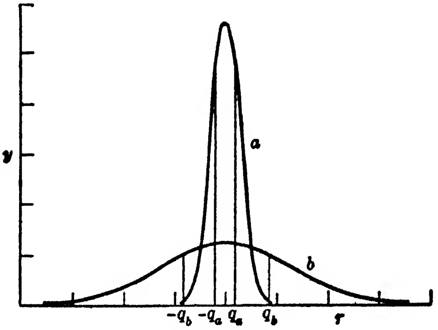

FIGURE 4

difference between a measured value, S_i, and the arithmetic mean of all measured values, m.

$$r_i = S_i - m$$

This substitution of variables shifts the maximum ordinate to a point corresponding to the zero of the abscissae.

Inspection of curves, such as 4*a*, 4*b*, and 3*y*, strongly suggests that y is a symmetrical, inverse function of r. In fact, it can be shown theoretically and has been demonstrated by innumerable experiments that the relation between y and r has the following form, which is called the "error function."

$$y = \frac{h}{\sqrt{\pi}} e^{-h^2r^2} \tag{1}$$

In this equation, h is an adjustable constant, called the "modulus of precision" and e and π have their usual significance. Strictly speaking, the error function applies to y and x rather than to y and r; however, x_i, the error of a single measurement, differs from r_i, the residual, only as much as the (unknown) true value of the measured quantity differs from the mean of the measurements. For all ordinary measurements which follow a normal distribution law, this difference, and therefore the distinction between error and residual, becomes relatively unimportant as the number of measurements becomes reasonably large.

BEST VALUE AND ITS RELIABILITY

From any series of measurements of a single quantity we can compute the best value of the quantity and estimate the reliability of that value. When the distribution of errors is in agreement with equation 1, as it is for practically all ordinary measurements, the best value is the arithmetic mean of the measurements, m.

$$m = \frac{1}{N} \sum_i S_i$$

A commonly used method of indicating the reliability of a series of measurements is to specify the probable error, q, of a single measurement. This quantity, q, has such a magnitude, that the probability that the error of a measurement, chosen at random, will be less than q is equal to the probability that it will be greater than q. It should be understood that this comparison between q and the error of a measurement is made without regard to sign; it concerns only the magnitudes of the quantities. Since the total area under an error function curve is unity, the area between q and $-q$ is 1/2. The probable errors corresponding to curves a and b are indicated in figure 4 by vertical lines which are erected at q_a and q_b. To obtain an analytical expression for q (or for the related quantity, h) it is necessary to solve the equation

$$\frac{h}{\sqrt{\pi}}\int_{-q}^{q} e^{-h^2r^2}dr = \frac{1}{2}$$

While this integral cannot be solved in terms of simple functions, it can be evaluated by means of a series. This calculation, which is beyond the scope of the present discussion, leads to the following formula:

$$\begin{aligned} q &= 0.674\sqrt{\frac{1}{N-1}\sum_i (S_i - m)^2} \\ &= 0.674\sqrt{\frac{1}{N-1}\sum_i r_i^2} \end{aligned} \qquad (2)$$

It can also be shown that the probable error is approximately equal to 0.845 of the arithmetic average of the magnitudes of the residuals.

$$q = \frac{0.845}{N}\sum_i \left| r_i \right| \qquad (3)$$

This expression is sufficiently accurate for most purposes, and its use involves less labor than the use of equation 2. The standard deviation, σ, is commonly employed in modern works on statistics and by students of biometrics and quality control. Since it is directly proportional to q,

$$q = 0.674\ \sigma$$

it is immaterial which measure of the precision is used. The probability that a given value of the residual, r_i, will fall within the limits $\pm\ \sigma$ is 0.68. Of the various functions which are measures of reliability, the simplest and possibly the most commonly used by chemists is the average error of a measurement, v; that is, the arithmetic average of all the residuals taken without regard to sign,

$$v = \frac{1}{N} \sum_i |r_i| \tag{4}$$

It is interesting to compare the values of m, v, and q for the three sets of data, I, I*A*, and II.

TABLE 2

QUANTITY	SERIES I	SERIES I*A*	SERIES II
N	150	50	150
ΔS	0.01 mm.	0.01	0.005
m	7.360 mm.	7.360+	7.360
$v = \frac{1}{N}\sum_i \lvert r_i \rvert$	0.014 mm.	0.014+	0.014
$q' \backsimeq 0.845\,v$	0.012 mm.	0.012	0.012
$q = 0.674\sqrt{\frac{\sum_i r_i^2}{N-1}}$	0.012 mm.	0.012+	0.012
$\sigma = \sqrt{\frac{\sum r^2}{N-1}}$	0.018 mm.	0.019	0.018

The parameters used in constructing the curve (figure 3) were $m = 7.360$ and $h = 40$, which corresponds to $q = 0.0119$. Within the limits to which it seems reasonable to record these data (i.e., the number of significant figures), the values of m, v, and q are the same for the three sets of measurements. However, it would be incorrect to conclude from this that the best values of the diameter based upon series I and upon series I*A* are equally reliable. The quantities, q and v, which we have computed, indicate the reliability of single determinations. For example, the fact that $q = 0.012$ signifies that the probability is equal to 1/2 that any of the 150 measured values of series I or of the 50 values of series I*A*, chosen at random, will have a residual between 0.012 and -0.012 mm. Since the measurements in these series were performed in the same way, it would be surprising if they were not equally reliable. On the other hand, it would be equally surprising if the mean value based upon the 150 measurements of series I was not more reliable than that based upon the 50 measurements of series I*A*.

Since the mean may be considered to be a function (see 14, also 28), $m = \frac{1}{N}\sum_i S_i$, of the several independently measured values, S_i, it can be demonstrated in terms of equation 9 that the error of a mean is inversely proportional to the square root of the number of measurements used to establish the mean. If we denote the probable error of the mean value by Q and the average error of the mean value by V, we may write

$$\begin{aligned} Q &= q/\sqrt{N} \\ &= 0.674\sqrt{\frac{\sum_i r_i^2}{N(N-1)}} \backsimeq \frac{0.674}{N}\sqrt{\sum_i r_i^2} \end{aligned} \tag{5}$$

$$\begin{aligned} V &= v/\sqrt{N} \\ &= \frac{1}{N^{3/2}}\sum_i |r_i| \end{aligned} \tag{6}$$

The values of Q for series I and IA are, respectively, 0.0010 and 0.0017. Frequently, this is indicated by writing

$$m_{IA} = 7.360 \pm 0.002$$

or more briefly

$$m_{IA} = 7.360 \pm 2$$

For some purposes it would be justifiable to retain one more significant figure, as

$$m_{IA} = 7.3604 \pm 0.0017$$

but this is neither customary nor useful in recording the results of ordinary chemical measurements.

APPLICATION OF ERROR THEORY TO EXPERIMENTAL DATA

These methods of determining the best value and the probable error apply only to those cases where the several measurements are of equal weight. For a discussion of the more general methods which must be used when the individual measurements are assigned different weights, consult any general treatise on the method of least squares. The practice of intuitively assigning arbitrary weights, other than 1 or 0, is seldom if ever justifiable and should not be followed. Occasionally an arbitrary weight of 0 may be assigned a measured value (i.e., the measurement may be rejected), but this should never be done without some sound reason. The mere fact that one or more measurement in a series departs widely from the mean is not sufficient justification for its rejection. A result should only be rejected when the observer has a definite reason for believing that the corresponding experiment was subject to some special uncertainty. In such cases it is preferable to reject the result immediately, before the observer's judgment is biased by a comparison of this result with the mean. (For a clear statement of a contrary view see "Theory of Measurements," Palmer (1912), pp. 124–30.) Of course some common sense has to be used in applying any such rules. If a beginner noticed that the first five of a series of ten measurements were much more discordant than the last five, he would probably be justified in rejecting the earlier measurements on the assumption that the discrepancies were due to his lack of experience with the technique. It is probably defensible to reject a discordant result when the discrepancy can be explained by assuming some definite and probable clerical error; such as writing an 8 for a 3 or recording a 5 mg. as a 50 mg. weight. Needless to say, all such adjustments must be considered as makeshifts and compromises; they detract seriously from the apparent reliability of the data. Some beginning students are occasionally tempted to reject all but two or three measurements from a set of rather scattered data merely because these measurements have values the same or similar. Such an arbitrary selection has no possible justification, it strongly suggests intellectual dishonesty, and should never be practiced.

It should be remembered that equations 2 to 6 apply only to measured quantities. There is no a priori reason for believing that the mean of a thousand guesses will be any more accurate than a single guess. It is advantageous to estimate the reading of an instrument to the nearest tenth, or in some cases fifth, of the smallest division. However, it would be useless to record the reading to a hundredth of the smallest division, since the last figure would have to be added entirely as a guess.

No series of measurements can yield a result more accurate than the calibration of the measuring instrument. Furthermore, the reading of an instrument is usually affected by the conditions under which it is used. The length of a scale varies with its temperature. The reading of a thermometer is affected by the temperature of its exposed stem and to a lesser extent by the total pressure upon its bulb. Whenever possible, an instrument should be recalibrated under the conditions of its use. In some cases, as in the change of length of a millimeter scale with temperature, a suitable correction can be applied in terms of the known properties of the instrument. Errors of this type as well as those due to an unconscious bias on the part of the observer are known as *systematic* or *persistent* errors. When they are due to faulty calibration of the instrument, they are known as *instrumental* errors. When they are due to the use of an instrument under conditions differing from those in which it was calibrated, they are sometimes referred to as *conditional* errors. Such errors are frequently more important than the erratic departures from the mean. When they are known or suspected, the experiment should be modified to minimize them. Frequently the measurements can be corrected for known instrumental or conditional errors. Examples of such corrections are outlined in Experiments 1, 4, 5, 10, 11, 12, 15, and 21. Valuable discussions can be found in K & S, pp. 262–70; "Theory of Measurements," Palmer, pp. 117–24; "Chemical Computations and Errors," Crumpler and Yoe, Chap. VII; and "Laboratory Manual of Physical Chemistry," Mack and France, pp. 13–8.

If a series of measurements of a given quantity have been made, it is always worth while to plot the measured values, or the corresponding residuals, in the order in which they were taken, or as a function of the time at which the measurements were made. If the values arranged in this way show a definite trend, it is convincing evidence that a *systematic* error is present. Under these conditions it is not justifiable to assume that the mean of the observations is the best value. The experimental procedure should be reviewed carefully in an attempt to discover any neglected source of conditional or instrumental error. If the systematic error can be estimated quantitatively, the data should be corrected for it before being averaged. If the sources of error is discovered but the magnitude of the correction is unknown (for example, the hysteresis of a thermometer bulb or a slow leak in a gas container) it may be that the best approximation to the true value is the last or first observation. In this case the experimental procedure should be modified to eliminate or reduce the systematic error, and the measurements repeated.

While constant errors cannot be detected by analysis of the data, they are frequently revealed by a change in experimental technique. For this reason, it is always worth while to repeat important measurements by at least two different and independent experimental methods.

APPLICATION OF ERROR THEORY TO FUNCTIONS OF A SINGLE VARIABLE

Many physical properties are most conveniently measured indirectly in terms of some related simpler property. In these cases it is necessary to determine the best value and the probable error of the computed quantity. As an illustration, let us assume that we wish to know the best value of the area of the ballbearing whose diameter (tables 1 and 2) is 7.360 ± 0.012. It can be shown to be a consequence of the theory of least squares, that the best value of a function is obtained by substituting the mean value of the measured quantity in the function; not by computing a value of the function corresponding to each observation and then averaging these computed values. Therefore the best value of the area, A, is

$$\begin{aligned} A &= \pi(7.360 \pm 0.012)^2 \\ &= 170.15 \pm 0.55 + 0.0005 \text{ mm.}^2 \\ &= 170.2 \pm 0.6 \text{ mm.}^2 \end{aligned}$$

Since 0.012 mm. is the probable error of the mean value of the diameter it is natural to assume that 0.6 mm.^{2} is the probable error of the best value of the area. That this is indeed true can be demonstrated as follows.

Let a certain derived property, p, be some function, f, of a measured quantity, S. Then corresponding to every measured value, S_i, there will be a derived value, $p_i = f(S_i)$. The best value, P, of the derived quantity is given by the equation

$$P = f(m),$$

where m is the arithmetic mean of all the measured values, S_i. Corresponding to the residual,

$$r_i = m - S_i$$

of each measured value, S_i, there will be a residual,

$$R_i = P - f(S_i) \tag{7}$$

of each derived value, p_i. When the residuals are small compared to the corresponding quantities, as they are in all except the crudest measurements, the following relation will be a close approximation.

$$\frac{R_i}{r_i} = \frac{df(S)}{dS} = \frac{dp_i}{dS_i}$$

Squaring both sides of this equation and rearranging it, we obtain

$$R_i^2 = \left(\frac{df(S)}{dS}\right)^2 r_i^2$$

Summing up for all values of i

$$\sum_i R_i^2 = \left(\frac{df(S)}{dS}\right)^2 \sum_i r_i^2$$

On taking the square root of both sides of the equation and multiplying through by $0.674/\sqrt{N-1}$, where N is the total number of measurements, it follows that

$$0.674\sqrt{\frac{1}{N-1}\sum_i R_i^2} = \left(\frac{df(S)}{dS}\right) 0.674\sqrt{\frac{1}{N-1}\sum_i r_i^2}$$

Substituting from equation 5, we may write

$$\mathbf{Q} = \left[\frac{df(S)}{dS}\right]_m Q \tag{8}$$

This is the general relation between the probable error, Q, of the mean, m, of a measured quantity, S, and the probable error, $\mathbf{Q}$, of the best value, P, of a derived quantity, $p = f(S)$.

The example which we have already considered will serve to illustrate the use of this equation. In this case,

$$f(S) = \pi S^2$$

and

$$\frac{df(S)}{dS} = 2\pi S$$

Substituting in equation 8, we obtain

$$\mathbf{Q} = 2\pi m Q$$

Since the mean value of S is 7.360 mm. and the probable error, Q, is 0.012 mm.

$$\begin{aligned}\mathbf{Q} &= 2\pi 7.360 \times 0.012 \text{ mm.}^2\\ &= 0.55 \text{ mm.}\end{aligned}$$

which is in agreement with the result previously obtained.

As a further illustration of the use of this equation (8), it has been applied to several typical functions and the results are given in the following table. It is assumed that the quantities A, B, and n which occur in this table are exactly known constants.

TABLE 3

APPLICATIONS OF THE EQUATION, $\mathbf{Q} = \frac{df(S)}{dS} Q$

$p = f(S)$	$\frac{dp}{dS} = \frac{df(S)}{dS}$	$\mathbf{Q} = \frac{df(S)}{dS} Q$
$A \cdot S$	A	AQ
S^n	nS^{n-1}	$nm^{n-1}Q$
$S^2 + AS + B$	$2S + A$	$(2m + A)Q$
$\ln S$	$1/S$	Q/m
e^S	e^S	$e^m Q$

APPLICATION OF ERROR THEORY TO FUNCTIONS OF SEVERAL VARIABLES

Most of the properties which are studied in the physico chemical laboratory are determined indirectly as functions of several variables, which are measured independently. It is essential therefore to be able to apply the theory of least squares to such cases. As in the case of the function of a single variable, the best value of the derived quantity is obtained by substituting the mean values of the several variables in the function. It can be demonstrated by a method similar to that used in deriving equation 8, that the probable error, $\mathbf{Q}$, of the best value, P, of the function,

$$p = f(S_1, S_2, S_3, \cdots, S_n)$$

is related to the probable errors, $Q_1, Q_2, \cdots, Q_n$, of the mean values, $m_1, m_2, \cdots, m_n$, of the several independently measured quantities, $S_1, S_2, \cdots, S_n$, by the following equation:

$$\mathbf{Q} = \sqrt{\sum_j \left(\frac{\partial p}{\partial S_j}\right)^2 Q_j^2} \qquad (9)$$

In experiments of this kind, it is seldom that a sufficiently large number of measurements of the several variables are made to permit the determinations of the probable errors, Q_j, by means of equation 5. Indeed, in some cases it is only possible to make a single measurement on a given sample. However, even in such cases it is usually possible to make a reasonably accurate estimate of the probable error of each measurement. As an illustration, let us assume that the density of a dilute aqueous solution was determined as follows: A 25-ml. pipet was calibrated with pure water at room temperature (20°C), using calibrated weights, an analytical balance, and a covered weighing bottle. To reduce errors due to the adsorption of moisture, the tare was made of glass and had approximately the same exposed surface as the weighing bottle. Ten determinations were made of the volume delivered, and the resulting best value was 24.98 ± 0.03 ml., where the uncertainty (0.03) is expressed as the probable error of a single measurement. The same pipet was filled with a dilute aqueous solution and was allowed to drain into the weighing bottle. The weight of the liquid, corrected for air buoyancy, was found to be 25.0832 gm. It is apparent that this method permits only one determination of the volume to be made on each sample. However, it is very likely that the probable error of a single determination of volume is the same for a dilute aqueous solution as it is for water. It is a matter of common knowledge, based upon the results of thousands of similar weighings, that the uncertainty of a single weighing, made with an analytical balance and calibrated weights, is about 0.2 mg. For want of a better estimate we may identify this uncertainty with the probable error of a single weighing. Substituting these values in equation 9, we find for the probable error, **Q**, of this determination of the density, *D*,

$$\begin{aligned}
\mathbf{Q} &= \sqrt{\left(\frac{\partial D}{\partial w}\right)^2 Q_w^2 + \left(\frac{\partial D}{\partial v}\right)^2 Q_v^2} \\
&= \sqrt{\left(\frac{1}{v}\right)^2 Q_w^2 + \left(-\frac{w}{v^2}\right)^2 Q_v^2} \\
&= \sqrt{\frac{1}{(24.98)^2}(0.0002)^2 + \left(\frac{25.083}{(24.982)^2}\right)^2 (0.03)^2} \\
&= \sqrt{6.4 \times 10^{-11} + 1.45 \times 10^{-6}} = 0.0012
\end{aligned}$$

The best value of the density is 1.0042 ± 0.0012 gm./ml. In estimating the error of the weighing, we have neglected the possibility that the tare was not exactly adjusted and that the correction for air buoyancy was made improperly. However, the omission of these contributions to the probable error, which are certainly of minor importance, is surely justifiable, since the computations show that the entire contribution of the error of weighing is quite negligible. We were also justified in neglecting the probable error of the calibration of the pipet, since the density was the result of a single measurement while the calibration was the mean of ten determinations. If we were to attempt to improve the accuracy of our value of the density by making several determinations, we would have to allow for the uncertainty of the calibration of the pipet in computing the probable error of the mean value of the density. In other words no measurement can be more accurate than the calibration of the instrument with which it is made. The probable error in the calibration of the pipet is $0.03/\sqrt{10}$ (see equation 5), or 0.01 ml. If there were no other source of error, the probable error of the density would be $(25.083/24.98^2)0.01$, or 4×10^{-4} gm./ml. This is the limiting value of the probable error which would be approached if a very large number of determinations of the density were performed with this calibrated pipet.

Another experiment which will serve to illustrate the application of equation 9 is the determination of the molecular weight of a vapor by the Dumas method (expt. 1, 53). In this method a flask of weight, w_1, is filled with vapor at barometric pressure, P_B, and the boiling point of water, T_B°A. It is sealed under these conditions and, after cooling, the total weight, w_2, of flask and vapor is determined. It is then filled with water, and its weight, w_3, determined with a Trip balance. To compute the molecular weight of the vapor, it is necessary to know the density of water, D_w, and the density of air, D_A, at the temperature and pressure of the laboratory. It can be readily shown that if the perfect gas law,

$$PV = nRT$$

(M, 32) holds, the molecular weight, M, is related to the measured quantities as follows.

$$M = \frac{[w_2 - w_1 + (w_3 - w_1)D_A/D_w]}{P_B(w_3 - w_1)} RT_BD_w$$

Let us assume that such an experiment has been performed and has yielded the following data.

$w_1 = 20.0000 \pm 0.0002$ gm.
$w_2 = 21.0000 \pm 0.0002$ gm.
$w_3 = 220.0 \pm 0.2$ gm.
$D_A = 0.00100 \pm 0.00001$ gm./ml.
$D_w = 1.000 \pm 0.001$ gm./ml.
$T_B = 373.0 \pm 0.1°A$,
$P_B = 1.0000 \pm 0.0003$ atm.

The room temperature was approximately 20°C. The indicated uncertainties are the probable errors of single measurements. As in the other illustration, the probable errors of the several variables have been estimated. The densities were obtained from tables; the errors of these quantities were estimated as due chiefly to the uncertainty in the observation of the room temperature. The expression for the molecular weight and the computation of the probable error can be simplified by explicitly introducing the weight of the water,

$$w_w = w_3 - w_1$$

The best value and the probable error of w_w can be computed as follows:

$$\begin{aligned} Q_{w_w} &= \sqrt{\left(\frac{\partial w_w}{\partial w_3}\right)^2 Q^2{}_{w_3} + \left(\frac{\partial w_w}{\partial w_1}\right)^2 Q^2{}_{w_1}} \\ &= \sqrt{Q^2{}_{w_3} + Q^2{}_{w_1}} = \sqrt{4 \times 10^{-2} + 10^{-8}} = 0.2 \\ w_w &= 200.0 \pm 0.2 \text{ gm.} \end{aligned}$$

In terms of this new quantity the equation for the molecular weight becomes

$$M = \frac{(w_2 - w_1 + w_w D_A/D_w)}{P_B w_w} RT_B D_w$$

The terms listed in the table on page 26 are those occurring in the expression for the probable error, Q, of M. These terms were obtained by combining the above equation with equation 9. The probable error of this determination of the molecular weight is equal to the square root of the sum of the terms listed in the last column.

$$\begin{aligned} \mathrm{Q} &= \sqrt{\sum_j \left(\frac{\partial p}{\partial S_j}\right)^2 Q^2{}_{S_j}} \\ &= \sqrt{0.142} = 0.38 \end{aligned}$$

The best value of M is 183.7 ± 0.4. Inspection of the table indicates that the chief source of error in the determination was the inaccurate value of D_A. Therefore it would be worthwhile in subsequent experiments to use a more accurate value for D_A, taking into account the humidity as well as the pressure and temperature of the air. It should be realized that this computation does not necessarily indicate the true accuracy of such an experiment. The success of the measurement depends upon the experimenter's

TABLE 4

APPLICATION OF EQUATION 9 TO A MOLECULAR WEIGHT MEASUREMENT

S_j	$\frac{\partial p}{\partial S_j}$		Q_j	$\left(\frac{\partial p}{\partial S_j}\right)^2 Q_j^2$
T_B	$\frac{M}{T_B}$	0.493	1×10^{-1}	0.002
P_B	$-\frac{M}{P_B}$	183.7	3×10^{-4}	0.003
w_1	$-\frac{RT_BD_w}{P_Bw_w}$	-153.0	2×10^{-4}	0.001
w_2	$\frac{RT_BD_w}{P_Bw_w}$	153.0	2×10^{-4}	0.001
w_w	$\frac{RT_BD_w}{P_B} \times \frac{w_1 - w_2}{w^2_w}$	0.765	2×10^{-1}	0.023
D_w	$\frac{RT_B}{P_Bw_w}(w_2 - w_1)$	139.2	1×10^{-3}	0.019
D_A	$\frac{RT_BD_w}{P_B}$	30600	1×10^{-4}	0.093

judgment in sealing the flask at a moment when it contains no liquid but is entirely filled with vapor; no allowance for this possible source of inaccuracy was made in the preceding computation. Unless the experimenter has had some practice with this operation, it is likely to be the largest source of error in the measurement. Furthermore the molecular weight so determined differs from the ideal molecular, or formula, weight due to the departure of the vapor from the perfect gas laws. However, it is quite reasonable to consider the experiment as a measurement of the apparent rather than the true molecular weight, and thereby to exclude departures from the gas laws from the sources of error.

Since the application of equation 9 to the results of complex experiments is frequently laborious and time consuming, certain approximate rules have come into common use. It will be instructive to examine their relation to equation 9. One of these rules concerns the product, p, of several measured quantities, S_j, whose mean values are $m_j \pm Q_j$.

$$p = S_i \cdot S_2 \cdot S_3 \cdots S_n$$

The partial derivative of p in respect to S_j is

$$\frac{\partial p}{\partial S_j} = \frac{p}{S_j}$$

Substituting this relation in equation 9 and introducing the best values, P and m_j, we obtain

$$\mathbf{Q} = \sqrt{\sum_j \left(\frac{P}{m_j}\right)^2 Q_j^2}$$

Dividing both sides of this equation by P, we may write

$$\frac{\mathbf{Q}}{P} = \sqrt{\sum_j \left(\frac{Q_j}{m_j}\right)^2} \qquad (10)$$

This relation applies to division as well as to multiplication. The student may verify this by substituting in the function, $p = f(S_1, S_2, \text{etc.})$ the quantity $(1/S_r)$ for any factor, S_k, and then taking the partial, $(\partial p/\partial S_r)$ and introducing the resulting expression in equation 9. The quantities $\mathbf{Q}/P$ and Q/m_j, which may be called the relative probable errors, are equal to the corresponding percentage errors divided by one hundred. It follows from equation 10, that the percentage error of the product is equal to the square root of the sum of the squares of the percentage errors of the variables. If one of the terms, $(Q_k/m_k)^2$, is much larger than the others, equation 10 reduces to the following simple form.

$$\mathbf{Q}/P \simeq Q_k/m_k$$

This leads to the common approximate rule, "In multiplication or division retain the largest percentage error." This rule gives reasonably good results even when the quantities, Q_j/m_j, are of the same order of magnitude. For example, in the case

$$p = a \cdot b$$

where the percentage errors of a and b are equal, the rule indicates that

$$\mathbf{Q}/P = Q_a/m_a$$

An application of equation 9 shows that the correct value is

$$\mathbf{Q}/p = \sqrt{2}\, Q_a/m_a$$

For many purposes, this difference would be unimportant. The rule breaks down completely only in those cases where p is the product of a large number of factors whose percentage errors are of the same order of magnitude.

In the case of addition or subtraction,

$$p = S_1 + S_2 + S_3 + \cdots + S_n$$

where S_j may be either positive or negative,

$$\frac{\partial p}{\partial S_j} = \pm 1$$

Substituting this result in equation 9, we obtain

$$\mathbf{Q} = \sqrt{\sum_j Q_j^2} \tag{11}$$

This equation leads directly to the approximate rule, "In addition or subtraction retain the largest absolute error." The application of this rule has about the same limitations as the rule for multiplication and division.

The approximate value of the probable error of any ordinary function of several measured quantities may be obtained by using these two rules with equation 8, or with the formulas of table 3. In the first illustration which we considered (22), the density was computed from a measured mass and volume. The percentage error, $\frac{0.03}{24.98} \times 100$, of this volume is obviously larger than that of the mass. Applying the approximate rule, we find that the probable error of the density is

$$\mathbf{Q} = \frac{0.03}{24.98} \times 1.0042 = 0.12$$

which is numerically identical with the value obtained by the exact method. In the case of the molecular weight determination (23), the approximate method may be applied as follows. The percentage error of the product $W_w D_A / D_w$ is equal to that of D_A or 1%. The corresponding absolute error is 0.002. This is the largest absolute error in the sum, $W_2 - W_1 + W_w D_A / D_w$. Therefore the percentage error of this sum is $100 \times 0.002/1.200$. Since this is larger than the percentage errors of any of the other factors, the approximate value of **Q** is

$$\mathbf{Q} = 183.7 \times \frac{0.002}{1.200} = 0.3$$

While this is slightly smaller than the value, 0.4, obtained by the exact method, the difference is relatively unimportant.

TABLE 5

SUMMARY OF FORMULAS AND RULES WHICH ARE IMPORTANT IN THE ANALYSIS OF ERRORS OF MEASUREMENTS

A. Concerning the Direct Measurement of a Single Quantity

a. The best value of the quantity is the arithmetic mean, m, of the N measurements, S_i (14).

$$m = \frac{1}{N}\sum_i S_i$$

b. The residual, r_i, of a measured value, S_i, (14) is

$$r_i = S_i - m$$

c. The probable error, q, of a measured value, S_i, (15) is

$$q = 0.674\sqrt{\frac{1}{N-1}\sum_i r_i^2} \tag{2}$$

or approximately

$$q \cong \frac{0.845}{N}\sum_i |r_i| \tag{3}$$

d. The standard deviation, σ, of a measured value, S_i, (15) is

$$\sigma = \sqrt{\frac{1}{N-1}\sum_i r_i^2}$$

e. The average error, r, of a measured value, S_i, (15) is

$$v = \frac{1}{N}\sum_i |r_i| \tag{4}$$

f. The probable error, Q, of the mean value, m, (17) is

$$\begin{aligned} Q &= q/\sqrt{N} \\ &= 0.674\sqrt{\frac{1}{N(N-1)}\sum_i r_i^2} \end{aligned} \tag{5}$$

g. The standard deviation, σ_m, of the mean value, m, (15) is

$$\sigma_m = \sigma/\sqrt{N}$$

h. The average error, V, of the mean value, m, (17) is

$$\begin{aligned} V &= v/\sqrt{N} \\ &= \frac{1}{N^{3/2}}\sum_i |r_i| \end{aligned} \tag{6}$$

B. Concerning the Indirect Measurement of a Quantity, p, Which Is Some Function, $f(S)$, of a Directly Measured Quantity, S.

a. The best value, P, of the derived quantity, p, (26) is

$$P = f(m)$$

b. The probable error, Q, of the best value, P, of the derived quantity, p, (20) is

$$Q = \left[\frac{df(S)}{dS}\right]_m Q \tag{8}$$

C. Concerning the Indirect Measurement of a Quantity, p, Which Is a Function, $f(S_1, S_2, \cdots, S_n)$, of Several Directly Measured Quantities, S_j.

a. The best value, P, of the derived quantity, p, (27) is

$$P = f(m_1, m_2, \cdots, m_n)$$

where m_j are the mean values of the directly measured quantities, S_j.

b. The probable error, Q, of the best value, P, of the derived quantity, p, (21) is

$$Q = \sqrt{\sum_j \left(\frac{\partial p}{\partial S_j}\right)^2 Q_{S_j}^2} \tag{9}$$

c. The following two rules (27) (28) may be used when only the approximate value of Q is required:

In multiplication or division retain the largest percentage error.
In addition or subtraction retain the largest absolute error.

EVALUATION OF THE CONSTANTS OF EMPIRICAL EQUATIONS

It is often necessary to determine the constants of equations which relate the physical properties of substances. The determination of these constants is next in importance to the measurement of the properties themselves. Sometimes the form of the equation is known or assumed, and it is only necessary to evaluate the coefficients. The determination of ΔH and B in the relation between vapor pressure and temperature (M, 88–9),

$$\ln p = -\Delta H/RT + B,$$

or of a and b in the van der Waals equation (M, 65),

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT,$$

are examples of this kind. Of course the resulting equations with numerical coefficients are valid only over the range of temperature and pressure used in evaluating the coefficients; they cannot be used for extrapolation. In other cases, exponents as well as coefficients are unknown and must be evaluated. Examples of this kind are reaction velocity equations (M, 420–1) and the Freundlich adsorption isotherm (M, 435),

$$\frac{x}{m} = kc^n$$

in which both k and n are adjustable constants. In a third group of equations, known as empirical equations, both the type of function and the values of the constants are unknown and must be determined from the experimental data. While the equations which make up this group are not of much theoretical significance, they are of the greatest practical importance; being used as interpolation formulas and to record experimental data in a very brief way. Power series are commonly used for this purpose, since they can represent any ordinary function. However, if the data obviously fit some simple function, as an exponential relation, it is usually advisable to adopt this function directly. The present discussion is limited to non-periodic functions of one independent variable. Most of the equations which are of interest to chemists belong to this class.

A linear equation is the simplest of empirical relations and is very commonly used, especially as an interpolation formula for a narrow range of values of the independent variable. It may be considered as a power series in which the coefficients are zero for all powers greater than one. As an illustration, let us assume that the specific heat, C, of a certain organic liquid has been determined at several temperatures, from 5 to 25°C, and that the best values of the coefficients of a linear interpolation formula are desired. The experimental data are given in the first two columns of the

TABLE 6

Application of a Linear Empirical Equation to Experimental Data

t	C	$\rho_A \times 10^4$	$\rho_B \times 10^4$	$\rho_C \times 10^4$	$\rho_D \times 10^4$	$\rho_G \times 10^4$
5.03	0.4002	0	+16	+8	+7	+9
7.10	.4009	−15	− 1	−8	−8	−7
9.24	.4040	− 7	+ 6	0	0	+1
11.38	.4061	− 9	+ 3	−3	−3	−2
13.41	.4091	− 1	+10	+4	+5	+5
15.36	.4103	−10	0	−5	−4	−4
17.89	.4133	− 7	+ 1	−2	−1	−2
19.21	.4151	− 4	+ 4	+1	+2	+1
22.00	.4178	− 7	0	−3	−1	−3
24.17	.4208	0	+ 5	+4	+6	+3
$0.674\sqrt{\dfrac{\sum \rho_i^2}{N-k}} \times 10^4$		5.7	5.0	3.4	3.4	3.4

table as shown on page 31. In determining the coefficients, C_0 and b, of the equation,

$$C = C_0 + bt$$

it should be remembered that the observed values are not exact and that furthermore the specific heat probably cannot be represented accurately by a linear function of temperature. If the data were exact and could be so represented, the values of the coefficients could be obtained by introducing any two pairs of measurements in the linear equation and solving the resulting simultaneous equations. While this method is extremely unreliable when applied to experimental data, it is quick and easy and, therefore, is sometimes used. It is known as the method of selected points. For example, if we select the extreme points, at 5.03 and 24.17°C., and substitute these values in the linear equation, we obtain

$$0.4002 = C_0 + 5.03\,b$$
$$0.4208 = C_0 + 24.17\,b$$

The solution of these simultaneous equations leads to the relation

$$C_A = 0.3948 + 0.001076\,t$$

To permit a comparison between the measured values of C and those computed with this equation, the residuals,

$$\rho_A = C - C_A$$

have been computed and are tabulated in the third column of table 6. It is apparent that the values of the coefficients and of C_A depend upon the arbitrary selection of the pair of points. For example, when the points at $t = 7.10$ and 22.00° are used, the resulting equation is

$$C_B = 0.3929 + 0.001134\,t$$

The values of the corresponding residuals are listed in column four. To avoid this arbitrary choice and to obtain better values of the coefficients, either the method of least squares or the method of averages may be used.

According to the theory of least squares, the best values of the coefficients are those which make the sum of the squares of the residuals,

$$\sum_i \rho_i^2 = \sum_i (C_i - C_0 - bt_i)^2$$

a minimum (compare 15). Since C_0 and b are the only two quantities which can be varied, the sum of the squares of the residuals will have a minimum value when its partials in respect to C_0 and b are equal to zero.

$$\frac{\partial}{\partial C_0}\sum_i \rho_i^2 = 0$$

$$\frac{\partial}{\partial b}\sum_i \rho_i^2 = 0$$

Introducing the values of ρ and carrying out the indicated operations, we obtain

$$-2\sum_i (C_i - C_0 - bt_i) = 0$$

or

$$\sum_i C_i - nC_0 - b\sum_i t_i = 0 \tag{12}$$

and

$$-2\sum_i (C_i - C_0 - bt_i)t_i = 0$$

or

$$\sum_i C_i t_i - C_0\sum_i t_i - b\sum_i t_i^2 = 0 \tag{13}$$

The quantity n in equation 12 is the number of measurements, equal to 10 in the present case. The following general equations, 14 and 15, which can be obtained by substituting the general variables x and y and the undefined constant a for the corresponding specific quantities in equations 12 and 13, can be used to determine the best values of the coefficients in any linear empirical equation,

$$y = a + bx$$

$$\sum_i y_i - na - b\sum_i x_i = 0 \tag{14}$$

$$\sum_i y_i x_i - a\sum_i x_i - b\sum_i x_i^2 = 0 \tag{15}$$

In applying equations 12 and 13 it is necessary to compute values of t^2 and Ct corresponding to each value of t, and then to add up all of the values of each of the following quantities t, t^2, C, and Ct.

Performing these computations and introducing the numerical values of the sums into equations 12 and 13, we obtain the following equations:

$$\begin{aligned} 4.0976 - \quad 10\,C_0 - \quad 144.79\,b &= 0 \\ 59.7323 - 144.79\,C_0 - 2463.60\,b &= 0 \end{aligned}$$

the expression resulting from the simultaneous solution of these equations is

$$C_c = 0.3939 + 0.001098\,t$$

These are the best values of the coefficients C_0 and b. The values of the residuals corresponding to this equation are given in the fifth column of table 6.

The method of averages, while less exact than the method of least squares, is satisfactory for many purposes and its application does not require as much labor. It is based upon the assumption that the correct values of the coefficients are those which make the sum of the residuals equal zero.

$$\sum_i \rho_i = \sum_i (C_i - C_0 - bt_i) = 0$$

This may be written in the form

$$\sum_i C_i - nC_0 - b\sum_i t_i = 0 \tag{16}$$

The general expression which corresponds to equation 16 is

$$\sum_i y_i - na - b\sum_i x_i = 0 \tag{17}$$

Since there are two unknowns, C_0 and b, and only one equation 17, it is necessary to divide the data into two groups. It is preferable to separate it into equal or nearly equal parts; the first, containing the first half of the data, and the second, the remainder of the data. To indicate this algebraically, we may replace equation 17 by the following equations:

$$\left.\begin{aligned} \sum_1^k y_i - ka - b\sum_1^k x_i &= 0 \\ \sum_{k+1}^n y_i - (n-k)a - b\sum_{k+1}^n x_i &= 0 \end{aligned}\right\} \tag{18}$$

where

$$k \simeq n/2$$

Applying this procedure to the present case, we obtain

$$\begin{aligned} 2.0203 - 5\,C_O - 46.16\,b &= 0 \\ 2.0773 - 5\,C_O - 98.63\,b &= 0 \end{aligned}$$

which leads to the following expression:

$$C_D = 0.3940 + 0.001086\,t$$

The values of the residuals based upon this equation are tabulated in the sixth column of table 6. Inspection of the tabulated residuals indicates that the equation obtained by the method of averages fits the data about as well as that based upon the method of least squares. On the other hand, the equations which were derived by the method of selected points are not only decidedly inferior, but differ widely from one another.

A convenient method of making a quantitative comparison of the fit of the several equations is to compute the quantity

$$0.674\sqrt{\frac{\sum \rho_i^2}{N - k}}$$

which is a measure of the "goodness of fit" of the equation to the data. (See Chemical Computations and Errors, Crumpler and Yoe, pp. 222–4.) In this equation, the ρ_i's are the residuals or differences between the observed and computed values of the dependent variable, N is the number of points used to evaluate the constants, and k is the number of adjustable constants in the equation (two in the present case). Numerical values of this quantity are given in the last row of table 6. They confirm the opinion which was based upon inspection of the table of residuals, that the equations obtained by the method of selected points are definitely inferior and that (in this case) the other equations are about equally good.

Some non-linear equations, which contain not more than two arbitrary constants, can be converted into linear equations by a suitable transformation or substitution of variables. For example, the relation between vapor pressure and temperature (M, 88–9),

$$\ln p = -\frac{\Delta H}{RT} + B$$

can be rendered linear by introducing the variables $u = \ln p$ and $v = 1/T$. The constants $\Delta H/R$ and B can then be determined by applying one of the standard methods to the resulting equation

$$u = -\frac{\Delta H}{R} v + B$$

In general, equations of the form

$$f(y) = a + bf'(x)$$

can be rectified by substituting $u = f(y)$ and $v = f'(x)$. Exponential equations,

$$y = ae^{bx}$$

can be put in linear form by first taking logarithms of both sides,

$$\ln y = \ln a + bx$$

and then substituting $u = \ln y$. Equations containing an arbitrary exponent, n, and a coefficient, a,

$$y = ax^n$$

can be rectified by first taking logarithms of both sides,

$$\ln y = \ln a + n \ln x$$

and then substituting $x = \ln y$ and $v = \ln x$. The process of rectification is frequently combined with a graphical method (45) of determining the values of the constants; however, either of the analytical methods may be used to evaluate the coefficients of the rectified equation. To obtain the best values of the coefficients of a rectified equation by an analytical method, it is commonly necessary to allow for the different weights of the coordinates of the several points. For a simple introduction to the methods of weighting see Theory of Measurements, Palmer, Chap. IX or Chemical Computations and Errors, Crumpler and Yoe, pp. 191–4.

In working with power series it is necessary, or at least very convenient, to have a method of deciding what is the highest power of the independent variable which must be retained in the equation. Whenever the values of the independent variable form an arithmetic progression (i.e., increase by some constant quantity) the highest exponent required for the power series can be determined by means of a table of successive differences. For example, let us consider some quantity $y = f(x)$ which can be represented by a power series in x,

$$y = a + bx + cx^2 + dx^3 + \cdots$$

and for which the successive values of x differ by a constant quantity, h. If the first value of x is denoted by x_0, the second by $x_0 + h$, and the kth by $x_0 + kh$, the differences between successive values of y are

$$\Delta_1^1 y = f(x_0 + h) - f(x_0)$$
$$\Delta_2^1 y = f(x_0 + 2\,h) - f(x_0 + h)$$

and

$$\Delta_k^1 y = f(x_0 + kh) - f(x_0 + [k - 1]h)$$

Correspondingly, the second differences in y are

$$\Delta_1^2 y = \Delta_2^1 y - \Delta_1^1 y$$
$$\Delta_2^2 y = \Delta_3^1 y - \Delta_2^1 y$$

and

$$\Delta_k^2 y = \Delta_{k+1}^{\,1} y - \Delta_k^1 y$$

The third and higher order differences are defined in an analogous manner. It can be readily demonstrated by a consideration of the general case, that the order of the difference which becomes constant corresponds to the highest power of the series which has a finite coefficient. For example, if the data can be represented by a quadratic equation, the second order differences, $\Delta_1^2 y$, will be sensibly constant; or if the data approximates to a cubic function, the third order differences, $\Delta_1^3 y$, are approximately constant. When the kth order differences, Δ_i^k, are constant, the $k + 1$ and all higher order differences are equal to zero. The data in the following table will serve to illustrate these relations. These data were not obtained by means of measurements; but the values of y were computed by means of the following cubic equation from an assumed series of values of x, for which $\Delta x = 0.100$.

$$y = 4 + 3\,x + 2\,x^2 + x^3$$

Corresponding to the fact that in the series the highest power with a finite coefficient is 3, the third order difference is constant. In the equation the coefficients of all powers of x higher than 3 are zero, and in the table all differences beyond the third are zero. The numerical values of the coefficients in the power series were chosen at random. While these coefficients determine the numerical values of the successive differences, the coefficients of the first three terms might have any finite positive or negative value or be equal to zero without affecting the constancy of the third order difference. So long as the coefficient of x^3 is finite and the coefficients of all higher powers are zero, the third order differences will be constant and finite.

In a difference table constructed from measured quantities, no order of differences will be exactly constant. Due to the erratic errors of the measurements, the difference column which would otherwise be constant will show erratic variations about a mean, and the next higher order of differences will be made up of small values of both signs, whose average will be approximately zero. The table, as shown on page 39 which is based upon measurements of the density, D, of an organic liquid at temperatures from 0 to 100°C., is typical of a difference table constructed from experimental data. It is apparent that the second order differences are constant, and that the third order differences, which are both positive and negative, have an average value of 0.0000. This indicates that, within the range of temperatures studied and within the limits of the experimental accuracy, the density may be represented by a quadratic function of the temperature,

TABLE 7

SUCCESSIVE DIFFERENCES CORRESPONDING TO A CUBIC FUNCTION

x_i	y_i	$\Delta_i y$	$\Delta_i^2 y$	$\Delta_i^3 y$
0	4.000			
		0.321		
0.100	4.321		0.046	
		.367		0.006
0.200	4.688		.052	
		.419		.006
0.300	5.107		.058	
		.477		.006
0.400	5.584		.064	
		.541		.006
0.500	6.125		.070	
		.611		.006
0.600	6.736		.076	
		.687		.006
0.700	7.423		.082	
		.769		.006
0.800	8.192		.088	
		.857		.006
0.900	9.049		.094	
		.951		
1.000	10.000			

$$D = a + bt + ct^2$$

In other words, we have determined that the coefficients of all higher powers of t are zero. The remaining problem is to determine the best values of the coefficients, a, b, and c.

In solving the problem by the method of selected points, it is necessary to choose three points, since three independent equations are required to determine the values of the unknowns, a, b, and c. If the method of least squares is applied, the three following simultaneous equations can be obtained from the fundamental postulate, that $\sum_i \rho_i^2$ is to be a minimum, by a procedure similar to that used on page 32.

TABLE 8

SUCCESSIVE DIFFERENCES CORRESPONDING TO MEASURED QUANTITIES

t_i°C	D_i	$-\Delta_i D$	$-\Delta_i^2 D$	$\Delta_i^3 D$	ρ_i
0.0	0.6454				0.0001
		0.0094			
10.0	.6360		0.0003		.0001
		.0097		0.0002	
20.0	.6263		.0001		−0.0001
		.0098		−0.0004	
30.0	.6165		.0005		0.0000
		.0103		0.0003	
40.0	.6062		.0002		.0000
		.0105		0.0000	
50.0	.5957		.0002		.0001
		.0107		−0.0002	
60.0	.5850		.0004		.0001
		.0111		0.0000	
70.0	.5739		.0004		.0002
		.0115		−0.0002	
80.0	.5624		.0006		.0003
		.0121		0.0001	
90.0	.5503		.0005		.0000
		.0126			
100.0	.5377				−0.0004

$$\sum_i D_i - na - b\sum_i t_i - C\sum_i t_i^2 = 0 \tag{19}$$

$$\sum_i D_i t_i - a\sum_i t_i - b\sum_i t_i^2 - C\sum_i t_i^3 = 0 \tag{20}$$

$$\sum_i D_i t_i^2 - a\sum_i t_i^2 - b\sum_i t_i^3 - C\sum_i t_i^4 = 0 \tag{21}$$

To obtain the values of a, b, and c, it is necessary to evaluate the several coefficients, $\sum_i t_i^4, \sum_i t_i^3, \sum_i D_i t_i^2$, etc., and then solve the equations 19, 20, and 21, simultaneously. To avoid the labor which the least squares solution demands, we shall evaluate the constants of the present quadratic expression by the method of averages. As was stated before (34), the postulate which is fundamental to this method of solution is, the best values of the coefficients are those which make the sum of the residuals equal to zero

$$\sum_i \rho_i = \sum_i (D_i - a - bt_i - ct_i^2) = 0$$

This may be written in the form

$$\sum_i D_i - na - b\sum_i t_i - c\sum_i t_i^2 = 0 \tag{22}$$

Since the postulate yields only one condition and there are three unknowns, a, b, and c, it is necessary to divide the data into three groups. It is convenient to take the first four points of table 8 as the first group, the next three for the second, and the last four for the third. In this way we can obtain the following three equations:

$$\begin{aligned} 2.5241 - 4\,a - 60\,b - 1{,}400\,c &= 0 \\ 1.7869 - 3\,a - 150\,b - 7{,}700\,c &= 0 \\ 2.2243 - 4\,a - 340\,b - 29{,}400\,c &= 0 \end{aligned}$$

Solving these simultaneously we obtain the following empirical equation

$$D = 0.6452 - 9.09 \times 10^{-4}\,t - 1.62 \times 10^{-6}\,t^2$$

The values of the residuals based upon this equation are given in the last column of table 8.

The application of these various methods to the evaluation of the coefficients of power series containing terms of higher order should be obvious. In any case the number of simultaneous equations required will be equal to the number of terms in the power series; two for a linear function, three for a quadratic, four for a cubic, etc. Since the labor involved in the application of the method of least squares to power series containing four or more terms is almost prohibitively great, the method of averages is used except when the highest accuracy is required.

GRAPHICAL METHODS OF COMPUTATION

Graphical methods of approximate computation are very convenient and well adapted to the purposes of physical chemistry. They are used frequently for interpolation, or as a substitute for a functional table or table of observed data. For data or functions involving only one independent variable, a single curve plotted on cartesian, or some other system, of coordinates is suitable. A network of scales can be used when there are two independent variables, and nomographs can be constructed to represent functions of several variables. While nomographs are perhaps the most useful and adaptable of all graphical systems, an adequate discussion of them is beyond the scope of this book, and the student is recommended to consult some standard treatise on the subject (for example, Davis, Empirical Equations and Nomography). Graphical methods of differentiation are used in the analysis of rates of complex reactions, in the computation of certain thermodynamic quantities, and for a variety of other purposes. While graphical integration is not utilized as commonly in chemistry as in some other sciences, it does have several valuable applications. Graphical methods are used so commonly in determining the best values of the constants of empirical equations that the entire process is sometimes referred to as curve fitting.

A curve which is to serve as a substitute for a table of data should be constructed with two objects in mind: first, to represent the data accurately, and second, to present it in as clear and graphic a manner as possible. The scale chosen should be consistent with these purposes. A scale which sets the smallest division of the coordinates equal to the average error of a single measurement, achieves the first object, but may not be consistent with the second. For very precise data such a scale would result in an impossibly large graph. If the same scale were applied to relatively inaccurate data the figure would either be inconveniently small, or would require coordinate paper with unusually coarse rulings. While no simple rule is satisfactory for all cases, the following generalization is sufficient for most purposes. Select a coordinate paper of a size and fineness of ruling which is consistent with the accuracy of the data and the purpose of the graph, and then choose scales which make the maximum ordinate approximately equal to maximum abscissa (i.e., if the plot were a straight line its slope would be 45°). It is not necessary to plot both ordinates and abscissae to the same scale. Scales should be so chosen that the ratio of the number of the divisions to the corresponding value of the quantity is a "convenient" number. Factors made up of the products of 1, 2 or 5 and 10^k, where k is any positive or negative integer, are convenient; but a scale where 10 divisions corresponded to (say) 70 units would be awkward. Such odd scales increase the labor of plotting, reading, and (especially) interpolation, and as a consequence frequently lead to mistakes in these operations. Beginners are sometimes of the opinion that every graph must include the origin. This is in general unnecessary, and is frequently quite inconvenient. For example, in a boiling point composition curve (compare experiment 21) in which the lowest recorded temperature is 57°C., it would be useless to start the ordinates at 0°C.; 50 or even 55°C. would be a much better choice for the smallest ordinate on the figure. It is common practice to plot the independent variable as abscissae, and the dependent variable or derived quantity as ordinates. Unless it is known that the data do not correspond to any continuous function (compare figure 6), a smooth curve should be drawn to represent the plotted points. Drawing the curve requires some judgment and practice. The best curve need not pass exactly through any of the points, but should be so placed as to make the sum of the residuals zero for each segment of the curve, providing that this is consistent with the curve being "fair" or smooth. Ordinarily, the best results can be obtained with a flexible spline and a hard pencil. If the plotted points can be represented by a straight line, a transparent straight edge should be used. The experimental points should be clearly indicated, either by a small cross or by a circle surrounding a central dot. If the graph is intended for display purposes, for publication, or for a formal report, the curve should be drawn in ink and the points should be represented by small circles, drawn with a compass.

GRAPHICAL DIFFERENTIATION AND INTEGRATION

In the study of reaction velocities, it frequently happens that the differential equation which represents the rate is fairly simple while the corresponding integrated equation is comparatively complicated and inconvenient. Furthermore, it is often necessary to compare the data to several different functions, and the time and labor which would be required to integrate these functions would be far from negligible. For these reasons, it is common practice to compare the data directly to the assumed differential equation. This is sometimes done by the crude analytical process of setting dC/dt equal to $(C_2 - C_1)/(t_2 - t_1)$, where C_2 and C_1 are the concentrations measured at times t_2 and t_1, respectively. Not only does this process lead to quite incorrect results when the curve is unsymmetrical, but it has the added disadvantage of greatly exaggerating the effect of the erratic errors of the several points. It is usually preferable to find the numerical values of the rate, dC/dt, graphically at a series of times, t_i, and to introduce these numerical values directly into the differential equation. To do this, first plot the data accurately; if possible, choose a scale such that the apparent uncertainty of an individual measurement corresponds to from 1 to 5 small divisions of the coordinate paper. Draw a smooth curve to represent the plotted points. There are three graphical methods of determining the slope of a curve at a point, which are in common use. In the simplest of these, a transparent straight edge is so placed that its edge mades contact with the curve at the point C_i, t_i, and it is then rotated about this point until it appears to be tangent to the curve. The tangent can then be drawn in, and its slope, $(C_b' - C_a'')/(t_b' - t_a'')$, read off of the coordinate axes. The dotted line, $C_a''t_b''$, of figure 5, was drawn through the experimental points on either side of C_i, t_i, and is included to demonstrate the error which can be introduced by the use of the approximate analytical method. With a little practice slopes can be determined accurately and rapidly by this simple graphical method. However, to avoid the effect of personal prejudice, it is advisable for at least two different people to estimate the slope at each point. The difficulty of estimating the slope can be considerably reduced by the use of a device consisting of a plane mirror fixed at right angles to a straight edge (Latashaw, J. Am.

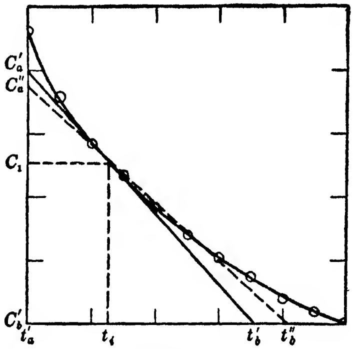

FIGURE 5

Chem. Soc. **47,** 793 (1925)). When the edge of the mirror rests on the curve, the reflection appears to be a continuation of the curve. Only when the mirror is at right angles to the curve do the curve and its image form a smooth continuous line; at any other angle there is a break or kink where the curve and image join. When the mirror is set perpendicular to the curve at a given point, the attached straight edge is parallel to the tangent of the curve at the point, and so determines the slope of the curve. A still more convenient device, called the "tangentmeter," is available commercially. It consists essentially of a triangular glass prism which can be placed with one face on the graph and its center over any point on the curve (Richards and Roope, Science **71,** 290 (1930)). If the prism is rotated until the line of contact between its other two faces is perpendicular to the curve, the curve appears smooth and continuous when viewed through the prism. At any other angle, the curve appears to be broken into disconnected segments at the vertex of the prism.

It is possible to obtain a crude estimate of the probable error of the slope by the following graphical method. If in addition to the best value of the slope, the experimeter estimates the largest and smallest values of the slope which he believes are consistent with the data, the difference between those extreme values will lie in the range 2 to 10 times the probable error, depending upon his unconscious bias. Accordingly one fourth of the difference between the extreme "possible" slopes will be an estimate of the probable error of the slope, which will be at least of the right order of magnitude. Obviously, this method can be applied to the slope of a straight line as well as to that of a curve.

The following example illustrates a common use of graphical integration in physical chemistry. In the study of photochemical reactions, it is often necessary to know the total radiant energy absorbed by a reacting system during a certain time interval. In the present example, the intensity of the absorbed light decreased as an unknown function of time, due partly to the gradual aging of the light source (a capillary mercury arc) and partly to the photochemical fading of the reacting solutions. Over a period of 3 hours the total intensity of the absorbed light was determined at 15 minute intervals with a calibrated thermopyle and galvanometer. In figure 6, these values of the intensity, in ergs per second, are plotted against time, in seconds. The successive points have been connected by straight lines, since due to fluctuations in line voltage the points do not lie on a smooth curve. The total energy, in ergs, absorbed by the reacting system in the 3 hour period is equal to the area under the broken line, *af*. This area may be readily computed by "counting squares." To facilitate this, the area has been divided into rectangles, whose widths correspond to the interval of 900 seconds between measurements. Since the area under the ordinate 1500 ergs/sec. is common to all of the rectangles, it is convenient to compute this first and then to add to it the sum of the areas of the quadrangles which extend above it. This common area is

$$1500 \text{ ergs/sec.} \times 10{,}800 \text{ sec.} = 1.620 \times 10^7 \text{ ergs}$$

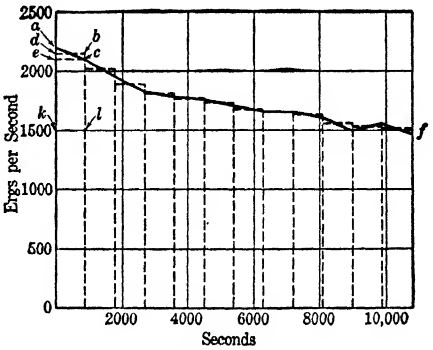

FIGURE 6

The area of the first quadrangle above the 1500 ordinate is the sum of the areas *eckl* and *aec*. This is equal to 900(*ke* + *ed*), where *ed* is 1/2 *ea*. Since in this figure the widths of the several rectangles are equal, we may add together the effective heights of these rectangles and multiply this sum by 900 sec. to obtain the total area above the 1500 ordinate. The total energy absorbed, evaluated in this way, is

$$(1.620 + 0.258) \times 10^7 = 1.878 \times 10^7 \text{ ergs}$$

In case the experimental points correspond to a smooth curve, the graphical integration can be made by breaking up the curve into a series of straight lines, and then treating the resulting broken line as in the present case. In general, the more sharply curved the graph is, the more rectangles will be required to represent a given area. For very precise calculations, a correction must be made for the error which is introduced by representing a segment of a curve by a straight line. However, this correction is seldom necessary in ordinary work. Graphical integration is also used to evaluate definite integrals which cannot be solved by ordinary methods. In addition to the simple process of counting squares, the area under a curve may be evaluated by special methods, such as the use of a planimeter. Numerical differentiation and integration are not limited to the graphical methods described here, but can be performed by any of a number of useful analytical methods. For a discussion of these analytical methods, it is recommended that the student consult any treatise on numerical calculations (such as Scarborough, Numerical Mathematical Analysis).

GRAPHICAL EVALUATION OF THE CONSTANTS OF AN EMPIRICAL EQUATION

Graphical methods are especially adapted to the determination of the coefficients of a linear equation. While modifications of these methods can be used to determine the coefficients of a power series, they are in general less convenient than the corresponding analytical methods. The first step in the graphical analysis of a set of measured values is the construction of an accurate plot of the data to a suitable scale. If the data can be represented by a linear equation,

$$y = a + bx$$

the plotted points will not show any systematic deviation from a straight line. The best straight line can then be drawn "through" the points with the aid of a transparent straight edge (43). The coefficient, b, corresponding to this line is equal to its slope,

$$b = (y_2' - y_1')/(x_2' - x_1') \tag{23}$$

The coordinates of the points y_1', x_1', and y_2', x_2' are read from the line; they are not selected from the original data. Although the constant a is the intercept on the y axis, it is neither convenient nor satisfactory to read it directly from the graph unless the value $x = 0$ is either included in the range of the measured values of x or involves only a short extrapolation. In any case, a may be evaluated as follows. Substitute into the linear equation any pair of values, $y_i'x_i'$, taken from the line and the value of b from equation 23, and then solve the resulting equation 24 for a.

$$a = y_i' - x_i' \frac{y_2' - y_1'}{x_2' - x_1'} \tag{24}$$

As an illustration we shall apply this process to the experimental data given in the first two columns of table 6. These data, which

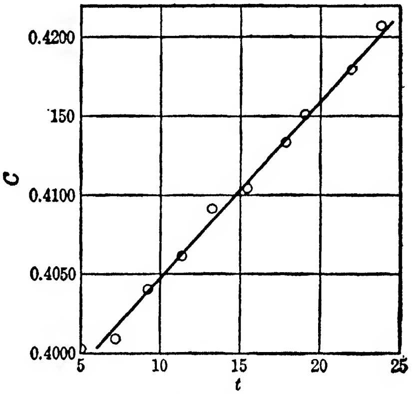

FIGURE 7

are plotted in figure 7, can be represented by a straight line within the limits of their apparent accuracy. It should be realized that figure 7 is a crude reproduction of the original plot, inasmuch as only every fortieth ordinate and every fiftieth abscissa are indicated. In the computer's judgment, the straight line which was drawn best represents the general trend of the data. Drawing the best line is the most important step in the computation, and its success depends entirely upon the skill and judgment of the computer. Choosing the following points from the line,

$$y_1' = 0.4000, \quad x_1' = 5.70$$
$$y_2' = 0.4200, \quad x_2' = 23.75$$

we may evaluate b by means of equation 23,

$$b = \frac{0.4200 - 0.4000}{23.75 - 5.70} = 0.001108$$

Substituting in equation 20, we obtain the corresponding value for a.

$$a = 0.4200 - 0.001108 \times 23.75 = 0.3937$$

The following empirical equation was obtained by introducing these values for a and b in the general linear equation and substituting the symbols C_G and t for y and x, respectively:

$$C_G = 0.3937 + 0.001108\, t$$

To test this equation and to permit its comparison to the equations which were determined analytically, the residuals,

$$\rho_G = C_i - 0.3937 - 0.001108\, t_i$$

have been computed and are listed in the last column of table 6. Inspection of this table reveals that the equation which was obtained graphically closely resembles that which was obtained by the method of least squares. We are justified in concluding, therefore, that the graphical method of evaluating the constants of an empirical equation is satisfactory in many cases, of which the present is typical. It is not satisfactory, however, when the highest accuracy is required or when the experimental data are so precise that it is impossible or impractical to employ a scale large enough to show the erratic variation of the data; i.e., to make the average error of a single measurement comparable to the smallest coordinate division. In the first case the method of least squares must be used; in the second, either the method of averages or of least squares.

Regardless of how the equation was obtained, it is always useful and instructive to plot the residuals against the independent variable. In figure 8, the residuals corresponding to the graphical solution of this case, to the least squares solution, and to the first solution by selected points are represented by the solid line G, the dotted line C, and the dash line A, respectively. This plot shows clearly and unmistakably that, in this case, the graphical solution is quite satisfactory and is far superior to the method of selected points.

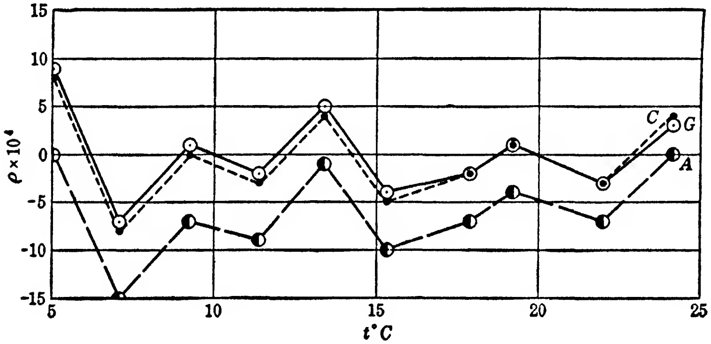

FIGURE 8

Graphical methods are frequently used in the evaluation of the constants of such non-linear equations as can be put in linear form by a simple transformation of substitution of variables. Such computations are particularly convenient when suitable special coordinate paper is available. For example, the coefficients of the equation

$$y = a + bu^2$$

could be evaluated in terms of the measured values of y and u by plotting corresponding values of y_i and u_i^2 on ordinary coordinate paper. The numerical values of a and b could then be obtained by drawing the best straight line through the points, substituting x for u^2, and applying equations 23 and 24. However, if a coordinate paper were available, which had its ordinates laid off on the usual linear scale but its abcissae so ruled that the distance from the origin to a given ruling was proportional to the square of its numerical value, we could obtain a straight line by plotting the original values of y_i and u_i. In this way the labor of squaring the several values of u_i could be avoided. This type of coordinate paper is illustrated in figure 9. The plotted points correspond to the equation

$$y = 14.00 - 0.750\,u^2$$

as may be easily verified by substituting two points read from the line in equation 23,

$$b = \frac{14.00 - 2.00}{0 - 4.00^2} = -0.750$$

and reading the value of a directly from the intercept on the y axis. The most commonly used and by far the most adaptable of the special coordinate papers are the logarithmic and semilogarithmic papers. In the former both coordinates are laid off on logarithmic scales, while in the latter one coordinate is linear and the other logarithmic. Data corresponding to any equation of the form

$$y = ax^b$$

will yield a straight line if plotted on logarithmic paper. Semilogarithmic paper is especially useful in the analysis of data corresponding to exponential or logarithmic functions. The methods of obtaining the constants from the best straight lines are analogous to those used in the cases already discussed.

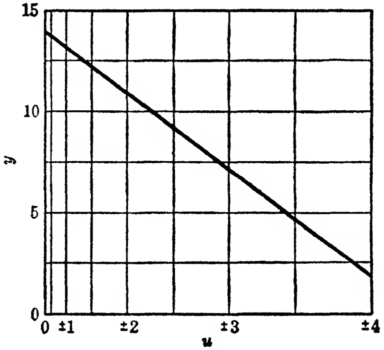

FIGURE 9

EMPIRICAL EQUATIONS WHICH ARE NON-LINEAR IN RESPECT TO THEIR CONSTANTS

All of the empirical equations which we have considered so far are linear in respect to their adjustable constants. While most of the equations which occur in physical chemistry are of this type, occasionally, particularly in the study of radioactive changes and of reaction kinetics, it is necessary to evaluate the constants of an equation which is non-linear in respect to its constants and which cannot be put into linear form by any simple transformation. The application of the method of least squares or of averages to such equations is possible though laborious, but is beyond the scope of the present discussion. Because of the labor which the other methods entail, the method of selected points (32) is commonly applied to equations of this type.

As an illustration of such a process, let us consider the evaluation of the constants of a typical non-linear two-constant equation

$$y = a(1 - e^{-bx})$$

in terms of the data which are recorded in the first two columns of the following table.

TABLE 9

DATA USED TO EVALUATE a AND b OF $y = a(1 - e^{-bx})$

x_i	y_i	$\rho_i \times 10^{+3}$
2.0	0.100	0
10.0	0.387	1
20.0	0.584	4
35.0	0.708	3
50.0	0.750	0

To minimize the effect of erratic errors, the first and last points have been used in obtaining the two simultaneous equations which are required to determine the values of the adjustable constants.

$$a_1 = \frac{0.100}{1 - e^{-2.0b}}$$

$$a_5 = \frac{0.750}{1 - e^{-50.0b}}$$

The required value of b is the one which makes a_1 equal a_5. This cannot be a large number, since a_1 and a_5 approach 0.100 and 0.750, respectively, as b is increased indefinitely. As a first trial, let us set b equal to 1. The corresponding values of a_1 and a_5 are, respectively, 0.12 and 0.75. Therefore, the correct value of b is certainly smaller than 1. When b is taken as 0.10, a_1 proves to be 0.55 and a_5, 0.75; but a value of 0.010 makes a_1 equal 5.00 and a_5, 1.93. Since for the first of these values a_5 is greater than a_1 and for the second a_5 is less than a_1 there must be some intermediate value of b which makes a_1 equal to a_5. This value can be found by the following graphical procedure. Compute values of a_1 and a_5 corresponding to an assumed series of values of b, between 0.010 and 0.100. Plot the values of a_1 and a_5 against those of b, and draw smooth curves through the plotted points. The coordinates of the intersection of these curves correspond to the desired values of a and b. Such a plot for the present case is given in figure 10. The small circles indicate computed values of a_1 and a_5. The curves intersect at the point $a = 0.775$, $b = 0.069$. We can test the corresponding equation by computing the residuals,

$$\rho_i = y_i - 0.775(1 - e^{-0.069x_i})$$

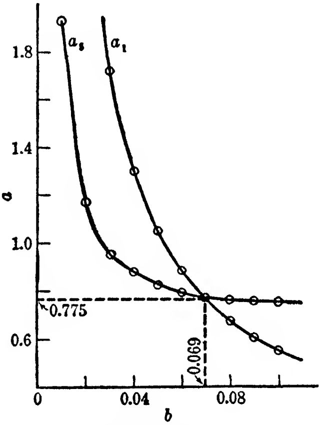

FIGURE 10

The values of the residuals are listed in the third column of table 9. As was to be expected, the first and last residuals are zero. The values of the others indicate that, while the equation is reasonably satisfactory, better values of the constants might be obtained by some more exact method or by means of successive approximations. This procedure is not a graphical method of evaluating the constants of an equation, but is a special application of the method of selected points and involves the usual uncertainty of this method (32). The graphical procedure is introduced merely to facilitate the solution of the simultaneous equations, and does not affect the final values of a and b.

REPORT WRITING

Scientific experiments whose results are known only to one man are relatively worthless. Anyone who makes systematic physical measurements is obligated to prepare a clear, readable report describing them. This is as necessary for the student working in a physical-chemistry laboratory as it is for the research scientist or the control chemist.

Student reports should contain brief but clear statements of the following: the purpose of the experiment, the experimental methods used, the data obtained, the computations performed, and the results and conclusions deduced. In addition, it is sometimes desirable to include an outline of the underlying theory, to mention related methods, and to discuss very briefly some of the more important applications of the methods used. It is good practice for the student to prepare a short abstract of the results of the experiment.

The report should be as concise as is consistent with clarity. Repetition should be avoided. Quotations from texts or journal articles should be included only when they simplify or shorten the discussion. When quotations are used, the source should be indicated. All references to source material should be given in sufficient detail to identify the volume and page referred to.

The outline of the experimental method should be complete enough to enable the reader to recognize the method and apparatus used, but need not include detailed directions for performing the experiment. Diagrams of apparatus should be included when they shorten or clarify the description of the experimental methods. Computations should be described clearly and in detail, preferably by means of equations. The meanings of all symbols used should be stated. The detail of the computations can be satisfactorily indicated by substituting one set of numerical data in each equation. Detailed arithmetic work should be omitted. The numerical results and the pertinent original data should be tabulated. The units in which each quantity is expressed should be stated explicitly. Plots or graphs of the results should be included whenever they contribute to the ease with which the results can be understood. A statement of the reliability of the final results (preferably in terms of the probable errors of numerical quantities) is an essential part of the report.

The adoption of a literary style is best left to the discretion of the student. However, it may be worth while to point out that it is both conventional and logical to describe properties of matter in the present tense and the particulars of experiments performed in the past tense. It is customary in American scientific journals to use the third person passive voice. Either this convention or a straightforward use of the first person singular active voice is appropriate for a student report.

Experiment 1

DETERMINATION OF THE MOLECULAR WEIGHT OF A VAPOR BY THE DUMAS METHOD

The Dumas method for the determination of the molecular weight of a vapor (M, 34) is simple but not very accurate. It consists of the following operations: A bulb, which is open to air, is weighed accurately. It is then filled with a vapor, at barometric pressure and at some known temperature, and sealed. After cooling to room temperature, it is weighed. The difference between these weighings, when properly corrected for the (important) effect of air buoyancy, is equal to the mass of the vapor. The bulb is then filled with water and weighed. Since the density of water is known, the volume of the bulb may be computed. These measurements yield the mass, m, volume, v, pressure, p, and temperature, T, of a sample of vapor. If it may be assumed that the vapor obeys the perfect gas law under the conditions of the experiment, its molecular weight, M, may be computed from the following relation:

$$M = \frac{mRT}{pv} = \frac{RT}{p}d$$

To avoid the errors which are inherent in the application of the perfect gas law, it would be necessary to use some experimental method which would permit the measurements to be made at several different pressures. (See Maass and Russel, J. Am. Chem. Soc. **40,** 1847 (1918); Cooper and Maass, Can. J. Research **2,** 388 (1930); D, M, and W, 3–7.) When the results of such measurements are available, the molecular weight can be computed by the method of limiting density (M, 37–8).

Apparatus and Materials: A Dumas bulb provided with a spring wire holder, a large beaker or a metal vessel suitable for use as a water bath. About 25 ml. of CCl_4.

Procedure: The neck of the Dumas bulb should end in a thin-walled capillary about 1 mm. in diameter; if it is larger than this, heat it with a Bunsen burner or blast lamp and draw it out until it reaches the desired dimension. Weigh the clean dry bulb on an analytical balance. (To dry the inside of the bulb, heat it with boiling water or a broad yellow flame, attach a dust-free rubber tubing to the tip, and alternately evacuate and allow the bulb to fill with air. This method will prove faster than merely heating the bulb when it is attached to an ordinary vacuum pump. It is unsafe to use alcohol and ether in drying a bulb of this type.) Introduce 10 or 15 ml. of CCl_4 into the bulb by heating it gently and allowing it to cool with its tip below the surface of the liquid. Using the spring holder (not shown in figure 11), clamp the bulb in the water bath, which should be approximately at 80°C. With the exception of a few centimeters of its tip, the bulb should be entirely immersed. Heat the bath to its boiling point and keep it boiling until the liquid CCl_4 is completely vaporized. Test this by seeing if there are vapors escaping from the tip of the bulb which will extinguish or disturb the flame of a match. When the liquid has been exhausted, keep the bulb boiling steadily and with a second burner gently heat the exposed stem to vaporize any liquid which may have condensed there. Then quickly seal the tip by heating it with the hottest part of the flame until it melts together. Read and record the barometric pressure. After allowing the sealed bulb to cool, weigh it on the analytical balance. Immerse the tip of the bulb in cool water (more than sufficient to fill the bulb) which has been recently boiled to drive off dissolved air. Cut off or break the tip with pliers. The bulb should fill completely; if there are more than 5 ml. of air in the bulb the experiment should be repeated. If there are a few ml. of air in the bulb, which got into it before it was sealed, no correction need be applied; however, if the air leaked in through a faulty seal, the volume of the air should be estimated and a suitable correction made for it. Weigh the water-filled bulb to the nearest 0.1 gm. (Do not use an analytical balance!)

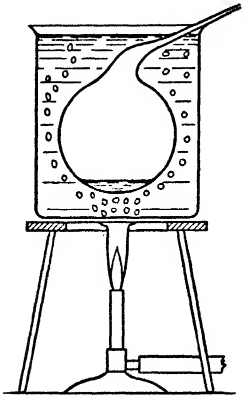
FIGURE 11
DUMAS BULB

The weighing of the empty and of the sealed bulb may be made more accurate by the use of a bulb or flask of similar size and weight as a counterpoise (K and S, 210–1). If this is done, the outside of the counterpoise should be treated in the same way as the Dumas bulb, to insure that the amount of adsorbed water is the same. It should be noted that in this experiment the use of a counterpoise will not render the buoyancy corrections unnecessary.

Computations: Correct the reading of the barometer to 0°C., for the cubical expansion of mercury and the linear expansion of the brass scale. Determine the boiling point of water corresponding to the corrected barometric pressure, p. Either consult tables, or use the following formula, which is accurate only near the normal boiling point:

$$t^{\circ}_{\text{B.P.}}\text{C.} = 100.0 + 0.0367(p - 760)$$

In computing the density of the CCl_4 vapor, the effect of air buoyancy on the glass vessel, the brass weights, and the water may be neglected. Why? However, the buoyant effect on the CCl_4 vapor (i.e., the weight of an equal volume of air) cannot be neglected but must be computed accurately. The density of air at 0°C. and 1 atm. is 0.001293 gm./ml. Assuming the perfect gas law, compute the density of air under laboratory conditions. If the relative humidity is high and known, this factor should also be taken into account (Dalton's law of partial pressures), since under otherwise equal conditions the density of humid air is less than that of dry air (R and R, vol. I, 60). From these quantities, compute the density of CCl_4 vapor at atmospheric pressure and the boiling point of water. Assuming the perfect gas law, compute the molecular weight of CCl_4. Compare this value to its formula weight (i.e., the weight which would be computed from its chemical formula). Make a quantitative estimate of the errors involved in the measurement, and compare this computed error to the difference between the measured molecular weight and the formula weight. Discuss the several approximations which were made in the computations.

USE OF THE BAROMETER

The simplest barometer is an ordinary closed-tube mercury manometer with the closed end evacuated and the other end open to the atmosphere. A common and entirely satisfactory type of barometer, figure 12, is provided with a Fortin cistern, a fixed brass scale, and a vernier.[1] In this instrument, the bottom of the

---

[1] See C. F. Marvin, Barometers and the Measurement of Atmospheric Pressure. U. S. Dept. of Agric., Circular F; also R and R, 386.

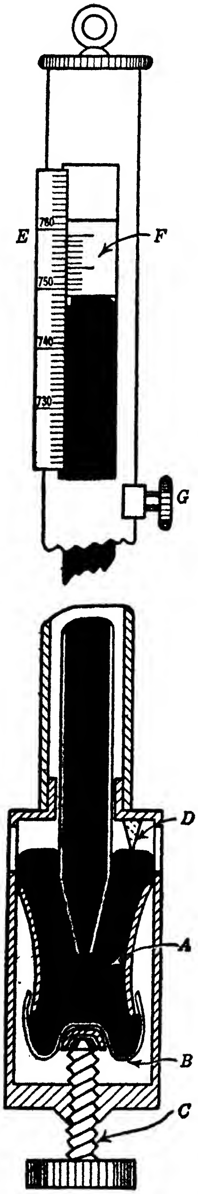

FIGURE 12
BAROMETER

cistern, A, is a bag of flexible leather, B, which is supported by a thumbscrew, C. By means of this screw, the surface of the mercury may be brought into contact with the ivory point, D. The fixed scale, E, is adjusted so that its zero point corresponds to the tip of the point, D.

To read the barometer, adjust the screw, C, until the surface of the mercury is just in contact with the point, D. Then by means of the screw, G, set the lower edge of the vernier, F, so that it coincides with the top of the mercury meniscus, and read the height of the mercury column to the nearest 0.1 mm. (or 0.05 mm.). The small correction for capillarity should not be applied to instruments of this type, since the scale is usually adjusted to eliminate this error. However, the correction for temperature, which is due to the cubical expansion of mercury and the linear expansion of the brass scale, is important. A thermometer is usually fastened to the barometer case to facilitate this correction. It may be readily shown that the following expression gives the barometric pressure corrected to 0°C., P, in terms of the observed pressure, P_{obs}, the cubical coefficient of expansion of mercury ($\alpha = 1.818 \times 10^{-4}$), and the linear coefficient of expansion of brass ($\beta = 1.84 \times 10^{-5}$):

$$P = \frac{1 + 1.84 \times 10^{-5}\, t°\text{C.}}{1 + 1.818 \times 10^{-4}\, t°\text{C.}} P_{obs}$$

The simplified formula,

$$P = (1 - 1.63 \times 10^{-4}\, t°\text{C.}) P_{obs}$$

is sufficiently accurate for most purposes. For an excellent discussion of the various errors which are inherent in the use of a barometer, see Mack and France, Laboratory Manual of Physical Chemistry, 13–8.

Experiment 2

DETERMINATION OF THE MOLECULAR WEIGHT OF A VAPOR BY THE VICTOR MEYER METHOD

The Victor Meyer method of determining the molecular weight of a vapor is moderately accurate and, once the student has mastered a few simple techniques, is quite rapid. It involves the following operations: A small sample, about 0.1 gm. of liquid, is weighed into a suitable bulb. The liquid is then transferred to the apparatus, where it vaporizes at a constant temperature above its boiling point, and displaces an equal volume of air. The volume of the displaced air, which is measured at room temperature and barometric pressure, is equal to the volume which the vapor would occupy under these conditions, if like air it obeyed the perfect gas laws. The molecular weight, M, of the vapor can be computed from the weight, w, of the sample and the volume, V, of the air, which was measured at the pressure, P, and the temperature, T, by means of the perfect gas law (M, 32–5)

$$\frac{w}{M} = n = \frac{PV}{RT}$$

where n is the number of moles of vapor of displaced air and R is the gas constant. A more convenient form of this equation is

$$M = \frac{wRT}{PV} \tag{1}$$

It should be noted that the molecular weight computed in this way is likely to be slightly high since the product, PV, shows a negative departure from the perfect gas laws for vapors near their boiling point. However, diffusion of the vapor into the air contained in the apparatus lowers the partial pressure of the vapor and thereby reduces this effect. For this reason it is difficult to estimate the magnitude of the correction which should be applied for departures from the perfect gas laws, but under the conditions of the present experiment they are probably less than 2%.

If the displaced air is collected over water, some correction should be made for the vapor pressure of water; the form of the correction depending upon the way in which the experiment is performed. If the apparatus is filled with dry air and the displaced air collected over water, the evaporation of the water into the dry air will increase its volume. Taking this effect into account, we obtain the following equation:

$$M = \frac{wRT}{(P - P_w)V} \tag{2}$$

If the apparatus is filled with laboratory air, its absolute humidity, P_h, affects the results. In this case, the correction will be smaller; it might, for very damp air and cold water, be of the opposite sign. The equation which corresponds to this procedure is

$$M = \frac{P - P_h}{P - P_w} \times \frac{wRT}{PV} \tag{3}$$

This equation can be put in the following approximate form, which is more convenient and is sufficiently accurate for most purposes, by dividing the numerator and denominator by $P - P_h$ and simplifying the remainder.

$$M = \frac{wRT}{(P - P_w + P_h)V} \tag{4}$$

A great many different modifications of the original Victor Meyer apparatus have been proposed; some of these are described in R and R, vol. II, 55–8. The various types of apparatus differ more in respect to simplicity and ease of operation than they do in the accuracy which may be attained with them. The apparatus which is described here has the advantage that it can easily be dried and freed of vapors between runs, without having to be dismantled or requiring awkward or difficult manipulations. It was also designed to ensure the breaking of the bulb at the required time, to eliminate the diffusion of condensible vapors to the cold part of the apparatus, and to facilitate the control of the temperature. A somewhat similar apparatus is described by D, M, and W, 7–10.

This apparatus can be easily modified to operate with smaller quantities of liquid, in the semi-micro range. A 2ml. graduated pipet can be used as a gas buret. The gas should be collected over mercury. A microbalance is required. While this modified apparatus gives good results in the hands of a competent student, it is not recommended for ordinary laboratory use, chiefly because of the difficulties involved in the making, filling, and weighing the tiny bulblets.

The small Victor Meyer's bulbs (figure 14), which are required for this experiment, should be about 6 mm. in diameter and be provided with a stem 4 cm. long and 1 mm. in diameter. They are made with a bent tail to facilitate breaking. They can be made quickly and cheaply by any glass blower; or, after a little directed practice, they can be prepared by the average student. The beginner may find it easier to make the type of bulb described by D, M, and W, 8–9; however, these have the disadvantage that they are harder to fill.

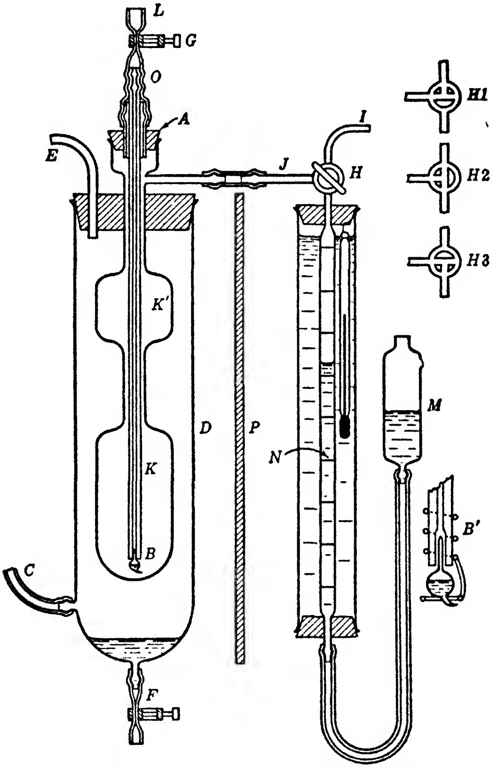

FIGURE 13. VICTOR MEYER APPARATUS

Apparatus and Materials: A complete Victor Meyer apparatus (figure 13), 3 or 4 small bulbs (figure 14), and a steam generator (figure 40). About 5 ml. of C_6H_6 or of some other suitably volatile liquid.

Procedure: Bend the stem of one of the small bulbs in a sharp angle about 1 cm. from the bulb. This operation and the filling of the bulb require a very small flame. A makeshift micro burner (figure 14, *B*), which can be easily made from a scrap of glass tubing and a screw clamp, will prove very convenient for the purpose. Weigh the bulb accurately on an analytical balance. Put the sample of the liquid in a small vial or in a vessel, *A*, made by cutting off the bottom of a small test tube. Place the stem of the bulblet against the inner wall of this vessel (surface tension will hold it in place). Force air out of the bulb by heating it gently with a tiny flame. When the flame is removed, the bulb will cool and draw up the liquid. The bulb should be filled 1/2 to 2/3 full with the liquid. If the stem is removed from the liquid while the bulb is still cooling, the liquid which is in the stem will be drawn into the bulb leaving the former empty. Seal the stem at the bend and pull off the rest of the stem. Heat the detached stem carefully to drive out any liquid which remains in it. Weigh the bulb and detached stem together.

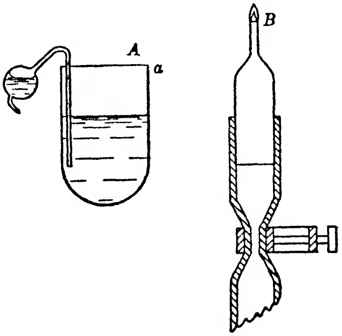

FIGURE 14

Set up the apparatus as is indicated in figure 13. Both the buret, *N*, and the steam-jacketed tube, *K*, can be supported by a single large ring stand. To render its manipulation convenient, support the leveling bulb, *M*, with a small ring or a clamp on a separate ring stand. Place a piece of cardboard or asbestos, *P*, between the steam jacket and the buret, to avoid heating the latter by radiation. Remove the stopper, *A*, and the system of tubes which it supports. Slip the stem of the sealed bulblet into the end of the capillary tube, *B*, as shown in detail *B′*, and support it there by means of a helical spring made of light-weight iron wire. Replace the stopper, *A*, in the apparatus. Connect a steam generator to the rubber tube, *C*. Pass steam into the jacket, *D*, rapidly enough so that it blows out of the vent tube, *E*. When water accumulates in the bottom of the jacket, allow it to escape by opening the pinch clamp, *F*. Open the screw clamp, *G*. Turn the three-way stopcock to position *H*1, so that it connects tubes *I* and *J*. With a rubber tube, connect the outlet, *I*, to the house vacuum or an aspirator pump. If you choose to use dry air in the experiment, connect a $CaCl_2$ tube to the rubber inlet tube, *L*. Otherwise, the instructor or student should determine the humidity of the laboratory air with a sling psychometer (ICT, Vol. I, 71). Maintaining a steady flow of steam through the jacket, draw air through the system until the bulbs, *K* and *K′*, and the connecting tubes are thoroughly dried. Then remove the rubber connection from the tube, *I*, close the screw clamp, *G*, and turn the stopcock to the position *H*2. By raising the leveling bulb, *M*, bring the water to the top of the 25 ml. gas buret, *N*. Turn the stopcock to the position *H*3, and test for leaks by lowering the bulb, *M*. If the apparatus proves to be tight, grasp the flexible rubber tube at the point *O*, and push the capillary tube down to break the bulblet on the bottom of the tube, *K*. Keeping the pressure in the buret equal to that of the atmosphere by means of the leveling bulb, read and record the position of the meniscus at 30 second intervals until it remains fixed for 2 or 3 minutes. Record the temperature of the water jacket surrounding the buret. Record the barometer reading (55–6), and the room temperature.

Repeat this process several times, or until the constancy of the values of the computed molecular weight indicates that you have mastered the technique. If so directed, determine the molecular weight of another substance or of a liquid unknown.

Computations: Compute a value of the molecular weight corresponding to each determination. In making this computation correct the barometer reading to 0°C. (56) and be sure that *P*, *V*, and *R* are expressed in consistent units. Prepare a table including the following quantities for each determination: the weights of the empty bulb, of the filled bulb and of the liquid, the measured volume, the temperature of the gas, the (corrected) barometric pressure, and the computed molecular weight and its percentage deviation from the formula weight.

Make a quantitative estimate of the errors pertaining to each of the several direct measurements. From these estimates calculate the probable error of the computed molecular weight. (Note: this computation of the probable error does not include the effect of any possible departures from the perfect gas laws.)

Experiment 3

EFFUSION OF GASES. THE MOLECULAR WEIGHT AND DIAMETER

Both the molecular weight and the molecular diameter of molecules can be determined from effusion experiments. The rate of effusion of a gas through a small hole in a thin wall is inversely proportional to the square root of its molecular weight (M, 39; E and R, 79). Therefore, the ratio of the times, t_i, required for equal volumes of different gases to escape through the same hole under the same conditions of temperature and pressure, is equal to the ratio of the square roots of the molecular weights of the gases.

$$t_1/t_2 = M_1^{1/2}/M_2^{1/2}$$

or

$$M_1^{1/2}/t_1 = M_2^{1/2}/t_2 = k \qquad (1)$$

where the constant, k, depends upon the characteristics of the apparatus as well as upon the pressure and temperature. For a given apparatus, such as is illustrated in figure 15, the constant, k, can be determined with a pure gas of known molecular weight, and the calibrated apparatus can then be used to measure the molecular weights of unknown gases.

The hole through which the gas escapes is usually a minute puncture made in a piece of Pt foil with a sharp pointed needle. The rest of the apparatus is devised to force a definite volume of gas through the hole under reproducible conditions of pressure and temperature. The diagram of figure 15 represents a common type of effusion apparatus. The pierced Pt foil is cemented to the end of a glass tube which is connected to the bulb, *B*. This bulb is filled with gas through the stopcock, *C*; the Hg which originally filled the bulb being displaced into the reservoir, *D*. When the stopcock, *C*, is closed and *E* is opened as indicated, the Hg forces the gas out through the small hole at *A*, and the time required for the Hg meniscus to pass from the first, *F*, to the second mark, *F'*, can be recorded. Although the pressure of the gas changes continuously during the process of effusion, this does not affect the ratio of the recorded times, although it does affect the value of k (compare the discussion in experiment 13). An improved form of

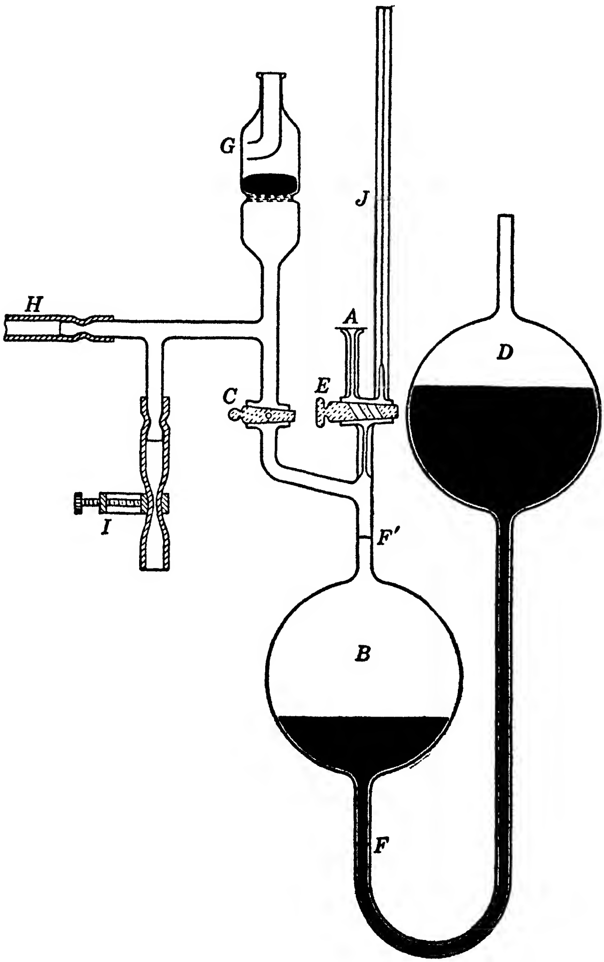

Figure 15. Gas Effusion Apparatus

this apparatus which is conveniently applicable to saturated vapors as well as gases is described by Eyring in J. Am. Chem. Soc. **50**, 2398 (1928); see also R and R, vol. II, 60–2; vol. I, 556–8. An extremely simple apparatus which can be used to determine the viscosity of a small sample of gas is described by Rankine, Pro. Roy. Soc. *A83*, 2651 (1910).

If the gas instead of passing through a pin hole in a thin wall escapes through a long narrow capillary, the time required for a given volume of gas to escape is a measure of its viscosity rather than of its molecular weight (M, 55–8; E and R, 78, 98–9).

$$\frac{\eta_1}{\eta_2} = \frac{t_1}{t_2}$$

It is a consequence of the kinetic theory of gases that the viscosity coefficient, η, is (approximately) related to the mean free path, l, by the following equation:

$$\eta = \frac{1}{3}\rho\bar{c}l \tag{2}$$

where ρ is the density of the gas and $\bar{c}$ is the mean velocity of its molecules.

For the comparison of two gases, we may write equation 2 in the following form:

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1\bar{c}_1l_1}{\rho_2\bar{c}_2l_2} \tag{3}$$

The two following relations can also be derived from the kinetic theory of gases:

$$\bar{c}_i^2 = \frac{8\,RT}{\pi M_i} \tag{4}$$

$$\sigma_i^2 = \frac{1}{\sqrt{2}\,\pi n_i l_i} \tag{5}$$

where n_i is the number of molecules per cc. and σ_i is the diameter of a molecule. Eliminating $\bar{c}$ between equations 3 and 4 and introducing the perfect gas law expression for ρ_i, we obtain

$$\frac{l_1}{l_2} = \left(\frac{\eta_1}{\eta_2}\right)\left(\frac{M_2}{M_1}\right)^{1/2} \tag{6}$$

The following equation can be obtained by eliminating l_i between equations 5 and 6:

$$\frac{\sigma_2}{\sigma_1} = \left(\frac{\eta_1}{\eta_2}\right)^{1/2}\left(\frac{M_2}{M_1}\right)^{1/4} \tag{7}$$

Molecular diameters, σ_i, determined from viscosity measurements are especially important in the study of reaction kinetics in gaseous systems (compare Hinshelwood, Kinetics of Chemical Changes, 13–5).

Apparatus and Materials: A special effusion apparatus, a Hg-filled safety valve, a $CaCl_2$-drying tower, a stopwatch, light-weight pressure tubing for connections, an O_2 cylinder fitted with a needle valve, and several other cylinders containing non-corrosive non-toxic gases such as N_2, CO_2, H_2, etc.

Procedure: Set up the effusion apparatus and Hg-filled escape valve as indicated in figure 15. Connect the tube, *H*, through a $CaCl_2$ drying tower to the needle valve of the O_2 cylinder. Place a plug of cotton in the top of the drying tower to prevent dust from being carried over into the apparatus. All of the rubber connections should be made with light-weight tight-fitting pressure tubing and should be wired on. It is also advisable to wire on the stoppers of the drying tower.

Open the stopcock, *E*, and the pinch clamp, *I*, and close the stopcock, *C*. With the needle valve closed, open the valve on the top of the O_2 tank, then cautiously open the needle valve until the gas blows slowly out of the tube, *I*. Allow the gas to wash through *I* for a few minutes to flush out any foreign gas present in the apparatus. Then open the stopcock, *C*, and cautiously close the pinch clamp, *I*. If the flow appears to be too rapid, partially close the needle valve. The gas will then escape by bubbling through the safety valve, *G*. Close the safety valve, *G*, by placing your finger on its outlet tube. Before the Hg is entirely forced out of the bulb, *B*, shut the stopcock, *E*. As soon as the Hg is forced a centimeter or two below the mark, *F*, close the stopcock, *C*, quickly remove your finger from the outlet, *G*, and close the valve on the tank. Then open the stopcock, *E*, to the tube leading to the diaphragm, *A*. When the Hg passes the mark, *F*, start the stopwatch; stop it when the Hg passes the upper mark, *F′*. Record this time interval.

Repeat this process at least four times, omitting only the preliminary flushing out of the apparatus with O_2. Following the same procedure, perform several determinations of the time required for the gas to escape through the capillary, *J*.

Repeat the entire process, including the initial flushing out of the apparatus, with several other gases. If inflammable gases are used, be sure that the apparatus is set up in a well ventilated part of the laboratory at a safe distance from flames or sparks. Mixed gases, such as air or illuminating gas, may be used, although the results obtained with these are perhaps less significant.

Computations: Compute the average time of efflux through the pierced diaphragm, *A*, for each gas studied. Taking the molecular weight of O_2 as 32.00, compute the molecular weights of the other gases by means of equation 1. Tabulate these results. If air was studied, compute the molecular composition (of O_2 and N_2) corresponding to the measured average molecular weight.

Compute the average time of efflux of each gas through the capillary, *J*. The viscosity, mean free path, and molecular diameter of O_2 have, respectively, the following values: $\eta_{23°} = 2.039 \times 10^{-4}$ gm./cm. sec., $l = 1.05 \times 10^{-5}$ cm., and $\sigma = 3.0 \times 10^{-8}$ cm. Using these values and equations 3, 6, and 7 compute values of these quantities for each of the gases studied. Tabulate your results.

Experiment 4

THE VAPOR PRESSURE AND THE HEAT OF VAPORIZATION OF A LIQUID

The heat of vaporization of a substance is related to the temperature coefficient of its vapor pressure (M, 81–2, 87–9; E and R, 274–7). For a restricted range of temperatures, the following equation holds with fair accuracy for most liquids:

$$\log P = -0.4343 \frac{\Delta H}{RT} + B$$

where B is a constant, ΔH is the average value of the molal heat of vaporization for the given temperature range, and the other symbols have their usual significance.

In the present experiment the vapor pressure is determined over a range of temperatures, and the heat of vaporization is computed from these data. The method used is a modification of the static method. This apparatus, the isotensiscope (see A. Smith and A. W. C. Menzie, J. Am. Chem. Soc. **32,** 1413 (1910)) has the advantage that trapped or dissolved gases may be readily removed from the liquid.

Apparatus and Materials: An isotensiscope tube, a 1/10° thermometer, a motor-driven stirrer, a 3 liter beaker, an open mercury manometer, a vacuum pump (either an oil pump or an efficient aspirator), a carboy to serve as a pressure stabilizer, and the necessary connecting tubing, screw clamps, etc. About 25 ml. of CCl_4 or some other liquid which has a boiling point in the same range.

Procedure: Assemble the apparatus as indicated in the diagram. The hand-controlled thermostat consists of a water-filled 3 liter beaker, provided with a motor-driven stirrer and a 1/10° thermometer. It should be mounted on a tripod so that it can be heated directly with a gas burner. When the temperature is above that of the room, it can be controlled by adjusting the size of the flame; lower temperatures may be maintained by adding small pieces of ice at frequent intervals. Clamp the isotensiscope, A, so that the bulb is near the center of the beaker, close to the thermometer bulb. Connect it by a short piece of rubber pressure tubing to the test tube, *B*, which serves as a condensate trap. In connecting this trap, *B*, to the manometer, *C*, and the carboy, *D*, which acts as a pressure reservoir, use only glass tubing and rubber pressure tubing. Be sure that all joints are "air-tight." Place a screw clamp, *F*, on the pressure tubing, *E*, which connects the carboy, *D*, to the vacuum pump, and a second clamp on the short piece of tubing which acts as an air inlet. To fill the isotensiscope, heat its terminal bulb moderately and then place its open end under the surface of the liquid, which will be sucked in as the bulb cools. Repeat, until the bulb is about two-thirds full and there is sufficient liquid in the U-tube to serve as a differential manometer.

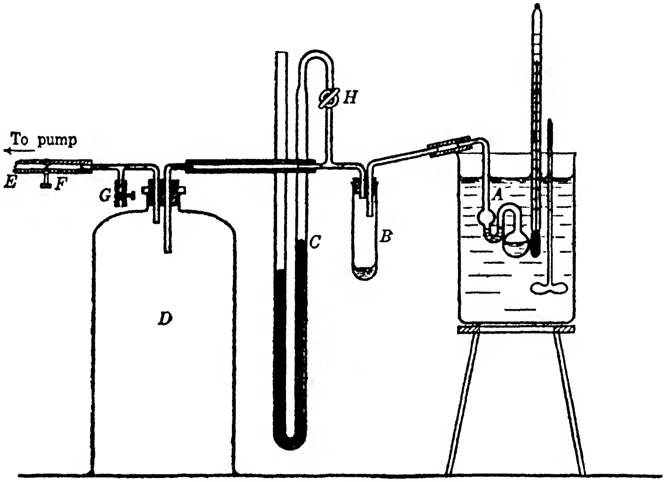

FIGURE 16. ISOTENSISCOPE

Leaving both screw clamps, *F* and *G*, and the stopcock, *H*, open, heat the bath to the highest temperature which is to be used in the experiment. Start the vacuum pump and adjust the screw clamps until the liquid begins to boil slowly. Let the liquid boil for 2 or 3 minutes to remove trapped and dissolved gases, but do not boil long enough to remove too much of the liquid from the U-tube. Read and record the barometric pressure at the beginning and end of the series of measurements. Adjust the temperature of the bath or the pressure of the system until the liquid stops boiling. The adjustment must be made cautiously to prevent air from bubbling back through the U-tube. If this does happen the air must be boiled out again. Record the temperature of the bath and the reading of the manometer at the instant when the differential manometer indicates no difference in pressure. To facilitate the reading of the manometer, its position may be retained by closing the stopcock, *H*. Since the bore of the manometer tube may not be uniform, the position of the mercury in both arms of the manometer should be read and recorded. Tap the manometer with a pencil frequently to keep the mercury from sticking. Reduce the temperature of the bath by a suitable amount, and repeat the determination of the vapor pressure. The temperature of the bath should be kept practically constant for several minutes before each reading; for if it is changing rapidly the temperature of the liquid in the isotensiscope will lag behind, and introduce an appreciable error. The error due to the temperature lag may be further reduced by using an isotensiscope bulb provided with a thermometer well.

Make 8 or 10 measurements at regular intervals of temperature. The highest temperature should correspond to a pressure slightly below atmospheric; and the lowest, to a pressure of 2 or 3 cm. of Hg.

Computations: Correct the thermometer readings for the effect of the exposed stem (70). For each measurement, compute the reciprocal of the absolute temperature, the vapor pressure in mm. of Hg, and the logarithm of the vapor pressure. Prepare a table containing these quantities in addition to the measured centigrade temperatures and the manometer readings. Make two accurate plots of the data, one of vapor pressure against temperature, and the other of the logarithm of the vapor pressure against the reciprocal of the absolute temperature. Make the latter plot on as large a scale as the accuracy of the data warrants. From the slope of this (logarithmic) plot, compute the molal heat of vaporization in calories. Compare this to the published value of the heat of vaporization at the boiling point. Discuss any difference between these values in terms of the specific heats of vapor and liquid (M292–3). Extrapolate the data, either analytically or graphically on the logarithmic plot, to a pressure of 1 atm. to obtain the normal boiling point. Estimate approximately (44) the probable error of the computed heat of vaporization and of the extrapolated boiling point.

CORRECTION OF A THERMOMETER READING FOR EXPOSED STEM

Accurate thermometers are calibrated with the entire stem immersed in the bath which determines the temperature of the bulb. However, for reasons of convenience it is common practice in using a thermometer to allow its stem to extend out of the apparatus. Under these conditions, both the glass and the mercury in the exposed stem are at a temperature differing from that of the bulb, and this introduces an error in the observed temperature. Since the coefficient of thermal expansion of mercury is greater than of glass, the observed temperature will be less than the true temperature if the bulb is hotter than the stem and greater than the true temperature, providing the thermal gradient is reversed. For exact work the magnitude of this error can be determined only by experiment. However, for many purposes it is sufficiently accurate to apply the following equation, which takes into account the thermal expansion of mercury and of the glass commonly used in thermometers:

$$t_c = t_0 + 1.6 \times 10^{-4} \Delta t_E (t_0 - t_M)$$

In this equation Δt_E is the length of the exposed column of mercury expressed in degrees and t_c, t_0, and t_M are, respectively, the corrected temperature, the thermometer reading, and the mean temperature of the exposed stem. The term "exposed stem" refers, of course, only to that part of the stem which is filled with mercury. The mean temperature of the exposed stem may be determined by fastening the bulb of a second thermometer against the midpoint of the exposed mercury column. However, with many experimental arrangements the reading of this auxiliary thermometer will not differ appreciably from room temperature. For this reason, the mean temperature of the exposed stem is frequently assumed to be equal to room temperature. For a more complete discussion of this and of the other corrections which must be applied in exact thermometry, see R and R, vol. I, 359–73 or D, M, and W, 421–2.

Experiment 5

SURFACE TENSION AS A FUNCTION OF TEMPERATURE

The relation between the temperature, t, and the surface tension, γ, of a normal or non-associated liquid is represented accurately by the Ramsay-Shields-Eötvös equation (M, 96–7),

$$\gamma\left(\frac{M}{\rho}\right)^{2/3} = 2.12(t_c - 6° - t)$$

In this equation, ρ is the density, M is the molecular weight, and t_c is the critical temperature. The quantity $\gamma(M/\rho)^{2/3}$ is sometimes called the molar free surface energy. The application of this equation to associated liquids, such as water or methyl alcohol, involves certain assumptions. If it be assumed that the value (2.12) of the coefficient applies to associated as well as to normal liquids, the equation may be used to compute the average molecular weight in the liquid state and therefore the degree of association, x.

For pure liquids, one of the most accurate methods of determining the surface tension is based upon the measurement of the height, above a flat surface, to which liquid will rise in a capillary of known cross section (M, 93–5; E and R, 158–64). However, this method is better adapted to research purposes, particularly to absolute measurements, than it is for use as an experiment in the physico chemical laboratory. It is difficult to determine the level of the flat surface of the liquid. This difficulty may be avoided by measuring the difference in height to which the liquid rises in two capillaries, of different but known cross sections. (See Adam, The Physics and Chemistry of Surfaces (1930), Chapter IX, also Sugden, J. Chem. Soc. **119,** 1483 (1921).) A simplified form of this technique is used in the present experiment. The difference in level of a liquid in the arms of a U-tube, which is made of two capillary tubes of different diameters (figure 17), is read directly on an attached scale. The same readings, when made at a series of temperatures, may be used to determine the change in density of the liquid. It is convenient to use capillaries having radii of approximately 1 mm. and 0.2 mm., respectively. The apparatus is difficult to clean if the radius of the smaller capillary is much less than 0.15 mm.

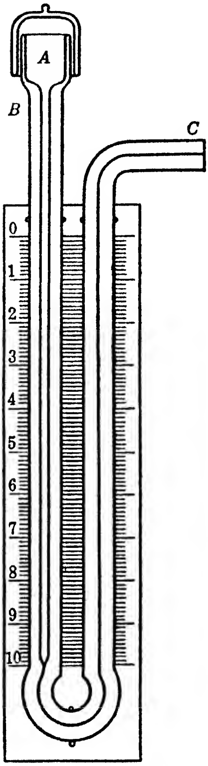

FIGURE 17. CAPILLARY U-TUBE

Apparatus and Materials: A special capillary U-tube with an attached millimeter scale, a meniscus reader, a 3 liter beaker, and a stirrer. About 5 ml. of pure toluene and 5 gm. of clean mercury.

Procedure: Clean the capillary U-tube thoroughly with a good grade of cleaning solution, by filling the cup, *A*, and allowing the liquid to flow through the capillary. (Don't spill cleaning solution on the brass scale.) Rinse the capillary with several ml. of distilled water. The flow of the liquid may be accelerated by applying air pressure, with the aid of a clean rubber tube slipped over the outside of the cup, *A*; however, blowing air through the capillary is very likely to contaminate it. A trace of oil or grease will greatly lower the surface tension of water.

Fill the 3 liter beaker with water and mount it on a tripod, so that it can be heated directly with a gas burner. Provide the beaker with a 100° thermometer and a stirrer, preferably motor driven. Clamp the U-tube, at *B*, and support it in a vertical position in the water-filled beaker. With the aid of a small pipet, or a short piece of tubing ending in a fine capillary, introduce enough pure water to fill 4 or 5 cm. of the larger capillary. Take care to avoid the trapping of air bubbles. If bubbles are trapped by a few small drops in the fine capillary, they may be removed by blowing gently at the end, *A*, of the coarse capillary and catching the droplets on a scrap of filter paper as they are forced out of the capillary tip, *C*. Attach a clean flexible piece of rubber tubing to the bent end, *C*, of the U-tube.

Keep the temperature of the bath constant, within 0.5°C. for about 10 minutes. Displace the meniscus in the small capillary by several millimeters, by applying gentle suction to the rubber tube attached to this capillary. As soon as the meniscus returns to its equilibrium position, which may require 1 or 2 minutes, read and record the positions on the scale of both menisci. These readings can be made to the nearest 0.1 mm. with the aid of a meniscus reader held close to the beaker. By blowing gently in the rubber tubing, displace the menisci in the opposite direction, and after waiting for equilibrium to be attained again read and record their positions. Repeat these readings several times, slightly displacing the menisci between each reading. Perform similar sets of readings at temperatures separated by 15 or 20° intervals from approximately 0 to 100°C.

At the end of this series of measurements displace the water by blowing into the larger capillary, and rinse the U-tube first with alcohol and then with toluene. Then repeat the whole series of measurements using toluene instead of water.

To determine the surface tensions and the temperature variation of density, it is necessary to know the radii of the capillaries and the volume of the U-tube. These quantities may be determined by measuring the lengths of a column of mercury of known weight when it is in various portions of the capillary. Remove the U-tube from the bath and dry it by drawing air through it for several minutes. Place a few grams of mercury in a weighing bottle and determine the total weight. With a capillary manipulator, transfer to the U-tube a few drops of mercury, sufficient to form a thread of several centimeters length in the fine capillary. The capillary manipulator or mercury dropper (figure 18) may be easily constructed from a piece of glass tubing and a scrap of flexible rubber tubing. Weigh the bottle and remaining mercury. With the aid of the meniscus reader, read and record the length of the mercury column (in the fine capillary) several times. The center of the mercury column should correspond approximately to the position formerly occupied by the menisci of water and of toluene, since the bore of the capillary may not be uniform. Force this mercury out of the capillary, and taking a second weighed quantity (of the same magnitude), repeat the measurements. Using proportionately larger samples of mercury, make similar measurements on the larger capillary. Force one of these samples

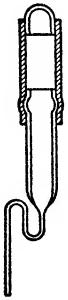

FIGURE 18. MERCURY MANIPULATOR

into the U-bend of the tube so that both menisci are on the scale, one being in the fine and the other in the coarse capillary. Read and record these positions of the menisci. This last pair of readings will enable you to compute the volume of the bent capillary and the section where the two capillaries join.

Computations: From the measured weights and (average) lengths of the mercury columns, compute the radii of the large and small capillaries. The density of mercury near room temperature is given by the following relation:

$$\rho_{\mathrm{Hg}} = 13.534 + (25^\circ - t^\circ\mathrm{C.})0.0024$$

The densities of the liquids at the temperatures of the several experiments, may be computed from the measurements, if the density of each liquid is known at one temperature (or if the weight of each sample of liquid is known). From the total lengths of the straight capillaries occupied by the liquid and the volume of the curved portion of the tube, compute the volume of each sample of liquid at each temperature used. For a given sample of liquid, the densities and volumes are, by definition, inversely proportional.

$$\rho_t = \rho_0 \frac{V_0}{V_t}$$

At 20°C. the density of toluene is 0.866 gm./ml. and the density of water is 0.998 gm./ml. Compute the densities of these liquids at the other temperatures used.

If the angle of contact is zero and the correction for the dimensions of the meniscus is neglected (M, 91–4), the relation between the surface tension, γ, of the liquid, its density, ρ, and the difference in height, Δh, to which it rises in the two capillaries, is given by the following equation:

$$\gamma = \frac{g}{2\left(\frac{1}{r_1} - \frac{1}{r_2}\right)} \rho \cdot \Delta h$$

where g is the acceleration of gravity, and r_1 and r_2 are the radii of the small and large capillaries, respectively. Using this relation and the values of ρ determined in this experiment, compute the surface tensions of water and of toluene at each temperature studied. Compute the corresponding values of the function, $\gamma(M/\rho)^{2/3}$. For each liquid tabulate the following quantities: t°C., Δh, ρ, γ, and $\gamma(M/\rho)^{2/3}$.

Plot $\gamma(M/\rho)^{2/3}$ against t°C. If the resulting graph appears to be a straight line, compare its slope to the standard value (2.12) of the Eötvös constant. Discuss any observed departure from linearity or from the expected slope. In your discussion of errors include a quantitative estimate of the errors introduced by the neglect of the thermal expansion of brass and of glass.

Experiment 6

SUBLIMATION PRESSURE AND HEAT OF SUBLIMATION

Vapor pressure, or sublimation pressure, is a characteristic property of a crystalline solid (M, 120; E and R, 276–7). It can be determined conveniently and accurately by the dynamic method (M, 83–4; R and R, vol. II, 6–9), since there is no danger of fog or spray formation when the saturating substance is a solid. In the present experiment, the vapor pressure of I_2 is to be measured at several different temperatures, within the range 0 to 40°C. The amount of I_2 carried over by a known volume of air is to be determined by absorbing it in a Na_2SO_3 solution, and precipitating and weighing the equivalent AgI (compare Baxter, Hickey, and Holmes, J. Am. Chem. Soc. **29**, 127 (1907)).

The relation between the vapor pressure and the molar heat of sublimation, L_s, is given, to a close approximation, by the following relation (M, 120):

$$\frac{d \ln p}{dT} = \frac{L_s}{RT^2}$$

If L_s is assumed to be independent of temperature, integration of this equation yields the following expression

$$\ln p = -\frac{L_s}{RT} + B$$

where B is a constant. This equation can be used to evaluate L_s in terms of the measured values of p and T.

Apparatus and Materials: A special U-tube for solid I_2; a suitable absorption tube; 2 small drying towers, one filled with NaOH pellets and the other with glass beads coated with concentrated H_2SO_4; a 10 liter bottle (a tubulated aspirator bottle is convenient); a 2-liter calibrated flask; a small open-tube mercury manometer; a thermostat; glass tubing for connections; a Gooch crucible, provided with an asbestos or sintered glass filter; a suction flask. About 50 gm. of pure I_2, 10 gm. of $Na_2SO_3 \cdot 7\,H_2O$, 40 ml. of 0.05 M $AgNO_3$, 5 ml. of 1 M HNO_3.

Procedure: Grind the I_2 to a coarse powder. Push a plug of clean glass wool into the constriction, *B*, of the special U-tube, *A*. Fill the U-tube with the coarsely ground I_2. When the iodine-filled tube is not being used, leave it unstoppered in a desiccator. Prepare about 100 ml. of approximately 0.02 *M* Na_2SO_3 solution. A fresh solution should be prepared for each determination, since Na_2SO_3 is rapidly oxidized to Na_2SO_4 when its solution stands in contact with air. Pour enough of this solution into the absorption tube to fill its inclined arm, *C*, three-quarters full. (The exact form of the absorption tube is not important.) Assemble the apparatus as indicated in figure 19. The tube, *D*, should be connected to two drying towers (not shown in the figure) by a short length of washed rubber tubing. Fill the first drying tower with pellets of NaOH, and the second with glass beads coated with concentrated H_2SO_4 to which a little $Na_2Cr_2O_7$ has been added. The purpose of the bent tube, *E*, is to bring the air to the temperature of the thermostat, *F*, before it enters the iodine tube. It is advisable to use an automatically controlled thermostat, since 2-1/2 to 3 hours are required to complete an experiment and

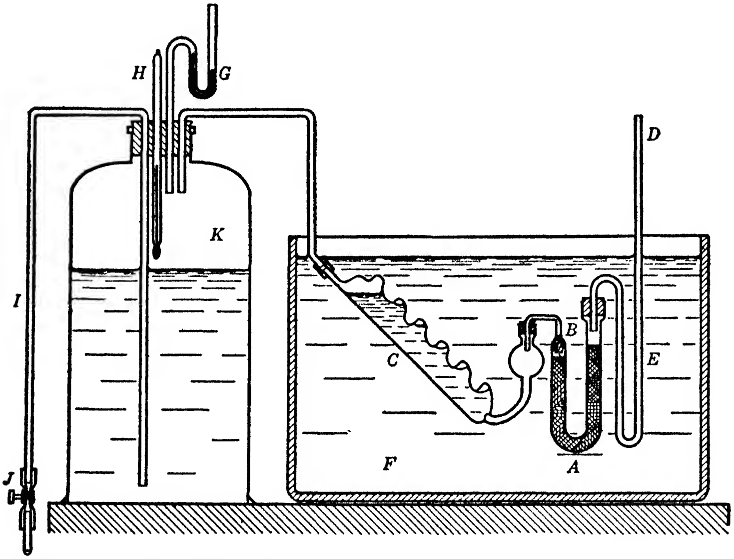

FIGURE 19. APPARATUS FOR DETERMINING VAPOR PRESSURE BY THE DYNAMIC METHOD

during that time the temperature must be kept constant within 0.1°. However, a hand-controlled thermostat may be used, if it is provided with an efficient stirrer. The small mercury-filled open manometer, *G*, can be easily made from a piece of glass tubing. A 100° thermometer divided in degrees is satisfactory for the thermometer, *H*. The siphon tube, *I*, is unnecessary if a tubulated aspirator bottle is used. The rate of flow of air through the tubes *A* and *C* is controlled by regulating the efflux of water with the screw clamp, *J*. All glass-to-rubber connections must be tight, and no long rubber connections should be used.

After arranging the apparatus as described and setting the thermostat to some convenient temperature, cautiously open the screw clamp, *J*, and allow water to flow into the 2 liter calibrated flask at a rate of from 2 to 2-1/2 liters per hour. In this way dry air is drawn through the heat exchanger, *E*, and saturated with I_2 in the U-tube, *A*; is freed of I_2 in the absorption tube, *C*; and finally is collected over water in the space, *K*. The volume of water collected equals the change of the volume, *K*, and when corrected for difference in pressure and temperature is equal to the volume of air drawn over the I_2. Allow 6 liters of water to escape, momentarily stopping the flow while you drain the calibrated flask. At half hour intervals, read and record the temperature and pressure of the air in the volume, *K*, reading both the barometer and the manometer, *G*. While the air is running through the system, prepare, dry, and weigh the Gooch crucible (K and S, 185–90). At the completion of the experiment, disconnect and remove the absorption tube, *C*, and drain its contents into a small beaker. Wash the tube carefully with several small portions of dilute HNO_3 and pour the washings into the beaker. Add slightly more (1 *M*) HNO_3 than is required to convert all of the Na_2SO_3 into H_2SO_3. Heat this solution almost to boiling, and precipate the I^- as AgI. Filter, wash, dry, and weigh the precipitate. Since the total amount of precipitate is small, follow the standard procedure (K and S, 307–13) closely; taking care to avoid loss of precipitate while it is being transferred and washed.

Repeat the experiment at two other temperatures. All of these temperatures should lie within the range 0 to 40°C., and the lowest and highest should differ by at least 15°. At temperatures below 15°C. it is advisable to pass 8 rather than 6 liters of air through the system.

Computations: From the volume of water collected, compute the volume of air which was passed over the I_2, taking into account the difference in temperature and in total pressure and the partial pressure of water vapor (M, 84). From the corrected volume of air and the corresponding weight of AgI, compute the vapor pressure of I_2 (M, 83–4). Repeat these computations for the other two measurements. Tabulate the following quantities for each of the three determinations: average reading of the barometer and of the small manometer, temperature of the air in the bottle, aqueous tension of water at this temperature, corrected volume of air, weight of AgI, vapor pressure of I_2, temperature of the thermostat.

Plot the logarithm of the pressure of I_2 against the reciprocal of the absolute temperature. Draw the best straight line through these three points. From the slope of this line, compute the molar heat of sublimation of I_2.

Experiment 7

THE LINEAR RATE OF CRYSTALLIZATION OF A MELT

The rate at which a melt crystallizes is determined in part by the number of crystal centers or seeds which form in unit time and in part by the speed with which these individual seed crystals grow. Some liquids may be cooled far below their melting points without the formation of crystal centers occurring spontaneously. If such a melt be seeded, the rate of growth of crystals from this center may be conveniently studied. The very fact that crystals occur with definite polyhedral forms is proof that the rate of growth of a single crystal is a function of the angle between the direction of growth and the crystal axes. While the rate of growth perpendicular to a crystal face can be measured, it is more convenient, although less significant, to measure the average linear rate of crystallization. This is done by filling a U-shaped glass tube with a liquid, cooling it below its melting point by immersing it in a constant temperature bath, inoculating it at one end of the tube with a crystal seed, and measuring the rate at which crystallization progresses along the tube.

The absolute value of this linear rate depends upon the temperature, the substance, and to some extent upon the diameter and wall thickness of the glass tube. For a given substance and experimental arrangement the rate depends upon the supercooling. As the temperature is lowered the rate increases to a flat maximum and if the temperature is sufficiently reduced decreases again (figure 20). Impurities decrease the rate. It was suggested by Tamman that there are five different types of linear crystallizations, the occurrence of which depends upon the degree of supercooling. In the first region, *A*, the melt crystallizes solidly in fine crystals oriented at random and the rate increases slowly with decreasing temperature. This region usually extends from the melting point to from 1 to 5° below. During the next 10 or 20° drop in temperature, region *B*, the rate increases more rapidly with falling temperature, and the crystals tend to form in long flat needles along the wall of the tube leaving the center of the melt liquid. For all substances except those which crystallize very slowly, this is followed by a region, *C*, in which the rate is independent of the temperature of the thermostat. In this region the melt crystallizes solidly, but with the crystals oriented along the axis of the tube.

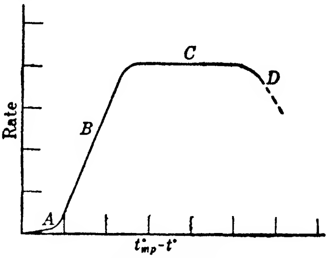

FIGURE 20

If the melt is further supercooled before inoculating the rate again decreases. At very low temperatures, the fifth region, it becomes extremely slow, but has a definite constant value for each temperature. At intermediate low temperatures there is a region, *D*, in which the rate is not constant even when the temperature of the thermostat is constant; this is especially marked for substances which crystallize rapidly. The constant or maximum rate, *C*, is least sensitive to the experimental conditions, and appears to be a definite property of the substance.

When the melt crystallizes on the face of a growing crystal the heat of crystallization is liberated, thereby raising the temperature at the liquid-solid interface. The rate of loss of heat from this surface is one of the factors which limits the rate of crystallization. It has been suggested, that when the rate is a maximum, the interface is at the melting point. At still lower temperatures, increasing viscosity of the melt and possibly other factors retard the crystallization. For further discussion of these phenomena see: Treatise of Physical Chemistry, H. S. Taylor, pp. 1035–8. Kristallisieren und Schmelzung, G. Tamman, 131–58.

The spontaneous formation of crystal centers may be demonstrated in a spectacular manner by pouring melted menthol (menthanol 3) into a warm watch glass and allowing it to cool slowly.

Apparatus and Materials: A 2 liter beaker, a motor-driven stirrer, a tenth degree thermometer, a stopwatch, and a special U-tube provided with protective caps and 1 cm. graduations. About 10 gm. of benzophenone.

Procedure: Mount the beaker on a tripod over a gas burner, and provide it with a thermometer and with a stirrer, which is efficient but does not produce too much vibration. Fill the beaker about three-fourths full of water and adjust its temperature to the desired value. Melt the benzophenone in a small beaker (about 50 ml.) and pour some of it into the shorter arm of the U-tube until the level of the liquid in the side tubes is one or two centimeters above the horizontal tube. Keeping the U-tube warm, tilt it carefully and tap it to remove all trapped air bubbles. After placing the protective caps on the tube, clamp it at a convenient height in the water bath. Keep the temperature constant (at some value 5° or more below the melting point) for about ten minutes before inoculating the melt. Pick up a seed on the end of a fine copper wire (from the material remaining in the beaker) and introduce this through the short arm of the U-tube. Start the stopwatch when the crystals reach the first etched ring, and record the time required for them to travel each centimeter. Record the temperature of the bath before and after each measurement of crystallization; it should not change by more than 0.1°C. Adjust the bath to a new temperature. Remove the U-tube, and melt the solid by heating the tube carefully with a gas flame. After getting rid of the trapped bubbles, return it to the water bath and determine the linear rate of crystallization at the new temperature. The measurements should be repeated at from 6 to 10 different temperatures between 0 and 45°C. At the end of the series, compare the graduations on the U-tube to an accurate millimeter scale.

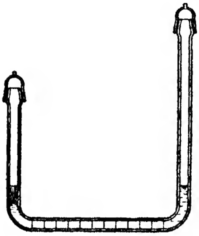

Figure 21

While benzophenone is particularly well fitted for use in this experiment, any substance which melts at a convenient temperature and does not have too great a tendency to crystallize spontaneously may be used. Salol (phenyl salicylate) is a good example of a substance which has a low maximum rate of crystallization.

Computations: Compute the average rate, in centimeters per minute, for each temperature studied. Tabulate the values, including the apparent average error of each average value. Plot the rate as a function of the number of degrees of supercooling.

Experiment 8

THE RADIOACTIVE DECAY LAW

The ionization produced by a single radioactive element is a measure of the amount of the element present. The ionization, unless it is extremely weak, can be readily measured with an electroscope (85–8).

The law which governs the rate of a radioactive disintegration (M, 169; E and R, 217) can be determined by measuring the ionization produced by a sample of a moderately short-lived element at a series of times; the measurements being continued for a period comparable to the half life of the element. This method can be applied not only to simple elements, but also to those whose decomposition is followed by several successive disintegrations, providing that the half lives of these unstable products is short compared to that of the parent element. In the latter case, a steady state, or "cascade equilibrium," is established quickly after the isolation of the parent element. The only measurable effect of the successive disintegration is an enhancement of the total ionization, which is still directly proportional to the amount of the original element present.

There are two parts to the present experiment. The first consists of the isolation of a moderately short-lived radioactive element. In the present experiment a naturally occurring radioactive element, AcB, is to be used; however, the use of artificial radioactive elements (M, 192; E and R, 224; Glasstone, Textbook of Physical Chemistry, 175–8), of suitable half life, increases the interest of the experiment and is practicable in those laboratories which have access to a cyclotron or electrostatic generator. The second part is the determination of the decay law of this element, by means of measurements of the ionization produced by it and its short-lived products, at a series of times after its isolation.

Starting with a preparation of Ac (or RaTh), AcB (or ThB) can be readily isolated. The active preparation gives off the short-lived gas, AcEm (or ThEm). When an atom ejects an α-particle or β-particle from its nucleus, the recoil atom loses one or more outer electrons and exists temporarily as an ion. If the ion is formed in an electric field it will migrate toward the cathode and be adsorbed upon it. In this way, AcB can be collected on a negatively charged disk or wire which is suspended over a solid preparation of Ac (compare F and W, 106). AcA, which is directly formed when AcEm decomposes, is very short lived, and decomposes before it reaches the cathode.

The applications of radioactivity which are chiefly of interest to chemists are the use of radioactive substances as tracers (M, 176; E and R, 226; Glasstone, loc. cit., 167–75; Thomas, Chem. Eng. News. **25,** 1572 [1947]) and their effects in inducing chemical reactions (Lind, The Chemical Effects of Alpha Particles and Electrons; Burton, Jour. Phys. Chem. **51,** 786 [1947]). Laboratory experiments illustrating the former use are described by D, M, and W, 260–9 and by Rosenblum, J. Chem. Educ. **11,** 622 (1934).

Apparatus and Materials: A Lind electroscope provided with an α-ray ionization chamber and a charging device, a stopwatch, an Ac (or RdTh) preparation, a metal disk and a flat metal dish provided with a glass spacer, a 200 to 300 volt B-Battery or B-battery eliminator, a resistance of several thousand ohms.

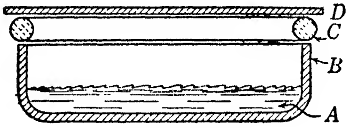

FIGURE 22

Procedure: Spread the Ac preparation, *A* (figure 22),[1] evenly in the small metal dish, *B*. By means of the glass ring or triangle, *C*, support the disk, *D*, over the dish. Attach the disk to the negative and the dish to the positive terminal of the B-battery or B-battery eliminator. To safeguard against short circuits, include a resistance of several thousand ohms in the circuit. Allow the disk to remain in place for an hour or longer.

Disconnect the battery, and transfer the disk to the bottom of the ionization chamber of the electroscope. Be sure that the surface covered with active deposit, which was facing the Ac preparation, is now turned up. Be careful not to touch this surface when transferring the disk. Allow 5 or 10 minutes to pass before making the first measurement. Measure (87–8) the ionization, in divisions per second, at 10 or 15 minute intervals for about 2 hours. (Note: if the longer-lived ThB is used, the measurements should be continued for at least 24 hours, but need not be made at such frequent

---

[1] The design of this simple and inexpensive device is due to Dr. D. Hull.

intervals.) In addition to measuring, with a stopwatch, the time interval required for the (partial) discharge of the electroscope, record the absolute time of the midpoint of each measurement with the laboratory clock or a watch. At the end of the hour period, remove the disk and determine the "natural leak" of the electroscope (88).

Computations: Compute the rate of discharge, in divisions per second, corresponding to each measurement. Subtract the rate of the natural leak from each of these values. Tabulate the (absolute) time corresponding to the midpoint of each measurement, the time interval recorded with the stopwatch, the observed rate of discharge, and the corrected rate.

Plot the logarithms of the corrected rate against the (absolute) time of the measurements. Since the corrected rate is directly proportional to the quantity of AcB present, the slope of a straight line drawn through these points will be directly proportional to the decay constant, λ, of AcB (M, 168–9). From this slope, compute the decay constant, the half life, and the average life of AcB. Compare your value of the half life to the accepted value.

USE OF THE LIND ELECTROSCOPE

At the present time most measurements of radioactivity are made with a Geiger-Mueller counter equipped with an automatic recorder (W, 1255–86). Electroscopes, while less sensitive, are simpler in principle and less expensive. Many different models of electroscopes have been developed and are used for various purposes (see for example, W 1252–4; Hevesy and Paneth, Radioactivity, 9–12; and Hoag, Electron Physics, Appendix E).

One of the simplest and most adaptable of these is the Lind electroscope (Lind, Ind. Eng. Chem. **7**, 406 (1915)). This instrument while not particularly sensitive is simple and rugged. It can be used to measure γ radiation, α or β radiations from a solid source, or the total radiation from radon. It is represented diagrammatically by figure 23. In this instrument a thin strip of Al foil, *A*, is attached to a metal rod, *B*, which is connected to the metal disk, *C*. The rod and disk are electrically insulated from the case, *D*, *D'*, being supported by the amber plug, *E*. The upper half of the case, *D*, is a horizontal metal cylinder, having shielded glass windows at either end. The lower half of the case, the ionization chamber, *D'*, is an upright metal cylinder. It is provided with a door through which the disk, *F*, covered with active deposit or any other radioactive substance, can be introduced.

In use the entire case is grounded. The system *A*, *B*, *C* can be raised to any desired potential with the aid of the charger, *G*. This is a bent piece of wire, passing through the ebonite bearing, *H*, and provided with an ebonite handle, *J*. When this wire is turned forward its end comes in contact with the rod, *B*. If a suitable potential, 200 to 300 volts, is applied to the wire at the point, *I*, the rod is raised to this potential, and the Al leaf, *A*, is repelled from the rod. If the charger is then turned backward until it contacts the case, the central system, *A*, *B*, *C*, is isolated. It can lose its charge only by conduction across the amber plug or through the gas to the grounded case. Introduction of a radioactive source into the ionization chamber ionizes the gas and greatly increases its conductivity. The rate at which the leaf, *A*, falls is a measure of the rate at which the central system loses its charge, and therefore of the intensity of the ionization. The motion of the leaf is observed with a short focus telescope (not shown in the figure), the eyepiece of which is equipped with a micrometer scale.

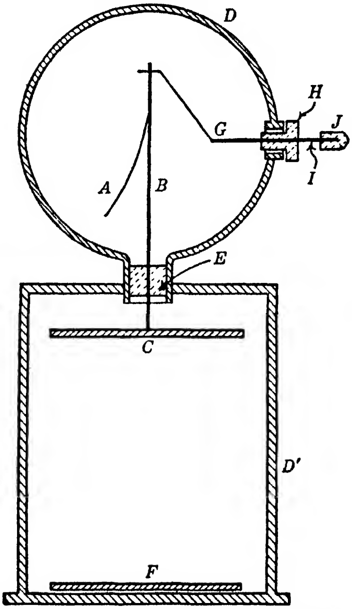

FIGURE 23. LIND ELECTROSCOPE

The insulation of an electroscope is never perfect and there is always some residual ionization of the air. This results in a slow rate of fall of the leaf even in the absence of any added radioactive material. This spontaneous rate of fall is known as the "natural leak" of the electroscope. In estimating the strength of an active source, this natural leak must be subtracted from the measured rate.

The simplest type of electroscope charger consists of an ebonite rod and a catskin. When the rod is rubbed with the fur it acquires an electrostatic charge, and this may be transferred to the electroscope by touching the rod to the wire at *I*. The successful use of this device requires some practice, and is particularly difficult in humid weather. It is much more convenient to use a set of B-batteries, which can be tapped off at different potentials between 200 and 300 volts, or a B-battery eliminator, which can be adjusted over the same range. If the B-batteries or "eliminator" are used, a resistance of several thousand ohms should be included in the circuit to minimize the effect of an accidental short circuit.

Although it is not so represented in the simplified diagram of figure 23, the construction of the Lind electroscope permits the removal of the head, *D*, from the body, or ionization chamber, *D'*. This makes it possible to use one head with several different ionization chambers. The ionization chamber used in experiment 8 is known as an α-ray chamber. Since the active material is introduced directly into the chamber all three types of radiation can pass through the gas. The ionizing power of α-rays is so much greater than that of β- or γ-rays, that when all three are present together the effect of the latter two is negligible. If the source is placed outside of a thick-walled chamber, only γ-rays can penetrate into the chamber and ionize the gas. β-ray electroscopes are provided with thin Al windows, which transmit most of the β-rays but absorb the α-rays (F and W, 108–12).

Apparatus and Materials: A Lind electroscope provided with an α-ray ionization chamber, a suitable charging device, a stopwatch, and a weakly radioactive source.

Procedure: Set up the electroscope with a frosted lamp 2 or 3 feet behind it. Adjust the charger to give about 200 volts. See that the case of the electroscope is grounded. Turn the charging wire, *G* (figure 23), forward until it makes contact with the rod, *B*. Touch the wire at *I* with the lead from the source of potential; note how far the leaf, *A*, moves. If the edge of the leaf is not in sharp focus, the telescope may be adjusted to bring it into focus, but this adjustment must not be changed during a series of measurements. When the potential is applied, the leaf should move almost across the scale, but it is inconvenient to have it go off of the scale. For example, if the scale is divided into 100 parts with the high numbers corresponding to large deflections, it will be convenient to adjust the charger so that the fully charged leaf comes to rest somewhere between divisions 90 and 100. When the charger has been adjusted to the right potential, charge the electroscope and then turn the wire, *G*, back until it touches the case. Allow the electroscope to remain charged from 5 to 15 minutes before making any measurements; this gives the insulation time to come into equilibrium (see Lind, loc. cit.).

Introduce the radioactive material through the door of the ionization chamber, and center it in the bottom of the chamber. Charge the electroscope. With a stopwatch, measure the time necessary for the leaf to fall across 40 or 50 divisions, somewhere in the middle of the scale. Since the rate of fall of the leaf may not be uniform, it is necessary to use the same scale interval in all succeeding experiments. For example, if the scale read from 0 to 100 and the fully charged position were 92, it would be convenient to take the time required for the leaf to fall from 80 to 40. The reciprocal of this time interval is directly proportional to the mean intensity of ionization.

Measurements with an electroscope yield only relative values of the intensity of ionization or of the strength of a radioactive source. To make an absolute measurement of the activity of a sample, a radioactive standard is necessary. The standard should be of the same general form and thickness as the unknown, and should be placed in the same position in the chamber.

It is necessary to correct all measured rates for the background rate or "natural leak." To determine the natural leak, remove the radioactive source from the electroscope, and measure the time required for the leaf to fall over the same portion of the scale as was used in the measurements.

Computations: Compute the rate of discharge, in mm. per second, for each measurement. Subtract the background rate from each of the measured rates. The ratios of the activities of the samples (or of the same sample at different times) are equal to the ratios of their corrected rates.

Experiment 9

ABSORPTION SPECTRA OF COLORED SOLUTIONS. USE OF THE SPECTROSCOPE

Spectroscopy (W, 738–820) has a great many important applications to chemistry. However, it has become both in theory and practice such a complex and intricate subject that it is practically impossible within the confines of a laboratory experiment to do more than indicate a few simple semi-quantitative applications of the ordinary "chemical" spectroscope. (Directions for a simple experiment using a quartz ultra-violet spectrograph are given in F and W, 145–6.)

In the first part of the present experiment the scale of a simple prism spectroscope is to be calibrated with the aid of the flame spectra of a few alkali elements, the arc spectrum of Hg, and the first three lines of the Balmer series (M, 149–50, 163) of H. The second part of the experiment consists of the determination of the absorption or Hartley curves of solutions of one or more colored substances (M, 204–6; Getman and Daniels, Theoretical Chemistry, 91–5).

Apparatus and Materials: A suitable spectroscope, a Hg arc, a H_2 discharge tube, a simple induction coil, a Baly tube, 3 Pt or nichrome wires or some other device for obtaining "monochromatic" flames. Samples of LiCl, NaCl, and KCl. A suitable colored solution.

Procedure: The spectroscope may be either of the single prism "chemical," or Bunsen, type or of the direct vision Amici prism type. It should be provided with a scale, the image of which can be made to coincide with the spectra. A simple spectrometer may be used in place of the spectroscope. While the spectrometer is capable of yielding more accurate determinations of wave length, its use requires a somewhat longer time. For diagrams of these instruments and more detailed descriptions of their adjustment and use, see R and R, vol. II, 289–304; Brode, Chemical Spectroscopy; J. Lewis, Spectroscopy, 11–21; or Weigert, Optische Methoden, 81–114.

Set up a Na flame in line with the collimator tube of the spectroscope, but not close enough to the slit to heat it. Open the slit to a width of at least 0.5 mm. Adjust the focus of the telescope or eyepiece until the image of the slit appears as a sharply defined yellow rectangle. Then narrow the slit until the image is just clearly visible. Illuminate the scale with a small incandescent lamp, and if necessary adjust the scale until its image is superimposed sharply upon the spectrum. Consult the instructor if it appears to be necessary to make other adjustments, such as orientation of the slit or prism, focus of the collimator lens, etc. Once the instrument has been properly adjusted, do not change its setting during the experiment.

To calibrate the scale, record the scale reading to a tenth of the smallest division corresponding to the position of each of the lines of the line sources used. Note the position of the NaD lines, and then replace the Na flame with a Li flame. (Note that if the spectroscope has a fairly high dispersive power, the D lines will be separated into a doublet, though the separation is not noticeable with an ordinary "chemical" spectroscope; compare table 10.) The flame spectrum of Li has only one strong line. Potassium gives two lines, one in the extreme red and the other in the extreme violet, which are particularly valuable for the calibrations. Since these lines are near the limits of visibility, it is advantageous to replace the short-lived flame which is obtained by introducing a KCl-coated wire into the bunsen flame with a steady source, such as a burner fed with a Gouy atomizer or a Pt wick (Baly, Spectroscopy, II, 55–176). The mercury arc should be of the medium pressure type, preferably made of glass which absorbs ultraviolet light. A GE AH4 is a convenient source. At least 6 lines in the Hg arc spectrum should be visible. The H_2 discharge tube can be operated by a small induction coil, such as is used to test vacuum lines for leaks. Many other sources can be used. A Cd amalgam arc is particularly valuable since it gives the lines of both Cd and Hg. A Ne discharge tube emits a number of lines in the red and orange, but due to the complexity of the Ne spectrum they are somewhat difficult to recognize. The flame spectra of the other alkalis as well as those of some of the alkaline earths and In and Tl may also be used. The wave lengths corresponding to these sources are given by Twyman and Smith, Wave Length Tables for Spectral Analysis, and also in the I.C.T. V, 277. Another simple and satisfactory method of calibrating the spectroscope is to use the dark Frauenhafer lines of the solar spectrum. To use these lines reflect sunlight parallel with the collimator tube into the slit, with a small mirror.

The quantitative determination of the absorption curve for a solution requires the use of a spectrophotometer (W, 773–88; R and R, 629–31; Brode, Chemical Spectroscopy, 117–216, 265–79; Weigert, loc. cit., 175–247; J. Lewis, loc. cit., 69–87). Spectrophotometric measurements can be made accurately and very conveniently with the aid of a modern commercial photoelectric spectrophotometer, such as the Beckman instrument. However, a semiquantitative result, in the form of a Hartley curve, may be obtained with a spectroscope and a Baly tube in the following manner: The Baly tube consists of two concentric glass tubes, *A* and *C*, fitted with plane glass or quartz ends. The inner tube, *A*, may be moved in or out through the rubber sleeve, *B*, thereby changing the thickness, *L*, of the solution through which the light must pass. The outer tube is provided with an etched millimeter scale (not shown in the figure), by means of which the length, *L*, can be measured. Slide the tube, *A*, out to the end of the scale, to make the thickness of the liquid layer, *L*, a maximum. Pour in enough of the colored solution to fill the tube, *C*, but to leave the bulb, *D*, empty. Clamp the Baly tube with its outer window, *E*, in front of the slit of the spectroscope, so that its axis, *KM*, is parallel to the axis of the collimator tube. At a point beyond the open end of the Baly tube but in line with its axis, fix a bright frosted incandescent lamp. The spectrum will now appear as one or more bright regions bounded or separated by dark bands.

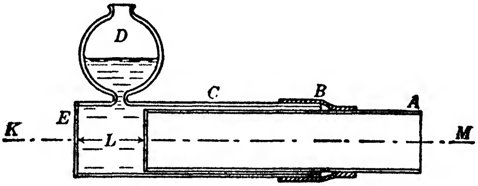

FIGURE 24. BALY TUBE

Estimate on the scale of the spectroscope, the positions of the edges of the bright bands. Record these positions and the corresponding thickness of the liquid layer, *L*. Repeat these measurements at 6 or 8 different settings of the Baly tube, ranging down to a thickness of a few mm. If the absorption due to the thinnest layer is still considerable, it may be necessary to replace the solution in the Baly tube with one which is only one-fifth as concentrated and repeat the measurements.

It is interesting to determine and compare the absorption curves for identical concentrations of different but closely related chemical compounds; such as, a two-color indicator in its acid and in its base form, a saturated aqueous solution of I_2 and the same solution to which solid KI has been added, or a dilute $CuSO_4$ solution before and after the addition of an excess of NH_4OH or KBr.

Computations: Using the data given in the following table, identify the wave lengths of the several lines observed in the first part of the experiment. Plot these wave lengths as a function of the scale readings, and draw a smooth curve through the points.

With the aid of this plot, determine the wave lengths corresponding to the edges of the absorption bands which were observed in the second part of the experiment. For each substance or concentration studied, tabulate the length of the absorption layer and the limits of the absorption bands in terms of wave lengths. Plot the thickness, *L*, as ordinates and the absorption limits, λ, as abscissae. If experiments were made with more than one concentration of the same substance, the results may be reduced to the same basis and plotted on the same curve, by means of Beer's law (M, 206–8).

TABLE 10

WAVE LENGTHS OF LINES SUITABLE FOR THE CALIBRATION OF THE SPECTROSCOPE

SOURCE	Å	SOURCE	Å
K	7699 7665	Hg H	5461 4862
Li	6708	Hg	4358
H	6563	H	4341
Na	5896 5890	H Hg	4102 4078
Hg	5791	Hg	4047
Hg	5769	K	4047 4044

Experiment 10

THE FREEZING POINT OF AN AQUEOUS SOLUTION AND THE MOLECULAR WEIGHT OF THE SOLUTE

The measurement of the freezing point lowering, produced by the addition of a small amount of a soluble substance to a solvent, is a convenient and relatively accurate method of determining the apparent molecular weight of the solute in a solution (M, 249–52; E and R, 305–9). For ideal solutions, the apparent molecular weight is equal to the weight which would be computed from the chemical formula: i.e., the formula weight. If the solute dissociates or ionizes in solution, the freezing point lowering will increase and the apparent molecular weight will be less than the formula weight. If it associates in solution, the apparent molecular weight will be greater than the formula weight. In many such cases the freezing point lowering may be used to determine the degree of dissociation or association of the solute (M, 263–9). The solvation of a solute increases the freezing point lowering and correspondingly decreases its apparent molecular weight. However, in dilute solutions the effect of solvation is not important.

The method used in this experiment is simpler and more accurate than the usual Beckmann method (103–07). When suitably refined (see for example Adams, Journ. Am. Chem. Soc. **37**, 381 (1915) it yields results of high precision. Unlike the Beckmann method it is not conveniently applicable to non-aqueous solutions. Its essential features are the use of a well insulated vessel and a large amount of the solid phase (ice), and the direct analysis of a sample of solution which is removed at the time the thermometer is read. The solute used should be a non-electrolyte, for which some simple analytical procedure is available. Solutions of sucrose, which can be analyzed polarimetrically (98–102), or boric acid, which can be titrated in the presence of mannitol or invert sugar (K and S, 560–1), are recommended. Solutions of many non-electrolytes may be analyzed with sufficient accuracy by means of an immersion refractometer (150) or an accurate pycnometer. If these methods are used, however, the relation between molality and refractive index or density must be determined with the aid of several solutions of known composition.

Apparatus: A Beckmann thermometer, a half pint Dewar tube fitted with a wooden stopper and a ring stirrer. The stopper should be water-proof and in addition to the hole for the stirrer should contain a central hole to admit the thermometer and another for the pipet.

Procedure: Prepare about 100 ml. of a solution of sugar (or boric acid), approximately 0.3 *M*, and set the flask containing the solution in an ice bath. Set a second flask containing a few hundred ml. of distilled water in the ice bath. Prepare three cotton filters, by plugging a small amount of cotton in the end of a short piece of rubber tubing which fits tightly on the end of a 25 ml. pipet. (If 25 ml. is insufficient for analysis use a larger pipet.) Rinse a lump (or two) of clear ice in distilled water, and crush it in a clean towel which has been washed free from starch. If the polarimetric method of analysis is to be used, care must be taken to avoid the introduction of even traces of dust or lint or anything which will render the solution cloudy. Adjust the Beckmann thermometer so that it reads between 2 and 5° when it is in the ice bath (95–8).

Fill the Dewar tube about two-thirds full of the finely crushed ice and add enough distilled water to cover the ice. Put the cover and stirrer in place. After placing a rubber guard ring on the thermometer for support (see figure 25), insert the thermometer through the central hole. Stir the mixture, tap the thermometer gently with a pencil, and read the temperature. Continue stirring until the temperature be-

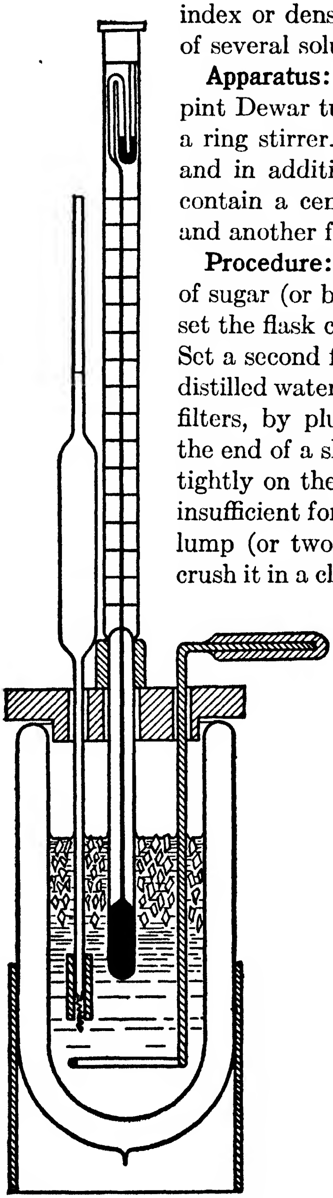

FIGURE 25. FREEZING POINT APPARATUS

comes constant. Record this temperature, which corresponds to 0°C. Then remove the cover and carefully pour the water off of the ice. Add enough chilled sugar (or boric acid) solution to cover the ice. Replace the cover, stirrer, and thermometer. Stir and read the temperature as before. After stirring for a few minutes, insert the pipet with its cotton filter, and withdraw a sample as quickly as possible. Record the temperature at the time of removing the sample. Remove the cotton filter from the pipet and discharge its contents into a small stoppered flask or bottle. Replace the solution which has been removed from the Dewar with an equal volume of chilled water. Again stir, remove a sample, and record the temperature. Add another portion of water to the Dewar and repeat the process. Analyze the three samples with the polarimeter (98–102); or, if some substance other than sucrose has been used, by an appropriate method.

Computations: From the results of the chemical analysis compute the number of grams of solute per 1000 gm. of water for each determination. Substitute these values in the following equation and obtain the apparent molecular weight of the solute.

$$M = \frac{1858\,W}{W_0\,\Delta T}$$

In this equation, which is valid only for dilute aqueous solutions, M is the apparent molecular weight, W is the weight of the solute, W_0 the weight of the solvent, and ΔT is the freezing point lowering in degrees centigrade. Tabulate your results and compare the apparent molecular weight to the formula weight of the solute.

USE OF A DIFFERENTIAL THERMOMETER

Differential thermometers are designed to measure small differences in temperature with relatively high precision. If the total difference in temperature is less than 0.1°C., it is necessary to use either a multiple-junction thermocouple (R and R, 389) or some special device. For ordinary purposes, mercury-in-glass thermometers, of the Beckmann or Philadelphia Differential types are satisfactory (compare Swietoslawski, Ebuliometric Measurements, 1945, 21, 37–9). These thermometers are provided with unusually large bulbs, with capillary stems graduated to 0.01°C., and with reservoirs at the upper end of the capillary which permit the amount of mercury in the bulbs (and thereby the setting of the thermometers) to be changed at will. The zero of this type of thermometer may be set to any temperature from − 10 to + 120°C. Their range is about 5°C. With the aid of a small magnifying glass, a "meniscus reader," they may be read with a precision of 0.001°C.

There are several precautions which should be observed in using a differential thermometer. The mercury column has a tendency to stick, but this may be largely prevented by tapping the thermometer with a pencil before each reading. After a sudden change in temperature, the glass bulb requires some time to come to equilibrium, and its gradual contraction or expansion produces a slow drift of the setting. A very sharp change in temperature may crack the ring seal where the bulb joins the stem. If a thermometer which is not provided with a safety bulb (see *d*, figure 26) is used at a temperature below that of the room, it must not be allowed to warm up to room temperature or the setting will be lost. For precise work a stem correction must be determined under the condition of use (Temperature, Its Measurement and Control in Science and Industry, A.I.P., 234–8).

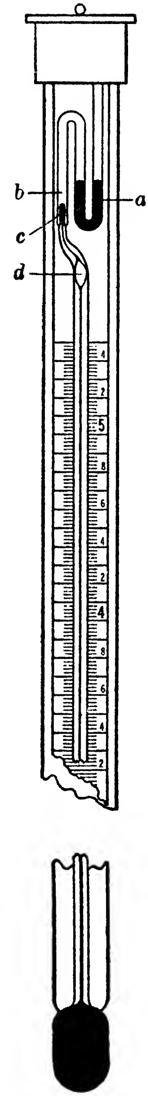

Figure 26
Beckmann Thermometer

The Beckmann Thermometer: The construction of the upper reservoir of an improved type of Beckmann thermometer is shown in Figure 26. The method of setting this thermometer can be most readily understood by considering the detailed procedure required to make a typical adjustment. Let us assume that the zero of the thermometer is set at 25°C. and that it is desired to make a new setting such that 0°C. will fall on the upper part of the scale. To begin with, the thermometer (proper) does not contain enough mercury, and if the bulb were immersed in ice water the mercury column would disappear into the bulb. To add more mercury to the thermometer, tilt it to transfer the mercury from the reservoir, *a*, to the space, *b*, above the fine capillary inseal, *c*. Now if the thermometer is held in an upright position, the mercury frequently can be caused to run down from the space, *b*, and join the main column by a quick jerk or sharp tap. If this does not occur readily, the bulb of the thermometer should be held in warm water until the main column rises to join the mercury at *b*. On cooling it will draw this mercury down with it. Next the bulb of the thermometer should be placed in an ice bath for a few minutes. The excess mercury remaining in the space, *b*, can then be returned to the reservoir, *a*, either by inverting the thermometer and giving it a sharp tap, or by a short swinging motion. This operation must be carried out quickly, before the mercury in the bulb has become appreciably warmer. Upon returning the thermometer to the ice bath it will probably be found that, due to the safety bulb, *d*, there is now too much mercury in the thermometer. This excess should be removed cautiously by heating the bulb, with warm water or even the palm of the hand, and thereby forcing the excess, drop by drop, out of the capillary inseal, *c*. In some thermometers each drop forced out lowers the scale reading by 1°C. If it is desired to adjust a thermometer to a temperature above that of the initial setting, the procedure will be similar to that just described, except that the first step is unnecessary since in this case the thermometer already contains an excess of mercury. For a description of an older type of Beckmann thermometer see (D, M, and W, 422–3 or R and R, vol. I, 618).

The Philadelphia Differential Thermometer: The Philadelphia differential and the Beckmann thermometers are similar in principle and general design, but differ in several important constructional details. While the Philadelphia thermometer is much more rugged, it is somewhat more difficult to set to a definite temperature. Its capillary stem is of solid glass and is lens shaped like a clinical thermometer. Because of this feature, it is easy to read to 0.01° (or possibly 0.005°) with the unaided eye. It can be read to 0.001°C. with a meniscus reader. The meniscus reader should be placed perpendicular to the flat side of the stem which bears the graduations. In this way an undistorted image of the meniscus is seen through the engraved scale. The usual precautions should be taken to avoid parallax.

While the following procedure for setting the thermometer can be applied in all cases, an experienced observer will discover short cuts which can be used in special cases. First, bring the bulb of the thermometer to the temperature at which it is to be used. If the mercury is too low on the scale or disappears into the bulb, more mercury must be added from the reservoir, H (figure 27). To do this, heat the bulb gradually until the mercury fills about one-third of the setting chamber, B. Quickly invert the thermometer and cool the bulb. Since the reservoir is gas filled, mercury will be forced into the setting chamber as the mercury in the bulb contracts. After a sufficient amount of mercury has been drawn into the setting chamber, reverse the thermometer and cool the bulb until all of the mercury in the setting tube has been drawn into the chamber. (The estimation of the amount of mercury which must be drawn into the setting chamber requires some practice. If the required adjustment of the zero is not more than a degree or two, mercury contained in the setting tube, B, will be sufficient.) Then tap or jerk the thermometer sharply, to shake the mercury down from the top of the chamber. If this mercury doesn't make direct contact with the mercury in the capillary, warm the bulbs slightly until such contact is established in the setting chamber. After contact has been established, bring the thermometer to the temperature of use, and check the position of the meniscus. If there is insufficient mercury, repeat the foregoing procedure. If there is too much mercury present, heat the bulb to a temperature several degrees above the temperature of use, quickly invert the thermometer, and tap or jerk it sharply to transfer the mercury in the setting chamber to its opposite (setting-tube) end. Return the thermometer to an upright position, and heat the bulb carefully to force the mercury, contained in the upper end of the setting chamber, into the reservoir. Since it is more difficult to remove a definite small quantity of mercury from the bulb than it is to add it, the final step in the adjustment will usually be the addition of mercury.

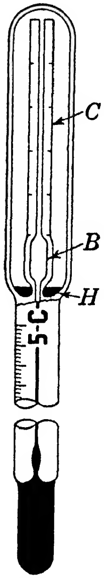

FIGURE 27

USE OF THE POLARIMETER

A polarimeter is used to measure the angle through which the plane of polarization, of plane polarized light, is rotated when it passes through a layer of optically active material (M, 201–4; W, 892–956). A simple polarimeter could be constructed from two Nicol prisms, so mounted that a beam of parallel light after being polarized by the first prism passed through a definite thickness of optically active material before going through the second prism (R and R, vol. II, 209–18). Such an instrument would be used by first setting the prisms for complete extinction (i.e., a minimum of transmitted light), then introducing the optically active substance between the prisms, and measuring the angle through which the second prism would have to be rotated to again obtain complete extinction. This angle is equal to the angle through which the plane of polarization is rotated by the optically active material. Since the visual determination of minimum intensity cannot be made with any accuracy, a modified apparatus which only requires the matching of adjacent fields is commonly used.

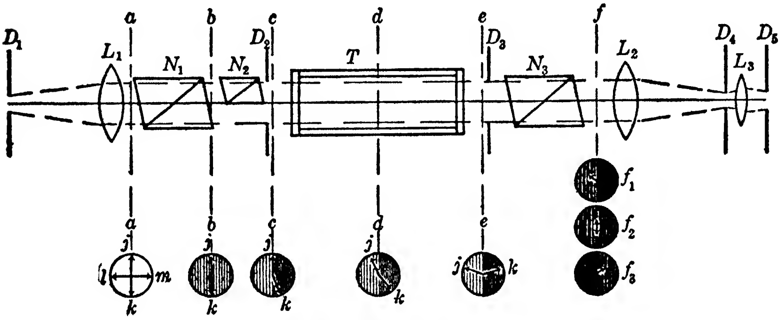

FIGURE 28. POLARIMETER

Of these modified instruments, the Lippich half shadow polarimeter is most frequently used for general work. Figure 28 is a diagram of its optical system. The circles which accompany this diagram represent the intensity and state of polarization of cross sections of the beam of light. In these circles the direction of the arrows coincides with the plane of polarization, and their length (as well as the density of shading) indicates the intensity of the light. The light from a monochromatic lamp, placed about 20 cm. in front of the diaphragm, D_1, is rendered parallel by the lens, L_1. At this point the light is unpolarized and has its full intensity (cross section *a*). Being unpolarized, it may be represented as the sum of two coincident plane polarized beams having their planes of polarization at right angles to one another (Wood, Physical Optics, 340). After passing through the first Nicol prism, N_1, the light loses half of its intensity and is plane polarized (cross section *b*). Half of the light beam now passes through a small Nicol prism, N_2, which is set at a slight angle to the first. That part of the beam which goes through this prism has its plane of polarization rotated through a slight angle and is correspondingly diminished in intensity (cross section *c*). The beam of light next enters a tube which contains optically active liquid. In passing through the liquid, the planes of polarization (represented by vectors j and k) in the two halves of the beam are continuously rotated, but the angle between them is not changed; likewise, the intensities of the two halves of the beam remain unchanged (cross sections *d* and *e*). What happens to the beam in passing through the third prism, N_3, depends upon its orientation relative to the planes of polarization (j and k of cross section *e*). In practice the prism is rotated until the field has a uniform low intensity. For this setting, the plane of polarization of the emergent beam (cross section f_2) (except for a small allowance for the initial difference in intensities of the two halves of the beam) bisects the angle between the two planes of polarization of the incident beam. If the prism is rotated slighty to the left, the right hand field will become completely dark and the left hand field somewhat brighter (cross section f_1); whereas, if it is rotated slightly to the right, the left hand field will be extinguished (cross section f_3). If the prism is rotated through 90° the fields will again have equal intensities; but at this position the fields will be bright, and the setting, under ordinary circumstances, will be less precise. The setting of the prisms is read directly on a graduated circle. This circle is usually divided in quarters of a degree and can be read to the nearest hundredth of a degree with the aid of the vernier. The angle between the two first prisms, N_1 and N_2, may be adjusted over a range of 15 or 20°. As this angle is increased the uniform (dark) field appears brighter, but the precision with which the setting may be established is decreased. For maximum precision, this angle should be kept as small as the intensity of the lamp and the transparency of the liquid will permit.

The light source must be practically monochromatic. A glass-walled mercury arc provided with a color filter to isolate the green line (D, M, and W, 394–7) is a useful source. Sodium flames, continuously fed with NaCl or Na_2CO_3, are frequently used. However, the sodium vapor arc has a greater intensity and is more convenient.

The determination of the specific rotation of a substance or of the concentration of a solution of an active substance, whose specific rotation is known (K and S, 685–6), involves the following steps: Fill the polarimeter tube with distilled water and place it in the polarimeter. Set the light source about 20 cm. from the instrument and in line with its axis. Rotate the analyzer until half of the field appears black. Then focus the instrument by adjusting the eyepiece, L_3, until the dividing line between the light and dark fields appears sharp. Turn the analyzer until the two fields are of low but equal brightness; and record the angle to 0.01°. Reset and record the reading of the analyzer several times. The average of these readings is the zero of the instrument. Replace the water in the tube with the solution or liquid to be measured. Again set the analyzer so the field is of low uniform intensity, and record the angle. The difference between the average of these readings and the zero reading is the angle of rotation, α. If the specific rotation, for the same temperature and wave length, is $[\alpha]$, the length of the tube in decimeters is l, and the density of the solution is d, then the weight, g, of the active solute in W grams of solution is given by the relation

$$g = \frac{\alpha W}{[\alpha] l d}.$$

The values of the density, d, may be determined with sufficient accuracy by means of the Westphall balance (116). However, if experiment 13 or 14 is to be performed, the determination of the density may be omitted in this experiment, and the densities obtained from a table. Convenient tables, listing the densities and the concentrations in gms./li of sugar solutions, are given in Lange's Handbook of Chemistry and in the Handbook of Chemistry and Physics. For exact work the variation of $[\alpha]$ with concentration must be considered; however, for most measurements in dilute solution this variation may be neglected and the above simple formula used. The specific rotation of sucrose at 20° using the Na D lines is 66.5°.

Several precautions must be observed in using a polarimeter. Be sure that the solution studied is clear, as even a slight turbidity results in a serious loss of precision. Rinse the tube with each new solution before filling it. If the bore of the tube is enlarged at one end, to fill the tube, remove the cap covering the other end. After filling the tube, screw on the cap and invert the tube to transfer the bubble to the enlarged end, where it will be out of the optical path. If the tube is of uniform diameter, remove the cap from one end and slip the cover glass out of the cap. Fill the tube until the liquid stands in an inverted meniscus above the end, then slide the cover glass in place, displacing the excess liquid, and screw on the cap. Care should be taken that no solution gets on the outside of the cover glass, and that a bubble is not left in the tube. The cover glasses must always be clean and dry, and the caps should not be screwed down hard enough to produce an optical strain in the glass. The zero reading of the polarimeter changes as the small angle between the first two nicol prisms, N_1 and N_2, is adjusted; therefore, do not change this angle during a series of measurements, without redetermining the zero angle. To minimize the effect of mechanical imperfection, always read both verniers, situated on opposite sides of the circle, and in setting the analyzer approach the setting from the same direction.

Experiment 11

FREEZING POINT LOWERING AND MOLECULAR WEIGHT (BECKMANN METHOD)

The Beckmann method of determining the freezing point is commonly applied to non-aqueous solutions. It is used chiefly to determine the molecular weights of organic compounds and the degree of association or dissociation of substances dissolved in organic solvents (M, 245–6, 250–2). The concentration of the solution is not determined analytically, but is computed from the weights of solvent and solute used in preparing the solution. Solutions nearly always supercool before freezing, and the effect of this supercooling on the concentration of the freezing solution must be taken into account.

Apparatus and Materials: A Beckmann freezing point apparatus, a Beckmann thermometer, a tablet press. About 50 ml. of pure dry benzene or cyclohexane, 5 gm. of camphor or anthracene, 5 gm. of benzoic acid.

Procedure: Before assembling the apparatus as indicated in figure 29, carefully clean and dry the inner tube, *A*, and weigh into it sufficient benzene (or cyclohexane) to fill it, when the thermometer is in place, to a height of about 7 cm. Set the Beckmann thermometer (95–8) so that a point on the upper part of the scale corresponds to 5.5°C (6.5° for cyclohexane). Be sure that the stirrer, *B*, operates freely and does not strike the bulb of the thermometer. With the aid of the tablet press (107) prepare two small pellets of camphor or anthracene. Each tablet should be of such a weight that a solution prepared by dissolving it in the solvent contained in the freezing tube will be from 0.05 to 0.10 *M*. Fill the outer jacket, *C*, of the apparatus with water at about 2°C. Keep this temperature constant during the entire experiment by frequent stirring, *F*, and by occasionally adding ice.

Before placing the tube containing the thermometer in the larger tube, *D*, which acts as an air jacket, cool the benzene to a temperature slightly above its melting point by immersing the tube directly in an ice bath. Dry the outside of the tube, *A*, and support it in the cork in the top of jacket, *D*. Stir the benzene steadily and read the temperature of the benzene at frequent intervals. When the temperature reaches a point 0.1° above the melting point, start recording the thermometer readings at 20 second intervals. The temperature will fall steadily to a point below freezing, and then, when crystallization starts, will rise rapidly to a steady value, the freezing point. If after the sudden rise, the temperature does not remain constant until the greater part of the liquid has crystallized, it is evidence that the benzene is impure. After ten or more readings of the steady value have been recorded, remove the freezing tube, *A*, from the air jacket, *D*, and warm it sufficiently to melt the solid. Then return it to the air jacket and repeat the measurements. Make at least three such determinations of the melting point. They ought to agree within a few thousandths of a degree.

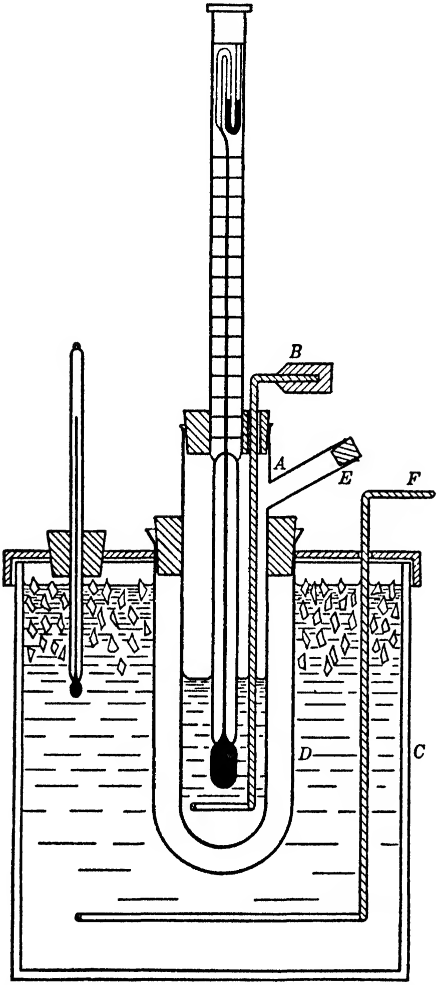

Figure 29. Beckmann Freezing Point Apparatus

Weigh one of the pellets of camphor, or anthracene. Unless the highest accuracy is desired, the pellet may be weighed on a weighing paper. Any piece of light-weight, uniform, glazed paper 5 or 6 cm. square will serve as a weighing paper. A second (similar) piece should be used as a tare. If a more accurate weighing is desired, place the pellet in a weighing bottle and determine the total weight; then, after removing the pellet, weigh the bottle again. If the substance is very volatile, or loses or gains water rapidly when in contact with the air, the weighing bottle technique must be used. Introduce the weighed pellet into the benzene through the side tube, *E*, and replace the cork. Stir the mixture until the solid goes into solution, and then place the freezing tube in the air jacket. Stir the solution and read and record the temperature as in the determination of the freezing point of the pure solvent. Unlike the solvent, the solution will not remain at a constant temperature during crystallization, since the removal of solvent from the liquid phase results in a continuous increase in the concentration of the solution. Make several determinations of the cooling curve for this solution. Then weigh and add the second pellet to the solution and again determine the cooling curve.

Repeat the entire determination using benzoic acid or some other substance which produces an abnormal lowering of the freezing point. If a liquid solute is used, it should be weighed out of a special weight pipet provided with a bent capillary delivery tube, which can be inserted through the side tube, *E*, of the apparatus (see F and W, 20 figure 5).

If the supercooling of a liquid is very pronounced, it is necessary to induce crystallization by adding a seed crystal of the solvent. The seed crystal may be prepared by freezing a few drops of the solvent in a test tube, and a small crystal may be transferred to the solution on the end of a thin glass rod or a wire through the side tube, *E*. The usual precautions (96) must be observed in using the Beckmann thermometer. The experiment is less laborious and frequently more consistent results are obtained when the ring stirrer, *E*, is operated mechanically. An electromagnet actuated by a make-and-break device (see F and W, 21–2) may be used to operate the stirrer. Another satisfactory and inexpensive device may be easily constructed from a pneumatic windshield wiper. An aspirator or the laboratory vacuum line can be used to operate the device, and the lever of the wiper can be attached to the stirrer by a thread running over an improvised pulley.

Computations: Draw the cooling curves for both solvent and solutions, plotting thermometer readings against time. From an inspection of the curves for the solvent, determine the best average value of the thermometer reading corresponding to the freezing point. In the case of a solution, the maximum reading obtained after the sharp rise in temperature corresponds to the freezing point of a solution slightly more concentrated than the initial solution. The correction which must be applied to the initial concentration may be obtained by computing the amount of solvent which crystallizes during the sharp rise in temperature. The heat liberated in this process is equal to the product of the latent heat of fusion per gram, λ_f, and the weight of the solid formed, W_f. This quantity must also equal the product of the rise in temperature (i.e., the degrees of supercooling, ΔT_c) and the heat capacity, C. While the heat capacity is usually not known exactly, it is given approximately by the following expression:

$$C = C_s(W_0 + W) + 15$$

when C_s is the specific heat of the solvent, W_0 is the weight of the solvent, W is the weight of the solute, and 15 is an estimate of the heat capacity of that part of the apparatus which is in thermal equilibrium with the solution. By equating the heat evolved to the heat absorbed, we may write

$$W_f = \frac{C_s(W_0 + W) + 15}{\lambda_f} \Delta T_c$$

For benzene $C_s = 0.41$ cal./gm. deg. and $\lambda_f = 30$ cal./gm. In the formula for the molal freezing point lowering, K_f,

$$K_f = \frac{MW_{0,\text{eq.}}\,\Delta T}{1000\,W}$$

ΔT is the difference between the freezing points of the solvent and the solution, M is the molecular weight of the solute, and $W_{0,\text{eq.}}$ is the weight of the solvent in the liquid phase.

$$W_{0,\text{eq.}} = W_0 - W_f$$

Taking the correction for supercooling into account, compute values of K_f corresponding to each determination of the freezing point of a camphor (or anthracene) solution. Compare the average of these values to the standard value (M, 252).

Using this average value of K_f, compute the apparent molecular weight and the van't Hoff factor, i (M, 263–5), for benzoic acid from the freezing point lowering of its solution.

USE OF THE TABLET PRESS

Most organic and many inorganic substances can be compressed into smooth coherent pellets by the application of moderate pressure. Such a pellet is to be preferred to a powder or a mass of loose crystals since it can be easily weighed and transferred without danger of loss. For many purposes, it is preferable to a large single crystal, since being compacted of a mass of fine crystals it dissolves more readily. While there are several different types of tablet presses manufactured for laboratory use, the one represented diagrammatically in figure 30 serves to illustrate all of the essential features. The use of the press in the preparation of a pellet is indicated in the following paragraph.

Procedure: Remove the drilled block, *A*, the cylindrical core, *B*, and the truncated conical plug, *C*, from the frame, *G*, and clean and dry them carefully. Replace the plug in the block and slide the latter into the frame. If necessary, grind the compound to a coarse powder. Weigh roughly, or estimate, the amount of material required, and pour this sample into the hole in the block. Insert the core, *B*, and compress the substance into a pellet, *H*, by turning down the screw, *F*. To remove the pellet from the block, turn up the screw, slide the block out of the frame and insert its keys, *D* and *D'*, into the upper grooves, *E* and *E'*. Then force the plug and the pellet out of the block by turning down the screw. Since it is difficult to get the mold perfectly clean, it is usually a wise precaution to discard the first pellet, which is likely to be contaminated. If the press is to be stored for more than a few days, it should be given a light coat of oil to prevent rust.

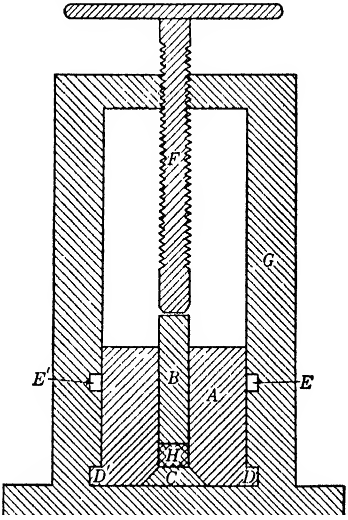

FIGURE 30. TABLET PRESS

Experiment 12

BOILING POINT ELEVATION AND MOLECULAR WEIGHT

The difference between the boiling point of a solution and of the pure solvent is, for dilute solutions of non-volatile solutes, directly proportional to the molality of the solute (M, 246–9; E and R, 305–9). In addition to their use in certain routine analyses, measurements of boiling point elevation are used chiefly to determine the apparent molecular weight of dissolved substances. The method is frequently applied to organic substances, using solvents such as benzene or carbon tetrachloride. Although these measurements as commonly performed are neither as accurate nor as convenient as measurements of the freezing point depression, they do greatly extend the temperature range and thereby make possible the study of some difficultly soluble substances. For a detailed discussion of this method and its applications, see "Ebuliometry," Swietoslawski (1945).

A special boiling point apparatus must be used to ensure that the thermometer is in contact with solution which is in equilibrium with its vapor. If the thermometer is suspended in the vapor phase it will attain a temperature equal to the boiling point of the pure solvent, which condenses upon it. If placed in the liquid phase it is very likely to be in error due to superheating. While superheating may be reduced by the use of an internal electric heater (D, M, and W, 79–80), more satisfactory results may be obtained by using the Cottrell apparatus (R and R, vol. I, 617–8), in which the thermometer is suspended in the vapor but is sprayed with the boiling solution by means of a vapor lift. A simplified modification of this apparatus (Davis, J. Chem. Educ. **10**, 47, (1933), which is relatively rugged and gives good results under laboratory conditions, is diagrammed in figure 31. This apparatus is heated with a small gas flame and utilizes indentations in the glass to prevent bumping. A Beckmann thermometer is used to measure the difference in temperature. The composition of the solution is computed from the weights of solvent and solute introduced into the apparatus.

For more exact measurements, the differential thermometer of

Menzies (R and R, vol. I, 619–20) is to be preferred to the Beckmann thermometer, since it makes the use of a monostat (D, M, and W, 310–1) unnecessary. If the concentration is computed from the weight of solvent and solute added, a correction must be applied for the amount of solvent which is in the gas phase or adhering to the walls of the condenser. This correction may be avoided by withdrawing a sample of the boiling solution, with a capillary siphon, and analyzing it.

Apparatus and Materials: A Davis boiling point apparatus, a Beckmann thermometer, a microburner, and a tablet press. About 200 ml. of pure dry C_6H_6 or CCl_4, about 5 gm. of camphor or anthracene, and of benzoic acid or naphthalene picrate.

Procedure: Clean and dry the apparatus and assemble it as indicated in figure 31. If rubber or neoprene stoppers, *A*, *B*, and *C*, are used in the apparatus, they must be protected with tin foil. Although neoprene stoppers do not swell badly when exposed to C_6H_6 or CCl_4 they do contain some substance which is soluble in these solvents and which may result in a gradual increase of the boiling point. The use of ground glass joints is to be preferred. Adjust the Beckmann thermometer (95–8) so that a point on the lower part of the scale corresponds to the boiling point of the solvent; 80.15°C. for C_6H_6 or 76.50° for CCl_4. Remove the stopper, *B*, which supports the condenser, and measure enough solvent into the apparatus to partly fill the bulge, *D*. The weight of the solvent should be

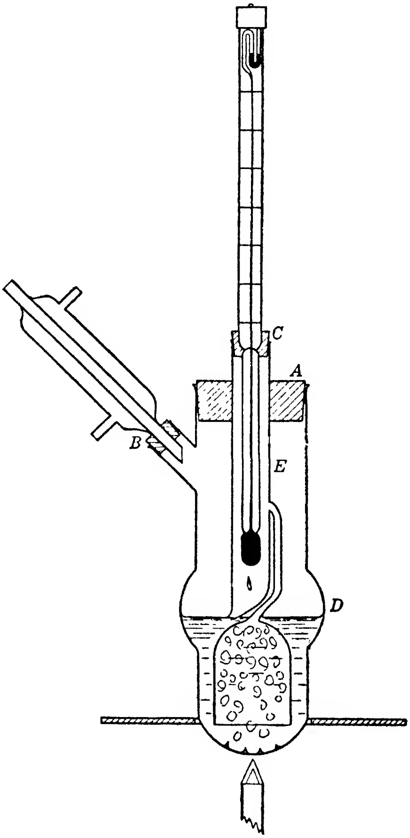

FIGURE 31. DAVIS BOILING POINT APPARATUS

known with an accuracy of about 0.5%. The bent tip of the inner tube, *E*, should be below the surface of the liquid. Heat the apparatus directly with a small flame from a microburner, shielding the flame and lower part of the apparatus from drafts, with a cylinder of asbestos paper.

Prepare two pellets of camphor, or anthracene, and two of benzoic acid, or some other abnormal solute, with the aid of a tablet press (107). Each pellet should be of such a weight that the solution prepared by dissolving it in the solvent contained in the apparatus will be from 0.05 to 0.10 *M*. Record the barometric pressure at 15 minute intervals throughout the experiment. Allow the solvent to boil for 15 or 20 minutes, recording the temperature (95–8) at regular intervals. While the temperature may drift slowly at first, due to the hysteresis of the thermometer bulb, it should reach a value which does not vary by more than 0.002°C. A small change in the rate of boiling should not produce an appreciable change in the temperature. While the solvent is boiling, weigh one of the pellets of camphor (or anthracene) to the nearest milligram (104–5). Remove the flame, and as soon as the boiling ceases, take out the stopper, *B*, and introduce the pellet through the side tube. Replace the condenser and the flame and again record the temperature at frequent intervals until it becomes constant. Then weigh out and introduce the second pellet of camphor, and determine the boiling point of the resulting solution.

Repeat the entire experiment, using the pellets of benzoic acid or naphthalene picrate.

Computations: Compute a value of K_b, the boiling point constant for each of the measurements with camphor (or anthracene) using the following equation:

$$K_b = \frac{W_0 M \Delta T}{1000\ W}$$

In this equation M is the molecular weight of the solute, ΔT is the elevation of the boiling point, and W_0 and W are the weights of solvent and solute, respectively. Compare your value of the boiling point constant to the measured values of Hoyt and Fink (J. Phys. Chem. **41,** 453 (1937)), who obtained for C_6H_6

$$K_b = 2.53 - (760 - P_{\text{Bar}})0.0007$$

and for CCl_4

$$K_b = 5.07 - (760 - P_{\text{Bar}})0.0013$$

where P_{Bar} is the barometric pressure in millimeters. Using the average of your values of K_b, determine the apparent molecular weight of benzoic acid (or naphthalene picrate) from your measurements with this substance. Compute values of the van't Hoff i (M, 263–5) for these two solutions. Tabulate your results, including in your table the principle observed and computed quantities.

It should be noted that the effect of variation of barometric pressure on the boiling point may be of the same magnitude as the difference between the boiling points of solution and solvent. The following equations relate the decrease in boiling point, ΔT_p, of the pure solvent to the barometric pressure, P_{Bar}, and may be used to correct for variations in pressure:

$$\text{for } C_6H_6, \qquad \Delta T_p = 73.96 \log \frac{760.0}{P_{\text{Bar}}}$$

$$\text{for } CCl_4 \qquad \Delta T_p = 81.10 \log \frac{760.0}{P_{\text{Bar}}}$$

These equations are based upon data given in the I. C. T. III, 215, 221.

Experiment 13

VISCOSITY OF A BINARY SOLUTION

The viscosity of a liquid may be determined by measuring its rate of flow through a capillary tube (M, 98–9; E and R, 68–9). The Ostwald viscosity pipet (figure 32) is a simple and convenient apparatus which is based upon this principle and commonly used to measure relative viscosities. The quantity measured is the time required for the liquid, contained between the marks A and B in the upper bulb, to flow into the lower reservoir. The fundamental equation used in computing the viscosity is Poiseuille's law:

$$\frac{dv}{dt} = \frac{\pi r^4 P}{8\,l\eta}$$

In this equation, dv/dt is the rate of flow produced by a pressure difference, P, acting across a capillary of length, l, and of radius, r. η is the coefficient of viscosity of the liquid, and π has its usual significance. In the Ostwald pipet the difference of pressure is not constant during the efflux of the liquid, but is given by the relation

$$P = gd_lh$$

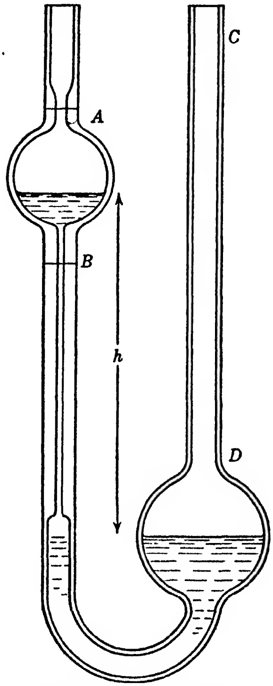

FIGURE 32. OSTWALD VISCOSITY PIPET

where g is the acceleration of gravity, d_l is the density of the liquid, and h is the difference in level of the liquid in the two arms of the pipet (see figure 32). The difference in level is a function of the volume of the liquid remaining in the upper bulb. This function depends upon the shape and size of the apparatus and the total amount of liquid contained in it, but is independent of the properties of the liquid. Therefore, we may write

$$P = gd_i f(v)$$

where $f(v)$ is the function of the volume, v, remaining in the bulb. Combining this equation and Poiseuille's law

$$\frac{dv}{f(v)} = \left(\frac{\pi r^4 g}{8l}\right)\frac{d_i}{\eta_i}dt$$

If we integrate this expression between the proper limits of v and t, corresponding to positions of the meniscus at A and B, we obtain

$$K = \left(\frac{\pi r^4 g}{8l}\right)\frac{d_i}{\eta_i}t_i$$

where t_i is the time of efflux for a particular liquid, and K is constant for a given apparatus and total volume of liquid. Therefore the ratio of the viscosities of two liquids may be computed when their densities are known and their times of efflux have been measured under comparable conditions.

$$\eta_2/\eta_1 = \frac{d_2t_2}{d_1t_1}$$

By choosing one substance as a standard, the viscosities of a series of liquids may be determined relative to it, and if its absolute viscosity is known the absolute viscosities of the others may be computed. For exact determination of the relative viscosity or the determination of the absolute viscosity, more elaborate apparatus must be used and several correction terms must be added to the simple formula (see R and R, vol. I, 542–54, also Hatscheck, The Viscosity of Liquids, 17–56).

The viscosity of a solution is not a simple function of its composition. Numerous empirical formulas have been proposed to represent the viscosity of solutions, but none of them have proved very useful (Hatscheck, loc. cit. 135–63). It has been proposed that the fluidity, or reciprocal of viscosity, is a simple function of composition for ideal solutions (Bingham, Fluidity and Plasticity, 81–105). However, this view has not been generally accepted.

Viscosity curves (η as a function of x_1) of simple solutions are usually sagged; i.e., fall below the straight line connecting the viscosities of their components. Many systems in which compound formation is known to occur have viscosity curves exhibiting a maximum. The maximum does not ordinarily occur at a composition corresponding to the compound, but is shifted toward the component of higher viscosity. The existence of a maximum should not be accepted as proof of compound formation, nor its absence as evidence that a compound does not exist.

The viscosities of solutions, of substances which are chemically similar but which differ in molecular weight, are a function of the molecular weight of the solute (W, 143–7). This fact is utilized in the determination of the molecular weights of polymers.

The purpose of the present experiment is to determine the curve of viscosity against mole fraction for a binary solution. Any pair of miscible liquids whose viscosities do not differ by more than two or three fold may be used. Aqueous solutions of acetone, methanol, ethanol, propanol, or acetic acid are recommended.

Apparatus and Materials: An Ostwald viscosity pipet, a stopwatch, a 2 liter beaker, and a Westphal balance. About 250 ml. of the assigned organic liquid.

Procedure: Prepare samples of not less than 50 ml. of each of several solutions of known mole fraction (120). The mole fraction should be known with an accuracy of at least 0.5%. Since the entire curve is to be determined, the mole fractions of the solutions should be distributed over the entire composition range. The minimum number and the compositions of the required solutions will depend upon the pair of liquids chosen, and in general can be determined only by trial. Decide on a volume of liquid which can be conveniently and accurately measured into the viscosity pipet, and which is satisfactory for its operation. For an ordinary pipet this volume will be between 5 and 10 ml. It should be large enough so that the bottom of the U-tube is filled when the liquid is drawn above the mark, *A* (figure 32), but not so large that liquid comes above the top, *D*, of the lower reservoir when it is in hydrostatic equilibrium. Clean the apparatus thoroughly with hot cleaning solution, and rinse it carefully with distilled water. After allowing it to drain, pipet the selected volume of distilled water into the apparatus through the tube, *C*. Clamp it in a 2 liter beaker filled with water, so that it is upright and both bulbs are immersed in the bath. Maintain this water at a constant temperature, preferably 25°, within 0.2°C. Allow several minutes for the liquid to come to the temperature of the bath. Force the liquid above the point, *A*, by blowing into a short rubber tube attached to the apparatus at *C*. With a stopwatch, determine the time required for the meniscus to pass from the mark, *A*, to the mark, *B*. Repeat this measurement three or four times. If the pipet is clean and the temperature constant, these measurements should agree within 1 part in 200. After emptying the apparatus, rinsing it with one of the solutions, and allowing it to drain, pipet the selected volume of this solution into it. Return the apparatus to the water bath and determine the time of efflux several times. Repeat this procedure with each of the other solutions and with the other pure component. With the aid of the Westphal balance (115–7), determine the density of each solution and of the component.

Computations: From the measurements of density and times of efflux, compute the viscosities, in millipoise, of the several liquids. The viscosity of water is 8.95 millipoise at 25.0°C. In this temperature range it decreases 2.3% for each degree rise in temperature. Tabulate mole fraction, density, average time of efflux, and viscosity for each liquid studied. Prepare a plot of viscosity as a function of mole fraction.

USE OF THE WESTPHAL BALANCE

The density of any liquid, which is not too viscous, may be determined, conveniently and with a precision of about 2 units in the fourth place, by means of the Westphal balance. The quantity measured is the buoyant effect on a glass plummet. This loss of weight is not measured in absolute units, but relative to the buoyancy of water at some standard temperature, usually 15°C. The weighing is made by means of a series of U-shaped riders and a notched beam. The plummet is supported by means of a fine platinum wire, whose displacement may be neglected. The error due to the surface tension acting on this wire may also be neglected. In the ordinary use of the balance the change of the volume of the glass plummet with temperature is neglected; however, if the liquid is at a temperature differing by more than 10 or 15° from the calibration temperature the expansion or contraction must be taken into account. The balance can be easily dismounted when it is to be stored or transported. (Apparatus which is similar in principle but slightly more accurate is described in R and R, vol. I, 498–502 and D, M, and W, 321.)

Procedure: Assemble the balance as in figure 33, but with the plummet, A, suspended in air and without any of the riders on the beam or hook. Adjust the balance, by means of the threaded counterpoise, B, and the leveling screw, C, until the rest point of the indicator, attached to the balance arm, coincides with the fixed point, D. Fill the glass cylinder, E, with distilled water at the standard temperature (usually 15°C.) which is indicated on the plummet or balance. Hang one of the (large) unit weights on the hook at the end of the beam. If the plummet is entirely immersed and is not grazing the wall of the cylinder the balance should still be exactly in adjustment. If it is not, it indicates that either the water is not at the right temperature or that the plummet and weights are not properly calibrated. When the balance has been adjusted in this way, the weight of the large rider is equal to the weight of the water (at the standard temperature) displaced by the plummet.

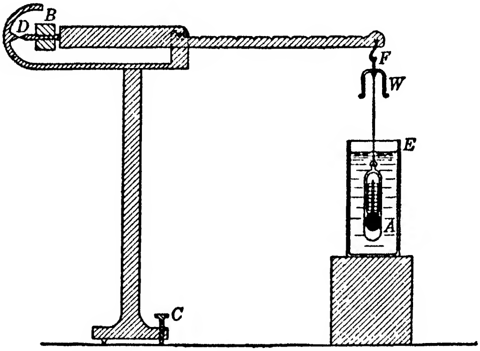

FIGURE 33. WESTPHAL BALANCE

Empty the cylinder, and, after drying the plummet and cylinder or rinsing them with the new liquid if it be miscible with water, fill it with the liquid whose density is to be determined. Place the graded riders on the notched beam so that the indicator points of the balance coincide. The weights of the various sized riders differ by a factor of 10. In addition to the (large) unit weight, the balance must be equipped with weights of 0.1000, 0.0100, and 0.0010. It is convenient to have duplicates of these weights. The notches divide the beam in 10 equal parts, so that a weight placed on a notch nearest to the center has an effect which is only one-tenth of that which it would have were it hung on the hook, F, at the end of the beam. To obtain the specific gravity of the liquid, add up the weights, taking into account their positions on the beam. For example if the 1.0000 and 0.0010 weights were on the ninth notch and the 0.1000 and 0.0100 weights were on the first and seventh notches, respectively, the specific gravity, S, of the liquid relative to water at the standard temperature (15°C.) is

$$\begin{aligned} S &= \frac{9}{10} \times 1.0000 + \frac{1}{10} \times 0.1000 + \frac{7}{10}\, 0.0100 + \frac{9}{10}\, 0.0010 \\ &= 0.9179 \end{aligned}$$

To convert the specific gravity to density, multiply it by the density of water at the standard temperature. The density of water at 15° is 0.99913 gm./ml.

Experiment 14

SURFACE TENSION OF A BINARY SOLUTION (DROP NUMBER METHOD)

The surface tension of a binary solution is not in general a linear function of its composition. (See Freundlich, Colloid and Capillary Chemistry, 46–71.) Substances which lower the surface tension of a solution are adsorbed at its surface and have, therefore, a greater effect on its surface properties than would be predicted upon the assumption of uniform distribution of the components throughout the solution. This effect is of particular importance in determining the behavior of dispersed systems, and has many applications in the biological sciences. It is also related to such industrial processes as flotation, stabilization of foams, etc. Systems in which one component is water and the other a water soluble organic compound are of special interest. The present experiment consists of the determination of the curve of surface tension against mole fraction for such a system. Any one of the following substances may be used as the second component: acetone, acetic acid, propionic acid, methanol, ethanol, or propanol.

The relative surface tension of a liquid may be determined conveniently with the aid of the Traube stalagmometer. This is a simple modification of the more precise, drop weight method (M, 95–6; W, 167–76). The measurement consists of counting the number of drops formed when a definite volume of liquid is allowed to flow slowly out of a capillary orifice. The ratio of the weight, w, of a drop of the liquid to that, w_0, of a drop of a reference substance (falling from the same capillary tip) is equal to the ratio of their surface tensions.

$$w/w_0 = \gamma/\gamma_0$$

If V is the volume delivered by the stalagmometer, ρ the density, and n_1 the number of drops, then the weight, w_1, of a single drop is given by the following equation:

$$w_1 = V\rho_1/n_1$$

Combining these equations we obtain

$$\gamma = \gamma_0 \frac{n_0 \rho}{n \rho_0} .$$

where the subscript 0 refers to the reference substance. To determine the surface tension of a liquid by this method we must know the number of drops and the density of the liquid and of the reference substance in addition to the surface tension of the latter. Of course all of these quantities must be measured at the same temperature.

Apparatus and Materials: A Westphal balance, a stalagmometer, a 100° thermometer, and a 2 liter beaker. About 200 ml. of the organic liquid.

Procedure: Set up the apparatus as indicated in figure 34. Support the stalagmometer by a two hole rubber stopper, which fits tightly in a short tube or small widemouthed bottle. Attach a thermometer capillary a few inches long to the upper end of the stalagmometer by a short piece of rubber tubing. The rubber tubing must be washed free from dust (boiling it in NaOH solution, if necessary) before it is used. The purpose of the thermometer capillary is to control the rate of flow of liquid by limiting the influx of air. Select a capillary which produces a rate of flow of about 20 drops a minute. A slower rate will not affect the results, but inaccurate results will be obtained if the rate is faster. Add a second piece of rubber tubing, provided with a pinch clamp, to the upper end of the capillary. Insert a piece of glass tubing in the other hole of the stopper, to serve as an air vent. Clean the stalagmometer thoroughly with hot cleaning solution (chromic acid), and rinse it with distilled water. [Be careful that the dropping tip does not subsequently come in contact with the hand, desk top, or anything else which might contaminate it with a trace of grease.] To fill the stalagmometer, open the pinch clamp, immerse the dropping tip

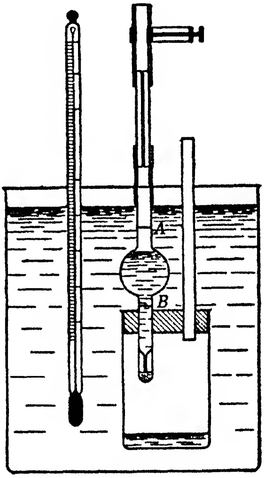

FIGURE 34. DROP NUMBER APPARATUS

in the liquid, suck on the rubber tube until the stalagmometer is filled above the upper etched ring, *A*, and then close the pinch clamp. Insert the stopper firmly in the small bottle, and support the assembly, by clamping the vent tube, in a 2 liter beaker filled with water. This water should be maintained at a constant temperature, preferably 25°, throughout the experiment.

Allow a few minutes for the liquid to come into thermal equilibrium with the water bath, then open the pinch clamp. Start counting the drops when the meniscus passes the upper mark, *A*, and stop when it passes the lower mark, *B*. Remove the assembly from the beaker, slip the stopper out of the bottle, and refill the stalagmometer. Return the apparatus to the water bath and repeat the measurement. Make three or four measurements with each liquid. Check results should not differ by more than one part in one hundred. It is not necessary to dry the stalagmometer between measurements, but it should be rinsed with each new solution before being filled. Care should be taken to have the stalagmometer vertical, and to avoid jarring it during a measurement. Determine the density of each solution and of the pure components with the Westphal balance (115–7).

As many solutions should be prepared and studied as are necessary to completely determine the form of the curve. In general, the number required can only be determined by trial. If they are properly distributed on the mole fraction and surface tension axes, four or five points in addition to the pure components should be sufficient.

In preparing a sample of *G* grams of a binary solution having a definite mole fraction (X_2), the following relation may be of service:

$$m_2 = \frac{X_2M_2}{X_1M_1 + X_2M_2}G$$

where m_2 is the mass of solute required, X_2 and X_1 are the mole fractions of solute and solvent, respectively; and M_2 and M_1 are their respective molecular weights. If you use this relation, show that it may be derived from the definition of mole fraction (M, 238)

$$X_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2}$$

Computations: Using the measured values of the density and the average numbers of drops, compute a value of the surface tension for each liquid studied. At 25°C. the surface tension of water is 72.0 dynes/cm. Tabulate the results, including mole fraction, density, average number of drops, and surface tension. Prepare a plot of surface tension as a function of mole fraction.

Experiment 15

HEATS OF IONIC REACTIONS

The heat of a reaction (M, 275–6, 284–91) occurring in solution can be determined by measuring the rise in temperature which results when solutions containing the reactants are mixed. In addition to the rise in temperature it is necessary to know the volumes, densities, concentrations, and temperatures of the initial solutions, the specific heats of the initial solutions or of the mixture, and the heat capacity of that part of the apparatus which is in thermal contact with the solution. In practice an added difficulty is introduced by the loss or gain of heat by the solutions to the surroundings. Although this effect can be reduced by using a well insulated calorimeter, it is always necessary to make some correction for it.

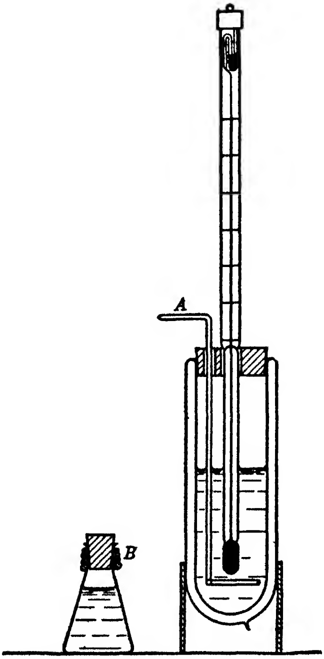

FIGURE 35. CALORIMETER

In the present experiment the solutions are to be mixed in a pint dewar flask ("food jar" type), provided with a cork stopper and a ring stirrer (figure 35). This type of calorimeter is well insulated, but has the disadvantage that its heat capacity (i.e., "water equivalent") varies with such factors as the amount of liquid in the calorimeter, the rate of heating, etc. The most accurate method of determining the water equivalent of the calorimeter is to calibrate it with a reaction whose heat is known, using the same volumes and procedures as are to be used in the later experiments. When, as in the present experiment, an accuracy of about 2% is sufficient, the heat capacity of the calorimeter may be estimated. The total weight of the glass in a one pint pyrex food jar varies from about 380 to 450 gm.; of this, probably less than one-third is in thermal contact with the solution. Taking the specific heat of pyrex as 0.2 cals./gm. deg., we obtain an average effective heat capacity of the flask of about 26 cals./deg. This quantity must be increased by about 2 cals./deg. to allow for the effect of the Beckmann thermometer (compare Findlay, Practical Physical Chemistry, 269). In this way, we estimate the average heat capacity of the calorimeter to be 28 cals./deg. If this estimate were in error by as much as 20%, the corresponding error in the total heat capacity would be approximately 1%. Verify this statement.

Before the solutions are mixed, one of them is to be contained in the dewar and the other in a small erlenmeyer. The same Beckmann thermometer is to be used to take the temperatures of both the solutions. Since it is difficult to determine the temperature of the liquid in the erlenmeyer with the same accuracy as that of the liquid in the dewar, a volume one-fourth as great, of a solution four times as concentrated, is to be used in the erlenmeyer.

It is impossible to determine directly the heats of all reactions with a calorimeter of this type (compare W, 333–46, 417–27; T, 290–4; also R and R, vol. I, 409–32.) To be measurable, the reaction should go practically to completion and be rapid. In this experiment the heats of the four following processes are to be measured: the neutralization of HCl and of CH_3COOH with $NaOH$, and the mixing of solutions of $NaCl$ with solutions of $Hg(NO_3)_2$ and of $Ca(NO_3)_2$, or $Ba(NO_3)_2$. From these measurements the heats of the following reactions are to be computed:

$$H^+ + OH^- = H_2O$$
$$H^+ + CH_3COO^- = CH_3COOH$$
$$Hg^{++} + 2\,Cl^- = HgCl_2$$

Apparatus and Materials: A pint large-mouthed dewar flask, fitted with a two-hole cork or wooden stopper; a Beckmann thermometer; and a 100 ml. pipet. A strip of asbestos paper or a short piece of asbestos rope. About 450 ml. each of standardized 0.24 *M* solutions of HCl and of CH_3COOH, and of a standardized 0.12 *M* solution of $Hg(NO_3)_2$ containing a slight excess of HNO_3 (K and S, 546); 250 ml. of a CO_2-free 1.00 *M* solution $NaOH$; 15 gm. of pure $NaCl$; and 10 gm. of $Ca(NO_3)_2$, or an equivalent amount of $Ba(NO_3)_2$.

Procedure: Prepare 250 ml. of a 1.00 *M* NaCl solution and 500 ml. of a 0.120 *M* solution of $Ca(NO_3)_2$. Allow these and all other solutions required for this experiment to come to room temperature before using them. Make a ring stirrer, *A* (figure 35), from light-weight glass tubing, passing it through the hole in the stopper before bending over the handle. Adjust a Beckmann thermometer (93–4) to record room temperature on the lower part of its scale. Wrap the neck, *B*, of a 125 ml. erlenmeyer flask with asbestos paper or cord.

With a 100 ml. pipet, transfer 400 ml. of the 0.24 *M* HCl to the dewar flask and 100 ml. of the 1.00 *M* NaOH to the small erlenmeyer flask. Weigh the erlenmeyer and solution to the nearest decigram. Determine the (relative) temperature of the acid with the Beckmann thermometer. Remove the thermometer, rinse it with distilled water, take off the excess water with filter paper, and insert it in the NaOH solution in the erlenmeyer. Record this temperature, and return the thermometer to the acid, rinsing and drying as before. Repeat these operations twice, at 5 minute intervals. During this time operate the stirrer slowly but continuously. On the second repetition, do not rinse or dry the thermometer but return it directly to the dewar. Then, holding the erlenmeyer by its insulated neck, quickly pour the base into the acid. Keeping the stirrer in regular motion, record the temperature at 60 second intervals until it becomes steady. Then record the temperature of the solution with an ordinary thermometer. To determine the weight of NaOH solution which was transferred to the dewar, weigh the erlenmeyer flask again.

Repeat this procedure using the following pairs of solutions: 100 ml. of 1.00 *M* NaOH and 400 ml. of 0.24 *M* CH_3COOH, 100 ml. of 1.00 *M* NaCl and 400 ml. of 0.120 *M* $Ca(NO_3)_2$, and 100 ml. of 1.00 *M* NaCl and 400 ml. of 0.120 *M* $Hg(NO_3)_2$.

Computations: The heat liberated by a reaction is equal to the product of the change in temperature and the total heat capacity of the system. The computation of the true rise in temperature can be made most simply by a graphical method. As an illustration of this method let us consider the following typical neutralization experiment. All of the temperature readings made in this experiment are plotted as a function of time (figure 36). In this case, the acid in the dewar flask was at a slightly higher temperature than the base in the erlenmeyer, but they were both below

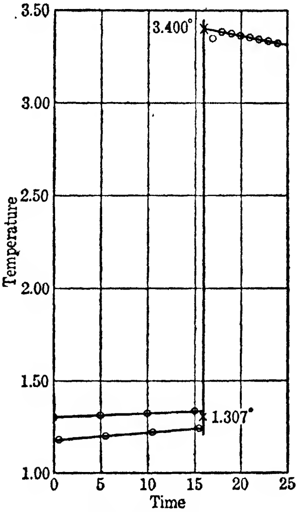

FIGURE 36

room temperature and were warming slowly. To determine their temperatures at the time of mixing (16 minutes in this case), draw straight lines through the two sets of points and extrapolate to this time. In this example, the extrapolated temperatures of acid and base are 1.322 and 1.242°, respectively. The effective mean temperature is the average of these values weighted by their respective heat capacities. In the present case the weight of the base was 103.0 gm., and its specific heat was 0.96 cals./gm. deg. The acid was contained in a calorimeter which had a heat capacity of 28 cals./deg. The volume of the acid was 400.0 ml., its density 1.004 gm./ml., and its specific heat 0.98 cals./gm. deg. Using these data and the temperatures obtained by extrapolation (figure 36), we may compute the effective initial temperature as follows:

$$\frac{(400.0 \times 1.004 \times 0.98 + 28)1.322 + 103.0 \times 0.96 \times 1.242}{(400.0 \times 1.004 \times 0.98 + 28) + 103.0 \times 0.96} = 1.307^\circ$$

In estimating the final temperature we must take into account the loss of heat which occurs while the system is attaining equilibrium. In the present case, since the (neutralization) reaction is extremely rapid and the stirring is fairly effective, we will not introduce much of an error by assuming that the heat is liberated instantaneously on mixing. On the basis of this assumption, we can obtain the corrected final temperature by drawing a straight line through the final series of points and extrapolating back to the time of mixing. Since the thermometer and calorimeter do not come into thermal equilibrium immediately, frequently the points corresponding to the first few measurements after mixing will not lie on a straight line and must be disregarded. In the present case, the extrapolated value is 3.400°, and the temperature rise is (3.400 − 1.307) or 2.093°C. The heat liberated by the reaction is equal to the product of this temperature rise and the heat capacity of the system. If the sum of the heat capacities of the initial solutions is used the quantity computed will correspond to the heat of the reaction at the final temperature; but, if the heat capacity of the final solution is used, the computed value will correspond to the heat of the reaction at the initial temperature (M, 292–4).

Using the method outlined above, compute, from the experimental data and the specific heats given in table 11 (126), the heat liberated on mixing, for each of the four experiments. From the number of moles of the substance present in least amount, compute the molar heat corresponding to each process measured. For the first two determinations, compute the molar heats of the following reactions (M, 277–8, 288–9):

$$H^+ + OH^- = H_2O$$
$$H^+ + CH_3COO^- = CH_3 \cdot COOH$$

Discuss the results of the third and fourth determinations (M, 288–9), and from these results compute the molar heat of the reaction

$$Hg^{++} + 2\,Cl^- = HgCl_2$$

In discussing the errors of this experiment, take into account the degree of ionization of the acetic acid, the possibility of the ionization of $HgCl_2$ or of the formation of the complex ion ($HgCl_4^=$), and the heat effects attendant upon the dilution which occurs on mixing the solutions.

TABLE 11

SPECIFIC HEATS AND DENSITIES OF CERTAIN SOLUTIONS

ELECTROLYTE	MOLARITY	$C_p, \frac{\text{cals.}}{\text{gm. deg.}}$	D(25°C.), gm./ml.
HCl	0.25	0.983	1.002
HNO_3	0.25	0.98	1 005
H_2SO_4	0.125	0.99	1.005
CH_3COOH	0.25	0.995	0.999
$CH_2ClCOOH$	0.25	0.994	1.006
C_2H_5COOH	0.25	0.995	0.999
$NaHSO_4$	0.25	0.975	1.013
NaOH	1.00	0.949	1.039
NaCl	1.00	0.935	1.037
NaCl	0.25	0.98	1.007
Na_2SO_4	0.125	0.975	1.013
CH_3COONa	0.25	0.985	1.007
$Ca(NO_3)_2$	0.125	0.98	1.012
$Hg(NO_3)_2$	0.125	(0.96)*	1.036

* Estimated only.

Experiment 16

HEATS OF COMBUSTION: THE BOMB CALORIMETER

The heats of combustion of solid or liquid organic compounds (M, 284), as well as those of certain elements and inorganic compounds, can be readily determined with a bomb calorimeter. In this method, the sample of combustible material and an excess of oxygen are confined in a corrosion resistant vessel, the "bomb." The bomb is placed in a thermally insulated metallic pail, containing a definite weight of water. The sample is ignited electrically, and the heat liberated is determined by measuring the rise of temperature of the water.

There are a number of types of bomb calorimeters available commercially (R and R, vol. I, 413–28). They are all similar in basic principle, differing chiefly in mechanical detail and in the precision which can be obtained in their use. There are two general types. In the adiabatic type, the calorimeter proper is surrounded by a water-filled jacket, the temperature of which is maintained continuously as close to the temperature of the calorimeter as possible. While this refinement is necessary in the measurement of heats of slow reactions, the advantages are slight in bomb calorimetry (W, 335–42, 383–4). In the common type of calorimeter, the jacket remains at approximately constant temperature, due either to automatic thermostating or more commonly due to its relatively high heat capacity. The instrument described here (see figure 37) is a Parr bomb calorimeter of the simple type. The calorimeter pail (*a*) is situated in an insulated plastic cylindrical container (*b*), which is fitted with a lid (*c*) of the same material. The lid supports a motor-driven stirrer (*d*) and a Beckmann (or special 1/100°) thermometer (*e*), which extends into the water in the pail. The bomb (*f*) is made of a resistant alloy (Illium), which is not attacked by oxygen or by the nitric acid which may be formed during the combustion. The bomb cover (*g*) is clamped in place by a heavy threaded ring (*h*). The cover is provided with a rubber compression gasket (*i*), which makes a tight seal when the ring is tightened by hand. (Other types of bombs require the use of a longhandled wrench to tighten the cover.) The cover is so constructed that it effectively protects the gasket from the flame during combustion.

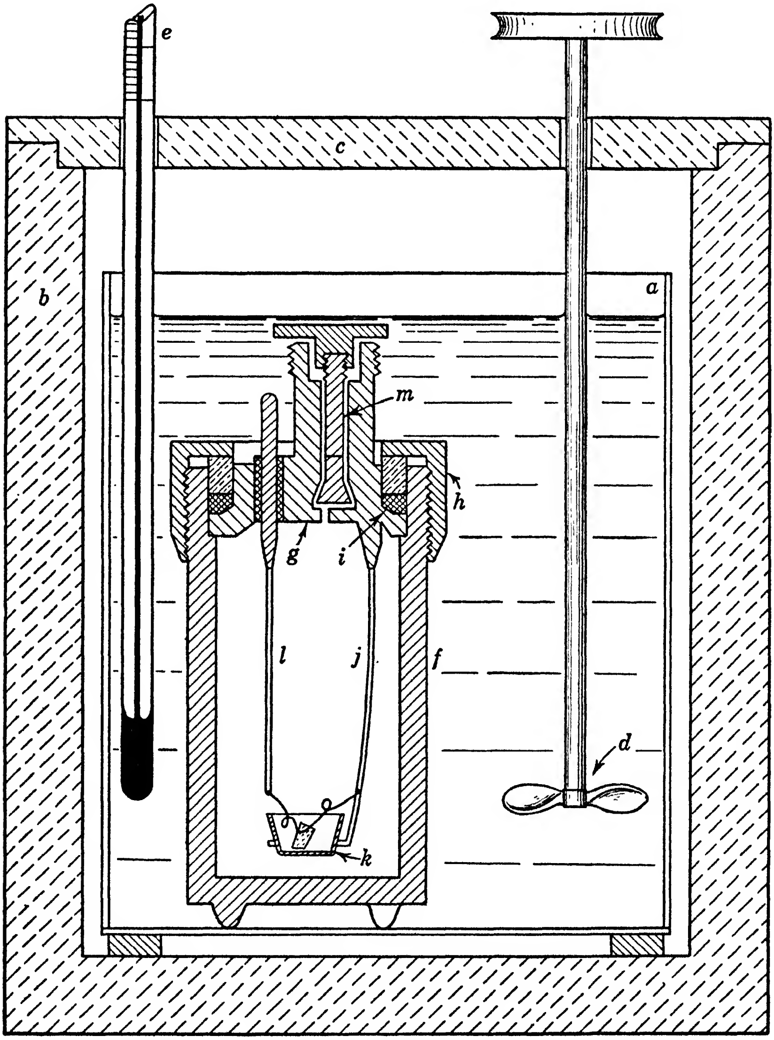

Figure 37

bustion. Two rods are fastened to the underside of the cover. One of these (*j*) supports a small receptacle (*k*) for the sample. The other (*l*) is electrically insulated from the bomb and serves as a lead to the fine iron wire which is used to fire the charge. The bomb is filled with oxygen (to a pressure of 20 or 30 atms.) through the check valve (*m*). Unless care is taken to flush the atmospheric nitrogen from the bomb, before the final filling with oxygen, it is necessary to determine (by titration) the amount of nitric acid formed during the combustion, and to subtract its heat of formation from the total heat evolved. The wire can be conveniently ignited with the 110 volt A. C. circuit, if a double pole switch and a resistance of approximately 20 ohms are connected in series with the iron wire.

To compute the heat evolved by the combustion of the sample, it is necessary to know the heat capacity of the calorimeter — including the bomb, pail, water, stirrer, and thermometer. For an absolute measurement, the heat capacity is determined by heating the calorimeter with a carefully measured quantity of electrical energy. Under ordinary conditions it is more accurate and much more convenient to calibrate the apparatus by the combustion of a weighed sample of pure benzoic acid, the heat of combustion of which has been determined very accurately by the U. S. Bureau of Standards. If the compound studied contains elements other than C, H, and O, it is necessary to analyze the products of combustion to determine the state of oxidation of these other elements.

An excellent discussion of the sources of error inherent in this method and the ways in which they can be eliminated or corrected for is presented by J. M. Sturtevant (W, 383–91). The applications of such measurements are discussed in the same reference (W, 375–83).

Apparatus and Materials: A Parr bomb calorimeter with accessories (including an oxygen tank equipped with reducing valve and pressure gauge), a Beckmann thermometer, and a tablet press. A 0.5M length of #32 (B & S) iron wire and about 5 gr. each of pure benzoic acid and of the substance whose heat of combustion is to be determined.

Procedure: Weigh a 50 cm. length of the fine iron wire on an analytical balance. Cut the wire into measured 5.0 cm. lengths. With the aid of a tablet press, prepare 3 or 4 approximately 1 gm. pellets of pure benzoic acid. The center of a length of iron wire should be imbedded in each pellet. To do this, place the piece of wire in the appropriate position in the tablet press mold (grooves are provided in the base plug of the mold, which make this possible) before adding the powdered charge. The wire may also be imbedded by heating it cautiously and then holding the hot wire against a corner of the pellet. Weigh the pellets with their attached wires on an analytical balance.

Disassemble the calorimeter, placing the insulating lid and the cover of the bomb on the special racks which are provided for the purpose. Place a weighed pellet in the receptacle which is suspended under the bomb cover. Attach the iron wire to the leads. Introduce 1.0 ml. of water from a pipet into the bomb. Set the bomb cover in place. Screw the ring clamp down tightly. With the aid of the flexible copper-tubing lead, connect the valve of the bomb to the reducing valve and gauge which are attached to the oxygen cylinder. Cautiously open the reducing valve until the gauge indicates a pressure of about 25 atm. Remove the coupling from the bomb valve, and screw the protective cap onto this valve. Weigh 2 ± 0.03% kgm. of water into the calorimeter pail. This water should be at approximately room temperature; preferably 1 or 2°C. below the temperature of the insulated calorimeter container. Place the bomb in the pail, centering it on the stud provided for that purpose. Make sure that no bubbles are escaping from the bomb. *Do not proceed with the experiment if there is any detectable leak!* (Leaks which cannot be eliminated by tightening the ring clamp may be due to a faulty gasket.) Connect the single electrical lead from the calorimeter case to the binding post on the bomb cover. Adjust the Beckmann thermometer so that the reading of the water temperature is on the lower part of its scale. Insert the thermometer through the hole in the lid, being sure that the thermometer bulb is completely covered with water.

Read and record the temperature for at least 15 minutes at 60-second intervals. Exactly at the end of a 1-minute interval close the switch to fire the charge. Open the switch as soon as the charge has fired. Record the temperatures at 30-second intervals for 5 minutes, and then at 60-second intervals for 15 minutes. Determine the temperature of the water with an ordinary thermometer.

Remove the bomb from the calorimeter pail and, after wiping off the water, unscrew the protective cap from the release valve. Vent the gas by depressing the escape valve. The screw clamp may then be removed safely.

Repeat this determination with one (or more) samples of benzoic acid. Make two or three similar measurements with another substance, whose heat of combustion is to be determined.

Computations: Plot the temperature readings as a function of time (cf. fig. 36). The points preceding the ignition should lie on a straight line, which by a short extrapolation gives the temperature at the instant of firing. Disregarding the first few points, while the temperature of the water was rising rapidly, draw a straight line through the points which correspond to the steady state following ignition, and extrapolate this line back to the time of ignition. The difference between these two extrapolated temperatures is a fairly accurate measure of the rise temperature due to the process of combustion (i.e., corrected for transfer of heat to or from the surroundings). The heats of combustion at constant volume of benzoic acid and of iron are, respectively, − 771.5 and − 189.8 kcal per mole. Using these valves and the weight of the samples and of the iron wire, compute the heat liberated by the reaction. From this compute the "water equivalent" or heat capacity of the calorimeter. Since the same weight of water is used in all determinations, it is unnecessary in the present experiment to subtract its heat capacity from the experimentally determined value for the calorimeter as a whole. Average the values for the heat capacity of the calorimeter based upon the several determinations with benzoic acid. Use this value to compute the heat of combustion, of the "unknown" at constant volume and at the initial temperature.

Taking into account the heat capacities (C_v) of the reactants and products, compute the heat of combustion at constant volume at 20°C. (M, 292–4). Assuming that O_2 and CO_2 act as perfect gases, compute the heat of combustion at 20°C. at constant pressure (M, 278–9). From this quantity and the known heats of formation of H_2O (1) and of CO_2 (g), compute the heat of formation of the compound at 20°C. at constant pressure (M, 280–4).

A detailed statement of the corrections which must be applied to the computed value, if the highest accuracy is to be obtained, is given by Washburn (J. Research Nat. Bur. Stds. *10,* 525 [1933]) and summarized by Sturtevant (W, 388–91). An extensive table of heats of combustion of organic compounds was published by Kharasch (J. Research Nat. Bur. Stds. *2,* 359 [1929]; see also E and R, 57–60). Heats of formation of inorganic compounds were evaluated critically and tabulated by Bichowsky and Rossini (The Thermochemistry of Chemical Substances, 1936).

Experiment 17

CHEMICAL EQUILIBRIUM IN A LIQUID PHASE

One of the first chemical equilibria to be studied quantitatively was the simple esterification reaction (M, 334–4)

$$C_2H_5OH + CH_3COOH = CH_3COOC_2H_5 + H_2O$$

At ordinary temperatures and in the absence of a catalyst, this reaction approaches equilibrium very slowly. Equilibrium may be attained in a reasonable time, either by allowing the reaction mixture to stand (in thick-walled sealed tubes) at a high temperature (about 200°C), or at room temperature in the presence of a strong acid which acts as a catalyst. The equilibrium constant can be determined by analyzing the equilibrium mixture.

In the present experiment 6 *M* HCl is to be used as a catalyst (D, M, and W, 137–40; Jones and Lapworth, J. Chem. Soc. **1911,** 1427) to avoid the danger of an explosion of the heated sealed tubes. The equilibrium is to be approached from both directions, starting with $CH_3COOC_2H_5$ and with a mixture of C_2H_5OH and CH_3COOH. The equilibrium concentrations can be determined by using known weights of the reactants and of the standardized 6 *M* HCl and titrating the total acid present in the equilibrium mixture. The mixtures are to be sealed in small ampules, to avoid loss by volatilization.

The relatively concentrated acid, which is used as a catalyst in this experiment, affects the equilibrium constant by changing the activity coefficients of the reactants (M, 322–4). A smaller value of the equilibrium constant would be obtained if the reaction were carried out in the absence of the catalyst. It is unnecessary to thermostat the reaction mixture, since the heat of the reaction is practically zero and the equilibrium constant is, therefore, independent of the temperature (M, 319–22).

Apparatus and Materials: A 50 ml. buret, 8 soft glass 25 ml. test tubes. 50 ml. of 6.0 *N* HCl, 500 ml. of standard 1.00 *N* NaOH, 15 ml. each of pure $CH_3COOC_2H_5$, glacial CH_3COOH, and absolute C_2H_5OH.

Procedure: Prepare 8 small ampules from clean dry soft glass 25 ml. test tubes. With the aid of an air-gas blast lamp or bunsen burner (R and R, vol. I, 271–3; or D, M, and W, 435) draw down the tubes to a neck, above the center of the tube. The constriction should be as small as will permit the entry of a 5 ml. pipet. Pipet 5 ml. of 6.0 *M* HCl into each of these 8 tubes, being careful to get all of the solution below the constriction. To each of the first 2 tubes add 5 ml. of distilled water. To the third and fourth, add 5 ml. of pure $CH_3COOC_2H_5$. To the fifth and sixth, add 3 ml. of glacial CH_3COOH and 2 ml. of absolute C_2H_5OH. To the seventh and eighth add 2 ml. of glacial CH_3COOH and 3 ml. of absolute C_2H_5OH. Seal each of the tubes at the constriction with a small pointed flame, being careful not to heat the contents of the tubes. Tubes 3 and 4 contain originally a heterogeneous mixture. To promote the reaction, shake these tubes occasionally.

Titrate at least two 2 ml. samples of glacial CH_3COOH with standard 1.0 *N* NaOH using phenolphthalein as an indicator. Using a small stoppered weighing bottle, determine the weights of the following liquids discharged by the pipets which were used in measuring out the samples: 5 ml. of 6.0 *N* HCl and of $CH_3COOC_2H_5$, 2 ml. of glacial CH_3COOH and of absolute C_2H_5OH, and 1 ml. of CH_3COOH and of C_2H_5OH. These several calibrations are necessary since pipets are calibrated to deliver water or dilute aqueous solutions only (Kolthoff and Stenger, Volumetric Analysis II, 9).

After 3 days or more analyze the contents of each tube as follows: Carefully scratch the neck of the tube with a file. Pipet 25 ml. of standard 1.0 *N* NaOH into a small erlenmeyer flask. Break off the top of the tube, using a hot rod if necessary, and pour its contents into the flask. With a wash bottle, rinse the inside of the tube, adding the rinsings to the flask. Titrate the excess of acid with 1.0 *N* NaOH. Do not attempt to obtain a permanent endpoint, since its fading is due to the saponification of the ester.

Computation: By comparing the results of the titrations and weighings of the 2 ml. samples of glacial CH_3COOH, compute the percentage of water present in the acid. Making allowance for this result, compute the weights of the reactants present in the initial mixtures. From the initial quantities and the total acid titrated, compute the number of moles of each of the reactants present at equilibrium. Compute a value of the equilibrium constant corresponding to each experiment. Tabulate your results.

Experiment 18

MUTUAL SOLUBILITY OF TWO LIQUIDS

Some pairs of liquids, such as aniline and water (M, 368–71), which are completely miscible in one temperature range are only partially miscible in others. Phenol and water, the system which is to be studied in the present experiment, has the advantage that its critical temperature is below the boiling point of water.

The purpose of this experiment is to determine the solubility limits of phenol and water as a function of temperature and composition at constant (atmospheric) pressure. Since this pressure is in excess of the total vapor pressure of the mixture, it is a condensed system (M, 381). A simple method of determining the miscibility limits of such a system consists of the preparation of a number of mixtures, representing the entire concentration range, and the determination, for each mixture, of the lowest temperature at which the second phase will disappear. For a further discussion of this method (known as the synthetic method) as well as a discussion of other possible methods, see Findlay, Practical Physical Chemistry, 282–5, and R and R, vol. I, 179. A modification of this method is to be followed in the present experiment. Two additional experiments are to be performed to determine the effect of typical impurities on the mutual solubility.

Apparatus and Materials: A 1/10° thermometer, a 2 liter beaker, two pyrex test tubes, one 2.5 × 20 cm. and the other about 4.0 × 20 cm. (The two inner tubes of a Beckmann freezing point apparatus will serve satisfactorily in place of the test tube assembly.) About 30 gm. of pure crystalline phenol, 2 ml. of methanol, and 2 gm. of NaCl.

Procedure: Assemble the apparatus as indicated in figure 38. Support the inner tube, *A*, in the jacket, *B*, by means of the ring, *C*, of cork or rubber. Fit the inner tube with a cork, *D*, equipped with a 1/10° thermometer and a simple ring stirrer, *E*. The ring stirrer can be made from light weight glass rod, and should move freely without striking the thermometer. Support the beaker on a tripod, and heat the water to boiling.

Prepare the first mixture by weighing 8 gm. of phenol from a weighing bottle and pipeting 7 ml. of water into the tube, *A*. (*Caution!* Phenol produces painful and dangerous burns. Don't allow it to come in contact with your skin!) Clamp the tube, *A*, in its air jacket in the beaker of boiling water. Stir the mixture regularly until it becomes homogeneous, then read and record the temperature. (Note: this temperature will be above 60°C.) Remove the tube and jacket from the boiling water and allow the mixture to cool slowly, stirring constantly. When the mixture becomes opalescent, due to the separation of a second phase, read and record the temperature. Return the tubes to the boiling water and repeat the determinations. The temperatures at which the opalescence appears and disappears should not differ by more than 0.1°C.

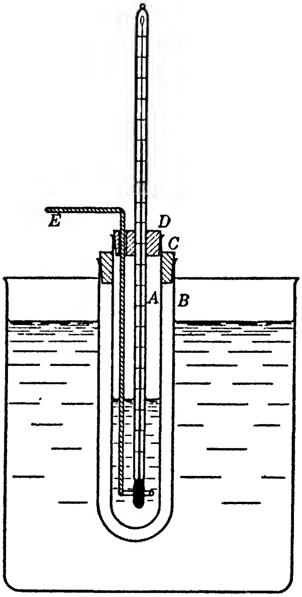

FIGURE 38

Repeat these measurements with each of a series of mixtures differing in composition by 2.5%. The (weight) percentage of phenol in these mixtures should not be greater than 55 nor less than 18%, since it is difficult to recognize the opalescence point for mixtures outside of this range. These several mixtures can be prepared conveniently by adding successively small quantities of distilled water to the original mixture (of 8 gm. of phenol and 7 gm. of water). The quantities of water required may be computed and added from a buret. However, it is satisfactory and easier to perform the dilutions by adding successively five 1 ml. samples of water, then five 2 ml. samples, and finally as many 4 ml. samples as are necessary to reduce the percentage of phenol below 20%. In computing the weight per cent it is sufficiently accurate to take the density of water as 1.0 gm./ml.

To observe the effect of a salt on the solubility of phenol (a nonelectrolyte) in water, determine the temperature at which 8 gm. of phenol dissolve in 12 ml. of a 1% NaCl solution. To find the effect of an impurity which is miscible both with water and phenol, repeat the determination using a 1% methanol solution in place of the salt solution.

Computations: Compute the weight per cent of phenol for each mixture prepared. For each experiment, correct the average thermometer reading for the effect of the exposed stem (69–70). Tabulate, for each mixture, the total volume of water, the weight per cent of phenol, and the observed and corrected thermometer readings. Plot the solution temperature as a function of the composition and draw a smooth curve through the points. On this same graph, plot and label the points representing the experiments performed with the methanol solution and with the salt solution. Indicate the significance of the areas above and below the curve. Discuss the effect of typical impurities on mutual solubilities.

Experiment 19

SOLUBILITY RELATIONS IN A THREE COMPONENT SYSTEM

At constant pressure and temperature the solubility relations of a three component system can be represented on any type of plane coordinates (M, 395–8; E and R, 334–9). While rectangular or even polar coordinates may be used, it is more convenient to use an equilateral triangular diagram, since this permits the percentages of each of the three components to be plotted to the same scale. Each vertex of the triangle represents a pure component, and the perpendicular distance from the opposite side to any point in the diagram is a measure of the percentage of this component in the mixture represented by the point. It is of course immaterial whether this distance is measured on a perpendicular to the opposite side or on a line parallel to one of the sides passing through the vertex, so long as one method is used consistently. The sum of the three distances, representing the percentages of the three components, is constant, regardless of the point selected, which corresponds to the fact that the sum of the three percentages must equal 100%. If the distances are measured perpendicular to the "opposite sides," the sum is equal to the altitude of the triangle; if it is measured parallel to a side passing through the vertex, the sum is equal to the side of the triangle. Just as each vertex represents a single component, so each side represents an isothermal isobaric two-component system. In a solubility diagram a curve represents the miscibility limits in the three component system, and the points of intersection of a curve with a side of the triangle represent the miscibility limits in the two component system which corresponds to the side. For a more detailed discussion of these diagrams see R and R, vol. I, 180–4.

The purpose of the present experiment is to determine the solubility limits in a system made up of water and two other liquids, one or both of which are only partly miscible with water. The solubility limits may be determined by preparing a series of solutions of two miscible liquids and titrating these mixtures with the third component to the first appearance of a second phase (i.e., cloudiness). The composition of the mixture at this end point will correspond to a point on the solubility curve, since the amount of the second phase which separates is presumably negligible. The ease with which the end point may be observed depends upon the difference in the refractive indices of the two phases. In some cases when the turbidity point is difficult to distinguish, it may be made more apparent by the addition of a small amount of some powder (such as jewelers' rouge) which separates out on the liquid-liquid interface. To simplify the technique, the present experiment may be performed at room temperature. If some other temperature is used, it should be remembered that, either the titrating liquid as well as the binary solution must be thermostated, or else the mixture must be returned to the thermostat after the addition of each portion of the third component.

The diagram (figure 39) represents the solubility limits for a typical system composed of water and two organic liquids, one of which is completely miscible and the other only partly miscible with water. If a mixture is prepared which has a total composition represented by the point *M*, it will separate into two phases having compositions *L* and *N*. Two phases formed in this way are called conjugate solutions, and the line which joins the points representing them on the diagram is called a tie line. In general tie lines are not parallel to a side of the triangle and their orientation must be determined experimentally. While the most direct way to do this is to separate the phases and analyze them, it may also be accomplished as follows: A mixture is prepared with the composition *M*, and the two resulting conjugate solutions are separated mechanically and weighed. The ratio of the weight, g_N, of the solution *N* to the total weight, g_M, of the mixture is equal to the ratio of the length, *LM*, to the total length, *LN*, of the tie line

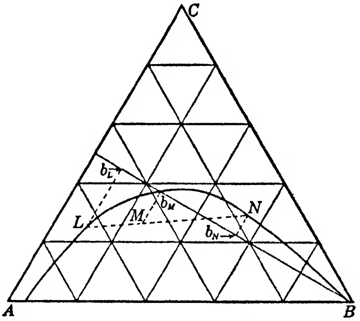

FIGURE 39. TYPICAL SOLUBILITY CURVE FOR A THREE COMPONENT SYSTEM

$$LM/LN = g_N/g_M \qquad (1)$$

The compositions of the conjugate solutions may be determined by finding (graphically) a line passing through M which satisfies equation 1. In some cases there are two lines which satisfy this equation, and in these cases it is necessary to supplement the method by a crude analysis of the solutions. However, this ambiguity can usually be avoided by choosing the point M off center, so that one of the solutions will constitute at least two-thirds of the total mass of the mixture.

Equation 1 may be readily derived as follows: Indicating the percentage of component B by b and mass by g, and using the subscripts M, L, and N to denote respectively the mixture and the separate conjugate solutions, we may write

$$g_M b_M = g_N b_N + g_L b_L \tag{2}$$

Substituting $(g_M - g_N)$ for g_L and rearranging the resulting equation we obtain

$$\frac{b_M - b_L}{b_N - b_L} = \frac{g_N}{g_M} \tag{3}$$

However,

$$\frac{b_M - b_L}{b_N - b_L} = \frac{LM}{LN} \tag{4}$$

since three parallel lines, Lb_L, Mb_M, and Nb_N, cut off proportional intercepts on any two transversals, LN and $b_L b_N$. Combining equations 3 and 4 we obtain the desired relation, 5.

$$LM/LN = g_N/g_M \tag{5}$$

While the following list does not begin to exhaust the number of suitable three component systems those included in it are known to be satisfactory for measurement at room temperature. It is to be understood in using the following list that water is component A and that the second component is to be selected from the B list and the third from the C list. B list: CH_3OH, C_2H_5OH, C_3H_7OH, $CH_3 \cdot CO \cdot CH_3$, and CH_3COOH. C list: $CHCl_3$, CCl_4, C_6H_6, $C_6H_5 \cdot CH_3$, $C_6H_5NO_2$, C_4H_9OH, and $C_5H_{11}OH$. Interesting systems which are represented by curves of a different type may be made up from water and any two of the following: $C_6H_5NH_2$, $C_5H_{11}OH$, and C_4H_9OH.

Apparatus and Materials: A 50 ml. buret, four 100 ml. glass stoppered bottles, and a small short-stemmed separatory funnel. About 150 ml. each of the two selected liquids.

Procedure: Prepare by weight four samples of about 25 gm. each of the two organic liquids, containing, respectively, 20, 40, 60, and 80 (weight) per cent of one component. Titrate each of these samples with water to the first appearance of turbidity. The danger of overstepping the endpoint may be minimized by the following procedure: Before beginning the titration, remove a small portion, about 1 ml. of the solution; titrate fairly rapidly to the first appearance of turbidity. Then replace the 1 ml. sample, which should clarify the solution. Titrate the resulting mixture carefully until a permanent endpoint is reached. It is necessary to shake the mixture vigorously after each addition of water. Do not confuse the small air bubbles which are introduced by shaking with the turbidity due to the presence of a second liquid phase. Compute the weight percentage of each component in the several mixtures. Plot these compositions on triangular coordinate paper, and decide what other data are necessary to complete the curve. Prepare the required two component solutions and titrate as before.

Select a point, *M*, on the diagram, lying in the heterogeneous region about midway between the center of this area and one side of the bounding curve (compare figure 39). Prepare a 50 ml. sample, the composition of which corresponds to the selected point. Shake the sample vigorously for several minutes. Allow the sample to stand until the phases form separate layers. Then with the aid of a small separatory funnel run each solution into a small weighed flask. Determine the weight of each solution to the nearest twentieth of a gram. If there is any doubt as to which of the two samples is the water-rich phase, add 1.0 ml. of water to each. The water-rich solution will remain homogeneous; the other will become heterogeneous.

Computations: Plot accurately on triangular coordinate paper the compositions representing the experimentally determined miscibility limits. Draw a smooth curve through the points. Indicate the meaning of the areas bounded by the curve (or curves) and of the points of intersection of the curve with the sides of the triangle.

Compute the ratio of the weight of one of the conjugate solutions to the total weight of the mixture, *M*, which was prepared in the second part of the experiment. Plot the point M, and lay a ruler on the diagram so that it passes through this point and intersects the curve twice. Rotate the ruler about the point M, until the ratio of the distance from M to one point of intersection with the curve to the total distance between the two points of intersection is equal to the ratio of the mass of one solution to the total mass of the mixture. Draw a line connecting the points of intersection. Discuss the significance of this line and of its points of intersection with the curve.

Experiment 20

STEAM DISTILLATION

When two immiscible liquids are heated together in an enclosed space the total pressure is the sum of their vapor pressures and is, therefore, independent of the relative amounts of the two liquids (M, 379–80). In steam distillation advantage is taken of this fact to distill substances at temperatures far below their boiling points. Whether steam distillation will prove to be practical or profitable in a given case depends upon the vapor pressure and molecular weight of the substance as well as upon its solubility in water. In the present experiment, the yield (i.e., the weight per cent of organic liquid in the distillate) which is obtained experimentally is to be compared to that which is computed from the properties of the pure liquids.

Apparatus and Materials: A 500 ml. Claisen flask, a steam generator, a short Liebig condenser, a 100° thermometer divided to 1/10°, 2–100 ml. calibrated flasks, and a 25 ml. buret or eudiometer. About 100 ml. of pure nitrobenzene or of some other organic liquid which has a boiling point around 200°C. and which is relatively insoluble in water.

Procedure: Assemble the apparatus as is indicated in figure 40. The open tube, *A*, is inserted in the steam generator to act as a safety valve and pressure indicator. The end of the steam injector, *B*, is bent at right angles and placed near the bottom of the flask. The right angle bend results in a violent rotary agitation of the nitrobenzene and water and thereby helps to keep the liquids in equilibrium with the vapor phase. It is not necessary to have the tube of the Claisen flask bent downward as is indicated in the figure, but the arrangement conserves desk space and reduces the amount of liquid held up by the condenser. Ordinary corks, providing that they fit tightly, serve satisfactorily for stoppers in the steam generator, Claisen flask, and condenser. It is advantageous to insulate the distilling flask by wrapping it with asbestos paper or a dry towel.

Place a beaker under the condenser and pass steam through the empty flask until the thermometer indicates a temperature constant within approximately 0.02°C. Record this temperature, and read and record the barometric pressure (53–4) and the room temperature (i.e., the temperature of the barometer). This part of the experiment is performed to enable you to calibrate the thermometer under the conditions of use.

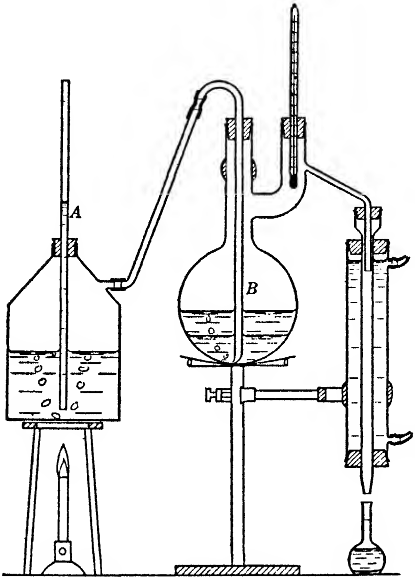

Figure 40. Apparatus for Steam Distillation

Pour about 100 ml. of nitrobenzene into the flask and again pass steam into it. Adjust the flame under the steam generator until the distillate is delivered at a rate of 1 or 2 drops per second. Discard about the first 25 ml. of distillate collected, then place one of the 100 ml. calibrated flasks under the condenser and allow it to fill to the 100 ml. mark. Then replace this flask with a second (empty) flask and again allow 100 ml. of distillate to collect. During the time that the distillate is being collected, read and record the temperature (to the nearest 0.02°) at 5 minute intervals. If the experiment is performed properly and the nitrobenzene is pure, the temperature will not vary more than a few hundredths of a degree. When the distillation is completed, read and record the barometric pressure and room temperature.

Stopper the calibrated flasks and let them remain for at least 2 hours to allow the liquid layers to separate. A 25 ml. buret, eudiometer, or measuring cylinder graduated to 0.1 ml. will serve to determine the volume of nitrobenzene. To avoid the error due to the flat meniscus, pour a few ml. each of nitrobenzene and water into the measuring vessel and record the position of the interface between the two liquids. Pour off most of the water contained in the flask and transfer the nitrobenzene to the measuring cylinder as quantitatively as possible. If necessary use several small volumes of water to rinse any nitrobenzene remaining in the flask into the buret. Dislodge any droplets of nitrobenzene adhering to the walls of the buret with a fine wire. Determine the volume of the nitrobenzene by reading the new position of the liquid interface. (A hand-driven centrifuge, provided with graduated tubes, would simplify this operation.) Using the same technique, measure the volume of nitrobenzene collected in the second flask.

Computations: Compute the weight per cent of nitrobenzene in each sample of the distillate, using the densities of nitrobenzene and water. Near room temperature the density of nitrobenzene is

$$\rho = 1.198 + (25^\circ - t^\circ\mathrm{C.})10^{-3}$$

Correct the first barometer reading to 0°C. (56) and look up the boiling point of water at this pressure. The difference between this boiling point and the thermometer reading when steam was passing through the empty flask is the correction which must be applied (at this temperature) to the thermometer. Since the temperature of the steam distillation (when a high-boiling liquid is used) is only slightly lower than the boiling point of water, this correction may be applied directly to the observed temperature of distillation. Look up the vapor pressure of water at the corrected distillation temperature. Compute the vapor pressure of nitrobenzene at the temperature of the distillation, by subtracting the vapor pressure of water from the barometric pressure. Compare this value to a value obtained by interpolation (M, 81–2) of the data tabulated in the I. C. T., volume III, 221. Compute the mole fraction and weight per cent of nitrobenzene which would be obtained in the distillate, if the liquids were completely immiscible and the vapors acted as perfect gases. Compare this weight per cent to the average of your experimental values.

Assuming a perfectly insulated distilling flask and neglecting the heat necessary to raise the flask and nitrobenzene from room temperature to the temperature of distillation, compute the heat (in calories) required to steam distill one kilogram of nitrobenzene. By how much does this exceed the heat required for the simple distillation of 1 kg. of nitrobenzene? The molar heat of vaporization of water and nitrobenzene at their boiling points are 9660 and 9700, respectively. While the heat of vaporization of nitrobenzene under the conditions of the experiment is slightly higher than this, it is sufficiently accurate for this computation to use the value given above.

Experiment 21

DISTILLATION OF SOLUTIONS OF TWO COMPLETELY MISCIBLE LIQUIDS

A plot of the compositions of vapor and liquid, which are in equilibrium at constant pressure, as a function of temperature is known as a boiling point diagram (M, 373–9; E and R, 316–8). Such diagrams are of interest not only in that they represent the characteristics of certain heterogeneous equilibria, but also because they are necessary in planning the separation of the components of a binary solution by fractional distillation. The boiling point curves of completely miscible binary mixtures can be separated into three classes: first, simple systems, the boiling points of which always occur between the boiling points of the pure components; second, systems exhibiting a minimum boiling point, which is below that of the lower boiling component; and third, systems exhibiting a maximum boiling point.

The present experiments are to be performed at barometric pressure and the composition of the residue and distillate (i.e., condensed vapor) are to be determined with the aid of an Abbé refractometer. The two chief difficulties in such determinations lie in the measurement of the equilibrium temperature and in obtaining a representative sample of the vapor. To indicate the correct temperature, the thermometer must be in thermal contact with the vapor and with liquid which has the composition of the residue. Entirely incorrect results may be obtained if the thermometer is suspended in the vapor phase. If, on the other hand, it is immersed in the liquid it is likely to be in error due to superheating. Superheating can be minimized by the use of an internal electric heater (D, M, and W, 79–80, 316). One of the most successful types of apparatus, which is a modification of Swieteslowski's ebuliometer (see Swieteslowski, Ebuliometry) utilizes Cottrell's principle (R and R, vol. I, 617–8) of spraying the thermometer with the boiling liquid. This is accomplished by means of a vapor lift (figure 41). The second source of error is more difficult to avoid, since in any simple apparatus the vapor undergoes some fractionation before it is condensed (compare Rosanoff, Bacon, and White, J. Am. Chem.

Soc. **36,** 1803 (1914)). This error is greatest when the equilibrium concentrations of vapor and liquid differ widely. It can be lessened by reducing the amount of contact between the vapor and the condensate which is returning to the pot.

While a large number of binary solutions may be studied by this method, the following pairs of liquids (each of which possesses either a minimum or maximum boiling point) have their boiling points in a convenient range and may be readily analyzed with the Abbé refractometer: $CH_3OH—CHCl_3$, $CH_3OH—CCl_4$, $CH_3OH—C_6H_6$, $C_2H_5OH—CHCl_3$, $C_2H_5OH—CCl_4$, $C_2H_5OH—C_6H_6$, $CH_3—CO—CH_3—CHCl_3$, $C_3H_7OH—C_6H_6$, $CH_3COOCH_3—CHCl_3$, $CH_3COOC_2H_5—CCl_4$.

Apparatus and Materials: A modified Swieteslowski boiling point apparatus, a 1/10° thermometer, 5 small sample vials, and an Abbé refractometer. About 150 ml. each of the two liquids chosen for the experiment.

Procedure: Prepare about 35 ml. each of three solutions whose mole fractions, which are to be known with an accuracy of 0.5%, are approximately 0.25, 0.50, and 0.75, in respect to one component. Determine the refractive indices of each of these solutions and of the pure components with the Abbé refractometer (150–3). Prepare an accurate plot of refractive index as a function of mole fraction (or weight per cent) for this binary mixture. This plot should be on a large enough scale to permit the determination of the mole fraction to the nearest half per cent, since it is to be used for the analysis of the several samples obtained in the latter part of the experiment.

Set up the boiling point apparatus as shown in figure 41. The thermometer well, *A*, should be partly filled with mercury to improve thermal contact. It has a thin glass spiral wound around the outside. To eliminate bumping, the inner surface of the bulb, *B*, is covered with finely ground glass which has been fused in place. If the bulb has not been so treated, it is advisable to use a few boiling chips. The flame should be protected from drafts by a shield, *C*, which can be made from a piece of asbestos paper. Use the same volume (about *35* ml.) of liquid in all determinations. It should be sufficient to fill the bulb and, when at rest, extend about *1* cm. up the tube, *D*. The bulb should be heated with a microburner (60) adjusted to give a very small flame in direct contact with the bulb. (The base of a bunsen burner will serve as a convenient and simple microburner.) When the volume of the liquid and the size of the flame are properly adjusted (to be determined by trial), plugs of liquid will be trapped between bubbles of vapor in the tube, *D*, and will be thrown against the thermometer well. The rate of boiling should be the same in all determinations. Do not boil the liquid so fast that there is danger of it being splattered into the small depression, *E*, which is under the condenser. After the temperature has become constant and has been recorded, withdraw the sample (0.10 to 0.15 ml.) of distillate which has collected in the depression, *E*. This can be done with a 1 ml. pipet or more conveniently with a sampler made by drawing out the tip of a medicine dropper into a long capillary tube. Stopper this sample and put it aside for analysis. Remove the burner, allow the liquid to cool for a few minutes, and withdraw a small sample of the residue through the tube, *F*. These samples should be analyzed as soon as is practicable. In no case should they be allowed to stand for over an hour, since evaporation through the cork stoppers will result in a change in composition.

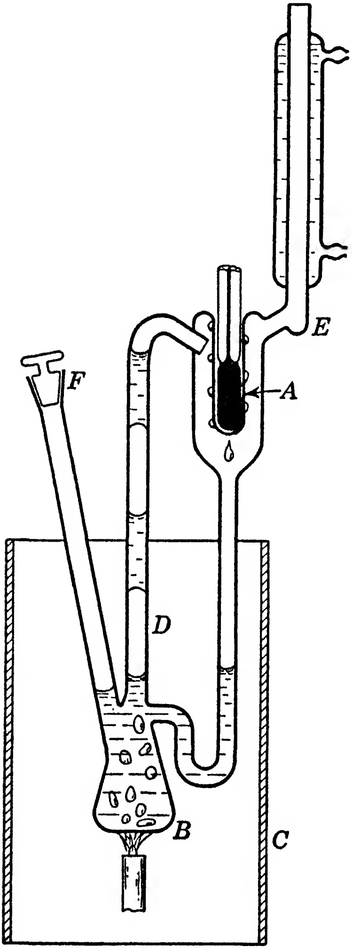

Figure 41

Following this procedure, determine the boiling points of each of the pure components. As a check on the purity of these compounds, collect samples of distillate and residue and determine their refractive indices. Determine the boiling points and the composition of residue and distillate for each of the three mixtures, which were prepared in the first part of the experiment. Make a rough plot (mole fraction against temperature) of this data. By inspection of this graph, decide what other mixtures must be studied to complete the curve. Prepare these mixtures, and determine their boiling points and the compositions of their residues and distillates. Since these solutions must be analyzed, it is not necessary to make them up to exactly known compositions. Instead of preparing a series of mixtures in this way, the following procedure may be followed. Make up a mixture rich in one component. Determine its boiling point, and take samples of its residue and distillate. Withdraw a volume of one or more ml. of the residue and replace it with an equal volume of the component which is (initially) present in small amount. Again determine the boiling point and the compositions. Repeat this procedure until you have covered the entire range of concentrations.

Computations: Correct each measured temperature for the effect of exposed stem (69–70). Prepare a table including the following quantities: recorded temperature, corrected temperature, refractive index of residue and of distillate, and mole fraction of residue and of distillate. Prepare a boiling point curve (M, 373–5), plotting the mole fractions of residue and of distillate against (corrected) temperature. Discuss the significance of the several lines and areas of this graph. Prepare an equilibrium diagram (B and M, 332–3) plotting the mole fraction of the distillate as a function of the mole fraction of the residue. Discuss the application of these curves to fractional distillation. Include your plot of mole fraction as a function of refractive index in your report of this experiment.

If the barometric pressure changes noticeably during the experiment, it will be necessary to correct the observed boiling points to some constant pressure; say, the average barometric pressure. This may be done for a pure liquid by applying the integrated form of the Clapeyron-Clausius equation (M, 82, 89). However, for the present purpose, it is sufficiently accurate to assume that Trouton's rule (M, 89) holds for the solutions as well as the pure liquids, and apply the following approximate relation:

$$\begin{aligned}\Delta T &= \frac{RT_B}{21}\frac{\Delta P}{P}\\ &= \frac{T_B}{10}\Delta P_{\text{atm}}\end{aligned}$$

where T_B is the boiling point in degrees absolute, ΔP_{atm} is the difference in pressure in atmospheres, and ΔT is the correction which must be applied to the measured boiling point.

USE OF THE ABBÉ REFRACTOMETER

The measurement of the refractive indices of liquids is of theoretical interest (M, 196–7), and in addition has many practical applications. Important among these is the analysis of binary solutions (K and S, 684). For precise analysis either the Dipping or the Pulfrich refractometer is commonly used (W, 683–718; R and R, vol. II, 229–31, 235–6). For approximate measurements, where a precision of 0.005 is sufficient, the relatively inexpensive Jelly-Fischer instrument is satisfactory. It requires only a small volume (about 0.1 ml.) of sample and is quick and convenient to operate. The Abbé refractometer is suitable for most routine physico-chemical measurements. In size of sample and speed of operation it is comparable to the Jelly-Fischer refractometer, but has the advantage that refractive indices varying from 1.3000 to 1.7000 can be measured with it to an accuracy of 0.0002. It has the following advantages: The refractive index may be read directly from the scale. A source of monochromatic light is not required. Only one or two drops of liquid are necessary for a determination, and the temperature of the liquid may be controlled, if so desired. The refractive indices (of prepared samples) of solids may also be determined with this instrument (W, 710; R and R, vol. II, 226).

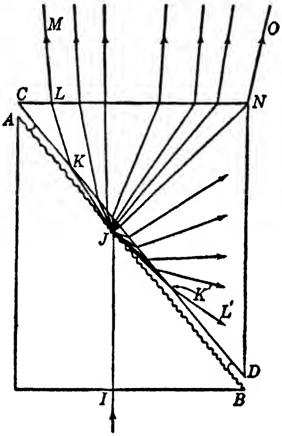

Figure 42

This refractometer consists, essentially, of a split rectangular prism (figure 42) of optically dense glass mounted directly beneath a short focus telescope. The telescope is fixed rigidly to a circular scale, and the prism, which may be rotated about an axis coincident with its upper surface, is attached to a pointer which moves along the scale. Light is reflected from a plane mirror up through the prism and into the telescope. The position of the pointer on the scale measures the angle which the ray of light makes with the normal to the upper surface, *CN*, as it emerges from the prism.

The liquid under investigation forms a continuous film between the diagonal surfaces of the halves of the prism. The diagonal surface, *AB*, of the lower half of the prism has a ground or matte finish, while the corresponding surface, *CD*, of the upper half is polished. When the incident light (represented by the ray *IJ*) strikes the matte surface, it is scatterd into the liquid in all directions. Every ray which strikes the lower surface, *AB*, will give rise in the upper half of the prism to a bundle of rays which will all lie within a restricted solid angle (in this case bounded by the rays *KL* and *K'L'*). The orientation and magnitude of this solid angle is not influenced by the angle at which the incident ray, *IJ*, strikes the matte surface, *AB*, but is dependent only upon the ratio of the refractive index of the liquid to that of the prism. The limiting rays, *KL* and *K'L'*, correspond to grazing incidence of the light upon the polished surface, *CD*, of the upper prism. If the prism is turned so that the telescope is parallel to any ray between *LM* and *NO*, the field in the eyepiece will appear bright, but if the angle between the axis of the telescope and a normal to the surface, *CN*, is outside of this range, the field will appear dark. Therefore, the angle which the bounding ray, *LM*, makes with the normal to the surface, *CN*, can be determined by rotating the prism (and its attached indicator arm) until the field in the eyepiece appears half dark and half light. Since both the angle *DCN* and the refractive index of the prism are known, the refractive index of the liquid can be computed from the angle through which the prism must be rotated to produce the divided field in the eyepiece. In most commercial instruments these computations are made in advance, and the circular scale is so graduated that it indicates the refractive index of the liquid directly.

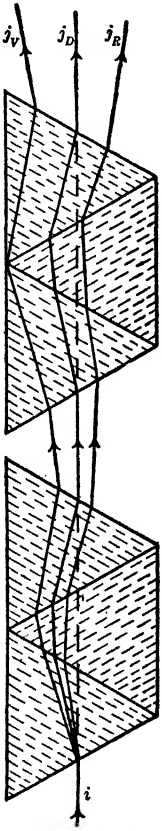

FIGURE 43
AMICI PRISMS

To eliminate the need for a source of monochromatic light, the telescope is provided with a dispersion compensator. This consists of two Amici prisms (figure 43), mounted one above the other, and arranged mechanically so that they can be rotated (about the axis ij_D) in opposite directions, by turning a knurled knob on the outside of the telescope tube. These compound prisms are of the type used in direct vision spectroscopes (R and R, vol. II, 298–9) . They disperse the light into a spectrum, but do not deviate a beam of light having the wave length of the sodium D lines. A ray of light of this wave length follows a path similar to the broken line ij_D. When the prisms are in the relative position indicated in the figure, they produce a maximum dispersion of the incident beam, as is indicated by the red and violet rays ij_R and ij_V. If they are rotated (in opposite directions) through an angle of 90°, they will exactly compensate one another and produce no dispersion. If they are rotated through an angle of 180° from the initial position, they will again produce maximum dispersion, but this time in the opposite direction. Since the dispersive power of the system can be varied continuously from zero to a maximum value, the system can be used to compensate for the dispersion which white light suffers in passing through the split prism of the refractometer. For a more complete description of this instrument, see R and R, vol. II, 224–7 and F and W, 132–5.

Procedure: Set up the Abbé refractometer, with the telescope and attached circular scale inclined at a convenient angle, in such a way that light from the sky or a frosted electric lamp is reflected by the small mirror into the split prism. Release the lock nut and open the prisms. Using a swab of soft cotton, wipe off the diagonal surfaces of this prism with alcohol and ether, taking particular care not to scratch the polished upper surface. To aid in the adjustment of this instrument, place two or three drops of pure water on the lower surface, close the prism, and fasten it with the lock nut. Move the indicator arm, which is attached to the prism, until the field seen through the eyepiece of the telescope appears part dark and part light. Focus the eyepiece by sliding it up or down in its sleeve, until the cross hairs are in sharp focus. If the line between the dark and light parts of the field is colored, turn the compensator screw, which is on the telescope tube, until the fringe of color disappears. If these adjustments are made properly, the line between the dark and light fields will be sharp and colorless. Move the indicator arm slowly until this borderline coincides exactly with the intersection of the cross hairs. With the aid of the reading glass, which is fixed to the arm, read the position of the indicator point (single cross hair or vernier) on the circular scale. This reading should be identical with the refractive index of water at room temperature. At 25°C. the refractive index of water for the *D* line is 1.3325, and in the range between 15 and 30° it decreases by 0.0001 for each degree rise in temperature. If your reading differs from the accepted value by more than a few units in the fourth place, it may be necessary to readjust the instrument. This can be done with the aid of the test piece of glass, provided with the instrument, by the method outlined in R and R, vol. II, 226. However, such an adjustment should be made only by an experienced worker.

When the highest accuracy is desired, it is necessary to control the temperature of the split prism to the nearest 0.2°. This can be done by circulating water from a thermostat through the hollow jacket which surrounds the prism. If a thermostat and circulating pump are not available, water may be siphoned slowly from a large beaker, while its temperature is controlled by hand. A thermometer which can be screwed into the hollow jacket is provided with the instrument. The analysis of the solutions, which are obtained in the experiment on distillation (146–50) may be performed with sufficient precision at room temperature.

When volatile solutions are being studied (W, 170), it is preferable to allow the liquid to run in between the halves of the closed prism, through the groove which is provided in the jacket for this purpose. It is easier to obtain a continuous film in this way, and there is less danger of the solution changing its composition by partial evaporation, which might introduce a serious error if the prism were opened and the liquid run onto the lower surface. The solvents, if they are free from non-volatile impurities, may be completely eliminated by opening the prism and allowing them to evaporate.

Some confusion is occasionally produced by light being reflected into the telescope from the top surface of the prism. This difficulty can be easily eliminated by changing the position of the light source relative to the instrument or by shading the upper part of the refractometer. In analyzing several samples of binary solutions, it should be remembered that the dispersive power of the sample depends upon its composition, and that the compensator must be readjusted for each sample.

Experiment 22

FUNDAMENTALS OF PLATE STILL FRACTIONATION

The object of this experiment is to illustrate the operation of a "plate still," to determine the difference in concentration which exists between the residue, the distillate, and a sample from the third plate, and to determine the effect of changing reflux ratio upon the degree of fractionation.

Although the still head used in these experiments differs greatly, both in respect to design and to operation, from a standard plate column, the essential characteristics of these columns are sufficiently related to justify the application of the theory of a plate column to the experimental results (compare Bruun, Ind. Eng. Chem. An. Ed. *8*, 226 (1936)). Since the following discussion of fractional distillation is necessarily brief, the student is advised to consult a standard treatise on this subject, such as Chapter IX of Badger and McCabe, Elements of Chemical Engineering.

A plate, in a fractionating column, is considered to be ideal when the vapor ascending from the plate is in equilibrium with the liquid descending from it. The number of moles of vapor, V_1, leaving the top or first plate in a given time equals the sum of the number of moles of liquid refluxed, L_0, and the number of moles distilled over or delivered, D.

$$V_1 = L_0 + D \tag{1}$$

While equation 1 applies to the sum of the moles of alcohol and water, a similar relation may be written for the number of moles of either compound

$$V_1Y_1 = (L_0 + D)X_D \tag{2}$$

For this first plate the mole fraction of alcohol in the vapor leaving the plate, Y_1, is equal to the mole fraction of alcohol in the condensate, X_D. To simplify the theory of fractionation we shall neglect minor changes in heat content occurring at each plate and shall assume that Trouton's rule may be extended to apply to each of the solutions. On the basis of this simplification we may write

$$V = L + D \tag{3}$$

That is, the total number of moles of vapor leaving the flask is not changed in passing up the column, and correspondingly the total number of moles of liquid which is condensed on the reflux condenser is not changed as it passes down the column. Since we distill off only a small fraction (less than 3%) of the total amount of liquid, we may neglect the effect of the changing concentration of the solution in the flask. (Note: In engineering practice, plate stills are operated continuously, and the "feed plate" takes the place of the "pot still" or flask.)

Therefore

$$VY_i = LX_{i-1} + DX_D \tag{4}$$

That is, the number of moles of alcohol leaving any plate, i, as vapor is equal to the sum of the number of moles of alcohol returning to the plate as liquid and the number of moles of alcohol distilled off. It is convenient to eliminate V between equations 3 and 4 and to write

$$Y_i = \frac{L}{L + D} X_{i-1} + \frac{D}{L + D} X_D \tag{5}$$

It is a consequence of this equation, that all of the possible points which have the coordinates X_i, Y_{i-1} will lie on a straight line having the slope $\frac{L}{L + D}$, and intercepting the diagonal of the equilibrium diagram at X_D. This straight line is known as the operating line. If we define the reflux ratio, R, by the relation

$$R = \frac{L}{D}$$

we may rewrite equation 5 as follows:

$$Y_i = \frac{R}{R + 1} X_{i-1} + \frac{1}{R + 1} X_D \tag{6}$$

With the aid of equation 6 and the equilibrium diagram, we may obtain a graphical solution of any simple problem involving the fractionation of a binary system in a column made up of ideal plates.

For example, we may determine, for the binary system whose equilibrium curve, *bdfh*, is plotted on figure 44, the minimum number of ideal plates required to produce a distillate of mole fraction 0.90 from an initial mixture whose mole fraction (in respect to the same component) is 0.20, when the reflux ratio is 3.0. Since the distillate undergoes no change in composition on condensation it may be represented by the point, *a*, on the diagonal. The composition, X_1, of the liquid descending from the first plate, which is in equilibrium with vapor having the composition of the distillate, may be obtained by finding the intersection, *b*, of the equilibrium curve with a horizontal line passing through *a*. The abscissa of this point, *b*, is X_1. Since the operating line, *ag*, is the plot of equation 6, Y_2 is the ordinate of the intersection of the operating line and a vertical line drawn through *b*. Since the liquid descending from the second plate is in equilibrium with vapor of composition Y_2, its composition, X_2, is the abscissa of the point of intersection, *d*, of the equilibrium curve with a horizontal line passing through *c*. Each intersection of such a horizontal line with the equilibrium curve represents a theoretical plate. By continuing this stepwise diagram, it may be seen that in this case four theoretical plates are sufficient to produce the desired fractionation.

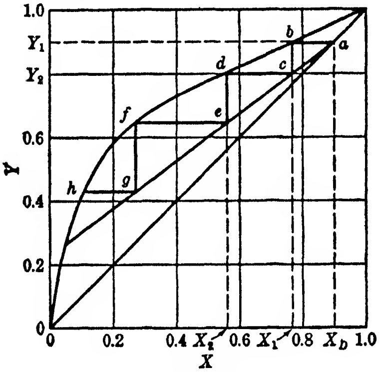

FIGURE 44

Apparatus and Materials: A four-plate glass still head equipped with a delivery condenser and an adjustable reflux condenser (see figure 44), two 100° thermometers graduated to 1°C., a 3 necked 2 liter flask, a strong ring stand, a small Sprengel pycnometer, 5 small sample vials. About 150 ml. of methanol.

Procedure: Prepare 1000 grams of an aqueous methanol solution in which the mole fraction of alcohol is 0.06. Pour this solution into the two liter flask and add a few pieces of broken porous porcelain (boiling chips). The flask, *A* (figure 45), should be supported on a wire gauze, at a height convenient for heating with a burner, and held in position by a clamp at the central neck. Press the cork, *B*, which supports the fractionating column, firmly into the central neck. Fasten the column in place with a condenser clamp. Since the column is rather fragile it is not advisable to remove it from the glass tube, *C*, which acts as a thermal insulator and protective jacket. It can be cleaned by rinsing with alcohol and drying with a stream of air. Insert a thermometer through a cork, *D*, into one of the side necks of the flask and adjust it so that its bulb is just below the surface of the solution. Insert the sampling tube, *H*, through a cork in the other side neck of the flask. Except when a sample is being removed, the small cork, *J*, should be kept in the top of this tube. Insert the second thermometer through the cork, *E*, in the top of the column. It is advisable to lag the tube which surrounds the bulb of this thermometer.

Start the water circulating through the condensers *F* and *G*. Push the reflux condenser, *G*, in as far as possible, to ensure a maximum reflux. Heat the flask with a burner until the solution starts boiling vigorously, then reduce the flame until the solution boils steadily but not violently; a fairly small flame should be sufficient. Boil the solution until the entire column has come into equilibrium. Under these conditions each of the bulbs (i.e., plates) will be about one-third filled with liquid, the rising vapor will bubble

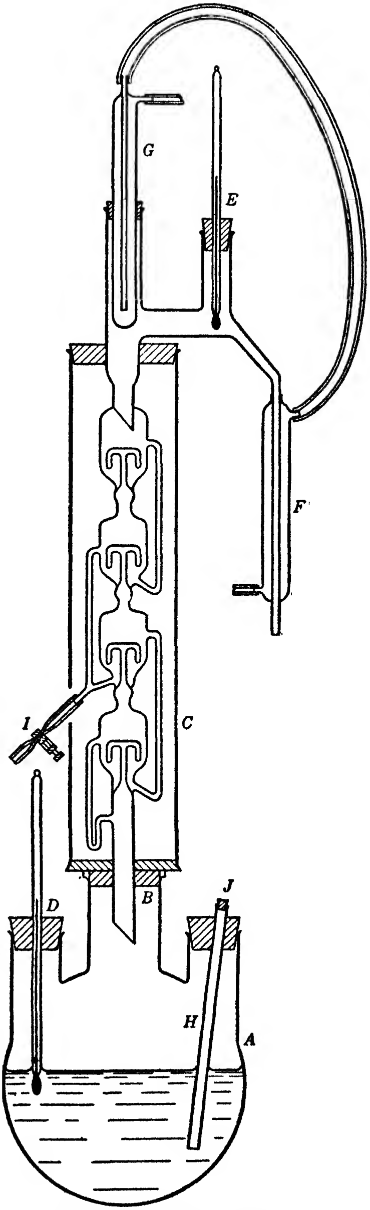

FIGURE 45. EXPERIMENTAL PLATE STILL

through the liquid contained in the bulbs, and there will be a steady reflux from the reflux condenser to the distillation flask. Record the temperature indicated by the thermometer in the flask. Adjust the reflux condenser until about 10 drops are refluxed for each drop distilled. This reflux ratio can be readily determined by counting the number of drops returned, or delivered, during a 100 second period. (Note: the rate of boiling as well as the position of the adjustable condenser affects the reflux ratio.) After allowing about 20 ml. to distill over, record the reading of both thermometers, and collect a sample (1.5 to 2 ml.) of the distillate in a small vial. Without disturbing the distillation, withdraw a sample from the third plate by opening the pinch clamp, *I*, on the short rubber tube; and, by means of a small pipet provided with a rubber tube, obtain a sample of the residue through the sampling tube, *H*. (Caution: do not suck directly on the pipet.) After the samples are taken, remove the flame, and allow the solution to cool slightly, then pour the excess distillate through one of the side necks into the flask. Return the flame and again allow the column to come into equilibrium under a condition of maximum reflux. Then adjust the reflux condenser to return about two drops for each drop delivered. After allowing 20 ml. to distill over, record the thermometer readings, and collect samples of distillate and residue. To analyze the samples determine their density with a small Sprengel pycnometer (160–1).

Computations: Compute the density of the five samples using the density of water as a standard and correcting for air buoyancy. Construct a plot of density as a function of mole fraction from the data given in table 12 of this experiment. These densities were measured at 20°. The change in weight of 1 ml. due to a 5° change in temperature is approximately 0.0009 gm. for pure water, 0.0033 gm. for a solution of mole fraction 0.5, and 0.0040 gm. for pure methyl alcohol. From this plot determine the composition of each of the samples.

From the data given in table 13 construct a graph, plotting the boiling point against the composition of liquid and of vapor. Also construct an equilibrium graph that is a plot of the composition of the vapor as a function of the composition of the liquid with which it is in equilibrium. All compositions are to be expressed as mole fraction.

This apparatus may be treated as a five plate still, in which the top bulb serves as the first plate and the flask as the fifth plate. It will not introduce too large an error if we assume that the "reflux ratio" L/D is equal to the ratio, r, of the number of drops refluxed in unit time to the number distilled off. On the basis of this assumption, for each reflux ratio, make a graphical computation, similar to that given in the introduction to this experiment, of the minimum number of theoretical plates necessary to effect a fractionation equal to that observed. The ratio of the number of ideal to the number of real plates is a measure of the average efficiency of the real plates. Compute the average efficiency of the real plates at each reflux ratio. Compare the theoretical value of X_3 with the composition of the sample withdrawn from the third plate. With the aid of the boiling point composition diagram, compare the thermometer readings to the corresponding concentrations of residue and distillate. Discuss these results.

TABLE 12

DENSITY OF AQUEOUS SOLUTIONS OF METHYL ALCOHOL AT 20°C.

MOLE FRACTION OF ALCOHOL	$d_{20°}$, gm./cc.	MOLE FRACTION OF ALCOHOL	$d_{20°}$, gm./cc.
0.000	0.9982	0.600	0.8650
.100	.9720	.700	.8453
.200	.9503	.800	.8263
.300	.9288	.900	.8085
.400	.9071	1.000	.7917
.500	.8858		

TABLE 13

BOILING POINT-COMPOSITION DATA FOR THE SYSTEM METHYL ALCOHOL-WATER, AT A PRESSURE OF 740 MM.

B. P.°C.	MOLE FRACTION OF ALCOHOL IN THE LIQUID PHASE	MOLE FRACTION OF ALCOHOL IN THE VAPOR PHASE
99.3	0.00	0.00
90.9	.06	.305
85.8	.12	.455
81.3	.20	.58
77.5	.30	.67
74.9	.40	.73
71.7	.55	.80
66.4	.85	.935
63.9	1.00	1.00

USE OF THE SPRENGEL PYCNOMETER

The density of a liquid may be determined simply and accurately by means of a pycnometer. While a simple weighing bottle provided with a stopper pierced by a capillary hole is commonly used, the Sprengel pycnometer is for many purposes more convenient and more accurate. For exact work the pycnometer should have a volume of at least 10 ml. However, a Sprengel pycnometer whose volume is as small as 1 ml. is capable of yielding results of an accuracy comparable to that which may be obtained with a Westphal balance. The following procedure and diagram (figure 46) refer to this small type of pycnometer. For a general discussion of pycnometers see Findlay's Practical Physical Chemistry, 60–4; R and R, vol. I, 491–7; or D, M, and W, 321–3.

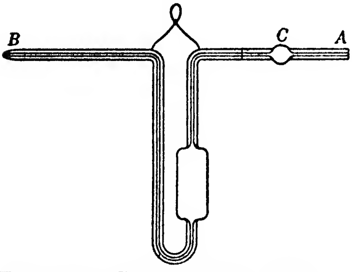

FIGURE 46. SPRENGEL PYCNOMETER

Procedure: Clean the pycnometer thoroughly, rinsing it first with distilled water and then with methanol, and finally drying it by drawing air through it for a few minutes. A 400 ml. beaker filled to within 1 cm. of the top with water, which has been allowed to come to room temperature, makes a convenient thermostat. A thermometer should be kept in the water and its temperature noted from time to time. When the capillary tubes of the pycnometer are allowed to rest on the rim of the beaker, its bulb will be immersed in the water. Before weighing the empty pycnometer, immerse it in the water and then wipe it dry with a lint-free cloth. In weighing the pycnometer, suspend it by means of its wire loop, from the hook at the end of the balance beam. Then fill the pycnometer with distilled water, which has been boiled and allowed to cool to room temperature shortly before using. To fill the pycnometer attach a short piece of light weight rubber tubing to the capillary tip, *A*, immerse the slightly constricted end, *B*, in the water and suck gently until the small bulb, *C*, in the capillary is about one-third full. Avoid introducing bubbles or getting liquid beyond the small bulb. Remove the rubber tubing, and place the pycnometer in the beaker of water, as described, and allow it to remain there for about 15 minutes, to permit its contents to come to the temperature of the water. At the end of that time adjust its contents until the capillary is filled, from the constricted tip (where the meniscus will be held by surface tension) to the scratch on the other arm. If the pycnometer contains too much liquid, the excess may be removed by touching the constricted tip with a scrap of filter paper. If it contains too little, catch a drop of liquid on the end of a stirring rod and bring it in contact with the constricted end of the capillary. Since the ends of the capillaries are not provided with protective caps, the weighings should be made promptly since there is an appreciable loss due to evaporation from the pycnometer. It should be noted that this modified Sprengel pycnometer can be used at temperatures below that of the room, since the expanding liquid must fill the safety bulb, *C*, before it can escape from the pycnometer.

Using the same technique, determine the weight of the pycnometer when filled with each of the liquids of unknown density. In computing the density of the liquids, correct for the effect of air buoyancy.

Experiment 23

THE FREEZING POINT CURVE OF A BINARY ALLOY

Freezing point diagrams (M, 380–95) are of primary importance in metallography; see Principles of Metallography, Williams and Homerberg; also Metals Handbook A. S. M. They are also very useful in the study of solutions, and in testing for compound formation, especially in organic chemistry. Likewise, the applications and limitations of the method of mixed melting points may be easily realized from an inspection of typical freezing point curves.

One of the simplest methods of constructing a freezing point diagram for a system is to determine the cooling curves for a series of mixtures of known (representative) compositions (see for example, Fundamentals of Physical Chemistry, Euken, Jette, and LeMer, 278). A cooling curve is a plot of temperature against time, beginning at a temperature where the entire mass is liquid and continuing until it has all solidified (W, 10–7). So long as no transition or change of phase is occurring, the rate of cooling will be, for a restricted range of temperature, practically constant, and the cooling curve will be approximately a straight line. However, when the temperature reaches a point where a solid phase begins to form, heat will be liberated and there will be a break or change of slope in the curve. Line *AD*, of figure 47, is a typical cooling curve for a pure substance. The segment *AB* corresponds to the steady cooling of the liquid. When the freezing point, T_B, is reached, the solid will form at a rate just sufficient to supply the heat lost by radiation and the temperature will remain constant (segment *BC*) until at a time, t_c, all of the melt has crystallized. The rest of the curve, *CD*, corresponds to the steady cooling of the solid. The lines *EI* and *JN* are typical cooling curves for a solution which forms a eutectic mixture. The first break, *F* or *K*, in the curve corresponds to the temperature at which one of the components, or a solid solution, starts to separate. Due to the liberation of heat by this process of crystallization, the temperature falls more slowly. However, it does not remain constant, since the composition of the solution, and therefore its freezing point, is changing continuously. When the eutectic temperature, T_G, is reached, the remainder of the melt crystallizes without further change in concentration, and the temperature remains constant (segment *GH* or *LM*) until this process is complete. This fact is utilized in the thermal analysis of simple alloys (see The Phase Rule, Findlay, 106–7 or T, 560–2). For a given set of experimental conditions, the time, called the eutectic halt, at which the cooling mixture remains at the eutectic temperature is directly proportional to the weight of the eutectic mixture present. Therefore, if no solid solutions are formed, the composition of an unknown sample may be determined, when the eutectic composition is known, by comparing the length of its eutectic halt to that of a sample of the same total weight which has the eutectic composition. For example, the weight of eutectic mixture in the sample corresponding to curve *EI* is only half as great as that in the sample corresponding to curve *JN*, since *LM* is twice as long as *GH*.

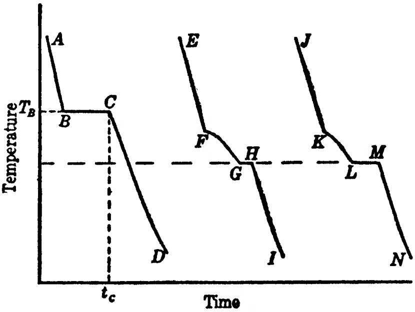

FIGURE 47. TYPICAL COOLING CURVES

In the complete study of an alloy system, thermal analysis must be supplemented by other measurements such as X-ray analysis (M, 108–18) or microscopic examination of polished and etched metallographic sections (T, 542). For the description of a simple experiment illustrating this latter method, the student is recommended to consult F and W, 97–9. It should be pointed out, that in the preparation of samples for X-ray or microscopic examination the cooling should be extremely slow, if a transformation of a solid phase (such as the change in composition of a solid solution) is involved.

Essentially, the determination of the cooling curve of an alloy involves the following steps, preparing a sample of known weight and composition, melting the sample, and measuring its temperature at regular intervals while it is cooling slowly. For this purpose the most generally useful apparatus consists of an insulated electric furnace and a thermocouple (M, 551–4). In using this apparatus, the current is passed through the furnace until the sample is melted, the current is then turned off and the sample allowed to cool in place, the temperature of the sample being recorded at regular frequent intervals. In the study of low melting alloys, a thermometer may be substituted for the thermocouple, and the sample may be heated in a crucible or tube directly over a gas flame until it is melted and then transferred to an insulated box for the cooling measurements. In the present experiment, this simple method of heating is to be combined with the use of a thermocouple.

While not of great importance in the simple alloy systems used in the present experiment, supercooling and spatial inequalities in the temperature and composition of the melt frequently disturb the determination of cooling curves. The latter effects are especially conspicuous in systems of low thermal conductivity which involve solid solutions. In working with such systems the melt must be stirred constantly.

The following alloy systems are recommended for the present experiment: Cd–Sn, Cd–Pb, Cd–Bi, and Bi–Sn.

Apparatus and Materials: A copper-constantan thermocouple and a suitable millivoltmeter or galvanometer (168); a small dewar flask; a stopwatch or a watch with a second hand; 7 pyrex test tubes, 18 or 20 mm. inside diameter; a test tube (or narrow beaker) about 5 cm. inside diameter and 10 or 12 cm. long; about 1.5 meters of 6 mm. pyrex tubing; asbestos paper, wool, and board. 400 gm. each of pure Cd and Sn (or of the metals selected for the experiment) and 5 or 10 gm. of ceresin wax.

Procedure: Prepare a copper-constantan thermocouple (167–70) and connect it to a sensitive millivoltmeter or a suitable galvanometer, provided with a shunt, telescope, and scale. For more accurate measurements, a simple potentiometer, circuit (216; W, 322–3; Temperature, Its Measurement and Control in Science and Industry, A.I.P. 265–78) may be used in place of the galvanometer. Cut off and seal at one end 6 or 7 pyrex tubes, 6 mm. in diameter and 1 cm. longer than the test tubes, to act as guards for the thermocouple junctions. Prepare the wide short test tube, or small narrow beaker, as is indicated in figure 48. Pack asbestos wool, *A*, loosely to a depth of 2 or 3 cm. in the bottom of this tube. Drop a large washer or ring, *B*, cut from heavy asbestos board, on top of the wool. The purpose of this washer is to center the bottom of the inner test tube, *C*. Wrap the outside of the tube with several layers of asbestos paper, *E*, and tie it in place. Make a stopper, *D*, for the top of the tube by fastening together two washers of asbestos board. This stopper in addition to closing the tube serves to support and center the inner tube, *C*. Weigh into labeled test tubes 100 gm. samples of each of the following: pure Sn, pure Cd, and mixtures containing, respectively, 20, 40, 60, and 80 mole per cent of Cd.

Slip the junctions of the thermocouples into their protective glass tubes. Fill a small dewar with cracked ice and place the cold junction of the thermocouple in it. Place the other junction in boiling water and record the reading of the millivoltmeter (or the displacement of the galvanometer). This reading will serve as the first calibration point for the thermocouple. The melting points of Sn and of Cd, 231.9 and 320.9°C., respectively, will serve to complete the calibration. These melting points can be obtained from the cooling curves of the pure components.

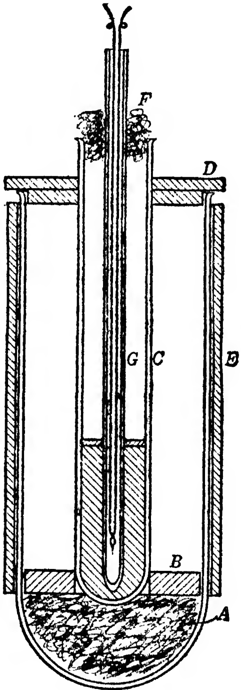

FIGURE 48

To determine the cooling curve of a sample proceed as follows: To prevent excessive oxidation of the metals, add a small lump of ceresin wax to the sample in the test tube. The wax is not entirely necessary when Sn and Cd are being used. Heat the tube with the direct flame of a gas burner until the sample is completely melted, but do not heat it much above the freezing point. Transfer the tube containing the melt to the center of the large insulated tube, as is indicated in figure 48. Insert the "hot junction" of the thermocouple, with its protective jacket, into the melt, and support it in place with a plug of asbestos wool, *F*. Record the readings of the millivoltmeter, or galvanometer, at 30 second intervals until the entire mass has solidified. This will be after the series of constant readings, corresponding to the freezing or eutectic point, has been passed, and the solid is cooling steadily. Take care to make the time interval between readings as constant as possible. If the cooling is very slow, the readings may be made at one minute intervals.

In some cases the thermocouple jacket may be released by remelting the sample. However, this is not always possible, since certain melts, particularly those rich in Cd, on solidifying will crack either the protective jacket, *G*, or the test tube, *C*. If this happens, slide the thermocouple junction out of its protective jacket and fit into a new one. This annoyance may be avoided, if a small steel tube, closed at one end and long enough to come about 2 cm. above the surface of the melt, is fitted over the end of the glass tube, *G*. If the same guard tube, whether of steel or glass, is transferred from one melt to another, it must be scraped or washed clean with acid (and dried) before being inserted in the new melt.

Following this procedure, determine the cooling curve for each of the 6 prepared samples. From a comparison of the eutectic halts of the 4 mixtures, estimate the eutectic composition for the system. Prepare a 100 gm. sample of this composition, and determine its cooling curve.

Computations: Plot the cooling curves, millivoltmeter readings as a function of cumulative time, for each of the 7 determinations. Prepare a calibration curve for the thermocouple by plotting (accurately and on a sufficiently large scale) millivoltmeter readings against temperature for the boiling point of water (at the observed barometric pressure) and for the melting points of Sn and Cd. The latter points can be obtained from the cooling curves for the pure metals. In drawing the calibration curve, remember that the millivoltmeter reading corresponding to 0°C. will be zero; that is, the curve passes through the origin. In place of this graphical method, the three pairs of values may be used to determine the constants, *A* and *B*, in the empirical equation (see I. C. T. vol. I, 57–9)

$$t\text{°C.} = AV + BV^2$$

where *V* is the reading of the millivoltmeter.

Using the cooling curves and the calibration data for the thermocouple, construct a freezing point diagram for the system Sn and Cd. Indicate the significance of the areas, lines, and points of intersection on this diagram.

From the known initial compositions and the eutectic composition, as determined from your freezing point diagram, compute the weight of eutectic mixture in each of the 5 mixed samples.

Divide the weight of the eutectic mixture by the length of the eutectic halt for each sample. Tabulate and discuss these results.

In place of the simple time temperature curves, inverse differential curves are sometimes used in thermal analysis. For this purpose, the time interval divided by the corresponding change in temperature, $\Delta t/\Delta T^\circ$, is plotted as a function of temperature. Since the time interval is constant in the present experiments, the same result may be obtained by plotting, as a function of temperature, the reciprocal of the difference between consecutive millivoltmeter readings. Prepare such a plot for at least one of your series of measurements on a mixed sample.

PREPARATION AND USE OF A THERMOCOUPLE

As an instrument for measuring temperature, the thermocouple has many special advantages (W, 321–6; Temperature, Its Measurement and Control in Science and Industry, A.I.P., 180–205, 219–27, 284–313). It may be used at very high or very low temperatures when the use of the mercury thermometer is impossible. Its heat capacity is low and there is therefore very little lag in its response to a change in temperature. It can be made extremely sensitive, by the use of multijunction couples.

When, in a circuit made up of two different metals, the junctions between these metals are kept at different temperatures, an electromotive force is set up in the circuit (M, 551–4). If one of these bimetallic junctions is kept at a reference temperature, usually in melting ice, the electromotive force in the circuit (figure 49) is a measure of the temperature of the other junction. While a circuit composed of any pair of elements or alloys will produce a thermal electromotive force, certain combinations of metals have proven to be particularly useful. The following combinations are frequently used: copper-constantan, iron-constantan, chromel-alumel, and platinum against a platinum-rhodium alloy. Constantan, cromel, and alumel are alloys which are obtainable commercially. In the low and moderate temperature range, the copper-constantan couple is particularly valuable. It has an unusually high thermal electromotive force, which is nearly a linear function of temperature, it has relatively a low resistance, and is inexpensive and easy to construct. The noble metal combination is used at high temperatures, especially in permanent installations. The other two base metal combinations are used in the intermediate range.

For exact work the thermal electromotive force is always measured with a potentiometer (216–21). The reading of this instrument is not influenced by any change in the resistance of the thermocouple or circuit and can be made on a spread-out scale. It has the disadvantage of requiring a manual adjustment for each reading. For many purposes a direct reading instrument, either a sensitive millivoltmeter or a suitable galvanometer, is preferable. A millivoltmeter in addition to having the required sensitivity, should have a resistance much higher than that of the thermocouple. The galvanometer should be of the volt-sensitive type, but should not have too low an internal resistance. Since in an ordinary thermoelectric circuit it is seldom necessary to use the full sensitivity of a galvanometer, the desired sensitivity as well as critical damping may be attained by the use of a suitable shunt and series resistance (see D, M, and W, 365–6; W, 322–3; Starling, Electricity and Magnetism, 81–6; Notes on Moving Coil Galvanometers, Leeds and Northrup Note-Book 2). The galvanometer should be provided with a telescope, or light projector, and scale.

Ordinarily the junctions between the unlike metals must be made by welding the wires together. This may be done by means of an electric arc (D, M, and W, 425), a "spot welder" is a convenience; or by twisting the ends of the wire together and then fusing their tips in a small hot flame from a blast lamp. A flux, such as borax, may be used to facilitate the welding with a gas flame, but the excess flux should be removed after the junction is formed. Copper-constantan junctions may be soldered, silver solder being required if the element is to be subjected to temperatures above 200°C. Short lengths of glass, quartz, or porcelain tubing (A, figure 49), can be used to insulate the wires which lead to the hot junction. While the cold junction may be insulated in the same way, narrow rubber tubing or any good insulating material will serve. The size of the wire to be used depends entirely upon the purpose for which the couple is intended. Couples which are to be used at high temperatures or are likely to be subjected to mechanical strain are frequently made from wire of #12 gauge or even heavier, whereas multiple junction couples are sometimes constructed from #40 wire. The use of heavy wire increases the thermal leak along the leads, while the fine wire has an inconveniently high resistance.

Thermocouples are usually calibrated in terms of fixed points, such as the melting points or boiling points of pure substances (R and R, vol. I, 356–8). However, in the moderate temperature range they may be calibrated by comparing them to a standard (certified) thermometer. An excellent review of the applications of thermocouples is given by Foote, Fairchild, and Harrison in the Bur. Std. Tech. Paper, 170 (1921). The following procedure gives detailed directions for the construction of a copper-constantan thermocouple suitable for use in the experiment (162–7) on the determination of the freezing point diagram of Sn and Cd.

Apparatus and Materials: A sensitive millivoltmeter, about 20 millivolt range and having not less than 100 divisions; a blast lamp; about 1 meter of #28 constantan wire; 2 or 3 meters of #28 copper wire; silver solder; powdered borax; 25 cm. of 6 mm. pyrex tubing; 15 cm. of thin-walled pyrex capillary; 15 cm. of rubber tubing which has an outside diameter of about 2 mm.

Procedure: Cut a 75 cm. length of constantan wire and a 30 cm. length of copper wire. Twist about 0.5 cm. of their ends together tightly. With a blast lamp, melt a little powdered borax on this twisted end to act as a flux. Cut a small chip of silver solder and stick it to the borax on the wires. Heat this assembly cautiously with a small hot flame from a blast lamp until the solder melts and coats the junction of the wires. While the couple is still hot plunge it into cold water to crack off the borax glass. Following the same procedure, join a piece of copper wire, about 1 meter long, to the other end of the constantan wire.

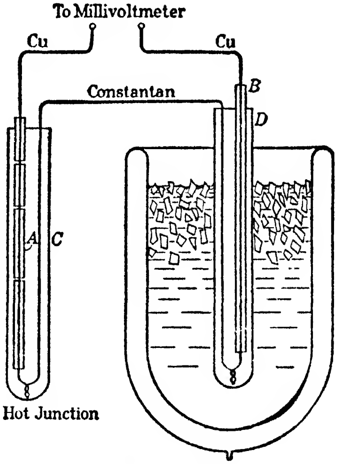

FIGURE 49

Slip about 15 cm. of narrow thin-walled pyrex capillary tubing, A, over the shorter piece of copper wire to insulate it from the constantan wire. Slide this pair of wires into a length of 6 mm. pyrex tubing, C, which is sealed at one end. This assembly is to serve as the "hot junction" of the thermocouple, the 6 mm. pyrex tubing, acting as a protective jacket. While thin-walled pyrex capillary can be obtained commercially, it can also be easily prepared by drawing out a pyrex test tube, or tubing, in an oxygen-gas flame; similarly to the preparation of melting point capillaries. To insulate the cold junction, pull a piece of narrow rubber tubing, *B*, of about 2 mm. outside diameter, over the copper wire. Slide this assembly into a protective jacket, *D*, made from 6 mm. glass tubing.

Connect the copper leads from the thermocouple to the millivoltmeter. If it is necessary to increase the length of either of the leads, solder the connection. Place the cold junction, with its protective jacket, in a dewar filled with cracked ice. A copper constantan thermocouple should produce about 0.04 millivolt for each degree difference in temperature (see I. C. T. vol. I, 57–9). Therefore, if a millivoltmeter with a 20 millivolt range and having 100 scale divisions is used, it should be possible to read the temperature to the nearest degree, by estimating to a fifth of a division. If a more extended scale is required, a student potentiometer (216–21), or a galvanometer with a telescope and scale should be used. The method of calibrating a thermocouple by means of the melting points of pure substances is described in experiment 23 (162–7). See also R and R, vol. I, 356–8, or F and W, 88–92. A copper-constantan thermocouple should not be subjected to temperatures above 400°C.

Experiment 24

THE RATE OF OXIDATION OF IODIDE ION BY HYDROGEN PEROXIDE. A CLOCK REACTION

In a slightly acid solution I^- is oxidized by H_2O_2 at a measureable rate, yielding I_3^- and H_2O.

$$H_2O_2 + 3\,I^- + 2\,H^+ = I_3^- + 2\,H_2O$$

The rate of this reaction, occurring in a buffered solution at constant temperature, can be represented by the following equation (M, 401–20; E and R, 382–6):

$$-\frac{d(H_2O_2)}{dt} = K(H_2O_2)^m(I^-)^n$$

where K, m, and n are constants, the latter two being small integers. The purpose of the present experiment is to find the best values of these constants, or in other words to determine the specific reaction velocity and the order of the reaction in respect to H_2O_2 and to I^-. The H^+ concentration is maintained constant by means of a buffer solution; and therefore, even if the rate is a function of the H^+ concentration, in these experiments the function will have a constant value and its value may be included in the constant, K.

The measurements are made by observing the times required for definite small amounts of iodine to be formed. This is done by adding successively small quantities of standard $Na_2S_2O_3$ solution to the reacting mixture (which contains starch) and recording the time required for the reappearance of the starch-iodine color. By this means the I^- concentration is kept practically constant, and the change in the H_2O_2 concentration may be computed. Under the conditions of the experiment, practically no oxygen is liberated, and the direct reaction between $S_2O_3^=$ and H_2O_2 is negligibly slow. The changes in the several concentrations due to the successive increases in the total volume are small and may be easily taken into account. Since the color reappears sharply after approximately constant intervals of time, this type of reaction is sometimes called a "clock reaction." The kinetic salt effect, or the variation of the rate with the total ion concentration (M, 439–42), is relatively small for a reaction of this ionic type, and is to be neglected in the present experiment. If $Na_2S_2O_3$ were not added to these reacting mixtures the iodine concentration would continue to increase until it was reduced by H_2O_2 at a rate equal to its rate of formation. At this steady-state the only measureable reaction would be the catalytic decomposition of H_2O_2 (compare experiment 25).

Apparatus and Materials: A 500 ml. calibrated flask and 2 stopwatches (the measurements may be made with one watch but are somewhat more difficult). About 125 ml. each of standardized 0.10 *N* solution of $KMnO_4$ and $Na_2S_2O_3$, about 50 ml. of 3% (approximately 1 *M*) H_2O_2 solution, 400 ml. of 0.10 *M* KI, 600 ml. of 2.0 *M* $NaOOC \cdot CH_3$, 100 ml. of 0.50 *M* CH_3COOH, 10 ml. of a tested (see K and S, 618–9) starch solution, and 40 ml. of approximately 6 *N* H_2SO_4.

Procedure: Prepare 500 ml. each of four KI solutions, which are 0.50 *M* in respect to $NaOOC \cdot CH_3$ and 0.020 *M* in respect to CH_3COOH. The first solution should be 0.0250 *M* in respect to KI, the second and third each 0.0125 *M*, and the fourth 0.00625 *M*. Before diluting the solutions to 500 ml., add 2 ml. of starch solution to each. While these concentrations need not be adjusted to the exact values indicated here, they should be known with an accuracy of at least 1%.

Since reaction velocity is a function of temperature, it is preferable to perform the experiments in a 25°C. thermostat. If this is not convenient, the experiments may be performed at room temperature, but in this case the temperature of each reacting solution should be recorded. Pour the first solution into a large beaker or flask. Add 1 ml. of the 0.10 *N* $Na_2S_2O_3$ solution and then 5 ml. of the 3% H_2O_2 solution, and stir vigorously. The reaction begins when the peroxide is added; therefore, start one stopwatch while adding the H_2O_2 solution. At the instant the blue color appears, stop this stopwatch and start the other. Immediately after this, add a second 1 ml. sample of $Na_2S_2O_3$ solution and stir vigorously. Read, record, and reset the first watch. Repeat this sequence of acts at each appearance of the blue color. The time interval which is recorded is the time between successive appearances of the blue color. From 10 to 20 such intervals should be recorded for each experiment. It should be noted that the stirring need not be continuous so long as the solution is thoroughly mixed after each addition of $Na_2S_2O_3$ solution. Since the drainage error of a 1 ml. pipet is large, care should be taken to add the $Na_2S_2O_3$ in as uniform a manner as possible (see K and S, 537–8).

The second, third, and fourth experiments should be performed in the same way, except that 10 ml. (rather than 5 ml.) portions of the H_2O_2 solution should be added to the third and fourth solutions.

Immediately after the performance of these experiments, analyze the stock solution of H_2O_2 as follows (see K and S, 505). Dilute the stock solution ten fold. Pipet 25 ml. of this diluted solution into approximately 10 ml. of 6 N H_2SO_4, and titrate with 0.10 N $KMnO_4$. This is necessary since H_2O_2 decomposes on standing.

Computations: For each of the four experiments, tabulate the time intervals, the cumulative times, the corresponding H_2O_2 concentrations, and the logarithms and reciprocals of these concentrations. With the aid of these tables, determine k_1 and k_2, which are defined by the following equations, for each of the four experiments (M, 399–402, 410–13):

$$-\frac{d(H_2O_2)}{dt} = k_1(H_2O_2)$$

$$-\frac{d(H_2O_2)}{dt} = k_2(H_2O_2)^2$$

The values of k_1 and k_2 may be computed by the method of least squares (32–4), method of averages (34–5), or by the graphical method (46–9). Of these, the last is the quickest and is sufficiently accurate. For the first order equation, the value of k_1 is -2.30 times the slope of the best straight line drawn through a plot of log (H_2O_2) against time. The second order coefficient, k_2, is the slope of the best straight line drawn through a plot of $1/(H_2O_2)$ against time.

If the reaction is carried beyond the first 10 or 20% of the total change, it should be possible to decide between a first or second order law (in respect to peroxide) from the curvature of the plots. If first order, the plot of logarithm of concentration will be a straight line and the plot of the reciprocal of concentration will be a curve. If second order, this relation will be reversed. However, if (as in the present case), the measurements are confined to the first 15% of the total reaction, it will be difficult to detect curvature in either of the plots. The order of the reaction in respect to each of the reactants must then be determined by comparing the average values of k_1 and k_2 for the several experiments.

Tabulate values of the initial concentrations of H_2O_2 and KI, and of k_1, k_2, $k_1/(I^-)$, $k_2/(I^-)$, $k_1/(I^-)^2$, and $k_2/(I^-)^2$. From the constancy or lack of constancy of the last four terms, determine the values of K, m, and n of the rate equation. Is your result consistent with the stoichiometric equation? If not, suggest an explanation (M, 402–3, 410–1; E and R, 399–405).

Experiment 25

THE RATE OF A HOMOGENEOUS CATALYZED REACTION

The rates of catalyzed reactions occurring in homogeneous solutions can be represented by laws of the same type as represent the rates of "simple" reactions (E and R, 405–7; Livingston, An Introduction to Chemical Catalysis in Homogeneous Solutions, J. Chem. Educ. **7,** 2887–902 (1930)). For example at constant temperature, the rate of the decomposition of H_2O_2 catalyzed by the $I_2^{-}I^{-}$ pair (M, 410–1) can be expressed by the following equation.

$$-\frac{d(H_2O_2)}{dt} = K(H_2O_2)^m(I^-)^n$$

In the present experiment, the progress of this reaction is to be followed by measuring the evolution of oxygen. The results of these measurements are to be used to determine the best values of the several constants, K, m, and n (where m and n are integers). The kinetic salt effect (M, 439–42) is not very great for a reaction of this type and is to be neglected in the present experiment.

Under the conditions of the experiment, a small portion of the I^- is oxidized to I_2 almost immediately after the solutions are mixed, but after this "steady-state" has been reached the $I_2^{-}I^{-}$ ratio remains constant and the only observable reaction is the decomposition of H_2O_2.

$$2\,H_2O_2 = 2\,H_2O + O_2$$

Apparatus and Materials: A 25° thermostat provided with a mechanical shaker, a eudiometer system, a 150 ml. Kjeldahl flask, and a stopwatch. About 75 ml. of 0.10 M KI, 40 ml. of 3% (approx. 1 M) H_2O_2, and 125 ml. of (standard) 0.10 N $KMnO_4$.

Procedure: In these experiments the reacting mixture is contained in a 150 ml. Kjeldahl flask, *A*, which is fastened to a shaker, *B*, in a 25° thermostat, *C* (figure 50). The shaker which oscillates the flask about the axis, *I*, is actuated by a motor-driven eccentric (not shown in the figure). The flask is closed by a one-hole rubber stopper and is attached to the eudiometer, *D*, by a flexible rubber tube. The eudiometer consists of two parallel tubes mounted together; one of these is graduated in ml. and is connected to the flask, the other is open at the top. At the bottom, a Y-tube joins both arms of the eudiometer to a rubber tube which leads to the reservoir bottle, *E*. A screw clamp, *F*, is placed on this rubber tube close to the Y-tube. A T-tube, *G*, is inserted between the eudiometer and the reaction flask. A short piece of rubber tubing equipped with a screw clamp, *H*, is attached to the open end of the T.

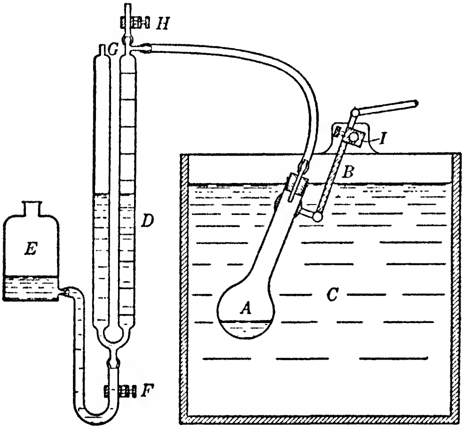

FIGURE 50

To begin an experiment open both screw clamps; raise the reservoir bottle so that the water rises to a point (which should be recorded) at about the top of the eudiometer tube; close the lower screw clamp, *F*; and place the reservoir below the level of the eudiometer tubes. Insert the stopper in the Kjeldahl flask and test the apparatus for leaks. If there are no leaks, place several short pieces of glass rod (with fire-polished ends) in the flask; pipet 10 ml. of 0.10 *M* KI, 15 ml. of water, and 10 ml. of the stock H_2O_2 solution into the dry flask; immediately insert the stopper, close the upper screw clamp *H*, and start the shaker. While the oxygen is being driven over into the eudiometer, keep the water in the two arms at nearly the same level by regulating the rate of flow of water into the reservoir, with the screw clamp. After several cubic centimeters of gas have been evolved, and the rate of evolution seems regular, record the eudiometer reading and simultaneously start the stopwatch. The reading may be conveniently made by temporarily reducing the rate of flow of water to the reservoir, and recording the time when one meniscus crosses the other at a given reading of the buret. Repeat these measurements for each 5 ml. until about 50 ml. have been evolved. Determine the room temperature and barometric pressure.

Repeat the experiment, first using 25 ml. of 0.10 *M* KI and 10 ml. of the stock solution of H_2O_2, and second using 25 ml. of 0.10 *M* KI and 5 ml. of water and 5 ml. of the H_2O_2 solution.

Immediately after the performance of these experiments analyze the stock solution of H_2O_2 as follows. (Compare K and S, 604.) Dilute the stock solution exactly 10 fold. Pipet 25 ml. of this diluted solution into approximately 10 ml. of 6 *N* H_2SO_4 and titrate with the standard 0.10 *N* $KMnO_4$. This is necessary since H_2O_2 decomposes on standing.

Computations: From the results of the titration compute the initial molarity of H_2O_2 in each of the reacting mixtures. Compute, for each reaction, the molarity of H_2O_2 corresponding to each reading of the eudiometer. Tabulate these values for each experiment, and include in the tables the values of the reciprocals and logarithms of each concentration. For each experiment, prepare a graph, plotting both the reciprocals and the logarithms of the concentrations against time.

If the reaction is first order, the logarithm of concentration is a linear function of time, and if it is second order, the reciprocal of concentration is a linear function of time. The value of the specific reaction rate, k, may be obtained from the slope of the appropriate straight line. For a first order reaction, k is -2.30 times the slope; for a second order it is equal to the slope (M, 403–4, 412–5). (For a description of analytical methods of determining k see 29–48.) Tabulate the values of the initial concentrations of H_2O_2 and of KI, and the values of k, $k/(I^-)$, and $k/(I^-)^2$. From the data contained in this table, evaluate K, m, and n of the rate equation.

Experiment 26

THE TEMPERATURE COEFFICIENT OF REACTION VELOCITY AND THE HEAT OF ACTIVATION

The rates of practically all reactions increase rapidly with increasing temperature. It has been demonstrated both experimentally and theoretically (M, 429–32; E and R, 386–94, 398–9) that the rate constants, k, of most reactions can be represented (at least approximately) by an equation of the following form:

$$k = Ke^{-\frac{A}{RT}} \tag{1}$$

where K and A are constants. For simple reactions (compare Hinshelwood, Kinetics of Chemical Changes, 41–69; also Kassel, Kinetics of Homogeneous Gas Reactions, 14–37) the constant K is proportional to the number of collisions between molecules of the reactants, and A is the energy of activation, or the energy which one mole of reacting molecules possesses in excess of the average energy of a mole of such molecules. When the rate constant for a reaction is known at several different temperatures, the heat of activation may be computed by means of equation 1. To simplify the computations, equation 1 may be put in the following form, by taking logarithms of both sides (36).

$$\ln k = \ln K - A/RT \tag{2}$$

In the present experiment, the rate of the reaction between I_2 and $CH_3 \cdot CO \cdot CH_3$ is to be measured at several different temperatures. For properly chosen concentrations this reaction has a conveniently rapid rate. Its heat of activation has been measured with great precision (Rice and Kilpatrick, J. Am. Chem. Soc. **45,** 1401 (1923); Rice, et al., ibid. **46,** 2405 (1924)). The rate of the reaction can be followed conveniently by titrating the free I_2 with a standard H_3AsO_3 solution in the presence of a borax-boric acid buffer (K and S, 590–1).

Although the stoichiometric equation for this reaction is

$$CH_3 \cdot CO \cdot CH_3 + I_2 = CH_3 \cdot CO \cdot CH_2I + H^+ + I^-$$

its rate is determined by the acid catalyzed enolization of acetone (see Moelwyn-Hughes, Kinetics of Reactions in Solutions, 45–8)

$$CH_3 \cdot CO \cdot CH_3 \xrightarrow{H^+} CH_2{=}COH{-}CH_3$$

and its rate can be represented by the following equation:

$$-\frac{d(I_2)}{dt} = k(C_3H_6O)(H^+)$$

The reaction is, therefore, an acid catalyzed process (M, 408–10; Brönsted, Chem. Rev. **5**, 231 (1928); Bell, Acid and Base Catalysis) and may be studied as a typical example of such a process. It is also an example of an auto-catalytic reaction, although in the presence of the concentrated acid used in the present experiment this autocatalytic behavior is not evident.

Apparatus and Materials: Four 250 ml. glass-stoppered volumetric flasks, a 50 ml. buret, a stopwatch, a 25° thermostat, two 1/10° thermometers, and two 2 li beakers. 100 ml. of 6.0 *N* HCl, 150 ml. of 0.10 *N* I_2 solution (0.25 *M* with respect to KI), 200 ml. of standard 0.010 *N* H_3AsO_3, about 25 ml. of tested starch solution (K and S, 618–9), 10 ml. of pure $CH_3 \cdot CO \cdot CH_3$, and 40 gm. of $Na_2B_4O_7 \cdot 10H_2O$.

Procedure: To 200 ml. of distilled water in each of four 250 ml. volumetric flasks add 20 ml. of 6.0 *N* HCl and 25 ml. of 0.10 *N* I_2 solution. Place one of these flasks in an ice bath, a second in a 25° thermostat, and the third in a water bath (2 li beaker) which is hand controlled (67) at 35°C. Make up the fourth solution to exactly 250 ml. with distilled water, and titrate at least two 25 ml. samples of this solution as follows. To a 250 ml. erlenmeyer flask, add 50 ml. of distilled water and 1.5 times as much borax as is required to convert the HCl in a 25 ml. sample into H_3BO_3. Pipet the sample into this prepared flask and titrate to a starch-iodine endpoint with standard H_3AsO_3 solution (K and S, 620–1, 625).

Keep the other three solutions in their respective thermostats, shaking them occasionally, until they reach their equilibrium temperatures. (In this experiment the temperatures should be controlled to the nearest 1/10°C.) When the temperature of the solution in the ice bath has become constant, pipet 2 ml. of CH_3COCH_3 into it and add enough water to make its volume exactly 250 ml. Shake the flask to mix the solution, then return it to the ice bath.

Record the time of addition of the $CH_3 \cdot CO \cdot CH_3$ and the temperature of the solution. While an ordinary watch or clock may be used in this experiment, the times of the two following shorter experiments must be recorded with a stopwatch. Repeat this procedure, first with the solution in the 25° thermostat and finally with the 35° solution.

Before mixing the 35° solution, prepare two 250 ml. erlenmeyer flasks by adding to each 50 ml. of water and the required amount of borax. Six or seven minutes after mixing the 35° sample, withdraw a 25 ml. sample and run it into a prepared flask. Record the time when half the contents of the pipet has run into the buffer solution, which stops the reaction. Three to five minutes later, withdraw a second sample. Measure the temperature of the remaining solution with a 1/10° thermometer. Titrate these samples with the 0.010 N H_3AsO_3 solution. About 25 minutes after starting the 25° reaction, withdraw two samples of this solution and titrate them, recording the times of withdrawal and the final temperature of the solution. The 0° solution should be allowed to stand for at least two hours, before withdrawing samples for analysis.

With the aid of a small stoppered weighing bottle, determine the weight of $CH_3 \cdot CO \cdot CH_3$ delivered by the 2 ml. pipet (Kolthoff and Stenger, Volumetric Analyses, II. 9).

Computations: From the average of the first two titrations, compute the molarity of the iodine present in the flask which was made up without acetone. This value may be taken as the initial concentration of iodine in each of the reaction mixtures. Compute the initial molarity of $CH_3 \cdot CO \cdot CH_3$. For each titration of a reaction mixture, compute the following quantities: the duration of the reaction, the instantaneous values of the molarities of iodine and $CH_3 \cdot CO \cdot CH_3$, and the rate constant. In computing the constant, remember that the reaction follows a first order equation, (M, 408–10) (i.e., a pseudomonomolecular law), since the rate is independent of the I_2 concentration and the acid concentration remains practically constant during the course of the reaction. Tabulate your results.

Corresponding to the measurements at each temperature, compute the average value of the rate constant, the logarithm of this average value, the average temperature, and the reciprocal of the corresponding absolute temperature. Plot the logarithm of the rate constant, log k, as a function of the reciprocal of the absolute temperature, $1/T$. Draw the best straight line through these points, and compute the heat of activation from the slope of this line.

In discussing the errors of this experiment, take into consideration the effect of using a pipet which was calibrated at 15 or 20° on solutions at 0° and 35°C.

Experiment 27

CATALYSIS AND INHIBITION OF A CHAIN REACTION

Although the most definite evidence for the existence of chain reactions comes from the study of photochemistry (M, 648, 655–6), it has been demonstrated that the mechanisms of many thermal reactions involve chain processes (see T, 1009–18; E and R, 405; also Semenoff, Chemical Kinetics and Chain Reactions). Chain reactions occur both in the gas phase and in solution. The study of gaseous explosions is closely associated with the subject of reaction chains. One of the striking characteristics of chain reactions, occurring in either gaseous or liquid media, is their sensitivity to the presence of inhibitors, or negative catalysts.

The oxidation of $SO_3^=$ by dissolved O_2 is a chain reaction which has been carefully studied (Schwab, Taylor, and Reed, Catalysis, 168–76; Fuller and Crist, Jour. Am. Chem. Soc. *63*, 1684 (1941)). Many substances are capable of acting as inhibitors for this reaction. It is also extremely sensitive to the action of such positive catalysts as Cu^{++}. $CuSO_4$ in concentrations as small as 10^{-8} *M* has a marked effect on the rate of oxidation. While inhibitors must be present in somewhat higher concentrations than this to have a noticeable effect, they can be detected in very dilute solutions. To demonstrate these effects it is necessary to use very pure reagents and water. For example, to show the effect of 10^{-8} *M* $CuSO_4$ on 0.10 *M* Na_2SO_3, the solid sulfite used should not contain more than $2 \times 10^{-6}\%$ of Cu nor the water, 6×10^{-4} mg. of Cu per ml.

The present experiment consists of a quantitative demonstration of the action of Cu^{++} as a catalyst and of benzyl alcohol as an inhibitor. The reaction is to be followed by measuring the diminution in gas volume which occurs when a sample of the solution is shaken with O_2 or air in a flask connected to a eudiometer. (A Warburg respiration apparatus (Dixon, Monometric Methods) can be used conveniently for these measurements.) Since the results obtained in this experiment depend largely upon the purity of the Na_2SO_3 and water used, it is difficult to give directions which will be generally applicable. The procedure which follows should prove satisfactory when ordinary conductivity water and the purest Na_2SO_3 which is commercially obtainable are used. Since Sn salts interfere with the reaction, the conductivity water should not be collected with a Sn condenser. If purer materials are available, the concentration of the $CuSO_4$ may be reduced. In this case it will probably prove more convenient to follow the (slower) reactions by titrating the $SO_3^{=}$. A number of other substances may be used as inhibitors and the catalytic effect of a mixture of $CuSO_4$ and $FeSO_4$ may be tested (see Titoff, Z. physik. Chem. **45**, 641 (1903); also Bäckström, J. Am. Chem. Soc. **49**, 1460 (1927)).

Apparatus and Materials: A Kjeldahl flask, a stopwatch, a water-jacketed 5 or 10 ml. eudiometer, and a 25° thermostat equipped with a shaker. 300 ml. of conductivity water, about 3 gm. of purified Na_2SO_3, 1 gm. of $CuSO_4 \cdot 5\,H_2O$, and 1 ml. of benzyl alcohol.

Procedure: Thoroughly clean a Kjeldahl flask and a few large glass beads. It is advisable to wash the flask with hot cleaning solution and then to rinse it, first with distilled water and finally with several portions of conductivity water. Prepare 100 ml. of a 0.10 *M* Na_2SO_3 solution by weighing the pure salt directly into 100 ml. of conductivity water contained in a carefully cleaned, glass-stoppered flask. This solution should not be kept for more than 2 or 3 hours after it is prepared. Prepare a 10^{-3} *M* solution of the catalyst by dissolving 0.025 gm. of $CuSO_4 \cdot 5\,H_2O$ in 100 ml. of distilled water. Clamp the Kjeldahl flask to a shaker in a 25° thermostat and connect it by means of a rubber stopper and tubing to a small eudiometer. Test this assembly for leaks.

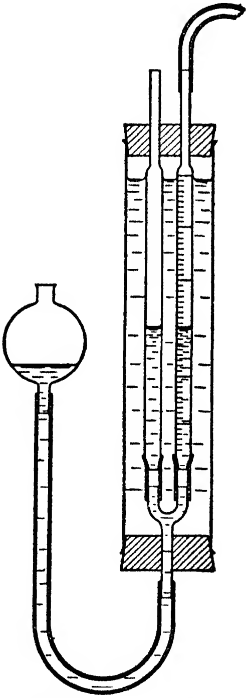

FIGURE 51. EUDIOMETER

This eudiometer, shown in figure 51, can be easily constructed from two 5 or 10 ml. graduated pipets, a small Y-tube, a leveling bulb, and a length of large tubing to serve as a water jacket.

Fill the eudiometer with water, taking care not to trap air bubbles in the connecting tubing.

Pipet 25 ml. of the Na_2SO_3 solution into the Kjeldahl flask. After allowing a few minutes for temperature equilibrium to be attained, insert the stopper which is connected to the eudiometer, and start the shaker. Record the volume, indicated by the eudiometer, every minute for about 15 minutes. After adding each of the following samples, redetermine the rate for 15 minutes, as outlined above. Add first 0.5 ml. of the 10^{-3} *M* $CuSO_4$, then 2 ml. more, and finally 1 drop (0.03 ml.) of benzyl alcohol.

Remove the flask from the thermostat and carefully clean and rinse it. Return it to the thermostat and add 25 ml. of 0.10 *M* Na_2SO_3. Measure the rate of absorption of O_2 as outlined above. Add 25 ml. of ordinary distilled water and repeat the measurements. Then add 2 drops of benzyl alcohol and again determine the rate.

Computations: Plot the eudiometer readings as a function of time for each of the seven 15 minute experiments. During each experiment, the concentration of the catalyst is constant, and the concentrations of $SO_3^{=}$ and dissolved O_2 change only slightly. For this reason the reaction may be treated as if it were of zero order, and the (relative) values of the specific reaction velocities obtained from the slopes of the best straight lines drawn through each set of points. Draw these lines, and compute their slopes. Prepare a table containing the following quantities for each experiment: molarity of (added) Cu^{++}, molarity of benzyl alcohol, and the reaction rate in ml./sec. Discuss your results from the standpoint of the theory of chain reactions. (Note: an estimate of the Cu content of the ordinary distilled water based upon the rate observed when it was present will probably be low, since Sn salts which act as inhibitors are nearly always present in ordinary distilled water.)

Experiment 28

THE RATE OF EVAPORATION OF A VOLATILE SOLUTE

The rates of many reactions which occur in heterogeneous systems are controlled by the speed at which one or more substances pass through a diffusion layer. For example, the rate at which a volatile solute escapes from a solution is limited by the rate of diffusion through two thin films, which are in contact with one another at the liquid-gas interface. The rate of diffusion in the liquid film must be equal to the rate in the adjacent gaseous film. Since the rate of diffusion is proportional to the concentration gradient (W, 277–95; T, 1022), the rate of evaporation, dw/dt, is given by the equation

$$\frac{dw}{dt} = k_1(C - C_s) = k_g(P_s - P) \tag{1}$$

where C is the concentration of the solute in the bulk of the solution, C_s is its concentration at the liquid-gas interface, P_s is its partial pressure at the interface, and P its partial pressure in the bulk of the gas. The coefficients k_1 and k_g are related to the diffusion constants, D_i, the area of the interface, A, and to the thicknesses of the diffusion films, X_i, as follows:

$$k_1 = D_1A/X_1 \qquad \text{and} \qquad k_g = D_gA/X_g \tag{2}$$

These coefficients are increased by an increase in the temperature or by mechanical agitation of the liquid surface. If the partial pressure of the solute in the body of the gas is negligibly small and the rate of diffusion in the gas film is relatively rapid, the concentration of the solute at the interface will be much smaller than its concentration throughout the solution, and equation 1 will reduce to the following form:

$$\frac{dw}{dt} = k_1C \tag{3}$$

On the other hand, if the diffusion in the gas film is the slow process and the partial pressure in the bulk of the gas is negligibly small, the partial pressure at the interface will be equal to the vapor pressure over the solution and we may write

$$\frac{dw}{dt} = k_g P_{eq} \tag{4}$$

If Henry's law (M, 341–2) holds for the solution,

$$P_{eq} = k_H C$$

we may rewrite equation 4 in the following form

$$\frac{dw}{dt} = k_g k_H C \tag{5}$$

In the present experiment, the rate of evaporation is followed by determining the concentration of the solute (either Br_2 or I_2) in the solution at known times. The rate of change of concentration is related to the rate of evaporation by the following equation

$$-\frac{dC}{dt} = \frac{k'}{V}\frac{dw}{dt} \tag{6}$$

where V is the volume of the solution and k' is a constant which becomes unity when w, V, and C are expressed in consistent units. Combining equations 1 and 6, we obtain

$$-\frac{dC}{dt} = \frac{k'k_1}{V}(C - C_s) = \frac{k'k_s}{V}(P_s - P) \tag{7}$$

The pressure of halogen in the air is practically zero. Therefore, if the overall rate is determined by diffusion in the liquid film

$$-\frac{dC}{dt} = \frac{(k'k_1)}{V}C$$

$$= K_1 C$$

and

$$\ln\frac{C_0}{C} = K_1 t \tag{8}$$

But if the rate is determined by diffusion through the gas film, and Henry's law holds for the solution

$$-\frac{dC}{dt} = \frac{(k'k_H k_g)}{V}C$$

$$= K_g C$$

and

$$\ln\frac{C_0}{C} = K_g t \tag{9}$$

It is worthy of note that a very similar treatment can be applied to the rate of solution of a gas; in fact, equations 1 and 7 may be applied without any change to measurements of the rate of absorption (i.e., solution) of a gas. A general discussion of these phenomena will be found in T, 1019–28, 1093–102. Experiments similar to the first three of this assignment are discussed by Polissar, J. Chem. Educ. **12,** 89 (1935). Although the apparatus and technique used in this experiment do not resemble those used in engineering practice, this experiment illustrates the general principles involved in "stripping" and the absorption of a gas (Badger and McCabe, Elements of Chemical Engineering, 383–96, 407–9).

Apparatus and Materials: Four 6 inch petri dishes (3 liter beakers may be used if petri dishes are not available), a stirring motor provided with a speed regulator, a T-shaped glass stirrer, three 250 ml. glass-stoppered bottles, and a block of wood 6 inches square and 3 inches thick. 500 ml. of saturated I_2 solution, 250 ml. of approximately 0.001 M Br_2 solution, 250 ml. of 0.10 M KI solution, about 15 ml. of standardized 0.10 N $Na_2S_2O_3$ solution, and 30 ml. of tested starch solution (K and S, 618–9).

Procedure: Dilute 10 ml. of the 0.10 N $Na_2S_2O_3$ solution exactly twenty fold. Add 25 ml. of the 0.10 M KI solution to 250 ml. of the saturated iodine solution. Using a 100 ml. graduate, add about 110 ml. of this triiodide solution to a clean petri dish. Keep the rest of the solution in a glass-stoppered bottle. With a pipet withdraw immediately 10 ml. of this solution, note the time, and drain the pipet into a small erlenmeyer flask which contains about 10 ml. of 0.10 M KI and 1 ml. of starch solution. Titrate this sample to the disappearance of the blue color with the diluted $Na_2S_2O_3$ solution. Place the petri dish on a desk top where it is exposed neither to direct drafts nor to the danger of being agitated. Withdraw and titrate a second sample at the end of one hour and a third sample at the end of two hours. Stir the solution gently before withdrawing each sample. Follow the same procedure with the saturated I_2 solution and with the 0.001 M Br_2 solution. These three experiments may be run simultaneously.

Place a petri dish containing 100 ml. of water on a block of wood about 3 inches thick and adjust the stirring motor until the cross piece of the stirrer is just submerged (figure 52). The block is used to permit the removal of the petri dish without disturbing the setting of the stirrer. Both the position and the speed of the stirrer should be the same in all three experiments. Set the speed regulator on the motor so that the stirrer rotates rapidly, but without scattering spray or greatly increasing the area of the surface. Add 10 ml. of 0.1 *N* KI and 1 ml. of starch solution to each of three small erlenmeyers. Slide the block from under the petri dish, and remove and dry it. Pour 110 ml. of the triiodide solution (which was prepared in the first part of the experiment) into the petri dish, and replace it on the block under the stirrer. Withdraw 10 ml. of this solution, start the stirrer, note accurately the time at which the stirrer was started, and drain the pipet into one of the prepared erlenmeyer flasks. After about 200 or 250 seconds have elapsed, stop the stirrer, note the time, and as rapidly as possible withdraw a 10 ml. sample and start the stirrer again. Drain the pipet into the second erlenmeyer. At the end of a second 200 (or 250) second interval again stop the motor and take a 10 ml. sample. Titrate the 3 samples with the 0.005 *N* $Na_2S_2O_3$ solution. Repeat this procedure with the saturated I_2 solution and with the 0.001 *M* Br_2 solution.

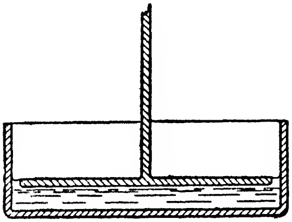

FIGURE 52. STIRRER AND PETRI DISH

If time permits repeat these experiments using different concentrations of Br_2 or I_2.

Computations: For each of the 6 (or more) experiments, tabulate time in seconds, volume of $Na_2S_2O_3$ solution used, concentration of halogen in moles per liter, and logarithms of this concentration. Plot the logarithm of concentration against time. Draw the best straight line through each set of 3 points, and determine the slopes of these lines.

Although the data available in the literature do not make an exact comparison of the diffusion coefficients of Br_2 in water, I_2 in water, and I_2 in KI solutions possible, it is very probable that these coefficients do not differ by as much as 50%. The Henry's law coefficients, k_H, expressed in atmospheres and moles per liter, are 1.5 and 0.30 for aqueous solutions of Br_2 and I_2, respectively. In KI solutions the vapor pressure of I_2 is depressed due to the formation of the I_3^-. In dilute solutions the equilibrium constant for the dissociation of I_3^- has the following value:

$$K_{I_3} = 1.4 \times 10^{-3} = \frac{C_{I_2} \cdot C_{I^-}}{C_{I_3^-}}$$

If the I^- concentration is considerably greater than the initial concentration of I_2, the above relation may be combined with Henry's law to give the following approximate relation:

$$P_{I_2} = \frac{4.2 \times 10^{-4}}{C^0_{I^-} + 1.4 \times 10^{-3}} C^0_{I_2}$$

The superscript ^{0} indicates that the concentrations are "initial" or stoichiometric values.

Compare the ratios of the slopes of the logarithmic plots for the three unstirred experiments to the corresponding ratios for the three stirred experiments. Approximately what ratios would be expected if the rate of evaporation were controlled entirely by diffusion in the gas film? in the liquid film? In light of these results, discuss your experiments in terms of the two film diffusion theory.

Experiment 29

THE DETERMINATION OF TRANSFERENCE NUMBERS

There are three general methods of determining transference numbers. One of these, which is to be used in the present experiment, involves the measurement of the changes in concentration which occur near the electrodes of a transference cell when a known quantity of electricity is passed through it (M, 451–7). A second depends upon the measurement of the EMF of certain types of concentration cells (experiment 35) (M, 587–9). The third consists of the direct measurement of the motion of a boundary between two solutions which are in direct contact in the same solvent (E and R, 424–6; R and R, vol. II, 408–11). An interesting laboratory experiment illustrating this third method is described by L. G. Longsworth (J. Chem. Educ. **11,** 420 (1934)).

Figure 53 is a diagram of the transference cell to be used in the present experiment. A number of other types of cells are illustrated in T, 681. Since in this experiment the transference numbers of Ag^+ and NO_3^- in a $AgNO_3$ solution are to be determined, the electrodes in the cell are of metallic Ag. The $AgNO_3$ solutions are to be analyzed with a standard KSCN solution using ferric alum as an indicator (K and S, 475–8, 573). The total amount of electricity passed through the cell is to be measured with a coulometer (M, 450–1; also D, M, and W, 376–7). It should be noted that in the present experiment no attempt is made to correct for the effect of transport of solvent by the hydrated ions.

The coulometer which is to be used in the present experiment has a Ag anode and an inert cathode. A mixture of KNO_3 and HNO_3 is to be used as the electrolyte. The number of faradays of electricity which flow through this coulometer can be determined by titrating the $AgNO_3$ which is formed by electrolytic solution of the Ag anode. The direct reaction between the metallic Ag and the dilute HNO_3 is very slow and may be safely neglected. While this type of coulometer is less accurate than the weight type Ag coulometer (T, 592–4) or the I_2 coulometer (T, 594–5), it is easy to operate and has the advantage that it uses the same standard solution (KCNS) as is used in the analysis of the contents of the transference cell.

Apparatus and Materials: A transference cell with Ag electrodes, a titration coulometer with one Ag electrode, a milliammeter, a rheostat of about 1000 ohms. 150 ml. of a chloride-free solution 0.25 *M* in respect to HNO_3 and 0.50 *M* in respect to KNO_3, 200 ml. of 0.050 *M* $AgNO_3$, 200 ml. of standard 0.050 *M* KSCN solution, and 20 ml. of a ferric alum indicator solution (K and S, 475–8).

Procedure: Set up and connect the apparatus as is indicated in figure 53. Fill the transference cell, *A*, with 0.050 *M* $AgNO_3$ and the coulometer, *B*, with a solution which is 0.50 *M* in respect to KNO_3 and 0.25 *M* in respect to HNO_3. Retain at least 25 ml. of the $AgNO_3$ solution for analysis. The coulometer electrode, *C*, is made of a piece of nichrome wire; it can be of any inert metal. The other three electrodes are short Ag rods to which Cu wires are soldered. The Ag rods are cemented into the ends of glass tubes, with any suitable sealing wax. To prevent them from eating off where they emerge from the tubes, the upper parts of the electrodes are covered with the sealing compound, leaving only about 5 mm. of the Ag rod exposed. If necessary, trim the wax back before inserting the electrodes in the cells. Be sure that the electrodes are clean and free from oxide. It is essential that the apparatus be set up where it will not be disturbed during the experiment. It should not be subjected to vibration or jars or exposed to drafts or direct sunlight. The stopcocks must be tight; clean and grease them if necessary.

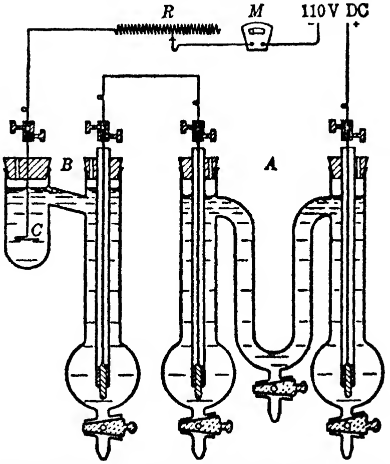

FIGURE 53. TRANSFERENCE CELL AND COULOMETER

Before connecting the circuit to the 110 volt power line, check the polarity of the latter with starch-iodide paper or with litmus paper moistened with a little NaCl solution. Adjust the 1000 ohm rheostat, *R*, for maximum resistance. Close the circuit, and read the milliammeter, *M*. The current should be between 6 and 12 milliamps. If it is less than this, decrease the resistance of the rheostat until it comes into the right range. Once the rheostat is set, the milliammeter may be removed from the circuit. Let the current pass through the system from 100 to 150 minutes. During this time, weigh 4 small numbered erlenmeyer flasks to the nearest hundredth of a gram. Soon after you shut off the current, run the solutions from the 3 parts of the transference cell into 3 of the weighed flasks. To avoid any possibility of mixing due to siphoning, draw off the central portion first. While it is ordinarily not necessary, the electrode compartments may be rinsed into their respective flasks with a few mls. of the original solution; but under no conditions should they be rinsed with water. Pipet about 25 ml. of the original solution into the fourth weighed flask. Weigh these 4 flasks to obtain the weights of the solutions. Run the solution from the coulometer into another flask, which need not be weighed. Carefully titrate (K and S, 475–8) these 5 solutions with standard 0.050 *M* KSCN solution, using 1 ml. of ferric ammonium sulfate solution as an indicator.

Computations: Compute the molality (M, 237) of the solution from the central part of the transference cell and of the original solution. If these two molalities differ, it is evidence that the concentration of the solution in the central part of the transference cell changed due to the electrolysis and that the experiment is unreliable and should be repeated.

Using the weights and titrations of the central and anode portions from the transference cell and the titration of the coulometer solution, compute (M, 455–7) the transference numbers of Ag^+ and NO_3^- in 0.050 *M* $AgNO_3$. Repeat the computations using the results obtained with the cathode portion instead of the anode portion. Tabulate your results.

Experiment 30

THE CONDUCTIVITY OF ELECTROLYTIC SOLUTIONS. THE IONIZATION CONSTANT OF ACETIC ACID

There are two common methods of measuring the conductance of electrolytic solutions, both of which utilize the wheatstone bridge principle (Starling, Electricity and Magnetism, Chap. IV). Solution of electrolytes, for which reversible electrodes are available, may be studied with direct current using a d'Arsonval galvanometer as a null instrument (M, 465–6; W, 1024; also J. N. Brönsted and R. F. Nielson, Trans. Farad. Soc. **31**, 1478 (1935)). However, an audiofrequency alternating current is generally used, with earphones serving as the null point indicator (M, 466–8; W, 1018–24). This latter method is to be used in the present experiment.

Figure 54 is a diagram of a wheatstone bridge circuit as applied to the measurement of the conductivity of electrolytic solutions. The line, *ABC*, represents a slide wire of uniform cross section, on which *B* is a sliding contact. *T* represents a pair of earphones and *F* a source of alternating current, having a frequency of about 1000 cycles. In order to increase the range of usefulness of the instrument, an adjustable resistance, such as a dial resistance box, is used as the standard resistance, R_{Std}. R_x represents the conductance cell. When the ratio of the resistance of the wire, *AB*, to the standard resistance, R_{Std}, equals the ratio of the resistance of *BC* to that of the unknown, R_x, the potentials of the terminals, *A* and *C*, are equal, and no current flows through the earphones. In practice, the standard resistance, R_{Std}, is set to a value which is estimated to be of the order of magnitude of the unknown resistance, R_x, and the sliding contact is adjusted until there is a minimum of sound in the earphones. Under the conditions, R_x can be computed from the following relation:

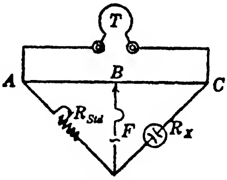

FIGURE 54

$$R_x = R_{Std}\frac{BC}{AB}$$

A factor which sometimes reduces the accuracy of such measurements (R and R, vol. II, 414–34) is polarization of the electrodes produced by an unbalanced component in the alternating current. This source of error can be minimized by using a generator which produces a pure sine wave current, by using platinized electrodes, and by using a very low current which is made audible by amplification. Platinized electrodes have the disadvantage that they are liable to change the concentration of dilute solutions by adsorbing the electrolyte. The capacitance of the conductance cell also renders these measurements less accurate, particularly for highly resistant solutions. This capacitance may be compensated by using a variable condenser parallel to the standard resistance.

Several different types of alternating current generators are available for conductance measurements. Of these, the simple "microphone hummer" is probably the most popular. It is simple, not too expensive, and fairly satisfactory. Its frequency is maintained constant by an electrically driven tuning fork. Small induction coils and buzzers are sometimes used, but are suitable only for crude measurements. All devices of this general type have the disadvantage of being rather noisy, and therefore must be placed at a distance from the observer. In recent years vacuum tube oscillators have come into common use. They are silent, cheap, and can be designed to have any required electrical characteristic. The circuit for such an oscillator, which is to be used in the present experiment, is represented in figure 56, between the terminals *FG* and *HI*.[1] When properly adjusted this circuit produces a fairly pure sine wave, having a frequency of about 1000 cycles. It operates directly from the 110 volt, 60 cycle power line and requires no batteries.

A conductance cell (M, 470–1; W, 1024–8) of the pipet type (figure 55) is to be used in the present experiment. This cell is intended for the intermediate resistance range, and is provided with lightly platinized electrodes. The cell is made with the long tube, *A*, so that it can be filled directly from a volumetric flask. The purpose of the test tube, *B*, is to prevent contamination of the cell by the water of the thermostat. The electrodes of the cell should not be allowed to dry; when not in use, the cell should be kept full

[1] See D. Hull, J. Chem. Educ. 17, 329 (1940).

of pure water. If the electrodes are accidentally dried or contaminated in any way, they must be replatinized.

Before platinizing the electrodes, dissolve off the old Pt black with aqua-regia under a fume hood. A suitable platinizing solution can be made from 3 gm. of chlorplatinic acid, 0.02 gm. of lead acetate, and 100 ml. of distilled water. The conductance cell should be filled with this solution and the electrodes connected to a dry cell through a reversing switch. If gas is evolved rapidly from the electrodes, a rheostat should be introduced into the circuit and the current diminished until there is only a slow evolution of gas. The direction of the current should be reversed about every 40 seconds. The process should be discontinued as soon as the bright electrodes appear to be covered with a thin gray or black coat of finely divided Pt. This should not require more than 5 or 10 minutes. After plating, the electrodes must be rinsed very carefully before they are used. (Note: the same solution will platinize a large number of electrodes.)

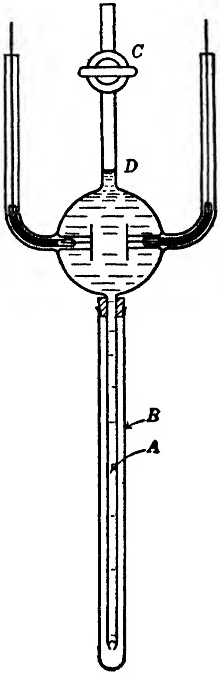

FIGURE 55. PIPET TYPE CONDUCTANCE CELL

In the present experiment, the cell constant is to be determined with the aid of a carefully prepared 0.01000 *N* KCl solution, and the conductivities of solutions of NaCl and of CH_3COOH are to be measured at several different concentrations. The behavior of the NaCl solution is typical of strong electrolytes, and the CH_3COOH of weak electrolytes. With the aid of the standard values of the ionic conductances of H^+ and CH_3COO^-, a value of the ionization constant is to be computed for each measurement of the conductance of a CH_3COOH solution. The use of the standard values of the ionic conductances can be avoided, by including in the experiment the measurement of the conductances of solutions of HCl and of $NaOOC \cdot CH_3$ at a number of different concentrations, since the equivalent conductance of CH_3COOH at infinite dilution, Λ_{0,CH_3COOH}, can be obtained from the relation—

$$\Lambda_{0,CH_3COOH} = \Lambda_{0,HCL} + \Lambda_{0,NaOOC \cdot CH_3} - \Lambda_{0,NaCL}$$

Apparatus and Materials: A rotary slide wire, a 4-dial 10,000 ohm resistance box, a pair of earphones, a key, a vacuum-tube oscillator, a 25° thermostat, a pipet-type conductance cell, and two 100 ml. calibrated flasks. 150 ml. each of 0.01000 *N* KCl, 0.100 *N* NaCl, and 0.100 *N* CH_3COOH. About 750 ml. of conductivity water (M, 473; W, 1029).

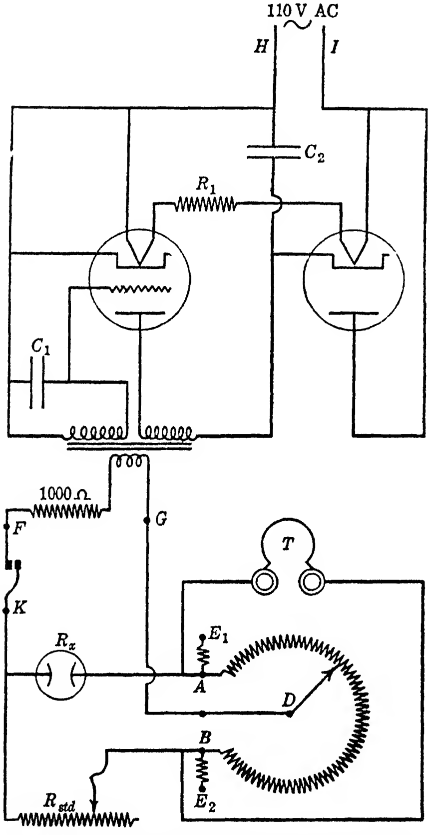

Figure 56. Conductance Bridge and Audio Frequency Oscillator

Procedure: Calibrate two 100 ml. volumetric flasks and a 50 ml. pipet. Connect the apparatus as indicated in figure 56. In this diagram, *F* and *G* are the output terminals of the oscillator, *K* is a key, R_x is a conductivity cell, R_{Std} is a 4 dial resistance box, *T* is a pair of earphones, and E_1ABE_2 is a rotary slide wire.

Drain the water from the cell and rinse it with several portions of the standard 0.01000 *N* KCl. To fill the cell, remove the protective tube, *B*, insert the tip, *A*, in the solution, open the stopcock, *C*, and suck the solution up to a point, *D*, in the upper tube. Be careful not to draw the solution into the stopcock. Clamp the cell in a 25° thermostat, with the point, *D*, below the level of the water bath. Set the bridge at its midpoint (i.e., 500) and adjust the resistance box, R_{Std}, to reduce the sound in the earphones as much as possible. Do not keep the key closed unnecessarily, as this heats the solutions and is also likely to increase polarization effects. Leaving the resistance box unchanged, adjust the slide wire until the sound is at a sharp minimum. If the adjustment corresponding to the minimum is very sharp, the end coils, AE_1 and BE_2, should be introduced into the circuit. Each of these coils has a resistance exactly 9/2 times greater than the resistance of the slide wire, AB. Therefore, making the connections to E_1 and E_2 instead of to A and B is equivalent to increasing the length of the slide wire tenfold, and "spreading out" the scale by the same factor. Of course, in this arrangement, only the middle tenth of the augmented wire is accessible to the slider. Record the readings of the resistance box and of the slide wire.

Remove the cell from the thermostat, and dry the outside of it before taking off the protective tube, B. Empty the cell, and refill it with a fresh portion of the 0.01000 N KCl. Replace the protective cap, return the cell to the thermostat, and after allowing time for it to attain thermal equilibrium again determine its resistance. If this result is appreciably different from the first, repeat the measurement with a fresh sample.

Empty the cell and rinse it several times with 0.100 N NaCl. Fill it with this solution and return it to the thermostat. After it comes to the temperature of the thermostat, determine its resistance. Pipet 50 ml. of the 0.100 N NaCl into one of the volumetric flasks and dilute it to 100 ml. Fill the cell with this diluted solution, rinsing several times as before. Pipet 50 ml. of the remainder of this solution into the other volumetric flask and dilute to 100 ml. In this way, perform 5 twofold dilutions, measuring the conductivity of each solution.

Similarly, perform 5 twofold dilutions of the 0.100 N CH_3COOH, and measure the conductivity of each of these 6 solutions. At the end of this series of experiments, rinse the cell thoroughly with conductivity water and determine the resistance of the cell when filled with this water. Drain and refill the cell several times, until changing the water produces no further increase in resistance.

Computations: From the measurement of the resistance of the cell when filled with 0.01000 N KCl, compute the cell constant (M, 471–2). The specific conductance, κ, of 0.01000 N KCl at 25°C. is 0.001411. Using this value of the cell constant, compute the specific conductance of each of the solutions studied, including the conductivity water.

Subtract the specific conductance of the water from that of each of the (dilute) NaCl solutions. Using these corrected values of the specific conductance, compute the equivalent conductance

(M, 469–70) of NaCl in each solution studied. For the measurements with the NaCl solutions, tabulate the following quantities: concentration, setting of the resistance box, reading of the slide wire, resistance of the conductance cell, measured specific conductance, corrected specific conductance, and equivalent conductance. Plot the equivalent conductance against the square root of the normality, and extrapolate to infinite dilution.

In the case of the acetic acid it is probably unnecessary to correct the measured conductance for the conductance of the water, since the conductivity of the water is due largely to the presence of H_2CO_3, the ionization of which is suppressed by an acid (W, 1029). Therefore, compute the equivalent conductance of the CH_3COOH solutions from the measured values of the specific conductance. At 25°C the ionic conductance, λ, of CH_3COO^- and H^+ are 41 and 350, respectively. Using these values and the measured values of the equivalent conductance, compute a value of the ionization constant (M, 488–9) of CH_3COOH for each solution studied. Tabulate the following quantities: normality, setting of the resistance box, reading of the slide wire, resistance of the conductance cell, specific conductance, equivalent conductance, and ionization constant. Plot the equivalent conductance against the square root of the normality on the same figure as the NaCl data.

Experiment 31

CONDUCTIMETRIC TITRATIONS

Since the specific conductance of a solution is a function of the concentrations of the ions in it, conductimetric methods can be used to determine the endpoints of ionic titrations (M, 497–8; E and R, 430–1; W, 1034–90). These methods can be applied to acidimetric titrations, to some precipitation titrations, and to titrations involving the formation of weak salts or complex ions. For a detailed discussion of such applications, see Kolthoff, P_H and Electro Titrations, 133–51; Kolthoff, Konductometrische Titrationen; T, 936–43; K and S, 509–12.

The same experimental methods can be used in conductimetric titrations as are used in any other type of conductance measurements. In routine titrations, a wheatstone bridge made from a simple slide wire and a suitable fixed resistance is sometimes used. In the present experiment, the electrical equipment and methods which are described in experiment 30 are to be used, except that a different type of conductance cell is required. Any cell may be used which permits of stirring by shaking or otherwise and to which the reagent can be added from a buret. The cell, which is represented by figure 57, is a convenient modification of the simple Ostwald type (M, 471, figures 79 and 80). In it the electrodes are supported by the glass stopper, which is ground to fit the cell. Conductimetric titrations can also be made in an ordinary beaker with the aid of a simple pair of dipping electrodes (F and W, 166). When CO_2 has to be excluded from the cell, it is convenient to stir the solution with

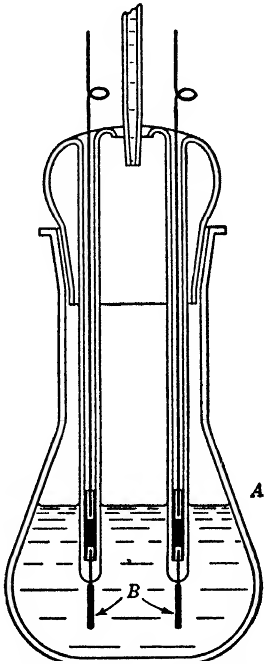

FIGURE 57. CONDUCTANCE CELL OF MODIFIED OSTWALD TYPE

CO_2-free air. It is usually convenient to avoid a large increase in volume during the titration by titrating with a reagent which is 10 or 20 times as concentrated as the unknown. This may require the use of a microburet.

The present experiment consists of two titrations; the first of a strong acid and the second of a weak acid, both with standard NaOH. For a number of other interesting and practical possibilities, see Kolthoff, P_H and Electro Titrations, 141–51.

Apparatus and Materials: An oscillator and conductivity bridge, as described in experiment 30; a special conductance cell for titrations; and a microburet. About 75 ml. each of standard 0.010 *N* HCl and CH_3COOH, 25 ml. of standard 0.20 *N* NaOH.

Procedure: Clean and dry the cell vessel, *A*. Do not dry the electrodes, *B*, but rinse them with a little of the 0.010 *N* HCl and remove the excess acid by touching them to a sheet of clean filter paper. Pipet exactly 50 ml. of the 0.010 *N* HCl into the cell vessel, and replace the electrodes. Set up and connect the oscillator and conductivity bridge (193, 196). Note the temperature of the conductance cell; or, better, keep it in a 25° thermostat while performing the titration. Measure (196–7) the resistance of the cell carefully. Add ten 0.50 ml. portions of the 0.20 *N* NaOH from the microburet, stirring the solution and measuring the resistance of the cell after each addition. The solution can be stirred conveniently by grasping the cell by its neck and giving it a short whirling motion, similar to that used in stirring the contents of an erlenmeyer flask.

Rinse and dry the cell vessel, and pipet 50 ml. of 0.010 *N* CH_3COOH into it. Titrate this sample, following the procedure which was used with the HCl solution.

Computations: At 25°C. the equivalent conductance, Λ, of 0.0100 *N* HCl is 412.0, and for concentrations in this immediate range (say, from 0.008 to 0.012 *N*) it can be represented by the following empirical formula—

$$\Lambda = 424.8 - 128\, N^{1/2}$$

where N is the normality Using this relation, compute Λ and κ, the specific conductance, for the standard HCl solution. From this value and the corresponding measured resistance, compute the cell constant, K (M, 471–2). Then compute the specific conductance corresponding to each measurement of the resistance.

For each titration, plot the specific conductance as a function of the volume of NaOH added. In routine titrations it is common practice to plot the resistance of the cell or even the bridge reading in arbitrary units, thus avoiding the computation of the specific conductance. Note the volumes at which the breaks occur in the curves, and compare these to the endpoints computed from the known concentrations of the solutions. Discuss the forms of the curves.

done graphically by plotting log C against the square root of the ionic strength for the measurements in water and in $NaNO_3$ solutions, expts. 1 to 4. It may also be done analytically by substituting in the Debye-Hückel relation (M, 529)

$$\log C_0 = \log C - \frac{0.5045\, S^{1/2}}{1 + 3.283 \times 10^7 a S^{1/2}}$$

where a is a constant which must be determined from the experimental data. From the relation,

$$\gamma = C_0/L^{1/2}$$

compute the mean activity coefficient γ for experiments 1 to 6. For these six experiments tabulate the following quantities: concentration of the added electrolyte, titre, solubility, ionic strength, solubility product, and mean activity coefficient.

Neglecting the ionization constant of CH_3COOH and assuming that the mean activity coefficient of $AgOOC \cdot CH_3$ is equal to unity, compute the solubility of $AgOOC \cdot CH_3$ in the HNO_3 solution (No. 7) from your value for *Co*. Repeat the computation assuming that the mean activity coefficient has a value in this solution equal to that found for a $NaNO_3$ solution of the same ionic strength. Neglecting the dissociation of $Ag(NH_3)_2^+$, compute the solubility of $AgOOC \cdot CH_3$ in NH_4OH (No. 8); first, assuming that the mean activity coefficient is equal to unity, and second, that it has a value similar to that found for a $NaNO_3$ solution of the same ionic strength. Discuss quantitatively the errors introduced by neglecting the ionization of CH_3COOH in No. 7, and the hydrolysis of CH_3COO^- in Nos. 1 to 4.

Experiment 33

DETERMINATION OF AN INDICATOR CONSTANT AND SOME PROPERTIES OF BUFFERED SOLUTIONS

A solution containing a weak base and its salt in a definite proportion has a fixed hydroxide ion, and therefore hydrogen ion, concentration. When the concentrations of the base and salt are comparable, the hydrogen ion concentration of the solution is but little affected by dilution or by the addition of a small amount of any acid or base (M, 521–23; K and S, 43–6). Such a solution is called a buffer solution. An indicator is a weak acid or base having different characteristic colors in the ionized and unionized forms (M, 536–43; K and S, 445–51). Although care must be taken in using an indicator in an unbuffered solution which is near the neutral point, the weakly acidic (or basic) indicator cannot appreciably change the hydrogen ion concentration of a buffered solution.

Thymol blue, the indicator which is used in this experiment, is a weak acid, which is partly converted from its yellow acid form to its blue salt form in an NH_4OH–NH_4Cl solution. In the interpretation of the results of the experiment, thymol blue is regarded as having a characteristic constant, K_I, which is defined by the equilibrium equation—

$$K_I = (H^+)\frac{X}{1 - X}$$

where X represents the fraction of the indicator existing in the blue salt form, $1 - X$ the fraction in the unionized yellow form, and (H^+) the molar concentration of the hydrogen ion. The value of K_I varies slightly with the total salt concentration, since in writing the indicator equation the activity coefficients (M, 503) of the several species were neglected. The alcohol contained in the stock solution of indicator likewise slightly affects the value of K_I. Both of these effects are to be neglected in the present experiment.

In this experiment, K_I for thymol blue is to be measured in terms of the known value of the ionization constant of NH_4OH.

This is done by determining colorimetrically the ratio of the ionized to the unionized form of the indicator which is present in an NH_4Cl–NH_4OH buffer solution of known concentration. A few additional experiments are included to demonstrate the characteristic properties of a buffer.

Since thymol blue is a two-color indicator, the usual apparatus of colorimetry, colorimeters, Nessler tubes, etc. (R and R, vol. II, 252–8) cannot be used to determine the relative concentrations of its two forms. The measurements can be made with a spectrophotometer (W, 276–88; R and R, vol. II, 304–6; D, M, and W, 64–7) or with a special two-color colorimeter (W, 861; Snell and Snell, Colorimetric Methods of Analysis, pp. 702–4, Van Nostrand, 1936; or Kolthoff and Furman, Indicators, pp. 154–9, Wiley, 1926). However, the measurements can be made with sufficient accuracy by means of a simple comparator block (figure 58) and a series of standard solutions, and this is the method which is to be used in the present experiment.

Apparatus and Materials: A comparator block, and 30 matched test tubes whose inside diameters do not differ by more than 2 or 3%. About 20 ml. of a 0.04% solution of thymol blue in 20% alcohol, 50 ml. each of 0.10 *M* solutions of NH_4OH and NH_4Cl, 25 ml. each of 0.10 *M* NaOH and HCl.

Procedure: Boil about half a liter of distilled water and allow it to cool in a loosely stoppered flask. Use this boiled water to make up the several solutions required in this experiment. Dilute part of the 0.10 *M* NaOH and HCl solutions to prepare 50 or 100 ml. each of 0.010 *M* NaOH and 0.0010 *M* HCl. Since an excess of these reagents is to be used in this experiment an error as great as 5% in their concentrations will not affect the results.

Mark two series of 10 matched test tubes (20 in all) with numbers running from 1 to 10. Using a small buret or graduated pipet, add 0.10 ml. of the stock indicator solution to the first tube of each series, 0.20 ml. to the second, 0.30 ml. to the third, and so on until you have two series of 10 tubes containing amounts of indicator solution increasing by a constant increment from 0.10 ml. to 1.00 ml. To each tube of one series add 1.0 ml. of 0.010 *M* NaOH, and to each of the other series add 1.0 ml. of 0.0010 *M* HCl. More concentrated acid should not be used since thymol blue undergoes a second color change in strongly acid solution. Dilute each standard to 10.0 ml. with boiled distilled water. If it is not possible to use the standards within an hour or two of the time of their preparation, the basic standards should be stoppered tightly to protect them from the CO_2 of the air. These two series of tubes constitute a series of color standards. In the acid standards the indicator is (practically) all in the unionized yellow form; in the basic standard it is all in the blue ionized form. By allowing light to pass through a basic tube containing 0.2 ml. of indicator and an acid tube containing 0.8 ml. of indicator, the resulting color is the same as that of a tube containing 1 ml. of indicator 80% of which is in the unionized form. The standard tubes are always to be used in pairs, so that the light passes through an acid and basic tube the total amount of indicator in which is 1 ml.

To determine the indicator constant perform the following experiments. Add 1 ml. of the indicator solution to each of four numbered test tubes. To three of these add 5 ml. of 0.10 *M* NH_4Cl and to the fourth 4 ml. To the first add 1 ml., to the second 2.5 ml., to the third 4 ml., and to the fourth 5 ml. of 0.10 *N* NH_4OH. Add sufficient boiled distilled water to make the volume of each of these 10 ml. Place the first buffered solution and a test tube of water in the two center holes of the comparator block. By comparing the color of this solution with that of the appropriate pairs of standard solutions, placed on either side of it, estimate what fraction of the indicator is in the ionized form. Repeat this comparison for the other three buffered solutions.

To demonstrate the action of a buffer in greatly reducing the change in H^+ concentration due to the addition of a small amount of acid or base, perform the following experiments. Add 1 ml. of the indicator solution to each of four numbered test tubes. To each of two of the tubes add 4 ml. of 0.1 *N* NH_4OH and 5 ml. of 0.1 *N* NH_4Cl solution. Add 9 ml. of boiled distilled water to each of the other tubes, and then adjust these solutions to about the same P_H as the buffered solutions by adding one drop (not more than 0.03 ml. from a pipet) of 0.010 *N* NaOH solution. Place one of the buffered solutions in the comparator block, and estimate what fraction of the indicator is in the ionized form. Add 0.10 ml. of 0.10 *N* HCl to the solution, stir, and again estimate what fraction of the indicator is in the ionized form. Repeat the experiment using the other buffer solution, but this time add 0.10 ml. of 0.10 *N* NaOH instead of the HCl. Perform a similar pair of experiments using the two tubes containing the dilute NaOH solution.

Computations: Compute the H^+ concentration of each of the first four buffered solutions, assuming that all of the salts present are completely ionized and that the ionization constants of water and NH_4OH are 1×10^{-14} and 1.8×10^{-5}, respectively. (For more exact work look up the values of these constants corresponding to the temperature of the solutions used.) From the H^+ concentration and the estimated degree of ionization of the indicator, compute the indicator constant, K_I, for each determination. Prepare a table containing values of the concentrations of NH_4OH, NH_4Cl, and H^+, of the P_H, of the degree of ionization of the indicator, and of the indicator constant, for each of the four experiments.

Compute the average value of the indicator constant. Using this value, and the estimated degree of ionization compute the H^+ concentration (or where necessary, its maximum or minimum limiting value) for each of the buffered and unbuffered solutions before and after adding a strong acid (or base). If the indicator is all in one or the other form, this indicates that the P_H of the solution is beyond the indicator range (M, 541–2). It is therefore not possible to determine the P_H, but it may be concluded that the P_H is greater or less than a certain value (the limiting value).

Using the ionization constants of NH_4OH and H_2O, compute the H^+ concentration for each of these six solutions. Compare these computed values with the values (or limits) based upon the experiments.

USE OF THE COLOR COMPARATOR

The color comparator is designed to facilitate the determination of the ratio of the concentrations of two differently colored substances which exist at a known total concentration in a solution, by the visual comparison of the color of this solution to that of suitably chosen color standards. For use with an ordinary comparator block, the standards are colored solutions contained in test tubes, which have been selected for constancy of internal diameter. Two series of color standards are required, each of which contains only one of the colored substances. In each series, the concentration of the colored substance is increased by a constant increment from zero to a value equal to the sum of the concentrations of the colored substances present in the unknown. Ten tubes in each series are usually sufficient. The standards are always used in pairs; one being chosen from each series so as to keep the sum of the concentrations of the colored substances equal to that in the unknown.

The comparator block (figure 58) is a wooden block containing six vertical holes (V_1 to V_6), large enough to admit the test tubes, and three smaller horizontal holes (H_1 to H_3) each of which passes through a pair of the vertical holes. A piece of frosted or milk glass covers the opening of the horizontal holes on one side of the block. The tubes containing the unknown and the selected pairs of standards are placed in vertical holes, and the colors are matched by looking simultaneously through the three horizontal holes when the block is placed in front of a uniform white light at a distance from the eye.

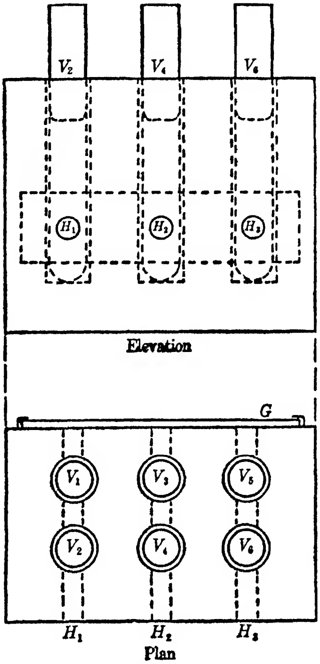

Figure 58. Comparator Block for Two-Color Colorimetry

The tube containing the unknown solution and a second filled with distilled water are placed in the center holes (V_3 and V_4). Tubes containing two consecutive pairs of standards are placed in the pairs of holes V_1, V_2 and V_5, V_6. The colors are compared, and the pairs of standards changed until the color appearing in the center horizontal hole is intermediate to those in the two outer holes. The color of the unknown is then estimated (to a fifth of the standard increment) and the concentration ratio computed.

Experiment 34

DETERMINATION OF THE DISSOCIATION CONSTANT OF TRIIODIDE ION BY PARTITION MEASUREMENTS

Iodine which is dissolved in moderately concentrated iodide solutions exists largely as the triiodide ion, I_3^-. The value of the dissociation constant, K, for this ion is given by the following equation

$$K = \frac{(I_2)(I^-)}{(I_3^-)} \times \frac{\gamma_{I_2}\gamma_{I^-}}{\gamma_{I_3^-}}$$

For dilute solutions the activity factor, $\gamma_{I_2}\gamma_{I^-}/\gamma_{I_3^-}$, is approximately equal to unity. (Why?) In the present experiment the equilibrium constant is to be determined for solutions prepared by shaking a known solution of KI with a solution of I_2 in CCl_4. In the resulting solution, the total iodide, $(I^-) + (I_3^-)$, is known; the total iodine, $(I_2) + (I_3^-)$, can be determined by titration with a standard $Na_2S_2O_3$ solution, and the concentration of the free iodine, (I_2), can be determined by distribution measurements (M, 349–54; W, 111). Similar distribution measurements have been used to determine the equilibrium constants of such processes as the ionization of weak acids and bases, the association of carboxylic acids in non-polar solvents, and the dissociation of various complex ions.

Apparatus and Materials: Six tall glass-stoppered bottles of approximately 500 ml. capacity. About 600 ml. of 0.100 M KI solution, 250 ml. of a 0.06 M solution of I_2 in CCl_4, 100 ml. of CCl_4, 250 ml. of standard 0.10 N $Na_2S_2O_3$ solution, and 25 ml. of a (tested) starch solution.

Procedure: Number the 6 bottles. Put 200 ml. of distilled water in each of the first 3, 200 ml. of 0.1 M KI in the fourth and fifth, and 50 ml. of 0.1 M KI and 150 ml. of water in the sixth bottle. Add 50 ml. of a 0.06 M solution of I_2 in CCl_4 to the first, fourth, and sixth bottles; 25 ml. of solution and 25 ml. of CCl_4 to the second and fifth; and 15 ml. of solution and 35 ml. of CCl_4 to the third. Stopper the bottles and shake them vigorously. Then fasten them in a 25° thermostat, so that they are immersed up to their necks in the thermostat water. Allow them to remain in the thermostat from 1 to 2 hours. At frequent intervals, remove the bottles one at a time, shake them vigorously for 1 or 2 minutes, and then return them to the thermostat. Before removing the samples for analysis, let each of the bottles remain in the thermostat for at least 20 minutes after its last shaking to allow the liquid layers to separate completely.

With the aid of a volumetric flask and a pipet, prepare 100 ml. of a 0.0100 *N* $Na_2S_2O_3$ solution from the standard 0.100 *M* solution. After the two liquids in the first bottle have separated into clear homogeneous layers, pipet a 50 ml. sample from the aqueous layer into a glass-stoppered 250 ml. erlenmeyer flask (or an iodine flask) which contains 10 ml. of 0.1 *N* KI and 1 ml. of starch solution (K and S, 618–9). It is important to avoid contamination of this sample by the CCl_4 layer, since in the first 3 mixtures the I_2 is so much more concentrated in the non-aqueous layer that even a drop of the CCl_4 solution would introduce an appreciable error in the titration of the aqueous phase. Pipet a 25 ml. sample of the CCl_4 layer into a second stoppered flask, which contains about 25 ml. of 0.1 *N* KI and 1 ml. of starch solution. To minimize contamination by the aqueous layer, blow a slow stream of air through the pipet while it is being introduced into the solution. Titrate each of these samples with the appropriate thiosulfate solution. In the two-phase titration, shake the flask vigorously after adding each portion of the thiosulfate solution. Analyze each phase of the other 5 bottles in the same way. If time permits, perform duplicate titrations.

Computations: Compute the total iodine concentration, $(I_2) + (I_3^-)$, for each of the 12 samples. Compute the partition coefficient for the first 3 mixtures. Using the average of these three values of the partition coefficient, compute the concentration of free iodine, (I_2), in the aqueous layers of the last three mixtures. For these same three solutions, compute the concentrations of the I^- and of the I_3^-, and the dissociation constant of the I_3^-. For the first three experiments, tabulate the following data: titration volumes for each phase, molar concentration of iodine in each phase, and distribution coefficient. For the last three experiments, tabulate the following data: titration volumes for each phase, molar concentration of the total titratable iodine in each phase, initial concentration of KI in the aqueous layer, the equilibrium concentrations of I_2, I_3^-, and I^- in the aqueous solutions, and the dissociation constant of the I_3^-.

Experiment 35

CONCENTRATION CELLS INVOLVING ZINC AMALGAMS AND ZINC CHLORIDE SOLUTIONS

Measurements of the EMF, or electromotive force, of cells are commonly made to determine either the free energy of a chemical reaction or the concentration, or more exactly the activity, of some substance occurring in the cell. Cells which are designed for the latter purpose are called concentration cells. In this experiment, four concentration cells which illustrate the principal types are to be constructed and measured.

The EMF of the first cell,

$$Zn \cdot Hg(2.0\%) \mid ZnCl_2(0.25\ M) \mid Zn \cdot Hg(0.20\%)$$

is determined by the ratio of the activities, or approximately of the concentrations, of the Zn in the amalgam electrodes (M, 583–6). The EMF of the second cell,

$$Zn \cdot Hg(2.0\%) \mid ZnCl_2(0.025\ M), HgCl(S) \mid Hg \mid HgCl(S), ZnCl_2(0.25\ M) \mid Zn \cdot Hg(2.0\%)$$

which is of the double concentration type (M, 591–4), is determined by the ratio of the mean activities of the $ZnCl_2$ in the two solutions. For sake of convenience it is to be constructed and measured in two parts. The third cell is a concentration cell with liquid junction (M, 586–7).

$$Hg \mid HgCl(S),\ ZnCl_2(0.025\ M) \mid ZnCl_2(0.25\ M),\ HgCl(S) \mid Hg$$

The fourth cell is similar to the third except that a "salt bridge," a saturated solution of KCl, is introduced between the two $ZnCl_2$ solutions. This cell is of less theoretical interest than the preceding ones, since no exact equation for its EMF exists. However, cells of this type (particularly those which measure differences in H^+ concentration) are of great practical interest, especially in biological studies and in industrial control processes. In treating such a cell the usual procedure is to assume that the saturated KCl eliminates the liquid junction potential and that the EMF of the cell is determined solely by the ratio of the concentrations (activities) of the Cl^- ions.

In an exact investigation of these cells it would be necessary to exclude air, since it reacts directly with the zinc amalgams. However, the construction and measurement of a cell in the absence of air requires rather elaborate apparatus, and will not be attempted in the present experiment. The following procedure is capable of yielding results which are reproducible and reasonably accurate. The accuracy of the experiment may be improved by suspending the cells in a 25° thermostat.

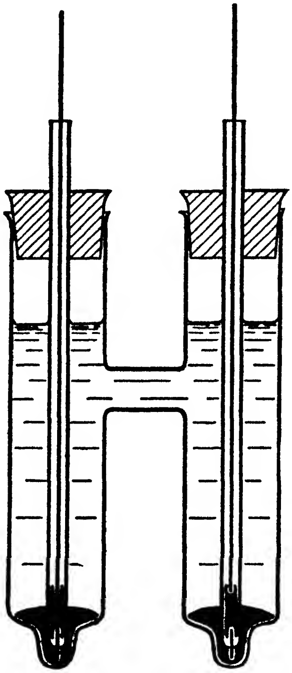

Figure 59. H-Cell

Apparatus and Materials: Potentiometer, galvanometer, rheostat, 2 dry cells, switch, 2 keys, 10,000 ohm resistance, and standard cell. H-cell, 3 half-cells, 4 Pt-point electrodes. About 10 ml. of 2.0% and 3 ml. of 0.2% Zn amalgam, 5 ml. each of pasty suspensions of calomel (W, 1056–7) in 0.25 *M* and 0.025 *M* $ZnCl_2$, 8 ml. of clean mercury, 150 ml. each of 0.25 *M* and 0.025 *M* $ZnCl_2$ solution.

Figure 60. Pt-Point Electrode

Procedure: Set up a "student" potentiometer and calibrate it with a standard cell (216–21).

Assemble the first cell (figure 59) by pouring a few ml. of 2.0% (by weight) Zn amalgam into one leg of a clean and dry H-cell and a similar amount of 0.2% amalgam into the other leg. To make electrical contact with amalgams use Pt-point electrodes (figure 60). These are prepared by sealing a short piece of Pt wire into one end of a piece of soft glass tubing. This seal must be water tight and mechanically strong, and the bare wire must project into the tube and beyond its end. Make electrical contact with the Pt wire by placing a few drops of mercury (sufficient to cover the wire) in the tube and then pushing a light weight bare copper wire down the tube. When the electrode is placed in the cell the projecting Pt wire should be entirely covered with the amalgam (W, 1057). Fill the cell vessel with 0.25 *M* $ZnCl_2$ solution. Connect the cell to the potentiometer (216–21) and measure and record its EMF at 3 minute intervals for 15 minutes. In this and in all cell measurements, record the polarity of the cell.

Each of the pair of cells, which constitutes the double concentration cell, should be made up as follows: Place a short piece of rubber tubing, provided with a pinch clamp, on the upper side arm of each of the half-cell vessels (figure 61). Add a few ml. of the 2% Zn amalgam, *A*, to one cell, and insert a Pt-point electrode, through a tightly fitting rubber stopper, into the amalgam. Fill this half-cell with 0.25 *M* $ZnCl_2$ by immersing the tip of the curved side arm into a small beaker containing the solution and sucking on the rubber tube. The rubber stopper and tube must make air-tight connection with the cell. Add a few ml. of mercury, *B*, to the other half-cell vessel, and cover it with a half centimeter layer of calomel, *C*, suspended in 0.25 *M* $ZnCl_2$. The calomel suspension is conveniently added by using a pipet with a coarse tip. Insert a Pt-point electrode through a rubber stopper and fill the vessel with 0.25 *M* $ZnCl_2$ by sucking. Support these two half-cells in clamps and immerse the tips of their side arms in 0.25 *M* $ZnCl_2$ contained in a small beaker. Determine the EMF as in the first part of the experiment. Remove the calomel half-cell and reserve it for use in the latter part of the experiment. Construct a cell similar to that just measured but containing 0.025 *M* $ZnCl_2$ throughout. Use the calomel suspension which was prepared with 0.025 *M* $ZnCl_2$ in the construction of this cell. Determine the EMF of the cell.

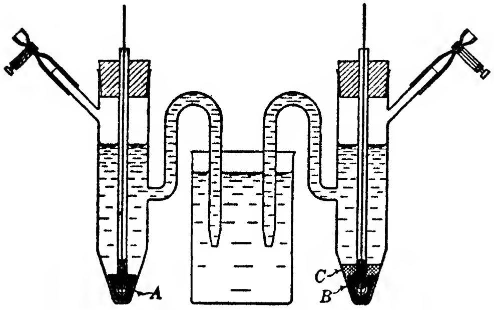

FIGURE 61

Insert the tips of the two calomel half-cells into a 0.25 *M* $ZnCl_2$ solution contained in a small beaker, and determine the EMF as before.

Replace the $ZnCl_2$ solution in the beaker with a saturated KCl solution and again determine the EMF.

Computations: Assume that the activity coefficients of Zn in 2.0% and 0.20% amalgams are equal and compute the EMF of the electrode concentration cell (M, 583–6).

$$\text{Zn} \cdot \text{Hg}(2.0\%) \mid \text{ZnCl}_2(0.25\ M) \mid \text{Zn} \cdot \text{Hg}(0.20\%)$$

Compare this computed value to the measured EMF of the cell. From this comparison, compute the ratio of the activity coefficients of Zn in the two amalgams. What effect would a change in the concentration of the $ZnCl_2$ solution have on the EMF of this cell?

Compute the ratio of the mean activity coefficients of $ZnCl_2$ in 0.025 *M* and in 0.25 *M* solution, using your measured value of the EMF of the double concentration cell.

$$\text{Zn} \cdot \text{Hg}(2.0\%) \mid \text{ZnCl}_2(0.025\ M),\ \text{HgCl(S)} \mid \text{Hg} \mid \text{HgCl(S)},\ \text{ZnCl}_2(0.25\ M) \mid \text{Zn} \cdot \text{Hg}(2.0\%)$$

When 2 faradays of positive electricity flow through this cell from left to right, 1 mole of $ZnCl_2$ is removed from the concentrated and introduced into the dilute solution.

$$\text{Zn}^{++}(0.25\ M\ \text{ZnCl}_2) + 2\ \text{Cl}^-(0.25\ M\ \text{ZnCl}_2) = \text{Zn}^{++}(0.025\ M\ \text{ZnCl}_2) + 2\ \text{Cl}^-(0.025\ M\ \text{ZnCl}_2)$$

The EMF corresponding to this process is (M, 589–92)

$$\begin{aligned} E &= \frac{RT}{2\,Fy} \ln \frac{a_{\text{Zn}^{++},C_2} \times a^2_{\text{Cl}^-,C_2}}{a_{\text{Zn}^{++},C_1} \times a^2_{\text{Cl}^-,C_1}} \\ &= \frac{RT}{2\,Fy} \ln \frac{(0.25)(2 \times 0.25)^2\gamma^3_{0.25}}{(0.025)(2 \times 0.025)^2\gamma^3_{0.025}} \\ &= \frac{3\,RT}{2\,Fy} \ln \frac{0.25\,\gamma_{0.25}}{0.025\,\gamma_{0.025}} \end{aligned}$$

where $\gamma_{0.25}$ and $\gamma_{0.025}$ are the mean activity coefficients of $ZnCl_2$ in 0.25 and 0.025 *M* $ZnCl_2$, respectively.

Using this value of the ratio of the mean activity coefficients and the observed EMF of the concentration cell with liquid junction,

$$\text{Hg} \mid \text{HgCl(S)},\ \text{ZnCl}_2(0.025\ M) \mid \text{ZnCl}_2(0.25\ M),\ \text{HgCl(S)} \mid \text{Hg}$$

compute the transference numbers of Zn^{++} and Cl^- in the $ZnCl_2$ solution (M, 586–7).

Assuming that the KCl bridge eliminates the liquid junction potential, compute the (approximate) ratio of the activity coefficients of Cl^- in 0.025 *M* and in 0.25 *M* $ZnCl_2$ solution, using the measured value of the EMF of the concentration cell with a salt bridge.

$Hg \mid HgCl(S),\ ZnCl_2(0.025\ M) \mid KCl\ (sat) \mid ZnCl_2(0.25\ M),$
$HgCl(S) \mid Hg$

The mean activity coefficient of $ZnCl_2$ in a 0.025 *M* solution is approximately 0.62 (Ladisalo, Gazz. chim. Ital. **64,** 261, 1934). Using this value compute E_0 for the cell

$$Zn \cdot Hg(2.0\%) \mid ZnCl_2(0.025\ M),\ HgCl(S) \mid Hg$$

What chemical reaction occurs when two faradays of positive electricity flow through this cell from left to right? State the mass action law for this reaction, giving the numerical value for the equilibrium constant.

USE OF THE STUDENTS' POTENTIOMETER

One of the simplest and most convenient ways of measuring the EMF of an easily polarizable cell is the potentiometric, or Poggendorf compensation, method (M, 563–5). The apparatus in its simplest form, which is diagrammed in figure 62, can be assembled from a uniform slide wire, *OPQ*, a working battery, *B*, a null point indicator such as a galvanometer, *G*, and a standard cell, *Std*. In use, the working battery sends a constant current through the uniform resistance, *OPQ*. The standard cell (M, 565–6) is placed in the circuit by means of the switch, *S*, and the contact is moved along the slide wire until the galvanometer shows no deflection. At this point the EMF of the standard cell, E_S, is equal to the drop in potential across the resistance, *OP*. Therefore, the total

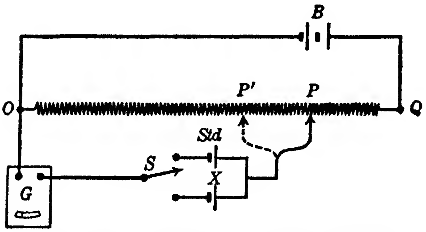

FIGURE 62: SIMPLE POTENTIOMETER CIRCUIT

potential drop across the resistance, OQ, equals $E_S(OQ/OP)$. Since the resistance is uniform, the potential drop per unit length is E_S/l_{OP}, where l_{OP} is the length of the wire OP. If the unknown cell, X, is put in the circuit, by throwing the switch to the other terminal, the sliding contact must be moved to some new position, P', to keep the galvanometer deflection zero. The EMF of the unknown cell, E_X, can now be computed by means of the equation

$$E_X = E_S \frac{l_{OP'}}{l_{OP}}$$

For sake of convenience, a "students' potentiometer" is commonly used in the routine measurement of the EMF of cells. The circuit included within the terminals, Ba^+, I, R, E^-, and E^+ (figure 63) is a simplified representation of a common form of the students' potentiometer. The two resistances ba and cd correspond to the slide wire, OQ, of figure 62. The resistance, ba, is made up of 15 equal resistances connected in series and arranged to be tapped off by means of the multiple contact switch, e. The uniform slide wire, cd, has a total resistance equal to that of one of the coils of the resistance, ba. The switch points, b to a, are numbered 0 to 1.5 with a uniform increment of 0.1, and the contact, f, is attached to a pointer moving on a circular scale, which reads from 0 at c to 0.100 at d. By means of these movable contacts, e and f, any

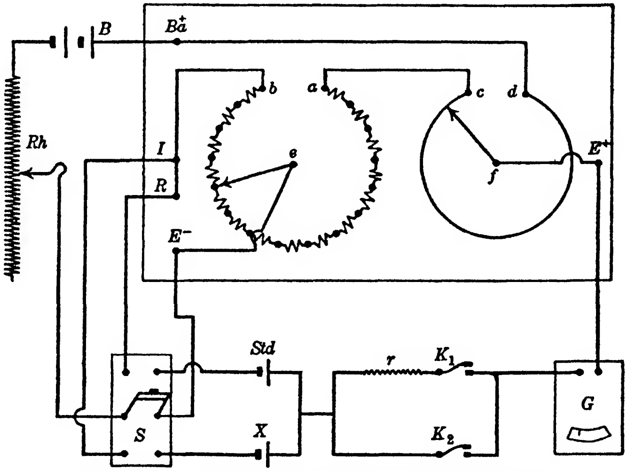

FIGURE 63. STUDENT'S POTENTIOMETER CIRCUIT

fraction of the total resistance, *bacd*, can be tapped off. The rheostat, *Rh*, is put in series with the working battery, *B*, to make it possible to vary the current flowing through the resistance of the potentiometer. While not essential, a double-pole double-throw switch, *S*, is used in this circuit. To prevent polarization of the cells and to safeguard the galvanometer against overloads, two keys, K_1 and K_2, have been introduced into the circuit. One of these, K_1, is connected in series with a resistance, *r*, of about 10,000 ohms. This key is depressed while the first rough adjustment of the contacts, *e* and *f*, is being made. After this approximate adjustment is made, the second key is closed while the circuit is adjusted more exactly. To facilitate the reading of the potentiometer it is customary to so adjust the current flowing through the resistance, *bacd*, that the sum of the readings of the pointers, *e* and *f*, is equal to the EMF of the cell in the circuit. This is done by introducing the standard cell, *Std*, into the circuit; setting the switch, *e*, at 1.0 and the rotary slider, *f*, at 0.0183; and then setting the rheostat, *Rh*, to some position which makes the deflection of the galvanometer zero even when the key, K_2, is closed. When calibrated in this way, the student potentiometer is capable of measuring EMF from 0 to 1.6 volts, with an apparent precision of 0.0001 volts.

It is sometimes necessary to measure the EMF of cells which give voltages higher than 1.6. For voltages less than 2.6, this may be done by connecting the unknown cell in opposition to a standard cell and measuring the EMF of the combination in the usual way. The desired EMF can then be obtained by adding the EMF of the standard cell to the measured value. However, it is usually more convenient to calibrate the potentiometer, in such a way that the range of measureable voltages is increased. This may be done by setting the indicators, *e* and *f*, so that the sum of their readings is equal to 1/2 (or some other simple fraction) of the EMF of the standard cell, and then adjusting the rheostat, *Rh*, until the galvanometer deflection is zero when the standard cell is in the circuit. In making this arrangement, a working battery of higher voltage than that used in the ordinary arrangement is necessary; if 2 dry cells were required for the 1.6 volt range, 4 cells would be needed for a 3.2 range. In using a potentiometer, which has been calibrated in this way, all of the readings must be multiplied by 2.

When small potentials are to be measured, the precision of the measurements can be increased by introducing a fixed resistance between the working battery and one end of the potentiometer resistance. However, this arrangement has the disadvantage that it requires a standard cell (or other source of potential) having an EMF within the range of the measurements, and such a standard is not commonly available in the laboratory. The process, of first calibrating the potentiometer in the usual way and then introducing a fixed resistance which is some known multiple of the potentiometer resistance, is not justifiable since it neglects the effect of the unknown and relatively inconstant internal resistance of the working battery. To avoid this difficulty an arrangement similar to that shown in figure 64 may be used. In this circuit, r_2 is equal to the resistance *OQ* and the r_1 is much greater than *OQ*. When contact is made between the terminals *C* and *M*, a certain fraction, say 10/11, of the total current passes through the resistance *OQ*. Under these conditions the rheostat, *Rh*, can be adjusted to make the potentiometer read directly in volts, as was done with the simple circuit, figure 63. If, after the rheostat has been set, the switch is thrown to connect the terminals *c* and *N*, only 1/11 of the current will flow through *OQ*, but the total current drawn from the battery will not change. The current now passing through *OQ* will be 1/10 as great as it was when the circuit was calibrated, and the total potential drop instead of being 1.6 volts will be 0.16 volts. Some commercial potentiometers are provided with arrangements of this sort which permit a one hundred fold change in their scale. However, it is not possible to take full advantage of this spread out scale for low voltages unless a more sensitive galvanometer is available than that which is commonly used with the ordinary arrangements of the potentiometer.

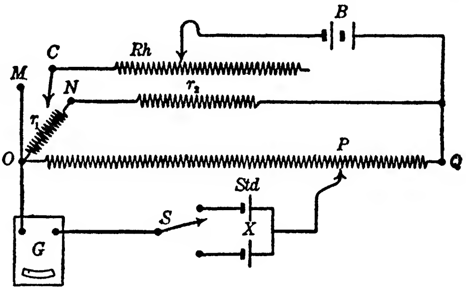

FIGURE 64. POTENTIOMETER CIRCUIT FOR LOW EMF'S

When a continuous indication of a changing EMF is desired, as in certain potentiometric titrations, a vacuum-tube voltmeter (D, M, and W, 433; Müller, Garman, and Droz, Experimental

Electronics, 163–87) can be used. The EMF of cells having high internal resistances, as those involving glass electrodes or non-aqueous solutions, can be measured with the aid of a vacuum-tube indicator, a suitable electrometer, or a circuit using a condenser and a ballistic galvanometer (compare Dole, the Principles of Experimental and Theoretical Electrochemistry, 211–20). For routine potentiometric titrations where the absolute value of the EMF is of little importance, a circuit in which the potentiometer is calibrated with a millivoltmeter can be used (D, M, and W, 201–2; Hildebrand, J. Am. Chem. Soc. **35**, 847 (1913)).

Apparatus and Materials: A students' potentiometer; a suitable galvanometer; a rheostat, preferably a 4-dial resistance box having a total resistance of 999.9 ohms; a double-pole double-throw switch; 2 keys; a fixed resistance of approximately 10,000 ohms; a standard cell; 2 dry cells; and copper annunciator wire for connections.

Procedure: Connect the apparatus as is indicated in figure 63. Set the switch, *e*, at the contact marked 1.0 and the indicator, *f*, at a point on the circular scale which makes the sum of the readings numerically equal to the EMF of the standard cell. If the EMF of the standard cell is not marked on its support, assume the average value of 1.0183 volts. Set the rheostat, *Rh*, at about 150 ohms and note the direction of the deflection of the galvanometer when the key, K_1, is depressed. Change the setting of the rheostat until the deflection of the galvanometer is no longer noticeable when K_1 is depressed. Then close K_2 and adjust the tenths dial of the rheostat until the galvanometer shows no deflection. If a balance is obtained with less than 100 ohms in the rheostat, this indicates that the dry cells are run down. It is advisable to replace the cells with fresh ones or to add a third cell. Recheck the setting of the rheostat against the standard cell at least every half hour, since changes in temperature or incipient polarization of the batteries is likely to result in a noticeable change in the potential drop across the potentiometer resistance. To measure the EMF of the unknown cell, throw the switch, *S*, to its other position, and leaving the rheostat unchanged adjust *e* and *f* until the galvanometer is not deflected when the key is depressed. As before, obtain an approximate balance using K_1 before closing K_2. Record the sum of the readings of *e* and *f* as the EMF of the cell. By comparison with the standard cell, note and record which pole of the unknown cell is positive. If, after the rheostat has been correctly balanced against the standard cell, the galvanometer deflects in the same direction for all settings of the potentiometer dials when the unknown cell is in the circuit, it is probable that the polarity of the cell is reversed. If this is observed, reverse the connections to the poles of the unknown cell. However, if it still proves impossible to get a balance and if the deflection of the galvanometer is now in the opposite direction, it indicates that the EMF of the unknown cell is greater than 1.6 volts. If at any time the galvanometer shows no deflection for a variety of settings of the potentiometer, it is very probable that there is a high resistance or poor contact in the circuit between the terminals E^+ and E^- (compare F and W, 189–92).

While a standard cell, such as is used for the calibration of a potentiometer, may be obtained commercially in a convenient form with its EMF certified, it may also be constructed in the laboratory from materials which are readily obtainable. Explicit directions for the construction of a standard cell are given in A Laboratory Manual of Physical Chemistry, by Mack and France, 237–43; also in R and R, vol. II, 453–5. The student who undertakes the construction of a standard cell should realize that extreme care must be taken in the purification of materials.

For ordinary measurements an inexpensive pointer galvanometer, with a sensitivity of approximately 1 microampere per mm. and a critical damping resistance of the order of 1000 ohms, is satisfactory. However, for measurements of low EMF's on the spread out scale of the potentiometer, or for measurements of cells with high internal resistances, the sensitivity of the galvanometer should be from 10 to 100 times greater and the critical damping resistance may be proportionately higher. For a general discussion of galvanometer characteristics, see Notes on Moving Coil Galvanometers, Leeds and Northrup Notebook 2; or D, M, and W, 365–6. In a permanent set up, the dry cells should be replaced by storage batteries.

Experiment 36

ELECTROMOTIVE FORCE AND THE EQUILIBRIUM CONSTANT

The equilibrium constant or the free energy of an ionic reaction may be determined either analytically or electrometrically. When the first method is used the reaction constituents are allowed to stand at a constant temperature until equilibrium has been attained, and then their concentrations are determined by analysis. When the second method is used a galvanic cell is so constructed that when current is allowed to flow through the cell the chemical reaction occurs in it. The equilibrium constant of the reaction can be computed from the observed electromotive force of the cell (M, 568–9, 599–607). In the present experiment the equilibrium constant, for the reaction

$$C_6H_4O_2 + 2\,Ag + 2\,H^+ = C_6H_4(OH)_2 + 2\,Ag^+$$

is to be determined by both methods.

Apparatus and Materials: A potentiometer, galvanometer, rheostat, 2 dry cells, switch, 2 keys, 10,000 ohm resistance, and standard cell. A small beaker or large-mouthed bottle provided with a two-hole rubber stopper, 2 half-cells, 2 platinum electrodes, and a 500 ml. round bottomed flask. About 0.1 gm. of quinhydrone, 5 gm. of hydroquinone, 2 gm. of finely divided Ag, 50 ml. each of standard 0.1 N $Na_2S_2O_3$, of 5% $AgNO_3$, and of a (tested) starch solution (K and S, 618–9), 75 ml. each of 6 N HCl and of 10% KI solution, 100 ml. of 0.100 M $AgNO_3$, and 300 ml. of 0.200 M HNO_3.

Procedure: (Part A. Potentiometric Determination.) Prepare a silver electrode by plating one of the platinum electrodes. Use a 5% $AgNO_3$ solution as the electrolyte, the other platinum electrode as the anode, and a dry cell as the source of current. The plating should require about 5 minutes, and, when complete, the electrode should be covered with a loose mass of fine silver crystals. Before using the electrode rinse it carefully with dilute HNO_3, but do not attempt to dry it. (For an alternative method see W, 1072–3.)

Since the cell is to be supported in a thermostat, it must be mechanically rigid and water tight (compare figure 65). Place a short piece of rubber tubing, provided with a pinch clamp, on the upper side arm of each half-cell vessel. Place the solid quinhydrone, *A*, in one half-cell and then insert the platinum electrode into it through a tightly fitting rubber stopper. Fill this half-cell with 0.100 *M* HNO_3 by immersing the tip of its curved side arm in the solution, contained in a small beaker, and sucking on the rubber tube. Insert the silver electrode, *B*, through a rubber stopper into the other half-cell, and fill this with a solution which is 0.100 *M* in respect to HNO_3 and 0.00100 *M* in respect to $AgNO_3$. Bring the two half-cells into electrolytic contact, by inserting their bent side arms through the holes of a two-hole rubber stopper into a small bottle, *C*, which is filled with 0.100 *M* HNO_3.

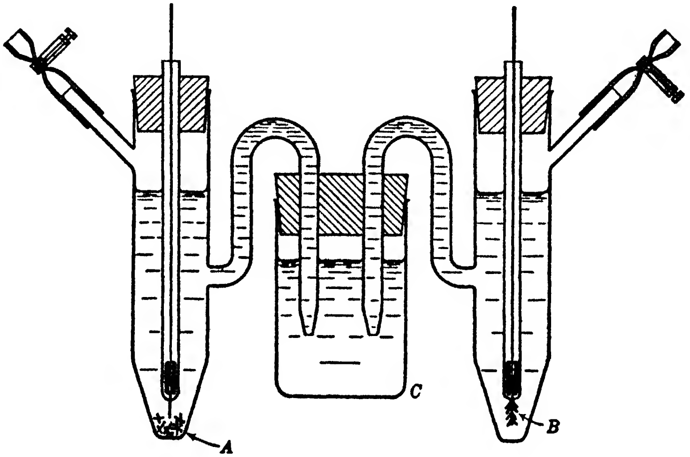

Figure 65

Support the cell in a 2 liter beaker, which is filled with water and provided with a thermometer and a hand stirrer. Adjust and maintain the temperature of the water at 25°C. Connect and adjust the potentiometer (216–21) and record its EMF (noting the polarity) at 5 minute intervals for about 30 minutes.

Change the temperature of the water in the beaker to 15°, and again measure and record the EMF of the cell, at 5 minute intervals, until it becomes constant.

(Part B. Analytical Method.) Prepare 300 ml. of a solution, 0.0250 *M* in respect to $AgNO_3$ and 0.1000 *M* in respect to HNO_3.

Weigh out and add to this solution sufficient hydroquinone to make its concentration 0.0250 *M*. Transfer this solution to a 500 ml. round bottomed flask, which contains a few glass beads to aid stirring and 2 gm. of finely divided Ag as a catalyst. Stopper the flask and set it in a shaker in a 25° thermostat. After the elapse of 20 minutes, stop the shaker for a few minutes to allow precipitated silver to settle and then remove a 10 ml. sample for analysis (see Livingston and Lingane, J. Chem. Educ. **15**, 320 (1938)). Start the shaker again, and allow a second 20 minute period to pass before taking another sample. Continue taking and analyzing samples at 20 minute intervals, until the constancy of the titer indicates that equilibrium has been reached. The rate of the reaction is strongly influenced by the condition of the Ag catalyst used; however, under the present conditions, at least 2 hours will be required for the titer to reach constancy.

The samples are to be analyzed for quinone as follows (Kolthoff and Menzel, Die Massanalyse, Vol. II, 492–4): Prepare 0.0100 *N* $Na_2S_2O_3$ solution by accurate dilution of standardized 0.1 *N* $Na_2S_2O_3$. Before removing each sample from the solution, prepare a 250 ml. erlenmeyer flask to receive it by adding 10 ml. each of 10% KI and 6 *N* HCl and from 2 to 5 ml. of starch solution. On adding the sample to this mixture the Ag^+ is precipitated as AgI and the quinone is rapidly reduced to hydroquinone. The liberated iodine is then titrated with thiosulfate to the starch endpoint. In a solution which is as strongly acid as this, I^- is rapidly oxidized by air to I_3^-. It is, therefore, necessary to prepare each mixture just before it is to be used and to titrate immediately after adding the sample. Agitate the solution continuously while adding the $Na_2S_2O_3$ solution. Determine the correction for the air oxidation of iodide by performing a titration as directed above, but adding 10 ml. of 0.10 *M* HNO_3 instead of the sample. Subtract the volume required for this blank titration from the titres of the other determinations (K and S, 287–8).

Computations: Since the cell was designed to reduce liquid junction potentials to a minimum, the observed EMF of the cell is related to the equilibrium constant of the reaction by the following equation (M, 568–9):

$$E = \frac{RT}{2Fy} \ln K - \frac{RT}{2Fy} \ln \frac{(\mathrm{Ag}^+)^2 \gamma^2_{\mathrm{Ag}^+} (\mathrm{H_2Q}) \gamma_{\mathrm{H_2Q}}}{(\mathrm{H}^+)^2 \gamma^2_{\mathrm{H}^+} (\mathrm{Q}) \gamma_{\mathrm{Q}}}$$

where Q stands for quinone and H_2Q for hydroquinone, the quantities in parentheses represent concentrations, and the γ's denote activity coefficients. Since quinone and hydroquinone are non-electrolytes, their activity coefficients (under the conditions of the experiment) may be taken as unity. While γ_{Ag^+} and γ_{H^+} are not equal to unity, it is very probable that no appreciable error is made by setting their ratio equal to one. It should be noted that this latter assumption is not generally true, but is approximately correct in the present case since H^+ and Ag^+ are both monovalent and occur in the cell in solutions of the same (relatively low) ionic strength. Making these assumptions, compute the equilibrium constants corresponding to the average EMF's measured at 25° and at 15°C.

From the measurements in the second part of the experiment, plot the corrected titer (i.e., ml. of $Na_2S_2O_3$ used) against time in minutes. Make a graphical estimate of the equilibrium value of the titer. From this, compute the equilibrium concentration of quinone, and combine this value with the known initial concentrations of Ag^+, H^+, and H_2Q to compute their equilibrium concentrations. Neglecting the activity corrections (for the reasons already discussed) compute the equilibrium constant for the reaction.

Compare the values and estimated probable errors of the equilibrium constants at 25° determined by the two methods. Compute the standard free energy, ΔF°_{298}, for the reaction. From the temperature coefficient of the cell, compute the heat, ΔH, of the reaction, using the Gibbs-Helmholtz relation (M, 569–70).

Experiment 37

POTENTIOMETRIC DETERMINATION OF THE ACTIVITY OF THE HYDROGEN ION

Either the P_H or the activity of the hydrogen ions, a_H, in a solution can be determined (approximately) by the use of a suitable concentration cell (M, 608–10; W, 1063–8). Theoretically the simplest cell which can be used for this purpose is one with two hydrogen electrodes—

$$\text{Pt, H}_2\text{ (1 atm)} \mid \text{H}^+(a_1) \parallel \text{H}^+(a=1) \mid \text{H}_2\text{ (1 atm), Pt}$$

In practice, the reference electrode, in which the activity of the H^+ is unity, is replaced by a normal calomel electrode (M, 574–5; W, 1056–8), and a saturated solution of KCl is used as a salt bridge (T, 820–1; W, 1060–2) to minimize the liquid junction potential (M, 587–90).

$$\text{Pt, H}_2\text{ (1 atm)} \mid \text{H}^+(a_1) \mid \text{KCl (sat)} \mid \text{KCl (1 }N\text{), HgCl (S)} \mid \text{Hg}$$

A hydrogen electrode consists of a Pt electrode which is covered with finely divided Pt (i.e., platinum black) and is immersed in a solution saturated with H_2. The Pt electrode is usually arranged to be partly or intermittently in contact with gaseous H_2. A wide variety of electrode vessels and types of electrodes have been suggested or are used for special purposes (see Clark, The Determination of Hydrogen Ions, 290–302). The electrode which is used in the present experiment is of the simple or Hildebrand type (figure 66).

For routine measurements, the quinhydrone electrode (M, 579–80; W, 1073–5; also Clark, loc. cit., 404–22) is frequently used in place of the hydrogen electrode. This electrode can be prepared very simply by adding a few milligrams of solid quinhydrone, an equimolar compound of quinone and hydroquinone, to the acid solution and inserting a gold or bright platinum electrode. This electrode attains equilibrium very rapidly, but has the disadvantage that it cannot be used in solutions of P_H greater than 8.5, since quinone decomposes rapidly in basic solution.

The antimony electrode can be used for approximate P_H determinations (Kolthoff and Furman, Potentiometric Titrations, 235–42). Its chief application is to certain industrial control operations. The electrode is prepared by inserting a stick of pure Sb into a solution, which may be either acidic or basic, and adding to the solution a small amount of pure Sb_2O_3. For titrations or rough measurements a rod of Sb lightly coated with Sb_2O_3 serves as an electrode. The half-cell reaction corresponding to this electrode may be written

$$Sb + H_2O + 3\,Fy = SbO^+ + 2\,H^+$$

In recent years the glass electrode has come into very wide use. It can be used in either acidic or basic solutions, and is not affected by oxidizing or reducing agents. However, a cell which contains a glass electrode has a high internal resistance and requires a more sensitive indicating device than the ordinary galvanometer. For this reason it will not be included in the present experiment. For an excellent discussion of the glass electrode see Dole, The Principles of Experimental and Theoretical Electrochemistry, 427–42; also Kolthoff and Furman, loc. cit., 247–52. Directions for a laboratory experiment using the glass electrode are given in D, M, and W, 205–11.

In the present experiment the EMF of each of the following cells is to be measured at 25°C., first when the HCl is 0.5 *M*, and second when it is 0.05 *M*.

$$\text{Pt, } H_2 \text{ (1 atm)} \mid \text{HCl(C)} \mid \text{KCl (sat)} \mid \text{KCl } (1\,N)\text{, HgCl(S)} \mid \text{Hg} \qquad \text{(A)}$$

$$\text{Pt, } H_2 \text{ (1 atm)} \mid \text{HCl(C)} \mid \text{HCl(C), quinhydrone (S)} \mid \text{Au} \qquad \text{(B)}$$

$$\text{Au} \mid \text{quinhydrone (S), HCl(C)} \mid \text{KCl (sat)} \mid \text{KCl } (1\,N)\text{, HgCl(S)} \mid \text{Hg} \qquad \text{(C)}$$

In a second part of the experiment, the cell A is to be used in a potentiometric titration of HCl with NaOH. The same cell may also be used to study the properties of buffer solutions.

Apparatus and Materials: A potentiometer and auxiliary equipment (220), a H_2 tank (W 1058–9), 2 half-cell vessels, a small large-mouthed bottle, a H_2 electrode, a Pt-point electrode, a Au electrode. 250 ml. of 0.50 *M* HCl, 100 ml. each of saturated and of 1.00 *N* KCl, 50 ml. of 0.500 *N* NaOH, 5 ml. of a pasty suspension of calomel in 1.00 *N* KCl, 4 ml. of clean Hg, about 0.5 gm. of quinhydrone.

Procedure: Prepare the calomel half-cell as follows. Place a short piece of rubber tubing equipped with a screw clamp on the side arm, *A* (figure 66), of the half-cell vessel. Set the Pt-point electrode in a one-hole rubber stopper which fits the top of the half-cell. Pour about 4 ml. of clean Hg, *B*, into the vessel, and insert the electrode so that its Pt point is covered by the Hg. With the aid of a glass tube or a pipet with a coarse tip, add enough of the HgCl suspended in KCl to form a layer, *C*, about 1 cm. thick on top of the Hg. Slip the stopper into place, and fill the cell with 1.00 *N* KCl by immersing its tip, *D*, in the solution and sucking on the tube, *A*. Then close the screw clamp. If the cell has been properly constructed, it will not leak. Fit the small large-mouthed bottle, *E*, with a 2-hole rubber stopper. Fill the bottle nearly to the top with saturated KCl solution. Make a U-tube, *F*, from 4 or 5 mm. tubing and insert one leg of it through the stopper. Put the tip, *D*, of the half-cell through the other hole. Push the stopper into place. This should force some of the solution out through the U-tube, thereby filling it. A salt-agar bridge (234) may be conveniently substituted for the inverted U-tube. If none of the glass-to-rubber joints leak, this assembly may be used throughout the experiment. However, it should not be kept for more than a few hours, since diffusion will gradually change the concentration of the KCl solution which is in contact with the HgCl and Hg.

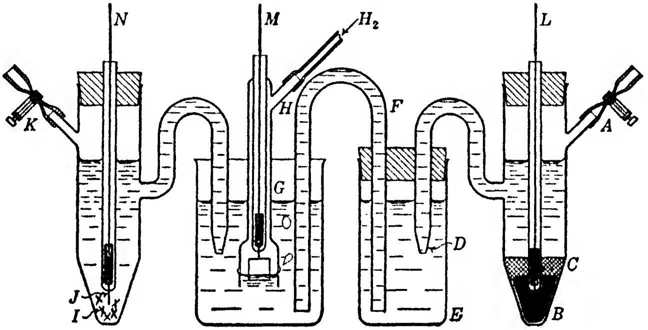

Figure 66

If the H_2 electrode has been properly platinized and has been kept in distilled water or dilute hydrochloric acid it may be used directly without further treatment. Rinse it with a little of the

0.50 *N* HCl and then support it in a small beaker containing this solution. Attach the side tube, *H*, of the electrode to the H_2 tank by a short piece of clean rubber tubing. The inside of this tubing should be free from sulfur dust; if new tubing is used, it should be washed with NaOH solution. Before attaching the rubber tube to the side tube, *H*, insert it into a beaker of clean water and cautiously open the needle valve on the H_2 tank until a slow steady stream of bubbles is formed. (Note: the tank H_2 may require purification. A properly constructed electrolytic generator is a convenient source of hydrogen for use with a hydrogen electrode. Hydrogen from a Kipp generator requires careful purification, and is not recommended.)

Prepare the quinhydrone electrode as follows. Place about 0.1 gm. of solid quinhydrone, *I*, in the bottom of a half-cell vessel. Insert a Au or bright Pt electrode, *J*, into the cell through a one-hole rubber stopper. Fill the cell with 0.50 *M* HCl by sucking on the rubber tube, *K*. Close the screw clamp on the rubber tube and insert the tip of the side tube into the beaker containing the H_2 electrode. To complete the cell insert the free arm of the inverted U-tube, *F*, into the beaker. Be sure that no air bubbles are trapped in the inverted U-tube or in the bent side tubes of the half-cell vessels.

Set up a student potentiometer and calibrate it with a standard cell (216–21). The experimental arrangement of the cell makes possible the simultaneous measurement of cells, A, B, and C (227). To determine the EMF of cell A, connect the terminals *L* and *M* to the potentiometer, and make the measurement in the usual way. Similarly, the terminals *M* and *N* correspond to cell B, and *L* and *N* to cell C. To facilitate changing the connections, the three wires may be inserted in mercury cups, and contact with the potentiometer made by dipping the leads from the switch, *S* (figure 63), into the appropriate pair of cups. The mercury cups may be three small holes in a block of paraffine, as in figure 67, or may be three short pieces of glass tubing sealed at one end and supported in holes drilled in a block of wood. Measure and record the EMF of each of these cells at 3 minute intervals for at least 15 minutes or until they become constant. The EMF of cell C should become constant within a few minutes; the other cells which involve the H_2 electrode may require as much as 30 minutes.

If these cells do not reach equilibrium approximately in this time, it is probable that the H_2 electrode has been poisoned. In this case, it should be removed from the cell and cleaned, or better replatinized. (Note: the H_2 electrode is readily poisoned by contact with mercury, calomel, many organic substances, the salts of certain heavy metals, etc. (W, 1068–9). It should not be touched with the hand or allowed to come in contact with the desk. Merely drying an electrode will usually render it inoperative.)

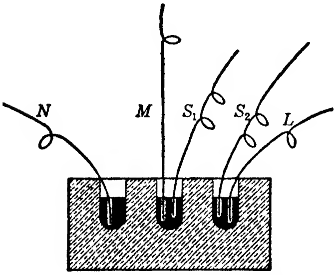

FIGURE 67. MERCURY-CUP SWITCH

Frequently, though not always, H_2 electrodes which have been dried but are otherwise uncontaminated can be restored to activity by a washing with alcohol and a thorough rinsing with distilled water. Contaminated electrodes can sometimes be regenerated by thorough cleaning with a strong oxidizing agent, followed by efficient rinsing and saturation with H_2. To clean an electrode allow it to remain in warm concentrated HNO_3 for 5 or 10 minutes. Next, rinse very thoroughly with distilled water. Finally, place it in a small beaker of dilute H_2SO_4 with a Pt-point electrode, connect the H_2 electrode to the negative pole of a dry cell and the other electrode to the positive pole, and liberate H_2 on the electrode for several minutes. If this process fails to regenerate the electrode it will be necessary to replatinize it. This may be done as follows. Dissolve off the Pt black with aqua regia under a fume hood. Watch the process, and remove the electrode as soon as it appears bright. Wash it thoroughly with distilled water. Place the H_2 electrode and a Pt-point electrode in a chlorplatinic acid solution, which contains 0.5 gm. of Pt in 100 gm. of solution. With the aid of two dry cells or a 4 volt storage battery, platinize the electrode for about 5 minutes or until it is covered with a uniform, adherent coating of finely divided Pt. Remove the electrode and rinse it thoroughly. Then saturate it with H_2 in a dilute H_2SO_4 solution as described above. The coating should be dark grey or black, but should not be thick or loose. If the coating is noticeably uneven, the electrode will probably be unsatisfactory and should be throughly cleaned and replatinized. (Note: it is not necessary to add Pb salt to the platinizing solution, nor is it advantageous to intermittently reverse the direction of the current.) For a more complete discussion of the technique of preparing H_2 electrodes see Clark, loc. cit., 285–90; W, 1059–60.

For the second part of the experiment, prepare 250 ml. of 0.050 *M* HCl by accurate dilution of the 0.50 *M* solution. Replace the 0.50 *M* HCl in the beaker, *Q*, and in the quinhydrone half-cell with 0.050 *M* solution. Use a fresh sample of quinhydrone. Reassemble the cell, and determine the EMF's of cells A, B, and C as before.

Measure exactly 100 ml. of 0.050 *M* HCl into a small beaker. Without interrupting the flow of H_2, quickly transfer the H_2 electrode to this beaker, and then insert the inverted U-tube, *F*, of the calomel-cell salt-bridge combination. The quinhydrone electrode is not used in this part of the experiment. Fill a 25 ml. buret with standardized 0.50 *M* NaOH solution. As soon as the EMF returns to its equilibrium value, record it, and then add 1.00 ml. of the NaOH solution. Stir the solution with a glass rod for about 10 seconds, then allow it to remain for about 1 minute before measuring the EMF. Since stirring the solution introduces O_2 from the air, and thereby lowers the EMF of the H_2 electrode, it will be necessary to follow this procedure of stirring and waiting in order to attain consistent results. This difficulty can be eliminated or at least minimized by using a closed titration vessel from which air is excluded. Record the EMF, add a second 1 ml. portion of 0.50 *M* NaOH, and proceed as before. Continue this procedure until the titration is within 1 ml. of the endpoint, then add a 0.5 ml. portion and determine the EMF. Next add 10 portions of 0.1 ml. each, measuring the EMF after each addition. Following this, add a 0.5 ml. and then, at least, four 1 ml. portions.

Computations: Tabulate the results of your experiments on cells, A, B, and C; including in the table the equilibrium values of the EMF, the concentration of the HCl, and the chemical equations which represent the cell reactions. Assuming that the EMF of the normal calomel half-cell is 0.2805 volts and that the saturated KCl bridge eliminates the liquid junction EMF, compute, from the data contained in your table, the following quantities: the standard half-cell EMF of the quinhydrone electrode, the a_H and the P_H of 0.050 *M* and 0.050 *M* HCl.

From the results of the titration, prepare a table including the (cumulative) volumes of NaOH added, the measured values of the EMF, and the corresponding (computed) values of the a_H. Compute and add to the table values of the molar concentration of the H^+ and of the logarithm of this concentration corresponding to each volume of NaOH added. In computing these concentrations, take into account the partial neutralization of the acid or the excess of base present, and the dilution of the solution. Assume that the ionization constant of water is

$$1 \times 10^{-14} = (H^+)(OH^-)$$

Construct a plot of EMF as a function of the volume of NaOH added. Indicate on this graph the end point, computed from the known concentrations of the NaOH and HCl solutions.

Experiment 38

POTENTIOMETRIC TITRATIONS

Potentiometric methods of determining the endpoint can be applied to almost any type of titration and frequently have special advantages over other methods (M, 610–2; W, 1075–1107; also Kolthoff and Furman, Potentiometric Titrations). Any cell made up from a reference electrode and a second electrode whose EMF is a function of the concentration of the ion being titrated, can be used for a potentiometric titration. For example, cell A of experiment 37

$$\text{Pt, } H_2 \text{ (1 atm)} \mid H^+ (a_1) \mid \text{KCl (sat)} \mid \text{KCl}(1\ N), \text{HgCl(S)} \mid \text{Hg}$$

could be used in acidimetric titrations. The EMF of this cell, neglecting the liquid junction EMF, is given by the expression

$$E = E_0 - \frac{RT}{2Fy} \ln \frac{a^2_{H^+} a^2_{Hg} a^2_{Cl^-}}{P_{H_2} \cdot a^2_{HgCl}}$$

Since the quantity $(a^2_{Hg} \cdot a^2_{Cl^-} / a^2_{HgCl} P_{H_2})$ is constant, the above equation may be written in the following simple form

$$E = E_0' - \frac{RT}{Fy} \ln (H^+)\gamma_H = E_0' + 2.303 \frac{RT}{Fy} P_H$$

It follows from this that the EMF is a linear function of the P_H. In an acid-base titration, the P_H changes most rapidly at the endpoint (M, 541–2). Therefore the endpoint of such a titration can be determined by finding the point of inflection on the curve which is obtained by plotting the EMF as ordinates and the (cumulative) volume, V_i, of reagent added as abscissae. This point of inflection is frequently referred to as the "jump" or "break" in the curve. The end point can also be determined by plotting $\Delta E_i / \Delta V_i$ against V_i, where ΔE_i is the change in EMF corresponding to the addition of a volume, $\Delta V_i = V_i - V_{i-1}$, of the reagent. This curve corresponds approximately to a plot of the differential of the first curve. It shows a sharp peak at the endpoint (Kolthoff and Furman, loc. cit., 147–8). The description of an interesting analytical method of finding the endpoint is given by Fenwick, Ind. Eng. Chem. Anal. Ed. **4,** 144 (1932). The general method of constructing the cell and the procedures for locating the endpoint are applicable to oxidation-reduction and precipitation titrations as well as to acidimetric determinations. Typical examples of each of these are described in the following procedures.

ACID–BASE TITRATIONS

Any of the electrodes (222–3) which measure the H^+ activity can be used as indicator electrodes in acidimetric titrations. The quinhydrone electrode (M, 579–80; Kolthoff and Furman, loc. cit., 220–4; Clark, The Determination of the Hydrogen Ion, 404–22), which is to be used in the present experiment is easy to set up and use, but has the disadvantage that it cannot be used in solutions which are more alkaline than $P_H = 8.5$. In using this electrode it is always necessary to start with the acid in the electrode vessel and titrate with the base.

In the present experiment the normal calomel electrode is to be used as the reference electrode. To prevent changes in the concentrations of the solutions due to siphoning, a salt-agar bridge is to be used to connect the two half-cells. Two titrations are to be performed, the first of a strong acid with a strong base, the second of a weak acid with a strong base. The results of the second titration can be used to compute the dissociation constant as well as the concentration of the weak acid.

Apparatus and Materials: A potentiometer and auxiliary equipment (216), a half-cell vessel, a Pt-point electrode, and a Au or bright Pt electrode. 150 ml. of 1 *N* KCl, 70 ml. each of 0.100 *M* HCl and of 0.100 *M* CH_3COOH (or of an unknown weak acid), 50 ml. of 0.500 *M* NaOH, 5 ml. of a pasty suspension of HgCl in 1 *N* KCl, 4 ml. of clean Hg, 0.5 gm. of quinhydrone, 1.5 gm. of agar, and 20 gm. of KCl.

Procedure: Prepare a calomel electrode, *A* (figure 68), as described in experiment 37. Make a U-tube, *B*, from 5 or 6 mm. tubing. To prepare the salt bridge, add 1.5 gm. of agar to 50 ml. of water and heat on a steam bath (not by direct contact with a flame) until the agar is completely dissolved. Add 20 gm. of solid KCl and stir until it goes into solution. Fill the U-tube and allow it to remain in an upright position until it cools and the agar gel sets. If the gel shrinks into the tube on cooling, scratch the ends of the tube with a file and break them off to expose the gel. Fill a small beaker, *C*, with 1 *N* KCl, and insert the side arm of the calomel half-cell into it. Pipet 50 ml. of 0.100 *M* HCl into a second beaker, *D*. Add about 0.1 gm. of quinhydrone (at least enough to saturate the solution) and stir for a few minutes. Insert a Au or bright Pt electrode, *E*. A Au electrode can be made by soldering a short piece of Au wire to a length of flexible Cu wire, slipping the wire into a glass tube, and sealing the Au wire in the end of the tube with any good acid-resisting sealing wax. Be sure that this seal is water tight. Connect this beaker with the calomel half-cell by means of the salt bridge, *B*.

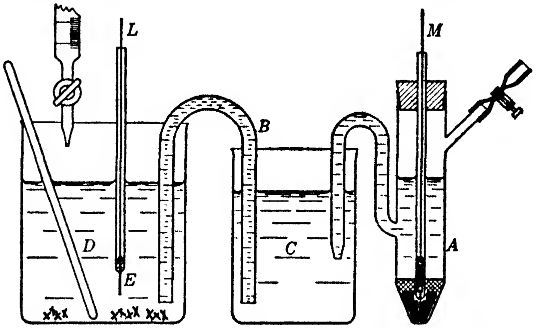

FIGURE 68. CELL FOR POTENTIOMETRIC TITRATIONS

Set up a student potentiometer and calibrate it with a standard cell (216–21). Connect the terminals *L* and *M* to the potentiometer and measure the EMF of the cell. Add 1 ml. of 0.500 *M* NaOH from a 25 ml. buret, stir for about 10 seconds and, after waiting for about half a minute, again measure the EMF of the cell. Continue to add 1 ml. portions of the base, stirring and measuring the EMF after each addition, until a point is reached within about 1 ml. of the expected endpoint. From this point, add the base in portions of 0.1 ml. or less, measuring the EMF after each addition. Continue the additions until the endpoint has been passed by 0.5 to 1.0 ml.

Using a dry beaker and fresh sample of quinhydrone, repeat the experiment with 50 ml. of 0.100 *N* CH_3COOH. (Note: If you are to perform the following experiment, save the calomel cell and agar salt bridge.)

Computations: Tabulate the (cumulative) volumes of NaOH added, V_i, and the corresponding values of the EMF, for both reactions. Compute values of $\Delta E_i/\Delta V_i$ for each value of V_i and add these to the table. Prepare plots of E against V and of $\Delta E/\Delta V$ against V for each of the experiments. Determine the endpoints of the titrations by locating the point of inflection in the first curve and the peak in the second. Compute the concentrations of the acid solutions and compare these to the standardization.

Assuming that the salt bridge eliminates the liquid junction potential, compute (M, 608–9) the P_H of the original weak acid solution. Since there are only weak electrolytes present in this solution, no appreciable error will be introduced by the assumption that the activity coefficients of all species present are equal to unity. Making this assumption, compute the dissociation constant of the weak acid in terms of the initial EMF and your value for the total concentration of the acid.

OXIDATION-REDUCTION TITRATIONS

A great variety of oxidation-reduction titrations (M, 611–2; Kolthoff and Furman, loc. cit., 232–308) can be performed potentiometrically. The indicator electrode which is used must be reversible for at least one of the two oxidation-reduction pairs involved in the reaction. However, an inert metal electrode, such as Au or Pt can be used in most of these titrations, since the substances which react are nearly always soluble.

The process to be studied in the present experiment is the titration of an iodide solution with standard $KMnO_4$. The equation corresponding to this reaction is

$$2\,MnO_4^- + 16\,H^+ + 10\,I^- = 2\,Mn^{++} + 8\,H_2O + 5\,I_2$$

Since the inert metal electrode may be treated as a reversible I_2 electrode, the following diagram represents a cell which may be used for the titration:

$$Pt \mid I_2(a_{I_2}),\ I^-(a_{I^-}) \mid KCl\ (sat) \mid KCl(1\ N),\ HgCl(S) \mid Hg$$

The following equation represents the chemical reaction which occurs when 2 faradays of positive electricity flow through the cell from left to right:

$$2\,I^-(a_{I^-}) + 2\,HgCl(S) = I_2(a_{I_2}) + 2\,Cl^-(1\ N) + 2\,Hg(l)$$

Therefore, if the liquid junction is neglected, the following equation represents the EMF of the cell:

$$E = E_0' - \frac{RT}{2Fy} \ln \frac{a^2_{\mathrm{Hg}}(\mathrm{l}) \cdot a^2_{\mathrm{Cl}^-}(N)}{a^2_{\mathrm{HgCl(S)}}} \cdot \frac{a_{\mathrm{I}_2}}{a^2_{\mathrm{I}^-}}$$

$$= E_0 - \frac{RT}{2Fy} \ln \frac{a_{\mathrm{I}_2}}{a^2_{\mathrm{I}^-}}$$

While the ratio $a_{\mathrm{I}_2}/a^2_{\mathrm{I}^-}$, increases throughout the titration, it changes most rapidly at the endpoint. Therefore, there is a "jump" in the EMF at the endpoint.

Apparatus and Materials: A potentiometer and auxiliary equipment (220), a half-cell vessel, and 2 Pt-point electrodes. 150 ml. of 1 N KCl, 100 ml. of 0.50 N H_2SO_4, 50 ml. of 0.100 N $KMnO_4$, 5 ml. of a pasty suspension of HgCl in 1 N KCl, 4 ml. of clean Hg, about 2 gm. of pure dry KI, 1.5 gm. of agar, and 20 gm. of KCl.

Procedure: Prepare a normal calomel half-cell (228) and an agar KCl bridge (234–5). Assemble the cell as indicated in figure 68. Add 50 ml. or more, of 0.50 N H_2SO_4 and an equal volume of distilled water to the small beaker, D. Insert a bright Pt electrode. Weigh accurately about 0.002 moles of pure KI into this solution, and stir until it dissolves.

Set up a student potentiometer and calibrate it with a standard cell (216–21). Measure the EMF of the cell. Add 1 ml. of 0.100 N $KMnO_4$ from a 25 ml. buret, stir, and measure the EMF. Since this indicator electrode attains its equilibrium EMF very quickly, it will not be necessary to wait after stirring before measuring the EMF, until you are within about 1 ml. of the endpoint. An automatic stirrer running continuously but at low speed is convenient though not necessary. When near the endpoint, allow about 1 minute to elapse after each addition of $KMnO_4$ before measuring the EMF. Add the $KMnO_4$ in 1 ml. volumes until you are within about 1 ml. of the endpoint, then 0.1 ml. or smaller portions until you have passed the endpoint by at least 0.5 ml.

Computations: Tabulate the (cumulative) volumes, V_i, of reagent added, and the corresponding values of the EMF and of $\Delta E/\Delta V$ (233–4). Prepare a plot of E against V. Using a spread out scale on the V axis, plot $\Delta E/\Delta V$ for the measurements in the immediate neighborhood of the endpoint. Estimate the endpoint from the position of the peak on this curve. Indicate this point on the E vs V curve, and note if it appears to coincide with the point of inflection. Treating the pure dry KI as a primary standard, compute the normality of the $KMnO_4$ solution. Compare this concentration to the standard value.

PRECIPITATION TITRATIONS

Potentiometric methods are frequently used to determine the endpoints of precipitation titrations (M, 612; Kolthoff and Furman, loc. cit., 164–203). In these titrations the indicator electrode must be reversible to one or the other of the ions which is being precipitated. For example, in the titration of a KI solution with standard $AgNO_3$, the electrode might be either a Ag electrode, reversible to Ag^+, or a Pt electrode in the presence of a little I_2 (that is, the I_2 electrode), which is reversible to I^-.

In this experiment, pure dry NaCl is to be used to standardize a $AgNO_3$ solution. The Ag electrode is to be used, and the salt bridge made with either KNO_3 or NH_4NO_3. The following diagram represents the cell

$$\mathrm{Ag} \mid \mathrm{AgCl(S)}, \mathrm{Cl^-}(a_{\mathrm{Cl^-}}) \mid \mathrm{KNO_3}(1\ N) \mid \mathrm{KCl}(1\ N), \mathrm{HgCl(S)} \mid \mathrm{Hg}$$

The following equation represents the chemical reaction which occurs when 1 faraday of positive electricity flows through the cell from left to right:

$$\mathrm{Ag(S)} + \mathrm{Cl^-}(a_{\mathrm{Cl^-}}) + \mathrm{HgCl(S)} = \mathrm{Hg(l)} + \mathrm{Cl^-}(1\ N) + \mathrm{HgCl(S)}$$

Neglecting the liquid junction EMF, the equation for the EMF of the cell may be written in either of the following forms, since the product $a_{\mathrm{Ag^+}} \cdot a_{\mathrm{Cl^-}} = K$ (M, 523–4):

$$\begin{aligned} E &= E_0 + \frac{RT}{Fy} \ln a_{\mathrm{Cl^-}} \\ &= E_0' - \frac{RT}{Fy} \ln a_{\mathrm{Ag^+}} \end{aligned}$$

In the titration, a jump in the EMF occurs at the endpoint, corresponding to the rapid change in $\ln a_{\mathrm{Cl^-}}$ at this point.

Apparatus and Materials: A potentiometer and auxiliary equipment (220), a half-cell vessel, a Pt-point electrode, and a Ag electrode. 150 ml. of 1 N KCl, 50 ml. of 0.100 M $AgNO_3$, 5 ml. of a pasty suspension of HgCl in 1 N KCl, 4 ml. of clean Hg, about 2 gm. of pure dry NaCl, 1.5 gm. of agar, and 10 gm. of KNO_3.

Procedure: Prepare a normal calomel half-cell (228). Prepare a KNO_3-agar bridge following the directions (234–5) given for the KCl-agar bridge, but substituting 5 gm. of KNO_3 for the KCl. If desired, a saturated NH_4NO_3-agar bridge may be used instead. Add about 100 ml. of distilled water to the beaker, *D* (figure 68), and accurately weigh into it 0.002 moles of pure NaCl. Insert the Ag electrode into this solution. (Note: the Ag electrode may be made from a short piece of Ag wire, using the same procedure as for the Au electrode (235), or a Pt electrode may be silver plated.) Using the salt bridge, assemble the cell as indicated in figure 68.

Titrate the NaCl solution with the standard $AgNO_3$, following the procedure outlined for the oxidation-reduction titration (237). Since this titration involves the separation of a second phase, it is important to have efficient stirring. It is advantageous, though not necessary, to use an automatic stirrer. Carry the titration at least 5 ml. past the endpoint.

Computations: Prepare a table of data and two plots, similar to those required for the oxidation-reduction titration (237). Compare your standardization of the $AgNO_3$ solution to the listed value.

With the aid of a plausible assumption, the data of this experiment can be combined with the standard EMF of the silver electrode (M, 581) to obtain the solubility product (M, 525–7) of AgCl. Using the EMF at the half titration point, perform this computation.

Experiment 39

ELECTROLYSIS AND POLARIZATION

When a direct current is passed between electrodes in an electrolytic solution, the applied EMF must overcome both the resistance of the cell and the back EMF which is set up at the electrodes (M, 618–29). If the electrodes are reversible and the current is small, the back EMF can be computed from the normal electrode EMF's and the concentrations of the several substances involved in the electrode processes. However, under ordinary conditions the electrodes become polarized, due to changes in concentration in the immediate neighborhood of the electrode or for other reasons. Polarization results in an increase in the back EMF and a decrease in the current passing through the cell.

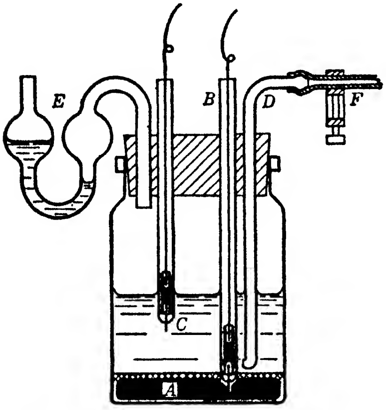

FIGURE 69. POLARIZATION CELL

The study of polarization effects may be simplified by the use of a reversible electrode with a large surface and a small inert electrode (Kolthoff and Lingane, Polarography, Chap. XXXII). In this way, the polarization is localized at the small electrode. In the present experiment, a large calomel electrode, *A* of figure 69, is used as the anode and a small Pt point, *C*, serves as the cathode. The solution is made up from TlCl and KCl; the concentration of the KCl being at least 100 fold greater than that of the Tl salt. The electrode reaction at the cathode is

$$\mathrm{Tl}^+ \rightarrow Fy + \mathrm{Tl}$$

and at the anode is

$$Fy + \mathrm{Hg} + \mathrm{Cl}^- \rightarrow \mathrm{HgCl}$$

Because of the low current density and the nature of the anode, the latter acts as a reversible electrode. Due to the high current density at the small cathode, the Tl^+ ions in the neighborhood of this electrode are rapidly depleted, resulting in a state of concentration polarization.

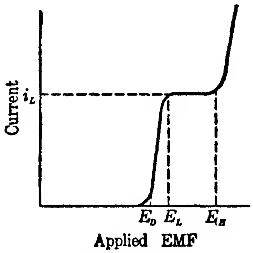

FIGURE 70

It may be helpful to consider what happens in a typical experiment of this kind (compare Kolthoff and Lingane, Chem. Rev. **24**, 1 (1939). Figure 70 is a plot of the current against the applied EMF. When the applied EMF is less than E_D, the decomposition EMF, the current is negligibly small, but at this point electrolysis sets in and the current increases rapidly with increasing applied voltage. Under these conditions, the current, i, is limited by the rate of diffusion (M, 670) of the Tl^+ ions to the cathode, and can be represented by the following expression:

$$i = k(C - C_c)$$

where C is the concentration of the Tl^+ ion in the bulk of the solution and C_c is its concentration at the surface of the cathode. The limiting current, i_L, corresponds to the condition where the Tl^+ ions are discharged as soon as they reach the surface of the cathode, and $C_c \ll C$. In this region the current, i_L, is independent of the applied potential, and is

$$i_L = kC$$

If k is independent of the applied potential, the limiting current is directly proportional to the concentration of Tl^+ ions in the solution. The assumption that k is independent of the applied potential is probably justifiable only when the concentration of the K^+ ions is much greater than that of the Tl^+ ions. In other words, k does not vary with changing EMF so long as the transference number of the Tl^+ ion in the solution is very small. The second rise in the curve at E_H corresponds to the liberation of H_2 at the cathode; that is, the break corresponds to the occurrence of the new cathode reaction

$$2\,H_2O \rightarrow 2\,Fy + H_2 + 2\,OH^-$$

Both the applied EMF and the current passing through the cell are to be measured with a student's potentiometer. Figure 71 is a diagram of the circuit which is to be used in this experiment. The part of the diagram which is below the dotted line is a standard potentiometer circuit for measuring EMF (216–21). As a source of potential, the battery, *B*, which consists of two dry cells, is connected through two tapped resistances, one of approximately 10 and the other of 1000 ohms. Either "potentiometer rheostats" or "radio potential dividers" may be used for this purpose. When the switch, S_3, is connected to the terminals, *g* and *h*, an adjustable fraction of the total EMF of the working battery, *B*, is applied to the polarization cell, *C*. This applied EMF can be measured by connecting the terminals, *a* and *b*, of the cell to the calibrated potentiometer circuit by means of the switches, S_1 and S_2. The current, *i*, passing through the cell can be determined by connecting the switch, S_1, to the terminals, *e* and *f*, and measuring the fall of potential across the standard resistance, R_s. This resistance should be approximately 20,000 ohms, and should be known with an accuracy of about one-half per cent. If the switch, S_1, is opened and S_3 is connected to *j* and *k*, the reversible EMF of the cell, which corresponds to E_D, can be measured directly.

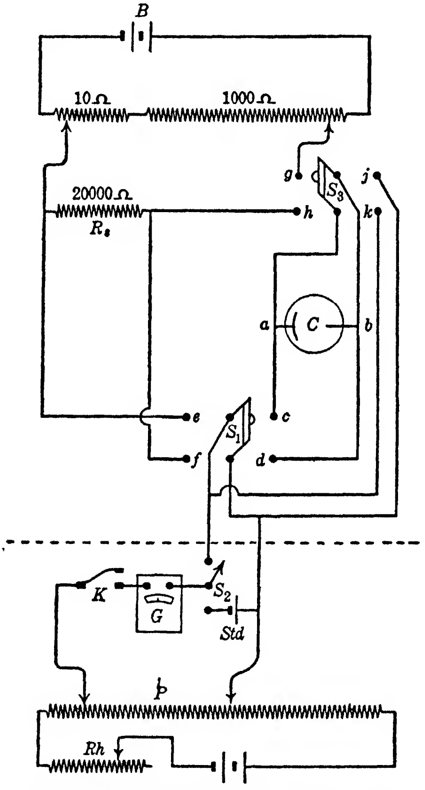

FIGURE 71. CIRCUIT FOR POLARIZATION EXPERIMENT

Apparatus and Materials: A student's potentiometer and auxiliary equipment (220), a standard 20,000 ohm resistance, a 10 ohm and a 1000 ohm potentiometer rheostat, 2 double-pole double-throw switches, 2 dry cells, a special polarization cell (figure 69), a tank of N_2 or H_2 fitted with a needle valve, a length of pressure tubing, and annunciator wire for connections. 100 ml. of a solution which is 0.10 *M* in respect to KCl and saturated with TlCl, 200 ml. of 0.10 *M* KCl, 10 ml. of pure Hg, and a few ml. of a suspension of HgCl in 0.10 *M* KCl.

Procedure: Assemble and connect the potentiometer and auxiliary equipment (216–21). Prepare the polarization cell (figure 69) as follows: Pour about 10 ml. of pure Hg, *A*, into the cell vessel. Place 1 ml. or less of a suspension of calomel in 0.10 *N* KCl on the Hg, and add about 50 ml. of the solution which is 0.10 *M* in respect to KCl and saturated with TlCl. Insert the rubber stopper which supports the electrodes, *B* and *C*, the gas inlet, *D*, and the gas trap, *E*. Connect the inlet tube, *D*, to the N_2 (or H_2) tank with a rubber tube which is provided with a pinch clamp, *F*. It is advisable to introduce a safety valve in this line. The exposed Pt point of the cathode, *C*, should be 3 or 4 mm. long. The other Pt electrode should be entirely covered by the Hg anode, *A*. Add a few ml. of water to the trap, *E*, to make a gas seal.

Since O_2 affects the results, pass N_2 (or H_2) through the cell for about 15 minutes to sweep out the air. During this time calibrate (216–21) the potentiometer with the standard cell, and connect the rest of the apparatus as indicated in figure 71. Then shut the valve on the gas tank and close the pinch clamp, *F*. If the tank is to be left connected to the cell the pinch clamp may be dispensed with. With the switch, S_3, in contact with the terminals, *g* and *h*, set the potentiometer rheostats to apply about 0.10 volts to the cell, *C*. Set the switch, S_1, to the terminals, *c* and *d*, and measure the applied EMF with the potentiometer. Then throw this switch to the terminals, *e* and *f*, and measure the drop in potential across the standard resistance, R_s. Increase the applied potential by about 0.10 volts, and again measure the applied EMF and the potential drop across the standard resistance. (Note: it is necessary that the voltage be applied stepwise, starting with a low value. If a high voltage is accidentally applied to the cell at the start of the experiment, the Pt electrode should be removed and cleaned with HNO_3 before proceeding with the experiment. Why?) It may be necessary to wait a few minutes after changing the applied EMF before making the measurements, since the equilibrium conditions are not established instantaneously. Increase the applied EMF by successive small amounts (0.10 volts or less) until the second break (at E_H, figure 70) is passed. Measure the applied EMF and the potential drop across the resistance for each setting of the potentiometer rheostats. During the course of the experiment, examine the cathode from time to time with a hand lens or meniscus reader, and note when gas bubbles first appear on the electrode. At the end of the run, open the switch, S_1, set the switch S_3 to the terminals, j and k, and measure the reversible EMF of the cell.

Prepare about 100 ml. each of two solutions, both of which are 0.10 M in respect to KCl, but which contain TlCl at concentrations which are 0.40 and 0.16, respectively, of the concentration used in the first experiment. Repeat the entire experiment with each of these solutions. The same Hg may be used in all three experiments, but at the completion of each run it and the cell should be thoroughly washed and rinsed with a portion of the new solution. The cathode should be cleaned with HNO_3.

Computations: Compute i, the value of the current passing through the cell, corresponding to each determination of the drop of potential across the standard resistance, R_s. For each of the three runs, plot the current, i, as a function of the applied EMF. Indicate on these plots the measured values of the reversible EMF. Compare these to the corresponding decomposition EMF's, E_D, obtained by extrapolating the first steeply rising part of the curve back to $i = 0$. Compute values of the reversible EMF's of the cells, from the standard electrode EMF's and the known concentrations (or better activities) of Tl^+ and Cl^- ions. Indicate on the curve the point where bubbles of H_2 were first formed. Plot the values of the diffusion current, i_L, as a function of the concentration, C, of the Tl^+ ions. Discuss the results.

Experiment 40

A STUDY OF THE FIRST AND SECOND LAWS OF PHOTOCHEMISTRY

The quantitative study of photochemical reactions requires specialized equipment and technique. However, it is possible to demonstrate the validity, in a semi-quantitative way, of the first two laws of photochemistry, using ordinary apparatus and simple technique. These fundamental laws of photochemistry can be stated as follows: Only that light which is absorbed by a system is capable of producing chemical action in it, and this action is directly proportional to the product of the intensity of the absorbed light and to the time of irradiation. Strictly speaking these laws apply only to the primary process (i.e., the interaction of a photon with a molecule) (M, 647–8). All cases of apparent exceptions to these laws, which have been carefully studied, have been explained definitely in terms of the secondary (thermal) reaction steps which follow the primary process. The substance which absorbs the light is not always identical with the compound which undergoes the chemical reaction. For example, when a solution which contains UO_2SO_4 and $(COOH)_2$ is illuminated with violet light, this light is absorbed by the uranyl compound but the chemical reaction is the decomposition of the $(COOH)_2$.

$$(COOH)_2 + h\nu \xrightarrow{UO_2^{++}} CO_2 + CO + H_2O$$

Either this reaction or a similar one, the oxidation of $(COOH)_2$ by Fe^{+++}, may be studied conveniently as an example of a photochemical process. When this latter reaction,

$$2\,Fe^{+++} + (COOH)_2 + h\nu \longrightarrow 2\,Fe^{++} + 2\,CO_2 + 2\,H^+$$

occurs in the presence of air, the Fe^{++} ion which is formed is rapidly oxidized back to Fe^{+++},

$$2\,Fe^{++} + \frac{1}{2}\,O_2 + 2\,H^+ \longrightarrow 2\,Fe^{+++} + H_2O$$

and the final result is the photosensitized oxidation of $(COOH)_2$ by the O_2 of the air,

$$(COOH)_2 + \frac{1}{2} O_2 + h\nu \xrightarrow[Fe^{++}]{Fe^{+++}} 2\,CO_2 + H_2O$$

It should be recognized that these equations are merely formal statements of the stoichiometry; they do not represent the mechanism of the reaction (compare Livingston, Jour. Phys. Chem. **44,** 601 (1940)).

While the following procedure applies to the reaction with Fe^{+++} ion it may be adapted to the UO_2^{++} reaction by a few minor changes (see D, M, and W, 274–6). If the UO_2SO_4 is used, a quartz-mercury arc, preferably of the horizontal 110 volt D. C. type, should be substituted for the incandescent lamp, and a 0.05 *M* $(COOH)_2$ solution should be used in place of the 0.10 *M* $Na_2C_2O_4$ stock solution. The $UO_2C_2O_4$ reaction has the advantage that it has been very carefully studied (see for example Leighton and Forbes, J. Am. Chem. Soc. **52,** 3139 (1930)), and is one of the most dependable of actinometric reactions (M, 651).

Apparatus and Materials: A 200 watt incandescent lamp with an unfrosted globe and a coiled filament, an 8 cm. evaporating dish, a 10 or 12 cm. petri dish, and a 50 ml. buret. 200 ml. each of 0.100 *M* $Na_2C_2O_4$ and of 0.0400 *M* $FeNH_4(SO_4)_2$, about 200 ml. of standard 0.05 *N* $KMnO_4$, and 35 ml. of 6 *N* H_2SO_4.

Procedure: Prepare 400 ml. of a solution 0.0500 *M* in respect to $Na_2C_2O_4$ and 0.0200 *M* in respect to $FeNH_4(SO_4)_2$. Keep this stock solution in a dark place. While it is fairly stable in the dark it should not be retained for more than a few days. Place a clean dry evaporating dish in the bottom of a larger dish or pan containing cold water. The purpose of the water-filled pan is to control the temperature of the solution during irradiation. If the water gets warm during the experiment it should be siphoned off and replaced with cold water. Since stray light interferes with the experiment, the apparatus should not be placed in sunlight or near a window; however, a dark room is not necessary. Pipet 25 ml. of the stock solution into the evaporating dish. Mount the 200 watt lamp above the center of the dish with its filament 10 cm. from the surface of the solution.

Record the time and turn on the lamp. Illuminate the solution for 45 minutes, stirring it with a glass rod at 10 or 15 minute intervals. During this time titrate a 25 ml. sample of the (unilluminated) stock solution with 0.05 *N* $KMnO_4$. As the change due to the photochemical reaction is relatively small, it is necessary that the titrations be performed carefully and in accordance with the standard procedure (see K and S, 592–4). At the end of the 45 minute period, turn off the light and wash the solution into a 250 ml. erlenmeyer flask. Titrate this sample with the standard $KMnO_4$.

Repeat the experiment doubling the time of illumination. Then raise the lamp until its filament is 20 cm. from the surface of the solution, and again illuminate a 25 ml. sample for 45 minutes, and then titrate it.

For the fourth experiment, return the lamp to its original position. Pipet 25 ml. of the stock solution into the evaporating dish, and reserve a second 25 ml. sample for a check analysis of the unilluminated solution. Pour the rest of the stock solution into a large petri dish, and place it on top of the evaporating dish. With this arrangement, the light which reaches the sample has already passed through a relatively thick layer of the same solution. While the first solution permits a fairly large amount of the total light to pass, it removes practically all of the light which the sample is able to absorb. The sample is thus exposed to an intense beam of light for which it is transparent. (It is interesting to examine the light, with a direct vision spectroscope, before and after it passes through the solution.) Irradiate under these conditions for at least 45 minutes, and then titrate the sample. During the period of illumination, analyze the 25 ml. sample of the stock solution.

Computations: Compute the number of moles of $(COOH)_2$ oxidized in each of the four experiments. Estimate the relative intensity of the light incident upon the solution when the lamp is at 10 and at 20 cm. from the surface of the solution, by applying the inverse square law. Since the lamp is not a point source of light an error is introduced by the application of the inverse square law. Discuss this. Tabulate your results. Discuss them in terms of the first two laws of photochemistry.

Experiment 41

ADSORPTION FROM SOLUTIONS. ACETIC ACID ON CHARCOAL

The adsorption of a solute on a porous solid (M, 681–3) may be studied by shaking a known weight of the solid with a standard solution and then analyzing the solution after the system has reached equilibrium. The weight, x, of solute adsorbed is equal to the change in molar concentration of the solution, $C_0 - C$, multiplied by the product of the molecular weight, M, of the solute and the volume of the solution.

$$x = (C_0 - C)MV$$

In the present experiment, the adsorption of CH_3COOH on active charcoal is to be measured and the results compared to the Freundlich adsorption isotherm,

$$\frac{x}{m} = kC^n \qquad (1)$$

where m is the weight of the charcoal and k and n are constants. The values of these constants depend upon the temperature and upon the nature of the solute, solvent, and adsorbent. The results may also be compared to the Langmuir equation (M, 434–5, 682). The last part of the experiment is introduced to demonstrate that this type of adsorption is reversible.

Apparatus and Materials: A 25 ml. buret, a 100 ml. calibrated flask, 2 small long-stemmed funnels, and 9 cm. filter paper. About 20 gm. of active charcoal (do not use bone charcoal), 250 ml. of 0.50 M CH_3COOH, and 150 ml. of standard 0.10 M NaOH.

Procedure: Weigh 2 gm. of charcoal into each of 6 numbered 250 ml. erlenmeyer flasks. While the weights need not be exactly 2 gm. they should be known to the nearest milligram. Add to each of the flasks 100 ml. of CH_3COOH solution; starting with a 0.50 M solution and diluting exactly two fold each time. That is, if the concentration of the first solution is exactly 0.500 M, the concentrations of the other 5 should have the following values: 0.250, 0.125, 0.0625, 0.0313, and 0.0156 M. Stopper these flasks, and let them stand for about an hour, shaking them at frequent intervals. If convenient, they may be kept in a 25° thermostat.

To standardize the original CH_3COOH solution in terms of the NaOH solution, titrate two 5 ml. samples with 0.100 M NaOH using phenolphthalein as an indicator. After the solutions have stood for about an hour, determine their equilibrium concentrations. If a finely powdered charcoal is used it will be necessary to filter the solutions before taking the samples. In any case filter the first, concentrated, solution through a 9 cm. filter paper, transferring the charcoal to the filter paper as quantitatively as possible without using wash water. Allow this charcoal to drain while you are performing the titrations. It will prove convenient to use a 5 ml. sample of the first, 10 ml. of the second, 25 ml. of the third, and 50 ml. of each of the last three. Duplicate titrations should be made on the first three, if time permits.

To demonstrate that this type of adsorption is reversible, proceed as follows: Puncture the filter paper containing the charcoal. With the aid of a wash bottle, wash as much as possible of it into a 100 ml. volumetric flask. Add enough distilled water to make the total volume 100 ml. Let this mixture stand for 20 to 30 minutes, shaking it at frequent intervals. Then filter off the charcoal, and titrate a 50 ml. sample with the standard NaOH solution. It should be realized that this last experiment is only semi-quantitative since no allowance is made for the original solution which adheres to the charcoal or for the true volume of the charcoal.

Computations: For each of the first 6 solutions, compute the following quantities: the equilibrium concentration, C; the common logarithm of this concentration, $\log C$; the total weight of CH_3COOH adsorbed, x; the ratio of this weight to that of charcoal, x/m; and the common logarithm of this ratio, $\log \frac{x}{m}$. Prepare a table containing these computed quantities and the experimental values upon which they were based. Construct two plots, the first of $\frac{x}{m}$ against C, and the second of $\log \frac{x}{m}$ against $\log C$. Draw the best straight line through the points of the logarithmic plot. From this line determine the values of k and n of the Freundlich adsorption isotherm.

Compute the equilibrium concentration of the seventh solution.

Assuming that all of the CH_3COOH present in this mixture was originally adsorbed on the charcoal, compute the weight of acid still adsorbed and the weight which was desorbed due to the addition of the water. Compare these results to the Freundlich adsorption isotherm, using the values of k and n which were obtained in the first part of the experiment. Discuss quantitatively the errors which were introduced by the neglect of the CH_3COOH solution which was adhering to the charcoal and the neglect of the true volume of the charcoal itself.

Experiment 42

SOLUBILIZATION BY A SOAP OF A WATER-INSOLUBLE DYE

In water, soaps form stable lyophilic colloidal solutions (M, 699–700). Although the soap colloids or micelles (M, 684; Glasstone, Textbook of Physical Chemistry, 1266–9) have colloidal dimensions, they show no tendency to settle out on standing. These colloidal solutions of detergents are able to "solubilize" water-insoluble materials. In other words, substances such as oils or hydrocarbons, which are negligibly soluble in water and form only unstable lyophobic colloids in it, dissolve readily in soap solutions. This property of detergent solutions is related to their cleansing action. It also finds an important application in the manufacture of synthetic rubber by the process of emulsion polymerization.

In the present experiment, which is based upon the researches of McBain (McBain and Woo, Jour. Am. Chem. Soc. *60*, 223 (1938)), the solubilization of the water-insoluble dye, butter yellow, by the soap, potassium laurate, is to be studied. A dye, rather than a simple hydrocarbon, is used, since its concentration can be determined colorimetrically. As an interesting variant of the experiment, a commercial detergent (such as a sulfonated oil) may be substituted for the potassium laurate.

Apparatus and Materials: A colorimeter, 8 oil sample bottles. About 250 ml. each of 0.20 *M* potassium laurate and of acetone. About 0.30 gm. of solid butter yellow (p-dimethylaminoazobenzene).

Procedure: By suitable dilutions, prepare 100 ml. each of potassium laurate solutions of the following molarities: 0.200, 0.150, 0.100, 0.050, 0.030, 0.015 and 0.005 *M*. Fill each of seven labelled oil sample bottles about two-thirds full with these solutions and an eighth bottle with distilled water. Add about 0.030 gm. of solid butter yellow to each bottle. Seal the bottles with neoprene stoppers or with clean rubber stoppers which have been boiled in dilute NaOH solution. Wire the stoppers securely in place. Place the bottles in the rotator in the 25°C. thermostat, and let them rotate for three days. Remove the bottles from the rotator, and allow them to stand in an upright position in the thermostat over night (or longer).

Withdraw samples of the several solutions, using a pipet equipped with a filter (203). Prepare a standard solution of butter yellow in acetone. The concentration of this solution should be known to the nearest per cent, and it should have about the same color (or one half as intense) as the 0.150 *M* potassium laurate solution. Determine, by means of the colorimeter (252), the concentrations of butter yellow in the several soap solutions and in pure water. In these determinations, use a series of standard solutions prepared by dilution of the primary standard solution so that all of the colorimeter readings are between 0.30 and 0.70.

Computations: For each solution, compute and tabulate the following quantities: concentration of potassium laurate, average colorimeter reading, concentration of the standard solution used, concentration of butter yellow in the sample, two-thirds power of the potassium laurate concentration, and the coefficient (K) in the empirical equation,

$$(\mathrm{BY}) = K\ (\mathrm{KL})^{2/3}$$

where (BY) and (KL) are the molarities of butter yellow and potassium laurate respectively. Plot (BY) against (KL) and against $(\mathrm{KL})^{2/3}$. Discuss your results, including an estimate of the precision of the colorimetric measurements.

USE OF THE COLORIMETER

Several solutions which obey Beer's law (M, 207) will appear to have identical colors when the products of the concentration, C_i, of the colored solute and the length, d_i, of the light path are the same for all of them.

$$c_i d_i = \text{constant}$$

A colorimeter (D, M, and W, 55–64; R and R, 252–62; W, 823–65) is a simple apparatus by means of which the relative lengths of the light paths in two solutions, of the same substance but at different concentrations, may be varied until the colors of the solutions appear to be identical.

Most commercial colorimeters are of the Duboscq type or are simple modifications of it. A typical colorimeter is represented schematically by figure 72. In this apparatus, two light beams, *lm* and *l'm'*, pass through the solutions contained in the cups, *D* and *D'*, and are then brought into contact by the prism system, *B*. When the condition $c_1d_1 = c_2d_2$ is satisfied, the field which is seen in the eyepiece, *A*, appears uniform in respect both to color and to intensity. Otherwise, the circular field appears to be divided into halves of unequal brightness or color.

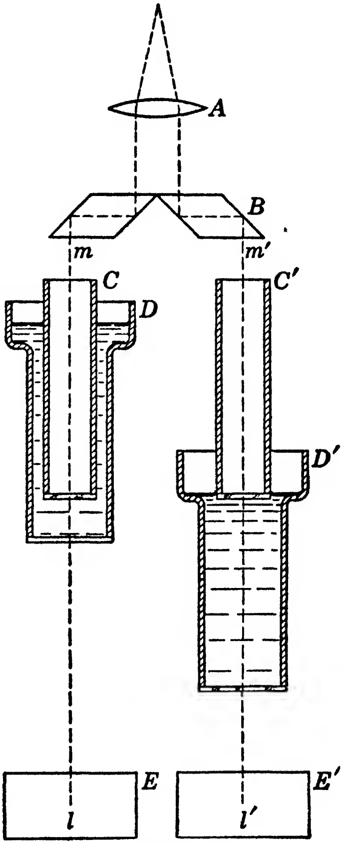

FIGURE 72

Both the hollow plungers, *C* and *C'*, and the cups, *D* and *D'*, are made of opaque tubing provided with transparent end plates. The plungers, *C* and *C'*, are fixed in position, but the cups, *D* and *D'*, can be moved up or down by means of a rack and pinion (not shown in the figure). By raising or lowering a cup, the thickness of the solution, through which the light passes, can be varied continuously from 0 to a maximum, usually 5.0 or 10.0 cm. This thickness can be read from a scale and pointer. In this way the concentration, c_x, of an unknown solution may be measured in terms of the concentration, c_s, of a standard solution, as

$$c_x = c_s \frac{d_s}{d_x}$$

In some colorimeters, light from the sky or from a uniformly illuminated white surface is reflected up into the cells by means of a pair of adjustable mirrors, *E* and *E'*. Since the mirrors are separately adjustable, the intensities of the two beams can be made identical. In other colorimeters, the mirrors are replaced by a piece of ground glass which is illuminated from below by an incandescent lamp.

Colorimeters of the Duboscq type have the disadvantage that the balance point at which the colors appear identical is determined subjectively. To increase the precision of the measurements and to avoid the systematic errors which personal bias can introduce into subjective determinations, a number of photoelectric colorimeters (D, M, and W, 58–63; W, 834–50) have been devised and are commercially available. In these instruments, a photocell and amplifier circuit is used to measure the intensity, relative to a standard, of the light beam, transmitted by a cell containing the unknown solution. The accuracy of the measurement is increased by using light of a narrow band of wave lengths which correspond approximately to the absorption maximum of the unknown solution. The band of light is isolated either by color filters or by means of a crude monochromator.

Procedure: Be sure that the windows of the plungers, C and C', and the cells, D and D', are clean. If they are marked with dust or fingerprints, wipe them carefully with lens paper. Fill both cells with the standard solution. Return the cells to their positions in the colorimeter, taking care to avoid trapping air bubbles under the windows of the plungers. Position the cups carefully to make the lengths of the light paths through the solution in the two cups equal. Then adjust the light source by changing the angles of the mirrors E and E' (or by shifting the incandescent light under the ground-glass plate), until the circular field in the eyepiece appears to be uniform. During the remainder of the experiment, do not change the adjustment of the light source.

Remove one of the cells, empty it, rinse it with the unknown solution, fill it, and return it to the colorimeter. Set the cell containing the more dilute solution so that the light path through it is of maximum length. With the rack and pinion, adjust the other cell until the field in the eyepiece appears uniform. Repeat this setting five or ten times, recording the measured path lengths. Use the average of these readings to compute the (relative) concentration of the unknown solution. Since subjective measurements of this type are peculiarly susceptible to personal error, every effort should be made to avoid bias in judging the balance point. Never look at the scale until you have decided that the field is uniform. Between measurements, displace the cup some distance from its previous setting. The precision with which one can match colors increases with practice; however, it decreases with fatigue or eyestrain.

The accuracy of the colorimetric determination of the concentration of the unknown is a maximum when the concentration of the unknown and standard solutions are practically equal. (Why?) Therefore, do not use a standard solution whose concentration differs from that of the unknown by more than five fold. If a wide range of concentrations are to be determined, prepare a series of standards. This may be done by starting with a standard solution, whose concentration is about as great as that of the most concentrated unknown, and performing several successive five-fold dilutions of it.

Appendix

ABBREVIATIONS AND REFERENCES

The texts and manuals which are referred to most frequently in this book are designated by abbreviations which are listed below. Other books are referred to by their full titles. The conventions used in referring to articles in scientific journals are those which have been adopted by Chemical Abstracts.

Abbreviations	
M	MacDougall, Physical Chemistry. Macmillan (1943)
E and R	Eastman and Rollefson, Physical Chemistry. McGraw-Hill (1947).
T	Taylor, Treatise on Physical Chemistry. Van Nostrand (1931).
D, M, and W	Daniels, Mathews, and Williams, Experimental Physical Chemistry. McGraw-Hill (1941).
F and W	Fajans and Wust, A Textbook of Practical Physical Chemistry. Dutton (1930).
W	Weissberger, Physical Methods of Organic Chemistry. Interscience Publishers (1945).
R and R	Reilly and Rae, Physico-Chemical Methods, Van Nostrand (1939).
K and S	Kolthoff and Sandell, Textbook of Quantititive Inorganic Analysis. Macmillan (1943).
I. C. T.	International Critical Tables. McGraw-Hill (1933).

In addition to the International Critical Tables, which are now in need of revision, the student will find it convenient to use one of the popular handbooks, such as Lange's Handbook of Chemistry. Handbook Publishers, Inc., or Handbook of Chemistry and Physics, Chemical Rubber Publishing Company.

NOTATION

With few exceptions the notation adopted in this manual is the same as that used by MacDougall, Physical Chemistry. While this notation is in general similar to that introduced by Lewis and

Randall, Thermodynamics, there are a few important differences. Several of these differences which seem most likely to cause confusion are recorded in the table below.

Quantity	Symbol (MacDougall)	Symbol (Lewis and Randall)
Mole fraction	x	$\mathbf{N}$
Ionic strength	S	μ
Chemical potential (M)	μ	$\bar{\mathbf{F}}$
Partial molal free energy (L & R)		
Faraday equivalent	F_y	$\mathbf{F}$
Electromotive force	E	$\mathbf{E}$
Electrical potential	π (See M, 547–51)	$\mathbf{E}$

ATOMIC WEIGHTS AND NUMBERS

	Symbol	Atomic Number	International Atomic Weights (1938)		Symbol	Atomic Number	International Atomic Weights (1938)
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231.
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222.
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.54	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.066
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0081	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

FOUR-PLACE LOGARITHMS

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	16	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	4	5	7	9	10	12	14	16
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	12	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	5	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	7	8	9	11	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	2	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	4	5	6	7	8	9	11
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	6	7	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	5	6	7	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	3	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	1	2	3	4	5	6	7	8	9

The proportional parts are stated in full for every tenth at the right-hand side. The logarithm of any number of four significant figures can be read directly by add-

FOUR-PLACE LOGARITHMS

N	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1 2 2	3 4 5	5 6 7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1 2 2	3 4 5	5 6 7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1 1 2	3 4 5	5 6 7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1 1 2	3 4 4	5 6 7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1 1 2	3 4 4	5 6 7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1 1 2	3 4 4	5 6 6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1 1 2	3 3 4	5 6 6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1 1 2	3 3 4	5 5 6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1 1 2	3 3 4	5 5 6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1 1 2	3 3 4	5 5 6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1 1 2	3 3 4	5 5 6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1 1 2	3 3 4	5 5 6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1 1 2	3 3 4	5 5 6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1 1 2	3 3 4	4 5 6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1 1 2	3 3 4	4 5 6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1 1 2	3 3 4	4 5 6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1 1 2	3 3 4	4 5 6
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1 1 2	3 3 4	4 5 6
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1 1 2	2 3 4	4 5 5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1 1 2	2 3 4	4 5 5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1 1 2	2 3 3	4 5 5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1 1 2	2 3 3	4 4 5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1 1 2	2 3 3	4 4 5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1 1 2	2 3 3	4 4 5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1 1 2	2 3 3	4 4 5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1 1 2	2 3 3	4 4 5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1 1 2	2 3 3	4 4 5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1 1 2	2 3 3	4 4 5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1 1 2	2 3 3	4 4 5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1 1 2	2 3 3	4 4 5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1 1 2	2 3 3	4 4 5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1 1 2	2 3 3	4 4 5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	1 1 2	2 3 3	4 4 5
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0 1 1	2 2 3	3 4 4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0 1 1	2 2 3	3 4 4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0 1 1	2 2 3	3 4 4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0 1 1	2 2 3	3 4 4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0 1 1	2 2 3	3 4 4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0 1 1	2 2 3	3 4 4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0 1 1	2 2 3	3 4 4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0 1 1	2 2 3	3 4 4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0 1 1	2 2 3	3 4 4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0 1 1	2 2 3	3 4 4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0 1 1	2 2 3	3 3 4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0 1 1	2 2 3	3 3 4
N	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9

ing the corresponding to the fourth figure to the tabular number

corresponding to the There may be an error of 1 in the last place.

INDEX

Abbé refractometer, 150–3
Abbreviations and reference (table), 257
Absorption spectrum of a solution, 89–92
Accuracy and precision, 18–9, 22–6
AcB, half life of, 83–5
Actinometer, 246
Activation energy, 178–81
Active deposit, 83–4
Activity coefficients of electrolytes, 203–4, 212–6, 226–32
Adsorption,
  from solution, 248–50
  isotherm, Freundlich, 248
Amici prism, 151–2
Analysis of binary solutions, 147, 158
Arc,
  mercury vapor, 90, 246
  sodium vapor, 100
Arrhenius reaction velocity equation, 178
Atomic weights and numbers (table), 259
Audiofrequency generator, 194–6
Average error,
  of a measurement, 16, 29
  of the mean, 17, 29

Balmer series, 89–92
Baly tube, 91
Barometer, 55–6
  correction to 0°C, 56
Beckmann thermometer, 96–7, 110
Beer's law, 92
Best value,
  of a derived quantity, 19, 22, 30
  of the mean, 16, 19, 29
Binary systems,
  analysis of, 147, 158
  boiling point-composition data (table), 159
  mutual solubility, 135–7
  surface tension, 71–5, 118–21
  viscosity, 112–5
Boiling point,
  apparatus, Cottrell, 108–9, 146–9
  apparatus, Davis, 108–9
  apparatus, Swicteslowski, 146–9
  constant, 110–1
  correction for change in pressure, 111
  elevation, 108–11
  maximum, 146–50
  minimum, 146–50
  of water, 55
Bomb calorimeter, 127–32
Buffer solutions, 207
Buoyancy of air, correction for, 55, 160–1

Calibration,
  of a Beckmann thermometer, 96–7
  of a conductivity cell, 195
  of a potentiometer, 218–9
  of a pycnometer, 160–1
  of a spectroscope, 90–1
  of a stalagmometer, 118–9
  of a thermocouple, 169–70
  of a viscosimeter, 112–3
  of the cross section of a capillary, 73–4
Calomel electrode, 214, 228
Calorimeter, 122–3, 127–30
Capillary,
  rise and surface tension, 71–5
  tube, measurement of radius of, 73–4
Catalysis,
  acid-base, 133, 179
  negative, 182–4
  oxidation-reduction, 175–7, 182–4
Cathodic polarization, 240–4
Cell,
  concentration, 212–6
  conductance, Ostwald type, 199
  conductance, pipet type, 194–5
  conductance, titration type, 199
  constant, 197
  H, 213

Cell—*Continued*
  polarization, 240
  standard, 221
  transference, 191–2
Chain reaction, 182–4
Clock reaction, 171–4
Color comparator, 208–9
Colorimeter, 252–5
Colorimetry, 206, 252–5
Combustion, 127–32
Comparator block, 208–9
Complex ion, dissociation constant of, 188–9, 210–1
Computations,
  approximate, 9–10
  graphical, 42–51
Conductance,
  apparatus, 193–8
  cell, Ostwald type, 199
  cell, pipet type, 194–5
  electrolytic, 190–201
Conductimetric titrations, 199–201
Conductivity water, 197
Constant boiling mixture, 143, 146, 149
Cooling curve, 162–7
Coulometer, 190–1
Crystallization,
  centers, spontaneous formation of, 80–1
  linear rate of, 80–2

Decay law, radioactive, 83–5
Density,
  of aqueous solutions (table), 126
  of gases, 53–5, 57–62
  of liquids, 74, 115–7, 159–61
  of Hg, 74
  of nitrobenzene, 145
  of the $H_2O—CH_3OH$ system (table), 159
  of water, 117, 158–9
Detergents, 251–2
Dewar tube, 94, 122–3
Differential thermometer, 95–8
Diffusion, 185–9
Dimensions, 4–6
Discharge tube, 90
Dispersion compensator of an Abbé refractometer, 151–2
Dissociation constant,
  of a complex ion, 188–9, 210–11
  of a weak acid, 193–8, 236
Distillation,
  fractional, 154–9
  of two miscible liquids, 146–50
  plate still, 154–9
  steam, 143–5
Distribution,
  coefficients, 210–11
  of errors, 10–4
Drop number method, 118–21
Drop weight method, surface tension, 118
Duboscq colorimeter, 252–5
Dumas bulb, 53–5
Dynamic method, vapor pressure, 76–9

Effusion of gases, 62–6
Electrodes,
  amalgam, 212–3
  antimony, 227
  calomel, 214, 228
  glass, 227
  hydrogen, 226, 228–9, 230–1
  iodine, 236
  platinum point, 213–4, 240
  quinhydrone, 223, 226, 229, 235
  silver, 222, 239
Electrolysis,
  and polarization, 240–4
  and transference, 190–2
Electrolytic conductance, 190–201
Electrometric titrations, 199–201, 233–9
Electromotive force,
  and activity, 212, 215, 224–5, 231–2
  and concentration, 212–6
  and equilibrium constant, 222–5
  and free energy, 225
  and heat of reaction, 225
  and transference number, 215–6
  decomposition, 241, 244
  liquid junction, 212–6, 231
  of chemical cells, 222–5
  of concentration cells, 212–6
Electroscope, 85–8
Empirical equations, 3, 30–40, 46–51
  rectification of, 35–6, 48–9
  solution of by graphical methods, 46–51
  solution of by least squares, 32–4, 39–40
  solution of by method of averages, 34–5, 40

Empirical equations—*Continued*
  solution of by method selected points, 32, 39, 51
End coils, 196–7
Equations, empirical, 3, 30–40, 46–51
Equilibrium,
  dissociation of a complex ion, 188–9, 210–1
  esterification, 133–4
  heterogeneous, 135–50, 162–7
  ionization, 198
  oxidation-reduction, 222–5
Equilibrium diagram (distillation), 149, 156
Error function, 14
Errors,
  average, 16–7, 29
  conditional, 19
  instrumental, 19
  persistent, 19
  probable, 15, 16–7, 29–30
  propagation of, 20–30
  random, 13–5
  systematic, 19
Esterification equilibrium, 133–4
Estimation of error, 44
Eudiometer, 59–61, 175–6, 183–5
Eutectic, 163
Evaporation, rate of, 185–9
Exponential notation, 7–9

Free energy and electromotive force, 222–5
Free surface energy (molar), 71–5
Freezing point,
  curve, 162–7
  lowering, Beckmann method, 103–6
  lowering, molar, 96, 106
  of an aqueous solution, 93–5
Freundlich adsorption isotherm, 248–50

Galvanometer, 168, 219, 221
Gases, effusion of, 62–6
"Goodness of fit," 35
Graham's effusion law, 62
Graphical,
  computations, 41–51
  differentiation, 42–4
  integration, 44–6
  solution of empirical equations, 46–9
Guoy "atomizer," 90

Half cell vessels, 214
Hartley curve, 91
Heat
  of activation, 178–81
  of ionic reactions, 122–6, 225
  of ionization, 122–6
  of neutralization, 122–6
  of sublimation, 76–9
  of vaporization, 67–9
Henry's law, 186
Hydrogen,
  electrode, 226, 228–9, 230–1
  generator, 229

Indicator constant, 205–8
Inhibition of a chain reaction, 182–4
Ionization,
  constant, 193–8, 234–6
  heat of, 122–6
Isotensiscope (Menzie's), 67–9

Laws physical, 3–4
Light,
  absorption of, 89–92
  chemical effect of, 245–7
  polarized, 98–102
Light sources,
  discharge tubes, 90
  mercury arc, 90, 100, 246
  monochromatic flames, 90
  sodium arc, 100
Lind electroscope, 85–8
Liquid,
  boiling point of, 69, 108–11
  density of, 74, 115–7, 159–61
  junction EMF, 212–6, 231
  molecular weight of, 71–5
  surface tension of, 71–5, 118–21
  vapor pressure of, 67–9
  viscosity of, 112–5
Logarithms (table), 260–1

Magnitude, 2
Manometer,
  differential, 68–9
  open mercury, 69, 77–8
Manostat, hand controlled, 68
Mean activity coefficient, 204, 212–6
Measurements, theory of, 2–4
Meniscus reader, 96
Menzie's isotensiscope, 67–9
Mercury arc, 90, 100, 246
Molecular diameters of gases, 64–5

Molecular weight,
  and boiling point elevation, 108–11
  and freezing point lowering, 93–5, 103–6
  of gases, 62–6
  of liquids, 71–5
  of solutes, 93–5, 101–3, 103–11
  of vapors, 53–5, 57–61
  the Dumas method, 53–5
  the effusion method, 62–6
  the Victor Meyer method, 57–61
Mole fraction, 120
Monochromatic flames, 90
Mutual solubility,
  of a binary system, 135–7
  of a ternary system, 138–42

Neutralization, heat of, 122–6
Nicol prism, 98–102

Optical activity, 98–102
Oscillator, audiofrequency, 194–7
Ostwald,
  conductance cell, 199
  pycnometer, 160–1
  viscosity pipet, 112–3
Overvoltage, 240–4

Partition measurements, 210–1
Pellet press, 107
P_H, 205–8, 212, 226–32, 234–6
Phase rule diagrams,
  distillation of a binary system, 146–50
  freezing point of a binary system, 162–7
  solubility of a binary system, 135–7
  solubility of a ternary system, 138–42
Philadelphia differential thermometer, 97–8
Photochemistry, laws of, 245–7
Photosensitized oxidations, 245–7
Plate still fractionation, 154–9
Platinizing,
  of conductance electrodes, 195
  of hydrogen electrodes, 230–1
Plotting data, 41–2
Poggendorf compensation method, 216–21
Polarimeter, 98–102
Polarization of an electrode, 240–4
Polarized light, rotation of the plane of, 98–102
Potentiometer,
  calibration of, 220–1
  simple, 216–8
  students, 217–8
Potentiometric titrations,
  acid-base, 234–6
  endpoint of, 233–4
  oxidation-reduction, 236–8
  precipitation, 238–9
Probable error,
  of a derived quantity, 20–30
  of a measurement, 15, 29
  of the mean, 16–7, 28–30
Propagation of errors, 20–30
Pycnometer, 160–1

Quinhydrone electrode, 223, 226, 229, 235

Radioactive decay law, 83–5
Rate,
  of a catalyzed reaction, 175–7, 178–81
  of a chain reaction, 182–4
  of an oxidation-reduction reaction, 171–4
  of crystallization (linear), 80–2
  of evaporation, 185–9
Reaction kinetics, 171–84
Reaction velocity, 171–84
  temperature coefficient of, 178–81
Refractometer, Abbé, 150–4
Report writing, 51–2
Residuals, 13–4, 32, 47–8
Resistance, electrical, 193

Salt bridge, 212, 228, 234–5, 239
Seed crystals, 80–1, 105
Significant figures, 6–7
Slide rule, 9
Sodium,
  arc, 100
  flame, 90
Soldering, hard, 169
Solubility,
  and common ion effect, 202–4
  and complex formation, 202–4
  and ionic strength, 202–4
  mutual, 135–7, 138–42
  of a sparingly soluble salt, 202–4
  product, 203

Solubilization by a soap, 251–5
Specific heats of aqueous solutions (table), 126
Spectroscope, 89–94
Sprengel pycnometer, 160–1
Standard,
  cell, 221
  deviation, 15–6, 29
  electromotive force, 216, 222–5
Steady state, 175
Stirrer,
  automatic, 105
  motor driven, 67–8, 81
  ring type, 122–4
  T-shaped, 187–8
Sublimation,
  heat of, 76–9
  pressure, 76–9
Successive differences, 36–9
Super cooling,
  and linear rate of crystallization, 80–2
  correction for in Beckmann FP method, 105–6
Super heating, 108, 146
Surface tension,
  as a function of temperature, 71–5
  capillary rise method, 71–2
  drop number method, 118–21
  of solutions, 118–21
Symbols and notation (table), 257–8

Tablet press, 107
Tangent meter, 44
Temperature coefficient,
  of crystallization velocity, 80–2
  of electromotive force, 223–5
  of mutual solubility, 135–7
  of reaction velocity, 178–81
  of surface tension, 71–5
  of vapor pressure, 67–9, 76–9
Ternary systems, solubility relations of, 138–42
Thermal analysis, 163
Thermocouple, 167–70
Thermometer,
  Beckmann, 96–7, 110
  correction for exposed stem, 70
  Menzie's differential, 108–9
  Philadelphia differential thermometer, 97–8
Thermostat, hand controlled, 67–8
Tie lines, 139–40
Titrations,
  conductimetric, 199–201
  potentiometric, 233–9
Transference,
  cell, 190–1
  numbers, 190–2, 215–6
Traube stalagmometer, 118–20
Triangular coordinates, 138–9

Ultraviolet light, 246
Units and dimensions, 2–3, 4–6

van't Hoff *i*, 106, 111
Vapor density, determination of,
  by Dumas method, 53–5
  by Victor Meyer method, 57–61
Vapor pressure,
  determination of by dynamic method, 76–9
  determination of by isotensiscope, 67–9
  temperature coefficient of, 67–9, 76–9
Victor Meyer apparatus, 57–61
Viscosity,
  of gases, 64
  of liquids, 112–5

Water equivalent of a calorimeter, 122–3, 129
Wave lengths for spectroscopic calibration (table), 92
Weighing paper, 104
Weighted mean, 17–8
Weston cell, 221
Westphall balance, 115–7
Wheatstone bridge, 193, 196