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# ACTIVITY EFFICIENTS IN ELECTROLYTE SOLUTIONS

Volume I

Wladyslaw M. Pytkowicz

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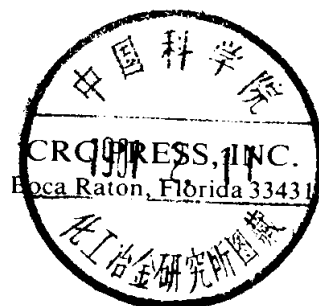
# Activity Coefficients in Electrolyte Solutions

Volume I

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## TABLE OF CONTENTS

### Volume I

Chapter 1	
Thermodynamics of Solutions .....	1
<b>R. H. Stokes</b>	
Chapter 2	
Introduction to the Statistical Mechanics of Solutions.....	29
<b>Robert M. Mazo and Chung Yuan Mou</b>	
Chapter 3	
Experimental Methods: Isopiestic .....	65
<b>Robert F. Platford</b>	
Chapter 4	
Experimental Methods: Potentiometric.....	81
<b>James N. Butler</b>	
Chapter 5	
Activity Coefficients and Hydration of Ions.....	95
<b>Brian E. Conway</b>	
Chapter 6	
Experimental Techniques: Cryoscopy and Other Methods.....	139
<b>Jacques E. Desnoyers</b>	
Chapter 7	
Theory: Ion Interaction Approach .....	157
<b>Kenneth S. Pitzer</b>	
Chapter 8	
Lattice Theories and a New Lattice Concept for Ionic Solutions .....	209
<b>Ricardo M. Pytkowicz and Kenneth S. Johnson</b>	
Index .....	265

### Volume II

Chapter 1	
Ion Association and Activity Coefficients in Multicomponent Solutions .....	1
<b>Kenneth S. Johnson and Ricardo M. Pytkowicz</b>	
Chapter 2	
Effects of Pressure and Temperature on Activity Coefficients .....	63
<b>Frank J. Millero</b>	

Chapter 3	
Activity Coefficients in Natural Waters .....	153
<b>Michael Whitfield</b>	
Chapter 4	
Activity Coefficients, Ionic Media, and Equilibria in Solutions. ....	301
<b>Ricardo M. Pytkowicz</b>	
Index .....	307

## Chapter 1

## THERMODYNAMICS OF SOLUTIONS

R. H. Stokes

## TABLE OF CONTENTS

I.	Basic Thermodynamic Functions $E$ $H$ $V$ $S$ $G$ $A$ and Their Physical Significance; Differential Relations .....	2
A.	Thermodynamic Functions .....	2
B.	Equations of State .....	3
C.	Conventional and Absolute Values of Thermodynamic Properties .....	3
D.	Physical Meaning of Thermodynamic Quantities .....	3
E.	The Laws of Thermodynamics .....	3
F.	Differential Relations Between Thermodynamic Functions .....	4
II.	Solutions: Partial Molar Quantities; Chemical Potentials .....	5
A.	Open Phases: the Chemical Potential .....	5
B.	Partial Molar Quantities .....	6
C.	Additivity of Partial Molar Quantities .....	6
III.	Chemical Potentials and Activity Coefficients; Standard States and Composi- tion Scales for Nonelectrolytes and Electrolytes .....	7
A.	Activities of Components .....	7
B.	Standard States .....	7
C.	Chemical Potentials in Electrolyte Solutions .....	8
D.	Activity, Activity Coefficients and Standard States .....	9
E.	Mean Activities and Activity Coefficients .....	10
F.	Relations Between Activity Coefficients on Different Scales .....	11
G.	The Solvent Chemical Potential, Solvent Activity and the Osmotic Coef- ficient .....	11
IV.	The Gibbs-Duhem Relation; Various Forms for Two- and Multi-Component Systems .....	12
A.	The Gibbs-Duhem Equation .....	12
B.	Relation Between Mean Activity Coefficient and Osmotic Coefficient	12
V.	Ideal Solutions; Entropy of Mixing on Various Statistics; Regular Solutions; Athermal Solutions .....	14
A.	Ideal Solutions .....	14
B.	The Entropy of Mixing .....	15
C.	Regular Solutions .....	16
VI.	Colligative Properties .....	17
A.	Freezing Point Depression .....	17
B.	Boiling-Point Elevation .....	18
C.	The Osmotic Pressure .....	19
D.	Derivation of Thermodynamic Quantities for Electrolyte Solutions from Electromotive Forces of Cells .....	20



VII.	Enthalpy and Volume Properties; Apparent Molar Quantities . . . . .	21
A.	Temperature and Pressure Dependence of Activity Coefficients . . . . .	21
B.	Pressure Dependence of Activity Coefficients . . . . .	22
C.	Partial Molar Enthalpies and Volumes . . . . .	22
VIII.	Excess Thermodynamic Properties . . . . .	24
IX.	Multi-Component Systems - Thermodynamic Relations; Salting-Out and Salt- ing-In Effects . . . . .	26
A.	Thermodynamic Relations for Multicomponent Solutions . . . . .	26
B.	Salting-Out Effects . . . . .	27
	References . . . . .	28

## I. BASIC THERMODYNAMIC FUNCTIONS $E$ $H$ $V$ $S$ $G$ $A$ 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 if the system for true equilibrium is 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 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	$C_p = \left( \frac{\partial H}{\partial T} \right)_p$
and at constant volume	$C_v = \left( \frac{\partial U}{\partial T} \right)_v$
The isothermal compressibility	$B_T = - \left( \frac{\partial \ln V}{\partial P} \right)_T$
The adiabatic compressibility	$B_s = - \left( \frac{\partial \ln V}{\partial P} \right)_s$
The thermal expansion coefficient	$\alpha = \left( \frac{\partial \ln V}{\partial T} \right)_p$

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  $V$ ,  $T$ ,  $P$  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  $25^\circ\text{C}$ .

### 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>6,7</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

$$q = C_p dT$$

whence

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

and

$$S(T_2, P) = S(T_1, P) + \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

$$\text{or, } S(T, P) = I + \int_0^T \frac{C_p}{T} dT \quad (3)$$

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

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

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

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

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

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

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

which may also be expressed as

$$\partial (G/T) / \partial (1/T) = H \tag{9}$$

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  $\bar{X}_j$ , by the relation:

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

(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:

$$\mu_j \equiv \bar{G}_j \quad (13)$$

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 one mole 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.

$$dX = \sum_i \bar{X}_i dn_i = \sum_i (n_i \bar{X}_i) dx$$

Now the  $n_i$  are constants during the integration (since they describe the final state, and the relative amounts of the components remain unchanged as the additions proceed); hence, the  $\bar{X}_i$  are also constant since they depend on the temperature, pressure, and composition. The integration therefore gives

$$\begin{aligned} X_{\text{final}} - X_{\text{initial}} &= \left( \int_0^1 dx \right) \cdot \sum_i n_i \bar{X}_i \\ &= \sum_i n_i \bar{X}_i \end{aligned}$$

Furthermore,  $X_{\text{initial}}$  refers to the start of the process, when the amount of the phase is zero, so clearly  $X_{\text{initial}}$  is zero. The result is

$$X = \sum_i n_i \bar{X}_i \quad (14)$$

showing that the value of the extensive property  $X$  for a phase is composed additively of the partial molar values of its components, each weighted by the number of moles present. In particular,

$$G = \sum_i n_i \mu_i \quad (15)$$

### III. CHEMICAL POTENTIALS AND ACTIVITY COEFFICIENTS; STANDARD STATES AND COMPOSITION SCALES FOR NONELECTROLYTES AND ELECTROLYTES

#### A. Activities of Components

The activity  $a_i$  of a component in a solution is a convenient alternative means of describing its chemical potential:

$$\mu_i = \mu_i^\theta + RT \ln (a_i/a_i^\theta) \quad (16)$$

Here the superscript  $\theta$  denotes an arbitrarily chosen standard state for the component  $i$ .  $\mu_i^\theta$  is then called the standard chemical potential of  $i$ . It is conventional to choose the corresponding standard activity  $a_i^\theta$  as unity, giving the simpler relation:

$$\mu_i = \mu_i^\theta + RT \ln a_i \quad (17)$$

The reason for the logarithmic form requires some comment. In the simplest case, that of a single component ideal gas phase containing  $n_i$  mol, Equations 14 and 7 give

$$G = n_i \mu_i$$

$$(\partial G / \partial P)_{T, n_i} = V = n_i RT / P_i$$

hence

$$dG = n_i RT d \ln P_i$$

and

$$\mu_i = \text{const} + RT \ln P_i \quad (18)$$

This means that the chemical potential approaches minus infinity as the pressure goes to zero, and the chemical potential is therefore an awkward quantity to discuss or tabulate for low pressures. Similar problems occur with solutions; in this case the logarithmic term involves the concentration instead of the pressure. However, when activities, with appropriately chosen standard states are considered, no infinite values occur; they are always positive, tending to zero at infinite dilution.

To avoid problems concerned with units, Equation 18 may be rewritten as

$$\mu_i = \mu_i^\theta + RT \ln (P_i/P^\theta) \quad (19)$$

where  $\mu_i^\theta$  is the chemical potential of the gas at the standard pressure  $P^\theta$ .

#### B. Standard States

It must be emphasized that the choice of standard state is arbitrary; indeed, it is sometimes convenient to use different standard states for the same substance in the same solution. There is nothing arbitrary about the chemical potential itself: for a

component of a given solution at a given temperature and pressure, its value is uniquely defined. It follows from Equation 17 that if we change the standard state, we also change the value of the activity.

In some cases it is convenient to use an actual physically realizable state as the standard state. In the thermodynamics of mixed liquid nonelectrolytes, the usual choice is the pure liquid component at the same temperature and pressure as the solution. With this choice, the activity of any component must lie between zero and 1 at equilibrium. This standard state is also almost invariably adopted for the solvent component of electrolyte solutions. Thus the activity of pure water is defined as unity, and the water activity in any solution is

$$a_w = P_w^* / P_w^\circ \approx P_w / P_w^\circ \quad (20)$$

The starred pressure symbol denotes the fugacity, an idealized partial pressure, which can be evaluated from the actual partial pressure  $P$  by the use of data on the nonideal gas behavior of the vapor.<sup>3</sup> The superscript zero refers to pure liquid solvent at the same temperature and hydrostatic pressure as the solution.

### C. Chemical Potentials in Electrolyte Solutions

For substances that are solids at the temperature of interest, the use of the pure liquid as the standard state is inconvenient since it represents a metastable or unstable condition. Nevertheless, if the enthalpy and free energy of fusion are known, it is possible to retain this standard state for the solution, as is done for example in Hildebrand's<sup>8</sup> treatment of the solubility of solid nonelectrolytes.

For electrolytes, however, a standard state is required which recognizes the ionic character of the solution. This raises a problem peculiar to electrolyte solutions, which must now be discussed. We may define the chemical potential of the ion of species  $i$  by

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{n_j, n_s, T, P} \quad (21)$$

where  $j$  refers to all ionic species other than  $i$  and  $s$  to the solvent. However, the physical operation represented by Equation 21 cannot be carried out: there is no way in which we can add to the solution ions of species  $i$  only, because only an electrolyte with equal amounts of positive charge on its cations and negative charge on its anions can be handled. For the electrolyte (formula B) as a whole there is no difficulty; the definition

$$\mu_B = \left( \frac{\partial G}{\partial n_B} \right)_{n_s, T, P} \quad (22)$$

represents a physically realizable process.

Equation 21 is actually incomplete in that it does not recognize that in adding charged ions of one species only, we will build up a charge in the solution. The free energy required to build up this charge from zero is in principle calculable from electrostatic theory, but will depend on the shape of the body of solution involved. Guggenheim<sup>3</sup> proposed the use of the "electrochemical potential" for individual ionic species as a way of avoiding this difficulty. The internal electrical potential  $\psi_{int}$  of any phase, charged or not, may be defined as the work done in bringing a unit electrical charge from infinity to the interior of the phase. Then the free energy of the phase is the electrochemical potential  $\mu_i'$ .

$$\mu_i^e = \mu_i + z_i F \psi_{\text{int}}$$

where  $F$  is the faraday and  $z_i$  is the (signed) charge number of the ion. This concept finds its main application in the study of electrodes and other charged interfaces. For the present problem, it suffices to note that provided the internal electrical potential is the same, differences in electrochemical potential are equal to differences in chemical potential defined by Equation 21. This overcomes the conceptual difficulty, but not the physical obstacle that we cannot actually add one kind of ion only. The consequence of this fact of life is that there is no rigorous method of measuring the chemical potential of a single ionic species; all experimental methods lead, if fully analyzed, to values for the chemical potential of an electrically neutral assemblage of ions, or else to differences between the chemical potentials of electrically equivalent amounts of ions of the same sign. Theoretical treatments, on the other hand, frequently lead to calculated values for the chemical potentials of single ionic species. In order to compare these with experiment, they must be combined to give the chemical potential of an electrically neutral assemblage.

#### D. Activity, Activity Coefficients, and Standard States

Accepting the conventional use of chemical potentials of individual ionic species, we may write

$$\mu_i = \mu_i^\theta + RT \ln a_i \quad (23)$$

This places no restriction on the choice of standard state. Several different choices are in common use for electrolytes.

First, when the composition of the solution is described in terms of the molality scale, the standard state is the "hypothetical one-molal solution" of the ion. It is so chosen that as the molality approaches zero, the ratio  $a_i/m_i$  tends to unity. This ratio is defined as the molal activity coefficient  $\gamma_i$ :

$$\gamma_i = a_i/m_i; \gamma_i \rightarrow 1 \text{ as } m \rightarrow 0 \quad (24)$$

and

$$\mu_i = \mu_i^\theta(m) + RT \ln (m_i \gamma_i) \quad (25)$$

The additional subscript ( $m$ ) has been added to  $\mu_i^\theta$  to emphasize that the standard state in question applies to the molality scale.

There is an awkward problem of dimensions concealed in Equations 24 and 25. The activity coefficient  $\gamma$  is a dimensionless quantity, tending to 1 at infinite dilution. The molality  $m_i$  on the other hand has dimensions  $\text{mol kg}^{-1}$ . Strictly speaking, then Equations 24 and 25 should be written

$$\begin{aligned} \gamma_i &= a_i m^\theta / m_i \\ \mu_i &= \mu_i^\theta(m) + RT \ln (m_i \gamma_i / m^\theta) \end{aligned}$$

where  $m^\theta$  is the unit molality, i.e.,  $1 \text{ mol kg}^{-1}$ . The inconvenience of inserting the  $m^\theta$  factor in all expressions deriving from Equation 25, including equilibrium constants, is, however, sufficient to deter all but the most rigorously minded from doing so, and we shall use the handier form Equation 25.



The standard state has the same composition as a real 1 molal solution, but its hypothetical character involves the imagined absence of all interactions between ions due to their charge, size, and other relevant properties. In this respect, the analogy between the ideal gas standard state of 1 standard atmosphere pressure and an actual gas at the same pressure is useful. In particular, the standard state must be such that Equations 24 and 25 hold at all temperatures and pressures. It follows from Equations 7 and 9 that the partial molar enthalpy and partial molar volume of the ion have the same values in the standard state as at infinite dilution. Also,  $\gamma_i$  must be unity in the standard state. We see that the standard state is an imaginary one in which the molality of the ion is 1 mol kg<sup>-1</sup>, but all the partial molar functions not involving the entropy have the same value as in the actual infinitely dilute solution.

Second, for the molarity scale ( $c_i$  = mol of ion  $i$ /l) a different standard state and activity coefficient are used; the hypothetical 1 molar solution and the molar activity coefficient ( $y_i$ ):

$$\mu_i = \mu_i^\theta(c) + RT \ln (c_i y_i) \quad (26)$$

Again the standard state is chosen so that  $y_i \rightarrow 1$  as  $c \rightarrow 0$ .

Some care is needed in the use of thermodynamic relations derived from Equation 26 by differentiation with respect to temperature or pressure, e.g., from Equation 6 or 7. It must be remembered that, unlike the molality,  $c$  varies with temperature and pressure.

Third, the mole fraction scale finds little application in the practical thermodynamics of electrolytes, but often appears in theoretical treatments. The standard state is now one that has unit mole fraction of the solute species concerned, but in other respects has the properties of the solute in infinitely dilute solution. This is an even more theological concept than the hypothetical molal and molar solutions.

$$\mu_i = \mu_i^\theta(x) + RT \ln x_i f_i \quad (27)$$

where  $f_i$  is the rational or mole-fraction scale activity coefficient.

### E. Mean Activities and Activity Coefficients

Thermodynamic measurements yield chemical properties not of individual ionic species but of electrolytes as a whole. Taking the general formula to be  $M_{\nu_1} X_{\nu_2}$  where the cation  $M$  has charge  $= z_1 e$  and the anion  $X$  has charge  $z_2 e$ , we have

$$\nu_1 z_1 = -\nu_2 z_2 \quad (28)$$

for electrical neutrality. The chemical potential of the electrolyte is

$$\begin{aligned} \mu(M_{\nu_1} X_{\nu_2}) &= \nu_1 \mu(M^{z_1 e}) + \nu_2 \mu(X^{z_2 e}) \\ &= \mu^\theta(M_{\nu_1} X_{\nu_2}) + \nu_1 RT \ln (m_1 \gamma_1) + \nu_2 RT \ln (m_2 \gamma_2) \end{aligned} \quad (29)$$

Here the  $\mu^\theta$  term is a combination of those for the separate ions.

$$\mu^\theta(M_{\nu_1} X_{\nu_2}) = \nu_1 \mu^\theta(M^{z_1 e}) + \nu_2 \mu^\theta(X^{z_2 e})$$

More briefly, putting B for the formula of the electrolyte and denoting the cation by 1 and the anion by 2:

$$\mu_B = \mu_B^\theta + RT \ln (m_1^{\nu_1} m_2^{\nu_2}) + RT \ln (\gamma_1^{\nu_1} \gamma_2^{\nu_2}) \quad (30)$$