THE PHYSICAL CHEMISTRY
OF
ELECTROLYTIC SOLUTIONS

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

GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

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

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

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

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

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

Preface to Second Edition

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

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

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

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

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New Haven, Conn.
June, 1949.

Preface

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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Glossary of Symbols

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

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

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

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

A few rules for subscripts and superscripts have been adopted.

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

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

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

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

$$\log f_\pm = -\boldsymbol{\mathcal{S}}_{(f)}\sqrt{\Gamma} = -\mathcal{S}_{(f)}\sqrt{c}$$
$$\overline{L}_2 = \boldsymbol{\mathcal{S}}_{(L)}\sqrt{\Gamma} = \mathcal{S}_{(L)}\sqrt{c}$$

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

A, work content per mol.
$\bar{A}$, partial molal work content.
$\bar{A}_1$, $\bar{A}_2$, etc., $\bar{A}_i$, $\bar{A}_j$, etc., partial molal work content of components, etc., and ion constituents, etc., indicated by subscripts.
A, contribution to, (1) ΔA (el), electrical contribution to the work content [Equation (3–2–1)]; (2) $\Delta A_{(s)}$, contribution to the work content caused by addition of electrolyte [Equation (3–10–7)].
A^*_w, van der Waals co-volume contribution to the work content [Chapter (12), Section (8)].
A, A', characteristic parameters of equations (5–2–7) and (5–2–9). Important functions. Note that $A'_m = A'\sqrt{d_0}$.
A, area
A, special function given by equation (4–7–19).
A, special function [Chapter (12), Section (7)].
$A\Delta\alpha$, special function in Table (5–2–6), defined by equation (5–2–17).
A, A_n, A_{n-1}, A^*_{n-1}, A', A^*, etc., empirical coefficients.
a, activity.
a_1, a_2, $\cdots$, activities of components indicated.
a_+, a_-, a_i, a_j, conventional activities of ionic constituents indicated.
$a_\pm$, mean ionic activity of an electrolyte [Equation (1–6–3)].
a_R, activity of a component in a reference solution.
a_w, activity of water.
a_{H}, a_{OH}, etc., activities of ionic constituents indicated.
a_N, a_m, a_c, activity on N-, m-, and c-, concentration scales.
a'_s, activity of solid solvent at T'.
$a_1^{0'}$, activity of pure liquid solvent at T'.
a'_1, activity of solvent in solution at T'.
a'_2, activity of solute in solution at T'.
a'_v, activity of solvent vapor at T'.
a, mean distance of approach of ions defined by equation (14–1–5).
$\mathring{a}$, same in Ångström units.
a_i, a_j, mean ionic distances of approach of ions indicated.
$\mathring{a}_i$, $\mathring{a}_j$, same in Ångström units.
a, distance of approach of ions in theory of ionic pair formation [Chapter (3), Section (7)].
a_3, distance in triple ion formation equation (3–7–21).

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

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

C_p, molal heat capacity at constant pressure.
C_{p_s}, molal heat capacity of solid.
C_{p_v}, molal heat capacity of vapor.
C_{p_1}, molal heat capacity of solvent.
$\bar{C}_p$, partial molal heat capacity.
$\bar{C}_{p_1}$, $\bar{C}_{p_2}$, partial molal heat capacities of components indicated.
$\bar{C}^0_p$, $\bar{C}^0_{p_1}$, $\bar{C}^0_{p_2}$, standard partial molal heat capacities.
C_n, function defined by equation (9–2–9).
C_n^*, function defined by equation (9–3–6).
C_{-2}, C_{-1}, C_0, C_1, C_2, coefficients in equation (11–9–3).
C', C^*, etc., coefficients of empirical equations.
c_p, c_p^0, c_v, etc., specific heat capacities at constant pressure, or volume.
c, molar concentration in mols per 1000 cc. solution.
c_+, c_-, c_i, c_j, molar concentrations of constituents indicated.
$c_\pm$, mean molar concentration [Equation (1–8–8)].
c^*, concentration in equivalents per 1000 cc. solution.
c_u, molar concentration of undissociated electrolyte.
c_A^*, normality of ion constituent, A.
c_I^*, normality of indicator solution.
$c_I^{*\prime}$, initial normality of indicator solution.
$c(x)$, concentration of solute at a distance, x, from boundary of solution [Chapter (3), Section (11)].
c, number of components (Gibbs) in a system.
c_0, c_1, c_2, c_n, etc., coefficients defined by equations (4–3–52) and (4–3–53).
c, c_0, c', c'', c''', c_1, etc., coefficients of empirical equations.

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

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

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

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

f, rational activity coefficient.
$f_{(s)}$, rational activity coefficient of non-electrolyte.
f_+, f_-, f_i, f_j, conventional rational activity coefficients of ions indicated.
$f_{\pm}$, mean rational activity coefficient [Equation (1–8–4)].
$f_{\pm(s)}$, rational activity coefficient of electrolyte in salting equation (3–10–10).
$f_{\pm(t)}$, rational activity coefficient of electrolyte in equation (3–10–13) for transfer of electrolyte.
$f_{ij}(\mathbf{r}_2, \mathbf{r}_{12}), f_{ji}(\mathbf{r}_1, \mathbf{r}_{21}), f_{ji}, f_{ij}$, distribution functions according to equation (2–1–4).
f^0_{ji}, f^0_{ij}, distribution functions for solution in unperturbed state.
f'_{ji}, f'_{ij}, distribution functions for perturbed solutions.
f_c, f_m, special functions given by equation (12–10–7).
$f(x)$, function in theory of Wien effect [Equation (4–6–45), Table (5–3–6)]

$G_{ji}, G_{ij}, G_{12}, G_{21}, G_{11}, G_{22}, G(\mathbf{r})$, functions used in theory of frequency and field effects (Wien effect) upon conductance [Chapter (4), Sections (5) and (6)].
g, rational osmotic coefficient [Equation (1–9–5)].
$g(x)$, function in theory of Wien effect [Equation (4–6–48), Table (5–3–5)].
$g(c)$, special function in equation (7–4–10).
$\mathbf{g}$, special function [Chapter (4), Section (7)].

H, molal heat content.
$H_1, H_2, \cdots H_c$, molal heat contents of components indicated.
$\bar{H}_1, \bar{H}_2, \cdots \bar{H}_c$, partial molal heat contents of components indicated.
$\bar{H}_i, \bar{H}_j$, conventional partial molal heat contents of ions indicated.
H^0, standard molal heat content.
$H^0_1, H^0_2, \cdots H^0_c$, standard molal heat contents of components indicated.
$\bar{H}^0_1, \bar{H}^0_2, \cdots \bar{H}^0_c$, standard partial molal heat contents of components indicated.
$\bar{H}^0_i, \bar{H}^0_j$, conventional standard partial molal heat contents of ions indicated.
h, height.
h_{ji}, h'_{ji}, elements of matrix [Chapter (4), Section (3)].
H, changes in, ΔH_D, heat of dilution; $\Delta H_{D(s)}, \Delta H_{D(a)}, \Delta H_{D(b)}$, heats of dilution of salt, acid and base; ΔH_n, heat of neutralization; $\Delta H^*_n = \Delta H_n - \Delta H_{D(s)}(m \to m')$; ΔH^0_i, heat of ionization.

I_0, intensity of light before traversing solution.
I, intensity of light after traversing solution.
$I(b_3)$, special function in theory of triple ion formation [Equation (3–7–25), Table (5–2–4)].
$\imath$, electric current.
$\mathbf{i}$, vector electric current.
i, characteristic constant in equation (8–7–28b)

$\mathcal{J}(\equiv\bar{C}_p-\bar{C}_p^0)$, relative partial molal heat capacity.

$\mathcal{J}_1, \mathcal{J}_2, \cdots \mathcal{J}_c$, relative partial molal heat capacities of components indicated.

$\mathcal{J}_{2(T_R)}=\mathcal{J}_2$, at a reference temperature, T_R.

$\mathbf{J}$, flow of ions [Equation (4–4–1)].

$\mathbf{J}_i$, $\mathbf{J}_j$, flow of i ion, j ion.

$(J_j)_{\mathrm{I}}$, $(J_j)_{\mathrm{II}}$, $(J_j)_{\mathrm{I}}(\kappa)$, special functions in Debye's theory of salting effect [Equations (3–10–44) to (3–10–49)].

$J(b_3, x)$, special function in theory of triple ion formation [Equation (3–7–26)].

j, function in freezing point theory [Equation (9–5–21)].

$\bar{K}_1, \bar{K}_2, \cdots \bar{K}_c$, partial molal compressibilities of components indicated.

$\mathbf{K}_i$, $\mathbf{K}_j$, total forces on ions.

K, equilibrium constant.

K_A, acid ionization constant.

K_B, base ionization constant.

K_w, ionization constant of water.

K_{2A}, second ionization constant of dibasic acid.

K_h, equilibrium constant of hydrolytic reaction.

K_θ, maximum value of ionization constant at temperature, θ.

K_A^*, specially defined ionization constants used in treatment of medium effects [Chapter (15), Section (7)].

K_3, dissociation constants for triple ions.

K_4, dissociation constants for quadruple ion aggregates.

$K(X)$, $K(0)$, ionization constants with, and without external field.

K^2, special function given by equation (4–5–9).

$\mathcal{K}_{(H)}$, special function given by equation (3–8–8).

$\mathcal{K}_{(V)}$, special function given by equation (3–9–5).

k, Boltzmann constant.

$\mathbf{k}_i$, $\mathbf{k}_j$, external forces on ions.

$\mathbf{k}_0$, force acting in molecules of solvent.

k, k_0, bulk compression of solution and solvent [Equation (8–7–16)].

$k(\equiv 2.3026\, RT/\mathbf{NF})$ [Equation (11–2–3), etc.].

k_1, constant in equation (4–1–18).

k_1, k_2, kinetic constants in equation (14–1–3).

k_s, k_m, k_N, salting coefficients on c-, m-, and N-scales.

$k_w(\equiv m_{\mathrm{H}}m_{\mathrm{OH}})$.

$k_A(\equiv m_{\mathrm{H}}m_{\mathrm{R}}/m_{\mathrm{HR}})$.

k_h $(\equiv m_{\mathrm{HR}}m_{\mathrm{OH}}/m_{\mathrm{R}})$.

k_A', k_{0A}', special functions [Chapter (15), Section (7)].

$\bar{L}_1$, $\bar{L}_2$, relative partial molal heat contents of components indicated.

$\bar{L}_{2(T_R)}$, $\bar{L}_2$ at reference temperature, T_R.

L_s', relative molal heat content of solid at T'.