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ACTIVITY COEFFICIENTS IN ELECTROLYTE SOLUTIONS

Volume II

Ricardo M. Pytkowicz

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Activity Coefficients in Electrolyte Solutions

Volume II

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TABLE OF CONTENTS

Volume I

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

Volume II

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

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

Chapter 1

ION ASSOCIATION AND ACTIVITY COEFFICIENTS IN
MULTICOMPONENT SOLUTIONS

Kenneth S. Johnson and Ricardo M. Pytkowicz

TABLE OF CONTENTS

I.	Introduction	2
II.	Development of Ion Pair Concept	3
A.	Theory of Ion Association	3
B.	Calculation of Free Activity Coefficients	4
C.	Measurement of Association Constants	5
1.	Conductivity	5
2.	Solubility	7
3.	Potentiometry	8
D.	Calculation of Activity Coefficients in Multicomponent Solutions ...	12
1.	NaCl-Na ₂ SO ₄ Solutions	12
2.	Garrels and Thompson Model	14
3.	Model of Pytkowicz and Hawley	17
III.	An Improved Ion Association Model	19
A.	Association of HCl	19
1.	Theory	20
2.	Results and Discussion	26
B.	Association of Alkali and Alkaline Earth Chlorides	32
1.	Theory	32
2.	Results and Discussion	33
C.	Association of Na ⁺ and K ⁺ with SO ₄ ²⁻	37
D.	Association of Mg ²⁺ with SO ₄ ²⁻	38
IV.	Properties of Multicomponent Solutions	40
A.	Activity Coefficients of Solutes in Multicomponent Solutions	40
1.	Theory	40
2.	Solutions with Two Solutes	43
3.	Speciation and Activity Coefficients in Seawater	46
B.	Activity Coefficient of the Solvent	48
C.	Conductance of Solutions	51
V.	Thermodynamic Association Constants, Comparison with Theory	53
A.	Thermodynamic Association Constants	53
B.	Fuoss Theory of Ion Association	53
C.	Activity Coefficients of Ion Pairs	57
VI.	Summary	58
	Acknowledgments	59
	References	59

I. INTRODUCTION

The purposes of this chapter are to review earlier works on ion pairs with emphasis on the effect of ion pairs upon activity coefficients, and to discuss in detail an ion association model we have recently developed.¹ This model is the first one to take into full account the association of chloride ions with alkali and alkaline earth metal ions, and it has proven useful in calculating activity coefficients in electrolyte mixtures. We will further expand the model in this chapter to include ion pairs of sulphate ions with the alkali and alkaline earth metal ions.

We should define what we mean by ion pairs at this point. We shall use the term ion pairs to describe entities formed in solution when cations and anions coalesce temporarily as the result of their mutual electrostatic attraction. The ions in such pairs may retain all, or only part of their water of hydration.

Our definition in theory excludes true complexes that result from covalent bonding, and pertains, therefore, primarily to what are known as strong electrolytes. In practice, however, ion pairs are defined operationally when we measure association constants. This means that we include all associated entities between pairs of ions, whether they are bonded covalently or electrostatically, in the measured concentration of a given ion pair (when the technique used does not distinguish between electrostatic and covalent bonding).²

Ion pairs are flickering entities in that two given ions may be free at one moment, may be associated for a brief period, and then become free again. Still, at any instant a given fraction of the ions in a solution are paired and the time-averaged concentration of pairs will remain constant as long as the temperature, pressure, and stoichiometric composition of the solution are invariant. One may, therefore, use the methods of equilibrium thermodynamics to study ion association.³

The existence of ion pairs in solutions of strong electrolytes has been verified directly, for example, by means of Raman spectroscopy⁴ and sound attenuation,⁵ and indirectly as a result of their effect upon activity coefficients,⁶ the electrical conductance,⁷ theoretical calculations,⁸ and the solubility of minerals in electrolyte solutions.⁹

The relationship between ion pairs and activity coefficients is easy to establish and will be derived formally later on. The activity of an electrolyte $C_e A_e$ that forms ion pairs can be expressed in two equivalent ways

$$a_{CA} = (\gamma_{C,T} m_{C,T})^c (\gamma_{A,T} m_{A,T})^a = (\gamma_{C,F} m_{C,F})^c (\gamma_{A,F} m_{A,F})^a \quad (1)$$

where γ is the molal activity coefficient and m is the molality, although other concentration units could have been used as well.¹⁰ The subscripts F and T refer to the free concentration and to the total or stoichiometric concentration of each species, respectively. The free concentration is defined to be the total concentration of a species less the number of moles of that species tied up in ion pairs. These concepts are illustrated below.

Consider a solution of a strong 1-1 electrolyte, such as NaCl or KCl, which is present at a total concentration of 1.0 m , and which has a total mean activity coefficient of 0.60. The activity of the electrolyte is

$$a = (0.6 \times 1.0)^2 = 0.36 \quad (2)$$

If the concentration of ion pairs is 0.10 m , then the mean free activity coefficient of the electrolyte is

$$\gamma_{\pm F} = \left(\frac{a}{(m_F)^2} \right)^{0.5} = \left(\frac{0.36}{0.9^2} \right)^{0.5} = 0.67 \quad (3)$$

We see, therefore, that ion pairs reduce the total activity coefficient of an electrolyte relative to the free value. Anomalously low activity coefficients in single electrolyte solutions have been frequently interpreted as indicating the formation of ion pairs.¹¹ The application of ion association models to multicomponent solutions — especially concentrated ones — has been more restricted than in the case of simpler solutions, because of difficulties in the determination of free activity coefficients and of degrees of association, although work in this area is accelerating at present.^{12,13}

We will first review the past work done with ion association models before proceeding to our present results discussed in the final three sections of this chapter.

II. DEVELOPMENT OF THE ION PAIR CONCEPT

A. Theory of Ion Association

The concept of ion pair formation was introduced by Bjerrum in 1926.¹⁴ He proposed that the coulombic attraction between ions of opposite charges could temporarily overcome the thermal energy that tends to separate ions after they have been hydrated in aqueous solutions.

A model was developed by Bjerrum to predict the degree of ion association based upon coulombic interactions alone.¹⁴ He used the Boltzmann distribution function to calculate the probability of finding an anion in a shell of volume $4\pi r^2 dr$ at a distance r from a cation. This probability function is

$$P_r = (4\pi n^\circ) r^2 \exp(z_- z_+ e^2 / \epsilon r kT) dr \quad (4)$$

where n° is the bulk concentration of anions, ϵ is the dielectric constant, and the other symbols have their usual meanings.

The probability function goes through a minimum with increasing distance from the cation and then increases with increasing r . The concentration of ion pairs may be found by integrating P_r with respect to r . The integration is extended between the limits $a_{max} = z_- z_+ e^2 / 2\epsilon kT$ and a_0 , which is the distance of closest approach of the cation and anion. The upper limit a_{max} corresponds to the minimum in the probability curve. Bjerrum, thus, defines all ion pairs to be those pairs of ions whose interaction energy is greater than two times the thermal energy (kT). a_0 is an adjustable parameter whose value is often taken to be the distance of closest approach calculated from the Debye-Hückel theory or the sum of the crystal radii of the ions. In reality, cosphere overlap must be taken into consideration.

The integration leads to an association constant at infinite dilution of the form

$$K = \frac{4\pi N_0}{1000} \left(\frac{z_- z_+ e^2}{\epsilon kT} \right) Q(b) \quad (5)$$

where $Q(b)$ is a complex integral whose values have been tabulated in a number of places.^{15,16} N_0 is Avogadro's number.

The association constants calculated from the above expression show a fair agreement with experimental values, particularly in nonaqueous solvents with low dielectric constants.¹⁷ Despite this, Bjerrum's theory has been criticized on a number of grounds, the most serious of which is the definition of a_{max} .¹⁶ The arbitrary choice of $a_{max} = z_- z_+ e^2 / 2\epsilon kT$ means that some ions will be counted as ion pairs, even though they are not in contact. Petrucci discusses these and other shortcomings of Bjerrum's theory in greater detail than is possible here.¹⁸

Fuoss proposed in 1958 a new model, which required that ions be in direct contact before they were to be counted as ion pairs, in order to overcome the ambiguity in

Bjerrum's definition of ion pairs.¹⁹ As in the Bjerrum theory, the distance at which ions come into contact is an adjustable parameter. This model will be discussed in detail in the final section of this paper, where we will compare the values predicted by it with those derived from our new model.

The concept of ion association may be used in conjunction with Equation 1 to calculate stoichiometric (total) activity coefficients and activities in multicomponent solutions.¹² Two types of information are required in order to do this; the free activity coefficient and the free concentration of each ion, as well as the stoichiometric concentration of all ions. We shall first consider the means that have been used in earlier works to obtain the free activity coefficients of electrolytes, and the techniques used to determine association constants.

B. Calculation of Free Activity Coefficients

There have been two approaches frequently used to calculate the free activity coefficients of ions in aqueous solutions. The first involves the use of some equation such as the Debye-Hückel one.¹¹ The Debye-Hückel theory, however, is only suitable at most up to ~ 0.003 M, as was shown by Frank and Thompson.²⁰ We shall be interested in solutions much more concentrated than this. As an example, the ionic strength of seawater, of concern to us, is about 0.7.

In an effort to increase the range of the Debye-Hückel limiting law, an empirical extended form was proposed by Davies¹¹

$$\log \gamma_{\pm F} = -0.5115 Z_- Z_+ \left(\frac{I^{0.5}}{1 + I^{0.5}} - 0.3 I \right) \quad (6)$$

where $\gamma_{\pm F}$ is the molar activity coefficient and I is the ionic strength. This equation was found to fit to within 10% of the measured activity coefficients of a number of salts — such as the alkali chlorides — at ionic strengths up to 0.10.¹¹ Most of these salts were thought not to associate and, therefore, the Davies equation has been used in many studies to calculate free activity coefficients.²¹ The results of our model, which will be discussed in Sections III and IV, show that the alkali chlorides do associate, and that the interpretation of the Davies equation in terms of free activity coefficients is in serious error. We do not, therefore, recommend its use.

There are no other rigorous theoretical models available by which free activity coefficients can be calculated. All current models contain an adjustable parameter of one type or another.

An alternative approach that has been used extensively in studies of seawater, involves the assumption that a given electrolyte does not associate.^{6,12} As an example, it has been assumed that the alkali and alkaline earth ions do not associate with chloride ions. The activity coefficients of these salts, which were obtained by dividing the activity measured in pure solutions of the salt by the total concentration of the salt, are then assumed to be free activity coefficients and serve as standards for the determination of the extent of association in other salts. There is a serious difficulty with this approach, because we have now found that chlorides of alkalis and alkaline earth ions do form ion pairs.

The relation between free activity coefficients and the composition of a solution must also be understood before they can be applied. One of the first suggestions for the dependence of free activity coefficients on solution composition was the ionic strength principle of Lewis and Randall.²² This principle states that the activity coefficient of an ion depends only upon the total ionic strength of a solution. The total ionic strength is defined as

$$I_T = \left[\sum_i |z_i|^2 m_i \right] \frac{1}{2} \quad (7)$$

where the summation is over the total concentrations of all ions in solution. The principle as stated above is not completely correct except in dilute solutions.⁶ We shall examine a modified form of it in conjunction with the work of Pytkowicz, Kester, and Hawley^{6,13} in this section, and in conjunction with our new model.¹

The modified form states that free activity coefficients depend only upon the effective ionic strength, which is defined as

$$I_e = \left[\sum_i |z_i|^2 m_{i,F} + \sum_p |z_p|^2 m_{p,F} \right] \frac{1}{2} \quad (8)$$

The first summation extends over the free concentration of the ions in solution and the second summation extends over the concentration of all ion pairs in the system. z_p is the net charge on the ion pair. This equation accounts for the change in the coulombic interactions in a solution, which occurs when ion pairs form.

We have recently used a third alternative to obtain free activity coefficients of electrolytes.¹ In this method the free activity coefficients are simply obtained from Equation 1 in pure solutions of the electrolytes where the total activity coefficients are known. This method requires that we know the ratio of free to total concentrations of the electrolytes to calculate the free activity coefficients from Equation 1. We shall examine this technique in more detail in Section IV.

C. Measurement of Association Constants

There are a number of methods available for the measurement of ion association constants. Each technique has its own peculiarities and limitations. Furthermore, each method may be suited to the measurement of only a limited number of ion pairs.² For example, not all ion pairs have a distinct frequency at which they absorb electromagnetic radiation. An additional complication is that two different methods may not give the same results when used to measure the concentration of the same ion pairs, if both methods are not equally sensitive to all forms of ion pairs of a given electrolyte.²

We will review three methods for measuring ion association that we believe have a general application. These methods are based upon conductivity, solubility, and potentiometric measurements. For a more general discussion of the measurements of ion association one should consult the references by Davies and by Nancollas.^{11,23} In Section III of this chapter, we will review a potentiometric method that we have recently introduced, which greatly simplifies the measurement of ion association constants and eliminates many assumptions used in the techniques discussed below.

1. Conductivity

Conductivity measurements are one of the methods used most frequently to obtain association constants,²⁴ but are limited to rather low concentrations. The determination of the association constant is based upon the measurement of the equivalent conductance of a solution Λ , which is defined to be

$$\Lambda = \frac{\kappa 1000}{M_{T,eq}} \quad (9)$$

κ is the conductivity of the solution and $M_{T,eq}$ is the total molar equivalent concentration. The factor 1000 appears because κ is defined in terms of cm^3 .

In solutions where the ion pairs bear zero net charge, it is assumed that only the free ions contribute to the equivalent conductivity.¹⁸ If this is true, the degree of ioni-

zation in solutions where the ion pairs have zero charge may be obtained from the ratio of the equivalent conductance measured experimentally to the equivalent conductance of the free ions

$$\alpha = \frac{M_F}{M_T} = \frac{\Lambda}{\Lambda^*} \quad (10)$$

where Λ^* is the equivalent conductivity defined in terms of the free ions. In order to apply this method the equivalent conductivity of the free ions must be known and this is where the difficulties of the method arise.

Theoretical expressions are generally used to evaluate Λ^* . Thus the accuracy with which the degree of ionization of a solution may be calculated depends on the accuracy of the theoretical expression used for the conductivity of solutions.

The theory that is commonly used to evaluate the equivalent conductivity of free ions is the one developed by Fuoss and Onsager.²⁵ They obtained an equation of the form

$$\Lambda^* = \Lambda^\circ - S(M_F)^{0.5} + E M_F \log M_F + J M_F \quad (11)$$

to predict the equivalent conductance of free ions in solution. The derivation of this equation is based upon a model that uses an ion atmosphere similar to that of the Debye-Hückel theory.²⁵ In this equation, Λ° is the equivalent conductivity at infinite dilution and S , E , and J are all parameters developed in the theory. The parameters S and E can be calculated from first principles and a knowledge of Λ° ; however, J is also a function of the distance of closest approach between the ions a_o .

The degree of ionization is related to the thermodynamic association constant K by the equation¹⁸

$$\alpha = 1 - K \alpha^2 M_T \frac{y_{C,F} y_{A,F}}{y_{CA}^\circ} \quad (12)$$

where y_{CA}° is the molar activity coefficient of the ion pair. $y_{C,F}$ and $y_{A,F}$ are the free molar activity coefficients of the ions. The activity coefficient of the ion pair is usually set equal to one, since we are considering only ion pairs with zero net charge. We will see later that an activity coefficient of unity is not necessarily true — even in dilute solutions — due to the dipolar nature of the pairs. The free activity coefficients of the ions are usually obtained from an equation such as Equation 6, which is related to the Debye-Hückel theory.

Equation 10 may now be written for electrolyte CA in the form

$$\begin{aligned} \Lambda_{CA} = \alpha \Lambda_{CA}^* &= \Lambda_{CA}^\circ - S(\alpha M_T)^{0.5} + E \alpha M_T \log (\alpha M_T) + J \alpha M_T \\ &\quad - K_{CA} \alpha^2 M_T \Lambda_{CA}^* y_{C,F} y_{A,F} \end{aligned} \quad (13)$$

where all terms with M_T raised to a power greater than 1.0 have been dropped. We see from this equation that the total equivalent conductivity of a solution, in theory, depends upon three unknown constants, (1) the equivalent conductivity at infinite dilution, (2) the distance of closest approach, and (3) the thermodynamic association constant of the ion pair.¹⁸ These three values may be obtained by using least squares fitting techniques to select values for these constants, which minimize the difference between the measured conductivity of a solution and the conductivity calculated from Equation 13. Petrucci discusses one method by which this may be done.¹⁸

The major difficulties with this method are that the Fuoss-Onsager equation is valid

only up to a concentration of 0.01 *M* for univalent electrolytes,²⁵ and that it cannot be applied to asymmetric electrolytes without making assumptions about the conductivity of ion pairs.²⁶ At concentrations as low as 0.01 *M*, the degree of ion association is not detectable for most ion pairs of univalent electrolytes. For electrolytes such as MgSO_4 , in which the ions bear a charge greater than one, conductivity measurements give accurate values for the thermodynamic association constants. The theory for conductivity is still under development, however, and the maximum concentration limit of the theory is gradually being extended. Even so, conductivity measurements are most suited for the determination of thermodynamic association constants and cannot be used to obtain the degree of ionization at high ionic strengths — except by indirect methods that require additional assumptions about activity coefficients, especially those of ion pairs.¹²

2. Solubility

The measurement of the solubility of minerals has been used by a number of workers to obtain ion association constants.^{9,21,27,28} In general, one measures the solubility of some relatively insoluble mineral in various solutions. The thermodynamic solubility product of a mineral such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is defined to be

$$K_{SP} = M_{\text{Ca},F} M_{\text{SO}_4,F} \gamma_{\text{Ca},F} \gamma_{\text{SO}_4,F} (a_{\text{H}_2\text{O}})^2 \quad (14)$$

The product of the free concentrations of the ions in the mineral will be a constant at a given temperature and pressure (when the mineral is at equilibrium in the various solutions), if the free activity coefficients are the same in all solutions. This will happen when the effective ionic strength does not vary.⁶ This product is termed the stoichiometric solubility product. Changes in the product of the total concentrations of calcium and sulphate, in different solutions, are assumed to be due to changes in the degree of ion association. The association constants of the various ion pairs are then obtained from an analysis of the changes in solubility. There are many different ways in which this technique may be applied.^{18,21,27} We shall consider only one to provide an example.

Elgquist and Wedborg examined the formation of ion pairs among the major ionic constituents of seawater from the solubility of gypsum in various solutions, all at a total ionic strength of 0.700.²⁸ We shall only consider the first portion of their work, in which they measured the solubility in 15 solutions containing Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , and ClO_4^- . The total concentration of each of these ions was known in the solutions, after the gypsum reached equilibrium.

Elgquist and Wedborg assumed that the free activity coefficients of the ions were a function only of the total ionic strength of the solution instead of the effective ionic strength, which takes ion pairs into consideration.⁶ Since all of their solutions were at the same total ionic strength, the free activity coefficients were assumed to be the same in each solution. The stoichiometric association constant of any ion pair CA^{n+} is defined to be

$$K_{\text{CA}}^* = \frac{M_{\text{CA}^{n+}}}{M_{\text{C},F} M_{\text{A},F}} \quad (15)$$

In Equation 15, $M_{\text{CA}^{n+}}$ is the concentration of the ion pair. If the free activity coefficients are the same in all solutions the stoichiometric association constant of each ion pair is also the same in each solution (Section III. A. 1.).⁶ Elgquist and Wedborg also

assumed that the only ion pairs that would form were CaSO_4° , MgSO_4° , NaSO_4^- , MgCl^+ , and CaCl^+ .

The distribution of ionic species in the solution may be obtained from a system of mass balance equations, an equation for the stoichiometric association constant of each type of ion pair, and the stoichiometric solubility product of gypsum. As an example, the mass balance equation for SO_4^{2-} is

$$M_{\text{SO}_4, T} = M_{\text{SO}_4, F} + M_{\text{NaSO}_4^-} + M_{\text{MgSO}_4^\circ} + M_{\text{CaSO}_4^\circ} \quad (16)$$

The stoichiometric association constant of CaSO_4° is

$$K_{\text{CaSO}_4}^* = \frac{M_{\text{CaSO}_4^\circ}}{M_{\text{Ca}, F} M_{\text{SO}_4, F}} \quad (17)$$

The stoichiometric solubility product is

$$K_{SP}^* = M_{\text{Ca}, F} M_{\text{SO}_4, F} \quad (18)$$

The complete system of equations is developed by Elgquist and Wedborg.²⁸ These equations can be used to calculate the total concentration of Ca^{2+} that would be present in each solution in equilibrium with gypsum, if all of the stoichiometric association constants and the stoichiometric solubility product of gypsum are known. Elgquist and Wedborg obtained the most probable values of all of the constants by finding the set that gave the minimum error in the prediction of the total concentration of Ca^{2+} present at equilibrium in each of the fifteen solutions they examined. The error in predicting $M_{\text{Ca}, T}$ is defined to be

$$E = \sum_i (M_{\text{Ca}, T}^{\text{obs}} - M_{\text{Ca}, T}^{\text{calc}})_i^2 \quad (19)$$

where the superscripts *obs* and *calc* indicate the total concentration of Ca^{2+} observed in the solution and that calculated to be present in the solution, respectively. The summation is extended over all 15 solutions in which measurements were made.

This method for determining stoichiometric association constants is simple and requires no complicated equipment except a computer for performing the calculations. However, the assumptions used in the example that we have considered tend to oversimplify the problem. We shall see later in this chapter that free activity coefficients are not constant at a given total ionic strength, since the effect of ion pairs upon the ionic strength must be taken into consideration. As a result, the stoichiometric association constants may not be the same in all of their solutions. This can only be determined by calculating the effective ionic strength in each solution after the association constants have been determined. Furthermore, in a study such as this, one should consider the formation of as many ion pairs as possible. Cl^- ion pairs with Na^+ and K^+ should play an important role, as should ion pairs with ClO_4^- , in the solutions used by Elgquist and Wedborg.¹

3. Potentiometry

Some of the most useful techniques for the determination of stoichiometric association constants are those based upon potentiometry. There are a number of different methods by which potentiometry can be used to measure ion association

constants.^{6,13,29,30} We will review only the method used by Pytkowicz and Kester to determine the association constant of Na^+ with SO_4^{2-} to illustrate potentiometric procedures.⁶

Equation 1 is common to any method based upon potentiometry that is used to determine ion association constants. This equation will be derived formally now, before we begin to examine its application. The derivation we present is based upon that given in Robinson and Stokes.¹⁰

The total free energy of a solution, per kilogram of water, is defined to be

$$G = 55.51 \mu_{H_2O} + \sum_i m_i \mu_i \quad (20)$$

where μ is the chemical potential.³ The summation extends over all the solutes in the solution, and m is the concentration of each component. This expression holds true for whatever form is attributed to the solutes.³ For example, in a solution of NaCl we could consider the solute to be NaCl or Na^+ and Cl^- ions. In a pure solution of a 1-1 electrolyte CA the total free energy may be expressed by

$$G = 55.51 \mu_{H_2O} + m_{C,T} \mu_{C,T} + m_{A,T} \mu_{A,T} \quad (21)$$

where the subscript T again refers to the total concentration of each ion. This equation is correct whether or not there is association in the solution, since the total free energy is independent of how we represent the solution. If there are ion pairs in the solution we may also write the free energy as

$$G = 55.51 \mu_{H_2O} + m_{C,F} \mu_{C,F} + m_{A,F} \mu_{A,F} + m_{CA^\circ} \mu_{CA^\circ} \quad (22)$$

where the subscript F refers only to the free ions and the subscript CA° refers to the ion pairs. Equating Equations 21 and 22 and cancelling the term representing the solvent we obtain

$$m_{C,T} \mu_{C,T} + m_{A,T} \mu_{A,T} = m_{C,F} \mu_{C,F} + m_{A,F} \mu_{A,F} + m_{CA^\circ} \mu_{CA^\circ} \quad (23)$$

The ion pairs are in equilibrium with the free ions and we can equate the chemical potential of the two free ions,³¹ yielding

$$\mu_{CA^\circ} = \mu_{C,F} + \mu_{A,F} \quad (24)$$

We now expand the chemical potentials in Equation 23 in terms of the standard state and of the activity of each component:

$$\begin{aligned} m_{C,T} (\mu_{C,T}^\circ + RT \ln m_{C,T} \gamma_{C,T}) + m_{A,T} (\mu_{A,T}^\circ + RT \ln m_{A,T} \gamma_{A,T}) = \\ m_{C,T} (\mu_{C,F}^\circ + RT \ln m_{C,F} \gamma_{C,F}) + m_{A,T} (\mu_{A,F}^\circ + RT \ln m_{A,F} \gamma_{A,F}) \end{aligned} \quad (25)$$

We have also taken Equation 24 into account, in order to eliminate the terms representing ion pairs.

The standard chemical potential of a species must be the same, whether or not we consider a portion of it to be involved in ion pairs.¹⁰ This is true because the standard chemical potentials are obtained by extrapolation from infinite dilution — where the concentration of ion pairs is zero — to an ideal state of unit molality of the solute —

where there are no ion-ion interactions.¹⁶ As a result of this, all terms involving the standard state may be cancelled in Equation 25. We are then left with a reduced version of Equation 1, in which c and a are equal to 1.

$$m_{C,T} \gamma_{C,T} m_{A,T} \gamma_{A,T} = m_{C,F} \gamma_{C,F} m_{A,F} \gamma_{A,F} \quad (26)$$

This equation can also be derived for multicomponent solutions, or for electrolytes with a higher valence. It is equally valid when the concentrations are defined on some other scale such as the molarity. Pytkowicz, Duedall, and Connors have also derived a form of Equation 1 that pertains only to the activities of single ions,³² i.e.,

$$m_{C,T} \gamma_{C,T} = m_{C,F} \gamma_{C,F} \quad (27)$$

Ion pairs must behave as distinct chemical entities in order for one to apply Equation 1, that is, ion selective electrodes must be insensitive to ion pairs. If this were not true, then there would be little point in discussing ion association from a potentiometric point of view. Ion pairs have been observed directly in solutions by a number of physical measurements. For example, the Raman spectra of MgSO_4° ion pairs have been detected in aqueous solutions.³³ The formation of Na^+ and Mg^{2+} ion pairs with SO_4^{2-} has also been detected indirectly through the effect of these ions on the Raman spectra of HSO_4^- .⁴ The anomalous adsorption of sound in MgSO_4 solutions can also be attributed directly to the dissociation of MgSO_4° pairs.⁵ Further evidence for the independent behavior of ion pairs can be found in the fact that potentiometric determinations of association constants usually give good agreement with other methods³⁴ and with theory.⁸

Pytkowicz and Kester made use of ion selective electrodes to measure the association constants of NaSO_4^- , MgSO_4° , and CaSO_4° .^{6,35} One important consequence of their work, which will have a strong influence on the model we will introduce in Section III, is the result that Harned's rule can be derived from an ion association model. We will examine this in greater detail after we review the procedure used by those authors to measure the stoichiometric association constant of NaSO_4^- .⁶

Pytkowicz and Kester assumed that Na^+ and Cl^- did not associate when they measured the stoichiometric association constant of NaSO_4^- . If this were the case, activity coefficients measured experimentally in pure NaCl solutions may be assumed to be free ones. Pure NaCl solutions were the standard, therefore, against which the degree of association in test solutions was measured. If, on the other hand, there is association in the NaCl solutions, then in $\text{NaCl-Na}_2\text{SO}_4$ mixtures, only the amount of association in excess of the NaCl° will be detected.

The degree of association in a solution consisting of NaCl and Na_2SO_4 was obtained by measuring the potential of a sodium-sensitive glass electrode vs. a saturated calomel electrode in the mixed solution. The potential of the same electrode pair was also measured in a solution of pure NaCl — whose composition was varied by titrating with a concentrated NaCl solution until the potential became the same as that measured in the $\text{NaCl-Na}_2\text{SO}_4$ mixture. The activity of Na^+ was then the same in both solutions when the potentials were equal if the liquid junction potential of the saturated calomel electrode had not changed, an assumption of the method. The activity of Na^+ in both solutions could, therefore, be equated by means of

$$a_{\text{Na}} = m_{\text{Na},F}^{(m)} \gamma_{\text{Na},F}^{(m)} = m_{\text{Na},F}^{(p)} \gamma_{\text{Na},F}^{(p)} \quad (28)$$

where superscripts p and m refer to the pure NaCl solution and to the mixture, respectively.