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*in*  
ELECTROLYTE  
SOLUTIONS  
2nd Edition

Kenneth S. Pitzer

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# Activity Coefficients in Electrolyte Solutions

2nd Edition

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## PREFACE

The progress toward a second edition of "Activity Coefficients in Electrolyte Solutions" was well advanced by Dr. R. M. Pytkowicz, the editor of the first edition, when he resigned in early 1989 for health reasons. After a substantial hiatus, I was asked to take over the editorship. Most of the chapters and authors remain as were planned by Dr. Pytkowicz, but a few changes in authorship or coauthorship were necessary and one new chapter (8) was added. I am responsible for the present organization of the book but am happy to acknowledge the role of Dr. Pytkowicz.

My evaluation concerning the general state of knowledge in this field and the opportunities for advances as well as certain specific comments concerning points of possible misunderstanding are given in the Introduction. At this point, I wish to thank all of the authors for the prompt completion of their chapters and my secretary, Peggy Southard, for assistance on various aspects of this project.

**Kenneth S. Pitzer**

## INTRODUCTION

It has been eight decades since activity coefficients came into use in the representation of the solute chemical potential in electrolyte solutions, together with the osmotic coefficient for the solvent chemical potential. While ionic solutions in other polar solvents have been and continue to be investigated, aqueous solutions dominate the electrolyte scene with respect to their importance in biological, geological, and industrial systems as well as in the range and intensity of scientific study. Although all of the concepts and theories are equally applicable to nonaqueous electrolytes, almost all of the particular systems that are considered here are aqueous.

In the earlier years, most research concerned pure, single-solute electrolytes at or near room temperature and at low and moderate concentration. Only a few systems were measured over the full molality range available. Subsequently, Robinson and Stokes and others through isopiestic measurements greatly extended the knowledge of a large number of electrolytes at 25°C. In their book Robinson and Stokes<sup>1</sup> summarize this information as well as presenting an excellent account of the principles and the methods of measurement for electrolytes.

While a few measurements of mixed electrolytes were made in very early years, it was Harned<sup>2</sup> and his associates that measured quite a number of mixed systems and stated the rules bearing his name concerning their behavior. Again, this work was confined to temperatures near 25°C and to moderate molalities. Many others made substantial contributions to experimental research on electrolytes prior to the first edition of this book published in 1979. It is impractical to list here all of the important contributors of that period; their names are cited in various chapters.

Even by 1910 it was recognized that the behavior of electrolytes in the dilute range differed from that of nonionic solutions. In 1912, Milner<sup>3</sup> explained theoretically the cause of this difference in terms of the long-range nature of ionic forces, but his mathematical expression was so complex that it received little attention. In 1923, however, Debye and Hückel<sup>4</sup> presented a simple expression that captured the essential consequence of the ionic forces. Subsequently, various theorists investigated the difficult problem of an electrolyte with greater rigor and confirmed the correctness of the limiting law of Debye and Hückel. As is described in certain chapters of this book, several of these later theories also contributed expressions for the behavior of more concentrated electrolytes.

The major advances in this field over the last fifteen years have been, first, in the area of mixed aqueous electrolytes of relatively high concentration extending to the limits of solid solubility, and second, for high temperatures up to 300°C and to pressures of hundreds of bars. Both of these advances are recognized in major additions to Chapter 3, a largely new chapter on natural waters, and new chapters on mineral solubilities and ion association at high temperatures and pressures.

With the ion-interaction (Pitzer) equations, including the theoretical terms for unsymmetrical mixing of ions of the same sign, together with ion-association equilibria where significant, it is now possible to predict activity coefficients and water activities accurately for mixtures of unlimited complexity and to the limits of solid solubility in most cases, provided, of course, that the solid properties are also accurately known. Computer programs are now available for such calculations.<sup>5</sup> Special recognition is due to Harvie and Weare<sup>6</sup> for their pioneering calculations of mineral solubility by these methods including the key case of CaSO<sub>4</sub> solubility in aqueous NaCl where this method gave good results, whereas older ion-association methods gave a qualitatively incorrect trend with NaCl molality. Also important are the numerous treatments extending to solid solubility by Filippov and associates.<sup>7</sup>

In past years, ion-interaction and ion-association methods have been regarded as competitive. The first edition of this book gives a good account of the status and viewpoints of

1979. Clegg and Whitfield discuss both the history and current status of these methods in Section II of Chapter 6. While the title of Chapter 6 is "Activity Coefficients in Natural Waters," this discussion is comprehensive and not limited to "Natural Waters".

For systems with little or no ion association, specific interionic effects are still significant at substantial molality and the ion-interaction method has proven to be excellent. Even where there is unquestioned association to a moderate degree, such as to  $\text{MgSO}_4$  in seawater and similar solutions, the inclusion of a special term in the ion-interaction equations has been found to be a better method at moderate temperatures than the inclusion of a formal association reaction. For  $\text{H}_2\text{SO}_4$ , however, the explicit inclusion of the association reaction to  $\text{HSO}_4^-$  is essential. Thus, when  $\text{HSO}_4^-$  or  $\text{HCO}_3^-$  or similar species are formed by strong association reactions, one requires a combination of ion-interaction and ion-association methods to obtain accurate results. Also, the tendency toward ion association increases at high temperature where the dielectric constant of water becomes small (see Chapter 8).

For pure electrolytes at room temperature, there has been a good database since the 1955 book of Robinson and Stokes,<sup>1</sup> although significant improvements have been made as well as extensions to additional solutes. The appearance of accurate values at high temperatures to 300°C and at high pressures is the second area of major recent advance. Particularly notable are the solvent vapor pressure measurements of Liu and Lindsay<sup>8</sup> for  $\text{NaCl(aq)}$  and the isopiestic measurements of Holmes and Mesmer for several other salt solutions. Heat capacity, heat of dilution, and volumetric measurements have also been made extending to 300°C or above. This has allowed comprehensive thermodynamic treatments; many of these are listed in Chapters 3, 7, and 8.

There have been a number of interesting theoretical advances including those allowing statistical calculations for more realistic physical models; these are reported in Chapter 2. Nevertheless, it remains necessary to use semi-empirical methods to represent data to the full experimental accuracy.

As described in Chapter 1, various measures of composition can be used for electrolytes: mole fraction, molality (moles per kg of solvent), molarity (moles per liter of solution), weight fraction, etc. Most electrolytes have a range of solubility limited to about  $15 \text{ mol} \cdot \text{kg}^{-1}$  or less, and for such solutions molality has been found to be by far the most convenient measurement system. Thus, molality is used very generally in this book, but for exceptional cases of extremely wide solubility range, mole fraction is used. Indeed, for a pure ionic liquid the molality is infinite; hence, the change to mole fraction is necessary.

The words "ideal" or "ideality" are ordinarily associated with behavior that corresponds to unit activity coefficients on the mole fraction basis. The behavior given by unit activity and osmotic coefficients on the molality basis is similar, has the same limiting property at infinite dilution, but is quantitatively different at other compositions. It is very convenient in either system to use expressions for an excess Gibbs energy defined as the difference of the actual Gibbs energy from that of the ideal or another simple reference pattern. In each system, mole fraction or molality, it is most convenient and useful to use, as the reference pattern, that of unit activity coefficients in the same system. Thus, two slightly different "excess Gibbs energies" are now used. No confusion need arise provided each system is used self-consistently and with clear statements and definitions.

That the advances of the last decade are important to geochemistry and chemical oceanography is clear from the results presented in various chapters, especially in Chapters 6 and 7. The application to aerosols which comprise aqueous electrolytes is less obvious but important; at low humidity these aerosol solutions become highly concentrated. This is recognized in Chapter 6.

There are many biologically important aqueous fluids where chemical thermodynamics has been applied and has been essential to an understanding of the complex array of processes taking place. Ions are present in most of these fluids; indeed, it is the activity of a particular



ion that is related to a biological function in many cases.<sup>9-16</sup> The ionic strength is rather low, however, so that a simple approximation for activity coefficients may suffice.

Thus, the numerous reactions involving adenosine mono-, di-, and triphosphates with various ions present and with varying pH constitute a very interesting system subject to treatment by the methods of chemical thermodynamics with equilibrium quotients for various reactions.<sup>9-11</sup> Some of the early treatments were for constant ionic strength. They omitted activity coefficients and used equilibrium quotients assumed to be valid for that fixed ionic strength. Other treatments consider data for different ionic strengths but assume that an activity coefficient depends only on the ion charge and the ionic strength and is independent of the specific ions present.

As the precision of thermodynamic measurements for biologically important systems increases, it will be necessary to recognize the specific effects of other ions on the activity coefficient of a given ion. Since these effects are now accurately known for many ions, this information can be included without introducing unknown parameters. There may be other interactions in a particular case which are not known independently, but it will be a better approximation to include the known ion-interaction terms than to ignore all interionic interactions and use only the ionic strength.

There is one area with a biological connection where highly concentrated electrolytes are involved. This is the use of concentrated solutions of NaCl or other salts to control the moisture content of foods in storage and its relationship to microbiological growth. Kitic et al.<sup>17</sup> have used the ion interaction equations and reported their methods in the literature for food science.

Some biologically oriented investigations are now using the ion-interaction equations (Chapter 7 of the 1st edition, Chapter 3 of this edition) in the treatment of their data. Indeed, Baumgarten<sup>18</sup> has published in a biological journal a simple computer program for this method. It seems probable that the more precise and complete treatments described in this volume will find increasing application in biological systems in the near future.

Finally, I note that in the geological area and in engineering there is great interest in aqueous electrolytes at still higher temperatures, far above 300°C, and this range requires a different theoretical approach from that used in this book. There is the phase separation of water and an appreciable salt solubility in the steam phase. Also, the compressibility of the solvent becomes infinite at its critical point. These aspects require the use of the Helmholtz energy rather than the Gibbs energy as the basic function. While several research contributions have been made, which are related to this higher temperature range, many aspects are still to be investigated. It will be an interesting field both theoretically and in applications in the near future.

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## THE EDITOR

**Kenneth S. Pitzer** was born in Pomona, California in 1914. He received his B.S. degree from the California Institute of Technology in 1935, his Ph.D. from the University of California, Berkeley in 1937, a D.Sc. from Wesleyan University in 1962, and an LL.D. from the University of California in 1963 and from Mills College in 1969. He was a member of the faculty at Berkeley from 1937 to 1960, serving also as Dean of the College of Chemistry from 1951 to 1960. On leave from the University of California, he was Technical Director of the Maryland Research Laboratory, a World War II entity from 1943 to 1944, and was Director of Research for the U.S. Atomic Energy Commission from 1949 to 1951. In 1961, he became President and Professor of Chemistry at Rice University, serving until 1968 when he became President of Stanford University until 1970. In 1971 he returned to the University of California, Berkeley, as Professor until 1984 and thereafter as Professor Emeritus but was recalled for continued service.

His advisory committee and other part-time service included the General Advisory Committee to the AEC, 1958 to 1965 (Chairman 1960 to 1962); President's Science Advisory Committee, 1965 to 1968; Commission on Chemical Thermodynamics of the International Union of Pure and Applied Chemistry, 1953 to 1961; NASA Science and Technology Advisory Committee, 1964 to 1965; Trustee, Harvey Mudd College, 1956 to 1961, Mills College, 1958 to 1961, Pitzer College 1966 to the present, Rand Corporation, 1962 to 1972; Member of the Board of Directors, Owens Illinois, Inc., 1967 to 1986; Federal Reserve Bank of Dallas, 1965 to 1968, the American Council on Education, 1967 to 1971; and Member of the Council of the National Academy of Sciences, 1964 to 1967 and 1973 to 1976.

His research has extended through many areas of physical chemistry and into topics of importance including inorganic and organic chemistry, chemical engineering, and geochemistry. In addition to work on aqueous electrolytes reflected in this volume, his research has included quantum theory and statistical mechanics as applied to chemical problems ranging from the potential restricting rotation about single bonds, to the bonding in polyatomic carbon molecules, and to the effects of relativity on chemical bonds involving very heavy atoms. In addition to many journal articles and several book chapters, his books include *Quantum Chemistry*, 1953; *Selected Values of Physical and Chemical Properties of Hydrocarbons and Related Compounds*, with F. D. Rossini and others, 1947, 2nd edition, 1953; *Thermodynamics*, 2nd edition with L. Brewer, 1961, and a revision of the 1st edition of G. N. Lewis and M. Randall.

His honors and awards include the National Medal of Science, 1975, the Robert A. Welch Award in Chemistry, 1984, the Alumnus of the Year Award, University of California, Berkeley, 1951, and the Alumni Distinguished Service Award, California Institute of Technology, 1966. From the American Chemical Society he received the Award in Pure Chemistry, 1943, in Petroleum Chemistry, 1949, the Gilbert Newton Lewis Medal, 1965, the Priestley Medal, 1969, and the Willard Gibbs Medal, 1976. Other recognitions include many special lectureships, a Guggenheim Fellowship, 1951, and election to the National Academy of Sciences in 1949.

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## Chapter 1

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## I. BASIC THERMODYNAMIC FUNCTIONS U H V S G A AND THEIR PHYSICAL SIGNIFICANCE; DIFFERENTIAL RELATIONS

### A. THERMODYNAMIC FUNCTIONS

The thermodynamic properties of a substance or system at equilibrium may be grouped into (1) intensive properties, of which the most familiar are the temperature and pressure, and (2) extensive quantities, of which the volume and mass are most familiar. The former are independent of the size of the sample taken for measurement and are constant throughout each phase of the system. The temperature, in fact, must be the same in all phases of the system for true equilibrium to exist, though the pressure may be different in different phases, as in osmotic equilibrium. Other intensive properties are the density, refractive index, dielectric constant, percentage composition, and the various molar quantities (see Section II.B).

Extensive quantities are directly proportional to the amount of the sample taken for measurement. The various energy quantities and the entropy are also extensive quantities when they refer to a phase or system as a whole, but their values per mole are intensive quantities.

The most frequently encountered thermodynamic functions in work on solutions are

The total energy or intrinsic energy	U
The enthalpy	$H = U + PV$
The entropy	S
The Gibbs free energy	$G = H - TS$
The Helmholtz free energy	$A = U - TS$
The heat capacities at constant pressure and at constant volume	$C_P = \left( \frac{\partial H}{\partial T} \right)_P$

The isothermal compressibility

The adiabatic compressibility

The thermal expansion coefficient

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

$$\beta_T = - \left( \frac{\partial \ln V}{\partial P} \right)_T$$

$$\beta_S = - \left( \frac{\partial \ln V}{\partial P} \right)_S$$

$$\alpha = \left( \frac{\partial \ln V}{\partial T} \right)_P$$

The last three properties above are intensive.

The thermodynamic properties and others defined in terms of them are functions of the state, that is, their values depend only on the existing state of the system and not on the route by which that state has been reached.

## B. EQUATIONS OF STATE

If the nature and amounts of substances are specified, the volume, temperature, and pressure are related by an equation of the form:

$$V = f(T, P)$$

known as the equation of state. Thus only two of  $V$ ,  $T$ , and  $P$  can be varied independently.

## C. CONVENTIONAL AND ABSOLUTE VALUES OF THERMODYNAMIC PROPERTIES

The existence of a true zero pressure, that of a perfect vacuum, is obvious, and the absolute zero temperature is equally familiar. The entropy of a pure substance also has a true zero, that of its pure crystalline solid form at zero (Kelvin) temperature, according to the third law of thermodynamics. The energy quantities  $U$ ,  $H$ ,  $G$ ,  $A$ , however, do not have a natural zero, and are consequently measured relative to arbitrarily chosen standard states. Thus the total energy  $U$  of a compound is usually referred to that of its constituent elements either at absolute zero or at 25°C.

## D. PHYSICAL MEANING OF THERMODYNAMIC QUANTITIES

Temperature, pressure, and volume need no discussion. The total energy  $U$  is defined by the first law of thermodynamics

$$dU = q + w \quad (1)$$

where  $q$  is the heat absorbed and  $w$  the work done on the system in an infinitesimal change. Hence,  $\Delta U$  is measurable as the heat absorbed at constant volume, e.g., in bomb calorimetry. Solution calorimetry, on the other hand, is usually carried out at constant (atmospheric) pressure, and the heat absorbed in this case is identified as  $\Delta H$ . The entropy, and the free energies that involve it, are the least obvious of the thermodynamic functions, and textbooks of general thermodynamics should be consulted for a full explanation.<sup>1-7</sup> The Gibbs free energy  $G$  is the most important function in dealing with chemical equilibria, being so defined that it is a minimum for equilibrium at constant temperature and pressure. It may be thought of as the chemical analogue of potential energy in a mechanical system, and, in particular, as closely related to electrical energy through the equation for reversible electrical cells

$$\Delta G = -nEF \quad (2)$$

where  $n$  is the number of electrons transferred and  $E$  is the reversible potential for a cell operating at constant temperature and pressure. The change  $\Delta G$  in a process at constant temperature and pressure is equal in magnitude to the maximum reversible work which can be done by the process.

### E. THE LAWS OF THERMODYNAMICS

The first law of thermodynamics, also known as the law of conservation of energy, says that the quantity  $U$  defined by

$$dU = q + w$$

is a function of the state of a system. Here  $q$  is the heat absorbed by, and  $w$  is the work done on, the system. The second law concerns the behavior of the entropy ( $S$ ), stating that in a natural or spontaneous process taking place at a Kelvin temperature  $T$ , in which the system absorbs heat  $q$  from its surroundings,

$$dS > \frac{q}{T}$$

and that in a reversible change

$$dS = \frac{q}{T}$$

Processes in which  $dS < q/T$  cannot occur according to the second law, and are called unnatural processes.

In measurements of the heat capacity  $C_p$  of a pure substance at constant pressure, heat is added at temperature  $T$  under reversible conditions, so that

$$q = C_p dT$$

where

$$dS = \frac{C_p}{T} dT$$

and

$$\begin{aligned} S(T_2, P) &= S(T_1, P) + \int_{T_1}^{T_2} \frac{C_p}{T} dT \\ \text{or } S(T, P) &= I + \int_0^T \frac{C_p}{T} dT \end{aligned} \quad (3)$$

where  $I$  is an integration constant.

The third law of thermodynamics states that for a pure crystalline solid the integration constant  $I$  is zero, i.e., the entropy itself is zero at the absolute zero. (In some cases allowance has to be made for the existence of different states of nuclear spin, which persist at the absolute zero.) This law arises from the statistical nature of entropy, expressed by Boltzmann's famous equation



$$S = k \ln W \quad (4)$$

where  $W$  is the number of complexions (distinguishable states) of the system.

In a perfect crystal,  $W = 1$ , so  $S = 0$ .

Some authorities refer to a zeroth principle of thermodynamics, which amounts to a statement of the existence of temperature. Guggenheim<sup>3</sup> formulates this as, "If two systems are both in thermal equilibrium with a third system, then they are in thermal equilibrium with each other."

## F. DIFFERENTIAL RELATIONS BETWEEN THERMODYNAMIC FUNCTIONS

For a closed system, i.e., one which no matter enters or leaves, the first and second laws are summed up by the equations

$$\begin{aligned} dU &= TdS - PdV \\ dH &= TdS + VdP \\ dA &= -SdT - PdV \\ dG &= -SdT + VdP \end{aligned} \quad (5)$$

The last of these is the most important in solution thermodynamics, giving the very useful results

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (6)$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad (7)$$

Equation 6 with  $G = H - TS$  yields the very important Gibbs-Helmholz equation:

$$\frac{\partial}{\partial T} \left(\frac{G}{T}\right)_P = -H/T^2 \quad (8)$$

which may also be expressed as

$$\partial(G/T)/\partial(1/T) = H \quad (9)$$

Equations 5 to 9 are used in treating change of equilibrium constants with temperature and pressure.

## II. SOLUTIONS: PARTIAL MOLAR QUANTITIES; CHEMICAL POTENTIALS

### A. OPEN PHASES: THE CHEMICAL POTENTIAL

An open phase is one which matter is able to enter or leave. When a chemical substance is added to or removed from a phase (e.g., when water evaporates from a solution), the thermodynamic properties of the phase are altered. These changes are described by adding to Equation 5 terms representing the energy, enthalpy, or free energy associated with each substance added. Each such term takes the form: chemical potential of substance  $\times$  differential quantity added. Thus

$$\begin{aligned}
dU &= TdS - PdV + \sum_i \mu_i dn_i \\
dH &= TdS + VdP + \sum_i \mu_i dn_i \\
dA &= -SdT - PdV + \sum_i \mu_i dn_i \\
dG &= -SdT + VdP + \sum_i \mu_i dn_i
\end{aligned} \tag{10}$$

where  $n_i$  denotes the number of moles of species  $i$  present in the phase. The last of these equations gives the clearest physical meaning to the chemical potential, since by considering the addition of  $dn_j$  mol of species  $j$  to a phase at constant temperature and pressure we find

$$\mu_j = \left( \frac{\partial G}{\partial n_j} \right)_{T, P, n_{i \neq j}} \tag{11}$$

The subscripts as usual denote which state variables are held constant during the partial differentiation;  $i \neq j$  means that the amounts of all species other than  $j$  are held constant.

## B. PARTIAL MOLAR QUANTITIES

For a phase such as a solution, any of the extensive thermodynamic properties (e.g.,  $V$ ,  $H$ ,  $U$ ,  $S$ ,  $A$ ,  $G$ ) can be regarded as a function of the state variables  $P$ ,  $T$ , and  $n_i$ . Using  $X$  to denote an extensive property in general, we can then define the partial molar value of  $X$  for component  $j$ , denoted  $\bar{X}_j$ , relation:

$$\bar{X}_j = (\partial X / \partial n_j)_{T, P, n_{i \neq j}} \tag{12}$$

(The term partial molal is often used instead of partial molar. In this context, either molar or molal means simply per mole, and has nothing to do with the molarity or molality concentration scales.)

The chemical potential of species  $j$  in the solution is thus identical with its partial molar Gibbs free energy:

$$\mu_j \equiv \bar{G}_j \tag{13}$$

A physical interpretation of the chemical potential of a substance is therefore that it is the free energy change per mole of substance added to the phase when the amount added becomes vanishingly small; or the Gibbs free energy change when 1 mol of the substance is added to an infinite amount of the phase, the temperature and pressure being held constant in either case.

## C. ADDITIVITY OF PARTIAL MOLAR QUANTITIES

Equation 12 can be integrated at constant temperature and pressure, with respect to the quantity of each component in turn. The components can be added in infinitesimal quantities, each proportional to the final amount of that component in the phase. This process can be described by

$$dn_i = n_i dx$$

where  $dx$  is the same for all components, and  $x$  increases from 0 to 1 during the integration.