The Excess Free Energy and Related Properties of Solutions Containing Electrolytes

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Abstract: Analytical expressions are developed for the excess free energy of solutions containing any number of electrolytes of any valence types, and those properties which may be derived from it by differentiation, such as the osmotic coefficient, the activity coefficients of the components, and the excess enthalpy. Approximations are discussed, such as Brønsted's principle of specific interactions of ions, Harned's rule, Young's rule, the cross-square rule, and Guggenheim's recent hypothesis. The use of ions as components and of equivalent concentrations is found very useful.

Recently there has been a renewed interest in mixed electrolyte solutions, much of it inspired by the desalination of sea water. From 1934 to 1964 there have been eight studies from the MIT laboratory of the osmotic coefficient of dilute aqueous solutions with more than two components.[1-8]

References 1-4 include measurements of freezing point depressions, ref 6 and 8 include measurements of isotonic (isopiestic) equilibrium, and ref 5 and 7 include no new experimental work. Reference 1 deals with two nonelectrolyte solutes, ref 2 and 4 concern mixtures of one electrolyte with one or two nonelectrolytes, and the rest deal with electrolyte solutions. I have also been coauthor of two papers from the Oak Ridge National Laboratory[9,10] on mixed electrolytes and consultant for several others. The practical objectives all were the same: to determine the osmotic coefficients from a limited number of measurements and to determine from these measurements the Gibbs free energy and the activity coefficients in electrolyte mixtures from those of solutions of single solutes, or somewhat better with the addition of mixtures with a common ion. The approaches have varied somewhat over the years, however, and it seems worthwhile to present a consistent approach to the whole field and to discuss more fully solutions of electrolytes of different valence types.

The use of ions as components, with the restriction that the total charge is zero, gives an excellent contrast to the earlier treatments. We did use this convention in ref 6, but the description was very terse and without explanation. It also contained an excessive number of misprints.

Solutions of Nonelectrolytes

Reference 1 inaugurated the policies of starting such studies with the total Gibbs free energy and of expressing the excess free energy of nonelectrolyte solutions as an integral power series in the molalities of the solutes. This is analogous to the virial expansion of $pV/RT\Sigma n_i$ for a gas or gas mixture in terms of the volume concentrations of the components. The corresponding expansion in terms of mole fractions is analogous to the more complicated virial expansion for a gas in terms of the partial pressures.

We take the pure solvent as the standard state of unit activity for itself and as the reference state of unit activity coefficient for each solute, and we write

$$G^e/RT = G/RT - \sum_j n_j(G_j{}^\circ/RT - 1 + \ln m_j) = W\sum_{jk} b_{jk}m_jm_k + W\sum_{jkl} d_{jkl}m_jm_km_l + \cdots \quad (1)$$

$$= W(\sum_i m_i)^2\sum_{jk} b_{jk}x_jx_k + W(\sum_i m_i)^3\sum_{jkl} d_{jkl}x_jx_kx_l + \cdots \quad (2)$$

in which G is the Gibbs free energy of the system, G^e is the excess free energy defined by eq 1, m_j is the molality of solute j, n_j/W, $G_j{}^\circ$ is its "standard molal free energy," n_j is the number of moles of j, W is the number of kilograms of solvent, and b_{jk}, d_{jkl}, etc. are coefficients which, like $G_j{}^\circ$, are functions of T and p and of the nature of the solvent, but not of the composition of the solute. The use of G^e/RT has the advantage that it is dimensionless.

In the first decade of this century, before G. N. Lewis, J. N. Brønsted, and N. Bjerrum began their studies of ion activities, there was much interest in nonelectrolyte mixtures. The theories ranged from van Laar's use of the van der Waals equation[11] to Dolezalek's purely chemical theory.[12] van Laar extended the van der Waals theory by making the excluded volume, b, a function of the solvation. He used only two parameters per mole, b and a. Dolezalek, on the other hand, attributed all deviation from ideality to chemical action; each irregularity in the curve demanded a new chemical species with a new constant.

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(1) G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **56**, 1486 (1934).
(2) G. Scatchard and S. S. Prentiss, *ibid.*, **56**, 2314 (1934).
(3) G. Scatchard and S. S. Prentiss, *ibid.*, **56**, 2320 (1934).
(4) G. Scatchard and M. A. Benedict, *ibid.*, **58**, 837 (1936).
(5) G. Scatchard, *Chem. Rev.*, **19**, 309 (1936).
(6) G. Scatchard and R. G. Breckenridge, *J. Phys. Chem.*, **58**, 596 1954; **59**, 1234 (1955).
(7) G. Scatchard, *J. Am. Chem. Soc.*, **83**, 2636 (1961).
(8) R. L. Yoest, Ph.D. Thesis, Massachusetts Institute of Technology, 1964.
(9) J. S. Johnson, G. Scatchard, and K. A. Kraus, *J. Phys. Chem.*, **63**, 787 (1959).
(10) R. M. Rush and G. Scatchard, *ibid.*, **65**, 2240 (1961).
(11) J. J. van Laar, *Z. Physik. Chem.*, **72**, 723 (1910); **83**, 599 (1913).
(12) F. Dolezalek, *ibid.*, **64**, 727 (1908).

It was realized that positive deviations from ideality were usually roughly proportional to m, and that negative deviations were roughly proportional to $m/(1 + bm)$. There was much interest in salting-out, which was attributed to the removal of solvent by solvation of the salt.

Reference 1 treats ethanol, glycine, and their mixtures. G^e/RT of ethanol is slightly negative and that of glycine is much more negative. To Dolezalek this would mean that glycine is largely associated and ethanol slightly associated. G^e/RT of their 1:2 and 2:1 mixtures, however, is positive, meaning solvation to Dolezalek. In ref 2, it is shown that ethanol is salted out by sodium chloride, but glycine is salted in. This would offer quite a problem to Dolezalek. The physical picture is that ethanol decreases the dielectric constant of water but glycine increases it. From ref 4, we find that dioxane gives almost ideal solutions with water but is salted out about three times as much as ethanol. Reference 3 deals with the reciprocal salt pair: KNO_3–LiCl.

Electrolyte Solutions. The Non-Debye–Hückel Term

There are two important differences between solutions containing only nonelectrolytes and those containing one or more electrolytes, both due to the charges on the ions. The first is that there cannot be a solution of a single solute because each equivalent of cation must be balanced by an equivalent of anion. The second is that the free energy per mole of solute, the osmotic coefficient, and the logarithms of the activity coefficients contain terms in the square root of the ionic strength which cannot be represented by integral power series in the concentrations. We will split G^e for an electrolyte solution into the Debye–Hückel term, G^{DH}, and the remainder G^n. We will consider G^{DH} in the next section.

If the neutral molecules are chosen as solute components, a series of arbitrary decisions is necessary. The first is for a mixture of two salts of different valence types with a common ion. It is seldom recognized because any chemist would choose the ions-as-solutes answer: that in sodium and magnesium chloride, for example, the number of equivalents of NaCl is equal to that of sodium ion, and the number of equivalents of $MgCl_2$ is equal to that of magnesium ion.

The next decision arises when there are two cations and two anions. The "reasonable choice" suggested in ref 7 is not a useful one, because it does not extrapolate correctly for mixtures with a common ion. If the Rubicon is crossed, however, and the ions are chosen as components, all further decisions fall into line.

If the ions are taken as components with the restriction that $\Sigma_i n_i z_i = 0$, it is necessary to distinguish between neutral solutes, cations, and anions. We will denote solutes in general with the subscripts i, j, k, l as in eq 1 and 2, which are also applicable to electrolyte solutions. We will use the subscripts a, b, c, d for cations, e, f, g, h for anions, and p, q, r, s for neutral molecules.

It is most convenient to express the quantity and concentration of an ion in equivalents: $n_i' = n_i\mathfrak{z}_i$, $m_i' = m_i\mathfrak{z}_i$, where $\mathfrak{z}_i$ is the absolute value of the valence, $\mathfrak{z}_i = |z_i|$. At any stage we may reconvert to concentrations, or convert to ionic strengths by use of the corresponding relation $m_i' = 2I_i/\mathfrak{z}_i$. We write the equivalent fraction $x_j' = m_j'/(\Sigma_i m_i'/2)$, so that in a solution of a single electrolyte, af, x_a' and x_f' are each unity. It is useful to separate the sums into those for cations only, for anions only, and for the different mixtures.

The non-Debye–Hückel free energy, G^n, in dilute solution is given by

$$(G^n/RTW)_2 = \textstyle\sum_j\sum_k m_j'm_k'b_{jk} \tag{3}$$

In a solution of a single electrolyte, af, $m_a' = m_f'$

$$\textstyle\sum_j\sum_k m_j'm_k'b_{jk} = m_a'm_f'(2b_{af} + b_{aa} + b_{ff}) \tag{4}$$

In general, since $\Sigma m_a' = \Sigma m_f'$, $\Sigma m_a'm_f' = \Sigma m_a'm_b' = \Sigma m_f'm_g'$, $(2b_{ii} - b_{ii} - b_{ii}) = 0$, and

$$\begin{aligned}(G^n/RTW)_2 = \textstyle\sum_j\sum_k m_j'm_k'b_{jk} = \sum_a\sum_f m_a'm_f'(2b_{af} +{}\\ b_{aa} + b_{ff}) + \textstyle\sum_a\sum_b m_a'm_b'(2b_{ab} - b_{aa} - b_{bb}) +{}\\ \textstyle\sum_f\sum_g m_f'm_g'(2b_{fg} - b_{ff} - b_{gg}) = \sum_j\sum_k m_j'm_k'B_{jk} ={}\\ (\textstyle\sum_i m_i/2)^2\sum_j\sum_k B_{jk}x_jx_k\end{aligned} \tag{5}$$

with

$$B_{jk} = (2b_{jk} - b_{jj} - b_{kk}) \tag{6a}$$

if $z_jz_k > 0$ and

$$B_{jk} = (2b_{jk} + b_{jj} + b_{kk}) \tag{6b}$$

if $z_jz_k < 0$.

$$\begin{aligned}(G^n/RTW)_3 = \textstyle\sum_j\sum_k\sum_l m_j'm_k'm_l'd_{jkl} ={}\\ (\textstyle\sum_i m_i'/2)^3[\sum_a\sum_f(D_{aaf}x_a'^2x_f' + D_{aff}x_a'x_f'^2) +{}\\ \textstyle\sum_a\sum_b(D_{aab}x_a'^2x_b' + D_{abb}x_a'x_b'^2)] +{}\\ \textstyle\sum_f\sum_g(D_{ffg}x_f'^2x_g' + D_{fgg}x_f'x_g'^2) +{}\\ \textstyle\sum_a\sum_b\sum_f 2D_{abf}x_a'x_b'x_f' + \sum_a\sum_f\sum_g 2D_{afg}x_a'x_f'x_g'\end{aligned} \tag{7}$$

$$(G^n/RTW)_4 = \textstyle\sum_i\sum_j\sum_k\sum_l m_i'm_j'm_k'm_l'{}_{ijkl} \tag{8}$$

The Debye–Hückel Free Energy

The Debye–Hückel equation assumes that all the ions have the same size. We will assume this as a first approximation, but we will follow our longtime customs[5,13] of using the ionic strength in moles per kilogram of solvent and of assuming that $ka/\sqrt{I} = a'$ is independent of temperature and pressure.

Then the Debye–Hückel free energy may be expressed as

$$G^{DH}/RT = WS\textstyle\sum_i I_i X/a' \tag{9}$$

in which S is the Debye–Hückel slope for ln $\gamma_\pm$ of a uniunivalent electrolyte, a function of T and p, $I_i = m_i'\mathfrak{z}_i'/2$, $x = \kappa a$, and

$$\begin{aligned}X = [x^2 - 2x + 2\ln(1 + x)]/x^2 = 2[(x/3) -{}\\ (x^2/4) + (x^3/5) - (x^4/6) + \cdots]\end{aligned} \tag{10}$$

We assume that for a single electrolyte, the deviations from this equation may be represented by an integral power series in I, or in m', which becomes part of the series discussed in the preceding section.

We have been moderately successful in describing the properties of solutions of simple ions with $a' = 1.5$. However, there is a large amount of evidence that more accurate expressions are given by assigning different values of a' to different electrolytes (equation in ref 7).

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(13) G. Scatchard and L. F. Epstein, *Chem. Rev.*, 30, 211 (1942).

For a mixture we take

$$G^{\mathrm{DH}}/RT = WS\sum_{\mathrm{a}}{}^{+}\sum_{\mathrm{f}}{}^{-}m_{\mathrm{a}}'m_{\mathrm{f}}'(\mathfrak{z}_{\mathrm{a}}/\sum_{\mathrm{g}}{}^{-}m_{\mathrm{g}}' + \mathfrak{z}_{\mathrm{f}}/\sum_{\mathrm{b}}{}^{+}m_{\mathrm{b}}')X_{\mathrm{af}}/a_{\mathrm{af}}' \quad (11)$$

This equation depends upon the assumptions that $a_{\mathrm{af}}' = (2a_{\mathrm{af}} + a_{\mathrm{aa}} + a_{\mathrm{ff}})\kappa/4I^{1/2}$ and that $a_{\mathrm{ab}}' = (2a_{\mathrm{ab}} - a_{\mathrm{aa}} - a_{\mathrm{bb}})\kappa/4I^{1/2} = 0$. This latter assumption is not necessarily contradictory to the "primitive model" treatment of Mayer[14] and Friedman[15] which includes much more than the electrostatic terms. It is discussed in detail in ref 7. We assume only that deviations from eq 11 may be included in the integral power series in the concentrations.

If H^{e} is the excess enthalpy and V^{e} is the excess volume, $H^{\mathrm{e}}/RT = -(\partial G^{\mathrm{e}}/RT)\partial \ln t$ and $pV^{\mathrm{e}}/RT = (\partial G^{\mathrm{e}}/RT)\partial \ln p$. The assumptions used in our laboratory since 1942[10] that each a_{af}' is independent of the temperature and pressure lead to expressions for H^{e}/RT and pV^{e}/RT of the same forms as those for G^{e}/RT with S and each b or b' replaced by its appropriate derivative. The differentiations may be carried further to give the heat capacity, the compressibility, or mixed quantities involving both temperature and pressure differentiation.

At constant temperature $\partial(G^{\mathrm{e}}/RT)/\partial n_{\mathrm{i}} = \ln \gamma_{\mathrm{i}}$, and $\partial(G^{\mathrm{e}}/RT)/\partial n_{\mathrm{s}} = \partial \ln \gamma_{\mathrm{s}} = -(\Sigma_{\mathrm{i}} n_{\mathrm{i}}/n_{\mathrm{s}})\phi$.

Approximate Rules

Most of the rules which follow have been given the names of men, though in no case has the man himself used this name.

Lewis Ionic Strength Rule. The boldest, and I think the oldest, approximation of G^{e}/RT or of one of its derivatives is that of Lewis[16] that the activity coefficient of an ion depends only on the ionic strength. There is no record in his published papers that there was any theory behind this assumption. Lewis was so impressed by the successes of the rule that the activity coefficient of an ion depends only on the ionic strength that he felt that it must be universal. However, Brønsted[17] showed that it requires that the activity coefficient be the same for all ions of the same valence type. With the perspective of almost half a century we can see that Brønsted proved that the ionic strength rule holds for one ion when it holds for all ions.

Brønsted's Principle of the Specific Interaction of Ions. In the same papers Brønsted presented the thesis that the electrostatic repulsion between ions of the same sign keeps them so far apart that the short-range attraction forces between them are zero. He assumed, however, that the forces due to solvation of the ions are unaffected. Since he limited his principle to 0.1 *N* solutions, it applies obviously to dilute solutions only. The confusion caused by an error in Brønsted's derivation is discussed fully in ref 6. We will treat Brønsted's principle as a special case of Harned's rule.

Harned's rule[18] states that, in a mixture of two electrolytes with a common ion at constant ionic strength, each $\ln \gamma_1$ is a linear function of the ionic strength fraction. In the special case of Brønsted's principle, the slope is the same for the two coions, and $\ln \gamma_{\mathrm{af(bf)}} = \ln \gamma_{\mathrm{bf(af)}}$ if $\ln \gamma_{\mathrm{af(bf)}}$ is the logarithm of the activity of af in bf, etc.

$$(G^{\mathrm{n}}/RTW)_2 = \frac{B_{\mathrm{af}}n_{\mathrm{a}}'n_{\mathrm{f}}' + B_{\mathrm{bf}}n_{\mathrm{b}}'n_{\mathrm{f}}' + B_{\mathrm{ab}}n_{\mathrm{a}}'n_{\mathrm{b}}'}{W^2} \quad (12)$$

$$\frac{\partial(G^{\mathrm{n}}/RTW)}{\partial n_{\mathrm{a}}'} + \frac{(\partial G^{\mathrm{n}}/RTW)}{n_{\mathrm{f}}'} = B_{\mathrm{af}}(n_{\mathrm{a}}' + n_{\mathrm{f}}') + B_{\mathrm{bf}}n_{\mathrm{b}}' + B_{\mathrm{ab}}n_{\mathrm{b}}' \quad (13)$$

$$= \frac{n_{\mathrm{f}}'}{W}[B_{\mathrm{af}}(2 - y) + B_{\mathrm{bf}}y + B_{\mathrm{ab}}y] \quad (14)$$

$$= \frac{n_{\mathrm{f}}'}{W}[2B_{\mathrm{af}} + (B_{\mathrm{bf}} - B_{\mathrm{af}} + B_{\mathrm{ab}})y] \quad (15)$$

if $y = n_{\mathrm{b}}'/n_{\mathrm{f}}'$, so

$$\frac{\mathrm{d}}{\mathrm{d}y}\left[\frac{\partial G^{\mathrm{n}}/RTW}{\partial n_{\mathrm{a}}'} + \frac{\partial G^{\mathrm{n}}/RTW}{\partial n_{\mathrm{f}}'}\right] = \frac{n_{\mathrm{f}}'}{W}(B_{\mathrm{bf}} - B_{\mathrm{af}} + B_{\mathrm{ab}}) \quad (16)$$

However, the Debye–Hückel activities are independent of the composition at constant ionic strength.

A very large majority of the measurements of ion activities are for the determination of single ion activities with a saturated potassium chloride bridge. Most physical chemists have always disliked such measurements for two reasons. They believe that the measurements are inexact and that the activity of a single ion cannot be determined. It is true that the inaccurate measurements are possible and many such are made every day. On the other hand, it is possible to make the error in the liquid junction smaller than that in the electrodes just as in a concentration cell with transference. To determine single ion activities, it is sufficient to have an operational definition for one cell, say the hydrogen–hydrogen ion electrode *vs.* the saturated potassium chloride bridge. I calculated this potential[19] with the MacInnes assumption that the liquid junction potential of the cell KCl (1 *m*)|KCl (satd) is zero.[20] Then the potential in millivolts for the cell HCl (1 *m*)|KCl (satd) is +0.09 at 0.2 *m*, −0.01 at 0.5 *m*, −0.15 at 0.6 *m*, −3.2 at 0.8 *m*, and −5.00 at 1 *m*. It must be remembered, however, that the assumptions underlying these calculations are very different from the previous ones.

Reference 3 contains the only published measurements I know on osmotic coefficients of a reciprocal salt pair. An objection has been raised[21] that the experimental results are not given in ref 3. I believe that publication of the parameters for a set of equations with deviations from these equations is the best way to present such results. Figure 6 in ref 3 shows that of 93 measurements with $I = 0.01$ or above on the single salts, 79 deviate less than 0.001 and 14 deviate between 0.001 and 0.002. Of 145 measurements on mixtures in the same concentration range, which depend also on the two-ion series, 134 deviate less than 0.001, 9 between 0.001 and 0.002, and 2 between 0.002 and 0.003.

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(14) J. E. Mayer, *J. Chem. Phys.*, **18**, 1426 (1950).

(15) H. L. Friedman, *ibid.*, **32**, 1351 (1960); "Ionic Solution Theory," Interscience Publishers, New York, N. Y., 1962.

(16) G. N. Lewis and M. Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921); "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.

(17) J. N. Brønsted, *J. Am. Chem. Soc.*, **44**, 877, 938 (1922); **45**, 289 (1923).

(18) H. S. Harned and B. B. Owen, "Electrolytic Solutions," McGraw-Hill Book Co., Inc., New York, N. Y., 1943.

(19) G. Scatchard, *J. Am. Chem. Soc.*, **47**, 696 (1925).

(20) D. A. MacInnes, *ibid.*, **41**, 1086 (1919).

(21) E. A. Guggenheim, "Applications of Statistical Mechanics," Clarendon Press, Oxford, 1966.

The equations used are not very convenient, however. They are of the form

$$\phi = 1 + 0.5M^{1/2}\sum_{\mathrm{J}}A_{\mathrm{J}}' + M\sum_{\mathrm{JK}}x_{\mathrm{J}}x_{\mathrm{K}}(B_{\mathrm{JK}}' + 1.5C_{\mathrm{JK}}'M^{1/2}) + M^2\sum_{\mathrm{JKL}}x_{\mathrm{J}}x_{\mathrm{K}}x_{\mathrm{L}}(2D_{\mathrm{JKL}}' + 2.5E_{\mathrm{JKL}}'M^{1/2}) \quad (17)$$

in which $M = 2I$ for 1:1 electrolytes. Then in our terms

$$\alpha_{\mathrm{J}} = 0.5(2I)^{1/2}A_{\mathrm{J}}' + (2I)B_{\mathrm{JJ}}' + 1.5(2I)^{3/2}C_{\mathrm{JJ}}' + 2(2I)D_{\mathrm{JJJ}}' + 2.5(2I)^{5/2}E_{\mathrm{JJJ}}' \quad (18)$$

$$\beta_{\mathrm{JK}} = (2I)(2B_{\mathrm{JK}}' - B_{\mathrm{JJ}}' - B_{\mathrm{KK}}') + 1.5(2I)^{3/2}(2C_{\mathrm{JK}}' - C_{\mathrm{JJ}}' - C_{\mathrm{KK}}') + 2(2I)^2(D_{\mathrm{JJK}}' + D_{\mathrm{JKK}}' - D_{\mathrm{JJJ}}' - D_{\mathrm{KKK}}') + 2.5(2I)^{5/2}(E_{\mathrm{JJK}}' + E_{\mathrm{JKK}}' - E_{\mathrm{JJJ}}' - E_{\mathrm{KKK}}') \quad (19)$$

For the KNO_3–KCl–$LiNO_3$–LiCl system, $(2B_{\mathrm{JK}}' - B_{\mathrm{JJ}}' - B_{\mathrm{KK}}')$ and $(2C_{\mathrm{JK}}' - C_{\mathrm{JJ}}' - C_{\mathrm{KK}}')$ are zero. Most readers will probably be satisfied, however, with the plots of $(\alpha_{\mathrm{J}} - \alpha_{\mathrm{K}})/I$ and β_{JK}/I in Figures 1–3 of ref 7. The freezing point constant is 0.001 too small. This leads to nearly constant errors of $+0.001$ in α and in β above 0.01 *m*.

Young and his students[22,23] have made many measurements of the heat of mixing at constant ionic strength of many 1:1 electrolytes, and Wood and his students[24–26] have extended the measurements to 2:1 and 1:2 electrolytes. These have the advantages over free-energy measurements that the ideal term is zero and that they measure directly the term corresponding to $B_{\mathrm{JK}}y_{\mathrm{J}}y_{\mathrm{K}}$, which we will call $B_{\mathrm{JK}}^{(\mathrm{H})}y_{\mathrm{J}}y_{\mathrm{K}}$.

From the measurements of his students, Young has arrived empirically at two important relations.

Young's rule states that the heat of mixing at constant ionic strength two 1:1 electrolytes with a common ion, af and bf, is independent of the common ion, f. It must hold for $(H^{\mathrm{m}}/RT)_2$ and it holds for $(H^{\mathrm{m}}/RT)_3$ if $d_{\mathrm{aaf}} + d_{\mathrm{bbf}} = 0$.

The cross-square rule states that for a reciprocal salt pair of 1:1 salts, af, bf, ag, bg, the heat of mixing 0.5 mole of af and ag, of bf and bg, of af and bf, and of ag and bg is the same as that of mixing 0.5 mole of af and bg and of ag and bf. In reply to Böttger at the Faraday Society Discussion,[22] Young said that the holding of Young's rule is a necessary but not a sufficient condition for the holding of the cross-square rule. No additional condition is necessary for the terms proportional to $(H^{\mathrm{m}}/RT)_2$ and to $(H^{\mathrm{m}}/RT)_3$.

Wood and Anderson[25] have calculated the terms in G^{e}/RT proportional to the first and second powers of the ionic strength. They say that triplet formation should lead to terms proportional to $I^{3/2}$, but they do not use this erroneous statement. They also copy the erroneous conclusion of ref 7 concerning the ionic strength fractions, but this has no effect because they apply it only to cases of the same valence type so that the ionic strength fraction is a constant times the ion-component fraction. The statement that the interactions of three ions of like charge lead to asymmetry is also erroneous.

Guggenheim's Recent Hypothesis.[21,27] Guggenheim starts with the hypothesis that up to 2 *m* the differences in *B* for most uniunivalent electrolytes are proportional to *I* and takes NaCl as standard. This hypothesis was examined in Figure 8 of ref 3 under the name "the Åkerlöf-Thomas Hypothesis" and found to hold better at higher concentrations that at lower ones. Then he states that up to 2 *m* the deviations from Brønsted's principle, our *B*'s, are small and proportional to *I*. He also rediscovered Young's rule. In Figures 1 and 2 of ref 7, the terms for B/I are small, but the constant term and that proportional to $I^{1/2}$ are zero, and at $I = 1$, $(B_{\mathrm{af}} - B_{\mathrm{bg}})$ is about as large as $(B_{\mathrm{af}} + B_{\mathrm{bg}})/2$, and $(B_{\mathrm{ag}} - B_{\mathrm{bf}})$ is about as large as $(B_{\mathrm{ag}} + B_{\mathrm{bf}})/2$. For the isopiestic results at 25°, only those in Figure 4 of ref 7 extend below 2 *m*. They are nearly linear from 1 to 4 *m*, but the slope is far from zero.

The worst difficulty with these papers for me is the statement that these conclusions are thermodynamic coming from one with such a high, and well-deserved, reputation for knowledge of thermodynamics as Guggenheim.

Our Later Work. Johnson[28] and Rush have corrected the errors in ref 7 and have measured the osmotic coefficients of mixtures of $NaClO_4$, $LiClO_4$, and $HClO_4$ up to very high concentraions.

Yoest[8] measured the osmotic coefficients of a reciprocal salt pair, $CuCl_2$–$NaClO_4$, with one bivalent cation, one univalent cation, and two univalent anions, with a very large spread in the osmotic coefficients of the two component systems.

Johnson, Scatchard, and Kraus[9] studied the system $BaCl_2$–HCl in the ultracentrifuge and applied eq 15 of ref 7 to the interpretation of the results. Rush and Scatchard[10] corrected the equation of Young and Smith[29] for a mixture of electrolytes of different valence types to complete the application of eq 15 of ref 7 in ref 9.

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(24) R. H. Wood and R. W. Smith, *ibid.*, **69**, 2974 (1965).

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