UNIVERSAL
LIBRARY
OU_156912
UNIVERSAL
LIBRARY

OSMANIA UNIVERSITY LIBRARY

Call No. 541.3 F12E Accession No. 16968

Author Falkenhagen, H.

Title Electrolytes.

This book should be returned on or before the date last marked below.

THE

INTERNATIONAL SERIES

OF

MONOGRAPHS ON PHYSICS

GENERAL EDITORS

R. H. FOWLER AND P. KAPITZA

THE INTERNATIONAL SERIES OF MONOGRAPHS ON PHYSICS

GENERAL EDITORS: R. H. Fowler and P. Kapitza

Already Published

THE PRINCIPLES OF QUANTUM MECHANICS

By P. A. M. DIRAC. 1930. Royal 8vo, pp. 268.

'Dr. Dirac's book has been eagerly awaited. . . . A book taking stock of the whole position, by one of the leaders in the advance, raises hope that our difficulties may be settled. The book fills this need admirably. For the first time wave mechanics is presented in a really coherent form with something like a philosophy of the new methods to support it.'
SIR ARTHUR EDDINGTON in the *Cambridge Review.*

'There can be no doubt that his [Dr. Dirac's] work ranks as one of the high achievements of contemporary physics.'—*Nature.*

CONSTITUTION OF ATOMIC NUCLEI AND RADIOACTIVITY. By G. GAMOW. 1931. Royal 8vo, pp. 122.

This is an important book which will be of great technical use to workers in the subject and in addition provide an informative and interesting account for more general readers.'—*Cambridge Review.*

'Il était donc utile de "faire le point" et c'est ce à quoi le livre de Gamow réussit parfaitement.'—*Journal de Physique.*

THE THEORY OF ELECTRIC AND MAGNETIC SUSCEPTIBILITIES. By J. H. VAN VLECK. 1932. Royal 8vo, pp. 396.

'Professor Van Vleck, in this volume, has made a valuable contribution to the Literature of Physics and this book is well worthy of the attention of those interested in the subject.'—*Chemical News.*

WAVE MECHANICS. ELEMENTARY THEORY

By J. FRENKEL. 1932. Royal 8vo, pp. 286.

WAVE MECHANICS. ADVANCED GENERAL THEORY. By J. FRENKEL. 1934. Royal 8vo, pp. 533.

THE THEORY OF ATOMIC COLLISIONS.

By N. F. MOTT and H. S. W. MASSEY. 1933. Royal 8vo, pp. 300.

RELATIVITY, THERMODYNAMICS, AND COSMOLOGY. By R. C. TOLMAN. 1934. Royal 8vo, pp. 518.

ELECTROLYTES

BY

HANS FALKENHAGEN

PROFESSOR IN THE UNIVERSITY OF KÖLN

TRANSLATED BY

R. P. BELL

FELLOW OF BALLIOL COLLEGE
OXFORD

OXFORD
AT THE CLARENDON PRESS
1934

OXFORD UNIVERSITY PRESS
AMEN HOUSE, E.C. 4
LONDON EDINBURGH GLASGOW
NEW YORK TORONTO MELBOURNE
CAPETOWN BOMBAY CALCUTTA
MADRAS SHANGHAI
HUMPHREY MILFORD
PUBLISHER TO THE UNIVERSITY

PRINTED IN GREAT BRITAIN

PREFACE

MY thanks are due to Professor P. Debye for suggesting the plan of this book. In the presentation of the material, it has been considered specially important not only to give the most important theoretical principles in the domain of electrolytes, but also to give the reader some idea of methods of experimental investigation and the reliable experimental results obtained.

The matter has been arranged with a view to familiarizing the reader first with the historical development of the science of electrolytes from an experimental point of view, neglecting all speculations, after which the possible theoretical explanations are discussed. The following review will serve as a guide to the contents of the book.

Faraday was the first to recognize the important part played by ions in the behaviour of an electrolytic solution. Some introductory remarks about certain definitions and energy relations in salt solutions (chapter I) and a presentation of Planck's theory of ideal dilute solutions (chapter II) are followed by a treatment of Arrhenius's theory (chapter III). This theory is, however, only valid for weak electrolytes, in which only a small proportion of the molecules are dissociated into ions. The behaviour of strong electrolytes, on the other hand, shows considerable departures from Arrhenius's theory, especially in the range of very dilute solutions. To aid in the interpretation of these anomalies, G. N. Lewis has developed an empirical thermodynamical theory of activities, which is thoroughly treated in chapter IV. The conductivity of strong electrolytes also exhibits anomalies which cannot be explained by Arrhenius's theory (chapter V). Earlier attempts at a theoretical explanation of the anomalous behaviour of strong electrolytes were bound to fail, since they did not take into account interionic action (chapter VI).

Van Laar, Bjerrum, Milner, and recently Debye, laid special weight on the action of the ions on one another. The ideas of Milner and more especially of Debye made it possible to explain those properties of strong electrolytes which follow the square root law, at least in sufficiently dilute solutions (chapters VII–X). It has in fact proved possible by means of the theory to predict new effects, such as the dependence of conductivity and dielectric constant upon frequency. Experimental work on these effects has been recently commenced (chapter IX). The characteristic behaviour of the viscosity of strong electrolytes, recently

discovered in America, also fits well into the picture of the ionic atmosphere (chapter X).

Even to-day it is only with difficulty that the theory can be extended from the field of dilute solutions to embrace concentrated solutions. Such an extended theory must take into account the polarization, dispersion, and repulsive forces between the ions, as well as the forces of interaction between the ions and the solvent molecules. The theoretical treatment of these complicated factors has so far been only partially successful. Various attempts to treat theoretically the properties of concentrated solutions are described shortly in chapter XI. The question of the true degree of dissociation of an electrolyte is closely connected with this problem, and a short section is therefore devoted to points connected with the optics of electrolytes and the detection of the undissociated part. In this connexion mention is made of the interesting attempts to study the structure of electrolyte solutions by means of the Raman effect.

In the final chapter (chapter XII) the statistical theories of R. H. Fowler and Kramers are developed. These theories show Debye's theory to be a direct and logical consequence of statistical laws, at least in the field of sufficiently dilute solutions.

The quantum mechanics of electrode processes, recently treated by R. W. Gurney are dealt with in an appendix by Professor R. H. Fowler. The field of reaction kinetics, in which particularly Brönsted has achieved so much, has been omitted, since there exist already several treatises on the subject, e.g. by G. M. Schwab. The study of colloidal electrolytes is at present only in the first stages of development, and it was not thought advisable to deal with it here.

I wish to take this opportunity of expressing my most sincere thanks to the Rockefeller Foundation for the award of research grants in Zürich, Leipzig, and Madison, Wisc., U.S.A. In this way I not only had the privilege of continuing my work under the valuable guidance of Professor Debye, but also had the opportunity of personal discussion with many American scientists who have contributed largely to solving the problem of electrolytes, and have shown me the greatest kindness in placing numerous separata at my disposal. My thanks are also due to the Notgemeinschaft der deutschen Wissenschaft for a research grant which made it possible for me to continue my studies on electrolytes.

I wish to thank Professor Wien (Jena) for a number of private communications. Especial thanks are due to my colleague E. Hückel (Stuttgart) for help in proof-reading and for much valuable advice.

Dr. Sack (Leipzig) and Dr. Burbach (Leverkusen) have been most kind in assisting with proof-reading. My colleague Herr Drucker (Leipzig) and Professors Brönsted and Bjerrum have very kindly placed numerous separata at my disposal. Finally, I wish to express my thanks to the publishers S. Hirzel for their extensive co-operation.

UNIVERSITY OF KÖLN, H. FALKENHAGEN
May 1932

TRANSLATOR'S NOTE

The present book is for the greater part a translation of the 1932 German edition, but has been revised, in consultation with the author, to bring it into line with the experimental and theoretical advances of the last two years. New topics treated in the English edition include the extension of Bjerrum's theory of ionic association by Kraus and Fuoss, Onsager's treatment of the dissociation field-effect, modern theoretical and practical work on transport numbers, and an appendix by Professor R. H. Fowler on the application of quantum mechanics to electrode processes. The references to the literature have also been brought up to date as far as possible.

R. P. B.

OXFORD,
July 1934

CONTENTS

I. SOME INTRODUCTORY REMARKS ABOUT ELECTROLYTES 1

1. Some Definitions: Electrolyte, Ions, Degree of Dissociation, Strong and Weak Electrolytes: Very Dilute, Moderately Dilute, and Concentrated Solutions 1
2. Energy Relations of Infinitely Dilute Salt Solutions . . 6
3. Notes and References 10

II. IDEAL DILUTE SOLUTIONS 13

4. Conditions of Equilibrium. The Thermodynamic Potentials . 13
5. The Theory of Ideal Dilute Solutions (Planck). The Law of Mass Action (Guldberg-Waage). The Equations of van 't Hoff . 16
6. The Laws of Osmotic Pressure, Depression of Freezing-point, Elevation of Boiling-point, and Vapour-pressure Lowering for Ideal Dilute Solutions 20

III. SOME CONSEQUENCES OF THE CLASSICAL THEORY OF ELECTROLYTES, AND THEIR APPLICATION TO WEAK ELECTROLYTES 25

7. The Doviations of Electrolytes from van 't Hoff's Equation for Osmotic Pressures and Raoult's Law for Freezing-point Depression and Boiling-point Elevation 25
8. Svante Arrhenius's Hypothesis of Electrolytic Dissociation in Aqueous Solution 26
   A. Explanation of osmotic and related phenomena . . 26
   B. The determination of the degree of dissociation from conductivity measurements. (Arrhenius and Planck) . 28
   C. Comparison of the degrees of dissociation calculated from osmotic measurements and from conductivity data (Arrhenius) 29
9. Ostwald's Dilution Law (The Variation of the Conductivity of Weak Electrolytes with the Concentration) . . . 30
10. Heterogeneous Ionic Equilibria. The Influence of Additions on the Solubility of Salts (Nernst) 34

IV. THE DEVIATIONS OF STRONG ELECTROLYTES FROM CLASSICAL THERMODYNAMICAL THEORY. THE EMPIRICAL ACTIVITY THEORY OF G. N. LEWIS. THE THERMODYNAMICS OF ACTIVITIES. THE REGULARITIES OBSERVED IN THE ACTIVITY COEFFICIENTS OF STRONG ELECTROLYTES AT SUFFICIENTLY HIGH DILUTIONS . 39

11. The Thermodynamic Anomalies of Strong Electrolytes in very Dilute Solution 39
   A. The impossibility of explaining the laws governing the osmotic coefficients by Arrhenius's theory . . 39
   B. The failure of the law of mass action for strong electrolytes 40
   C. Anomalies in the solubility relations of strong electrolytes 41
12. Definition of the Activity 43

13. The Thermodynamic Potential of Real Solutions and the Thermodynamics of Activities 45
14. The Osmotic Pressure, Freezing-point Depression, Boiling-point Elevation, and Lowering of Vapour Pressure of Strong Electrolytes, and their Relation to the Activity of the Solvent . 48
15. The Relation between the Activity Coefficients of the Solvent and the Solute. (Gibbs's Equation) 49
16. Activities from the Electromotive Force of Reversible Cells . 50
17. The Activity and Activity Coefficients of Strong Electrolytes . 51
18. Rational and Practical Activity Coefficients 53
19. The Experimental Determination of the Activity of Strong Electrolytes 56
A. Determination of activities from the vapour pressure of the electrolyte 56
B. Determination of activities from the vapour pressure of the solvent 57
C. Determination of activities from electromotive force measurements 58
D. Determination of the activity of electrolytes from freezing-point measurements. (G. N. Lewis) 62
E. The definition of activity coefficients in mixtures of electrolytes. The determination of activity coefficients in mixtures of electrolytes by means of solubility measurements. The principle of ionic strength. (Lewis and Randall) . . 68
20. Summary of the Laws found empirically for Activity Coefficients in Dilute Aqueous Solutions 70

V. ANOMALIES IN THE CONDUCTIVITY OF STRONG ELECTROLYTES 73
21. The Conductivity of Strong Electrolytes in Weak Stationary Fields 73
A. The variation of conductivity with concentration in aqueous solutions. The failure of Ostwald's dilution law for strong electrolytes 73
B. The conductivity of non-aqueous solutions . . 78
22. The Effect of Field-strength and Frequency on the Conductivity of Strong Electrolytes 82
A. The dependence of the conductivity of electrolytes on the electric field-strength (Wien effect) 82
B. The variation of the conductivity of strong electrolytes with the frequency of the field 90

VI. EARLY THEORIES OF THE ANOMALIES OF STRONG ELECTROLYTES 93
23. Chemical Theories (Drucker, Roth). The Conception of the Complete Dissociation of Strong Electrolytes (van Laar, Sutherland, Liebenow, Kjellin, Noyes, Hantzsch, and especially Bjerrum) 93
24. The Theories of P. Hertz, S. R. Milner, C. Ghosh, and Malmström 95

VII. THE PRINCIPLE OF THE DEBYE-MILNER THEORY OF STRONG ELECTROLYTES 99
25. Introductory Remarks 99
26. The Mean Electric Potential surrounding a Dissolved Ion. The Ionic Atmosphere and its Characteristic Properties . . 100
A. The distribution of the mean electric potential about an ion in a dilute electrolyte solution. The ionic atmosphere caused by the interionic forces 100
B. The thickness of the ionic atmosphere . . . 105
C. The time of relaxation of the ionic atmosphere . . 107

VIII. THE THERMODYNAMICS OF STRONG ELECTROLYTES ACCORDING TO DEBYE'S THEORY . . . 110
27. The Mean Potential Energy of the Central Ion. . . . 110
28. The Electric Energy of the Ionic Solution . . . 110
29. Calculation of the Electric Work W necessary to discharge and recharge the Ions. The Limiting Law for Osmotic Coefficients 111
30. The Limiting Law for Activity Coefficients . . . 120
31. Solubility Influences for Completely Dissociated Electrolytes, according to Debye's Theory 126
32. Salt Effects, according to Debye's Theory. Osmotic Pressure and Activities in Dilute Mixtures of Electrolytes and Non-electrolytes. Salting-out Effects. Neutral Salt Action . 136
A. Introductory Remarks 136
B. Osmotic pressure and activity in dilute mixtures (salting-out effect) 138
C. More exact theory of the salting-out effect . . 143
D. Neutral salt effects 152
33. The Heat of Dilution of Strong Electrolytes . . . 154
A. The theoretical limiting law 154
B. Experimental methods for measuring the heat of dilution (Nernst and Orthmann, Lange and Messner) . . 157
C. Comparison of the experimental data with theory . . 159

IX. DEBYE'S THEORY OF THE CONDUCTIVITY OF STRONG ELECTROLYTES 163
34. Conductivity Phenomena interpreted qualitatively in Terms of the Properties of the Ionic Atmosphere . . . 163
35. The General Fundamental Equations for Non-stationary Processes in Dilute Strong Electrolytes 165
36. The Special Case of Electrolytic Conductivity . . . 170
37. The Special Case of Simple Electrolytes with Two Sorts of Ions 172
38. Application to the Potential Distribution round an Ion in the Absence of External Influences 173
39. The Time of Relaxation of the Whole Ionic Atmosphere . 176
40. Calculation of the Electrophoretic Force upon an Ion (Debye, Hückel, and Onsager) 179

41. The Dependence of the Conductivity and the Dielectric Constant of Strong Electrolytes upon the Frequency. The General Theory of Debye and Falkenhagen 182
A. The fundamental equations when only two kinds of ion are present 182
B. Calculation of the asymmetric potential of the oscillating ion 186
C. Calculation of the force acting on the oscillating ion . 187
D. The general formulae for the dependence of conductivity and dielectric constant upon the frequency . . 189
42. The Conductivity of Electrolytes for the Special Case of Stationary Fields. Experimental Results and the Theory of L. Onsager 192
A. Test of Onsager's theory for aqueous solutions . . 193
B. The dependence of conductivity upon temperature and pressure 200
C. Comparison of Onsager's theory with experimental data in non-aqueous solvents 202
D. Onsager's theory of transport numbers . . . 209
43. Results of the Theory of Dispersion for the Conductivity and Dielectric Constant of Strong Electrolytes . . . 211
A. General calculation of the dispersion effect for conductivity 211
B. Applications of the theory of conductivity dispersion . 214
C. General formulae and interpolation tables for the dependence of dielectric constants upon frequency . . 219
D. Applications of the theory of the dispersion of dielectric constants 220
44. The Experimental Determination of the High-frequency Conductivity of Electrolytes and the Variation of Dielectric Constant with Frequency 222
A. The method of Sack and his collaborators for measuring the high-frequency conductivity of electrolytes . . 223
B. Zahn's method of conductivity measurement . . 226
C. Deubner's method for conductivity measurements at high frequencies 229
D. The method of M. Wien and his collaborators for measuring simultaneously the conductivity and dielectric constant of electrolytes 231
E. The method of Malsch for the absolute determination of high-frequency conductivites 234
F. Comparison of results by different methods . . 235
45. The Theory of the Wien Effect 235

X. THE MODERN THEORY OF THE VISCOSITY OF STRONG ELECTROLYTES 243
46. Historical 243
47. The Work of Jones and Dole 245
48. The Theoretical Limiting Law for the Viscosity of Strong Electrolytes, and its Experimental Confirmation . . . 245

XI. MORE CONCENTRATED SOLUTIONS 250
49. Introductory Remarks 250
50. The Theory of Debye and Hückel and its Applications . . 250
51. Theories of Ionic Association (Bjerrum, Müller, Gronwall, La Mer, and Sandved) 257
A. Bjerrum's theory. Formation of ion triplets (Bjerrum, Fuoss, Kraus) 258
B. The relation of Bjerrum's theory to the theories of both Müller, and Gronwall, La Mer, and Sandved . . 267
C. The theory of Gronwall, La Mer, and Sandved . . 270
52. The Heat of Dilution of More Concentrated Solutions according to the Theories of Debye and Hückel; Hückel; and La Mer, Gronwall, and Sandved 280
53. Nernst's Theory of Electrolytic Dissociation. Approximate Determination of the True Degree of Dissociation . . 289
54. General Considerations Involved in a Treatment of more Concentrated Solutions 295
55. Approximate Determination of the True Degree of Dissociation from Conductivity Measurements (Onsager, Nernst, Davies, McInnes, Fuoss, and Kraus) 297
56. Wien's Method for determining the True Degree of Dissociation 308
A. Wien's first method 308
B. Wien's method for determining the true degree of dissociation from the Debye-Falkenhagen dielectric constant effect 311
C. Degree of dissociation and field effect . . . 312
57. The Determination of the Degree of Dissociation of Electrolytic Solutions from their Optical Properties . . . 312
A. The absorption spectra of strong electrolytes (Bjerrum, v. Halban, J. Franck, Ebert, Scheibe and Eisenbrand, Gross and Goldstern, Fromherz and collaborators) . . 313
B. Refractometric investigations (Fajans, Kohner, and Geffcken) 316
C. The Raman effect and the structure of electrolytic solutions 322
58. Brönsted's Principle of the Specific Interaction of Ions . . 325

XII. THE STATISTICAL FOUNDATIONS OF DEBYE'S THEORY 331
59. General Statistical Considerations 331
60. Kramers's Theory 332

APPENDIX. RECENT APPLICATIONS OF QUANTUM MECHANICS TO THE THEORY OF ELECTROLYTES. By R. H. FOWLER
Introduction 336
The experimental data on overvoltage . . . 337
The behaviour of an ion near a metal 337
The effect of interface potentials 338
Theory of the current-voltage relationship . . . 340

TABLE OF THE MOST IMPORTANT SYMBOLS 344

INDEX 347

INTRODUCTION

THE classical theory of electrolyte solutions is characterized by a complete neglect of the forces between the ions, and thus corresponds to the theory of perfect gases. It is therefore not surprising that the theory was found to be incapable of describing the behaviour of electrolytes which are dissociated to a great extent.

It is known that the Coulomb forces existing between ions in virtue of their electric charges are considerably greater than the intermolecular forces usually met with, and fall off much more slowly with the distance. The problem thus arises of investigating the effect of these forces and devising methods which are suited to their special nature. Just as van der Waals's theory of real gases involves no contradiction of the theory of perfect gases, the modern theory of electrolytes is not incompatible with the ideas of Arrhenius. It seeks only to introduce certain refinements which are necessary to explain the anomalies, just as it is necessary to take into account the ordinary intermolecular forces to obtain an equation of state for gases which will make plausible the phenomena of the critical point and liquefaction.

The special nature of interionic forces appears most clearly in the domain of very dilute solutions. It is just in this range that it has proved possible to formulate certain characteristic laws such as the laws of Kohlrausch for the conductivity and of G. N. Lewis for the activity, some of which were based solely upon experimental data long before the existence of any extension to the classical theory. It was found that the square root of the concentration was specially prominent both in these laws and in many others relating to the properties of electrolyte solutions, and it was one of the first successes of the modern theory that it connected this special type of dependence directly with the inverse square law of the Coulomb forces.

Apart from the formulation of such quantitative laws much insight has been gained from the qualitative picture of ionic distribution which is a necessary consequence of the existence of interionic forces. The ions in solution are not distributed completely at random. If we consider a given ion, the probability of finding an ion of the same sign in the neighbourhood of this ion is less than the probability of finding an ion of the opposite sign. This gives the mean charge distribution in the solution a structure which bears some resemblance to the charge distribution in a rock-salt crystal, and which gives rise to the characteristic

behaviour of the solution. Milner was the first to work out this idea clearly, and it is this structure which we now describe in terms of the ionic atmosphere, characterized by its spatial extension on the one hand, and its time of relaxation on the other. The most recent developments have taken place along these lines. The properties of the ionic atmosphere have provided an explanation of the dependence of conductivity upon field strength discovered by M. Wien. The same theory predicts that the conductivity should also depend upon the frequency, and this prediction has now been satisfactorily verified.

The subject has thus reached a certain provisional stage of finality, though there are many questions yet to be answered, and their number is continually increasing. The time is certainly ripe for a presentation of modern electrolyte theory reviewed from a consistent standpoint, such as the present work provides. It is highly satisfactory that the considerable labour involved has been undertaken by such an expert as Falkenhagen, who has himself been a valuable contributor to the development of the theory.

P. DEBYE

LEIPZIG,
May 11th, 1932

I

SOME INTRODUCTORY REMARKS ABOUT ELECTROLYTES

1. Some Definitions: Electrolyte, Ions, Degree of Dissociation, Strong and Weak Electrolytes: Very Dilute, Moderately Dilute, and Concentrated Solutions

THE chief token by which an electrolyte is recognized, its electrical conductivity, was long ago traced to the transport of electrically charged matter. Salts, acids, and bases possess this special kind of conductivity. In 1832 Faraday† discovered *the law of electrolysis* known by his name, according to which one gram-equivalent of any substance transports a fixed amount of electricity, 96,494 coulombs. This amount of electricity, $\mathfrak{F}$, is called the *electrochemical equivalent* or the *faraday*. A current of 9·6494 amperes flowing for 10,000 seconds through any electrolyte will liberate 1·008 gm. of univalent hydrogen, $\frac{16}{2}$ gm. of divalent oxygen, 107·88 gm. Ag, etc. All investigations have confirmed Faraday's law with great accuracy and shown that the amount liberated is independent of the temperature, pressure, the concentration, the solvent, the presence of other electrolytes, and other factors.

Hermann v. Helmholtz‡ was the first, in his famous 1881 Faraday lecture, to explain Faraday's law by the assumption of *atoms of electricity* bearing a simple numerical relation to the atoms or groups of atoms. Following Faraday, these charged atoms or groups of atoms are termed *ions*, and those ions which migrate in an electric field towards the cathode are called *cations*, while those which move towards the anode are called *anions*. Electrolytic conductivity thus differs from metallic conductivity, in that it is not the *electrons* but the positive and negative *ions* which are responsible for the conduction. The ions are formed by the loss or gain of an electron by the corresponding uncharged atoms or groups of atoms, and in an electric field they constitute the carriers of the electric current.

† M. Faraday, *Phil. Trans.* **123** (1833), 379; **124** (1834), 481; *Experimental Researches in Electricity*, 3rd–5th and 6th–8th series, Electrochemical Decomposition (1833 and 1834) republished in Ostwald's *Klassiker*, nos. 86 and 87. See also W. Ostwald, *Elektrochemie, ihre Geschichte und Lehre*, Leipzig, 1896 (Weit).

‡ H. v. Helmholtz, *Wied. Ann.* **11** (1880), 737; *Proc. Roy. Soc. Edinb.* 1880–1, p. 202. See also *Wissenschaftliche Abhandlungen*, vol. iii, p. 52 (Leipzig, 1895) and *Vorträge und Reden*, 5th edition, vol. ii, p. 249 (Braunschweig, 1903). Grotthus, Williamson, and more especially Clausius and Hittorf had mentioned the idea of the existence of free ions before v. Helmholtz. For further historical details see the book by M. Roloff, *Die Theorie der elektrolytischen Dissoziation* (Springer, Berlin, 1902).

The *valency* of an ion is determined by the number of electrons it has gained or lost. These electrons are termed *valency electrons*, and always come from the outer part of the atom. A divalent cadmium ion is thus a cadmium atom which has lost two electrons, and a sulphate ion is an atomic complex SO_4 with two extra electrons. The classical work of Hittorf† was the first occasion on which the nature of the ions into which a molecule dissociates was deduced from the concentration changes caused by electrolysis, which are due to the different velocities of migration of the different ions. A $CdSO_4$ solution is termed a *binary electrolyte* since one molecule dissociates into two ions, Cd^{++} and $SO_4^{=}$, $BaCl_2$ is a ternary electrolyte, since one molecule dissociates into one Ba^{++} ion and two Cl^- ions. $LaCl_3$ is an example of a quaternary electrolyte, giving one La^{+++} ion and three Cl^- ions.‡ Each of the above electrolytes is a *simple electrolyte*, but mixtures of electrolytes are often met with.

In 1876 Kohlrausch formulated the law that the conductivity of a number of simple electrolytes can be expressed as the sum of two quantities, each characteristic of one of the component ions. This law was named by him the law of *independent migration of ions*. It is strange that this discovery did not lead directly to the ionic theory.

Svante Arrhenius§ was the first to propose and demonstrate that the molecules of an electrolyte are dissociated to a certain extent into free ions even when no external field is acting on them. He was led to this conclusion by van't Hoff's theory of solution and his own extensive researches on the conductivity of electrolytic solutions. Berzelius thought that the electric current tore the molecules apart, and thus caused the polarity of the two groups of ions. If this were so, no current would flow through the electrolyte below a certain limiting voltage, and when the voltage reached this limit, a current would suddenly start, which is in complete contradiction to experiment. Even with the smallest applied e.m.f., the current flowing through the electrolyte obeys Ohm's law. Clausius|| was the first to point out this discrepancy

† W. Hittorf, *Pogg. Ann.* **89** (1853), 117–211; **98** (1856), 1; **103** (1858), 1; **106** (1859), 337, 513; *Z. f. phys. Chem.* **39** (1901), 612; **43** (1903), 49. See also Ostwald's *Klassiker*, nos. 21 and 22, Leipzig, 1891. For further references to work on transport numbers, see *Note 1*, p. 10.

‡ Many electrolytes, especially acids and salts of the higher types, exhibit a more complicated dissociation into intermediate ions. Such behaviour is termed 'stepwise dissociation'. For references to the literature, see especially the books of Taylor and Jellinek quoted in *Note 1*, p. 10.

§ Sv. Arrhenius, *Bih. Svensk. Akad. Handl.* **8** (1884), nos. 13 and 14; *Z. phys. Chem.* **1** (1887), 631.

|| R. Clausius, *Pogg. Ann.* **101** (1857), 338. Similar ideas had been expressed by Grotthus in 1806, though not so clearly. See Th. v. Grotthus, *Ann. chim.* **58** (1806), 54.

between the older ideas and experiment, and also to propose the hypothesis of the electrolytic dissociation of molecules. Clausius believed, however, that ions occurred only rarely in solution, by far the greater part of the salt being present as undissociated molecules. This idea of Clausius is quite incorrect.

The great service performed by Arrhenius lies in the fact that he placed the *Dissociation Theory* on a sound basis, and thereby made possible the subsequent widespread development which has been of such importance for physical chemistry.

The dissociation theory gave the first exact definition of acids and bases. It was known previously that H and OH were the significant groups, but this gave no real understanding of the nature of acids and bases, since many compounds were known which contained H or OH without possessing an acidic or basic character. The dissociation theory was the first to show that H^+ or OH^- must be present in solution in order to give rise to acidic or basic properties respectively.

This definition of acids and bases is only valid for aqueous solutions. Thus aniline, for example, exhibits basic properties in non-aqueous solutions in which there is no possibility of the formation of OH^- ions, and a solution of ammonia in ether behaves in many ways just like an aqueous solution of NH_3, although it contains no OH^- ions. Further, the H^+ ion (i.e. the proton) cannot exist as such in any solvent. Thus in aqueous solution the H_3O^+ ion is formed, and is commonly termed the hydrogen ion. In ethyl alcohol the $C_2H_5OH_2^+$ ion acts as the hydrogen ion.

Brönsted has devoted himself specially to this question in some recent papers, and has given a definition of the acid-base function which is valid independent of the solvent and is more generally applicable than that of Arrhenius. Brönsted inquires whether the classical theory really does express the fundamental nature of acids and bases. He proposes instead the following definition as being universally characteristic of acids and bases:

$$\underset{\text{Acid}}{A} \rightleftharpoons \underset{\text{Base}}{B} + H^+.$$

This scheme shows clearly how the interrelation between acids and bases depends on the unique nature of the proton. According to Brönsted, an acid is a substance having a tendency to split off a proton, and a base is a substance having a tendency to take up a proton. The above equation does not, however, represent a stoichiometric process actually taking place, since the proton cannot exist in a free state. B can only be completely transformed into A in the presence of a third molecule which can give up the proton, and is therefore an acid.

Similarly, A can only be completely converted into B in the presence of a basic molecule which takes up the proton liberated. The reaction of an acid with a base takes place according to the equation.

$$\underset{\text{(Acid 1)}}{A_1} + \underset{\text{(Base 2)}}{B_2} \rightleftharpoons \underset{\text{(Acid 2)}}{A_2} + \underset{\text{(Base 1)}}{B_1}$$

If the acid is acetic acid, the *corresponding base* is the negatively charged acetate

ion, according to the equation

$$\underset{\text{(Acid)}}{CH_3COOH} \rightleftharpoons \underset{\text{(Base)}}{CH_3COO^-} + H^+.$$

When acetic acid is dissolved in water, the process of ionization is represented by the scheme,

$$\underset{\text{(Acid 1)}}{CH_3COOH} + \underset{\text{(Base 2)}}{H_2O} \rightleftharpoons \underset{\text{(Base 1)}}{CH_3COO^-} + \underset{\text{(Acid 2)}}{H_3O^+}.$$

If the base is ammonia, the *corresponding acid* is the positively charged ammonium ion, according to

$$\underset{\text{(Acid)}}{NH_4^+} \rightleftharpoons \underset{\text{(Base)}}{NH_3} + H^+,$$

and the process taking place on dissolving the base NH_3 in water is given by

$$\underset{\text{(Base 1)}}{NH_3} + \underset{\text{(Acid 2)}}{H_2O} \rightleftharpoons \underset{\text{(Acid 1)}}{NH_4^+} + \underset{\text{(Base 2)}}{OH^-}.$$

It appears from these considerations that it is only in aqueous solution that the 'hydrogen ion' H_3O^+ and the hydroxyl ion OH^- are of special significance for the theory of acids and bases.

We have retained Arrhenius's theory in the following treatment, since the thermodynamic reasoning involved remains unaffected by Brönsted's modification.

In considering kinetic phenomena such as hydrogen ion and hydroxyl ion catalysis, Brönsted's theory necessitates certain changes which we shall briefly mention here. It is well known that certain chemical reactions are catalysed by hydrogen ions and hydroxyl ions, such reactions being in fact often used to determine the concentration of H^+ ion or OH^- ion. If it is remembered, however, that the H_3O^+ ion is only one of many acids and does not occupy any unique position, it is not to be expected that it will prove unique in its catalytic powers. Such reactions must also be catalysed by any other acids present in the solution. Similar remarks apply to hydroxyl ion catalysis. On these grounds Brönsted has developed an *extended theory of acid and basic catalysis* in which the tendency to lose or gain a proton is shown to be the factor governing catalytic properties. For references, see *Note 2*, p. 11.

Salts can be considered as compounds which form ions other than H^+ and OH^-. It is an aid to the extension of our ideas on electrolytes to introduce the *degree of dissociation* as a measure of the dissociation of the molecules. The degree of dissociation is defined as the ratio of the number of molecules dissociated to the total number of molecules present in the solution. *Strong electrolytes* are those which are much more than half dissociated even at high concentrations. *Weak electrolytes* are those which have a degree of dissociation very much less than unity. A survey of some of the important groups of electrolytes is given in the following paragraph.†

† The conventional classification of the strength of electrolytes is based upon the order of magnitude of the mass law constant K_γ (cf. p. 32). If $K_\gamma > 1$, the electrolyte is strong, if $K_\gamma < 10^{-2}$, it is weak. Electrolytes of medium strength correspond roughly to $10^{-2} > K_\gamma > 1$, and very weak ones to $K_\gamma \ll 10^{-7}$. See e.g. the section by L. Ebert in *Handb. d. Experimentalphysik*, vol. xii, part 1, p. 85, 1932. We may mention in passing two groups of electrolytes which differ from ordinary electrolytes in many of their properties, i.e. *pseudo-electrolytes* and *amphoteric electrolytes*. According to Hantzsch, a

The strong electrolytes include most salts dissolved in water, including ammonium and substituted ammonium salts. Among the exceptions are the halides of mercury, cadmium, tin, and antimony. Other strong electrolytes are the strong acids HCl, HBr, HI, HNO_3, $HClO_4$, H_2SO_4, H_2F_2, and all sulphonic acids. H_2SO_4 and H_2F_2 are, however, dissociated less than those preceding them in the list. Strong bases (hydroxyl compounds) include the quaternary substituted amine bases, while ammonia and the primary, secondary, and tertiary substituted amine bases are weak electrolytes. The weak electrolytes also comprise ammonia, the majority of organic acids, many organic bases, and many inorganic acids and bases as well as the hydroxides of divalent and trivalent metals (with the exception of mercury, cadmium, and zinc). Examples of the weak salts mentioned above are $CdCl_2$, $CdBr_2$, CdI_2, $HgCl_2$, $Hg(CN)_2$, $Fe(CNS)_3$, FeF_3, $(CH_3COO)_3Fe$, etc. The phenols, the alcohols, aniline, and water are extremely weak electrolytes.

Since the degree of dissociation depends very much on the concentration, there are naturally many intermediate types between the strong and weak electrolytes, which only represent extreme cases. Thus we may class as intermediate the salts of the heavy metals and the strongest carboxylic acids, such as citric, tartaric, oxalic, and formic acids and many halogen and nitro-carboxylic acids. As examples of extremely weak electrolytes we may mention the acids hydrogen sulphide, silicic acid, boric acid; the bases aniline, pyridine, etc.; and water. The following point is of importance in this connexion. The class to which an electrolyte belongs is not determined by the electrolyte alone, but by its behaviour in solution. Thus a salt may very well be a strong electrolyte in water, but a weak electrolyte in acetone, and extremely weak in benzene.† This depends to some extent on the fact that the dielectric constant of water (about 80) is much greater than those of acetone (21) and benzene (2·3), so that the Coulomb forces between the ions in water are correspondingly smaller than in acetone and benzene. The dissociating power of water is much greater than that of acetone or benzene, as was first pointed out by Nernst and Thomson.‡

pseudo-electrolyte is one which only exhibits acid or basic character after being transformed to an ionizable form, or after reaction with the solvent. An amphoteric electrolyte is one which can split off either a H^+ ion or an OH^- ion. If both these ions are split off simultaneously, the resulting ion is known as a '*zwitterion*'. We shall exclude these special classes of electrolytes from the following discussion, and only mention that an electrostatic theory of the 'zwitterion' has been given by G. Scatchard and J. G. Kirkwood (*Phys. Z.* **33** (1932), 297). For further information see A. Thiel, *Samml. chem. u. chem.-techn. Vorträge*, **16** (1911), 307; H. Lundén, ibid. **29** (1927), 265. See also L. Michaelis, *Die Wasserstoffionkonzentration*, 2nd edition, part I, p. 59, Berlin, 1922, and appropriate text-books of chemistry, especially W. Nernst, *Theoretische Chemie*, 8th–10th edition, p. 440, and H. S. Taylor, *A Treatise on Physical Chemistry*, 2nd edition, vol. i, p. 700, 1931.

† See p. 202 in this book; also a review of the dissociation of strong electrolytes in non-aqueous solutions by R. Schingnitz, *Z. f. Elektrochem.* **36** (1930), 861.

‡ W. Nernst, *Gött. Nachr.* (1893), no. 12; *Z. f. phys. Chem.* **13** (1894), 531; *Z. f.*

P. Walden† has succeeded in confirming the Nernst-Thomson rule very elegantly, e.g. for the salt $N(C_2H_5)_4I$, which dissolves fairly readily in a number of solvents, he found a certain relation between dissociation and dielectric constant, though the parallelism is not complete on account of other specific influences, such as the formation of complex ions or the association of the ions with solvent molecules.

The definition of degrees of dilution is also closely connected with considerations of this kind. A solution is termed *infinitely dilute* or ideally dilute when the attractive and repulsive forces between the ions have no appreciable effect upon the properties of the solution, and the interaction between an ion and the molecules of the solvent is not appreciably affected by the presence of the other ions. If these effects are present but only to a small extent, Drucker‡ proposes to term the solutions *moderately dilute*, while in *concentrated solutions* the effects are very large. In the latter case the interaction between the ions and the solvent molecules are of importance. The actual magnitudes of the concentrations corresponding to these classes again depend very much on the solvent. Thus a solution containing 0·01 gram-molecules per litre would be termed very dilute in water, while it would be hardly dilute at all in acetone and very concentrated in benzene, corresponding to the Nernst-Thomson rule for the effect of the dielectric constant.

Before continuing with the main plan of the present work, we shall give a second introductory paragraph dealing with the energy relations involved in the solution of salts, as treated by Haber and Fajans.

2. Energy Relations of Infinitely Dilute Salt Solutions

We shall now consider the problem of how a salt solution actually comes into existence.§ When a small crystal of common salt is placed in water, the ions of the salt act upon the water molecules, each ion tending to become surrounded by a sheath of water molecules. P. Debye‖ has shown that the water molecule is a dipole. Although we know very

Elektrochem. **8** (1902), 484. J. J. Thomson's paper on the same subject appeared almost simultaneously; *Phil. Mag.* **36** (1893), 320.

† P. Walden, *Z. f. phys. Chem.* **54** (1905), 228; **55** (1906), 683; **94** (1920), 263. For further literature see P. Walden, *Z. f. phys. Chem.* A, **147** (1930), 1, and p. 80 of this book.

‡ K. Drucker calls an electrolyte solution moderately dilute when the ions exhibit departures from ideal behaviour, but the concentration of the solvent is effectively constant. See K. Drucker, *Die Anomalie der starken Elektrolyte*, Stuttgart, 1906.

§ The matter is considerably more complicated in the case of acids and bases. See especially K. Fajans, *Naturwiss.* **9** (1921), 729; also H. G. Grimm in Geiger-Scheel's *Handbuch d. Physik*, xxlv, p. 550.

‖ See P. Debye's recent monograph on this subject: *Polare Molekeln*, S. Hirzel, Leipzig, 1929.

little about the structure of highly associated liquids like water, it seems reasonable to assume that the water dipole is attracted and oriented by the field of the ion. The interaction between the ion and the dipole will be greater the smaller the distance between them, and the orienting influence of the ion will increase with increasing charge and decreasing radius. Fajans† takes the *heat of hydration of gaseous ions* as a quantitative measure of the action of the ions upon the dipoles. This quantity can be defined as the heat evolved by the combination of free gaseous ions with liquid water to form hydrated ions, the existence of which has now been definitely established.‡ We can carry out the following *Born's cycle.*§ One gram-molecule of salt is first converted to gaseous ions, the necessary energy being termed the *lattice energy.* This can be calculated theoretically for the NaCl type of lattice by the method of Born, but can also be easily obtained from the following experimental

$$\begin{array}{ccc} [\mathrm{K}]+\frac{1}{2}(\mathrm{Cl_2}) & \xrightarrow{Q_B} & [\mathrm{KCl}] \\ \uparrow Q_S \quad \uparrow D_i & & \uparrow U_g \\ (\mathrm{K})+(\mathrm{Cl}) & \xleftarrow[-E_A]{J_K} & (\mathrm{K^+})+(\mathrm{Cl^-}) \end{array}$$

FIG. 1. The Born cycle.

data: the *heat of sublimation*, the *energy of ionization*, the *heat of formation*, and the *electron affinity* of chlorine. The method is as follows.

The compound (e.g. KCl) is formed from the elements in two distinct ways (cf. Fig. 1). The first way is the direct union of the elements, liberating the heat of formation Q_B. The second way consists of four steps. (1) The element K is sublimed by supplying the heat of sublimation Q_S. (2) One electron is removed from the K atom, the energy necessary being the work of ionization, J_K. (3) The chlorine molecules are split up into atoms by supplying energy D_i (dissociation energy) per gram-atom. Each chlorine atom is then converted into a chlorine ion by the addition of an electron thereby liberating an amount of energy E_A (electron affinity) per gram-atom. (4) The separate gaseous ions K and Cl now unite to give the solid KCl lattice, liberating the lattice energy U_g. The direction of the arrows in Fig. 1 indicates which alterations of the system are accompanied by an evolution of heat. The figure leads immediately to the relation

$$Q_B = U_g - J_K - Q_S - D_i + E_A. \qquad (1)$$

The quantities in this equation refer to one gram-atom or one gram-molecule of KCl. (Cf. Table 1.)

† K. Fajans, *Verh. d. Dtsch. Phys. Ges.* **21** (1919), 549, 709, 714; F. Haber, ibid. **21** (1919), 750.

‡ See W. Nernst, *Theoretische Chemie*, 11th–15th edition, p. 447, 1926; also H. S. Taylor, loc. cit., p. 686.

§ M. Born, *Verh. d. Dtsch. Phys. Ges.* **21** (1919), 13, 679.

The gaseous ions are then dissolved in water, liberating the sum of the heats of hydration of the anion (Q_a) and the cation (Q_k).

The cyclic process then gives

$$Q_a + Q_k = Q_L + U_g, \tag{2}$$

where Q_L is the heat of solution as experimentally determined.

The following table, taken from recent investigations by E. Lange and K. P. Miščenko,[1] gives the values of U_g and Q_L for various salts.

TABLE 1

Lattice energy (U_g) and heat of solution (Q_L) of the alkali halides, in kg. cal.

	J_{M_g}[2]	$-El.Aff.$[3]	$+Q_S$[4]	$+D_i$[5]	$+Q_B$[6]	$= U_g$[7]	U_g'[8]	U_g''[9]	Q_L[10]
LiF	123	(94)	40	..	120	..	..	231	— 1·04
LiCl	123	85	40	29	97	204	..	189	+ 8·76
LiBr	123	82	40	22	87	190	..	180	+11·72
LiI	123	75	40	17	71	176	..	..	+14·76
NaF	118	(94)	27	..	111	..	..	..	— 0·6
NaCl	118	85	27	29	98	187	183	178	— 1·7
NaBr	118	82	27	22	90	175	173	169	— 0·2
NaI	118	75	27	17	76	163	160	..	+ 1·3
KF	99	(94)	23	..	109	..	..	182	+ 4·24
KCl	99	85	23	29	104	170	164	164	— 4·29
KBr	99	82	23	22	97	159	157	157	— 4·91
KI	99	75	23	17	85	149	146	148	— 4·98
RbF	96	(94)	22	..	108	..	..	..	+ 5·80
RbCl	96	85	22	29	105	167	156	..	— 4·5
RbBr	96	82	22	22	99	157	149	152	— 5·96
RbI	96	75	22	17	87	107	140	147	— 6·5
CsF	89	(94)	20	..	107	..	..	..	+ 8·37
CsCl	89	85	20	29	106	159	..	..	— 4·75
CsBr	89	82	20	22	101	150	..	..	— 6·73
CsI	89	75	20	17	90	141	..	..	— 8·25

[1] E. Lange and K. P. Miščenko, *Z. f. phys. Chem.* A, **149**, (1930), 1.

[2] Ionization energies of the metals (from recent spectroscopic data): E. Rabinowitsch and E. Thilo, *Z. phys. Chem.* B, **6** (1930), 288.

[3] The values for the electron affinities are mean values from spectroscopic data (E. v. Angerer and A. Müller, *Physikal. Z.* **26** (1925), 643), and the theory of the crystal lattice (M. Born, *Atomtheorie des festen Zustandes*, p. 752, Leipzig, 1923).

[4] Heats of sublimation of the elements (calculated from data in Landolt-Börnstein by E. Rabinowitsch and E. Thilo, loc. cit., p. 298).

[5] Heats of dissociation of the halogens (from spectroscopic data by H. Sponer, *Ergebn. d. exakt. Naturw.* **6** (1927), 75.

[6] Heats of formation of the salts (Landolt-Börnstein, *Phys.-chem. Tabellen*, p. 1505).

[7] Lattice energies calculated from the above data by equation (1).

[8] Lattice energies calculated from the electrostatic lattice theory (Na and K salts, E. Lange, *Z. phys. Chem.* **116** (1925), 337; Rb salts, H. G. Grimm, *Handbuch d. Physik*, xxiv, p. 440).

[9] Lattice energies according to J. C. Slater, *Phys. Rev.* **23** (1924), 488.

[10] Heats of solution from Landolt-Börnstein and E. Lange. The figures refer to one gram-molecule at infinite dilution.

The lattice energies of KCl and KBr are respectively 164 and 157 kg. cal./gm. mol. The corresponding heats of solution are −4·3 and −4·9 kg. cal./gm. mol.; hence

$$(Q_a+Q_k)_{\mathrm{KCl}} = 159{\cdot}7 \text{ kg. cal./gm. mol.}$$
$$(Q_a+Q_k)_{\mathrm{KBr}} = 152{\cdot}1 \text{ kg. cal./gm. mol.}$$

The work necessary to break up the crystal is thus chiefly furnished by the heat of hydration.

We shall not here deal with the thermochemistry of the hydration of ions, which treats the polarization of the water molecules by the ions as the essential part of the process. (For details see M. Born, *Z. f. Physik*, **1** (1920), 45; T. J. Webb, *Proc. Nat. Acad. Wash.* **12** (1926), 524; *J. Am. Chem. Soc.* **48** (1926), 2589; Latimer and R. M. Buffington, ibid. **48** (1926), 2297; W. M. Latimer, ibid. **48** (1926), 1234; N. Bjerrum, *Z. phys. Chem.* **127** (1927), 369. See also the monograph by A. E. van Arkel and J. H. de Boer, *Chemische Bindung als elektrostatische Erscheinung*, p. 203, Hirzel, Leipzig, 1931). Extended use has been made of M. Born's idea, according to which the maximum work performed by transferring a spherical ion of radius r and charge e from a vacuum to a medium of dielectric constant D_0 is given by the expression

$$\frac{e^2}{2r}\left(1-\frac{1}{D_0}\right).$$

We may mention the considerations of Scatchard on the effect of the medium on the electromotive force of cells (see *J. Am. Chem. Soc.* **47** (1925), 2098; *Trans. Farad. Soc.* **23** (1927), 454; *Chem. Rev.* **3** (1927), 383, and the work of Bjerrum and Larsson (*Z. phys. Chem.* **127** (1927), 358) on the distribution of ions between different media. References may also be made in this connexion to a paper by Hammerschmid and E. Lange (*Z. phys. Chem.* **155 A** (1931), 85) containing a criticism of the views of Fredenhagen, *Z. phys. Chem.* **152 A** (1931), 321; *Z. f. Electrochem.* **37** (1931), 257, on the solution process for electrolytes. (See also subsequent polemical papers by both these authors in the *Z. phys. Chem.*) Fajans and Born have frequently emphasized the fact that the energy of solvation of a gaseous ion can only be roughly calculated in this way, and actually depends on several additional factors, such as chemical linkages between the ion and one or more of the surrounding water molecules. The forces between two ions very close together, and between an ion and the solvent molecules in its immediate neighbourhood are very specific in character, and do not only depend on the dielectric constant and the distance. Individual variations are therefore also found in the solvent power and power of dissociation of different media. The long distance forces between two ions can, however, be approximately represented as Coulomb forces, and it is therefore possible to calculate approximately the change of free energy on dilution by the Debye-Hückel limiting law (see p. 120). H. Ulich (*Z. f. Elektrochem.* **36** (1930), 497) has recently calculated the degree of hydration of ions from ionic entropies, and finds good agreement with the figures obtained from ionic mobilities (see H. Ulich, 'Über die Beweglichkeit elektrolytischer Ionen', *Fortschr. d. Chem. u. phys. Chem.* **18** (1926), no. 10; *Trans. Farad. Soc.* **23** (1927), 388; Ulich and Birr, *Z. angew. Chem.* **41** (1928), 443).

A further point of interest is the following. If we vary the anion, but not the cation, we have for the difference between the heats of hydration

of the anions,

$$\Delta Q_{a'a''} = \Delta Q_{La'a''} + \Delta U_{ga'a''}.$$

Similarly, by varying the cation,

$$\Delta Q_{k'k''} = \Delta Q_{Lk'k''} + \Delta U_{gk'k''}.$$

It is thus possible to determine these differences. The following table gives the results of Fajans for the differences between the heats of hydration of gaseous ions. The figures are in kg. cal. per gm. mol., and stand between the two ions concerned.

TABLE 2

Differences between the heats of hydration of gaseous ions, according to Fajans

			F			Cl			Br			I			
				40			11			10					
H			Li			Na			K			Rb			Cs
		113			27			21			3			8	
						Mg			Zn			Cd			
							30			25					

It is found that the difference calculated in this way for any pair of anions or cations is independent of the nature of the oppositely charged ions with which they are associated.

3. Notes and References

Note 1. Numerous references to work on transport numbers are given in the section by J. R. Partington in Taylor's *Treatise on Physical Chemistry*, 2nd edition, vol. i, p. 607, 1930, and also in Jellinek's *Lehrbuch der physikal. Chemie*, 1st and 2nd editions, vol. iii, p. 437, 1929, P. Walden's 'Das Leitvermögen der Lösungen' in Ostwald-Drucker, *Handbuch der allgemeinen Chemie*, vol. iv, Leipzig, 1924, Akad. Verlagsges., and L. Ebert's 'Überführungszahlen in flüssigen Elektrolyten', *Handbuch der Experimentalphysik*, vol. xii, part I, pp. 291 ff., 1932. The moving boundary method, first employed by O. Lodge (*Brit. Ass. Rep.*, p. 389, 1886), has subsequently been greatly refined, especially by McInnes and J. A. Beattie (*J. Am. Chem. Soc.* **42** (1920), 1117; D. A. McInnes and E. R. Smith (ibid. **45** (1923), 2246; **46** (1924), 1398; **47** (1925), 1009); McInnes, J. A. Cowperthwaite, and K. C. Blanchard (ibid. **48** (1926), 1909); McInnes, Cowperthwaite, and T. C. Huang (ibid. **49** (1927), 1711); McInnes and T. B. Brighton (ibid. **47** (1925), 994; **48** (1926), 1909); and L. G. Longsworth and McInnes (*J. Opt. Soc. Am.* **19** (1929), 50); see also Longsworth, *J. Am. Chem. Soc.* **52** (1930), 1900, and the review by McInnes and Cowperthwaite, *Chem. Rev.* **11** (1932), no. 2, 171. McInnes, Cowperthwaite, and T. Shedlowsky (ibid. **51** (1929), 2671) succeeded in showing by means of this method that, contrary to what is often assumed, the chloride ion shows no trace of complex formation in mixtures of KCl and NaCl up to 0·1 N. An approximate theory of the moving boundary method has been given by F. Kohlrausch (*Ann. d. Phys.* (3) **62** (1897), 209), H. Weber (*Berl. Ber.* 936, (1897)), W. L. Miller (*Z. phys. Chem.* **69** (1909), 437), and especially M. v. Laue (*Z. anorg. Chem.* **93** (1915), 329).

J. W. McBain and P. J. Rysselberghe (*J. Am. Chem. Soc.* **50** (1928), 3009; **52** (1930), 2336) and J. W. McBain, P. J. Rysselberghe, and W. A. Squance (*J. Phys. Chem.* **35** (1931), 999) find that on electrolysing a mixture of 0·05 M.

magnesium sulphate and 0·95 M. potassium sulphate, the magnesium migrates to the anode instead of to the cathode. They conclude from this that strong electrolytes contain undissociated molecules and complex ions. It should, however, be emphasized that transport numbers are very sensitive to errors in the analytical methods employed, so that a fresh confirmation of the results of McBain and Rysselberghe would be desirable. C. Drucker (*Z. f. Elektrochem.* **18** (1913), 797; *Z. phys. Chem.* **121** (1926), 326; cf. dissertation by Düsedau, Leipzig, 1931) concludes from his own measurements and values given in the literature (cf. Landolt-Börnstein) that the transport number of the anion in solutions of ternary salts passes through a minimum (about 0·01 M. for $BaCl_2$), from which he deduces the presence of singly charged cations. Jones and Dole (*J. Am. Chem. Soc.* **51** (1929), 1073) have recently found that no such minimum exists, the transport number of the anion rising continuously with the concentration. (The results in dilute solution conform approximately to a square-root law, which is what we should expect theoretically: cf. equations (550) and (565). See also M. Dole, *J. Phys. Chem.* **35** (1931), 3647, and especially L. Ebert (loc. cit., p. 346) who has given a complete treatment of dilute solutions.)

S. Freed and Ch. Casper (*J. Am. Chem. Soc.* **52** (1930), 2632) have recently shown an interesting relationship between the nature of complex ions and their magnetic properties. The magnetic susceptibility of $MgSO_4$ and of similar electrolytes is independent of concentration, and this constancy makes the formation of complex ions very improbable. Freed and Casper consider that the reversal in the direction of the magnesium ion found by McBain and Rysselberghe can probably be explained on the basis of ionic interaction. For a further discussion of transport numbers, see p. 203.

Note 2. See J. N. Brönsted, *Rec. Trav. Chim. Pays-Bas*, **42** (1923), 718; Brönsted and K. Pedersen, *Z. phys. Chem.* **108** (1924), 185; Brönsted and H. C. Duus, ibid. **117** (1925), 299; Brönsted, *J. Chim. Phys.* **30** (1926), 777; Brönsted and E. A. Guggenheim, *J. Am. Chem. Soc.* **49** (1927), 2554; Brönsted, *Chem. Rev.* **5** (1928), 284 (many references to literature); *Trans. Farad. Soc.* **24** (1928) 630; Brönsted and W. F. K. Wynne-Jones, *Trans. Farad. Soc.* **25** (1929), 59; Brönsted and R. P. Bell, *J. Am. Chem. Soc.* **53** (1931), 2478; Brönsted and N. L. Ross-Kane, ibid. **53** (1931), 3624; Brönsted and K. Volquartz, *Z. phys. Chem.* **155 A** (1931), 211; A. Hantzsch, *Z. f. Elektrochem.* **29** (1923), 229, and succeeding volumes; Hantzsch and Weissberger, *Ber.* **125** (1927), 251; Hantzsch and Voigt, *Chem. Ber.* **62** (1929), 975; Hantzsch and Burawoy, ibid. **63** (1930), 1181; L. P. Hammett, *J. Am. Chem. Soc.* **50** (1928), 2666; T. M. Lowry, *Chem. and Ind.* **42** (1923), 43; *Trans. Farad. Soc.* **20** (1924), 58; *J. Chem. Soc.* (1927), 2554; Lowry and G. F. Smith, ibid. (1927), 2539; J. B. Conant and N. F. Hall, *J. Am. Chem. Soc.* **49** (1927), 3047, 3062; Hall, 'New views on acids and bases', *The Nucleus* (Boston), Jan. 1929; *J. Chem. Education*, **7** (1930), 782; *Chem. Rev.* **8** (1931), 191; Hall and T. H. Werner, *J. Am. Chem. Soc.* **50** (1928), 2367; N. F. Hall and M. R. Sprinkle, ibid. **54** (1932), 3469; K. J. Pedersen, Kgl. Danske Vid. Selsk. **12** (1932), 1; A. W. Davidson, ibid. **50** (1928), 1890; **52** (1930), 507, 519; **53** (1931), 1341; V. K. La Mer and H. C. Downes, ibid. **53** (1931), 888; **55** (1933), 1850; *Chem. Rev.* August, 1933; Wynne-Jones, *Proc. Roy. Soc.* **140 A** (1933), 440; Halford, *J. Am. Chem. Soc.* **53** (1931), 2939; **55** (1933), 2272. See also P. Walden, *Salts, acids, and bases*, McGraw Hill, New York, 1929. Numerous references are given by G. M. Schwab in his book *Katalyse vom Standpunkt d. chemischen Kinetik*, Berlin, 1931.

II

IDEAL DILUTE SOLUTIONS

4. Conditions of Equilibrium. The Thermodynamic Potentials†

Considering any system (e.g. a solution of sodium chloride) in a rigid enclosure impermeable to heat, we wish to determine under what conditions this thermodynamic system is in equilibrium. It is known from the principles of thermodynamics that the entropy S of an isolated system always tends to increase. If the entropy has reached a maximum value it can increase no further, and will therefore remain stationary. The system is then in a state of thermodynamic equilibrium. Since S is a function of the state of the system, i.e. of the absolute temperature T and the generalized coordinates $x_1, x_2, \ldots, x_n$, the system can only be in equilibrium if the first-order differential of the entropy S is zero. The necessary condition for *equilibrium* is thus

$$\delta S = 0. \tag{3}$$

The premises underlying this condition are that the energy U is constant, and the volume V is constant, since the system is isolated.‡ This corresponds to the assumption of a rigid, non-conducting envelope. In actual practice the conditions U = constant, V = constant are never fulfilled, and it is therefore necessary to find conditions of equilibrium which apply to ordinary experimental conditions. The most important quantities in this connexion are the *free energy* introduced by v. Helmholtz, and the *thermodynamic potential* of Gibbs. We shall first consider the free energy. Consider a system Σ in which the volume V and the temperature T are kept constant. In order to find the equilibrium conditions for this case, imagine the system Σ extended to form the isolated system $\Sigma+\Sigma'$. Since nothing is stipulated about the processes taking place in Σ, any surface may be taken as the adiabatic envelope. The equilibrium condition for the isolated system $\Sigma+\Sigma'$ is

$$\delta(S+S') = \delta S+\delta S' = 0, \tag{4}$$

where S and S' are respectively the entropies of Σ and Σ'.

† For further information see specially M. Planck, *Vorlesung über Thermodynamik*, Berlin and Leipzig, 1927, 8th edition; G. N. Lewis and M. Randall, *Thermodynamics*, McGraw Hill Book Co., 1923; W. Schottky, H. Ulich, and C. Wagner, *Thermodynamik*, Berlin, 1929. See also the appropriate articles in the large text-books of physics by Geiger-Scheel, Wien-Harms, and Müller-Pouillet.

‡ This represents the simplest case of one generalized coordinate V, which is sufficient for the purposes of further development. The extension to several coordinates follows as a matter of course. See p. 14.

By definition,

$$\delta S' = \frac{d'Q'}{T'}, \tag{5}$$

where $d'Q'$ is the amount of heat received by the system Σ'.† At equilibrium, the temperature of Σ and Σ' must be equal, i.e. $T = T'$. Since the outer envelope is non-conducting, the heat $d'Q'$ received by Σ' can only come from Σ, and therefore $d'Q = -d'Q'$. Consequently,

$$\delta S' = -\frac{d'Q}{T}. \tag{5'}$$

Combining this relation with the equilibrium condition (4) we have

$$\delta S - \frac{d'Q}{T} = 0. \tag{6}$$

From the first law of thermodynamics,

$$d'Q = \delta U + p\,\delta V \quad (p = \text{pressure}). \tag{7}$$

Since V is assumed to be constant,

$$\delta S - \frac{\delta U}{T} = 0,$$

or, since T is also constant,

$$\delta(U - TS) = \delta F = 0 \tag{8}$$

the *free energy* F being defined by the equation

$$F = U - TS. \tag{9}$$

Since $S + S'$ and hence also $TS - U$ must be a maximum at equilibrium, the free energy $U - TS$ must be a minimum.

We shall now deal briefly with the *thermodynamic potential* of Gibbs. In the majority of physical and chemical experiments, the pressure p and the absolute temperature T are constant. Consider again the system Σ combined with the system Σ'. Exactly as in the case of the free energy we arrive at the condition of equilibrium,

$$\delta S - \frac{d'Q}{T} = \delta S - \frac{\delta U + p\,\delta V}{T} = 0.$$

In the present case, however, p and T are constant, and therefore

$$\delta(TS - U - pV) = 0. \tag{10}$$

The function $TS - U - pV$ is therefore a maximum, and the function

$$\Phi = U - TS + pV \tag{11}$$

a minimum. Φ is called the *thermodynamic potential*.‡ The condition

† The sign d' serves as a reminder that $d'Q$ is not a total differential, but only an infinitesimal quantity.

‡ The symbol G is often used in the literature in honour of Gibbs. Planck uses the function $-(U - TS + pV)/T$, which he denotes by Φ.

for equilibrium at constant temperature and pressure is therefore that the first-order differential of the chemical potential Φ shall be zero, i.e.†

$$\delta\Phi = 0. \tag{12}$$

The formulae for the free energy and thermodynamic potential can readily be extended to the case where the external work can be expressed in the form

$$d'A = \sum_h X_h \, \delta x_h. \tag{13}$$

The expression for the free energy remains unaltered (9), while that for the thermodynamic potential becomes

$$\Phi = U - TS - \sum_h X_h x_h. \tag{14}$$

By combining equations (6), (7), (9), and (14) with the first and second laws of thermodynamics, we arrive at the frequently used relations,

$$\left.\begin{aligned} \frac{\partial U}{\partial S} &= T & \frac{\partial U}{\partial x_h} &= X_h \\ \frac{\partial F}{\partial T} &= -S & \frac{\partial F}{\partial x_h} &= X_h \\ \frac{\partial \Phi}{\partial T} &= -S & \frac{\partial \Phi}{\partial X_h} &= -x_h \end{aligned}\right\}. \tag{15}$$

We might now be inclined to consider the *thermodynamic potentials* U, S, F, and Φ as convenient mathematical abstractions without any concrete physical significance. This is, however, not the case. The energy U represents a perfectly intelligible conception and the entropy can be interpreted on the basis of the kinetic theory as the probability of a certain distribution, as was first pointed out by Boltzmann. This treatment of thermodynamics requires, however, a knowledge of the elementary components of the system, e.g. molecules, which is often inaccessible. We shall therefore refrain from further treatment of this point of view‡ except in dealing with the statistical foundations of the Debye theory, where we shall return to the relation of free energy to probability.§

To arrive at the significance of free energy, consider a system which

† Our formulae $\delta S = 0$, $\delta F = 0$, $\delta\Phi = 0$, give no information as to whether the equilibrium is stable or unstable. For a discussion of this point, see text-books of thermodynamics.

Classical thermodynamics tells us nothing of how rapidly the maximum is reached.

‡ It is also necessary to know something of the nature of the atoms and molecules present in the practical applications of thermodynamics. Thus, in order to specify the thermodynamic potential of an ideal solution, we must know the nature of the elementary particles present. (See p. 16.)

§ Cf. Chap. XII.

passes from one state to another state at the same temperature. The change in free energy corresponding to this process is then according to (9)

$$dF = dU - T\,dS. \tag{16}$$

According to the second law of thermodynamics, $T\,dS$ represents the heat $d'Q$ supplied to the system when the change is reversible. The first law states that the total external work performed by the system in the course of this reversible process is given by

$$-d'A = d'Q - dU = -dF. \tag{17}$$

The external work done by the system is therefore $-dF$ for any other isothermal process taking place between the same initial and final states. In practice, the external work performed by the system during any isothermal process is less than $-dF$, on account of friction and other irreversible processes. $-dF = -dA'$ thus represents the *maximum external work done by the process*, which is only obtained when the process is completely reversible. If the system is at constant pressure, and undergoes a volume change dV during the process, an amount of work $p\,dV$ will always be done against the external pressure, and must be subtracted in order to obtain the available external work $-d'A'_N$. The *available work* is therefore given by

$$-d'A_N = -d'A - p\,dV. \tag{18}$$

If the process is reversible, $-d'A$ reaches its maximum value $-dF$, and we have

$$-d'A_N = -d'A - p\,dV = -d\Phi. \tag{19}$$

Thus for any process taking place at constant temperature and constant pressure, $\Phi_A - \Phi_B$ represents the maximum external work available for use when the process takes place between the two states A and B. It may be noted that in the case of liquids, dF and $d\Phi$ do not differ greatly numerically since $p\,dV$ is small.

The applications of these results cover an extremely wide range, not only for *homogeneous systems* (e.g. the theory of the galvanic cell and the thermo-element), but also for *heterogeneous systems*. Thus the phase rule of Gibbs appears as one of the consequences of the theory. The applications of thermodynamics to gaseous mixtures and dilute solutions are of special importance, and we shall use in connexion with the theory of electrolytes the *theory of ideal dilute solutions*. We shall deal briefly with the application of this theory to *the laws of osmotic pressure, depression of freezing-point, elevation of boiling-point*, and *lowering of vapour pressure*, after which we shall treat thoroughly the *deviations* from these laws exhibited by *electrolytes*.

5. The Theory of Ideal Dilute Solutions (Planck). The Law of Mass Action (Guldberg-Waage). The Equations of van't Hoff

In dilute solutions the amount of one component is very large compared with the amounts of all the other species in the same phase.† The system may consist of many phases, and the theory can easily be extended to cover this case.‡ We shall first, however, treat the simple case of one phase, and investigate the criteria of thermodynamic equilibrium and the nature of its dependence on temperature and pressure. Let the phase contain l species, the amount of the λth species being M_λ moles. M_1 is taken as being very great compared to all other M_λ's, and the component 1 is termed the solvent. If U is the energy of the solution, we may write in general

$$\frac{U}{M_1} = \chi\left(\frac{M_2}{M_1}, \frac{M_3}{M_1}, \ldots, \frac{M_l}{M_1}\right). \tag{20}$$

The function χ can be expressed as a series by Taylor's theorem, and we can neglect terms containing higher powers of M_λ/M_1, than the first, since $M_1 \gg M_2, M_3, \ldots, M_l$. This gives

$$\frac{U}{M_1} = \chi_1 + \sum_{\lambda=2}^{l} \frac{M_\lambda}{M_1}\left(\frac{\partial \chi}{\partial M_\lambda/M_1}\right)_0. \tag{21}$$

If we define the quantities u_1 and u_λ (which are independent of concentration for small values of the latter) by the equations

$$u_1 = \chi_1, \qquad \left(\frac{\partial \chi}{\partial M_\lambda/M_1}\right)_0 = u_\lambda \quad (\lambda = 2, 3, \ldots, l), \tag{22}$$

we have

$$U = \sum_{\lambda=1}^{l} M_\lambda u_\lambda. \tag{23}$$

The energy U is thus a homogeneous linear function of the quantities M_λ. The physical significance of this linear dependence is that the properties of a dilute solution depend, to a first approximation, only on the interaction between the molecules of the solute and the molecules of the solvent, and not on the action of the solute molecules upon one another. The latter effect is taken into account by retaining the terms in Taylor's series containing M_λ/M_1, to the second and higher powers. Solutions for which it is necessary to consider only the first-named effect will be termed '*ideal dilute solutions*'. The u_λ's are functions of the temperature and pressure and also of the nature of the

† M. Planck, *Wied. Ann.* **34** (1888), 139–54. See also *Vorlesungen über Thermodynamik*, Berlin and Leipzig, 1927.

‡ We shall return to this point later (see p. 18).

substances present in the solution. Thus u_1 depends upon p, T, and the solvent; u_2 upon p, T, the solvent, and the first dissolved substance, and so on for u_3, etc. In the same way, the volume of the solution V can be written in the form

$$V = \sum_{\lambda=1}^{l} M_\lambda v_\lambda, \tag{24}$$

where the v_λ's depend upon p, T, and the substances present in exactly the same way as the u_λ's above. We wish now to calculate the entropy of the ideal dilute solution. According to (6) and (7)

$$dS = M_1 \frac{du_1 + p\,dv_1}{T} + M_2 \frac{du_2 + p\,dv_2}{T} + \ldots. \tag{25}$$

Since u_λ and v_λ depend only on p and T, and not on $M_1, \ldots, M_l$, the coefficients of M_1, M_2,... in (25) must each be total differentials, i.e.

$$ds_1 = \frac{du_1 + p\,dv_1}{T}, \text{ etc.} \tag{26}$$

Therefore,
$$dS = \sum M_\lambda\, ds_\lambda, \tag{27}$$

and on integrating,
$$S = \sum_{\lambda=1}^{l} M_\lambda s_\lambda + C. \tag{28}$$

The integration constant C is not a function of p and T, but may depend on $M_1, \ldots, M_l$. Its value is readily determined. We imagine that the whole system, both solvent and solutes, is converted to the ideal gas state by increasing the temperature and decreasing the pressure. This process cannot be realized in practice, since changes would occur in the state of aggregation and chemical composition of the system, i.e. the M_λ's would not remain constant and the equilibrium of the solution would be disturbed. This is, however, immaterial for the present calculation, since the change is theoretically feasible.† The entropy of the ideal gas thus obtained may be easily calculated. We have l different gases in amounts $M_1, \ldots, M_l$ moles present in volume V. Calling the partial pressures $p_1, \ldots, p_l$ and the specific heats per mole at constant pressure $C_{p_1}, \ldots, C_{p_l}$, the entropy of the gas mixture is

$$(S) = \sum_{\lambda=1}^{l} M_\lambda (C_{p_\lambda} \log T - R \log p_\lambda + b_\lambda), \tag{29}$$

where b_λ is an integration constant, and R is the universal gas constant, $8{\cdot}31 \times 10^7$ ergs per degree.

† This method of determining C, due to Planck, is not quite unexceptionable, since it assumes that the system remains ideal for all values of T and p. The same result may be obtained rigidly by statistical methods, which we shall, however, omit for the sake of brevity. See especially R. H. Fowler, *Statistical Mechanics*, 1929, and E. A. Guggenheim, *Proc. Roy. Soc.* **135** (1932), 181.

Introducing the mole fraction η_λ and the total pressure p we have

$$p_\lambda = \frac{M_\lambda p}{\sum M_\lambda} = \eta_\lambda p, \tag{30}$$

and the entropy of the gas is†

$$(S) = \sum_{\lambda=1}^{l} M_\lambda (C_{p_\lambda} \log T - R \log p + b_\lambda) - \sum_{\lambda=1}^{l} M_\lambda R \log \eta_\lambda, \tag{31}$$

or, more shortly, $(S) = \sum (s_\lambda) M_\lambda - \sum M_\lambda R \log \eta_\lambda$. (31′)

If the gas is now converted again to the liquid state without changing the M_λ's and η_λ's, comparison of (28) and (31) gives

$$C = R \sum_{\lambda=1}^{l} M_\lambda \log \eta_\lambda, \tag{32}$$

since on varying p and T, (s_λ) becomes s_λ.

If we now write $$\phi_\lambda = u_\lambda - T s_\lambda + p v_\lambda, \tag{33}$$

ϕ_λ being a function of p and T, the thermodynamic potential of the ideal dilute solution can be written in the form‡

$$\bar{\Phi} = \sum_{\lambda=1}^{l} M_\lambda \phi_\lambda + \sum_{\lambda=1}^{l} RT M_\lambda \log \eta_\lambda. \tag{34}$$

If the system contains κ different phases $(1, 2, \ldots, \sigma, \ldots, \kappa)$ each of which constitutes an ideal solution, then we have for the phase σ,

$$\bar{\Phi}^{(\sigma)} = \sum_{\lambda=1}^{l} M_\lambda^{(\sigma)} \phi_\lambda^{(\sigma)} + RT \sum_{\lambda=1}^{l} M_\lambda^{(\sigma)} \log \eta_\lambda^{(\sigma)}, \tag{35}$$

and for the total thermodynamic potential, which is equal to the sum of those in the separate phases,

$$\bar{\Phi} = \sum_{\sigma=1}^{\kappa} \bar{\Phi}^{(\sigma)}, \tag{36}$$

or

$$\bar{\Phi} = \sum_{\sigma=1}^{\kappa} \sum_{\lambda=1}^{l} M_\lambda^{(\sigma)} \phi_\lambda^{(\sigma)} + RT \sum_{\sigma=1}^{\kappa} \sum_{\lambda=1}^{l} M_\lambda^{(\sigma)} \log \eta_\lambda^{(\sigma)}. \tag{37}$$

We shall now use this expression to derive the *conditions for equilibrium* of the system. According to previous considerations (see p. 13) when p and T are kept constant, $\bar{\Phi}$ must be a minimum, i.e. the differential of the thermodynamic potential $\delta\bar{\Phi}$ must be zero. The $\phi_\lambda^{(\sigma)}$'s are

† The brackets in equations (29), (31), and (31′) refer to the gaseous state.

‡ This form (34) will be used later in the development of modern electrolyte theory, cf. p. 120. The thin bar over the Φ shows that the symbol refers to an ideal solution. A thicker bar, on the other hand, would mean that the quantity in question refers to one mole (see e.g. p. 44).

functions of p and T only, and are not changed by variations of $\bar{\Phi}$. We thus have

$$\sum_{\sigma=1}^{\kappa}\sum_{\lambda=1}^{l}\phi_\lambda^{(\sigma)}\delta M_\lambda^{(\sigma)}+RT\sum_{\sigma=1}^{\kappa}\sum_{\lambda=1}^{l}\delta M_\lambda^{(\sigma)}\log\eta_\lambda^{(\sigma)}+RT\sum_{\sigma=1}^{\kappa}\sum_{\lambda=1}^{l}M_\lambda^{(\sigma)}\frac{\delta\eta_\lambda^{(\sigma)}}{\eta_\lambda^{(\sigma)}}=0.$$

Since by definition,

$$\eta_\lambda^{(\sigma)}=\frac{M_\lambda^{(\sigma)}}{\sum_{\lambda=1}^{l}M_\lambda^{(\sigma)}}, \tag{38}$$

the condition for equilibrium is

$$\sum_{\sigma=1}^{\kappa}\sum_{\lambda=1}^{l}\phi_\lambda^{(\sigma)}\delta M_\lambda^{(\sigma)}+RT\sum_{\sigma=1}^{\kappa}\sum_{\lambda=1}^{l}\delta M_\lambda^{(\sigma)}\log\eta_\lambda^{(\sigma)}=0. \tag{39}$$

From this the equilibrium condition can easily be obtained in terms of the $\eta_\lambda^{(\sigma)}$'s. The variations $\delta M_\lambda^{(\sigma)}$ are related by the *reaction equations* which have the form†

$$\mu_1^{(\sigma)}A_1^{(\sigma)}+\mu_2^{(\sigma)}A_2^{(\sigma)}+\ldots+\mu_l^{(\sigma)}A_l^{(\sigma)}=0. \tag{40}$$

$A_1^{(\sigma)}$, $A_2^{(\sigma)}$, etc. are the chemical formulae of the substances, and $\mu_\lambda^{(\sigma)}$ is proportional to $\delta M_\lambda^{(\sigma)}$. Each reaction is also characterized by definite relationships between the numbers of moles concerned, i.e.

$$\delta M_1^{(\sigma)}:\delta M_2^{(\sigma)}:\ldots:\delta M_\lambda^{(\sigma)}:\ldots=\mu_1^{(\sigma)}:\mu_2^{(\sigma)}:\ldots:\mu_\lambda^{(\sigma)}:\ldots, \tag{41}$$

where $\mu_1^{(\sigma)}$, $\mu_2^{(\sigma)}$, etc. are positive or negative integers according as the species in question is formed or destroyed in the reaction.

Equation (39) therefore becomes finally

$$\sum_{\sigma=1}^{\kappa}\sum_{\lambda=1}^{l}\mu_\lambda^{(\sigma)}\log\eta_\lambda^{(\sigma)}=-\sum_{\sigma=1}^{\kappa}\sum_{\lambda=1}^{l}\frac{\mu_\lambda^{(\sigma)}\phi_\lambda^{(\sigma)}}{RT}=\log K(p,T). \tag{42}$$

This may be written in a slightly different form,

$$\prod_{\sigma=1}^{\kappa}\prod_{\lambda=1}^{l}(\eta_\lambda^{(\sigma)})^{\mu_\lambda^{(\sigma)}}=K(p,T). \tag{43}$$

Equation (43) is the law of mass action of Guldberg and Waage in its usual form.‡

The two equations of van't Hoff can easily be derived from these

† $\delta M_\lambda^{(\sigma)}$, etc., need not refer to a reaction in the phase σ, but can also correspond to a transference from one phase to another. We can then treat (a) the equilibrium for reactions in one phase, and (b) the equilibrium for transference between two phases. If there is equilibrium (a) in one phase and equilibrium (b) with respect to all transferences between this phase and other phases, then there must also be equilibrium (a) for all phases.

‡ The papers of C. M. Guldberg and P. Waage, 1864–79, have been translated and edited by R. Abegg in Ostwald's *Klassiker*, no. 104, Leipzig, 1899.

considerations. These equations express the dependence of the equilibrium constant K on temperature and pressure, as follows:

$$\frac{\partial \log K}{\partial T} = \frac{Q}{RT^2} \tag{44}$$

$$\frac{\partial \log K}{\partial p} = -\frac{\Delta V}{RT}. \tag{45}$$

Q is the total amount of heat absorbed at constant pressure during the reaction characterized by the $\mu_\lambda^{(\sigma)}$'s, and ΔV is the corresponding change of volume of the whole system.

6. The Laws of Osmotic Pressure, Depression of Freezing-point, Elevation of Boiling-point, and Vapour-pressure lowering for Ideal Dilute Solutions

If a vessel contains a layer of cane sugar solution covered by a layer of pure water, the system will not remain in this state. The entropy will continue to increase until equilibrium is reached, which will be when the sugar is distributed completely evenly throughout the system. Let the solution now be separated from the pure water by a semi-permeable membrane permeable to water but not to sugar. The solution will now have a tendency to become more dilute, but the transference of water can be prevented by exerting a pressure upon the solution. The pressure necessary exactly to maintain equilibrium is termed the *osmotic pressure of the solution*. We shall now apply the general considerations of the previous section to this simple system. The solvent 0† constitutes the first phase, which we shall designate by one dash. The second phase, designated by two dashes, is the solution consisting of the solvent 0 and the solute 1. The only reaction taking place is the transfer of one mole of water so that

$$\mu_0' = -1, \quad \mu_0'' = +1, \quad \mu_1'' = 0.$$

The corresponding mole fractions are

$$\eta_0', \ \eta_0'', \ \eta_1'',$$

and we have from (42),

$$\log \eta_0'' = -\frac{1}{RT}(\phi_0'' - \phi_0'). \tag{46}$$

This equation determines the osmotic pressure. Since we are dealing with a dilute solution, η_0'' is approximately unity, and $\log \eta_0''$ has a very small negative value. In the absence of any cane sugar, $\phi_0'' = \phi_0'$, but when some is dissolved, our equation shows that $\phi'' \neq \phi_0'$ and also that

† The solvent will from now onwards be designated as 0.

$\phi_0'' > \phi_0'$. The thermodynamic potential of the water in the solution must thus be greater than that of the pure water. This is due to the external pressure applied, the magnitude of which can easily be evaluated as follows.

We write $$\phi_0'(p, T) = f(p, T). \tag{47}$$

To preserve equilibrium, the external pressure p must be increased by the amount of the osmotic pressure $\bar{P}$, so that

$$\phi_0'' = f(p+\bar{P}, T). \tag{48}$$

We shall take the temperature as constant. Now since $\log \eta_0''$ is very small, ϕ_0'' and ϕ_0' differ very little, and we can use Taylor's series, retaining only the first two terms, giving

$$\phi_0'' = f(p, T)+\bar{P}\frac{\partial f(p, T)}{\partial p}. \tag{49}$$

Then we have from (11) and (15), introducing the molar volume of water, v_0,

$$\phi_0''-\phi_0' = \bar{P}v_0, \tag{50}$$

or,

$$\frac{\bar{P}v_0}{RT} = -\log \eta_0''. \tag{51}$$

Also, from (38)

$$\eta_0''+\eta_1'' = 1. \tag{52}$$

So that

$$\frac{\bar{P}v_0}{RT} = -\log(1-\eta_1''). \tag{53}$$

Since we are dealing with dilute solutions, the equation for the *osmotic pressure* becomes

$$\bar{P} = \frac{RT}{v_0}\eta_1''. \tag{54}$$

If several different substances are dissolved in water—η_i moles of the ith substance per mole of water—then the osmotic pressure of the ideal dilute solution becomes by an extension of (54),

$$\bar{P} = \frac{RT}{v_0}\sum{}' \eta_i, \tag{54'}$$

the summation extending over all the dissolved species.

The osmotic pressure of any dilute solutions is thus directly proportional to the concentration of dissolved substance and to the absolute temperature. η_1'' moles of solute are dissolved in $1-\eta_1''$ moles of water. For very dilute solutions, we can write one mole in place of $1-\eta_1''$ moles, and the volume in which one mole of solute is dissolved then becomes

$$\frac{v_0}{\eta_1''} = v_1. \tag{55}$$

On introducing this volume $\mathfrak{v}_1$ into equation (54), we obtain van't Hoff's equation for the osmotic pressure,

$$\bar{P}\mathfrak{v}_1 = RT. \tag{56}$$

One mole of the solute contains $6{\cdot}06 \times 10^{23} = \mathbf{N}$ molecules, and

$$R = \mathbf{N}k, \qquad (k = 1{\cdot}37 \times 10^{-16} \text{ ergs/degree}).$$

Equation (56) can thus also be written

$$\bar{P}\mathfrak{v}_1 = \mathbf{N}kT.$$

Introducing the number of molecules in one c.c., n, we have

$$n = \frac{\mathbf{N}}{\mathfrak{v}}.$$

$$\bar{P} = nkT. \tag{56'}$$

This equation corresponds to the well-known equation for the pressure of an ideal gas in the kinetic theory of gases.

In a similar way we can use the general treatment of § 5 to derive the equations for the *freezing-point depression*, *boiling-point elevation*, and *vapour-pressure lowering* for ideal dilute solutions. We shall confine ourselves to the results, since the derivations follow exactly the same lines as that given in detail for the osmotic pressure. The equation for the freezing-point lowering $(\overline{\Delta T})_g$ of an ideal dilute solution is

$$(\overline{\Delta T})_g = -\frac{RT_g^2}{r_g}\eta_1'', \tag{57}$$

where T_g is the freezing-point and r_g the molar heat of fusion of the solvent. This is *Raoult's equation for the freezing-point depression*, and states that to a first approximation the freezing-point depression is proportional to the concentration of the solute.† In practice the concentration of the solute is not expressed as mole fractions, but as moles per 1,000 gm. solvent or *molarity*. If the molarity is m and the molecular weight of the solvent G_0, we have

$$\eta_1'' = \frac{m}{(1{,}000/G_0) + m}. \tag{58}$$

For sufficiently small concentrations this becomes

$$\eta_1'' = \frac{G_0}{1{,}000}m, \tag{58'}$$

† It is assumed that the solid phase consists of pure solvent. If more than one solute is present, η_1'' in equations (57), (61), and (63) must be replaced by $\sum' \eta_1''$. (Cf. formulae (54) and (54').)

and the freezing-point depression is given by

$$(\overline{\Delta T})_g = -\frac{RT_g^2}{r_g}\frac{G_0}{1{,}000}m. \tag{59}$$

For water, we have

$$G_0 = 18{\cdot}02, \quad r_g = 1{,}438 \text{ cal.}, \quad T_g = 273{\cdot}2°,$$

which gives for the freezing-point depression

$$(\overline{\Delta T})_g = -1{\cdot}858m \tag{60}$$

agreeing well with the observed value, $1{\cdot}860m$.

Equation (60) is used in practice for determining molecular weights. A known amount of substance is dissolved in a known quantity of water, and the molecular weight of the substance can be calculated from the observed freezing-point depression. Many substances, especially organic compounds, give a value very near 1·86 for $(\overline{\Delta T})_g/m$. On the other hand, salts and strong acids and bases give higher values, which in general increase with decreasing concentration, and approach an integral multiple of 1·86. These discrepancies can be explained by Arrhenius's theory of electrolytic dissociation, which will be treated in the next chapter.

The *boiling-point elevation* for ideal dilute solutions is given by the corresponding equation,

$$(\overline{\Delta T})_s = \frac{RT_s^2}{r_s}\eta_1''; \tag{61}$$

where r_s is the molar heat of evaporation, and T_s is the boiling-point of the pure solvent. For water at a pressure of one atmosphere,

$$r_s = 539{\cdot}1 \text{ cal.}, \quad T_s = 373{\cdot}2, \quad \eta'' = \frac{18{\cdot}02m}{1{,}000},$$

$$(\overline{\Delta T})_s = 0{\cdot}512m, \tag{62}$$

agreeing well with the observed value $0{\cdot}511m$. The change in boiling-point is thus not so great as the change in freezing-point (cf. (60)). Molecular weights are also determined by measuring the boiling-point elevation. Strong salts, acids, and bases again show considerable departures from equation (62), which will be discussed in the next chapter.

The *vapour-pressure lowering* $-\overline{\Delta p}$ is given by

$$-\overline{\Delta p} = +\eta_1''\frac{RT}{v_0}, \tag{63}$$

and is thus also proportional to the concentration. v_0 is the molar

volume of the vapour. If the vapour can be considered as an ideal gas, then

$$pv_0 = RT$$

and

$$\frac{\overline{\Delta p}}{p} = -\eta_1''. \tag{63'}$$

The vapour-pressure lowering expressed as a fraction of the vapour-pressure of the solvent is thus equal to the mole fraction of the solute. Anomalies are again observed in the vapour-pressure lowerings for dissociated substances.

III

SOME CONSEQUENCES OF THE CLASSICAL THEORY OF ELECTROLYTES, AND THEIR APPLICATION TO WEAK ELECTROLYTES†

7. The Deviations of Electrolytes from van't Hoff's Equation for Osmotic Pressures and Raoult's Law for Freezing-point Depression and Boiling-point Elevation

If a salt or a fairly strong acid or base is dissolved in water, the osmotic pressure, freezing-point depression, boiling-point elevation, and vapour-pressure lowering are all greater than they should be according to the equations of the preceding section. In Table 3 the experimental values

TABLE 3

m in $\frac{gm.\ mol.}{1{,}000\,gm.\ H_2O}$	$(\Delta T)_g$	$\frac{\lvert(\Delta T)_g\rvert}{m}$	i	α
		KCl		
0·0010	−0·00365°	3·65	1·97	0·97
0·0050	−0·0182	3·64	1·96	0·96
0·0100	−0·0361	3·60	1·94	0·94
0·0497	−0·176	3·54	1·91	0·91
0·0867	−0·299	3·45	1·86	0·86
		$BaCl_2$		
0·000214	−0·00119°	5·57	2·99	0·99
0·000872	−0·00464	5·32	2·86	0·93
0·00273	−0·0144	5·27	2·83	0·915
0·01142	−0·0577	5·05	2·72	0·86
0·11358	−0·5319	4·68	2·52	0·76
		$La(NO_3)_3$		
0·00132	−0·00915	6·93	3·75	0·92
0·00354	−0·02345	6·62	3·56	0·84
0·00806	−0·0509	6·32	3·40	0·80
0·0177	−0·103	5·8	3·12	0·71
0·0430	−0·235	5·5	2·96	0·65
		CH_3COOH		
0·00952	−0·001946°	2·05	1·10	0·10
0·003007	−0·006062	2·01	1·08	0·08
0·01002	−0·0196	1·96	1·054	0·054
0·03535	−0·06839	1·93	1·04	0·04
0·0951	−0·1811	1·90	1·02	0·02

† We shall not attempt to give an account of all the results and applications of Arrhenius's theory, since this has already been done in many excellent text-books and

of $(\Delta T)_g/m$ are given for various electrolytes at different concentrations. The ratio

$$\frac{(\Delta T)_g}{M} : 1{\cdot}86 \qquad (64$$

is called i.

The boiling-point elevation, the vapour-pressure lowering, and the osmotic pressure give values of i which agree with those in Table 3 within the experimental error. The osmotic pressure, freezing-point depression, boiling-point elevation, and vapour-pressure lowering are thus all i times as great as the values calculated from the equations of the preceding paragraph. This abnormality factor i was first introduced by van 't Hoff in his theory of solutions, and is therefore usually called the *van 't Hoff factor*. Arrhenius succeeded in showing that the van 't Hoff factor i is a measure of the increase in the number of particles caused by the dissociation of the molecules into ions.

8. Svante Arrhenius's Hypothesis of Electrolytic Dissociation in Aqueous Solution†

A. *Explanation of osmotic and related phenomena.*

It is seen from the considerations of the preceding paragraph that the van 't Hoff factor i is the factor by which the number of moles of solute added must be multiplied in order to account for the observed osmotic phenomena, e.g. the freezing-point depression. Arrhenius interpreted this abnormality factor i in the following manner. Let the fraction of the total number of molecules which break up into ions be α, and the fraction remaining undissociated therefore $1-\alpha$. One mole of the electrolyte containing $\mathbf{N}$ $(= 6{\cdot}06 \times 10^{23})$ molecules therefore gives on solution $\mathbf{N}(1-\alpha)$ undissociated molecules and $\nu\alpha\mathbf{N}$ ions, where ν is the number of ions formed by the dissociation of one molecule. Since the

monographs, e.g. W. Nernst, *Theoretische Chemie*; A. Eucken, *Lehrbuch der chemischen Physik*, 1930. Complete references to the literature are given by K. Jellinek, *Lehrbuch der physikalischen Chemie*, vol. ii, 1928, vol. iii, 1929; H. S. Taylor, *A Treatise on Physical Chemistry*, New York, 1931, 2nd edition. In this chapter we shall only deal with the fundamental principles of the classical theory, which are important in connexion with modern electrolyte theory.

† The ionic theory has also been frequently applied successfully to non-aqueous solutions. Often, however, matters are complicated by the presence of specific factors, which are not at present understood. We shall therefore omit any treatment of non-aqueous solutions except for an occasional reference to results for solvents resembling water. (For further details, see the following monographs: Ch. A. Kraus, *Electrically Conducting Systems*, 1922; P. Walden, *Elektrochemie nichtwässriger Lösungen*, 1924; also H. S. Taylor, loc. cit. p. 25, L. Ebert, loc. cit. p. 10, and the symposium in *Chem. Rev.* 8, April, 1931.)

total number of particles Ni is equal to the number of molecules plus the number of ions, we have

$$iN = N(1-\alpha)+\nu\alpha N$$

and

$$i = (1-\alpha)+\nu\alpha = 1+(\nu-1)\alpha. \tag{65}$$

We find in fact by referring to Table 3 that with increasing dilution the van 't Hoff factor i approaches the value 2 for 1-1 valent electrolytes ($\nu = 2$), the value 3 for 1-2 valent electrolytes ($\nu = 3$), and the value 4 for 1-3 valent electrolytes ($\nu = 4$). Conversely, we can calculate the *degree of dissociation* α from the experimental values of i, thus obtaining the figures given in Table 3. It is found that for strong electrolytes, e.g. KCl, KOH, HCl, $BaCl_2$, $La(NO_3)_3$, the degree of dissociation is almost unity, while for weak electrolytes, e.g. CH_3COOH, it is very much less than unity, i.e. only a very small proportion of the dissolved acetic acid molecules are dissociated into the ions CH_3COO^- and H^+.† Arrhenius's hypothesis of electrolytic dissociation thus explains the abnormally high values of osmotic pressure, etc. exhibited by electrolyte solutions as being due to an increase in the number of dissolved particles, brought about by the dissociation of the dissolved molecules into ions. Van 't Hoff's application of the laws of ideal gases to the solute leads to the conclusion that the number of dissolved particles does determine the osmotic pressure and the thermodynamically related quantities freezing-point depression, boiling-point elevation, and vapour-pressure lowering. Now it is actually found that the osmotic pressures, etc. have values smaller than those corresponding to complete dissociation (cf. Table 3), and we must therefore assume that the number of dissolved particles varies according to the law of mass action with the concentration, temperature, and pressure. The nature of this dependence on concentration and the anomalous behaviour of strong electrolytes will be dealt with shortly.

Arrhenius and Planck showed almost simultaneously that the degree of dissociation must also be related directly to the electrical conductivity, which will increase with increasing dissociation. We shall now investigate further this relationship between the electrical conductivity and the thermodynamic properties of electrolytes.

† A few electrolytes do not behave like those in Table 3. Thus hydrogen fluoride has the properties of a weak electrolyte at concentrations higher than one molar, and only approaches complete dissociation at much lower concentrations. There is complex formation at higher concentrations. See H. Pick, *Nernst Festschrift*, p. 360, 1912; C. W. Davies and L. J. Hudleston, *J. Chem. Soc.* **125** (1924), 260.

B. *The determination of the degree of dissociation from conductivity measurements.* (*Arrhenius and Planck.*)†

The conduction of electricity through an electrolyte is effected by the ions. The molar conductivity‡ is therefore proportional to the degree of dissociation, i.e.

$$\Lambda = C\alpha. \tag{66}$$

At infinite dilution we can consider the molecules as completely dissociated into ions. The degree of dissociation is then unity, and the molar conductivity has reached the limiting value Λ_∞. We thus have

$$C = \Lambda_\infty,$$

and for the *degree of dissociation* α

$$\alpha = \frac{\Lambda}{\Lambda_\infty}. \tag{67}$$

As the concentration increases, the number of conducting ions decreases.

Arrhenius and Planck thus put the *conductivity coefficient*

$$f_\Lambda = \frac{\Lambda}{\Lambda_\infty} \tag{67'}$$

equal to the degree of dissociation.§

According to the classical theory it is thus possible to use measurements of the quotient f_Λ to calculate the degree of dissociation α, and to compare these values with those obtained from measurements of osmotic pressure or freezing-point determinations.‖ Table 4 contains such data for solutions of potassium chloride in water. The values of the conductivity are from measurements by Kohlrausch at 18°. The

TABLE 4

The conductivity coefficient (f_Λ) *for* KCl *in water at* 18° *C.*

γ(*moles/litre*)	Λ(*rec. ohms/cm.*^{2})	$f_\Lambda(\alpha)$	γ(*moles/litre*)	Λ(*rec. ohms/cm.*^{2})	$f_\Lambda(\alpha)$
0	130	1·0	5×10^{-3}	124·34	0·956
10^{-4}	129	0·992	10^{-2}	122·37	0·941 (0·94)
2×10^{-4}	128·7	0·990	2×10^{-2}	119·90	0·922
5×10^{-4}	128·04	0·985	5×10^{-2}	115·69	0·889
10^{-3}	127·27	0·979 (0·97)	10^{-1}	111·97	0·861
2×10^{-3}	126·24	0·971			

† Sv. Arrhenius, *Bih. Svensk. Akad. Handl.* **8** (1884), nos. 13 and 14; M. Planck, *Ann. d. Physik*, **32** (1887), 462; *Z. phys. Chem.* **1** (1887), 577.

‡ The molar conductivity is equal to the specific conductivity (the conductivity of 1 c.c.) divided by the concentration in moles per c.c.

§ This assumption is not strictly true for strong electrolytes; cf. p. 283.

‖ This calculation is, however, based upon an exact knowledge of Λ_∞, which can only be obtained by extrapolation to infinite dilution.

values of f_Λ are compared with the values of α (in brackets) calculated from the freezing-point data in Table 3. The two sets of values agree well, as predicted by Arrhenius.

It may be noted that the value of Λ/Λ_∞ is approximately the same for all uni-univalent salts at the same concentration. These salts can therefore according to Arrhenius be considered as having the same degree of dissociation at the same molar concentration (γ).

C. *Comparison of the degrees of dissociation calculated from osmotic measurements and from conductivity data.* (*Arrhenius.*)

Arrhenius was the first to express clearly the hypothesis of electrolytic dissociation and to show its approximate validity by an intercomparison of the values obtained for the degree of dissociation from conductivity and freezing-point data respectively. Later and more accurate measurements with salts, acids, and bases have confirmed Arrhenius's original calculations. Table 5† shows side by side the values from measurements of freezing-point depression (§ 8 A) and those from conductivity data (§ 8 B).

The two sets of values α_1 and α_2 agree so well to a first approximation that we can consider Arrhenius's dissociation hypothesis as essentially correct.‡ The decrease in molar conductivity caused by increasing the concentration can thus be expressed to a first approximation as being due to a decrease in the number of ions carrying the current. A closer inspection of Table 5 reveals, however, small differences between α_1 and α_2 which cannot be due to experimental error in the measurements of freezing point and conductivity. These differences are greater for electrolytes of higher valence type, i.e. in Table 5 they are least for the mono-monovalent electrolytes (KCl, etc.) and greatest for $MgSO_4$. These discrepancies, which are not very noticeable in the present case, are due to the neglect of the interionic forces, and will be dealt with in

† The value of $\alpha_1(f_\Lambda)$ are taken from the results of A. A. Noyes and K. G. Falk (*J. Am. Chem. Soc.* **34** (1912), 462). It is doubtful whether it is justifiable to apply a viscosity correction as these authors have done. See e.g. B. F. E. King and J. R. Partington, *Trans. Farad. Soc.* **23** (1927), 531; D. A. McInnes and I. A. Cowperthwaite, ibid. **23** (1927), 400; Gr. Jones and M. Dole, ibid. **52** (1930), 2245. Since, however, the correction is practically negligible at the concentrations to which Table 5 refers, no alterations have been made.

‡ See C. Drucker, *Samml. chem. u. chem.-techn. Vorträge*, **10** (1906), 1; A. A. Noyes and G. Falk, loc. cit.

There are a number of other methods for measuring the degree of dissociation, e.g. by measuring the e.m.f. of a concentration cell. (The general formulae involved are given on p. 51, using activities instead of concentrations.) The values obtained agree approximately with those given here.

detail later. We shall now pass on to the quantitative treatment of the variation of conductivity with concentration, as given by the classical theory of Arrhenius. It will be found that the discrepancies appear especially for strong electrolytes, while the classical theory applies very well to weak electrolytes.

TABLE 5

The degree of dissociation from conductivity measurements (α_1) *and from freezing-point measurements* (α_2), *calculated according to the classical dissociation theory*

Solvent water. Conductivity data at 18° C. used.

γ^* = concentration in gramme equivalents per litre of solution.

Electrolyte	$\gamma^* =$	5×10^{-3}	10^{-2}	2×10^{-2}	5×10^{-2}	10^{-1}
KCl	$\alpha_1 = f_\Lambda$	0·956	0·941	0·922	0·889	0·860
($\nu = 2$)	α_2	0·963	0·943	0·918	0·885	0·861
NaCl	$\alpha_1 = f_\Lambda$	0·952	0·936	0·914	0·878	0·852
($\nu = 2$)	α_2	0·953	0·938	0·922	0·892	0·875
LiCl	$\alpha_1 = f_\Lambda$	0·949	0·931	0·908	0·870	0·846
($\nu = 2$)	α_2	0·944	0·937	0·928	0·912	0·901
HCl	$\alpha_1 = f_\Lambda$	0·981	0·973	0·962	0·944	0·923
($\nu = 2$)	α_2	0·991	0·972	0·957	0·933	0·912
KOH	$\alpha_1 = f_\Lambda$	0·964	0·956	..	..	0·893
($\nu = 2$)	α_2	0·992	0·982	..	..	0·858
$MgSO_4$	$\alpha_1 = f_\Lambda$	0·739	0·666	0·592	0·498	0·434
($\nu = 2$)	α_2	0·694	0·618	0·536	0·420	0·324
$BaCl_2$	$\alpha_1 = f_\Lambda$	..	0·882	0·848	0·794	0·751
($\nu = 3$)	α_2	0·899	0·878	0·855	0·819	0·788

9. Ostwald's Dilution Law
(The Variation of the Conductivity of Weak Electrolytes with the Concentration)

Arrhenius assumed further that the equilibrium existing between the molecules and the ions of an electrolyte was governed by the Guldberg-Waage law of mass action (43). We shall suppose that a molecule of the electrolyte dissociates directly (without intermediate stages) into ν_+ positive ions and ν_- negative ions. If the mole fractions corresponding to these three species are respectively η, η_+, and η_-, the law of mass action gives

$$\frac{(\eta_+)^{\nu_+}(\eta_-)^{\nu_-}}{\eta} = \bar{K}_\eta(p, T), \tag{68}$$

where $\bar{K}_\eta$ is a quantity depending on p and T. If M moles of solute are added to M_0 moles of solvent, and the degree of dissociation is α, we

have by definition,

$$\left.\begin{aligned} \eta &= \frac{(1-\alpha)M}{M_0+\{1+(\nu-1)\alpha\}M} \\ \eta_+ &= \frac{\nu_+\alpha M}{M_0+\{1+(\nu-1)\alpha\}M} \\ \eta_- &= \frac{\nu_-\alpha M}{M_0+\{1+(\nu-1)\alpha\}M} \end{aligned}\right\} \tag{69}$$

where

$$\nu = \nu_+ + \nu_-. \tag{70}$$

Defining the concentration σ by

$$\frac{M}{M_0} = \sigma, \tag{71}$$

and introducing the van 't Hoff factor i, we have from (65), (68), and (69),

$$\frac{\alpha^\nu}{1-\alpha}\sigma^{\nu-1} = \frac{(1+i\sigma)^{\nu-1}}{(\nu_+)^{\nu_+}(\nu_-)^{\nu_-}}\bar{K}_\eta.$$

For very dilute solutions we can replace $(1+i\sigma)^{\nu-1}$ by 1, so that the right-hand side of the equation is again a quantity depending only upon temperature and pressure. We therefore write

$$\frac{\alpha^\nu}{1-\alpha}\sigma^{\nu-1} = K_\sigma(p, T), \tag{72}$$

which for binary electrolytes ($\nu = 2$) simplifies to

$$\frac{\alpha^2}{1-\alpha}\sigma \doteq K_\sigma(p, T). \tag{73}$$

It is obviously possible to use any other scale of concentration in place of σ in equations (72) and (73), e.g. moles per litre of solution (γ), or equivalents per litre of solution (γ^*). The value of K (the *dissociation constant*) will, however, depend on the concentration scale chosen, since σ, γ, and γ^* are all different, though directly proportional to one another in dilute solutions. If we use moles per litre of solution, we shall write (73) as

$$\frac{\alpha^2}{1-\alpha}\gamma = K_\gamma(p, T), \tag{74}$$

the subscript of the dissociation constant referring to the concentration scale used. On introducing the molar conductivities by means of (67), we obtain the *Ostwald dilution law*

$$\frac{\Lambda^2\gamma}{\Lambda_\infty(\Lambda_\infty-\Lambda)} = K_\gamma. \tag{75}$$

This law governs the variation of the molar conductivity of weak electrolytes with concentration. Ostwald† has verified equation (75) for a very large number of organic acids, and weak organic bases follow the same law.‡ As examples of the accuracy with which the law applies, we shall take acetic acid (Table 6) and ammonia (Table 7), both dissolved in water.§ In order to show the dependence of K_γ upon the temperature, we have given values for 18° and 25°. In Table 6 v_γ is the molar dilution, i.e. the number of litres of solution which contains 1 mole of electrolyte,

$$v_\gamma = \frac{1}{\gamma}. \tag{76}$$

For acetic acid at 25° $K_\gamma = 1{\cdot}78 \times 10^{-5}$. It is seen that the law of mass action is fairly well obeyed by acetic acid and ammonium hydroxide, both of which are weak electrolytes. Although the concentration varies through a range of 10^4, K_γ remains fairly constant. The Ostwald dilution law has been confirmed by an extremely extensive mass of data. Reference to the numerous tables in Landolt-Börnstein or other books of reference will show that an extremely large number of weak organic acids and bases obey the law of mass action in the concentration range for which its derivation is valid.

The limits of accuracy of the Ostwald dilution law are illustrated by the recent data of Kendall.‖ We shall again take acetic acid in water at 25° as an example. Table 8 contains the values of K_γ calculated by using the recent value for Λ_∞ obtained by Kraus and Parker†† (392), as well as the values originally calculated by Kendall using $\Lambda_\infty = 387{\cdot}9$. The latter value has also been used by Ostwald in Table 6, but is too low according to Kraus and Parker. It is apparent from Table 8 that the K_γ values rise gradually with increasing concentration. This tendency is extremely marked in the case of strong electrolytes, as we shall show later.‡‡ Organic acids stronger than acetic acid show a correspondingly greater rise in the values of K_γ. This is illustrated by the figures for cyanacetic acid also given in Table 8.

† Wilh. Ostwald, *Z. phys. Chem.* **2** (1888), 36, 270; **3** (1889), 170, 241, 418; M. Planck, *Wied. Ann.* **34** (1888), 139.

‡ G. Bredig, *Z. phys. Chem.* **13** (1894), 289; H. G. Goldschmidt and R. Salcher, ibid. **29** (1899), 89.

§ The Ostwald dilution law is valid for weak electrolytes up to about 0·1 N. See H. C. Jones and G. F. White, *Am. Chem. J.* **42** (1909), 520; H. C. Jones and E. P. Wightman, ibid. **46** (1911), 56.

‖ J. Kendall, *J. Chem. Soc.* **101** (1912), 1275.

†† C. A. Kraus and H. C. Parker, *J. Am. Chem. Soc.* **44** (1922), 2429. See also D. A. McInnes and Th. Shedlovsky, *J. Am. Chem. Soc.* **54** (1932), 1429.

‡‡ See p. 41.

TABLE 6

Test of the Ostwald dilution law. Acetic acid in water

$t = 18°$ C.

γ moles per litre	Λ	$100\alpha = \frac{100\,\Lambda}{\Lambda_\infty}$	$K_\gamma = \frac{1-\alpha}{\alpha^2}\gamma$
0	349·5	..	..
0·0001	107·0	30·6	$1{\cdot}31\times10^{-5}$
0·001	41·0	11·8	$1{\cdot}50\times10^{-5}$
0·01	14·3	4·1	$1{\cdot}70\times10^{-5}$
0·1	4·6	1·32	$1{\cdot}70\times10^{-5}$
1	1·32	0·38	$1{\cdot}40\times10^{-5}$
			Mean $1{\cdot}52\times10^{-5}$

$t = 25°$ C.

v_γ	Λ	K_γ
0·989	1·443	$1{\cdot}405\times10^{-5}$
1·977	2·211	$1{\cdot}652\times10^{-5}$
3·954	3·221	$1{\cdot}759\times10^{-5}$
7·908	4·618	$1{\cdot}814\times10^{-5}$
15·82	6·561	$1{\cdot}841\times10^{-5}$
31·63	9·26	$1{\cdot}846\times10^{-5}$
63·26	13·03	$1{\cdot}846\times10^{-5}$
126·52	18·30	$1{\cdot}847\times10^{-5}$
253·04	25·60	$1{\cdot}843\times10^{-5}$
506·1	35·67	$1{\cdot}841\times10^{-5}$
1012·2	49·50	$1{\cdot}844\times10^{-5}$
2024·4	68·22	$1{\cdot}853\times10^{-5}$
∞	387·9	..
		Mean $1{\cdot}78\times10^{-5}$

TABLE 7

Test of the Ostwald dilution law. Ammonia in water

$t = 18°$ C.

γ	Λ	100α	K_γ
0	238·4	..	..
0·0001	66	27·7	$1{\cdot}06\times10^{-5}$
0·001	28	11·7	$1{\cdot}56\times10^{-5}$
0·01	9·6	4·1	$1{\cdot}68\times10^{-5}$
0·1	3·3	1·4	$1{\cdot}92\times10^{-5}$
1·0	0·89	0·37	$1{\cdot}40\times10^{-5}$
			Mean $1{\cdot}51\times10^{-5}$

We shall now turn to a further application of Arrhenius's theory, which will be of value later. The scope of the classical theory is extremely wide. It has, for example, been applied to the electromotive

TABLE 8

Test of the Ostwald dilution law. Acetic and cyanacetic acids in water at 25°C.

Acetic Acid				*Cyanacetic Acid*		
γ	Λ	$K_\gamma \times 10^5$ ($\Lambda_\infty = 387{\cdot}9$)	$K_\gamma \times 10^5$ ($\Lambda_\infty = 392$)	γ	Λ	$K_\gamma \times 10^3$ ($\Lambda_\infty = 386{\cdot}1$)
0·07369	6·086	1·845	1·835	0·003716	238·7	3·72
0·03685	8·591	1·851	1·825	0·003005	252·4	3·72
0·01842	12·091	1·849	1·818	0·001858	282·6	3·72
0·009208	16·98	1·849	1·810	0·001503	294·9	3·72
0·004606	23·81	1·851	1·811	0·0009287	320·0	3·73
0·002303	33·22	1·849	1·807	0·0007515	329·2	3·72
0·001151	46·13	1·850	1·806	0·0004644	347·1	3·73
0·0005757	63·60	1·854	1·807	0·0003757	353·2	3·71
0·0002879	86·71	1·855	1·807	0·0002322	364·8	3·78

force of reversible cells by Nernst and others,† and also to the equilibrium in mixtures of electrolytes. It is always found that while weak electrolytes conform to the theory, strong electrolytes show deviations from the classical laws.‡ Heterogeneous ionic equilibria, the subject of the next section, constitutes only one of the numerous applications of Arrhenius's theory to thermodynamic phenomena.

10. Heterogeneous Ionic Equilibria. The Influence of Additions on the Solubility of Salts (Nernst)

In analytical chemistry it is often necessary to detect the presence of the ions of an electrolyte and to determine quantitatively the number of ions present. This is usually done by adding certain reagents to the solution to be investigated, and observing the resulting changes in the appearance of the mixture. This change may be due to the formation of ions or soluble molecules having a different colour, or to the formation of a sparingly soluble precipitate. In the first case we are dealing with a colour reaction depending upon changes of equilibrium in homogeneous systems, e.g. oxidation and reduction processes, or indicator reactions. We shall here deal only with the second case, a precipitation

† This subject will be treated from the standpoint of modern theory in the chapter on activities. See p. 39.

‡ The interpretation of the experimental data for homogeneous equilibria on the basis of the classical theory (cf. *Z. phys. Chem.* **2** (1888), 284; **5** (1890), 1) led to difficulties, as shown by Bjerrum (*Samml. chem. u. chem.-tech. Vorträge*, **21** (1915), 1). Other anomalies were found by Michaelis (see L. Michaelis and A. Gyemant, *Biochem. Z.* **109** (1920), 187). For full references to the literature on the deviations of strong electrolytes from Arrhenius's theory see the following articles: L. Ebert, *Jahrb. d. Radioakt. und Elektronik*, **18** (1921), 134; F. Auerbach, *Ergebn. d. exakt. Naturw.* **1** (1921), 228; E. Baars, *Handb. d. Phys. von Geiger-Scheel*, **13** (1927), 397. See also the text-books referred to on p. 10.

reaction in which a solid salt takes part in the equilibrium, and the system is heterogeneous. An example of such a heterogeneous precipitation reaction is

$$KCl + AgNO_3 = AgCl(solid) + KNO_3.$$

Silver chloride is precipitated when the concentrations of the Ag^+ and Cl^- ions exceed a certain minimum value. The remaining ions, i.e. K^+ and NO_3^-, take no part in the precipitation, and we can write the reaction more simply in terms of ions,

$$Ag^+ + Cl^- = AgCl\ (solid),$$

neglecting the other components. In a precipitation reaction we have always a solution saturated with respect to the precipitated substance. If a saturated solution of AgCl is in equilibrium with the solid phase AgCl, there will be a certain equilibrium (dependent on temperature) between the solid salt and the dissolved AgCl molecules, and also between the latter and the Ag^+ and Cl^- ions in solution. We can write

$$AgCl(solid) \rightleftharpoons AgCl(dissolved) \leftrightharpoons Ag^+ + Cl^-.$$

If we apply the law of mass action (43) to the equilibrium

$$AgCl(dissolved) \rightleftharpoons Ag^+ + Cl^-,$$

we obtain the equation

$$\gamma_{Ag^+}\gamma_{Cl^-} = K_\gamma \gamma_{AgCl\ (dissolved)}. \tag{77}$$

It has been pointed out by Nernst† that the concentration of the undissociated molecules in solution has a definite (though sometimes extremely small) value, determined by the equilibrium of the solution with the solid phase, i.e. by the vapour pressure of the solid at the temperature in question. $\gamma_{AgCl\ (dissolved)}$ is therefore constant, and we have from (77)

$$\gamma_{Ag^+}\gamma_{Cl^-} = K_\gamma \gamma_{AgCl\ (dissolved)} = \mathbf{P}_{AgCl} = \text{const.} \tag{78}$$

The quantity $\mathbf{P}_{AgCl}$ is equal to the product of the dissociation constant and the concentration of undissociated molecules γ_{AgCl}, and is termed the *solubility product*. The solubility product should therefore be constant at constant temperature and pressure, independent of the presence of other ions or molecules in the solution. For sparingly soluble substances the concentrations are very small, and it can be assumed that the dissolved molecules are completely dissociated. We then have the following very simple relation between the solubility product and the solubility in moles per litre,

$$\gamma_{AgCl\ (total)} = \gamma_{Ag^+} = \gamma_{Cl^-} = \sqrt{\mathbf{P}}. \tag{79}$$

† W. Nernst, *Z. phys. Chem.* **4** (1889), 372.

(For more easily soluble substances which are not completely dissociated

$$\mathbf{P} = \alpha^2\gamma^2,$$

where α is the degree of dissociation and γ the concentration in moles per litre at saturation.) If it is impossible to measure γ directly, the specific conductivity λ is measured. The equivalent conductivity Λ^* is known from the ionic mobilities† and can be identified with Λ^*_∞ in very dilute solutions. γ is then given by the equation $1{,}000\lambda = \gamma z_e \Lambda^*_\infty$, where z_e is the electrochemical valency. Kohlrausch has carried out a very great number of such measurements. The solubilities and solubility products are known for very slightly soluble binary electrolytes in water.‡ Thus if the solubility L is measured in grammes of anhydrous substance per 100 grammes solution, we have

$$\gamma = 10d(L)/G_E,$$

where G_E is the molecular weight of the electrolyte, and α the density of the solution. Taking as an example a solution of silver bromide saturated at 18°, (L) is given by

$$(L) = \frac{\gamma G_E}{10d} = 4{\cdot}5\times10^{-7}\frac{79{\cdot}9+107{\cdot}9}{10}$$
$$= 8{\cdot}4\times10^{-6}\text{ gm. AgBr per 100 gm. solution.}$$

The solubility product $\mathbf{P}$ is given by (78) as 2×10^{-13}.

We shall now consider how the solubility of a binary electrolyte is changed by the addition of a second binary electrolyte having a common ion. Let γ_1 be the concentration of one of the ions of the first electrolyte, so that in the absence of additions

$$\mathbf{P} = \gamma_1^2. \tag{80}$$

If the second electrolyte is now added in concentration γ_2, then since the solubility product is unaltered at the same temperature and pressure,

$$\mathbf{P} = \gamma_1'(\gamma_1+\gamma_2). \tag{81}$$

It is obvious that $\gamma_1' < \gamma_1$, i.e. the solubility is decreased. We may take as an example a saturated solution of AgCl in which the concentration of Ag^+ ion has been increased by the addition of $AgNO_3$ solution. The value of $\mathbf{P}$ is about 10^{-10}, so that the addition of normal $AgNO_3$ solution will depress γ_{Cl^-} from 10^{-5} to 10^{-10} ($\gamma_{Ag^+} = 1$).

† The specific conductivity λ, the equivalent concentration γ^*, and the equivalent conductivity Λ^* are by definition related by the equation $1{,}000\lambda/\gamma^* = \Lambda^*$. In general Λ^* is given by multiplying the sum of the ionic mobilities by the true degree of dissociation. (See (674) and (686).)

‡ See e.g. Landolt-Börnstein, ii, 1180; Ergbd. i, 662, ii b, 1109.

Nernst† has investigated more complicated solubility effects both theoretically and practically, and there are many more recent studies, especially by A. A. Noyes.‡ The change of solubility was investigated for the addition of salts having a common ion and salts without a common ion. For example, it was found that the equivalent amounts of $AgNO_3$ and $KBrO_3$ caused the same decrease in the solubility of silver bromate, and in general the results obtained agree approximately with the predictions of the classical theory. Noyes has also investigated ternary salts, e.g. the decrease in the solubility of lead chloride caused by the addition of the chlorides of magnesium, calcium, tin, and manganese.

Noyes§ has also shown both theoretically and experimentally that an increase in solubility is often brought about by adding a salt not having a common ion. The added ions will in general combine to a certain extent with those of the opposite sign already present, e.g. on adding potassium nitrate to silver bromate a certain number of silver nitrate and potassium bromate molecules will be formed in the solution. In this particular example the number of undissociated molecules which can exist in the solution is relatively low, and the increase of solubility is therefore small. In some cases, however, very great increases are found, e.g. when nitric acid is added to a saturated solution of silver acetate. In this case large amounts of undissociated acetic acid molecules are formed since its degree of dissociation is very small, and a considerable amount of the solid silver acetate must go into solution in order to maintain the solubility product for the silver and acetate ions. The fact that many salts which are sparingly soluble in water dissolve readily in acids and bases is to be explained in the same way.‖ A similar effect can be observed in the action of suitable salt solutions on sparingly soluble acids and bases.†† Thus calcium oxalate is very soluble in strong acids, but practically insoluble in acids as weak as acetic acid. This may

† W. Nernst, *Z. phys. Chem.* **4** (1889), 372.

‡ A. A. Noyes, *Z. phys. Chem.* **6** (1890), 241; **9** (1892), 603; **16** (1895), 125 (with C. G. Abbott); **27** (1898), 267; see also R. Griessbach, ibid. **97** (1921), 22. For further references, see V. Rothmund, *Löslichkeit und Löslichkeitsbeeinflussung*, Leipzig, 1907; J. H. Hildebrand, *Solubility*, Chem. Cat. Co., New York, 1924; also standard works on physical chemistry and pp. 41 and 124 of the present book.

§ Noyes and collaborators, *J. Am. Chem. Soc.* **33** (1911), 1643, and subsequent papers.

‖ See A. A. Noyes and D. Schwartz, *J. Am. Chem. Soc.* **20** (1898), 742; Noyes and E. S. Chapin, ibid. **20** (1898), 751; *Z. phys. Chem.* **27** (1898), 279. For further references, see H. S. Taylor, *A System of Physical Chemistry*.

†† See J. M. Loven, *Z. anorg. Chem.* **11** (1896), 404; A. A. Noyes and E. S. Chapin, *J. Am. Chem. Soc.* **20** (1898), 751; *Z. phys. Chem.* **27** (1898), 442; **28** (1899), 518; E. Larsson, ibid. **127** (1927), 233.

be explained as follows. If the hydrogen ion concentration of the solution is so great that the product $\gamma_{C_2O_4^=} \times \gamma_{H^+}$ exceeds the permitted value, H^+ and $HC_2O_4^-$ combine to form undissociated $H_2C_2O_4$. In order to maintain equilibrium, fresh $C_2O_4^=$ ions must go into the solution from the solid phase, and the calcium oxalate thus dissolves more and more. If a weak acid is added, the hydrogen ion concentration is not high enough to bring about the above process, and the precipitate remains practically unaltered. Similar reasoning applies to the solubility of $Mg(OH)_2$ and $Ca(OH)_2$ in NH_4Cl solutions. If the concentration of NH_4^+ ions is sufficiently high, the undissociated base NH_4OH is formed in solution, and more $Mg(OH)_2$ or $Ca(OH)_2$ dissolves to maintain the equilibrium.

Strong electrolytes exhibit deviations from this classical interpretation of solubility effects. These deviations will now be dealt with in detail. It was found at an early date that the fall in solubility caused by the addition of a salt containing a common ion was not so great as would be expected according to the classical theory.† These deviations lead to the conception of *activity coefficients*, which will be dealt with in the following chapter.

† For details, see e.g. H. Karplus, *Die Löslichkeitsbeeinflussung*, Dissertation, Berlin, 1907. Cases of very great increase in solubility, e.g. AgCN in KCN are due to the formation of complex ions. We shall omit these cases from consideration. See e.g. A. Jaques, *Complex ions in aqueous solutions*, Longmans, London, 1914, and the works on solubility previously quoted.

IV

THE DEVIATIONS OF STRONG ELECTROLYTES FROM CLASSICAL THERMODYNAMICAL THEORY. THE EMPIRICAL ACTIVITY THEORY OF G. N. LEWIS. THE THERMODYNAMICS OF ACTIVITIES. THE REGULARITIES OBSERVED IN THE ACTIVITY COEFFICIENTS OF STRONG ELECTROLYTES AT SUFFICIENTLY HIGH DILUTIONS

11. The Thermodynamic Anomalies of Strong Electrolytes in very Dilute Solution†

A. *The impossibility of explaining the laws governing the osmotic coefficients by Arrhenius's theory.*

For a molecule which dissociates completely into ν ions, van 't Hoff's equation for the ideal osmotic pressure gives

$$\bar{P} = \nu nkT, \tag{82}$$

where n is the number of salt molecules per c.c. Following Bjerrum‡ we shall introduce the *osmotic coefficient* g as a measure of the deviation of the osmotic pressure P of real solutions from the ideal value. This coefficient is defined by the equation

$$P = g\nu nkT \tag{83}$$

or

$$\frac{\bar{P}-P}{\bar{P}} = 1-g. \tag{84}$$

If we introduce the van 't Hoff factor i or the degree of dissociation α (according to Arrhenius's theory) into (84) we have

$$i = 1+(\nu-1)\alpha = \nu g \tag{85}$$

or

$$1-g = \frac{\nu-1}{\nu}(1-\alpha). \tag{86}$$

On introducing Ostwald's dilution law (72), equation (86) becomes, for sufficiently dilute solutions,

$$1-g = \gamma^{\nu-1}\frac{(\nu-1)}{K_{\gamma}{}^{\nu}}. \tag{87}$$

If therefore $1-g$ is plotted as a function of the molar concentration γ, the curve obtained for binary electrolytes should have a finite slope at the origin. For ternary and more complex electrolytes ($\nu > 2$) the curve

† Arrhenius himself has acknowledged these anomalies. See *Conférences sur quelques problèmes actuels de la chimie physique et cosmique*, Paris, 1923.

‡ N. Bjerrum, *Z. f. Elektrochem.* **24** (1907), 259.

should approach the origin as a tangent to the γ-axis, the order of contact being higher the greater the value of ν. In Fig. 2 the values of $1-g$ are plotted for four salts of different ionic types, the values being taken from the reliable freezing-point measurements of Adams, Hall, and Harkins.† In Fig. 2, $\nu\gamma$ has been chosen as abscissa, since according to van 't Hoff completely dissociated electrolytes with the same value of $\nu\gamma$ must have the same osmotic pressures, the valency of the ions being assumed to have no effect. Fig. 2 shows that it is very unlikely that the curves for the binary electrolytes KCl and $MgSO_4$ have a finite slope at the origin, as required by the classical theory. In the case of the ternary electrolyte K_2SO_4 and the quaternary electrolyte $La(NO_3)_3$, it is quite obvious that the curves do not conform to the law of mass action by becoming tangential to the γ-axis at the origin. They appear in fact to become tangential to the $1-g$ axis. Fig. 2 shows other points of interest, for example, the part played by the valency of the ions. Thus for the same value of $\nu\gamma$, KCl has a very much smaller value of $1-g$ than $MgSO_4$, i.e. the osmotic pressure of $MgSO_4$ will be lower than that of KCl. It should also be noted that if the points for other representatives of the valency types shown in Fig. 2 were inserted, it would be found that at low concentrations they would coincide with the curves already there, e.g. the pairs KCl and NaCl, $MgSO_4$ and $CaSO_4$ give the same curves. Individual discrepancies only appear at higher concentrations. These facts make it very probable that an important part is played by the electric charges of the ions, which are ignored in the classical theory.

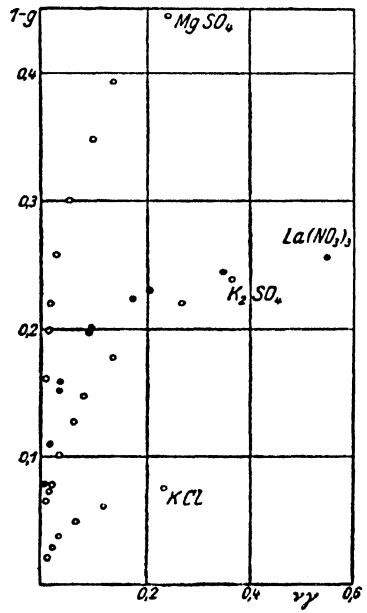

FIG. 2. Osmotic coefficients from freezing-point measurements.

B. *The failure of the law of mass action for strong electrolytes.*

According to the law of mass action (74) the quantity $K_{\gamma+}$ should remain a constant. In order to test this in the case of strong electrolytes,

† L. H. Adams, *J. Am. Chem. Soc.* **37** (1915), 494; R. E. Hall and W. D. Harkins, ibid. **38** (1916), 2658.

we shall take the values of the degree of dissociation α already given in Table 5 (p. 30) and calculate the values of $\alpha^2\gamma^*/(1-\alpha) = K_{\gamma^*}$. Table 9 contains the values of K_{γ^*} for some strong electrolytes at different concentrations. It is obvious that K_{γ^*} shows no constancy whatever. Once again we find that the behaviour of strong electrolytes is at variance with the classical theory.

We shall now turn to solubility effects, and show that here also strong electrolytes exhibit anomalous behaviour.

TABLE 9

Values of $K_{\gamma^*} = \alpha^2\gamma^*/(1-\alpha)$ *for various strong electrolytes*

$t = 18°$ C., solvent water.

	NaCl		KCl		LiCl		$BaCl_2$		$MgSO_4$	
γ^*	α	K_{γ^*}	α	K_{γ^*}	α	K_{γ^*}	α	K_{γ^*}	α	K_{γ^*}
0	1		1		1		1		1	
10^{-4}	0·9921	0·0123	0·9923	0·0128	0·9915	0·0116	..	..	0·9607	0·00235
2×10^{-4}	0·9895	0·0185	0·9900	0·0196	0·9886	0·0171	..	..	0·9447	0·00323
5×10^{-4}	0·9836	0·0294	0·9849	0·0322	0·9819	0·0266	0·9678	0·0145	0·9109	0·00466
10^{-3}	0·9772	0·0419	0·9790	0·0456	0·9751	0·0382	0·9562	0·0209	0·8732	0·00601
2×10^{-3}	0·9686	0·0598	0·9711	0·0652	0·9660	0·0549	..	..	0·8229	0·00764
5×10^{-3}	0·9523	0·0952	0·9565	0·1051	0·9489	0·0881	..	..	0·7389	0·01046
10^{-2}	0·9355	0·1358	0·9413	0·1510	0·9309	0·1254	0·8823	0·0661	0·6662	0·01329
1×10^{-2}	0·9141	0·1947	0·9223	0·2190	0·9084	0·1802	0·8481	0·0947	0·5916	0·01714
5×10^{-2}	0·8784	0·3173	0·8899	0·3597	0·8701	0·2915	0·7944	0·1535	0·4976	0·02464
10^{-1}	0·8444	0·4584	0·8613	0·5349	0·8328	0·4148	0·7509	0·2263	0·4343	0·03334

C. *Anomalies in the solubility relations of strong electrolytes.*

It was formerly assumed that in Nernst's theory of solubility effects it was quite necessary to assume a constant solubility product.† This constancy should also be maintained in the presence of added electrolytes, independent of the nature and quantity of the addition. Taking thallium chloride as an example, the solubility product at 18° should always be

$$\mathbf{P}_{TlCl} = \gamma_{Tl^+}\gamma_{Cl^-} = 2{\cdot}1\times10^{-4},$$

or the common logarithm of $10^5\times\mathbf{P}$ should be

$$\log_{10}(\mathbf{P}_{TlCl}\times10^5) = 1{\cdot}32.$$

However, on adding varying quantities of KCl to a saturated solution of thallium chloride, it is found that the solubility product is by no means constant, but rises.‡ As an example of these experimental

† See p. 35.

‡ This variation in the solubility product has been observed by many American workers. See e. g. A. E. Hill and J. P. Simmons, *J. Am. Chem. Soc.* **31** (1909), 821; Hill, ibid. **32** (1910), 1186; A. A. Noyes and W. C. Bray, ibid., **33** (1911), 1643; Bray and Winninghoff, ibid., **33** (1911), 1663; Hill, ibid. **39** (1917), 218; W. D. Harkins, ibid. **33** (1911), 1807. For further literature, see p. 124 in connexion with the electrostatic theory.

results, if we add $3{\cdot}35\times10^{-2}$ moles KCl per litre to saturated thallium chloride solution it is found that the concentration of thallium ions is $1{\cdot}65\times10^{-2}$, that of the chlorine ions being also $1{\cdot}65\times10^{-2}$. The total *ionic concentration*†

$$\sum z_i^2 \gamma_i = \Gamma \tag{88}$$

is in this case

$$\Gamma = \sum \gamma_i = 3{\cdot}30\times10^{-2}+6{\cdot}7\times10^{-2} = 10^{-1}.$$

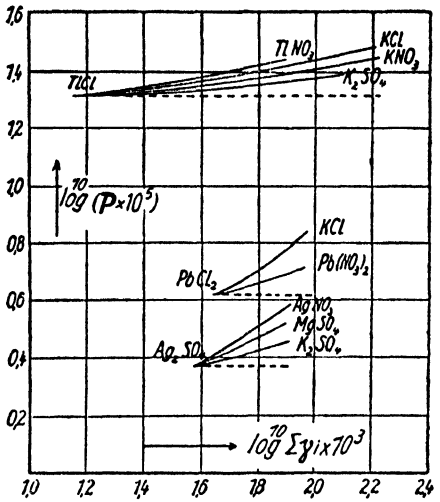

FIG. 3. The effect of added salts on the solubility product **P**.

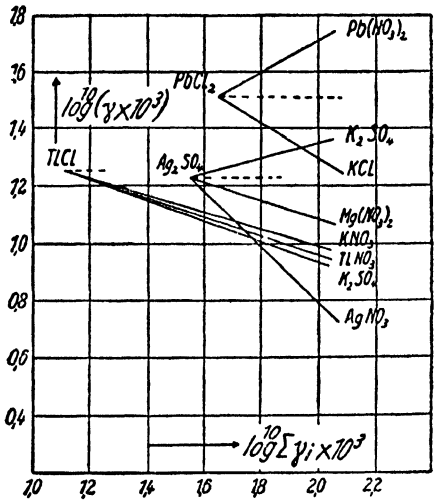

FIG. 4. The effect of added salts on the solubility γ.

The solubility product corresponding to the amount of added KCl mentioned is

$$2{\cdot}8\times10^{-4},$$

so that

$$\log_{10}(\mathbf{P}\times10^5)_{\Gamma=0{\cdot}1} = 1{\cdot}45.$$

If we choose as ordinate $\log_{10}(\mathbf{P}\times10^5)$ and as abscissa $\log_{10}(\sum\gamma_i\times10^3)$, the example given above corresponds to an ordinate 1·45 and an abscissa 2. In Fig. 3 the values obtained for additions of KCl, $TlNO_3$, KNO_3, and K_2SO_4 to TlCl are plotted in this way. The dotted horizontal line at a height of 1·32 corresponds to the requirements of the law of mass action. It is seen that the law of mass action is by no means exactly obeyed, the solubility product depending on the nature and quantity of salt added. The second assumption of Nernst's theory has already been dealt with in detail.‡ As a test of this, Fig. 4 shows the dependence of the concentration of the undissociated salt molecules in

† The ionic concentration is used here in anticipation of the theory dealt with later. (See p. 128.)

‡ See p. 35.

solution on the quantity $\sum \gamma_i \times 10^3$ in the case of the slightly soluble salts TlCl, $PbCl_2$, and Ag_2SO_4. The ordinates are $\log_{10}(\gamma \times 10^3)$ and the abscissae $\log_{10}(\sum \gamma_i \times 10^3)$. Nernst's theory is represented by the horizontal dotted lines. γ is in no case strictly constant.† While **P** always increases with increasing ionic concentration γ may also decrease, e.g. in the case of TlCl. It is also seen that the curves are more steeply inclined when the saturating salt is composed of ions of higher valencies: this again suggests the influence of the interionic forces, which are neglected in the classical theory. Many more examples of the thermodynamic behaviour of solutions could be taken, and it is always found that strong electrolytes behave anomalously according to the classical laws.‡ G. N. Lewis evolved an empirical theory of these anomalies by introducing the concept of activity, and he showed on purely experimental grounds the importance of the 'ionic concentration' (as defined above) for the thermodynamic behaviour of strong electrolytes. We shall now turn to the theory of activities.

12. Definition of the Activity

We shall take as an example the solubility effects just described. For a slightly soluble salt, e.g. TlCl, the solubility product **P** is defined by (78). We know, however, from experiment that **P** is actually not always constant, but increases with increasing concentration of added salt. It might be concluded from this that only a certain fraction of the ions Tl^+ and Cl^- take an active part in the equilibrium between solid and solution. These fractions we shall term f_{Tl^+} and f_{Cl^-}. In order to describe the deviations of electrolyte solutions from the ideal laws holding at infinite dilution, it is found convenient to retain the form of the ideal laws even for the real solutions. To effect this, it is only necessary to use, instead of the concentration of any ion γ_i, the apparent concentration

$$a_i = \gamma_i f_i \tag{89}$$

as a measure of the chemical 'activity' of the ion in question. The law of mass action and related formulae can then be used as before; thus in the case just mentioned, we write

$$a_{Tl^+} a_{Cl^-} = \mathbf{P}_{a\,(TlCl)}, \tag{90}$$

or, by (89)

$$(\gamma_{Tl^+} f_{Tl^+})(\gamma_{Cl^-} f_{Cl^-}) = \mathbf{P}_{a(TlCl)}. \tag{91}$$

† Arrhenius pointed out this lack of constancy in the data of A. A. Noyes for silver salts. See *Z. phys. Chem.* **31** (1899), 197, and also J. Stieglitz, *J. Am. Chem. Soc.* **30** (1908), 946.

‡ For literature, see p. 91.

a_i is termed the *activity* and f_i the *activity coefficient* of the ions of the ith sort. At infinite dilution,

$$a_i = \gamma_i, \tag{92}$$

i.e.

$$f_i = 1. \tag{93}$$

As the concentration increases, f_i becomes less than unity. We see immediately from equation (91) that

$$\gamma_{Tl^+}\gamma_{Cl^-} = \mathbf{P}_{TlCl} > \mathbf{P}_{a(TlCl)}, \tag{94}$$

which corresponds to the experimental facts. Activity coefficients of this kind were introduced by G. N. Lewis, purely as a formal conception and without reference to any theoretical considerations. Their properties have been further studied by Lewis and Randall† since 1912, and by Brönsted‡ since 1915, and received a theoretical interpretation at the hands of Debye and Hückel.§ Lewis|| introduced the activity in the following way. Let the thermodynamic potential of one mole of component A (e.g. a certain species of ion) be $\bar{\Phi}_A$ in the real solution, and let $\bar{\Phi}^0_A$ be the thermodynamic potential of one mole of the same component in any arbitrary standard state. Lewis then defines the activity a by the following relation,

$$\bar{\Phi}_A - \bar{\Phi}^0_A = RT \log a. \tag{95}$$

The activity is thus a relative magnitude: it is usually defined so that for very small concentrations it becomes in the limit equal to the concentration, i.e. the activity coefficient becomes unity. When $\bar{\Phi}_A = \bar{\Phi}^0_A$, a is by definition unity. Now we have previously seen†† that $\bar{\Phi}_A - \bar{\Phi}^0_A$ represents a work term, being in fact the change of free energy per mole of the component in question caused by the change from one state to another. (The compressibility of the electrolyte can be always neglected in practice.) Thus in the case of a concentration cell, the change of free energy is the electrical work corresponding to the electromotive force. Any phenomena connected directly with free energy can therefore be used in the determination of activities. Thus measurements of lowering of vapour pressure, freezing-point depressions, or the electromotive force of suitable cells can be used to calculate activities. G. N. Lewis

† G. N. Lewis and M. Randall, *Thermodynamics and the free energy of chemical substances*, McGraw Hill Book Co., 1923.

‡ J. N. Brönsted, *D. kgl. danske Vidensk. Selsk. Skrifter* (7), **12** (1915), 241; *Medd. k. Vet. Akad. Nobel Institut*, **5** (1919), no. 25; *D. kgl. danske Vidensk. math.-fys. Medd.* III, 9, 1920; *Lectures on Contemporary Developments in Chemistry*, Columbia University Press, 1927.

§ See p. 126.

|| G. N. Lewis, *Proc. Am. Acad.* **37** (1901), 45; **43** (1907), 259; *Z. phys. Chem.* **61** (1907), 129.

†† See p. 15.

and his collaborators have in this way measured the activities of numerous electrolytes and their ions, and an account of their work will be given shortly. First, however, we shall investigate the part played by the concept of activity in thermodynamics.

13. The Thermodynamic Potential of Real Solutions and the Thermodynamics of Activities

In evolving a theory of real solutions, it is convenient to consider what changes must be made in the laws of ideal solutions. We have seen previously† that the thermodynamic potential must be a homogeneous linear function of the mole fractions. The same must therefore be true of the term W which must be added to the thermodynamic potential $\bar{\Phi}$ of the ideal solution, i.e.

$$W = \sum_{\sigma} W^{(\sigma)} = \sum_{\sigma} \sum_{\lambda} M_{\lambda}^{(\sigma)} w_{\lambda}^{(\sigma)}, \tag{96}$$

where the $w_{\lambda}^{(\sigma)}$'s are functions of temperature, pressure, and concentration. We therefore have

$$\frac{\partial W}{\partial \bar{M}_{\lambda}^{(\sigma)}} = w_{\lambda}^{(\sigma)} + \sum_{\lambda=1}^{l} M_{\lambda}^{(\sigma)} \frac{\partial w_{\lambda}^{(\sigma)}}{\partial \bar{M}_{\lambda}^{(\sigma)}}. \tag{97}$$

From (37) and (96), the thermodynamic potential of the real solution is

$$\Phi = \sum_{\sigma=1}^{\kappa} \sum_{\lambda=1}^{l} M_{\lambda}^{(\sigma)} \{\phi_{\lambda}^{(\sigma)} + RT \log \eta_{\lambda}^{(\sigma)} + w_{\lambda}^{(\sigma)}\}. \tag{98}$$

If we now consider the variation in thermodynamic potential caused by a small arbitrary variation $\delta M_{\lambda}^{(\sigma)}$ in the molar quantity at constant pressure and temperature, we have from (97) and (98)

$$\delta\Phi = \sum_{\sigma=1}^{\kappa} \sum_{\lambda=1}^{l} \delta M_{\lambda}^{(\sigma)} \left\{\phi_{\lambda}^{(\sigma)} + RT \log \eta_{\lambda}^{(\sigma)} + \frac{\partial W}{\partial \bar{M}_{\lambda}^{(\sigma)}}\right\}. \tag{99}$$

This expression can be converted to a simpler form by writing

$$\frac{\partial W}{\partial \bar{M}_{\lambda}^{(\sigma)}} = RT \log f_{\lambda}^{(\sigma)*} \tag{100}$$

so that

$$\delta\Phi = \sum_{\sigma=1}^{\kappa} \sum_{\lambda=1}^{l} \delta M_{\lambda}^{(\sigma)} \{\phi_{\lambda}^{(\sigma)} + RT \log (f_{\lambda}^{(\sigma)*} \eta_{\lambda}^{(\sigma)})\}. \tag{101}$$

Following Gibbs‡ the factor

$$\phi_{\lambda}^{(\sigma)} + RT \log (f_{\lambda}^{(\sigma)*} \eta_{\lambda}^{(\sigma)}) \tag{102}$$

† See p. 19.

‡ J. W. Gibbs, *Trans. Connecticut Acad.* **3** (1875–8); *Scientific Papers*, vol. i, Longmans, 1906; *Collected Works*, Longmans, Green & Co., New York, 1928.

is termed the *chemical potential* of the component λ in the phase σ. According to (93), the chemical potential for an ideal solution is

$$\phi_\lambda^{(\sigma)} + RT \log \eta_\lambda^{(\sigma)}. \tag{103}$$

The expression for a real solution (102) differs from this only in the replacement of the real concentration $\eta_\lambda^{(\sigma)}$ by the apparent concentration $f_\lambda^{(\sigma)} * \eta_\lambda^{(\sigma)}$. In a real solution the chemical potential of the component λ in the phase σ is thus

$$\frac{\partial \Phi}{\partial M_\lambda^{(\sigma)}} = \phi_\lambda^{(\sigma)} + RT \log (f_\lambda^{(\sigma)} * \eta_\lambda^{(\sigma)}). \tag{104}$$

$f_\lambda^{(\sigma)} * \eta_\lambda^{(\sigma)}$ is termed the *activity* $a_\lambda^{(\sigma)}$ of the component λ in the phase σ, and $f_\lambda^{(\sigma)}*$ the corresponding *rational activity coefficient.*† Introducing the activities $a_\lambda^{(\sigma)}$, the change in the thermodynamic potential of the real solution becomes

$$\delta\Phi = \sum_{\sigma=1}^{\kappa} \sum_{\lambda=1}^{l} \delta M_\lambda^{(\sigma)} \{\phi_\lambda^{(\sigma)} + RT \log a_\lambda^{(\sigma)}\}. \tag{105}$$

The relation of this formula to Lewis's definition follows from the fact that in the standard state $a_\lambda^{(\sigma)}$ is unity. The change of thermodynamic potential in the standard state is therefore

$$\delta\Phi^0 = \sum_{\sigma=1}^{\kappa} \sum_{\lambda=1}^{l} \delta M_\lambda^{(\sigma)} \phi_\lambda^{(\sigma)}, \tag{106}$$

and we can write for the real solution,

$$\delta\Phi = \delta\Phi^0 + RT \sum_{\sigma=1}^{\kappa} \sum_{\lambda=1}^{l} \delta M_\lambda^{(\sigma)} \log a_\lambda^{(\sigma)} \tag{107}$$

or,

$$\delta\Phi - \delta\Phi^0 = RT \log \Big\{ \prod_{\sigma=1}^{\kappa} \prod_{\lambda=1}^{l} (a_\lambda^{(\sigma)})^{\delta M_\lambda^{(\sigma)}} \Big\}. \tag{108}$$

At equilibrium, by (12), $\delta\Phi = 0$.

Each reaction is further characterized by certain values for the $\delta M_\lambda^{(\sigma)}$'s (see (41)). We then obtain from (12), (106), (107), and (108),

$$\sum_{\sigma=1}^{\kappa} \sum_{\lambda=1}^{l} \mu_\lambda^{(\sigma)} \log a_\lambda = -\sum_{\sigma=1}^{\kappa} \sum_{\lambda=1}^{l} \frac{\mu_\lambda^{(\sigma)} \phi_\lambda^{(\sigma)}}{RT} = \log K_a(p, T). \tag{109}$$

The Guldberg-Waage law of mass action can therefore be written more generally,

$$\prod_{\sigma=1}^{\kappa} \prod_{\lambda=1}^{l} (a_\lambda^{(\sigma)})^{\mu_\lambda^{(\sigma)}} = K_a(p, T). \tag{110}$$

For the special case of a single phase, the generalized law of mass action can be deduced more simply from Lewis's definition of activity (95). Let μ_1 moles of the substance A_1, μ_2 moles of the substance A_2, etc.,

† See p. 54 for the relation between rational and practical activity coefficients.

react at constant temperature and pressure to give μ_1' moles of the substance A_1', μ_2' moles of the substance A_2', etc., so that the equation of the reaction can be written,

$$\mu_1 A_1+\mu_2 A_2+\ldots = \mu_1' A_1'+\mu_2' A_2'+\ldots. \tag{111}$$

According to (95) we have:

$$\left.\begin{aligned}
(\Phi-\Phi^0)_{A_1} &= \mu_1 RT\log a_{A_1}\\
(\Phi-\Phi^0)_{A_2} &= \mu_2 RT\log a_{A_2}\\
&\cdots\cdots\cdots\\
(\Phi-\Phi^0)_{A_1'} &= \mu_1' RT\log a_{A_1'}\\
(\Phi-\Phi^0)_{A_2'} &= \mu_2' RT\log a_{A_2'}\\
&\cdots\cdots\cdots
\end{aligned}\right\} \tag{112}$$

In order to find the change of thermodynamic potential for the reaction we have

$$(\Phi-\Phi^0)_{A_1}+(\Phi-\Phi^0)_{A_2}+\ldots-(\Phi-\Phi^0)_{A_1'}-(\Phi-\Phi^0)_{A_2'}-\ldots = RT\log\frac{a_{A_1'}^{\mu_1'}a_{A_2'}^{\mu_2'}\ldots}{a_{A_1}^{\mu_1}a_{A_2}^{\mu_2}\ldots}. \tag{113}$$

Writing now
$$\Phi_{A_1'}-\Phi_{A_1}+\Phi_{A_2'}-\Phi_{A_2}+\ldots = \Delta\Phi \tag{114}$$

$$\Phi^0_{A_1'}-\Phi^0_{A_1}+\Phi^0_{A_2'}-\Phi^0_{A_2}+\ldots = \Delta\Phi^0, \tag{115}$$

$\Delta\Phi$ is the change in thermodynamic potential for the reaction in general, and $\Delta\Phi-\Delta\Phi^0$ the change referred to the standard state as zero. At equilibrium,

$$\Delta\Phi = 0$$

so that we have as in (108)

$$\Delta\Phi^0 = -RT\log\frac{a_{A_1'}^{\mu_1'}a_{A_2'}^{\mu_2'}\ldots}{a_{A_1}^{\mu_1}a_{A_2}^{\mu_2}\ldots}. \tag{116}$$

Since $\Delta\Phi^0$ depends only on temperature and pressure, we have for the *general law of mass action*

$$\frac{a_{A_1'}^{\mu_1'}a_{A_2'}^{\mu_2'}\ldots}{a_{A_1}^{\mu_1}a_{A_2}^{\mu_2}\ldots} = K_a(p,T). \tag{117}$$

In principle, any thermodynamic equilibrium can be used in order to measure activities; e.g. osmotic pressures, freezing-point depressions, electromotive force of concentration cells should all lead to the same results. Before illustrating this further we shall deal with some theoretical considerations which are of assistance in interpreting these investigations. We shall then give a few applications of the thermodynamical relations derived above in order to illustrate the significance of activity coefficients. In practice it is necessary to differentiate between processes involving transfer of the solvent and processes

involving transfer of the solute. The first type includes osmotic pressure, freezing-point depression, boiling-point elevation, and lowering of vapour-pressure; the second type phenomena connected with the law of mass action, such as solubility, change of solubility, electromotive force, etc.

14. The Osmotic Pressure, Freezing-point Depression, Boiling-point Elevation, and Lowering of Vapour Pressure of Strong Electrolytes, and their Relation to the Activity of the Solvent

In order to obtain the laws of osmotic pressure of real solutions, we must generalize the considerations of p. 21 by introducing activities in place of concentrations. The solvent is again the first phase, and will be characterized by a single dash. The solvent 0 and the solute 1 constitute the second phase (the solution). From (51) we have for the osmotic pressure P of the real solution,

$$\frac{P\mathfrak{v}_0}{RT} = -\log(\eta_0 f_0^*), \tag{118}$$

where f_0^* and η_0 are respectively the activity coefficient and mole fraction of the solvent in the solution.† We have from (38)

$$\sum \eta_i = 1,$$

so that

$$\eta_0 = 1 - \sum{}' \eta_i.$$

Hence

$$P\mathfrak{v}_0 = -RT \log\{(1 - \sum{}' \eta_i) f_0^*\}. \tag{119}$$

If the concentration of the solutes $\sum' \eta_i$ is small compared to unity, (119) can be expanded as a series giving

$$P = RT\left(\frac{1}{\mathfrak{v}_0}\sum{}' \eta_i - \frac{1}{\mathfrak{v}_0}\log f_0^*\right). \tag{120}$$

In our earlier treatment of ideal dilute solutions, we arrived at the equation

$$\bar{P} = \frac{RT}{\mathfrak{v}_0}\sum{}' \eta_i \tag{121}$$

for the osmotic pressure.‡ Since in an ideal dilute solution $f_0^* = 1$, $\log f_0^* = 0$, this appears as a special case of (120).

The osmotic pressure of a real solution thus differs from that of an ideal dilute solution by the term $-(RT/\mathfrak{v}_0)\log f_0^*$ and is smaller than the ideal osmotic pressure when f_0^* is greater than unity. On introducing

† The equation for the osmotic pressure of a real solution can also be obtained easily from equation (98) for the thermodynamic potential and the equilibrium condition (12). See e.g. E. Hückel, *Ergeb. d. exakten Naturwiss.* 3 (1924), 199.

‡ See p. 21, formula (54′).

the osmotic coefficient g, we have from (83), (120), and (121),

$$1-g = \frac{\log f_0^*}{\sum' \eta_i}, \tag{122}$$

or,

$$g = 1 - \frac{\log f_0^*}{\sum' \eta_i}. \tag{122'}$$

The osmotic coefficient g can thus be expressed in terms of the activity coefficient of the solvent f_0^*. The activity is actually the more fundamental conception, although the osmotic coefficient is often more convenient to use in practice.

In exactly the same way the freezing-point depression $(\Delta T)_g$, the boiling-point elevation $(\Delta T)_s$, and the lowering of vapour pressure Δp of real solutions can be expressed in terms of the activity coefficient f_0^* and the corresponding quantities for ideal dilute solutions, $(\overline{\Delta T})_g$, $(\overline{\Delta T})_s$, and $\overline{\Delta p}$. The following equations are obtained:

$$\frac{(\overline{\Delta T})_g-(\Delta T)_g}{(\overline{\Delta T})_g} = \frac{(\overline{\Delta T})_s-(\Delta T)_s}{(\overline{\Delta T})_s} = 1-g = \frac{\log f_0^*}{\sum' \eta_i}, \tag{123}$$

$$\frac{\overline{\Delta p}-\Delta p}{\overline{\Delta p}} = 1-g = \frac{\log f_0^*}{\sum' \eta_i}. \tag{124}$$

15. The Relation Between the Activity Coefficients of the Solvent and the Solute. (Gibbs's Equation)

Our starting-point is the equation (96) for the additional term to be added to the thermodynamic potential of an ideal dilute solution in order to obtain the thermodynamic potential of a real solution. Since we are now dealing with only one phase, the index σ can be omitted, and the sum $\sum_\sigma$ becomes a single term. We then have

$$W = \sum M_\lambda w_\lambda, \tag{125}$$

and from (100)

$$\frac{\partial W}{\partial M_\lambda} = RT \log f_\lambda^*. \tag{126}$$

This equation gives immediately

$$\frac{\partial \log f_\lambda^*}{\partial M_\nu} = \frac{\partial \log f_\nu}{\partial M_\lambda}. \tag{127}$$

If we now put $\lambda = 0$, we obtain the following equation for the activity coefficient f_0^* of the solvent in terms of the activity coefficient f_ν^* of the component ν†

$$\frac{\partial \log f_0^*}{\partial M_\nu} = \frac{\partial \log f_\nu^*}{\partial M_0}. \tag{128}$$

† We shall return later to equations (128) and (130). See p. 63.

It is interesting to note that the above considerations are closely connected with an equation derived by Gibbs. From (125) and (97),

$$W = \sum M_\lambda \frac{\partial W}{\partial M_\lambda} = \sum M_\lambda w_\lambda. \tag{129}$$

We now form the total differential of W at constant temperature and pressure,

$$dW = \sum M_\lambda dw_\lambda + \sum w_\lambda dM_\lambda.$$

Also, since

$$W = W(M_1, M_2, \ldots, M_l)$$

$$dW = \sum \frac{\partial W}{\partial M_\lambda} dM_\lambda = \sum w_\lambda dM_l.$$

Hence,

$$\sum M_\lambda dw_\lambda = 0,$$

or

$$\sum M_\lambda d\log f_\lambda^* = 0. \tag{130}$$

Equation (130) is known as the generalized Gibbs-Duhem-Margules equation. On introducing activities ($a_\lambda = f_\lambda^* \eta_\lambda$) it becomes

$$\sum M_\lambda d\log a_\lambda = 0. \tag{130'}$$

since

$$\sum M_\lambda d\log \eta_\lambda = 0.$$

The truth of the last equation follows from

$$\sum \eta_\lambda d\log_\lambda = \frac{1}{M_1 + \ldots + M_l} \sum M_\lambda d\log \eta_\lambda = \sum d\eta_\lambda = 0,$$

since

$$\sum \eta_\lambda = 1.$$

16. Activities from the Electromotive Force of Reversible Cells

We shall now apply our previous considerations of the maximum external work available in a process to the case of a galvanic cell. In this case $-\Delta\Phi$ is simply equal to the maximum electrical work which the cell can produce. If $\mathfrak{H}$ is the electrochemical equivalent (96,494 coulombs) and z_e the number of such equivalents which flow through the cell, we have when the cell is working reversibly,

$$\Delta\Phi = -z_e \mathfrak{H} \mathbf{E}, \tag{131}$$

where $\mathbf{E}$ is the electromotive force of the cell. If $\mathbf{E}_0$ is the e.m.f. of the cell in the standard state, equations (113), (114), (115), and (131) lead to the following general equation relating the e.m.f. and the activities†

$$E = E_0 - \frac{RT}{z_e \mathfrak{H}} \log \frac{a_{A_1}^{\mu_1'} \ldots}{a_{A_1}^{\mu_1} \ldots}. \tag{132}$$

† It must be mentioned that the activity may refer to a hydrated ion in the solution and to a non-hydrated ion in the electrode. Since the equilibrium between the hydrated and non-hydrated ions is governed by the generalized law of mass action (117), the activity of the solvent will also occur in the expressions derived. See N. Bjerrum, *Z. anorg. Chem.* **109** (1920), 275; *Z. phys. Chem.* **104** (1923), 406; E. Hückel, *Phys. Z.* **26** (1925), 99; L. Ebert, *Handbuch d. Experimentalphysik.*

This relation is of very widespread application. It can, for example, be applied to cells for which the electromotive force depends only on the nature and state of the electrodes. Thus Richards and Daniels† investigated a cell containing two different thallium amalgams. They were able to show that the simple Nernst equation (obtained by replacing the activities in (132) by concentrations) is not valid. Such discrepancies between the classical theory and experiment can be expressed in terms of activities.

17. The Activity and Activity Coefficients of Strong Electrolytes‡

We shall now apply the generalized law of mass action (117) to simple binary electrolytes. The activity of the undissociated part of the dissolved electrolyte will be termed a_2, and that of the cation and anion a_+ and a_- respectively. (117) then becomes

$$\frac{a_+ a_-}{a_2} = K_a, \tag{133}$$

where K_a is constant at constant temperature and pressure. In practice the effect of pressure can be neglected. Equation (133) takes no account of the part played by the solvent, which is permissible up to moderately concentrated solutions. The interaction between the molecules or ions of the electrolyte and the solvent molecules can be approximately expressed by means of mean hydration numbers. Most methods give directly the activity of the solvated forms. At infinite dilution the activity of any ion is equal to the molar concentration of that ion, which is equal to the molar concentration of the binary electrolyte if we assume (with Lewis) that dissociation is complete. We shall follow the practice of Lewis and his school by defining the molar concentration or molarity as the number of moles dissolved in 1,000 gm. water, which will be represented by m. In the case of strong electrolytes we have no reliable information as to the concentration of the undissociated salt present. We shall therefore choose the standard state so that K_a in equation (133) is equal to unity. This is allowable since the activities always contain an indeterminate factor independent of concentration, and the normalizing factor can be included in ϕ_λ, the part of the chemical potential which is independent of

† T. W. Richards and F. Daniels, *J. Am. Chem. Soc.* **41** (1919), 1732; cf. Lewis and Randall, ibid. **43** (1921), 233. Further applications of (132) to strong electrolytes will be dealt with later. Discrepancies between Nernst's equation and experimental results had also been found much earlier by Bjerrum, *Z. f. Elektrochem.* **17** (1911), 392.

‡ See Lewis and Randall's *Thermodynamics*, also the detailed account in Jellinek's *Lehrbuch der physikalischen Chemie*, vol. iii, p. 562, 1930.

concentration, cf. (102). We thus define the activity of the binary electrolyte a_2 as being equal to the product of the activities of its ions, i.e.

$$a_+ a_- = a_2. \tag{134}$$

At infinite dilution the concentrations of cations and anions are equal, so that

$$a_+ = a_- = a_2^{\frac{1}{2}}. \tag{135}$$

If we introduce the geometric mean of the two ionic activities†

$$a_\pm = (a_+ a_-)^{\frac{1}{2}}, \tag{136}$$

we have from (134)

$$a_\pm = a_2^{\frac{1}{2}} \tag{137}$$

even in concentrated solutions.

The *mean ionic activity* $a_\pm$ divided by the molar concentration m is termed the activity coefficient f' of the electrolyte,‡ i.e.

$$\frac{a_\pm}{m} = f'. \tag{138}$$

If we are dealing with ions of higher valency, e.g. $LaCl_3$ or K_2SO_4, the relations corresponding to (137) and (138) are somewhat more complicated. If the molecule dissociates into ν ions, ν_+ positive and ν_- negative, the equilibrium condition is according to (117)

$$a_+^{\nu_+} a_-^{\nu_-} = a_2, \tag{139}$$

and the mean value of the two ionic activities is given by

$$a_\pm = a_2^{1/\nu}. \tag{140}$$

The activity coefficient f' must now be suitably defined. If, for example, we are dealing with a very dilute solution of $LaCl_3$, we have

$$a_+ = m, \qquad a_- = 3m$$

$$a_\pm = \{m(3m)^3\}^{\frac{1}{4}} = 3^{\frac{3}{4}} m.$$

If we define the activity coefficient by the equation

$$f' = \frac{a_\pm}{3^{\frac{3}{4}} m},$$

† Although it is convenient to introduce the activity coefficients of the individual ions, they can never be determined experimentally, since on account of the condition of electric neutrality in each phase, it is the undissociated molecules and not the ions which are the true independent components. If it were possible to determine the potential of single electrodes, individual ionic activities could be calculated. For literature, see p. 71.

‡ The dash in f' signifies that the activity coefficient refers to the molarity concentration scale. Cf. p. 53.

it will become unity at infinite dilution. In general we shall define the activity coefficient by the equation

$$f' = \frac{a_\pm}{m(\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}}. \tag{141}$$

The meaning of this definition appears more clearly if we introduce the activity coefficients of the individual ions according to the equations

$$f'_+ = \frac{a_+}{m_+}, \qquad f'_- = \frac{a_-}{m_-}, \tag{142}$$

where m_+ and m_- are the stoichiometric molarities of the solution with respect to the positive and negative ions. If we define a mean molarity of the ions $m_\pm$ (corresponding to the mean activity) by

$$m_\pm = (m_+^{\nu_+} m_-^{\nu_-})^{1/\nu}, \tag{143}$$

the relations

$$m_+ = \nu_+ m, \quad m_- = \nu_- m \tag{144}$$

lead to the expression

$$m_\pm = m(\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}. \tag{145}$$

Introducing (141), we then have

$$f'_\pm = f' = \frac{a_\pm}{m_\pm} = (f'^{\nu_+}_+ f'^{\nu_-}_-)^{1/\nu} \tag{146}$$

which may be more conveniently written as

$$\nu \log f' = \nu_+ \log f'_+ + \nu_- \log f'_-. \tag{146'}$$

18. Rational and Practical Activity Coefficients

Before going into the regularities revealed by an experimental study of the activity coefficients of electrolyte solutions we shall discuss the relation between the thermodynamic system of activity coefficients and the system generally used in practice. In the thermodynamic equations in their original form, concentrations are expressed as mole fractions η_i, and the activity coefficient f_i^* may be defined as the factor by which the concentration terms η_i in the laws of ideal dilute solutions must be multiplied in order that the same laws may hold for real solutions. These activity coefficients f_i^* are termed *rational activity coefficients*. The activity coefficients most used in practice differ from these and are termed practical activity coefficients. This is due to the fact that concentrations are not usually expressed as mole fractions but as moles per litre of solution (γ_i) or moles per 1,000 gm. of solvent (m_i). Practical activity coefficients thus differ from rational activity coefficients by a factor depending upon the relation between η_i and γ_i or m_i. We shall therefore derive the relations existing between these three concentration

scales.† Let V be the volume of the solution in c.c. and d its density. Let the various species present be designated by 0, 1,..., i,..., s, the corresponding number of molecules of each species being

$$N_0, N_1, \ldots, N_i, \ldots, N_s.$$

Then if $\mathbf{N}$ is Loschmidt's number ($6{\cdot}06 \times 10^{23}$), the number of moles of each species present is

$$\frac{N_0}{\mathbf{N}}, \frac{N_1}{\mathbf{N}}, \ldots, \frac{N_i}{\mathbf{N}}, \ldots, \frac{N_s}{\mathbf{N}}.$$

Finally, let the molecular weights of the various species be

$$G_0, G_1, \ldots, G_i, \ldots, G_s.$$

The mole fractions η_i are then defined by (38),

$$\eta_i = \frac{N_i}{N_0 + \sum_{i=1}^{s} N_i} = \frac{N_i/\mathbf{N}}{\frac{N_0}{\mathbf{N}} + \sum_{i=1}^{s} \frac{N_i}{\mathbf{N}}}. \tag{147}$$

The concentration in moles per litre of solution is given by

$$\gamma_i = \frac{N_i}{\mathbf{N}V} 1{,}000, \tag{148}$$

and the concentration in moles per 1,000 gm. solvent by

$$m_i = \frac{N_i}{N_0 G_0} 1{,}000 = \frac{N_i/\mathbf{N}}{N_0 G_0/\mathbf{N}} 1{,}000. \tag{149}$$

We also have for the density of the solution,

$$d = \frac{\frac{N_0 G_0}{\mathbf{N}} + \sum_{i=1}^{s} \frac{N_i G_i}{\mathbf{N}}}{V}. \tag{150}$$

These four equations give the following relations between the different concentration scales:

$$\gamma_i = \frac{m_i d}{1 + \sum_{i=1}^{s} \frac{G_i m_i}{1{,}000}}, \tag{151}$$

$$m_i = \frac{\gamma_i}{d - \sum_{i=1}^{s} \frac{G_i \gamma_i}{1{,}000}}, \tag{152}$$

$$\eta_i = \frac{G_0 \gamma_i}{1{,}000} \frac{1}{d - \sum_{i=1}^{s} (G_i - G_0) \frac{\gamma_i}{1{,}000}}, \tag{153}$$

† Cf. A. Macfarlane and O. Gatty, *Phil. Mag.* **13** (1932), 283, 291.

$$\eta_i = \frac{G_0 m_i}{1{,}000} \frac{1}{1 + G_0 \sum_{i=1}^{s} \frac{m_i}{1{,}000}}. \tag{153'}$$

These relations hold quite generally. For sufficiently dilute solutions concentrations measured in the three scales are proportional to one another, according to the following equations.

$$\eta_i = \frac{\gamma_i}{1{,}000} \frac{G_0}{d_0} = \frac{m_i G_0}{1{,}000}. \tag{154}$$

G_0/d_0 is the molar volume v_0 of the solvent. For water, $d_0 = 1$, $v_0 = G_0$, so that in this case γ_i and m_i are identical at sufficiently low concentrations.

The activity must be independent of the concentration scale used. This gives

$$\eta_i f_i^* = \gamma_i f_i = m_i f_i' \tag{155}$$

so that

$$f_i = \frac{f_i^* G_0}{1{,}000} \frac{1}{d - \sum_{i=1}^{s} (G_i - G_0) \frac{\gamma_i}{1{,}000}}, \tag{156}$$

$$f_i' = \frac{f_i^* G_0}{1{,}000} \frac{1}{1 + G_0 \sum_{i=1}^{s} \frac{m_i}{1{,}000}}. \tag{157}$$

We have already seen that activity coefficients are only relative, and may be multiplied by a constant factor independent of concentration.† (The logarithm of this factor can be included in the term ϕ_i of equation (98).) We shall normalize f_i and f_i' so that on approaching zero concentration they become equal to f_i^*. At low concentrations, however, the three concentration scales give values directly proportional to one another, so that if we are to have

$$f_i^* = f_i = f_i',$$

the following relation must hold

$$f_i^* \frac{\gamma_i G_0}{1{,}000 d_0} = f_i \gamma_i = f_i' \gamma_i, \tag{158}$$

according to (154) and (155); that is, the activity coefficient f^* must be multiplied by $1{,}000 d_0/G_0$ in order to obtain the practical activity

16968

† See p. 51.

coefficients f_i and f_i'. If we write in general,

$$f_i = f_i^* \frac{1}{\frac{d}{d_0} - \frac{1}{d_0}\sum_{i=1}^{s}(G_i - G_0)\frac{\gamma_i}{1{,}000}}, \tag{159}$$

$$f_i' = f_i^* \frac{1}{1 + G_0 \sum_{i=1}^{s} \frac{m_i}{1{,}000}}, \tag{160}$$

f_i, f_i^*, and f_i' become identical at infinite dilution, and have practically identical values in sufficiently dilute solutions.†

19. The Experimental Determination of the Activity of Strong Electrolytes

The experimental determination of the activity of strong electrolytes has been studied systematically since 1907 by G. N. Lewis and his collaborators.‡ We shall consider here a few of the most frequently used methods for determining activities. While any thermodynamic property can be used for this purpose, especially accurate results are obtained from measurements of electromotive force, freezing-point depressions and solubilities.

A. *Determination of activities from the vapour pressure of the electrolyte.*

From the definition of the thermodynamic potential (15) we have

$$\left(\frac{\partial \Phi}{\partial p}\right)_T = V,$$

where V is the volume. For an isothermal process, this gives

$$\int d\Phi = \int V\, dp. \tag{161}$$

We can apply this equation to a substance which exists in two different states at the same temperature but different pressures. Let the pressure and volume in the first state be p_A and V_A, and in the second state p_B and V_B. The difference in thermodynamic potential is then

$$\Phi_B - \Phi_A = \int_A^B V\, dp. \tag{161'}$$

† A number of numerical examples have been worked out by G. Hückel (*Physikal. Z.* **26** (1925), 93). He finds that for mono-monovalent electrolytes, f_i^* and f_i differ by less than ½ per cent. for $\gamma = 0{\cdot}1$, and by about 1·7 per cent. for $\gamma = 1$.

‡ See Lewis and Randall's *Thermodynamics*, and the section by H. S. Harned in H. S. Taylor's *System of Physical Chemistry*, 2nd edition, vol. i, p. 731, 1931. Cf. also Randall, *Trans. Farad. Soc.* **23** (1927), 502. For bibliography, see K. Jellinek, *Lehrb. d. physikal. Chem.*, 1st and 2nd editions, vol. iii, pp. 521 and 708, 1929.

We shall now apply this equation to a vapour which behaves as a perfect gas. If we identify the volume V with the molar volume $\mathfrak{v}$,

$$\mathfrak{v}\,dp = \frac{RT\,dp}{p},$$

so that

$$\int_A^B \mathfrak{v}\,dp = RT\log\frac{p_A}{p_B}. \tag{162}$$

If we compare this with (95), we see that in this case the activity is identical with the vapour pressure, so that if we are dealing with sufficiently volatile electrolytes, their vapour pressures can be used to measure their activities. As an example, we may take the results of Bates and Kirschman† on the vapour pressures of the three hydrogen halides in aqueous solution at 25° C. The activity a_2 of the undissociated acid is proportional to its vapour pressure. The mean activity coefficient of its ions is given by (137) as

$$p^{\frac{1}{2}}/m \text{ is proportional to } f',$$

i.e.

$$\frac{p^{\frac{1}{2}}}{m} = k'f'. \tag{163}$$

The limiting value of $p^{\frac{1}{2}}/m$ in very dilute solutions gives the value of k', since the activity coefficient becomes unity. In this case it is impossible to obtain values for the vapour pressure in very dilute solutions, and recourse must be had to other methods, e.g. freezing-point depression.‡

B. *Determination of activities from the vapour pressure of the solvent.*

It is also possible to obtain the activity a_2 of the solute from that of the solvent, a_0. We employ equation (130′), which in this case becomes

$$\int d\log a_2 = -\int \frac{\eta_0}{\eta_2}\,d\log a_0. \tag{164}$$

This equation enables us to use, for example, measurements of the vapour pressure of water p_0 over electrolyte solutions to calculate the activity a_2. If the vapour pressure of pure water is p_0^0, the activity of the solvent is given by (95) and (162) as

$$a_0 = \frac{p_0}{p_0^0}. \tag{165}$$

† S. J. Bates and H. D. Kirschman, *J. Am. Chem. Soc.* **41** (1919), 1991. For further examples (alkali halides), see J. N. Pearce and A. F. Nelson, *J. Am. Chem. Soc.* **57** (1932), 3544. J. V. Butler (*Proc. Roy. Soc.* **129A** (1930), 519) has used this method to determine the activities of LiCl in alcohol-water mixtures.

‡ See p. 62.

Knowing the mole fractions η_0 and η_2, (164) can be integrated graphically to give a_2. Randall and White† have used this method to calculate the activity coefficients of KCl from measurements of Lovelace, Frazer, and Sease.‡ Grollmann and Frazer§ have used in the same way the results of Brönsted‖ on the vapour pressure of water over solutions of sulphuric acid. Similarly, Scatchard†† has calculated activity coefficients of LiCl from the data of Lovelace, Bahlke, and Frazer.‡‡

The methods so far described are very inaccurate in dilute solutions, which is the region which especially interests us. We shall now turn to the determination of activities by measurements of electromotive force and freezing-points. These methods are considerably more accurate in dilute solutions.

C. *Determination of activities from electromotive force measurements.*§§

The fundamental equation for the electromotive force of a reversible galvanic cell has been derived in § 16. Equation (13) may be used to determine the activity of an electrolyte. We shall take as an example one electrode consisting of mercury and solid mercurous chloride and the second a hydrogen electrode with a partial pressure of hydrogen of one atmosphere, both electrodes being immersed in an electrolyte, e.g. a solution of hydrochloric acid of known concentration. If the temperature and the partial pressure of hydrogen are fixed the electromotive force **E** depends only on the molarity of the acid. According to (131), the change in free energy associated with the passage of one equivalent of electricity is given by

$$\Delta\Phi = -\mathfrak{F}\mathbf{E}.$$

We now consider a combination of two such cells having different concentrations of HCl. Such a combination is termed a *concentration cell without liquid junctions*, since no two liquids of different compositions are in direct contact with one another.

No entirely satisfactory theory of liquid junction potentials has yet been proposed. The Nernst-Planck theory (W. Nernst, *Z. phys. Chem.* **2** (1888), 163;

† M. Randall and A. M. White, *J. Am. Chem. Soc.* **48** (1926), 2514.

‡ B. F. Lovelace, J. C. W. Frazer, and V. B. Sease, *J. Am. Chem. Soc.* **43** (1921), 102.

§ A. Grollmann and J. C. W. Frazer, ibid. **47** (1925), 712.

‖ J. N. Brönsted, *Z. phys. Chem.* **68** (1910), 693.

†† G. Scatchard, *J. Am. Chem. Soc.* **47** (1925), 648.

‡‡ B. F. Lovelace, W. H. Bahlke, and J. C. W. Frazer, ibid. **45** (1923), 2930.

§§ See G. N. Lewis and M. Randall, *Thermodynamics*, and the section by H. S. Harned ('The Electrochemistry of Solutions') in H. S. Taylor's *System of Physical Chemistry*, vol. i, p. 731. Numerous references to the literature are given by K. Jellinek, *Lehrb. d. physikal. Chem.*, vol. iii, p. 699, 1929, and by R. Kremann and R. Müller, 'Elektromotorische Kräfte', in Ostwaldwalden-Drucker, *Handb. d. allg. Chem.*, vol. viii, Leipzig, 1930.

M. Planck, *Wied. Ann.* **39** (1890), 161) made it possible to calculate the potential difference in a given strong electrolyte of non-uniform concentration. At high concentrations the concentrations should be replaced by activities. This theory fails, however, when two solutions of different concentrations are in contact, since here there is no concentration gradient, since the concentration changes discontinuously. The surface of discontinuity is therefore replaced by a transition layer of small but finite thickness δ. The concentrations are now continuous functions, and the concentration gradient assumes very high values in the transition layer. Different expressions may now be obtained for the potential difference, according to the nature of the transition layer. (For the sake of simplicity, the interionic forces are neglected.) Planck (*Wied. Ann.* **40** (1890), 561; *Sitzungsber. d. preuss. Akad. d. Wiss.* (1930) 367; (1931) 3; (1933) 3) considers the transition layer to be formed by diffusion from a boundary which is initially infinitely sharp. Henderson (*Z. phys. Chem.* **59** (1907), 118) assumes that the transition layer is continuous, the solution at any point in the layer being composed additively of the fraction β of the solution 2, and the fraction $1-\beta$ of the solution 1. β is here any function of the position in the layer which is zero for $x = 0$, and unity for $x = \delta$. There is no foundation for Henderson's assumption that β is proportional to x. This generalization (due to Planck) does, however, lead to Henderson's formula for the potential difference. Measurements by P. F. Büchi (*Z. Elektrochem.* **30** (1924), 443) and V. Plettig (*Ann. d. Phys.* (5) **5** (1930), 735) have shown that if one solution is carefully poured on to the other, the potential after a short interval is that given by Henderson's formula. In the course of time the state of the transition layer will be changed by diffusion, and hence the potential will change (cf. Shu-Tsu-Chang, *Ann. d. Phys.* (5) **16** (1933), 513). Guggenheim (*J. Am. Chem. Soc.* **52** (1930), 1315) has shown that the transition layer is only stable and reproducible when there is cylindrical symmetry. Guggenheim has also described experimental methods for obtaining the continuous and diffuse layers. (For further details of theory and experiment, see B. Taylor, *J. Phys. Chem.* **31** (1927), 1478; the section by H. S. Harned in H. S. Taylor's text-book, and Jellinek, *Lehrbuch d. physikalischen Chemie.*

If m and m' are the molarities of HCl in the first and second cells respectively, then the change of thermodynamic potential† caused by transferring one mole of acid from m' to m is given by

$$\Delta\Phi = \bar{\Phi}_2 - \bar{\Phi}_2' = RT\log\frac{a_2}{a_2'} = -\mathfrak{F}(\mathbf{E}-\mathbf{E}'). \tag{166}$$

If the HCl in one cell is in the standard state,

$$\bar{\Phi}_2' = \bar{\Phi}_2^0, \qquad \mathbf{E}' = \mathbf{E}^0, \qquad a_2' = 1, \tag{167}$$

and hence by (166) $\bar{\Phi}_2$, the partial molal free energy of the acid at a given concentration, is given by

$$\bar{\Phi}_2 - \bar{\Phi}_2^0 = RT\log a_2 = -\mathfrak{F}(\mathbf{E}-\mathbf{E}^0). \tag{168}$$

Introducing the mean ionic activity, $a_\pm = a_2^{\frac{1}{2}}$ (see (137)),

$$2RT\log a_\pm = -\mathfrak{F}(\mathbf{E}-\mathbf{E}^0). \tag{169}$$

† Following G. N. Lewis, a heavy bar over Φ_2 shows that the thermodynamic potential refers to one mole.

(169) enables us to calculate activities a_2 or $a_\pm$, directly from measurements of the electromotive force of cells of this type. Such measurements have now been carried out in very great numbers, especially at 25°. Owing to the difficulty of extrapolating to infinite dilution to obtain the value of $\mathbf{E}^0$, the relative values of a are more accurate than the absolute values.†

The first measurements with hydrochloric acid were carried out by Tolman and Ferguson,‡ and the concentration range extended considerably by Ellis§ and by Linhart.|| Using the silver silver-chloride electrode in place of mercury and calomel, Noyes and Ellis†† and especially Linhart‡‡ have investigated dilute solutions of hydrochloric acid with great accuracy. Their results are shown in Fig. 5. Using common logarithms, equation (169) becomes

$$0{\cdot}1183 \log_{10} a_\pm = \mathbf{E}^0 - \mathbf{E}. \qquad (170)$$

Subtracting $0{\cdot}1183 \log_{10} m$ from this equation, and introducing the activity coefficient

$$\frac{a_\pm}{m} = f',$$

we have

$$0{\cdot}1183 \log_{10} \frac{a_\pm}{m} = 0{\cdot}1183 \log_{10} f' = \mathbf{E}^0 - (\mathbf{E} + 0{\cdot}1183 \log_{10} m). \qquad (171)$$

At infinite dilution, $\quad 0{\cdot}1183 \log_{10} \dfrac{a_\pm}{m} = 0.$

We now write $\quad \mathbf{E}^0 + 0{\cdot}1183 \log_{10} m = \mathbf{E}^{0\prime} \qquad (172)$

and plot $\mathbf{E}^{0\prime}$ as a function of $m^{\frac{1}{2}}$.

According to Linhart the limiting value of $\mathbf{E}^{0\prime}$ at infinite dilution is 0·2234 volt. Nonhebel§§ obtained the value 0·2228 volt, and Scatchard|||| found later 0·2226 volt. According to Randall and Young††† the value 0·2221 volt is probably more accurate. By subtracting 0·2221 from the ordinate corresponding to any concentration, we obtain the corresponding value of

$$-0{\cdot}1183 \log_{10} f'.$$

† This constitutes the chief difficulty of the method: cf. Tables 12 and 13. More accurate absolute values are given by measurements of freezing-point and solubilities, cf. pp. 62, 69, and 128.

‡ R. C. Tolman and A. L. Ferguson, *J. Am. Chem. Soc.* **34** (1912), 232.

§ J. H. Ellis, *J. Am. Chem. Soc.* **38** (1916), 737.

|| G. A. Linhart, *J. Am. Chem. Soc.* **39** (1917), 2601.

†† A. A. Noyes and J. H. Ellis, *J. Am. Chem. Soc.* **39** (1917), 2532.

‡‡ G. A. Linhart, *J. Am. Chem. Soc.* **41** (1919), 1175.

§§ G. Nonhebel, *Phil. Mag.* (7) **2** (1926), 1085.

|||| G. Scatchard, *J. Am. Chem. Soc.* **47** (1925), 641.

††† M. Randall and L. E. Young, *J. Am. Chem. Soc.* **50** (1928), 989.

The abscissa in Fig. 5, has been chosen as $m^{\frac{1}{2}}$ because at low concentrations the ordinate varies linearly with $m^{\frac{1}{2}}$. As will be shown later, in dealing with modern electrolyte theory, Debye has succeeded in calculating quantitatively the slope of this limiting straight line.† Fig. 5 contains the results for both the silver chloride and the calomel cells. On account of the difference in the values, the ordinates for the calomel curve are higher than those for the silver chloride curve by a constant difference of 0·0466 volt. The activities and the activity coefficients

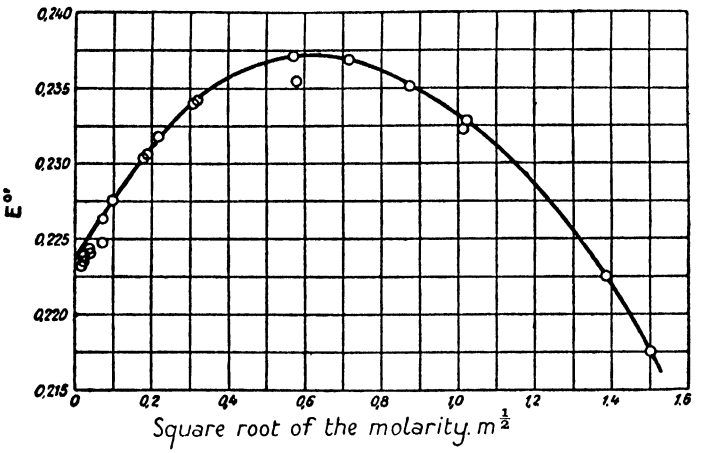

FIG. 5. The e.m.f. of the silver chloride cell at different concentrations.

of hydrochloric acid‡ can be calculated from the curve by equation (171). The results obtained are given in Table 10.

In Table 10 the values enclosed in brackets (f') correspond to the value $\mathbf{E}^{0\prime} = 0{\cdot}2234$ volt used by Linhart. Using the more accurate value $\mathbf{E}^{0\prime} = 0{\cdot}2221$ volt, the unbracketed values in Table 10 are obtained.§ Similarly, more accurate values for $a_{\pm}$, a_2, and $\bar{\Phi}_2 - \bar{\Phi}_2^0$ can be calculated from equations (168), (169), (171), and (172), giving

$$a_{\pm} = 0{\cdot}975(a_{\pm})$$

$$a_2 = a_{\pm}^2 = 0{\cdot}9506(a_2)$$

$$\bar{\Phi}_2 - \bar{\Phi}_2^0 = RT \log a_2 = RT \log(a_2) + RT \log 0{\cdot}9506$$

$$= (\bar{\Phi}_1 - \bar{\Phi}_2^0) - 30.$$

† See p. 120.

‡ The activity coefficient of HBr behaves similarly to that of HCl; see G. N. Lewis and Storch, *J. Am. Chem. Soc.* **39** (1917), 2544; R. S. Livingston, ibid. **48** (1926), 45. HI has also been investigated; see J. N. Pearce and A. R. Fortsch, ibid. **45** (1923), 2852.

§ These values agree well with those in Table 12.

TABLE 10

The activity of aqueous† hydrochloric acid solutions at 25° C.

m	(f')	f'	$(a_\pm)$	(a_2)	$(\bar{\Phi}_2 - \bar{\Phi}_2^0)$
0·0005	0·991	0·965	0·000496	0·000000246	−9,022
0·001	0·984	0·959	0·000984	0·000000909	−8,204
0·002	0·971	0·946	0·001942	0·00000377	−7,403
0·005	0·947	0·923	0·00474	0·0000228	−6,336
0·01	0·924	0·901	0·00924	0·0000855	−5,552
0·02	0·894	0·872	0·01788	0·000319	−4,772
0·05	0·860	0·839	0·0430	0·00185	−3,732
0·1	0·814	0·794	0·0814	0·00664	−2,977
0·2	0·783	0·763	0·1566	0·0246	−2,197
0·3	0·768	0·749	0·2304	0·0530	−1,742
0·4	0·763	0·744	0·305	0·0929	−1,409
0·5	0·762	0·743	0·381	0·145	−1,144
0·6	0·770	0·751	0·462	0·213	− 917
0·75	0·788	0·768	0·591	0·348	− 625
1	0·823	0·802	0·823	0·676	− 232
2	1·023	0·997	2·064	4·17	846

These more accurate values have been omitted from Table 10 for the sake of brevity. It is seen from the table that the activity coefficient f' of HCl is unity at infinite dilution, passes through a minimum a little below $m = 0{\cdot}5$, and then increases rapidly. This behaviour is frequently observed with strong electrolytes. The method described here has been applied to many other cells.

D. *Determination of the activity of electrolytes from freezing-point measurements.* (G. N. Lewis.‡)

(*a*) *Dilute solutions.* The determination of activities from freezing-point data is more accurate for dilute solutions than the methods described under A, B, and C. Equation (123) gives the relation between the freezing-point depression and the activity of the solvent, and (128) gives the relation between the activities of the solvent and solute. It

† The activity coefficients of HCl have also been investigated in non-aqueous solution by measurements of electromotive force. See e.g. P. S. Danner, *J. Am. Chem. Soc.* **44** (1922), 2832 (ethyl alcohol); H. S. Harned and M. H. Fleysher, ibid. **47** (1925), 82; G. Scatchard, ibid. **47** (1925), 2098 (mixtures of water and alcohol); G. Nonhebel and H. B. Hartley, *Phil. Mag.* (6) **50** (1925), 298, 729 (methyl alcohol); W. W. Lucasse, *Z. phys. Chem.* **121** (1926), 254 (methyl alcohol, ethyl alcohol, mixtures of glycerine and water); J. H. Wolfenden, C. P. Wright, N. L. Ross Kane, and P. S. Buckley, *Trans. Farad. Soc.* **23** (1927), 491 (methyl alcohol); J. W. Woolcock and H. B. Hartley, *Phil. Mag.* (7) **5** (1928), 1133 (mixtures of water and ethyl alcohol).

‡ G. N. Lewis, *J. Am. Chem. Soc.* **34** (1912), 1631. This method was employed for dilute solutions by Lewis and Linhart (ibid. **41** (1919), 1951) and extended to more concentrated solutions by Lewis and Randall (ibid. **43** (1921), 1112). For details, see G. N. Lewis and M. Randall, *Thermodynamics.* Numerous experimental data are given in the second supplementary volume to Landolt-Börnstein's tables, p. 1113, 1931.

is therefore possible to determine the variation of activity with concentration by determining the freezing-point depression at different concentrations.

In developing the method of Lewis, we shall start with equation (123). If we write for the freezing-point depression of the real solution

$$(\Delta T)_g = \vartheta, \tag{173}$$

(123) becomes

$$1 - \frac{\vartheta}{(\Delta T)_g} = \frac{1{,}000 \log f_0}{G_0 m\nu}, \tag{174}$$

since

$$\Sigma' \eta_1 = \frac{G_0}{1{,}000} m\nu.$$

Differentiating

$$d\vartheta = -\frac{1{,}000\, d\log f_0}{G_0 m\nu} (\overline{\Delta T})_g.$$

For water $(\overline{\Delta T})_g = 1{\cdot}858\nu m$ and $G_0 = 18{\cdot}02$, so that for dilute solutions

$$d\log f_0 = -0{\cdot}009696\, d\vartheta \tag{175}$$

or

$$\log f_0 = -0{\cdot}009696\vartheta. \tag{175'}$$

In dilute solutions the mole fraction of the solvent is practically unity, and on introducing the activity of the solvent a_0 equation (175) becomes

$$d\log a_0 = -0{\cdot}009696\, d\vartheta \tag{176}$$

or

$$\log a_0 = -0{\cdot}009696\vartheta. \tag{176'}$$

Introducing the activity of the solute a_2 (130') gives

$$\eta_0\, d\log a_0 + \eta_2\, d\log a_2 = 0. \tag{177}$$

We also have

$$\eta_2 = \frac{G_0}{1{,}000} m,$$

and since $1{,}000/G_0$ for water is 55·51,

$$d\log a_2 = -\frac{55{\cdot}51}{m}\, d\log a_0.$$

Combining this with (176),

$$d\log a_2 = -\frac{55{\cdot}51}{m}(-0{\cdot}009696\, d\vartheta) = \frac{d\vartheta}{1{\cdot}858m}. \tag{178}$$

If each molecule of the electrolyte forms ν ions on complete dissociation, (140) gives

$$\frac{1}{\nu} d\log a_2 = d\log a_2^{1/\nu} = d\log a_\pm = \frac{d\vartheta}{1{\cdot}858m}. \tag{179}$$

We now introduce the abbreviation

$$j = 1 - g = 1 - \frac{\vartheta}{1{\cdot}858\nu m}, \tag{180}$$

then since $$dj = -\frac{d\vartheta}{1{\cdot}858\nu m} + (1-j)d\log m$$

we have $$d\log\frac{a_\pm}{m} = d\log f' = -dj - j\,d\log m. \tag{181}$$

Equation (181) can be written as

$$\frac{\partial \log f'}{\partial m} = \frac{\partial j}{\partial m} - \frac{j}{m}, \tag{182}$$

in which form it was first derived by Bjerrum.†

An empirical relation between j and m can be obtained from freezing-point determinations. Lewis and Linhart found that the relation

$$j = Bm^A \tag{183}$$

was obeyed by all salts in dilute solutions up to about $m = 0{\cdot}01$. A and B are constants for any given electrolyte. At higher concentrations the values of j are always smaller than those given by the above formula, and in many cases pass through a maximum. We shall consider here only dilute solutions, for which from (182) and (183)

$$\log_{10} f' = -\frac{B(A+1)m^A}{2{\cdot}303A}. \tag{184}$$

Lewis and Linhart‡ have used this formula to calculate the activity coefficients of a number of electrolytes in dilute solution. Table 12 contains their results, together with data from other sources mostly calculated by the same method. Table 11 gives the values of A and B for a few of the electrolytes considered by Lewis and Linhart.

TABLE 11

Electrolyte	KCl	KNO_3	KIO_3	K_2SO_4	$BaCl_2$	$MeSO_4$	$La(NO_3)_3$
A	0·535	0·565	0·500	0·374	0·364	0·38	0·42
B	0·329	0·427	0·417	0·572	0·477	1·44	1·148

Me = Mg, Zn, Cd.

It may be mentioned that the electrostatic theory leads to a value of

† N. Bjerrum, *Proc. Int. Cong. Applied Chem.* (1909), section 10; *Z. Elektrochem.* **24** (1918), 321.

‡ G. N. Lewis and G. A. Linhart, *J. Am. Chem. Soc.* **41** (1919), 1951. Their calculations are based on the very accurate freezing-point determinations of H. Hausrath, *Ann. d. Physik*, **9** (1902), 522; P. G. Bedford, *Proc. Roy. Soc.* A, **83** (1909), 454; L. H. Adams, *J. Am. Chem. Soc.* **37** (1915), 494; W. D. Harkins and W. A. Roberts, ibid. **38** (1917), 2676; R. E. Hall and Harkins, ibid. **38** (1916), 2658; M. Randall and A. P. Vanselow, ibid. **46** (1924), 2433. Further refinements in technique are described by G. Scatchard, P. T. Jones, and S. S. Prentiss, ibid. **54** (1932), 2676, 2690, 2696.

0·5 for the exponent A.[1] The same result was arrived at as an empirical limiting law by Lewis and by Brönsted.[2] The data in Table 11 do not lead to the constant value 0·5 for A because the solutions studied were not sufficiently dilute. The first data which provided a general confirmation of the theoretical law were those of Brönsted and La Mer[3] on solubility effects in very dilute solution. Table 11 also shows that the values of B for mono-monovalent electrolytes are much smaller than those for di-divalent electrolytes. This again suggests some effect due to the forces between the ions, and foreshadows the electrostatic theory.

TABLE 12

The activity coefficients of very dilute solutions of electrolytes (0°–25° *C.*)

m = concentration in moles per 1,000 gm. H_2O; Me = Mg, Zn, Cd.

m =	0·0001	0·0005	0·001	0·005	0·01
KCl, NaCl	0·993	0·984	0·977	0·946	0·922
KCl[4]	..	..	0·961	0·926	0·903
KCl[5]	..	..	0·965	0·926	0·899
NaCl[4]	..	..	0·963	0·928	0·906
NaCl[5]	..	..	0·965	0·928	0·903
LiCl[5]	..	..	0·965	0·927	0·901
HCl[6]	..	..	0·965	0·928	0·904
TlCl[7]	0·990	0·979	0·970	0·935	0·910
KNO[6]	0·994	0·984	0·976	0·943	0·916
HNO_3[8]	..	..	..	0·930	0·905
KIO_3, $NaIO_3$	0·988	0·972	0·961	0·915	0·882
K_2SO_4	0·935	0·885	0·853	0·749	0·687
H_2SO_4[9]	..	0·912	0·876	0·734	0·648
$BaCl_2$	0·939	0·894	0·865	0·771	0·716
$CoCl_2$	0·943	0·900	0·873	0·784	0·731
$Ba(NO_3)_2$[9]	..	0·915	0·884	0·770	0·701
$Pb(NO_3)_2$[7]	0·964	0·921	0·890	0·770	0·692
$MeSO_4$	0·85	0·75	0·69	0·50	0·40
$CdSO_4$[10]	..	0·774	0·699	0·476	0·383
$K_3Fe(CN)_6$	0·922	0·853	0·808	0·657	0·571
$La(NO_3)_3$	0·922	0·853	0·808	0·657	0·571

(*b*) *The activity of electrolytes in concentrated solutions.* The calculation of activity coefficients for concentrated electrolytic solutions is a

[1] See p. 124. [2] J. N. Brönsted, *J. Am. Chem. Soc.* **44** (1922), 938.

[3] See p. 128. [4] H. Harned, *J. Am. Chem. Soc.* **44** (1922), 252.

[5] G. Scatchard, ibid. **47** (1925), 648. Harned and Scatchard have used the results of F. Flügel, *Z. phys. Chem.* **79** (1912), 577, and H. Jahn, ibid. **50** (1905), 144; **59** (1907), 33.

[6] M. Randall and L. E. Young, *J. Am. Chem. Soc.* **50** (1928), 989.

[7] M. Randall and A. P. Vanselow, ibid. **46** (1924), 2418.

[8] E. Abel, O. Redlich, and B. v. Lengyel, *Z. phys. Chem.* **132** (1928), 189.

[9] M. Randall and G. N. Scott, *J. Am. Chem. Soc.* **49** (1927), 647.

[10] V. K. La Mer and W. G. Parks, ibid. **53** (1931), 2040.

very laborious process, and we shall only deal with it briefly. G. N. Lewis has studied this subject with the greatest care, and it is to him that the concept of activity largely owes its present prominent position in the physical chemistry of solutions.

The method of Lewis (which is given fully in Lewis and Randall's *Thermodynamics*) is briefly as follows. The generalized form of van 't Hoff's equation (44) gives

$$\left(\frac{\partial \log a_h}{\partial T}\right)_p = -\frac{\bar{L}_h}{RT^2}.$$

$\bar{L}_h$ is the partial molal heat content of the component h, usually referred to infinite dilution, where $\bar{L}_h = 0$. The activity of the solute (a_2) in aqueous solution is given by

$$d \log a_2 = \frac{d\vartheta}{1{\cdot}858m} + 0{\cdot}00057\frac{\vartheta\, d\vartheta}{m},$$

cf. (177) and (179). This is sufficient to determine the activity and therefore the activity coefficient. The variation with temperature of the heat dilution and of the difference between the specific heat of the solution and the pure solvent lead to corrections, which are specially important in concentrated solution. Activities are usually referred to a temperature other than the freezing-point (usually 25°), so that the equation given above must be employed.

Lewis and his collaborators have calculated activities for a large number of electrolytes, the results of freezing-point measurements being later extended by electromotive force data. The three methods described above agree very well.† Table 13 gives a selection of the results obtained, which serves to show the characteristic change of activity coefficient with concentration. The activity coefficients first decrease with increasing concentration to a minimum value, and then increase again. $CdCl_2$, $CdBr_2$, and CdI_2 have recently been investigated by Getnam, and have activity coefficients in dilute solutions differing from those of $BaCl_2$. This is probably due to the fact that the cadmium halides cannot be considered as strong electrolytes, especially CdI_2 and $CdCl_2$, which show tendencies to complex formation even in relatively dilute solution. Hydrofluoric acid also behaves like a weak electrolyte in dilute solutions and exhibits complex formation in more concentrated ones. The activity coefficients of these electrolytes change with concentration in a characteristic manner.‡

† E.m.f. measurements in the region of 0·001 N. can rarely be used for extrapolating to $\gamma = 0$, since unavoidable side reactions often interfere. Activity coefficients from e.m.f. data thus often fail to agree with those from freezing-point data in this concentration range. Above about 0·03 N. (for mono-monovalent electrolytes) the two methods agree very well.

‡ For numerous references, see H. Harned in H. S. Taylor's *System of Physical Chemistry*.

TABLE 13

The activity coefficients of some electrolytes in water at 25° C.

$m =$	0·01	0·05	0·1	0·2	0·5	1	3
KCl[1]	0·922	0·840	0·794	0·749	0·682	0·634	..
NaCl[1]	0·922	0·842	0·798	0·752	0·689	0·650	0·704
LiCl[1]	0·922	0·843	0·804	0·774	0·754	0·776	1·20
HCl[1]	0·924	0·860	0·814	0·783	0·762	0·823	1·35
KNO_3[1]	0·916	0·806	0·732	..	..	..	..
$AgNO_3$[1]	0·902	0·783	0·723	0·655	0·526	0·396	..
KOH[2, 3, 4]	0·901	0·815	0·772	0·739	0·723	0·743	1·041
NaOH[5]	0·901	0·809	0·765	0·723	0·679	0·667	0·812
LiOH[6]	0·899	0·794	0·742	0·685	0·602	0·541	0·482
$BaCl_2$[7, 8, 9]	0·723	0·554	0·495	0·439	0·395	0·398	..
$SrCl_2$[7, 8, 9]	0·729	0·571	0·512	0·465	0·427	0·449	1·083
$CaCl_2$[7, 8, 9]	0·732	0·582	0·528	0·492	0·510	0·725	3·385
$CdCl_2$[1]	0·532	0·30	0·219	(0·158)	(0·098)	(0·065)	..
$CdBr_2$[10]	0·50	0·23	0·17	(0·134)	(0·079)	(0·053)	(0·031)
CdI_2[10]	0·39	0·14	0·09	0·059	0·031	0·020	..
K_2SO_4[9]	0·720	0·504	0·420	0·326	0·233	..	..
Na_2SO_4[9]	0·721	0·51	0·435	0·356	0·267	0·206	..
Li_2SO_4[9]	0·722	0·522	0·447	0·380	0·306	0·267	..
H_2SO_4[1]	0·617	0·397	0·313	0·244	0·178	0·150	..
$MgSO_4$[1]	0·404	0·225	0·166	0·119	..	..	..
$CuSO_4$[1]	0·404	0·216	0·158	0·110	0·067	..	..
$La(NO_3)_3$[1]	0·571	0·591	0·326	0·271	..	..	..

For further data, see Lewis and Randall, *Thermodynamics*, and the tables edited by O. Redlich and P. Rosenfeld in the second supplement of Landolt-Börnstein, ii, p. 1113, 1931.

[1] G. N. Lewis and M. Randall, *J. Am. Chem. Soc.* **43** (1921), 1112. The values in brackets are from W. W. Lucasse, ibid. **51** (1929), 2597. $LaCl_3$ has recently been measured by E. Proskauer (Diss., Leipzig, 1932); the values obtained are very close to those for $La(NO_3)_3$.

[2] Scatchard, ibid. **47** (1925), 648.

[3] M. Knobel, ibid. **45** (1923), 70.

[4] Randall and Young, ibid. **50** (1928), 989.

[5] Harned, ibid. **47** (1925), 676.

[6] Harned and F. E. Swindells, ibid. **48** (1926), 126.

[7] W. W. Lucasse, ibid. **47** (1925), 743.

[8] Harned, ibid. **48** (1926), 326.

[9] Harned and G. Åkerlöf, *Physik. Z.* **27** (1926), 411.

[10] F. H. Getman, *J. Phys. Chem.* **32** (1928), 91; **33** (1929), 1781. Ca salts have recently been investigated by R. J. Fosbinder (*J. Am. Chem. Soc.* **51** (1929), 1345). New data have been obtained for $PbCl_2$ by W. R. Carmody (ibid. **51** (1929), 2905), see also H. D. Crockford and H. C. Thomas (ibid. **55** (1933), 572), for the cadmium halides by Getman (loc. cit) and by Lucasse (*J. Am. Chem. Soc.* **51** (1929), 2597), and for $ZnCl_2$ by Scatchard and R. F. Tefft (ibid. **52** (1930), 2272). $SnCl_2$ has been investigated by Randall and S. Murakami (ibid. **52** (1930), 3967). Silver halides and silver cyanide in HCN and NH_4OH have been recently studied by Randall and J. O. Halford (ibid. **52** (1930), 178, 192). Complex formation takes place, and can be treated by the generalized law of mass action (117).

E. *The definition of activity coefficients in mixtures of electrolytes. The determination of activity coefficients in mixtures of electrolytes by means of solubility measurements. The principle of ionic strength (Lewis and Randall).*

We shall now deal briefly with solutions containing more than one electrolyte. The activity coefficient of an electrolyte in a mixture of electrolytes can be defined in a manner analogous to that employed for a single electrolyte. If m_+ and m_- are the molar concentrations of positive and negative ions respectively in the solution, the activity coefficients are given by

$$f'_+ = \frac{a_+}{m_+} \qquad f'_- = \frac{a_-}{m_-}.$$

If one molecule of a particular electrolyte in the solution dissociates into ν_+ positive and ν_- negative ions, the mean activity coefficient of the electrolyte is defined by (146) as

$$f' = (f'^{\nu_+}_+ f'^{\nu_-}_-)^{1/\nu} = \frac{a_\pm}{m_\pm}$$

where $$\nu = \nu_+ + \nu_-.$$

Thus in a mixture containing 0·1 N. NaCl and 0·1 N. $BaCl_2$,

$$m_+ = 0{\cdot}1 \text{ for } Na^+ \text{ and } Ba^{++}$$

while $$m_- = 0{\cdot}3 \text{ for } Cl^-.$$

The mean molar concentration is thus for NaCl

$$m_\pm = (0{\cdot}1 \times 0{\cdot}3)^{\frac{1}{2}},$$

and for $BaCl_2$

$$m_\pm = (0{\cdot}1 \times 0{\cdot}3)^{\frac{1}{2}}.$$

The object of the first investigations of activity coefficients in mixed electrolytes was to discover whether the activity coefficient depended only on the total equivalent concentration or whether more complex relations held. Lewis and Sargent† were able to show that the activity depended only on the total electrolyte concentration. They measured the e.m.f. of a gold electrode in a potassium chloride solution containing small amounts of ferrocyanide and ferricyanide. Harned‡ investigated

† Lewis and L. W. Sargent, *J. Am. Chem. Soc.* **31** (1909), 355. See also E. P. Schoch and W. A. Folsing, ibid. **38** (1916), 1928; Linhart, ibid. **39** (1917), 615.

‡ Harned, *J. Am. Chem. Soc.* **37** (1015), 2460; **38** (1916), 1986. The same considerations were later extended to more concentrated solutions, where they are no longer valid. See Harned, ibid. **42** (1920), 1808; **47** (1925), 648, 689; **48** (1926), 326; *Z. phys. Chem.* **117** (1926), 1; Harned and N. J. Brumbaugh, *J. Am. Chem. Soc.* **44** (1922), 2729; Harned and R. D. Sturgis, ibid. **47** (1925), 945; Harned and F. E. Swindells, ibid. **48** (1926), 126; Harned and G. M. James, *J. Phys. Chem.* **30** (1926), 1060; Harned and O. E. Schapp, *J. Am. Chem. Soc.* **52** (1930), 3886, 3892; Harned and G. Åkerlöf, *Phys. Z.* **27** (1926), 411; Åkerlöf, *J. Am. Chem. Soc.* **48** (1926), 1160; Güntelberg, *Z. phys. Chem.* **123** (1926),

a cell consisting of a hydrogen electrode and a calomel electrode in 0·1 N. hydrochloric acid in the presence of varying concentrations of potassium chloride. A very extensive series of measurements showed that in dilute solutions the activity coefficient of hydrochloric acid depended only on the total electrolyte concentration, and not on the relative proportions of the two electrolytes. Thus in solutions of NaCl up to 0·5 N. and of other chlorides up to 0·2 N., the activity coefficient of HCl is the same as in a pure hydrochloric acid solution of the same total concentration. It may be assumed that this principle holds good for other electrolytes of the same valency type. We shall, however, show that this limiting law is actually a special case of a more general law. This may be shown by the methods described above, i.e. by the determination of activities in mixed electrolytes from electromotive force or freezing-point measurements. There is, however, an especially important method for determining activities which has led to the discovery of important limiting laws in dilute solutions. The method consists of measuring the effect of one salt upon the solubility of another, and has been developed especially by A. A. Noyes and his collaborators,† G. N. Lewis,‡ and Brönsted.§

If a solid salt is in equilibrium with a solution at a given temperature, the activity of the salt in the solution is fixed, and cannot be altered by any alteration in the nature of the solution, e.g. by the addition of another salt. We have therefore that a_2 is constant for the salt which is present as a solid, and therefore by (140) $a_\pm$ is also constant. (Cf. p. 43.) The activity coefficient of the salt is given by (146),

$$f' = \frac{a_\pm}{m_\pm},$$

199; Randall and C. T. Langford, *J. Am. Chem. Soc.* **49** (1927), 1445; Randall and G. F. Breckenridge, ibid. **49** (1927), 1435. Harned and his collaborators have later evolved a method for determining the activity coefficients of weak acids and bases in salt solutions from the e.m.f. of cells without liquid-junctions. This method eliminates the uncertainty of the liquid-liquid junction potential. See Harned and R. A. Robinson, *J. Am. Chem. Soc.* **50** (1928), 3157; Harned and J. M. Harris, ibid. **50** (1928), 2633; Harned and B. B. Owen, ibid. **52** (1930), 5079, 5091; E. J. Roberts, ibid. **52** (1930), 3877; Harned and Ehlers, ibid. **54** (1932), 1350; Harned and C. M. Mason, ibid. **54** (1932), 1439, 3112; Harned and W. J. Hamer, ibid. **55** (1933), 2194; Harned and H. R. Copson, ibid. **55** (1933), 2206.

† A. A. Noyes, *Z. phys. Chem.* **6** (1890), 241; Noyes and W. C. Bray, *J. Am. Chem. Soc.* **33** (1911), 1643; Bray and W. J. Winninghoff, ibid. **33** (1911), 1663; W. D. Harkins and Winninghoff, ibid. **33** (1911), 1827; Harkins and H. M. Paine, ibid. **41** (1919), 1155; Harkins and W. T. Pearce, ibid. **38** (1916), 2679. ‡ See Lewis and Randall, *Thermodynamics*.

§ Brönsted, *J. Am. Chem. Soc.* **42** (1920), 761; **44** (1922), 938. It was these measurements which later gave valuable support to Debye's theory of electrolytes. For further references, see p. 124.

and since $a_\pm$ is constant, the activity coefficient must be inversely proportional to the mean molarity of the ions, $m_\pm$, whatever alterations take place in the solution. As an example we shall consider the solubility of a 1-1-valent in presence of another 1-1-valent salt having no common ion. In this case $m_\pm$ is simply equal to the solubility.† We have just shown that the activity coefficient is proportional to $1/m_\pm$, and the proportionality factor can thus be found by plotting $1/m_\pm$ against the total molarity of the solution, or better, the square root of the total molarity, and extrapolating to infinite dilution. It is found experimentally that the plot against the square root of the molarity approximates to a straight line at high dilutions. If we call the value of $1/m_\pm$ at infinite dilution $(1/m_\pm)_0$, the activity coefficient at any concentration is obtained by dividing the corresponding value of $1/m_\pm$ by $(1/m_\pm)_0$, since the activity coefficient tends to unity at infinite dilution.

Lewis and Randall‡ have found a simple general rule connecting the activity coefficient and the ionic strength. They showed that the activity coefficient of a given strong electrolyte had the same value in all dilute solutions of the same ionic strength. The *ionic strength* J' is defined by

$$J' = \tfrac{1}{2} \sum_i m_i z_i^2, \tag{185}$$

where m_i is the stoichiometric molarity of an ion i of valency z_i in any solution of strong electrolytes. If $1/m_\pm$ is plotted against $\sqrt{J'}$, the curves obtained practically coincide in dilute solution. Since we have just shown that the activity coefficient f' is proportional to $1/m_\pm$, f' will show a similar dependence on $\sqrt{J'}$.§

Lewis and Randall's principle of the ionic strength holds only for sufficiently dilute solutions. Brönsted|| has proved thermodynamically from equation (130) that it must fail at higher concentrations.

20. Summary of the Laws Found Empirically for Activity Coefficients in Dilute Aqueous Solutions

We shall now give a brief summary of the laws governing the activity coefficients of dilute aqueous solutions, as formulated by Lewis and Brönsted on purely experimental grounds. It is extremely remarkable that both Lewis and Brönsted have refrained completely from specu-

† In the presence of a salt having a common ion, similar relations hold. Thus it is found that the solubility of TlCl in the presence of 0·05 N. KCl is 0·0059. We thus have $m_+ = 0{\cdot}0059$, $m_- = 0{\cdot}0559$, and from (145), $m_\pm = (0{\cdot}0059 \times 0{\cdot}0559)^{\frac{1}{2}} = 0{\cdot}0181$.

‡ G. N. Lewis and M. Randall, *J. Am. Chem. Soc.* **43** (1921), 1112.

§ Cf. Figs. 25–8, which show in a striking manner the dependence of activity coefficients on the ionic strength.

|| See p. 315.

lating as to the theoretical interpretation of these experimental laws, and it was left to Debye to develop a theory which succeeded in explaining practically all the regularities established by experiment.†

I. For dilute solutions of simple salts (up to about 0·01 N.)

$$\log f = -\frac{B(A+1)m^A}{A},$$

and hence

$$1-g = Bm^A$$

where g is the osmotic coefficient.‡ The experimental values of the exponent A for uni-univalent electrolytes vary between 0·50 and 0·565. Electrolytes of higher valence types give lower values of A down to 0·364. Brönsted found that at very high dilutions the behaviour of an electrolyte was determined only by its valence type; thus for uni-univalent electrolytes

$$1-g = a'\sqrt{\gamma}$$

$$\log f = -3a'\sqrt{\gamma}.$$

The constant a' varies only slightly with temperature, and has empirically the value 0·32 at 0°.

At higher concentrations§ deviations from the square root law appear, which can be approximately represented by an additional linear term, i.e.

$$1-g = a'\sqrt{\gamma}-b\gamma$$

$$\log f = -3a'\sqrt{\gamma}+2b\gamma.$$

b is a positive constant depending on the electrolyte.

II. In dilute solution, the activity coefficient of a given electrolyte has the same value in all solutions of the same ionic strength J', where

$$J' = \tfrac{1}{2}\sum m_i z_i^2.$$

In sufficiently dilute solutions, the logarithm of the activity coefficient is proportional to the square root of the ionic strength.

III. The hypothesis of independent ionic activity coefficients (which only possesses a limited validity‖) states that in dilute electrolyte solution the activity coefficient of an ion depends only on the total ionic strength. This hypothesis enables us to calculate the activity coefficient of one salt from the known activity coefficients of the other salts. If

† See p. 120.

‡ In dilute solution it is permissible to replace m by γ and f' by f, cf. p. 55.

§ See p. 131 for additional experimental results.

‖ It is impossible by pure thermodynamics to calculate the individual ionic activities from e.m.f. data. Cf. p. 52. See P. B. Taylor, *J. Phys. Chem.* **31** (1927), 1478; L. Onsager, ibid. **32** (1928), 1461; E. A. Guggenheim, ibid. **33** (1929), 842; **34** (1930), 1758. See also H. S. Harned in H. S. Taylor's *Treatise on Physical Chemistry*, vol. i, p. 731, 1931.

we make the plausible assumption that the activity coefficient of the K^+ ion is equal to that of the Cl^- ion under the same conditions, it is possible to calculate the activity coefficients of the individual ions at different ionic strengths.

Brönsted found that in dilute solutions the logarithms of the activity coefficients of ions of different valency in a solution of the same composition were proportional to the squares of the valencies.

It must be emphasized that while certain of the results mentioned rest on a purely thermodynamical basis, others are of a more hypothetical nature. Thus the methods of calculating activity coefficients from solubilities, electromotive force, etc., are purely thermodynamical. Assumption II has been shown by Brönsted to be incompatible with strict thermodynamics.† Hypothesis III (the independence of activity coefficients) cannot be strictly true in concentrated solutions, since the behaviour of an ion will certainly depend upon its nature.

We have now given an account of the most important thermodynamic phenomena, and the anomalies exhibited by strong electrolytes. All thermodynamic laws which involve (according to Arrhenius's theory) the concentration will exhibit anomalies in the case of strong electrolytes, since here the concentrations must be replaced by activities, as defined by G. N. Lewis.

We shall now leave reversible thermodynamic phenomena, and give a brief account of the anomalies of the electrical conductivity of strong electrolytes.

† See p. 315.

V

ANOMALIES IN THE CONDUCTIVITY OF STRONG ELECTROLYTES

21. The Conductivity of Strong Electrolytes in Weak Stationary Fields

A. *The variation of conductivity with concentration in aqueous solutions. The failure of Ostwald's dilution law for strong electrolytes.*

We shall now give a short account of the anomalies in the conductivity of strong electrolytes, first from a purely empirical standpoint. Aqueous solutions have been very thoroughly studied by F. Kohlrausch and his collaborators, and also by Ostwald, Bredig, Heydweiller, Jones, Noyes, Lorenz, Walden, Kraus, Davies, and their collaborators.† Table 14 contains data for the equivalent conductivity of a number of electrolytes, chosen with a view to the subsequent theoretical discussion.

TABLE 14

Equivalent conductivities in water at 18° *C.*

Electrolyte	$\gamma^* = 0$	10^{-4}	5×10^{-4}	10^{-3}	5×10^{-3}	10^{-2}	5×10^{-2}	10^{-1}	0·5	1	5	10
LiCl	98·88	98·14	97·19	96·52	93·92	92·14	86·12	82·42	70·71	63·36	33·3	11·3
$LiIO_3$	67·36	66·66	65·87	65·27	62·89	61·23	55·28	51·50	38·98	31·21	..	..
$LiNO_3$	95·18	94·46	93·52	92·87	90·33	88·61	82·72	79·19	67·98	60·77	..	..
NaCl	108·99	108·10	107·18	106·49	103·78	101·95	95·71	92·02	80·94	74·35	42·2	..
$NaIO_3$	77·42	76·69	75·83	75·19	72·62	70·87	64·43	60·45	..	..	..	..
$NaNO_3$	105·33	104·55	103·53	102·85	100·06	98·16	91·43	87·24	74·05	..	..	..
KCl	130·10	129·07	128·11	127·34	124·41	122·43	115·75	112·03	102·41	98·27	..	..
KBr	132·30	131·15	130·15	129·38	126·40	124·43	117·78	114·22	105·37	..	..	..
KI	131·10	129·76	128·95	128·23	125·33	123·44	117·26	113·98	106·2	103·6	..	..
KIO_3	98·49	97·64	96·72	96·04	93·19	91·23	84·06	79·67	..	..	..	..
$KClO_3$	119·70	118·63	117·68	116·92	113·84	111·64	103·74	99·19	85·28	..	..	..
KNO_3	126·50	125·5	124·44	123·65	120·47	118·19	109·86	104·79	89·24	80·46	..	..
KCNS	121·30	120·22	119·38	118·65	115·81	113·95	107·74	104·28	95·69	91·61	..	..
CsCl	133·60	132·3	131·38	130·68	127·47	125·2	..	113·55	..	..	..	..
$AgNO_3$.	115·80	115·01	113·89	113·15	110·04	107·81	99 51	94 33	77·5	..	..	..
$TlNO_3$	127·75	126·62	125·60	124·68	121·10	118·39	107·93	101·19	..	..	..	..
CH_3COONa	77·4*	(76·8)	(75·8)	(75·2)	(72·4)	70·2	64·2	61·1	49·4	41·2	(10·5)	..
NaOH	217·4*	..	..	208	..	200	..	183	..	160	20·2	..
KOH	238·5*	..	..	(234)	230	228	219	213	197	184	105·8	44·8
HCl	378	..	..	(377)	373	370	360	351	327	301	152·2	64·4
HNO_3	377	..	..	(375)	371	368	357	350	324	300	156	65·4
CH_3COOH	349·5*	107	57	41	20	14·3	6·48	4·6	2·01	1·32	0·285	0·049
NH_3	242	(66)	38	28	13·2	9·6	4·6	3·3	1·35	0·89	0·202	0·054
$MgCl_2$	110·88	109·43	107·68	106·35	101·30	98·14	88·48	83·42	69·87	61·45	..	..
$CaCl_2$	116·69	115·17	113·34	111 95	108·69	103·37	93·29	88·19	74·92	67·54	35·6	(11)
$Ca(NO_3)_2$	113·56	111·91	109·92	108·47	103·03	99·53	88·41	82·48	65·70	55·86	21·5	..
$Sr(NO_3)_2$	113·42	111·74	109·75	108·30	102·72	99·03	87·30	80·93	62·72	52·07	16·4	..
$Ba(NO_3)_2$	116·95	115·32	113·3	111·72	105·29	100·96	86·81	78·94	56·6	..	..	..
K_2SO_4	132·23	130·71	128·53	126·88	120·26	115·8	101·93	94·93	78·48	71·59	..	..
H_2SO_4	384·5*	..	372	361	..	309	253·5	233·3	..	..	..	..
$MgSO_4$	113·5	109·85	104·16	99·84	84·49	76·21	56·92	49·68	..	28·91	8·8	..
$CdSO_4$	113·9	109·84	102·93	97·72	79·70	70·32	49·60	42·21	28·74	23·58	..	..
$ZnSO_4$	113·5	(110·1)	103·15	98·4	(82·5)	72·75	(53·4)	45·34	..	(26·6)	..	..
$CuSO_4$	113·85	109·95	103·54	98·54	91·91	71·72	51·16	43·85	37·66	25·77	..	..
$La(NO_3)_3$	125	..	..	..	..	..	..	..	..	..	..	..
$K_4Fe(CN)_6$	189	..	173·1	..	146·9	135·35	108·3	98·2	..	..	..	..
$Ca_2Fe(CN)_6$	147	..	..	..	..	49·9	38·5	35·1	..	..	..	..
$CdCl_2$	113·9*	..	..	..	91	83	59	50	30·8	22·4	5·3	..
CdI_2	113·3*	..	..	..	86·5	76·3	53·2	44·6	25·3	18·3	5·3	..

* Calculated from the ionic mobilities. The values in brackets are interpolated.

† For references to the literature, see *Note 1*, p. 91.

The data are mostly taken from the book by F. Kohlrausch and L. Holborn (see *Note 1*, p. 91). The conductivity of the water has been taken into account and subtracted. According to Sv. Arrhenius (*Z. phys. Chem.* **11** (1893), 401) and F. Kohlrausch (*Wied. Ann.* **26** (1885), 181) a simple subtraction is allowable for

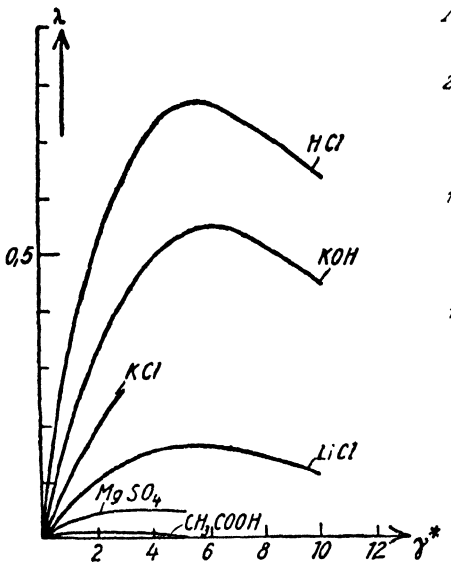

FIG. 6. The variation of specific conductivity with concentration.

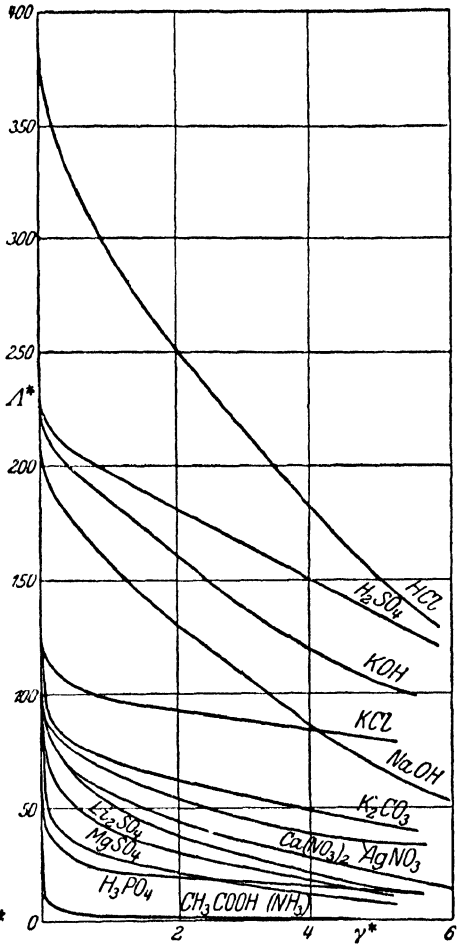

FIG. 7. The variation of equivalent conductivity with concentration.

salts, but not for acids and bases, which greatly modify the conductivity of the water. The error involved is especially important at high dilutions, and in this case it is essential to use extremely pure water. For a discussion of experimental methods and the effect of temperature and pressure on conductivity, see the literature quoted in *Note 1*, p. 91.

Figs. 6 and 7† show the variation with concentration of the specific

† It must be remembered that $\gamma^* = z_e\gamma$, $\Lambda^* = \Lambda/z_e$, $\Lambda = 1{,}000\lambda/\gamma$, where z_e is the electrochemical valency.

conductivity λ and the equivalent conductivity Λ^* for some of the electrolytes in Table 14. Qualitatively, the curves obtained show the same behaviour for all the electrolytes shown. The specific conductivity begins at zero, and increases with increasing concentration up to a maximum. The concentration corresponding to this maximum varies for different electrolytes and in some cases, e.g. KCl and $AgNO_3$, the maximum is not reached since these salts are not sufficiently soluble. Acids and bases behave very differently to salts. With a few exceptions, salts give relatively well-conducting solutions, the maximum values of the specific conductivity being all of the same order of magnitude. Acids and bases, on the other hand, give conductivities ranging from very high values for HCl, HNO_3, KOH, etc. to extremely low ones, e.g. phenol and hydrazine. It will be seen that a weak acid like CH_3COOH gives quite small specific conductivities.

The difference between the strong and weak electrolytes appears clearly from Fig. 7, which shows the equivalent conductivity as a function of the equivalent concentration. The equivalent conductivity of weak electrolytes decreases very rapidly with increasing concentration.

According to Ostwald's dilution law (75), which holds well for weak electrolytes, the relation between the equivalent conductivity Λ^* and the equivalent concentration γ^* is given by

$$\frac{a'-\Lambda^*}{\Lambda^{*2}} = b'\gamma^*,$$

where a' and b' are characteristic constants for each electrolyte. This equation fails completely for strong electrolytes, especially in dilute solution. According to Arrhenius's theory, if one molecule of an electrolyte dissociates into ν ions, (86) and (87) give for dilute solutions,

$$(\nu-1)\frac{1-f_\Lambda}{\nu} = \frac{\nu-1}{\nu}\frac{\gamma^{\nu-1}}{K_\gamma}, \tag{186}$$

where $f_\Lambda = \Lambda/\Lambda_\infty$. Thus for a binary electrolyte,

$$1-f_\Lambda = \frac{\gamma}{K_\gamma}, \tag{186'}$$

or, from (67),

$$\Lambda = \Lambda_\infty - \gamma\frac{\Lambda_\infty}{K_\gamma}. \tag{186''}$$

The Λ-curves for binary electrolytes should thus have a finite slope at Λ_∞, while electrolytes which dissociate into more than two ions should give curves which become horizontal at this point. It is obvious from Fig. 7 that neither of these predictions is fulfilled, so that the classical

theory fails completely for very dilute solutions of strong electrolytes. It is of great interest that Kohlrausch† as early as 1900 proposed the empirical formula

$$\Lambda^* = a'' - b''\sqrt{\gamma^*} \tag{187}$$

for very dilute solutions. This relation was found to reproduce the experimental data for all strong salts, acids, and bases, as may be seen

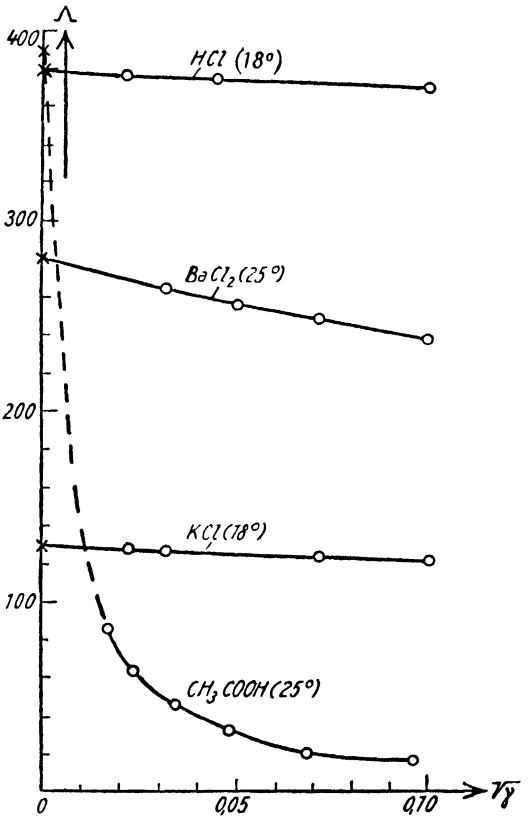

FIG. 8. The equivalent conductivity of strong and weak electrolytes.

from Figs. 8 and 9.‡ Fig. 8 shows Λ as a function of $\gamma^{\frac{1}{2}}$ for several electrolytes. The values for HCl and KCl are at 18°, those for $BaCl_2$ and CH_3COOH at 25°. It will be seen that the valency of the ions has a great effect on the curve of the $(\Lambda, \gamma^{\frac{1}{2}})$ curve, in that 1-2 valent salts exhibit linearity at lower concentrations than the 1-1 salts and also give steeper curves. These facts will subsequently be interpreted on the basis of

† F. Kohlrausch and M. E. Maltby, *Wiss. Abh. d. Phys.-techn. Reichsanstalt*, **3** (1900), 156.

‡ See also Figs. 40–50.

Debye's theory;† for the present it is sufficient to state that in general both the range of validity of (187) and the steepness of the curve are largely determined by the valency of the ions concerned. It is important to note that Kohlrausch's law has so far only been thoroughly verified for the simplest types of electrolytes, i.e. the 1-1 valent and 1-2 valent. Measurements with electrolytes of higher valence types are not very accurate, although the changes of Λ with the concentration are much larger. Fig. 9 shows $100\Lambda/\Lambda_\infty$ plotted against $\sqrt{\gamma^*}$ for electrolytes of various valency types. The curves are only linear over a considerable range for the 1-1- and 1-2-valent electrolytes.

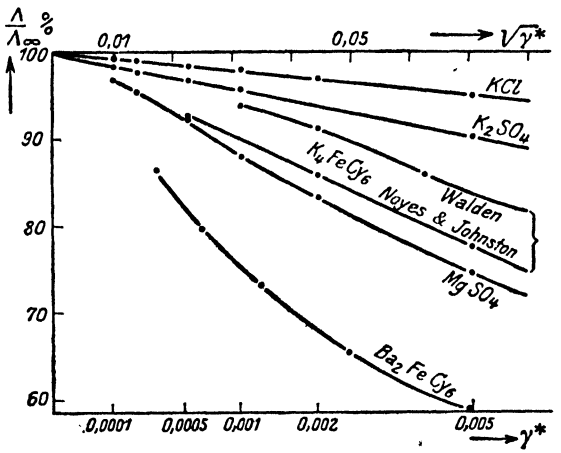

FIG. 9. Equivalent conductivities in dilute solution.

Weak electrolytes exhibit a very marked disagreement with Kohlrausch's law, as may be seen from the curve for CH_3COOH in Fig. 8.

It will be seen that in the concentration range shown in Figs. 8 and 9, the equivalent conductivity without exception decreases with increasing concentration. In very concentrated salt solutions the (Λ^*, γ^*) curve may change its direction, especially at higher temperatures and in non-aqueous solvents.‡

Attempts have also been made to represent the dependence of equivalent conductivity on concentration in dilute solutions by a cube root law of the form

$$\Lambda^* = a''' - b'''\sqrt[3]{\gamma^*}. \tag{188}$$

† See p. 163. W. Ostwald (*Z. phys. Chem.* **1** (1887), 74), P. Walden (ibid. **1** (1887), 529), and G. Bredig (ibid. **73** (1894), 191) were the first to point out this regular effect of the valency. The effect was first attributed definitely to the electrical forces between the ions by v. Laar and Bjerrum (see p. 94).

‡ See the references in *Note I*, p. 200, especially P. Walden and H. S. Taylor.

This relation fails completely, however, for extremely dilute solutions, as may be easily shown by reference to experimental data.†

B. *The conductivity of non-aqueous solutions.*

Non-aqueous solutions have been much studied recently especially by Carrara, Dutoit, Jones, Walden, Franklin, Kraus, Sachanov, Goldschmidt, Müller, etc.‡ It is of special interest here that the square root law often holds for very dilute solutions in non-aqueous solvents. The lower the dielectric constant of the solvent, the lower the concentration at which the law holds. Walden has given an approximate equation for the smallest dilution ($v = 1/\gamma$) at which the square root law holds, according to which $D_0 v^{\frac{1}{2}} = 272$. This relation is only valid for the so-called 'normal' electrolytes (mostly tetra-alkylammonium salts), for which Walden's rule holds. Walden's rule states that $\Lambda_\infty \eta_0 = \text{const.}$ when η_0 is changed by changing the solvent or the temperature, and its validity has been shown especially by measurements of Müller in a number of organic solvents.§ Excellent agreement with the square root law is shown by the measurements of Frazer and Hartley|| on the conductivity of electrolytes in methyl alcohol at 25°.

It is interesting to compare the conductivities of a given salt in a number of different solvents. Fig. 10 shows the equivalent conductivity of tetraethylammonium picrate at different concentrations in water, methyl alcohol, acetone, and ethylene chloride. D is the dielectric constant of the solvent.

Nernst and Thomson†† were the first to point out the effect of the

† See the reference in *Note 1*. p. 91. For empirical interpolation formulae applicable to moderately dilute solutions, see R. T. Lattey (*Phil. Mag.* **4** (1927), 831), and T. Shedlovsky (*J. Am. Chem. Soc.* **54** (1932), 1405, 1411).

‡ See *Note 1*, p. 91, and P. Walden, *Elektrochemie nichtwässriger Losungen*, Leipzig, 1924; R. Müller, *Elektrochemie der nichtwässrigen Losungen*, Stuttgart, 1923; *Chem. Rev.* **8** (1931), 167; L. Ebert, *Handbuch d. Experimentalphysik*, vol. xii, p. 169, 1932. A special discussion of the specific part played by the solvent is given by H. Ulich, *Z. Elektrochem.* **39** (1933), 489.

§ See e.g. the article by R. Schingnitz, *Z. Elektrochem.* **36** (1930), 861. According to measurements by other workers, Walden's rule does not hold accurately even for the 'normal' electrolytes. Further work is needed to clear up these discrepancies. For references, see *Note 1*, p. 91, and Ulich, 'Über die Beweglichkeit elektrolytischer Ionen', *Fortschr. d. Chem.* 1926; Ulich and Birr, *Z. angew. Chem.* **41** (1928), 443, 467, 1075, 1141.

|| J. E. Frazer and H. Hartley, *Proc. Roy. Soc.* **109 A** (1925), 351, 1163.

†† Loc. cit. p. 5. The Nernst-Thomson rule is often obeyed, cf. e.g. B. H. Schlundt and R. C. Palmer, *J. Phys. Chem.* **15** (1911), 381; A. Sachanov and I. Prsheborowski, *Z. Elektrochem.* **20** (1914), 39; H. Joachim, *Ann. d. Phys.* (4) **60** (1919), 570. There are, however, other factors which influence ionization, especially the chemical nature of the solvent. Thus although the dielectric constant of HCN is 95, salts in HCN are bad conductors, while HBr and HI, with low dielectric constants, give highly conducting solutions with certain organic acids. See L. Kahlenberg, *J. Phys. Chem.* **3** (1899), 13;

dielectric constant of the solvent (D_0) upon the conductivity coefficient. The greater D_0 is, the smaller will be the Coulomb forces between the ions. Table 15 shows the parallelism between dielectric constant and conductivity coefficient for tetraethylammonium picrate and tetra-amylammonium picrate, from measurements by Walden†. These two picrates are comparatively strong electrolytes, at least in solvents of fairly high dielectric constant. Walden‡ has established this parallelism for uni-univalent electrolytes on the basis of his own very extensive

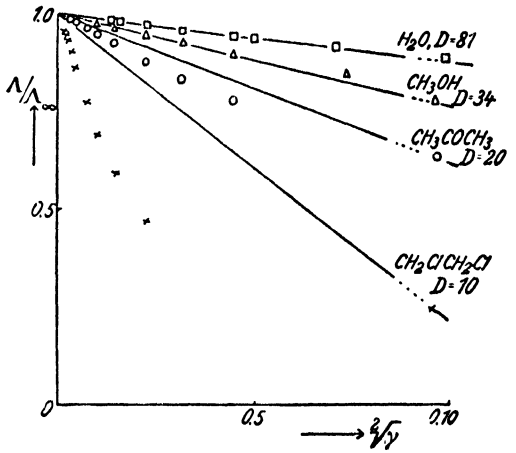

FIG. 10. Equivalent conductivities in different solvents.

investigations. He has also succeeded in finding some approximately quantitative relationships. Thus the conductivities of solutions of a uni-univalent salt in various solvents will be approximately the same if the dielectric constants of the solvents are inversely proportional to the cube root of the molar dilution, i.e. if f_Λ is constant, we have approximately§ and with some exceptions||

$$D_0 v^{\frac{1}{3}} = \text{const.} \sim \frac{41{\cdot}5}{1-\alpha}. \tag{189}$$

Since it is known empirically that 1-1-valent salts in the same medium at the same concentration have the same degree of dissociation,†† the

O. C. Schäfer and Schlundt, ibid. **13** (1909), 669; Sachanov, *J. Russ. Phys. Chem. Soc.* **42** (1910), 1363; *Z. phys. Chem.* **80** (1912), 1320; I. Plotnikow and W. E. Rokotjan, *J. Russ. Phys. Chem. Soc.* **45** (1913), 193.

† P. Walden, *Z. phys. Chem.* **147** (1930), 1.

‡ P. Walden, ibid. **54** (1905), 228; **55** (1906), 683; **70** (1910), 569; **94** (1920), 263, 374.

§ For references, see *Note 1*, p. 91; also footnotes p. 78.

|| S. Partington, *Trans. Farad. Soc.* **15** (1919), 113; Kraus, *The Properties of Electrically Conducting Systems*, New York; L. B. Turner and C. C. Bissett, *J. Chem. Soc.* **105** (1914), 947.

†† Cf. p. 29.

product $D_0 v^{\frac{1}{2}}$ should have the same constant value for all electrolytes of this type.

The simple relation (189) has no validity for salts of higher valence types, and matters are much more complicated in the case of acids and bases. Thus hydrochloric acid is an extremely bad conductor in formic acid ($D_0 = 58{\cdot}5$), acetonitrile ($D_0 = 36$), and nitrobenzene ($D_0 = 35$), while it constitutes one of the strongest electrolytes in water and is also considerably dissociated in certain other solvents, e.g. the alcohols and liquid ammonia. The dependence on dielectric constant thus fails completely, since the dielectric constant of alcohol is lower than that of formic acid. The same holds for other acids, e.g. picric and trichloracetic. These complications are due to the fact that an acid can only dissociate in a medium which can solvate the free hydrogen ion H^+, giving in the solvents named above the ions H_3O^+, $C_2H_5OH_3^+$, and NH_4^+ respectively.†

Affairs are much more complicated in concentrated solutions, where maxima and minima are often observed in the curves, especially with solvents of low dielectric constant and weak electrolytes. An increase of equivalent conductivity with increasing concentration is often found, e.g. with $N(C_2H_5)_4Br$ in chloroform.

Most acids and bases behave abnormally in non-aqueous solutions. Thus the hydrogen halides, which are very good conductors in water, are bad conductors in non-aqueous solvents (with the exception of the alcohols) and exhibit an anomalous change of equivalent conductivity with concentration. The majority of substances which are weak electrolytes in water have not been studied in other solvents. A phenomenon often observed in non-aqueous solutions is that a substance is found to conduct in certain media although its composition is such as to make the formation of ions very improbable. Examples of this are Br_2 in liquid SO_2, ether in liquid SO_2,‡ and nitro and amino-compounds in liquid ammonia.§ These phenomena probably depend upon a purely chemical interaction between the solvent and the solute.

† For references, see Hall, *Chem. Rev.* **8** (1931), 191. We shall not deal further with considerations of this kind; see also *Note 2*, p. 11.

‡ See P. Walden, *Ber.* **34** (1901), 4194; **35** (1902), 1771, 2022; *Z. phys. Chem.* **43** (1903), 407; L. Bruner and E. Bekier, ibid. **84** (1913), 572; T. Henderson, E. L. Hirst, and A. K. Macbeth, *J. Chem. Soc.* **123** (1923), 1130.

§ See E. C. Franklin and C. A. Kraus, *J. Am. Chem. Soc.* **27** (1905), 191, and subsequent papers. For a review of the subject, see W. C. Fernelius and W. C. Johnson, *J. Chem. Education*, **5** (1928), 664, 828; **6** (1929), 20, 441; **7** (1930), 981, 1291, 1602, 1850, 2600.

3595.7 M

TABLE 15

The relation between Λ_v/Λ_∞ and the dielectric constant

Solvent $t = 25°$	*D.C.* ($t = 20°$)	*Dipole moment in* D†	*Binary salt*	Λ^t_∞	Λ_v $v = 1{,}000$	Λ_v $v = 10{,}000$	$\left(\frac{\Lambda_v}{\Lambda_\infty}\right)$ $v = 1{,}000$	$\left(\frac{\Lambda_v}{\Lambda_\infty}\right)$ $v = 10{,}000$
Water H_2O (18°)	81	1·9	$N(C_2H_5)_4$ picrate	53·3	51·4	52·9	0·965	(0·992)
Methyl alcohol CH_3OH	35	1·7	$N(C_2H_5)_4$,,	103·0	96·1	100·7	0·933	0·978
Acetonitrile CH_3CN	36	3·1	$N(C_2H_5)_4$,,	163·8	152·0	160·1	0·928	0·978
Ethyl alcohol C_2H_5OH	25	1·7	$N(C_2H_5)_4$,,	51·45	43·85	48·97	0·852	0·952
Acetone CH_3COCH_3	20·7	2·8	$N(C_2H_5)_4$,,	177·3	148·1	167·8	0·835	0·946
Methyl ethyl ketone $CH_3COC_2H_5$	17·8	2·8	$N(C_2H_5)_4$,,	139·7	113·5	131·7	0·812	0·943
Methylamine CH_3NH_2 (−15°)	10	1·2	$N(C_2H_5)_4$,,	182	..	107·5	(0·28)	0·59
Tetrachlorethane $C_2H_2Cl_4$	8·15	..	$N(C_5H_{11})_4$,,	25·3	7·1	(14)	0·25	0·553
Ethylamine $C_2H_5NH_2$ (0°)	6·17	1·3	$N(C_2H_5)_4$,,	165	0·75	17·8	0·045	0·108
Chloroform $CHCl_3$	4·95	1·2	$N(C_2H_5)_4$,,	105	0·16	0·55	0·0015	0·0053
Ether $(C_2H_5)_2O$ (0°)	4·3	1·1	$N(C_5H_{11})_4$,,	150	..	0·367	0·001	0·0025
Pentachlorethane C_2HCl_5	3·76	1·0	$N(C_5H_{11})_4$,,	19	0·013	..	0·0007	0·001
Trichlorethylene C_2HCl_3	3·42	..	$N(C_5H_{11})_4$,,	75	0·01	..	0·0001	..
Benzene C_6H_6 (72°)	2·1	0	$N(C_5H_{11})_4$,,	117	Appreciable but very small.			..

From measurements of Walden, *Z. phys. Chem.* **147** (1930), 1. The values of Λ_∞ were determined by the square root law (187).

† 1 Debye = 1 D = 10^{-18} electrostatic units. This nomenclature has been recently proposed in honour of Debye.

22. The Effect of Field-Strength and Frequency on the Conductivity of Strong Electrolytes

We shall now turn to two phenomena which have only been recently discovered, and investigate whether they can be explained by Arrhenius's theory. The first is the dependence of the conductivity of electrolytes upon the strength of the electric field, and the second the dependence of the conductivity on the frequency of the field. The first effect was discovered experimentally by M. Wien,† while the second was predicted theoretically by Debye and Falkenhagen, the prediction being verified experimentally by Sack. This latter effect has been much studied of late, especially by Zahn, Rieckhoff, Brendel, Deubner, Mittelstädt, M. Wien, Malsch, and Gärtner. The classical theory is unable to account for these phenomena, while they may be explained by the modern electrostatic theory.‡

A. *The dependence of the conductivity of electrolytes on the electric field-strength (Wien effect).*

(*a*) *Experimental methods.*§ The ordinary methods of determining the conductivity of electrolytes employ a field of the order of 1 volt/cm. The velocities of the ions are under these conditions extremely small, e.g. for a K^+ ion in a field of 1 volt/cm., 0·00068 cm./sec. A sodium ion in a field of 1 volt/cm. has a velocity of about 0·00044 cm./sec. and thus moves about 1·6 cm. in an hour. For these small velocities the current is proportional to the applied potential, and Ohm's law therefore holds. The question now arises whether the conductivity of electrolytes remains constant with very high field-strengths and consequently high ionic velocities. This question has been studied recently by M. Wien, who has used fields of the order of 100,000 volts/cm. and discovered deviations from Ohm's law, which are of great significance for the theoretical development of the problem of electrolytes. In these strong fields the ions have velocities of several metres per second.

We shall first describe briefly the experimental arrangement used by Wien. A difficulty arises, because if the current continues for any appreciable time, the enormous heat evolution and electrolysis make it

† M. Wien, *Ann. d. Phys.* (4) **83** (1927), 327; (4) **85** (1928), 795. See also p. 229. Milner was the first to deal with the dependence of the conductivity upon the field in his fundamental work on the interionic theory.

‡ See p. 216.

§ My colleague Herr Malsch has been kind enough to look through section (*a*).

impossible to carry out any measurements. The only possibility remaining is therefore to use extremely short surges of current lasting about 10^{-6} seconds.

It would, of course, be most convenient if the potential E remained constant during the time t, corresponding to the full curve in Fig. 11. Actually, however, the potential varies in the manner represented by the dotted line in Fig. 11. In order to arrive at the relation between the conductivity and the field-strength it is possible to take the time average

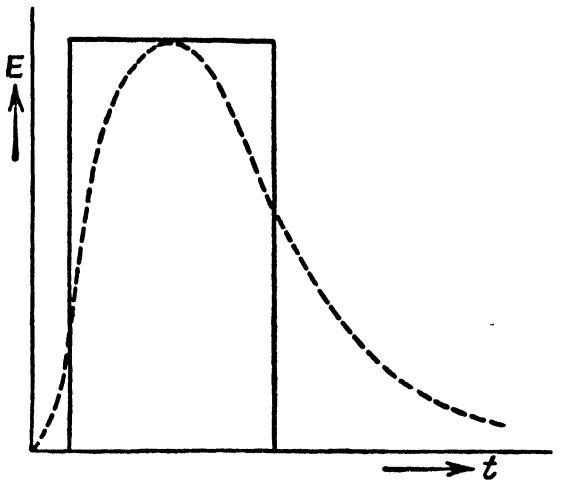

FIG. 11. The variation of voltage with time in the electric discharge.

of the potential during the experiment and to calculate the mean field-strength from this and the observed resistance.† W. Fucks‡ has recently described a method for determining directly the dependence of the conductivity upon the field-strength. The results justify the method of calculating the mean value employed by Malsch and Wien. The method used is shown diagrammatically in Fig. 11A. r_1 is the electrolyte resistance to be investigated, and c_1 the electrode capacity of the cell. The electrodes are movable, so that the distance between them can be varied. r_2 is a constant resistance which does not vary with the temperature, and c_2 is a variable capacity to compensate for the electrode capacity of the cell. The resistances and capacities must first be adjusted with small potential differences (for which the effect does not appear) so that $r_1 = r_2$ and $c_1 = c_2$. The method then consists in comparing the distribution of potential between AB and BC by means of an oscillo-

† See J. Malsch and M. Wien, *Ann. d. Phys.*, **83** (1927), 317.
‡ W. Fucks, *Ann. d. Phys.* [5] **12** (1932), 306.

graph, from which the ratio of the resistances can be deduced. The maxima of the deflexions are now observed, their height being varied by altering the applied potential. Fig. 11 B shows an oscillogram obtained using barium ferrocyanide.† The specific conductivity of the electrolyte for low field-strengths was 4×10^{-4} and the maximum field during the discharge was 180 kilovolts per cm. The upper curve was obtained by connecting the oscillogram to BC, and the lower curve by connecting it to the electrolyte. The ratio of the deflexions gives the change in the resistance at a field-strength determined by the position on the curve. The oscillogram shown here shows an effect of 20 per cent. at the maximum potential. We shall describe briefly the experimental arrangement first devised by Wien and later improved by Wien and Malsch. The apparatus first used is sketched in Fig. 12.‡ There are two circuits, the oscillation circuit containing the electrolyte and a liquid resistance for comparison, and the receiving circuit which is coupled inductively to the oscillation circuit. The inductance of the oscillation circuit is so chosen that the condenser discharges aperiodically through a spark gap and the electrolyte being investigated. The measurement of resistance is effected by observing the time integral of the heat effect produced in the receiving circuit by a single discharge. The receiving circuit is aperiodically damped and is coupled loosely to the oscillation circuit. The heating effect is measured with a thermo-element and galvanometer. The resistance being investigated is then replaced by a known resistance

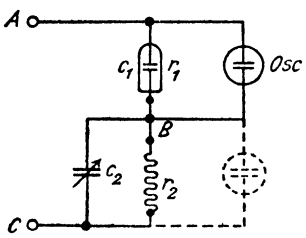

FIG. 11 A. Cathode oscillograph method of measuring the Wien effect.

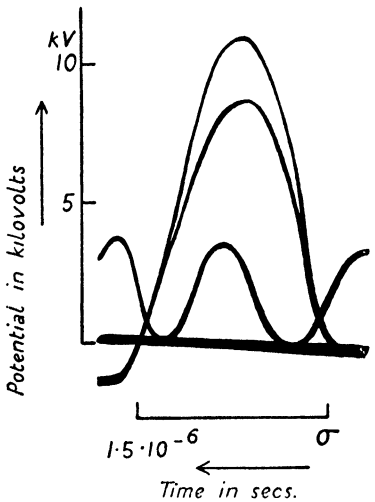

FIG. 11 B. Oscillogram of the Wien effect for barium ferrocyanide. Conductivity at low field-strengths $= 4{\cdot}0 < 10^{-4}(\Omega\ \text{cm.})^{-1}$. Maximum field during discharge: 180 kV. cm. Maximum effect: 20 per cent.

† This oscillogram has been kindly provided by Dr. Fucks.

‡ See further O. Meisser, *Jahrb. d. drahtlos. Telegraphie und Telephonie*, **22** (1923), 204.

which does not vary with the field. This latter resistance is then adjusted until the deflexion of the galvanometer is the same for the unknown and the known resistances. The potential is then increased by increasing the spark-gap, and the alteration of the resistance with the potential can be determined. The accuracy of this method is about 1 per cent. Difficulties arising from the lack of constancy of the thermo-element have been avoided by a new null-method devised

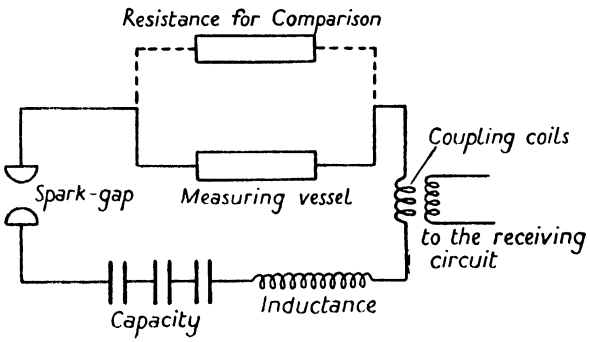

FIG. 12. First method of Malsch and Wien for measuring the Wien effect.

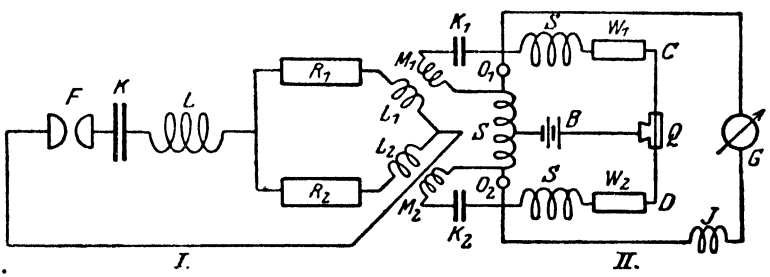

FIG. 13. Second method of Malsch and Wien for measuring the Wien effect.

by Wien and Malsch† which gives an accuracy of 0·1 per cent. The principle of this method is illustrated in Fig. 13. I is the oscillation circuit, resembling that used in the deflexion method. It contains two branches, one of which includes the resistance R_1 and the other the adjustable resistance R_2 and the electrolyte being studied R_E. Each of these branches is coupled to one of the branches of a barretter circuit by means of the coupling coils L_1, L_2, M_1, M_2. (B is a battery, Q a mercury contact, K_1 and K_2 large condensers.) If the oscillation circuit is completely symmetrical, there will be no deflexion in the galvanometer G in the barretter circuit. R_1 is first adjusted so that no deflexion is

† J. Malsch and M. Wien, *Ann. d. Phys.* (4) **83** (1927), 305. Cf. also J. Malsch, *Ann. d. Phys.* (5) **3** (1929), 803.

produced when R_E is inserted. R_E is then replaced by R_2 which is adjusted until there is again no deflexion. R_E is then equal to R_2. For further details, see Malsch and Wien, loc. cit.

(*b*) *Experimental results for the dependence of conductivity on field-strength.* It was found that all electrolytes exhibited an increase in conductivity with increasing potential. If we call the specific conductivity for very small fields λ_0† and that for the high field-strength λ_E, M. Wien introduces the following quantity as a measure of the effect of the field,

$$\Delta\lambda_E = \frac{\lambda_E - \lambda_0}{\lambda_0} 100. \tag{190}$$

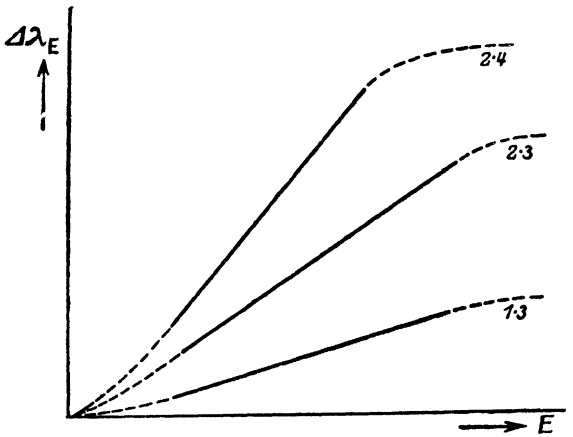

FIG. 14. The variation of conductivity with field-strength.

Changes in conductivity up to 50 per cent. were observed. The variation of $\Delta\lambda_E$ with the field-strength E for three electrolytes of different types is shown in Fig. 14. The conductivity first rises slowly with increasing field, corresponding to the lower dotted part of the curves, and then increases approximately linearly with the field, as shown by the full part of the curves in Fig. 14. Finally the curves bend over again at high field-strengths, as shown by the upper dotted portion. The first dotted part of the curves, corresponding to weak fields can be represented empirically by an equation of the type

$$\Delta\lambda_E = AE^2(1 - BE^2). \tag{191}$$

The following points emerge from M. Wien's results:‡

The initial effect (AE^2 in (191)) increases rapidly with the valency of the ions, and is approximately proportional to the product of the

† This is normally called λ (cf. § 21).

‡ For further details and a theoretical discussion, see p. 229.

squares of the valencies, $z_1^2 z_2^2$. A increases with increasing dilution, and is approximately inversely proportional to the square root of λ_0. If the field is measured in volts/cm., the proportionality factor is $1{\cdot}74 \times 10^{-14}$.

The second term in (191) can also be obtained with some accuracy. B increases with the valency of the ion, though not so rapidly as A, the increase being more marked at high dilutions. B increases more rapidly with decreasing conductivity and concentration, and its mean value for $\lambda_0 = 0{\cdot}000125$ is about three times the value for $\lambda_0 = 0{\cdot}001$.

The following table contains the results for solutions of $CoCl_2$ and KI in acetone solution.

TABLE 16

Solvent—acetone

	$\lambda_0 = 0{\cdot}0002$	$0{\cdot}0004$	$0{\cdot}0008$
$CoCl_2$	$A = 0{\cdot}93 \times 10^{-11}$	$0{\cdot}62 \times 10^{-11}$	$0{\cdot}39 \times 10^{-11}$
	$B = 0{\cdot}35 \times 10^{-12}$	$0{\cdot}35 \times 10^{-12}$	$0{\cdot}35 \times 10^{-12}$
KI	$A = 0{\cdot}33 \times 10^{-11}$	$0{\cdot}33 \times 10^{-11}$	$0{\cdot}26 \times 10^{-11}$
	$B = 0{\cdot}44 \times 10^{-12}$	$0{\cdot}53 \times 10^{-12}$	$0{\cdot}53 \times 10^{-12}$

The data in Table 16 show that for ions of the same valency, the field effect is considerably greater in acetone than in water. Thus for $\lambda_0 = 0{\cdot}0002$, KI in water has $A = 0{\cdot}12 \times 10^{-11}$, and in acetone

$$A = 0{\cdot}33 \times 10^{-11}.$$

The curves for $\Delta\lambda_E$ resemble those for water, and can be represented by equation (191) the B-coefficients being considerably smaller than those in water. It is reasonable to suppose that all these differences depend on the fact that the dielectric constant of acetone is one-quarter that of water.†

We must now turn to the upper dotted portion of the curve in Fig. 14, corresponding to very strong fields. The field-strength at which the curve begins to bend downwards depends very much upon the concentration. In very dilute solutions, the initial slope is very great, after which the curve becomes almost horizontal. In more concentrated solutions the initial slope is less, but it persists up to quite high field-strengths and the curve bends downwards only with very strong fields. This is illustrated by Fig. 15, which shows the results for barium ferricyanide. The rate of increase of conductivity with field-strength always decreases with increasing fields, and the results seem to indicate that a limiting conductivity is reached at very high field-strengths. The limiting value is more easily reached in very dilute solutions than in

† See further p. 232.

more concentrated ones, and Wien was only able to measure it in very dilute solutions on account of sparking through the electrolyte. It was found that the limiting values of the conductivity thus obtained coincide with the conductivities at infinite dilution within the limits of experimental error. Table 17 shows the observed limiting values of the increase in conductivity together with the values calculated from the conductivity at infinite dilution.

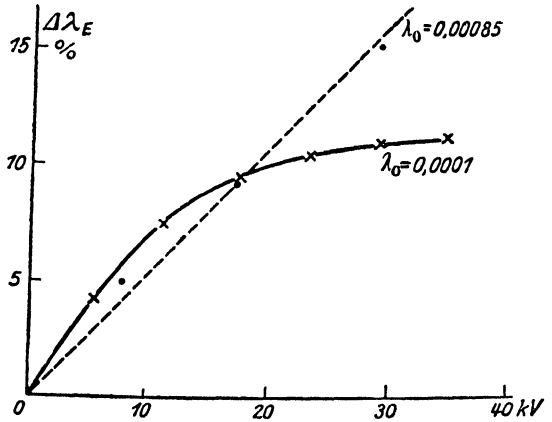

FIG. 15. Wien effect for barium ferricyanide.

TABLE 17

γ^* = Equivalent concentration

	$z_1 z_2$	$\gamma^* . 10^3$	$\Delta\lambda_\gamma$	$\Delta\lambda_\infty$
		$\lambda_0 = 2{\cdot}3 \times 10^{-5}$		
$Li_3[Fe(CN)_6]$	1.3	0·18	2·8%	2·4%
$MgSO_4$	2.2	0·21	4·0%	5·3%
$Ba_3[Fe(CN)_6]$	2.3	0·15	6·2%	7·0%
		$\lambda_0 = 9{\cdot}2 \times 10^{-5}$		
$Li_3[Fe(CN)_6]$	1.3	0·74	5·5%	4·9%
$MgSO_4$	2.2	0·93	9·0%	11·2%
$Ba_3[Fe(CN)_6]$	2.3	0·73	14·2%	15·0%

It appears from the table that the agreement is satisfactory.

A. Gyemant† has observed an increase of conductivity with field-strength in the case of badly conducting liquids, which is probably related to the Wien effect. Since the liquids studied conduct so badly that there is very little electrolysis or evolution of heat, it was possible to apply a strong field for a longer period.

According to the classical theory it is impossible to explain the Wien

† A. Gyemant, *Phys. Z.* **29** (1928), 289.

effect as being due to a hydrodynamic effect† or the effect of a chemical reaction. This may be shown roughly by the following considerations. The heat of reaction corresponding to the dissociation of complexes, e.g. $Ag(CN)_2$ or $Fe(CN)_6$, is of the order of magnitude of 1 volt-electron,‡ or 23,070 cals. The mean free path in a liquid is of the order of magnitude 10^{-8} cm., so that a field of 10^5 volts/cm. will only produce velocities corresponding to 10^{-3} volt-electrons. While the energy of dissociation of any salt molecules present will probably be less than the figure given above, it will still be much greater than the kinetic energy acquired by an ion. In any case this explanation would require a greater Wien effect at higher concentrations, owing to the presence of more molecules, whereas exactly the opposite is found experimentally.

Weak acids and salts also exhibit a marked Wien effect, but matters are somewhat more complex in this case.§

We may refer here to an observation made by M. Wien|| which led subsequently to another important discovery, the dependence of the conductivity upon the frequency. In his preliminary experiments on the deviations of electrolyte solutions from Ohm's law, he found an effect which appeared at the time incomprehensible, but which has been subsequently very simply explained by the modern electrostatic theory.†† The duration of the electric discharge was varied through wide limits by altering the capacity and inductance of the oscillation circuit, the damping being kept as far as possible constant by selecting a suitable ratio between the capacity and the inductance. Experiments with beryllium sulphate, lithium ferrocyanide, barium ferrocyanide, and calcium ferricyanide showed that the Wien effect increases with increasing duration of the discharge, the effect being especially marked for very short durations. For longer durations, the effect approached a limiting value. The great decrease observed with very short durations is partly due to the effect of the capacity of the liquid resistance used for comparison, which decreases the damping. There is, however, clear evidence that the conductivity depends on the duration of the discharge.

† Cf. p. 230.

‡ Cf. Randall and J. O. Halford, *J. Am. Chem. Soc.* **52** (1930), 178.

§ Cf. p. 234. The explanation of this effect (discovered by Herr Schiele in Wien's laboratory) is not yet fully cleared up. This 'dissociation field effect' is the chief factor at at high field-strengths (cf. p. 233). This interesting effect offers a wide field for theoretical and experimental investigation. (See the theoretical treatment recently given by Onsager, p. 241.)

|| M. Wien, *Ann. d. Phys.* (4) **83** (1927), 327; **85** (1928), 795.

†† Cf. p. 181.

B. *The variation of the conductivity of strong electrolytes with the frequency of the field.*

The dependence of conductivity upon frequency was predicted by Debye and Falkenhagen on the basis of modern electrostatic theory, and will be dealt with later in detail in connexion with this theory.† For the present we shall only describe some of the essential features of this dispersion effect. It is found experimentally that the conductivity in an alternating field increases with increasing frequency, the lowest

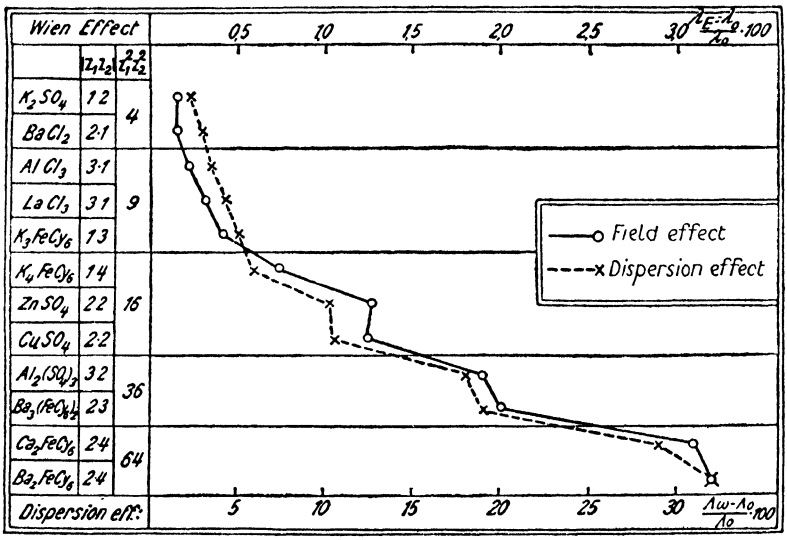

FIG. 16. Comparison of the field effect and the dispersion effect.

frequency at which this effect becomes apparent being about 10^6 per sec., corresponding to a wave-length of a few metres. The conductivity does not increase so much as in the Wien effect, and does not reach the value corresponding to infinite dilution.

The increase in conductivity is easily measured, and of the same order of magnitude as the Wien effect. The dependence of the dispersion effect upon the frequency is qualitatively exactly the same as the dependence of the Wien effect upon the field-strength. The variation of both effects on the valency of the ions is shown in Fig. 16. The Wien effect is characterized by the quantity

$$\Delta\lambda_E = \frac{\lambda_E-\lambda_0}{\lambda_0}\,100$$

corresponding to $\lambda_0 = 0{\cdot}001$, $E = 10^4$ volts/cm. The corresponding

† Cf. pp. 182, 209.

quantity for the dispersion effect is given by

$$\Delta\Lambda_\omega = \frac{\Lambda_\omega - \Lambda_0}{\Lambda_0} 100, \qquad (192)$$

where Λ_ω is the conductivity corresponding to a frequency ω. The values of $\Delta\Lambda_\omega$ given in Table 18 and Fig. 16 correspond to a frequency of 10^8 hertz, i.e. a wave-length of about one metre. It is seen that there is a close connexion between the Wien effect and the dispersion effect.†

TABLE 18

$(\lambda_0)_{18°} = 0{\cdot}001\,\Omega^{-1}\,\text{cm.}^{-1}$	$z_1 z_2$	$z_1^2 z_2^2$	$100\,\Delta\lambda_E$	$100\,\Delta\Lambda_\omega$
K_2SO_4	1.2	4	0·16	2·3
$BaCl_2$	2.1	4	0·16	3
$LaCl_3$	3.1	9	0·33	4·4
$AlCl_3$	3.1	9	0·23	3·5
$K_3Fe(CN)_6$	1.3	9	0·42	5·1
$K_4Fe(CN)_6$	1.4	16	0·75	6
$CuSO_4$	2.2	16	1·24	10·5
$ZnSO_4$	2.2	16	1·27	10·3
$Al_2(SO_4)_3$	2.3	36	1·9	18
$Ba_3[Fe(CN)_6]_2$	2.3	36	2·0	19
$Ca_2Fe(CN)_6$	2.4	64	3·1	29
$Ba_2Fe(CN)_6$	2.4	64	3·2	32

Note 1. Literature on the conductivity of solutions

F. Kohlrausch and L. Holborn, *Das Leitvermögen der Elektrolyte*, 2nd edition, Leipzig and Berlin, 1916; P. Walden, *Das Leitvermögen der Lösungen*, Leipzig, 1924; L. Holborn, 'Elektrolytische Leitung', in Graetz, *Handb. d. Elektrizität u. d. Magnetismus*, vol. iii, Leipzig, 1923; Ostwald-Luther-Drucker, *Physiko-chemische Messungen*, 4th edition, Leipzig, 1925; G.Pfleiderer,'Leitfähigkeitsmessungen', in Staehler, *Handb. d. Arbeitsmethoden in der anorganischen Chemie*, vol. iii, Leipzig, 1914; E. Baars, 'Elektrizitätsleitung in Flüssigkeiten' and 'Elektrochemische Messungen', in Geiger-Scheel, *Handb. d. Physik*, vols. xiii and xvi; Ch. A. Kraus, *The Properties of Electrically Conducting Solutions*, Chem. Catalog Co., New York; C. W. Davies, *The Conductivity of Solutions*, Wiley & Sons, New York, 1933; H. E. Jones and A. A. Noyes, *Carnegie Institute Reports*; J. R. Partington, 'Conductance, Ionization and Ionic Equilibria' in H. S. Taylor, *A Treatise on Physical Chemistry*; H. Hartley, O. Gatty, W. A. McFarlane, and D. M. Murray-Rust, 'The Electrical Conductivity of Solutions', *Chem. Soc. Ann. Reports*, 1930; F. H. Newman, *Electrolytic Conduction*, Chapman & Hall, London, 1931; E. Darmois, *Leçons sur la conductibilité des électrolytes*, Paris, 1929; H. Jahn, *Grundriss der Elektrochemie*, 2nd edition, 1905; H. J. Creighton, *Electrochemistry*, New York, 1925; M. Le Blanc, *Lehrbuch der Elektrochemie*, 11th and 12th editions,

† A parallelism between these two effects was first suggested by the author (*Phys. Z.* **30** (1929), 163) on theoretical grounds, and was later confirmed by Rieckhoff (*Ann. d. Phys.* (5) **2** (1929), 596). Wien, in a private communication to the author, has pointed out that this parallelism breaks down for very intense fields, on account of the appearance of a dissociation field effect in addition to the effect due to the ionic atmosphere. (Cf. the theoretical treatment on p. 236.)

Leipzig, 1925; G. Grübe, *Grundzüge der Elektrochemie*, 2nd edition, 1930; F. Foerster, *Elektrochemie wässriger Lösungen*, 4th edition, Leipzig, 1925; and the section by L. Ebert, 'Leitfähigkeit der Elektrolyte', in *Handb. d. Experimentalphysik*, vol. xii, 1932. Numerous data are given in Landolt-Börnstein, *Physikalisch-chemische Tabellen*, 5th edition, Berlin, 1923, and supplementary volumes 1 and 2, Berlin, 1927 and 1931. An interesting study of the sources of error in conductivity measurements has been given by G. Jones and his collaborators. See Jones and R. C. Josephs, *J. Am. Chem. Soc.* **50** (1928), 1049; Jones and G. M. Bollinger, ibid. **51** (1929), 2407; **53** (1931), 411, 1207; Jones and B. C. Bradshaw, ibid. **55** (1933), 1780. McInnes and his collaborators have recently increased the accuracy of conductivity measurements to 0·02 per cent. For results, see p. 196. The historical development of electrochemistry has been treated in detail in W. Ostwald's *Elektrochemie* (*Ihre Geschichte und Lehre*), Leipzig, 1906.

VI

EARLY THEORIES OF THE ANOMALIES OF STRONG ELECTROLYTES

23. Chemical Theories (Drucker, Roth). The Conception of the Complete Dissociation of Strong Electrolytes (van Laar, Sutherland, Liebenow, Kjellin, Noyes, Hantzsch, and especially Bjerrum)

The theories proposed to explain the anomalies of strong electrolytes can be classified as chemical and physical. On the chemical side, numerous attempts have been made to explain these anomalies by assuming complex formation and solvation of ions. Complex formation certainly takes place in many cases, and it is sometimes possible to determine the concentration of complex present by a combination of various methods, e.g. conductivity, e.m.f., solubility and transference determinations. The deviations from classical theory are often reduced by taking complex formation into account.† It may, however, be easily shown that the assumption of complex formation leads always to a linear limiting law in very dilute solutions, and never to the square root law which is found experimentally.‡ A. Roth§ attempted to explain the apparent deviations from the law of mass action by taking into account the hydration of the ions. Very little is yet known about hydration, so that no quantitative explanation can be attempted. Moreover, considerations of this kind again lead to a linear law in dilute solutions, in opposition to experiment.‖

† See C. Drucker, *Z. Elektrochem.* **11** (1905), 211; **17** (1911), 398; **18** (1912), 562; **19** (1913), 8, 797; *Z. phys. Chem.* **96** (1920), 381; Drucker and G. Riethof, ibid. **111** (1924), 1; Drucker and R. Schingnitz, ibid. **122** (1926), 149; Drucker, *Akad. d. Wiss.* (II b) **138** (1929), Suppl. 62. For further references, see *Note 1*, p. 91; also the articles by L. Ebert, *Jahrb. d. Radioakt.* **18** (1921), 134; K. F. Herzfeld, *Enzykl. d. math. Wissensch.* V, No. 11 (1921), §§ 16, 19, 24; Fr. Auerbach, *Ergeb. d. exakt. Naturw.* **1**, 228; C. Drucker, *Samml. chem. Vorträge*, **10** (1906).

‡ Cf. p. 242.

§ A. Roth, *Z. phys. Chem.* **79** (1912), 599.

‖ We shall not deal further with these chemical theories. A few numerical examples will show sufficiently the great difficulties associated with their quantitative application. Moreover there is no experimental evidence for the existence of complex ions in dilute solutions of typical strong electrolytes such as NaCl. See e.g. the investigations of M. Taylor, *J. Am. Chem. Soc.* **48** (1926), 599, who showed from transport determinations that no complex formation takes place in mixtures of HCl and NaCl. R. F. Schneider and S. A. Brayley (ibid. **45** (1923), 1121) claimed to have shown the presence of complexes, but it has been shown by Bjerrum (*Kgl. Danske Vid. Selsk.* **6** (1925), No. 9) that their conclusions are incorrect. Complex formation can of course occur in non-aqueous solvents, especially in concentrated solutions. (Thus LiBr and LiCl form complex ions in acetone,

While the chemical theories assume the simple law of mass action to hold for ionic solutions, the physical theories throw doubt upon its validity, and seek to explain the discrepancies by taking into account the interaction between the charged and uncharged particles present in the solution. The first important step towards a quantitative theory was the assumption that strong electrolytes are practically completely dissociated, so that the equilibrium between ions and undissociated molecules is only of subsidiary importance. Noyes, Bjerrum,† and almost simultaneously Hantzsch‡ were the first to assume complete dissociation on the basis of the optical behaviour of coloured electrolyte solutions. The light absorbed by a given amount of solute is in many cases independent of the concentration, i.e. Beer's law is obeyed. Unless the undissociated molecules absorb in exactly the same way as the ions, it must be assumed that the degree of dissociation is practically independent of the concentration. Bjerrum made the simple assumption that strong electrolytes are practically completely dissociated, an appreciable number of undissociated molecules being only present for weak electrolytes. The variation of many properties (conductivity, osmotic properties, etc.) with concentration was explained by van Laar, Noyes, and Bjerrum as being due to the interaction of electrically charged ions, which will prevent the free motion of the ions and thereby cause the anomalous behaviour of electrolytes.

Before the work of Bjerrum, Sutherland§ had attempted to explain the variation of conductivity with concentration on a similar basis. He also assumed complete dissociation, and attributed the decrease of the equivalent conductivity with increasing concentration to an increase in the friction opposing the motion of the ions, due to the electrical forces. A rough calculation of this effect led to an approximate agreement with experiment. It can, however, be easily shown that Sutherland's derivation is not correct.||

It may be mentioned that there are other early attempts to explain

while NaI does not. See S. W. Serkov, *Z. phys. Chem.* **73** (1910), 557; J. W. McBain and F. C. Coleman, *Trans. Farad. Soc.* **15** (1919), 27; P. Walden, *Z. phys. Chem.* **123** (1926), 467; W. Birkenstock, ibid. (A) **138** (1928), 432.

† N. Bjerrum, *D. Kgl. Danske Vid. Selsk. Skrifter* (7) **4** (1906), 1; *Proc. 7th Int. Cong. Appl. Chem.* London, 1909, section X; *Z. anorg. Chem.* **63** (1909), 146; *Fys. Tidskr.*, Copenhagen, **15** (1916), 59; *Z. Elektrochem.* **24** (1918), 321.

‡ A. Hantzsch, *Ber.* **39** (1906), 3080, 4153; **41** (1908), 1216, 4328; *Z. phys. Chem.* **63** (1908), 367; **72** (1910), 362; **84** (1913), 321. See also H. Kayser, *Handb. d. Spektroskopie III* (1905), 109–28; G. Rudorf, *Samml. chem. u. chem.-techn. Vorträge*, **9** (1904), 1; *Jahrb. d. Radioakt.* **3** (1906), 422; **4** (1907), 380.

§ W. Sutherland, *Phil. Mag.* **3** (1902), 161; **9** (1905), 781; **12** (1906), 1; **14** (1907), 1; **16** (1908), 497.

|| See p. 249.

the behaviour of strong electrolytes from an electrical standpoint, assuming complete dissociation.†

Specially worthy of mention is the fact that van Laar as early as 1894 emphasized clearly the importance of the extremely powerful electrostatic fields of the ions.

24. The Theories of P. Hertz, S. R. Milner, C. Ghosh and Malmström

P. Hertz‡ attempted in 1912 to calculate the effect of collisions upon the paths of the ions. He took into account the coulomb forces between the ions, and calculated the ionic mobilities by kinetic considerations. Neglecting the Brownian movement, the ions will move in straight lines, but will be deflected by the interionic forces, especially when two ions approach one another closely. They will thus describe hyperbolae of varying curvatures, just like the planets. This effect will slow down the ions and thus account for the decrease of mobility with increasing concentration.

A strict test of this theory is not possible, since certain quantities, e.g. the mass of an ion in solution, are not known.§ If ionic masses calculated from the atomic weights are employed, there is no agreement between theory and experiment. This may be interpreted as being due to the solvation of ions. If the constants in Hertz's formula which depend upon the ionic mass (and other quantities not directly accessible) are calculated empirically from conductivity measurements, the very complex function given by Hertz reproduces the data of Kohlrausch over a large concentration range. It thus serves well as an interpolation formula,|| but does not agree with the experimental results for very dilute solutions. From a theoretical point of view it may be doubted whether it is permissible to transfer the considerations of the kinetic theory of gases to ionic solutions, especially in dealing with such concepts as the mean free path of the ions among the solvent molecules.

Milner†† obtained more reliable results in his calculation of the effect

† See C. Liebenow, *Z. Elektrochem.* **8** (1902), 931; **11** (1905), 301; R. Malmstrom, *Diss.*, Berlin, 1905; F. A. Kjellin, *Z. phys. Chem.* **77** (1911), 192; J. J. van Laar, ibid. **15** (1894), 457; **17** (1895), 245; **18** (1895), 274; **19** (1896), 318; *Arch. Musée Teyler*, series II, (1900), 59; *Z. anorg. Chem.* **139** (1924), 108.

‡ P. Hertz, *Ann. d. Phys.* **37** (1912), 1.

§ It is interesting to note that Debye has recently devised a method for determining the mass of the ions by the potential differences caused by supersonic vibrations. See p. 170.

|| See R. Lorenz, *Raumerfüllung und Ionenbeweglichkeit*, p. 163, Leipzig, 1922.

†† R. Milner, *Phil. Mag.* (6) **23** (1912), 551; **25** (1913), 742; **35** (1918), 214, 352; *Trans. Farad. Soc.* **15** (1919), 148.

of the attractive and repulsive forces between the ions upon the osmotic pressure. Using statistical principles, he obtained a method for calculating graphically the variation of the free energy of a dilute electrolyte solution with concentration. This is related to the osmotic pressure by equation (243). Milner found that for very small concentrations, $1-g$ was proportional to the square root of the concentration. The principle of Milner's theory is identical with that of P. Debye, but the latter author employed a much simpler and more convenient mathematical method.

The work of Ghosh,† 1918–21, attracted at the time considerable attention. His calculations (and those of Malmström) are based upon the following doubtful assumption. The work obtained in diluting a solution of a strong electrolyte depends upon the work of separation of two oppositely charged ions, it being assumed that the ions have a certain fixed configuration in the solution. The variation of the conductivity and the osmotic phenomena with concentration can then be calculated in the following way.

It is known from X-ray analysis that the ions in a solid salt form a lattice. In solution, on account of the interionic forces, the ions will not be able to move freely. Only those ions having a sufficiently great kinetic energy to overcome the electric field will be in free motion. Ghosh and Malmström calculate the work necessary to separate the ions completely in the following simple manner. If two electric charges ϵ and $-\epsilon$ are at a distance r in a medium of dielectric constant D_0, their mutual potential energy is

$$-\frac{1}{D_0}\frac{\epsilon^2}{r}.$$

We shall consider a binary electrolyte‡ such as NaCl, one gram mole being dissolved in volume V. The space distribution is the same for both positive and negative ions, and since the volume corresponding to one ion is $V/2N$ the mean distance r between two oppositely charged ions is given by

$$r = \left(\frac{V}{2N}\right)^{\frac{1}{3}}, \tag{193}$$

assuming the statistical distribution of the ions in solution to be given

† I. C. Ghosh, *J. Chem. Soc.* **113** (1918), 449, 627, 707, 790; **117** (1920), 828, 1390; *Trans. Farad. Soc.* **15** (1919), 154; *Z. phys. Chem.* **98** (1921), 211. The same law had previously been deduced by Malmström, *Z. Elektrochem.* **11** (1905), 797.

‡ For electrolytes of other types the space lattice will be different, and the expression for U_0 will also be changed. The same law is, however, finally obtained for the variation with concentration.

by the NaCl-lattice. The electrical energy U_e of the solution is then

$$U_e = -\frac{N\epsilon^2}{D_0}\left(\frac{2N}{V}\right)^{\frac{1}{3}}. \tag{194}$$

This energy U_e is the basis of the calculations of Ghosh and Malmström. It is, however, quite incorrect to calculate the energy of the solution from the mean distance between two oppositely charged ions in a lattice. The determining factor is actually quite a different length which depends on the temperature as well as the concentration and the charges,† since the mean distribution of the ions varies with the temperature, and cannot be compared to a space lattice which changes very little with the temperature. It is fortuitous that these two characteristic lengths have the same order of magnitude in the range of temperatures and concentrations usually studied and it is owing to this fortuitous agreement that the theory of Ghosh gives results of the right order of magnitude in a certain concentration range. The calculations of Born on the electrical energy of the crystal lattice cannot be extended to solutions, for which it is necessary to consider the difference between the probabilities of finding a positive and a negative ion in an element of volume near a given ion. In this way it is found that the characteristic length, and hence the electrical energy of the solution, depends upon the temperature.

In order to calculate the conductivity, Ghosh and Malmström assume that only a fraction $e^{-U_e/\nu RT}$ of the ions of an electrolyte which dissociates into ν ions are sufficiently free to take part in the conduction of electricity, i.e.

$$\frac{\Lambda}{\Lambda_\infty} = f_\Delta = e^{-U_e/\nu RT}. \tag{195}$$

On introducing U_e from (194), it is seen that a cube-root limiting law is obtained for the conductivity of dilute solutions. As has been shown previously,‡ this is in direct contradiction to the experimental results.

Ghosh also employed Clausius' virial theorem to evaluate the effect of the interionic forces upon the osmotic pressure. We have

$$pV = \nu RT - \tfrac{1}{3}U_e,$$

and hence from (194), for very small concentrations,

$$i = \frac{pV}{RT} = \nu(1 - A\gamma^{\frac{1}{2}}), \tag{196}$$

where i is van 't Hoff's factor, and A is a constant. As has been shown previously,§ the limiting law actually observed is of another form.

† See p. 105.

‡ See pp. 77, 79, and 193.

§ See p. 64.

We have thus been able to show that on the one hand the Ghosh-Malmström theory is theoretically unsound, and on the other hand that it leads to conclusions which are incompatible with the experimental results in very dilute solutions. The literature contains articles which claim to show both agreement and disagreement between the Ghosh-Malmström theory and the experimental results.†

† See J. R. Partington, *Trans. Farad. Soc.* **15** (1919), 98; D. L. Chapman and H. J. George, *Phil. Mag.* (6) **41** (1921), 799; H. Kadlcowa, *Chem. Listy*, **15** (1921), 109; *Chem. Abstr.* **15** (1921), 2374; H. Kallmann, *Z. phys. Chem.* **98** (1921), 433; C. A. Kraus, *J. Am. Chem. Soc.* **43** (1922), 2514; Sv. Arrhenius, *Z. phys. Chem.* **100** (1922), 9; J. Kendall, *J. Am. Chem. Soc.* **44** (1922), 717; H. J. S. Sand, *Phil. Mag.* (6) **43** (1923), 281; A. Brodsky, *Z. phys. Chem.* **108** (1924), 293; L. Klemensiewicz, ibid. **113** (1924), 28; P. Debye and E. Hückel, *Phys. Z.* **24** (1923), 185; W. Nernst, *Theoretische Chemie.*

VII

THE PRINCIPLES OF THE DEBYE-MILNER THEORY OF STRONG ELECTROLYTES

25. Introductory Remarks

The most recent developments of the theory of electrolytes depend upon the fundamental work of Debye and Milner,† which has been greatly extended in collaboration with Hückel, Onsager, and Falkenhagen. The Debye-Milner theory is now able to account quantitatively for practically all properties of electrolyte solutions in the range of extreme dilution, and is free from any assumptions of doubtful validity in this concentration range. The advances represented by this theory correspond roughly to the advances made by using the theory of real gases in place of the perfect gas laws. In van der Waals' equation of state the pressure is smaller than that calculated from the perfect gas laws, owing to the intermolecular forces of attraction. Similarly, in the Debye-Milner theory, the decrease in osmotic pressure is attributed to the electrical forces between the ions. In the case of electrolytes, however, the mathematical treatment is more complicated, since the electrostatic force varies inversely as the square of the distance while in a gas the attractive force between the molecules falls off much more rapidly with increasing distance. As a further complication, the ions are separated by solvent.

We shall deal specially with Debye's theory‡ first describing its fundamental principles and then its numerous applications. It must be noted that the development given will apply primarily only to very dilute solutions, since it is difficult to extend the theory to more concentrated solutions.§

Arrhenius's theory of electrolytic dissociation only considers the equilibrium between undissociated molecules and ions in solution. It can therefore only apply to weak electrolytes dissociated to a slight extent in which the most important forces are those of a truly chemical nature, i.e. the resonance forces of quantum mechanics. In the case of strong electrolytes conditions are quite different, since there are present large numbers of ions which exert electrical forces on one

† For references, see *Note 1*, p. 109.

‡ Milner's theory is identical with Debye's in its fundamental assumptions, but employs graphical methods and a statistical treatment. Further, Debye's theory leads much more readily to expressions of practical application. We shall deal with Debye's theory in the form in which he presented it himself.

§ A short chapter will be devoted to more concentrated solutions (cf. Chapter XI).

another. This ionic interaction is the determining factor in dilute solutions of strong electrolytes, but can be neglected for weak electrolytes. The modern theory of electrolytes is characterized by the importance attributed to the Coulomb forces between the ions. Milner and Debye have shown that these forces prevent a completely random distribution of the ions. The actual distribution may be characterized by an ionic atmosphere of electric density surrounding each ion. The following section deals with the properties of this *ionic atmosphere*, which is of great importance for the recent development of electrolyte solutions.

26. The Mean Electric Potential Surrounding a Dissolved Ion. The Ionic Atmosphere and its Characteristic Properties

A. *The distribution of the mean electric potential about an ion in a dilute electrolyte solution. The ionic atmosphere caused by the interionic forces.*

Before carrying out any calculations, we shall give a qualitative picture of the ionic atmosphere, which is characterized by a certain regularity in the distribution of the ions. Owing to the interionic forces, the probability of two ions approaching one another is greater when they are of opposite signs than when they are of the same sign. Consider any short radius vector (10^{-5}–10^{-7} cm.) drawn from a given ion, which we shall take as being positive. At the other end of the vector is a very small element of volume dV. We consider now the electric charge of this volume element, observations being carried out over a time which is large compared with the fluctuations of the Brownian movement (*c.* 10^{-12} sec.). On taking a time average, it will be found that the volume element has a negative charge density. The probability of finding a negative ion at a given distance from the central positive ion is by Boltzmann's theorem greater than the probability of finding a positive ion at the same distance. The positive ion thus has in a sense a connexion with the negative ions, which decreases with increasing distance, and is quite different from the chemical combination of the two ions to form a molecule. Just as in Arrhenius's theory the energy of ionization is of great importance for the degree of dissociation, in the present instance the potential of an ion with respect to its surroundings is a measure of the strength with which it is connected to all the surrounding ions, and therefore determines the thermodynamic properties

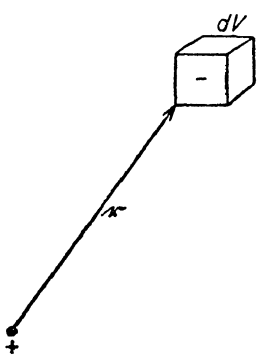

FIG. 17.

of the solution. Before we investigate the characteristic properties of the ionic atmosphere from this point of view, we shall give a quantitative treatment of the preceding qualitative ideas.

For the sake of simplicity we shall consider a mono-monovalent salt, of which N molecules are dissolved in volume V and dissociate completely into ions. ϵ is the absolute value of the charge on an ion ($4{\cdot}77 \times 10^{-10}$ electrostatic units), and D_0 is the dielectric constant of the solvent. We shall consider one of these ions† having a charge $+\epsilon$. We wish to obtain the time average of the potential in the neighbourhood of this ion. Taking a point P at a fixed distance from the central ion, we shall call the mean potential at this point Ψ; the work of bringing a positive ion to P is then $+\epsilon\Psi$, and the corresponding work for a negative ion is $-\epsilon\Psi$.

Considering a small volume element dV surrounding P, Boltzmann's theorem gives for the average number of positive ions in this volume

$$n_+ \, dV = ne^{-\epsilon\Psi/kT} \, dV, \tag{197}$$

and for the average number of negative ions

$$n_- \, dV = ne^{+\epsilon\Psi/kT} \, dV, \tag{197'}$$

where

$$n = \frac{N}{V} \tag{198}$$

is the number of positive or negative ions per c.c. of solution. Equation (197) must fulfil the condition that in the limit when $T = \infty$, the distribution must become uniform, i.e. the factor before the exponential expression must be n. (197) is, however, not sufficient alone to solve the problem, since the potential Ψ of the point P is as yet undetermined. The further solution is effected by means of Poisson's differential equation, according to which

$$\Delta\Psi = -\frac{4\pi}{D_0}\Pi, \tag{199}$$

where Π is the true charge density in a medium of dielectric constant D_0. Π can be easily obtained from (197), which gives for the amount of electricity in the volume element dV,

$$n\epsilon \, dV(e^{-\epsilon\Psi/kT} - e^{+\epsilon\Psi/kT}) = -2n\epsilon \, dV \sinh\frac{\epsilon\Psi}{kT}, \tag{200}$$

† Milner (*Phil. Mag.* **23** (1912), 551; **25** (1913), 743) has attempted to consider each possible arrangement of the ions, and to calculate its probability by Boltzmann's theorem. Fowler and Kramers have succeeded in carrying out the calculations of Debye and Hückel using strict statistical mechanics; they obtain in this way the same equation (204) for the potential in the neighbourhood of an ion, at least for dilute solutions. (Cf. Chapter XII.)

and hence for Π

$$\Pi = -2n\epsilon \sinh \frac{\epsilon\Psi}{kT}. \tag{201}$$

The potential Ψ is then given by the solution of the differential equation†

$$\Delta\Psi = \frac{8\pi n\epsilon}{D_0} \sinh \frac{\epsilon\Psi}{kT}. \tag{202}$$

If the energy of an ion $\epsilon\Psi$ is small compared with the mean energy of thermal agitation, kT, the above differential equation can be considerably simplified. This assumption,

$$\frac{\epsilon\Psi}{kT} \ll 1, \tag{203}$$

becomes more nearly true as the distance from the central ion increases, and Ψ decreases. It is in any case valid for dilute electrolyte solutions.‡ A strict statistical treatment leads to the simplified form of (202)§ which also follows from (202) and (203), and is

$$\Delta\Psi = \frac{8\pi n\epsilon^2}{D_0 kT}\Psi = \kappa^2\Psi. \tag{204}$$

In this equation κ has the dimensions of a reciprocal length. The corresponding length,

$$\frac{1}{\kappa} = \left(\frac{D_0 kT}{8\pi n\epsilon^2}\right)^{\frac{1}{2}} \tag{205}$$

is an important and characteristic quantity in Debye's theory, and replaces the mean separation of the ions in Ghosh's theory.‖ Before entering into a further discussion of the quantity $1/\kappa$ we shall show how the distribution of the mean potential round an ion of charge $+\epsilon$ can be calculated.

We shall call the distance of the point P from the ion in question r, and introduce polar coordinates. There is no reason to suppose that the potential depends upon the direction of the radius vector, and we shall assume the potential distribution to be symmetrical about the origin. We then have

$$\frac{\partial\Psi}{\partial x} = \frac{d\Psi}{dr}\frac{x}{r}, \qquad \frac{\partial\Psi}{\partial y} = \frac{d\Psi}{dr}\frac{y}{r}, \qquad \frac{\partial\Psi}{\partial z} = \frac{d\Psi}{dr}\frac{z}{r},$$

and hence

$$\Delta\Psi = \frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{dz^2} = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\Psi}{dr}\right).$$

† The full form of (202), corresponding to the most general case, is obtained from (199) and (215). See p. 270.

‡ The unsimplified form of (202) leads to the theory of more concentrated solutions developed by Grönwall, La Mer, and Sandved. (See p. 270.)

§ See Chapter XII.

‖ See p. 94.

Equation (204) thus becomes

$$\frac{1}{r}\frac{d^2}{dr^2}(r\Psi) = \kappa^2\Psi. \tag{206}$$

The solution of this equation is

$$\Psi = \frac{Ae^{-\kappa r}}{r} + \frac{A'e^{\kappa r}}{r} \tag{207}$$

as may be verified by substitution in (206). Since (206) is a second order differential equation, A and A' are arbitrary constants.

Since Ψ must vanish for infinite values of r,

$$A' = 0. \tag{208}$$

The constant A can be determined by considering the state of affairs in the immediate neighbourhood of the ion. If we are dealing with very dilute solutions, we can consider the distance r as great compared with the radius of the ion, i.e. we can consider the ion as being a point charge. In the absence of other ions, the potential due to a point charge $+\epsilon$ at a distance r in a medium of dielectric constant D_0 is $\epsilon/D_0 r$. The potential in (207) must approach this value for very small values of r, and the required expression for the mean potential is

$$\Psi = \frac{\epsilon}{D_0}\frac{e^{-\kappa r}}{r}. \tag{209}$$

This potential can be divided into two parts, the first Ψ_{I} being the potential which would be found in absence of the surrounding ions, and the second Ψ_{II} being the potential due to the ionic atmosphere. We therefore write

$$\Psi = \Psi_{\mathrm{I}} + \Psi_{\mathrm{II}} = \frac{\epsilon}{D_0}\frac{e^{-\kappa r}}{r}, \tag{209'}$$

where

$$\Psi_{\mathrm{I}} = \frac{\epsilon}{D_0}\frac{1}{r} \tag{210}$$

and

$$\Psi_{\mathrm{II}} = -\frac{\epsilon}{D_0}\left(\frac{1-e^{-\kappa r}}{r}\right). \tag{211}$$

The potential Ψ_{II}, caused by the ionic atmosphere, is the characteristic feature of the modern electrostatic theory.

In order to find how the electric density in the ionic atmosphere varies with the distance r from the central ion, we write

$$\Delta\Psi_{\mathrm{II}} = \kappa^2\Psi = \frac{\kappa^2\epsilon}{D_0}\frac{e^{-\kappa r}}{r}; \tag{212}$$

i.e. the electric density Π is

$$\Pi = -\frac{D_0 \kappa^2}{4\pi} \frac{\epsilon}{D_0} \frac{e^{-\kappa r}}{r} = -\frac{\kappa^2 \epsilon}{4\pi} \frac{e^{-\kappa r}}{r} \tag{213}$$

from (199) and (212). Π is very great near the ion, and decreases with increasing distance r. It is negative for a positive ion, i.e. the ionic atmosphere surrounding the given positive ion is negatively charged. Similarly, a negative ion will be surrounded by a positive ionic atmosphere. The decrease of electric density in the ionic atmosphere is determined by the characteristic length $1/\kappa$, which is often referred to simply as the thickness of the ionic atmosphere.

We shall now generalize the above calculation of the potential distribution round a given ion to include an electrolyte solution containing the ionic species $1,\ldots,i,\ldots,s$. The number of each of these species is respectively

$$n_1,\ldots,n_i,\ldots,n_s,$$

and the corresponding valencies

$$z_1,\ldots,z_i,\ldots,z_s.$$

These valencies may be either positive or negative. Since the total charge must be zero, we have

$$\epsilon \sum n_i z_i = 0. \tag{214}$$

We shall again consider a given central ion, and denote by Ψ the potential at a point P. Just as above, Boltzmann's theorem gives for the density of ions of the ith species

$$n_i e^{-z_i \epsilon \Psi / kT}.$$

The total density in a volume element near the central ion is thus

$$\Pi = \epsilon \sum_i n_i z_i e^{-z_i \epsilon \Psi / kT}. \tag{215}$$

We can introduce this expression for Π in Poisson's equation (199). Again considering only the first two terms in the expansion of the exponential function, we obtain for Ψ the equation

$$\Delta \Psi = \kappa^2 \Psi, \tag{216}$$

where in the general case†

$$\kappa^2 = \frac{4\pi\epsilon^2}{D_0 kT} \sum_i n_i z_i^2. \tag{217}$$

If the ion in question has the charge $z_i \epsilon$, the solution of equation (216)

† This value of κ^2 is written κ_0^2 in Chapter XI, where the term κ^2 is reserved for the value of (217) when the dielectric constant of the solution is inserted in place of D_0.

can be obtained exactly above, and we obtain for the potential round the ion i

$$\Psi = \frac{z_i \epsilon}{D_0} \frac{e^{-\kappa r}}{r}. \tag{218}$$

The electric density Π in the ionic atmosphere surrounding the ion i is given by

$$\Pi = -\frac{\Delta\Psi}{4\pi} D_0 = -\frac{D_0 \kappa^2 \Psi}{4\pi} = +\frac{n^2 z_i \epsilon}{4\pi} \frac{e^{-\kappa r}}{r}. \tag{219}$$

If we integrate to find the total charge present in the ionic atmosphere, we obtain

$$\int_0^\infty \Pi 4\pi r^2 \, dr = -z_i \epsilon, \tag{220}$$

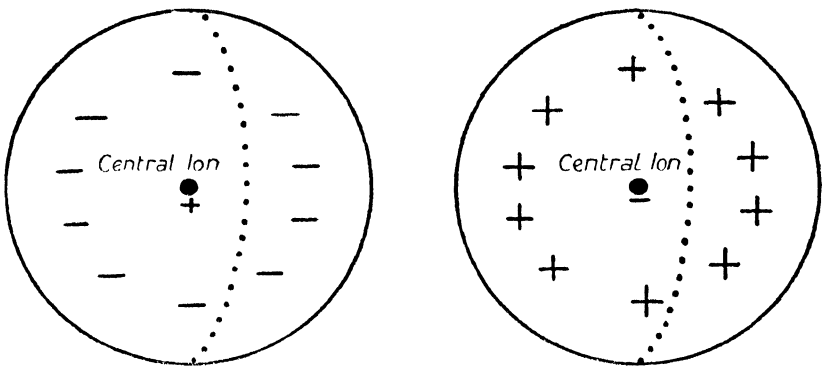

FIG. 18. The ionic atmosphere.

i.e. the total charge in the ionic atmosphere is equal to the charge on the central ion, but has the opposite sign.

We shall now consider further the characteristic length $1/\kappa$.

B. *The thickness of the ionic atmosphere.*

We have seen that the characteristic length $1/\kappa$ (defined by (217)) determines the decrease of the electric density in the ionic atmosphere. Fig. 18 shows this diagrammatically for a positive and a negative ion. $1/\kappa$ is the distance necessary for the electric density to decrease by the factor $1/e$. The formula for this thickness of the ionic atmosphere,

$$\frac{1}{\kappa} = \left(\frac{D_0 kT}{4\pi\epsilon^2 \sum n_i z_i^2} \right)^{\frac{1}{2}}, \tag{221}$$

can be somewhat simplified by means of the concept of ionic strength J introduced by Lewis and Randall.† If there are present in the solutions ν_1 ions, of species 1,..., ν_i of species i,..., ν_s of species s, we may

† Cf. p. 70.

introduce the molar concentration γ in moles per litre by the equation

$$\gamma_i = \frac{n_i \times 1{,}000}{\mathbf{N}} \quad (\mathbf{N} = 6{\cdot}06 \times 10^{23}), \tag{222}$$

the ionic strength being defined by the equation

$$J = \tfrac{1}{2} \sum \gamma_i z_i^2. \tag{223}$$

Combining (221) and (223), the characteristic length $1/\kappa$ can be expressed in terms of the ionic strength as

$$\frac{1}{\kappa} = \left(\frac{D_0 T}{2J}\right)^{\frac{1}{2}} 2{\cdot}81 \times 10^{-10} \text{ cm}. \tag{224}$$

If we are dealing with a single electrolyte which dissociates into ν_i ions we can write

$$\gamma_i = \nu_i \gamma \tag{225}$$

and

$$J = \tfrac{1}{2}\gamma \sum \nu_i z_i^2. \tag{226}$$

The thickness $1/\kappa$ will then be inversely proportional to the square root of the molar concentration γ. We can thus write (224) as

$$\frac{1}{\kappa} = 2{\cdot}81 \times 10^{-10} \left(\frac{D_0 T}{\gamma \sum \nu_i z_i^2}\right)^{\frac{1}{2}} \text{cm}. \tag{227}$$

The valency and the dielectric constant are thus the essential factors which determine the thickness $1/\kappa$ and are of paramount importance in the practical significance of the Coulomb forces between the ions. Given the temperature and the nature of the solvent and electrolyte, we can calculate the thickness of the ionic atmosphere at different molar concentrations. For water we have for

$$T = 291{\cdot}2 \qquad D_0 = 81{\cdot}3$$

$$T = 298{\cdot}2 \qquad D_0 = 78{\cdot}8,$$

and the thickness of the ionic atmosphere is given for single electrolytes by the formulae

$$\frac{1}{\kappa} = \frac{4{\cdot}33 \times 10^{-8}}{(\gamma \sum \nu_i z_i^2)^{\frac{1}{2}}} \quad (18°); \qquad \frac{1}{\kappa} = \frac{4{\cdot}31 \times 10^{-8}}{(\gamma \sum \nu_i z_i^2)^{\frac{1}{2}}} \quad (25°). \tag{228}$$

Table 19 shows the value of the thickness of the ionic atmosphere in water for different valence types, taking $\gamma = 0{\cdot}001$, $T = 291{\cdot}2$.

According to (228), the order of magnitude of the thickness of the ionic atmosphere is given by

$$\frac{1}{\kappa} \sim \frac{10^{-8}}{\gamma^{\frac{1}{2}}} \text{cm}. \tag{229}$$

It therefore increases with decreasing concentration and is increased tenfold in going from $\gamma = 0{\cdot}01$ to $\gamma = 0{\cdot}0001$.

TABLE 19

The thickness of the ionic atmosphere $1/\kappa$.

$\gamma = 0{\cdot}001$, $T = 18°$ C., solvent water.

Valency type	*Thickness* $1/\kappa$ *in cm.*
1-1 valent	$96{\cdot}6 \times 10^{-8}$
1-2 ,,	$55{\cdot}9 \times 10^{-8}$
2-2 ,,	$48{\cdot}4 \times 10^{-8}$
1-3 ,,	$39{\cdot}5 \times 10^{-8}$
1-4 ,,	$30{\cdot}4 \times 10^{-8}$
2-4 ,,	$27{\cdot}8 \times 10^{-8}$

We shall now deal with the second important property of the ionic atmosphere, its time of relaxation.

C. *The time of relaxation of the ionic atmosphere.*

The time of relaxation of the ionic atmosphere was first calculated by Debye and Falkenhagen† for certain simple electrolytes. It is of great importance in the irreversible phenomena of electrolytic conduction, and is the cause of certain special effects which have subsequently been verified experimentally, e.g. the dependence of conductivity upon frequency.‡ The meaning of the term 'time of relaxation of the ionic atmosphere' may be illustrated as follows. If we imagine the charge of the central ion suddenly removed at a certain instant ($t = 0$) the cause of the uneven distribution in the ionic atmosphere is also removed. If we now observe the electric intensity in the atmosphere surrounding the point from which the central charge was removed at $t = 0$, its variation with time can be characterized by a time Θ which we term the time of relaxation. The following considerations show its quantitative significance. Let dQ_e be the amount of electricity enclosed between two spheres of radii r and $r+dr$, where r is the distance from the central ion. If the charge of the central ion is e_1, it will be shown later§ that

$$dQ_e = -y\kappa e_1 \, dr. \tag{230}$$

y is a measure of the electric density in a spherical shell of radius r and thickness dr. Fig. 19 shows y as a function of κr for the times

$$t = 0, \quad t = 0{\cdot}25q\Theta, \quad t = q\Theta.$$

† P. Debye and H. Falkenhagen, *Phys. Z.* **29** (1928), 401. ‡ See p. 222.

§ P. Debye and H. Falkenhagen, *Phys. Z.* **29** (1928), 121. This paper gives only a qualitative calculation of the disappearance of the equilibrium condition. Debye gave later (*Sommerfeld Festschrift*, p. 52, Leipzig, 1928) a quantitative calculation for the special case of binary electrolytes with ions of equal mobility. The more general treatment in the present work (see p. 176) is due to the author.

Θ is the time of relaxation and q is a factor depending on the valencies and mobilities of the ions. The value of q lies between

$$\frac{|z_1|}{|z_1|+|z_2|} \quad \text{and} \quad \frac{|z_2|}{|z_1|+|z_2|},$$

and is $\frac{1}{2}$ for binary electrolytes. Θ is defined so that the electric density in the ionic atmosphere has practically speaking disappeared after time $4q\Theta$. In the case of binary electrolytes the electric density is thus practically zero after time 2Θ. Θ is not only dependent on the factors which determine the thickness of the ionic atmosphere $1/\kappa$ (see (227)), but depends also upon the mobilities of the ions. Calculation shows

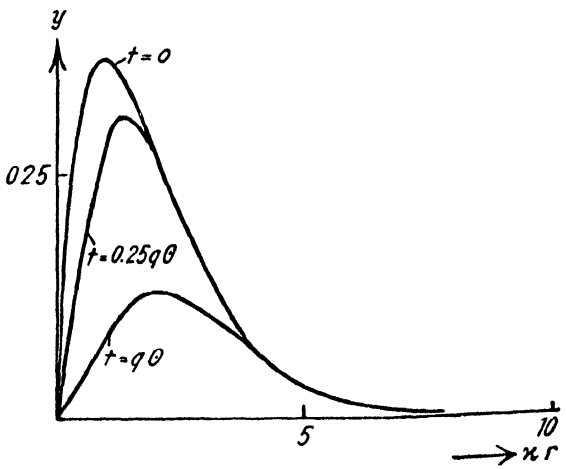

FIG. 19. Variation of electric density with time.

that the time of relaxation is given by

$$\Theta = \frac{|z_1||z_2|}{|z_2|l_1+|z_1|l_2}\,\frac{15{\cdot}34\times10^{-8}}{kTq}\,\frac{1}{\kappa^2}, \tag{231}$$

where q is defined by† $$\frac{|z_1||z_2|}{|z_1|+|z_2|}\,\frac{l_1+l_2}{|z_2|l_1+|z_1|l_2}, \tag{232}$$

and the square of the thickness of the ionic atmosphere by (227), i.e.

$$\frac{1}{\kappa^2} = \frac{7{\cdot}90\times10^{-20}\,D_0\,T}{\gamma(\nu_1 z_1^2+\nu_2 z_2^2)}. \tag{233}$$

For simple electrolytes the order of magnitude of the time of relaxation Θ is given by†

$$\Theta \sim \frac{10^{-10}}{\gamma}\ \text{sec.} \tag{234}$$

† l_i, the mobility of the ion at infinite dilution, is defined by $\Lambda_\infty^* = \sum l_i$.

‡ In a series of papers to appear shortly the author and W. Fischer have extended the treatment to the general case of mixtures. The results serve to explain the interesting experimental results of Spaght (*Phys. Z.* **33** (1932) 534).

The following table gives the numerical values of Θ in water for $\gamma = 0{\cdot}001$.

TABLE 20

The time of relaxation for some salts in aqueous solution.

$\gamma = 0{\cdot}001$.

Electrolyte	*Time of relaxation* Θ, *seconds*	*Temperature, °C.*	*Corresponding wave-length, metres*
KCl	$0{\cdot}553 \times 10^{-7}$	18°	16·6
HCl	$0{\cdot}189 \times 10^{-7}$	18°	5·67
LiCl	$0{\cdot}732 \times 10^{-7}$	18°	22·0
$MgCl_2$	$0{\cdot}324 \times 10^{-7}$	18°	9·72
$CdSO_4$	$0{\cdot}315 \times 10^{-7}$	18°	9·45
$LaCl_3$	$0{\cdot}162 \times 10^{-7}$	18°	4·86
$K_4Fe(CN)_6$	$0{\cdot}102 \times 10^{-7}$	25°	3·06
$Ca_2Fe(CN)_6$	$0{\cdot}113 \times 10^{-7}$	25°	3·39

The meaning of the wave-lengths given in Table 20 will be explained later in connexion with the dependence of conductivity on frequency.†

Of the two essential properties of the ionic atmosphere the thickness $1/\kappa$ is the determining factor in reversible thermodynamic phenomena, while the time of relaxation Θ is of importance in dealing with the phenomena of conductivity. The plan of the next few chapters is based on this division, the thermodynamics of strong electrolytes being dealt with first, and then the phenomena of conductivity.

Note 1. Literature on the Debye-Milner theory of strong electrolytes

S. R. Milner, *Phil. Mag.* (6) **23** (1912), 551; **25** (1913), 742; **35** (1918), 214, 352; *Trans. Farad. Soc.* **15** (1919), 148; P. Debye, *Hand. XIXe Nederlandsch Natuur- en Geneeskundig Congres*, Maastricht, 1923; Debye and E. Hückel, *Phys. Z.* **24** (1923), 185; L. Onsager, ibid. **27** (1926), 388; **28** (1927), 277; Debye and H. Falkenhagen, ibid. **29** (1928), 121, 401. See also the following reviews: E. Huckel, *Ergebn. d. exakt. Naturwiss.* **3** (1924), 199; N. Bjerrum, ibid. **5** (1926), 125; W. Orthmann, ibid. **6** (1927), 155; E. Baars, *Handb. d. Phys. von Geiger-Scheel*, xiii (1928), 397–516; V. K. La Mer, *Trans. Am. Electrochem. Soc.* **41** (1927), 507; A. A. Noyes, *J. Am. Chem. Soc.* **46** (1924), 1080, 1098; *Trans. Farad. Soc. Symposium* (1927), 334–544; reviews by M. Wien, G. Joos, and E. Lange, *Phys. Z.* **29** (1928), 751; Ulich and Birr, *Z. angew. Chem.* **41** (1928), 443, 467, 1075; F. Förster, ibid. **41** (1928), 1013; N. Bjerrum, *Ber.* **62** (1929), 1091; H. van Veldhuizen, *Chem. Weekblad*, **27** (1930), 486, 681; H. Falkenhagen, *Chemiker-Kalender*, III (1931), 346; *Rev. Modern Phys.* **3** (1931), 412; Debye, *Z. Elektrochem.* **39** (1933), 478; 'Symposium on electrolytes', *Chem. Rev.* August 1933.

† See p. 182.

VIII

THE THERMODYNAMICS OF STRONG ELECTROLYTES ACCORDING TO DEBYE'S THEORY

27. The Mean Potential Energy of the Central Ion

We shall again begin by considering a mono-monovalent electrolyte. (209) gives the mean potential in the neighbourhood of a given positive ion of charge $+\epsilon$. The potential due to the ionic atmosphere is given by the second part of (209), which becomes $-\epsilon\kappa/D_0$ for small values of r; i.e. the potential due to the ionic atmosphere at the point occupied by the central ion is $-\epsilon\kappa/D_0$. In other words, in a dilute solution the potential produced at a given ion by all the other ions is equal to that which would be produced by a single ion having a charge equal and opposite to that of the first ion, and separated from it by a distance equal to the thickness of the ionic atmosphere.

We shall now calculate the potential energy u of the central ion with respect to its surroundings. This is given by

$$u = \int_0^\infty \frac{\epsilon \Pi}{D_0 r} 4\pi r^2 \, dr,$$

where Π is the electric density in the ionic atmosphere, given by (213). Integration gives

$$u = -\frac{\epsilon^2}{D_0}\kappa. \tag{235}$$

The same value for u follows directly from (211).

We shall now derive the expression for the potential energy of an ion with respect to its ionic atmosphere. (218) gives the value of the potential due to the ionic atmosphere. For small values of r this leads to

$$\Psi_i = -\frac{z_i \epsilon \kappa}{D_0} \tag{236}$$

for the potential at an ion with charge $z_i \epsilon$. The potential energy of the central ion with respect to its surroundings is therefore

$$u_i = -\frac{z_i^2 \epsilon^2 \kappa}{D_0}. \tag{237}$$

28. The Electric Energy of the Ionic Solution

We shall first consider the total mutual potential energy of the ions with respect to their ionic atmospheres, again considering mono-monovalent electrolytes first for the sake of simplicity. The potential energy

of one ion of charge $+\epsilon$ is given by (235). We have altogether N positive ions, at a potential $-\epsilon\kappa/D_0$ with respect to their surroundings, and N negative ions at a potential $\epsilon\kappa/D_0$.

The total potential energy† is therefore

$$U_e = \frac{N\epsilon}{2}\left(-\frac{\epsilon\kappa}{D_0}\right) - \frac{N\epsilon}{2}\left(+\frac{\epsilon\kappa}{D_0}\right) = -\frac{N\epsilon^2\kappa}{D_0}, \tag{238}$$

since if we have a number of charges e_i at points where the potentials are Ψ_i', the total potential energy is given by

$$U_e = \tfrac{1}{2}\sum e_i \Psi_i'. \tag{238'}$$

(227) shows that κ, and therefore also the potential energy of the solution U_e, is proportional to the square root of the concentration.‡

This result can easily be generalized for an electrolyte containing $N_1,\ldots,N_i,\ldots,N_s$ ions of valencies $z_1,\ldots,z_i,\ldots z_s$. In this case the potential energy of the central ion with respect to its ionic atmosphere is given by (237) and the potential energy of the solution is then given by (236) and (238') as

$$U_e = -\sum_i \frac{N_i z_i^2 \epsilon^2 \kappa}{2D_0}. \tag{238''}$$

In this case the reciprocal length κ is defined by the generalized equation (227).

29. Calculation of the Electric Work W necessary to discharge and recharge the Ions. The Limiting Law for Osmotic Coefficients

We shall now calculate the electric work W necessary to remove and replace the charges on the ions. In order to clarify the somewhat obscure considerations involved, we shall deal with the osmotic pressure of the solution. We have previously§ derived the equation of van 't Hoff for the osmotic pressure of ideal dilute solutions. If n' is the

† Since we need only the mutual potential energy of the ions with respect to their ionic atmosphere, (238') contains only the portion of the potential energy due to the charges in the atmosphere, i.e. the portion corresponding to Ψ_n' in (209'). We obtain therefore the potential at the point occupied by the charge e_i.

‡ Ghosh finds that the potential energy of the solution is proportional to the cube root of the concentration, which cannot be the case. Milner's formula agrees with (235) except for the numerical factor: he finds

$$u = -\frac{e^2\kappa}{D_0}\sqrt{(\tfrac{1}{2}\pi)}.$$

The difference between the two factors probably depends upon the less accurate graphical method employed by Milner. T. S. Wheeler (*Phys. Z.* **32** (1931), 674) has shown that the factor in Milner's formula should be $(\frac{1}{8}\pi)^{\frac{1}{2}}$ instead of $(\frac{1}{2}\pi)^{\frac{1}{2}}$.

§ See p. 20.

number of molecules and ions contained in 1 c.c., then the ideal osmotic pressure is given by (56′) as

$$\bar{P} = n'kT. \tag{239}$$

We have previously seen† that the actual osmotic pressure of an electrolyte solution differs from this ideal value. This difference can be interpreted in terms of Debye's theory of the interionic forces in the following way.‡

We begin by considering a practically infinitely dilute solution containing the same amounts of dissolved solute as the final solution of finite concentration, i.e. $N_1,\ldots,N_i,\ldots,N_s$ particles of species having charges $e_1,\ldots,e_i,\ldots,e_s$. The particles may be either ions, molecules, or atoms, so that some of the charges may be zero. This infinitely dilute solution may be converted isothermally and reversibly into the solution of finite concentration in two ways. According to the laws of thermodynamics, the work obtained in the two cases must be the same, and must be equal to the difference in the free energies of the infinitely dilute solution, and the solution of volume V.

The first way consists of compressing the solution infinitely slowly and isothermally with a semi-permeable piston, thereby transforming it from the original state of very high dilution and volume Ω to the final state of volume V. The piston is permeable to solvent, but not to solute. At any stage of the process the pressure upon the piston is the osmotic pressure P, and the work corresponding to a volume change dV is $P\,dV$. The total work done during the compression is therefore

$$A = -\int_{\Omega}^{V} P\,dV. \tag{240}$$

The second way is as follows. We first consider the very dilute solution, and imagine the charges e_i on the ions removed infinitely slowly. This process would be impossible in practice, since it is impossible to sub-divide the charge on the electron. This fact does not, however, constitute an objection against the employment of the process in a theoretical argument, any more than the impossibility of obtaining semi-permeable membranes precludes their use in theory. Since the charges are now absent, the solution may be considered as being perfect. It is now compressed isothermally and infinitely slowly by means of a

† See p. 48.

‡ P. Debye, *Phys. Z.* **25** (1924), 97. Gross and Halpern (*Phys. Z.* **26** (1925), 403) have criticized Debye's derivation. It can, however, easily be shown that Debye's result is correct by employing the mean value of the potential introduced on p. 100.

semi-permeable piston to the volume V, and finally the charges e_i are restored infinitely slowly. The total work done in this process may be divided into two parts. The work done during the isothermal compression is

$$\bar{A} = -\int_{\Omega}^{V} \bar{P}\, dV, \tag{241}$$

where $\bar{P}$ is the ideal osmotic pressure. The electrical work done in removing and restoring the charges will be termed W, so that the total work done in the second type of process is $\bar{A}+W$. By the laws of thermodynamics, this work must be equal to the work done in the first process, i.e.

$$A = \bar{A}+W. \tag{242}$$

We can now consider the same two processes, but this time with compression to $V+dV$ instead of V. Equations (240) and (241) then hold with the substitution of $V+dV$ for V, and the required osmotic pressure is obtained by subtraction. The same result is easily obtained by differentiating (241) and (242) with respect to V at constant temperature. This gives

$$\frac{\partial A}{\partial V} = -P, \qquad \frac{\partial \bar{A}}{\partial V} = -\bar{P} \tag{243}$$

and

$$P = \bar{P} - \frac{\partial W}{\partial V}. \tag{244}$$

Thus if we know $\partial W/\partial V$ (the dependence on the volume of the work done in carrying out the discharging and recharging process) as a function of the temperature, the osmotic equation of state of the solution is determined.

We shall now proceed to calculate W, and it will be found that for fairly dilute solutions, work is actually obtained in carrying out the discharging and recharging process. Further, the amount of work obtained increases as the final volume of the solution V decreases. $\partial W/\partial V$ is therefore positive, and the actual osmotic pressure P is less than the ideal value $\bar{P}$.

The electric work W is made up of two parts, the first of which is the work necessary to discharge the ions in the infinitely dilute solution, and the second the work necessary to recharge them in the solution of finite concentration. We shall imagine the operations of charging and discharging carried out in such a way that the charge on the ion i at any moment is given by the product λe_i. λ is a function of the time, which decreases gradually from 1 to 0 in the discharging process, and increases from 0 to 1 in the process of charging. If a sphere of radius b_i is given

a charge of e_i in a medium of dielectric constant D, it can be shown that the work done is $e_i^2/2Db_i$. Thus if we consider the ion as a sphere of radius b_i, the potential at its surface at the moment characterized by λ is given by

$$\Psi_i''(\lambda) = \frac{e_i \lambda}{Db_i},$$

and the corresponding work done in discharging the ion in infinitely dilute solution is

$$-e_i \int_0^1 \Psi''(\lambda)\, d\lambda = -\frac{e_i^2}{2D_0 b_i}, \tag{245}$$

where D_0 is the dielectric constant of the pure solvent. In the second part of the process, the ions are recharged in the solution of finite concentration, and the work done is analogously $c_i^2/2Db_i$, where D is the dielectric constant of the solution. On account of alterations in the electrical nature of the surroundings of the ion, D will in general differ from D_0. Investigations of the variation of the dielectric constant with concentration have led to very contradictory results, and the question is not yet by any means cleared up. It is, however, justifiable in sufficiently dilute solutions to identify D with D_0, the dielectric constant of the pure solvent. The difference between the two is certainly so small that the corresponding work term will be small compared with the term arising from the Coulomb forces between the ions. We can thus write for sufficiently dilute solutions.

$$-\frac{e_i^2}{2D_0 b_i} + \frac{e_i^2}{2Db_i} = 0. \tag{246}$$

Recent investigations by Wien appear to show (in opposition to previous results) that the dielectric constant of ionic solutions is greater than that of the pure solvent, the increase being proportional to the square root of the concentration in dilute solution, as required by the theoretical predictions of Debye and Falkenhagen (see p. 182). Wien's results also show that the expression in (246) probably differs very little from zero even in more concentrated solutions. These considerations probably do not apply to non-aqueous solutions.

The above derivation assumes that the dielectric constant does not change during the charging of the ions. This is not strictly true, and actually we should employ a mean value, which could be calculated from the final value D, if the dependence of the dielectric constant on the charge e_i were known. It is, however, allowable to use the value D in fairly dilute solutions. It is also strictly speaking necessary to take into account the fact that the dielectric constant in the neighbourhood of an ion is not the same as the macroscopic dielectric constant of the solution. Any error introduced on this account will, however, be the same in both the charging and the discharging process, and will therefore cancel out.

We shall now evaluate the work term arising from the Coulomb forces, making use of equation (236), which gives the value of the potential at

the point occupied by an ion of the ith sort, due to its ionic atmosphere. If at any moment the charges have reached the values

$$\lambda e_1, \ldots, \lambda e_i, \ldots, \lambda e_s,$$

the potential will have the value $\lambda^2 \Psi_i$, since κ is by (221) proportional to λ. The increase in the charge of an ion of the ith sort during an element of time may be written as $e_i\, d\lambda$, and the work done on the ion during this element is therefore

$$e_i \Psi_i \lambda^2\, d\lambda;$$

i.e. the product of the potential and the alteration in charge. The total electric work is then given by integrating from $\lambda = 0$ to $\lambda = 1$, and summing over all the particles contained in the liquid, i.e.

$$W = \sum \frac{N_i e_i \Psi_i}{3} = -\sum \frac{N_i e_i^2 \kappa}{3D_0}, \tag{247}$$

where W is the required total electric work.

The difference between U_e (cf. (238)) and W may be explained as follows. $-U_e$ is the work done in removing the charge from the ions, keeping them fixed in their original configuration, and then restoring the charge at infinite dilution. W, on the other hand, is the energy necessary when at any stage of the discharging process the ions have the distribution corresponding to their degree of charge at that instant. The energy necessary to separate the ions is smaller in the latter case, since in setting up each distribution the thermal motion does work against the interionic forces.

In order to calculate the osmotic pressure, we must differentiate the electrical work W with respect to the volume V. It must be noted that the expression for κ (221) contains V implicitly, since

$$n_i = \frac{N_i}{V}. \tag{248}$$

We have

$$\frac{\partial W}{\partial V} = \frac{\partial W}{\partial \kappa}\frac{\partial \kappa}{\partial V} = -\sum \frac{N_i e_i^2}{3D_0}\frac{\partial \kappa}{\partial V}, \tag{249}$$

and from (221)

$$\frac{\partial \kappa}{\partial V} = -\frac{\kappa}{2V}; \tag{250}$$

so that

$$\frac{\partial W}{\partial V} = \sum \frac{n_i e_i^2 \kappa}{6D_0}, \tag{251}$$

and from (244)

$$P = \bar{P} - \sum \frac{n_i e_i^2 \kappa}{6D_0}. \tag{252}$$

Since the osmotic pressure of the ideal dilute solution is given by

$$\bar{P} = \sum n_i kT, \tag{253}$$

the osmotic pressure of the real solution becomes

$$P = \sum \left(1 - \frac{e_i^2 \kappa}{6D_0 kT}\right) n_i kT. \tag{254}$$

The actual osmotic pressure can therefore be obtained from the equation for ideal solutions if we employ in place of the real volume concentrations fictive concentrations obtained by multiplying the real values by the factors

$$g_i = 1 - \frac{e_i^2 \kappa}{6D_0 kT}. \tag{255}$$

The osmotic pressure of the real solution can thus be written in the form

$$P = \sum g_i n_i kT. \tag{256}$$

The factors g_i, which will differ from unity for all charged particles, have been termed by Bjerrum the osmotic coefficients of the ions. If a solution contains n molecules of a salt in 1 c.c. giving νn ions in infinitely dilute solution, Bjerrum† defines the osmotic coefficient of the salt by the equation

$$P = g \sum n_i kT. \tag{257}$$

We thus have

$$g = \frac{\sum g_i n_i}{\sum n_i} = \frac{\sum \nu_i g_i}{\sum \nu_i}, \tag{258}$$

which can be written as

$$1 - g = 1 - \frac{\sum n_i g_i}{\sum n_i}, \tag{259}$$

or, from (255),

$$1 - g = \frac{\sum n_i e_i^2 \kappa}{6D_0 kT \sum n_i}. \tag{259'}$$

(224) gives the relation between κ^2 and the ionic strength J, leading to the relation

$$1 - g = \frac{1{\cdot}39 \times 10^6}{(D_0 T)^{\frac{3}{2}}} \frac{\sum \nu_i z_i^2}{\nu} \sqrt{J}. \tag{259''}$$

Introducing the valency factor w defined by

$$w = \left(\frac{\sum \nu_i z_i^2}{\nu}\right)^{\frac{3}{2}} \tag{260}$$

we have

$$1 - g = \frac{0{\cdot}985 \times 10^6}{(D_0 T)^{\frac{3}{2}}} w(\nu\gamma)^{\frac{1}{2}}. \tag{261}$$

For the special case of water at 0° ($D_0 = 88{\cdot}2$, $T = 273$) this becomes

$$1 - g = 0{\cdot}263 w(\nu\gamma)^{\frac{1}{2}}. \tag{262}$$

These formulae contain several important predictions, which have in most cases been verified for extremely dilute solutions.‡ Formulae (261)

† N. Bjerrum, *Fysisk Tidsskr.* **15** (1916), 66; *Z. f. Elektrochem.* **42** (1918), 325.

‡ For certain discrepancies which arise, see pp. 119, and 270. G. Scatchard and S. S. Prentiss (*J. Am. Chem. Soc.* **54** (1932), 2696) have recently found that the chloride,

and (262) for the osmotic coefficient can of course also be tested by measurements of freezing-point depression, boiling-point elevation, and lowering of vapour pressure. The points to be tested are the dependence of the osmotic coefficient upon concentration, valency, dielectric constant and temperature, as well as the absolute values of the constants in (259′) and (259″). A series of excellent measurements are available for the freezing-point depression of very dilute solutions of strong electrolytes.† Fig. 20 shows the values of $1-g$ for four electrolytes of different types, plotted against the square root of the ionic concentration $(\nu\gamma)^{\frac{1}{2}}$. The straight lines in the figure represent the theoretical limiting law, their slopes being given by the factor $0{\cdot}263w$ (cf. (262)). The valency factor w is given by (260) and has the following values for the salts considered,

$$\mathrm{KCl} : w = 1 \qquad \mathrm{BaCl_2} : w = 2\sqrt{2}$$
$$\mathrm{La(NO_3)_3} : w = 3\sqrt{3} \qquad \mathrm{MgSO_4} : w = 4\sqrt{4}.$$

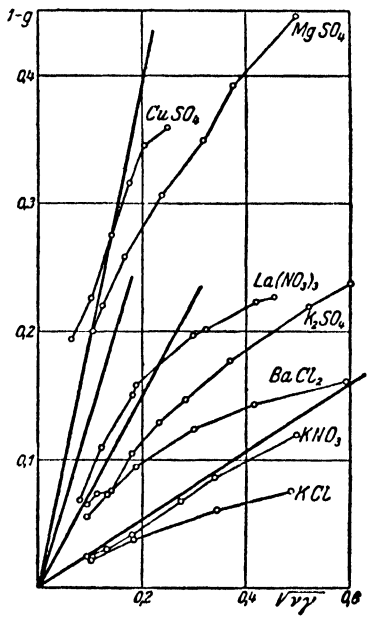

FIG. 20. Osmotic coefficients of electrolytes in water.

Fig. 20 shows that the observed values approach the limiting theoretical straight line at very small concentrations. There are, however, undoubted deviations from the limiting law even at lowest concentrations measured, and it must be emphasized that no real proof of the square-root law can be obtained from freezing-point measurements. (Such a proof was first afforded by solubility measurements, see § 31.)

Recent experimental work‡ has shown that the lower the concentration, the better is the agreement between the experimental results and equation (262). This is illustrated by Figs. 21–3. Fig. 21 shows $1-g$ for mono-monovalent electrolytes plotted against $\sqrt{\gamma}$, the results being taken from Hovorka and Rodebush, Randall and Vanselow, and Adams.

bromide, iodide, nitrate, and sulphate of ammonium deviate considerably from the Debye-Huckel limiting law for osmotic coefficients. This fact remains at present unexplained.

† See e.g. B. T. G. Bedford, *Proc. Roy. Soc.* **83** (1909), 454; L. H. Adams, *J. Am. Chem. Soc.* **37** (1915), 481; R. E. Hall and W. D. Harkins, ibid. **38** (1916), 2658.

‡ See e.g. W. H. Rodebush and F. Hovorka, *J. Am. Chem. Soc.* **47** (1925), 1614; M. Randall, ibid. **48** (1916), 2512; Randall and A. M. L. White, ibid. **48** (1926), 2514; Randall and A. P. Vanselow, ibid. **46** (1924), 2418; Randall and G. N. Scott, ibid. **49** (1927), 647.

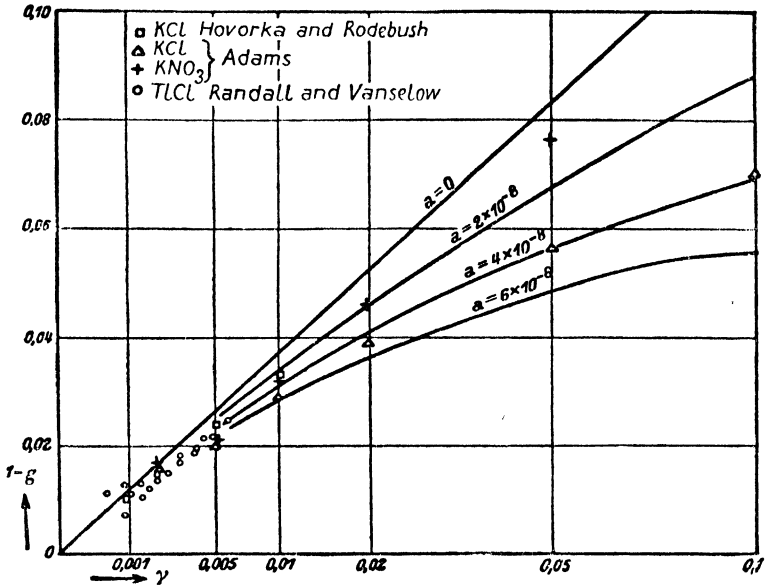

FIG. 21. Osmotic coefficients in dilute solution.

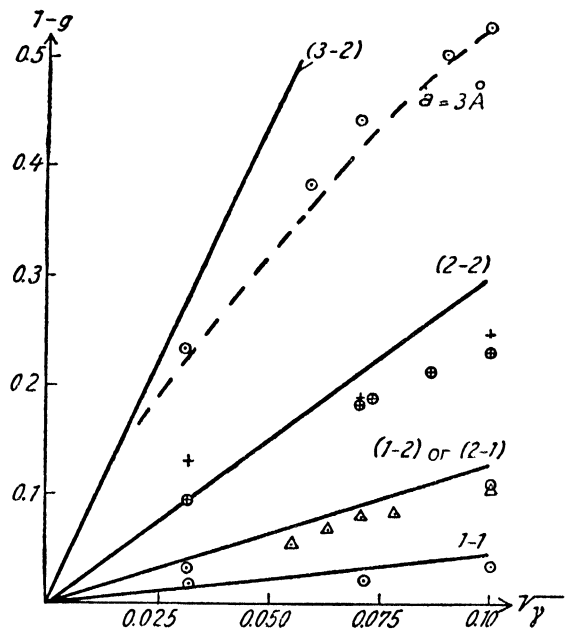

FIG. 22. The effect of valency on the osmotic coefficients.

The figure shows that the curves connecting the experimental points approach very near to the limiting straight line. (The meaning of the a-values in the figure will be explained in § 51.) Fig. 22 shows the results

of Hall and Harkins for K_2SO_4 (Δ ⊙) and those of Adams for KCl (⊙). $MgSO_4$ (⊕) and $CuSO_4$ (+) are taken as examples of 2-2-valent electrolytes, and $La_2(SO_4)_3$ as a 3-2-valent. Fig. 23 illustrates the principle of the ionic strength, $1-g$ being plotted against $\sqrt{J'}$ for electrolytes of different valency types.

The work of Baxter† with water at 75° shows that the theory predicts correctly the effect of temperature.

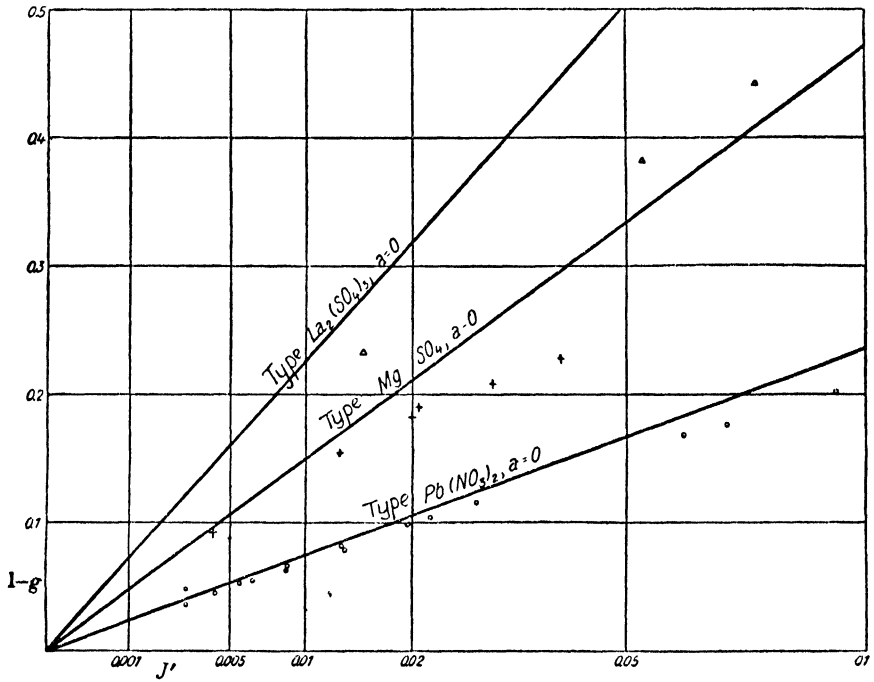

FIG. 23. The variation of osmotic coefficient with ionic strength.

According to (261) the osmotic coefficient should depend largely upon the dielectric constant, $1-g$ being inversely proportional to $D_0^{\frac{3}{2}}$. Frivold‡ measured the boiling-point elevation for solutions of LiCl down to 0·005 N. in methyl, ethyl, and propyl alcohols, having dielectric constants of 22·7, 18·7, and 8·4. The concentrations were, however, too high, and the accuracy too low to make it possible to test the Debye-Hückel limiting law. The measurements do, however, appear to approach the theoretical straight line, and the slope increases with decreasing dielectric constant, as required by the theory. Frivold§ then

† W. P. Baxter, *J. Am. Chem. Soc.* **48** (1926), 615.
‡ O. E. Frivold, *Phys. Z.* **25** (1924), 465.
§ O. E. Frivold, *J. Phys. Chem.* **30** (1925), 1153.

extended his measurements to $CoCl_2$ and $La(NO_3)_3$ and obtained much steeper curves which again appear to approach the limiting theoretical straight lines.

Schreiner and Frivold† tested the theory by carrying out freezing-point measurements with lithium salts in cyclohexanol. This solvent has a dielectric constant of 15 and melts at 23·4°, and is thus a very suitable solvent for such a test. Calculation shows that $1-g$ should be theoretically 12·4 times as great as in water. Fig. 24 shows that the theory appears to be confirmed. Schreiner, Frivold, and Ender‡ subsequently extended their measurements in cyclohexanol to include salts

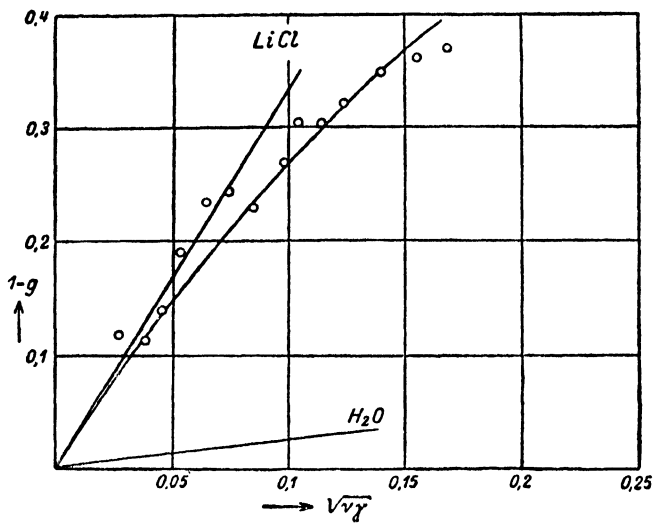

FIG. 24. The osmotic coefficient of lithium chloride in cyclohexanol.

with di- and tri-valent cations, i.e. LiCl, $VO_2(C_2H_3O_2)_2$, $La(NO_3)_3$, and mixtures of LiCl and $La(NO_3)_3$. In the case of $La(NO_3)_3$, the results obtained appear to be incompatible with the theory.§ It should, however, be pointed out|| that these measurements were carried out with a Beckmann thermometer, and not with the more reliable thermo-element.

30. The Limiting Law for Activity Coefficients

According to the laws of thermodynamics, the work done upon a system at constant temperature is equal to the increase in the free energy F of the system (cf. (17)). We have just calculated the work

† E. Schreiner and O. E. Frivold, *Z. phys. Chem.* **124** (1926), 1.

‡ E. Schreiner, O. E. Frivold, and F. Ender, *Phil. Mag.* (7) **8** (1929), 669.

§ The curve obtained resembles that shown in Fig. 83, p. 255.

|| Cf. V. K. La Mer, *Trans. Am. Electrochem. Soc.* **51** (1927), 507.

done upon an electrolytic solution when the concentration is changed isothermally and reversibly by means of a semi-permeable piston (cf. (247)).† In the case of an ideal solution, the increase in free energy is measured by the work term $\bar{A}$. Since at infinite dilution there is no difference between the ideal and the real solution, the term W represents the quantity which must be added to the free energy of the ideal system in order to obtain the free energy of the real system. We can therefore write

$$F = \bar{F} + W, \tag{263}$$

where $\bar{F}$ represents the ideal free energy of the solution. Gibbs has shown that since most measurements are carried out at constant temperature and pressure, it is more convenient to use the thermodynamic potential Φ. This is defined by (9) and (11) as

$$\Phi = F + pV.$$

Hence if we can neglect the term pV, any relation between the real and ideal free energy will also apply to the real and ideal thermodynamic potentials. Since we can regard the electrolyte as incompressible, we can therefore write

$$\Phi = \bar{\Phi} + W. \tag{264}$$

The thermodynamic potential of an ideal solution is defined by (35) as‡

$$\bar{\Phi} = \sum_0^s N_i(\bar{\phi}_i + kT \log \eta_i), \tag{265}$$

where N_0 molecules of the solvent contain $N_1, \ldots, N_s$ molecules, atoms, or ions. The $\bar{\phi}_i$'s depend only on the pressure and temperature, and not on the concentrations.

The thermodynamic potential of the real solution then follows from (247), (264), and (265),

$$\Phi = \sum_0^s N_i\left(\bar{\phi}_i + kT \log \eta_i - \frac{e_i^2 \kappa}{3D_0}\right). \tag{266}$$

The term added to Φ is thus

$$-\sum_0^s \frac{N_i \kappa e_i^2}{3D_0},$$

the single terms of which are proportional to $N_i \kappa$, i.e. to the $\frac{3}{2}$th power of the concentration. It is thus clear that older attempts to represent Φ as a power series involving only integral powers of N_i were bound to

† The whole system comprises both the solution below the semi-permeable membrane and above it.

‡ Remembering that $\phi_i/\mathbf{N} = \bar{\phi}_i$, $\mathbf{N}k = R$, and $M_i\mathbf{N} = N_i$.

fail.† The change of the thermodynamic potential with changing N_i, temperature and pressure being kept constant, is given by (266) as

$$\delta\Phi = \sum_{i=0}^{s} \delta N_i \left[\bar{\phi}_i + kT \log \eta_i - \frac{e_i^2 \kappa}{3D_0} - \sum_{j=0}^{s} \frac{e_j^2}{3D_0} N_j \frac{\partial \kappa}{\partial N_j} \right]. \tag{267}$$

We have also from (217)

$$\sum_j N_j e_j^2 \frac{\partial \kappa^2}{\partial N_i} = \sum_j \frac{4\pi}{D_0 kT} \frac{N_j e_j^2}{V} = e_i^2 \kappa^2. \tag{268}$$

If the index i refers to the dissolved particles, i.e. one of the values $i = 1,\ldots, s$, we have

$$\sum_{j=0}^{s} \frac{e_j^2}{3D_0} N_j \frac{\partial \kappa}{\partial N_i} = \frac{e_i \kappa}{6D_0} \qquad \text{for } i = 1,\ldots, s. \tag{269}$$

If, on the other hand, $i = 0$, i.e. we are dealing with variations in the solvent, we may proceed as follows. We can write the total volume of the solution V in the linear form

$$V = v_0 N_0 + \sum_1^s N_i v_i, \tag{270}$$

where v_0 and v_i represent the changes in the total volume caused by adding respectively a molecule of the solvent or a particle of the ith sort to the solution. We then have from (250) and (270)

$$\frac{\partial \kappa}{\partial N_0} = \frac{\partial \kappa}{\partial V} \frac{\partial V}{\partial N_0} = v_0 \frac{\partial \kappa}{\partial V} = -\frac{v_0}{2V} \kappa, \tag{271}$$

and hence,

$$\sum_j \frac{e_j^2}{3D_0} N_j \frac{\partial \kappa}{\partial N_0} = -v_0 \frac{n_j e_j^2 \kappa}{6D_0}. \tag{272}$$

The total variation in thermodynamic potential is thus

$$\delta\Phi = \delta N_0 \left[\bar{\phi}_0 + kT \log \eta_0 + v_0 \sum_j \frac{n_j e_j^2 \kappa}{6D_0} \right] + \\ + \sum_1^s \delta N_i \left[\bar{\phi}_i + kT \log \eta_i - \frac{e_i^2 \kappa}{2D_0} \right]. \tag{273}$$

In connexion with equation (270) it may be mentioned that O. Redlich and P. Rosenfeld (*Z. phys. Chem.* **155 A** (1931), 65; *Naturwiss.* **19** (1931), 231; *Z. Elektrochem.* **37** (1931), 705) have recently derived a square-root law for the variation of the partial molal volume of the dissolved electrolyte with concentration. If M_0 moles solvent and M moles electrolyte are contained in volume V we have

$$V = M_0 \frac{\partial V}{\partial M_0} + M \frac{\partial V}{\partial M}.$$

† See H. Jahn, *Z. phys. Chem.* **37** (1901), 490; **38** (1901), 125; **41** (1902), 257; **50** (1905), 129; W. Nernst, ibid. **38** (1901), 484.

where $\partial V/\partial M$ is the partial molal volume of the electrolyte. We have from (265) and (266)

$$\frac{\partial V}{\partial M}-\frac{\partial V_\infty}{\partial M}=\frac{\partial}{\partial p}\left(\frac{\partial \Phi}{\partial M}\right)-\frac{\partial}{\partial p}\left(\frac{\partial \bar{\Phi}}{\partial M}\right)=\frac{\partial}{\partial p}\left(\frac{\partial W}{\partial M}\right),$$

where V_∞ is the volume of an infinitely dilute solution. $\partial W/\partial M$ can be easily calculated, giving

$$\frac{\partial V}{\partial M}-\frac{\partial V_\infty}{\partial M}=RT\left(\sum\frac{v_i z_i^2}{2}\right)^{\frac{3}{2}}\left(\frac{\epsilon^2}{D_0 RT}\right)^{\frac{3}{2}}\left(\frac{2\pi N}{1{,}000}\right)^{\frac{1}{2}}\left(\frac{3}{D_0}\frac{\partial D_0}{\partial p}+\frac{1}{V}\frac{\partial V}{\partial p}\right)\gamma^{\frac{1}{2}}.$$

The experimental evidence on the variation of $\partial V/\partial M$ with concentration appears to be somewhat conflicting. Thus D. O. Mason (*Phil. Mag.* (7) **8** (1929), 218) and W. Geffcken (*Z. phys. Chem.* **155**A (1931), 1) found a square-root law to be obeyed up to very high concentrations, but the slopes of the lines obtained showed individual variations, even for electrolytes of the same valence type. Redlich and Rosenfeld (loc. cit.) conclude, however, on examining the best experimental data that these apparent straight lines are actually curves, which approach the theoretical slope at high dilutions. (The above formula should of course only be valid for dilute solution.) The influence of the valency type also appears to be accounted for by the theory. Further work on the subject is needed.

Equation (266) leads also by purely thermodynamical relationships to the following expression for the specific heat per mole

$$C_p-C_{p\infty}=\frac{3}{4}\left(\frac{\pi \mathbf{N}}{1{,}000k}\right)^{\frac{1}{2}}\frac{\mathbf{N}\epsilon^3}{(D_0T)^{\frac{3}{2}}}(\sum v_i z^2)^{\frac{1}{2}}[\quad]\sqrt{\gamma},$$

where the expression in square brackets is given by

$$[\quad]=\left[1+2\frac{T}{D_0}\frac{\partial D_0}{\partial T}+5\left(\frac{T}{D_0}\frac{\partial D_0}{\partial T}\right)^2-2\frac{T^2}{D_0}\frac{\partial^2 D_0}{\partial T^2}+\right.$$
$$\left.+\left(\frac{2}{D_0}\frac{T^2}{V}\frac{\partial D_0}{\partial T}+\frac{2}{3}\frac{T}{V}\right)\frac{\partial V}{\partial T}-\frac{2}{3}\frac{T^2}{V}\frac{\partial^2 V}{\partial T^2}+\left(\frac{T}{V}\frac{\partial V}{\partial T}\right)^2\right].$$

A similar expression was given by Messner (*Z. Elektrochem.* **33** (1927), 440) and by M. Randall, and F. D. Rossini (*J. Am. Chem. Soc.* **51** (1929), 323), but without taking into account the variation of the volume with temperature. It has, however, been shown by H. Hammerschmidt and E. Lange (*Z. phys. Chem.* **160 A** (1932), 445), and by La Mer and Cowperthwaite (*J. Am. Chem. Soc.* **55** (1933), 1004) that the terms involving the thermal expansion make a difference of 16 per cent. in water at 25°, i.e. more than in the case of heats of dilution (cf. p. 155). The expression in square brackets cannot at present be evaluated with any accuracy, but the predicted square-root law and the effect of the valency type appear to be confirmed by experiment; see F. D. Rossini (*Bur. Stand. Res.* **7** (1931), 47); F. T. Gucker and H. K. Schminke (*J. Am. Chem. Soc.* **54** (1932), 1358; **55** (1933), 1013). La Mer and Cowperthwaite (loc. cit.) have calculated the specific heats for $ZnSO_4$ from e.m.f. measurements, and compared them with the above expression, using the values of Wyman (*Phys. Rev.* **35** (1930), 623) to evaluate the expression [ ]. This leads to $C_p-C_{p\infty}=4{\cdot}69(\sum v_i z_i^2)^{\frac{1}{2}}\sqrt{\gamma}$. In a subsequent paper La Mer and Cowperthwaite have applied the results of the La Mer-Gronwall-Sandved theory (cf. p. 280) to this problem. It appears that the Debye-Hückel limiting law will only be obeyed for extremely small concentrations ($\sqrt{\gamma}<0{\cdot}004$). (A review of the subject has been given by F. T. Gucker, *Chem. Rev.* August, 1933.)

F. Zwicky (*Proc. Nat. Acad. Sci.* **12** (1926), 86; *Phys. Z.* **27** (1926), 271) has developed a theory of the specific heat of electrolytes which depends essentially

on the changes of pressure caused by the non-homogeneous electric field in the neighbourhood of the ions. It appears, however, to be theoretically unsound, and not to be supported by experiment (see F. T. Gucker, *J. Am. Chem. Soc.* **50** (1928), 1005). The compressibility of electrolytes is also of interest in this connexion. At Professor Debye's suggestion, the author and his collaborators have commenced work upon this problem, using the optical method with supersonic waves developed by Debye and F. W. Sears (*Proc. Nat. Acad. Washington*, **18** (1932), 409; P. Debye, *Sächs. Akad. Math.* **84** (1932), 125; *Phys. Z.* **33** (1932), 849; S. E. Heidmann and H. R. Asbach, ibid. **34** (1933), 494). The problem of compressibilities from the point of view of the interionic theory has also been treated by other authors. (Cf. the article by F. T. Gucker in *Chem. Rev.* August, 1933.)

The coefficient of δN_i in (273) is termed the chemical potential. In the case of ideal dilute solutions, the chemical potential ξ is given by

$$\xi_i = \bar{\xi}_i = \bar{\phi}_i + kT \log \eta_i.$$

Equation (273) thus shows how the ideal chemical potential is modified by the presence of the electrostatic forces. The chemical potential of the real solution is obtained by replacing the concentration η_i by the activity $f_i^* \eta_i$, f_i^* being the activity coefficient. We then have

$$\xi_i = \bar{\phi}_i + kT \log (f_i^* \eta_i), \tag{274}$$

and thus from (273),

$$\log f_i = -\frac{e_i^2 \kappa}{2 D_0 kT}. \tag{275}$$

In dilute solutions, f_i^* can be replaced by f_i.†

The activity of the solvent is also affected by the dissolved ions, the activity coefficient being given by

$$\log f_0 = v_0 \sum_j \frac{n_j e_j^2 \kappa}{6 D_0 kT}. \tag{276}$$

Thus the electrostatic forces decrease the activity coefficient of the ions, but increase that of the solvent.

Equations (275) and (276) can be deduced somewhat more simply from the general thermodynamical considerations on p. 45. Thus the total work of charging can be written according to (96) or (125) in the form

$$W = \sum N_i \bar{w}_i, \tag{277}$$

where

$$\bar{w}_i = \frac{w_i}{\mathbf{N}}.$$

By comparing with (247), this gives

$$\bar{w}_i = -\frac{\epsilon^2 z_i^2}{3 D_0} \kappa. \tag{278}$$

We now introduce the activity potential, h_i, defined by

$$\log h_i = \frac{\bar{w}_i}{kT} = -\frac{\epsilon^2 z_i^2}{3 D_0 kT} \kappa. \tag{279}$$

† See p. 46.

$\log h_0$, which refers to the solvent, has the value zero. Equations (97), (100), and (279) then give

$$\log f_i = \log h_i + \sum_j N_j \frac{\partial \log h_j}{\partial N_i}, \tag{280}$$

which leads to

$$\log f_i = -\frac{\epsilon^2 z_i^2}{2D_0 kT}\kappa.$$

The activity coefficient of the solvent can be shown to be given by

$$\log f_0 = \sum_i N_i \frac{\partial \log h_i}{\partial N_0} = \frac{v_0 \epsilon^2 \kappa}{6D_0 kT} \sum n_i z_i^2. \tag{281}$$

The last two formulae are deduced in detail as follows. We have

$$\frac{\partial \log h_j}{\partial N_i} = -\frac{\epsilon^2 z_j^2}{3D_0 kT}\frac{\partial \kappa}{\partial N_i},$$

and from (217) and (270),

$$\frac{\partial \kappa}{\partial N_i} = \tfrac{1}{2}\kappa\left[\frac{z_i^2}{\sum n_k z_k^2} - \frac{v_i}{V}\right],$$

so that

$$\sum_j N_j \frac{\partial \log h_j}{\partial N_i} = -\tfrac{1}{2}\kappa \frac{\epsilon^2 z_i^2}{D_0 kT} + \tfrac{1}{2}\kappa \frac{\epsilon^2 v_i}{3D_0 kT} \frac{\sum N_k z_k^2}{V} \tag{282}$$

$$\sum N_i \frac{\partial \log h_j}{\partial N_0} = v_0 \frac{\epsilon^2 \kappa}{6D_0 kT} \sum N_i z_i^2.$$

Equations (275) and (276) are then obtained by neglecting the term

$$\tfrac{1}{2}\kappa \frac{\epsilon^2}{3D_0 kT} v_i \frac{\sum N_k z_k^2}{V}$$

in (282), which is permissible in dilute solution, where the volume of the ions is small compared to the total volume V.

The logarithm of the activity coefficient of an ion in a sufficiently dilute electrolyte solution is thus related to the ionic strength J by equations (224) and (275), which give (283).

$$\begin{aligned} \log_{10} f_i &= -\frac{\epsilon^2 z_i^2}{2D_0 kT}\kappa . 0{\cdot}4343 \\ &= -\frac{1{\cdot}28 \times 10^6}{(D_0 T)^{\frac{3}{2}}} z_i^2 (2J)^{\frac{1}{2}}. \end{aligned} \tag{283}$$

This equation agrees with the hypothesis of the independent activity coefficients of ions, formulated empirically by Lewis† long before the advent of the Debye theory. According to this principle, the activity coefficient of a given ion depends only upon the total ionic strength of the solution. In the case of a single electrolyte, the ionic strength is proportional to the molarity γ, so that in this case

$$\log_{10} f_i = -\frac{1{\cdot}28 \times 10^6}{(D_0 T)^{\frac{3}{2}}} z_i^2 (\gamma \sum \nu_i z_i^2)^{\frac{1}{2}}. \tag{283'}$$

† See p. 73. The empirical considerations of Lewis and Randall gave the variation of the activity coefficients with the concentration and the charge. The theoretical limiting law gives in addition the numerical factor and the variation with the dielectric constant and the temperature.

In the special case of binary electrolyte of valency z, this becomes

$$\log_{10} f_i = -\frac{1{\cdot}815\times 10^6}{(D_0 T)^{\frac{3}{2}}}|z|^2\gamma^{\frac{1}{2}} \qquad (283'')$$

since in this case, $2J = z^2\gamma$.

We shall now turn to the application of the theory to solubility data, which are especially suitable for testing it.

31. Solubility Influences for Completely Dissociated Electrolytes, according to Debye's Theory†

We shall now consider the bearing of the above deductions on the solubility product **P** of a completely dissociated electrolyte.‡ We wish to investigate the change in solubility caused by the addition of other completely dissociated electrolytes, the ions of which will not combine with those of the first electrolyte to form molecules.

We shall first consider the equilibrium between the electrolyte and the solid phase without any added electrolyte. As before, we suppose one molecule of the salt to dissociate into $\nu_1,\ldots,\nu_i,\ldots,\nu_s$ ions designated by $1,\ldots,i,\ldots,s$. The solution contains N molecules. We have then from (273), (275), and (276) that the variation in the thermodynamic potential is given by

$$\delta\Phi = \delta N_0\phi_0 + \delta N_0 kT\log(n_0 f_0) + \delta N\sum{}' \nu_i\{\bar{\phi}_i + kT\log(n_i f_i)\}, \qquad (284)$$

where the sign $\sum'$ refers to summation over the solutes, but not the solvent. The variation in the thermodynamic potential of the solid is given by

$$\delta\Phi' = \sum{}' \nu_i \bar{\phi}'_i\,\delta N', \qquad (285)$$

where N' is the number of molecules in the solid phase. If we consider the transfer of one molecule from the solid phase into the solution, we have

$$\delta N_0 = 0, \quad \delta N = \delta N', \quad \delta N_i = \nu_i\delta N.$$

The equilibrium condition

$$\delta(\Phi+\Phi') = 0$$

thus becomes

$$\sum{}' \nu_i\{\bar{\phi}_i + kT\log(n_i f_i)\} - \sum{}' \nu_i\bar{\phi}'_i = 0,$$

i.e.

$$\sum{}' \nu_i\log(n_i f_i) = \log K_l, \qquad (286)$$

where

$$\log K_l = \frac{1}{kT}\sum{}' \nu_i(\bar{\phi}'_i - \bar{\phi}_i). \qquad (287)$$

$\log K_l$ depends only on the temperature and the pressure, and determines the solubility of the solid phase in the pure solvent. K_l is there-

† This theory was first given by Debye, *Chem. Weekblad*, **20**, No. 42 (1923), 562.

‡ This subject has already been treated from a different point of view. See p. 73.

fore termed the solubility constant.† (286) can also be written in the form

$$\prod_i{}' (n_i f_i)^{\nu_i} = K_l. \tag{288}$$

By a generalization of (78), the solubility product is defined by

$$\log \mathbf{P} = \sum{}' \nu_i \log \eta_i \tag{289}$$

or

$$\mathbf{P} = \prod{}' \eta_i^{\nu_i}. \tag{289'}$$

We thus see that at constant temperature and pressure it is not the solubility product **P** which remains a constant, but the expression in (288), in which the concentrations in (289') have been replaced by activities. It is again convenient (cf. (146')) to introduce the mean activity coefficient for the whole electrolyte defined by

$$\nu \log f = \sum{}' \nu_i \log f_i \qquad (\nu = \sum \nu_i) \tag{290}$$

or

$$f^\nu = \prod_i{}' f_i^{\nu_i}. \tag{290'}$$

Introducing this relation, (288) becomes

$$\log \mathbf{P} + \nu \log f = \log K_l \tag{291}$$

or,

$$\mathbf{P} f^\nu = K_l. \tag{291'}$$

If we now add a second electrolyte, the activities of the ions corresponding to the solid phase will be altered, and the equilibrium will be disturbed. This effect will be present even when the added electrolyte and the first electrolyte have no ions in common. If after the addition of the second electrolyte the concentrations and activities of the ions of the solid phase are $\bar{\eta}_i$ and $\bar{f}_i$, we arrive just as before at the relation

$$\sum{}' \nu_i \log(\bar{\eta}_i \bar{f}_i) = \log K_l. \tag{292}$$

Introducing again the solubility product

$$\log \mathbf{P} = \sum{}' \nu_i \log \bar{\eta}_i \tag{293}$$

and the total activity coefficient for the dissolved salt

$$\nu \log \bar{f} = \sum{}' \nu_i \log f_i, \tag{294}$$

we have

$$\bar{\mathbf{P}} \bar{f}^\nu = K_l. \tag{295}$$

The ratio of the activity coefficient of the dissolved salt in presence of added electrolyte to its activity coefficient in the pure solvent is then given by (291') and (295) as

$$\frac{\bar{f}}{f} = \left(\frac{\mathbf{P}}{\bar{\mathbf{P}}}\right)^{1/\nu}. \tag{296}$$

Before we continue with the calculation of solubility effects, we shall try to give a picture of how the interionic forces cause the solubility to be increased by the addition of salts. Consider first a saturated solution

† The same relation follows from the treatment on p. 47.

to which a second electrolyte having a common ion is added. According to the classical theory, this should always bring about a decrease in solubility.† We may consider equilibrium to be characterized by the fact that the probability of the simultaneous transfer of the ions of the solid phase to the solution is equal to the probability of the reverse process. If now the number of one of the species of ions is increased, the first probability will become greater, and if this increase is the only way in which the probability of transfer can be affected by additions, then the decrease of solubility predicted by the classical theory will be the only effect produced. Looked at from a somewhat different point of view, the addition will repress the dissociation of the salt, and tend to increase the concentration of undissociated molecules. Since, however, this last concentration must remain constant in presence of solid salt, solid must separate out, and the total solubility is decreased.

These considerations neglect the presence of the interionic forces, the effect of which will be to promote the passage of ions from the solid to solution, and to hinder the reverse process. Moreover, this effect will be greater the more concentrated the solution, so that the addition of electrolyte will increase the probability of the transfer of an ion from the solid to the solution, and decrease the probability of the reverse process. (This is another way of stating the fact that the activity concentration of an ion decreases with increasing ionic concentration.) The effect due to the interionic forces is thus opposite in sign to the effect caused by increasing the concentration of one of the ions which constitute the solid phase. It is thus clear that the net effect may be either an increase or a decrease in solubility according to which effect is the greater. An increase in solubility will be observed much more often when the added salt is of a high valency type, since in this case the interionic forces are much greater. In some cases complex formation also occurs, which will decrease the concentration of the undissociated part, and hence increase the solubility.‡

We shall deal here with the cases in which complex formation is very improbable, especially the work of Brönsted and La Mer§ which deals with the effect of salts not having a common ion. Their results provide a most elegant confirmation of the Debye-Hückel theory of activity coefficients.

† See p. 37. ‡ See note to p. 38.

§ Brönsted and La Mer, *J. Am. Chem. Soc.* **46** (1924), 555. S. Popoff and E. Neumann (*J. Phys. Chem.* **34** (1930), 1853) have recently determined the solubility of silver chloride in extremely dilute solutions (down to 2×10^{-8}N.) and find excellent agreement with Debye's limiting law.

Equation (296) can be written in the form

$$\left(\frac{\bar{f}}{f}\right)^{\nu} = \frac{\mathbf{P}}{\bar{\mathbf{P}}}. \tag{296'}$$

For the small concentrations we are dealing with here we may replace η_i by γ_i. Brönsted and La Mer used four saturating salts of valency-types 1-1, 1-2, 1-3, and 3-3. In these cases we have from (289) and (296),

$$\frac{\bar{f}}{f} = \frac{\gamma}{\bar{\gamma}} \qquad \text{i.e. } -\log\frac{\bar{f}}{f} = \log\frac{\bar{\gamma}}{\gamma}, \tag{297}$$

where γ and $\bar{\gamma}$ are the solubilities in pure water and salt solution respectively, expressed as molarity. The ratio of the activity coefficients is thus simply equal to the reciprocal of the ratio of the solubilities. According to (283), the limiting law for the activity coefficients of binary salts in water is

$$\left.\begin{aligned} 0° \quad & \log_{10} f = \log_{10} f_1 = \log_{10} f_2 = -0{\cdot}486\sqrt{J} = -0{\cdot}344\sqrt{\Gamma} \\ 15° \quad & \log_{10} f = \log_{10} f_1 = \log_{10} f_2 = -0{\cdot}498\sqrt{J} = -0{\cdot}352\sqrt{\Gamma} \\ 20° \quad & \log_{10} f = \log_{10} f_1 = \log_{10} f_2 = -0{\cdot}505\sqrt{J} = -0{\cdot}357\sqrt{\Gamma} \end{aligned}\right\}, \tag{298}$$

where Γ is the total ionic concentration (see p. 42). Similarly, for 1-2-valent salts at 15°

$$\log_{10} f = \tfrac{1}{3}(2\log_{10} f_1 + \log_{10} f_2) = -2\times 0{\cdot}352\sqrt{\Gamma}, \tag{299}$$

and for 1-3-valent salts at 15°

$$\log_{10} f = \tfrac{1}{4}(3\log_{10} f_1 + \log_{10} f_2) = -3\times 0{\cdot}352\sqrt{\Gamma}. \tag{300}$$

The summation in (223) extends over both dissolved salt and added electrolyte. Thus if Γ is the ionic concentration in the pure solvent saturated with salt, and $\bar{\Gamma}$ the same quantity in the presence of added electrolyte, equations (297)–(300) become

$$\begin{aligned} \log_{10}\frac{\bar{\gamma}}{\gamma} = -\log_{10}\frac{\bar{f}}{f} &= 0{\cdot}352(\sqrt{\bar{\Gamma}} - \sqrt{\Gamma}) \text{ for 1-1-valent salts at 15°,} \\ \log_{10}\frac{\bar{\gamma}}{\gamma} = -\log_{10}\frac{\bar{f}}{f} &= 2\times 0{\cdot}352(\sqrt{\bar{\Gamma}} - \sqrt{\Gamma}) \text{ for 1-2-valent salts at 15°,} \\ \log_{10}\frac{\bar{\gamma}}{\gamma} = -\log_{10}\frac{\bar{f}}{f} &= 3\times 0{\cdot}352(\sqrt{\bar{\Gamma}} - \sqrt{\Gamma}) \text{ for 1-3-valent salts at 15°.} \end{aligned} \tag{301}$$

Thus if $\log_{10}\bar{\gamma}/\gamma$ is plotted against $\sqrt{\bar{\Gamma}}$, the points for each saturating salt should fall on a straight line, independent of the nature of the added electrolyte, and the three straight lines should have the slopes 0·352, $2\times 0{\cdot}352$, and $3\times 0{\cdot}352$. If these straight lines are extrapolated to

$\sqrt{\bar{\Gamma}} = 0$, they will cut the ordinate axis at the point $\log_{10} f$, since when $\sqrt{\bar{\Gamma}} = 0$, $\log_{10} f = 0$. When measurements are available in very dilute solution, this extrapolation can be carried out very accurately. Then we can write

$$-\log_{10} \bar{f} = \log_{10} \frac{\bar{\gamma}}{\gamma} - \log_{10} f \tag{302}$$

and plot the values of $-\log_{10} \bar{f}$ thus obtained against $\sqrt{\bar{\Gamma}}$. Fig. 25 shows

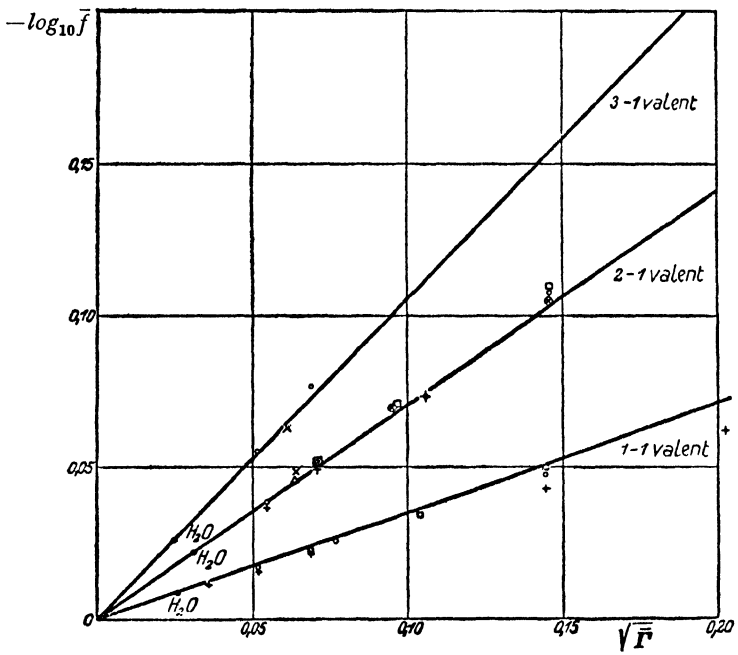

FIG. 25. Activity coefficients of complex cobalt salts from solubility measurements.

some of Brönsted and La Mer's experimental results plotted in this way, the different points on the three straight lines corresponding to the addition of salts of widely differing valency types.† The 1-1-valent saturating salt used was

$$[Co(NH_3)_4(NO_2)(CNS)][Co(NH_3)_2(NO_2)_2C_2O_4]$$

(Thiocyanato-nitro),

the 2-1-valent salt

$$[Co(NH_3)_4(C_2O_4)]_2(S_2O_6)$$

(Oxalato-dithionato),

† For the 1-1-valent salt the additions were NaCl (+), KNO_3 (.) and $K_3Co(CN)_6$ (□); for the 2-1-valent salt NaCl (+), KNO_3 (⊙), K_2SO_4 (△), $BaCl_2$ (×), $MgSO_4$ (⊗), and $K_3Co(CN)_6$ (□); and for the 3-1-valent salt KNO_3 (⊙) and $BaCl_2$ (×).

and the 3-1-valent salt

$$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_2(C_2O_4)]_3$$

(Luteo-dinitro).

Fig. 25 shows that these measurements not only verify the predicted dependence on concentration, but also the dependence on the ionic strength, the effect of the valency and (within the limits of experimental error) the numerical factors in (301).

Table 21 contains all the necessary data for the effect of NaCl upon the solubility of the thiocyanato-nitro salt in water at 15°. It will be seen that the observed solubility $\bar{\gamma}$ increases with increasing salt addition. The solubility in pure water is

$$\gamma = 0{\cdot}0003355 \text{ moles/litre},$$

so that

$$-\log_{10} f = 0{\cdot}0088$$

from which the activity coefficients can be calculated at different ionic strengths from (302).

TABLE 21

The effect of added NaCl on the solubility of the thiocyanato-salt in water at 15° C.

Conc. of NaCl Eq./litre	*Solubility Eq./litre* $\times 10^4$	$\bar{J} = \frac{1}{2}\bar{\Gamma}$	$\sqrt{\bar{J}}$	$\log_{10}\frac{\bar{\gamma}}{\gamma}$	$\log_{10}\bar{f}$	$\bar{f}_{obs.}$	$f_{calc.}$	*Diff. calc.*
0·0000	3·355	0·0003355	0·01831	0·0000	0·0088	0·980	0·979	0·001
0·0003	3·377	0·0006375	0·0252	0·0028	0·0116	0·975	0·971	0·004
0·0010	3·405	0·001340	0·0366	0·0065	0·0153	0·965	0·959	0·006
0·0020	3·451	0·002345	0·0484	0·0124	0·0212	0·952	0·946	0·006
0·0100	3·627	0·010363	0·1015	0·0340	0·0428	0·906	0·890	0·016
0·0200	3·790	0·020379	0·1428	0·0531	0·0619	0·867	0·848	0·019

Recent investigations by La Mer, King, and Mason† show that the effect of added KNO_3 and $MgSO_4$ upon the solubility of the 3-3-valent salt

$$[Co(NH_3)_6][Fe(CN)_6]$$

agree well with the Debye-Hückel theory up to an ionic strength of $\bar{J} = 0{\cdot}007$. This is seen from Fig. 26, where $\log_{10}(\bar{\gamma}/\gamma)$ is plotted against $\sqrt{\bar{J}}$. (The circles refer to KNO_3, and the squares to $MgSO_4$.) $-\log_{10} f$

† V. K. La Mer, C. V. King, and C. F. Mason, *J. Am. Chem. Soc.* **49** (1927), 363, 410. See also La Mer and F. H. Goldman, ibid. **51** (1929), 2632 (solubility of $La(IO_3)_3$ and $TlIO_3$) and B. H. Peterson and E. L. Meyers, ibid. **52** (1930), 4853 (solubility of $Cu(IO_3)_2$). E. W. Neumann, ibid. **54** (1932), 3195; **55** (1933), 879 (solubility of AgCl in aqueous solutions of the sulphates of H, K, Ca, Mg, and La, and the nitrates of K, Ba, and La: also the solubility of $BaSO_4$ in aqueous solutions of KCl, KNO_3, $MgCl_2$, $Mg(NO_3)_2$, $La(NO_3)_3$, $LaCl_3$).

can be calculated from (302), or read directly from Fig. 26. Fig. 27 illustrates the fact that the slope of the line is very much greater for 3-3-valent salts than for the types previously mentioned.

Matters are not so simple in the case of the unsymmetrical complex salts

$$[Co(NH_3)_6][Co(NO_2)_4(NH_3)_2]_3$$

$$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_2C_2O_4]_3.$$

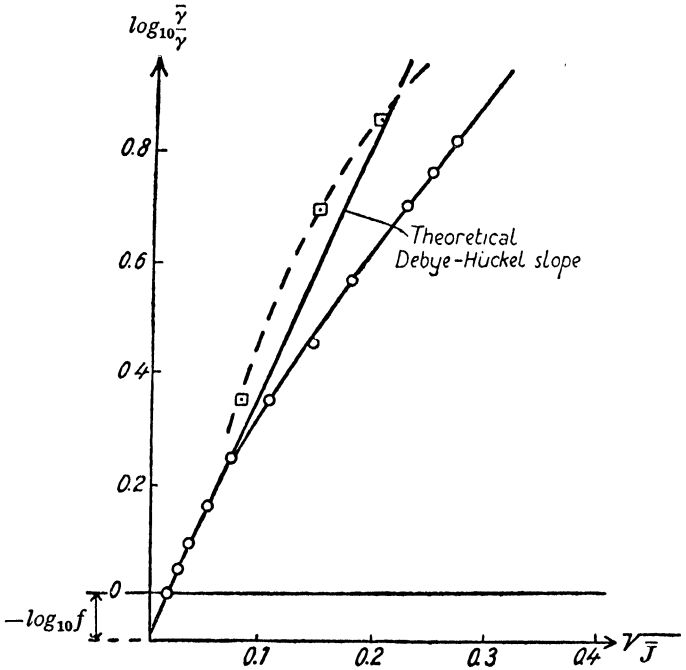

FIG. 26. Solubility of a 3-3-valent complex cobalt salt in salt solutions.

If the added electrolytes contain only univalent anions (e.g. KNO_3, $BaCl_2$, $NaNO_3$), the results obtained with these salts agree excellently with the Debye-Hückel limiting law. If, however, anions of higher valencies are introduced (e.g. K_2SO_4, $MgSO_4$, $K_3Fe(CN)_6$) considerable discrepancies are observed. This is illustrated by Fig. 28, in which $-\log f$ is plotted against $\sqrt{\bar{J}}$ for the second of the complex salts shown above. It will be seen that the experimental curves show no signs of approaching the theoretical limiting law, even at concentrations somewhat below $\bar{J} = 0{\cdot}0005$.

These discrepancies between theory and experiment may be expressed as a term proportional to $\bar{J}$, agreeing with the theory of Gronwall,

La Mer, and Sandved, which we shall deal with later in the chapter on concentrated solutions.†

The theory appears to predict correctly the effect of temperature: see e.g. the measurements of Baxter‡ on the solubility of silver iodate in various salt solutions at 75°.

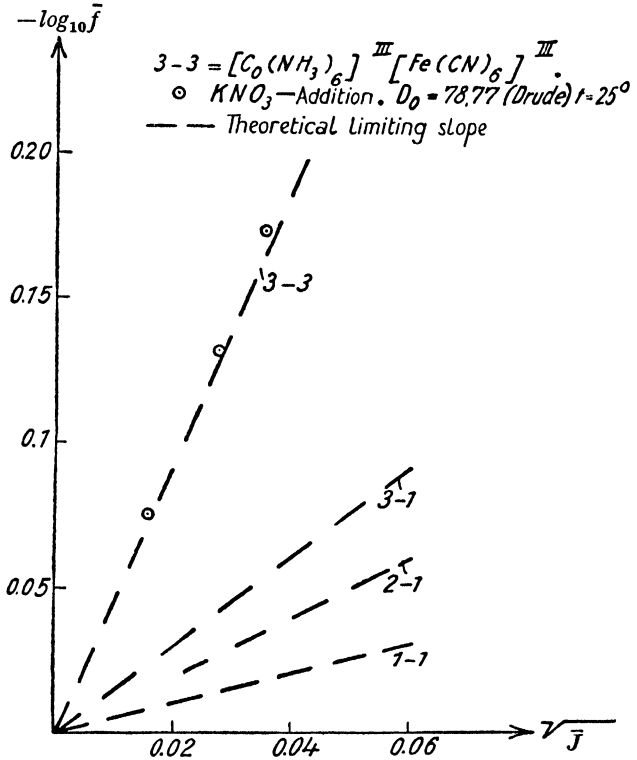

FIG. 27. The effect of valency on the activity coefficients of complex salts.

The effect of the dielectric constant has been tested by a number of investigations in non-aqueous solvents, chiefly methyl and ethyl alcohol and their mixtures with water.§ These investigations were carried out partly by means of e.m.f. determinations, and partly by solubility

† See p. 270.

‡ W. P. Baxter, *J. Am. Chem. Soc.* **48** (1926), 615.

§ See W. P. Baxter, *J. Am. Chem. Soc.* **48** (1926), 615; G. Scatchard, ibid. **47** (1925), 2098; A. A. Noyes and W. P. Baxter, **47** (1925), 2122; G. Nonhebel and H. Hartley, *Phil. Mag.* **50** (1925), 729; J. W. Woolcock and H. Hartley, ibid. (7) **5** (1928), 1133; J. A. V. Butler, *Proc. Roy. Soc.* **129 A** (1930), 519; J. N. Brönsted and J. W. Williams, *J. Am. Chem. Soc.* **50** (1928), 1338; Brönsted, A. Delbanco, and K. Volqvartz, *Z. phys. Chem.* **162 A** (1932), 128; Williams, *J. Am. Chem. Soc.* **51** (1929), 1112; Hansen and Williams, ibid. **52** (1930), 2759.

measurements. In many cases the results obtained agree well with the theory, but deviations are more frequent than in water. Thus J. W. Williams (loc. cit.) found that the effect of added salts on the solubility of 1-1-valent salts in methyl alcohol agrees well with the Debye-Hückel limiting law, while for 1-2-valent salts there were considerable discrepancies between the observed values and the theory even at the lowest concentrations studied.†

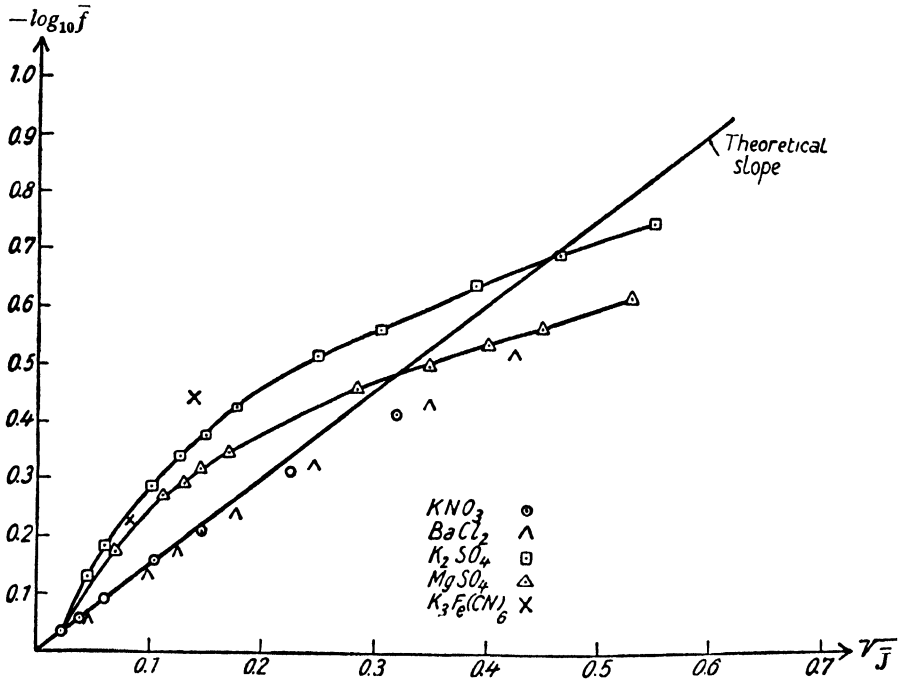

FIG. 28. The activity coefficients of the unsymmetrical salt $[Co(NH_3)_6]^{+++}[Co(NH_3)_3(NO_2)_2C_2O_4]_3^-$ in salt solutions.

This may be illustrated in the following manner. The dielectric constant of methyl alcohol at 20° is about 30, which gives on substituting in (283) and (290)

$$-\log_{10} f = 2|z_1 z_2|\sqrt{\bar{J}}.$$

Table 22 contains a comparison of the theoretical and experimental values of $2|z_1 z_2|$ for saturating salts of different types (1-1, 2-1, 3-1), and various added electrolytes.

† R. P. Seward and W. C. Schumb (*J. Am. Chem. Soc.* **52** (1930), 3692) and C. A. Kraus and Seward (*J. Phys. Chem.* **32** (1928), 1294) found deviations from the theoretical laws even for 1-1-valent salts in ethyl and isopropyl alcohols. See also Robinson, ibid. **32** (1928), 1089. Differences of the same kind were found by Harned and M. H. Fleysher (*J. Am. Chem. Soc.* **47** (1925), 82) for HCl in ethyl alcohol.

TABLE 22

Complex salt	*Type*	*Salt added*	*Observed value*	*Calc. value* $= 2\|z_1 z_2\|$
Croceochloride	1-1	$C_6H_5SO_3Na$	1·7	2
Croceochloride	1-1	KSCN	1·7	2
Croceochloride	1-1	$Ba(ClO_3)_2$	2·5	2
Croceochloride	1-1	$(C_6H_5COO)_2Sr$	1·7	2
Xanthochloride	2-1	KSCN	4	4
Xanthochloride	2-1	$Ba(ClO_3)_2$	6	4
Xanthochloride	2-1	$(C_6H_5COO)_2Sr$	6	4
Luteobromide	3-1	KSCN	11·5	6

The deviations from the theoretical value are particularly marked for the higher valence types. They resemble the deviations found in aqueous solutions, and are probably theoretically explicable on the basis of the theory of Gronwall, La Mer, and Sandved.† In any case, in solvents of low dielectric constant difficulties arise (which are absent for aqueous solutions) due largely to the fact that the solute molecules are not completely dissociated, and it is necessary to take into account the association and solvation of the ions, besides other factors.

The available experimental data on solubilities thus lead to the conclusion that the Debye-Hückel limiting law holds more or less exactly at high dilutions for aqueous solutions, and to a more limited extent for non-aqueous solutions. We shall return later to the deviations observed for somewhat more concentrated solutions and non-aqueous solvents. The possibility of a theoretical explanation of these deviations will also be dealt with.‡

† See p. 270. A decrease in dielectric constant will have a similar effect to an increase in the valency. In a private communication to the author, Professor La Mer states that the mathematical series occurring in his theory are much less convergent for low values of the dielectric constant, so that the theory cannot at present be applied in these cases. R. P. Seward and C. H. Hamblet (*J. Am. Chem. Soc.* **54** (1932), 554) measured the solubility of $KClO_4$ and KNO_3 in solutions of 1-1-valent salts in acetic acid (dielectric constant about 6·3), and found that their results could be explained fairly well by the Debye-Hückel theory (cf. p. 250) by assuming a fairly large a-parameter (*c.* 9×10^{-8} cm.). The theory of La Mer, Gronwall, and Sandved (see p. 270) gives still better agreement.

‡ See p. 250. It should be emphasized that neither the polarization of the solvent by the ions nor the unequal size of the ions (see Scatchard, *Phys. Z.* **33** (1932), 22) nor the departure of the potential from spherical symmetry (see Scatchard and Kirkwood, *Phys. Z.* **33** (1932), 297) have any effect upon the limiting law.

32. Salt Effects, According to Debye's Theory. (Osmotic Pressure and Activities in Dilute Mixtures of Electrolytes and Non-electrolytes. Salting-out Effects. Neutral Salt Action.)

A. *Introductory remarks.*

The deviations of strong electrolytes from classical laws are not confined to their behaviour in solutions containing only electrolytes, but extend also to mixtures of electrolytes and non-electrolytes. A familiar example of this is the salting-out effect (and the reverse effect of increased solubility). A further interesting set of phenomena is met with in the effect of adding a salt containing a common ion to a solution of a weak electrolyte when the repression of dissociation is less than that predicted by the classical theory. These phenomena (usually termed neutral salt effects) are closely connected with the effect of added salts on hydrolysis.

All these phenomena can be explained on the basis of interionic forces. The characteristic properties of strong electrolytes are due to the large number of free electric charges formed by their dissociation. All the phenomena mentioned above can be classified together under the name of 'salt effects' or 'electrolyte effects'. The salt effects which refer to states of equilibrium can be divided into two main classes, according to the type of phenomena involved.

The first class comprises those phenomena in which only the solvent is directly involved in the equilibrium measured, while in the second class of phenomena the solute undergoes changes in concentration. Examples of the first type are osmotic pressure, freezing-point depression, etc., while the second class includes mass action phenomena, solubility effects, electromotive force, etc. An example of the first class is the interaction of an electrolyte and a non-electrolyte, which was first observed by Tammann† and Abegg‡ in cryoscopic results. Thus suppose that a solution containing γ moles of a non-electrolyte per litre exhibits a freezing-point depression Δ_N, and a solution containing γ' moles of an electrolyte per litre a freezing-point depression Δ_E. If now a solution is taken containing simultaneously γ moles of non-electrolyte and γ' moles of electrolyte per litre, it is found in general that the freezing-point depression Δ observed is greater than the sum $\Delta_N+\Delta_E$.

The salting-out effect is the decrease in the solubility of a non-electrolyte caused by the addition of an electrolyte. Often an increase of solu-

† G. Tammann, *Z. phys. Chem.* **9** (1892), 108.
‡ R. Abegg, ibid. **11** (1893), 259.

bility results, in which case we may speak of a 'salting-in effect'. From a thermodynamic point of view the two effects are closely related.

The effect of added salts may be seen most clearly by considering the osmotic pressure. To take a concrete example, we shall consider why the osmotic pressure of a solution containing a mixture of sugar and salt is greater than the sum of the osmotic pressures exerted by the same amounts of sugar and salt when present separately. We shall confine ourselves to dilute solutions, since it is only in the dilute range that a valid theory can be obtained. The solution of sugar and salt can be brought to any desired concentration by means of a semi-permeable piston, which is permeable to water, but impermeable to both solutes. If during a small displacement of the piston the volume of the solution changes by dV, the work done is $-P\,dV$, where P is the osmotic pressure. If the electric charges on the ions are not taken into account, we must have

$$P = P_N + P_E,$$

where P_N and P_E are the osmotic pressures which would be exerted by the non-electrolyte and the electrolyte respectively if present alone.

The ions are surrounded by an electric field, which will possess a certain energy. If $\mathfrak{E}$ is the field strength in a given volume element, electrostatic theory gives the energy per unit volume as

$$\frac{D\mathfrak{E}^2}{8\pi} \quad \text{or} \quad \frac{(D\mathfrak{E})^2}{8\pi D}.$$

The electric displacement $D\mathfrak{E}$ is proportional to the charge, and hence remains constant during the movement of the piston. An additional amount of work will, however, be necessary if the concentration increase brought about by the movement of the piston causes a decrease of dielectric constant. Since actually most non-electrolytes do lower the dielectric constant of water, we may attribute the interaction of electrolyte and non-electrolyte (which appears in many cases as an increase in the osmotic pressure) to the work necessary to increase the energy of the electric field. It should be mentioned that a few non-electrolytes increase the dielectric constant of water. In these cases the osmotic pressure of the solution will be less than the sum of the osmotic pressures of the single solutions, and the solubility of the non-electrolyte will be greater in the salt solution than in pure water. It should also be emphasized that the use of the macroscopic dielectric constant to characterize the dielectric action of the solvent corresponds to a highly simplified picture, which we are forced to use in the absence of any microscopic theory of the processes involved. Making this simplification,

we can as before calculate the electrical work term which must be added to the classical expression for the free energy. The corrected free energy expression can then be employed to obtain the activity coefficients of the various species present. It is found that when the non-electrolyte lowers the dielectric constant of the solvent, the addition of the electrolyte will increase the activity coefficient of the non-electrolyte. If the non-electrolyte is present as a solid phase, its activity will be constant at constant temperature, and since the activity is equal to the product of the concentration and the activity coefficient, the increase in the activity coefficient will cause a decrease in the solubility. This corresponds to the ordinary salting-out effect.

B. *Osmotic pressure and activity in dilute mixtures (salting-out effect).*†

In order to find the additional free energy caused by the presence of the ionic charges, we shall proceed in the same way as before (p. 112). We imagine the ions discharged in an infinitely dilute solution, and recharged in a solution of finite concentration. The work necessary to carry out this process is the additional term required. If the solution contains $N_1,\ldots, N_i,\ldots, N_s$ ions of the species $1,\ldots, i,\ldots, s$ having charges $e_1,\ldots, e_i,\ldots, e_s$ the work W is given as before by‡

$$W = -\sum \frac{N_i e_i^2}{2D_0 b_i} + \sum \frac{N_i e_i^2}{2D_m b_i} - \sum \frac{N_i e_i^2 \kappa}{3D_m}. \tag{303}$$

For the sake of simplicity, an ion of the ith sort is considered as a sphere of radius b_i which is charged first in pure water of dielectric constant D_0, and subsequently in the solution of given concentration and dielectric constant D_m. The third term in (303) represents to a first approximation the work done against the interionic forces. κ is the reciprocal thickness of the ionic atmosphere (221). Since we are dealing only with a first approximation, we can represent the dielectric constant of the mixture D_m by the linear interpolation formula

$$D_m = D_0(1-\tilde{\alpha}n-\beta n'), \tag{304}$$

where n and n' represent the number of molecules of non-electrolyte and electrolyte respectively per c.c., and $\tilde{\alpha}$ and β are two constants which may be determined from experiment. It is known with certainty that the addition of a non-electrolyte as a rule lowers the dielectric constant. In the case of electrolytes, the experimental data do not as yet permit

† See P. Debye and J. McAulay, *Phys. Z.* **26** (1925), 22; G. Scatchard, *J. Am. Chem. Soc.* **47** (1925), 2098; *Chem. Rev.* **3** (1927), 384; P. Debye, *Z. phys. Chem.* Cohen-Festband (1927), p. 56.

‡ Cf. p. 115. κ is defined by (217); D_0 is replaced by D_m.

any definite conclusion to be drawn†. We shall, however, show in the following treatment that the constant β is of no importance in the first approximation term. We introduce (304) in (303) and expand $1/D_m$ in the second term in powers of n and n', retaining only the first term of the expansion, and write D_0 for D_m in the third term. We then have‡

$$W = \tilde{\alpha} n \sum \frac{N_i e_i^2}{2D_0 b_i} + \beta n' \sum \frac{N_i e_i^2}{2D_0 b_i} - \sum \frac{N_i e_i^2 \kappa_0}{3D_0}. \tag{305}$$

We shall now use the expression for W to obtain the corrected osmotic equation of state. It has been previously shown§ that the osmotic pressure is given by (244), where $\bar{P}$ is the classical expression for the osmotic pressure of the ideal solution and $-\partial W/\partial V$ represents the correction due to the interionic forces. V is the volume of the solution which we imagine altered by dV by means of a semi-permeable piston. The two first terms of (305) depend upon V, since

$$n = \frac{N}{V}, \quad n_1' = \frac{N'}{V}, \tag{306}$$

where N and N' are the numbers of molecules of non-electrolyte and electrolyte respectively present in the whole solution. The third term in (305) contains κ_0 and therefore depends upon the volume.|| We thus have from (250)

$$-\frac{\partial W}{\partial V} = \tilde{\alpha} n \sum \frac{n_i e_i^2}{2D_0 b_i} + \beta n' \sum \frac{n_i e_i^2}{2D_0 b_i} - \sum \frac{n_i e_i^2 \kappa}{6D_0}.$$

According to the classical theory we have

$$\bar{P} = nkT + \sum n_i kT. \tag{307}$$

If one molecule of the electrolyte dissociates into ν_1 of the species $1,\ldots,\nu_s$ of the species s, having valencies $z_1,\ldots,z_i,\ldots,z_s$, we have

$$n_i = \nu_i n' \quad e_i = z_i \epsilon. \tag{308}$$

Introducing the abbreviations

$$\left.\begin{aligned} \nu &= \sum \nu_i \\ P_N &= nkT \\ P_E &= \nu n' kT\left(1 - \frac{n_0 \epsilon^2}{6D_0 kT} \frac{\sum \nu_i z_i^2}{\nu}\right) \\ p &= \tilde{\alpha} \frac{n \nu n' \epsilon^2}{2D_0 \nu} \sum \frac{\nu_i z_i^2}{b_i} \end{aligned}\right\} \tag{309}$$

† See footnote, p. 283.

‡ The quantity previously termed κ (221) is called κ_0 in this section.

§ See p. 113. || Since $n_i = N_i/V$.

we can write for the osmotic pressure†

$$P = P_N + P_E + p. \tag{310}$$

We can thus consider the osmotic pressure as being composed of three parts. The first is the osmotic pressure P_N which would be exerted by the non-electrolyte if present alone in the solution. The second, P_E, is by (254) the osmotic pressure which the $\nu n'$ ions of the electrolyte would exert if present alone in the solution. The third term is positive or negative according to the sign of $\tilde{\alpha}$. (309) may be written in a somewhat more convenient form by introducing a mean radius b defined by

$$\sum \frac{\nu_i z_i^2}{b_i} = \frac{\sum \nu_i z_i^2}{b}. \tag{311}$$

We may compare the value found for p with the osmotic pressure $\bar{P}$ which would be exerted according to the classical theory (see (307)). We then have

$$\frac{p}{\bar{P}} = \tilde{\alpha} \frac{n\nu n'}{n + \nu n'} \frac{\sum \nu_i z_i^2}{\nu} \frac{\epsilon^2}{2D_0 b kT}. \tag{312}$$

According to this formula the ratio $p/\bar{P}$ is proportional to the product of the concentrations of the two components, and inversely proportional to their sum. Other factors are the valency factor $\sum \nu_i z_i^2/\nu$ and the ratio of the electrical energy of the central ion $\epsilon^2/2D_0 b$ to the thermal energy kT. The proportionality factor $\tilde{\alpha}$ is a measure of how much the dielectric constant of water is lowered by the addition of the non-electrolyte. If $\tilde{\alpha}$ is positive, a positive abnormal change in the osmotic pressure is produced, while if $\tilde{\alpha}$ is negative, there is an abnormal decrease.

We shall now calculate the effect of the electrolyte on the activity of the non-electrolyte, using the general considerations developed on p. 121. If we write the electrical energy contribution W in the form

$$W = \sum N_i \bar{w}_i, \tag{313}$$

the activity potentials h_i are defined by (278). Using equations (303) for W this gives

$$\log h_i = \frac{\tilde{\alpha} n e_i^2}{2D_0 b_i kT} + \beta \frac{n' e_i^2}{2D_0 b_i kT} - \frac{e_i^2 \kappa_0}{3D_0 kT}. \tag{314}$$

The activity potential of the non-electrolyte is thus unity, and only activity potential of the ions differs from unity. The general considerations of pp. 45 and 123 give for the activity coefficient f_i of any

† The term $\beta n' \frac{\epsilon^2}{2D_0 kT} \sum \frac{\nu_i z_i^2}{b_i}$ has been omitted in P_E, which is permissible in the approximation we are employing.

component i

$$\log f_i = \log h_i + \sum_j N_j \frac{\partial \log h_j}{\partial N_i}. \tag{315}$$

Symbols referring to the non-electrolyte will be distinguished by having no index. As stated above,

$$h = 1, \qquad \log h = 0. \tag{316}$$

Again introducing $N = nV$ for the non-electrolyte, (314) and (315) give

$$\log f = \tilde{\alpha} \sum \frac{n_j e_j^2}{2D_0 b_j kT}. \tag{317}$$

If we employ the mean ionic radius b defined by (311) and replace e_j by $z_j \epsilon$, $\log f$ can be written in the form

$$\log f = \tilde{\alpha} \nu n' \frac{\sum \nu_i z_i^2}{\nu} \frac{\epsilon^2}{2D_0 bkT}. \tag{318}$$

Thus as long as $\tilde{\alpha}$ is positive, the activity coefficient of the non-electrolyte is increased by an amount proportional (as a first approximation) to the number of ions added. Since the activity is the determining factor in the equilibrium between the solid phase and the solution, the increase in activity coefficient necessitates a decrease in the concentration if the equilibrium is to be maintained, i.e. the non-electrolyte is salted out. If its solubility is (L_0) before the addition of electrolyte and (L) after the addition

$$(L)f = (L_0), \text{ i.e. } \frac{(L_0)}{(L)} = f. \tag{319}$$

We shall now compare the experimental data on freezing-point depressions with the theoretical predictions. As an example we shall take the data of Rivett† on the freezing-points of solutions containing cane sugar and various electrolytes, e.g. KCl. In Table 23 the first two columns contain the concentrations of the electrolyte and non-electrolyte respectively in moles per litre (γ' and γ). The freezing-point observed in the mixture is termed Δ, and the freezing-points for the electrolyte and non-electrolyte when present alone, Δ_E and Δ_N, respectively. The difference

$$\delta = \Delta - (\Delta_E + \Delta_N) \tag{320}$$

is given in the third column of Table 23. δ is here always positive, as originally found by Tammann. The fourth column contains $\bar{\Delta}$, the freezing-point of the mixture calculated according to the classical van 't Hoff laws. The fifth column gives the ratio $\delta/\bar{\Delta}$, which is equal to $p/\bar{P}$. For small concentrations, (312) should hold.

† A. C. D. Rivett, *Medd. K. Vetensk.-akad. Nobelinstitut*, vol. 2 (1913), No. 9.

Introducing γ and γ' in place of n and n'

$$n = \frac{\mathbf{N}}{1{,}000}\gamma. \tag{321}$$

Further, D_m can be defined by

$$D_m = D_0(1-\tilde{\alpha}n) = D_0(1-A\gamma), \tag{322}$$

where

$$A = \frac{\mathbf{N}}{1{,}000}\tilde{\alpha}.$$

(312) thus becomes

$$\frac{\delta}{\bar{\Delta}} = A\frac{\gamma\nu\gamma'}{\gamma+\nu\gamma'}\frac{\sum\nu_i z_i^2}{\nu}\frac{\epsilon^2}{2D_0 bkT}. \tag{323}$$

In our case $\nu = 2$. The sixth column of Table 23 contains the ratio of $\delta/\bar{\Delta}$ to $2\gamma\gamma'/(\gamma+2\gamma')$, and it is seen that the value obtained varies but little with concentration. On drawing a curve through these points (which involves a certain degree of arbitrariness), it is seen that the limiting value for low concentrations should be about 0·22. If we insert the numerical values of ϵ and k in (323) and put $D_0 = 88{\cdot}2$, $T = 273$, we have

$$\frac{\delta/\bar{\Delta}}{\gamma\nu\gamma'/(\gamma+\nu\gamma')} = \frac{A\sum\nu_i z_i^2}{\nu}\frac{3{\cdot}45\times10^{-8}}{b}. \tag{324}$$

TABLE 23

γ' (*Salt*)	γ (*Sugar*)	δ	$\bar{\Delta}$	$\frac{\delta}{\bar{\Delta}}$	$\frac{\delta/\bar{\Delta}}{2\gamma\gamma'/(\gamma+2\gamma')}$
0·1402	0·3717	0·038	1·213	0·0313	0·196
0·2359	0·6108	0·116	2·014	0·0576	0·216
0·3690	0·8571	0·272	2·967	0·0917	0·231
0·4667	0·7562	0·282	3·144	0·0897	0·215
0·7030	0·5114	0·269	3·566	0·0756	0·201
0·9414	0·2639	0·177	3·993	0·0443	0·191

In the present instance

$$\frac{\sum\nu_i z_i^2}{\nu} = 1.$$

According to measurements by Harrington† the dielectric constant of sugar solutions can be expressed by the formula

$$D_m = D_0(1-0{\cdot}079\gamma)$$

so that

$$A = 0{\cdot}079.$$

(311) then gives for the mean radius of the K^+ and Cl^- ions

$$b = \frac{0{\cdot}079}{2{\cdot}2}\times 3{\cdot}45\times10^{-8} = 1{\cdot}24\times10^{-8}\text{ cm.}$$

This radius is of the order of magnitude expected. Similarly, Rivett's data for the effect of K_2SO_4, $Mg(NO_3)$, and $CuSO_4$ upon the sugar solu-

† E. A. Harrington, *Phys. Rev.* **8** (1916), 581.

tion lead to reasonable values for the mean ionic radii. If we remember that the idea of a homogeneous medium of known dielectric constant extending right up to the ion is a very crude one, this result must be regarded as satisfactory. We can at least consider the general theory of salt action described above as probably correct.† It is especially interesting that Harrington found urea to be one of the few substances which raise the dielectric constant of water. Harrington's data at low concentrations are represented by the formula

$$D_m = D_0(1+0{\cdot}038\gamma).$$

We should therefore expect that a mixture of urea and a strong electrolyte would give a smaller freezing-point lowering than the sum of the separate lowerings. McAulay found experimentally that this actually was so.

Introducing the molar concentration γ' into (318) we obtain

$$\log f = A\nu\gamma' \frac{\sum v_i z_i^2}{\nu} \frac{3{\cdot}45\times 10^{-8}}{b}.$$

Taking the case of KCl and sugar and using the value given above $A = 0{\cdot}079$, this gives an increase of 19 per cent. in the activity coefficient of sugar for an addition of 0·4 mole KCl per litre.

C. *More exact theory of the salting-out effect.*

We shall now consider in more detail the question of the salt effect‡ and at the same time obtain an improvement on equation (318). It is possible to obtain a clearer picture of the state of affairs in the neighbourhood of an ion, if we assume that the interionic forces are the only forces acting. We shall show that it is possible to account for a considerable part of the salting-out effect, though this fact in no way excludes the existence of other forces or chemical combinations which may be of importance.

† For further examples, see the article by G. Scatchard, *Chem. Rev.* **3** (1927), 383. Scatchard shows that various dielectrics lead to approximately the same values for b. For the case given above he obtains $b = 1{\cdot}3\times 10^{-8}$ cm. F. H. MacDougall and D. R. Blumer (*J. Am. Chem. Soc.* **55** (1933), 2236) found approximate agreement with the theory of Debye and McAulay in the case of aqueous solutions of acetic and sulphuric acids. The formulae of Debye and McAulay are also applicable to the solubility of gaseous non-electrolytes in electrolyte solutions. See e.g. the investigations of M. S. Sherrill and E. J. Izard (*J. Am. Chem. Soc.* **53** (1931), 1667) on the solubility of chlorine in strong electrolytes.

‡ The theory was given by Debye, *Z. phys. Chem.* **130** (1927), 56. For a summary and discussion of earlier investigations, see *Handb. d. angew. phys. Chem.*, edited by G. Bredig, vol. vii; V. Rothmund, *Löslichkeit und Löslichkeitsbeeinflüssung*, p. 48, Leipzig, 1907. See also M. Randall and C. Failey, *Chem. Rev.* **4** (1927), 271 and 285; G. Scatchard, ibid. **3** (1927), 383; *Trans. Farad. Soc.* **23** (1927), 454. For other references, see p. 149.

For the sake of simplicity we consider an ion as a sphere of radius b and charge e, surrounded by a mixture consisting of N_1 molecules of substance 1 and N_2 molecules of substance 2. Further, let n_1 and n_2 be the corresponding numbers of molecules per c.c., and

$$\eta_1 = \frac{n_1}{n_1+n_2}, \qquad \eta_2 = \frac{n_2}{n_1+n_2} \tag{325}$$

the mole fractions. For an ideal mixture,

$$n_1 v_1 + n_2 v_2 = 1, \tag{326}$$

where v_1 and v_2 are volume constants for the two sorts of molecules. If the mixture is not ideal, v_1 and v_2 are not constant, and it is necessary to introduce activities. The free energy of a volume element dV of an ideal mixture is according to (265)

$$[n_1(\bar{\phi}_1 + kT\log\eta_1) + n_2(\bar{\phi}_2 + kT\log\eta_2)]\,dV. \tag{327}$$

In order to calculate the corresponding free energy for the real solution, we must take into account the energy of the electric field surrounding the ion. For a volume element dV distant r from the ion, this has the value†

$$\frac{(D_m\mathfrak{E})^2}{8\pi D_m}\,dV = \frac{\left[\frac{\partial}{\partial r}\left(\frac{e}{r}\right)\right]^2}{8\pi D_m}\,dV = \frac{e^2}{8\pi r^4}\frac{1}{D_m}\,dV, \tag{328}$$

where D_m is the dielectric constant of the mixture. All quantities in this formula are in electrostatic units. The thermodynamic potential of the whole system is thus

$$\Phi = \int dV\left[n_1(\bar{\phi}_1 + kT\log\eta_1) + n_2(\bar{\phi}_2 + kT\log\eta_2) + \frac{e^2}{8\pi r^4}\frac{1}{D_m}\right], \tag{329}$$

where the integration must be extended over the whole volume of the solution. Φ depends upon the spatial distribution of components 1 and 2 relative to the ion. The equilibrium distribution (see p. 14) is that for which Φ is a minimum. Subject to the conditions that the numbers of molecules,

$$N_1 = \int n_1\,dV \qquad N_2 = \int n_2\,dV \tag{330}$$

must remain constant, and that at any point the values of n_1 and n_2 must satisfy (326). We now vary n_1 by δn_1 and n_2 by δn_2; since the

† More accurately, the potential of the ionic atmosphere (209′) must also be taken into account, giving the value

$$e^2\,dV\frac{\left[\frac{\partial}{\partial r}\left(\frac{e^{-\kappa_0 r}}{r}\right)\right]^2}{8\pi D_m} = \frac{e^2}{8\pi r^4}\frac{1}{D_m}(1+\kappa_0 r)^2 e^{-2\kappa_0 r}\,dV. \tag{328′}$$

The calculation can also be easily carried out in this case. See P. Gross, *Monatsh. d. Chem.* **53** (1929), **54**, 445.

dielectric constant depends upon the composition of the mixture, we have

$$\delta\Phi = \int dV\Big[\delta n_1\Big(\bar{\phi}_1 + kT\log\eta_1 - \frac{e^2}{8\pi r^4}\frac{1}{D_m^2}\frac{\partial D_m}{\partial n_1}\Big) + \\ + \delta n_2\Big(\bar{\phi}_2 + kT\log\eta_2 - \frac{e^2}{8\pi r^4}\frac{1}{D_m^2}\frac{\partial D_m}{\partial n_2}\Big)\Big].$$

Also, from (326) $$v_1\delta n_1 + v_2\delta n_2 = 0. \tag{331}$$

In order to satisfy (331), we write

$$\delta n_1 = v_2\delta\chi; \quad \delta n_2 = -v_1\delta\chi, \tag{332}$$

where $\delta\chi$ is an arbitrary variation. Consequently,

$$\delta\Phi = \int dV\delta\chi\Big[v_2\Big(\bar{\phi}_1 + kT\log\eta_1 - \frac{e^2}{8\pi r^4}\frac{1}{D_m^2}\frac{\partial D_m}{\partial n_1}\Big) - \\ - v_1\Big(\bar{\phi}_2 + kT\log\eta_2 - \frac{e^2}{8\pi r^4}\frac{1}{D_m^2}\frac{\partial D_m}{\partial n_2}\Big)\Big]. \tag{333}$$

Applying the variations to (330), and remembering that (332) must hold, we have

$$\int dV d\chi = 0. \tag{334}$$

Since at equilibrium $d\Phi = 0$, the solution of the problem is obtained by multiplying (334) by an arbitrary constant, adding (333), and equating the factor of $\delta\chi$ inside the integral to zero. Thus for any distance r from the ion

$$v_2\Big(\bar{\phi}_1 + kT\log\eta_1 - \frac{e^2}{8\pi r^4}\frac{1}{D_m^2}\frac{\partial D_m}{\partial n_1}\Big) - \\ - v_1\Big(\bar{\phi}_2 + kT\log\eta_2 - \frac{e^2}{8\pi r^4}\frac{1}{D_m^2}\frac{\partial D_m}{\partial n_2}\Big) = \text{const.} \tag{335}$$

At great distances from the ion the concentrations are naturally unaffected by the electric field of the ion; if these concentrations are η_1^0 and η_2^0, we have for the constant in (335)

$$\text{const.} = v_2(\bar{\phi}_1 + kT\log\eta_1^0) - v_1(\bar{\phi}_2 + kT\log\eta_2^0). \tag{336}$$

Inserting this value in (335) we obtain the distribution equation

$$v_2\log\frac{\eta_1}{\eta_1^0} - v_1\log\frac{\eta_2}{\eta_2^0} = \frac{e^2}{8\pi kT}\frac{1}{D_m^2}\Big(v_2\frac{\partial D_m}{\partial n_1} - v_1\frac{\partial D_m}{\partial n_2}\Big)\frac{1}{r^4}. \tag{337}$$

Thus if we know the dielectric constant D_m as a function of the composition of the mixture, (337) enables us to determine the concentration of both components at any distance r from the ion. It is assumed that D_m is independent of r, i.e. we are neglecting any phenomena of electric saturation in the neighbourhood of the ion.

(337) can thus be evaluated in any case, and the resulting curve for

η_1 as a function of r used to carry out the integration over the whole of the space surrounding the ion, and thus to obtain the total effect due to the ion. For the sake of simplicity, we shall consider a mixture which contains only small quantities of the component 2. Writing η and η^0 in place of η_2 and η_2^0, we have also

$$\eta_1 = 1-\eta, \qquad \eta_1^0 = 1-\eta^0. \tag{338}$$

The left hand side of (337) then becomes

$$v_2 \log \frac{1-\eta}{1-\eta_0} - v_1 \log \frac{\eta}{\eta_0}\, v_2(\eta^0-\eta) - v_1 \log \frac{\eta}{\eta^0}. \tag{339}$$

If we now assume that the substance 2 is being salted out, η^0 is small, and $\eta/\eta^0 \ll 1$. We can therefore neglect the first term in the right-hand side of (339) and retain only $-v_1 \log \eta/\eta^0$. We also write

$$\tilde{R}^4 = \frac{e^2}{8v_1 \pi k T} \frac{1}{D_m^2} \left(v_2 \frac{\partial D_m}{\partial n_1} - v_1 \frac{\partial D_m}{\partial n_2} \right), \tag{340}$$

where $\tilde{R}$ is a characteristic length. Integration then gives immediately

$$\eta = \eta^0 e^{-\tilde{R}^4/r^4}. \tag{341}$$

This equation shows that the salting-out effect decreases rapidly with increasing r. We shall further assume that for the small concentrations being considered, the dielectric constant D_m is a linear function of η_1 and η_2, i.e.

$$D_m = \eta_1 D_1 + \eta_2 D_2. \tag{342}$$

This gives

$$v_2 \frac{\partial D_m}{\partial n_1} - v_1 \frac{\partial D_m}{\partial n_2} = (D_1-D_2) \frac{v_1 n_1 + v_2 n_2}{(n_1+n_2)^2} = \frac{D_1-D_2}{(n_1+n_2)}.$$

Referring back to (338), since the concentration of the second component is small

$$\frac{1}{n_1+n_2} = \frac{1}{n_1} = v_1.$$

If we further replace D_m by the dielectric constant of the first component D_1, (340) becomes

$$\tilde{R}^4 = \frac{e^2 v_1}{8\pi k T} \frac{D_1-D_2}{D_1^2} \quad \text{or} \quad \tilde{R}^4 = \frac{e^2 V_1}{8\pi R T} \frac{D_1-D_2}{D_1^2}. \tag{343}$$

V_1 is the volume of one mole of the first component, and R the gas constant. We shall for the moment assume that all the simplifications introduced are justified. The linear law (342) may be tested by measuring the dielectric constants of mixtures of 1 and 2. Since

$$\eta_1 = 1-\eta_2 = 1-\eta,$$

D_m can be written

$$D_m = D_1 - (D_1-D_2)\eta. \tag{344}$$

If the dielectric constant D_m is lowered by the addition of component 2, $D_1 - D_2 > 0$ and hence from (343) $\tilde{R}^4$ is positive. If addition of the second component causes an increase in the dielectric constant, $D_1 - D_2 < 0$ and $\tilde{R}^4$ is negative. From (341), these two cases correspond respectively to a decrease and an increase in the concentration of the second component in the neighbourhood of the ion. We shall now calculate the total decrease or increase in concentration (i.e. salting-out effect or the reverse) caused by an ion in virtue of its electric field. We have in general

$$n_1 = \frac{\eta_1}{v_1\eta_1 + v_2\eta_2}, \qquad n_2 = \frac{\eta_2}{v_1\eta_1 + v_2\eta_2},$$

so that for small concentrations of the second component,

$$n_2 = \frac{\eta_2}{v_1} = \frac{\eta}{v_1}.$$

(341) gives the concentration η as a function of r. Thus if we have a saturated solution of component 2 in component 1, also containing p ions per unit volume, the mean number of molecules of component 2 surrounding an ion is given by

$$\int n_2\, dV = \frac{\eta^0}{v_1}\int e^{-\tilde{R}^4/r^4}\, dV = \frac{\eta^0}{v_1}\left\{\int dV - \int (1 - e^{-\tilde{R}^4/r^4})\, dV\right\}, \quad (345)$$

where the integration is to be extended over the volume at the disposal of one ion. If we make the assumption that at a great distance from the ion the concentration is the same as it would be in the absence of the ion, then η^0 is the concentration at any point of a mixture containing no ions. The volume which corresponds to one ion after the addition of salt will thus contain (before this addition)

$$\frac{\eta^0}{v_1}\int dV \quad (346)$$

molecules of 2. Thus if Z_2 and Z_2' are the numbers of molecules present in the solution respectively before and after the addition of salt, we have from (345),

$$\frac{Z_2'}{Z_2} = 1 - \frac{\int (1 - e^{-\tilde{R}^4/r^4})\, dV}{\int dV}. \quad (347)$$

The integration is to be extended over the volume available for one ion, so that

$$\int dV = \frac{1}{p}. \quad (348)$$

Since the integrand in (347) converges rapidly to zero for large values of

r, the integration in the numerator can be extended from b to ∞. Introducing a salt factor σ defined by

$$\sigma = \int_b^\infty (1-e^{-\tilde{R}^4/r^4})4\pi r^2\, dr \tag{349}$$

the salting-out effect is given by

$$Z_2' = Z_2(1-\sigma p). \tag{350}$$

Since we have calculated the effect of the added ions only for small salt concentrations, the effect is proportional to p, the number of ions per c.c.

We now write $$\sigma = \frac{4\pi}{3}\tilde{R}^3 s, \qquad \rho = \frac{r}{\tilde{R}}, \tag{351}$$

so that $$s = s\left(\frac{\tilde{R}}{b}\right) = 3\int_{b/\tilde{R}}^\infty (1-e^{-1/\rho^4})\rho^2\, d\rho. \tag{352}$$

For large values of $\tilde{R}/b$ this gives the series

$$s = 3{\cdot}626-\left(\frac{b}{\tilde{R}}\right)^3+\left(\frac{b}{\tilde{R}}\right)^3 e^{-\tilde{R}^4/b^4}\left\{\frac{3}{4}\left(\frac{b}{\tilde{R}}\right)^4-\frac{3}{4}\frac{7}{4}\left(\frac{b}{\tilde{R}}\right)^8+\ldots\right\}. \tag{353}$$

Small values of $\tilde{R}/b$ lead to

$$s = \frac{3\tilde{R}}{b}\left\{1-\frac{1}{2!}\frac{1}{5}\left(\frac{\tilde{R}}{b}\right)^4+\frac{1}{3!}\frac{1}{9}\left(\frac{\tilde{R}}{b}\right)^8-\frac{1}{4!}\frac{1}{13}\left(\frac{\tilde{R}}{b}\right)^{12}+\ldots\right\}. \tag{354}$$

Since the integral in (349) cannot be expressed explicitly in a finite form, it is necessary to employ the series (353) and (354). The treatment given in the preceding section corresponds to the approximation

$$s = \frac{3\tilde{R}}{b}, \tag{355}$$

as may be seen by reference to (350). Numerical values for the function s are given in Table 24.

TABLE 24

$\frac{\tilde{R}}{b}$	0	0·5	1·0	1·5	2·0	∞
s	0	1·49	2·75	3·33	3·50	3·63

It is seen that s approaches a limiting value of 3·63 for high values of $\tilde{R}/b$, i.e. even an infinitely small ion can only produce a finite effect.

We shall now discuss some examples of the salting-out effect, beginning with the case of ethyl ether in water. For water at 23°, $D_1 = 80{\cdot}3$

and according to measurements of J. W. Williams, D_m for the saturated solution of ether is 74·5. If the linear law (342)

$$D_m = D_1\eta_1 + D_2\eta_2$$

applies, $D_1 = 80{\cdot}3$ and $D_2 = -295$, since from measurements by Osaka† the saturated solution at 23° contains 6·07 gm. ether and 93·93 gm. water, which gives

$$\eta_1 = 1 - 0{\cdot}0154$$

$$\eta_2 = 0{\cdot}0154.$$

If we add one mole of KCl to one litre of solution, then neglecting any volume change, the number of ions in one c.c. is $\rho = 12{\cdot}1 \times 10^{20}$. For the limiting case of small ions, the salt factor σ is given by

$$\sigma = 3{\cdot}63\frac{4\pi}{3}\tilde{R}^3.$$

Inserting in equation (343) the values

$$e = 4{\cdot}77 \times 10^{-10}, \qquad R = 8{\cdot}31 \times 10^{7}, \qquad D_1 - D_2 = 375,$$

$$V_1 = 18, \qquad T = 296, \qquad D_1 = 80{\cdot}3,$$

we obtain for the characteristic length

$$\tilde{R} = 2{\cdot}49 \times 10^{-8}\ \text{cm.}$$

and hence

$$p\sigma = 0{\cdot}285.$$

If all our assumptions are allowable in such concentrated solutions, (350) predicts that 28 per cent. ether should be salted out. Measurements by Euler‡ at 18° give salting-out effects of 33 per cent., 42 per cent., and 40 per cent. by one mole per litre of LiCl, NaCl, and KCl respectively. Thus in spite of the many approximations, the electric effect seems to be an important factor in the salting-out effect.

The salting-out effect has recently been the subject of much study.§

† Y. Osaka. *Mem. Coll. of Science, Kyoto Univ.* **2** (1910), 21.

‡ Euler, *Z. phys. Chem.* **31** (1894), 360; **49** (1904), 303.

§ See K. Linderström-Lang, *Compt. Rend. Lab. Carlsberg*, **15** (1924), No. 4; **17** (1929), No. 13 (hydroquinone, quinone, succinic acid, boric acid); S. Glasstone and J. Pound, *J. Chem. Soc.* (1925), 2660; Glasstone, D. W. Dimond, and E. C. Jones, ibid. (1926), 2935 (ethyl acetate); Glasstone, J. Bridgman, and W. R. P. Hodgson, ibid. (1927), 635 (aniline); Kwantero Endo, *J. Chem. Soc. Jap.* **47** (1926), 374; *Bull. Chem. Soc. Jap.* **2** (1927), 24 (phenol); W. Herz and E. Stanner, *Z. phys. Chem.* **128** (1927), 399 (distribution of acetone, phenol, benzoic acid, and trimethylamine); J. S. Carter and R. K. Hardy, *J. Chem. Soc.* (1928), 127 (*m*-cresol); G. Åkerlöf, *J. Am. Chem. Soc.* **51** (1929), 984 (distribution of diacetone alcohol); N. Schlesinger and W. Kubasowa, *Z. phys. Chem.* **142** (1929), 25 (ethyl acetate); E. Abel and E. Neusser, *Monatsh. f. Chem.* **53/54**, (1929) 855; *Sitz. Akad. d. Wiss. Wien* (IIb), **138** (1929), 855 (Suppl.) (nitrous acid); J. N. Brönsted, *Z. phys. Chem.* **103** (1929), 160; *Chem. Rev.* **5** (1928), 278; M. Randall and C. F. Failey, *Chem. Rev.* **4** (1927), 291; P. Gross, *Monatsh. f. Chem.* **53/54** (1929), 449; *Sitz. Akad. d. Wiss. Wien* (IIb), **138** (1929), 449 (Suppl.); P. Gross and K. Schwarz,

In connexion with this work we shall continue from equation (350)

$$Z_2' = Z_2(1-p\sigma) \tag{356}$$

$p\sigma$ can be written

$$p\sigma = \frac{4\pi \mathbf{N}}{1{,}000} \sum J_j \gamma_j, \tag{357}$$

where the γ_j's are the molar concentrations of the ions of the added electrolytes. The J_j's are defined as follows. According to (344)

$$D_m = D_1\left(1-\frac{D_1-D_2}{D_1}\eta\right) = D_1(1-\alpha' c), \tag{358}$$

where c is the volume concentration and

$$c = \frac{\eta}{V_1}, \qquad \alpha' = \frac{D_1-D_2}{D_1}V_1. \tag{359}$$

The fourth power of the characteristic length can then be written in the form

$$\tilde{R}_j^4 = \frac{z_j^2 \epsilon^2}{8\pi RT}\frac{\alpha'}{D_1}. \tag{360}$$

In this case we shall employ the integral

$$(J_j)_1 = \int_{b_j}^{\infty} (1-e^{-\tilde{R}_j^4/r^4})r^2\, dr \tag{361}$$

(b_j = radius of an ion of the jth sort), which according to (353) and (354) can be expanded as one of the following two series,

$$(J_j)_1 = \tilde{R}_j^3\left\{1{\cdot}21-\frac{1}{3}\left(\frac{b_j}{\tilde{R}_j}\right)^3-\ldots\right\} \quad (\tilde{R}_j > b_j), \tag{361'}$$

$$(J_j)_1' = \frac{\tilde{R}_j^4}{b_j}\left\{1-\frac{1}{2!\,5}\left(\frac{\tilde{R}_j}{b_j}\right)^4+\ldots\right\} \quad (\tilde{R}_j > b_j). \tag{361''}$$

We have supposed here that $\alpha' > 0$. We can, however, also have $\alpha' < 0$, i.e.

$$D_m = D_1(1+\alpha' c). \tag{362}$$

In this case (361) is replaced by

$$(J_j)_2 = \int_{b_j}^{\infty} (1-e^{\tilde{R}_j^4/r^4})r^2\, dr. \tag{363}$$

Monatsh. d. Chemie, **55** (1930), 287, 329; *Sitz. Akad. d. Wiss. Wien* (II b), **139** (1930), 179; P. Gross and M. Iser, ibid. (II b), **139** (1930), 221; E. Larsson, *Z. phys. Chem.* **148 A** (1930), 148, 304; **153** (1931), 299 (benzoic acid). See also M. Kolthoff and W. Bosch, *J. Phys. Chem.* **36** (1932), 1885. In the theory developed above the ions have been assumed to be spheres with charges at their centres. In the case of most organic ions this assumption is certainly not true, which may lead to the deviations from the theory observed in this case. Certain anomalies which cannot be explained by Debye's theory have been discussed by P. M. Gross (*Chem. Rev.*, August, 1933), who also gives a general account of the salting-out phenomena.

This gives e.g. if $b_j > \tilde{R}_j$ the series

$$(J_j)_2 = -\frac{R_j^4}{b_j}\left\{1+\frac{1}{2!\,5}\left(\frac{\tilde{R}_j^4}{b_j}\right)^4+\ldots\right\}. \tag{363'}$$

The formula

$$Z_2' = Z_2\left(1-\frac{4\pi\mathbf{N}}{1{,}000}\sum J_j\gamma_j\right) \tag{364}$$

becomes on introducing the activity coefficient f,

$$\frac{1}{f} = \frac{Z_2'}{Z_2} = 1-\frac{4\pi\mathbf{N}}{1{,}000}\sum J_j\gamma_j. \tag{365}$$

As an example we shall take the salting-out effect for aqueous solutions of acetone and hydrocyanic acid, recently investigated by Gross (loc. cit.). For acetone, a somewhat arbitrary interpolation gives for low concentrations

$$D_m = D_1(1-0{\cdot}0367c),$$

while for hydrocyanic acid,

$$D_m = D_1(1+0{\cdot}0039c).$$

According to our general considerations, acetone should be salted out while hydrocyanic acid should show the reverse effect. The characteristic length for acetone is given by (360) as

$$\tilde{R}_{(\text{acetone})} = 2{\cdot}03\times10^{-8}\text{ cm.}$$

Since further in the limit $(J) = \tilde{R}^3 1{\cdot}21$,

we have from (365)

$$\frac{1}{f} = 1-0{\cdot}158\gamma_s\text{ (acetone)}$$

or

$$\frac{1}{f} = 1-\frac{0{\cdot}27\times10^{-8}}{b}\gamma_s,$$

according to whether we use (361') or (361''). For hydrocyanic acid the corresponding characteristic length is

$$\tilde{R}_{\text{HCN}} = 1{\cdot}2\times10^{-8}\text{ cm.},$$

i.e.

$$\frac{1}{f} = 1+\frac{0{\cdot}027\times10^{-8}}{b}\gamma_s.$$

Gross confirmed experimentally the order of magnitude of the theoretical values for the activity coefficients. He determined the partition of acetone and hydrocyanic acid between benzene and water. If $(c_b/c_w)_0$ is the partition coefficient in the absence of electrolytes, and $(c_b/c_w)_s$ the same coefficient after salt has been added, we have

$$f = \left(\frac{c_b}{c_w}\right)_s\Big/\left(\frac{c_b}{c_w}\right)_0.$$

The magnitude of the effect observed with acetone and hydrocyanic acid agrees approximately with the theory for the nitrates of lithium, sodium, potassium, caesium, and magnesium, the chlorides of lithium, sodium, and potassium, and the sulphates of potassium, magnesium, and lanthanum. A comparison of the measurements on acetone and hydrocyanic acid in presence of potassium nitrate and caesium nitrate show that the requirements of Debye's theory (in particular the inversion of the salting-out effect) are satisfied (cf. (358) and (362)). It is interesting to note that with a few exceptions† (e.g. lithium nitrate and magnesium chloride) hydrocyanic acid exhibits the anticipated inversion of the salting-out effect. The salting-out effect depends on the nature of the salt, but the effects referred to the same ionic strength are of approximately the same magnitude. The salting-out effect is but little dependent on the temperature and the concentration of the non-electrolyte, but is approximately proportional to the concentration of the salt, i.e. the quantity $(1/f-1)/\gamma_s$ is approximately constant and of the order of magnitude expected from (365). The inversion of the effect for hydrocyanic acid is, however, met with much less frequently at higher salt concentrations.‡

D. *Neutral salt effects.*

We shall now treat shortly the effect of a neutral salt upon the degree of dissociation of a weak electrolyte.§ Arrhenius's theory showed that

† See also P. M. Gross, *Chem. Rev.*, August, 1933.

‡ The formulae for the salting-out effect can also be developed from (328′). It is then found that the effect of the ionic atmosphere amounts to about 20 per cent. even in dilute solutions. See especially the work of P. Gross and his collaborators, loc. cit.

§ The effect of neutral salts upon the hydrolysis of salts can be treated in a similar manner. Brönsted has shown that this may be considered as a particular case of the general acid-base equilibrium. $A \leftrightharpoons B+H^+$.

If the valencies of the acid and base are respectively z_A and z_B, we have

$$z_B = z_A + 1,$$

and the dissociation equilibrium is governed by the equation

$$\log K_\gamma = \log K_a - z_B \sqrt{J} + \text{const.} \times J,$$

where a further linear term in J has been added. Thus, in the case of the dissociation of NH_4^+,

$$z_B = 0$$

and the square-root term vanishes, so that in this case the addition of neutral salts will have no effect at very small concentrations.

In a similar manner it may be easily shown that the dissociation equilibrium of bases is governed by the equation

$$\log K_\gamma = \log K_a + z_A \sqrt{J} + \text{const.} \times J.$$

Brönsted and his collaborators have treated yet more general cases, e.g. the equilibrium between four charged or uncharged molecules,

$$A+B \rightleftharpoons C+D$$

the dissociation of a weak electrolyte is strongly repressed by the addition of a neutral salt having a common ion. We shall, however, now show that on account of the interionic forces, this repression of the degree of dissociation in not so great as predicted by the classical theory. The dissociation of a weak acid is governed by the generalized law of mass action, which we may write

$$K_a = \frac{a_{H^+}\, a_{S^-}}{a_{HS}}. \tag{366}$$

If we now introduce the activity coefficients of the ions, and identify the activity a_{HS} of the undissociated acid in dilute solution with its concentration γ_{HS}, we have

$$K_a = \frac{\gamma_{H^+}\gamma_{S^-}}{\gamma_{HS}} f_{H^+} f_{S^-} = K\gamma f_{\pm}^2, \tag{366'}$$

$f_{\pm}$ is the mean activity coefficient according to (136). According to the Debye-Hückel theory, if we are dealing with dilute aqueous solutions at 20°, $\log_{10} f_{\pm}$ is related to the ionic strength J by the equation

$$\log_{10} f_{\pm} = -0{\cdot}50\sqrt{J}.$$

We then have from (366'),

$$\log_{10} K_\gamma = \log_{10} K_a + \sqrt{J}. \tag{367}$$

At constant pressure and temperature, K_a is a constant, so that it follows from (367) that on increasing the concentration of neutral salt the dissociation of the weak electrolyte must be increased. Cohn, Heyroth, and Menkin† were in fact able to confirm (367) experimentally as a limiting law for small ionic strengths. They chose acetic acid as the weak electrolyte, and sodium acetate as the neutral salt. Fig. 29 shows the experimental values of $\log_{10} K_\gamma$ plotted against the square root of the ionic strength. The K_γ values were determined electrometrically by using mixtures of sodium acetate and acetic acid in a hydrogen ion concentration cell. (See equation (168).) This gives a_{H^+}; γ_{S^-}, γ_{HS}, and γ_{Na^+} are known, and hence the ionic strength J (223) which determines the activity coefficient of the hydrogen ion f_{H^+}. This leads to γ_{H^+} and finally K_γ.

in which case the limiting law is

$$\log K_\gamma = \log K_a - (z_C z_D - z_A z_B)\sqrt{J}.$$

For details, see J. N. Brönsted, *Rec. Trav. Chim. Pays-Bas.* **42** (1923), 718; *J. Phys. Chem.* **30** (1926), 777; *Chem. Ber.* **61** (1928), 2049; *Chem. Rev.* **5** (1928), 231; *Trans. Farad. Soc.* **24** (1928), 630; J. N. Brönsted and C. V. King, *Z. phys. Chem.*, Cohen Festb. (1927), 699; J. N. Brönsted and K. Volqvartz, ibid. **134** (1928), 97; **155 A** (1931), 211. See also the symposium in *Chem. Rev.* **10** (1932), 1–264.

† E. J. Cohn, F. F. Heyroth, and M. F. Menkin, *J. Am. Chem. Soc.* **50** (1928), 696.

In conclusion, we may give some numerical values to illustrate the order of magnitude of the neutral salt effect. In the example quoted above, K_γ according to the classical theory is $1{\cdot}84\times10^{-5}$, which gives by (366') $\gamma_{H^+} = 1{\cdot}62\times10^{-4}$ in a mixture of 0·008 molar sodium acetate and 0·072 molar acetic acid. We shall show that this value is actually too low, since the interionic forces have not been taken into account. We have

$$\gamma_{HS} = 0{\cdot}072, \qquad \gamma_{Na^+} = 0{\cdot}008,$$
$$\gamma_{S^-} = 0{\cdot}008+\gamma_{H^+} \sim 0{\cdot}008+0{\cdot}00016.$$

Experimentally it was found that the activity of the hydrogen ion was

$$a_{H^+} = 0{\cdot}000179.$$

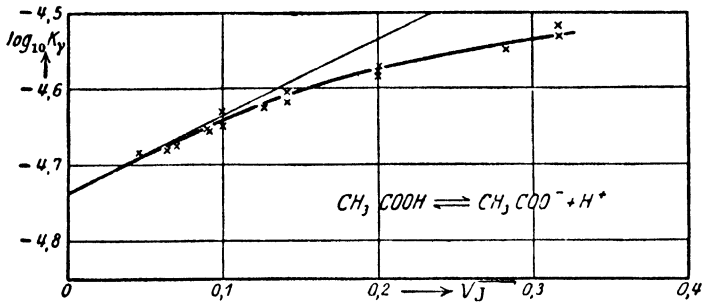

FIG. 29. Variation of dissociation constant with ionic strength.

The ionic strength in this case is

$$J = \tfrac{1}{2}(0{\cdot}008+0{\cdot}00818+0{\cdot}00016) = 0{\cdot}0082.$$

According to the results of Lewis, this corresponds to an activity coefficient for the hydrogen ion of $f_{H^+} = 0{\cdot}913$, so that

$$\gamma_{H^+} = 0{\cdot}000179/0{\cdot}913 = 0{\cdot}000196.$$

The interionic action thus causes an increase of about 20 per cent. in the hydrogen ion concentrations.

33. The Heat of Dilution of Strong Electrolytes

A. *The theoretical limiting law.*

The integral heat of dilution† which we shall term L when it refers to an arbitrary number of moles, and $\bar{L}$ when it refers to one mole, is

† The expression for the heat of dilution can also be readily obtained from the general form of van 't Hoff's equation (44),

$$\left(\frac{\partial \log a_h}{\partial T}\right)_p = \frac{-\bar{L}_h}{RT^2},$$

where $\bar{L}_h$ is the partial molal heat content of the component h, and a_h is its activity. This gives immediately for the heat of dilution, $\bar{L} = -\nu RT^2 \partial \log f/\partial T$, and in conjunction with (275) and (290) leads to (373). For numerous references, see E. Lange, 'Über

equal to the decrease in U, the internal energy of the solution. If we term the difference between the real and ideal free energy of the solution W, (217) and (247) give

$$W = \frac{VkT}{12\pi}\kappa^3, \tag{368}$$

where V is the volume of the solution. The Gibbs-Helmholtz equation (9) connecting the free energy F and the total energy U then gives for the integral heat of dilution,

$$L = U = W - T\left(\frac{\partial W}{\partial T}\right)_v = \frac{VT\epsilon^2}{D_0}\sum n_i z_i^2 \frac{\partial \kappa}{\partial T}. \tag{369}$$

Introducing the value of κ^2 from (217),†

$$L = -\frac{V\epsilon^2}{2D_0}\sum n_i z_i^2 \kappa\left(1 + \frac{T}{D_0}\frac{dD_0}{dT}\right). \tag{370}$$

If there are γ_i moles of ions present,

$$Vn_i = \mathbf{N}\gamma_i, \tag{371}$$

and hence

$$L = -\epsilon^2\mathbf{N}\frac{\sum \gamma_i z_i^2}{2D_0}\kappa\left(1 + \frac{T}{D_0}\frac{dD_0}{dT}\right). \tag{372}$$

We therefore have for the heat of dilution per mole‡

$$\bar{L} = -\frac{\epsilon^2\mathbf{N}}{2D_0}\sum \nu_i z_i^2 \kappa\left(1 + \frac{T}{D_0}\frac{dD_0}{dT}\right). \tag{373}$$

In the case of simple electrolytes the molar heat of dilution becomes,

$$\bar{L} = -\left(\frac{\sum \nu_i z_i^2}{2}\right)^{\frac{3}{2}}\frac{\mathbf{N}\epsilon^2}{D_0}\left(\frac{8\pi\epsilon^2\mathbf{N}}{1{,}000 D_0 kT}\right)^{\frac{1}{2}}\left(1 + \frac{T}{D_0}\frac{dD_0}{dT}\right)\gamma^{\frac{1}{2}}. \tag{374}$$

If, as is usual, the heat of dilution is measured in calories,

$$\bar{L} = -\frac{0{\cdot}239}{10^7}\left(\frac{\sum \nu_i z_i^2}{2}\right)^{\frac{3}{2}}\frac{\mathbf{N}\epsilon^2}{D_0}\left(\frac{8\pi\epsilon^2\mathbf{N}}{1{,}000 D_0 kT}\right)^{\frac{1}{2}}\left(1 + \frac{T}{D_0}\frac{dD_0}{dT}\right)\gamma^{\frac{1}{2}} \text{ cals./mol.} \tag{375}$$

Lösungs- und Verdünnungswärmen einiger starker Elektrolyte', *Fortschr. d. Chem., Phys. u. phys. Chem.* **19** (1928), No. 6. The significance of the dielectric constant in the thermodynamic derivation of the free energy and heat of dilution of electrolyte solutions was first recognized by Cavanagh (*Phil. Mag.* (6) **43** (1922), 625). Gross and Halpern (*Phys. Z.* **26** (1925), 403) gave the first thorough treatment of the problem of heats of dilution on the basis of statistical mechanics.

† It is not specified in (370) whether the term in brackets involves $(\partial D/\partial T)_p$ or $(\partial D/\partial T)_v$. If L represents ΔU the differentiation should be carried out at constant volume, while the temperature coefficient usually measured is at constant pressure. O. Gatty (*Phil. Mag.* **11** (1931), 1082) has investigated the error introduced in this way, and finds that it is small in the case of water, but may be considerable for some non-aqueous solvents.

‡ The ionic strength J (223) can be introduced in (372). Since, however, mixtures have not been investigated experimentally, we shall not deal with them here.

It is interesting to consider the physical interpretation of (375). In an ideal solution, no heat changes take place on adding water, since (as for ideal gases) the total energy is independent of the volume. We should, however, expect in this case that on diluting work must be done against the attractive forces between the ions, so that we should anticipate a cooling of the solution which would depend chiefly upon the charge and concentration of the dissolved particles, and for the same type of electrolyte should be independent of any individual properties. On this view we should expect a negative heat of dilution for dilute solutions, while actually a positive heat is found.† The alteration in electrostatic energy for one mole of solute in dilute solution of concentration γ moles per litre is given by (227) and (238′) as

$$U_e = -\frac{1}{2}\frac{\mathbf{N}\epsilon^2}{D_0}\left(\frac{4\pi\epsilon^2\mathbf{N}}{1{,}000 D_0 kT}\right)^{\frac{1}{2}}\left(\sum \nu_i z_i^2\right)^{\frac{1}{2}}\gamma^{\frac{1}{2}}.$$

U_e is thus equal to the value obtained for the heat of dilution (374) by omitting the term in dD_0/dT.

Bjerrum‡ and Gross and Halpern§ have pointed out that the mutual electrostatic energy of the ions cannot be identified with the heat of dilution, since a further amount of energy is involved in the effect of the electric fields of the ions upon the solvent, which varies with the concentration. By considerations of this kind Bjerrum was able to show that the heat of dilution involved the temperature coefficient of the dielectric constant, and arrived at equation (375), which, as we have seen, can be derived directly from the Gibbs-Helmholtz equation. Bjerrum was probably the first to point out that the individual properties of different ions were much more prominent in their heats of dilution than e.g. in their osmotic coefficients $(1-g)$. Thus in the measurements of Richards and Rowe‖ on uni-univalent salts for concentrations between 0·139 and 0·227, the values of $1-g$ show good mutual agreement, while the heats of dilution are sometimes positive and sometimes negative. Negative heats of dilution are actually in the majority while according to (374) they should be positive and of the same magnitude for all mono-monovalent electrolytes. It is thus necessary to carry out measurements at much lower concentrations than Richards and Rowe in order to be able to test the validity of Debye's

† See p. 159.

‡ N. Bjerrum, *Z. phys. Chem.* **119** (1926), 145.

§ P. Gross and P. Halpern, *Phys. Z.* **26** (1925), 403.

‖ T. W. Richards and A. W. Rowe, *J. Am. Chem. Soc.* **43** (1921), 770; **44** (1922), 684. Richards and his collaborators later improved the experimental technique considerably; see Richards and F. T. Gucker, ibid. **47** (1925), 1876; **51** (1929), 712; Richards, B. J. Mair, and L. P. Hall, ibid. **51** (1929), 727.

theory of heats of dilution. Such measurements were first carried out by Nernst and Orthmann, and later still more accurately by Lange. Before comparing the results obtained with the theoretical predictions we shall give a short account of the experimental methods employed.

B. *Experimental methods for measuring the heat of dilution.* (*Nernst and Orthmann, Lange and Messner.*†)

Nernst and Orthmann were the first to develop a very accurate method for measuring heats of dilution, which made it possible to measure very small amounts of heat. The improved apparatus is sketched in Fig. 30. The differential calorimeter‡ which was used in measuring the heat change contained a set of 100 iron-constantan thermo-elements. The junctions of these stuck into small tubes filled with mercury placed alternately in each of the two calorimeter vessels, which were stirred at the same speed by two identical glass stirrers driven by the same motor. The solution to be diluted was contained in test-tubes with the bottom cut off, closed by means of a small piece of rubber tube and a glass plate. To mix the solutions, the glass plate was pushed down by means of a glass rod, and thorough mixing brought about by stirring with the glass plate. As a protection against external temperature variations, the whole inner part was surrounded by a thick copper casing, which was itself contained in a Dewar flask, and closed at the top by a layer of cotton wool 10 cm. thick. The temperature could be kept extremely constant. The sensitivity of the measurements was 0·00318 cals. per millimetre on the galvanometer scale. The accuracy of each measurement was about 1 mm., corresponding to a temperature difference of 5×10^{-6} degrees. Each half of the calorimeter contained two test-tubes each containing 10 c.c. of solution, which were

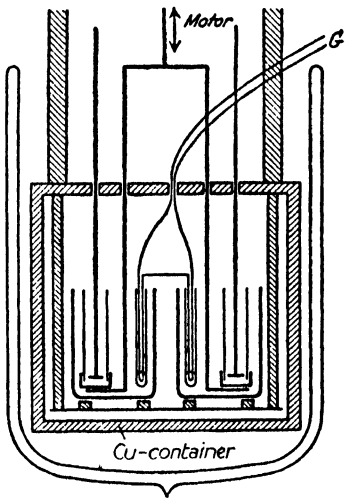

FIG. 30. The method of Nernst and Orthmann for measuring heats of dilution.

† W. Nernst and W. Orthmann, *Ber. d. Berl. Akad.* (1926), p. 51; (1927), p. 136; E. Lange and G. Messner, *Naturwiss.* **15** (1927), 521; see also *Lecture to the Bunsengesellschaft*, May, 1927.

‡ H. v. Steinwehr (*Z. phys. Chem.* **38** (1901), 185) and G. Rümelin (ibid. **58** (1907), 449) had previously described differential calorimeters, but their further development is due to Nernst and Orthmann.

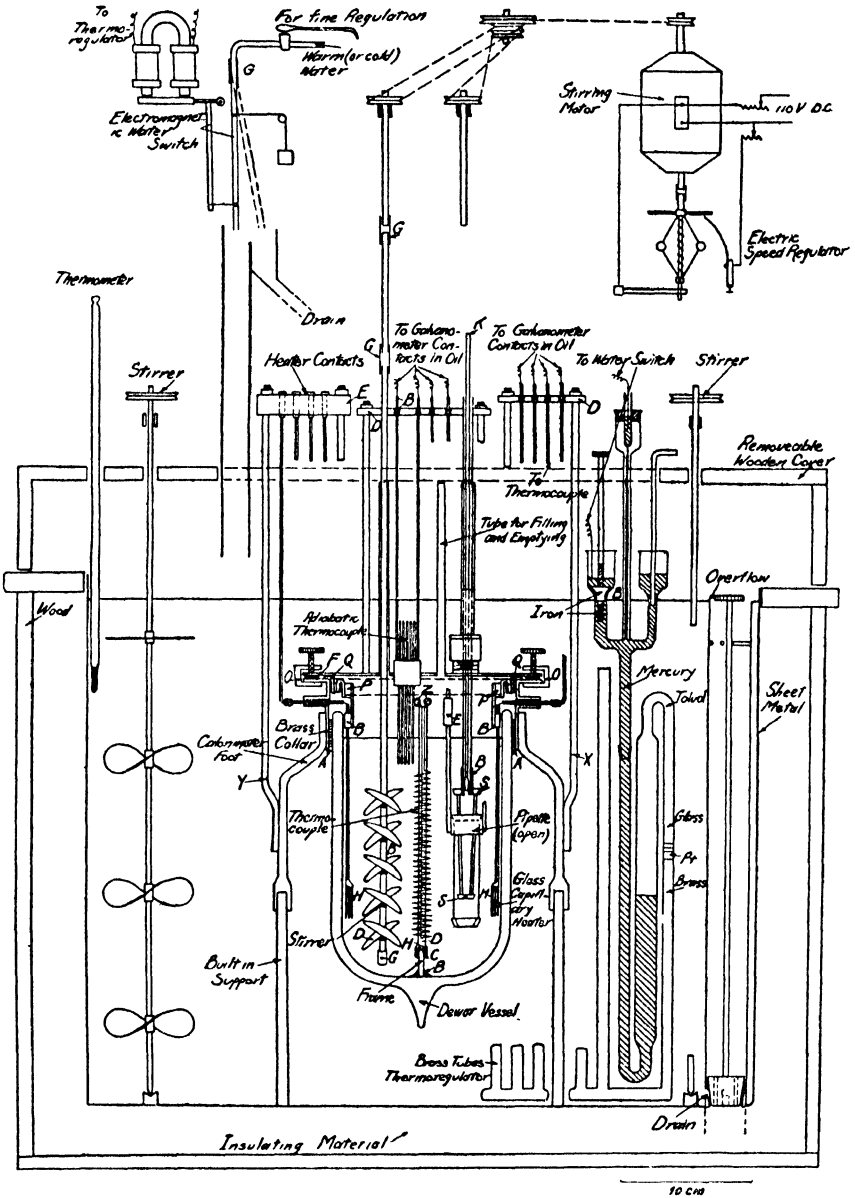

FIG. 31. Adiabatic differential calorimeter (Lange).

diluted one after another. Surrounding these was 500 c.c. conductivity water. The most important result of these investigations is that for all the electrolytes investigated at high dilution the sign found for the heat of dilution agrees with that predicted theoretically.

E. Lange and G. Messner used a similar apparatus (see Fig. 31). A Dewar flask was divided in two by a plate of hard rubber, thus forming the two calorimeter vessels. Each side contained the junctions of 1,000 thermo-elements. By means of a mirror galvanometer, the temperature difference between the two halves of the calorimeter could be measured to $1 \times 10^{-6}°$. Each half contained a metal pipette, which was surrounded by the contents of the calorimeter, and contained the solution to be diluted. The calorimeter was in a water bath which could be regulated to within 0·001° of the temperature of the interior of the calori-

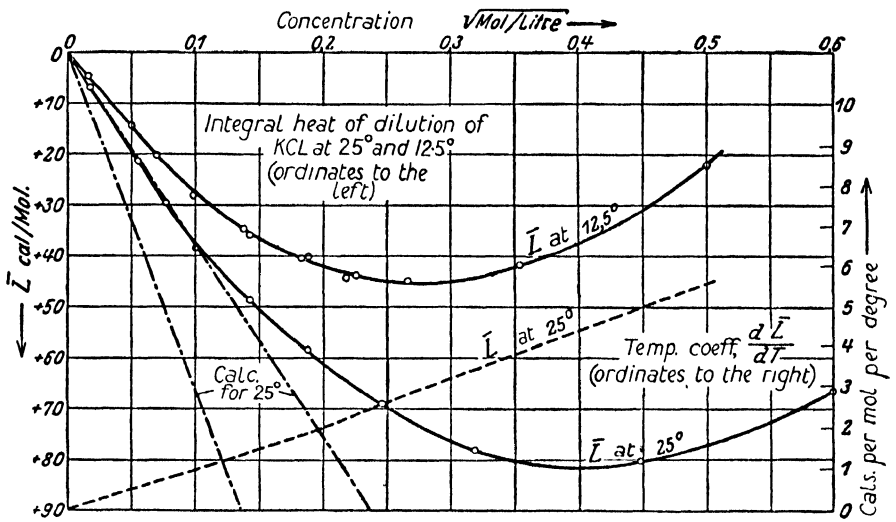

FIG. 32. Heat of dilution of KCl.

meter, thus eliminating any external disturbances. Lange and Messner worked at 25°, while the measurements of Nernst and Orthmann are at 18°. The agreement between the results of the two sets of authors is excellent in every respect, especially considering the difference in these temperatures.

We shall now turn to the experimental results.

C. *Comparison of the experimental data with theory.*

The theory requires (see (375)) that the heat of dilution should be proportional to the square root of the molar concentration. Fig. 32 shows the experimental results for KCl, and it is seen that the theory is confirmed to within 5 per cent. up to $\gamma = 0{\cdot}01$. Fig. 32 also shows the temperature coefficient $d\bar{L}/dT$ as a function of the concentration.

The theory also requires that the heats of dilution of all salts of the

same type (e.g. 1-1-valent) should be the same within the square root range. From careful measurements of the heat of dilution for a number of very dilute solutions, E. Lange was able to show that this is confirmed for a number of salts (KF, KCl, CsCl, LiBr, etc.) within the experimental accuracy (see Fig. 33). KNO_3 shows considerable deviations even at $\gamma = 0{\cdot}01$, but it may be assumed that at still higher dilutions it will coincide with the other uni-univalent salts. For other salts, e.g. KCl, CsCl, and KF, this is approximately true even at higher con-

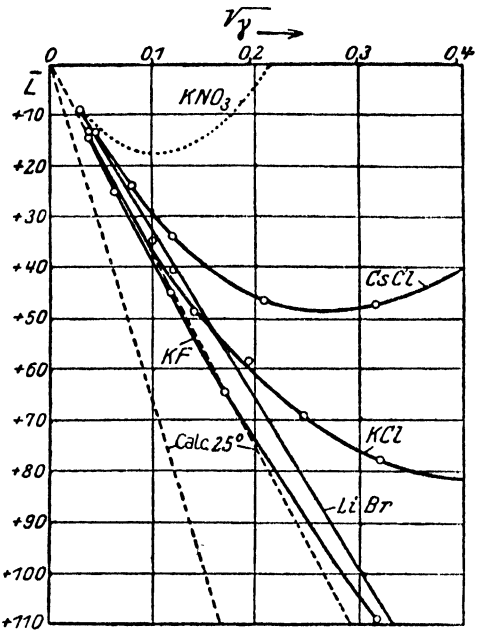

FIG. 33. Heat of dilution of different salts.

centrations. A number of measurements with salts of higher valencies, e.g. Na_2SO_4 and $Ca(NO_3)_2$, show approximate agreement with the theory. The deviations found in the case of 2-2-valent salts are probably (as for KNO_3) due to the fact that the square root range has not yet been reached. (See also Table 25.)

Thirdly, the heats of dilution of salts of the same molarity but different valence types should differ in the square root range by a calculable factor. Thus from (375) the theoretical ratio for the 1-1-valent group and the 1-2-valent group is

$$\left(\frac{\sum \nu_i z_i^2}{z}\right)^{\frac{3}{2}} = 3^{\frac{3}{2}} = 5{\cdot}2,$$

while the value found experimentally is 4·3. The small discrepancy between theory and experiment is again probably due to the fact that the true square root range has not yet been reached for the salts of higher valence types.

Finally, the value of the constant A in the theoretical law (375)

$$\bar{L} = A\sqrt{\gamma}$$

can be predicted. A depends very much upon the temperature coefficient of the dielectric constant of the solvent, dD_0/dT. In the case of water the numerical value of the term $(T/D_0)dD_0/dT$ is greater than one, so that the term $1+(T/D_0)dD_0/dT$ is negative and the heat of dilution positive. As previously stated, the interaction between the ions alone would lead to a negative heat of dilution, since work must be done to separate the ions; however the polarization of the solvent molecules by the ions also plays an important part, and the net effect is a positive heat of dilution. Unfortunately, the temperature coefficient for water is only known with an accuracy of about 8 per cent., which leads to an uncertainty of 30 per cent. in the heat of dilution (cf. (375)). Drude† gives at 25°, $dD_0/dT = -0{\cdot}349$, Kockel,‡ on the other hand,

$$dD_0/dT = -0{\cdot}384.$$

The resulting values for the expression $1+(T/D_0)dD_0/dT$, according to Drude, are $-0{\cdot}329$ at 25° and $-0{\cdot}269$ at 12·5°, while the corresponding values, according to Kockel, are $-0{\cdot}474$ at 25° and $-0{\cdot}393$ at 12·5°.§ Equation (375) then gives the following values for 1-1-valent salts:

Drude	25°	$\bar{L} = 457\sqrt{\gamma}$;
	12·5°	$\bar{L} = 351\sqrt{\gamma}$;
Kockel	25°	$\bar{L} = 664\sqrt{\gamma}$;
	12·5°	$\bar{L} = 513\sqrt{\gamma}$.

The dotted straight lines in Fig. 33 show the limits of uncertainty of the theoretical values,‖ e.g. at 25° the theoretical values vary from $374\sqrt{\gamma}$ to $664\sqrt{\gamma}$. Table 25 contains the results of Lange solutions of a

† P. Drude, *Wied. Ann.* **59** (1896), 48.

‡ L. Kockel, *Ann. d. Phys.* **77** (1926), 430.

§ J. Wyman (*Phys. Rev.* **35** (1930), 623) has recently obtained the following values at 25°,

$$D_0 = 78{\cdot}54, \qquad \frac{dD_0}{dT} = -0{\cdot}361, \qquad \left(1+\frac{T}{D_0}\frac{dD_0}{dT}\right) = -0{\cdot}371,$$

$$\bar{L} = 513\sqrt{\gamma},$$

thus agreeing fairly well with Drude. See also p. 282.

‖ A table containing all the experimental values for D_0, dD_0/dT and $1+(T/D_0)dD_0/dT$ is given by E. Lange, *Z. Elektrochem.* **36** (1930), 772.

series of electrolytes of various types. It is seen that the results agree moderately with the theory.

The behaviour of the heat of dilution in more concentrated solutions will be dealt with in Chapter XI.

TABLE 25

The heat of dilution $\bar{L}$ of aqueous electrolyte solutions at 25° C.

Type	*Salt*	γ_a *Initial conc.*	γ_e *Final conc.*	$\bar{L}_{\gamma_a}-\bar{L}_{\gamma_e}$ *cal./mol.*	*Maximum experimental error*	$\bar{L}_{\gamma_a}-\bar{L}_{\gamma_e}$ *theor. (Drude)*	$\bar{L}_{\gamma_a}-\bar{L}_{\gamma_e}$ *theor. (Kockel)*
1-1	KCl(11°)	0·01	0·00138	+16	±2	+21	+28
	KCl	0·01	0·00138	+23	±2	+33	+41
	NaCl	0·01	0·00138	+23	±2	+33	+41
	LiCl	0·01	0·00138	+24	±2	+33	+41
	LiBr	0·01	0·00138	+21	±2	+33	+41
	,,	0·01	0·0016	+48	±3	+74	+94
	KNO_3	0·01	0·00138	+5	±2	+33	+41
	,,	0·02	0·00275	+3	±1	+46	+59
	,,	0·063	0·0087	−28	±1	+81	+102
1-2	$Ca(NO_3)_2$	0·001	0·00014	+50	±7	+55	+70
	$Ca(NO_3)_2$	0·002	0·00028	+62	±13	+76	+96
	Na_2SO_4	0·001	0·00014	+50	±6	+55	+70
2-2	$MgSO_4$	0·002	0·00028	+170	±7	+112	+145
	$CaSO_4$	0·00236	0·000328	+235	±20	+125	+158
1-3	$La(NO_3)_3$	0·0005	0·0000695	+140	±30	+106	+136
	$CeCl_3$	0·0005	0·0000695	+142	±30	+106	+136

Note on the theory of the surface tension of strong electrolytes.

The increase of surface tension caused by electrolytes was first correctly interpreted by C. Wagner† as being due to the electrostatic mirror forces at the surface. Further calculations on this problem have been carried out by Oka‡ and by Onsager and Samaras.§ The calculations of the latter authors agree essentially with those of Wagner in giving as the limiting law for the increase of surface tension

$$\Delta\sigma = \text{const.} \times \gamma l_n(\kappa q_0),$$

where q_0 is the ionic distance occurring in Bjerrum's theory (see equation (585)). From a comparison of the theory with experiment Onsager and Samaras conclude that the mirror forces obey Coulomb's law for distances greater than 3 Å from the surface. This conclusion is of importance for the study of dipole liquids, and is incompatible with Sack's theory‖ of electrostatic saturation by ions.

† C. Wagner, *Phys. Z.* **25** (1924), 474.

‡ Gyoten Oka, *Proc. Phys.-Math. Soc. Japan*, **14** (1932), 441, 527, 649; **15** (1933), 407.

§ L. Onsager and Samaras, *J. Chem. Phys.* 1934 (in the press).

‖ See P. Debye, *Polare Molekeln*, p. 133.

IX

DEBYE'S THEORY OF THE CONDUCTIVITY OF STRONG ELECTROLYTES

34. Conductivity Phenomena Interpreted Qualitatively in Terms of the Properties of the Ionic Atmosphere

We shall now turn to the various phenomena connected with the conductivity of electrolytic solutions. These irreversible phenomena can also be treated theoretically by Debye's theory. Before developing the theory of conductivity quantitatively, we shall present the fundamental ideas upon which the subsequent calculations are based. If an ion is moved through the solution by means of an external field, the surrounding ions will be continually changing their distribution in order to maintain the ionic atmosphere. If we imagine a charge created suddenly in the interior of the solution, the formation of the ionic atmosphere will take a certain time, which is termed the time of relaxation of the ionic atmosphere.† In the same way the atmosphere surrounding a moving ion will not possess its equilibrium distribution, and hence cannot be calculated from the Maxwell-Boltzmann law. It can, however, be derived from a suitable interpretation of Einstein's equations‡ for the Brownian movement. The qualitative effect of this finite time of relaxation can be seen at once. At a point in front of the moving ion (i.e. a point towards which it is moving) the electric density must increase with time, while at a point behind the ion the density will decrease with time. On account of the finite time of relaxation, the density in front of the ion will be somewhat smaller than the equilibrium value, while behind the ion it will not yet have fallen to its equilibrium value. Hence during motion there will always be a somewhat greater electrical density behind the ion than in front of it. This additional unsymmetrical charge distribution, which will be superimposed upon the original symmetrical ionic atmosphere, is shown at the right of Fig. 34. Since the ion and its atmosphere are always oppositely charged, the result will be a force which tends to oppose the motion of the ion, independently of the sign of its charge. This retarding effect will obviously increase with increasing concentration. This is the first effect which acts in the same direction as a decrease in the degree of dissociation.

There is, however, another effect present, which must also be taken

† See pp. 107 and 176.

‡ A. Einstein, *Ann. d. Phys.* **17** (1905), 549; **19** (1906), 289, 371.

into account. We have seen that in the immediate neighbourhood of an ion, there is present an excess of ions of the opposite sign, which will move in the opposite direction under the influence of the applied field. These ions will carry with them a certain amount of the solvent, and hence the central ion has to be moved not through a stationary solvent, but through a medium, moving in the opposite direction. This effect obviously increases with increasing concentration, so that we have a second effect acting in the same direction as a decreased degree of dissociation. The second effect may be calculated according to the same principles as those employed by von Helmholtz in treating electrophoresis. We shall show shortly that both effects are closely connected

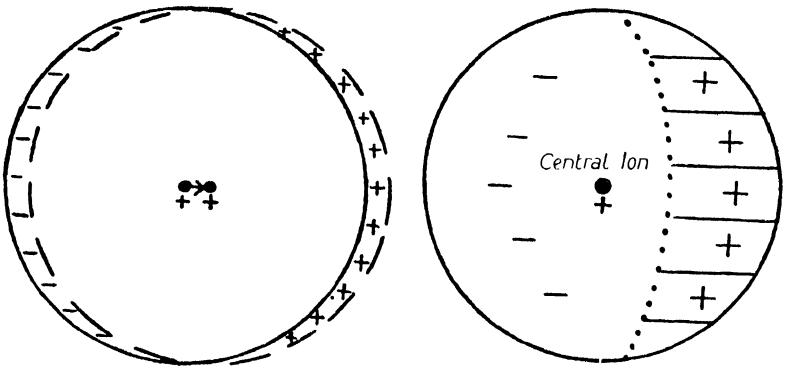

FIG. 34.

with the thickness of the ionic atmosphere, and that for very dilute solutions the force exerted is in both cases proportional to the square root of the concentration. This explains the law found many years ago by Kohlrausch, that the percentage deviation of the equivalent conductivity from its limiting value at infinite dilution is proportional to the square root of the concentration at high dilutions.† In this way the characteristic properties of strong electrolytes which were previously referred to as 'anomalies', can be explained theoretically, at least in the range of dilute solutions. Further, the variation of conductivity with frequency and field strength, which is very difficult to explain by Arrhenius's theory has been to a great extent accounted for by these modern theories of conductivity. The last effect was first predicted theoretically and later confirmed experimentally.‡

We shall now derive the fundamental equations for treating the problems of conductivity.

Debye and Hückel§ first derived strictly the average forces acting

† See p. 77. ‡ Cf. p. 182. § Loc. cit. p. 109.

upon an ion moving with constant velocity in a straight line. It has, however, been shown by Onsager† that this method gives too high a value for the resistance met with by the ion. Actually the ion does not move in a straight line, but is continually changing its direction on account of the Brownian movement, which modifies the retarding force. Thus in treating the ionic atmosphere, it is necessary to take into account the Brownian movement of the central ion. Although the force is again found to be proportional to the square root of the concentration, the coefficients are altered.

We shall first deal with the way in which the thermal equilibrium between the frequencies of different configurations is disturbed by the motion of the ions. This disturbance is only annulled by the thermal motion after a finite time of relaxation. The electrophoretic effect will be thoroughly dealt with later. As a necessary preliminary, we shall first derive the general fundamental equations for non-stationary processes in dilute strong electrolytes.

35. The General Fundamental Equations for Non-stationary Processes in Dilute Strong Electrolytes‡

Let the solution contain ions of the species $1,\ldots,i,\ldots,s$ with charges $e_1,\ldots,e_i,\ldots,e_s$, and let the numbers of ions present in 1 c.c. be on a time average $n_1,\ldots,n_i,\ldots,n_s$. We consider (see Fig. 35) two volume elements dV_P and dV_Q fixed in space at the points P and Q which have the coordinates x_P, y_P, z_P and x_Q, y_Q, z_Q. We shall take a time τ which is great compared with the time for a single displacement of an ion due to its Brownian movement.§ During this time τ we note the intervals of time during which an ion of species i is in dV_P or an ion of species j in dV_Q. Occasionally, of course, dV_P or dV_Q may contain simultaneously ions of both species i and species j, and still less often will three sorts of ions, e.g. i, j, k, be found simultaneously in one of the volume elements. If, however, we make the volume elements

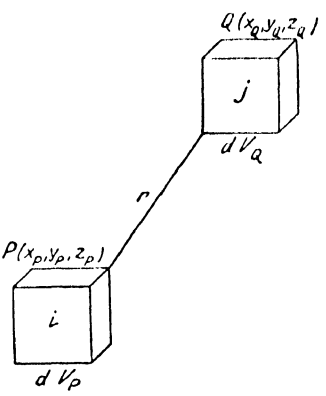

FIG. 35.

† Loc. cit. p. 109.

‡ P. Debye and H. Falkenhagen, *Phys. Z.* **29** (1928), 401. L. Onsager has derived equations (398) for the special case of stationary processes using another method. See L. Onsager, *Phys. Z.* **28** (1927), 277.

§ This last time is of the order 10^{-12} sec.

sufficiently small, we may neglect these contingencies, particularly the latter,† in sufficiently dilute solutions. If t_i is the sum of the intervals (in the time τ) during which an ion of the ith sort is in dV_P, then for sufficiently large values of τ,

$$\frac{t_i}{\tau} = n_i \, dV_P. \tag{376}$$

Similarly, the sum of the intervals up to τ during which dV_Q contains an ion of species j is given by

$$\frac{t_j}{\tau} = n_j \, dV_Q. \tag{377}$$

We now consider the intervals during which there is simultaneously an ion of species i in dV_P and an ion of species j in dV_Q. The sum of these intervals during the time τ is termed t_{iP}^{jQ}. Then if n_{iP}^{jQ} is the average number of j ions per c.c. in the neighbourhood of an i ion, and n_{jQ}^{iP} the corresponding number of i ions in the neighbourhood of j ion we have

$$\frac{t_{iP}^{jQ}}{t_i} = n_{iP}^{jQ} \, dV_Q, \qquad \frac{t_{jQ}^{iP}}{t_j} = n_{jQ}^{iP} \, dV_P, \tag{378}$$

where t_{jQ}^{iP} is the sum of the intervals (during τ) during which there is simultaneously a j ion in dV_Q and an i ion in dV_P. When dV_P and dV_Q have fixed positions, the times t_{iP}^{jQ} and t_{jQ}^{iP} must be identical, i.e.

$$t_{iP}^{jQ} = t_{jQ}^{iP}. \tag{379}$$

(376), (377), and (378) lead to the relation

$$t_{iP}^{jQ} = n_i \, n_{iP}^{jQ} \tau \, dV_P dV_Q = n_j n_{jQ}^{iP} \tau \, dV_P dV_Q, \tag{380}$$

i.e.

$$n_i \, n_{iP}^{jQ} = n_j n_{jQ}^{iP}.$$

We shall introduce the abbreviation

$$n_i \, n_{iP}^{jQ} = n_j n_{jQ}^{iP} = w_{iP}^{jQ} = w_{jQ}^{iP}, \tag{381}$$

where w_{iP}^{jQ} is a distribution function for the frequency of those configurations in which there is simultaneously an i ion in dV_P and a j ion in dV_Q. If this probability function w_{iP}^{jQ} is known, then for a given value of $dV_P dV_Q$ (380) gives the period of time t_{iP}^{jQ} during the period of observation τ during which there is simultaneously an i ion in dV_P and a j ion in dV_Q. We now consider a very great number of combinations of volume elements dV_P and dV_Q during time τ. This number will

† It would be interesting to take into account these relatively improbable events which would certainly be of importance in a theory of concentrated solutions. They will be neglected here, since we are dealing only with dilute solutions. General distribution functions of this kind have recently been introduced by Onsager (*Chem. Rev.*, August, 1933) and applied to certain problems in more concentrated solutions.

be for the moment termed N. We consider again t_{iP}^{jQ}, the sum of the time intervals during which there is simultaneously an i ion in dV_P and a j ion in dV_Q, and we note also N_{iP}^{jQ}, the corresponding number of double elements $dV_P\,dV_Q$. We then have,

$$\frac{N_{iP}^{jQ}}{N} = \frac{t_{iP}^{jQ}}{\tau} = w_{iP}^{jQ}\,dV_P\,dV_Q. \tag{382}$$

The observations described above were carried out in a small time τ following the moment t. We may now carry out exactly similar observations in the time τ following the moment $t+\Delta t$. We now find instead of N_{iP}^{jQ} combinations a number $N_{iP}^{jQ}+\Delta N_{iP}^{jQ}$. This is the number of double elements which during the time τ were occupied in such a way that dV_P contained an i ion and dV_Q a j ion, being at the moment $t+\Delta t$. The distribution function w_{iP}^{jQ} thus changes with the time for all non-stationary processes. The change ΔN_{iP}^{jQ} can be calculated in the following way. While dV_P contains an i ion, a j ion can enter dV_Q; this we suppose to take place A_{i0}^{ij} times during τ. Or alternatively, while dV_Q contains a j ion, an i ion enters dV_P; this second process takes place A_{0j}^{ij} times during τ. We then write

$$A_{0j}^{ij}+A_{i0}^{ij} = Z_+. \tag{383}$$

Alternatively, while dV_P contains an i ion, a j ion can leave dV_Q, and while dV_Q contains a j ion, an i ion leaves dV_P. We suppose these processes to take place respectively A_{ij}^{i0} and A_{ij}^{0j} times during τ. Writing

$$A_{ij}^{i0}+A_{ij}^{0j} = Z_- \tag{384}$$

we have

$$\frac{\Delta N_{iP}^{jQ}}{N} = \frac{Z_+-Z_-}{\tau}\,\Delta t. \tag{385}$$

Abbreviating,

$$Z_+-Z_- = Z, \tag{386}$$

we have

$$\frac{\Delta N_{iP}^{jQ}}{N} = \frac{Z}{\tau}\,\Delta t, \tag{387}$$

and hence from (382)

$$\frac{\partial w_{iP}^{jQ}}{\partial t}\,dV_P\,dV_Q = \frac{Z}{\tau}. \tag{388}$$

We now need an expression for Z. For this purpose we introduce $\mathfrak{v}_{iP}^{jQ}$, the mean velocity of the j ions in the neighbourhood of an i ion. The excess of the j ions entering the volume element dV_Q per unit time over those which leave it during the same period is given by

$$-\left\{\frac{\partial(n_{iP}^{jQ}\mathfrak{v}_{iPx}^{jQ})}{\partial x_Q}+\frac{\partial(n_{iP}^{jQ}\mathfrak{v}_{iPy}^{jQ})}{\partial y_Q}+\frac{\partial(n_{iP}^{jQ}\mathfrak{v}_{iPz}^{jQ})}{\partial z_Q}\right\}dV_Q = -\mathrm{div}_Q(n_{iP}^{jQ}\mathfrak{v}_{iP}^{jQ})\,dV_Q. \tag{389}$$

This expression is easily obtained by calculating how many j ions enter and leave through the surfaces of the volume element dV_Q.† The index Q signifies that the partial differential coefficients forming the divergence refer to the coordinates x_Q, y_Q, z_Q. If we multiply (389) by t_i, the sum of all the intervals in τ during which dV_P actually contains an i ion, we obtain

$$-t_i \operatorname{div}_Q(n_{iP}^{jQ} \mathfrak{v}_{iP}^{jQ})\, dV_Q.$$

This is, however, the excess of j ions in the neighbourhood of an i ion during the time τ, and must be equal to $A_{i0}^{ij} - A_{ij}^{i0}$, i.e.

$$A_{i0}^{ij} - A_{ij}^{i0} = -t_i\, dV_Q \operatorname{div}_Q(n_{iP}^{jQ} \mathfrak{v}_{iP}^{jQ}). \tag{390}$$

In the same way, the excess of i ions in dV_P during the presence of a j ion in dV_Q, in the time τ, is

$$A_{0j}^{ij} - A_{ij}^{0j} = -t_j\, dV_P \operatorname{div}_P(n_{jQ}^{iP} \mathfrak{v}_{jQ}^{iP}). \tag{391}$$

Equations (383), (384), (386), (390), and (391) then give

$$\frac{Z}{\tau} = -\{n_i \operatorname{div}_Q(n_{iP}^{jQ} \mathfrak{v}_{iP}^{jQ}) + n_j \operatorname{div}_P(n_{jQ}^{iP} \mathfrak{v}_{jQ}^{iP})\}\, dV_P\, dV_Q. \tag{392}$$

In conjunction with (388) this gives,

$$\frac{\partial w_{iP}^{jQ}}{\partial t} = -\{\operatorname{div}_Q(w_{iP}^{jQ} \mathfrak{v}_{iP}^{jQ}) + \operatorname{div}_P(w_{jQ}^{iP} \mathfrak{v}_{jQ}^{iP})\}. \tag{393}$$

The indices P and Q attached to the operator div indicate that the partial differential coefficients refer respectively to x_P, y_P, z_P and x_Q, y_Q, z_Q. According to (381)

$$w_{iP}^{jQ} = w_{jQ}^{iP}.$$

We shall now adapt equation (393), which is fundamental for non-stationary processes, to the cases to be dealt with later. Since we shall treat the conductivity of electrolyte solutions, the possible causes for the motions of the ions are firstly the electric forces present, and secondly the thermal agitation. A third cause is the possible presence of streaming in the liquid, which, however (since it depends on the motion of the liquid in which the particles are suspended), can be neglected in considering the motion of the particles, at least for very dilute solutions. Strictly speaking, the streaming of the liquid should be taken into account in calculating the distribution function.‡ It will be seen later that the potential round the moving ion differs but little from that round a stationary ion, so that we can treat the relaxation of the atmosphere and the electrophoretic effect separately. In order to treat the

† In hydrodynamics, the amount of liquid contained in a volume element is calculated in an exactly analogous manner. See e.g. the article by L. Prandtl and H. Falkenhagen in Wien-Harms, *Handbuch der Experimentalphysik*, vol. iv, part I, 1931.

‡ This is necessary in dealing with viscosity: see p. 245.

action of the forces present and the thermal agitation, we shall follow Debye and Hückel† in employing the equations for Brownian movement, modified to take into account the forces present. In this way it is possible to use the ordinary macroscopic laws for migration and diffusion. For each ion j let there be a corresponding resistance ρ_j, and let the force acting upon a j ion in dV_Q be $\mathfrak{K}_{iP}^{jQ}$, the j ion being in the neighbourhood of an i ion. The velocity of the j ion due to this force is therefore

$$\frac{\mathfrak{K}_{iP}^{jQ}}{\rho_j}. \tag{394}$$

If T is the absolute temperature and k Boltzmann's constant, then according to Fick's law‡ the mean velocity of the j ion due to thermal motion or diffusion§ is given by

$$-\frac{kT}{\rho_j w_{iP}^{jQ}} \operatorname{grad}_Q w_{iP}^{jQ}. \tag{395}$$

There will thus only be a velocity of diffusion when there is a gradient in the distribution function w_{iP}^{jQ}, and the mean velocity will be proportional to this gradient. The total velocity of the j ion is thus

$$\mathfrak{v}_{iP}^{jQ} = \left\{\mathfrak{K}_{iP}^{jQ} - \frac{kT}{w_{iP}^{jQ}} \operatorname{grad}_Q w_{iP}^{jQ}\right\}\frac{1}{\rho_j}. \tag{396}$$

The velocity of the i ion in P in the neighbourhood of a j ion is similarly given by

$$\mathfrak{v}_{jQ}^{iP} = \left\{\mathfrak{K}_{jQ}^{iP} - \frac{kT}{w_{jQ}^{iP}} \operatorname{grad}_P w_{jQ}^{iP}\right\}\frac{1}{\rho_i}. \tag{397}$$

Our fundamental equation (393) thus becomes

$$\frac{\partial w_{iP}^{jQ}}{\partial t} = -\frac{1}{\rho_j}\operatorname{div}_Q\{w_{iP}^{jQ}\mathfrak{K}_{iP}^{jQ} - kT\operatorname{grad}_Q w_{iP}^{jQ}\} - \\ -\frac{1}{\rho_i}\operatorname{div}_P\{w_{jQ}^{iP}\mathfrak{K}_{jQ}^{iP} - kT\operatorname{grad}_P w_{jQ}^{iP}\}. \tag{398}$$

It can be easily shown that in treating conductivity it is permissible to neglect the forces due to the dynamical reactions in comparison to the viscosity forces. The viscosity forces are given by $\rho\mathfrak{v}$, where ρ is of the order of magnitude 2×10^{-9} (for water), while the dynamical reactions are given by $m(d\mathfrak{v}/dt)$. If we consider an ion in a field of frequency ω, the ratio of the viscosity forces to the inertial

† P. Debye and E. Hückel, *Phys. Z.* **24** (1933), 344.

‡ A. Fick, *Pogg. Ann.* **94** (1855), 59.

§ The problem of the diffusion of electrolytes, which represents a much more general case than that of conductivity, has recently been treated by Onsager and Fuoss (*J. Phys. Chem.* **36** (1932), 2689), who obtained an expression for the limiting law for the diffusion coefficient of a single electrolyte. There are no data of sufficient accuracy available for dilute solutions to permit of a test of the equations obtained, and since the mathematical difficulties involved are considerable, we shall not deal with the subject here.

forces is $\rho/\omega m$. If we put $m \sim 10^{-22}$ gm., then the two forces are of the same order of magnitude for $\omega \sim 10^{13}$, i.e. in the infra-red region, while the dispersion of conductivity is usually observed at very much longer wave-lengths. Although the effect of the dynamical reactions of the ionic masses is much too small to be detected in ordinary high-frequency measurements, it is, however, possible to produce potential differences in an electrolyte by means of supersonic vibrations. Debye (*J. Chem. Phys.* **1** (1933), 13) has shown that it should be possible in this way to measure the mass of electrolytic ions, and hence the number of solvent molecules attached to the ion. Debye obtains the following expression for the amplitude of the potential difference in the potential wave.

$$\frac{m_{\mathrm{H}}}{\epsilon} G\alpha_0 \frac{\sum \nu_j z_j M_j/\rho_j}{\sum \nu_j z_j^2/\rho_j} \frac{\dfrac{4\pi}{D_0\omega}\sum \dfrac{n_j e_j^2}{\rho_j}}{\left[1+\left\{\dfrac{4\pi}{D_0\omega}\sum \dfrac{n_j c_j}{\rho_j}\right\}^2\right]^{\frac{1}{2}}}.$$

If we consider a KCl solution of concentration $\gamma = 10^{-3}$ and put $\rho = 2\times 10^{-9}$, the specific conductivity is of the order of magnitude $\sum \dfrac{n_j e_j^2}{\rho_j} \sim 10^9$ e.s.u. Taking ω as 10^8 per second (wave-length 30 m.) and $D_0 = 80$, we have $\dfrac{4\pi \sum n_j e_j^2/\rho_l}{D_0\omega} \sim 1$.

For a somewhat lower frequency, $\dfrac{\dfrac{4\pi}{D_0\omega}\sum n_j e_j^2/\rho_l}{[1+\ldots]^{\frac{1}{2}}} \sim 1$. Taking the latter case, if the velocity of the supersonic waves is given by $= 1{\cdot}4\times 10^5$ cm./sec., the amplitude of the potential difference in this special case is given by

$$1{\cdot}4\times 10^{-7}\alpha_0 \frac{M_1/\rho_1 - M_2/\rho_2}{1/\rho_1 + 1/\rho_2} \text{ volts.}$$

The velocity of the medium oscillates between $\pm\alpha_0$, which corresponds to a quartz plate producing 0·005 joules per sq. cm. per sec. The potential difference of the order of magnitude 10^{-6} volts can easily be measured by means of the usual amplifying arrangements.

The dynamical reactions are also of importance in the case of gaseous ions, see K. F. Niessen, *Phys. Z.* **33** (1932), 705; D. Gabor, ibid. **34** (1933), 38.

36. The Special Case of Electrolytic Conductivity

In the case of conductivity, if the external field strength is $\mathfrak{E}$, then

$$\left.\begin{aligned} \mathfrak{R}_{iP}^{jQ} &= -e_j \operatorname{grad}_Q \Psi_{iP}^{Q} + e_j \mathfrak{E} \\ \mathfrak{R}_{jQ}^{iP} &= -e_i \operatorname{grad}_P \Psi_{jQ}^{P} + e_i \mathfrak{E} \end{aligned}\right\}. \tag{399}$$

Ψ_{iP}^{Q} is the potential at the j ion due to the ionic atmosphere of i ions; similarly Ψ_{jQ}^{P} is the potential at the i ion due to the ionic atmosphere of j ions. These two potentials must satisfy Poisson's equations,

$$\left.\begin{aligned} \operatorname{div}_Q \operatorname{grad}_Q \Psi_{iP}^{Q} &= -\frac{4\pi}{D_0}\sum_j n_{iP}^{jQ} e_j = -\frac{4\pi}{n_i D_0}\sum_j w_{iP}^{jQ} e_j \\ \operatorname{div}_P \operatorname{grad}_P \Psi_{jQ}^{P} &= -\frac{4\pi}{D_0}\sum_i n_{jQ}^{iP} e_i = -\frac{4\pi}{n_j D_0}\sum_i w_{jQ}^{iP} e_i \end{aligned}\right\}. \tag{400}$$

Taking the special case of equilibrium, i.e. considering a homogeneous electrolyte with no current passing, we have from (396), (397), and (399)

$$-w_{jQ}^{iP} e_i \operatorname{grad}_P \Psi_{jQ}^{P} - kT \operatorname{grad}_P w_{jQ}^{iP} = 0. \tag{401}$$

The distribution functions are therefore in this case

$$\left.\begin{aligned} w_{iP}^{jQ} &= n_i n_j e^{-e_j \Psi_{iP}^{Q}/kT} \\ w_{jQ}^{iP} &= n_i n_j e^{-e_i \Psi_{jQ}^{P}/kT} \end{aligned}\right\} \tag{402}$$

or, from (381),

$$\left.\begin{aligned} n_{iP}^{jQ} &= n_j e^{-e_j \Psi_{iP}^{Q}/kT} \\ n_{jQ}^{iP} &= n_i e^{-e_i \Psi_{jQ}^{P}/kT} \end{aligned}\right\}. \tag{403}$$

The factor $n_i n_j$ in (402) is chosen so that at a great distance from the central ion the distribution becomes a random one, and corresponds to the concentrations given. The result obtained shows that any concentration changes caused by an ion are relatively small outside the immediate neighbourhood of the ion. If therefore the ionic atmospheres of ions interpenetrate, we are not committing any large error by supposing that the changes in concentration caused by the two ions are merely superimposed. The average force acting upon one ion in this configuration is therefore given by the average field in the atmosphere of the other ion, and we may use equation (399). Writing

$$\Psi_{iP}^{Q} = e_i g(r), \quad \Psi_{jQ}^{P} = e_j g(r), \tag{404}$$

where g depends only on the distance r of the i ion from the j ion, (400), (402), and (404) give the following differential equation for $g(r)$,

$$\Delta g(r) = g(r) \frac{4\pi}{D_0 kT} \sum n_j e_j^2 = \kappa^2 g(r). \tag{405}$$

The exponential function in (402) has been replaced by

$$w_{iP}^{jQ} = n_i n_j \left(1 - \frac{e_j \Psi_{iP}^{Q}}{kT}\right).$$

A corresponding equation holds for w_{jQ}^{iP}, and the relation (381) is then satisfied. As previously described† equation (405) was first obtained by Debye and Hückel for the case of a stationary ion.‡

† See p. 100.

‡ Equation (404) leads to the relation

$$e_i \Psi_{jQ}^{P} = e_j \Psi_{iP}^{Q}.$$

The Poisson-Boltzmann equation (403) will only be valid (and hence applicable to more concentrated solutions) when this relation holds. This is, however, only possible in certain symmetrical cases. If the ions have considerably different charges, there will be a discrepancy between (403) and (381). The question has been treated in detail by Onsager in a critical discussion of the basis of the interionic theory (*Chem. Rev.* August, 1933).

We return now to the general case. Substituting (399) in (398),

$$\frac{\partial w_{iP}^{jQ}}{\partial t} = \frac{1}{\rho_j}\mathrm{div}_Q(e_j w_{iP}^{jQ}\,\mathrm{grad}_Q\,\Psi_{iP}^{Q}+kT\,\mathrm{grad}_Q\,w_{iP}^{jQ}-e_j\mathfrak{E}w_{iP}^{jQ})+$$
$$+\frac{1}{\rho_i}\mathrm{div}_P(e_i w_{jQ}^{iP}\,\mathrm{grad}_P\,\Psi_{jQ}^{P}+kT\,\mathrm{grad}_P\,w_{jQ}^{iP}-e_i\mathfrak{E}w_{jQ}^{iP}). \quad (406)$$

To simplify this expression, we write

$$w_{iP}^{jQ} = w_{jQ}^{iP} = n_i n_j + f_{ij}, \quad (407)$$

where f_{ij} determines the deviation from a completely random distribution of the ions. (400) and (406) lead to the following differential equation for the distribution function

$$\frac{\partial f_{ij}}{\partial t} = \frac{1}{\rho_j}\left(kT\Delta_Q f_{ij} - \frac{4\pi n_j e_j}{D_0}\sum_p f_{ip}\,e_p - e_j\mathfrak{E}\,\mathrm{div}_Q f_{ij}\right)+$$
$$+\frac{1}{\rho_i}\left(kT\Delta_P f_{ij} - \frac{4\pi n_i e_i}{D_0}\sum_p f_{pj}\,e_p - e_i\mathfrak{E}\,\mathrm{div}_P f_{ij}\right), \quad (408)$$

where the approximation $w_{iP}^{jQ} = w_{jQ}^{iP} = n_i n_j$ is used in deriving the second and fifth terms.

We may express the function f_{ij} in terms of the relative coordinates x, y, z

$$f_{ij} = F_{ij}(x, y, z), \quad (409)$$

where
$$x = x_Q - x_P, \quad y = y_Q - y_P, \quad z = z_Q - z_P, \quad (410)$$

and hence

$$\frac{\partial f_{ij}}{\partial x_Q} = \frac{\partial F_{ij}}{\partial x}, \qquad \frac{\partial f_{ij}}{\partial x_P} = -\frac{\partial F_{ij}}{\partial x}, \text{ etc.}$$
$$\frac{\partial^2 f_{ij}}{\partial x_Q^2} = \frac{\partial^2 F_{ij}}{\partial x^2}, \qquad \frac{\partial^2 f_{ij}}{\partial x_P^2} = \frac{\partial^2 F_{ij}}{\partial x^2}, \text{ etc.}$$

If further the electrical field is assumed to act along the x-axis and $\mathfrak{E}_X$ is written X, then (408) becomes

$$\frac{\partial F_{ij}}{\partial t} = kT\left(\frac{1}{\rho_i}+\frac{1}{\rho_j}\right)\Delta F_{ij}+\left(\frac{e_i}{\rho_i}-\frac{e_j}{\rho_j}\right)X\frac{\partial F_{ij}}{\partial x}-$$
$$-\frac{4\pi}{D_0}\left(\frac{n_i e_i}{\rho_i}\sum_p e_p F_{pj}+\frac{n_j e_j}{\rho_j}\sum_p e_p F_{ip}\right). \quad (411)$$

37. The Special Case of Simple Electrolytes with Two Sorts of Ions

Equation (411) is the general fundamental equation underlying conductivity problems, also for non-stationary states.† We shall here make

† It is also possible to develop the theory of the dispersion of conductivity and dielectric constants in the general case of a mixture containing any number of strong electrolytes (see H. Falkenhagen and W. Fischer, *Phys. Z.* **33** (1932), 941; *Nature*, **130** (1932), 128). The detailed treatment is very involved in the general case. M. E. Spaght (*Phys. Z.* **33** (1932), 354) has investigated experimentally mixtures of $Ca_2Fe(CN)_6$ with

the simplifying assumption that only two sorts of ions are present. We then have the four functions $F_{11}, F_{22}, F_{12}, F_{21}$, which must satisfy the following four equations.†

$$\left.\begin{aligned}
\frac{\partial F_{11}}{\partial t} &= \frac{2kT}{\rho_1}\Delta F_{11} - \frac{4\pi n_1 e_1}{D_0\rho_1}(e_1 F_{11}+e_2 F_{21}) - \frac{4\pi n_1 e_1}{D_0\rho_1}(e_1 F_{11}+e_2 F_{12}) \\
\frac{\partial F_{22}}{\partial t} &= \frac{2kT}{\rho_2}\Delta F_{22} - \frac{4\pi n_2 e_2}{D_0\rho_2}(e_1 F_{12}+e_2 F_{22}) - \frac{4\pi n_2 e_2}{D_0\rho_2}(e_1 F_{21}+e_2 F_{22}) \\
\frac{\partial F_{12}}{\partial t} &= kT\left(\frac{1}{\rho_1}+\frac{1}{\rho_2}\right)\Delta F_{12} + \left(\frac{e_1}{\rho_1}-\frac{e_2}{\rho_2}\right)X\frac{\partial F_{12}}{\partial x} - \\
&\qquad - \frac{4\pi}{D_0}\left\{\frac{n_1 e_1}{\rho_1}(e_1 F_{12}+e_2 F_{22}) + \frac{n_2 e_2}{\rho_2}(e_1 F_{11}+e_2 F_{12})\right\} \\
\frac{\partial F_{21}}{\partial t} &= kT\left(\frac{1}{\rho_1}+\frac{1}{\rho_2}\right)\Delta F_{21} + \left(\frac{e_2}{\rho_2}-\frac{e_1}{\rho_1}\right)X\frac{\partial F_{21}}{\partial x} - \\
&\qquad - \frac{4\pi}{D_0}\left\{\frac{n_2 e_2}{\rho_2}(e_1 F_{11}+e_2 F_{21}) + \frac{n_1 e_1}{\rho_1}(e_1 F_{21}+e_2 F_{22})\right\}
\end{aligned}\right\}. \qquad (412)$$

We shall now give a number of applications of these partial differential equations.

38. Application to the Potential Distribution round an Ion in the Absence of External Influences

As our first example we shall consider the case of an ion subjected to no external influences,‡ and assume that the F_{ij}'s are independent of the time. With these assumptions,

$$\frac{\partial F_{ij}}{\partial t} = 0, \qquad X = 0, \qquad (413)$$

equations (412) become very much simpler. In order to solve the system of equations obtained, we shall assume that the F_{ik}'s satisfy the equations

$$\Delta F_{ik} - K^2 F_{ik} = 0. \qquad (414)$$

KCl, HCl, and KOH. His results have been discussed from the point of view of the theory by H. Falkenhagen and W. Fischer, *Phys. Z.* **34** (1933), 593; *Z. Elektrochem.* **39** (1933), 517.

† The meaning of the F_{ij}'s may be briefly restated here. $w_{ij} = n_i n_j + F_{ij}$ (see (407) and (409)) is a distribution function defined as follows. Consider a volume element dV_P at the point P and a volume element dV_Q at the point Q, both fixed in space. The probability that there is simultaneously a j ion in dV_Q and an i ion in dV_P is then given by $w_{ij}\,dV_P\,dV_Q$. Hence if the ions exert no forces upon one another, then $w_{ij} = n_i n_j$, where n_i and n_j are the average numbers of i ions and j ions respectively per c.c. The w_{ij}'s also satisfy the differential equations (412).

‡ This case has previously been treated, but without taking into account the Brownian movement (cf. p. 98). Apart from this, the result is the same as that obtained in § 38.

Introducing the abbreviations

$$u_1 = \frac{1/\rho_1}{1/\rho_1+1/\rho_2} = \frac{\rho_2}{\rho_1+\rho_2}, \qquad u_2 = \frac{1/\rho_2}{1/\rho_1+1/\rho_2} = \frac{\rho_1}{\rho_1+\rho_2} \tag{415}$$

$$\frac{4\pi}{D_0 kT} n_1 e_1^2 = \kappa_1^2, \qquad \frac{4\pi}{D_0 kT} n_2 e_2^2 = \kappa_2^2, \qquad \kappa_1^2+\kappa_2^2 = \kappa^2, \tag{416}$$

the F_{ik}'s must satisfy the following system of linear equations,

$$\left.\begin{aligned}
(K^2-\kappa_1^2)F_{11} &= \frac{2\pi}{D_0 kT} n_1 e_1 e_2 (F_{12}+F_{21}) \\
(K^2-\kappa_2^2)F_{22} &= \frac{2\pi}{D_0 kT} n_2 e_1 e_2 (F_{12}+F_{21}) \\
\{K^2-(u_1\kappa_1^2+u_2\kappa_2^2)\}F_{12} &= \frac{4\pi}{D_0 kT} e_1 e_2 (n_2 u_2 F_{11}+n_1 u_1 F_{22}) \\
\{K^2-(u_1\kappa_1^2+u_2\kappa_2^2)\}F_{21} &= \frac{4\pi}{D_0 kT} e_1 e_2 (n_2 u_2 F_{11}+n_1 u_1 F_{22})
\end{aligned}\right\}. \tag{417}$$

Hence if $$K^2 \neq u_1\kappa_1^2+u_2\kappa_2^2 \tag{418}$$

then $$F_{12} = F_{21} = F. \tag{419}$$

In conjunction with the first two equations of (417) this gives for K^2

$$(K^2-\kappa_1^2)(K^2-\kappa_2^2)\{K^2-(u_1\kappa_1^2+u_2\kappa_2^2)\} = \kappa_1^2\kappa_2^2\{K^2-(u_1\kappa_1^2+u_2\kappa_2^2)\}. \tag{420}$$

Since now $$K^2 \neq u_1\kappa_1^2+u_2\kappa_2^2,$$

we obtain as the equation for K^2

$$(K^2-\kappa_1^2)(K^2-\kappa_2^2) = \kappa_1^2\kappa_2^2, \tag{421}$$

which has the two roots

$$K^2 = 0 \qquad K^2 = \kappa^2.$$

For our purpose, only the root

$$K^2 = \kappa^2$$

has any meaning, and F must satisfy the equation

$$\Delta F = \kappa^2 F. \tag{422}$$

The solution of this equation has been given previously. F_{11} and F_{22} can be obtained from the first two equations of (417), giving

$$\left.\begin{aligned}
F_{11} &= \frac{4\pi}{D_0 kT} \frac{n_1 e_1 e_2}{\kappa_2^2} F = \frac{n_1 e_1}{n_2 e_2} F = -F, \\
F_{22} &= +F_{11} = -F.
\end{aligned}\right\} \tag{423}$$

The solution of equation (422) must be of the form

$$F = C\frac{e^{-\kappa r}}{r}, \tag{424}$$

so that it remains only to determine the constant C. The electric density in the atmosphere surrounding the ion is given by (400), (407), and (409) as

$$\Pi_1 = -\frac{D_0}{4\pi}\Delta\Psi_1' = \frac{1}{n_1}\sum_p e_p F_{1p} = \frac{1}{n_1}(e_1 F_{11}+e_2 F_{12}). \tag{425}$$

Similarly, the electric density of the atmosphere surrounding the ion 2 is

$$\Pi_2 = -\frac{D_0}{4\pi}\Delta\Psi_2' = \frac{1}{n_2}\sum_p e_p F_{2p} = \frac{1}{n_2}(e_1 F_{21}+e_2 F_{22}). \tag{426}$$

In conjunction with (419) and (423) this gives for the electric densities

$$\Pi_1 = \frac{1}{n_1}(-e_1 F+e_2 F) = \frac{F}{n_1}(e_2-e_1),$$
$$\Pi_2 = \frac{F}{n_2}(e_1-e_2). \tag{427}$$

The potentials Ψ_1' and Ψ_2' must thus satisfy the equations

$$\Delta\Psi_1' = \frac{C'e^{-\kappa r}}{r}, \qquad \Delta\Psi_2' = \frac{C''e^{-\kappa r}}{r}, \tag{428}$$

the solutions of which are

$$\Psi_1' = \frac{Ae^{-\kappa r}}{r}, \qquad \Psi_2' = \frac{Be^{-\kappa r}}{r}. \tag{429}$$

Since in the immediate neighbourhood of the ion 1 $\Psi_1' = e_1/D_0 r$ and in the neighbourhood of the ion 2 $\Psi_2' = e_2/D_0 r$, we must have

$$A = \frac{e_1}{D_0}, \qquad B = \frac{e_2}{D_0}, \tag{430}$$

i.e. using (424–30) the constant C becomes

$$C = \frac{n_2^2 e_2^2}{D_0 kT} = \frac{n_1^2 e_1^2}{D_0 kT}. \tag{431}$$

The F_{ik}'s are thus given by the following two equations,

$$F_{11} = F_{22} = -\frac{n_2^2 e_2^2}{D_0 kT}\frac{e^{-\kappa r}}{r}, \tag{432}$$

$$F_{12} = F_{21} = \frac{n_2^2 e_2^2}{D_0 kT}\frac{e^{-\kappa r}}{r}. \tag{433}$$

These two equations prove the existence of an ionic atmosphere surrounding each ion and having a charge opposite to that of the central ion.†

† See p. 98.

Reference must be made to the root

$$K^2 = u_1\kappa_1^2 + u_2\kappa_2^2.$$

This root of the equation for K^2 can have no meaning in the present problem, which possesses central symmetry. (417) gives for this root

$$F_{11} = F_{22} = 0, \qquad F_{12} = -F_{21},$$

and hence from (425) and (426) the electric densities are given by

$$\Pi_1' = \frac{e_2}{n_1}F_{12}, \qquad \Pi_2' = \frac{e_1}{n_2}F_{21} = -e_2 F_{12}$$

which do not describe an ionic atmosphere with central symmetry. We must therefore reject this root, but it may be remarked that it is of the greatest importance for stationary states in the treatment of conductivity.† As a further example of the application of the fundamental equations (412), we shall now calculate the time of relaxation of the whole ionic atmosphere.

39. The Time of Relaxation of the Whole Ionic Atmosphere‡

We consider the ions in Brownian movement in the solution, no external field being initially present. We have seen that each ion is surrounded by an ionic atmosphere having a charge opposite to that of the central ion. We imagine the charge of the central ion removed at time $t = 0$, and we wish to investigate how the ionic atmosphere disappears round the point from which the charge was removed. It is again assumed that only two kinds of ions are present in the solution. Since no external field is present, the general equations (412) become in this case

$$\left.\begin{aligned}
\frac{\partial F_{11}}{\partial t} &= \frac{2kT}{\rho_1}\Delta F_{11} - \frac{4\pi n_1 e_1}{D_0\rho_1}(e_1 F_{11} + e_2 F_{21}) - \frac{4\pi n_1 e_1}{D_0\rho_1}(e_1 F_{11} + e_2 F_{12}) \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\frac{\partial F_{21}}{\partial t} &= kT\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right)\Delta F_{21} - \frac{4\pi}{D_0}\left\{\frac{n_2 e_2}{\rho_2}(e_1 F_{11} + e_2 F_{21}) + \frac{n_1 e_1}{\rho_1}(e_1 F_{21} + e_2 F_{22})\right\}.
\end{aligned}\right\} \tag{434}$$

† See p. 185.

‡ This problem was first treated by P. Debye and H. Falkenhagen (*Phys. Z.* **29** (1928), 121), who did not, however, treat the Brownian movement strictly, and thus obtained results which are only qualitatively correct. P. Debye (*Sommerfeld Festschrift*, S. Hirzel, 1928) has treated a similar problem. For the special case of an electrolyte with ions of equal mobilities, he investigates how an electrolyte which is initially in a completely random state, will attain its equilibrium state. This problem can also be treated by the general methods described here, giving the same result as that obtained by Debye.

It is now necessary to find solutions of equations (434) which are suited to the problem in hand. In the first place, there is no reason to suppose that the charge distribution will lose its central symmetry on removing the central ion, so that equations (419) and (423) will also hold here. Since also

$$n_1 e_1 = -n_2 e_2,$$

the four equations (434) become

$$\frac{\partial F}{\partial t} = kT\left(\frac{1}{\rho_1}+\frac{1}{\rho_2}\right)\Delta F - \frac{4\pi F}{D_0}(n_1 e_1^2 + n_2 e_2^2)\left(\frac{1}{\rho_1}+\frac{1}{\rho_2}\right), \tag{435}$$

or, introducing the characteristic quantity κ^2 (see (221))

$$\frac{\partial F}{\partial t} = kT\left(\frac{1}{\rho_1}+\frac{1}{\rho_2}\right)(\Delta F - \kappa^2 F). \tag{435'}$$

Since there is central symmetry, F depends only on r and upon the time t. F is connected by (427) with the charge density Π_1, of the atmosphere surrounding the ion 1 and the corresponding charge density Π_2 surrounding the ion 2 according to the equations

$$\Pi_1 = -e_1 F\left(\frac{1}{n_1}+\frac{1}{n_2}\right), \qquad \Pi_2 = -e_2 F\left(\frac{1}{n_1}+\frac{1}{n_2}\right).$$

We shall now write equation (435) in a dimensionless form, for which purpose we introduce the quantity $\bar{\Theta}$, which has the dimensions of a time, and is defined by

$$\bar{\Theta} = \frac{\rho_1 \rho_2}{\rho_1+\rho_2}\frac{1}{kT\kappa^2}. \tag{436}$$

If we now write

$$\frac{t}{\bar{\Theta}} = \tau, \qquad \kappa r = s, \tag{437}$$

(435') becomes

$$\frac{1}{s^2}\frac{\partial}{\partial s}\left(s^2\frac{\partial F}{\partial s}\right) - F = \frac{\partial F}{\partial \tau}. \tag{438}$$

We now wish to find a solution of this equation which will fulfil the condition that at time $t = 0$ the ion in question is surrounded by its characteristic ionic atmosphere, the charge on the central ion being removed at the same instant; i.e. at time $t = 0$, F must be given by

$$(F)_{t=0} = F_0 = \frac{n_2^2 e_2^2}{D_0 kT}\frac{e^{-\kappa r}}{r}, \tag{439}$$

which by (424) and (431) can be written

$$F_0 = \frac{\kappa^3}{4\pi}\frac{e^{-s}}{s(1/n_1+1/n_2)}. \tag{440}$$

It may be easily shown that the only solution which satisfies all the necessary conditions is

$$F = \frac{\kappa^3}{4\pi s} \frac{e^{-s}}{(1/n_1+1/n_2)} \frac{1}{\sqrt{\pi}} \int_{\sqrt{\tau}-s/2\sqrt{\tau}}^{\infty} e^{-x^2}\, dx. \tag{441}$$

Writing

$$\frac{1}{\sqrt{\pi}} \int_{\sqrt{\tau}-s/2\sqrt{\tau}}^{\infty} e^{-x^2}\, dx = J(\tau, s), \tag{442}$$

this becomes

$$F = \frac{\kappa^3}{4\pi s} e^{-s} \frac{J(\tau, s)}{\frac{1}{n_1}+\frac{1}{n_2}}. \tag{443}$$

$J(\tau, s)$ can be calculated, and hence the distribution function F obtained for all values of the time and s. J has the value $\frac{1}{2}$ when

$$\sqrt{\tau} - \frac{s}{2\sqrt{\tau}} = 0,$$

i.e.

$$s = 2\tau,$$

or

$$\kappa r = \frac{2t}{\bar{\Theta}}, \qquad \text{i.e.} \quad t = \frac{\kappa r}{2}\bar{\Theta}.$$

The disappearance of the equilibrium state may be visualized more readily by calculating the amount of electricity dQ_e between two spheres of radii r and $r+dr$. This varies with the time, and is given by

$$dQ_e = \Pi_1 4\pi r^2\, dr = y e_1 \kappa\, dr, \tag{444}$$

where

$$y = s e^{-s} J(\tau, s). \tag{445}$$

In Fig. 19 (p. 108) y is plotted as a function of κr for the times†

$$t = 0, \quad t = 0{\cdot}25\bar{\Theta}, \quad t = \bar{\Theta}.$$

y is a measure of the charge density in a spherical shell of thickness dr distance r from the central ion of charge e_1. The corresponding charge density round the ion of charge e_2 is obtained by replacing e_1 by e_2 in (444). It may be seen that after time $4\bar{\Theta}$, y has become practically zero. If $\rho_1 = \rho_2$ then

$$\bar{\Theta} = \frac{1}{2} \frac{\rho}{kT\kappa^2},$$

and in the special case of KCl,

$$\bar{\Theta} = \frac{0{\cdot}276}{\gamma} 10^{-10} \text{ sec.}$$

† Here $\bar{\Theta} = q\Theta$, cf. (436) and (466).

We may also mention the problem which Debye has treated in a special case, i.e. how quickly an electrolyte attains its equilibrium distribution from a completely random state. It may be easily seen that in this more generalized case the distribution function F is given by

$$F = \frac{\kappa^2}{4\pi\left(\frac{1}{n_1}+\frac{1}{n_2}\right)} \frac{e^{-\kappa r}}{r}\left\{\frac{1}{\sqrt{\pi}} \int_{\sqrt{\tau}-s/2\sqrt{\tau}}^{\infty} e^{-x^2}\,dx - 1\right\}. \tag{446}$$

As will be shown later, the time of relaxation $\bar{\Theta}$ defined by equation (436), is of very great importance for the theory of the conductivity of strong electrolytes. Before dealing with this, we shall first calculate the electrophoretic effect.

40. Calculation of the Electrophoretic Force upon an Ion (Debye, Hückel, and Onsager)†

It has already been pointed out that according to the laws of hydrodynamics, ions moving in an electric field will carry solvent with them, and this effect will extend to relatively great distances from the ions. Now we know that there is in the neighbourhood of any given ion an excess of ions of the opposite sign, so that the ion in question is not moving relative to a stationary solvent, but relative to solvent streaming in the opposite direction. The velocity of the ion will therefore be less than that calculated on the basis of the electrical forces and the forces due to viscosity. It may at first appear somewhat unjustifiable to employ the ordinary macroscopic hydrodynamic laws to a problem involving ions of molecular dimensions. It must, however, be remembered that the processes which would cause deviations from these laws take place essentially in the immediate neighbourhood of the ion. It is thus allowable to assume the validity of the fundamental equations of hydrodynamics at a certain distance (two or three molecular diameters) from the central ion. We shall show in the next paragraph that the unsymmetrical charge distribution set up round the moving ion can be neglected in calculating the electrophoretic effect, and we may assume a distribution symmetrical about the central ion. If the charge of the central ion is e_j, the charge distribution round the central ion is given by (219),

$$\Pi = -\frac{e_j}{4\pi}\frac{\kappa^2 e^{-\kappa r}}{r}.$$

† P. Debye and E. Hückel (*Phys. Z.* **24** (1923), 305) were the first to calculate the electrophoretic force by integrating the hydrodynamic equations. We shall follow here the simpler derivation given later by Onsager (*Phys. Z.* **27** (1926), 388.)

In presence of an external field of strength $\mathfrak{E}$, the force $\mathfrak{F}$ acting on unit volume is

$$\mathfrak{F} = -\mathfrak{E}\frac{e_j}{4\pi}\frac{\kappa^2 e^{-\kappa r}}{r}. \tag{447}$$

This force $\mathfrak{F}$ is thus everywhere opposed to the direction of the electric field (see Fig. 36). We must now investigate the hydrodynamics of this system, assuming that the ordinary hydrodynamic laws hold throughout the liquid. If $\mathfrak{v}$ is the velocity, p the pressure, and η_0 the viscosity of the liquid, Stokes's equation of motion gives†

$$\eta_0 \operatorname{curl}\operatorname{curl}\mathfrak{v} = -\operatorname{grad} p + \mathfrak{F}. \tag{448}$$

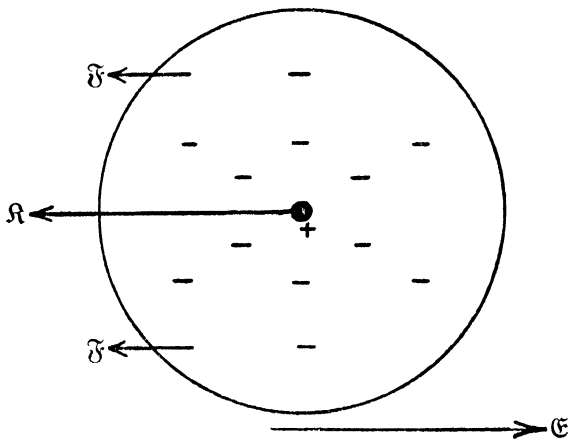

FIG. 36.

Further, the equation of continuity of an incompressible liquid gives

$$\operatorname{div}\mathfrak{v} = 0. \tag{449}$$

The following boundary conditions must also hold:

(1) The velocity of the liquid at an infinite distance from the ion must be zero,

(2) The liquid immediately at the surface of the ion must have the same velocity as the ion.

We may now divide the velocity $\mathfrak{v}$ into two parts,

$$\mathfrak{v} = \mathfrak{v}_1 + \mathfrak{v}_2, \tag{450}$$

where $\mathfrak{v}_1$ corresponds to the case

$$\mathfrak{K}_1 = \mathfrak{K}, \quad \mathfrak{F}_1 = 0. \tag{451}$$

† For a proof of these equations, see H. Falkenhagen, 'Klassische Hydrodynamik', in Wien-Harms, *Handb. d. Experimentalphysik*, vol. iv, part I, p. 68, 1931.

$\mathfrak{K}$ is simply the force which will give the ion a velocity

$$\mathfrak{V}_1 = \frac{\mathfrak{K}}{\rho_j} = \frac{e_j \mathfrak{E}}{\rho_j}. \tag{452}$$

Since we are only interested in the velocity of the ion, we shall not go into the details of the $\mathfrak{v}_1$ system. $\mathfrak{v}_2$ corresponds to

$$\mathfrak{K} = 0, \quad \mathfrak{F}_2 = \mathfrak{F}, \tag{453}$$

where $\mathfrak{F}$ is the force per unit volume due to the action of the external field upon the ionic atmosphere. We therefore wish to find $\mathfrak{V}_2$, which is the velocity due to the system of forces $\mathfrak{F}$. We divide the ionic atmo-

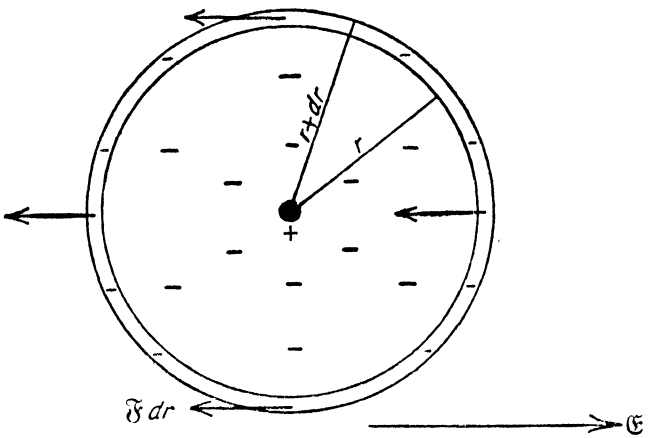

FIG. 37.

sphere into thin concentric spherical shells, radius r and thickness dr and investigate the velocity $d\mathfrak{v}_2$ caused by the forces between the two spheres. According to Stokes† a sphere of radius r subjected to a force K' moves through the liquid with a velocity $K'/6\pi\eta_0 r$. Further, the force per sq. cm. exerted by the liquid upon the sphere (which is partly a pressure and partly a viscosity effect) is distributed uniformly over the surface of the sphere, and acts everywhere in the opposite direction to the direction of motion. The distribution of force has this same property, and is given by (447) (cf. Fig. 37) as

$$\mathfrak{F}\,dr = -\frac{\mathfrak{E} e_j}{4\pi} \frac{\kappa^2 e^{-\kappa r}}{r}\, dr. \tag{454}$$

The interior of the spherical shell will thus move through the liquid just as if it were a rigid sphere, quite independent of the presence of the

† For deviations, see e.g. H. Falkenhagen, 'Klassische Hydrodynamik', in Wien-Harms, *Handb. d. Experimentalphysik*, vol. iv, part I, p. 206, 1931.

central ion. The total force acting upon the shell is

$$4\pi r^2 \mathfrak{F}\, dr.$$

This force causes the sphere of liquid (and hence also the ion) to move with a velocity

$$d\mathfrak{V}_2 = \frac{4\pi r^2 \mathfrak{F}\, dr}{6\pi\eta_0 r} = \frac{2}{3}\frac{r\mathfrak{F}\, dr}{\eta_0} = \frac{2}{3\eta_0}\frac{\mathfrak{E} e_j \kappa^2 e^{-\kappa r}\, dr}{4\pi}. \tag{455}$$

In order to obtain the total velocity caused by the system of forces $\mathfrak{F}$, (455) must be integrated, giving

$$\mathfrak{V}_2 = \int_{r=0}^{r=\infty} d\mathfrak{V}_2 = -\frac{e_j \mathfrak{E}\kappa}{6\pi\eta_0}. \tag{456}$$

This velocity is the additional velocity due to the electrophoretic effect, and the retarding electrophoretic force is thus

$$-\frac{e_j \mathfrak{E}\kappa\rho_j}{6\pi\eta_0}. \tag{457}$$

This electrophoretic term (equation (457)) has recently been the subject of much discussion. According to v. Smoluchowski (for references, see H. Freundlich, *Kapillarchemie*, vol. i (Leipzig, 1930), and W. Pauli and E. Válko, *Elektrochemie der Kolloide* (Wien, 1929)), 6π should be replaced by 4π for large particles, while according to Debye and Hückel (*Phys. Z.* **25** (1924), 49) 4π is correct only for cylindrical particles and 6π for spherical ones. According to Debye and Hückel the mobility should thus depend on the shape of the particle; this is not confirmed by experiment (see H. Freundlich and H. Abramson, *Z. phys. Chem.* **128 A** (1927), 25; **133 A** (1928), 51). The question has been to some extent cleared up by a paper of D. C. Henry (*Proc. Roy. Soc.* **133 A** (1931), 106). For very large spheres he finds instead of $1/6\pi$ the factor $\frac{1}{6\pi}\frac{3\lambda}{2\lambda+\lambda'}$, where λ is the specific conductivity of the liquid and λ' that of the particle. If $\lambda' \ll \lambda$, the lines of flow of the current are tangential to the particle, and we obtain v. Smoluchowski's equation. If $\lambda' = \lambda$, we obtain the expression of Debye and Huckel, which should therefore be valid when the lines of flow of the current are not affected by the particle. (See also J. J. Bikerman, *Z. phys. Chem.* **163 A** (1933), 378; *Z. Elektrochem.* **39** (1933), 526.)

41. The Dependence of the Conductivity and the Dielectric Constant of Strong Electrolytes upon the Frequency. The General Theory of Debye and Falkenhagen

A. *The fundamental equations when only two kinds of ion are present.*

We shall now treat the general case of the dependence of the conductivity of electrolytic solutions upon the frequency. This effect was first predicted theoretically by Debye and Falkenhagen† and subse-

† P. Debye and H. Falkenhagen, *Phys. Z.* **29** (1928), 121, 401; *Z. Elektrochem.* **34** (1928), 562. For other articles of a more general character, see H. Falkenhagen and

quently verified (with approximate quantitative agreement with the theory), first by Sack, and later by a number of other authors.† The case of stationary fields, which was first treated by Debye, Hückel, and Onsager‡ may be considered as a particular case of the general problem, the frequency of the alternating electric field becoming zero. We shall first discuss the principles and chief results of the theory and subsequently give the calculations.

It must again be pointed out that on account of the long range electrostatic forces between the ions, there are two factors which tend to hinder the motion of an ion and thus cause a diminished mobility, even in a completely dissociated electrolyte. In the first place the ion is surrounded by an oppositely charged ionic atmosphere. The electric field thus causes the solvent to move in the opposite direction to the ion, and gives rise to the effect known as electrophoresis, which increases the ordinary viscosity resistance. In the second place, an ion moving with constant velocity must always be building up the ionic atmosphere in the regions to which it moves, while at points behind it the charge distribution is continually returning to a random one. The mean charge distribution in the ionic atmosphere therefore no longer possesses central symmetry with respect to the ion, but there will be an increased charge density in front of the ion, and a decreased density behind it. It will be shown later that the asymmetry of the charge distribution increases with increasing ionic velocity. It gives rise to a retarding force, termed the relaxation force, which is proportional to the ionic velocity for small velocities of the order of 10^{-3} cm./sec. Both effects are inversely proportional to the thickness of the ionic atmosphere and, since this thickness is itself inversely proportional to the square root of the concentration (see (227)), the total decrease in the conductivity is directly proportional to the square root of the concentration, thus agreeing with the law discovered experimentally by Kohlrausch.§

Now suppose the electrolyte to be in an alternating field. Each ion will then execute a periodic to and fro motion. For small frequencies the symmetry of the charge distribution in the ionic atmosphere will at any moment correspond to the instantaneous velocity of the ion. If, however, the frequency is so great that the time of an oscillation is comparable to (or even smaller than) the time of relaxation, practically

J. W. Williams, *Z. phys. Chem.* **137 A** (1928), 399; *J. Phys. Chem.* **33** (1929), 1121; *Chem. Rev.* **6** (1929), 317.

† For references, see pp. 222–235.

‡ P. Debye and E. Hückel, *Phys. Z.* **24** (1923), 305; L. Onsager, ibid. **27** (1926), 388; **28** (1927), 285.

§ See p. 77.

no asymmetry will be set up in the charge distribution. The relaxation force will therefore increase with increasing frequency of the alternating field. Hence for wave-lengths of the order of magnitude velocity of light $\times$ time of relaxation, we may anticipate a conductivity greater than that found for stationary fields.

We shall now develop the quantitative treatment of the dispersion conductivity effect, using for this purpose the fundamental equations (412) for the case of two sorts of ions. The four distribution functions F_{11}, F_{22}, F_{12}, F_{21} must satisfy the four equations (412). We shall assume that the field X is very small, and oscillates periodically with a frequency ω, i.e.

$$X = Ee^{i\omega t}. \tag{458}$$

We shall also write

$$F_{ij} = F^0_{ij} + g_{ij}, \tag{459}$$

where g_{ij} is small compared to F^0_{ij}. This assumption can be shown to be true for the range in which Ohm's law is obeyed, i.e. for small field-strengths, F^0_{ij} is then given by (407), (432), and (433) as

$$F^0_{ij} = n_i n_j \left(1 - \frac{e_i e_j}{D_0 kT} \frac{e^{-\kappa r}}{r}\right). \tag{460}$$

The deviation of the distribution function g_{ij} will also execute periodic oscillations with the same frequency ω, so that we write

$$g_{ij} = G_{ij} e^{i\omega t}. \tag{461}$$

Introducing these quantities into (412), the following four equations are obtained,

$$\left.\begin{aligned}
&\frac{2}{\rho_1} kT\Delta G_{11} - i\omega G_{11} - \frac{4\pi n_1 e_1}{D_0 \rho_1}(e_1 G_{11} + e_2 G_{21}) - \\
&\qquad - \frac{4\pi n_1 e_1}{D_0 \rho_1}(e_1 G_{11} + e_2 G_{12}) = 0 \\
&\frac{2}{\rho_2} kT\Delta G_{22} - i\omega G_{22} - \frac{4\pi n_2 e_2}{D_0 \rho_2}(e_1 G_{12} + e_2 G_{22}) - \\
&\qquad - \frac{4\pi n_2 e_2}{D_0 \rho_2}(e_1 G_{21} + e_2 G_{22}) = 0 \\
&\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) kT\Delta G_{12} - i\omega G_{12} - \frac{4\pi n_1 e_1}{D_0 \rho_1}(e_1 G_{12} + e_2 G_{22}) - \\
&\qquad - \frac{4\pi n_2 e_2}{D_0 \rho_2}(e_1 G_{11} + e_2 G_{12}) = -\left(\frac{e_1}{\rho_1} - \frac{e_2}{\rho_2}\right) E \frac{\partial F^0_{12}}{\partial x} \\
&\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) kT\Delta G_{21} - i\omega G_{21} - \frac{4\pi n_2 e_2}{D_0 \rho_2}(e_1 G_{11} + e_2 G_{21}) - \\
&\qquad - \frac{4\pi n_1 e_1}{D_0 \rho_1}(e_1 G_{21} + e_2 G_{22}) = \left(\frac{e_1}{\rho_1} - \frac{e_2}{\rho_2}\right) E \frac{\partial F^0_{21}}{\partial x}
\end{aligned}\right\}. \tag{462}$$

It is now necessary to find the solutions of (462) appropriate to the dispersion problem. As long as the field strength is not too high (i.e. well under 100,000 volts per cm.), Ohm's law holds. In this case it may be easily shown by investigating all the possible solutions† that the root which is of importance in the present case is

$$K^2 = u_1\kappa_1^2+u_2\kappa_2^2+\frac{2iu_1u_2\omega(\rho_1+\rho_2)}{2kT}$$

$$=\frac{\rho_1\kappa_1^2+\rho_2\kappa_2^2}{\rho_1+\rho_2}+\frac{2i\rho_1\rho_2}{\rho_1+\rho_2}\frac{\omega}{2kT}, \tag{463}$$

corresponding to the root mentioned on p. 176. This means that now we have

$$G_{12} = -G_{21}, \qquad G_{11} = G_{22} = 0. \tag{464}$$

The physical significance of (464) is that the ionic atmospheres of the two sorts of ions are changed asymmetrically by the field, as will appear more precisely from the following calculations. The other roots only give density distributions having central symmetry, and thus will not lead to a solution of the conductivity problem. The differential equations (462) thus give the following equation, which governs the dispersion conductivity effect,

$$\left(\frac{1}{\rho_1}+\frac{1}{\rho_2}\right)kT\,\Delta G_{12}-i\omega G_{12}-\frac{4\pi}{D_0}\left(\frac{n_1e_1^2}{\rho_1}+\frac{n_2e_2^2}{\rho_2}\right)G_{12} = -\left(\frac{e_1}{\rho_1}-\frac{e_2}{\rho_2}\right)E\frac{\partial F_{12}^0}{\partial x}. \tag{465}$$

To develop this equation further, we introduce Θ, the time of relaxation of the ionic atmosphere round the ion 1 or the ion 2, defined by

$$\Theta = \frac{\rho_1\rho_2}{\rho_1+\rho_2}\frac{1}{kT\kappa^{*2}}, \tag{466}$$

where

$$\kappa^{*2} = q\kappa^2, \tag{467}$$

$$q = \frac{e_1/\rho_1-e_2/\rho_2}{(e_1-e_2)(1/\rho_1+1/\rho_2)}; \tag{468}$$

so that (cf. (436))

$$q\Theta = \bar{\Theta}. \tag{469}$$

Writing the complex root K^2 as

$$K^2 = \kappa^{*2}(1+i\omega\Theta), \tag{470}$$

(465) becomes

$$\Delta G_{12}-K^2G_{12} = -\frac{e_1\rho_2-e_2\rho_1}{\rho_1+\rho_2}\frac{E}{kT}\frac{\partial F_{12}^0}{\partial x}. \tag{471}$$

† As on p. 173.

According to (460)

$$F_{12}^0 = n_1 n_2 - \frac{n_1 n_2}{D_0 kT} \frac{e_1 e_2 e^{-\kappa r}}{r}. \tag{472}$$

We now introduce Ψ_1', the additional potential round the ion 1.† From equations (400), (407), (409), (459), (461), and (464),

$$G_{12} e^{i\omega t} = -\frac{D_0}{4\pi} \frac{n_1}{e_2} \Delta\Psi_1'. \tag{473}$$

This potential (due to the applied field) is superimposed upon the potential (429) which exists in the absence of external field. According to (471), (472), and (473), the potential Ψ_1' must satisfy the differential equation

$$\Delta\Delta\Psi_1' - K^2 \Delta\Psi_1' = \Omega\kappa^{*2} \frac{\partial}{\partial x} \frac{e^{-\kappa r}}{r} e^{i\omega t}, \tag{474}$$

where

$$\Omega = E \frac{e_1 e_2}{D_0 kT}. \tag{475}$$

Equation (474) is now in the same form as the equation used by Onsager‡ in his work on the conductivity of strong electrolytes, the only difference being that K^2 is complex in the non-stationary case which we have considered. We shall show that this leads directly to the dispersion effect for the conductivity and the dielectric constant. The asymmetric potential of the oscillating ion will first be calculated.

B. *Calculation of the asymmetric potential of the oscillating ion.*

From (464), (473), and corresponding equations for Ψ_2',

$$n_1 e_1 \Psi_1' + n_2 e_2 \Psi_2' = 0. \tag{476}$$

Since

$$n_1 e_1 = -n_2 e_2,$$

$$\Psi_1' = \Psi_2', \tag{477}$$

i.e. the additional potential caused by the alteration of the symmetrical ionic atmosphere of one of the ions is on a time average equal to the same potential for the ionic atmosphere of the other ion. We can thus write as a particular solution of (474),

$$\Psi_1' = \frac{q\Omega}{\kappa^2 - K^2} \frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r}\right) e^{i\omega t}. \tag{478}$$

We must now add to (478) an arbitrary solution of the homogeneous equation

$$\Delta(\Delta\Psi' - K^2\Psi') = 0 \tag{479}$$

† It is not actually necessary to introduce this potential since the additional electric density can be obtained from (471), and the force (490). This method is, however, hardly any simpler for the dispersion effect, though it is much more suitable for solving the viscosity problem (cf. p. 245).

‡ Loc. cit. p. 165.

giving as the general solution of (474)†

$$\Psi_1' = \left\{\frac{q\Omega}{\kappa^2-K^2}\frac{d}{dr}\left(\frac{e^{-\kappa r}}{r}\right)+A'\frac{d}{dr}\left(\frac{e^{-Kr}}{r}\right)+\frac{B'}{r^2}\right\}e^{i\omega t}\cos\vartheta, \tag{480}$$

where ϑ is the angle between the direction of the field and the radius vector r. The potential of the oscillating ion at the point $r = 0$ (i.e. the point occupied by the ion itself) must have a finite value, and the charge density at the same point must also be finite. Using the expansion

$$\frac{d}{dr}\left(\frac{e^{-\kappa r}}{r}\right) = -\frac{1}{r^2}+\frac{\kappa^2}{2}-\frac{\kappa^3 r}{3}+\ldots \tag{481}$$

these two conditions give for the constants A' and B'

$$A' = -\frac{q\Omega}{\kappa^2-K^2}\frac{\kappa^2}{K^2}, \qquad B' = A'+\frac{q\Omega}{\kappa^2-K^2}. \tag{482}$$

This gives for the additional potential near the ion,

$$\begin{aligned}\Psi_1' &= -\left(\frac{q\Omega}{\kappa^2-K^2}\frac{\kappa^3 r}{3}+\frac{A'K^3}{3}r\ldots\right)e^{i\omega t}\cos\vartheta \\ &= -\frac{\Omega q\kappa^2}{3(\kappa+K)}re^{i\omega t}\cos\vartheta.\end{aligned} \tag{483}$$

C. *Calculation of the force acting on the oscillating ion.*

Equation (483) gives for the field strength at the origin, i.e. the point occupied by the ion 1, the value

$$\frac{\Omega q\kappa^2}{3(\kappa+K)}e^{i\omega t}. \tag{484}$$

Substituting from (467), (470), and (475),

$$K = \kappa\sqrt{q}(1+i\omega\Theta)^{\frac{1}{2}}, \tag{485}$$

the field strength at the origin can be written in the form

$$\frac{e_1 e_2}{3D_0 kT}\frac{q\kappa E e^{i\omega t}}{1+\sqrt{q}(1+i\omega\Theta)^{\frac{1}{2}}}. \tag{486}$$

In the limiting case of infinitely dilute solutions, we have

$$\rho_1 v_1 = e_1 E, \tag{487}$$

where $v_1 e^{i\omega t}$ is the velocity of the ion 1. The force on the ion can thus

† The two other particular solutions

$$A''\cos\vartheta\frac{d}{dr}\left(\frac{e^{+Kr}}{r}\right) \quad \text{and} \quad B''r^2\cos\vartheta$$

must both be equal to zero, since otherwise the additional potential would become infinite at an infinite distance from the central ion.

be written with sufficient accuracy as

$$\frac{e_1 e_2}{3D_0 kT} \frac{\kappa \rho_1 v_1 q e^{i\omega t}}{1+\sqrt{q}(1+i\omega\Theta)^{\frac{1}{2}}} \tag{488}$$

or

$$\frac{e_1 e_2}{3D_0 kT} \kappa \sqrt{q} \rho_1 v_1 \frac{a-ib}{a^2+b^2} e^{i\omega t}, \tag{488'}$$

where

$$\frac{1}{\sqrt{q}} + (1+i\omega\Theta)^{\frac{1}{2}} = a+ib. \tag{489}$$

The force on the ion 2 can be obtained in an exactly analogous manner, introducing $\rho_2 v_2 = e_2 E$ in place of $\rho_1 v_1 = e_1 E$. The force acting on

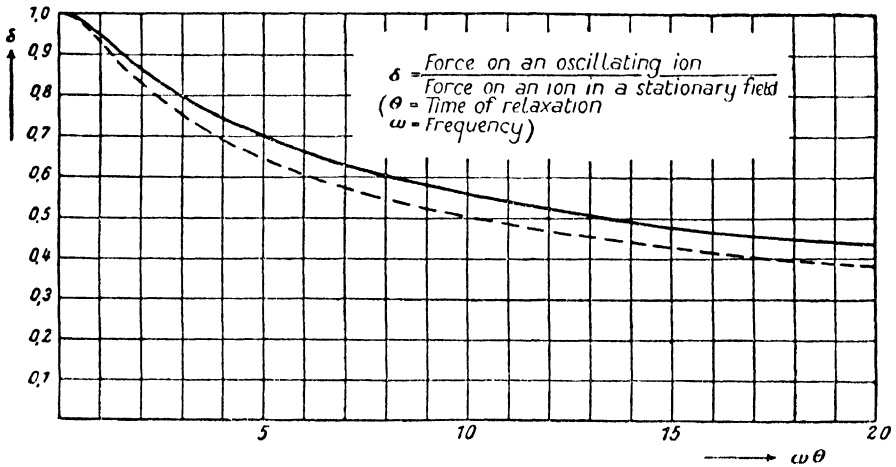

FIG. 38. The force acting on an ion in an oscillating field.

the ion 1 is given by

$$-K^* e^{i(\omega t+\Delta)} = K^* e^{i(\omega t+\Delta+\pi)}, \tag{490}$$

where the absolute value of the force K^* is given by

$$K^* = \frac{|e_1 e_2|}{3D_0 kT} \frac{\kappa \rho_1 v_1 \sqrt{q}}{(a^2+b^2)^{\frac{1}{2}}}, \tag{491}$$

and the phase Δ by

$$\tan\Delta = -\frac{b}{a}. \tag{492}$$

$\pi+\Delta$ is the phase difference between the force acting on the oscillating ion and its velocity. For a given simple electrolyte the absolute value of the force K^* and the phase Δ can be calculated as functions of $\omega\Theta$ from equations (491) and (492). If the quantities q, κ, and Θ have been calculated (cf. Table 33, p. 213), (491) and (492) give K^* and Δ as functions of the frequency ω or the wave-length of the alternating electric field. In the special case of a stationary field ($\omega = 0$), the

absolute value of the force acting upon the ion 1 is given by

$$\frac{e_1 e_2}{3D_0 kT}\kappa\rho_1 v_1 \frac{q}{1+\sqrt{q}}. \tag{493}$$

Onsager was the first to obtain this result for the stationary case, using a different method.

Formulae (491) and (493) give the ratio δ of the absolute value of the force on an oscillating ion to the value for the ion in a stationary field.† For small values of ω this ratio is very nearly unity. For small values of $\omega\Theta$ the δ–$\omega\Theta$ curve begins as a parabola with a horizontal tangent at $\omega\Theta = 0$, while for very high values of $\omega\Theta$, δ increases linearly

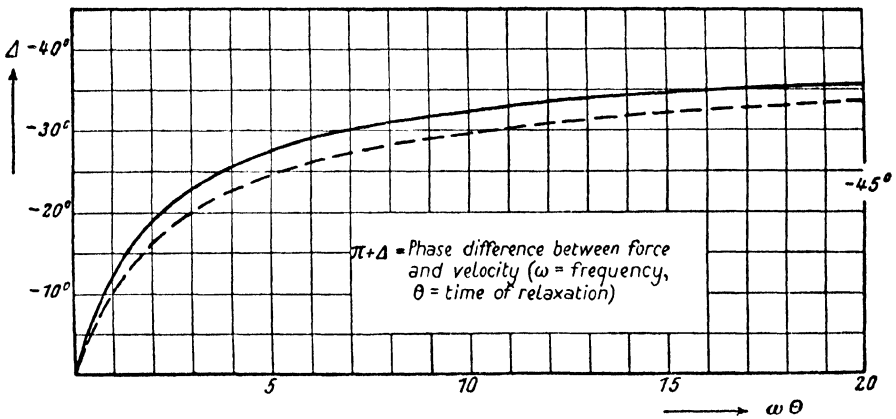

FIG. 39. The phase difference between the force and the velocity at different frequencies.

with $1/\omega\Theta$. Similarly, the negative phase difference Δ increases linearly for very small values of $\omega\Theta$, and approaches the value $-45°$ for very great values of $\omega\Theta$. Figs. 38 and 39 illustrate these relations for binary electrolytes, for which $q = 0{\cdot}5$. In the stationary case the absolute value of the forces is‡

$$\frac{e^2\kappa}{6D_0 kT}(2-\sqrt{2})E. \tag{494}$$

The dotted lines in Figs. 38 and 39 correspond to an approximate method of taking the Brownian movement into account.§

D. *The general formulae for the dependence of conductivity and dielectric constant upon the frequency.*

It is now necessary to calculate the conduction and displacement current, for which purpose we must evaluate the velocities of the two

† This ratio is the same for both ion 1 and ion 2.

‡ The curves are very similar for more complicated electrolytes, for which $q \neq 0{\cdot}5$.

§ See P. Debye and H. Falkenhagen, *Phys. Z.* **29** (1928), 121.

ions, $v_1 e^{i\omega t}$ and $v_2 e^{i\omega t}$. The force due to the electric field, the Stokes force, the electrophoretic force, and the relaxation force must then be in equilibrium. It can be shown† that, in the frequency range we shall consider, the electrophoretic force is independent of the frequency. Similarly, the time of relaxation of the ionic atmosphere has no effect upon the viscosity coupling between the ions, and other effects (connected with solvation) can also be neglected. Equations (457) and (488) thus give

$$\left.\begin{aligned} e_1 E-\rho_1 v_1+\frac{e_1 e_2 \kappa}{3D_0 kT}\,\frac{\rho_1 v_1 \sqrt{q}}{\dfrac{1}{\sqrt{q}}+(1+i\omega\Theta)^{\frac{1}{2}}}-e_1\frac{E\kappa\rho_1}{6\pi\eta_0}=0,\\ e_2 E-\rho_2 v_2+\frac{e_1 e_2 \kappa}{3D_0 kT}\,\frac{\rho_2 v_2 \sqrt{q}}{\dfrac{1}{\sqrt{q}}+(1+i\omega\Theta)^{\frac{1}{2}}}-e_2\frac{E\kappa\rho_2}{6\pi\eta_0}=0. \end{aligned}\right\} \tag{495}$$

The required velocities are then given by

$$v_j e^{i\omega t}=E\left(e_j\omega_j+\frac{e_1 e_2}{3D_0 kT}\kappa e_j\omega_j\chi-\frac{e_j\kappa}{6\pi\eta_0}\right)e^{i\omega t}, \tag{496}$$

where j is 1 or 2 according to which ion is being considered, and χ and ω_j are defined by

$$\chi(q,\omega\Theta)=\frac{\sqrt{q}\{(1+i\omega\Theta)^{\frac{1}{2}}-1/\sqrt{q}\}}{1+i\omega\Theta-1/\sqrt{q}}, \tag{497}$$

$$\omega_j=\frac{1}{\rho_j}. \tag{498}$$

χ is thus connected with the part depending on the frequency, and depends only on q and the product $\omega\Theta$. The current density $\mathfrak{i}$ (cf. (496)) is thus given by

$$\mathfrak{i}=\sum_j n_j e_j v_j e^{i\omega t}=Ee^{i\omega t}\left\{\sum_j n_j e_j^2\omega_j+\frac{e_1 e_2}{3D_0 kT}\kappa\sum_j n_j e_j^2\omega_j\chi-\sum_j\frac{n_j e_j^2\kappa}{6\pi\eta_0}\right\}. \tag{499}$$

The total current density $\mathfrak{J}$ must be equal to the sum of the conduction current and the displacement current, i.e.

$$\mathfrak{J}=\lambda\mathfrak{E}+\frac{D_\omega}{4\pi}\dot{\mathfrak{E}}=\lambda Ee^{i\omega t}+\frac{i\omega}{4\pi}D_\omega Ee^{i\omega t} \tag{500}$$

and

$$\mathfrak{J}=\frac{D_0}{4\pi}i\omega Ee^{i\omega t}+\left\{\sum n_j e_j^2\omega_j+\frac{e_1 e_2}{3D_0 kT}\kappa\sum n_j e_j^2\omega_j\chi-\sum\frac{n_j e_j^2\kappa}{6\pi\eta_0}\right\}Ee^{i\omega t}. \tag{501}$$

† Unpublished calculations by the author; see also J. Schiele, *Phys. Z.* **34** (1933), 61.

D_0 is the dielectric constant of the solvent. The conductivity $\bar{\lambda}_\omega$ is obtained from the real part of the right-hand side of (501), i.e.

$$\bar{\lambda}_\omega = \sum n_j e_j^2 \omega_j + \frac{e_1 e_2}{3 D_0 kT} \kappa \sum n_j e_j^2 \omega_j \times \text{real part of } \chi - \sum \frac{n_j e_j^2 \kappa}{6\pi\eta_0}, \tag{502}$$

while the imaginary part of (501) is connected with the increase in dielectric constant $D_\omega - D_0$ by the equation

$$D_\omega - D_0 = \frac{4\pi}{\omega} \frac{e_1 e_2}{3 D_0 kT} \kappa \sum n_j e_j^2 \omega_j \times \text{imaginary part of } \chi. \tag{503}$$

The dispersion effects for the conductivity and the dielectric constant are thus determined by the behaviour of χ. The general formulae for the conductivity $\bar{\lambda}_\omega$ and the increase in dielectric constant $D_\omega - D_0$ can now be derived.

The part of the specific conductivity $\bar{\lambda}_\omega$ depending on the relaxation forces of the ionic atmosphere is given by

$$\bar{\lambda}_{\text{I}\omega} = \frac{|e_1 e_2|}{3 D_0 kT} \kappa \bar{\lambda}_\infty \times \text{real part of } \chi, \tag{504}$$

where $\bar{\lambda}_\infty$ is the specific conductivity at infinite dilution. The part due to the electrophoretic effect is

$$\bar{\lambda}_{\text{II}} = \sum \frac{n_j e_j^2 \kappa}{6\pi\eta_0}, \tag{505}$$

the total conductivity thus being

$$\bar{\lambda}_\omega = \bar{\lambda}_\infty - \bar{\lambda}_{\text{I}\omega} - \bar{\lambda}_{\text{II}}. \tag{506}$$

The real part of χ is readily obtained, and is

$$\text{real part of } \chi = \frac{\sqrt{q}}{(1-1/q)^2 + \omega^2\Theta^2} \{(1-1/q)(\bar{R} - 1/q^{\frac{1}{2}}) + \omega\Theta\bar{Q}\}, \tag{507}$$

where

$$\bar{R} = \frac{1}{\sqrt{2}} \{(1+\omega^2\Theta^2)^{\frac{1}{2}} + 1\}^{\frac{1}{2}}, \qquad \bar{Q} = \frac{1}{\sqrt{2}} \{(1+\omega^2\Theta^2)^{\frac{1}{2}} - 1\}^{\frac{1}{2}}. \tag{508}$$

For stationary fields, i.e. $\omega = 0$, (507) becomes

$$(\text{real part of } \chi)_{\omega=0} = \frac{q}{1+\sqrt{q}}. \tag{509}$$

In practice one usually deals with the molar conductivity in practical units. If the molar conductivity at infinite dilution is Λ_∞, (506) can be written

$$\Lambda_\omega = \Lambda_\infty - \Lambda_{\text{I}\omega} - \Lambda_{\text{II}}, \tag{510}$$

where $\Lambda_{I\omega}$ and Λ_{II} are given by

$$\Lambda_{I\omega} = \frac{|e_1 e_2|}{3D_0 kT}\kappa\Lambda_\infty \times \text{real part of } \chi, \tag{511}$$

$$\Lambda_{II} = \sum \frac{n_j e_j^2 \kappa}{6\pi\eta_0}\frac{1{,}000}{\gamma}\frac{1}{9\times 10^{11}}. \tag{512}$$

The increase in dielectric constant is given by (503) as

$$D_\omega - D_0 = \frac{4\pi e_1 e_2}{3D_0 kT}\kappa\bar{\lambda}_\infty \frac{\Theta\sqrt{q}}{\omega\Theta\{(1-1/q)^2+\omega^2\Theta^2\}}\{\bar{Q}(1-1/q)-\omega\Theta(\bar{R}-1/\sqrt{q})\}. \tag{513}$$

Equation (510) for the dispersion conductivity effect will be discussed in detail later (see p. 211). Quite recently M. Wien† has confirmed experimentally the predictions of the Debye-Falkenhagen theory of the increase of dielectric constant, the results agreeing well with equation (513). For the sake of brevity, we shall not enter into a detailed discussion of this effect.‡ It may, however, be noted that the increase in dielectric constant is greatest for $\omega = 0$, and is proportional to the square root of the concentration in very dilute solutions.

Before comparing with experiment the general equation for the dependence of the molar conductivity upon the concentration, we shall first deal with the special case of stationary fields, first treated by Onsager.

42. The Conductivity of Electrolytes for the Special Case of Stationary Fields. Experimental Results and the Theory of L. Onsager§

If in equation (510) the frequency of the alternating field becomes zero, we obtain the molar conductivity (in practical units) for a stationary field, which we shall term Λ. For dilute solutions

$$\Lambda = \Lambda_\infty - \Lambda_{I0} - \Lambda_{II}, \tag{514}$$

where Λ_{I0} and Λ_{II} are given by the relations (see (511) and (512)),

$$\Lambda_{I0} = \frac{|e_1 e_2|}{3D_0 kT}\kappa\Lambda_\infty \frac{q}{1+\sqrt{q}}, \tag{515}$$

$$\Lambda_{II} = \sum \frac{n_j e_j^2}{6\pi\eta_0}\frac{1{,}000}{\gamma}\frac{1}{9\times 10^{11}}\kappa. \tag{516}$$

† M. Wien, *Ann. d. Phys.* (5) **11** (1931), 429.

‡ For such a discussion, see H. Falkenhagen and L. Vernon, *Phys. Z.* **33** (1932), 218. Cf. also p. 219 and Figs. 54–60.

§ L. Onsager, *Phys. Z.* **28** (1927), 277.

Introducing the value for κ given by (227), (515) and (516) become

$$\Lambda_{10} = \frac{0{\cdot}985\times 10^6}{(D_0 T)^{\frac{3}{2}}} \frac{2q}{1+\sqrt{q}} |z_1 z_2| \Lambda_\infty (\sum \nu_i z_i^2)^{\frac{1}{2}} \sqrt{\gamma}. \tag{517}$$

$$\Lambda_{11} = \frac{29}{(D_0 T)^{\frac{1}{2}} \eta_0} (\sum \nu_i z_i^2)^{\frac{1}{2}} \sqrt{\gamma}. \tag{518}$$

The molar conductivity Λ is thus given by an expression of the form

$$\Lambda = \Lambda_\infty - \alpha\sqrt{\gamma}, \tag{519}$$

where

$$\alpha = \frac{0{\cdot}985\times 10^6}{(D_0 T)^{\frac{3}{2}}} \frac{2q}{1+\sqrt{q}} |z_1 z_2| \Lambda_\infty (\sum \nu_i z_i^2)^{\frac{1}{2}} + \frac{29}{(D_0 T)^{\frac{1}{2}} \eta_0} (\sum \nu_i z_i^2)^{\frac{1}{2}}. \tag{520}$$

The law discovered experimentally by Kohlrausch (cf. (187)) is thus accounted for theoretically on the basis of the interionic forces.† Onsager uses the corresponding expression for the equivalent conductivity Λ^*, which is

$$\Lambda^* = \Lambda^*_\infty - \alpha^*(|z_1| + |z_2|)^{\frac{1}{2}} \sqrt{\gamma}, \tag{521}$$

where

$$\alpha^* = \frac{0{\cdot}985\times 10^6}{(D_0 T)^{\frac{3}{2}}} \frac{2q}{1+\sqrt{q}} |z_1 z_2| \Lambda^*_\infty + \frac{29{\cdot}0(|z_1| + |z_2|)}{(D_0 T)^{\frac{1}{2}} \eta_0}, \tag{522}$$

z_1 and z_2 being the valencies of the ions. Using the values of Drude for the dielectric constant of water at 18° and 25°, i.e.

$$D_0 = 81{\cdot}3 \text{ at } 18°$$

$$D_0 = 78{\cdot}8 \text{ at } 25°,$$

and for the viscosities‡

$$\eta_0(18°) = 0{\cdot}01056, \qquad \eta_0(25°) = 0{\cdot}00895$$

we obtain for α^* the values

$$\left.\begin{aligned} 18°.\quad \alpha^* &= 0{\cdot}270 \frac{2q}{1+\sqrt{q}} |z_1 z_2| \Lambda^*_\infty + 17{\cdot}85(|z_1| + |z_2|) \\ 25°.\quad \alpha^* &= 0{\cdot}274 \frac{2q}{1+\sqrt{q}} |z_1 z_2| \Lambda^*_\infty + 21{\cdot}14(|z_1| + |z_2|). \end{aligned}\right\} \tag{523}$$

A. *Test of Onsager's theory for aqueous solutions.*

We shall now compare the values of Kohlrausch§ with the above equations. Debye and Hückel have calculated a number of limiting slopes from the conductivity data of Kohlrausch at 18°. Tables 26 and 27 show the experimental and theoretical values side by side, and

† See p. 76. This law was predicted by v. Laar as early as 1900; see *Arch. Teyler*, pp. 14, 19, and 37.

‡ These values are taken from the work of Drake, Pierce, and Dow (*Phys. Rev.* **35** (1930), 613) and agree well with the values given in *Int. Crit. Tab.* **5** (1929), 10.

§ Cf. p. 73.

TABLE 26

Conductivity data for 1-1-valent electrolytes in water

$t = 18°$ C. $\alpha^*_{theor} = 35{\cdot}7 + 0{\cdot}159\,\Lambda^*_\infty$

Electrolyte	Λ^*_∞	α^*_{exp}	α^*_{theor}	$\alpha^*_{exp} - \alpha^*_{theor}$
LiCl	98·9	57·4	51·4	6·0
$LiIO_3$	67·4	48·3	46·4	1·9
$LiNO_3$	95·2	56·3	50·9	5·4
NaCl	108·9	54·7	53·0	1·7
$NaIO_3$	77·4	51·4	48·0	3·4
$NaNO_3$	105·3	58·3	52·5	5·8
KCl	129·9	59·9	56·4	3·5
KBr	132·0	62·2	56·7	5·5
KI	130·5	51·5	56·5	−5·0
KIO_3	98·4	54·2	51·4	2·8
$KClO_3$	119·5	58·2	54·7	3·5
KNO_3	126·4	65·7	55·8	9·9
KCNS	121·0	54·1	55·0	−0·9
CsCl	133·1	53·8	56·9	−3·2
$AgNO_3$	115·8	62·4	54·1	8·3
$TlNO_3$	127·6	63·4	56·0	7·4

TABLE 27

Conductivity data for 1-2-valent electrolytes in water

$t = 18°$ C. $\alpha^* = 53{\cdot}55 + 1{\cdot}084\,\frac{q}{1+\sqrt{q}}\,\Lambda^*_\infty$

Electrolyte	Λ^*_∞	α^*_{exp}	α^*_{theor}	$\alpha^*_{exp} - \alpha^*_{theor}$
$Ba(NO_3)_2$	117·0	92·8	86·9	5·9
$Sr(NO_3)_2$	113·4	97·8	85·5	12·3
$CaCl_2$	116·7	88·0	86·1	1·9
$Ca(NO_3)_2$	113·6	97·4	85·6	11·8
$MgCl_2$	110·9	83·2	84·1	− 0·9
K_2SO_4	132·2	81·0	92·1	−11·1

it is seen that the deviations are practically speaking always within the experimental error.† The difference between the theoretical and experimental slopes is slightly greater for 1-2-valent than for 1-1-valent salts. This is probably due to the fact that in the former case five conductivity values, corresponding to $\gamma^* = 0{\cdot}0001$, $0{\cdot}0002$, $0{\cdot}0005$, $0{\cdot}001$, and $0{\cdot}002$ were used for extrapolation, while in the latter case the six concentrations $0{\cdot}0001$, $0{\cdot}0002$, $0{\cdot}0005$, $0{\cdot}001$, $0{\cdot}002$, and $0{\cdot}005$ were employed. The 1-2 salts are also probably not quite so completely dissociated as the 1-1 salts. Fig. 40 shows the conductivity curves and the theoretical limiting slopes for a number of electrolytes. It is seen that

† It is improbable that KNO_3 forms complex ions, as assumed by Drucker (*Z. Elektrochem.* **26** (1920), 463). The results for $KMnO_4$ agree well with Onsager's equation; see R. Pederson (*Abh. Norske Videnskabs. Akad.* 1932, No. 13).

the limiting slope increases more slowly than Λ^*_∞, e.g. the absolute decrease in conductivity is greater for HCl than for $LiIO_3$, but the relative decrease is much less.

Fig. 40 really extends to much too high concentrations, since the theory has so far only been developed for dilute solutions. The following point

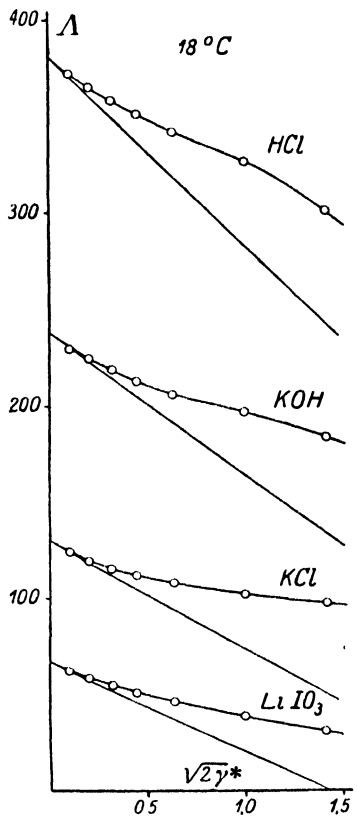

FIG. 40. Equivalent conductivity of aqueous solutions.

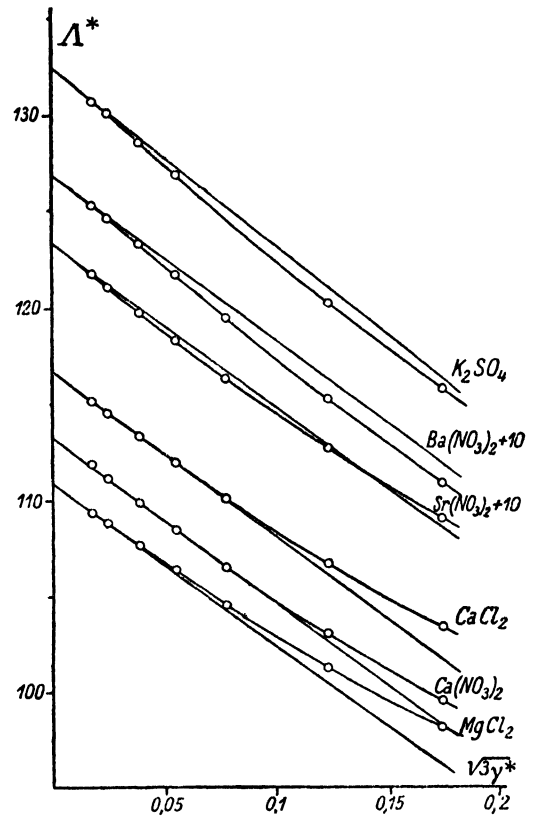

FIG. 41. Equivalent conductivity of dilute solutions.

is of interest. It is seen in Fig. 40 that the experimental points at higher concentrations lie above the limiting straight line, There are, however cases, e.g. the thallous salts, where the observed points lie below the limiting straight line (cf. Fig. 42). These salts have long been known to have a tendency to association.† Conductivity measurements have been recently carried out in the Rockefeller Institute which are accurate to 0·02 per cent., and must thus supersede Kohlrausch's values. It has been found that the Onsager equation is obeyed within the

† See the chapter on more concentrated solutions, p. 250.

experimental error in the range $\gamma = 0{\cdot}00003$ to $\gamma = 0{\cdot}001$ for 1-1-valent electrolytes.† Fig. 41 A shows the results for KCl and NaCl. The calculated slopes are shown by dotted lines. KNO_3 and $AgNO_3$ also agree with Onsager's theory up to 0·002 N.

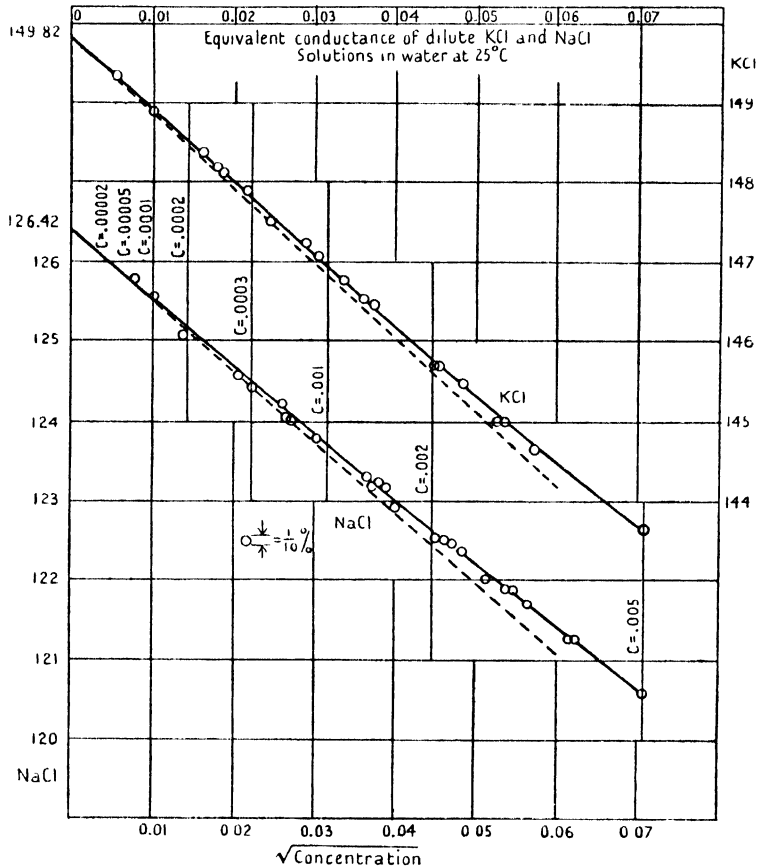

FIG. 41 A.

† T. Shedlovsky, *J. Am. Chem. Soc.* **54** (1932), 1411. This author proposes an empirical extension of Onsager's equation which represents the experimental data up to 0·07 N. for most 1-1-valent electrolytes (KNO_3, $AgNO_3$, and similar electrolytes are exceptions). Transport numbers have also been determined with an accuracy of 0·02 per cent. by the moving boundary method (MacInnes and Longsworth, *Chem. Rev.* **11** (1932), 171) and also obey Onsager's equation in very dilute solutions.

By combining the results of conductivity measurements with the transport numbers, the mobilities of ions at infinite dilution can be calculated with great accuracy (see McInnes, Shedlovsky, and Longsworth, *J. Am. Chem. Soc.* **54** (1932), 2758). In this connexion it is also found that Kohlrausch's law of the independent mobility of ions is valid for the K^+ ion up to 0·01 N. The K^+ ion in KNO_3 is an exception (see McInnes, Shedlovsky, and Longsworth, *Chem. Rev.*, August, 1933).

Fig. 41 shows the conductivity curves for 1-2-valent salts. (For the sake of clearness, the curves for $Sr(NO_3)_2$ and $Ba(NO_3)_2$ have been displaced vertically 10 units). K_2SO_4 and $Ba(NO_3)_2$ show undoubted signs of association, while the chlorides appear to be fairly completely dissociated, which agrees with previous ideas on the subject.

For salts of higher valency types, it seems as if there are not yet sufficient data in dilute solutions, since the values for the limiting slope are higher than the theoretical. This may be seen from Table 28.

TABLE 28

Conductivity data for 2-2-valent electrolytes in water

$t = 18°$ C. $\alpha^*_{\text{theor}} = 71{\cdot}4 + 0{\cdot}636\,\Lambda^*$

Electrolyte	Λ^*_∞	α^*_{exp}	α^*_{theor}	$\alpha^*_{\text{exp}} - \alpha^*_{\text{theor}}$
$MgSO_4$	114·7	242·7	144·4	98·3
$CdSO_4$	118·0	270·7	145·1	125·6

It would be of great interest to extend the data for this type of electrolyte to yet more dilute solutions. In the case of $MgSO_4$ it may in fact be shown that the extrapolation is incorrect, as the value obtained for Λ^*_∞ does not agree with that calculated from the mobilities of Mg^{++} and $SO_4^{=}$, taken from the data for 1-2-valent salts. Thus by adding the equivalent conductivities of $MgCl_2$ and K_2SO_4 and subtracting that of KCl, we obtain

$$110{\cdot}9 + 132{\cdot}2 - 129{\cdot}8 = 113{\cdot}3,$$

while the extrapolated value is 114·7, the difference being well outside the experimental error. Fig. 43 shows how extrapolation to the theoretical line involves a point of inflexion. The experimental points actually do show a slight S-shaped bending, and the curve can be drawn without violence as a continuation of the theoretical straight line $113{\cdot}3 - 143{\cdot}3\sqrt{(4\gamma^*)}$. Similar considerations apply to $CdSO_4$.

Before going on to the results in other solvents, we shall illustrate the application of the Onsager theory to a few acids. Accurate measurements of the conductivity of dilute solutions of acids have been carried out with HIO_3 by Kraus and Parker† and with HCl by Parker,‡ both

† C. Kraus and H. C. Parker, *J. Am. Chem. Soc.* **44** (1922), 2429.

‡ H. C. Parker, *J. Am. Chem. Soc.* **45** (1923), 2017. Data are also available for the conductivity of acids in methyl and ethyl alcohol. Murray-Rust and Hartley (*Proc. Roy. Soc.* **126** (1929), 84) showed that some 1-1-valent acids (e.g. HCl) are strong electrolytes in both alcohols, and agree approximately with Onsager's theory, the deviations being greater in ethyl than in methyl alcohol. Other acids, e.g. HNO_3 and thiocyanic acid, are weak acids in ethyl alcohol. Very few measurements exist of the conductivity of acids in non-hydroxylic solvents. Practically all acids appear to be weak in these solvents, the only exception being perchloric acid (see C. P. Wright, D. M. Murray-Rust, and H.

at 25°. Fig. 44 shows the values for HCl plotted against $\sqrt{(2\gamma^*)}$, and the most probable limiting straight line,

$$\Lambda^* = 427{\cdot}1 - 111{\cdot}0\sqrt{(2\gamma^*)}. \qquad (524)$$

The circles and crosses in Fig. 44 refer to different series of measurements. There is satisfactory agreement with theory. In the case of

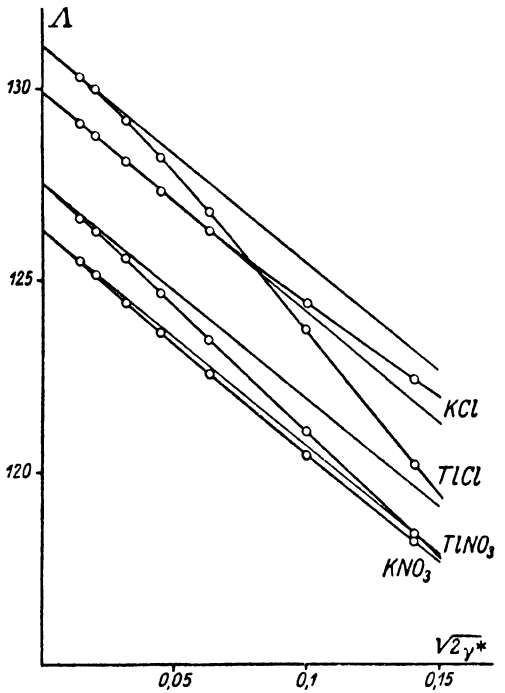

FIG. 42.

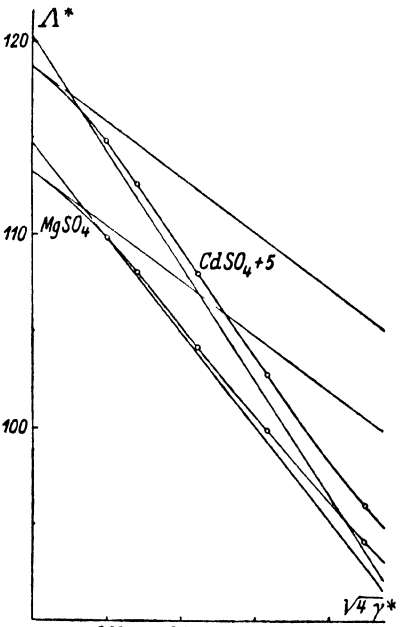

FIG. 43. Equivalent conductivity of 2-2-valent electrolytes.

iodic acid (cf. Fig. 45) there is obviously incomplete dissociation, even in highly dilute solutions. A conductivity curve of this form is found for a large class of electrolytes, and will be discussed in the chapter on more concentrated solutions.†

Hartley, *J. Chem. Soc.* (1931), 199. See also the section by H. Hartley, O. Gatty, W. A. Macfarlane, and D. M. Murray-Rust on the electrical conductivity of solutions, *Ann. Rep.* 1931). Goldschmidt and his collaborators (see H. Goldschmidt and H. Aarflot, *Z. phys. Chem.* **117** (1925), 312; **119** (1926), 439; Goldschmidt and F. Aas, ibid. **112** (1924), 423) find that the dissociation constants of acids which are weak in water are considerably smaller in methyl and ethyl alcohol than in water. H. Hunt and H. T. Briscoe (*J. Phys. Chem.* **33** (1929), 190, 1495) find that the conductivity of acids in alcohols decreases with increasing molecular weight of the alcohol.

† See p. 299. For HIO_3, see also G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.* (1932), 400.

Large deviations are found on comparing the results for 1-2-valent acids with the Debye-Onsager theory. Thus for H_2SO_4 at 18° the theoretical value, $\alpha^* = 148{\cdot}3$ (cf. (523)), is about three times as great as the experimental value. To obtain a more exact comparison, it would

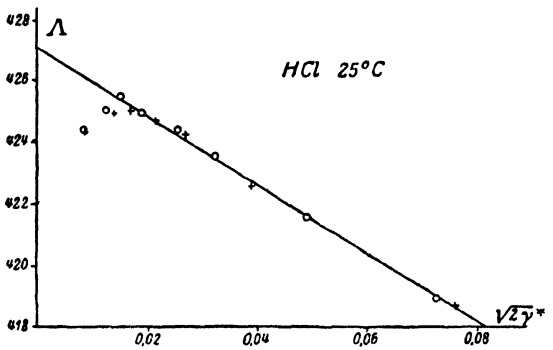

FIG. 44. Equivalent conductivity of HCl at 25°C.

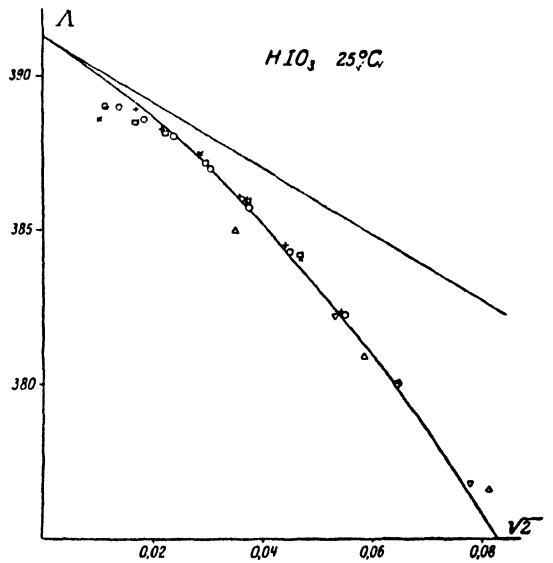

FIG. 45. Equivalent conductivity of HIO_3 at 25°C.

be necessary to extend the measurements to include the more dilute range.

Onsager and Fuoss† have recently extended the theory to the case of mixture by employing matrix algebra. The treatment is extremely complicated, and has so far only been carried out for the simplest case

† *J. Phys. Chem.* **36** (1932), 2689.

(three different sorts of ions). There are at present hardly any accurate measurements which can be compared with the theory. One of the most interesting effects has been observed by Bray and Hunt† who determined the conductivities of mixtures of NaCl and HCl. They found (in agreement with the theory) that at constant total ionic concentration the conductivities were not additive, although in NaCl and HCl separately the mobility of the chlorine ion is independent of the cation.‡ The rapid hydrion is retarded more than in the single electrolyte, while the slower K ion is accelerated. The Cl ions retain their normal velocity. The nature of this effect was first theoretically discussed by Bennewitz, Wagner, and Küchler.§ On account of the high concentrations studied by Hunt and Bray, their results agree only qualitatively with the calculations of Onsager and Fuoss. More recent measurements by R. A. Kay-Smith and R. A. Gärtner|| appear to agree quantitatively with the theory within the experimental error.

B. *The dependence of conductivity upon temperature and pressure.*

For 1-1-valent electrolytes, Onsager's theory is very successful in predicting the dependence of conductivity upon temperature. For aqueous solutions at 0° the theoretical equation is

$$\Lambda = \Lambda_\infty - (0{\cdot}2186\Lambda_\infty + 29{\cdot}47)\sqrt{\gamma} \tag{525}$$

and at 100°

$$\Lambda = \Lambda_\infty - (0{\cdot}2758\Lambda_\infty + 201{\cdot}1)\sqrt{\gamma}. \tag{526}$$

Thus for KCl the theoretical slope is 47·3 at 0° and 313·4 at 100°. The results of Walden and Ulich†† for 1-1-valent electrolytes agree well with Onsager's theory within the experimental error.

It is of interest to consider the variation of the equivalent conductivity over a greater temperature range. For dilute solutions, this is obtained by differentiating (521) with respect to temperature. The first term of the expression thus obtained will then contain the differential coefficient of the equivalent conductivity at infinite dilution, which is positive, since the viscosity of the solvent decreases with increasing temperature. Since, however, the dielectric constant of the solvent decreases with rise of temperature the second term will be negative, so that the increase of conductivity expressed by the first

† *J. Am. Chem. Soc.* **33** (1911), 781.

‡ See Kohlrausch-Holborn, *Leitvermögen der Elektrolyte*, McInnes and Cowperthwaite, *Trans. Farad. Soc.* **23** (1927), 400.

§ *Phys. Z.* **30** (1929), 623.

|| *J. Phys. Chem.* **37** (1933), 29.

†† P. Walden and H. Ulich, *Z. phys. Chem.* **106** (1923), 49.

term will be largely compensated, especially at higher concentrations. The increase in Λ^*_∞ is balanced by an increase in the difference $\Lambda^*_\infty - \Lambda^*$. Further, the considerable decrease in dielectric constant may lead to a decrease in the true degree of dissociation.† The last two effects may be so large that the equivalent conductivity no longer increases, but decreases with increasing temperature. Fig. 46 shows how the equivalent conductivity of NaCl solutions of different concentrations varies with the temperature. The temperature at which the equivalent conductivity reaches a maximum becomes lower with decreasing dielectric constant and increasing concentration, as would be expected from the theory. For 1-1-valent salts in water this maximum occurs at a very

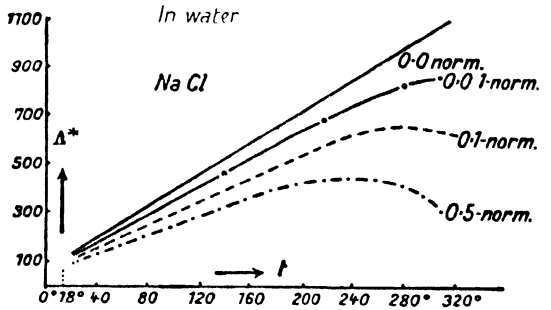

FIG. 46. Effect of temperature upon conductivity curves.

high temperature near the critical point. For salts of higher valency types the maximum occurs at lower temperatures. This is due to the fact that the Coulomb forces are stronger than for 1-1-valent salts, and hence the difference $\Lambda^*_\infty - \Lambda^*$ becomes equal to the increase in Λ^*_∞ at a lower temperature. A more detailed examination of the effect of temperature requires more accurate data on the variation of the dielectric constant of electrolyte solutions with temperature.

The effect of pressure upon the equivalent conductivity can be similarly treated. Zisman‡ has recently published an experimental and theoretical treatment of the effect of pressure upon the conductivity of salt solutions in water. He employs, however, the inaccurate conductivity theory of Debye and Hückel, and his conclusions are thus open to some modification.

† See p. 297.

‡ W. A. Zisman, *Phys. Rev.* **39** (1932), 151. See also E. Brander (*Soc. Sci. Fenn. Comm. Phys.-Math.* **6** (1932), 8) for a very complete list of the literature. For a further discussion of the effect of temperature and pressure, see L. Ebert, *Handb. d. Experimentalphysik*, pp. 246, 256.

C. *Comparison of Onsager's theory with experimental data in non-aqueous solvents.*

We shall now proceed to test Onsager's theory in other solvents, with special reference to some points of interest. For methyl alcohol at 25° (dielectric constant 30), the Onsager theory gives for α^*

$$\alpha^* = 1{\cdot}15\frac{2q}{1+\sqrt{q}}|z_1 z_2|\Lambda^*_\infty + 55{\cdot}3(|z_1|+|z_2|). \qquad (527)$$

Onsager has employed the conductivity data of Frazer and Hartley† and found a good confirmation of the theory for 1-1-valent salts over the range of concentrations studied, $\gamma^* = 0{\cdot}0001$ to $\gamma^* = 0{\cdot}002$. Table 29 shows the comparison between the theoretical and experimental slopes; the agreement is fair except in the case of the nitrates, which are not completely dissociated at a concentration of 0·0001 in methyl alcohol. It would be of great interest to extend the measurements with nitrates to yet higher dilutions, in order to test the theory in a more satisfactory manner. The activity coefficients probably show similar deviations from the theory. The halides, on the other hand, are much more completely dissociated, as may be seen from Table 29 and Fig. 47.

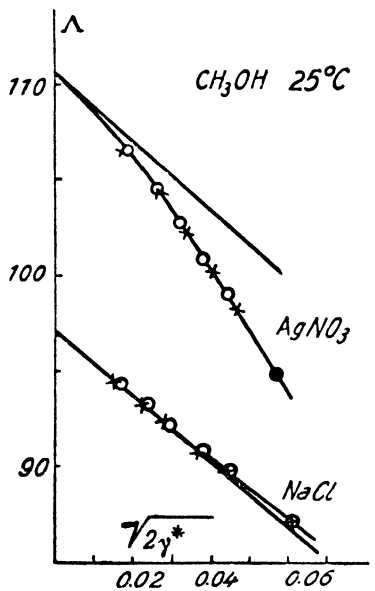

FIG. 47. Conductivity of salts in methyl alcohol.

Unmack, Murray-Rust, and Hartley‡ and Copley and Hartley§ have recently measured the conductivity of a number of thiocyanates and perchlorates in methyl alcohol. The results for 1-1-valent salts agree excellently with the Onsager theory, but the experimental limiting slopes for Ca, Sr, Ba, and Mg salts are much greater than the theoretical values. 1-2-valent salts thus have a tendency to associate in methyl alcohol. A comparison of the results for the chlorides, nitrates, and thiocyanates of the alkali metals shows that the deviations from the Onsager equation increase with increasing atomic weight of the metal. The mobilities of the cations increase in the same order. If it is assumed that the mobilities increase with decreasing

† J. E. Frazer and H. Hartley, *Proc. Roy. Soc.* **109 A** (1925), 351.

‡ A. Unmack, D. M. Murray-Rust, and H. Hartley, *Proc. Roy. Soc.* **127 A** (1930), 228.

§ E. D. Copley and H. Hartley, *J. Chem. Soc.* (1930), 2488.

size of the solvated ions, it appears that the deviations from theoretical behaviour are greatest for the smallest cations. (This agrees with Bjerrum's ideas on ion association, see p. 258.)

TABLE 29

Conductivity data for 1-1-valent electrolytes in methyl alcohol

$t = 25°C$. Dielectric constant = 30. $\alpha^*_{theor} = 109 + 0{\cdot}674\,\Lambda^*_\infty$

	Λ^*_∞	α^*_{exp}	α^*_{theor}	$\alpha^*_{exp}-\alpha^*_{theor}$		Λ^*_∞	α^*_{exp}	α^*_{theor}	$\alpha^*_{exp}-\alpha^*_{theor}$
LiCl	90·9	158	170·3	−12·3	$LiNO_3$	100·3	177	176·7	0·3
NaCl	97·0	163	174·3	−11·3	$NaNO_3$	106·5	204	180·8	23·2
KCl	105·1	185	179·8	5·2	KNO_3	114·6	244	186·2	57·8
RbCl	108·7	199	182·2	16·8	$RbNO_3$	118·2	251	188·7	62·3
CsCl	113·6	200	185·5	14·5	$CsNO_3$	123·0	268	191·8	76·2
KF	94·0	167	172·3	− 5·3	$AgNO_3$	113·0	319	185·1	133·9
KBr	109·4	185	182·7	2·3	NaBr	101·5	170	177·4	− 7·4
KI	114·9	184	186·4	− 2·4	$NaOCH_3$	98·4	157	175·3	−18·3
NH_4Cl	111·0	187	183·7	3·3	$NaClO_4$	115·1	198	186·5	+11·5
HCl	193·5	260	239·4	20·6					

Walden, Ulich, and Laun† have carried out sufficiently accurate measurements at extremely high dilutions in a number of non-aqueous solvents, and were able in many cases to confirm the Onsager theory. The salts employed were tetraethylammonium picrate, isobutylammonium chloride, diethylammonium chloride, and tetramethylammonium chloride, all of which are practically completely dissociated up to 0·001 N. In many cases the limiting slope of the (Λ^*, $\sqrt{\gamma^*}$) curve agrees well with the Onsager equation. Fig. 48 contains some examples with widely differing solvents, the points representing the experimental values and the lines the theoretical limiting slopes. Only 1-1-valent salts are included, and only solvents with a dielectric constant about 30. For lower dielectric constants systematic deviations from the Onsager theory occur.‡ This may be seen from the results of Walden, Ulich, and Laun in ethyl alcohol (D.C. = 24) (cf. Fig. 49). In order to show more clearly the effect of the dielectric constant upon the Λ curves, we may take the ratio Λ/Λ_∞ for the same salt in different solvents. The Onsager theory gives for this ratio,

$$\frac{\Lambda}{\Lambda_\infty} = 1 - \left\{ \frac{0{\cdot}818 \times 10^6}{(D_0 T)^{\frac{3}{2}}} z^2 + \frac{82{\cdot}0z}{(D_0 T)^{\frac{1}{2}} \Lambda_\infty \eta_0} \right\} \sqrt{\gamma}, \qquad (528)$$

for a z-valent binary electrolyte. Taking as an example tetraethylammonium picrate at 25°, we have from Walden's rule (see p. 79)

† P. Walden, H. Ulich, and F. Laun, *Z. phys. Chem.* **114** (1924), 275.

‡ Cf. Figs. 49 and 50. The dotted lines represent the theoretical limiting slopes.

$\Lambda_\infty \eta_0 = 0{\cdot}561$, and the only remaining variables are D_0 and $\sqrt{\gamma}$. This gives

$$\frac{\Lambda}{\Lambda_\infty} = 1 - \left\{\frac{159}{D_0^{\frac{3}{2}}} + \frac{0{\cdot}47}{D_0^{\frac{1}{2}}}\right\}\sqrt{\gamma}. \tag{529}$$

Λ/Λ_∞ has been previously shown as a function of $\sqrt{\gamma}$ in Fig. 10 (p. 79).

Fig. 50 shows two examples of conductivity curves in solvents having

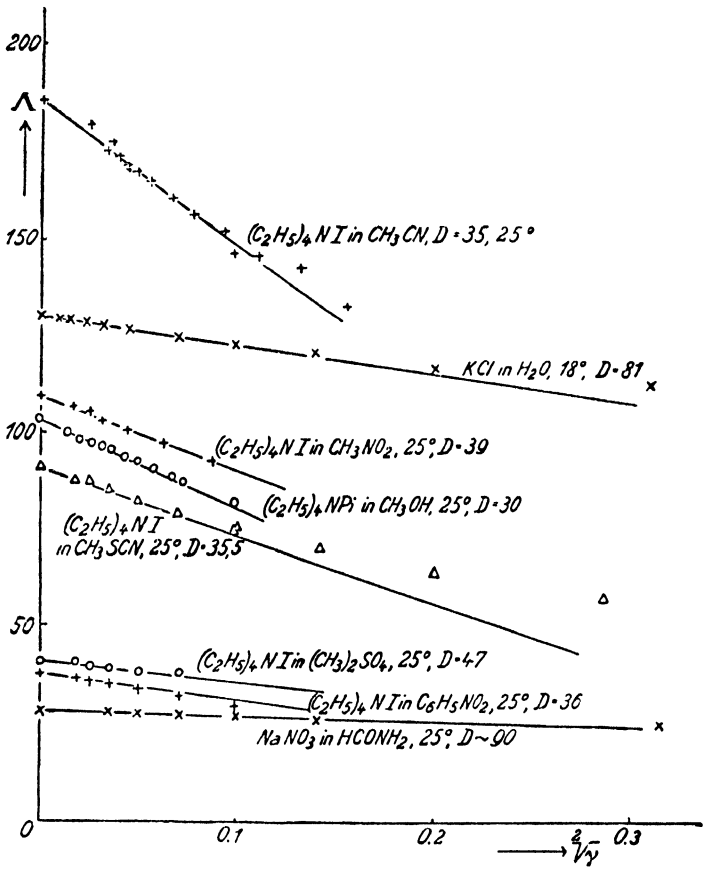

FIG. 48. Conductivity of salts in different solvents.

dielectric constants lower than 30, i.e. KBr in liquid ammonia and KCl in acetone. Tetraethylammonium iodide, potassium iodide, and other salts have been studied in nitromethane by a number of authors,† and potassium iodide appears to be partly associated. Thus in spite of the fact that the dielectric constant of nitromethane is greater than

† J. C. Philip and H. R. Courtman, *J. Chem. Soc.* **97** (1910), 1261; J. C. Philip and H. B. Oakley, ibid. **125** (1924), 1189; C. P. Wright, Murray-Rust, and Hartley, ibid. (1931), 199; Walden, *Z. phys. Chem.* **163 A** (1933), 263, 321.

that of methyl alcohol, there is less association in methyl alcohol. This point is well illustrated by Figs. 50A and 50B, which represent the results of Hartley and his collaborators for the alkali thiocyanates in methyl alcohol and nitromethane. Acetonitrile (D.C. = 36) and nitrobenzene† (D.C. = 35) resemble nitromethane in their behaviour.

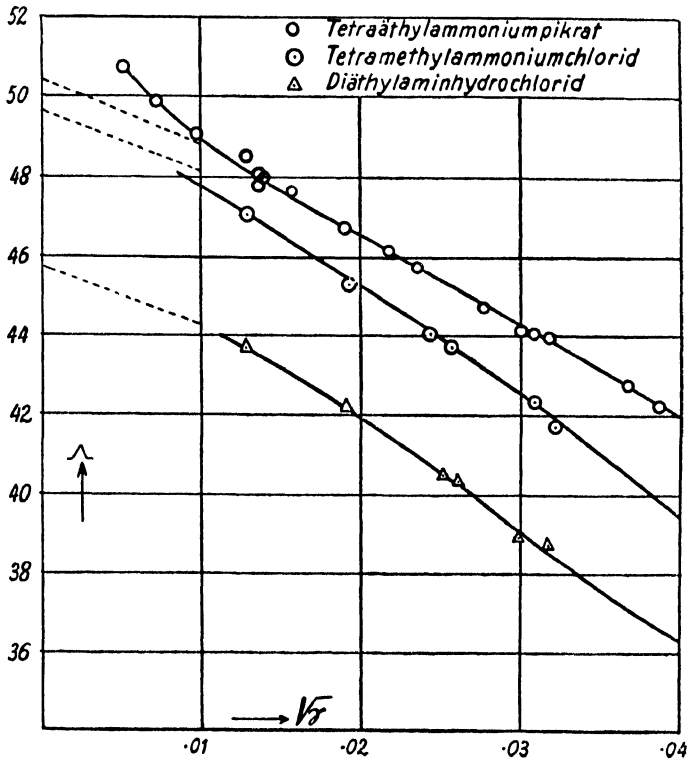

FIG. 49. Conductivity of salts in ethyl alcohol.

Franklin and Kraus‡ have investigated a number of 1-1-valent salts in liquid ammonia (D.C. = 22). All the salts appear, however, to be quite weak.

Walden, Ulich, and Busch§ have investigated 1-1-valent salts in acetone at 25° C. (D.C. = 21·2). They find that the square root law is obeyed, but that the slopes are much steeper than the theoretical

† P. Walden, *Z. phys. Chem.* **54** (1905), 203; **78** (1911), 275; P. Walden and E. J. Birr, *Z. phys. Chem.* **144** (1929), 269; **153 A** (1931), 1; ibid. **163 A** (1933), 281, 321; Murray-Rust, H. J. Hadow, and Hartley, *J. Chem. Soc.* (1931), 215.

‡ E. C. Franklin and C. A. Kraus, *Am. Chem. J.* **23** (1900), 277; *J. Am. Chem. Soc.* **27** (1905), 191.

§ P. Walden, H. Ulich, and G. Busch, *Z. phys. Chem.* **123** (1926), 429.

straight lines. Again the salts are presumably incompletely dissociated.

Martin† has measured various 1-1-valent salts in acetonitrile (D.C. = 26), and found them to be incompletely dissociated.

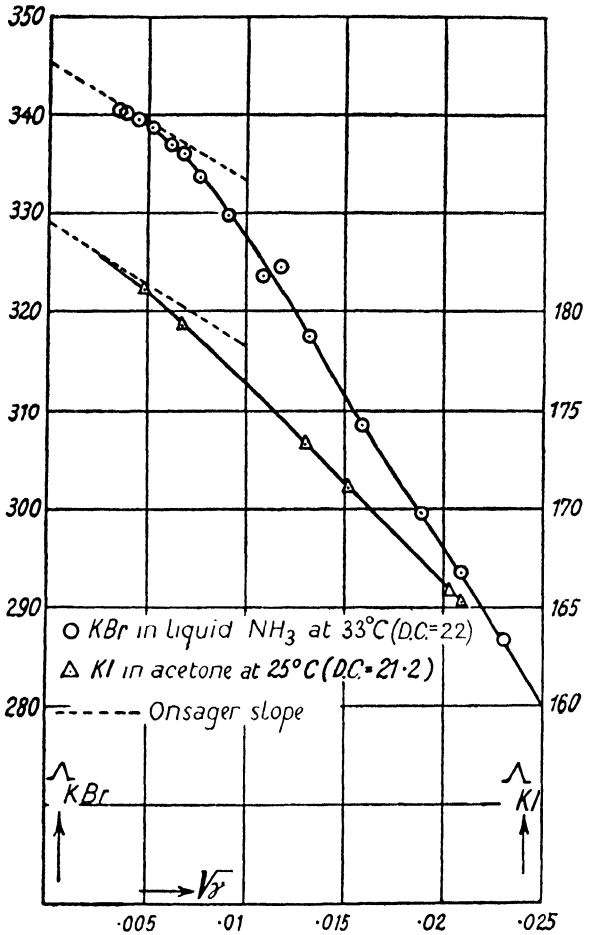

FIG. 50. Conductivity of salts in acetone and liquid ammonia.

Morgan and Lammert‡ have investigated KI in acetophenone (D.C. = 18), and find that it resembles a weak electrolyte in its behaviour.

Frivold§ has measured LiCl, LiBr, $LiClO_4$ and guanidine nitrate in cyclohexanol, and finds no agreement with the Onsager theory.

† A. R. Martin, *J. Chem. Soc.* (1928), 3270.

‡ J. L. R. Morgan and O. M. Lammert, *J. Am. Chem. Soc.* **46** (1924), 1126.

§ O. E. Frivold, *J. Franklin Inst.* **208** (1929), 627.

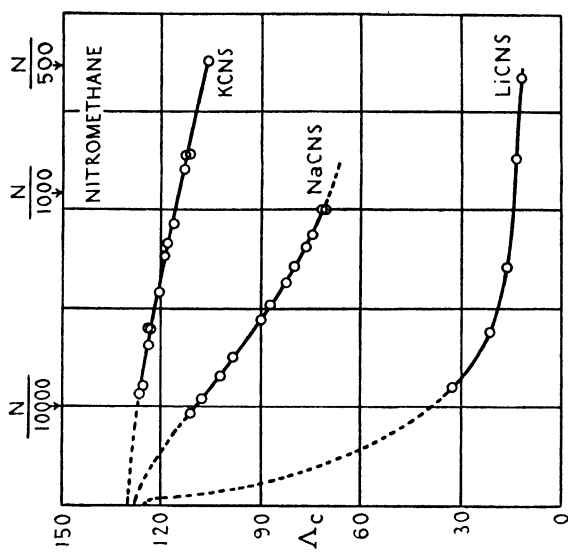

FIG. 50 B. Conductivity of thiocyanates in nitromethane.

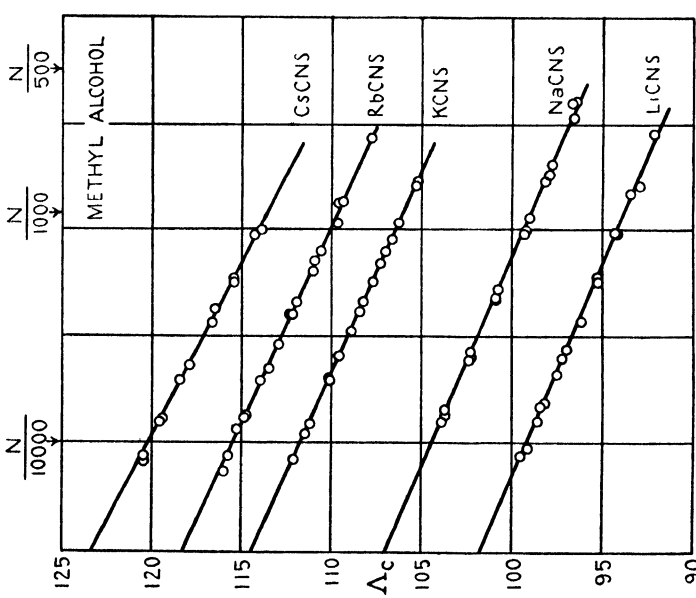

FIG. 50 A. Conductivity of thiocyanates in methyl alcohol.

Measurements have also been carried out in solvents of still lower dielectric constant.† No salts behave as strong electrolytes in these solvents.

The experimental data for non-aqueous solutions show that very specific effects often come into play, and the dielectric constant is often only of subsidiary importance in determining the degree of dissociation. The solvents which have been studied fall into two groups.‡ Hydroxylic solvents (water and the alcohols) form one group, in which the dielectric constant is the chief factor in determining the course of the conductivity curves. The other group comprises solvents of other types, e.g. nitrobenzene, nitromethane, and acetone, in which most 1-1-valent salts behave as weak electrolytes, and the conductivity curves vary in a very individual way from solvent to solvent.§ In these cases the Debye-Onsager theory is not able to give a complete picture of the behaviour of the electrolytic solution. It will probably be necessary to take into account the chemical nature of the solvent and the quantum-mechanical

TABLE 30

Percentage deviations from the Onsager theory at 25°

Electrolyte	*Water*‖	*Methyl alcohol*	*Ethyl alcohol*	*Nitro-methane*	*Aceto-nitrile*	*Acetone*
KCNS	— 1·7	0	37	180	..	122
KI	— 8·8	—10	38	73	17	58
$LiClO_4$	—12	— 2	10	430	..	54
Li-picrate	—32	..	16	..	410	270
Na-picrate	..	3	104	..	106	190
$LiNO_3$	~ 0	~ 0	21	..	..	..
$AgNO_3$	15	70	130	..	84	weak
$NI(C_2H_5)_4$	..	23	102	2	5·7	98
$N(C_2H_5)_4$-picrate	—10	17	75	— 1·5	6	34
HCl	~ 0	7	88	weak	weak	weak

† See P. Walden and G. Busch, *Z. phys. Chem.* **140** (1929), 89; Walden and H. Gloy, ibid. **144** (1930), 395. The solvents studied were tetrachlorethane (D. = 8), symm. dichlorethylene (D. ~ 7) and ethylene dichloride (D. ~ 10).

‡ See P. Walden, L. F. Audrieth, and E. J. Birr, *Z. phys. Chem.* **160 A** (1932), 337.

§ For the behaviour of acids, see p. 197, especially footnote. It may be mentioned here that while hydrogen has an extremely high mobility in water and the alcohols, its mobility is quite normal in non-hydroxylic solvents. This fact supports the theory of Hückel (*Z. Elektrochem.* **34** (1928), 546) who has proposed a chain mechanism involving the transfer of a proton from one water molecule to another. However, according to Hückel, at a frequency of about 3×10^{10} this transfer should take place in all directions with practically the same probability, so that only the normal mobility should remain. H. Zahn (*Z. f. Phys.* **58** (1929), 470) finds no decrease in the mobility of the hydrogen ion in water at these frequencies. See also P. Walden, *Z. phys. Chem.* Bodenstein Festband (1931), p. 19.

‖ These figures refer to 18°.

forces between the molecules and ions in order to account for these specific effects. Table 30 shows the percentage deviation from the Onsager slope for some typical salts in various solvents.† It will be seen that in differentiating solvents the calculated values usually differ considerably from the observed values. Only strong salts exhibit satisfactory agreement with the theoretical limiting law.

D. *Onsager's theory of transport numbers*

All the ions present contribute to the specific conductivity of an electrolyte. The equation of conduction for an electrolyte leads to the following equation connecting the specific conductivity of the solution λ with the mobilities of the ions l_i,‡

$$1{,}000\lambda = \sum \gamma_i^* l_i \text{ (in ohm}^{-1} \text{ cm.}^{-1}\text{).} \qquad (529\,a)$$

Each sort of ion is thus characterized by a perfectly definite contribution to the total conductivity; this contribution is proportional to the transport number of the ion, defined by the equation

$$u_i = \frac{\gamma_i^* l_i}{\sum \gamma_i^* l_i}, \qquad (529\,b)$$

so that $\sum u_i = 1$. It may be expected that the transport numbers will obey Onsager's theory to the same extent as mobilities or conductivities. As an example we shall take the case of some 1-1-valent salts in water at 25°, the transport numbers of which have been determined by Longsworth§ by the moving boundary method. According to equations (519) and (520), Onsager's theory gives for the equivalent conductivity and mobility,

$$\begin{aligned} \Lambda &= \Lambda_\infty - (a\Lambda_\infty + b)\sqrt{\gamma} \\ l &= l_\infty - (al_\infty + b)\sqrt{\gamma}, \end{aligned} \qquad (529\,c)$$

† The values in Table 30 are in many cases only approximate, since in non-aqueous solvents the extrapolation of the conductivity curve to infinite dilution is often inaccurate.

‡ The current density i is given by $i = \sum n_i e_i v_i = \sum \frac{n_i e_i^2 E}{\rho_i}$ and hence the specific conductivity by $\lambda = \sum \frac{n_i e_i^2}{\rho_i} \frac{1}{9\times 10^{11}}$.

Introducing the mobilities (referred to molar concentrations) by the relation

$$\frac{1}{\rho_i} = \frac{l_i}{\mathrm{N}e^2|z_i|} 9\times 10^{11}$$

and the molar concentration γ^* by

$$n_i = \frac{\mathrm{N}\gamma_i^*}{1{,}000|z_i|}$$

equation (529 a) follows at once.

§ L. G. Longsworth, *J. Am. Chem. Soc.* **54** (1932), 2741.

where $a = 0{\cdot}2274$; $b = 29{\cdot}9$. The transport number of the cation is thus given by

$$u_+ = \frac{l_+}{l_+ + l_-} = \frac{l_{+\infty} - (al_{+\infty} + b)\sqrt{\gamma}}{l_{+\infty} + l_{-\infty} - \{a(l_{+\infty} + l_{-\infty}) + 2b\}\sqrt{\gamma}}, \tag{529 d}$$

where $l_{+\infty}$ and $l_{-\infty}$ are the mobilities at infinite dilution. If we now write for the transport number of the cation at infinite dilution

$$u_{+\infty} = \frac{l_{+\infty}}{l_{+\infty} + l_{-\infty}}, \tag{529 e}$$

and make the further abbreviation

$$\begin{aligned} \Lambda' &= l_{+\infty} + l_{-\infty} - \{a(l_{+\infty} + l_{-\infty}) + 2b\}\sqrt{\gamma} \\ &= \Lambda_\infty - (a\Lambda_\infty + 2b)\sqrt{\gamma}, \end{aligned} \tag{529 f}$$

then (529 d) becomes

$$u_+ = u_{+\infty} - \frac{(1 - 2u_{+\infty})b\sqrt{\gamma}}{\Lambda'}. \tag{529 g}$$

If therefore we plot u_+ against $\sqrt{\gamma}$, the slope at infinite dilution should be given by

$$\left(\frac{du_+}{d\sqrt{\gamma}}\right)_{\gamma \to 0} = \frac{(2u_{+\infty} - 1)b}{\Lambda_\infty}. \tag{529 h}$$

Fig. 50 c shows u_+ plotted against $\sqrt{\gamma}$ for HCl, KCl, NaCl, and LiCl. The circles represent the experimental points, and the curves correspond to the more general equation

$$u_+ = u_{+\infty} - \frac{(1 - 2u_{+\infty})b\sqrt{\gamma}}{\Lambda'} + A\gamma\left(1 + \frac{2b\sqrt{\gamma}}{\Lambda'}\right). \tag{529 i}$$

The limiting slopes are also shown in the figure. The experimental results for KCl agree with Onsager's theory up to a concentration of several hundredths normal. Jones and Dole† have proposed for the transport number of $BaCl_2$ a formula which represents the experimental results up to high concentrations. Their equation does not, however, reduce to that of Onsager at high dilutions, and the same applies to the empirical equation used by Jones and Bradshaw‡ to represent the experimental results for LiCl.

It is probable that a more accurate study of the transport numbers for 1-2-valent salts would confirm the Onsager equation for sufficiently dilute solutions. In the case of 2-2-valent salts and non-aqueous solutions, we should anticipate similar deviations to those found for conductivities.§

† G. Jones and M. Dole, *J. Am. Chem. Soc.* **51** (1929), 1073.
‡ G. Jones and B. C. Bradshaw, ibid. **54** (1932), 138.
§ See preceding section.

43. Results of the Theory of Dispersion for the Conductivity and Dielectric Constant of Strong Electrolytes

A. *General calculation of the dispersion effect for conductivity.*

We have already seen that when an ion moves in a stationary electric

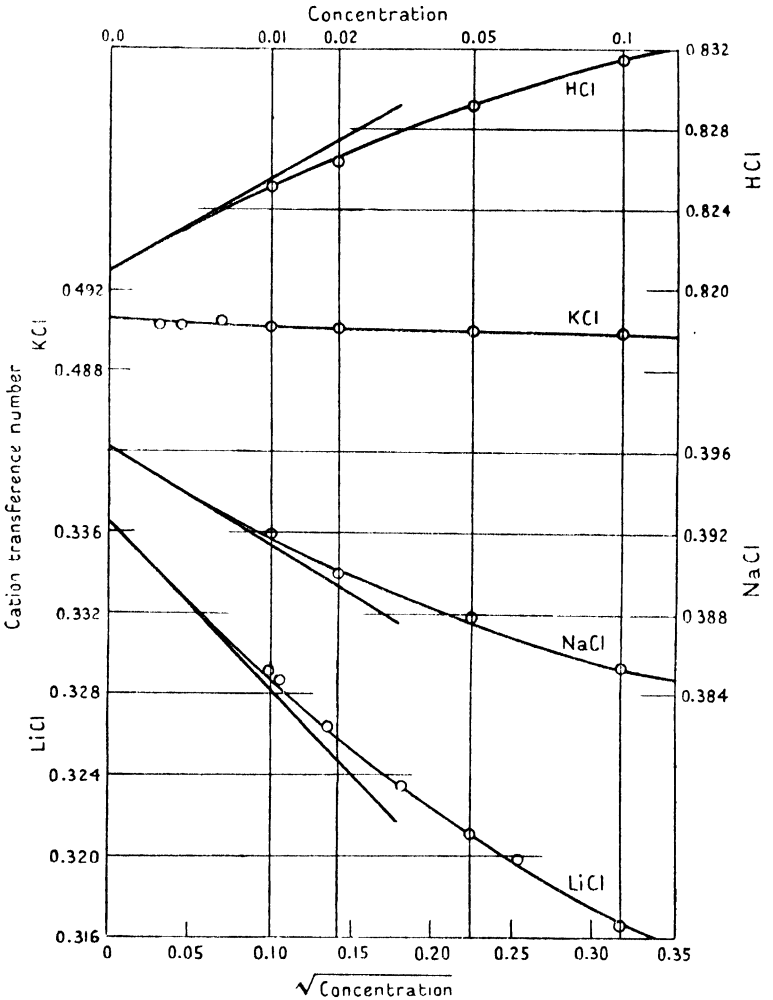

FIG. 50 c. Variation of transport number with concentration.

field the charge distribution loses its symmetry, and thus produces a retarding effect which is partly responsible for the decrease of equivalent conductivity with increasing concentration. If the applied field is cut off at a given moment ($t = 0$), the ion will come to rest in about 10^{-13} sec., and hence will hardly move from the point corresponding to

$t = 0$. It can be shown† that the disappearance of the unsymmetrical charge distribution in the ionic atmosphere is governed by a similar law to that which determines Θ, the time of relaxation of the whole ionic atmosphere. After a time 4Θ the unsymmetrical charge distribution will have practically disappeared, leaving only the symmetrical ionic atmosphere, which exerts no retarding force upon the ion. The formation and disappearance of the unsymmetrical distribution thus require a certain time of the order of magnitude Θ. The cause of the dispersion effect is now obvious. If an external electric field of frequency ω is acting upon the ions in the solution, each ion (apart from its Brownian movement) will describe a to and fro movement. If the frequency of the alternating field is small compared with $1/\Theta$, the unsymmetrical charge distribution in the ionic atmosphere at any moment will correspond to the instantaneous velocity of the ion, i.e. the relaxation force will be the same as in the stationary case. If we now consider the other extreme, in which ω is very large compared with $1/\Theta$, there will not be enough time for the formation of any unsymmetrical charge distribution, and hence the retarding relaxation force will be zero. The conductivity therefore increases with increasing frequency. The molar conductivity (cf. (510)) can be written in the form

$$\Lambda_\omega = \Lambda_\infty - \Lambda_{I\omega} - \Lambda_{II}, \tag{530}$$

where

$$\Lambda_{I\omega} = \Lambda_{I0}\,\chi(\omega\Theta, q), \tag{531}$$

$$\Lambda_{II} = \frac{29}{(D_0 T)^{\frac{1}{2}}\eta_0}(\sum \nu_i z_i^2)^{\frac{1}{2}}\sqrt{\gamma}, \tag{532}$$

and from (517)

$$\Lambda_{I0} = \frac{0{\cdot}985\times 10^6}{(D_0 T)^{\frac{3}{2}}}\frac{2q}{1+\sqrt{q}}|z_1 z_2|(\sum \nu_i z_i^2)^{\frac{1}{2}}\sqrt{\gamma}, \tag{533}$$

$$\chi(\omega\Theta, q) = \frac{1+\sqrt{q}}{\sqrt{q}\{(1-1/q)^2+\omega^2\Theta^2\}}\left\{\left(1-\frac{1}{q}\right)\left(\bar{R}-\frac{1}{\sqrt{q}}\right)+\omega\Theta\bar{Q}\right\}, \tag{534}$$

where $\bar{R}$ and $\bar{Q}$ are defined by (508).

Introducing the mobilities l_i defined by

$$\Lambda_\infty^* = \sum l_i,$$

Θ and q can be written in the form (cf. (466) et seq.)

$$\Theta = \frac{|z_1 z_2|}{|z_1|l_1+|z_2|l_2}\frac{15{\cdot}34\times 10^{-8}}{kTq\kappa^2}, \tag{535}$$

$$q = \frac{|z_1 z_2|}{z_1+z_2}\frac{l_1+l_2}{|z_2|l_1+|z_1|l_2}, \tag{536}$$

† Unpublished work by the author.

TABLE 31

Values of $\Lambda_{I\omega}/\Lambda_{I0}$

$\omega\Theta$	$q = 0{\cdot}5$	$q = 0{\cdot}45$	$q = 0{\cdot}40$	$q = 0{\cdot}35$	$q = 0{\cdot}30$
0	1·00	1·00	1·00	1·00	1·00
0·2	0·997	0·997	0·997	0·997	0·997
0·5	0·980	0·981	0·981	0·981	0·981
0·75	0·956	0·959	0·962	0·965	0·968
1	0·930	0·934	0·938	0·942	0·946
1·25	0·904	0·909	0·913	0·918	0·922
1·5	0·876	0·882	0·888	0·894	0·900
2	0·826	0·833	0·841	0·848	0·856
2·5	0·783	0·791	0·799	0·808	0·817
3	0·745	0·753	0·763	0·773	0·785
4	0·682	0·691	0·701	0·713	0·727
6	0·593	0·603	0·614	0·628	0·643
8	0·531	0·540	0·553	0·565	0·582
10	0·486	0·496	0·507	0·520	0·537
15	0·409	0·417	0·428	0·442	0·458
20	0·360	0·368	0·378	0·390	0·406
25	0·326	0·334	0·344	0·354	0·369
30	0·299	0·307	0·317	0·327	0·342
35	0·279	0·286	0·295	0·305	0·318
40	0·261	0·267	0·277	0·287	0·299
45	0·247	0·254	0·263	0·272	0·288
50	0·235	0·242	0·250	0·259	0·271
75	0·193	0·199	0·206	0·214	0·223
100	0·168	0·173	0·179	0·186	0·195
150	0·138	0·142	0·147	0·153	0·160
200	0·1195	0·1232	0·1278	0·1328	0·1394
300	0·0983	0·1011	0·1046	0·1088	0·1145
500	0·0759	0·0783	0·0812	0·0844	0·0888
700	0·0643	0·0663	0·0688	0·07165	0·0751
1,000	0·0538	0·0555	0·0576	0·0599	0·0629
5,000	0·0241	0·0249	0·0258	0·0269	0·0282
10,000	0·01706	0·01755	0·01824	0·0190	0·0199

where for a single electrolyte (cf. (233))

$$\kappa^2 = 12{\cdot}16\times 10^{18}\frac{\gamma(\nu_1 z_1^2+\nu_2 z_2^2)}{D_0 T}. \tag{537}$$

Substituting in (535) the values of q and κ^2 from (536) and (537), and remembering that $\nu_1 z_1 \gamma = \nu_2 z_2 \gamma = \gamma^*$, the expression for Θ becomes†

$$\Theta = \frac{8{\cdot}85\times 10^{-11}}{\gamma^* \Lambda_\infty^*} D_0. \tag{535'}$$

The dependence of the conductivity upon the frequency is governed by the function χ, which depends upon $\omega\Theta$ and q. When $\omega = 0$, $\Lambda_{I\omega} = \Lambda_{I0}$,

† This simple expression for Θ was first given by Schiele; cf. M. Wien, *Ann. d. Phys.* (5) **11** (1931), 432.

and $\chi = 1$. The dispersion effect is simply expressed by means of the ratio $\Lambda_{I\omega}/\Lambda_{I0}$. We shall show briefly how this ratio can be rapidly calculated for any given electrolyte, given the solvent, temperature, concentration, valencies (z_i), and mobilities (l_i) The quantities q and Θ can be calculated from (535′) and (537). Since now $\Lambda_{I\omega}/\Lambda_{I0}$ depends only upon q and $\omega\Theta$ (see (531)), we can construct a table of values of $\Lambda_{I\omega}/\Lambda_{I0}$ which can be used to calculate this ratio for any electrolyte and any value of ω. The wave-length l in metres is introduced by the relation

$$l = \frac{18{\cdot}85 \times 10^8}{\omega\Theta}\Theta.$$

The decrease in conductivity caused by the relaxation effect in the stationary case and the decrease due to the electrophoretic effect may be easily calculated from equations (533) and (532) for Λ_{I0} and Λ_{II}. The conductivity can thus be calculated for any frequency and any concentration.

Table 31 contains values of $\Lambda_{I\omega}/\Lambda_{I0}$, correct to better than 1 per cent.

B. *Applications of the theory of conductivity dispersion.*

(*a*) *Mobilities, q-values, and thicknesses and times of relaxation of the ionic atmosphere in some particular cases.* Tables 32 and 33 contain values for the mobilities and the quantities $1/\kappa$, κ^2, q, and $\Theta\gamma$. $1/\kappa$ and Θ can be obtained directly from Table 33 for sufficiently dilute solutions.

Some values for the mobilities, thickness and time of relaxation of the ionic atmosphere, and q-factors

TABLE 32

Ion	18° *C.*	25° *C.*
H^+	315	349·72
Cl^-	65·4	76·32
K^+	64·6	73·5
Li^+	33·4	38·68
Na^+	43·5	50·1
NO_3^-	61·8	71·42
Mg^{++}	45·5	53
Cd^{++}	47·5	..
Cu^{++}	46	55
Ca^{++}	51·5	59
$SO_4^=$	68·5	81
La^{+++}	50	72·7
$Fe(CN)_6^{----}$	..	95·5

TABLE 33

Electrolyte	$\frac{1}{\kappa}10^8\sqrt{\gamma}$	$\frac{\kappa^2}{\gamma}\times 10^{-16}$	q	$\Theta\gamma\times 10^{10}$	
HCl	3·06	0·107	0·5	0·190	
KCl	3·06	0·107	0·5	0·553	
LiCl	3·06	0·107	0·5	0·727	
$MgCl_2$	1·77	0·321	0·421	0·323	
H_2SO_4	1·77	0·321	0·366	0·0942	
$CdSO_4$	1·53	0·428	0·5	0·310	18° C.
$MgSO_4$	1·53	0·428	0·5	0·315	
$CuSO_4$	1·53	0·428	0·5	0·311	
$LaCl_3$	1·25	0·642	0·352	0·207	
$La(NO_3)_2$	1·25	0·642	0·356	0·217	
$K_4Fe(CN)_6$	0·96	1·08	0·344	0·103	
$Ca_2Fe(CN)_6$	0·88	1·29	0·482	0·113	25° C.

(*b*) *The effect of concentration, temperature, and dielectric constant upon the dispersion of conductivity.* We shall take as our example KCl in water at 18° C., so that $D_0 = 81{\cdot}3$. For the concentrations

$$\gamma = 0{\cdot}01, \qquad \gamma = 0{\cdot}001, \qquad \gamma = 0{\cdot}0001$$

Table 33 gives for the times of relaxation

$$\Theta = 0{\cdot}553\times 10^{-8} \text{ sec.}, \quad \Theta = 0{\cdot}553\times 10^{-7} \text{ sec.},$$

$$\Theta = 0{\cdot}553\times 10^{-6} \text{ sec.}$$

and for the corresponding values of κ^2

$$\kappa^2 = 0{\cdot}107\times 10^{-14} \quad \kappa^2 = 0{\cdot}107\times 10^{-13} \quad \kappa^2 = 0{\cdot}107\times 10^{-12}.$$

Since we are dealing with a symmetrical electrolyte, $q = 0{\cdot}5$. The ratio $\Lambda_{I\omega}/\Lambda_{I0}$ can now be obtained from Table 31 as a function of l, the wave-length in metres. The effect of concentration upon the dispersion effect is shown in Fig. 51, where $\Lambda_{I\omega}/\Lambda_{I0}$ is plotted against l, the abscissae being plotted on a logarithmic scale. Thus it is seen from the figure that the value $\Lambda_{I\omega}/\Lambda_{I0} = 0{\cdot}5$ is reached at wave-lengths $l = 1{\cdot}16$ m., 11·6 m., and 116 m., corresponding to the concentrations $\gamma = 0{\cdot}01$, 0·001, and 0·0001 respectively. In general, if the concentration is decreased U times, the wave-length corresponding to a given value of $\Lambda_{I\omega}/\Lambda_{I0}$ will be increased U times. This is due to the fact that the time of relaxation (535′) is inversely proportional to the concentration. It may also be easily seen that for a given wave-length there is a certain concentration for which the increase in molar conductivity is a maximum. This maximum has been observed experimentally (see p. 225).

If the temperature is raised, the same $\Lambda_{I\omega}/\Lambda_{I0}$ value is reached at a shorter wave-length. This is due to the fact that the time of relaxation

(535') decreases with increasing temperature, since the mobilities increase more rapidly than the dielectric constant decreases.†

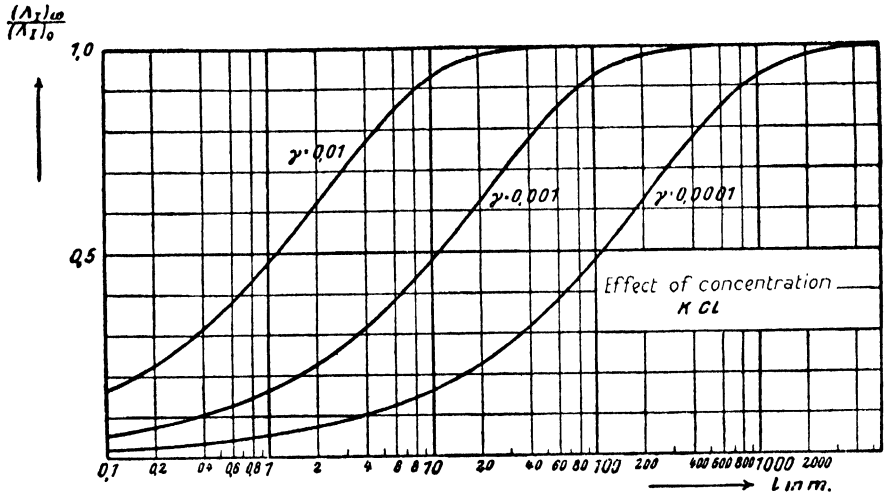

FIG. 51. Variation of the dispersion effect with concentration.

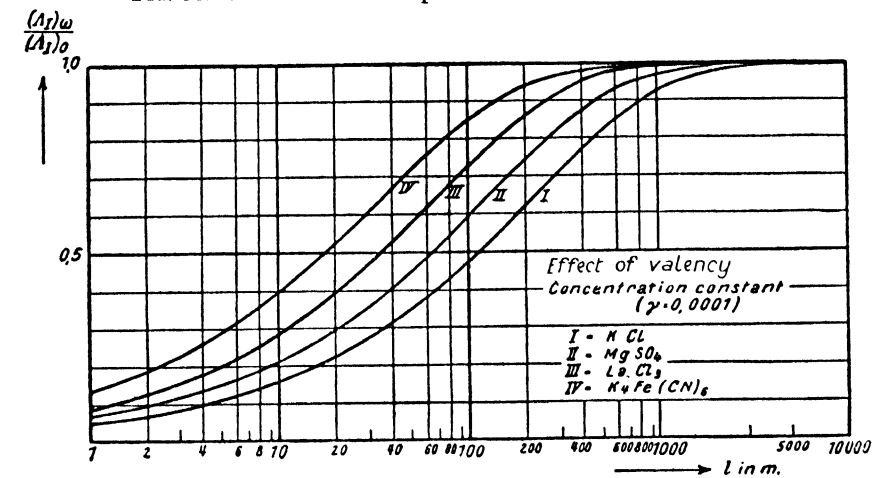

FIG. 52. Effect of the valency upon the dispersion effect.

In the same way, a decrease of dielectric constant displaces the dispersion curve in the direction of shorter wave-length.

(c) *The effect of the valency upon the dispersion effect.* We have so far dealt only with electrolytes of symmetrical valency types. For unsymmetrical types, $q \neq 0{\cdot}5$ (see (536)). This variation in the q-values and also in the times of relaxation cause the dispersion effect to vary with the valency type. Fig. 52 shows the dispersion curves for the

† See H. Falkenhagen and J. W. Williams, *Z. phys. Chem.* **137** (1928), 412.

electrolytes KCl, $MgSO_4$, $LaCl_3$, and $K_4Fe(CN)_6$ at a concentration of $\gamma = 0{\cdot}0001$ in water. The curve for $CdSO_4$ coincides with that for $MgSO_4$. The curve for $MgCl_2$ would lie a little to the left of the curve for $MgSO_4$, and the curve for $Ca_2Fe(CN)_6$ between the curves for $K_4Fe(CN)_6$ and $LaCl_3$. Table 34 gives the values of $\Lambda_{I\omega}/\Lambda_{I0}$ at different wave-lengths for the above electrolytes.

TABLE 34

Values of $\Lambda_{I\omega}/\Lambda_{I0}$ *for different wave-lengths* ($\gamma = 0{\cdot}0001$)

l in m.	KCl	$MgSO_4$	$MgCl_2$	$LaCl_3$	$Ca_2Fe(CN)_6$	$K_4Fe(CN)_6$
1	0·055	0·070	0·070	0·08	0·116	0·138
2	0·073	0·098	0·102	0·12	0·167	0·190
5	0·115	0·154	0·162	0·19	0·260	0·295
10	0·163	0·216	0·225	0·28	0·353	0·400
20	0·230	0·300	0·309	0·39	0·478	0·530
50	0·355	0·455	0·465	0·58	0·676	0·730
100	0·480	0·600	0·610	0·72	0·815	0·860
200	0·630	0·750	0·758	0·85	0·925	0·950
500	0·820	0·910	0·915	0·96	0·983	0·986
1,000	0·925	0·970	0·970	0·98	0·997	0·997
2,000	0·978	0·994	0·994	1	1	1
5,000	1	1	1	1	1	1
10,000	1	1	1	1	1	1

The values of Λ_{II} and Λ_{I0} are given by (532) and (533). Some of the values are given in Table 35.

TABLE 35

Values of Λ_{I0} *and* Λ_{II}

Valency type	Λ_{II}	Λ_{I0}	$t°$ C.
1-1	$50{\cdot}5\sqrt{\gamma}$	$0{\cdot}224\Lambda_\infty\sqrt{\gamma}$	18°
1-2	262·4 ,,	0·677 ,,	18°
2-2	404·4 ,,	1·79 ,,	18°
1-3	743·0 ,,	1·52 ,,	18°
1-4	1,890·0 ,,	2·12 ,,	25°
2-4	2,485·0 ,,	6·32 ,,	25°

Inserting the appropriate values of Λ_∞ and putting $\gamma = 0{\cdot}0001$, the values in Table 36 are obtained.

The magnitude of the dispersion effect is conveniently expressed as the percentage $100(\Lambda_\infty - \Lambda_\omega)/(\Lambda_\infty - \Lambda_0)$. We shall take as examples $CdSO_4$ at 18° and $K_4Fe(CN)_6$ at 25°, both at a concentration $\gamma = 0{\cdot}0001$. Curve I, Fig. 53, refers to $K_4Fe(CN)_6$ and curve II to $CdSO_4$. The molar conductivity of $CdSO_4$ has been taken as 224 (cf. Table 14), and we have

$$\Lambda_{I0} = 4{\cdot}09 = 1{\cdot}8 \text{ per cent. } \Lambda_\infty$$

$$\Lambda_{II} = 4{\cdot}04 = 1{\cdot}8 \text{ per cent. } \Lambda_\infty.$$

TABLE 36

Values of Λ_{II} *and* Λ_{I0} *for various electrolytes* ($\gamma = 0{\cdot}0001$)

Electrolyte	Λ_∞	Λ_{II}	Λ_{I0}	$t°$ C.
KCl	130	0·505	0·29	18°
HCl	380	0·505	0·85	18°
LiCl	98	0·505	0·22	18°
$MgCl_2$	222	2·62	1·5	18°
H_2SO_4	767	2·62	5·2	18°
$MgSO_4$	229	4·04	4·1	18°
$CuSO_4$	229	4·04	4·1	18°
$LaCl_3$	345	7·43	5·25	18°
$K_4Fe(CN)_6$	680	18·9	14·4	25°
$Ca_2Fe(CN)_6$	620	24·9	39·2	25°

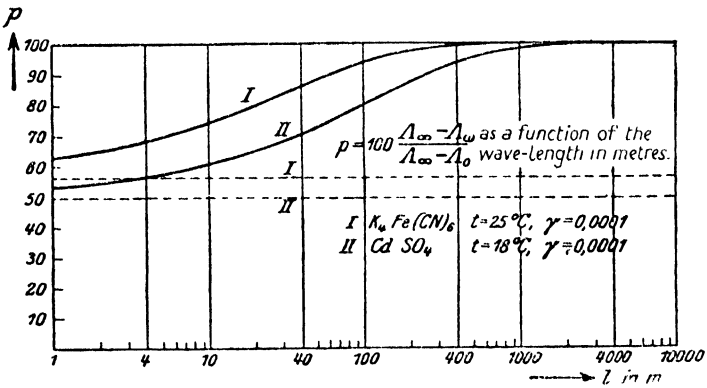

FIG. 53. Variation of the dispersion effect with the frequency.

The total decrease in the conductivity is thus 3·6 per cent. $\Lambda_{I\omega}$ is due to the relaxation forces, and decreases with decreasing wave-length. Thus at $l \sim 60$ m., for which $\Lambda_{I\omega}/\Lambda_{I0} = 0{\cdot}5$, an increase of 0·9 per cent. will be observed in the molar conductivity.

In the case of $K_4Fe(CN)_6$, Λ_∞ at 25° is 680, and

$$\Lambda_{I0} = 13{\cdot}7 = 2 \text{ per cent. } \Lambda_\infty$$

$$\Lambda_{II} = 18{\cdot}9 = 2{\cdot}8 \text{ per cent. } \Lambda_\infty.$$

The total decrease in conductivity is here 4·8 per cent. At a wave-length $l = 16{\cdot}3$ m., $\Lambda_{I\omega}/\Lambda_{I0} = 0{\cdot}5$, and hence the molar conductivity will be increased by about 1 per cent. It can be easily shown† that at higher concentrations the dispersion effect is relatively larger at suitable wave-lengths.

† See e.g. P. Debye and H. Falkenhagen, *Phys. Z.* **29** (1928), 423.

C. *General formulae and interpolation tables for the dependence of dielectric constants upon frequency.*

Equation (513) can be written in the form

$$D_\omega - D_0 = \frac{1{\cdot}97\times10^6 z_1 z_2(\nu_1 z_1^2+\nu_2 z_2^2)^{\frac{1}{2}}\sqrt{q}}{D_0^{\frac{1}{2}}T^{\frac{3}{2}}\omega\Theta\{(1-1/q)^2+\omega^2\Theta^2\}}\left\{\bar{Q}\left(1-\frac{1}{q}\right)-\omega\Theta\left(\bar{R}-\frac{1}{\sqrt{q}}\right)\right\}\sqrt{\gamma}. \tag{538}$$

In the special case of stationary fields, $\omega = 0$, and (538) becomes

$$D_{\omega=0} - D_0 = \frac{1{\cdot}97\times10^6|z_1 z_2|(\nu_1 z_1^2+\nu_2 z_2^2)^{\frac{1}{2}}}{2D_0^{\frac{1}{2}}T^{\frac{3}{2}}(1+1/\sqrt{q})^2}q^{\frac{1}{2}}\gamma^{\frac{1}{2}}. \tag{539}$$

Introducing γ^*, the equivalent concentration, (539) becomes

$$D_{\omega=0} - D_0 = \frac{1{\cdot}97\times10^6|z_1 z_2|(|z_1|+|z_2|)^{\frac{1}{2}}}{2D_0^{\frac{1}{2}}T^{\frac{3}{2}}(1+1/\sqrt{q})^2}(q\gamma^*)^{\frac{1}{2}}, \tag{539'}$$

since $$\nu_1|z_1|\gamma = \nu_2|z_2|\gamma = \gamma^*.$$

TABLE 37

$\omega\Theta$	$q = 1{\cdot}0$	$q = 0{\cdot}75$	$q = 0{\cdot}5$	$q = 0{\cdot}45$	$q = 0{\cdot}40$	$q = 0{\cdot}35$	$q = 0{\cdot}30$
0	1	1	1	1	1	1	1
0·1	0·992	0·996	0·999	0·999	0·999	0·999	0·999
0·2	0·988	0·988	0·989	0·989	0·989	0·9895	0·990
0·35	0·966	0·974	0·974	0·974	0·974	0·975	0·975
0·5	0·931	0·935	0·940	0·941	0·943	0·944	0·946
0·75	0·863	0·870	0·879	0·882	0·885	0·887	0·890
1·0	0·789	0·799	0·813	0·816	0·820	0·824	0·830
1·25	0·718	0·731	0·748	0·752	0·757	0·763	0·768
1·5	0·662	0·668	0·689	0·694	0·700	0·706	0·713
2	0·544	0·561	0·585	0·591	0·598	0 605	0·615
2·5	0·459	0·477	0·502	0·510	0·517	0·525	0·535
3	0·393	0·411	0·437	0·444	0·452	0·460	0·471
4	0·300	0·317	0·342	0·349	0·356	0·365	0·375
6	0·196	0·209	0·231	0·237	0·244	0·251	0·261
8	0·1411	0·1521	0·1703	0·1753	0·1811	0·1877	0·1957
10	0·1080	0·1175	0·1326	0·1369	0·1419	0·1477	0·1546
15	0·0651	0 0716	0·0822	0·0853	0·0889	0·0931	0·0983
20	0·0448	0 0496	0·0576	0·0600	0·0627	0·0660	0·0700
25	0 0334	0·0371	0·0434	0·0453	0·0475	0·0501	0·0533
30	0·0261	0·0292	0·0343	0·0358	0·0376	0·0398	0·0425
35	0·0212	0·0237	0·0280	0·0293	0·0316	0·0327	0·0350
40	0·01764	0·01979	0·0235	0·0246	0·0259	0·0275	0·0295
45	0·0150	0·01686	0·0201	0·0210	0·0222	0·0236	0·0253
50	0·01296	0·01459	0·01741	0·01826	0·0193	0·0205	0·0220
75	0·00735	0·00832	0·01001	0·01053	0·01114	0·01190	0·01284
100	0·00489	0·00555	0·00672	0·00707	0·00750	0·00803	0·00869
150	0·00273	0·00312	0·00380	0 00401	0·00426	0·00457	0·00497
200	0·001805	0·00206	0·00252	0·00267	0·00284	0·00302	0·00332
300	0·000999	0·001148	0·001411	0·001493	0·001592	0·001714	0·001870
500	0·000475	0·000545	0·000674	0·000713	0·000762	0·000822	0·000899
700	0·000289	0·000333	0·000413	0·000437	0·000467	0·000505	0·000553
1,000	0·0001710	0·0001971	0·000245	0·000259	0·000278	0·000300	0·000329
5,000	0·0000157	0·00001814	0·0000227	0·0000241	0·0000258	0·0000280	0·0000308
10,000	0·00000558	0·00000646	0·00000808	0·00000859	0·00000922	0·00000999	0·0000110

Equation (539) for the stationary case can be employed directly for any single electrolyte. For the dispersion effect, however, it is convenient to construct an interpolation table showing the values of

$$(D_\omega - D_0)/(D_{\omega=0} - D_0)$$

corresponding to different values of $\omega\Theta$ and q. Table 37 has been constructed for this purpose.

This table, in conjunction with values of $D_{\omega=0} - D_0$ from (539), makes it possible to calculate the dielectric constant of any solution of a single electrolyte at any frequency. Some examples are given in the next section.

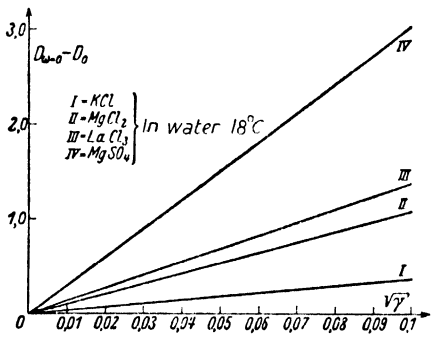

Fig. 54. Theoretical dependence of the dielectric constant upon the salt concentration.

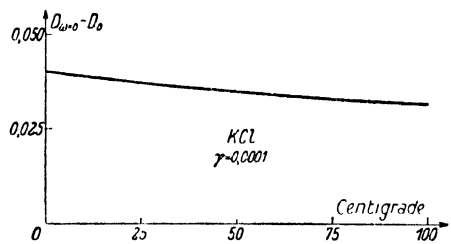

FIG. 55. Variation of the dispersion of dielectric constant with temperature.

D. *Applications of the theory of the dispersion of dielectric constants.*

The values taken for the mobilities and the dielectric constant of the pure solvent are the same as those previously employed.†

(*a*) *The stationary case.* Equation (539) gives the following formulae for KCl, $MgCl_2$, $LaCl_3$, and $MgSO_4$ in water at 18°.

$$D_{\omega=0} - D_0 = 3{\cdot}79\sqrt{\gamma}\ (\mathrm{KCl})$$
$$D_{\omega=0} - D_0 = 10{\cdot}9\sqrt{\gamma}\ (\mathrm{MgCl_2})$$
$$D_{\omega=0} - D_0 = 13{\cdot}8\sqrt{\gamma}\ (\mathrm{LaCl_3})$$
$$D_{\omega=0} - D_0 = 30{\cdot}3\sqrt{\gamma}\ (\mathrm{MgSO_4}).$$

Fig. 54 illustrates this square root law for the increase in dielectric constant for the same four salts.

As a further example we have calculated the variation of $D_{\omega=0} - D_0$ with temperature for KCl at a concentration of $\gamma = 0{\cdot}0001$. The result

† See p. 215; also the papers by Debye, Falkenhagen, and Williams referred to on p. 182. The results given in paragraphs (*a*) and (*b*) above have not yet been subjected to a thorough experimental test. Cf. p. 231.

is shown in Fig. 55. The mobilities, dielectric constants, etc., are given in Table 38.

TABLE 38

$t°$ C.	0°	18°	25°	50°	75°	100°
$D_0(H_2O)$	88·2	81·3	78·8	69·9	62·2	55·3
l_{K^+}	40·6	64·4	74·8	115	159	198
l_{Cl^-}	41·3	65·5	76·3	116	160	208
$\Theta \times 10^{10} \times \gamma$	0·952	0·554	0·461	0·268	0·172	0·120
$\kappa_2 \times 10^{-14} \times \gamma^{-1}$	10·51	10·77	10·78	11·21	11·70	12·27

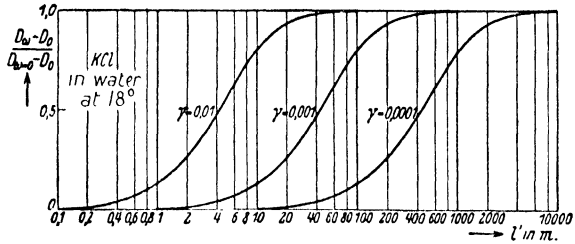

FIG. 56. Effect of concentration on the dispersion of dielectric constant.

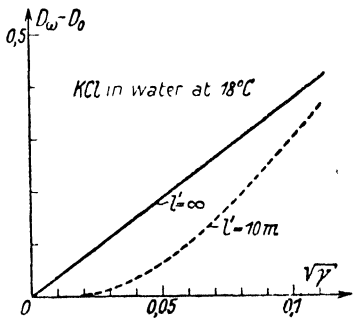

FIG. 57. Variation of dielectric constant with salt concentration at different wave-lengths.

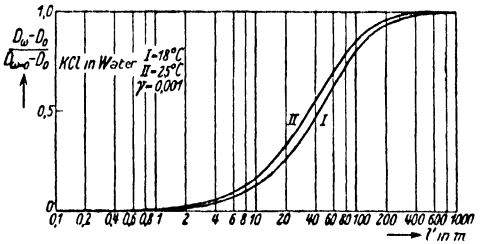

FIG. 58. Effect of temperature on the dispersion of dielectric constant.

(*b*) *The effect of concentration, temperature, valency, and solvent upon the dispersion of dielectric constants.* The first example we shall take is KCl in water at 18° C. Fig. 56 shows the variation of $(D_\omega - D_0)/(D_{\omega=0} - D_0)$ with the wave-length for the three concentrations $\gamma = 0{\cdot}01$, $0{\cdot}001$, $0{\cdot}0001$. The displacement of the dispersion curves towards shorter wave-lengths with increasing concentration is due to the decrease in the time of relaxation of the ionic atmosphere (cf. (535′)). Fig. 57 shows the increase in dielectric constant $D_\omega - D_0$ plotted against $\sqrt{\gamma}$ for KCl in water at 18°, first for the stationary case $l' = \infty$,

and secondly for $l' = 10$ m. It is seen that the curve for $D_\omega - D_0$ approaches the concentration axis more and more as the wave-length decreases.

Figs. 58, 59, and 60 show the effect of the temperature, the dielectric constant, and the valency upon the dispersion of dielectric constants. The dielectric constant of methyl alcohol at 25° is taken as $D_0 = 30$, the time of relaxation as $0{\cdot}245 \times 10^{10}/\sqrt{\gamma}$ and κ^2 as $28{\cdot}3 \times 10^{-14}/\gamma$. The mobilities in methyl alcohol are taken from the work of Hartley and Raikes.†

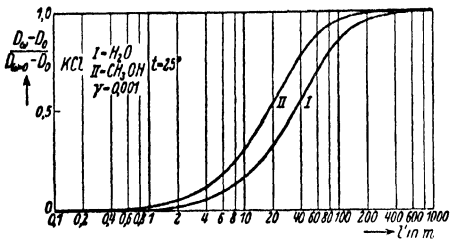

FIG. 59. Effect of dielectric constant on the dispersion of dielectric constant.

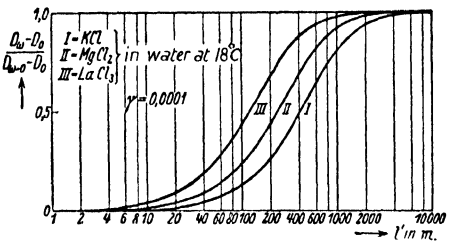

FIG. 60. Effect of valency on the dispersion of dielectric constant.

44. The Experimental Determination of the High-frequency Conductivity of Electrolytes and the Variation of Dielectric Constant with Frequency

As previously mentioned in § 22, M. Wien‡ obtained experimental evidence for the variation of conductivity with frequency long before the first theoretical treatment of the effect by Debye and Falkenhagen. Sack§ was the first to obtain results of any accuracy at sufficiently high frequencies, and he found an increase in conductivity of the order of magnitude predicted by the theory. It may be noted that most of the earlier methods used for determining conductivities with direct currents are inapplicable to high frequencies. Thus Nernst's well-known bridge method is not sufficiently accurate to demonstrate with certainty the small effect predicted by the theory. As the frequency increases it becomes more and more difficult to maintain the symmetry in the bridge system which is necessary to obtain a sharp minimum. We shall now describe the experimental methods which have been developed recently by Sack, Zahn, Deubner, M. Wien, Malsch, and their collaborators.

† H. Hartley and H. Raikes, *Trans. Farad. Soc.* (1927) 393.
‡ M. Wien, *Ann. d. Phys.* **83** (1927), 840 (cf. p. 82).
§ H. Sack, *Phys. Z.* **29** (1928), 627.

A. *The method of Sack and his collaborators for measuring the high-frequency conductivity of electrolytes.*†

The method first employed by Sack, and subsequently developed in collaboration with Mittelstaedt and Brendel‡ can be conveniently described as a deflexion method. The principle of the method is as follows. If we have a resonance circuit consisting of an inductance and a capacity with a resistance in parallel, the resonance current depends upon the magnitude of the resistance, provided that the potential induced in the circuit is kept constant. If $\omega^2C^2W^2 \gg 1$ (where ω is the frequency, C the capacity, and W the resistance), a given percentage decrease in the resistance corresponds to the same percentage increase in the current.§ It is thus possible to deduce the resistance from the magnitude of the resonance current. The apparatus used by Brendel, Mittelstaedt, and Sack gave a relative accuracy of 0·15 per cent. for the high-frequency conductivity in the range of wave-lengths 10–30 m. The apparatus is shown schematically in Fig. 61. A Holborn transmitter is used (wave-length 6–60 m., intensity constant to 0·1 per cent.) with a Telefunken R.V. 218 valve. The oscillations in the transmitter are transferred by means of a variable coupling to an untuned intermediate circuit (I), the current in which is measured by an aperiodically damped circuit (II). The actual measuring circuit (III) consists of a coil, a variable condenser, and the conductivity cell in parallel, and is coupled to the intermediate circuit (I). The circuit (II) consists of a wire loop and a thermocouple with galvanometer. The resonance deflexion was measured in an aperiodic circuit (IV) with a thermo-element and a mirror galvanometer sensitive to 10^{-8} amp. All precautions are taken to prevent the transfer of energy from circuit I to circuit IV. The energy in circuit I is kept constant by varying the coupling. The resonance deflexion can be measured to 0·05 per cent. At the high frequencies employed, the dielectric losses in the glass of the conductivity cells are considerable, and vary with the frequency and the distance between the plates. Hence only one cell is used, of the form shown in Fig. 62. In carrying out measurements, the cell is filled successively with a number

† The bridge method has recently been refined so as to give an accuracy of 0·01 per cent. (see W. Geyer, *Ann. d. Phys.* (5) **14** (1932), 299). The heating of the electrolyte is reduced by employing very small energies, and the current induced in the null branch is highly amplified. Solutions of $MgSO_4$ and NaCl were compared at wave-lengths between 39 m. and 185 m., the results being in good agreement with the theory. For details of the very complicated apparatus, see the original paper.

‡ B. Brendel, O. Mittelstaedt, and H. Sack, *Phys. Z.* **30** (1929), 576.

§ A cell containing liquid corresponds to a resistance W with a capacity C in parallel. The real part of the resistance operator is thus $W/(1+\omega^2C^2W^2)$.

of KCl solutions of slightly different concentrations, and the corresponding resonance deflexions measured. (The dielectric constant of the solutions used, and hence the capacity of the cells, remains effectively constant over the small range of concentrations employed.) Simultaneously the low-frequency conductivities of the same solutions are measured with a Wheatstone bridge to about 0·2 per cent. In this way a curve is obtained connecting the resonance deflexion with the low-frequency conductivity. A curve of this kind is shown in Fig. 63. The

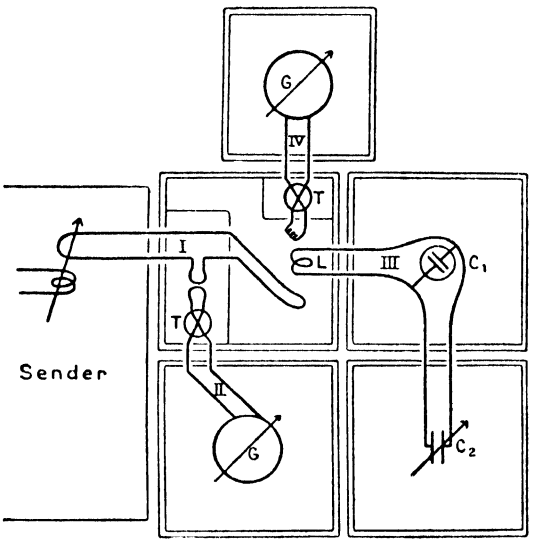

FIG. 61. The method of Sack for determining the high-frequency conductivity.

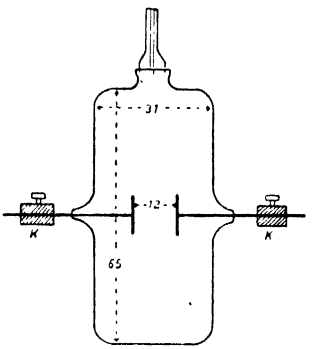

FIG. 62. Cell for high-frequency conductivity determinations.

cell is now filled with another solution, e.g. $MgSO_4$, the concentration being chosen so that the low-frequency conductivity falls in the range previously measured. The resonance deflexion and the low-frequency conductivity are then measured as before. The result of such a measurement with $MgSO_4$ is shown by the point ⊙ in Fig. 63. It is seen that the point does not lie on the original curve for KCl; i.e. the resonance deflexions of the $MgSO_4$ and KCl solutions are different. Hence the two solutions have different high-frequency conductivities, although their conductivities at low frequencies are the same. $\Delta\Lambda$, the percentage difference in the conductivities of solutions which have the same low-frequency conductivity, is readily obtained from the curve. Fig. 63 also contains one point (○) referring to NaCl, which falls on the curve $\Delta\Lambda = 0$, i.e. the high-frequency conductivity of NaCl does not differ from that of KCl, in agreement with the theory. Fig. 64 shows the results for

$MgSO_4$ at 20° and 25°, $\Delta\Lambda$ being plotted against the concentration. The points at 25° are marked +, and the corresponding theoretical curve as a dotted line. At 20° the effect is slightly greater; the theoretical curve for 18° is shown by the full curve in the figure. The agreement between theory and experiment is satisfactory.

Quite recently Sack and Brendel† have succeeded in confirming the theory for $CuSO_4$, $K_4Fe(CN)_6$, $La(NO_3)_3$, and the acids HCl and H_2SO_4. The theory was also confirmed for the shorter wave-length of 16 m.

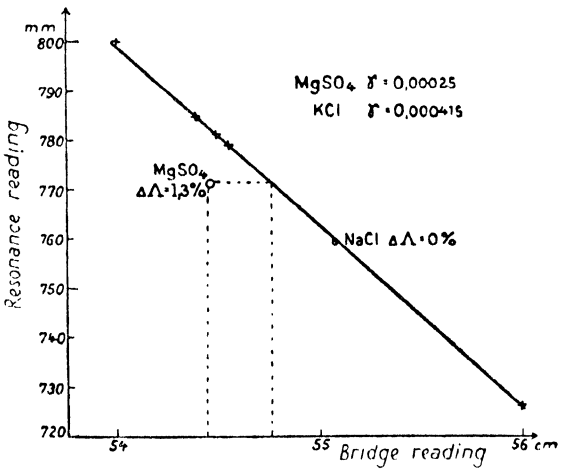

FIG. 63. Calibration with KCl.

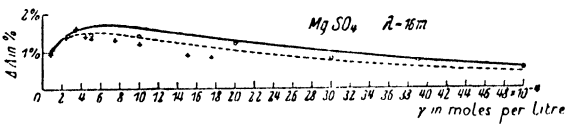

FIG. 64. Difference between the high-frequency conductivities of KCl and $MgSO_4$.

Gärtner has recently studied the dispersion of aqueous solutions of $MgCrO_4$, $CaCrO_4$, $Ca_2Fe(CN)_6$, and $N(CH_3)_4.OH_2C_6(NO_2)_3$ and found good agreement with the theoretical values.

The study of weak electrolytes would be of great interest in this connexion.‡

† H. Sack and B. Brendel, *Phys. Z.* **31** (1930), 345; B. Brendel, ibid. **32** (1931), 327.

‡ It can be predicted that weak electrolytes will not exhibit any effect corresponding to the dissociation field effect (see p. 240). Only the ionic atmosphere is of importance in determining the dispersion effect. This prediction has recently been confirmed by B. G. Whitmore (*Phys. Z.* **34** (1933), 649). For most of the weak electrolytes investigated, the increase in high-frequency conductivity is of the same order of magnitude as that calculated by the Debye-Falkenhagen theory for the ions present in the solution. Since,

Gärtner† has recently tested the Debye-Falkenhagen theory for non-aqueous solutions. For $MgSO_4$ at a concentration of 0·072 N. in methyl alcohol, the increase of conductivity relative to KCl was 5·5 per cent. with a wave-length of 15·5 m. The concentration is, however, too high for the legitimate application of the theory. It is of especial interest that $Ca_2Fe(CN)_6$ in Kahlbaum glycerine gives an increase in high-frequency conductivity five times that for KCl. In spite of the magnitude of this effect, it seems probable that it is chiefly due to interionic action.

Gärtner also showed that e.g. for glycerine at high frequencies there is anomalous dipole absorption in addition to the normal absorption due to the ionic conduction. In Gärtner's experiments this dipole absorption was several times as great as the electrolytic conductivity, while in some experiments carried out by Whitmore (loc. cit. footnote, p. 225) it was several hundred times as great. According to Debye, the dipoles take a certain time to become oriented in the direction of the electric field. This time of relaxation causes a phase difference between the field and the polarization, and hence an absorption of energy. Gärtner has also pointed out the possibility that in the range of abnormal absorption the Stokes viscosity forces acting on the ion may be modified, since they involve solvation. This effect would lead to an increased conductivity at high frequencies. The effect of temperature on the dispersion of conductivity has recently been investigated‡ and agrees with the theoretical predictions.

B. *Zahn's method of conductivity measurement.*§

Zahn and his collaborators measure the conductivity by means of the loss due to the oscillatory currents set up when the electrolyte is subjected to an alternating magnetic field. This loss increases with the conductivity of the solution. If two electrolytes exhibit the same loss, then neglecting any effect due to differences in their dielectric constants, they will have the same conductivity at the frequency in question. In practice, an untuned circuit was excited by means of an undamped sender, and the damping caused by placing the electrolyte at the point of maximum magnetic flux was measured. The frequencies used were as high as possible, the limit being set by the difficulty of obtaining suffici-

however, the ionic concentration is not in general known accurately, an accurate calculation of the effect is not possible.

† H. Gärtner, *Phys. Z.* **32** (1931), 919.

‡ H. Geest, ibid. **34** (1933), 660.

§ H. Zahn, *Z. Phys.* **51** (1928), 350; H. Rieckhoff and Zahn, ibid. **53** (1929), 619; Rieckhoff, Diss. Kiel, 1929, *Ann. d. Phys.* (5) **2** (1929), 577.

ently constant wave-length and intensity at high frequencies. Special precautions were taken to ensure constant frequency and intensity, especially the latter. The apparatus is shown diagrammatically in Fig. 65. The exciting circuit induces oscillations in a system of parallel wires terminated at one end by a copper loop, and at the other end by a copper plate W. The copper plate is fixed, and adjustment to resonance is effected by moving the parallel wire system. The solution L being investigated is placed inside the loop D_r. The solution is contained in

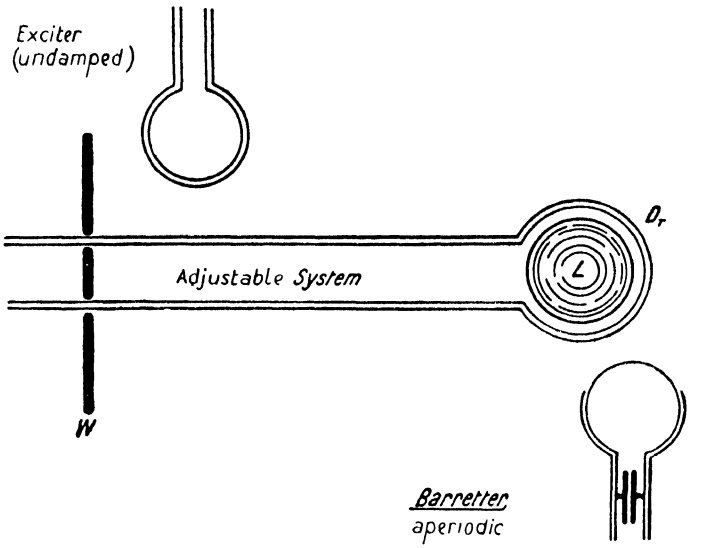

FIG. 65. Zahn's method for determining high-frequency conductivities.

a thin-walled glass cell. It is important that both the quantity of liquid and the position of the cell should be strictly reproducible. The intensity of the oscillations in the parallel wire system was measured by the effect of the current induced in a Wollaston wire, which constituted part of one arm of a balanced Wheatstone bridge. The induced current alters the resistance of the Wollaston wire, and thus unbalances the bridge, the resulting current being measured by a hot-wire mirror galvanometer. It was found that the resonance amplitude depended very little upon whether the cell was empty or filled with distilled water, i.e. small changes of dielectric constant will have no measurable effect upon the resonance amplitude. Just as in Sack's method, only comparative measurements of the high-frequency conductivity could be made, KCl being again chosen as standard. The method of comparison is exactly the same as that used by Sack and described in the preceding paragraph.

In order to determine the total dispersion effect for a given salt, it is

necessary to know the effect for the KCl solution which is found to have the same high-frequency conductivity. Table 39 gives the theoretical values for KCl; these must be added to the percentage deviations w.r.t. KCl in order to obtain the total effect.

TABLE 39

γ	$100\frac{\Lambda_\omega-\Lambda_0}{\Lambda_0}$	γ	$100\frac{\Lambda_\omega-\Lambda_0}{\Lambda_0}$
10^{-4}	0·22%	5×10^{-3}	1·15%
2×10^{-4}	0·34%	1×10^{-2}	1·25%
5×10^{-4}	0·47%	2×10^{-2}	1·31%
1×10^{-3}	0·59%	5×10^{-2}	1·06%
2×10^{-3}	0·79%	1×10^{-1}	0·66%

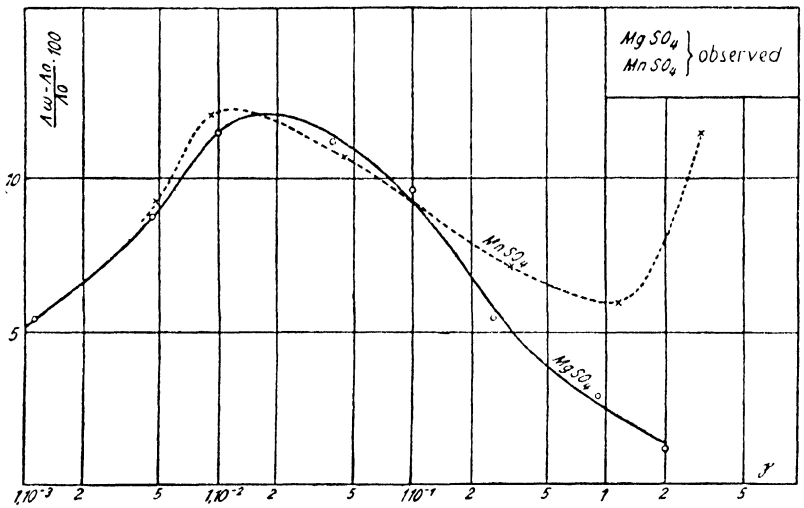

FIG. 66. High-frequency conductivity of $MgSO_4$ and $MnSO_4$ (Zahn).

About twenty electrolytes of different valency types were investigated. The results show in general fair agreement with the Debye-Falkenhagen theory of dispersion, and the agreement is in many cases excellent. Deviations from the theory are especially prominent for solutions containing ions of high valency, which is not surprising, since it is just in these cases that the conductivities in stationary fields deviate from Onsager's theory.† Fig. 66 shows the results for $MgSO_4$ and $MnSO_4$ at a wave-length of about 1 metre. The results for $MgSO_4$ agree excellently with the calculated curves, while the points for $MnSO_4$ show a tendency to rise again in very concentrated solutions. $MnSO_4$ is, however, one of the electrolytes for which the specific conductivity

† See p. 198.

shows a marked maximum when plotted against the concentration. In any case, the theory cannot be expected to be valid for such high concentrations.

The effect of temperature has also been studied, and it is found that the predictions of the theory are in general fulfilled.

C. *Deubner's method for conductivity measurements at high frequencies.*†

The methods so far described depend on the measurement of the resonance amplitude in an undamped circuit. In Sack's method the electrolyte is in a condenser, while in Zahn's method it is placed in the electromagnetic field of the oscillatory circuit. In both cases the determination of the conductivity depends upon the damping effect caused by the electrolyte solution.

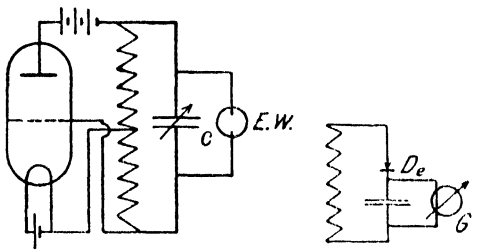

FIG. 67. Deubner's method for determining high-frequency conductivities.

The above two methods may be termed deflexion methods; Deubner's method, on the other hand, is better described as a null method. Its principle is as follows. An ordinary valve transmitter with variable reaction (see Fig. 67) contains an electrolyte resistance EW in parallel with the condenser C. The capacity of the electrolyte resistance when filled with water is about 5 per cent. that of C. A simple aperiodic receiving circuit with a detector D_e and a galvanometer G serves to measure (as galvanometer deflexion) the intensity of the oscillations. If the reaction is adjusted so that the transmitter is just on the point of oscillating, the intensity of the oscillation is very sensitive to small changes in the resistance of the electrolyte. Thus by inserting different electrolyte solutions it is possible to compare their high-frequency conductivities very accurately. Since a small relative change in the quantity being measured causes a large relative change in the galvanometer reading, the method may be legitimately described as a null method. In fact the positive damping effect of the electrolyte resistance is

† A. Deubner, *Phys. Z.* **30** (1929), 946; *Ann. d. Phys.* (5) **5** (1930), 305.

balanced by the negative damping of the transmitter resistance. In order to obtain actual oscillation it is necessary to over-compensate slightly, and the resulting small deflexion is measured. To illustrate the sensitivity of the method, it may be mentioned that the deflexion of the galvanometer changes from 30 to 90 divisions when the conductivity of the electrolyte changes by 2 per cent. If a number of NaCl solutions differing very little from one another are compared in this way, it is found that an approximately straight line is obtained on plotting the galvanometer deflexions against the low-frequency conductivities. If now a $MgSO_4$ solution is taken, the deflexion obtained is considerably less than for a NaCl solution having the same low-frequency conductivity. The high-frequency conductivity can be obtained by interpolation, just as described in the methods of Sack and Zahn. The galvanometer deflexions are so accurately reproducible that the accuracy of Deubner's method is about 0·03 per cent., i.e. higher than the accuracy of low-frequency conductivity measurement by the Kohlrausch bridge method, which is about 0·5 per cent.

It is, of course, very important that alterations in the dielectric constant should not affect the results. This is, however, taken care of by the properties of the transmitter. By adjusting the main condenser, a maximum oscillation intensity can be obtained, and it is found that in the neighbourhood of this maximum the variable condenser can be turned through several degrees without altering the galvanometer deflexion. The effect of small changes in the dielectric constant can therefore be assumed to be practically negligible. One special advantage of Deubner's method is that the electrolyte can be changed without making any alterations in the apparatus. A streaming method was used in which the electrolyte being used flows continuously through the cell. When another electrolyte is to be used, the first solution is displaced by the second, and the cell rinsed out with the second solution until the first is entirely removed. This operation takes place without removing the electrolyte resistance from the circuit, and is effected by a system of distant controls to avoid disturbing the constancy of the oscillations.

Fig. 68 shows the results for $CaSO_4$ and $CuSO_4$, the increase of conductivity with respect to NaCl being plotted against the low-frequency conductivity of the solution. (The latter values can of course be replaced by the concentrations.) The curve represents the theoretical values. $CuSO_4$ and $CaSO_4$ give exactly the same curve. The results are in essential agreement with the Debye-Falkenhagen theory of the dispersion effect, though small deviations are found.

As recognized by Deubner, better temperature regulation is desirable. It may be noted that the hydrolysis of $CuSO_4$ has had no effect, since the results agree with those for $CaSO_4$, which is certainly not hydrolysed.

Deubner has subsequently described† an interesting method for comparing the high-frequency conductivities of two electrolytes which have the same conductivity at low frequencies. The method depends upon measuring the heat developed, and has an accuracy of 0·1 per cent. The same idea has later been developed by Malsch‡ and used for the

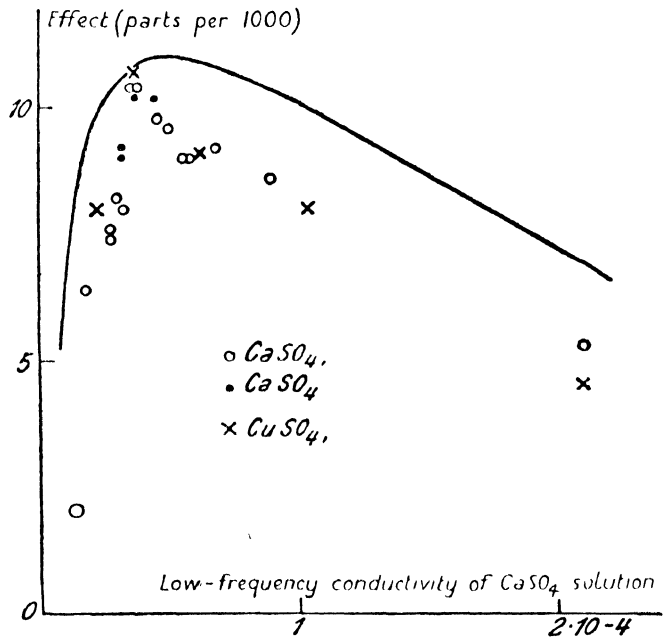

FIG. 68. High-frequency conductivity of $CaSO_4$ and $CuSO_4$ (Deubner).

absolute determination of high-frequency conductivities. Deubner was able to confirm his previous results with $MgSO_4$, and to measure the dependence of the dispersion effect upon the frequency. His results are in close agreement with the Debye-Falkenhagen theory.

D. *The method of M. Wien and his collaborators for measuring simultaneously the conductivity and dielectric constant of electrolytes.*

Wien§ employs the barretter method previously described‖ but with a valve transmitter in place of a spark gap. This method has been

† A. Deubner, *Phys. Z.* **33** (1932), 223. ‡ See p. 234.

§ M. Wien, *Phys. Z.* **31** (1930), 793; **32** (1931), 183; *Ann. d. Phys.* (5) **11** (1931), 429.

‖ See p. 85.

specially developed by Neese† in Wien's laboratory for the simultaneous determination of the conductivity and the dielectric constant. The principle of the method is shown in Fig. 69. A high-frequency current is induced in two branches of a circuit, one containing the system to be measured, and the other for comparison. The equality of the two branches can be ascertained by means of a barretter arrangement. The liquid resistance is represented schematically in Fig. 69 by the combination R_1, c. By altering the capacity C_1, a resonance curve is obtained (cf. Fig. 70) the height and position of which serve as a measure of the conductivity and the dielectric constant. The maximum deflexion in

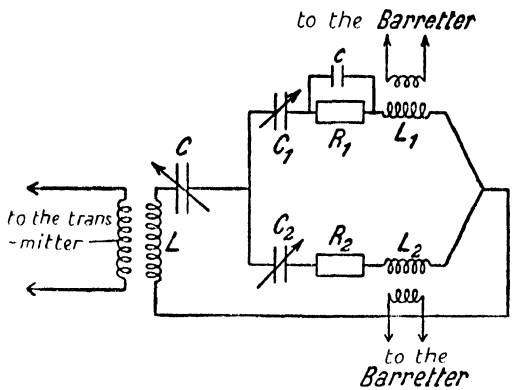

FIG. 69. Wien's method for measuring conductivities and dielectric constants at high frequencies.

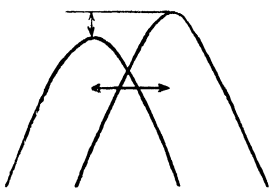

FIG. 70. Resonance curves.

the barretter circuit is obtained when the capacity of the circuit is balanced by the inductance. The determinations were carried out as follows. The electrolyte cell was first filled with NaCl or HCl, and the resonance curve obtained. The cell was then filled with a second electrolyte, having the same low-frequency conductivity as the first, and a different resonance curve obtained. In order to obtain again a resonance curve identical with the first, it was necessary to alter both the conductivity and capacity of the second solution. The conductivity was changed by altering the concentration slightly, and the capacity by a condenser in parallel. This condenser consisted of a cell fused directly on to the electrolyte cell (cf. Fig. 73), containing alcohol-water mixtures of varying compositions.

By means of this method Wien measured the conductivity and dielectric constants of solutions of $MgSO_4$ and $Ba_3(Fe(CN)_6)_2$ at different concentrations, using wave-lengths of 10, 20, and 40 metres. The

† O. Neese, *Ann. d. Phys.* (5) **8** (1931), 929.

results are essentially in agreement with the Debye-Falkenhagen theory. Figs. 71 and 72 illustrate the change in conductivity and dielectric con-

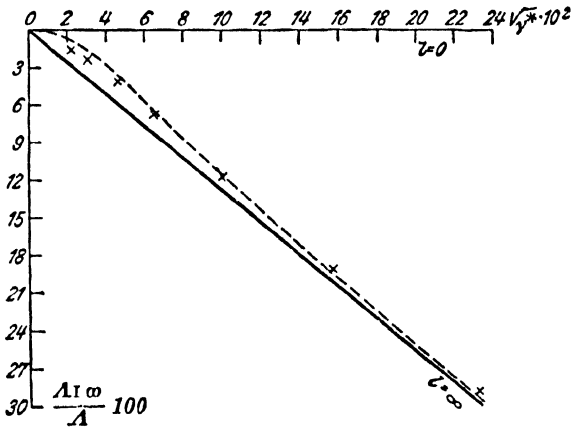

FIG. 71. High-frequency conductivity of $MgSO_4$ (Wien).

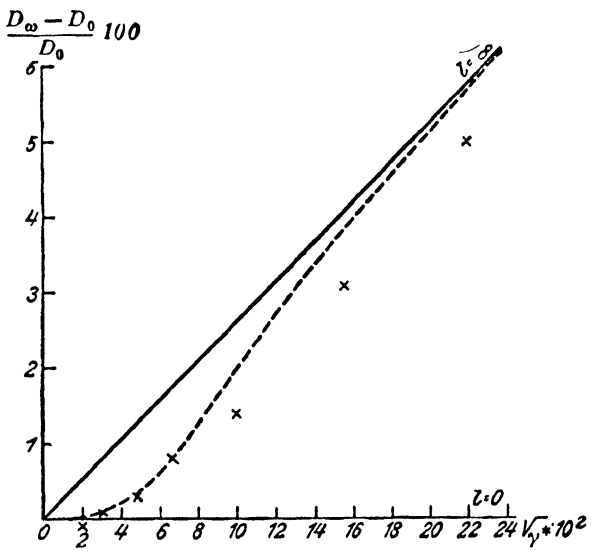

FIG. 72. Dielectric constant of $MgSO_4$ solutions (Wien).

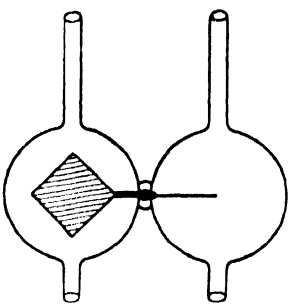

FIG. 73. Cell for high-frequency measurements.

stant for $MgSO_4$. It is seen that the experimental values lie near the theoretical curve.† The continuous curve corresponds to the stationary

† Orthmann (*Ann. d. Phys.* (5) **9** (1931), 537) also finds at low concentrations an increase in dielectric constant corresponding to the theory. M. Tezewski (*Phys. Z.* **34** (1933), 88, 561) using a resonance method obtained results for the dispersion of the dielectric constant for HCl, NaCl, KCl, $MgSO_4$, and $CuSO_4$ which agree with the theory.

case. The values obtained for the change in conductivity agree throughout with the values obtained in Debye's laboratory.

E. *The method of Malsch for the absolute determination of high-frequency conductivities.*

All the methods so far described are relative in character, i.e. they compare the effect produced by 1-1-valent electrolytes with the effect of electrolytes of higher valency types. Recently Malsch† has devised a method for determining the absolute value of the effect, the current and the potential being measured simultaneously. The cell with the platinum electrodes *EE* (see Fig. 74) is converted into a thermometer by fusing on a capillary, and is connected directly by short leads to the terminals of a string galvanometer. The whole arrangement is surrounded by an earthed metal shield to protect it from external disturbances. The rate of heat evolution is measured alternately at high and low frequencies, using different potentials. The wavelength varied between 28 and 80 metres. For solutions of $AgNO_3$ and $FeCl_3$ in C_2H_5OH, Malsch found an effect of the order of magnitude predicted by the Debye-Falkenhagen theory. The main part of the work dealt with the high-frequency heating effect of the solvent itself, which constitutes the chief source of error in these measurements. In spite of the very small times of relaxation of the dipoles (10^{-10}–10^{-11} sec.), in some cases the change in conductivity due to the high-frequency heating of the solvent‡ is several times as great as the Debye-Falkenhagen effect in dilute solutions. Malsch found that different dipole liquids behave very differently. He distinguishes between two classes; those which exhibit large heating effects (e.g. the alcohols), and those with small effects (water, glycerine, acetone). The latter group are specially suitable for absolute measurements.

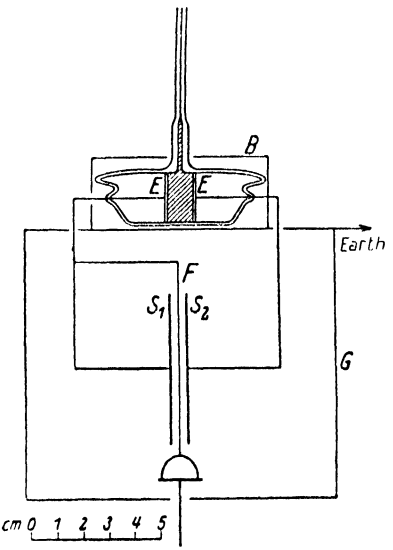

FIG. 74. Malsch's method for high-frequency conductivity determinations.

† J. Malsch, *Phys. Z.* **33** (1932), 19; *Ann. d. Phys.* (5) **12** (1932), 865.

‡ See P. Debye, *Polare Molekeln*, p. 88, 1929.

F. *Comparison of results obtained by different methods.*

Measurements of the dispersion of conductivity have now been carried out at wave-lengths of 40 m., 30 m., 20 m., 16 m., 10 m., and below 1 m. The agreement of the results obtained by different methods is shown in Fig. 74 A,† which shows the percentage dispersion effect for $MgSO_4$ at 18° at a concentration of 0·001 mole/litre. The curve represents the theory of Debye and Falkenhagen, and the points represent the experimental results of different authors.

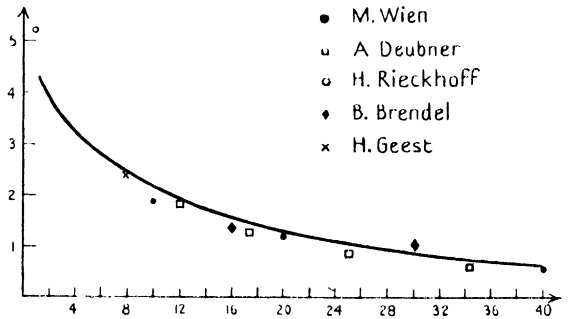

FIG. 74 A. Variation of the dispersion effect with frequency. $MgSO_4$, $\gamma = 0{\cdot}001$.

45. The Theory of the Wien Effect‡

As previously described§ the results of Wien's investigations can be represented schematically by Fig. 75, in which the quantity δ defined by

$$\delta = \frac{\Lambda_E - \Lambda_{E=0}}{\Lambda_{E=\infty} - \Lambda_{E=0}} \tag{540}$$

is plotted against the field strength E. Writing

$$\Delta_E = 100\frac{\Lambda_E - \Lambda_{E=0}}{\Lambda_{E=0}}, \tag{541}$$

$$\Delta_{E=\infty} = 100\frac{\Lambda_{E=\infty} - \Lambda_{E=0}}{\Lambda_{E=0}}, \tag{542}$$

we have

$$\delta = \frac{\Delta_E}{\Lambda_{E=\infty}}. \tag{543}$$

A very important result of Wien's investigations is that for very high fields, the conductivity becomes practically equal to the conductivity at infinite dilution, i.e.

$$\Lambda_{E=\infty} = \Lambda_\infty. \tag{544}$$

† The figure is taken from a paper by Geest, *Phys. Z.* **34** (1933), 660.

‡ See p. 82 for experimental methods; also the review by M. Wien, *Phys. Z.* **34** (1933), 60.

§ See p. 86.

From (514)
$$\Delta_{E=\infty} = 100\frac{\Lambda_{I0}+\Lambda_{II}}{\Lambda_{\infty}-\Lambda_{I0}-\Lambda_{II}}. \qquad (545)$$

The quantities Λ_{I0} and Λ_{II} can be calculated theoretically (cf. Table 36), but these theoretical values have not yet been confirmed for electrolytes of high valence types. We shall therefore in the following employ the quantity Δ_E.† Δ_E varies with E in a similar way to δ, but the limiting value is not unity but $\Delta_{E=\infty}$. As previously described, Wien has obtained Δ_E as a function of the concentration, valency, dielectric constant, etc., just as in our treatment of the dispersion effect (p. 211). The entire behaviour of the Wien effect can in fact be represented

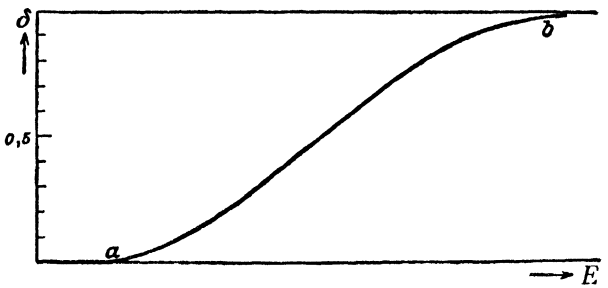

FIG. 75. The Wien effect.

qualitatively by replacing the frequency by the field strength.‡ Thus the curves in Figs. 51–3 retain their general characteristics when applied to the Wien effect.

We shall now consider the theoretical interpretation of the Wien effect. According to Joos and Blumentritt§ it is possible to calculate theoretically the portion a of the curve in Fig. 75. It can also be shown|| that for very high fields the conductivity will become equal to the conductivity at infinite dilution. It should be noted that the field-strength must not be too high, since otherwise velocities will be reached for which Stokes's law is no longer obeyed. Oseen†† has carried out the necessary hydrodynamic calculations, and finds that for a velocity of 1 metre per sec. the correction amounts to only 0·1 per cent. In special cases it is possible to calculate theoretically the whole course of the curve obtained by Wien.‡‡

† Δ_E is identical with the quantity previously termed $\Delta\lambda_E$. See p. 86.

‡ See H. Falkenhagen, *Phys. Z.* **30** (1929), 163; **32** (1931), 353; also Rieckhoff, *Ann. d. Phys.* (5) **2** (1929), 596.

§ G. Joos and M. Blumentritt, *Phys. Z.* **28** (1927), 836; M. Blumentritt, *Ann. d. Phys.* **85** (1928), 812. || P. Debye and H. Falkenhagen, *Phys. Z.* **29** (1928), 401.

†† For an account of Oseen's calculations and comparison with experiment, see H. Falkenhagen, *Handbuch d. Experimentalphysik* von Wien-Harms, vol. iv, part I, 1931.

‡‡ See H. Falkenhagen, *Phys. Z.* **30** (1929), 163; **32** (1931), 353.

We shall first show that on account of the finite time of relaxation of the ionic atmosphere† the conductivity for high field strengths approaches the value at infinite dilution (cf. *b* in Fig. 75), taking as an example KCl. From the relation‡

$$\rho|\mathfrak{v}| = \epsilon E \tag{546}$$

the velocity of a K^+ or Cl^- ion in a field of 100,000 volts/cm. is $|\mathfrak{v}| = 67{\cdot}5$ cm./sec. ($l = 65$, and hence $\rho = 0{\cdot}236\times10^{-8}$ c.g.s. units). If we take the concentration $\gamma = 0{\cdot}0001$, then from p. 178 the time of relaxation of the ionic atmosphere is $\bar{\Theta} = 0{\cdot}276\times10^{-6}$ sec. From (228), the thickness of the ionic atmosphere is $1/\kappa = 3{\cdot}06\times10^{-6}$ cm. Thus during the time of relaxation $\bar{\Theta}$ the ion will have travelled $18{\cdot}6\times10^{-6}$ cm., i.e. about six times the thickness of the ionic atmosphere. During the time necessary for the complete formation of the ionic atmosphere (see p. 178) the ion will have travelled about 25 times the thickness of the atmosphere. Under these conditions, the atmosphere can hardly be formed at all. In other words, the conductivity for high field-strengths will assume the value it has at infinite dilution, since the forces due to relaxation and electrophoresis disappear. While the dispersion effect depends on the disappearance of asymmetry in the ionic atmosphere, the Wien effect is due to the fact that at high field-strengths the ionic atmosphere is not formed at all. But see note on p. 335.

By applying successive approximations, Joos and Blumentritt have employed equations (411) to calculate the initial portion of the curve in Fig. 75.§ The Brownian movement is taken into account just as in Onsager's theory. The calculations are somewhat involved, and we shall give here only the results. Writing

$$\Delta_E = \Delta\lambda_E = 100AE^2(1-BE^2), \tag{547}$$

then

$$\left.\begin{aligned} A &= \frac{6{\cdot}61\times10^{-5}\Lambda_\infty|z_1z_2|(|z_1|+|z_2|)^{\frac{1}{2}}q^{\frac{2}{3}}}{T^{\frac{1}{2}}(D_0\gamma^*)^{\frac{1}{2}}(1-q)^3\Lambda}k_1 + \\ &\qquad + \frac{6{\cdot}3\times10^{-11}|z_1z_2|(|z_1|+|z_2|)^{\frac{1}{2}}q^{\frac{1}{3}}D_0^{\frac{1}{2}}}{T^{\frac{1}{2}}\gamma^{*\frac{1}{2}}(1+\sqrt{q})^2\Lambda\eta_0} \\ k_1 &= -0{\cdot}2q^{\frac{1}{2}}+0{\cdot}075+0{\cdot}15q-0{\cdot}025q^2, \end{aligned}\right\} \tag{548}$$

where q is given by (536).

† See p. 176.

‡ The quantity ρ_1 is related to the mobility l_1 and the valency z_1 of the ion by the relation

$$\rho_1 = \frac{1{\cdot}54\times10^{-7}|z_1|}{l_1}.$$

§ Putting $\partial F_{ij}/\partial t = 0$.

Further,

$$B = 1{\cdot}09\times10^{-11}\frac{D_0(|z_1|+|z_2|)q}{\gamma^*(1-q)^2}\times$$
$$\times\frac{-0{\cdot}00558+0{\cdot}06696q+0{\cdot}10045q^2-0{\cdot}02232q^3+0{\cdot}00335q^4-0{\cdot}14286q^{1{\cdot}5}}{-0{\cdot}2q^{\frac{1}{2}}+0{\cdot}075+0{\cdot}15q-0{\cdot}025q^2}. \qquad (549)$$

Table 40 shows the values of A and B for a number of electrolytes, the theoretical values of Joos and Blumentritt being compared with the experimental values of Wien. It will be seen that there is approximate agreement between the theoretical and experimental values. λ_0 is the specific conductivity for $E = 0$. The values of A and B increase rapidly as the valencies of the ions increase, and also increase with increasing concentration, in agreement with equations (548) and (549).

TABLE 40

Water at 18°

	$\lambda_0 = 0{\cdot}0005$ $A.10^{11}$		$\lambda_0 = 0{\cdot}00025$ $A.10^{11}$		$\lambda_0 = 0{\cdot}000125$ $A.10^{11}$	
	obs.	*calc.*	*obs.*	*calc.*	*obs.*	*calc.*
$MgSO_4$	1·12	1·49	1·50	1·96	2·0	2·5
$MgCrO_4$	1·14	1·21	1·55	1·60	2·1	1·8
K_3FeCy_6	0·73	0·44	1·0	0·70	1·4	0·77
K_4FeCy_6	1·07	0·88	1·50	1·17	2·0	(0·82)
$Ba_3(FeCy_6)_2$	3·2	3·9	4·2	5·1	5·4	5·6
Ba_2FeCy_6	4·2	6·6	5·5	10·9	7·2	11·6
	$B.10^{11}$		$B.10^{11}$		$B.10^{11}$	
	obs.	*calc.*	*obs.*	*calc.*	*obs.*	*calc.*
$MgSO_4$	1·2	1·7	2·8	2·3	6·0	6·0
$MgCrO_4$	1·3	3	2·8	3·6	6·0	7·5
K_3FeCy_6	2·0	1·1	4·2	1·5	8·7	3·4
K_4FeCy_6	2·1	2·3	4·5	2·9	9·4	3·8
$Ba_3(FeCy_6)_2$	1·7	2·1	3·8	4·5	9·2	7·5
Ba_2FeCy_6	2·2	3·2	5·0	3·9	12	(6·9)

Recent work of Bauer† on acetone solutions shows that the effect of the dielectric constant is also predicted at least qualitatively by the theory. As in aqueous solutions, the first part of the curve (see *a*, Fig. 75) can be expressed by equation (547), but the values of A and B are respectively greater and smaller than in aqueous solution, as predicted by the theory. Fig. 76 shows the effect $\Delta\lambda_E$ as a function of the field E for KI and LiBr at different concentrations.‡ Specially interest-

† F. Bauer, *Ann. d. Phys.* (5) **6** (1930), 253.

‡ In the case of LiBr and the 1-2-valent salts, complications arise owing to the so-called dissociation field effect. Cf. the following paragraph.

ing from a theoretical point of view are the results of Bauer on the variation of the effect with the duration of the discharge. He found that the curve relating $\Delta\lambda_E$ to E became steeper as the duration of the discharge increased. This result follows qualitatively from Debye's theory; in fact it is possible† by making the same approximations as on p. 237 to calculate the dependence of the Wien effect upon the frequency over the whole range of field-strength. The results agree qualitatively with Bauer's curve.

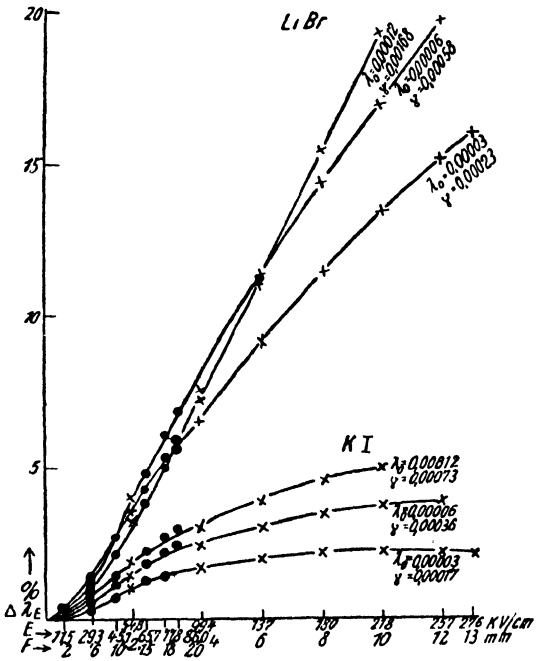

FIG. 76. The field effect for KI and LiBr (Bauer).

The existence of a finite time of relaxation thus provides an explanation of the Wien effect. In principle it should also provide a method for eliminating the interaction of the ions due to the Coulomb forces, and thus enable a study of the true degree of dissociation.‡ It would be of the greatest interest to develop such investigations and to compare the values obtained for the degree of dissociation with e.g. the values of Nernst,§ obtained by combining Debye's theory with Arrhenius's classical theory.

A very important phenomenon, known as the dissociation field effect,

† H. Falkenhagen, *Phys. Z.* **32** (1931), 353. It should be noted that according to Wien, the results of Bauer are unreliable, especially with regard to the effect of the duration of the discharge. A more accurate method has since been developed by Wien and Schiele, cf. footnote p. 240. ‡ See also p. 312. § See p. 289.

has been recently discovered by Wien and his collaborators.† The nature of this effect is best understood by reference to Figs. 77 and 78. Fig. 77 shows that with strong acids the field effect is small and agrees with the theory. The heavy line in Fig. 77 represents the effect for sul-

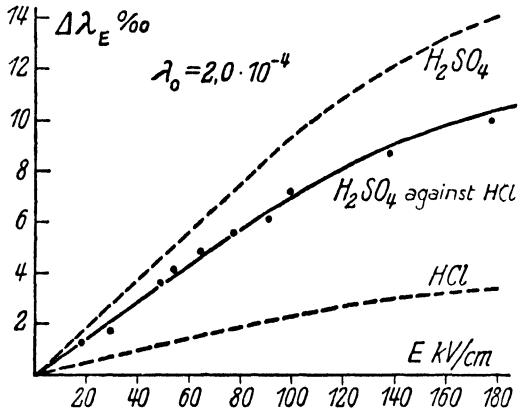

FIG. 77. The field effect for strong acids.

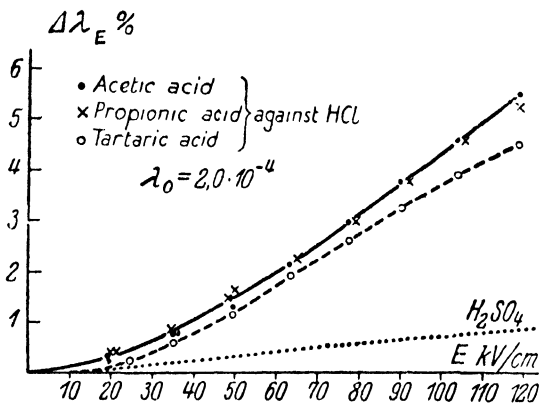

FIG. 78. The field effect for weak acids.

phuric acid relative to hydrochloric acid. It was found that the field effect with fields of 100,000 to 200,000 volts/cm. increased to about 1 per cent., and was approximately the same for the various 1-2-valent acids.

Weak acids and salts behave quite differently, the effects observed being five to ten times as great as for strong acids. Fig. 78 shows the field effect for acetic, propionic, and tartaric acids, relative to HCl. The effect is much too great to be attributed to the ionic atmosphere. There must be an entirely new type of action, causing an increased degree of

† M. Wien and J. Schiele, *Phys. Z.* **32** (1931), 545.

ionization of weak acids and salts in strong fields. According to Wien and Schiele, other acids, e.g. monochloracetic, dichloracetic, and aminoacetic acids also exhibit very marked field effects, presumably due to an increase in the number of ions. The saturation effect, observed specially in the case of aminoacetic acid, indicates that the strong field has caused a decrease in the number of molecules. As the field increases still more, dissociation should finally become complete, and in this way it should be possible to measure the true degree of dissociation. In the case of aminoacetic acid, the limiting effect is about 2 per cent., while at the dilution in question the degree of dissociation is 93 per cent., which should give rise to a limiting effect of 7 per cent. In Wien's opinion, the very rapid recombination of the ions to form molecules prevents complete dissociation. It is a very interesting question whether the velocity of this recombination bears any relation to the time of relaxation of the ionic atmosphere. It should be possible to decide this by measurements of the time effect in the dissociation field effect. According to unpublished calculations by Onsager (private communication to the author) the time of recombination of the ions should be of the same order of magnitude as the time of relaxation. In the author's opinion, however, other factors, probably of a quantum-mechanical nature, will be of importance in many cases.

It is also of interest that polybasic acids exhibit the dissociation field effect for the different stages of their dissociation.

As regards the problem of separating the ionic atmosphere effect from the dissociation field effect, this is probably impossible, since both effects are operative simultaneously. The effect due to the ionic atmosphere is predominant for comparatively weak fields, but is largely displaced by the dissociation field effect for stronger fields.† The dispersion effect is of course due solely to the ionic atmosphere.

The dissociation field effect has recently been treated theoretically by Onsager.‡ The mutual approach and separation of an ion pair is treated in terms of the Brownian movement. In the absence of an electric field, diffusion can take place to an unlimited extent. If, however, a field is present, the ions are separated to a certain distance by the field, this distance being determined by the fact that the electrical energy must be of the order of magnitude kT. The mass-law equilibrium will be modified by the external field. The calculations are based on

† The author's thanks are due to Herr Wien for these considerations.

‡ Thanks are due to Herr Onsager for placing an unpublished manuscript at the author's disposal, and also for many private communications.

equations (396) and (397). $\mathfrak{R}_{iP}^{jQ}$ and $\mathfrak{R}_{jQ}^{iP}$ are replaced by the values in (399), i.e. the ionic atmosphere is neglected, and only the Coulomb potential taken into account. Making the abbreviations

$$q_0 = \frac{-e_1 e_2}{2D_0 kT}$$

$$\beta_0 = \frac{\mathfrak{E}\left(\frac{e_1}{\rho_1} - \frac{e_2}{\rho_2}\right)}{kT\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right)}$$

the differential equation can be put into the form

$$\operatorname{div}\operatorname{grad} f = \operatorname{grad} f \operatorname{grad}\left(\frac{2q_0}{r} + 2\beta_0\right).$$

In this equation, the quantity f is the distribution function, previously denoted by $w_{iP}^{jQ} = w_{ij}$. By introducing the correct boundary conditions it is possible to obtain a unique solution of this equation. The result of Onsager's calculation is that the dissociation constant K increases with increasing field-strength, since the recombination of the ions takes place independently of the field in a time of the same order of magnitude as the time of relaxation. The ratio of the dissociation constant $K(E)$ at field-strength E to the dissociation constant at zero field-strength is given by

$$\frac{K(E)}{K(0)} = \frac{+I_1\{4i\sqrt{(-\beta_0 q_0)}\}}{2i\sqrt{(-\beta_0 q_0)}},$$

where I_1 is the Bessel function of the first order with a purely imaginary argument. On developing the above expression as a series, we obtain

$$\frac{K(E)}{K(0)} = 1 + 2\beta_0 q_0 + \frac{(4\beta_0 q_0)^2}{2!\,3!} + \frac{(4\beta_0 q_0)^3}{3!\,4!} + \ldots. \qquad (549\,a)$$

The dissociation constant should thus be a linear function of the field for not too strong fields, and the same should apply to the change in conductivity. The parabolic course of $\Delta\lambda_E$ per cent. at small field-strengths shown in Fig. 78 would probably be obtained by a refinement of Onsager's theory. The approximation involved in equation (549 a) is that for very weak electrolytes the characteristic thickness of the ionic atmosphere $1/k$ is very much greater than q_0, i.e. $kq_0 \ll 1$ and hence $e^{-kq_0} \simeq 1$. A variation of the dissociation field effect with the concentration would only be obtained by assuming a finite value for k. It would appear that both the nature and the order of magnitude of the effect agree with the experiments of Wien (loc. cit.) and of Gyemant.†

† Gyemant, *Wiss. Veröff. Siemens-Konzern*, **7** (1928), vol. 1. p. 134.

NOTE.—For further experimental work on the dissociation field-effect, see p. 335.

X

THE MODERN THEORY OF THE VISCOSITY OF STRONG ELECTROLYTES

46. Historical

POISEUILLE,† the great pioneer of experimental work on the viscosity of liquids, was the first to show that the viscosity of salt solutions was in some cases greater and in other cases less than the viscosity of the pure solvent. Sprung‡ found that the viscosity of barium chloride solutions is greater than that of pure water. Arrhenius§ carried out some viscosity determinations and proposed the relation

$$\frac{\eta}{\eta_0} = A\gamma, \tag{550}$$

where A is a constant for a given salt and a given temperature, η is the viscosity, and γ the concentration. Equation (550) was later tested by Reyher,‖ Wagner,†† and other workers, who found that between $\frac{1}{8}$ N. and $\frac{1}{2}$ N. it reproduces the results to within a few parts per thousand, and up to 1 N. to within 1 per cent. Sutherland‡‡ suggested that the depolymerization of the water molecules by the ions brought about a decrease in the viscosity. Gruneisen§§ has made a very careful and critical study of the viscosity of 16 salts in water over a wide range of concentration embracing much more dilute solutions than those previously studied. He found that in very dilute solutions η/η_0 is not proportional to γ, but that the function $(\eta/\eta_0 - 1)/\gamma$ plotted against γ bends upwards at low concentrations. If η/η_0 were proportional to γ, then $(\eta/\eta_0 - 1)/\gamma$ should retain a constant value right down to zero concentration. Fig. 79 shows the actual course of the curves in different cases. Curves A, B, and F refer respectively to magnesium sulphate, lithium iodate, and potassium iodide, all from Gruneisen's measurements at 18°. Curve D represents the results of Applebey for lithium nitrate at 18°, and curves G and E measurements of Merton on caesium nitrate at 0° and 25°. Curve C refers to recent results of Jones and Dole for barium chloride at 25°. These results appear to show that $(\eta/\eta_0 - 1)/\gamma$ decreases rapidly with increasing concentration in very dilute solutions,

† J. L. M. Poiseuille, *Ann. chim. phys.* (3) **21** (1847), 76.
‡ A. Sprung, *Ann. d. Phys.* **159** (1876), 1.
§ Sv. Arrhenius, *Z. phys. Chem.* **1** (1887), 285.
‖ R. Reyher, ibid. **2** (1888), 744. †† J. Wagner, ibid. **5** (1890), 31.
‡‡ W. Sutherland, *Phil. Mag.* (5) **50** (1900), 481.
§§ Gruneisen, *Wiss. Abh. Phys.-Tech. Reichsanst.* **4** (1905), 151, 237.

passes through a minimum, and then increases slowly. Gruneisen attempted to represent these curves by the equation

$$\eta/\eta_0 - 1 = A\alpha\gamma + B(1-\alpha)\gamma + C\gamma^2, \qquad (551)$$

where α is the degree of dissociation and A, B, and C constants for a given salt and a given temperature. He was able to reproduce the experimental results fairly well by equation (551), though it was sometimes necessary to give A and B negative values. Gruneisen's

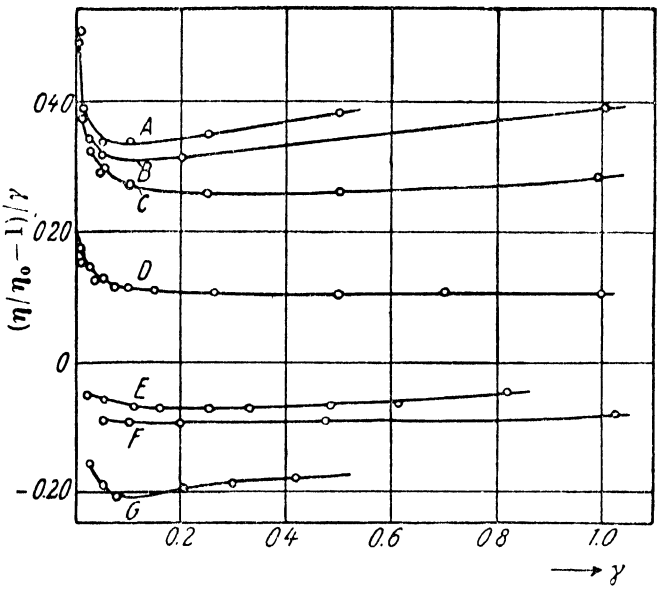

FIG. 79. The viscosity of aqueous solutions.

equation is, however, not of any practical service for interpolating or explaining the experimental results; the degree of dissociation α is itself a function of the concentration, and for very dilute solutions, since $\alpha \sim 1$, $\eta - \eta_0$ again becomes a linear function of the concentration, in contradiction to the experimental results. Schneider† has investigated a large number of other salts and found curves resembling those in Fig. 79, with a convex curvature at low concentrations. He made, however, no advance in the interpretation of this phenomenon. The theory of Applebey‡ gives no satisfactory explanation of the facts, since he assumes that the friction with the water is greater for the ions than for the undissociated molecules, which can hardly be the case, since the viscosity depends upon the volume of the particle.

† Schneider, Diss. Rostock, 1910.

‡ N. P. Applebey, *J. Chem. Soc.* **97** (1910), 2000.

47. The Work of Jones and Dole

Jones and Dole† have quite recently investigated the viscosities of very dilute salt solutions in the hope of obtaining results which might be treated by the modern theory of electrolytes.‡ Jones and Dole found that their own results, as well as those of Gruneisen and Applebey could be represented by a simple relation. Introducing $\phi = \eta_0/\eta$, the relative fluidity, the equation of Jones and Dole is

$$\phi = 1 - A\sqrt{\gamma} + B\gamma, \tag{552}$$

or, for the viscosity itself at low concentrations,

$$\eta = \frac{\eta_0}{\phi} = \eta_0\{1 + A\sqrt{\gamma} + (A^2 - B)\gamma + \ldots\}. \tag{553}$$

The value of A is zero for non-electrolytes, and positive for all strong electrolytes. B can be either positive or negative, but is negative for most salts; e.g. for $BaCl_2$, $A = 0{\cdot}0201$, $B = -0{\cdot}2009$.

48. The Theoretical Limiting Law for the Viscosity of Strong Electrolytes, and its Experimental Confirmation

This theory, which will be treated quite shortly here, was suggested by the results of Jones and Dole, and developed by Falkenhagen.§

The irreversible processes involved in the viscosity of strong electrolytes can be treated from the point of view of the ionic atmosphere. Thus if we assume that there is a linear decrease of velocity in the electrolyte, so that the ions in different layers are moving with different velocities, it is clear that the original symmetrical charge distribution in the ionic atmosphere will be deformed. This appears in more detail by considering Fig. 80. The central ion is taken as positive, and the charge in the ionic atmosphere is originally negative. We wish to investigate the changes in the charge density in the atmosphere caused by a velocity gradient parallel to the z-axis. The arrows show the velocities of different parts of the ionic atmosphere relative to the central ion, the direction of

† G. Jones and M. Dole, *J. Am. Chem. Soc.* **51** (1929), 2950.

‡ This has since been done; cf. § 48.

§ H. Falkenhagen and M. Dole, *Phys. Z.* **30** (1929), 611; *Z. phys. Chem.* **6 B** (1929), 159; H. Falkenhagen, *Phys. Z.* **32** (1931), 365; **32** (1931), 745; Falkenhagen and E. L. Vernon, ibid. **33** (1931), 140; *Phil. Mag.* (7) **14** (1932), 537. The theory has recently been extended by Onsager and Fuoss (*J. Phys. Chem.* **36** (1932), 2688) to the case of a solution containing any number of electrolytes. There are, however, no experimental data on this point, and we shall therefore not deal with their treatment.

In this connexion it would be interesting to investigate theoretically and experimentally the effect of an electric field upon the viscosity. Cf. L. Ebert, *Handb. d. Experimentalphysik*, loc. cit., p. 220.

motion being parallel to the x-axis. It is clear that e.g. in the upper right-hand quadrant there will be an additional negative charge density, since the negative charges are coming from a portion of the atmosphere which originally had a greater charge density, and on account of the finite time of relaxation there will be an excess of negative ions. In the same way we can determine the charge distribution in the three other quadrants. As shown in Fig. 80, two quadrants have an additional positive charge density, and two a negative. The additional charge density in the atmosphere surrounding the central ion is proportional to a spherical function S of the second order. Introducing polar coordinates,

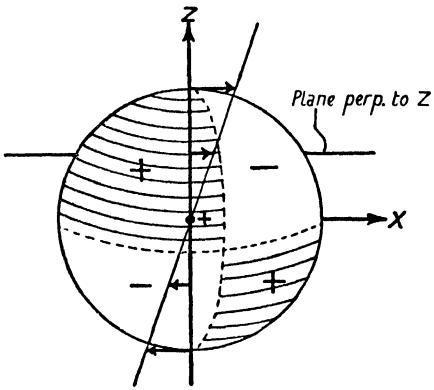

FIG. 80.

$$x = r\sin\theta\cos\phi, \qquad y = r\sin\theta\sin\phi, \qquad z = r\cos\theta, \tag{554}$$

the additional charge density round the ion 1† which we shall term Π_1 is given by

$$\Pi_1 = S(\theta,\phi)R(r), \tag{555}$$

where

$$S = -3\sin\theta\cos\theta\cos\phi. \tag{556}$$

In the special case of a simple electrolyte with ions of equal mobilities, the radial function R is given by

$$R = \frac{e}{u'}\frac{\tilde{b}re^{-\kappa r}\kappa^2}{96D_0kT}, \tag{557}$$

where r is the distance from the central ion, $\tilde{b}$ the velocity gradient, and u' the mobility of the ion. The thickness of the ionic atmosphere $1/\kappa$ is in this special case given by (227) as

$$\frac{1}{\kappa} = \frac{2{\cdot}81\times10^{-10}}{\sqrt{\gamma}}\left(\frac{D_0T}{2z^2}\right)^{\frac{1}{2}}\text{cm.} \tag{558}$$

The value of u' in c.g.s. units is related to l the mobility in rec. ohms per sq. cm. by the equation

$$u' = \frac{l}{15{\cdot}4z^2}10^8 \text{ c.g.s. units.} \tag{559}$$

The form of the radial function is shown in Fig. 81; it depends of course on the properties of the particular electrolyte solution considered, i.e. the concentration, etc. If we take a plane perpendicular to the velocity

† In this special case Π_2, the additional charge density round the ion 2, is equal to Π_1.

gradient, it will be seen from Fig. 80 that on account of the lines of force of the additional charge density, the layers above the plane will exert a force upon the central ion parallel to the positive x-axis. Similarly, the layers below this plane will exert an equal force parallel to the negative x-axis. The total force has the character of a tensor. It is now required to calculate the total shearing force transmitted through one square centimetre at right angles to the velocity gradient, taking also into account the distortion of the ionic atmospheres of the negative ions. This force is proportional to the velocity gradient, and the proportionality factor is the amount added to the coefficient of viscosity on account of the interionic forces. If η_γ is the viscosity of an electrolyte

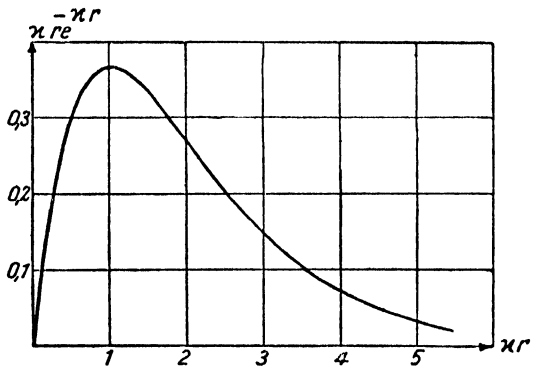

FIG. 81.

of concentration γ (expressed in moles per litre) and η_0 is the viscosity of the pure solvent, we arrive at the relation

$$\eta_\gamma = \eta_0(1+A\sqrt{\gamma}). \tag{560}$$

The value of A was first calculated theoretically for the special case of a binary electrolyte with ions of equal mobility† and the calculations were subsequently extended to embrace the case of any simple electrolyte.‡ The distribution of the additional charge density is again qualitatively just the same as in Fig. 80, and the charge density is again proportional to the spherical function of the second order given in (556). The radial function has a form similar to that shown in Fig. 81, but is now represented by a much more complicated function than (557). Further, the additional charge density round the ion 1 is no longer equal to the corresponding additional charge density round the ion 2, as was the case in the particular case treated above. The viscosity still follows

† See Falkenhagen and Dole, loc. cit.
‡ See Falkenhagen and Vernon, loc. cit.

the simple law expressed by (560), but the coefficient A is now a very complicated function of the valency type of the salt and the mobilities of the ions.

The theoretical expression obtained for A is

$$A = \frac{1{\cdot}45}{\eta_0(D_0T)^{\frac{1}{2}}}\left(\frac{\nu_1 z_1}{|z_1|+|z_2|}\right)^{\frac{1}{2}} \times \times \left[\frac{l_1 z_2^2 + l_2 z_1^2}{4 l_1 l_2} - \frac{(|z_2|l_1 - |z_1|l_2)^2}{l_1 l_2\left\{(l_1+l_2)^{\frac{1}{2}} + (|z_2|l_1 + |z_1|l_2)^{\frac{1}{2}}\left(\frac{|z_1|+|z_2|}{z_1 z_2}\right)^{\frac{1}{2}}\right\}}\right]. \quad (561)$$

For the special case of binary electrolytes with ions of equal mobility, i.e. $|z_1| = |z_2|$, $l_1 = l_2 = l$, this expression simplifies to

$$A = \frac{51{\cdot}2 \times 10^{-2} z^2}{l\eta_0(D_0T)^{\frac{1}{2}}}. \quad (562)$$

These theoretical expressions have received experimental confirmation for 1-1-valent salts by the work of Joy and Wolfenden† and later by the measurements of Jones and Talley,‡ who used a photoelectric method of timing accurate to 0·01 sec. Table 41 contains the experimental and theoretical values of A.

TABLE 41

Electrolyte	*Type*	*Observer*	*t° C.*	A_{obs}	A_{calc}
$LiNO_3$	1-1	Gruneisen and Applebey	18°	0·0082	0·0069
$RbNO_3$	1-1	Joy and Wolfenden	18°	0·0050	0·0049
$LiNO_3$	1-1	Gruneisen	18°	0·0108	0·0094
KI	1-1	..	..	..	0·0048
KCl	1-1	Joy and Wolfenden	18°	0·0052	0·0049
HCl	1-1	..	..	..	0·0020
HNO_3	1-1	Joy and Wolfenden	18°	0·0023	0·0021
$KClO_3$	1-1	„ „	18°	0·0050	0·0052
$KBrO_3$	1-1	Jones and Talley	25°	0·0058	0·0058
KNO_3	1-1	„ „	25°	0·0051	0·0052
$CsNO_3$	1-1	„ „	25°	0·0043	0·0051
$BaCl_2$	1-2	Jones and Dole	25°	0·020	0·015
$MgSO_4$	2-2	Cox and Wolfenden	18°	0·0048	0·022
$LaCl_3$	1-3	„ „	18°	0·0215	0·032
$K_4Fe(CN)_6$	1-4	..	..	..	0·039

The effect of the ionic mobility appears clearly in Table 41, e.g. by comparing the coefficients for KCl and HCl. The effect of the valency type is also apparent. The values for $LaCl_3$ and $MgSO_4$ are taken from recent work of Cox and Wolfenden.§ In the case of $MgSO_4$ there is a

† W. E. Joy and J. H. Wolfenden, *Proc. Roy. Soc.* **134 A** (1931), 413.
‡ G. Jones and S. K. Talley, *J. Am. Chem. Soc.* **55** (1933), 624.
§ W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc.* (1934).

large discrepancy between the theoretical and experimental values; this corresponds to the discrepancies found for the conductivities of 2-2-valent salts; cf. p. 197. Cox and Wolfenden have also carried out some measurements in non-aqueous solvents, and find that for tetra-ethylammonium picrate in nitrobenzene and sodium iodide in ethyl alcohol the predictions of the theory are verified.

All the above investigations show that in sufficiently dilute solutions the viscosity effect is positive, i.e. the viscosity of the solution is greater than that of the pure solvent. The negative viscosity effect which sets in at higher concentrations must be due to other causes, e.g. the depolymerization of the solvent molecules by the ions. Finkelstein† has calculated the effect of the relaxation of the dipole molecules of the solvent upon the viscosity and finds a positive effect which should vary linearly with the concentration. While the writer is not convinced of the quantitative validity of Finkelstein's theory, investigations in this direction will obviously be of great importance in elucidating the structure of electrolyte solutions.

In order to represent their results over a greater concentration range, Jones and Dole (loc. cit.) introduced a linear term into equation (560), and wrote

$$\eta_\gamma = \eta_0(1+A\sqrt{\gamma}+B'\gamma).$$

While it is not yet possible to calculate B with certainty from theoretical considerations, a study of the deviations from the simple equation (560) is of great interest in connexion with the state of electrolytes in solution.‡

It may be noted that the effect of the ionic atmosphere upon the viscosity is very small according to (560), so that the previously mentioned theory of Sutherland§ fails completely.

† B. N. Finkelstein, *Phys. Z.* **31** (1930), 130, 165.
‡ See W. M. Cox and J. H. Wolfenden, loc. cit.
§ See p. 94.

XI

MORE CONCENTRATED SOLUTIONS

49. Introductory Remarks

THE formulae derived theoretically in the preceding chapters are valid only for very dilute electrolyte solutions. In the present state of the theory the various effects involved can only be predicted quantitatively for dilute solutions. Deviations from the theoretical limiting laws set in at quite low concentrations, e.g. about $\gamma = 0{\cdot}005$ for 1-1-valent salts in water. Although no rigid theory of more concentrated solutions has hitherto been developed, we shall describe briefly here some of the attempts to extend the theory to embrace more concentrated solutions. Such attempts have been made by Debye and Hückel, Hückel, H. Müller, Gronwall, La Mer, and Sandved, Bjerrum, Nernst, Onsager, Davies, Brönsted,† and Scatchard.‡ While the first six authors do not employ the law of mass action, Bjerrum attempts to show that it can be applied, even though undissociated molecules (in the classical sense) do not exist. Nernst, Onsager, and Davies combine formally the theories of Arrhenius and Debye. Before the advent of the electrostatic theory of electrolytes, Brönsted had developed the interesting empirical theory of the specific interaction of ions.

We are still a long way from a strict theory of more concentrated solutions, and the above theories will therefore be treated only briefly in this chapter.

50. The Theory of Debye and Hückel and its Applications

We shall once more consider the characteristic length $1/\kappa$, which at a concentration of 0·1 mole per litre is only about ten times the dimen-

† P. Debye and E. Huckel, *Phys. Z.* **24** (1923), 185. E. Huckel, ibid. **26** (1925), 93. H. Müller, ibid. **28** (1927), 324. T. H. Gronwall, K. La Mer, and Sandved, ibid. **28** (1928), 358. N. Bjerrum, *Dansk. Vid. Selsk. Medd.* **7** (1926), No. 9. W. Nernst, *Z. Elektrochem.* **33** (1927), 428, *Berl. Akad. Ber.* **2** (1928), 4, *Z. phys. Chem.* **135** (1928), 237. W. Orthmann, *Ergeb. d. exakt. Naturw.* **6** (1927), 155. W. Nernst and W. Orthmann, *Z. phys. Chem.* **135** (1928), 199. Naudé, *Z. Elektrochem.* **33** (1927), 532, *Z. phys. Chem.* **135** (1928), 209. L. Onsager, *Phys. Z.* **28** (1927), 277, *Chem. Rev.* August, 1933. C. W. Davies, *The Conductivity of Solutions*, 1930, *Trans. Farad. Soc.* **23** (1927), 351, **25** (1929), 129, 133, **26** (1930), 592, **27** (1931), 621, *J. Chem. Soc.* **149** (1930), 2410, 2421. J. N. Brönsted, *J. Am. Chem. Soc.* **44** (1922), 877, **45** (1923), 2898.

‡ G. Scatchard, *Phys. Z.* **33** (1932), 22; *Chem. Rev.* August, 1933. We shall not deal with this theory here. Scatchard derives expressions to take into account the mutual potential energy of two ions, an ion and a neutral molecule, and two neutral molecules. The equations obtained are, however, only qualitative, and are too complex for practical use for interpolation. Moreover, there appear to be some theoretical objections to Scatchard's theory.

sions of a molecule.† At concentrations of this magnitude it is obviously not permissible to replace an ion of finite dimensions by a point charge, as we have done for more dilute solutions. If we are to retain our previous treatment on the basis of Poisson's equation, there is no point in introducing a detailed picture of the way in which two ions approach one another. Debye and Hückel‡ therefore pictured the ion as being a sphere of fixed radius with a dielectric constant D in its interior. In the case of a 1-1-valent electrolyte (which we shall consider first), a charge of $+\epsilon$ or $-\epsilon$ is situated at the centre of the sphere. We introduce a quantity a, which is not identical with the radius of the ions, but represents the mean distance to which the surrounding positive and negative ions can approach. For positive and negative ions of identical dimensions, we should expect a to be of the order of magnitude of an ionic diameter.§ We have previously deduced the expression (207) for the potential round a given ion.‖ The constant A in this expression must now be determined afresh. On the assumptions just formulated, the potential at a point distant r from the centre inside the ionic sphere can be written

$$\Psi = \frac{\epsilon}{D}\frac{1}{r} + B, \tag{563}$$

since it is a well-known theorem in electrostatics that the potential inside a uniformly charged sphere is constant. In order to determine the constants A and B, we employ the boundary conditions at the surface of the sphere. Since we have assumed that the dielectric constant is the same inside and outside the sphere, there is no charge on the surface, and the boundary conditions are that both Ψ and $d\Psi/dr$ shall be continuous across the surface of the sphere. This gives

$$A = \frac{\epsilon}{D}\frac{e^{-\kappa r}}{1+\kappa a}, \qquad B = -\frac{\epsilon\kappa}{D(1+\kappa a)} = \Psi_b. \tag{564}$$

† Cf. p. 105. ‡ Loc. cit., p. 250.

§ We shall show later (p. 255) how far this expectation is fulfilled by the experimental facts.

‖ In place of D_0 we shall introduce D, the dielectric constant of the solution, so that in this chapter κ^2 signifies equation (217) with D in place of D_0. The value of (217) with D_0 will be termed κ_0^2. The distinction is without practical significance, since the dielectric constant which determines the interaction of the ions in solution is certainly not to be identified with the macroscopic dielectric constant of the solution. Moreover, it is only for quite concentrated solutions (several moles per litre) that the dielectric constant of the solution differs appreciably from that of the pure solvent (cf. Hückel's theory, p. 272). There is therefore no point in emphasizing the difference between κ and κ_0 for the concentrations which we shall deal with in this chapter.

It has been shown by Debye and Pauling (*J. Am. Chem. Soc.* **47** (1925), 2129) that the limiting law is not affected by the assumption that the dielectric constant in the neighbourhood of the ion is not the same as that of the solvent.

B represents the potential Ψ_b produced by the ionic atmosphere at the centre of the ionic sphere, as may be seen by reference to (563). The potential energy of a positive ion due to its surroundings is given by

$$u = -\frac{\epsilon^2\kappa}{D(1+\kappa a)}. \tag{565}$$

A comparison with (235) shows that taking into account the finite size of the ion introduces the factor $1/(1+\kappa a)$. For small concentrations, κ is by (227) small compared to unity, and the energy approximates to the value given in (235) for infinitely small ions. For higher concentrations, i.e. larger values of κ, u approaches the value $-\epsilon^2/Da$, i.e. the characteristic length $1/\kappa$ gives way to the quantity a in determining the energy. In the same way as on p. 110, it can be shown that the total electrical energy of the ionic atmospheres is given by

$$U_e = -\frac{N\epsilon^2\kappa}{2D}\left\{\frac{1}{1+\kappa a_1}+\frac{1}{1+\kappa a_2}\right\}, \tag{566}$$

where a_1 and a_2 are the characteristic diameters for the positive and negative ions respectively.

In the general case, where we have $N_1,\ldots,N_i,\ldots,N_s$ ions of different species and charges $z_1\epsilon,\ldots,z_i\epsilon,\ldots,z_s\epsilon$, the total electrical energy of the electrolyte solution is given by

$$U_e = -\sum_i \frac{N_i z_i^2}{2}\frac{\epsilon^2\kappa}{D(1+\kappa a_i)}. \tag{567}$$

We can now derive the free energy of a 1-1-valent electrolyte from the potential Ψ_b at the point occupied by the central ion, just as was done on p. 112. Following Debye, we consider the system central ion + ionic atmosphere as a kind of galvanic element which can be discharged infinitely slowly, isothermally, and reversibly. The maximum work obtained in this discharging process is then obviously equal to the difference between the thermodynamic potentials of the real solution and the ideal solution. Let the charge on the central ion at any moment of the discharging process have fallen from ϵ to $\lambda\epsilon$. From (564) and (217) the potential at the same moment will have fallen from Ψ_b to $\lambda^2\Psi_b$. The differential work obtained in decreasing the charge $\lambda\epsilon$ by $d(\lambda\epsilon)$ is therefore

$$\Psi_b\lambda^2\, d(\lambda\epsilon) = \Psi_b\epsilon\lambda^2\, d\lambda.$$

Since λ varies from 1 to 0 during the process of discharging, the total work obtained from one central ion and its atmosphere is

$$-\int_0^1 \Psi_b\epsilon\lambda^2\, d\lambda = -\frac{e^2\kappa}{D}\int_1^0 \frac{\lambda^2\, d\lambda}{1+\lambda\kappa a}.$$

This result can easily be generalized. If one c.c. of the solution contains n_i ions of the sort i and charge $z_i\epsilon$, the total electrical work A' is given by†

$$A' = -\frac{1}{D}\epsilon^2\kappa V \sum n_i z_i^2 \int_1^0 \frac{\lambda^2\, d\lambda}{1+\lambda\kappa a}$$

$$= \frac{kTV\kappa^3}{4\pi}\int_0^1 \frac{\lambda^2\, d\lambda}{1+\lambda\kappa a}. \tag{568}$$

The diameter of the various ions has been replaced here by a mean diameter a.‡ On integrating (568) we obtain

$$A' = -\frac{1}{4\pi}\frac{kTV}{a^3}\left\{\log(1+a\kappa) - a\kappa + \frac{(a\kappa)^2}{2}\right\}$$

$$= \frac{VkT\kappa^3}{12\pi}\{1-\tfrac{3}{4}a\kappa+\tfrac{3}{5}(a\kappa)^2+\ldots\}. \tag{569}$$

From (244), (253), and (257),

$$1-g = \frac{1}{\bar{P}}\frac{\partial A'}{\partial V}, \tag{570}$$

where g is the osmotic coefficient. Then from (569),

$$1-g = -\frac{1}{4\pi a^3 \sum n_i}\left\{\log(1+a\kappa) - \frac{a\kappa}{2(1+a\kappa)} - \frac{(a\kappa)^2}{2}\right\}, \tag{571}$$

or as a series,

$$1-g = \frac{\kappa^3}{24\pi \sum n_i}\{1-\tfrac{3}{2}a\kappa+\tfrac{9}{5}(a\kappa)^2+\ldots\}. \tag{572}$$

The activity coefficients may be calculated as follows. As we have seen, the term to be added to the free energy of the solution is A' plus A'', the work of charging the ions against their own potential. From p. 114

$$A'' = \sum \frac{z_i^2\epsilon^2 N_i}{2Db_i} - \sum \frac{z_i^2\epsilon^2 N_i}{2D_0 b_i}. \tag{573}$$

The thermodynamic potential of the real solution is thus

$$\Phi = \bar{\Phi} + A' + \sum \frac{z_i^2\epsilon^2 N_i}{2Db_i} - \sum \frac{z_i^2\epsilon^2 N_i}{2D_0 b_i}. \tag{574}$$

If we now vary the number of molecules, keeping the pressure and temperature constant,

$$\delta\Phi = \delta\bar{\Phi} + \frac{\partial A'}{\partial N_i}\delta N_i + \frac{\partial}{\partial N_i}\left(\sum \frac{z_i^2\epsilon^2 N_i}{2Db_i} - \sum \frac{z_i^2\epsilon^2 N_i}{2D_0 b_i}\right)\delta N_i. \tag{575}$$

† A' corresponds to W in equation (247) for very dilute solutions.

‡ For the case of different values of a, see G. Scatchard, *Phys. Z.* **33** (1932), 22.

$\delta\bar{\Phi}$ for ideal solutions is known from (265). If we assume that the dielectric constant is independent of concentration, $\delta\Phi$ for the real solution is given by

$$\delta\Phi = \sum_i \{\bar{\phi}_i + kT\log(\eta_i f_i^*)\}\,\delta N_i, \tag{576}$$

where the f_i^*'s are activity coefficients.† Combining this with (575),

$$\log f_i^* = \frac{1}{kT}\frac{\partial A'}{\partial N_i} \tag{577}$$

or

$$\log f_i^* = -\frac{z_i^2\epsilon^2\kappa}{2DkT(1+\kappa a)}. \tag{578}$$

Combining (578) and (224), the logarithm of the activity coefficient in water at 20° is given by

$$\log_{10} f_i^* = -\frac{z_i^2 . 0{\cdot}505\sqrt{J}}{1+0{\cdot}327\times 10^8 a\sqrt{J}}. \tag{579}$$

Introducing the ionic concentration (88),

$$\log_{10} f_i^* = -\frac{0{\cdot}354 z_i^2\sqrt{\Gamma}}{1+0{\cdot}232\times 10^8 a\sqrt{\Gamma}}. \tag{580}$$

For 1-1-valent electrolytes this becomes

$$\log_{10} f^* = -\frac{0{\cdot}505\sqrt{\gamma}}{1+0{\cdot}327\times 10^8 a\sqrt{\gamma}}. \tag{581}$$

Applications.

We shall first apply the theory to some of the chlorides and nitrates of the alkali metals. Fig. 82 shows the experimental curves for $1-g$ plotted against $\sqrt{(2\gamma)}$. The theoretical Debye-Hückel limiting straight line is also drawn, and the dotted line represents the theory of Ghosh.‡ It will be seen that individual curves of this kind can be well represented by equation (571), the value of a being fixed from a few measurements at higher concentrations. It has been shown, especially by Schärer,§ that up to several tenths of a mole per litre very many solubility measurements can be fitted by the above equation using suitable values for the ionic diameters. The curves in Fig. 83 were calculated from equations (571), using the following values of a, which were calculated from the points corresponding to the highest concentration.

† For concentrated solutions it is necessary to distinguish between the rational activity coefficients f_i^* and the practical activity coefficients f_i and f_i'. (See p. 53.) The difference is negligible up to 0·1 N., but amounts to a few per cent. at 1 N. (See e.g. E. Hückel, *Phys. Z.* **26** (1925), 124.

‡ Cf. p. 95.

§ O. Schärer, *Phys. Z.* **25** (1924), 145.

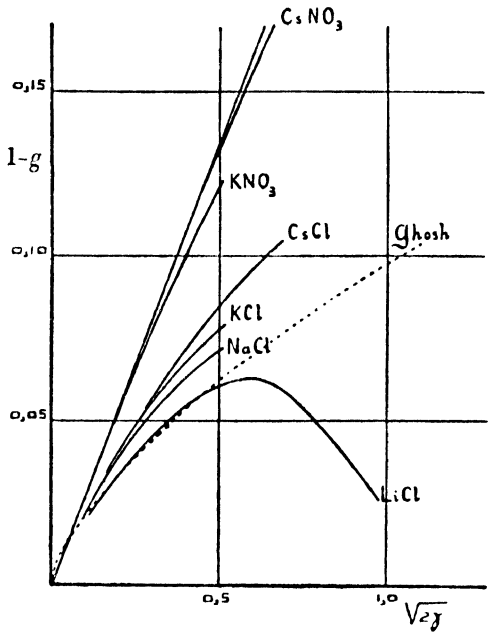

FIG. 82. Osmotic coefficients in aqueous solution.

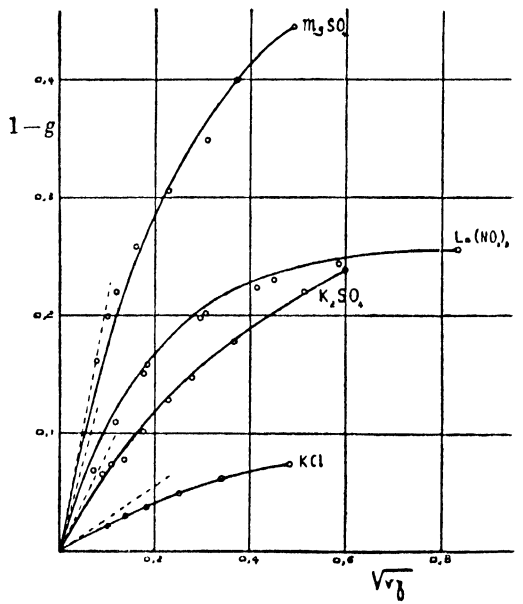

FIG. 83. Osmotic coefficients in aqueous solutions.

NaCl	$a = 4{\cdot}02 \times 10^{-8}$ cm.
KCl	$a = 3{\cdot}76 \times 10^{-8}$ cm.
K_2SO_4	$a = 2{\cdot}69 \times 10^{-8}$ cm.
$La(NO_3)_3$	$a = 4{\cdot}97 \times 10^{-8}$ cm.
$MgSO_4$	$a = 3{\cdot}35 \times 10^{-8}$ cm.

The distance between two neighbouring ions in the crystal lattice is e.g. $3{\cdot}14 \times 10^{-8}$ cm. for KCl and $2{\cdot}82 \times 10^{-8}$ cm. for NaCl. The agree-

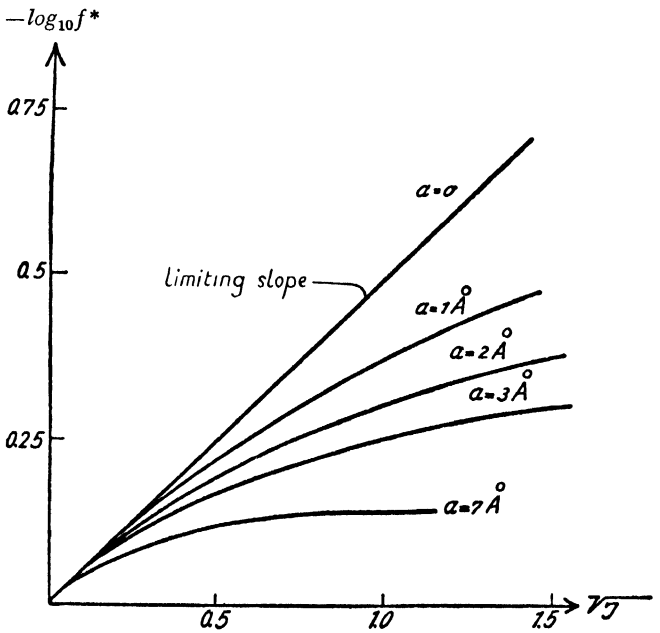

FIG. 84. Effect of ionic diameter on the activity coefficient.

ment for KCl is as good as could be expected, and the large a-value found for NaCl is probably due to hydration.

The results of some more recent measurements of $1-g$ for 1-1-valent electrolytes are shown in Fig. 21. Taking into consideration the great experimental difficulties in carrying out cryoscopic measurements in very dilute solutions, the agreement with equation (571) for concentrations above about 0·01 N. may be considered satisfactory. The experimental results are on the whole well represented by the curves, and the ionic diameters obtained are of the expected order of magnitude.

For the electrolytes so far considered, the effect of the finite ionic radius results according to (580) in a decrease in the activity coefficient. Fig. 84

illustrates this point; $-\log_{10} f^*$ is plotted against $\sqrt{J}$, taking various values for the ionic diameter.

In other cases, the values obtained for a are not at all of the expected magnitude. Thus the activity coefficients of the alkali nitrates and iodates are so small that the ionic diameters derived from the Debye-Hückel equations are impossibly small or even negative.† Table 42 gives the values of Lewis and Randall for $-\log_{10} f$ at 25° for KNO_3. The fifth column contains the values calculated from (581) with

$$a = 0{\cdot}43 \times 10^{-8}.$$

For KIO_3 and $NaIO_3$ it is necessary to take practically zero values of a. It is thus seen that the Debye-Hückel theory appears to break down completely for small ionic radii. As we shall show later, this is due to the tendency of small ions to associate, the activity coefficient being considerably lowered by the formation of ion-pairs. The association effect is thus in the opposite direction to the radius effect.

TABLE 42‡

m	*Lewis and Randall*	*Corrected by Bjerrum*	*Bjerrum's theory*	*Debye-Huckel theory*
0·01	0·038	0·048	0·047	0·048
0·02	0·056	0·066	0·068	0·067
0·05	0·094	0·104	0·105	0·105
0·1	0·136	0·146	0·145	0·147

51. Theories of Ionic Association (Bjerrum, Müller, Gronwall, La Mer, and Sandved)

In order to explain the difficulties met with above, several theories have recently been developed based upon the idea of association of the ions. While Bjerrum introduces association as an additional hypothesis, Müller, Gronwall, La Mer, and Sandved have succeeded in developing a theory on the basis of the original Debye theory, thus rendering superfluous Bjerrum's hypothesis. We shall now treat these theories separately.

† See p. 269.

‡ It should be mentioned that Bjerrum has corrected the values of Lewis and Randall so that they agree with the freezing-point determinations of Adams. As previously stated (p. 64), it is possible that all the values of $-\log_{10} f$ obtained experimentally by Lewis and Randall are in error by a constant amount. While the differences between the values obtained are quite reliable, the extrapolation from 0·01 N. to infinite dilution was carried out on the basis of equation (184) without sufficient experimental confirmation. By adding 0·01 to all the values of Lewis and Randall, Bjerrum obtained values which agree excellently with the theoretical values calculated from either Bjerrum's theory or the Debye-Hückel theory. (Cf. Table 42.) At the concentrations dealt with here, f may be identified with f^*, and m with γ.

A. *Bjerrum's theory. Formation of ion triplets (Bjerrum, Fuoss, Kraus).*

Debye's original considerations, which depend upon the integration of the differential equation (216) in Ψ, can only be approximately correct, since in place of a strict statistical treatment they employ Poisson's equation (199) and assume mean values. Strictly speaking it is necessary to take into account all the possible configurations and energies of the ions in solution in order to calculate the additional free energy term. Milner† was the first to attempt such a calculation, using a not very accurate graphical method of calculation. Milner himself considers that the treatment of Debye and Hückel is less open to criticism than his own.‡

Recently Kramers§ has attempted an investigation of the limits of validity of the Debye theory, using strict statistical mechanics. Kramers finds that the additional free energy term at sufficiently low concentrations is independent of the ionic radius, and approaches a limiting function identical with that of Debye and Hückel. According to Kramers it appears that this state of statistical distribution (independent of the ionic radius) is realized below a certain limiting concentration. For KCl in water at 15° this maximum concentration is about 0·03 N., while salts of higher valency types give much smaller values. At higher concentrations the distribution of the ions becomes dependent upon their radii, on account of the great tendency of oppositely charged ions to associate. The method employed by Debye and Hückel for introducing a correction term involving the ionic sizes is inadmissible according to Kramers, since it considers the atmosphere of free ions and neglects the effect of association. Kramers has not, however, carried out any exact treatment for solutions of higher concentrations.‖

An earlier improvement upon the calculations of Debye and Hückel is due to Bjerrum,†† whose theory of ionic association is supported by the statistical considerations of Kramers. Many experimental results at higher concentrations can be more satisfactorily accounted for by Bjerrum's theory than by the second approximation of Debye and Hückel.

† R. Milner, *Phil. Mag.* **23** (1912), 551.

‡ Cf. the discussion between Scatchard (*Phil. Mag.* **2** (1926), 577) and Nonhebel and Hartley (ibid. **2** (1926), 586) as to whether the results of measurements by the latter authors agree better with the Milner theory or the Debye-Huckel theory.

§ H. A. Kramers, *Proc. Amsterdam*, **30**, 145, 197. See Chapter XI.

‖ Such a treatment would be of great value in connexion with the theory of Gronwall, La Mer, and Sandved (cf. p. 270).

†† N. Bjerrum, *D. Kgl. Dansk. Vid. Selsk. Medd.* **7** (1926), No. 9. See also *Ergeb. d. exakt. Naturwiss.* **6** (1926), 125.

Debye and Hückel chose an arbitrary value for the ionic radius so as to give the best possible agreement between theory and experiment. This, as we have seen, led to the difficulty that very small or negative radii had to be assumed for some salts. Bjerrum's theory has the advantage that the radii assumed are always possible, though sometimes small. Bjerrum first calls attention to the following point, which is of importance at higher concentrations. Debye and Hückel make the assumption† ,

$$\frac{z_i \epsilon \Psi}{kT} \ll 1. \tag{582}$$

This assumption, which also occurs in the statistical treatment of Fowler‡ makes it possible to integrate the differential equation (216). The higher the valencies of the ions, the lower the dielectric constant, and the smaller the mean distance between the ions, the less are we justified in assuming (582). This assumption becomes particularly inadmissible in the case of small ions, which can approach one another very closely. Bjerrum calls two ions which are very close together 'associated', and treats the problem quantitatively as follows. If r has such a value that the effect of other ions can be neglected, then for sufficiently low concentrations the number of i ions in a spherical shell of radius r and thickness dr is given by

$$H = n_i 4\pi r^2 e^{-U/kT}\, dr, \tag{583}$$

the j ion being at the centre of the sphere. In this equation, n_i is the number of i ions per c.c., $-U$ is the energy required to separate the two ions, and $e^{-U/kT}$ is the Boltzmann factor which determines to what extent the configuration in question is favoured by the electrical forces. Bjerrum now assumes that the solvent is a continuous medium of dielectric constant D_0 and that the mutual potential energy of the two ions is determined by Coulomb's law, i.e.

$$-U = \frac{-z_i z_j \epsilon^2}{D_0 r}, \tag{584}$$

where z_i and z_j are the valencies of the ions. This assumption implies that the ions are spheres with the charge situated centrally, and that the solvent may be treated as a continuous medium of dielectric constant D_0. Bjerrum himself has pointed out that it is certainly inaccurate to assume the validity of Coulomb's law down to such small interionic distances. The potential energy at such small distances must also largely depend upon quantum-mechanical exchange forces, as well as polarization and dispersion forces, which are known to follow quite

† See p. 102. ‡ See p. 332.

different laws. A more exact statistical treatment of electrolyte solutions is only possible on the basis of a more detailed knowledge of these laws.

Fig. 85 illustrates the relative probability of ion-pairs with different interionic distances calculated by Bjerrum for monovalent ions in water at 18°. Curve I shows the distribution for uncharged particles, i.e. $U = 0$. Curve III shows the frequency of ionic pairs formed from ions of like charges, i.e. $-U$ is negative (see (584)). These pairs are of course considerably less frequent than those formed from uncharged

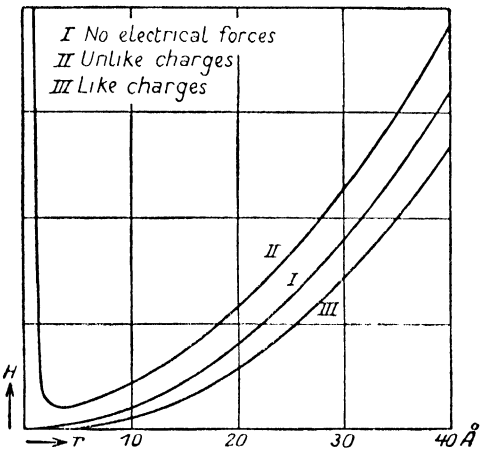

FIG. 85. The distribution of ion-pairs (Bjerrum).

particles. Curve II is the most important: it shows that the number of ion pairs formed from oppositely charged ions ($-U > 0$) first decreases with decreasing distance r, passes through a minimum, and then increases again rapidly, becoming infinite for $r = 0$. Bjerrum points out that a more exact quantum-mechanical treatment would probably lead to a curve similar to that in Fig. 85, so that the following deductions should be qualitatively correct, though there may be quantitative differences. This supposition is supported by the success of Bjerrum's treatment, which can of course be tested by calculation. If we call the interionic distance corresponding to the minimum in the curve q_0, then a simple calculation gives†

$$q_0 = \frac{\epsilon^2 z_i z_j}{2D_0 kT}. \tag{585}$$

From (584) the work of separating two oppositely charged ions at a distance q_0 is $2kT$, i.e. the energy necessary to dissociate the ion-pair is four times as great as the mean kinetic energy per degree of freedom.

† By putting $\partial H/\partial r = 0$.

For smaller values of r this energy increases very rapidly. In water at 18° the minimum for monovalent ions is at $q_0 = 3{\cdot}52$ Å. Large ions such as K^+ and Cl^-, for which the sum of the ionic radii is greater than 3·5 Å., will thus have but little tendency to associate. For such ions, the method of treatment employed by Debye and Hückel will be approximately correct. On the other hand, for ions which are smaller or have a higher ionic charge, the interionic forces will lead to a considerable association even in water, and in non-aqueous solvents of lower dielectric constant, association to groups of two or more ions will be very considerable. Bjerrum now arbitrarily terms as associated all ion-pairs which are closer than the minimum distance in (585), all other ions being termed free. This distinction between free and associated ions is made quite arbitrarily, since in the association due to interionic forces there is no discontinuity such as is often met with in chemical processes. Thus in the thermal dissociation of hydrogen iodide, the degree of dissociation can be stated accurately, since transitional states between dissociated and undissociated molecules are not present in appreciable concentrations. In the case of free and associated ions as defined by Bjerrum, such transition states occur in finite though small amounts. The smallest amounts correspond to the minimum in the probability curve III in Fig. 85. According to Bjerrum, there can be 100 per cent. ionization without 100 per cent. dissociation, and the ions associate together without any appreciable deformation of their electron orbits,† and without the formation of any more permanent chemical linkage.

If the true degree of association $1-\alpha^*$ is known, the activity coefficient of the solution is determined solely by the free ions which may not approach one another more closely than the distance q_0. As long as this distance is very small, $1-\alpha^*$ can be obtained by integrating (583) from q_0 up to the sum of the ionic radii. For 1-1-valent electrolytes this gives

$$1-\alpha^* = \frac{4\pi \mathrm{N}}{1{,}000}\gamma \int_{q_0}^{a} e^{-U/kT} r^2\, dr, \tag{586}$$

or, introducing the abbreviations

$$y = \frac{\epsilon^2}{rD_0 kT}, \qquad b = \frac{\epsilon^2}{aD_0 kT}, \qquad Q(b) = \int_2^b e^y y^{-4}\, dy, \tag{587}$$

† Fajans is of the opinion that this assumption is incorrect. Recent work on the absorption of light by the alkaline earth halides provides strong evidence for the formation of Bjerrum ion pairs. There are, however, undoubtedly cases in which a more permanent chemical linking plays a part.

$$1-\alpha^* = \gamma \frac{4\pi \mathbf{N}}{1{,}000}\left(\frac{\epsilon^2}{D_0 kT}\right)^3 Q(b), \tag{588}$$

where a is the sum of the ionic radii. In order to be able to carry out the calculations for greater degrees of association, Bjerrum proceeds as follows.

It is thermodynamically permissible to apply the law of mass action to the equilibrium between free and associated ions provided that the appropriate activities of the ions are introduced correctly. If a_1 and a_2 are the activities of the free ions and a_{12} the activity of the product of association, then by (133)

$$\frac{a_{12}}{a_1 a_2} = \frac{1}{K_a}. \tag{589}$$

The concentration of the association product is $\gamma(1-\alpha^*)$, and that of the free ions $\gamma\alpha^*$. The associated ion pairs can be considered as neutral molecules, and their activity coefficients taken as unity, so that

$$a_{12} = \gamma(1-\alpha^*). \tag{590}$$

For the activity coefficients (f) of the free ions we shall employ the formulae of Debye and Hückel, taking the concentration as $\alpha^*\gamma$ and the ionic diameter as q_0. If the centres of two oppositely charged ions approach to a distance less than q_0, they are no longer to be considered as free ions, and the effects of their charges upon the free ions cancel out. It is assumed that the Debye-Hückel equations are applicable taking the ionic diameter as q_0. We thus have

$$a_1 = a_2 = \gamma\alpha^*(f). \tag{591}$$

Then from (589), (590), and (591),

$$\frac{(1-\alpha^*)\gamma}{\{\gamma\alpha^*(f)\}^2} = \frac{1}{K_a}. \tag{592}$$

For sufficiently small values of $1-\alpha^*$ and γ (592) reduces to

$$1-\alpha^* = \gamma/K_a. \tag{593}$$

In order to calculate K_a, Bjerrum proceeds as follows. Substituting in (592) the value of K_a obtained from (588), we have

$$\frac{1-\alpha^*}{\alpha^{*2}} = (f)^2\gamma \frac{4\pi \mathbf{N}}{1{,}000}\left(\frac{\epsilon^2}{D_0 kT}\right)^3 Q(b). \tag{594}$$

Since (f) is a fairly complicated function of $1-\alpha^*$, (594) cannot be solved explicitly, but the value of $1-\alpha^*$ may be obtained by a few successive approximations.

Table 43 gives some values calculated by Bjerrum for the degree of association of univalent ions in water at 18°.†

† e.g. for 0·1 N. KNO_3 the degree of association is about 10 per cent., since from

TABLE 43

Values for the degree of association of univalent ions in water at 18° C. (Bjerrum)

Sum of the ionic radii	*Concentration in moles per litre*								
	0·0001	0·0005	0·001	0·005	0·01	0·05	0·1	0·5	1
2·82 Å.	..	..	..	0·002	0·005	0·017	0·029	0·090	0·138
2·35 Å.	..	..	0·001	0·004	0·008	0·028	0·048	0·140	0·206
1·76 Å.	..	..	0·001	0·007	0·012	0·046	0·072	0·204	0·286
1·01 Å.	..	0·002	0·004	0·016	0·030	0·105	0·163	0·360	0·457
0·70 Å.	0·001	0·006	0·011	0·048	0·083	0·240	0·336	0·568	0·651
0·47 Å.	0·027	0·106	0·177	0·418	0·529	0·741	0·804	0·901	0·928

If $1-\alpha^*$ and (f) are known, the activity coefficient of the electrolyte considered as completely dissociated is given by

$$f = (f)\alpha^*. \tag{595}$$

In the calculation described above, higher types of association have been neglected, which is permissible for fairly dilute solutions. Comparison with experiment shows excellent agreement up to a few tenths of a mole per litre. It is especially noteworthy that in Bjerrum's theory the ionic radii are always positive and have much more probable values than those obtained in the theories of Debye and Hückel or Hückel (cf. Table 44). Bjerrum supposes that at higher concentrations, and especially in solvents of lower dielectric constants, association complexes containing more than two ions are formed. In this case the methods of calculation described above will fail. Bjerrum's ideas are in excellent qualitative agreement with the measurements of Walden.† It has been recently shown by Fuoss and Kraus‡ that in solvents of low dielectric constant, salts are very much associated and the dependence of the conductivity upon the concentration shows peculiarities (observed also in water at very high concentrations). Thus, for a symmetrical electrolyte, while the ion pairs formed contribute nothing to the conductivity, higher unsymmetrical association products will be charged and hence conduct current. Thus if the transformation of ionic pairs to higher association products involves the production of conducting aggregates, this will account for the rise of equivalent conductivity with increasing concentration often observed at high con-

Table 42 the sum of the ionic radii is 1·57 Å. It is of interest to compare this value with the considerably smaller value obtained by Nernst (cf. p. 289).

† P. Walden, *Z. phys. Chem.* **94** (1920), 295; *Z. Elektrochem.* **26** (1920), 61; *Kolloid Z.* **27** (1920), 97. See also p. 79.

‡ Fuoss and Kraus, *J. Am. Chem. Soc.* **55** (1933), 2387.

centrations. Gross and Halpern† have shown that the behaviour of salts in solvents of low dielectric constant is accounted for at least qualitatively by Debye's theory.

This formation of ion-triplets has recently been treated in detail by Fuoss and Kraus.‡ As an example we may consider the case of the conductivity of tetraisoamylammonium nitrate in mixtures of dioxane and water. On examining the curves given by these authors, it will be noted that when the dielectric constant becomes about 10, the curve

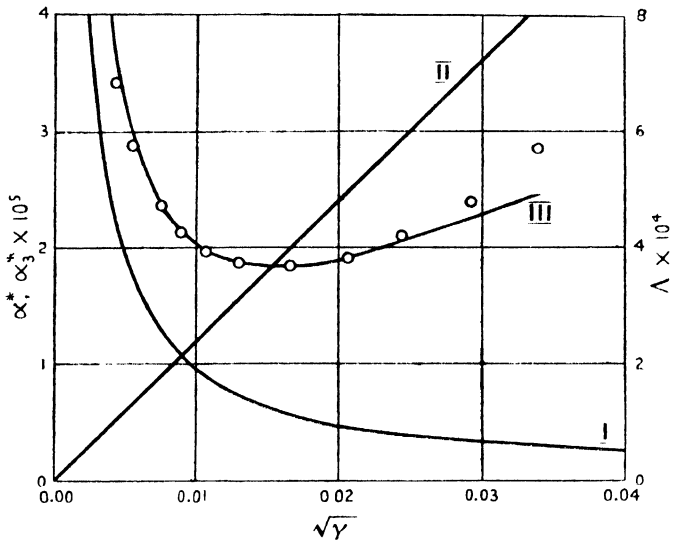

FIG. 85 A. Conductivity and ionization curves for tetraisoamylammonium nitrate in dioxane containing 1·26 per cent. water.

exhibits a new behaviour at moderate concentrations: the molar conductivity passes through a minimum and subsequently increases with increasing concentration. This conductivity minimum was observed long ago by Walden, but as it usually occurs at concentrations of 0·01 N. or higher, it has usually been considered as a property of concentrated solutions. Kraus and Fuoss have, however, shown that, as the dielectric constant decreases, the minimum is displaced to lower concentrations, and can very well appear at concentrations which are usually considered as dilute.§

The question now arises as to how this phenomenon is to be explained.

† P. Gross and O. Halpern, *Phys. Z.* **26** (1925), 636.

‡ Fuoss and Kraus, *J. Am. Chem. Soc.* **55** (1933), 2387.

§ The limiting equivalent conductivity of the salt in question is about 30. It is seen from the curve that in a mixture containing 0·6 per cent. of water ($D \sim 2{\cdot}38$) the ionic concentration corresponding to the minimum is extremely small.

The solution contains a few free ions, but a comparatively large number of ion-pairs. The latter are electrically neutral, but are dipoles, and hence possess an external field. We may therefore anticipate an interaction between the ions and the dipoles, leading to the formation of ion triplets according to one of the equations

$$(+-)+(+) \leftrightharpoons (+-+)$$
$$(-+)+(-) \leftrightharpoons (-+-).$$

If we assume for the sake of simplicity that the equilibrium constants of both these reactions are equal to k_3, then the formation of ion triplets assumed by Fuoss and Kraus leads to a conductivity function which agrees with the experimental data (cf. Fig. 85 A). Let the total concentration be γ, the fraction of free ions be α^*, and the fraction of ion triplets α_3^*. We may then write the following approximate mass-law equations

$$\frac{[+][-]}{[+-]} = K \simeq \gamma\alpha^{*2}, \qquad \text{i.e.} \quad \alpha^* \simeq \left(\frac{K}{\gamma}\right)^{\frac{1}{2}},$$
$$\frac{[+-][-]}{[-+-]} = k_3 \simeq \gamma\frac{\alpha^*}{\alpha_3^*}, \qquad \text{i.e.} \quad \alpha_3^* \simeq \frac{K^{\frac{1}{2}}\gamma^{\frac{1}{2}}}{k_3},$$

the activity coefficients being for the present put all equal to unity. The molar conductivity Λ is then given by

$$\Lambda = \alpha^*\Lambda_\infty + \alpha_3^*\Lambda_{3\infty} = \Lambda_\infty K^{\frac{1}{2}}\gamma^{-\frac{1}{2}} + \frac{\Lambda_{3\infty}K^{\frac{1}{2}}\gamma^{\frac{1}{2}}}{k_3} = A\gamma^{-\frac{1}{2}} + B\gamma^{\frac{1}{2}}, \quad (595\,a)$$

neglecting the interionic forces. In this equation $\Lambda_{3\infty}$ is the limiting equivalent conductivity of $(+-+)$ or $(-+-)$, and Λ_∞ that of $(+-)$. The necessary condition for a minimum is

$$A = B\gamma_{\min},$$

which gives for the quantities k_3 and K

$$k_3 = \frac{\Lambda_{3\infty}}{\Lambda_0}\gamma_{\min}, \qquad (595\,b)$$
$$K = (\gamma\Lambda^2)_{\min}/4\Lambda_\infty^2.$$

For solvents of diclectric constant less than about 3, the interionic forces must be taken into account both in the conductivity and the mass-law expressions. This treatment leads to the conductivity function

$$\frac{\Lambda\gamma^{\frac{1}{2}}\exp\left\{-\dfrac{\beta''}{0{\cdot}4343}\left(\dfrac{\gamma\Lambda}{\Lambda_\infty}\right)^{\frac{1}{2}}\right\}}{\left\{\Lambda-\alpha''\left(\dfrac{\gamma\Lambda}{\Lambda_\infty^3}\right)^{\frac{1}{2}}\right\}\left(1-\dfrac{\Lambda}{\Lambda_\infty}\right)^{\frac{1}{2}}} = \Lambda\gamma^{\frac{1}{2}}g(\gamma)$$
$$= \Lambda_\infty K^{\frac{1}{2}} + \frac{\Lambda_{3\infty}K^{\frac{1}{2}}}{k_3}\left(1-\frac{\Lambda}{\Lambda_\infty}\right)\gamma, \qquad (595\,c)$$

where β'' is Debye's constant

$$\beta'' = \frac{\epsilon^2}{2D_0 kT}\left(\frac{8\pi N\epsilon^2}{1{,}000 D_0 kT}\right)^{\frac{1}{2}} \tag{595 d}$$

and α'' is Onsager's constant

$$\alpha'' = \frac{8{\cdot}18\times 10^5 \Lambda_\infty}{(D_0 T)^{\frac{1}{2}}} + \frac{82}{\eta(D_0 T)^{\frac{1}{2}}}. \tag{595 e}$$

Equation (595 c) can be tested by means of the data shown in Fig. 85 A, by plotting $\Lambda\gamma^{\frac{1}{2}}g(\gamma)$ against $\{1-(\Lambda/\Lambda_\infty)\}\gamma$. Fuoss and Kraus have shown

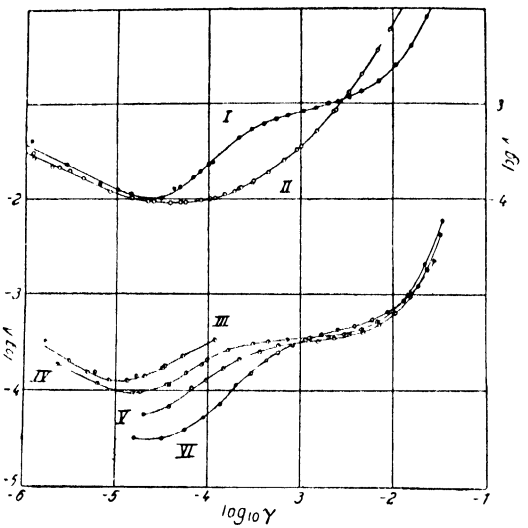

FIG. 85 B. The conductivity of tetraisoamylammonium salts in benzene.

that a straight line is obtained, from which they conclude that the assumption of ion triplets leads to a conductivity function in agreement with the experimental data. Fig. 85 A shows the molar conductivity, Λ (curve III), the fraction of the solute present as ions, α^* (curve I), and the fraction present as ion triplets, α_3^* (curve II), all plotted against the square root of the molar concentration γ. The equilibrium constant k_3 for the formation of ion triplets has the value $k_3 = 8\times 10^{-5}$. The circles represent the observed points, and curve III is calculated from equation (595 c). On the other side of the minimum, the experimental conductivities increase more rapidly than proportional to $\gamma^{\frac{1}{2}}$: this is probably due to the formation of higher complexes, which would introduce higher terms into the conductivity function. To illustrate this point further, Fig. 85 B shows the conductivity curves for various

tetraisoamylammonium salts dissolved in benzene. In the case of the nitrate and the picrate, terms in $\gamma^{\frac{3}{2}}$ and $\gamma^{\frac{5}{2}}$ must be introduced in order to represent the experimental results. For specially symmetrical salts it is necessary to introduce both negative terms in even powers of $\gamma^{\frac{1}{2}}$ and positive terms in odd powers of $\gamma^{\frac{1}{2}}$. If the salt is unsymmetrical with respect to the charge or size of its ions, the minimum appears less or not at all. In solvents of low dielectric constant, the conductivity function can in general be expressed as a power series of the form

$$\Lambda = a_{-1}\gamma^{-\frac{1}{2}} + a_1\gamma^{\frac{1}{2}} - a_2\gamma + a_3\gamma^{\frac{3}{2}} - \ldots .$$

By applying Bjerrum's considerations on ion association to the formation of ion triplets† it is possible to treat theoretically the dependence of the conductivity minimum upon the dielectric constant, and thus to obtain a theoretical basis for Walden's rule $D^3 = \text{const.}\,\gamma_{\min}$. It is in fact found that for dielectric constants greater than 23·2, the ion triplets are no longer stable to the thermal motion, and the conductivity minimum no longer appears.

We shall return in the next section to a comparison of Bjerrum's theory with experiment.

B. *The relation of Bjerrum's theory to the theories both of Müller, and Gronwall, La Mer, and Sandved.*

While Bjerrum avoids the integration of equation (202) by invoking the law of mass action, Müller‡ has solved the unabbreviated form of equation (202) by graphical means and Gronwall, La Mer, and Sandved§ have developed an analytical method for carrying out the same integration. In this way they have succeeded in obtaining the complete expression for the mean value of the total potential of an ion in solution for ions of any dimensions. It is of interest that this work renders superfluous the hypothesis of association introduced by Bjerrum. Müller showed that the critical ionic diameter, above which the Debye-Hückel approximation is valid, is 1·76 Å. for 1-1-valent electrolytes, while Bjerrum obtained the value 3·52 Å. for this limit. However, the work of Müller (and also that of Kramers) provided a justification of the method of approximation used by Bjerrum, especially as Bjerrum was able to show that the results are not much dependent upon the exact value taken for the interionic distance which separates free and

† See Fuoss and Kraus, loc. cit., p. 2398.

‡ H. Müller, *Phys. Z.* **28** (1927), 324.

§ Gronwall, La Mer, and Sandved, *Phys. Z.* **28** (1928), 358; La Mer, Gronwall, and Greiff, *J. Phys. Chem.* **35** (1931), 2245.

associated ions.† Fig. 86 shows $-\log_{10} f$ as a function of $\sqrt{\gamma}$ according to the theories of Debye and Hückel (dotted curves) and of Bjerrum.‡ The figure refers to 1-1-valent electrolytes in water at 18°. The curves obtained by Müller (not shown in the figure) lie a little lower than those of Bjerrum. For ionic diameters above 3·5 Å., all three theories are in good agreement. For smaller diameters differences appear: the curves of Bjerrum and Müller become much higher than the Debye limiting straight line, and give activity coefficients which decrease rapidly with

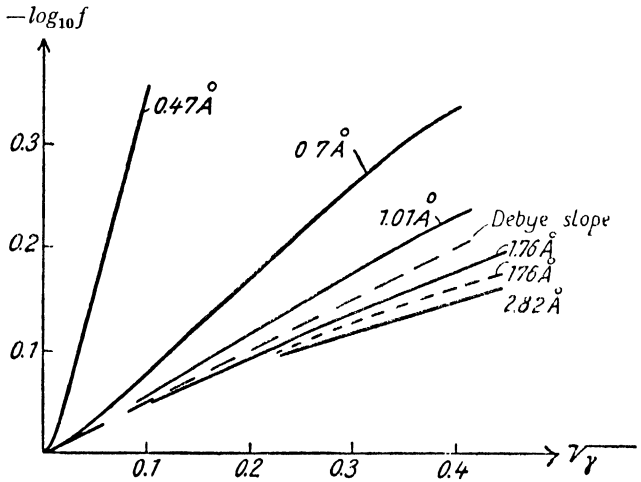

FIG. 86. The effect of the ionic diameter on the activity coefficients (Bjerrum).

decreasing ionic radius. The effect of ionic association is always to decrease the activity coefficients, while the radius effect acts in the opposite direction. According to Bjerrum, all the curves become tangential to the Debye limiting straight line at the origin, but this

† Müller used a graphical method, and derived the activity coefficients by means of the Güntelberg principle (see N. Bjerrum, *Z. phys. Chem.* **119** (1926), 145.) This principle states that the work of discharging one ion is equal to the electrostatic part of the thermodynamic potential of that ion. Gronwall, La Mer, and Sandved have employed Debye's charging process (see p. 113), and were of the opinion that the method used by Muller would give widely different results. Muller has, however, shown that the difference between the two methods is practically negligible. (See Muller, *Phys. Z.* **29** (1928), 78.) It has been recently shown by Onsager (*Chem. Rev.*, August 1933) in a critical examination of the problem that both methods of treatment are correct, and that the discrepancy lies in the application of the Poisson-Boltzmann equation, which is not strictly correct, especially for unsymmetrical electrolytes.

‡ It is interesting to compare Fig. 86 with the corresponding curves obtained from the theory of Gronwall, La Mer, and Sandved (Fig. 88). The curves of the latter authors resemble very much those of Bjerrum.

occurs at lower concentrations the more the ionic radius deviates above or (more especially) below a certain value.

By means of simple transformations the theories of Bjerrum and Müller can be applied to the general case of z-z-valent (and also unsymmetrical) electrolytes.† The minimum in the association curve and the limit of validity will be z^2 times as high as for 1-1-valent electrolytes, so that association has a much greater effect for polyvalent ions. We shall show shortly that the theory of Gronwall, La Mer, and Sandved gives for this limiting value

$$r_{\min} = \frac{4{\cdot}16 \times 10^{-4}}{D_0 T} z_i^2 \text{ cm.} \tag{596}$$

It will thus be seen that the dielectric constant has a great effect upon this critical distance. Bjerrum has carried out a thorough comparison of his theory with experimental results. Just as in the theory of Debye and Hückel there is only one arbitrary constant, the ionic diameter a. The great advantage of the theories both of Bjerrum and of Gronwall, La Mer, and Sandved is that they give much more probable values for the ionic diameters than the theory of Debye and Hückel. For large ionic diameters, all three theories give substantially the same values. For the alkali nitrates and nitrates, however, very different results are obtained. Table 44 shows the values of the ionic diameters necessary to reproduce the experimental activity coefficients according to the three theories.

TABLE 44

Ionic diameters in Å., calculated from activity coefficients by Bjerrum; Debye and Hückel; Gronwall, La Mer, and Sandved

Electrolyte	KIO_3 $NaIO_3$	KNO_3	KCl	NaCl	K_2SO_4	$MgSO_4$ $CdSO_4$ $CuSO_4$	$La(NO_3)_3$
Bjerrum	1·33	1·57	3·40	4·02	3·8	4·2	6·4
Debye-Hückel	0·03	0·43	3·40	4·02	2·69	3·0	4·97
Gronwall-La Mer-Sandved	1·25	1·40	3·40	4·02	3·6	3·7	..

† See N. Bjerrum, *Kgl. Dansk Vid. Selsk.* **7** (1926), 9, 32. Bjerrum showed that the activity coefficients are approximately the same for all electrolytes having the same values of

$$\gamma \frac{|z_1|+|z_2|}{2} \left(\frac{|z_1 z_2|}{D_0 T}\right)^3 \quad \text{and} \quad \frac{a}{z_1 z_2} D_0 T.$$

It would be of interest to compare this point with experiment, and also with the theory of Gronwall, La Mer, and Sandved. It seems probable that the latter theory will in general give results at variance with Bjerrum's theory.

The theories of Bjerrum and of Gronwall, La Mer, and Sandved give for $NaIO_3$ and KNO_3 ionic diameters of 1·3 and 1·5 Å. respectively, which still seem rather small. The reason for this has not been further investigated. A comparison with the experimental results for $MgSO_4$, $CdSO_4$, and $CuSO_4$ shows that for large diameters the agreement is better than with the Debye-Hückel theory. The table also shows that for unsymmetrical electrolytes, e.g. K_2SO_4 and $La(NO_3)_3$, the theories of Bjerrum and of Gronwall, La Mer, and Sandved lead to greater ionic diameters than the theory of Debye and Hückel.

C. *The theory of Gronwall, La Mer, and Sandved.*

(*a*) *General Theory.* Gronwall, La Mer, and Sandved succeeded in obtaining a mathematical series for the potential and free energy of more concentrated solutions, and hence also for the osmotic coefficient and the logarithm of the activity coefficient. They started with the differential equation resulting from (199) and (215), first obtained by Debye, i.e.

$$\Delta\Psi = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\Psi}{dr}\right) = -\frac{4\pi}{D}\Pi = -\frac{4\pi}{D}\epsilon\sum_{j=1}^{s} n_j z_j e^{-z_j\epsilon\Psi/kT}. \qquad (597)$$

Developing the electric density Π as a series, we have

$$\Pi = \frac{\epsilon}{kT}\sum_{1}^{s} n_j z_j - \frac{\epsilon^2\Psi}{kT}\sum_{1}^{s} n_j z_j^2 + \frac{\epsilon^3\Psi^2}{2k^2T^2}\sum_{1}^{s} n_j z_j^3 - \ldots. \qquad (598)$$

Since the solution is electrically neutral, $\sum n_j z_j = 0$: further, for any mixture of symmetrical electrolytes it will be seen that all terms in (598) involving odd powers of z_j will vanish. In this case (598) reduces to the simple series

$$\Pi = -\sum n_j \epsilon_j z_j \sinh\frac{\epsilon z_j \Psi}{kT}. \qquad (599)$$

For symmetrical electrolytes, $\sum n_j z_j^3 = 0$. If, however, the valencies of the cations are not equal to those of the anions, as e.g. in some solubility measurements previously referred to,† then we may have either $\sum n_j z_j^3 > 0$ or < 0. The deviations from Debye's theory observed in these cases are probably due to this fact. The solution of the differential equation (597) must satisfy the following conditions,

$$\Psi = 0 \quad \text{for} \quad r \to \infty$$

$$\frac{d\Psi}{dr} = -\frac{\epsilon z_i}{D}\frac{1}{a_i^2} \quad \text{for} \quad r = a_i. \qquad (600)$$

† See p. 134. Cf., however, the critical discussion of L. Onsager, *Chem. Rev.*, August 1933.

The subsequent calculations consist merely of replacing (597) by a single integral equation† with the boundary conditions (600). The solution of this equation may be obtained in the form of a series. Just as in the treatment of Debye previously described,‡ in order to calculate the free energy, we need the potential Ψ_i at the ion i. Introducing the abbreviation

$$x_i = \kappa a_i \tag{601}$$

it is found that the potential at the point x_i is given by the equation

$$\Psi_i(x_i) = \frac{kT}{\epsilon} \sum_{m=1}^{\infty} \left(\frac{\epsilon^2 z_i}{-Da_i kT} \right)^m \psi_m(x_i, x_i), \tag{602}$$

where the ψ_m's are functions which can be evaluated by means of recurrence formulae. By means of the charging process previously described, the electrical part of the free energy F_e can be calculated, giving

$$\frac{F_e}{kT} = \sum_{j=1}^{s} N_j \int_0^1 \epsilon z_j \Psi_j^{(\lambda)} \, d\lambda - \sum_{j=1}^{s} \frac{N_j z_j^2 \epsilon^2}{2D_0 a_j kT}. \tag{603}$$

The functions $\Psi_i^{(\lambda)}$ are derived from (602) by replacing ϵ by $\lambda\epsilon$. Combining (602) and (603),

$$\frac{F_e}{kT} = -\sum_{j=1}^{s} N_j z_j \sum_{m=1}^{\infty} \left(\frac{\epsilon^2 z_j}{-Da_j kT x_j^2} \right)^m \int_0^x x^{2m-1} \psi_m(x, x) \, dx - \sum_{j=1}^{s} \frac{N_j z_j^2 \epsilon^2}{2D_0 a_j kT}. \tag{604}$$

The activity coefficient of an ion of the ith sort is given by (577) as

$$\log f_i = \frac{1}{kT} \frac{\partial F_e}{\partial N_i}. \tag{605}$$

If the solution contains M moles of a salt,

$$N_i = \mathbf{N} M \nu_i \tag{606}$$

and the activity coefficient of the salt is given by

$$(\nu_1 + \nu_2) \log f = \frac{\partial}{\partial M} \frac{F_e}{\mathbf{N}kT}. \tag{607}$$

(*b*) *Symmetrical electrolytes.* For a symmetrical electrolyte

$$(z_1 = -z_2 = z, \quad \nu_1 = \nu_2 = 1)$$

† See Courant-Hilbert, *Methoden d. mathematischen Physik*, 2nd edition, 302, 1931.

‡ See p. 111.

making the assumption $a_1 = a_2 = a$, (604) and (605) give†

$$\log f = z\sum_{m=0}^{\infty}\left(\frac{\epsilon^2 z}{DkTa}\right)^{2m+1}\left[\frac{1}{2}\left(1-10^{-3}\gamma\frac{\partial V}{\partial M}\right)\left(1-\frac{\gamma}{D}\frac{\partial D}{\partial \gamma}\right)\psi_{2m+1}(x,x)-\right.$$

$$\left.-\left(2m-10^{-3}(2m+1)\gamma\frac{\partial V}{\partial M}\right)\frac{1}{x^{4m+2}}\int_0^x x^{4m+1}\psi_{2m+1}(x,x)\,dx\right]-\frac{\epsilon^2 z^2}{2kTD_0 a}, \tag{608}$$

where by (601) $x = \kappa a.$

The quantity $10^{-3}\gamma\partial V/\partial M$ is for dilute solutions negligible compared to unity and the integer $2m$. It is also permissible (at least for concentrations below 0·01 N.) to write

$$1-\frac{\gamma}{D}\frac{dD}{d\gamma} = 1.$$

Introducing these simplifications into (608), we obtain

$$\log f = z\sum_{m=0}^{\infty}\left(\frac{\epsilon^2 z}{D_0 kTa}\right)^{2m+1}\left[\tfrac{1}{2}\psi_{2m+1}(x,x)-\right.$$

$$\left.-\frac{2m}{x^{4m+2}}\int_0^x x^{4m+1}\psi_{2m+1}(x,x)\,dx\right]-\frac{\epsilon^2 z^2}{2kTD_0 a}. \tag{609}$$

Above 0·01 N. the term $\frac{\gamma}{D}\frac{\partial D}{\partial \gamma}$, which represents the variation of the dielectric constant with concentration, is probably not negligible. The experimental evidence on this point is fragmentary and contradictory, but it would be of interest to investigate this point in the theory of Gronwall, La Mer, and Sandved with reference to the recent measurements of Wien (loc. cit., p. 226). An attempt to take into account the variation of dielectric constant with concentration has also been made by Huckel (*Phys. Z.* **26** (1925), 93). The correction for variation in dielectric constant occurs in Huckel's theory in a less general form than in (608), but the problem which he has attacked is a very important one. While most of the effects dealt with in this chapter result in a decrease in the activity coefficient (only the radius effect causes an increase), Huckel seeks to explain the increase in activity coefficient which is often met with at high concentrations, values greater than unity being often obtained. This must be due to some large effect which in concentrated solutions quite outweighs the effects dealt with in this chapter. In an attempt to elucidate the factors which are most important in concentrated solutions, Hückel entirely neglects all effects except the variation of dielectric constant. (A detailed treatment taking all effects into account

† Miss Greiff has pointed out (private communication from Professor La Mer) that there are minor errors in equations (34) and (34 a) of the Gronwall-La Mer-Sandved paper. In equation (34), $m-1-10^{-3}\gamma(\partial V/\partial M)$ should be replaced by $m-1-10^{-3}m\gamma(\partial V/\partial M)$, and in equation (34 a), $2m-10^{-3}\gamma(\partial V/\partial M)$ should be replaced by

$$2m-10^{-3}(2m+1)\gamma(\partial V/\partial M).$$

appears hopeless.) Hückel assumes a linear relation between the dielectric constant and the concentration, and on this basis attempts to account for the activity coefficients up to very high concentrations (1 N.). Hückel's formulae reproduce the experimental results surprisingly well, though it is doubtful whether they can be considered as more than convenient empirical formulae for interpolation. Hückel's theory is also able to account for the behaviour of mixtures, provided that no complicating ions such as $SO_4^{=}$ and OH^- are present. See especially H. S. Harned and G. Åkerlöf, *Phys. Z.* **27** (1926), 411; J. E. Hawkins, *J. Am. Chem. Soc.* **54** (1932), 4481; also G. Scatchard, *J. Am. Chem. Soc.* **47** (1925), 2098; E. Güntelberg, *Z. phys. Chem.* **123** (1926), 199; W. W. Lucasse, *J. Am. Chem. Soc.* **48** (1926), 626; *Z. phys. Chem.* **121** (1926), 254; H. S. Harned, *J. Am. Chem. Soc* **48** (1926), 326; H. S. Harned and S. M. Douglas, ibid. **48** (1926), 3095. Later measurements by M. Randall and C. T. Langford (*J. Am. Chem. Soc.* **49** (1927), 1445) differ considerably from Åkerlöf's results for H_2SO_4 and Na_2SO_4, so that the constants employed by Hückel need revision. See further G. B. Bonino, *Atti d. Soc. Ligustica d. Sci. e. Lett. d. Genova*, Fasc. III, p. 1, 1926; A. W. Hutchison and G. C. Chandlee, *J. Am. Chem. Soc.* **53** (1931), 2881; G. Åkerlöf, ibid. **52** (1930), 2353; H. S. Harned and O. E. Schupp, ibid. **52** (1930), 3886; J. J. Johnston and C. Grove, ibid. **53** (1931), 3976; H. S. Harned and C. M. Mason, ibid. **54** (1932), 1439; H. S. Harned and L. F. Nims, ibid. **54** (1932), 423. The last paper shows especially plainly that the constants of Hückel's theory vary considerably with the temperature. B. Saxton and R. P. Smith (ibid. **55** (1933), 2626) have applied Hückel's theory to KCl solutions at 100°. H. S. Harned and R. W. Ehlers (ibid. **55** (1933), 2179) have combined Hückel's theory with that of Gronwall, La Mer, and Sandved, and are thus able to account excellently for the activity coefficients of HCl from 0–4 M. over a temperature range of 0–60°. The values deduced for the specific heats by the Gibbs-Helmholtz equation (cf. p. 123) agree well with the experimental results of Rossini. In many cases, e.g. HCl and LiCl, the constants in Hückel's equation would lead to a negative dielectric constant at very high concentrations, which is of course absurd. Again, Huckel's theory can hardly be reconciled with Brönsted's principle of specific interaction (see E. Güntelberg, *Z. phys. Chem.* **125** (1926), 245). The measurements of Wien mentioned above, and also recent work by Malsch (*Ann. d. Phys.* **84** (1927), 841; (2) **3** (1929), 803; *Phys. Z.* **29** (1928), 770; **30** (1929), 837) on the effect of the electric fields upon dielectric constants, appear to be in opposition to Huckel's theory, although the matter needs further elucidation. The effect of the dielectric constant will be greater in non-aqueous solvents, but the above considerations have yet to be tested in this case. It should be specially noted that the dielectric constant which governs the interionic forces is not to be identified with the macroscopic dielectric constant of the solution. We shall not deal further with Hückel's theory here. (For details, see W. Orthmann, *Ergeb. d. exakt. Naturwiss.* **6** (1927), 155.)

Bjerrum (*Z. anorg. u. allg. Chem.* **109** (1920), 275) considers that hydration involves a chemical combination between the ions and the water, and hence a decrease in the content of free water. This should increase the mole fraction of the ions, and hence their activity coefficient, the predicted effect depending linearly upon the concentration. Bjerrum employs, however, the incorrect cube root law for the activity coefficient of the unhydrated ions. Hückel has used the correct limiting law, and has shown that the hydration effect acts in the same direction

as the dielectric constant effect, but is much too small to explain the observed increase of activity coefficients. (See E. Hückel, loc. cit., and W. Schottky, *Thermodynamik*, p. 435, Berlin 1929.) It may be hoped that a method recently described by Debye (see p. 170) will give valuable information about hydration. Hydration appears optically as a displacement of the water bands towards longer wave-lengths, caused by the effect of the fields of the ions upon the vibrating water molecules (see especially the accurate work of R. Suhrmann and F. Breyer, *Z. phys. Chem.* **20 B** (1933), 17).

We also have for a binary electrolyte†

$$\left.\begin{aligned} &\psi_{2m} = 0, \quad \psi_{2m+1} = X_{2m+1}(x)z^{2m+1} \quad (m = 0, 1, \ldots) \\ &X_1 = \frac{1}{1+x} - X_3 = \frac{1}{6}\frac{x^2}{(1+x)^4}\{1 - 4xe^{4x}E(4x)\}\ldots \end{aligned}\right\}. \tag{610}$$

If we also write

$$Y_{2m+1}(x) = \frac{1}{x^{4m+2}}\int_0^x x^{4m+1}X_{2m+1}(x)\,dx \tag{611}$$

we obtain the following expression,

$$\log f = -\frac{\epsilon^2 z^2}{2D_0 kTa}\frac{x}{1+x} + \sum_{m=1}^{\infty}\left(\frac{\epsilon^2 z^2}{D_0 kTa}\right)^{2m+1}\{\tfrac{1}{2}X_{2m+1}(x) - 2mY_{2m+1}(x)\}. \tag{612}$$

Gronwall, La Mer, and Sandved have tabulated the values of the functions X_{2m+1} and Y_{2m+1} for various values of x up to $m = 2$. Fig. 88 shows the behaviour of $-x/(1+x)$, $\frac{1}{2}X_3 - 2Y_3$, and $\frac{1}{2}X_5 - 4Y_5$. For water at 25°, insertion of numerical values gives

$$-\log_{10} f = 1{\cdot}53636\frac{z^2}{10^8 a}\frac{x}{1+x} - 0{\cdot}15382\left(\frac{z^2}{10^8 a}\right)^3 10^3\{\tfrac{1}{2}X_3(x) - 2Y_3(x)\} -$$

$$-0{\cdot}0770\left(\frac{z^2}{10^8 a}\right)^5 10^5\{\tfrac{1}{2}X_5(x) - 4Y_5(x)\} \tag{613}$$

$$x = 10^{-8}\kappa\, 10^8 a, \quad 10^{-8}\kappa = 0{\cdot}3283z\sqrt{\gamma}. \tag{614}$$

Fig. 88 shows $-\log_{10} f$ as a function of x for different values of a, the solvent being water at 25°. In this figure it is of special interest to note that for small ionic diameters the curve for $-\log_{10} f$ lies above the Debye limiting straight line. Fig. 89 illustrates in particular $-\log_{10} f$ plotted against $\sqrt{m}$ for $CdSO_4$ at 25°. Up to $m = 0{\cdot}01$ there is excellent agreement between theory and experiment. The values of the activity

† Writing $E(x) = \int_x^{\infty}\frac{e^{-u}}{u}\,du$.

coefficient of $CdSO_4$ are taken from the e.m.f. measurements of La Mer and Parks.† The value taken for a was 3·65 Å.‡

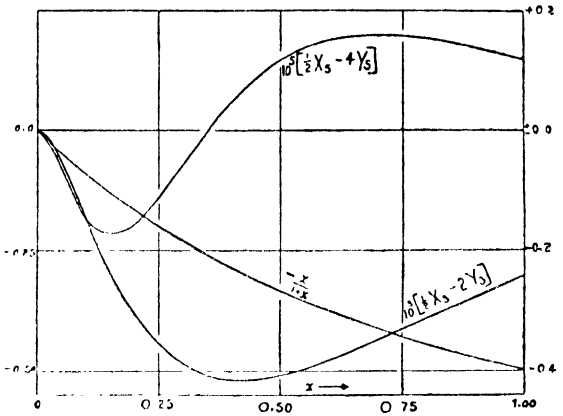

FIG. 87.

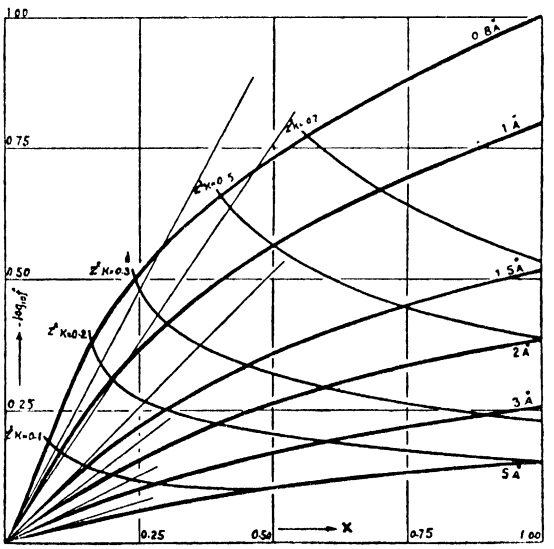

FIG. 88. Variation of activity coefficient with concentration according to the Gronwall-La Mer-Sandved theory.

† V. K. La Mer and W. G. Parks, *J. Am. Chem. Soc.* **53** (1931), 2040. While the activity coefficient of $ZnSO_4$ agrees well with the theory (see Cowperthwaite and La Mer, *J. Am. Chem. Soc.* **53** (1931), 4333), $CuSO_4$ offers great difficulties in this respect (see M. Quintin, *Compt. rend.*, p. 767, 1933).

‡ a was found to vary less than 0·1 Å. between 0° and 25°. a must therefore be considered as the distance of closest approach of two ions without their surrounding hydrate sheaths; otherwise a should decrease with increasing temperature. See especially J. A. Cowperthwaite, *Diss. Columbia University*, 1930.

The deviations from the limiting laws found by Scatchard and Tefft† for $ZnCl_2$, $PbCl_2$, and $CdCl_2$ can probably also be interpreted in terms of the theory of La Mer, Gronwall, and Sandved. Another possible explanation is provided by assuming incomplete dissociation and the formation of intermediate ions, as has been proposed specially by C. W. Davies.‡

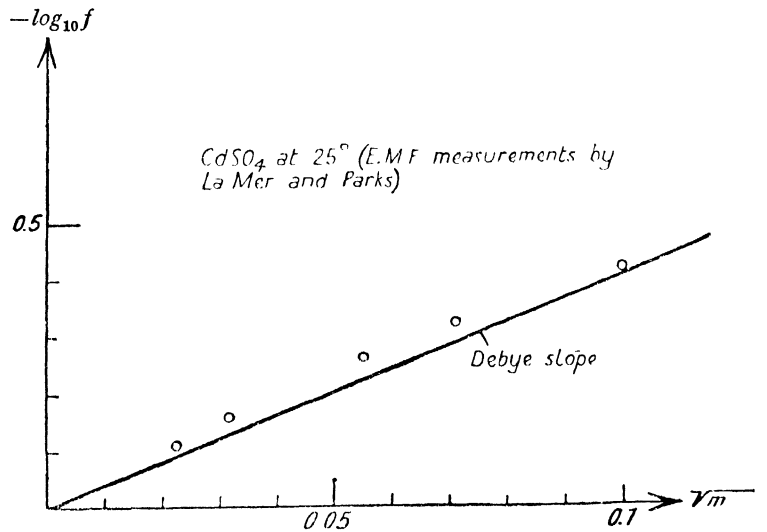

FIG. 89. The activity coefficient of $CdSO_4$.

For the osmotic coefficient g in water at 25° the theory gives the expression

$$1-g = 3{\cdot}44716\frac{z^2}{10^8a}\left\{\frac{2}{x}-\frac{1}{1+x}-\frac{2}{x^2}\log(1+x)\right\}-$$
$$-0{\cdot}16384\left(\frac{z^2}{10^8a}\right)^3 10^3\{X_3(x)-6Y_3(x)\}-$$
$$-0{\cdot}07790\left(\frac{z^2}{10^8a}\right)^5 10^5\{X_5(x)-10Y_5(x)\}. \quad (615)$$

Table 45 gives some data for $NaIO_3$ KNO_3, $ZnSO_4$, and $MgSO_4$.§ The electrolytes contained in these tables give according to Debye's approximation values for the ionic diameters which vary considerably with the concentration and often become negative. These values are

† G. Scatchard and Tefft, *J. Amer. Chem. Soc.* **52** (1932), 2272.

‡ See p. 280, footnote. The method of M. Wien described in § 56 offers a possibility of distinguishing between these two explanations.

§ Data for K_2SO_4 and $BaCl_2$ are included; cf. the following section. KCl also obeys the theory; see H. M. Spencer, *J. Am. Chem. Soc.* **54**, (1932), 4490.

given in Table 49 under the heading a_0. The values of 10^8a at the head of each table are those employed in the La Mer-Gronwall-Sandved expression, for calculating the freezing-point lowering Δ. It is seen that the agreement between the observed and calculated values of Δ is satisfactory throughout.†

TABLE 45

m	Δ_{obs}	10^8a_0 (Debye-Huckel)	$\Delta_{obs}-\Delta_{calc}$
	$NaIO_3$; $10^8a = 1{\cdot}25$		
0·00212	0·00770	−11·70	−0·00004
0·00499	0·01785	− 9·08	−0·00018
0·00929	0·03310	− 2·74	−0·00011
0·01502	0·05300	− 1·59	−0·00006
0·02868	0·0997	− 0·29	+0·0001
0·06329	0·2129	− 0·08	+0·0000
0·101	0·3317	+ 0·13	−0·0002
	KNO_3; $10^8a = 1{\cdot}40$		
0·00443	0·0161	+ 0·54	0·0000
0·01565	0·0558	+ 2·10	+0·0003
0·03874	0·1343	+ 0·91	+0·0007
0·05766	0·1960	+ 0·41	+0·0001
0·12270	0·4017	+ 0·56	−0·0002
	$ZnSO_4$; $10^8a = 3{\cdot}60$		
0·0003988	0·001387	− 3·60	+0·00001
0·001081	0·00350	− 7·83	−0·00003
0·005160	0·01499	− 2·46	+0·00004
0·01391	0·03701	+ 1·99	−0·00016

m	Δ_{obs}	10^8a_0 (Debye-Hückel)	$\Delta_{obs}-\Delta_{calc}$
	$MgSO_4$; $10^8a = 3{\cdot}70$		
0·003201	0·0100	1·10	+0·0002
0·00535	0·01595	1·42	+0·0003
0·00746	0·02165	2·04	+0·0005
0·01310	0·03615	2·77	+0·0005
0·02668	0·06730	2·98	0·0000
	K_2SO_4; $10^8a = 3{\cdot}6$		
0·001	0·00526	−10·7	+0·00009
0·005	0·02565	2·39	+0·00003
0·01	0·05005	2·96	+0·00003
	$BaCl_2$; $10^8a = 3{\cdot}4$		
0·001	0·00531	− 4·96	0·00004
0·004	0·02048	− 0·28	0·00018
0·01	0·05000	+ 2·86	0·00008

(*c*) *The case of unsymmetrical electrolytes.* La Mer, Gronwall, and Greiff‡ have obtained the following expressions for unsymmetrical electrolytes

$$-\log f = -z_1z_2\left\{\frac{1}{10^8a}B_1(x)+\left(\frac{1}{10^8a}\right)^2(z_1+z_2)^2B_2(x)-\right.$$
$$-\frac{1}{(10^8a)^3}(z_1^2+z_1z_2+z_2^2)(z_1+z_2)^2B_3^*(x)-$$
$$\left.-\frac{1}{(10^8a)^3}(z_1^2+z_1z_2+z_2^2)^2B_3(x)\right\}, \qquad (616)$$

† It is specially interesting that La Mer and W. C. Eichelberger (*J. Am. Chem. Soc.* **54** (1932), 2763) have recently shown that the activity coefficients of H_2SO_4 in glacial acetic acid obey the La Mer-Gronwall-Sandved theory, taking the *a*-parameter as 11 Å. It is assumed that the acid dissociates into H^+ and HSO_4^-.

‡ V. K. La Mer, T. H. Gronwall, and L. J. Greiff, *J. Phys. Chem.* **35** (1931), 2245. A method has been recently developed for determining the solubility of sparingly soluble inorganic salts in aqueous solutions (see E. W. Neumann and Popoff, *J. Phys. Chem.* **34** (1930), 1853; also the papers quoted on p. 131). It has been found that symmetrical electrolytes obey the La Mer-Gronwall-Sandved theory fairly well, but that its extension by Greiff to unsymmetrical types does not appear to agree with the experimental results.

$$\left.\begin{aligned} B_1(x) &= \frac{10^8\epsilon^2}{2D_0kT}\frac{x}{1+x},\quad B_2(x) = \left(\frac{10^8\epsilon^2}{D_0kT}\right)^2\{\tfrac{1}{2}X_2(x)-Y_2(x)\} \\ B_3^*(x) &= \left(\frac{10^8\epsilon^2}{D_0kT}\right)^3\{\tfrac{1}{2}X_3^*(x)-2Y_3^*(x)\} \\ B_3(x) &= \left(\frac{10^8\epsilon^2}{D_0kT}\right)^3\{\tfrac{1}{2}X_3(x)-2Y_3(x)\}. \end{aligned}\right\} \quad (617)$$

The functions $X_2,\ldots, X_3^*$ and $Y_2,\ldots, Y_3^*$ occurring in these equations have been tabulated. For the special case of water at 25° the equation becomes

$$\begin{aligned} \frac{-\log_{10}f}{(-z_1z_2)} = 1{\cdot}53636\frac{1}{10^8a}\frac{x}{1+x} &+ \frac{0{\cdot}2174}{(10^8a)^2}(z_1+z_2)^2 10^2(\tfrac{1}{2}X_2-Y_2)- \\ &-0{\cdot}15382\frac{1}{(10^8a)^3}(z_1^2+z_1z_2+z_2^2)(z_1+z_2)^2 10^3(\tfrac{1}{2}X_3^*-2Y_3^*)- \\ &-0{\cdot}15382\frac{1}{(10^8a)^3}(z_1^2+z_1z_2+z_2^2)10^3(\tfrac{1}{2}X_3-2Y_3). \end{aligned} \quad (618)$$

For the osmotic coefficient in water at the same temperature,

$$\begin{aligned} \frac{1-g}{-z_1z_2} = \frac{3{\cdot}44716}{10^8a}&\left\{\frac{2}{x}-\frac{1}{1+x}-\frac{2}{x^2}\log(1+x)\right\}+ \\ &+0{\cdot}47532\frac{(z_1+z_2)^2\,10^2}{(10^8a)^2}(\tfrac{1}{2}X_2-2Y_2)- \\ &-0{\cdot}3279(z_1+z_2)^2\frac{(z_1^2+z_1z_2+z_2^2)\,10^3}{(10^8a)^3}(\tfrac{1}{2}X_3^*-3Y_3^*)- \\ &-0{\cdot}3279\frac{(z_1^2+z_1z_2+z_2^2)^2\,10^3}{(10^8a)^3}(\tfrac{1}{2}X_3-3Y_3). \end{aligned} \quad (619)$$

Greiff was able to show that the agreement between theory and experiment is again excellent.

The case of mixtures has also been treated by Greiff. We shall take as an example the case previously mentioned† of the effect of added K_2SO_4 upon the solubility of a 3-1-valent complex cobalt salt (see Fig. 90). It is especially interesting that the new theory is able to clear up the discrepancy between the experimental results and the simple Debye theory (see Figs. 90 and 28). The ionic strength $\bar{J}$ (cf. p. 133) is connected with κ by (224), giving $\sqrt{J} = 3{\cdot}05\times10^{-8}\kappa$. Thus if the abscissae in Fig. 90 are multiplied by 3·05, the square roots of the corresponding ionic strengths are obtained. The behaviour of the osmotic

† See p. 133.

coefficients is illustrated in Fig. 49; here again there is good agreement between theory and experiment.

(*d*) *General considerations.* The theoretical foundations of the theory of Gronwall, La Mer, and Sandved can only be tested by an extension of Kramer's statistical treatment of electrolyte solutions† to embrace the case of finite ionic radii. The good agreement between theory and experiment makes it probable that the next approximation in the statistical treatment will give values very near those obtained by Gronwall, La Mer, and Sandved. It is especially noteworthy that the theory

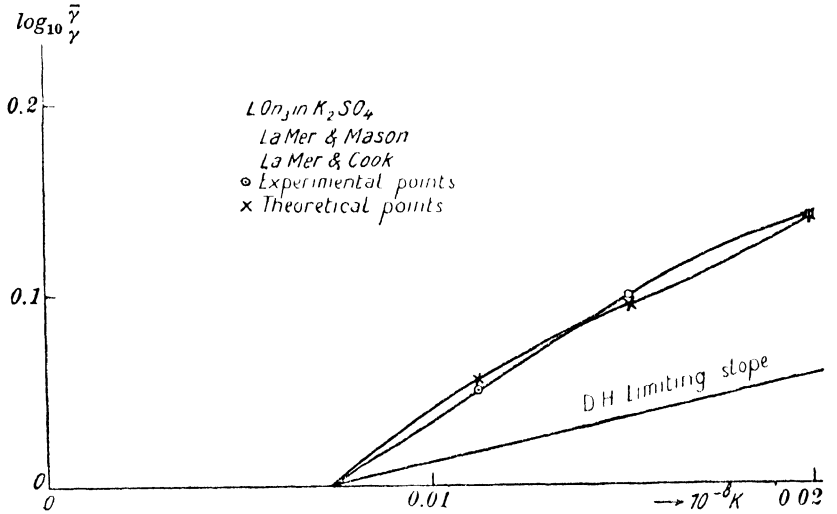

FIG. 90. Solubility of $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_2C_2O_4]_3$ in K_2SO_4 solution.

is able to account for the behaviour of unsymmetrical electrolytes of high valence types, for which the original Debye theory failed completely. It is, however, strange that the *a*-parameter, which represents some kind of a closest distance of approach between two ions in contact, should assume the value 1·6 Å. when dealing with the complex ion $[Co(NH_3)_2(NO_2)_2(C_2O_4)]$, the radius of which is certainly at least 3 Å. A further difficulty was found by E. W. Neumann (loc. cit) in his experiments on the solubility of AgCl in salt solutions. For unsymmetrical solvent salts (especially sulphates) equation (618) does not lead to constant values for the parameter *a*. This point requires further investigation. It would also be of considerable interest to extend the same treatment to conductivity phenomena, though in this case the mathematical difficulties would be very great.

† See p. 332.

In spite of the great success of the theory of Gronwall, La Mer, and Sandved, one other point needs consideration.† It is not very probable that at the concentrations considered the interaction between the ions is entirely determined by the Coulomb forces. We should expect that the quantum-mechanical dispersion forces, and in many cases also the true quantum-mechanical chemical forces will be of importance. Unfortunately, very little is known of these latter forces in solution, but it may be anticipated that they will introduce modifications in La Mer's calculations. The solvent may also exert some effect upon the ions, the nature of which is not yet fully understood.

We shall now consider the heat of dilution of more concentrated solutions, which is closely connected with the theory of La Mer, Gronwall, and Sandved.

52. The Heat of Dilution of More Concentrated Solutions according to the Theories of Debye and Hückel; Hückel; and La Mer, Gronwall, and Sandved

In order to obtain the heat of dilution, we shall begin with F_e, the electrical part of the free energy of the ions in solution, which we have previously obtained by considering a reversible discharging process.‡

If we have V c.c. solution containing M_1, M_2, ..., M_s, moles of ions of the sorts 1, 2,..., s, valencies z_1, z_2 ..., z_s, and diameters a_1, a_2,..., a_s, the Debye-Hückel theory gives from (569)

$$A' = \sum_{j=1}^{s} \frac{\mathbf{N}M_j z_j^2 \epsilon^2}{\kappa^2 D_0 a_j^3} \left\{ -\log(1+a_j\kappa) + a_j\kappa - \frac{(a_j\kappa)^2}{2} \right\}. \tag{620}$$

According to Hückel's theory§ D_0 in equation (620) should be replaced by a dielectric constant D depending on the concentration, and an additional work term

$$A'' = \sum_{j=1}^{s} \left(-\frac{z_j \epsilon^2 \mathbf{N} M_j}{2D_0 b_j} + \frac{z_j \epsilon^2 \mathbf{N} M_j}{2Db_j} \right) \tag{621}$$

† It may be noted that C. W. Davies and his collaborators account for the behaviour of electrolytes in more concentrated solutions by assuming incomplete dissociation (see p. 301, and in connexion with La Mer's theory, H. E. Blayden and C. W. Davies, *J. Chem. Soc.* (1930), 949; C. W. Davies, ibid. (1930), 2410). Even the great deviations from the Debye-Huckel theory exhibited by dilute solutions of unsymmetrical electrolytes are explained by Davies on the basis of incomplete dissociation, while they appear as typical ion effects in the theory of La Mer and his collaborators. See C. W. Davies, *J. Chem. Soc.* (1930) 2421; W. H. Banks, E. C. Righellato, and C. W. Davies, *Trans. Farad. Soc.* **27** (1931), 621; R. W. Money and C. W. Davies, ibid. **38** (1932), 609; Davies, ibid. **38** (1932), 607.

‡ See p. 113.

§ For a criticism of this theory, see p. 272.

should be added to (620). F_e is then equal to $A'+A''$. We shall for the present neglect the variation of D with concentration, i.e. put $A''=0$ and employ equation (620). The heat of dilution of M moles of salt is then given by the Gibbs-Helmholtz equation (9), giving

$$M\bar{L} = F_e - T\frac{\partial F_e}{\partial T} = -\sum \frac{\mathbf{N}M_j\epsilon^2 z_j^2}{2D_0}\frac{\kappa}{1+a_j\kappa}\left(1+\frac{T}{D_0}\frac{dD_0}{dT}\right). \quad (622)$$

This assumes that the ionic diameters a_j are independent of temperature, and also neglects the effect of a term in $\partial \log V/\partial T$ resulting from the thermal expansion.† The integral heat of dilution per mole $\bar{L}$ is then given by

$$\bar{L} = -\frac{1}{M}\sum \frac{\mathbf{N}M_j}{2D_0}\frac{z_j^2\epsilon^2\kappa}{1+a_j\kappa}\left(1+\frac{T}{D_0}\frac{dD_0}{dT}\right). \quad (623)$$

It may be seen from this equation that the introduction of a finite ionic diameter will decrease the positive heat of dilution, but can never change its sign. Such a change of sign can, however, be accounted for by taking into account the dependence of the ionic diameters upon the temperature. Gross and Halpern‡ and Bjerrum§ have shown that the effect is to add a term to (623) which for low concentrations is proportional to the concentration and to the temperature coefficient da_j/dT. If, therefore, a_j decreases with rising temperature, the additional term is positive, while if a_j increases with rising temperature, the additional term is negative. Bjerrum has calculated the values of da_j/dT from the experimental heats of dilution of a number of 1-1-valent electrolytes. It was found that for the strongly hydrated electrolytes HCl, LiOH, LiCl, $LiNO_3$, a decreases with increasing temperature,‖ while for the unhydrated electrolytes KOH, HNO_3, NaOH, KCl, KNO_3, and $CsNO_3$ with smaller values of a, a was found to increase with rising temperature.†† It is impossible to develop Bjerrum's theory quantitatively, since a number of approximations are made which are not permissible in more concentrated solutions. The chief objection to Bjerrum's treatment is the fact that the Debye-Hückel theory is certainly not applicable

† See O. Gatty, *Phil. Mag.* **11** (1931), 1082; G. Scatchard, *J. Am. Chem. Soc.* **53** (1931), 2037. For water the correction is of the order of magnitude of the experimental error (*c.* 7 per cent.), but it is much greater in some non-aqueous solvents.

‡ P. Gross and O. Halpern, *Phys. Z.* **26** (1925), 403; P. Gross, *Akad. d. Wiss. Wien* IIb, **136** (1927), 243.

§ N. Bjerrum, *Trans. Farad. Soc.* **23** (1927), 445.

‖ For $\frac{10^8 da}{d\log T}$ Bjerrum finds the values −0·86, −0·62, −0·55.

†† The corresponding values of $10^8 da/d \log T$ are 0·12, 0·25, 0·43, 0·60, 2·06, 2·20. The more recent investigations of La Mer and his collaborators indicate that a does not vary nearly as much with temperature as assumed by Bjerrum. See specially J. A. Cowperthwaite and V. K. La Mer, *J. Am. Chem. Soc.* **53** (1931), 4333.

at such high concentrations. The effect is also much too small at about 0·01 N. to explain the observed individualities in the heats of dilution.†

We shall now investigate the results obtained from Hückel's theory, taking the case of 1-1-valent electrolytes for the sake of simplicity. Equation (621) gives for A'' per mole

$$A'' = -\frac{\epsilon^2}{2D_0 b}\mathbf{N} + \frac{\epsilon^2}{2Db}\mathbf{N}. \tag{624}$$

We also have from (569)

$$A' = -\frac{VkT}{4\pi a^3}\left\{\log(1+a\kappa) - a\kappa + \frac{(a\kappa)^2}{2}\right\}. \tag{625}$$

In (622) and (625) D may be written in the form $D = D_0(1-\delta\gamma)$. If $a\kappa \ll 1$, this gives for A'

$$A' = -\frac{VkT}{12}\kappa_0^3(1+\tfrac{3}{2}\delta\gamma). \tag{626}$$

We now have

$$A'' - T\frac{\partial A''}{\partial T} = \frac{N\epsilon^2}{b}\left\{\left(1+\frac{T}{D_0}\frac{dD_0}{dT}\right) - \frac{T}{\delta}\frac{d\delta}{dT}\right\}\frac{\delta\gamma}{D_0}. \tag{627}$$

$A' - T\dfrac{dA'}{dT}$ can be similarly calculated from (626) and (217). We shall now take the case of water at 18° and use Drude's value‡

$$1+\frac{T}{D_0}\frac{dD_0}{dT} = -0{\cdot}315,$$

which gives for $\bar{L}$

$$L = \frac{N\epsilon^2}{b}\left(-0{\cdot}315 - \frac{T}{\delta}\frac{d\delta}{dT}\right)\frac{\delta\gamma}{D_0} - 1{,}328\sqrt{\gamma}\left(-0{\cdot}315 - \delta\gamma\frac{d\delta}{dT}\right)(1+\tfrac{3}{2}\delta\gamma). \tag{628}$$

Inserting Sack's value $\delta = 6{\cdot}6$ and putting $b = 2$ Å., (628) becomes

$$\bar{L} = -1{,}328\sqrt{\gamma}\left(-0{\cdot}315 - 6{\cdot}6\gamma\frac{T}{\delta}\frac{d\delta}{dT}\right)(1+9{\cdot}9\gamma) + \\ + 13{,}600\left(-0{\cdot}315 - \frac{T}{\delta}\frac{d\delta}{dT}\right)\gamma. \tag{629}$$

It will be seen that the variation of the dielectric constant with concentration introduces a term proportional to the concentration. Unfortunately there exists very little experimental data on the quantity δ, and still less on the term $\dfrac{T}{\delta}\dfrac{d\delta}{dT}$. If we neglect the latter term,

† See p. 160. ‡ Cf. p. 161.

(629) becomes

$$\bar{L} = 1{,}328 \times 0{\cdot}315\sqrt{\gamma}(1+9{\cdot}9\gamma) - 13{,}600 \times 0{\cdot}315\gamma. \qquad (630)$$

The negative second term can thus give rise to a negative heat of dilution, even at $\gamma = 0{\cdot}01$. By taking into account the term $\frac{T}{D_0}\frac{d\delta}{dT}$, any values of the heat of dilution could no doubt be accounted for. It can, however, be easily shown that if the formulae here are applied to the calculation of osmotic coefficients, the results obtained are at variance with experiment.† Further, it is impossible to explain the fact that the negative heat of dilution increases rapidly with increasing concentration, since the values of δ become 30–100 times smaller at high concentrations, and the negative term in (629) will correspondingly decrease in importance. It can also be easily shown that the individuality of the heats of dilution cannot be explained in this way.‡

Lange and Meixner§ have recently attempted to explain the individuality of the integral heats of dilution by applying the theory of Gronwall, La Mer, and Sandved. To simplify matters, the dielectric constant is assumed independent of the concentration, and the ionic radius and the volume assumed independent of the temperature. To make the subsequent considerations clearer, we shall first consider equation (622), the expression for the molar heat of dilution derived from the second approximation of Debye and Hückel. The potential at the central ion for $r = a_j$ is given by

$$\Psi_j = \frac{\epsilon z_j}{D_0 a_j}\frac{1}{1+\kappa_0 a_j}. \qquad (631)$$

Introducing this in (622), we obtain for the integral molar heat of dilution

$$\bar{L} = \frac{1}{M}\sum_{j=1}^{s}\frac{\mathbf{N}M_j z_j \epsilon}{2}\left(\Psi_j - \frac{\epsilon z_j}{D_0 a_j}\right)\left(1+\frac{T}{D_0}\frac{dD_0}{dT}\right) \text{ ergs per mole salt.} \qquad (632)$$

The potential energy of an ion of charge ϵz_j and potential Ψ_j is given by

$$U_j = \frac{\epsilon z_j \Psi_j}{2}, \qquad (633)$$

† See p. 231 for a discussion of the difficulties connected with Sack's conclusions. It is now known (especially from the work of Wien) that for very dilute solutions the dielectric constants follow a square-root law, and that at high concentrations the δ-values for water are very much smaller than those obtained by Sack. For literature, see R. T. Lattey and W. G. Davies, *Phil. Mag.* **12** (1931), 1111.

‡ See E. Lange and A. L. Robinson, *Chem. Rev.* **9** (1931), 89.

§ Lange and Meixner, *Phys. Z.* **30** (1929), 670; *Z. Elektrochem.* **36** (1930), 772; A. L. Robinson, *J. Am. Chem. Soc.* **54** (1932), 1311; H. Hammerschmid and Lange, ibid. **54** (1932), 3120.

while at infinite dilution it has the value

$$U_{j\infty} = \frac{\epsilon z_j^2}{2D_0 a_j}, \tag{634}$$

since only the potential $\epsilon z_j/D_0 a_j$ is operative. Introducing U_j and $U_{j\infty}$ into (632), it becomes

$$\bar{L} = \frac{\mathbf{N}}{M}\sum_{j=1}^{s} M_j(U_j - U_{j\infty})\left(1+\frac{T}{D_0}\frac{dD_0}{dT}\right) \text{ ergs per mole salt.} \tag{635}$$

(632) thus expresses the integral molar heat of dilution as the difference between the electrical potential energies of the ions at the initial concentration γ and at infinite dilution, multiplied by $1+\frac{T}{D_0}\frac{dD_0}{dT}$. We shall now show that the heat of dilution can be expressed in the same form in the theory of Gronwall, La Mer, and Sandved.

By means of the charging process previously described, the electrical part of the free energy of M moles of the electrolyte is calculated to be

$$\frac{F_e}{\mathbf{N}kT} = -\sum_{j=1}^{s} M_j z_j \sum_{m=1}^{\infty}\left(\frac{-\epsilon^2 z_j}{-D_0 a_j kT x_j^2}\right)^m \int_0^{x_j} x^{2m-1}\psi_m(x, x)\,dx - \sum_{j=1}^{s}\frac{M_j z_j^2 \epsilon^2}{2D_0 a_j kT}. \tag{636}$$

We also have

$$\frac{\partial}{\partial T}\left(\frac{F_e}{T}\right) = \frac{1}{T}\frac{\partial F_e}{\partial T} - \frac{F_e}{T^2} = -\frac{1}{T^2}\left(F_e - T\frac{\partial F_e}{\partial T}\right) = -\frac{M\bar{L}}{T^2}, \tag{637}$$

so that the heat of dilution $\bar{L}$ is given by

$$\bar{L} = -\frac{T^2}{M}\frac{\partial}{\partial T}\left(\frac{F_e}{T}\right). \tag{638}$$

Equation (638) is easily evaluated, giving the result

$$\begin{aligned}\bar{L} &= \frac{\mathbf{N}kT}{M}\left(1+\frac{T}{D_0}\frac{dD_0}{dT}\right)\times \\ &\quad\times\left\{-\sum_{j=1}^{s}\frac{M_j z_j}{2}\sum_{m=1}^{s}\left(\frac{\epsilon^2 z_j}{-D_0 a_j kT}\right)^m \psi_m(x_j, x_j) - \sum_{j=1}^{s}\frac{M_j z_j^2 \epsilon^2}{2D_0 a_j kT}\right\} \\ &= \frac{\mathbf{N}}{M}\sum_{j=1}^{s}\frac{M_j z_j \epsilon}{2}\left(\Psi_j - \frac{z_j \epsilon}{D_0 a_j}\right)\left(1+\frac{T}{D_0}\frac{dD_0}{dT}\right).\end{aligned} \tag{639}$$

It will be seen that (639) is in formal agreement with (632), so that the same rule applies. There is, however, an essential difference, since (632) employs an approximate value for Ψ_j, while (639) contains the exact value. The numerical results are therefore different. In the case of

symmetrical z-valent electrolytes, assuming the radii of the cation and the anion to be equal, the formula for $\bar{L}$ becomes very much simpler. Using the relations (610) we obtain†

$$\bar{L} = \mathbf{N}kT\left(1+\frac{T}{D_0}\frac{dD_0}{dT}\right)\left\{\sum_{m=0}^{\infty}\left(\frac{\epsilon^2 z^2}{D_0 akT}\right)^{2m+1} X_{2m+1}(x) - \frac{\epsilon^2}{D_0 akT}\right\}\text{ergs/mole}. \tag{640}$$

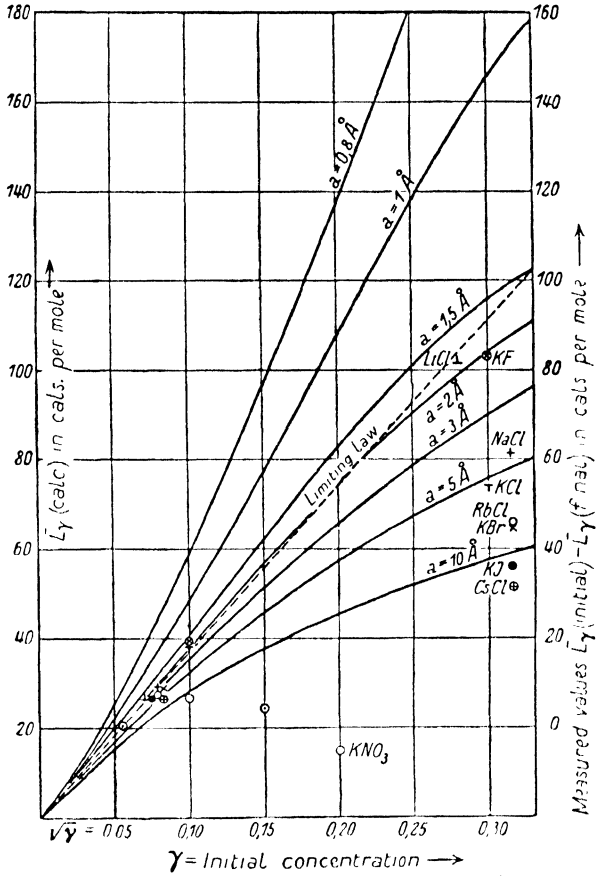

FIG. 91. Heats of dilution of 1-1-valent salts in water.

For values of $a > 2z^2 \times 10^{-8}$ it is permissible to neglect X_7, X_9, and higher terms. We then obtain the curves shown in Fig. 91, in which the heat of dilution in cal./mole is plotted against $\sqrt{\gamma}$. For small radii, the

† If the temperature variations of the volume and the ionic radius are taken into account, $\left(1+\frac{T}{D_0}\frac{dD_0}{dT}\right)X_{2m+1}(x)$ must in general be replaced by

$$\left(1+\frac{T}{D_0}\frac{dD_0}{dT}\right)X_{2m+1} + \frac{d\log V}{dT}\{X_{2m+1}-(2m+1)2Y_{2m+1}\} - \frac{d\log a}{dT}\{X_{2m+1}-3(2m+1)Y_{2m+1}\}.$$

See G. Scatchard, *J. Am. Chem. Soc.* **53** (1931), 2037.

neglect of the higher terms introduces considerable errors. The limiting law (373) is obtained from (640) by neglecting the terms X_3, X_5, etc. and putting $a = 0$ in X_1. The second approximation is obtained by retaining only $X_1 = 1/(1+x)$. The curves corresponding to the second approximation are hyperbolae, which all lie below the limiting straight

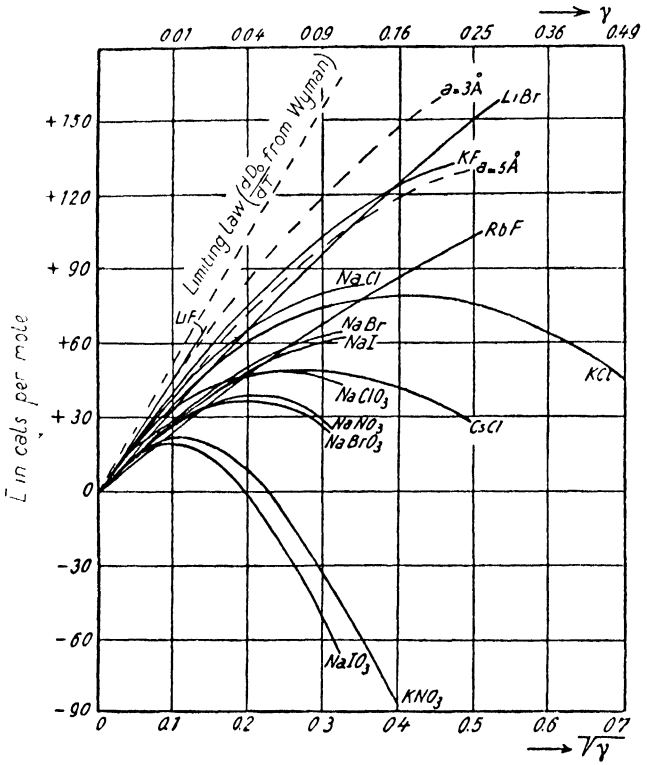

FIG. 92. Heats of dilution of 1-1-valent salts in water.

line and become tangential to it at the origin. Hence for small concentrations and finite values of a, X_3, etc. can be neglected. At higher concentrations this is no longer the case, since small values of a lead to positive deviations, and large values of a to negative deviations. The second Debye-Hückel approximation cannot account for positive deviations. Fig. 92 shows the experimental results for a number of 1-1-valent salts. The limiting straight line is also shown, using Wyman's† value $dD_0/dT = -0{\cdot}361$. Fig. 92 also shows the theoretical curves from (640) with $a = 3$ Å. and $a = 5$ Å. It should be specially noticed that a negative heat of dilution is never to be expected according to the theory of Gronwall, Sandved, and La Mer. Figs. 93, 94, and 95 show

† J. Wyman, *Phys. Rev.* **35** (1930), 623.

the results for the molar heat of dilution $\bar{L}$ for 2-1, and 2-2-valent salts in water at 25°. The theoretical curves for $a = 3$ Å. and $a = 4$ Å lie very near the experimental curves for $CaSO_4$ and $MgSO_4$, respectively, using Wyman's value $dD_0/dT = -0{\cdot}361$.† (The uncertainty in this value leads to a considerable uncertainty in the absolute theoretical

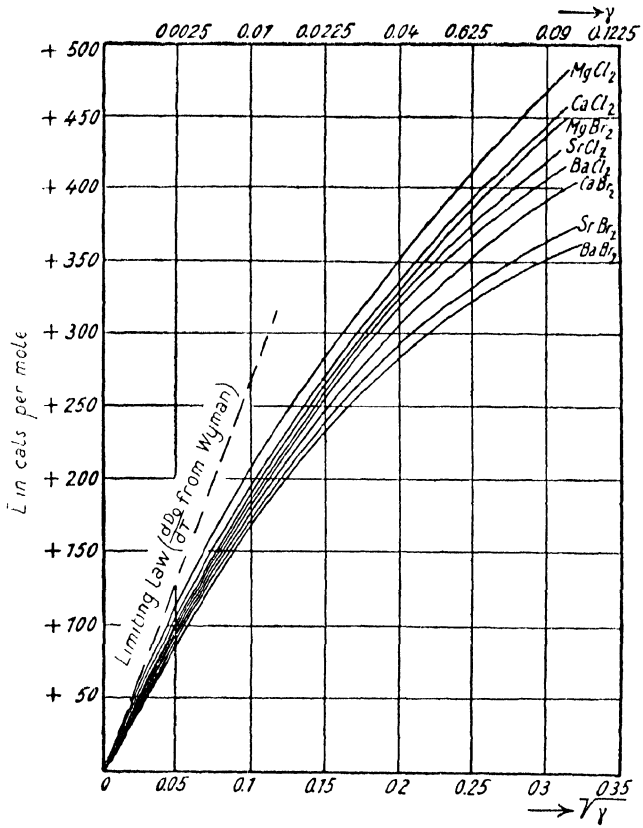

FIG. 93. Heats of dilution of 2-1-valent salts in water.

values.) The Debye-Hückel second approximation is powerless to explain such large positive deviations from the limiting law. Ca must be assigned a smaller ionic radius than Mg, which is in the opposite order to their atomic weights, but is probably due to hydration. For 1-1-valent salts up to $\gamma = 0{\cdot}01$ the order found is

$$a_{LiCl} < a_{NaCl} < a_{KCl} < a_{RbCl} < a_{CsCl}$$

$$a_{KF} < a_{KCl} < a_{KBr} < a_{KI}$$

$$a_{LiF} < a_{KF} < {}_{RbF}; \; a_{NaCl} < a_{NaBr} < a_{NaI}$$

† See E. Lange, *Z. Elektrochem.* **36** (1930), 775.

and similarly for 2-1-valent salts, where we have

$$a_{MgBr_2} < a_{SrBr_2} < a_{BaBr_2}$$
$$a_{MgCl_2} < a_{CaCl_2} < a_{SrCl_2} < a_{BaCl_2}$$
$$a_{Mg(NO_3)_2} < a_{Ca(NO_3)_2} < a_{Sr(NO_3)_2} < a_{Ba(NO_3)_2}$$
$$a_{Li_2SO_4} < a_{Na_2SO_4} < a_{K_2SO_4} < a_{Rb_2SO_4} < a_{Cs_2SO_4}.$$

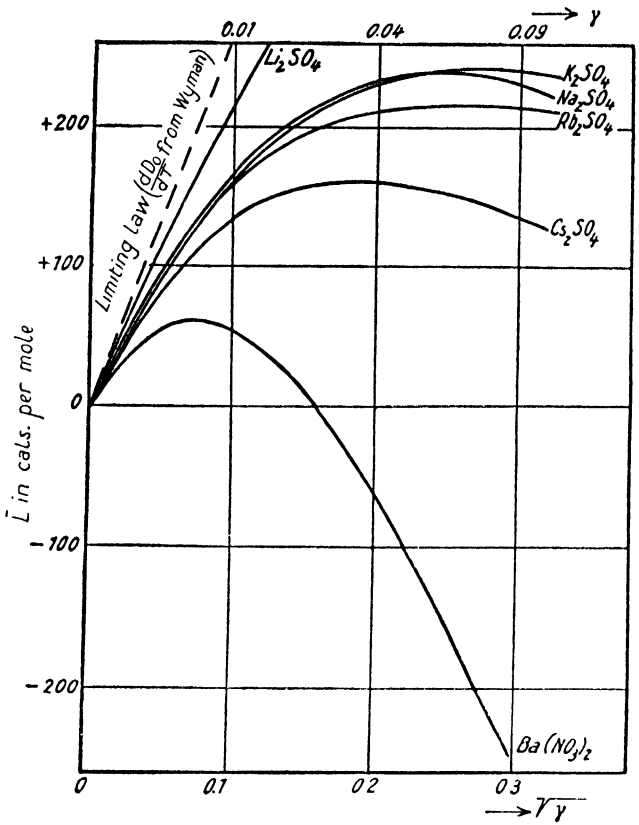

FIG. 94. Heats of dilution of 1-2-valent salts in water.

These orders seem plausible, but unfortunately a consideration of activity coefficients and ionic mobilities leads to the reverse order.† Further, the a-values found for $MgCl_2$ and $CaCl_2$ are in the reverse order to those found for $MgSO_4$ and $CaSO_4$. Hence unless the order becomes reversed at great dilutions in the case of the sulphates, the a-values depend not only upon the radii of the single ions, but also upon the nature of the oppositely charged ions present.

† See E. Lange and H. Streck, *Naturwiss.* **19** (1931), 359.

Matters are far more complicated at higher concentrations. Thus it is important to note that the Gronwall-La Mer-Sandved theory can never account for the negative heats of dilution which are frequently met with. We have previously shown that these negative values can be explained by assuming that the ionic radii depend upon the temperature, or that the dielectric constant depends upon the concentration.

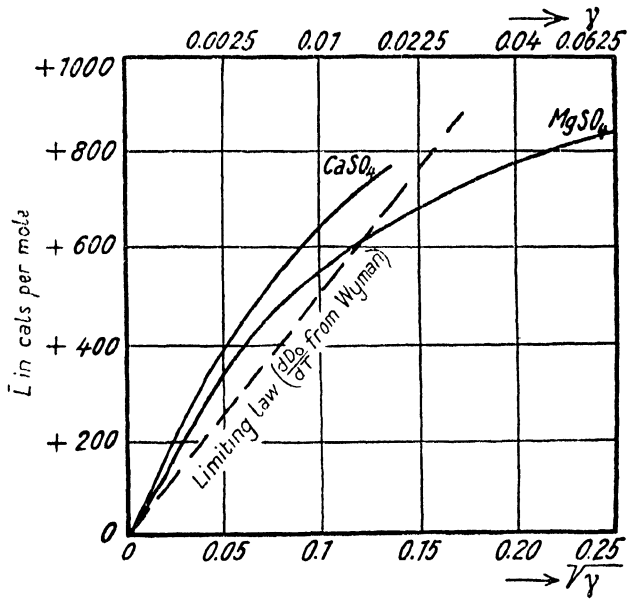

FIG. 95. Heats of dilution of 2-2-valent salts in water.

These hypotheses will not, however, explain the discrepancies met with in the initial slopes. It may be easily shown that the theory of Nernst, dealt with in the next section, also fails in this respect.†

53. Nernst's Theory of Electrolytic Dissociation. Approximate Determination of the True Degree of Dissociation

Nernst has recently proposed a theory‡ to account (at least in the simplest cases) for the occurrence of large negative heats of dilution without having recourse to the introduction of ionic radii or the variation of the dielectric constant with concentration. Nernst's theory is

† The molar heat of dissociation is of the order of magnitude 10,000 cal., i.e. the contribution to the heat of dilution in 0·01 N. solution is 10 cal., which is hardly enough to explain the observed discrepancies.

‡ W. Nernst, *Z. Elektrochem.* **33** (1927), 428, and later papers. See also J. Zirkler, *Z. f. Phys.* **69** (1931), 515; *Z. phys. Chem.* **163 A** (1932), 1; **164 A** (1933), 134; Plake, ibid. **162 A** (1932), 257.

based on the idea that negative heats of dilution are most simply referred to heats of dissociation, solutions of strong electrolytes being assumed to contain appreciable amounts of undissociated molecules, as in Arrhenius's original theory. These molecules are in mass law equilibrium with the ions. The true degree of dissociation can be deduced from measurements of heats of dilution and their temperature coefficients, and quite independently from osmotic and conductivity measurements. Since dissociation is complete at infinite dilution the heat of dilution is determined by the energy which is necessary during dilution to break up the undissociated molecules into their ions. In addition to this negative heat of dilution, there is also a positive effect due to interionic action, which for high degrees of dissociation can be calculated on the assumption that all the molecules are dissociated. If Q is the molar heat of dissociation of the binary electrolyte, α^* its true degree of dissociation and B the factor in the Debye limiting law (375), the molar heat of dilution is given by

$$\bar{L} = -Q(1-\alpha^*)+B\alpha^*(\alpha^*\gamma)^{\frac{1}{2}}. \tag{641}$$

The factor $\alpha^*\sqrt{\alpha^*}$ must be introduced into the Debye expression† since only the fraction α^* of the molecules is dissociated into ions. The thermodynamic mass action expression for binary electrolytes is given by (133)

$$\frac{f^2\alpha^{*2}}{1-\alpha^*}\gamma = K \qquad (f = \text{activity coefficient}). \tag{642}$$

For values of α^* near unity, $1-\alpha^*$ may be assumed to be proportional to γ. The measurements of Nernst and Orthmann can in fact be expressed in this form. The validity of (641) is not, however, proved until Q and α^* can be determined independently. Nernst succeeded in doing this as follows. If the Debye effect is known, experimental values of the heat of dilution $\bar{L}_1$ and $\bar{L}_2$ at two different temperatures T_1 and T_2 can be used to calculate $Q(1-\alpha_1^*)$ and $Q(1-\alpha_2^*)$. Van 't Hoff's isochore (44) gives on integration (Q being assumed independent of the temperature)

$$\log\frac{K_1}{K_2} = \log\frac{f_1^2\alpha_1^{*2}(1-\alpha_2^*)}{f_2^2\alpha_2^{*2}(1-\alpha_1^*)} = \frac{Q}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right). \tag{643}$$

The activity coefficients f_1 and f_2 cancel out, since it has been shown by Scatchard‡ that for a given concentration the activity coefficients vary very little with temperature. As a first approximation we put

$$(\alpha_1^*/\alpha_2^*)^2 = 1.$$

† This expression is hardly valid at the high concentrations considered by Nernst.

‡ G. Scatchard, *J. Am. Chem. Soc.* **47** (1925), 650.

Equation (643) then gives Q_0, and since $(1-\alpha_1^*)Q_0$ and $(1-\alpha_2^*)Q_0$ are known from the heats of dilution, approximate values of α_{10}^* and α_{20}^* are obtained.

We can now correct the heats of dilution $\bar{L}_1$ and $\bar{L}_2$ by $B\alpha^*(\alpha^*\gamma)^{\frac{1}{2}}$ instead of $B\sqrt{\gamma}$, thus obtaining better values for $Q(1-\alpha^*)$. These calculations are then repeated, using the values α_{10}^* and α_{20}^*, and this method of successive approximation is continued until constant values are obtained for the heat of dissociation Q and the true degrees of dissociation α_1^* and α_2^*.

The degree of association $1-\alpha^*$ varies much more with the temperature than does Q. Equation (44) enables us to estimate how far the relative temperature coefficient of Q can be neglected in comparison to that of $1-\alpha^*$. Integrating over a small temperature interval, we have

$$\log \frac{\alpha^{*2}}{1-\alpha^*} = -\frac{Q}{RT} + \text{const.} \tag{644}$$

Differentiating this with respect to T, we obtain for small degrees of association,

$$\frac{d\log(1-\alpha^*)}{dT} : \frac{d\log(Q/RT)}{dT} = \frac{Q}{RT}, \tag{645}$$

i.e. the relative temperature of the association is Q/RT times as great as the relative temperature coefficient of Q/T. Table 47 shows that Q is much greater than RT; further $1-\alpha^*$ varies much more rapidly than T, so that the degree of association $1-\alpha^*$ varies much more rapidly with the temperature than does Q.

The necessary measurements of the heat of dilution at different temperatures have been carried out by Naudé, using the calorimeter of Nernst and Orthmann previously described.† For the sake of simplicity the 1-1-valent salts KCl, NaCl, KNO_3, and $NaNO_3$ were first considered. The first four salts showed a definite decrease in the heat of dilution with decreasing temperature specially marked in the case of KNO_3. If B is assumed constant, $Q(1-\alpha^*)$ must therefore increase with decreasing temperature; i.e. the degree of association increases with decreasing temperature, which is what we should expect.

In contrast to the other salts, LiCl appears to be completely dissociated in 0·1 N. solution. The Debye theory, leading to a positive heat of dilution, may thus be applied to this salt. It was found empirically that the expression $320\sqrt{\gamma}$ expresses the results at 18° up to 0·1 N. The square-root law is thus retained from Debye's theory‡ but the factor is determined experimentally (Bjerrum gives the theoretical value 418).

† See p. 157. ‡ See equation (375).

At the highest concentrations the observed values are lower than those given by the formula; this is interpreted as being due to the presence of a small amount of undissociated salt. On account of the uncertainty in dD_0/dT the theoretical values of B are not accurately known.† Naudé has therefore determined experimentally the value of B for LiCl as a function of the temperature. The measured heat evolutions for the other salts are then corrected to infinite dilution by the use of these coefficients. The heat of dissociation Q and the degree of dissociation α^* can then be obtained from equations (641) and (642) as described above.

TABLE 46

Electrolyte	*Conc. (moles per litre)*	*Obs. heat of dilution* $\bar{L}$ *corr. to* $\gamma = 0$ *by* $320\sqrt{\gamma}$ *(cal.)*	*Heat absorption* $(1-\alpha^*)Q$ *calc. (cal.)*	*Debye effect* $320\alpha^*(\alpha^*\gamma)^{\frac{1}{2}}$ *(cal.)*	$\bar{L}$ *calc. from columns 4 and 5 (cal.)*
NaCl	1	−101·6	−372·2	+272·0	−100·2
	0·83	+ 37·2	−124·1	+174·8	+ 50·7
	0·1	+ 55	− 37·2	+100	+ 62·8
	0·04	+ 57	− 15	+ 64	+ 49
	0·033	+ 39	− 12	+ 58	+ 46
	0·013	+ 35	− 4	+ 37	+ 33
	0·004	+ 19	− 1	+ 20	+ 19
KCl	0·333	+ 31·4	−133·0	+166·6	+ 32·7
	0·1	+ 52	− 40	+ 98	+ 58
	0·013	+ 33	− 5	+ 37	+ 32
	0·004	+ 22	− 2	+ 20	+ 18
$NaNO_3$	0·333	−128·3	−287·9	+159·7	+128·2
	0·1	+ 4	− 86	+ 97	+ 11
	0·033	+ 22	− 29	+ 57	+ 28
	0·013	+ 26	− 11	+ 37	+ 26
	0·004	+ 20	− 3	+ 20	+ 17
KNO_3	0·333	−327·3	−474·8	+146·9	−327·9
	0·1	+ 76	−143	+ 94	− 49
	0·013	+ 24	− 19	+ 37	+ 18
	0·004	+ 18	− 6	+ 20	+ 14

Using the values of the heat of dissociation Q and the degree of association $1-\alpha^*$ thus obtained, (641) enables us to calculate the heats of dilution for different concentrations at 18°. These calculated heats are then compared with the observed heats of dilution, corrected to infinite dilution by the formula $320\sqrt{\gamma}$. Table 46 contains the results obtained by Naudé for the electrolytes NaCl, KCl, $NaNO_3$, and KNO_3. It is seen that there is good agreement between the observed heats of dilution in the third column and the calculated values in the sixth. Even the point at which the negative heat of dilution changes to a

† See p. 161.

positive one is well reproduced by Nernst's theory. Equation (641) enables us to calculate the heat of dilution at different temperatures. It is found that there is again good agreement between the observed and calculated values, especially taking into account the difficulty of the measurements. Naudé has also investigated the heat of dilution of non-electrolytes. It was found that while the Bjerrum-Debye-Hückel theory predicts a heat of dilution of 42 cal., per mole for a 0·01 N. 1-1-valent electrolyte, the corresponding heat of dilution of non-electrolytes was zero within the experimental error, as may be expected in the absence of interionic forces. Table 47 gives the values calculated by Nernst for the degree of association of some electrolytes at 0° and 18° at a concentration of $\gamma = 0{\cdot}1$. The values of Q used in the calculations are also given.

TABLE 47

($\gamma = 0{\cdot}1$ N.)

Electrolyte	Q	$1-\alpha^*$	
		0°	18°
KNO_3	3,100	0·063	0·048
$NaNO_3$	3,130	0·036	0·028
KCl	2,160	0·025	0·019
NaCl	3,500	0·015	0·011
LiCl	..	0	0

Nernst has also calculated the true degree of dissociation from measurements of osmotic pressure and conductivity, allowing for the Debye effect. The values obtained are in approximate agreement with those derived from the heats of dilution. We shall give a short account of Nernst's treatment.†

It appears from the heats of dilution that the Debye effect can be taken as practically the same for all 1-1-valent salts. If we use (86) and (262) to calculate the Debye effect for 0·1 N. KCl, which is only slightly associated, we obtain the value 0·134. Table 47 gives for the true degree of dissociation $1-\alpha^* = 0{\cdot}025$. The degree of association as calculated by Arrhenius is therefore given by

$$1-\alpha = 0{\cdot}134+0{\cdot}025 = 0{\cdot}159.$$

Actually, freezing-point determinations give by (86) and (123)

$$1-\alpha = 0{\cdot}161.$$

Table 48 gives the corresponding values of $1-\alpha^*$ and $1-\alpha$ calculated by Nernst for other 1-1-valent electrolytes.

† See also J. Zirkler, *Z. Elektrochem.* **37** (1931), 252; *Z. f. Physik*, **69** (1931), 50; *Z. phys. Chem.* **163 A** (1932), 1; **164 A** (1933), 134; Plake, ibid. **162 A** (1932), 257.

TABLE 48

(Concentration $\gamma = 0{\cdot}1$ N.)

Electrolyte	$1-\alpha$* 0°	$1-\alpha$ (*calc.*)	$1-\alpha$ (*obs.*)	$1-\alpha$ (100°)	$1-\alpha$ (100° and $\gamma = 0{\cdot}333$)
KNO_3	0·063	0·197	0·217	0·17	0·29
$NaNO_3$	0·036	0·170	0·154	0·19	0·25
KCl	0·025	0·159	0·161	0·17	0·19
NaCl	0·015	0·149	0·161	0·12	0·17
LiCl	0	0·134	[0·13]	0·15	0·15

The values of $1-\alpha$ obtained from freezing-point data are unavoidably uncertain, so that the agreement may be considered as good throughout.

Nernst has obtained practically the same results for the true degree of dissociation from conductivity data. The same method was first described by Onsager† whose treatment we shall follow.

We have previously seen that not all deviations from the theoretical square-root relation between equivalent conductivity and concentration can be attributed to association, since the square-root law is only a first approximation applicable to very dilute solutions. In treating more concentrated solutions, it would be necessary to develop the differential equations of Onsager, Debye, and Hückel (474) in more detail. Redlich‡ has carried out such calculations for the original equations of Debye and Hückel, assuming complete dissociation. His equations agree with experiment up to 0·1 N. for the alkali halides, the conductivity curves of which resemble those in Fig. 40. Unfortunately, the original Debye-Hückel equations are not completely accurate, and actually the differential equations of Onsager (which take into account the Brownian movement) should be treated in the same way. The qualitative result of such a treatment would presumably be the same as that found by Redlich, i.e. it would lead to a conductivity curve lying above the limiting straight line. There are, however, certainly cases, e.g. the thallous salts, in which the conductivity curves curve down below the Onsager limiting slope (cf. Fig. 42). This is probably due to association, just as we found in considering activity phenomena (p. 257), and the question arises whether it is not possible to deduce at least approximate values for the degree of association from the conductivity curves. This has been done by Onsager§ and independently somewhat later by Nernst.‖

† L. Onsager, *Phys. Z.* **28** (1927), 277.

‡ O Redlich, *Phys. Z.* **26** (1925), 199; **27** (1926), 528.

§ L. Onsager, *Phys. Z.* **28** (1927), 277.

‖ W. Nernst, *Berl. Akad. Ber.* (1928), 4.

If there are two salts having equal conductivities at infinite dilution and the same transport numbers, then all the factors determining the interionic forces are the same for the two salts. If therefore they differ in their behaviour at higher concentrations, this must be attributed to chemical differences. Onsager has carried out comparisons of this kind. The salts are not strictly identical, and it may be doubted whether the individual deviations of the alkali halides are not due to these small differences. There can, however, be no doubt that abnormal curves are obtained in some cases, e.g. for the thallous salts, which have long been known to form complexes in aqueous solution.† Before treating these questions in detail, it is of interest to consider for a moment the difficulties which are involved in the problem of developing a theory of more concentrated solutions.

54. General Considerations Involved in a Treatment of more Concentrated Solutions

We shall first enumerate the most important simplifications which have been made in deriving the limiting laws for the conductivity of dilute solutions. These simplifications are no longer valid for more concentrated solutions.

In the first place Boltzmann's equation has been employed at the beginning of the derivation.‡ A second simplification is involved in neglecting the interaction between the interionic forces and the electrophoretic effect. Onsager§ has shown that the error thus introduced in equation (519) is approximately of the form

$$\beta \log \frac{\gamma_0^*}{\gamma^*}, \tag{646}$$

where γ_0^* depends upon the ionic diameter.

It would be interesting to calculate the quantity β in (646) accurately. It can, however, be shown definitely that in the range

$$10^{-4} < \gamma^* < 0{\cdot}5 \times 10^{-2}$$

the effect of the expression (646) is negligible, or can be expressed with sufficient accuracy by a term linear in γ^*. If the highest concentration we wish to consider is termed γ_1^*, we can write

$$\beta\gamma^* \log \frac{\gamma^*}{\gamma_0^*} = \beta\gamma^* \log \frac{\gamma_1^*}{\gamma_0^*} + \Delta = \beta_1 \gamma^* + \Delta, \tag{647}$$

† According to Drucker (*Z. Elektrochem.* **28** (1922), 463) the behaviour of thallium salts is largely due to the equilibrium $2Tl^+ \leftrightharpoons Tl^{+++}$.

‡ See p. 101.

§ L. Onsager, *Phys. Z.* **28** (1927), 277.

where $\Delta = \beta\gamma^* \log \frac{\gamma^*}{\gamma_1^*}$ and β_1 is a constant. The error is zero for $\gamma^* = 0$ and for $\gamma^* = \gamma_1^*$, but has an intermediate maximum value of

$$\Delta_{\max} = \beta\gamma_1^*/2{\cdot}718 \quad \text{at} \quad \gamma^* = \gamma_1^*/2{\cdot}718.$$

If we take 1-1-valent electrolytes in water and put $\gamma_1^* = 0{\cdot}005$, then the value of $\Delta_{\max}$ is less than 0·1 per cent. of the mobility, and hence is outside the limits of accuracy of conductivity measurements by the Kohlrausch method. The value of $\Delta_{\max}$ is greater for electrolytes of higher valency types, but the experimental accuracy is correspondingly lower. A rough calculation shows further that the ratio of the correction term to the square-root term in (519) is of the same order of magnitude as the ratio of the square-root term to the mobility itself. For 1-1-valent electrolytes in water at a concentration $\gamma = 0{\cdot}01$, the relative decrease in mobility corresponding to the square-root term is about 0·1. The correction term will therefore be about 1 per cent., and is thus hardly of importance at this concentration.

A further simplification implied in the limiting law is the assumption of complete dissociation. We know, however, that at somewhat higher concentrations undissociated molecules are also present, which will lead to deviations from the limiting law. This point has been dealt with in the previous section in connexion with heats of dilution. The effect of the undissociated part upon the conductivity curves will be treated in the next section.

A complete theory of more concentrated solutions must also take into account the fact that Coulomb's law cannot be assumed to hold for more concentrated solutions, since very considerable deviations must be anticipated when the ions approach closely together. These deviations appear partly as repulsive forces, and partly as increased attractive forces. Unfortunately nothing is known of the magnitude of these forces, and it is thus impossible to predict their effect upon the mobility of the ions. It would be of very great interest to obtain further information about these forces, which will include polarization forces, quantum-mechanical dispersion forces,† and the discontinuous quantum-mechanical forces of a purely chemical nature. The following qualitative predictions may be made. The repulsive forces will hardly extend beyond the first layer of molecules surrounding an ion. Their effect upon the mobility will thus be of the same order of magnitude as the effect of an increase in the ionic diameter, i.e. at the most a 100

† Corresponding to the van der Waals forces in gases.

per cent. decrease in the probability of the ion-pair configurations. It is quite impossible to predict the effect of the attractive forces which are superimposed upon the Coulomb forces. They may very well increase the probability of the ion-pair configurations by several hundred per cent. Although we know that for sufficiently small concentrations these forces are negligible compared to the Coulomb forces, it is impossible to state over what range of concentration this statement is valid. It is known from a theoretical point of view that these forces decrease with increasing distance much more rapidly than the Coulomb forces, and will hardly extend further than the first layer of molecules surrounding the ion. The effect of these forces upon the mobility can therefore probably be expressed approximately as a term directly proportional to the concentration.

A further simplification is introduced in employing Boltzmann's equation at the beginning of the deduction of the limiting law. It is, of course, possible in principle to extend the calculations of Gronwall, La Mer, and Sandved to the treatment of conductivity phenomena. This would presumably lead to both positive and negative deviations from the limiting law, just as in the case of heats of dilution. It is, however, probable that a strict statistical treatment employing the correct law of force would introduce some modifications into the calculations of Gronwall, La Mer, and Sandved.

Finally, we must consider the possibility that the ions may associate together to form larger ions in more concentrated solutions. The interaction with the solvent has also been neglected.

These considerations are intended to illustrate the extremely great difficulties associated with any theory of more concentrated solutions. Progress in this direction is bound to be gradual, and in the author's opinion there is no immediate prospect of an exact theory of more concentrated solutions, any more than it has proved possible to obtain a general equation of state for gases. All attempts which have so far been made to determine the true degree of dissociation must therefore be only approximate in character. We shall now turn to the methods developed by Onsager, Nernst, and recently by Davies and Wien for determining the true degree of dissociation.

55. Approximate Determination of the True Degree of Dissociation from Conductivity Measurements (Onsager, Nernst, Davies, McInnes, Fuoss, and Kraus)

We shall now show that for electrolytes with a tendency to association, the true ionic concentrations can be calculated approximately by means

of the law of mass action. This has been done especially by Onsager and Nernst. They have pointed out that better values for the true degree of dissociation could be obtained by using the generalized law of mass action, and this idea has been developed further by Davies, McInnes, Fuoss, and Kraus.† We shall first follow Onsager, and calculate how great the dissociation constant of a 1-1-valent electrolyte must be in order to cause a decrease in apparent mobility of the same order of magnitude as the decrease caused by the electrical forces. The effect of the incomplete dissociation will be calculated according to the classical law of mass action, i.e. we shall not take into account the effect of the activities, as has been done by Davies. The effect of the interionic forces will be calculated according to Onsager's limiting equation (519).

Let $1-\alpha^*$ be the true fraction of undissociated molecules. If $1-\alpha^*$ is small, the mass law for binary electrolytes becomes approximately

$$1-\alpha^* = \frac{\gamma^*}{K}. \tag{648}$$

The decrease in mobility caused by this decrease in the number of ions is

$$\frac{l_{j\infty}\gamma^*}{K}. \tag{649}$$

According to Onsager's limiting law, the decrease in mobility caused by interionic action is given by (519) as $\alpha_j\sqrt{\gamma}$.‡ The two effects therefore cause equal decreases in mobility at a concentration given by

$$\gamma^* = \frac{K^2\alpha_j^2}{l_{j\infty}^2}. \tag{650}$$

In more dilute solutions the effect of the electrical forces will be more prominent, while in more concentrated solutions the effect of association will predominate. The ratio of the two effects is

$$\frac{1}{K}l_{j\infty}\gamma^*/\alpha_j\sqrt{\gamma^*} = \frac{l_{j\infty}}{K\alpha_j}\sqrt{\gamma^*}, \tag{651}$$

which approaches to the value zero with decreasing concentration. For 1-1-valent electrolytes in water (520) shows that the value of α_j is of the same order of magnitude as l_j, α_j being greater then l_j for all ions except the hydrogen and hydroxyl ions, for which it is a little smaller. If the dissociation constant is $K = 0{\cdot}01$, (651) shows that incomplete

† For references see p. 250. Previous to the work of Onsager, the combined use of the law of mass action and interionic action for strong electrolytes had been proposed by Gross and Halpern (*Phys. Z.* **26** (1925), 403), Sherrill and Noyes (*J. Am. Chem. Soc.* **48** (1926), 1861), McInnes (ibid. **48** (1926), 2068), and Davies (*J. Phys. Chem.* **29** (1925), 277.)

‡ We do not need the exact expression for α_j given in (520).

dissociation is the determining factor for concentrations $\gamma^* > 0{\cdot}0001$. If, on the other hand, $K = 1$, the effect of the electrical forces is the predominating effect for all concentrations less than $\gamma^* = 1$.

Combining (649) and (519), the conductivity curve appears as a parabola,

$$\Lambda = \Lambda_\infty - \alpha\sqrt{\gamma^*} - \frac{\Lambda_\infty}{K}\gamma^*. \tag{652}$$

It should be possible to obtain an approximate value for the dissociation constant from the curvature of this parabola. The equation possesses, however, only a very limited validity, since the factors mentioned in the preceding paragraph have not been taken into account. A further uncertainty is also introduced by the fact that the change of viscosity with concentration will affect the term linear in γ^*. The effect of this correction could be estimated: it is, however, uncertain how far the macroscopic viscosity should be employed in (520), or whether a microscopic viscosity determines the motion of the ions.† If the mobility decreases more rapidly in dilute solutions than demanded by (519), we may always conclude that some association is present. It may be anticipated that the tendency to association will in general be greater for media of low dielectric constant and ions of higher valencies.

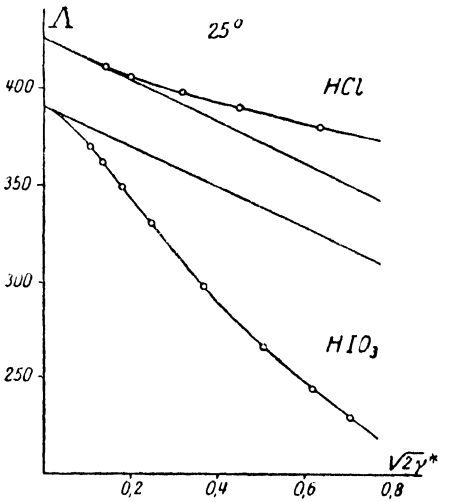

FIG. 96. Equivalent conductivity of acids in water.

In the case of iodic acid, incomplete dissociation becomes apparent even in very dilute solutions, and we can therefore represent the conductivity curve by a parabola which has the theoretical slope at $\gamma^* = 0$. Fig. 45 shows the observed values up to $\gamma^* = 0{\cdot}004$ compared with the theoretical parabola

$$\Lambda = 396{\cdot}3 - 105{\cdot}3\sqrt{(2\gamma^*)} + 2{\cdot}2 \times 10^3\gamma^*,$$

which corresponds to a dissociation constant $K = 0{\cdot}17$. The two series shown with triangles were carried out with less pure water. At higher concentrations the limiting formula fails, no doubt owing to neglect of the factors mentioned in the preceding paragraph. Fig. 96 shows the

† Cf. § 46, also footnote 1, p. 29.

conductivity curves of HCl and HIO_3 up to $\gamma^* = 0{\cdot}3$. Good agreement with the limiting formula extends only up to $\gamma^* = 0{\cdot}004$. The curve for HIO_3 has one interesting property. There is a point of inflexion, and between $\gamma^* = 0{\cdot}005$ and $\gamma^* = 0{\cdot}05$ the plot against $\sqrt{\gamma^*}$ is almost exactly linear. In the absence of measurements for more dilute solutions it would be easy to extrapolate this portion of the curve to $\Lambda_\infty = 400$ and thus obtain an incorrect limiting slope, just as was the case for 2-2-valent electrolytes.† It is certain that the variation of mobility with concentration cannot be wholly explained by the Coulomb interionic forces. To illustrate this we shall consider the four electrolytes KCl, KNO_3, TlCl, and $TlNO_3$. The extrapolation employed by Debye and Hückel gives for their conductivities at infinite dilution the values 129·9, 126·5, 131, and 127·6, and equations (519) and (520) give the values 56·4, 55·8, 56·6, and 56 for the theoretical limiting slopes, which are thus practically identical within the experimental error. The transport numbers are all in the neighbourhood of 0·5. We should therefore expect that any second-order effects, such as the interaction between the ionic forces and the electrophoretic effect, will be almost identical for all four salts. A comparison of the experimental results for the four salts should thus enable us to recognize the presence of effects other than those due to Coulomb forces. Fig. 42 shows the values of Λ plotted against $\sqrt{\gamma^*}$ up to $\gamma^* = 0{\cdot}01$. There are obvious individual differences between the different curves: while the KCl curve is bent above the limiting straight line, the curves for the other three salts are bent downwards. The KNO_3 curve has only a very slight curvature, while the curves for the two thallium salts bend downwards over the whole concentration range. The differences between the viscosities of the different solutions amount to less than 0·05 per cent. over the whole range, and are thus negligible. The differences in the ionic diameters are also probably fairly small, and the observed individualities must therefore be attributed to ion association. This conclusion is perhaps somewhat doubtful in the case of KNO_3 since the effect is very small. If we assume that KCl is completely dissociated, the dissociation constants for the three other salts KNO_3, $TlNO_3$ and TlCl can be calculated. Onsager uses the values 129·9, 126·3, 127·5, and 131·1 for Λ_∞ for the salts KCl, KNO_3, $TlNO_3$, and TlCl respectively. For $\gamma^* = 0{\cdot}01$, Λ for KCl is 120·43, i.e. 0·5 units greater than the value calculated from the limiting expression $\Lambda_\infty - \alpha\sqrt{(2\gamma^*)}$. If the other salts were completely dissociated, the considerations given above would lead

† See p. 197.

us to expect that in these cases also Λ for $\gamma^* = 0{\cdot}01$ would be 0·5 unit greater than the value given by the limiting expression. The amounts by which the observed values of $\Lambda_{0{\cdot}01}$ are less than the calculated values may thus be used to calculate the effective ionic concentrations and hence the dissociation constants. Table 49 gives the results of these calculations.†

TABLE 49

Salt	KCl	KNO_3	$TlNO_3$	TlCl
Λ_∞	129·9	126·3	127·5	131·1
$\Lambda_{0{\cdot}01} - \Lambda_\infty + a\sqrt{0{\cdot}02}$	+ 0·5	− 0·2	− 1·2	− 2·1
Deficit in $\Lambda_{0{\cdot}01}$	0	− 0·7	− 1·7	− 2·6
Degree of dissociation α^*	1	0·994	0·987	0·980
Fraction undissociated	0	0·006	0·013	0·020
K_a	∞	1·4	0·59	0·40

The more accurate method of Davies,‡ which we shall now deal with, leads to approximately the same results for the examples given above. Davies employs the exact form of the law of mass action (133) involving activities. Consider first a 1-1-valent electrolyte which dissociates according to the scheme

$$AB \rightleftharpoons A^- + B^+. \tag{653}$$

For any concentration γ the concentrations of B^+, A^-, and AB are respectively $\alpha^*\gamma$, $\alpha^*\gamma$, and $(1-\alpha^*)\gamma$, where α^* is the true degree of dissociation. The molar conductivity Λ is then given by

$$\Lambda = \alpha^*(l_A + l_K), \tag{654}$$

or writing

$$\Lambda_x = l_A + l_K, \tag{655}$$

then

$$\Lambda = \alpha^* \Lambda_x. \tag{656}$$

Davies uses Onsager's equation (519) for Λ_x, which gives for water at 25°

$$\Lambda_x = \Lambda_\infty - (\alpha^*\gamma)^{\frac{1}{2}}(0{\cdot}2271\Lambda_\infty + 59{\cdot}78). \tag{657}$$

† In order to calculate $K_a = f^2K$ Onsager uses the value 0·89 for the activity coefficients f of all three electrolytes at $\gamma^* = 0{\cdot}01$, which agrees only approximately with more recent measurements. Onsager's values of K_a are therefore somewhat inaccurate. The slightly different values given in Table 49 were obtained by the author by repeating Onsager's calculations.

‡ See also Wien's method, § 56. Measurements of departures from Beer's law lead to values of the same order of magnitude for α^*. (See v. Halban and Eisenbrand, *Z. phys. Chem.* **132** (1928), 412: also p. 313.) An interesting point has been raised by Ebert. While e.g. $CuSO_4$ obeys Beer's law well, deviations are observed in the ultra-violet which may be related to the Onsager-Davies conception. (See R. Mecke and H. Ley, *Z. f. anorg. Chem.* **173** (1928), 287.) It is therefore not safe to conclude that a system is chemically unchanged from its optical constancy in a particular range of wave-lengths. One can in fact use the sensitivity of a given absorption range to concentration changes to obtain information about the situation of the absorbing centres, e.g. for $CuSO_4$ they may lie deep in the ion $Cu(H_2O)_4$, so that ion association has no effect.

Davies's method is thus only strictly correct when equation (657) holds, i.e. up to a concentration of $\alpha^*\gamma = 0{\cdot}002$. From (656) and (657)

$$\Lambda_x = \Lambda_\infty - \left(\frac{\Lambda}{\Lambda_x}\gamma\right)^{\frac{1}{2}}(0{\cdot}2271\Lambda_\infty + 59{\cdot}78). \tag{658}$$

From this relation Λ_x may be obtained by a series of successive approximations.† We first put $\Lambda = \Lambda_\infty$ in the term $(\Lambda\gamma/\Lambda_x)^{\frac{1}{2}}$ and calculate an approximate value of Λ_x from (658). This approximate value is introduced in the right-hand side of (658) and a second approximate value calculated. By continuing in this way a fairly accurate value for Λ_x (and hence from (656) for α^*) may be rapidly obtained. As an example we shall take the weak electrolyte formic acid in water at 18°. In this case $\Lambda_\infty = 364{\cdot}5$, and for $\gamma = 0{\cdot}03208$ the value $\Lambda = 27{\cdot}36$ was observed. Calculation from (658) then gives $\Lambda_x = 361$, and for the true degree of dissociation $\alpha^* = 0{\cdot}0764$.

We now introduce the generalized law of mass action (133)

$$\frac{a_A - a_{B^+}}{a_{AB}} = K_a, \tag{659}$$

where the a's are activities. If γ_i is the concentration of the ions and γ_u the concentration of the undissociated molecules, then introducing the corresponding activity coefficients,

$$\frac{\gamma_i^2}{\gamma_u}\frac{f_A - f_{B^+}}{f_{AB}} = K_a. \tag{660}$$

We have just seen that it is possible by making certain assumptions to calculate the true degree of dissociation α^*, and hence $\gamma_i = \alpha^*\gamma$. We therefore have

$$\gamma_u = (1-\alpha^*)\gamma = \gamma - \gamma_i. \tag{661}$$

It has been previously shown‡ that the values of f_{A^-} and f_{B^+} can be calculated from e.g. freezing-point measurements, as has been done by Lewis and his collaborators. f_{AB} cannot be obtained directly without knowing K_a: we may, however, assume for dilute solutions

$$f_{AB} = 1, \quad a_{AB} = \gamma_u. \tag{662}$$

This assumption is supported by the success of the ionic theory, which explains the variation in the activity of an ion as due entirely to its charge. There is thus no reason to suppose that the activity coefficient of a neutral molecule changes appreciably in dilute solution. Lewis and Randall§ found that the activity coefficient of glycerine in aqueous

† Also Schreiner (*Z. anorg. Chem.* **115** (1921), 185) has pointed out that the degree of dissociation can be obtained from the conductivity by means of successive approximations.

‡ See p. 62.

§ Lewis and Randall, *Thermodynamics*, p. 288.

solution only changes from 1 to 1·006 in a concentration range 0–0·1 N. Similarly, Randall and Failey† showed from a large amount of experimental material that the activity coefficients of neutral molecules in salt solutions vary very little, the effect being negligible in dilute solutions. If the electrolyte has a tendency to polymerization, the method outlined here will not give constant values for K_a. In exceptional cases of this kind, further investigation of the molecular state of the substance is necessary.

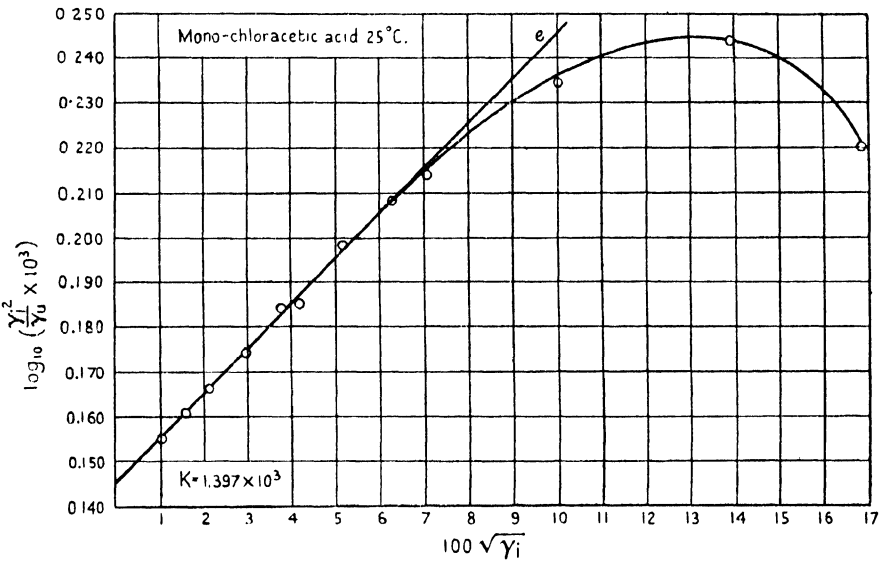

FIG. 97. Variation of the dissociation constant of monochloracetic acid with concentration.

Assuming $f_{AB} = 1$, (660) becomes

$$\frac{\gamma_i^2}{\gamma_u} f_A - f_{B^+} = K_a. \tag{663}$$

The Debye-Hückel theory gives for dilute solutions (283″)

$$\log_{10} f_i = -A\sqrt{\gamma_i}, \tag{664}$$

where $A = 0{\cdot}5$ for water at 18°. Combining this with (663),

$$\log_{10} \frac{\gamma_i^2}{\gamma_u} = \log_{10} K_a + 2A\sqrt{\gamma_i}. \tag{665}$$

Fig. 97 shows $\log_{10}(10^3\gamma_i^2/\gamma_u)$ plotted against $100\sqrt{\gamma_i}$ for monochloracetic acid, the data being taken from recent accurate measurements by

† M. Randall and C. E. Failey, *Chem. Rev.* **4** (1927), 271.

McInnes and his collaborators.† The theoretical value of 0·5 was found for A.

Data for salts in liquid ammonia, acetone, and benzonitrile show that all salts are fairly weak electrolytes in these solvents,‡ and it might be thought that Davies's treatment could be applied in these cases. The difficulty arises, however, that the Λ_∞-values are not accurately known; further, the Onsager equation is only valid for a very limited concentration range.§ Ostwald's dilution law (74) can often be used for very weak electrolytes in non-aqueous solutions.‖ Davies (loc. cit.) has attempted to determine the true degree of dissociation in more concentrated solutions by employing an equation for the sum of the mobilities which differs from (657). The values thus obtained are, however, uncertain for several reasons; they also disagree with the values obtained by Nernst.

The method of Kraus and Fuoss.

Kraus and Fuoss†† have recently evolved a very interesting method of applying the correction for the interionic forces and the law of mass action to conductivity data. Equations (578), (592), and (519) respectively can be written in the form

$$-\log_{10} f = \frac{0{\cdot}4343\beta''(\alpha^*\gamma)^{\frac{1}{2}}}{1+\delta''(\alpha^*\gamma)^{\frac{1}{2}}}, \tag{665 a}$$

$$\frac{\gamma\alpha^{*2}f^2}{1-\alpha^*} = K_a, \tag{665 b}$$

$$\Lambda = \alpha^*\{\Lambda_\infty - \alpha''(\alpha^*\gamma)^{\frac{1}{2}}\}, \tag{665 c}$$

† For references, see p. 196. The results of C. W. Davies are less accurate, since he employs a value of A differing from 0·5 (see the German edition of this book, p. 297). Davies has applied his method to a series of acids, the thallous salts, and aqueous solutions of 2-2-valent salts: his values of K_a show good constancy. See C. W. Davies, *The Conductivity of Solutions* (New York 1930), p. 93; *J. Chem. Soc.* (1930) 2421; W. H. Banks, E. C. Righellato, and C. W. Davies, *Trans. Farad. Soc.* **27** (1931), 621. It may be noted that Bjerrum (*Z. Elektrochem.* **24** (1918), 321) used a similar method for calculating the dissociation constant of picric acid, but made use of the cube-root law for the variation of the activity coefficient with concentration. McInnes (*J. Am. Chem. Soc.* **48** (1926), 2068) treated weaker electrolytes in a similar way, apparently without knowledge of Bjerrum's work. M. Randall and C. F. Failey (*Chem. Rev.* **4** (1927), 305) have similarly obtained the values $K_a = 1{\cdot}39\times10^{-3}$ and $5{\cdot}53\times10^{-2}$ for mono- and di-chloracetic acids at 25°. A. A. Noyes and M. S. Sherrill (*J. Am. Chem. Soc.* **48** (1926), 1861) have treated acids of medium strength in the same way, and find e.g. for the first dissociation of H_3PO_4 $K_a = 8{\cdot}3\times10^{-3}$ at 18°.

‡ For references, see p. 205.

§ See the next section.

‖ See e.g. H. Goldschmidt and H. Aarflot, *Z. phys. Chem.* **117** (1925), 312; **119** (1926), 439; Goldschmidt and Aas, ibid. **112** (1924), 423.

†† Fuoss and Kraus, *J. Am. Chem. Soc.* **55** (1933), 476.

where β'' and α'' are given by equations (595 d) and (595 e), and δ'' is given by the equation

$$\delta'' = \left(\frac{8\pi N\epsilon^2}{1{,}000 D_0 kT}\right)^{\frac{1}{2}} a.$$

Equations (665 a), (665 b), and (665 c) represent implicitly an expression for the molar conductivity Λ in terms of the concentration γ. However, on account of the form of these equations, it is difficult to obtain an explicit solution. Introducing a new variable x by the equation

$$x = \frac{1-\alpha^*}{\alpha^{*2}} = \frac{\gamma f^2}{K_a}, \tag{665 d}$$

it is possible to transform the equations to a more convenient form. We obtain

$$\frac{\Lambda}{\Lambda_\infty} = \alpha^* - \frac{\alpha'' K_a^{\frac{1}{2}} x^{\frac{1}{2}} \alpha^{*\frac{3}{2}}}{\Lambda_\infty f} \tag{665 e}$$

$$-f \log_{10} f = \frac{\beta'' K_a^{\frac{1}{2}} (x\alpha^*)^{\frac{1}{2}}}{1+\delta''(\alpha^*\gamma)^{\frac{1}{2}}}. \tag{665 f}$$

By solving equation (665 d), we also have

$$x^{\frac{1}{2}} = \frac{(1-\alpha^*)^{\frac{1}{2}}}{\alpha^*}, \qquad \alpha^* = \{(1+4x^2)^{\frac{1}{2}} - 1\}/2x, \tag{665 g}$$

which for small values of x can be expanded as the series

$$\alpha^*(x) = 1 - x + 2x^2 - 5x^3 + 14x^4 - 42x^5 + \ldots .$$

The values of Λ_∞ and K_a are obtained from the conductivity data in the following way. As a first approximation α^* under the root in (665 c) is replaced by Λ/Λ_∞, giving

$$\alpha^{*\prime} = \frac{\Lambda/\Lambda_\infty}{1-\alpha''\Lambda_\infty^{-\frac{3}{2}}(\gamma\Lambda)^{\frac{1}{2}}}.$$

This expression is then evaluated using a value for Λ_∞ obtained by extrapolating the $(\Lambda, \gamma^{\frac{1}{2}})$ curve: this value need not be very accurate, since the final results are independent of the value initially assumed for Λ_∞. This value for $\alpha^{*\prime}$ is again substituted under the square root in (665 c), and a second approximation obtained. By repeating this process, the values of α^* finally converge to a constant value, which is substituted in (665 g) to give $x^{\frac{1}{2}}$, and in (665 a) to give $x^{\frac{1}{2}}$. $f\gamma^{\frac{1}{2}}$ is then plotted against $x^{\frac{1}{2}}$. According to equation (665 d), this should give a straight line passing through the origin with a slope of $K_a^{\frac{1}{2}}$. If the value chosen for Λ_∞ is greater than the true value, the $(f\gamma^{\frac{1}{2}}, x^{\frac{1}{2}})$ curve will have a positive intercept on the $x^{\frac{1}{2}}$ axis. It is thus possible by interpolation to obtain the true value of Λ_∞. The slope of the line thus obtained is then equal to $K_a^{\frac{1}{2}}$. Since the $(f\gamma^{\frac{1}{2}}, x^{\frac{1}{2}})$ curves (except in very dilute solutions) are very

nearly linear, it is sufficient to take only two suitable concentrations in the above calculations. When Λ_∞ and K_a are known, the conductivity curve is calculated as follows. The corresponding values of α^*, $x^{\frac{1}{2}}\alpha^{*\frac{1}{2}}$ and $(x\alpha^*)^{\frac{1}{2}}$ are obtained graphically or by means of tables in terms of $x^{\frac{1}{2}}$. If now $f\log_{10}f$ is plotted against f, approximate values of f can be calculated from the equation

$$-f'\log_{10}f' = \beta''K_a^{\frac{1}{2}}(x\alpha^*)^{\frac{1}{2}}.$$

Using these values for f, approximate values of the concentration are calculated from the equation

$$\gamma'^{\frac{1}{2}} = \frac{K_a^{\frac{1}{2}}x^{\frac{1}{2}}}{f'}.$$

These values γ' are then used to calculate the correction term in (665 f), from which a second set of approximate values can be obtained for f by the equation

$$-f''\log_{10}f = \frac{\beta''K_a^{\frac{1}{2}}(x\alpha^*)^{\frac{1}{2}}}{1+\delta''(\gamma\alpha^*)^{\frac{1}{2}}}.$$

This method of approximation converges rapidly, and when finally a constant set of values has been obtained for f, $\gamma^{\frac{1}{2}}$, and Λ are calculated from equations (665 b) and (665 e). Fig. 97 A shows how well the calculated curve agrees with the experimental points. The constants employed are given in Table 50.

TABLE 50

	I	II	III	IV	V
Solvent	H_2O	NH_3	$C_5H_{11}OH$	$C_2H_4Cl_2$	NH_3
Electrolyte	HIO_3	$NaBrO_3$	NaI	$(C_5H_{11})_4NNO_3$	KNH_2
$t°$ C.	25	−33·5	25	25	−33·5
D_0	78·57	22	16	10·4	22
η	0·00895	0·00256	0·038	0·00785	0·00256
α''	148·75	1052	59·19	500	1191
δ''	0·0153	1·54	2·80	2·86	1·26
β''	0·5044	4·742	5·517	10·52	4·742
Λ_∞	391·19	286·2	11·246	65·8	351·3
K_a	0·1686	0·00253	0·00295	0·00115	0·000070

Two limiting cases may be noted. If K_a is very large, $\alpha^* \simeq 1$ and (665 c) reduces to Onsager's equation (652). In the other limiting case when K_a is very small and hence $\alpha^* \ll 1$, (665 b) can be written (since $f \simeq 1$)

$$\gamma\alpha^{*2} = K_a. \qquad (665\,\text{h})$$

Further in this case we have approximately

$$\alpha^* = \frac{\Lambda}{\Lambda_\infty},$$

so that (665 h) can be written

$$\gamma\Lambda^2 = K_a\Lambda_\infty^2.$$

Hence if we plot $\log_{10}\Lambda$ against $\log_{10}\gamma$, a straight line of slope $-\frac{1}{2}$ should be obtained. This corresponds to what is actually found. As an example, Fig. 97 B shows the conductivity curves† for tetraisoamylammonium

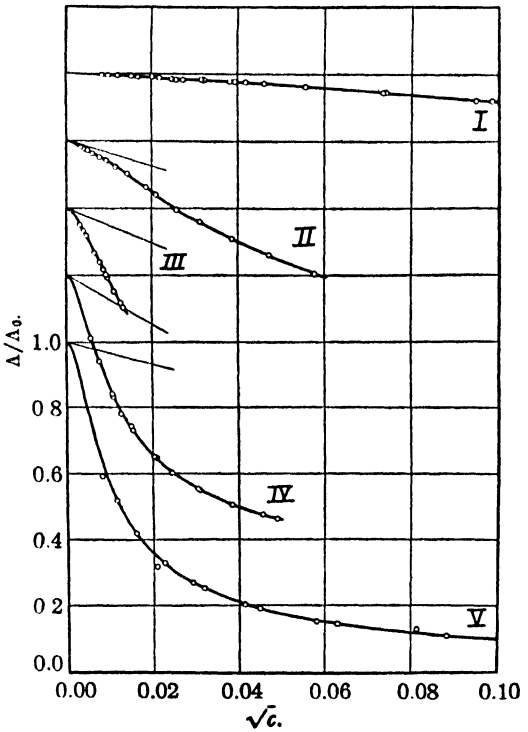

FIG. 97 A. Comparison of conductivity data with the theory of Kraus and Fuoss.

nitrate in mixtures of dioxane ($D_0 = 2{\cdot}2$) and water ($D_0 = 78$). The percentage water by weight is shown below the corresponding curves. The slope of the curves at low concentrations approaches the theoretical value of $-0{\cdot}5$, indicated on the figure by straight lines.

In another paper, Kraus and Fuoss‡ have applied the mass law and the correction for interionic forces to conductivity data for a number of other salts and solvents, and showed that their treatment represented the conductivity curves well. The dissociation constant is a unique function of the dielectric constant of the solvent and the parameter a

† From measurements by Kraus and Fuoss, *J. Am. Chem. Soc.* **55** (1933), 26.

‡ Fuoss and Kraus, *J. Am. Chem. Soc.* **55** (1933), 476.

corresponding to the ionic diameter.† Bjerrum's conception of ion pairs agrees well with the observed values. a depends on the properties of the electrolyte and those of the solvent, and is roughly an additive function of the ions present. Fuoss and Kraus have also succeeded in obtaining a quantitative interpretation of conductivities in solvents of dielectric constant less than 10, in which a minimum point appears in the conductivity curve.

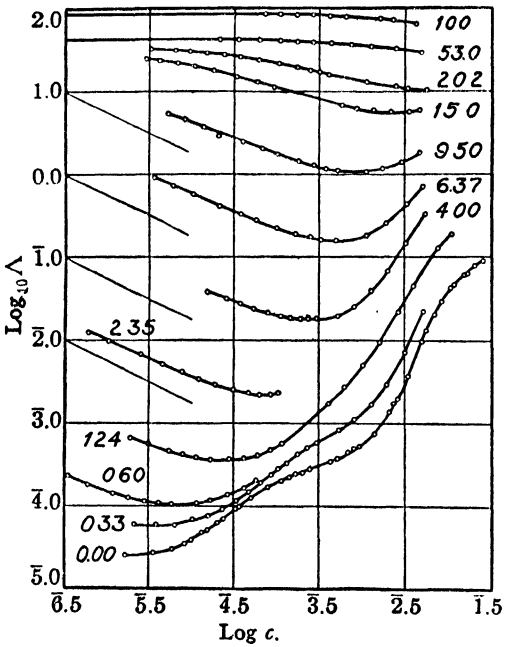

FIG. 97 B. The conductivity of tetraisoamylammonium nitrate in dioxane-water mixtures.

56. Wien's Method for determining the True Degree of Dissociation

The considerations in this paragraph are based on unpublished work by M. Wien, which he has kindly communicated to the author. Like Davies's theory, Wien's treatment depends upon the validity of the limiting laws, and is hence only approximately correct for solutions of finite concentration.

A. *Wien's first method.*

This method is essentially the same as the treatment of Davies described in the preceding paragraph, but employs a different method of

† Fuoss and Kraus, *J. Am. Chem. Soc.* **55** (1933), 1019.

calculation. If Λ^* and γ^* are the equivalent conductivity and equivalent concentration respectively, and $\alpha^* = \gamma_i^*/\gamma^*$ then (656) and (657) become

$$\frac{\Lambda^*}{\Lambda_\infty^*} = \alpha^*\{1-\beta(\alpha^*\gamma^*)^{\frac{1}{2}}\}, \tag{666}$$

where β may be calculated from the Debye-Onsager theory by (522). Equation (666) expresses the fact that the equivalent conductivity is decreased in two ways by increasing the concentration; firstly by the relative decrease in the number of ions, and secondly by the decrease in the velocities of the ions due to the Debye effect. Equation (666) is a cubic in α^*: writing

$$x = \frac{1}{\alpha^*}$$

it becomes

$$x^3 - \frac{\Lambda_\infty^*}{\Lambda^*}x + \frac{\Lambda_\infty^*}{\Lambda^*}\beta\sqrt{\gamma^*} = 0.$$

This is of the form

$$x^3 - px + q = 0,$$

and provided that $4p^3 > 27q^2$ the solution is

$$\frac{1}{\alpha^*} = x = \frac{2\sqrt{p}}{\sqrt{3}}\sin(60-\phi) = \frac{2}{\sqrt{3}}\left(\frac{\Lambda_\infty^*}{\Lambda^*}\right)^{\frac{1}{2}}\sin(60-\phi), \tag{667}$$

where

$$\sin 3\phi = \frac{3}{2}\frac{q}{p}\frac{\sqrt{3}}{\sqrt{p}} = \frac{3\beta}{2}\left(3\gamma^*\frac{\Lambda^*}{\Lambda_\infty^*}\right)^{\frac{1}{2}}.$$

We shall now give some applications of this treatment. We shall not deal with strong electrolytes, for which the degree of dissociation is very near unity, and hence the plot of Λ^* against $\sqrt{\gamma^*}$ lies very near the theoretical Debye-Onsager straight line.† This is the case for NaCl and $CoCl_2$ in water; for $MgSO_4$ the initial part of the $(\Lambda_\infty, \sqrt{\gamma})$ curve is steeper than the calculated line, which is probably connected with the uncertainty of determinations at great dilutions. It is characteristic of all these curves that they lie above the Debye-Onsager limiting straight line.

We shall also exclude from consideration the case of weak acids in water. Although they are strongly associated, the Debye effect is of little importance at the ionic concentrations involved, since most of the acids are 1-1-valent.

There are, however, a large number of solutions in non-aqueous solvents (such as the alcohols and acetone) in which both effects are simultaneously of importance. As examples of the calculation of the true degree of dissociation we shall take the strongly associated solutions LiBr in acetone and $CoCl_2$ in ethyl alcohol. Fig. 98 shows the

† See p. 192.

results for LiBr. The lowest curve gives the values of $\Lambda^*/\Lambda^*_\infty$ obtained by the ordinary method of calculation, and the dotted line above it gives the true degree of dissociation. The straight line is calculated from the Debye-Onsager equation (519), and the uppermost dotted line is the Debye curve corrected according to (666). As an example of the calculation, take the point $\gamma^* = 0{\cdot}01$. $\Lambda^*/\Lambda^*_\infty = 0{\cdot}257$, which gives from (667) $\alpha^* = 0{\cdot}335$, using the values for acetone $D_0 = 20{\cdot}5$ and

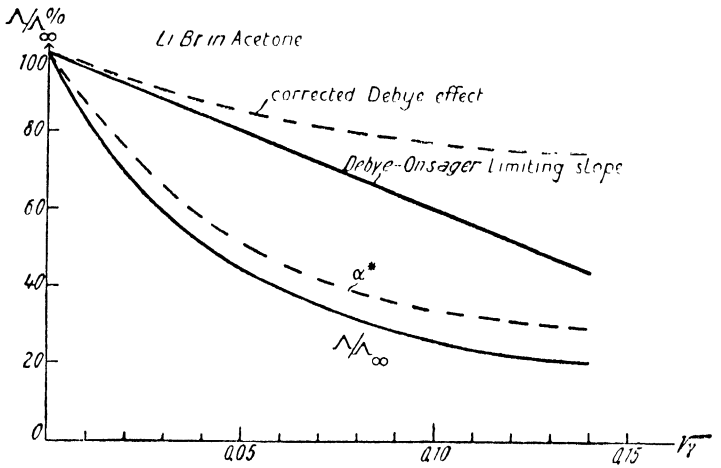

FIG. 98. The dissociation of LiBr in acetone.

$\eta_0 = 0{\cdot}0037$, and hence from (522), $\beta = 4{\cdot}1$. Table 51 gives the results for $CoCl_2$ in ethyl alcohol, for which case $\beta = 6{\cdot}25$.

TABLE 51

$\sqrt{\gamma^*}$	$\left(\frac{\Lambda^*}{\Lambda^*_\infty}\right)_{\text{calc}}$	α^*	*Debye-Onsager limiting law*	*Corrected Debye-Onsager law*
0·01	0·640	0·670	0·938	0·948
0·02	0·460	0·515	0·873	0·907
0·03	0·365	0·426	0·811	0·870
0·04	0·308	0·369	0·750	0·835
0·05	0·270	0·332	0·688	0·805
0·075	0·221	0·299	0·530	0·735
0·10	0·187	0·290	0·375	0·663
0·12	0·166	0·275	0·250	0·610
0·14	0·150	0·262	0·130	0·556

In both these examples the true degrees of dissociation are considerably greater than the values calculated by the classical Arrhenius theory. Similarly, the curve for the corrected Debye effect lies higher than the uncorrected curve; i.e. the effect is decreased by the decrease in the ionic concentration.

B. *Wien's method for determining the true degree of dissociation from the Debye-Falkenhagen dielectric constant effect.*

The preceding calculations are subject to uncertainty for two reasons, which are particularly important for polyvalent ions and strongly associated electrolytes. In the first place the value of Λ_∞ is often un-uncertain. Secondly, the electrophoretic effect has been little investigated: for the solvents dealt with above it constitutes the greater part of the Debye effect and is subject to further uncertainty because it involves Λ_∞ (see (519) and (522)). It is therefore of special interest that other methods exist for determining the true ionic concentration. Debye and Falkenhagen† have shown that the presence of ions changes the dielectric constant according to a square-root law. Electrophoresis plays no part in this effect, and there is no uncertainty due to Λ_∞. On the other hand, the effect of concentration upon the dielectric constant is comparatively small and difficult to measure. It is also dependent upon the frequency, except in the regions of high concentrations and long wave-lengths. This introduces a great difficulty, since the methods for measuring the dielectric constant fail for high concentrations (i.e. high conductivities) and become more difficult the longer the wave-length. However, in cases where other methods fail, the alteration in dielectric constant may give some information about the true degree of dissociation.

As an example we shall calculate the degree of dissociation of LiBr at two concentrations in acetone, by comparing with KI, which is practically completely dissociated in acetone. (539′) gives for symmetrical electrolytes at 18°

$$\frac{D_{\omega=0}-D_0}{D_0} = \frac{33{\cdot}7\, z^{5/2}}{D_0^{3/2}}\sqrt{\gamma_i^*}, \tag{668}$$

which becomes for acetone ($D_0 = 20{\cdot}5$)

$$\gamma_i^* = 7{\cdot}6\left(\frac{D_{\omega=0}-D_0}{D_0}\right)^2. \tag{669}$$

Measurements with a wave-length of 10 m. using the barretter method give for LiBr relative to KI

$$\gamma^* = 0{\cdot}0069 \qquad \lambda_0 = 2{\cdot}8\times 10^{-4} \qquad \frac{D_\omega - D_0}{D_0} = 0{\cdot}0163$$

$$\gamma^* = 0{\cdot}06 \qquad \lambda_0 = 9\times 10^{-4} \qquad \frac{D_\omega - D_0}{D_0} = 0{\cdot}048.$$

† See p. 220.

Taking into account the theoretical dependence upon the frequency (equation (538)) we obtain for $\gamma^* = 0{\cdot}0069$ the value

$$\frac{D_{\omega=0}-D_0}{D_0} = 0{\cdot}017,$$

which with (669) gives

$$\gamma_i^* = 0{\cdot}0022 \quad \text{i.e.} \quad \alpha^* = 0{\cdot}33.$$

For the second concentration $\gamma^* = 0{\cdot}06$ we get similarly

$$\gamma_i^* = 0{\cdot}0176 \quad \text{i.e.} \quad \alpha^* = 0{\cdot}29.$$

These values fit fairly well into the curve obtained by the first method, and may be considered quite satisfactory considering the difficulties associated with dielectric constant measurements.

Results of the right order of magnitude are also obtained for the degree of dissociation of $CoCl_2$, but in this case no reliable comparison can be made, since the experimental values of Λ^* and Λ_∞^* are very inaccurate.

C. *Degree of dissociation and field effect.*

The presence of ionic association can also be detected by the fact that the field effect will exceed the normal effect predicted by the Debye-Onsager-Blumentritt theory. This abnormal field effect† is due to the increase of dissociation caused by the powerful electric field. If the abnormal effect is considerably greater than the normal effect, this may be safely attributed to association. If, however, dissociation is almost complete (especially in concentrated aqueous solutions) the increase cannot be detected with certainty, since Debye's theory is not sufficiently valid for more concentrated solutions. No conclusions can be drawn from the form of the curve, since the same type of curve is obtained for the normal field effect and the dissociation field effect. The two effects are superimposed and are difficult to separate. It is therefore not yet possible to make any quantitative deductions about the degree of dissociation from the abnormal field effect. These considerations of Wien do, however, open up an interesting field for further investigation.

57. The Determination of the Degree of Dissociation of Electrolytic Solutions from their Optical Properties

In connexion with the above methods for studying the true degree of dissociation, it is of interest to consider what information can be obtained by measurements of optical properties, i.e. absorption spectra,

† See p. 240.

refractive indices and Raman spectra. We may hope that such methods may enable us to differentiate between the dissociated and undissociated fractions in an electrolytic solution, and hence to measure the true degree of dissociation. Although the problem is by no means solved,† it offers a fruitful field for future investigations.

A. *The absorption spectra of strong electrolytes* (*Bjerrum, v. Halban, J. Franck, Ebert, Scheibe and Eisenbrand, Gross and Goldstern, Fromherz and collaborators.*)

Many indicators, e.g. litmus and phenolphthalein, undergo colour changes under certain circumstances. These visible optical changes can often be attributed to the dissociation of molecules into free ions, often caused merely by dilution. While weak electrolytes often exhibit considerable optical effects upon changing the concentration, Bjerrum‡ and Hantzsch§ were able to show that the colour and absorption spectra of strong electrolytes hardly change in the dilute range. This fact led Bjerrum to the view that strong electrolytes are completely dissociated, their thermodynamical and electrical behaviour being attributed to interionic effects. As we have previously shown, this idea has proved extremely fruitful in dilute solutions, especially in the hands of Debye. According to Bjerrum, the extinction coefficient of a strong electrolyte for a given wave-length has a constant value.‖ H. v. Halban and Ebert and Gross and Goldstern†† have recently worked on the optical

† For a critical study of the subject, see M. B. Jacobs and C. V. King, *J. Phys. Chem.* **34** (1930), 1013, 1303.

‡ N. Bjerrum, *D. Kgl. Dansk Vid. Selsk.* **4** (1906), 1. For further literature, see the review by H. Ley, *Handb. d. Physik. v. Geiger-Scheel*, **21** (1929), 1. Both the optical rotation (P. Walden, *Monatsh.* **53–4** (1929), 14) and the refractivity (see p. 316) of salts remain very constant when the concentration is changed. Since the optical activity is in general very susceptible to disturbances (see W. Kuhn and K. Freudenberg, *Hand- u. Jahrbuch d. chem. Physik*, **8**, 111, Leipzig 1932), Walden's discovery is very good evidence for complete dissociation, since e.g. the formation of complexes by the ions should be detectable by this means.

§ A. Hantzsch and collaborators in *Ber.*, *Z. phys. Chem.*, and *Z. Elektrochem.* from 1906 onwards.

‖ These conclusions are only valid on the assumption that the absorption observed originates in a simple ion. A constant absorption is in general no proof that the ions give no complex chemical reaction with increasing concentration, since the absorption may take place in a part of the molecule far removed from the part which undergoes chemical reaction. A complex chemical process may thus remain undetected owing to the restriction of the experimental conditions to too narrow a field.

†† P. Gross and A. Goldstern, *Monatsh.* **55** (1930), 316; Gross, Goldstern, and P. Kuzmany, *Z. Elektrochem.* **36** (1930), 786. These authors have used the square-root law (283′) for the logarithm of the activity coefficient, while v. Halban and Ebert (*Z. phys. Chem.* **112** (1924), 359) used the cube-root law, which is without theoretical foundations.

determination of electrolytic dissociation in very dilute solutions. They investigated lithium picrate and picric acid in ethyl alcohol, using a wave-length of 436 $\mu\mu$. In agreement with Bjerrum's view, it was found that the extinction coefficient for lithium picrate is practically constant over the whole concentration range. Picric acid, on the other hand, exhibited a large increase in extinction coefficient with increasing concentration. There is a relation between the extinction coefficient and the degree of dissociation, and since the latter is connected by the generalized law of mass action (133) with the activity coefficients of the ions, it should be possible to deduce the degree of dissociation from measurements of the extinction coefficient. Gross and Goldstern used the equations of Debye's theory for the activity coefficients of the ions.

H. v. Halban and Ebert,† Scheibe,‡ Hantzsch,§ and v. Halban and Eisenbrand|| have shown that at high concentrations the optical properties of strong electrolytes vary slightly with the concentration. This variation is fairly marked in the range above 1 N. where the thermodynamic and electrical phenomena can no longer be accounted for by Debye's theory. H. v. Halban has introduced an important criterion for deciding whether or not undissociated molecules are present. We assume that both the free ions and the undissociated molecules possess characteristic absorption spectra, and that the curves representing the extinction coefficients of these spectra intersect at a certain wave-length. If we now gradually dilute the solution, more and more molecules will dissociate into ions, and hence the absorption spectrum of the solution (always referred to one mole of the solute) will gradually change from the molecule spectrum to the ion spectrum. The resulting extinction coefficients will consequently change continuously for all wave-lengths except the wave-lengths corresponding to the point of intersection of the two separate curves, where it will remain unaltered. H. v. Halban's results show approximately this behaviour, and hence lend strong support to the assumption that definite changes of molecular state take place. It cannot, however, be maintained that the experimental material at present available proves quite conclusively the existence of undissociated molecules in solutions of strong electrolytes.

The absorption spectra of the alkali and alkaline earth halides have

† H. v. Halban and L. Ebert, *Z. phys. Chem.* **112** (1924), 321; v. Halban, ibid. **120** (1926), 268; *Z. Elektrochem.* **34** (1928), 489.

‡ G. Scheibe, *Z. Elektrochem.* **34** (1928), 497.

§ A. Hantzsch, *Ber.* **58** (1925), 941; **59** (1926), 1106.

|| H. v. Halban and J. Eisenbrand, *Z. phys. Chem.* **132** (1928), 401, 433.

recently been investigated by Scheibe† and by Fromherz.‡ These authors came to the important conclusion that the association of the alkali and alkaline earth halides in aqueous solution consists chiefly of the formation of aggregates caused by the interionic forces, as pictured by Bjerrum. This conclusion is based on the following evidence. The absorption spectra of the alkali halides have been investigated in the vapour state by Franck, Kuhn, and Rollefson.§ It was found e.g. that the iodides exhibit two absorption bands at 324 mμ and 270 mμ. The distance between these two bands corresponds to the difference in energy between the stable and metastable iodine atoms. In aqueous solutions more dilute than 1 N., two distinct absorption bands were again observed, with maxima at 226 mμ and 194 mμ. The corresponding energy difference agrees very nearly with that in the vapour state. On the basis of this analogy, Franck and Scheibe were able to show that the spectrum of a halogen ion in aqueous solution is an electron affinity spectrum, the differences in the two cases quoted above being due to the effect of solvation upon the electron affinity spectrum of the iodine ion.‖ It is therefore probable that in this limiting case the ions associate by the action of the interionic forces without changing their electron shells, giving rise to non-stoichiometric and continually changing swarms. If the gaseous molecule forms in solution a molecule-like product (NaI. aq.) we should expect this to possess an absorption band between 324 mμ and 226 mμ. No such band is actually observed.

There are, of course, also cases in which a more powerful interaction causes a larger spectral displacement, due to a change in the electron terms.

Finally, yet stronger interaction will give rise to molecular vibrations, and hence to the appearance of new bands between the infra-red and

† Loc. cit.; see also E. Lederle, *Z. phys. Chem.* **10 B** (1930), 121.

‡ H. Fromherz and W. Menschick, *Z. phys. Chem.* **7 B** (1930), 439; H. Diamond and H. Fromherz, ibid. **9 B** (1930), 289.

§ J. Franck, H. Kuhn, and G. Rollefson, *Z. f. Phys.* **43** (1927), 155; cf. also Franck, *Z. phys. Chem.*, Haber-Band, **22** (1928).

‖ Other interesting examples have been discussed by S. Kato (*Sci. Papers Inst. Phys. and Chem. Res. Tokio*, **6** (1927); **12** (1930), 230; **15** (1931), 161). It is interesting to note that K. Butkow (*Z. f. Phys.* **63** (1930), 71) has observed the photoelectric effect predicted by Franck and Scheibe, corresponding to the processes

$$X^- + h\nu_1 = X + \text{electron}$$
$$X^- + h\nu_2 = X^* + \text{electron},$$

where ν_1 and ν_2 are the frequencies of the two absorption maxima, X^- the halogen ion, X the neutral atom, and X^* the metastable state of the halogen atom. The observed photoelectric thresholds agree well with the edges of the absorption bands of the halogen ions.

the ultra-violet, as well as new Raman lines.† Examples of this behaviour have been found in the halides of lead and thallium by Fromherz and Kun-Hou-Lih.‡

B. *Refractometric investigations (Fajans, Kohner, and Geffcken).*

The assumption of the existence of undissociated molecules appears also to be supported by the refractometric investigations of Fajans, Kohner, and Geffcken.§ For most of the numerous electrolytes which he investigated, Heydweiller‖ was not able to detect any variation of refractivity with concentration in dilute solutions. The refractivity is defined as the value per mole of the Lorentz-Lorenz expression

$$R = \frac{n^2-1}{n^2+2}\frac{G}{d} = \frac{4\pi}{3}N\alpha_e, \qquad (670)$$

where n is the refractive index, G the molecular weight, d the density, N Loschmidt's number, and α_e the polarizability of the molecule, which is a measure of the deformability of the electron shells by an electric field. Fajans and his collaborators found that at higher concentrations the refractivity depends slightly upon the concentration. Before dealing with this point, we shall describe Fajans's views on the deformation of ions. Fig. 99 illustrates the diagram given by Fajans and Joos†† for the refractivities of the free gaseous ions as a function of the atomic number. The refractivity R is a measure of the deformability of the electronic system of the ion, which may undergo a change in its equilibrium electrical distribution when subjected to an electric field. If we compare the value of R for iodine with that for fluorine or chlorine, it is seen that the refractivity is greater the more loosely the outer electrons are bound, or, to employ a rough picture, the larger the ion. Fig. 99 also shows that the electron shells of the anions Cl^-, Br^-, etc. are bound more firmly by the presence of a neighbouring cation, since on passing from Cl^- to HCl the refractivity decreases. The more firmly the electrons in the anion are bound, the greater will be this decrease in refractivity. Thus conversion of the I^- ion to HI is accompanied by a much greater decrease in refractivity than the conversion of Cl^- into HCl. The stronger the electric field of the cation, i.e. the smaller its radius and the

† See p. 322.

‡ H. Fromherz and Kun-Hou-Lih, *Z. phys. Chem.* **153 A** (1931), 321.

§ For literature, see K. Fajans, *Z. Elektrochem.* **34** (1928), 502. Cf. also P. Hölemann and H. Kohner, *Z. phys. Chem.* **13 B** (1931), 338; Fajans, Z. Shibata, and P. Hölemann, ibid. 347, 354.

‖ A. Heydweiller, *Phys. Z.* **26** (1925), 526.

†† K. Fajans and G. Joos, *Z. f. Phys.* **23** (1924), 1.

higher its charge, the more firmly will the electrons in the anion be bound. This may also be easily demonstrated by examples. On the other hand, the electron shells of a cation will be repelled and loosened by the electric field of the anion. In practice these two effects will be superimposed, the negative effect being usually predominant. The combination of ions to form crystals or molecules is thus usually accompanied by a decrease of refractivity, since the binding effect of the cation usually exceeds the loosening effect of the anion. This is illustrated by Fig. 100, which shows the total change in refractivity in

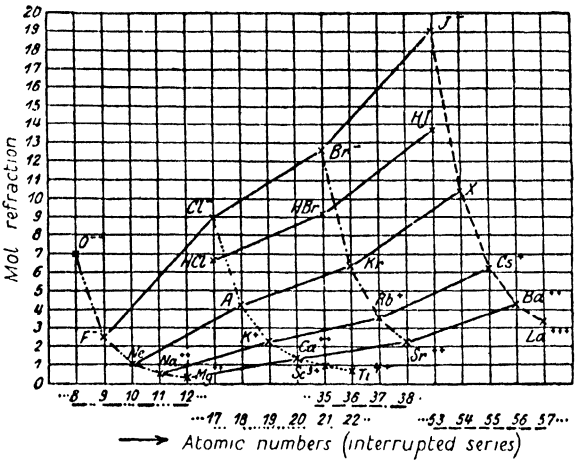

FIG. 99. The refractivities of the ions.

passing from the gaseous ion to the solid crystal. In the case of the large anions Br^- and I^- a large decrease in refractivity takes place. The binding of the electrons is naturally stronger the more deformable the anion and the smaller the cation. For large cations such as Rb^+ combined with small anions such as F^- the reverse positive effect comes into prominence, with the result that for KF and RbF a total positive effect is found. The compounds of the alkaline earth metals with the elements of the oxygen group and the alkaline earth fluorides show similar sequences, as is shown by Fig. 101 and Table 52.

We shall now deal with the variation of the refractivity with the concentration in aqueous solutions of salts. Thus $HClO_4$ is completely dissociated in very dilute aqueous solution, and has a refractivity $R = 12{\cdot}65$. In the pure liquid state, i.e. 100 per cent. solution, on the other hand, the acid is largely undissociated, and has a refractivity $R = 13{\cdot}25$. The problem now arises of how we are to interpret this change of $+0{\cdot}6$ unit of refractivity which accompanies the transition

from a very dilute solution of perchloric acid to the pure acid. The H^+ nucleus has no electrons, and hence contributes nothing to the refractivity. From the above considerations, we should expect that the hydrogen nucleus will cause a closer binding of the electrons in the anion, which will lead to a decrease in refraction. On the other hand, it must be remembered that the small hydrogen ion will exert a binding influence upon the surrounding water molecules, which will also cause

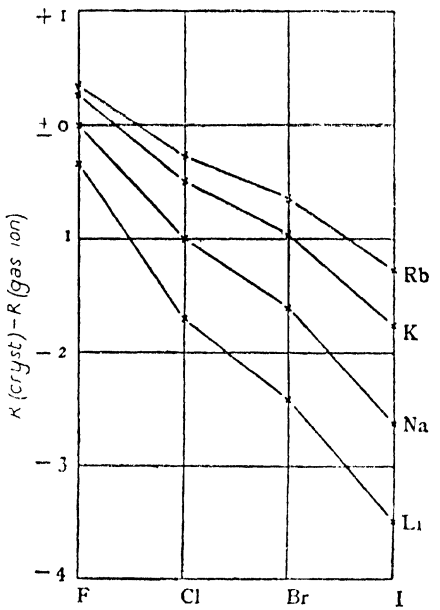

FIG. 100. The difference in the refractivities of ions in the crystalline and gaseous states.

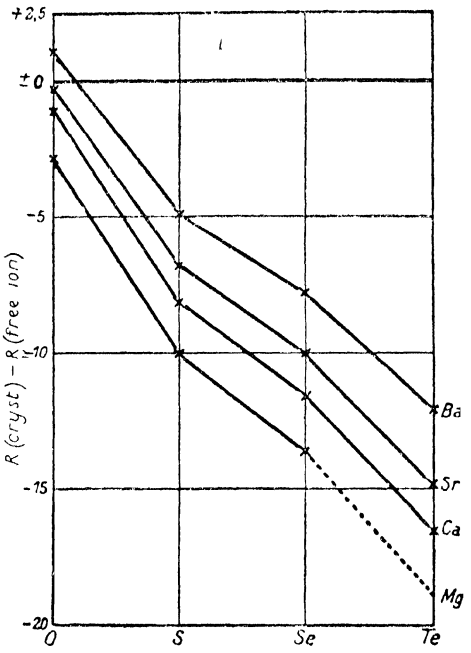

FIG. 101. The difference in the refractivities of ions in the crystalline and gaseous states.

a decrease in the refraction. The free hydrated H^+ ion causes a negative refractivity of $-0{\cdot}6$ unit (see column 2, Table 53). If now undissociated molecules are formed, the H^+ ion will (at least partially) lose its water of hydration, and in doing so will make a positive contribution to the refractivity of $+0{\cdot}6$ unit. The total change may thus be either positive or negative, according to whether or not the negative effect due to the binding of the electrons in the anion outweighs the positive effect due to the dehydration of the hydrogen ion. The fifth column in Table 53 shows that the total change in refractivity is negative for most of the acids taken, and especially so for the large halogen ions. Perchloric acid, on the other hand, exhibits a total positive effect, since

the ClO_4 ion has a low deformability, and hence the positive effect caused by the dehydration of the hydrogen ions predominates.

TABLE 52

Refractivity for the D-line.

	MgF_2	CaF_2	SrF_2	BaF_2
R_{cryst}	4·84	6·39	..	10·08
$R_{gas\text{-}ion}$	5·28	6·33	7·24	9·24
Δ	−0·44	+0·06	..	+0·80

TABLE 53

Acid	R_{H^+diss}	R_{X^-}	$R_{H^+diss.}+R_{X^-}$	ΔR $HR_{und}-(H^+_{diss.}+X^-)_\infty$	R_{HX} undiss.	ΔR $[NaX_{sn.}-(Na^+ + X^-)_\infty]$
HI	−0·6	19·24	18·64	−4·90	13·74	−0·225
HBr	−0·6	12·67	12·07	−2·93	9·14	−0·085
HCl	−0·6	9·07	8·47	−1·80	6·67	−0·053
HAc	−0·6	14·36	13·76	−0·74	13·02	−0·05
HNO_3	−0·6	11·01	10·41	−0·4	10·0	−0·027
$\frac{1}{2}H_2SO_4$	−0·6	7·42	6·82	−0·07	6·75	−0·0
$HClO_4$	−0·6	13·25	12·65	+0·6	13·20	+0·042

Fig. 102, which is taken from the work of Fajans, Kohner, and Geffcken† shows that small changes in refractivity also take place in concentrated salt solutions. In the experimental investigations the refractive index and density of salt solutions above 2 N. were measured. By subtracting the refractivity of the water a value is obtained for the refractivity of the dissolved salt, which includes the hydration effect. These refractivities were extrapolated to infinite dilution, and it was found that the extrapolated values were additive with respect to the single ions, to within one unit in the second decimal place. This is illustrated by Table 54, which gives the observed refractivity at infinite dilution for the *D*-line for a number of salts, and also the values obtained by assuming certain additive values for the single ions. The agreement is excellent.

TABLE 54

Refractivity (D-line) per gram-equivalent at infinite dilution.

	KCl	NH_4Cl	KNO_3	$NaNO_3$	$Al(ClO_4)_3$
$R_{abs.}$	11·31	13·37	13·23	11·21	12·43
$R_{calc.}$	11·31	13·35	13·25	11·21	12·40

Fig. 102 shows the differences between the observed refractivities at

† K. Fajans, H. Kohner, and W. Geffcken, *Z. Elektrochem.* **34** (1928), 1.

higher concentrations and the extrapolated infinite dilution values, expressed as units in the second place of decimals of the refractivity. Analogously to the case of the union of ions to form a crystal, KF

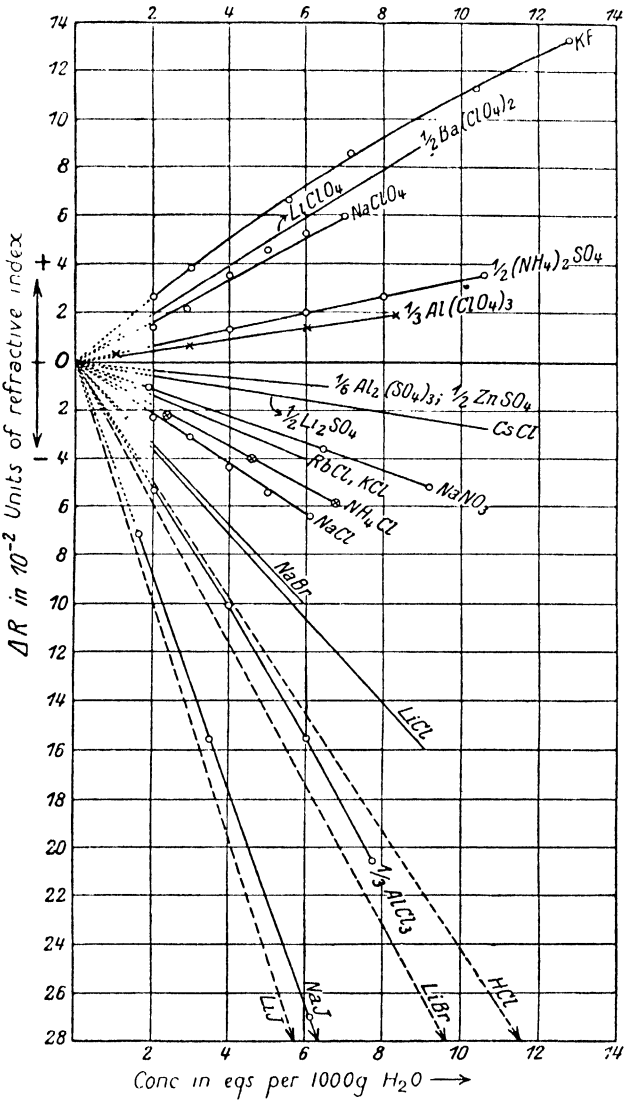

FIG. 102. The refractive index of salt solutions.

exhibits an increase of refractivity with increasing concentration, and LiCl a decrease. This analogy also holds good e.g. for $NaClO_4$ and NaI. Thus in passing from infinite dilution to saturated solution, the refractivity of KF increases by 0·13 unit, while that of NaI decreases by

more than 0·3 unit. It is of interest to compare these results with those previously dealt with for solutions of acids and the formation of crystals. Some results for the sodium salts of the acids in Table 53 are given in column 7, which contains the difference between the refractivities of these salts at infinite dilution and in 5 N. solution. There is an obvious parallelism between columns 5 and 7 of Table 53, both as regards the order and the sign of the differences in refractivity. Fajans concludes from this fact that the salts as well as the acids give rise to some undissociated molecules in solution. As we have previously shown, the same parallelism exists between the results for crystals and salt solutions (cf. Figs. 100 and 102). Fajans therefore concludes that the optical effects observed in solution are due to direct contact between pairs of oppositely charged ions, i.e. to a partial association to undissociated molecules. In his opinion the variation of refractivity with concentration would not reach the observed values if it were caused by pairs of ions separated by a water molecule. It may be objected that these changes in refraction may be due to the interionic forces. Fajans has, however, estimated the probable magnitude of this interionic effect and finds that it is too small to account for the observed changes in refractivity. Thus if we consider a 5 N. NaI solution, and imagine as a first approximation that the ions are distributed through the solution in the form of a lattice, the mean distance between two ions will be 5·5 Å. The corresponding distance in the crystal is 3·2 Å, i.e. 1·7 times smaller than in the solution. Experimental evidence shows that the decrease in refractivity is inversely proportional to the fourth power of the interionic distance. A decrease of the distance by a factor of 1·7 will therefore make the lowering of refractivity (*in vacuo*) 8·3 times smaller than it is in the crystal. The value in this case will be (see Fig. 102) $2{\cdot}67/8{\cdot}3 = 0{\cdot}32$. This value is still too high, since the attractive forces in solution will be reduced greatly by the intervening water molecules. If we take the very small value $D_0 = 5$ (in place of the macroscopic value $D_0 = 80$) the calculated value for the decrease in refractivity becomes 0·06. The observed value is considerably greater, namely $-0{\cdot}27$. Taking into consideration the partial dehydration of the ions, i.e. the optical effects in the water sheath which accompany the process of association, will change the value 0·06 in a positive direction, and hence cause it to deviate still more from the observed value $-0{\cdot}27$. Fajans therefore considers that concentrated solutions contain appreciable amounts of association products in which there are no water molecules between the ions. At the moment it is impossible to say anything

more definite on this subject.† It is quite possible that valuable information about the structure of electrolyte solutions may be obtained by the method recently developed by Debye for studying the structure of liquids and gases by means of X-rays and electron rays.

C. *The Raman effect and the structure of electrolytic solutions.*‡

Attempts have recently been made to elucidate the structure of electrolyte solutions by means of the Raman effect. This effect was predicted some years ago by Smekal, Kramers, and Heisenberg,§ and was discovered experimentally in 1928 by Raman|| and almost simultaneously by Landsberg and Mandelstam.†† If monochromatic light of frequency ν_0 falls on a substance, the scattered light contains not only the original frequency ν_0 but also light of a different frequency ν_1. The energy of the exciting line is $h\nu_0$, and the energy of the emitted Raman line is $h\nu_1$. The difference

$$h\nu_0 - h\nu_1 = h\nu \tag{671}$$

is hence the amount of energy taken up by the molecule during the process of scattering. This energy $h\nu$ is used in exciting the vibrations of the atoms or groups of atoms in the scattering molecule. Amounts of energy of this order of magnitude are also involved in the infra-red part of the spectrum, and have long been interpreted as due to intramolecular vibrations of atoms or groups of atoms. The Raman effect should thus in suitable cases enable a study of the phenomena of electrolytic dissociation by measuring the intensity of the Raman lines. We suppose that the electrolyte is AB and that B gives rise to a Raman line.

† It should be noted that it is possible to obtain an approximate value for the degree of dissociation of weak electrolytes from refractometric measurements. Acetic and dichloracetic acids have been treated in this way by Schreiner (*Z. phys. Chem.* **133** (1928), 420) and trichloracetic acid by Frivold (*Abhandl. Norsk. Vidensk. Akad. Oslo*, No. 12 (1932)). The formula used by Schreiner assumes that the refractivity of a solution is an additive function for the constituents of the solution. For dichloracetic acid the dissociation constant found refractometrically differs considerably from that obtained by other methods. The Raman effect has not yet provided any information in this respect (see next section). Present experimental methods do not permit of a sharp distinction between ion-pairs held together by electrostatic forces and association products involving chemical forces, though the latter appear to be present in weak electrolytes.

‡ An excellent review with numerous references to the literature has been given by L. A. Woodward, *Phys. Z.* **32** (1931), 777.

§ A. Smekal, *Naturwiss.* **11** (1923), 873; *Z. f. Phys.* **32** (1925), 241; H. A. Kramers and W. Heisenberg, *Z. f. Phys.* **31** (1925), 681.

|| C. V. Raman, *Ind. J. Phys.* **2** (1928) 387. For summaries of recent literature, see S. Bhagavantam, *The Raman Effect* (Calcutta University Press); C. Schaefer and F. Matossi, *Fortschr. d. Chem., Phys. u. phys. Chem.* (Berlin 1930); F. Kohlrausch, *Der Smekal-Ramaneffekt* (Berlin 1931).

†† G. Landsberg and L. Mandelstam, *Z. f. Phys.* **50** (1928), 769.

Then if $(N_B)_\gamma$ is the number of B ions present at a concentration γ and $(J_B)_\gamma$ the intensity of the Raman line at the same concentration, then

$$(N_B)_\gamma = \text{const.}\ (J_B)_\gamma. \tag{672}$$

If the corresponding quantities at infinite dilution are $(N_B)_\infty$ and $(J_B)_\infty$, then the true degree of dissociation is given by

$$\alpha^* = \frac{(N_B)_\gamma/\gamma}{(N_B)_\infty/\gamma_\infty} = \frac{(J_B)_\gamma/\gamma}{(J_B)_\infty/\gamma_\infty}. \tag{673}$$

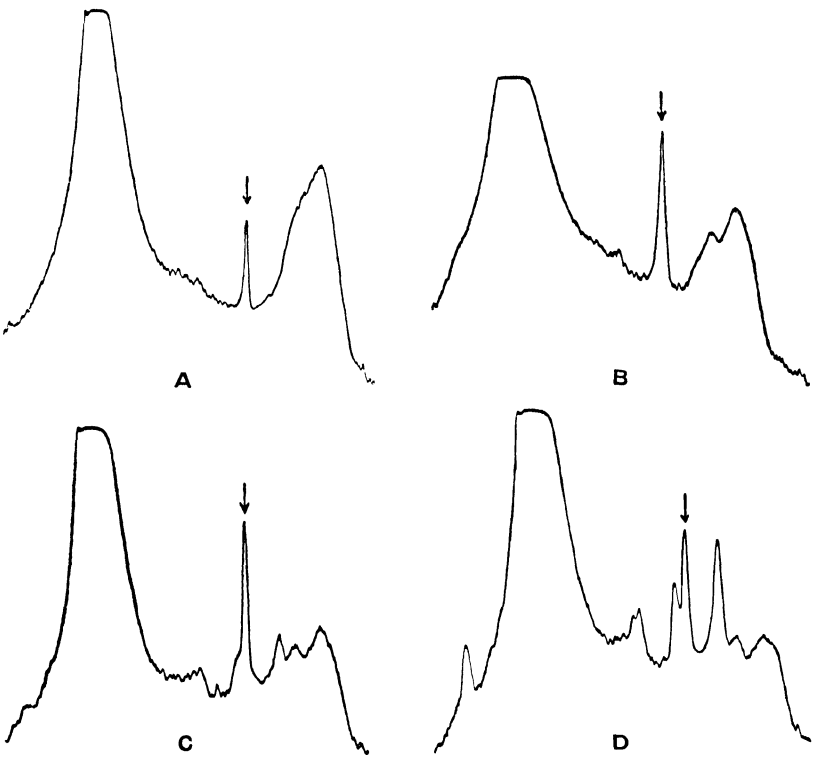

FIG. 103. The Raman effect of nitric acid solutions.

Measurements of the intensity of Raman lines at different concentrations should thus make it possible to determine the degree of dissociation provided that matters are as simple as we have assumed above. It should be possible to develop a precision method on these lines. Rao† and Woodward‡ have recently carried out such intensity measurements with nitric acid. Fig. 103 shows the behaviour of the line having a wave-number difference 1,050 cm.$^{-1}$ at different concentrations. Figs. 103 A, B, C, and D correspond to concentrations of 1·5, 5·2, 9·6, and 14 moles

† I. R. Rao, *Nature*, **124** (1929), 762; *Proc. Roy. Soc.* **127 A** (1930), 279.

‡ L. A. Woodward, *Phys. Z.* **32** (1931), 212.

per litre, using the same exposure, and it is seen that the intensity of the line of the nitrate ion (↓) first increases to a maximum and then exhibits an abnormal decrease. This behaviour is undoubtedly due to the decrease in the degree of ionization with increasing concentration. The other lines ($\Delta\nu = 961, 697, 643$ cm.$^{-1}$) belong to the HNO_3 molecule and not to the NO_3^- ion. They had been previously observed in HNO_3, $NaNO_3$, and NH_4NO_3 by Carelli, Pringsheim, and Rosen† who ascribed them to the NO_3^- ion. H_2SO_4 solutions have been studied by Bell and Fredrickson,‡ Nisi,§ and more accurately by Woodward (loc. cit.), who succeeded in recognizing the two stages of ionization. At very high concentrations a Raman line $\Delta\nu = 1{,}046$ cm.$^{-1}$ appears, which must be attributed to the HSO_4^- ion, and which is also observed in $KHSO_4$ solutions. At a concentration of 25 vol. per cent. a line appears ($\Delta\nu = 987$ cm.$^{-1}$) which belongs to the $SO_4^=$ ion, and is also found in solutions of all normal sulphates.‖ It is important to note that the work of a number of investigators†† has shown that many simple electrolyte exhibit no Raman effect due to undissociated molecules, which agrees with modern theories of complete dissociation. The undissociated molecules which many theories assume to be present in a concentrated solution of e.g. KCl have not yet been detected by means of the Raman effect. This is in complete contradiction to Nernst's conclusions.

Special interest attaches to the investigation of the Raman effect of comparatively weak electrolytes. Woodward‡‡ has carried out such measurements with $HgCl_2$ and $Hg(CN)_2$, which are only slightly dissociated. On account of the low solubility of these salts, rather weak Raman lines were obtained. Woodward first investigated a saturated solution of $HgCl_2$, which is 0·2 N. A Raman line was found at $\Delta\nu = 320$ cm.$^{-1}$ This proves the existence of undissociated $HgCl_2$ molecules,

† A. Carelli, P. Pringsheim, and Rosen, *Z. f. Phys.* **51** (1928), 511.

‡ R. M. Bell and W. R. Fredrickson, *Nature*, **125** (1930), 892.

§ H. Nisi, *Jap. J. Phys.* **5** (1929), 119.

‖ See e.g. Table (4), A. Hollaender and J. W. Williams, *Phys. Rev.* **38** (1931), 1739.

†† Carelli, Pringsheim, and Rosen, loc. cit.; P. Pringsheim and M. Yost, *Z. f. Phys.* **58** (1929), 1; R. G. Dickenson and R. T. Dillon, *Proc. Nat. Acad. Am.* **15** (1924), 334; J. N. Mukherjee and Sen-Gupta, *Ind. J. Phys.* **3** (1927–8), 503; A. M. Taylor, *Farad. Soc. Discussion*, Sept. 1929, p. 830; Bell and Fredrickson, loc. cit.; P. Daure, *Ann. d. Phys.* **12** (1929), 375; W. Gerlach, *Naturwiss.* **18** (1930), 182; *Nature*, **125** (1930), 819; *Ann. d. Phys.* **5** (1930), 196; *Phys. Z.* **31** (1930), 695; W. D. Harkins, D. M. Gans, and H. E. Bowers, *Nature*, **125** (1930), 464; E. L. Kinsey, *Phys. Rev.* **35** (1930), 284; I. Kishi, *Mem. Coll. Sci. Kyoto*, **13 A** (1930), 163; M. Leontowitsch, *Z. f. Phys.* **54** (1929), 155; H. Nisi loc. cit.; C. Ramaswamy, *Ind. J. Phys.* **5** (1930), 193.

‡‡ L. A. Woodward, *Phys. Z.* **31** (1930), 792.

since if they were completely dissociated into ions, no Raman effect would be possible, just as in the case of KCl. Matters are a little more complicated for $Hg(CN)_2$, since the CN group itself gives a Raman effect. Thus a concentrated solution of KCN (7 N.) gives a line 2,081 cm.$^{-1}$ which must be attributed to the ionized CN group. Dadieu and Kohlrausch† found a somewhat greater value ($\Delta\nu = 2{,}200$ cm.$^{-1}$) for the combined CN group. Woodward found for 0·35 N. $Hg(CN)_2$ the value 2,195 cm.$^{-1}$ which agrees well with the figure given by Dadieu and Kohlrausch, and hence leads to the conclusion that $Hg(CN)_2$ is present chiefly in the undissociated form.

58. Brönsted's Principle of the Specific Interaction of Ions

Previous to Debye's theory of electrolytes, Brönsted‡ had put forward an interesting empirical theory which he termed the principle of the specific interaction of ions. We may begin by considering the principle of the independent activity coefficients of ions, first stated by G. N. Lewis§ according to which e.g. the activity coefficient of KCl in mixtures of KCl and NaCl has a constant value, provided that the total molality is kept constant. Lewis and Randall themselves recognized that this hypothesis is only approximately valid. Thus it was found that at equal concentrations, $f_{NaCl} > f_{KCl}$, while at least for dilute solutions (below 0·1 N.) $f_{NaIO_3} = f_{KIO_3}$ and $f_{NaOH} < f_{KOH}$. Apart from the experimental evidence, Brönsted was also able to show on thermodynamic grounds that Lewis and Randall's principle must fail in more concentrated solutions. Consider a mixture of total molarity m containing mx moles NaCl and $m(1-x)$ moles KCl. Applying the Gibbs-Duhem equation ((95) and (130)), we have‖

$$mx\, d\bar{\Phi}_{NaCl} + m(1-x)d\bar{\Phi}_{KCl} + 55{\cdot}51 d\bar{\Phi}_{H_2O} = 0. \qquad (674)$$

† A. Dadieu and K. W. F. Kohlrausch, *Wien Ber.* **138** (1929), 613, 804; see also *Ber.* **63** (1930), 251; *Z. angew. Chem.* **43** (1930), 800; *J. Opt. Soc.* **21** (1931), 286. A large number of investigations of the Raman effect of the CN group have recently been published, which agree with Woodward's results. See N. N. Pal and P. N. Sen-Gupta, *Ind. J. Phys.* **5** (1930), 13; A. Dadieu, *Wien. Ber.* **139** (1930), 629; P. Krishnamurti, *Ind. J. Phys.* **5** (1930), 651; A. Petrikaln and J. Hochberg, *Z. phys. Chem.* **8 B** (1930), 440. The co-valent CN group always gives a higher value (2,195 cm.$^{-1}$) than the CN^- ion (2,080 cm.$^{-1}$), and only the complex ions give intermediate values. Woodward (*Phys. Z.* **32** (1931), 777) has recently investigated HCl, HF, HIO_3, CCl_3COOH, $CHCl_2COOH$, NaOH, and KOH, and finds no connexion between the electrolytic dissociation and the Raman effect.

‡ J. N. Brönsted, *J. Am. Chem. Soc.* **44** (1922), 877; **45** (1923), 2898.

§ See p. 70.

‖ 55·51 is the number of moles H_2O in 1,000 gm. water.

By the definition of $\bar{\Phi}$, this becomes†

$$\left.\begin{aligned} \bar{\Phi}_{KCl} &= RT\log(a_K a_{Cl}) = RT\log\{m.m(1-x)f^2_{KCl}\} \\ \bar{\Phi}_{NaCl} &= RT\log(a_{Na}a_{Cl}) = RT\log\{m.mxf^2_{NaCl}\}, \\ 55{\cdot}51\bar{\Phi}_{H_2O} &= -2RTmg \end{aligned}\right\} \quad (675)$$

introducing the osmotic coefficient g as defined by Bjerrum in (83).

Since $$d\log(1-x) = -\frac{dx}{1-x}, \qquad d\log x = \frac{dx}{x},$$

(674) becomes $$x\,d\log f_{NaCl} + (1-x)d\log f_{KCl} = dg \quad (676)$$

or $$x\,d\log f_{Na} + (1-x)d\log f_K + d\log f_{Cl} = 2dg. \quad (676')$$

Hence if f_{NaCl} and f_{KCl} are constant for a given total molarity, (676) shows that the osmotic coefficient g must also be constant. Thus on changing gradually from a solution of NaCl (containing very little KCl) to a solution of KCl (containing very little NaCl), no change in freezing-point should be observed. This is quite at variance with the experimental facts and hence it must be concluded that f_{NaCl} and f_{KCl} are not constant for a given total concentration. The same conclusion holds good for any mixture of electrolytes of the same type at constant total concentration. Brönsted's principle of the specific interaction of ions makes it possible to account for these facts.

Brönsted begins by assuming that, for a constant total molarity, $\log f$ varies linearly with the ratio NaCl/KCl i.e.

$$d\log f_{KCl} = -adx = d\log f_{NaCl}. \quad (677)$$

A linear change of this kind was found by Güntelberg‡ for 0·1 N. solutions, and by Harned§ for more concentrated solutions. Equation (677) gives for the difference of the osmotic coefficients of the two pure solutions

$$g_{NaCl} - g_{KCl} = -a. \quad (678)$$

Güntelberg found for 0·1 N. mixtures

$$g_{NaCl} - g_{KCl} = 0{\cdot}0097, \quad (678')$$

in agreement with measurements of osmotic coefficients. Equation (678) follows directly from (676) and (677) by integrating between $x = 0$ and $x = 1$. Similarly, Güntelberg's results for the variation of the activity

† The third equation of (675) is obtained as follows. From (180) $\delta = g\nu RTm$, and from (95) $RT\log a_0 = \bar{\Phi}_{H_2O}$. Thus on multiplying (177′) by 55·51, we obtain

$$55{\cdot}51\,\bar{\Phi}_{H_2O} = -\nu RTmg,$$

and since for the present case $\nu = 2$, this leads directly to the equation above.

‡ E. Guntelberg, *Z. phys. Chem.* **123** (1926), 199.

§ Harned, *J. Am. Chem. Soc.* **48** (1926), 326.

coefficient of HCl in mixtures with KCl give for the difference between the osmotic coefficients of the two pure solutions

$$g_{KCl} - g_{HCl} = -0{\cdot}0194, \tag{679}$$

while very accurate osmotic measurements by Adams† for KCl and by Vanselow‡ for HCl give the value $-0{\cdot}0195 \pm 0{\cdot}0005$, in excellent agreement.

Returning to equation (677), integration gives

$$\log f_{KCl} = -ax + \text{const.} \tag{680}$$

For pure KCl solution, $x = 0$, and hence,

$$\log f_{KCl} - \log f^0_{KCl} = -ax, \tag{681}$$

where f^0_{KCl} is the activity coefficient of KCl in its pure solution. In pure NaCl solution, $x = 1$, so that we can write

$$\log f_{KCl(NaCl)} - \log f_{NaCl(KCl)} = -a = g_{NaCl} - g_{KCl}. \tag{682}$$

The above hypothesis of the linear variation of the logarithms of the activity coefficients (and the osmotic coefficients) at constant total molarity is not, however, generally valid. If it were so, the ratio of the activity coefficients of a sparingly soluble salt in two salt solutions should be independent of the nature of the sparingly soluble salt, since the derivation of (682) is quite independent of the nature of the electrolytes concerned (e.g. whether or not they contain a common ion). Thus for KCl and $NaNO_3$ we should have

$$\log f_{NaNO_3(KCl)} - \log f_{(NaNO_3)(NaNO_3)} = g_{KCl} - g_{NaNO_3} \tag{682'}$$

and similarly

$$\log f_{NaNO_3(LiCl)} - \log f_{NaNO_3(NaNO_3)} = g_{LiCl} - g_{NaNO_3} \tag{682''}$$

and hence by subtraction

$$\log f_{NaNO_3(KCl)} - \log f_{NaNO_3(LiCl)} = g_{KCl} - g_{LiCl}. \tag{683}$$

In equation (683) the right-hand side is quite independent of the nature of $NaNO_3$, which can be replaced by any salt of the same ionic type. Brönsted found from his solubility measurements that the experimental results did not support an hypothesis of such wide generality. Measurements with KCl and NaCl give

$$\log_{10} f_{(NaCl)} - \log_{10} f_{(KCl)} = 0{\cdot}0045,$$

and we should thus always have

$$\frac{f_{(NaCl)}}{f_{(KCl)}} = 1{\cdot}01, \tag{684}$$

† J. H. Adams, *J. Am. Chem. Soc.* **37** (1915), 481.

‡ M. Randall and A. P. Vanselow, *J. Am. Chem. Soc.* **46** (1924), 2418.

where e.g. $f_{(NaCl)}$ is the activity coefficient of any sparingly soluble salt of the same valency type. For another chloride, oxalatotetrammine cobaltic chloride, Brönsted found the same ratio 1·01, although the complex cobalt ion is very different from the sodium ion. Dichlorotetrammine cobaltic iodate, on the other hand, gave the value 1·005, and tetranitrodiammine cobaltiate 1·033. These facts are accounted for by the principle of specific interaction, which predicts that f_{NaCl}/f_{KCl} will have one constant value for all chlorides, but a different constant value for all nitrates. It also predicts many other properties in mixtures of salts of the same ionic type.

Brönsted's original formulation of the principle of specific interaction was based upon the conception of individual ionic activity coefficients. It has since been realized that no physical significance can be attached to the activities of individual ions, and Guggenheim† has recently shown that it is possible to derive the specific interaction principle on much simpler assumptions than those originally employed by Brönsted. Guggenheim's derivation is as follows.

The mutual potential energy between any two ions α and β in the solution can be expressed as the sum of two parts, i.e.

$$W_{\alpha\beta} = W^0_{\alpha\beta} + W'_{\alpha\beta}, \tag{685}$$

where $W^0_{\alpha\beta}$ is due to the Coulomb forces, and $W'_{\alpha\beta}$ to the short range forces which lead to the individual behaviour of the different ions. In the same way, F_{in}, the contribution of the interionic forces to the free energy of the solution can be written

$$F_{in} = F^0_{in} + F'_{in}, \tag{686}$$

where again F^0_{in} refers to the Coulomb forces and F'_{in} to the short range forces. It can be easily shown‡ that for short range forces F'_{in} can be written in the form

$$F'_{in} = \frac{1}{V} \sum_{\alpha,\beta} n_\alpha n_\beta \epsilon_{\alpha\beta}, \tag{687}$$

where n_α and n_β are the numbers of α and β ions present in volume V, and $\epsilon_{\alpha\beta}$ is a constant for each pair of ionic species in a given medium at a given temperature. Brönsted's assumption is essentially that $\epsilon_{\alpha\beta}$ is zero when α and β have like charges, but is finite for oppositely charged ions. The reason for this assumption is that oppositely charged ions will tend to approach one another so closely that short range forces will come into play, while ions of like charges will rarely come closely

† E. A. Guggenheim, *18th Scandinavian Naturalist Congress* (Copenhagen 1929).

‡ See e.g. R. H. Fowler, *Statistical Mechanics*, Chapter 8.

together, and hence interact in the same way as two point charges. We thus have

$$F'_{\text{in}} = \frac{1}{V}\sum_{k,a} n_k n_a \epsilon_{ka}, \tag{688}$$

where k is any cation and a any anion.

To relate this expression to the mean activity coefficient of any salt A^+B^-, we note that

$$2RT \log f_{AB} = \left(\frac{\partial F_{\text{in}}}{\partial n_A}\right) + \left(\frac{\partial F_{\text{in}}}{\partial n_B}\right), \tag{689}$$

where F_{in} is the contribution of the interionic forces to the total free energy of the system. Hence from (686), (688), and (689),

$$\log f_{AB} = \log f^0 + \sum_a \frac{n_a}{V}\frac{\epsilon_{Aa}}{2RT} + \sum_k \frac{n_k}{V}\frac{\epsilon_{kB}}{2RT}, \tag{690}$$

where

$$\log f^0 = \frac{1}{2RT}\left(\frac{\partial F^0_{\text{in}}}{\partial n_A}\right) + \frac{1}{2RT}\left(\frac{\partial F^0_{\text{in}}}{\partial n_B}\right). \tag{691}$$

f^0 is governed only by the Coulomb forces, and hence is independent of the nature of A and B. Writing $n_\alpha/V = x_\alpha m$, where m is the total salt concentration, and $\epsilon_{\alpha\beta}/2RT = \lambda_{\alpha\beta}$ (690) becomes

$$\log f_{AB} = \log f^0 + \sum_a \lambda_{Aa} x_A m + \sum_k \lambda_{kB} x_B m. \tag{692}$$

Equation (692) leads to all the results which are obtainable from the principles of specific interaction and linear variation. We may note first that for a single salt AB (692) becomes

$$\log f_{AB(AB)} = \log f^0 + 2\lambda_{AB}\, m, \tag{693}$$

i.e. the λ's in (692) can be obtained from measurements of the activity coefficients of the salts present singly. If we now have one salt AB present in small amount in a solution of XY, (693) gives

$$\log f_{AB(XY)} = \log f^0 + (\lambda_{AY} + \lambda_{XB})m, \tag{694}$$

from which it immediately follows that

$$f_{AB(XY)} = f_{XY(AB)}. \tag{695}$$

By applying (694) to two solute salts AB and $A'B$ having the common anion B, both present in small amount in XY of constant concentration, we have

$$\log \frac{f_{AB(XY)}}{f_{A'B(XY)}} = (\lambda_{AY} - \lambda_{A'Y})m, \tag{696}$$

i.e. the ratio of the activity coefficients of AB and $A'B$ present in small

quantity in a solution of XY is independent of X and also of B. For example,

$$\frac{f_{AgCl(KNO_3)}}{f_{TlCl(KNO_3)}} = \frac{f_{AgCl(NaNO_3)}}{f_{TlCl(NaNO_3)}} = \frac{f_{AgBr(NaNO_3)}}{f_{TlBr(NaNO_3)}} = \frac{f_{AgBr(KNO_3)}}{f_{TlBr(KNO_3)}}.$$

Similarly, for a single solute salt AB present in small amount in two solvent salts XY and $X'Y$ with a common anion Y,

$$\log\frac{f_{AB(XY)}}{f_{AB(X'Y)}} = (\lambda_{XB}-\lambda_{X'B})m, \tag{697}$$

i.e. the ratio of the activity coefficients of AB in XY and $X'Y$ is independent of the common anion Y of the solvent and also of the cation A of the solute. Thus for example

$$\frac{f_{AgCl(KNO_3)}}{f_{AgCl(NaNO_3)}} = \frac{f_{TlCl(KNO_3)}}{f_{TlCl(NaNO_3)}} = \frac{f_{HCl(KNO_3)}}{f_{HCl(NaNO_3)}} = \frac{f_{AgCl(KCl)}}{f_{AgCl(NaCl)}} = \frac{f_{AgCl(KClO_4)}}{f_{AgCl(NaClO_4)}}, \text{ etc.}$$

All these conclusions have been amply verified by Brönsted by means of solubility measurements. La Mer and his collaborators† have tested the specific interaction principle for sparingly soluble salts of the valency types 3-1 and 3-3 in presence of 0·1 N. solutions of salts of the types 1-1, 1-2, 2-1, 2-2, and 3-1. They found that the principle applies also to these salts of higher valencies, provided that the ratio of the ionic strengths of the solvent salts remains constant, the common ion of the solvent salts being changed at constant equivalent concentration. Recent investigations by Friedman and La Mer‡ appear to show that Brönsted's principle does not hold so well for an electrolyte such as $CdCl_2$ which has a strong tendency to complex formation.

The specific interaction principle is also able to account for the limited validity of the principle of linear variation of osmotic coefficients. It can be easily shown§ that the linear variation principle only holds for two salts having a common ion. In the general case, the osmotic coefficient is a quadratic function of x.

† V. K. La Mer and R. G. Cook, *J. Am. Chem. Soc.* **51** (1929), 2622; La Mer and F. H. Goldman, ibid. **51** (1929), 2632.

‡ H. B. Friedman and V. K. La Mer, *J. Am. Chem. Soc.* **53** (1931), 103.

§ See E. Güntelberg, *Z. phys. Chem.* **123** (1926), 199.

XII

THE STATISTICAL FOUNDATIONS OF DEBYE'S THEORY

59. General Statistical Considerations

THE formal treatment of the statistics of any solution can be most conveniently presented by the partition function method of Fowler.† Consider a system of total volume V containing N_α particles of the sort α, N_β of the sort β, etc. Let the coordinates of the α particles be $(x_\alpha, y_\alpha, z_\alpha)_r$, where r can have the values $1,\ldots,N_\alpha$, and let U be the total potential energy as a function of the configuration of all the particles in the phase space. U is considered to be independent of the velocities of the particles and the kinetic energy need not be considered. The partition function is then defined by

$$B(T) = \int_{(V)} \ldots \int e^{-U/kT} \prod_{r=1}^{N_\alpha} (dx_\alpha dy_\alpha dz_\alpha)_r \prod_{r=1}^{N_\beta} (dx_\beta dy_\beta dz_\beta)_r \ldots, \quad (698)$$

where the integration extends over the whole of the configuration space, i.e. over all possible arrangements of the particles in the volume V. Making the abbreviation

$$\prod_{r=1}^{N_\alpha} (dx_\alpha dy_\alpha dz_\alpha)_r \prod_{r=1}^{N_\beta} (dx_\beta dy_\beta dz_\beta)_r \ldots = \prod_\kappa (d\omega_\kappa)^{N_\kappa} \quad (699)$$

(698) becomes

$$B(T) = \int_{(V)} \ldots \int e^{-U/kT} \prod_\kappa (d\omega_\kappa)^{N_\kappa}. \quad (700)$$

It can be shown‡ that the partition function $B(T)$ and the free energy F of the solution are related by the equation

$$F = -kT \log B(T). \quad (701)$$

Provided $B(T)$ can be evaluated, it is thus possible to calculate e.g. the equation of state of a gas or the osmotic pressure of a solution.

For dilute gaseous systems and short-range forces, (700) is easily evaluated as a convergent series.§ For more concentrated gases, liquids, or long-range forces, the evaluation of $B(T)$ offers considerable difficulties. Guggenheim‖ has treated the case of perfect and dilute solutions, but the more general problems of imperfect solutions have not yet been attacked.

† R. H. Fowler, *Statistical Mechanics*, Cambridge, 1929.

‡ For a very simple derivation of (701), see P. Debye, *Polar Molecules*, chapter VI.

§ See R. H. Fowler, *Statistical Mechanics*, chapter VIII.

‖ E. A. Guggenheim, *Proc. Roy. Soc.* **135** (1932), 181. Guggenheim has pointed out that the derivation given by Fowler (loc. cit., chapter XIII) is erroneous.

In the case of an electrolyte solution, the most important contribution to U is due to the long-range Coulomb forces, and $B(T)$ can no longer be evaluated as a convergent series. The two chief contributions to the problem have been made by Fowler and by Kramers. Fowler† has attempted to investigate the conditions under which the employment of Poisson's equation is a valid substitute for a strict statistical treatment, and has come to the conclusion that this is only so in solutions so dilute that the limiting law holds. Onsager‡ has, however, recently shown that Fowler's method needs modification, and we shall therefore give no account of his treatment here. Kramers's theory is described in the next section.

60. Kramers's Theory

Kramers§ has attempted to obtain an exact solution of (700) in the case of electrolytes. The usual method of expanding $e^{-U/kT}$ as a series and retaining only the first term is not applicable here. When the ionic radii are very small the terms of this series become very large, though it may be easily shown‖ that for sufficiently small concentrations the partition function (700) must approach a function which is independent of the ionic radii. If the ionic radii are put equal to zero, then (700) becomes divergent. Kramers solves these difficulties in two ways, as follows:

(1) If we assume that the ionic radii are finite, all configurations of the ions may be formally considered as possible provided that we add to the energy expression

$$U = \frac{1}{D_0} \sum_{k,l} \frac{e_k e_l}{r_{kl}} \tag{702}$$

a function which becomes infinite when the centres of the ions k and l approach more closely than $a_k + a_l$.

(2) By means of a less physical treatment, Kramers modifies the energy expression (702) so that the integral representing the mean value for all configurations is no longer divergent, but the energy is still a homogeneous function of degree -1.

We shall not reproduce here Kramers's somewhat involved calculations, but shall confine ourselves to the results obtained. Kramers shows that below a certain maximum concentration there exists a stable

† R. H. Fowler, *Proc. Camb. Phil. Soc.* **22** (1925), 861; *Trans. Farad. Soc.* **23** (1927), 434.

‡ L. Onsager, *Chem. Rev.*, August 1933.

§ H. A. Kramers, *Proc. Amsterdam*, **30** (1927), 145.

‖ See N. Bjerrum, *Copenhagen Acad. Math. fys. Medd.* **7**, 9.

statistical distribution which is independent of the ionic radii. This maximum concentration is about 0·03 N. for 1-1-valent electrolytes in water. The change in the free energy of the solution due to the inter-ionic forces, which Debye's theory gives as

$$-\sum \frac{N_i z_i^2 \epsilon^2}{3D_0}\kappa$$

is given by Kramers's theory as

$$\tfrac{1}{2}NkT\log\omega(x), \tag{703}$$

where

$$\left.\begin{aligned} x &= \left(\frac{\kappa^2}{4\pi}\right)^3 n \\ \omega &= e^t(1+3t)^{-1}, \qquad \frac{4\pi}{9}x = t^2(1+3t)^{-3}. \end{aligned}\right\} \tag{704}$$

The osmotic coefficient g is then given by

$$g = 1-\frac{t}{2}, \tag{705}$$

and the activity coefficient of an i ion by

$$f_i = \frac{1}{(1+3t)^{\frac{1}{2}}}. \tag{706}$$

It is easily seen that in the limit for very dilute solutions, all these expressions are equivalent to the Debye limiting laws. They are, however, only valid under a certain maximum concentration which is about 0·03 N. for 1-1-valent electrolytes in water, and about 0·0075 N. for 2-2-valent electrolytes. For ions of small radius it is only legitimate to speak of an atmosphere of free ions below this limiting concentration.

Fig. 104 shows the course of the osmotic coefficient according to Debye's limiting formula (262) and Kramers's more rigid formula (705). Reference to experimental values of g (cf. p. 255) shows that Kramers's formula (like Debye's) is quite unable to explain the individualities observed in the osmotic coefficients. Kramers's results bear an interesting formal analogy to Heisenberg's treatment of ferromagnetism.† The critical point corresponding to $\alpha^3 n = 27/\pi$ is in many ways analogous to the Curie point which occurs in Heisenberg's theory. Above the Curie point the magnetic moment depends in a fairly simple manner upon the magnetic field-strength, and the Curie constant is related simply to the exchange integral. Below the Curie point, on the other hand, matters are very complicated: it becomes impossible to evaluate the partition function, and spontaneous magnetization sets in. The

† W. Heisenberg, *Z. f. Phys.* **49** (1928), 619.

state of affairs is very similar for electrolyte solutions. Kramers's method does not enable us to calculate the partition function above the critical concentration, since in the first place the random distribution of the ions makes the problem much more complicated than that of a magnetic crystal, and in the second place the partition function will not lead to any satisfactory result without the introduction of a finite ionic radius, which would add enormously to the mathematical difficulties. It appears probable that for concentrations only a little smaller than the critical concentration the introduction of a finite ionic radius would

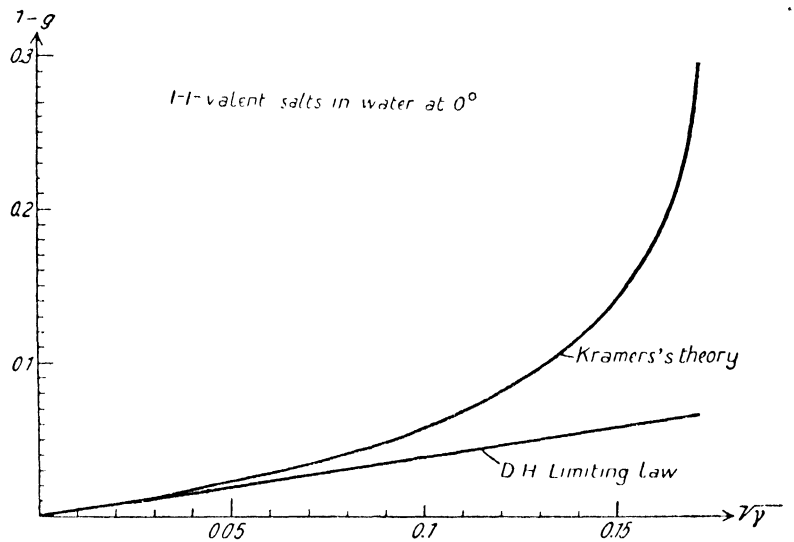

FIG. 104. Theoretical curves for the osmotic coefficient of 1-1-valent salts in water at 0°.

introduce considerable modifications into Kramers's results, while for concentrations below $\gamma_{\text{crit}}/2$ the only effect would probably be to introduce a small term proportional to the concentration and depending on the radii, just as in the theory of Debye and Hückel. Above the critical concentration we must always allow for a pseudo-association of the ions, as pictured by Bjerrum. It is probably possible to develop a satisfactory theory by combining Bjerrum's ideas with those of Kramers. This aspect of the question presents a number of problems of great importance but considerable mathematical difficulty.

The statistical method of Kramers is undoubtedly more exact than the treatment of Gronwall, Sandved, and La Mer, although the latter theory has met with more success from an empirical point of view. Kramers's treatment has unfortunately not yet been extended to the

case of finite ionic radii: such an extension would make it possible to judge the validity of the approximations of Gronwall, Sandved, and La Mer. By employing statistical mechanics, a knowledge of the exact law of force between the ions would make it possible in principle to evolve a theory of more concentrated solutions. The difficulties mentioned above in connexion with the convergence of the expressions obtained would automatically disappear in this case. The development of such a theory must be considered as one of the most interesting problems for future investigation.

APPENDIX I

Note on the dissociation field-effect (p. 242)

Fig. 105 shows the experimental results of Schiele (loc. cit., p. 240) for two weak acids in water compared with Onsager's theory, the relative increase in

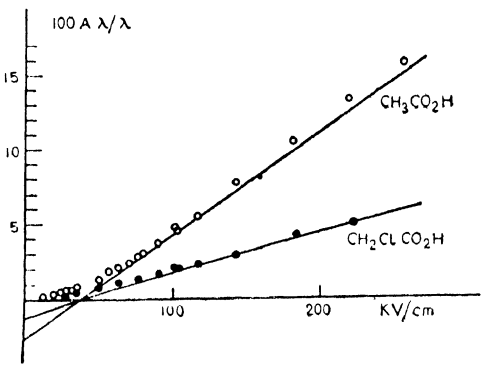

FIG. 105.

conductivity being plotted against the field-strength. The initial course of the curve is due to the action of the ionic atmosphere. Onsager† has recently published a discussion of the results of Schiele for water, of Bauer for acetone,‡ of Poole and Schiller for solid electrolytes,§ of Gemant for benzene,‖ and of a number of authors for transformer oil.

Note on the quantitative treatment of the Wien effect (p. 237).

According to a private communication from Professor Onsager, the derivation of Joos and Blumentritt (see p. 237) is in error, and their result is only correct as regards the order of magnitude.

† L. Onsager, *J. Chem. Phys.* 1934 (in the press).

‡ Bauer, loc. cit., p. 238.

§ H. H. Poole, *Phil. Mag.* **32** (1916), 112; **34** (1917), 204; **42** (1921), 488. H. Schiller, *Ann. d. Physik* **81** (1926), 32.

‖ Gemant, *Elektrophysik der Isolierstoffe*, p. 78 (Berlin 1930).

APPENDIX II

Recent applications of quantum mechanics to the theory of electrolytes

By R. H. FOWLER

Introduction.

THE specific molecular or electronic processes occurring in a solution of an electrolyte have in general hitherto proved too complicated to admit of discussion by the application of quantum mechanics to precise models in any exact manner. Naturally enough, the processes concerned being molecular, one is confident that quantum-mechanical theories must apply, but it has not appeared hitherto that they would apply so as to yield results in any way significantly different from the results of classical mechanical theories applied to the same or similar models. Recently, however, since the appearance of the German edition of this book, some work by Gurney† has made a start in showing that the general principles of quantum mechanics can be applied in a significant and important way, at least to the discussion of various processes that must occur at the electrodes of an electrolytic solution.

The considerations brought forward by Gurney have perhaps hardly yet been sufficiently discussed and criticized for us to estimate confidently their importance, and we shall therefore not give a full account of them here. But his quantum-mechanical discussion of overvoltage, in particular of the current-voltage relationship (especially for small currents) during the electrolysis of water from a dilute acid using inert electrodes, should not be passed over. The discussion is simple and successful, and is an excellent example of the way in which we may be able in future to use the general principles of quantum mechanics in an elementary way in order to interpret a complex phenomenon.

In any phenomenon in which a current flows from a metal electrode to an electrolyte and back again, no matter what the detailed mechanism of conversion at the electrode, such a current is carried in the metal by electrons and in the electrolyte by positive and negative ions. Electrons must, therefore, be continually emerging from a cathode into the solution and neutralizing positive ions in the layer next to the surface in order that the observed current may flow. In the same way, at an anode

† R. W. Gurney, *Proc. Roy. Soc.* A, **134** (1931), 137; **136** (1932), 378. See also J. H. Wolfenden, *Ann. Rep. Chem. Soc.* (1932), 34.

electrons are being continually delivered up to the anode by negative ions in order that current may flow, the ions being thereby neutralized. It is the essential point of Gurney's theory to examine the conditions, suggested by quantum mechanics, under which such processes can occur on an electrode surface at the proper rate.

The experimental data on overvoltage.

The most valuable data for our purpose are those of Bowden and his collaborators† on the overvoltage of hydrogen and oxygen at different inert electrodes. As is well known, the overvoltage was found to vary very much with the chemical composition and the physical state of the electrode, and also depended upon whether hydrogen or oxygen was being discharged. More interesting from our point of view is the variation of the overvoltage with the current density and with the temperature. Bowden found that, for any one electrode, if the logarithm of the current density $\log i$ is plotted against the overvoltage V, straight lines are obtained over the range of current densities measured (10^{-7}–10^{-3} amps per sq. cm.). The slopes of the straight lines obtained are the same for all the electrodes studied, and are independent of whether the electrode is used as anode or cathode. The results may be expressed by the equation

$$\left(\frac{d\log i}{dV}\right)_T = \frac{\alpha}{T}, \tag{1}$$

where α is a constant independent of the nature of the electrode.

When the electrode remains the same and the temperature is altered, Bowden obtained results which may be represented by the following equation

$$\left(\frac{d\log i}{dT}\right)_V = \beta, \tag{2}$$

where β decreases slightly with decreasing V, but has the value 0·05–0·06 for all electrodes studied in the range 14–80° C.

Any theory of overvoltage must thus reproduce correctly the interdependence of overvoltage, current density, and temperature, as expressed in the above two equations.

The behaviour of an ion near a metal.

We start by considering the behaviour of a free atom or free positive or negative ion near a metal surface *in vacuo*. If the ionization energy I of the atom or ion is less than χ, the work function of the metal, the

† F. P. Bowden and E. K. Rideal, *Proc. Roy. Soc.* **120 A** (1928), 59; Bowden, ibid. **125** (1929), 446; **126** (1929), 107; Bowden and O'Connor, ibid. **128** (1930), 317.

electron can and will make a transition to an empty level in the metal when the ion is still some way away from the surface, a distance perhaps of the order of 10^{-7} cm. At such distances, transitions take place quite readily through the potential barrier, by what is commonly called the quantum-mechanical tunnel effect.† Atoms or negative ions for which $I < \chi$ cannot exist permanently as such near a metal at ordinary temperatures, for there are very few metallic electrons above the level (of depth χ below free space) at which Sommerfeld's set of occupied free electron levels ends, and only such electrons can jump back to the ion. If, however, $I > \chi$ the positive ion cannot exist as such near the metal but will be neutralized while still some distance away from the surface. It cannot lose its electron again since the metallic levels at this height are normally full. Thus when $I > \chi$ only neutral or negative ions, and when $I < \chi$ only positive ions, survive near the metal.

The situation is slightly different for ions in solution, since any positive or negative ion in solution has lost energy by interaction with the water molecules compared with its state in free space (hydration). This loss of energy is comparable to the work functions and ionization potentials themselves. This last energy W must be replaced as the ion is neutralized, when its energy becomes comparatively unaffected by being in solution. The condition for the survival of a positive ion in solution is that there are no suitable metallic electrons of the energy required to neutralize it, i.e. none of an energy greater by W than the energy required to neutralize a free ion, i.e. none of an energy $I-W$ below the standard zero. This condition will be written

$$E_+ = I_+ - W_+ < \chi.$$

The condition for the survival of a negative ion is that the level to which the ion wants to jump shall be full. The electron must take with itself the energy of a level $I+W$ below the standard zero. Hence survival is possible if

$$E_- = I_- + W_- > \chi.$$

The conditions $\qquad E_+ > \chi \qquad E_- < \chi$

are the conditions that electron transfers shall be possible to discharge positive and negative ions respectively, so that current can flow.

The effect of interface potentials.

The foregoing paragraph refers to a standard state in which electrical double layers are absent (or have some standard value). When, however,

† See e.g. Condon and Morse, *Quantum Mechanics*, chapter VII; Frenkel, *Wave Mechanics*, vol. i, p. 111.

the electrode is an anode, so that the positive current must flow from the electrode into the solution and negative ions are being neutralized at the surface, we shall expect to have a double layer set up (metal + —solution) which will assist the current by assisting the discharge of the negative ions by depressing the metallic electron levels relative to those of the solution. The condition for continued neutralization is then

$$E_- < \chi + \epsilon V_a.$$

Similarly when the electrode is a cathode and positive ions are being neutralized we shall have a double layer (metal— +solution) set up assisting neutralization, so that the condition for continued neutralization becomes

$$E_+ > \chi - \epsilon V_c.$$

V_a, V_c are the interface potentials at the anode and cathode respectively. If either an anode or a cathode is left to adjust itself to equilibrium with the ions in the solution, then it will do so as follows. The ions will be held close to the surface by image forces and, provided the supply is not limited, will accumulate until they build up such a double layer that neutralization is just possible. The electrode in such a state is reversible, and for the ideally simple cases discussed so far here the conditions are $E_- = \chi + \epsilon V_a$ or $E_+ = \chi - \epsilon V_c$, respectively. But the reversible electrode can only pass an infinitesimally small current, and in order to pass significant currents we must have the foregoing inequalities. These give the so-called overvoltages, and the important point to grasp is that these overvoltages are primary and essential to the passage of appreciable currents—they are not in any way due to secondary effects such as the need to overcome the resistance of obstructive layers of gas, as has often been argued.

A simple general argument shows that electrolysis cannot proceed without building up these interface potentials to some degree; for to proceed with $V_a = V_c = 0$ we must have $E_+ > \chi$ and $E_- < \chi$ (or ideally in the limit $E_+ = \chi = E_-$) and therefore $E_+ \geqslant E_-$. But this is impossible in an electrolyte, which by hypothesis is a solution in which the state of ionization plus hydration is of lower energy than that of neutralization, i.e.

$$I_+ - I_- - W_+ - W_- < 0$$

$$E_+ < E_-.$$

When an electrically neutral surface is immersed in the electrolyte both positive and negative ions are attracted to the metal by image forces, so that the surface concentration of ions of both signs is greater than in the bulk of the solution. But if the metal is made positive with

respect to the solution, negative ions are more strongly held than positive ones, and their concentration increases at the expense of the positives. This double layer accommodates the applied potential difference V_a between the metal and the solution, which is thus confined to a surface double layer metal+ —solution, assisting the neutralization of negative ions. Bowden's measurements show that the total transient current required to build up an overvoltage of one volt is about equal to the charge required to establish this potential difference between the plates of a condenser whose area is that of the electrode, whose separation is about 2×10^{-8} cm. and whose dielectric constant is unity.† The excess number of ions required is of the order of 3×10^{13} per sq. cm. and the total number in the surface layer may well be 10^{15}, so that the relative change is small. There is little doubt that these extra interface potentials are present, being superposed on those necessary for the reversible state, and are built up by the accumulation of ions until the conditions are adjusted to carry the proper steady current.

Theory of the current-voltage relationship.

We can now see how the theory leads at once to a current-voltage relationship of roughly the right type. We consider throughout only the current to a single electrode, whose potential relative to the solution is fixed by measurement relative to the potential of an undisturbed electrode in another part of the solution carrying no current. Current can only flow when the electrode is a cathode (positive current solution → electrode) if

$$E_+ > \chi-\epsilon V_c,$$

or when an anode if

$$E_- < \chi+\epsilon V_a.$$

If we start applying a voltage making the electrode a cathode say when the electrode is in a state different from that of the reversible cathode, then at first no current will flow in the electrode. As soon, however, as the voltage V_c exceeds $(\chi-E_+)/\epsilon$ the current can immediately jump to a large value. But this is just what we require, when we remember that our formulation has so far ignored all temperature distributions over a range of energy levels, taking all energy levels or limits as ideally sharp, as they would be at absolute zero.‡

† Though water has a dielectric constant of 80 in bulk, the water dipoles will be fully orientated by the ions, and a dielectric saturation will set in, so that the constant will have far less than its bulk value.

‡ If for a moment we cease to concentrate on a single electrode and consider the cell as a whole, this point can be made yet clearer. The voltage applied to the cell is V_a+V. Current can only flow if $\epsilon V_c < \chi-E_+$, $\epsilon V_a < -\chi+E_-$, i.e. if $\epsilon V > E_--E_+$. Once this condition is satisfied we get a sudden increase of current.

Actually the hydrated ions instead of lying in a sharp energy level or sharply bounded band, will be distributed over a wide band of energies almost continuously, and the distribution must be given approximately by Boltzmann's law. The spread lies in the hydration energy W. Thus if $N_+(E)\,dE$ is the number of positive ions with neutralization energy between E and $E+dE$,

$$\begin{aligned} N_+(E) &= N_0^+ e^{(E_0^+ - E)/kT} && (E > E_0^+ = I_+ - W_0^+) \\ &= 0 && (E < E_0^+), \end{aligned}$$

where W_0^+ is the (negative) energy of the ground state of the hydrated ions. Similarly,

$$\begin{aligned} N_-(E) &= N_0^- e^{(E - E_0^-)/kT} && (E < E_0^- = I_- + W_0^-) \\ &= 0 && (E > E_0^-). \end{aligned}$$

Strictly there may be weight factors multiplying the exponential factors by some simple polynomial in E, but this complication is not of much importance at present.

In the same way, the metallic electron levels are not all full below χ, nor all vacant above. The Sommerfeld distribution law gives accurately enough for the present purpose that the number of electrons $n(w)dw$ having kinetic energy between w and $w+dw$ is

$$\begin{aligned} n(w) &= A w^{\frac{1}{2}} e^{(w^* - w)/kT} && (w \gg w^*) \\ &= A w^{\frac{1}{2}} \{1 - e^{(w - w^*)/kT}\} && (w \ll w^*). \end{aligned}$$

The region $w \sim w^*$ in which these formulae do not hold is not important here. The level of kinetic energy w^* corresponds to a total negative energy χ when there is no interface potential, or $\chi - \epsilon V_c$, $\chi + \epsilon V_a$ when there is one. More explicitly, we can write for the distribution law for electrons of given total (negative) energy E, neglecting the unimportant weight factor $w^{\frac{1}{2}}$,

$$\begin{aligned} n(E, \chi - \epsilon V_c) &= A e^{(E - \chi + \epsilon V_c)/kT} && (E < \chi - \epsilon V_c) \\ &= A\{1 - e^{-(E - \chi + \epsilon V_c)/kT}\} && (E > \chi - \epsilon V_c). \end{aligned}$$

Similarly, the distribution of empty electron levels in the anode can be written

$$\begin{aligned} \nu(E, \chi + \epsilon V_a) &= A\{1 - e^{(E - \chi - \epsilon V_a)/kT}\} && (E < \chi + \epsilon V_a) \\ &= A e^{-(E - \chi - \epsilon V_a)/kT} && (E > \chi + \epsilon V_a). \end{aligned}$$

In order that appreciable current shall flow at a cathode, it is necessary that $N_+(E)$ and $n(E, \chi - \epsilon V_c)$ should have an appreciable overlap. At ordinary temperatures $N_+(E)$ and $n(E, \chi - \epsilon V_c)$ fall to very small values

within a tenth of a volt of E_0^+ and $\chi-\epsilon V_c$ respectively, but while N_+ diminishes exponentially as E increases, n increases by the same factor until E reaches $\chi-\epsilon V_c$, when further increase stops. Thus if $P(E)$ is the probability of a jump per unit time by an electron of energy E from the metal to a positive ion (strictly speaking $P(E)$ must be averaged for all distances), we can express the current i which flows at a cathode in the form

$$i_c = \int_{E_0^+}^{\chi-\epsilon V_c} n(E, \chi-\epsilon V_c) N_+(E) P(E)\, dE.$$

The conditions for an anode are similar. We require an appreciable overlap of $\nu(E, \chi+\epsilon V_a)$ and $N(E)$, and the current at an anode can be expressed in the form

$$i_a = \int_{\chi+\epsilon V_a}^{E_0^-} \nu(E, \chi+\epsilon V_a) N_-(E) P'(E)\, dE.$$

These integrals are easy to evaluate approximately, and give

$$\log i_c \sim \frac{E_0^+-\chi+\epsilon V_c}{kT}, \qquad \log i_a \sim \frac{\chi-E_0^-+\epsilon V_a}{kT}. \tag{3}$$

By differentiating equation (3) with respect to V and T, we at once obtain equations (1) and (2), which were found experimentally, i.e. the theory gives equations of the right form. Numerically, the agreement is good, but not quite perfect. Thus the value of the constant α in equation (1) is found experimentally to be about $\epsilon/2k$, instead of ϵ/k as required by the theory. Further, β in equation (2) is found experimentally to have a value of 0·05–0·06, while if we give the numerator in (3) the reasonable value of one electron volt, the value 0·11 is obtained.

It appears, however, that complete numerical agreement may be attained by taking into account one theoretical point hitherto overlooked, namely the Franck-Condon principle.† In order to neutralize a positive or negative hydrated ion by supplying an electron we may not be and in general are not able to dissociate it into a water molecule and neutral atom at rest, but only into a water molecule and a neutral atom with a definite amount of surplus energy determined roughly at least by the principle that the transition takes place between states of equal separation of the atomic nuclei. The negative energies W of the hydrated ion govern the Boltzmann distribution laws $N_+(E)$ and $N_-(E)$

† See e.g. Condon and Morse, *Quantum Mechanics*, § 53.

as before, but the energies that have to be supplied or removed by the electron are greater than these E's. Over the important range of energies we may suppose that the distribution law energies are a fraction $1/\gamma$ of the energies to be supplied, where it is necessary that $\gamma > 1$.

It is not necessary to go into details. The effect is easily shown to add a factor γ to the denominators in equation (3), and there is no reason to believe that this factor may not have the value 2, which would at once give complete agreement between the theory and Bowden's results.

TABLE OF THE MOST IMPORTANT SYMBOLS

A	work in general.
a	activity in general. (In Chapter XI also ionic diameter.)
a_λ	activity of the species λ.
$a_\pm$	mean ionic activity.
$\mathbf{D}$	10^{-18} e.s.u. (1 Debye).
D	dielectric constant of the solution.
D_ω	dielectric constant of the solution at frequency ω.
D_0	dielectric constant of the solvent.
d	density of the solution.
$d'A$	infinitesimal amount of work done upon the system.
$d'Q$	infinitesimal amount of heat absorbed by the system.
E	electric field strength.
$\mathbf{E}$	electromotive force of a cell.
e_i	electric charge of an ion of the ith sort.
$\mathfrak{F}$	value of the Faraday.
F	free energy in general.
f_λ, f'_λ, or f^*_λ	activity coefficient of the species λ, related by the equation $\eta_\lambda f^*_\lambda = \gamma_\lambda f_\lambda = m_\lambda f'_\lambda$.
f_0	activity coefficient of the solvent.
$f_\lambda = \Lambda/\Lambda_\infty$	conductivity coefficient.
G_0	molecular weight of the solvent.
G_E	molecular weight of the electrolyte.
G_λ	molecular weight of the species λ.
g	osmotic coefficient.
i	van't Hoff factor.
$J = \frac{1}{2}\sum \gamma_i z_i^2$	ionic strength.
$J' = \frac{1}{2}\sum m_i z_i^2$	ionic strength.
K	mass law equilibrium constant, equation (42).
K_a	equilibrium constant of the generalized law of mass action, equation (117).
$k = 1{\cdot}37 \times 10^{-16}$	ergs per degree, Boltzmann's constant.
L	heat of dilution in general.
$\bar{L}$	molar heat of dilution.
(L)	solubility.
l_i	ionic mobility at infinite dilution.
M_λ	number of moles of the species λ.
m	molarity, i.e. moles of solute per 1,000 g. solvent.
m_λ	molarity of the species λ.
$\mathbf{N} = 6{\cdot}06 \times 10^{23}$	Loschmidt's number per mole.
N_λ	number of particles of the species λ.
N_0	number of molecules of the solvent.
n	number of particles per c.c.
n_i	number of ions of the ith sort per c.c.
P	osmotic pressure of a real solution.

$\bar{P}$	osmotic pressure of the ideal dilute solution.
$\mathbf{P}$	solubility product.
p	pressure in general.
Q	quantity of heat in general.
q	quantity defined by equation (232).
$R = 8{\cdot}31 \times 10^7$	ergs per degree, universal gas constant.
S	entropy in general.
T	absolute temperature.
U	energy in general.
U_e	electrical energy of an electrolyte solution.
V.	volume.
v_γ	molar dilution, i.e. number of litres which contain one mole of electrolyte.
$\mathfrak{V}_0$	molar volume of the solvent.
W	electrical work of charging and discharging the ions (also termed F_e).
z_i	valency of the ion i.
z_e	electrochemical valency.
α	degree of dissociation according to Arrhenius.
α^*	true degree of dissociation.
$\Gamma = 2J$	ionic concentration.
γ	concentration of electrolyte in moles per litre of solution.
γ^*	concentration of electrolyte in equivalents per litre of solution.
γ_i	molar concentration of the species i.
$(\overline{\Delta T})_0$	freezing-point depression in an ideal dilute solution.
$(\Delta T)_0 = \vartheta$	freezing-point depression in a real solution.
$\Delta\lambda_E$	quantity characterizing the Wien effect.
$\epsilon = 4{\cdot}77 \times 10^{-10}$	e.s.u. electric charge of an electron.
η	viscosity of the solution.
$\eta_\lambda^{(\sigma)}$	mole fraction of the species λ in the phase σ.
η_0	mole fraction of the solvent; viscosity of the solvent.
Θ	time of relaxation of the ionic atmosphere.
κ	characteristic quantity in Debye's theory. $1/\kappa$ = thickness of the ionic atmosphere.
Λ	molar conductivity in ohms^{-1} per sq. cm. (with a stationary field).
Λ^*	equivalent conductivity in ohms^{-1} per sq. cm. (with a stationary field).
Λ_ω	molar conductivity at the frequency ω.
λ	specific conductivity in ohms^{-1} per sq. cm.
λ_E	specific conductivity at field strength E.
λ_0	specific conductivity at zero field strength.
ν	number of ions formed by the dissociation of one molecule.
ν_+	number of positive ions formed by the dissociation of one molecule.
ν_-	number of negative ions formed by the dissociation of one molecule.
ν_i	number of ions of the ith sort formed by the dissociation of one molecule.
ξ	chemical potential.

Π	electric density.
ρ_i	frictional coefficient for an i ion.
Φ	thermodynamic potential in general.
$\overline{\Phi}$	thermodynamic potential of an ideal dilute solution.
$\overline{\Phi}$	thermodynamic potential of the electrolyte per mole.
$\overline{\Phi}_A$	thermodynamic potential of the component per mole.
Ψ	electric potential round an ion.
$\omega_j = 1/\rho_j$	frequency of an alternating electric field.

INDEX

Absorption spectra of electrolytes, 313–16.
Acids, definition of, 3.
Activity, definition of, 43; thermodynamics of, 45–8; of strong electrolytes, 51–3; relation to osmotic pressure, &c., 48; determination of—from E.M.F. data, 50, 58–62; from vapour pressures, 56–8; from freezing-points, 62–5.
Activity coefficients, rational and practical, 55–6; of strong electrolytes, 51–3; empirical laws governing, 70; in mixtures of electrolytes, 68; determination from solubility measurements, 69, 126–35; limiting law of, 120–6.
Anomalies of strong electrolytes, 40–3, 73–8.
Association, theories of, 257–80.
Atmosphere, *see* Ionic atmosphere.

Bases, definition of, 3.

Conductivity, literature on, 91; of strong electrolytes, 73–91, 163–242; of aqueous solutions, 193–201; of non-aqueous solutions, 78–81, 202–9; Onsager's theory of, 192–209; variation with field-strength, 82–9, 235–9; variation with frequency, 90, 182–92; variation with pressure and temperature, 200.
Cycle, Born's, 7.

Dielectric constant of electrolytes, dependence on frequency, 189–92; measurement of, 231.
Diffusion of strong electrolytes, 169.
Dilution law, Ostwald's, 30–4.
Dispersion of conductivity and dielectric constant, 90, 182–92; calculation of, 211–22; measurement of, 222, 235.
Dissociation, true degree of, 289–312.
Dissociation field-effect, 240.

Electromotive force measurements, determination of activities from, 50, 58–62.
Electrophoretic effect, 179–82.

Faraday's laws, 1.
Freezing points, determination of activities from, 62–5.

Heat of dilution of strong electrolytes: limiting law of, 154–7; in more concentrated solutions, 280–9; measurement of, 157–9.
Hydration of ions, thermochemistry of, 6–10.

Ideal solutions, thermodynamics of, 16–24.
Ion pairs, Bjerrum's theory of, 258–63.
Ion triplets, 263–7.
Ionic atmosphere, 100; thickness of, 105; time of relaxation of, 107, 176–9.
Ionic strength, principle of, 70.

Lattice energies, 7.

Mass of ions, determination of, 169.
Mass action, law of, 16–20, 47.

Neutral salt effects, 152–4.
Non-aqueous solutions, conductivity of, 78–81, 202–9; osmotic coefficients of, 119; solubility effects in, 133–5.

Optical properties of electrolytes, 94, 312–25.
Osmotic coefficients, definition of, 39; limiting law for, 116–20; in non-aqueous solutions, 119.
Ostwald's dilution law, 30–4.
Overvoltage, 337.

Quantum mechanics of electrode processes, 336–43.

Raman effect of electrolyte solutions, 322–5.
Refractive index of electrolyte solutions, 316–22.

Salt effects, 136–54.
Salting-out effect, 138–52.
Solubility of salts, 34–8, 41–3.
Solubility effects according to Debye's theory, 126–31.
Solubility measurements, determination of activity coefficients from, 69, 126–35.
Specific heats of electrolytes, 123.
Specific interaction, principle of, 325–30.
Statistical mechanics of electrolyte solutions, 331–5.
Supersonic vibrations in electrolytes, 170.

Thermodynamic potentials, 12.
Thermodynamics of ideal solutions, 16–24; of activities, 45–8.
Transport numbers, theory of, 209.

Van 't Hoff factor, 25.
Vapour pressures, determination of activities from, 56–8.
Viscosity of strong electrolytes, 243–9.
Volume, partial molal, of electrolytes, 122.

Walden's rule, 78.
Wien effect, 82–9, 225–39.

PRINTED IN
GREAT BRITAIN
AT THE
UNIVERSITY PRESS
OXFORD
BY
JOHN JOHNSON
PRINTER
TO THE
UNIVERSITY