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THERMODYNAMIC PROPERTIES OF MOLTEN-SALT SOLUTIONS

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INTRODUCTION

I.1 General

In this chapter the physical description of molten-salt solution thermodynamics will be discussed. Because of the large volume of work in this field this chapter cannot be comprehensive. As the field of molten-salt solution chemistry is still in a rudimentary state, this must be considered as an interim report on some of its aspects.

The Gibbs free energy G and the Helmholtz free energy A are related to the chemical potential of the component i, μ_i, of a solution by the relation

$$\left(\frac{\partial G}{\partial n_i}\right) T,P,n_k + n_i = \left(\frac{\partial A}{\partial n_i}\right) T,V,n_k + n_i = \mu_i \; . \tag{I.1.1}$$

For pure liquid and solid i the symbols μ_i^0 and $\mu_i^\square$, respectively, will be used to represent the chemical potential. Rational forms can be deduced for expressing the chemical potentials of components of solutions by considering a hypothetical ideal solution. In choosing such a hypothetical ideal solution, one must be careful to have it bear some resemblance to real mixtures, and the equations derived should conform to the limiting laws which are valid for dilute solutions. Since the equations derived should conform to the limiting laws, we will discuss these before discussing ideal solutions.

I.2 The Limiting Laws

Limiting laws can be derived for any solution that is dilute enough so that the enthalpy of solution per mole of solute is essentially independent of the concentration of solute and the equation

$$H = n_1 H_1^0 + n_2 \bar{H}_2^* \tag{I.2.1}$$

holds, where H is the total enthalpy of the solution, n_1 and H_1^0 are the number of moles and enthalpy of pure solvent, and n_2 and $\bar{H}_2^*$ are the number of moles and partial molar enthalpy of solute.

If the solute has no ions in common with the solvent, then the ideal limiting laws may be derived from statistical considerations.[107,123] If a solute molecule dissolves to form k different species with ν_k particles (or ions) of kind k, then the number of ways of arranging the ions of the solute in solution, or the number of configurations Ω is given by

$$\Omega = \prod_{k+1} \frac{(B_k)^{\bar{n}_k}}{\bar{n}_k!} \; , \tag{I.2.2}$$

where $\bar{n}_k$ are the number of particles of type k, where B_k is the number of ways of placing one particle k in the solvent, and, if the solution is dilute enough, $(B_k)^{\bar{n}_k}$ is the number of ways of placing $\bar{n}_k$ distinguishable particles k. The $\bar{n}_k!$ in the denominator corrects for the indistinguishability of all the particles of a given type. The B_k may be all different but are all proportional to $\bar{n}_1$, the number of molecules of solvent. The entropy of mixing may be calculated from the relation

$$\frac{\Delta S_T}{k} = \ln \Omega \, . \qquad (1.2.3)$$

By using Stirling's approximation one obtains

$$\begin{aligned} \frac{\Delta S_T}{k} &= \Sigma \bar{n}_k \ln \bar{n}_1 + \Sigma \bar{n}_k \ln \beta_k - \Sigma \bar{n}_k \ln \bar{n}_k + \Sigma \bar{n}_k \\ &= \Sigma \nu_k \bar{n}_2 \ln \bar{n}_1 + \Sigma \nu_k \bar{n}_2 \ln \beta_k - \Sigma \nu_k \bar{n}_2 \ln (\nu_k \bar{n}_2) + \Sigma \nu_k \bar{n}_2 \, , \qquad (1.2.4) \end{aligned}$$

where $B_k = \bar{n}_1 \beta_k$ and $\bar{n}_k = \nu_k \bar{n}_2$, and where $\bar{n}_2$ is the number of molecules of solute. From Eqs. (1) and (4) the ideal limiting laws for the solvent are

$$\mu_1 - \mu_1^0 = -T_1(\bar{S}_1 - S_1^0) = -T \frac{\partial \Delta S_T}{\partial n_1} = -RT \frac{n_2}{n_1} \Sigma \nu_k \cong RT \ln (1 - N_2 \Sigma \nu_k) \, , \qquad (1.2.5)$$

where N_2 is the mole fraction of the solute. For the solute the ideal limiting law is

$$\mu_2 - \mu_2^* = -T \frac{\partial \Delta S_T}{\partial n_2} = \Sigma \nu_k RT \ln \frac{n_2}{n_1} \cong \Sigma \nu_k RT \ln N_2 \, , \qquad (1.2.6)$$

where the term $\mu_2^* [= \bar{H}_2^* + \Sigma \nu_k \ln (\beta_k / \nu_k)]$ is the partial molar free energy of a standard state chosen so that a solution of component 2 will behave ideally at extremely high dilutions. The term μ_2^* is a function of the concentration scale used. Equations (5) and (6) express the fact that in a dilute solution the solvent obeys Raoult's law and the solute obeys Henry's law. The limiting laws given by Eqs. (5) and (6) are independent of the specific properties of the solvent (except for the value of μ_2^*) unless the solvent has an ion or particle in common with one of the species. If the ions or particles formed from the solute upon dissolution which are already present in the solvent are designated as l, then

$$\Omega = \frac{\prod_k (B_k)^{\bar{n}_k} (K_l \bar{n}_1)!}{\prod_{k \neq l} \bar{n}_k! \prod_l (\bar{n}_l + K_l \bar{n}_1)!} \, , \qquad (1.2.7)$$

where K_l is the number of l particles per molecule of solvent. If the K_l are not very small, then it may be shown that

$$\mu_1 - \mu_1^0 \cong RT \ln (1 - N_2 \nu) \qquad (1.2.8)$$

$$\mu_2 - \mu_2^* \cong \nu RT \ln N_2 \, , \qquad (1.2.9)$$

where $\nu = \sum_{k+l} \nu_k$ and is equal to number of independent particles which differ from those already present in the solvent which are introduced upon the dissolution of one molecule of solute. To illustrate this the solute KCl in the solvent $AgNO_3$ leads to a value of $\nu = 2$,[37] but KNO_3 and Ag_2SO_4 in $AgNO_3$ lead to a value of $\nu = 1$.[37] Partially ionized solvents such as water can be described by using more than one value of ν. The dissolution of HCl in H_2O at concentrations of HCl much lower than the concentration of H^+ from the self-ionization of water leads to a value of $\nu = 1$. At concentrations of HCl high enough so that the self-ionization of water is suppressed, $\nu = 2$. Thus by choosing an ionic solute with a common ion, a distinction can be made between an ionizing and a non-ionizing solvent by testing the limiting laws. Care must be taken before using this as a criterion of the ionic nature of the solvent to apply these considerations to solutions that are dilute enough so that the limiting laws are valid.

I.3 The Temkin Ideal Solution[127]

Liquid salts are similar to solids in some of their aspects and differ considerably from solids in important ways. A molten salt must be considered as an assembly of ions with the expected alternation of charge as in solids, with the cations having anions as nearest neighbors and the anions having cations as nearest neighbors. The enthalpies and energies of formation of solids and liquids from the gaseous ions do not differ greatly, since the enthalpy and energy of fusion is very small relative to the total lattice energy of the solid. The sharp increase of conductance upon melting indicates that the melting process leads to ions of greater mobility than in the solid.

In the Temkin model, salts are considered as completely ionized. The strong Coulombic forces in a molten salt lead to a strong tendency for the alternation of charges such that cations are surrounded by anions and the anions are surrounded by cations. If a mixture of the two monovalent cations A^+ and B^+ and the two monovalent anions X^- and Y^- is considered, then the anions reside in a region adjacent to the cations and the cations reside in a region adjacent to the anions and the molten salt might be considered as a quasi-lattice. If the two cations and the two anions respectively have the same physical properties, then the cations can mix randomly in the cation region of positions which is adjacent to the anions, and the anions can mix randomly in the anion region of positions which is adjacent to the cations. The total enthalpy and energy of the solution is the same as that of the pure components, and the heat of mixing and energy of mixing are zero. The total entropy of mixing, ΔS_T, can be calculated from the total number of possible equivalent and distinguishable configurations, ω_T,

$$\frac{\Delta S_T}{k} = \ln \omega_T = \ln \left\{ \left[\frac{(\bar{n}_A + \bar{n}_B)\,!}{\bar{n}_A!\,\bar{n}_B!} \right] \left[\frac{(\bar{n}_X + \bar{n}_Y)\,!}{\bar{n}_X!\,\bar{n}_Y!} \right] \right\}, \tag{I.3.1}$$

where the $\bar{n}_i$ are the number of cations of kind i^+ and $\bar{n}_j$ are the number of anions of kind j^-. By using Stirling's approximation

$$\ln (\bar{n}!) \cong \bar{n} \ln \bar{n} - \bar{n} \; ; \tag{I.3.2}$$

then

$$\frac{-\Delta S_T}{R} = n_{\mathrm{A}} \ln N_{\mathrm{A}} + n_{\mathrm{A}} \ln N_{\mathrm{B}} + n_{\mathrm{X}} \ln N_{\mathrm{X}} + n_{\mathrm{Y}} \ln N_{\mathrm{Y}} \;, \tag{I.3.3}$$

where n_i and n_j are the number of gram moles of ions i^+ and j^-, and N_i and N_j are the ion fractions of cation i^+ or anion j^- respectively.

$$N_{\mathrm{A}} = \frac{n_{\mathrm{A}}}{n_{\mathrm{A}} + n_{\mathrm{B}}} \,, \qquad N_{\mathrm{X}} = \frac{n_{\mathrm{X}}}{n_{\mathrm{X}} + n_{\mathrm{Y}}} \,,$$

$$N_{\mathrm{B}} = \frac{n_{\mathrm{B}}}{n_{\mathrm{A}} + n_{\mathrm{B}}} \,, \qquad N_{\mathrm{Y}} = \frac{n_{\mathrm{Y}}}{n_{\mathrm{X}} + n_{\mathrm{Y}}} \,. \tag{I.3.4}$$

For any number of monovalent species

$$N_{\mathrm{A}} = \frac{n_{\mathrm{A}}}{\Sigma n_i} \,,$$

$$N_{\mathrm{X}} = \frac{n_{\mathrm{X}}}{\Sigma n_j} \,, \tag{I.3.5}$$

$$\frac{-\Delta S_T}{R} = \Sigma n_i \ln N_i + \Sigma n_j \ln N_j \,.$$

The partial molar entropy of solution is then

$$-\frac{(\bar{S}_{ij} - S^0_{ij})}{R} = \ln N_i N_j = -\frac{\partial \Delta S_T}{\partial n_{ij}} = -\frac{\partial \Delta S_T}{\partial n_i} - \frac{\partial \Delta S_T}{\partial n_j} \,, \tag{I.3.6}$$

and the chemical potential can be expressed by

$$\mu_{ij} - \mu^0_{ij} = RT \ln N_i N_j \,. \tag{I.3.7}$$

Equation (7) is compatible with (I.2.8), when ij is the solvent; if ij is the solute, μ_{ij} differs from μ_2 in (I.2.9) by a constant. By defining the activity of the component ij, a_{ij}, by the equation

$$\mu_{ij} - \mu^0_{ij} = RT \ln a_{ij} \,, \tag{I.3.8}$$

then for a Temkin ideal solution

$$a_{ij} = N_i N_j \,. \tag{I.3.9}$$

If the solution contains only one anion as X^- and a number of cations, then for any component such as AX for example, $N_{\mathrm{X}} = 1$ and

$$a_{\mathrm{AX}} = N_{\mathrm{A}} = N_{\mathrm{AX}} \,, \tag{I.3.10}$$

where N_{AX} is the mole fraction of the component AX. A similar relation holds if the cation A is the only cation. Thus, if in a mixture of several simple* salts containing two ions each, and if all of the components of the mixture contain one ion in common, the Temkin ideal activity of a component is equal to its mole fraction. In an ideal mixture of one mole of AX with one mole of BX, for example, the activity of AX and of BX are both $\frac{1}{2}$.

On the other hand, in an ideal mixture of one mole of AX with one mole of BY, the activities of AX and BY are both $\frac{1}{4}$. Thus the activity of a given mole fraction of an ionizing salt in a mixture depends strongly on whether it has an ion in common with other salts in the mixture. Even though the salts AY and BX have not been used, the activities of AY and BX are also $\frac{1}{4}$. There are four different ions in this solution, and the restriction imposed by the condition of electroneutrality reduces the number of independent thermodynamic components to three. If, as is unlikely, in all equilibria and phases $n_A = n_X$ and $n_B = n_Y$, then another restriction is imposed on the solution and it is a two-component system. If, in some equilibria this condition is true, the solution may be termed a quasi-binary system for that equilibrium.

The condition of electroneutrality makes it necessary to choose electrically neutral components. In the three-component system A^+, B^+, X^-, Y^-, for example, there are four possible ways of choosing components

AX-BX-BY
AY-BX-BY
AX-AY-BX
AX-AY-BY

all of which are correct. For some compositions and choices of components a negative concentration of one of the components would have to be used. For example a mixture of 1 mole of AX, 1 mole of AY, and 1 mole of BY, if described in terms of the components AX, BX, and BY, would be composed of 2 moles of AX, 2 moles of BY and −1 mole of BX. Although this is a thermodynamically valid method of description, it is usually more convenient to avoid negative concentrations of components. Any partial molar value of the thermodynamic function T for the component ij containing monovalent ions can be calculated in two ways by

$$\bar{T}_{ij} = \left(\frac{\partial T}{\partial n_{ij}}\right) = \left(\frac{\partial T}{\partial n_i}\right) + \left(\frac{\partial T}{\partial n_j}\right), \tag{1.3.11}$$

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*Simple salts contain only two atomic ions.

where n_{ij} is the number of moles of the component ij. The use of the sum $(\partial T/\partial n_i) + (\partial T/\partial n_j)$ permits one to avoid stating a choice of components. In general, the partial derivative of any thermodynamic function T for a component A_rX_s will be given by

$$\left(\frac{\partial T}{\partial n_{A_rX_s}}\right) = r\left(\frac{\partial T}{\partial n_A}\right) + s\left(\frac{\partial T}{\partial n_X}\right) .$$

An ideal mixture of two different salts of the same charge type as a mixture of A_rX_s and B_rY_s would give an expression for the total entropy of mixing of

$$\frac{-\Delta S_T}{R} = n_A \ln N_A + n_B \ln N_B + n_X \ln N_X + n_Y \ln N_Y \tag{1.3.12}$$

and

$$\frac{-(\bar{S}_{ij} - S_{ij}^0)}{R} = r \ln N_i + s \ln N_j \ , \tag{1.3.13}$$

so that

$$\mu_{ij} - \mu_{ij}^0 = RT \ln N_i^r N_j^s \tag{1.3.14}$$

and

$$a_{ij} = N_i^r N_j^s . \tag{1.3.15}$$

Another interesting definition of an ideal solution is that which is derived under the assumption that all cations and anions are randomly mixed despite the differences in the sign of the charge. Although this is undoubtedly a poor picture of any molten salt, it can give an idea of the effect of the interchange of cations and anions on the cation and anion positions; since a molten salt is not a rigid lattice, some ions of the same charge must occasionally be near neighbors. For the pure salts ij containing only monovalent cations the entropy of mixing is

$$-\frac{\Delta S_{ij}^0}{R} = n_i \ln 2 + n_j \ln 2 = -\frac{\Delta S_i^0}{R} - \frac{\Delta S_j^0}{R}, \tag{1.3.16}$$

and for a random mixture of the four ions A^+, B^+, X^-, and Y^-

$$\frac{-\Delta S_T'}{R} = n_A \ln \frac{n_A}{n_A + n_B + n_X + n_Y} + n_B \ln \frac{n_B}{n_A + n_B + n_X + n_Y}$$
$$+ n_X \ln \frac{n_X}{n_A + n_B + n_X + n_Y} + n_Y \ln \frac{n_Y}{n_A + n_B + n_X + n_Y} , \tag{1.3.17}$$

and, since $n_A + n_B = n_C + n_D$, it can be shown that

$$-\frac{\Delta S_T}{R} = -\frac{\Delta S_T' - \Sigma n_i \Delta S_i^0 - \Sigma n_j \Delta S_j^0}{R} = \Sigma n_i \ln N_i + \Sigma n_j \ln N_j \ , \tag{1.3.18}$$

which is the same as Eq. (5). Thus, the assumption of random mixing of all the ions leads to the same definition of an ideal solution for mixtures of monovalent ions as does the Temkin model in this case.

This conclusion may be generalized since the configurational integral for $\bar{n}$ molecules of uni-univalent salt is

$$Z_{ij} = \int \cdots \int \frac{e^{-BU_{ij}}}{(\bar{n}\,!)^2} (d\tau)^{2\bar{n}} \,, \tag{1.3.19}$$

where $d\tau$ is a volume element in configurational space $B = (1/kT)$ and U_{ij} is the total potential energy of a salt, ij, in a given configuration and the integration is overall configurations. For a mixture of anions, j, and cations, i,

$$Z_{\text{mixture}} = \int \cdots \int \frac{e^{-BU_{\text{mix}}}}{\pi\bar{n}_i\,!\;\pi\bar{n}_j\,!} (d\tau)^{2\bar{n}} = \frac{(\bar{n}\,!)^2}{\pi\bar{n}_i\,!\;\pi\bar{n}_j\,!} \int \cdots \int \frac{e^{-BU_{\text{mix}}}}{(\bar{n}\,!)^2} (d\tau)^{2\bar{n}} \,, \tag{1.3.20}$$

where $\bar{n} = \Sigma\bar{n}_i = \Sigma\bar{n}_j$. The total free energy of mixing per mole is

$$\Delta A_m = A_{\text{mixture}} - \Sigma\Sigma N_i N_j A_{ij} = -kT \ln Z_{\text{mixture}} + \Sigma\Sigma N_i N_j\, kT \ln Z_{ij} \,. \tag{1.3.21}$$

For the case in which the quantity

$$\left[\ln \int \cdots \int e^{-BU_{\text{mix}}} (d\tau)^{2\bar{n}} - \Sigma N_i N_j \ln \int \cdots \int e^{-BU_{ij}} (d\tau)^{2\bar{n}} \right]$$

is zero,* then

$$-\Delta A_m = T\Delta S_T = -RT(\Sigma n_i \ln N_i + \Sigma n_j \ln N_j) \,, \tag{1.3.22}$$

which is equivalent to Eqs. (5) and (18) but has been derived without a model.

1.4 Salts Containing Ions of Different Charge

Although the laws of ideal solution are unambiguous for ionizing salts of the same charge type, expressions for salts of different charge types present a problem. Førland[58] has given an extensive discussion of this. For a system A^+, B^{2+}, X^- for example one can consider that a quasi-lattice exists with the anions occupying the anion region of the lattice and the cations mixing on the cation portion of the lattice. For every B^{2+} ion added from BX to a solvent A_2X a "vacancy" is also added. If, as is reasonable, there is a very large "concentration of vacancies"

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*One obvious condition for which this is true is when the two cations and the two anions respectively have the same physical properties. In this case, for any given geometric configuration of the ions, the potential energy of the mixture (U_{mix}) is the same as the potential energy of any one of the salts (U_{ij}).

or "holes" in the solvent liquid, then the added hole at very low concentrations will have no effect on the properties of the solution just as the presence of a common ion in the solvent suppresses the effect of a solute ion on the limiting laws. The total ideal entropy of mixing would then be

$$\frac{-\Delta S_T}{R} = n_\mathrm{A} \ln N_\mathrm{A} + n_\mathrm{B} \ln N_\mathrm{B} \tag{I.4.1}$$

and

$$\left(\frac{\bar{S}_1 - S_1^0}{R}\right) = -\ln N_\mathrm{A}^2 \left(\frac{\bar{S}_2 - S_2^0}{R}\right) = -\ln N_\mathrm{B} \,, \tag{I.4.2}$$

where salt 1 is A_2X and salt 2 is BX. These equations will be valid as long as the "concentration of vacancies" in the solvent is large enough to buffer the added "vacancies." Equations (1) and (2) would hold for any valence types in such cases.

Førland has also considered the cases, analogous to those found in solid solutions, in which a divalent cation salt BX will dissolve in a monovalent cation salt A_2X by occupying one site and creating a vacant site. If the vacant site associates with the B^{2+} cation, then the cation lattice behaves as a mixture of monomers and dimers and an approximate expression stated by Førland and based on the calculations of the ideal entropy of mixing of molecules of different sizes[55,62] is

$$\frac{-\Delta S_T}{R} = n_\mathrm{A} \ln N'_\mathrm{A} + n_\mathrm{B} \ln N'_\mathrm{B} \,, \tag{I.4.3}$$

where N_i is an ion equivalent fraction of the ith ion.

$$N'_\mathrm{A} = \frac{n_\mathrm{A}}{n_\mathrm{A} + 2n_\mathrm{B}} \,, \qquad N'_\mathrm{B} = \frac{2n_\mathrm{B}}{n_\mathrm{A} + 2n_\mathrm{B}} \,,$$

$$\frac{-(\bar{S}_1 - S_1^0)}{R} = 2 \ln N'_\mathrm{A} + N'_\mathrm{B} \,, \tag{I.4.4}$$

$$\frac{-(\bar{S}_2 - S_2^0)}{R} = \ln N'_\mathrm{B} - N'_\mathrm{A} \,. \tag{I.4.5}$$

The assumption in Eqs. (3), (4), and (5) is that the divalent ion B^{2+} and the associated vacancy are twice as large as the A^+ cation so that the entropy of mixing of cations is that of the "dimer" (B^{2+}-vacancy) and the "monomer" A^+. Førland has discussed a small correction term to these expressions to account for the fact that at high B^{2+} concentrations, where more than one vacancy may be near a given B^{2+}, one cannot distinguish which one should be part of the "dimer." If the cation vacancy dissociates from the B^{2+} ion, then

$$\frac{-\Delta S_T}{R} = n_A \ln N'_A + n_B \ln N'_B , \tag{1.4.6}$$

$$\frac{\bar{S}_1 - S_1^0}{R} = -2 \ln N'_A , \tag{1.4.7}$$

$$\frac{\bar{S}_2 - S_2^0}{R} = -2 \ln N'_B . \tag{1.4.8}$$

Equations (7) and (8) have been derived for solid solutions and are probably not reasonable pictures of liquids where "vacancies" must exist even in the pure salts.

The very careful study of the $CaCO_3$-M_2CO_3 systems, where M = Na or K, by Førland and coworkers appeared to be inconsistent only with Eq. (6)[57,58] and were consistent with Eqs. (1) and (3).

Equations (1) through (8) are useful largely to obtain convenient forms for the expression of chemical potential and may be generalized for mixtures of ions with different valences. The large differences in the Coulombic interactions of ions of different valence make it improbable, except for very special cases, that the entropy expressions (1) through (8) will be valid over a large range of concentrations for real systems.

1.5 Standard States and Units of Concentration

As seen by the preceding paragraphs, reasonable concentration scales are the mole fraction, equivalent fraction, ion fraction, and ion equivalent fraction although this chapter will, generally, use mole and ion fractions. The mole ratio defined by $R_2 = n_2/n_1$, where n_2 and n_1 are the number of moles of solute and solvent, is sometimes convenient in dilute solutions when it differs little from a mole fraction. The molarity scale (moles/liter) is sometimes convenient in a case, for example, where experiments are compared with theoretical calculations made for a constant volume process. The expression of concentrations on a molality scale (moles/1000 g solvent), because of the large number of different solvents of different molecular weights, does not seem to be well-chosen if one wishes ultimately to compare phenomena in different solvents.

Some definitions of the activity and activity coefficients of, for example, the salt B_rX_s are

$$\mu_2 = \mu_2^0 + RT \ln a_2 = \mu_2^* + RT \ln a_2 = \mu_2^\square + RT \ln A_2^\square , \tag{1.5.1}$$

$$\gamma_2 = \frac{a_2}{N_B{}^r N_X{}^s} = \gamma_B{}^r \gamma_X{}^s , \tag{1.5.2}$$

$$\gamma_2' = \frac{a_2}{(N_B')^r \, (N_X')^s} = (\gamma_B')^r \, (\gamma_X')^s \, , \tag{1.5.3}$$

$$\gamma_2^* = \frac{a_2}{N_B{}^r \, N_X{}^s} = \gamma_B^{*r} \, \gamma_X^{*s} \, , \tag{1.5.4}$$

$$\gamma_2^{\square} = \frac{a_2^{\square}}{N_B{}^r \, N_X{}^s} = (\gamma_B^{\square})^r \, (\gamma_X^{\square})^s \, , \tag{1.5.5}$$

where the standard chemical potential μ_2^0 is the chemical potential of the pure liquid salt, μ_2^* is the chemical potential of a standard state chosen so that γ_2^* approaches unity as the concentration of all the solutes approaches zero, and $\mu_2^{\square}$ is the chemical potential of pure solid. It should be noted that the value of μ_2^* depends on the concentration scale used and unless otherwise stated, the definition of μ_2^* derived from the use of the ion fraction scale expressed in (4) will be used here.* For the comparison of the solution properties of different mixtures containing salts of different melting points, the most convenient standard state is the pure liquid (supercooled if necessary) since there will be no break in the temperature dependence of some of the derived activities at temperatures at which there are transitions in the solids. It is probably more meaningful to compare liquid solution properties of a component with those of the pure liquid component. The standard chemical potential μ_2^* is often conveniently used in dilute solutions. The usefulness of any chosen standard state should be measured by the ultimate ability to measure the value of μ in that state.

It should be noted that the single ion activity coefficients, γ_B, γ_X, γ_B^*, γ_X^*, etc., do not have a strict thermodynamic significance except as a product for the ions in a neutral species or as a quotient for ions with the same total charge. The use of single ion activity coefficients may often be confusing and should be avoided if possible.

Excess chemical potentials may be defined by

$$\mu_2^E = RT \ln \gamma_2 \, . \tag{1.5.6}$$

By considering the equality

$$\mu_2^* - \mu_2^0 = RT \ln \frac{\gamma_2}{\gamma_2^*} \, , \tag{1.5.7}$$

then since γ_2^* approaches 1 as the concentration of B^{+s} and X^{-r} ions both approach zero, $\mu_2^* - \mu_2^0$ is the excess chemical potential of the salt B_rX_s at infinite dilution and may be termed an excess chemical potential of pure liquid B_rX_s at infinite dilution.

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*To convert from one scale to the other, the relations μ_2^* (mole fraction) $= \mu_2^*$ (molarity) $- RT \ln V_1 = \mu_2^*$ (molality) $+ RT \ln (1000/M_1)$ may be used, where V_1 is the volume of one mole of solvent and M_1 is the gram molecular weight of the solvent.

SOLUTIONS WITH COMMON ANIONS OR COMMON CATIONS

II.1 Cryoscopic Methods of Investigation

The limiting laws have been investigated mainly by cryoscopy and with emf measurements. A description of the theory and experimental applications of these methods is given in sections II.1 and II.2.

Cryoscopic measurements have been made from thermal halts, visual observations, and by filtration and analysis of solutions at equilibrium with a solid. For an equilibrium between a pure solid A_rX_s (component 1) and a liquid mixture

$$\frac{d \ln a_1}{d(1/T)} = \frac{d \ln N_A{}^r N_X{}^s}{d(1/T)} + \frac{d \ln \gamma_1}{d(1/T)} = -\frac{\Delta H_f}{R}, \qquad \text{(II.1.1)}$$

where ΔH_f is the enthalpy of fusion of A_rX_s and a_1 is the activity of the component A_rX_s in a solution at equilibrium with the pure solid at the temperature T. This relation may be re-expressed for the solubility of a slightly soluble salt A_rX_s.

$$\frac{d \ln a_2}{d(1/T)} = \frac{d \ln N_A{}^r N_X{}^s}{d(1/T)} + \frac{d \ln \gamma_2^*}{d(1/T)} = -\frac{(\bar{H}_2^* - H_2^\square)}{R}, \qquad \text{(II.1.2)}$$

where $(\bar{H}_2^* - H_2^\square)$ is the heat of the solution of solid A_rX_s to infinite dilution. In general, γ_1 and γ_2^* are not constant except in solutions dilute enough for the limiting laws to apply, and they must be known in order to evaluate ΔH_f and $(\bar{H}^* - H^\square)$ from cryoscopic or solubility measurements. The term ΔH_f is a function of temperature:

$$\Delta H_f = \Delta H_f^0 - \int_T^{T^0} \Delta C_p \, dt, \qquad \text{(II.1.3)}$$

where ΔH_f and ΔH_f^0 are the heats of fusion at the temperatures T and the melting temperature T_0 respectively and $\Delta C_p = C_p(\text{liq}) - C_p(\text{solid})$. If the heat capacities of the pure solid and the pure liquid A_rX_s can be expressed by

$$C_p = a + bT + cT^{-2};$$

then

$$\Delta C_p = \Delta a + T\Delta b + \frac{\Delta c}{T^2}. \qquad \text{(II.1.4)}$$

By introducing Eq. (1) and integrating one obtains

$$\ln a_1 = \frac{-\Delta H_f^0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \Delta a\left(\frac{T_0}{T} - 1 - \ln\frac{T_0}{T}\right)$$

$$+ \frac{\Delta b}{2}\left(\frac{T_0^2}{T} - 2T_0 + T\right) + \frac{\Delta c}{2R}\left(\frac{1}{T^2} - \frac{1}{T_0^2}\right). \qquad \text{(II.1.5)}$$

The considerable deviations from ideality of most mixtures of molten salts make it essential that ΔH_f be obtained from calorimetric measurements except for a limited number of cases. The use of phase diagrams to obtain a "cryoscopic" heat of fusion under the assumption of ideal solution behavior has been shown to be often in error.[45,73] The terms containing the correction for ΔC_p must be included in a calculation of a_1 from measurements of the liquidus temperature. For example, if $\Delta C_p = 2$ cal/deg mole at all temperatures and $T_0/T = 1.2$, the error in a_1 would be about 2% if the ΔC_p correction were excluded. For $T_0/T = 1.5$ the error is about 10%, and when $T_0/T = 2$ the error in a_1 is about 31%. Since the values for the heat capacity for pure liquid have to be extrapolated below the melting point, any errors in the extrapolation can be appreciable at large values of T_0/T. Table 1 gives a summary of selected values of ΔH_f^0 and the parameters for C_p for solid and liquid.[45,73]

Cryoscopic measurements have been used to test the limiting law expressed by Eq. (I.2.8). Combining Eqs. (I.2.8) and (5) and expanding the logarithms in the relation obtained, one obtains the van't Hoff relation,

$$\Delta T \simeq \frac{RT_0^2}{\Delta H_f} \nu N_2 = (T_0 - T)\,, \tag{II.1.6}$$

for small values of N_2 and for values of ΔT small relative to T_0. Equation (6) has been used to investigate the limiting laws in many systems. The freezing point lowering of $NaNO_3$ by NaCl obeys Eq. (6) to about 7 mole % of NaCl for $\nu = 1$.[129,130] The compounds Na_2CO_3, Na_2SO_4, $NaBrO_3$, Na_2WO_4, Na_2MO_4, $Pb(NO_3)_2$, and $LiNO_3$ also gave apparent values of $\nu = 1$ in $NaNO_3$; KIO_4, LiCl, and CsCl led to values of $\nu = 2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ led to apparent values of $\nu = 3$, and $LaCl_3$ to $\nu = 4$ in $NaNO_3$.[*,129] In molten $AgNO_3$ the solutes Ag_2SO_4, KNO_3, and $Pb(NO_3)_2$ led to values of $\nu = 1$, and $PbCl_2$, $K_2Cr_2O_7$, $HgCl_2$, $HgBr_2$, and HgI_2 led to values of $\nu = 3$.[80] In molten KNO_3 the limiting law has been demonstrated for a number of cases, mostly at concentrations of solute less than 1 mole %.[80] And Na_2SO_4 in a solution with NaCl and NaBr obeys the limiting law[52] and Eq. (I.2.8) at all concentrations.

II.2 Electromotive Force Measurements

Measurements have been made in concentration cells with liquid junctions such as

$$\mathrm{A}\left|\begin{array}{l}\mathrm{AX}_n(N_2')\\ \mathrm{BX}\end{array}\right\|\left.\begin{array}{l}\mathrm{AX}_n(N_2)\\ \mathrm{BX}\end{array}\right|\mathrm{A}\,. \tag{II.2.A}$$

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[*] It should be noted that in most other cases of systems consisting of a solvent containing a foreign cation and a foreign anion, deviations from ideality are large at the lowest concentrations of the studies cited so that the limiting laws cannot be tested.

Table 1. Melting Points, Heats of Fusion, and Heat Capacities of Some Salts[45,73]
$(C_p = a + bT + c/T^2)$

Composition	T_m (°K)	H_f or H_{tr} (kcal/mole)	C_p(solid)			C_p(liq)
			a	$b \times 10^3$	$c \times 10^{-5}$	a
LiF	1121	6.47	10.41	3.90	− 1.38	15.50
LiCl	883	4.76	(11.00)[a]	(3.40)		
LiBr	823	4.22	(11.50)	(3.02)		
LiI	742	3.50	(12.30)	(2.44)		
$LiNO_3$	525	6.12	14.98	21.20		26.60
NaF	1268	8.03	10.40	3.88	− 0.33	16.40
NaCl	1073	6.69	10.98	3.90		16.00
NaBr	1020	6.24	11.87	2.10		
NaI	933	5.64	(12.50)	(1.62)		
$NaNO_3(\alpha)$	549(Tr)	0.81(Tr)	6.34	53.32		
$NaNO_3(\beta)$	579	3.49	35.70			37.00
KF	1131	6.75	11.88	2.22	− 0.72	16.00
KCl	1043	6.34	9.89	5.20	0.77	16.00
KBr	1007	6.10	10.65	4.52	0.49	
KI	954	5.74	11.36	4.00		
$KNO_3(\alpha)$	401(Tr)	1.40(Tr)	14.55	28.40		
$KNO_3(\beta)$	611	2.80	28.80			29.50
RbF	1068	6.15	(11.33)	(2.55)		
RbCl	995	5.67	(11.50)	(2.49)		
RbBr	965	5.57	(11.89)	(2.22)		
RbI	920	5.27	(11.93)	(2.27)		
CsF	976	5.19	(11.30)	(2.71)		
CsCl	918	4.84	(11.90)	(2.28)		
CsBr	909	5.64	(11.60)	(2.59)		
CsI	899	5.64	(11.60)	(2.68)		
AgCl	728	3.08	14.88	1.00	− 2.70	16.00
AgBr	703	2.19	7.93	15.40		14.90
$AgNO_3(\alpha)$	433(Tr)	0.61(Tr)	8.76	45.20		
$AgNO_3(\beta)$	484	2.76	25.50			30.60

[a] Numbers in parentheses are estimated values (K1).

The emf of the cell can be given by

$$\Delta E = \frac{RT}{nF} \ln \frac{a_2}{a_2'} + \Delta\phi_{\mathrm{diff}} , \qquad \text{(II.2.1)}$$

where $\Delta\phi_{\mathrm{diff}}$ is the diffusion potential and the prime (′) denotes the left-hand electrode. In a binary system, all that need be known in order to evaluate a_2/a_2' from the emf of cell (A) are the Hittorf transference numbers of the components. For a system containing more than two components, the gradients of concentration for each component across the liquid junction between the left- and right-hand compartments need also be known.

To give an idea of the magnitude of $\Delta\phi_{\text{diff}}$ for salts containing only monovalent ions for example, let us consider the approximate equation for mixtures of AX and BX dilute in AX

$$\Delta\phi_{\text{diff}} = \frac{RT}{F}\left(\frac{b_{\text{AX}} - b_{\text{BX}}}{b_{\text{BX}}}\right)(N_2 - N_2') = \frac{RT}{F}\frac{b_{\text{AB}}}{b_{\text{BX}}}(N_2 - N_2') \,, \tag{II.2.2}$$

where b_{ij} is the mobility of the ion of species i relative to j. We may cite three pertinent examples:

1. The ion A^+ interacts so strongly with X^- that it has a low mobility relative to $\text{X}^-(b_{\text{AX}} \simeq 0)$. In this case $\Delta\phi_{\text{diff}}$ is small only when $(N_2 - N_2')$ is small.
2. The relative mobilities of A^+ and B^+ are the same. In this case $\Delta\phi_{\text{diff}}$ is zero.[83]
3. The A^+ ion is relatively more mobile than the B^+ ion. If $b_{\text{AX}} = mb_{\text{BX}}$, then

$$\Delta\phi_{\text{diff}} \simeq \frac{RT}{F}(m-1)(N_2 - N_2') \,. \tag{II.2.3}$$

If m is large, one must be especially careful to either correct for $\Delta\phi_{\text{diff}}$, or to work in extremely dilute solutions.

For solutions dilute enough so that $\Delta\phi_{\text{diff}}$ is small, then the emf of the Daniell cell

$$\text{A}\left|\begin{array}{l}\text{AX}_n\\ \text{BX}\end{array}\right|\left|\begin{array}{l}\text{CX}_m\\ \text{BX}\end{array}\right|\text{C} \tag{II.2.B}$$

is given by

$$\Delta E = \Delta E^* + \frac{RT}{F}\ln\frac{\left(a_{\text{CX}_m}\right)^{1/m}}{\left(a_{\text{AX}_n}\right)^{1/n}} \,, \tag{II.2.4}$$

where

$$\Delta E^* = +\left(\frac{RT}{mF}\mu^*_{\text{CX}_m} - \frac{RT}{nF}\mu^*_{\text{AX}_n}\right) \,.$$

For cells of the type

$$\text{A}\left|\begin{array}{l}\text{BX (solid)}\\ \text{AX }(N_{\text{X}}')\\ \text{AY}\end{array}\right|\left|\begin{array}{l}\text{BX (solid)}\\ \text{AX }(N_{\text{X}})\\ \text{AY}\end{array}\right|\text{A} \tag{II.2.C}$$

in which BX is very insoluble and for concentrations of solutes low enough so that $\Delta\phi_{\text{diff}}$ can be neglected, the emf can be expressed by

$$\Delta E = -\frac{RT}{F}\ln\frac{a_{\text{AX}}}{a_{\text{AX}}'} \,, \tag{II.2.5}$$

where a_{AX}' denotes the activity of AX in the left-hand electrode.

At concentrations where $\Delta\phi_{\mathrm{diff}}$ is negligible and low enough for the limiting laws to apply, the emf of concentration cells (A) and (C) obey the Nernst equation

$$\Delta E = \pm \frac{RT}{nF} \ln \frac{N_{\mathrm{AX}}}{N'_{\mathrm{AX}}}, \tag{II.2.6}$$

and cell (B) will obey the equation

$$\Delta E = \Delta E^{*} + \frac{RT}{F} \ln \frac{(N_{\mathrm{CX}_m})^{1/m}}{(N_{\mathrm{AX}_n})^{1/n}}. \tag{II.2.7}$$

The validity of Eqs. (6) and (7) are proof of the validity of Eq. (I.2.9) for the solute. Many examples of concentration cells and Daniell cells exist in the literature which illustrate the limiting Nernst laws up to concentrations at least as high as 0.5 mole % and often for solutes of the same valence type to more than 1 mole %. Some examples are $AgNO_3$ in $NaNO_3$-KNO_3,[46,60] in $NaNO_3$ (Fig. 1)[70] and in KNO_3;[11] AgCl, $CoCl_2$, $PbCl_2$, $ZnCl_2$, $NiCl_2$, $CdCl_2$, TlCl, CuCl,

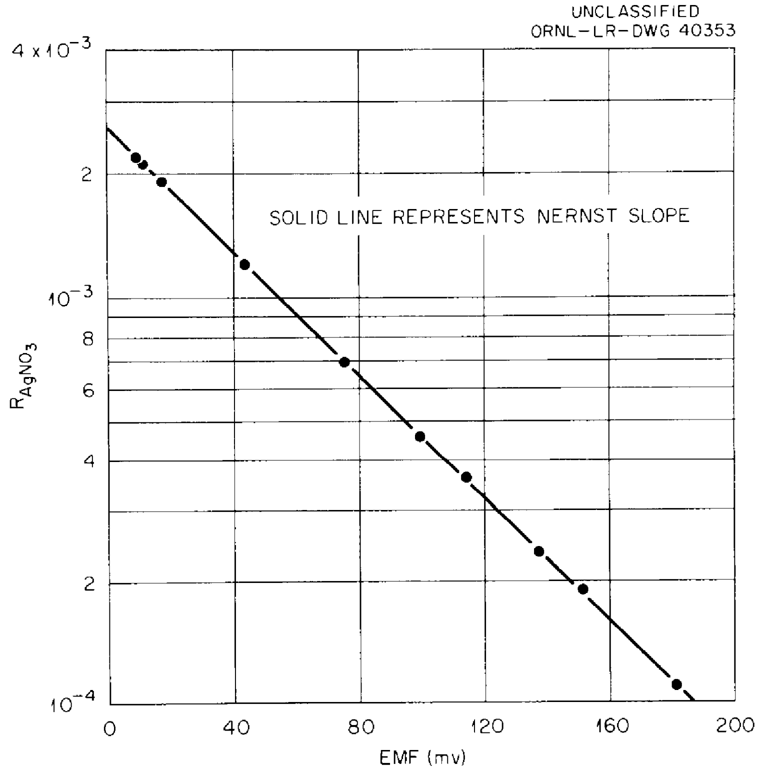

Fig. 1. Demonstration of the Nernst Equation in $AgNO_3$-$NaNO_3$ Mixtures from the Cell

$$\mathrm{Ag} \left| \begin{array}{c} \mathrm{AgNO_3}(N_1') \\ \mathrm{NaNO_3} \end{array} \right| \left| \begin{array}{c} \mathrm{AgNO_3}(N_1) \\ \mathrm{NaNO_3} \end{array} \right| \mathrm{Ag}\,.$$

$CrCl_2$, $MnCl_2$, $FeCl_2$, and $SnCl_2$ in NaCl-KCl mixtures;[47,48] and $PtCl_2$, $PdCl_2$, $BiCl_3$, AgCl, $NiCl_2$, CuCl, $PbCl_2$, $FeCl_2$, $CdCl_2$, and TlCl in LiCl-KCl mixtures.[82] From cells of type (C) the Nernst law, with silver solid-silver-halide electrodes, has been demonstrated for KCl in $LiNO_3$-KNO_3,[22] KBr and KI in KNO_3 and in $NaNO_3$-KNO_3 mixtures.[25]

These illustrations indicate that for mixtures with a common anion the solvents obey Raoult's law and the solute obeys Henry's law in dilute solutions,* even for solutes with polyvalent cations. The high concentrations of charges in a molten salt, composed of monovalent ions, apparently swamps out or partially cancels the high local-charge density of a given polyvalent cation and, in a sense, the solvent must behave like a medium of very high dielectric constant in cases where the solution contains only one anion. These cases in dilute solutions also indicate that the effect of any "holes" introduced into the solvent by the addition of polyvalent cations is suppressed by the presence of "holes" in the solvent. Although a molten salt seems to be a highly concentrated ionic solution if the solvent ions are included, the effects of the solvent on the ionic solutes having a common anion seem to be such as to make the properties of these solutions simpler in less dilute solutions, than is the case with water or other non-electrolytes as a solvent for salts. Similar checks of the limiting laws for ionic solvents containing polyvalent ions are unavailable. Although measurements do not appear to lead to results of interest in fairly dilute solutions, measurements in concentrated solutions are of more interest.

II.3 Strongly Ionic Salts Containing Monovalent Cations and a Common Anion

The most revealing experimental work on mixtures of salts with monovalent ions are the calorimetric measurements of the molar enthalpies of mixing of the alkali nitrates by Kleppa,[76] and Kleppa and Hersh.[78] Although the alkali nitrates cannot be considered as good a prototype of an ionic salt as the alkali halides, they are analogous to the alkali halides.

The molar enthalpy of mixing of two salts 1 and 2 is given by

$$\Delta H_m = N_1(\overline{H}_1 - H_1^0) + N_2(\overline{H}_2 - H_2^0) , \tag{II.3.1}$$

where $\overline{H}_1$ and $\overline{H}_2$ are the partial molar enthalpies of components 1 and 2. Enthalpies of mixing of all of the ten possible mixtures of alkali nitrates were reported with measurements for seven of the mixtures being reported in detail. In Figs. 2–4 are plotted some typical data for ΔH_m and $\Delta H_m/N_1N_2$. The data may be represented by the expression

$$H_m = N_1N_2(a + bN_1 + cN_1N_2) . \tag{II.3.2}$$

In Table 2 a summary of the values of a, b, and c representing the data is given.

All of the observed enthalpies of mixing in mixtures of alkali nitrates are negative and are more negative the greater the separation of the two alkali metals in the periodic system (and

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*Molality is about an order of magnitude larger than mole or ion fraction in these cases. By standards used for aqueous solutions, these are concentrated solutions.

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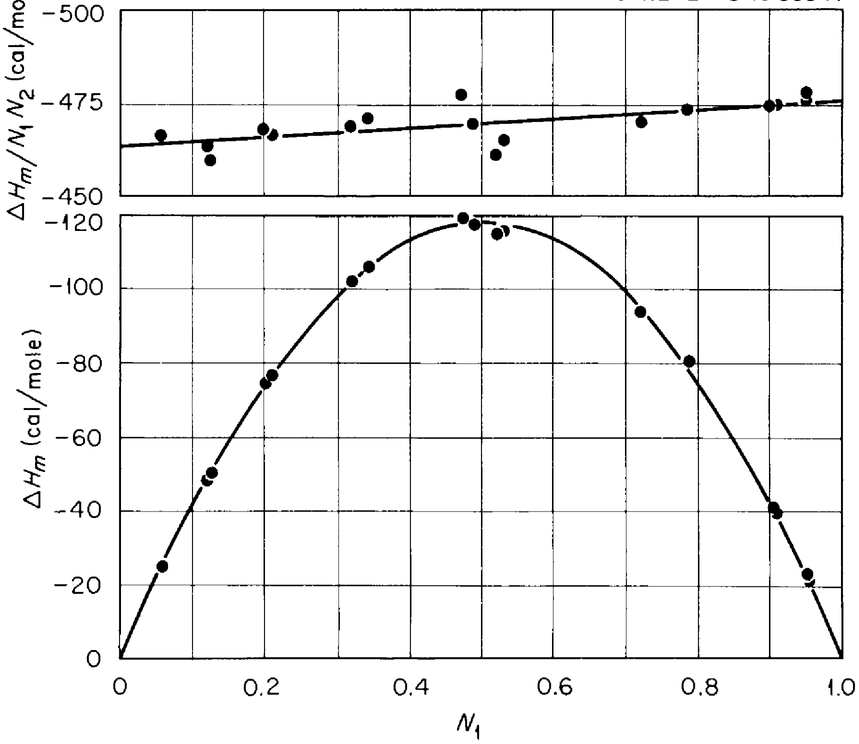

Fig. 2. Total Molar Heats of Mixing (ΔH_m) in $NaNO_3LiNO_3$ Mixtures ($LiNO_3$ Is Component 1).

also the greater the difference in size of the two cations). In all the systems an *energetic asymmetry* in the enthalpies of mixing is present so that for a given pair of nitrates, the value of ΔH_m is more negative in a mixture dilute in the large-cation nitrate than in a mixture dilute in the small-cation nitrate. The parameter b is a measure of the *energetic asymmetry*. Assuming that the form of Eq. (2) is correct, then the partial molar enthalpies are given by

$$\bar{H}_1 - H_1^0 = (a + 2b - c)N_2^2 + (4c - 2b)N_2^3 - 3cN_2^4 , \tag{II.3.3}$$

$$\bar{H}_2 - H_2^0 = (a - b - c)N_1^2 + (2b + 4c)N_1^3 - 3cN_1^4 , \tag{II.3.4}$$

at $N_2 = 1$, $\bar{H}_1 - H_1^0 = a$, and $N_1 = 1$, $\bar{H}_2 - H_2^0 = (a + b)$, where component 1 has a smaller cation than component 2. Since both the a and the b are negative, the partial molar enthalpy of solution can be seen to be asymmetric. Only for systems in which the absolute value of ΔH_m is small does it appear that the parameter c is negligible and that the term containing the concentrations to the fourth power are not necessary to represent the data.

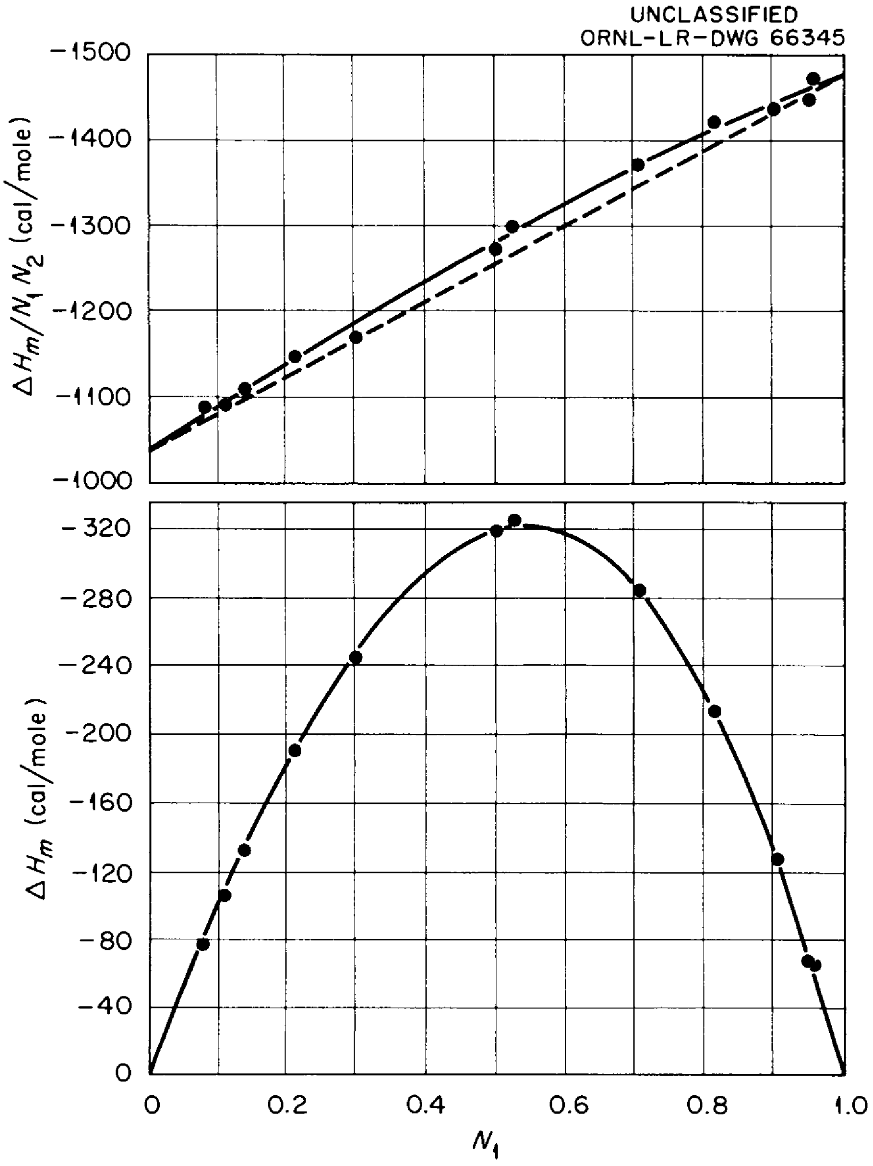

Fig. 3. Total Molar Heats of Mixing (ΔH_m) in $CsNO_3$-$NaNO_3$ Mixtures ($NaNO_3$ Is Component 1).

Kleppa, by using the enthalpy of mixing of 50-50 mixtures of the nitrates as a measure of the magnitude of the effect, demonstrated the empirical relation

$$4\Delta H_m^{0.5} \cong U\left(\frac{d_1 - d_2}{d_1 + d_2}\right)^2 = U\delta^2 = -140\delta^2 \,, \tag{II.3.5}$$

where $\delta = (d_1 - d_2)/(d_1 + d_2)$, and d_i is the sum of the radii of the cation and anion indicated, and U is about −140 kcal. The value of U is about the same magnitude as the lattice energy of

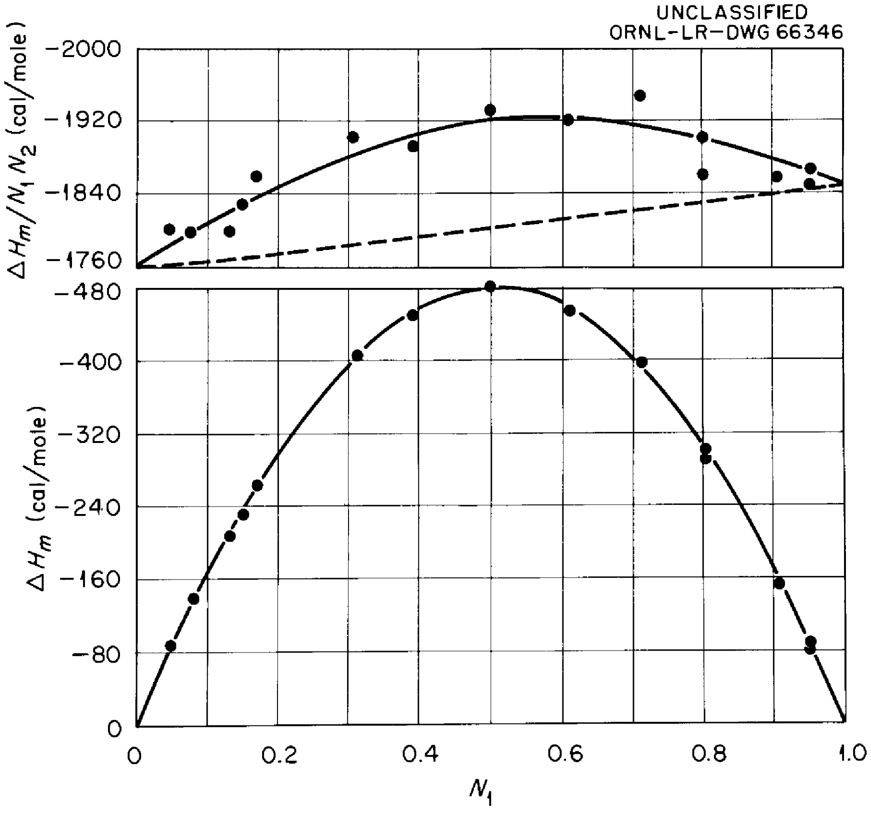

Fig. 4. Total Molar Heats of Mixing (ΔH_m) in KNO_3-$LiNO_3$ Mixtures ($LiNO_3$ Is Component 1).

the alkali nitrates. The results of Kleppa may be rationalized in terms of simple concepts. Since the simplest binary mixtures are those containing monovalent cations and anions, simple solution theories are more likely to apply to these mixtures than to mixtures containing polyvalent ions.

Although some of the relations discussed below will be naive, they will serve the main objective of this discussion, which is to relate the solution behavior of molten salts to fundamental physical laws.

As discussed in a previous section, a molten salt may be compared to a quasi-lattice. Because of the alternation of charge, the quasi-lattice consists of two sublattices, one of cations, and the other of anions which interlock so that the anions have cations as nearest neighbors and the cations have anions as nearest neighbors. For a mixture of salts with a common anion, the cation sublattice may be considered as being imbedded in a sea of anions. The anions are not excluded from consideration, since the cation environment of a given anion will greatly affect its relative position and energy. Since the solute and solvent in a mixture both have the same anions as nearest neighbors as they do in the pure state, any solution effects are caused by ions further away although these ions further away may, indirectly, affect the nearest-neighbor anions.

Table 2. A Summary of the Parameters *a*, *b*, and *c* Derived from the Heat of Mixing Data for Binary Nitrate Systems

System	*T* (°C)	*a* (cal/mole)	*b* (cal/mole)	*c* (cal/mole)
(Li-Na)NO_3	345	−464	−11.5	~0
(Li-K)NO_3	345	−1759	−87	−463
(Li-Rb)NO_3	345	−2471	−178	−945
(Li-Cs)NO_3	450	(−3000)[a]		
(Na-K)NO_3	345–450	−408.5	−68	~0
(Na-Rb)NO_3	345	−744.5	−268	−36
(Na-Cs)NO_3	450	−1041	−435	−93
(K-Rb)NO_3	345	(−60)		
(K-Cs)NO_3	450	−89.5	−87.5	~0
(Rb-Cs)NO_3	450	(−14)		
(Li-Ag)NO_3	350	702	−108	0
(Na-Ag)NO_3	350	677	−156	0
(K-Ag)NO_3	350	−303	−294	0
(Rb-Ag)NO_3	350	−944	−337	−297
(Li-Tl)NO_3	350	−901	178	−294
(Na-Tl)NO_3	350	131	241	~0
(K-Tl)NO_3	350	447	−17	~0
(Rb-Tl)NO_3	350	240	−15	~0

[a] Parentheses indicate uncertain data.

Molten-salts solutions differ from solid-salt solutions in an important respect. In order to place a large cation in solution in a solid salt having a small cation the structure near the foreign cation must be distorted. In a solid, such a distortion is difficult as evidenced by the rigidity of the lattice. Although there is some ability of the ions in a solid to adjust their positions to minimize the energy,[44] the net effect is that the enthalpy of mixing of ionic solids is positive, and there is a strong tendency for ionic solids having a common anion to be mutually insoluble if the cations are very different in size. The structures of molten salts are much less rigid, and the salt can easily accommodate cations of different size.

The theory which can most easily be applied to mixtures of molten salts with monovalent ions is the quasi-chemical theory of Guggenheim[63] which is based on a quasi-lattice model. Since it may safely be assumed that cations almost exclusively have anions as nearest neighbors in a solution containing only one kind of anion, all the nearest neighbors of the cations will be the same as in the pure salts, and solution effects will be caused by ions further away than nearest nieghbors. The nearest cation neighbors which are next nearest neighbors in the salt quasi-lattice might be considered as a first approximation.

If salt 1 is AX and salt 2 is BX, then the potential energy of the ion triplet $A^+X^-A^+$ may be designated by V_{11}, of $B^+X^-B^+$ by V_{22} and of $A^+X^-B^+$ by V_{12}.[78] To validly apply the quasi-chemical theory to the model, V_{11}, V_{22}, and V_{12} must be assumed independent of the local environment of the ionic triplets. Although this assumption is not correct, it may serve as an initial working hypothesis. The molar excess free energy of solution and molar heat of mixing of solution as calculated from the quasi-chemical theory will be given by[68]

$$\frac{\Delta A^E}{RT} = N_1 N_2 \lambda \left(1 - N_1 N_2 \frac{\lambda}{Z'RT} + \ldots\right), \tag{II.3.6}$$

$$\frac{\Delta H_m}{RT} = N_1 N_2 \lambda \left(1 - N_1 N_2 \frac{2\lambda}{Z'RT} + \ldots\right), \tag{II.3.7}$$

where $\lambda = (\mathfrak{N} Z'/2)(2V_{12} - V_{11} - V_{22}) = \mathfrak{N} Z'\Delta\epsilon'/2$, $\mathfrak{N}$ is Avogadro's number, and Z' is the number of cation next-nearest neighbors of a cation.

Førland[57,58] has discussed the quantity $(2V_{12} - V_{11} - V_{22}) \equiv \Delta\epsilon'$ in terms of the change of the repulsions of next-nearest-neighbor cations. Førland represents the configuration of next-nearest-neighbor cations and a nearest-neighbor anion as in Fig. 5 and calculates the Coulombic energy change, $\Delta\epsilon_c$, for mixing the cations in these two arrays of three hard spherical ions.

$$\Delta\epsilon_c = -e^2 \left(\frac{1}{d_1} + \frac{1}{d_2}\right)\left(\frac{d_1 - d_2}{d_1 + d_2}\right)^2, \tag{II.3.8}$$

where e is the electronic charge. The term $-e^2[(1/d_1) + (1/d_2)]$, for a real ionic salt, can be related to the average lattice energy of the two salts composing the mixture and is analogous to the

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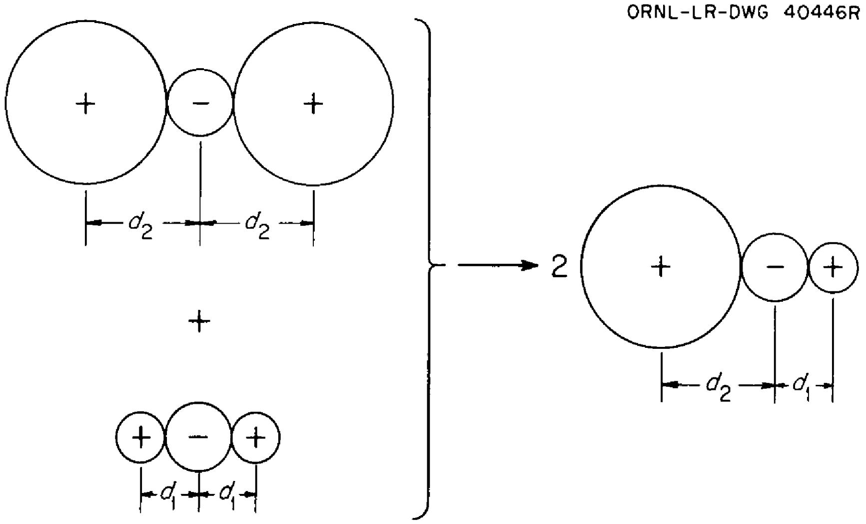

Fig. 5. Configuration of Ions for the Calculation of Førland on the Change of Repulsions of Next-Nearest Neighbors.

empirical parameter U in Eq. (5). $\Delta\epsilon_c$ is always negative and tends to be more negative the greater the differences in the cationic radii. Except for small factors the form of Eq. (8) is obviously related to the empirical relation (5).

Blander[15] has extended Førland's calculations to a hypothetical salt mixture which is extremely dilute in one component and which is represented by an infinite linear array of hard-charged spheres. Although this model is unrealistic for a real three-dimensional salt, it does serve to assess the effect of Coulombic interactions of longer range than the next-nearest neighbors. The inset of Fig. 6 is a picture of a portion of the solution of one mole of the solute with an interionic distance d_2 in an infinite amount of solute. In Fig. 6 are plotted calculated values of $-\Delta\epsilon_c d_1/e^2$ vs Δ, where $d_2 = d_1(1 + \Delta)$, and where $\Delta\epsilon_c$ is the energy of mixing per molecule of solute. The values of $\Delta\epsilon_c$ are always negative and become more negative the greater the value of Δ and are only about 0.4 times the magnitude of the values calculated from Førland's simple model. If the mutual dissolution of two salts 1 and 2 where salt 1 has the smaller cation is considered, then Blander's calculation indicates that a dilute solution of 2 in 1 will lead to a more negative value of $\Delta\epsilon_c$ than for a dilute solution of 1 in 2. Since Førland's calculation predicts a symmetry in the energy of mixing, the effect of the long-range interactions is to decrease the total calculated value of $|\Delta\epsilon_c|$ and to lead to a small asymmetry in the energy of solution. The asymmetry effect means that the parameter λ cannot be independent of composition.

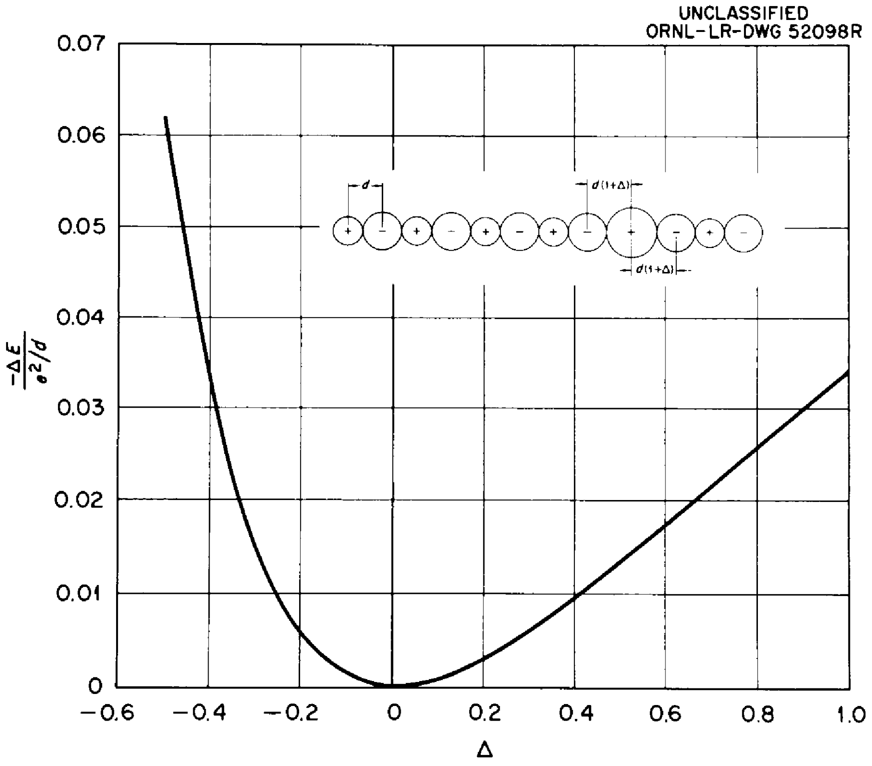

Fig. 6. Values of the Energy of Solution at Infinite Dilution (ΔE) in Units of (e^2/d) Calculated from an Infinite One-Dimensional Solidlike Model.

Care must be taken not to ascribe the observed negative deviations from ideal solution behavior or an asymmetry to only Coulombic effects. For example, polarization may also contribute to the energy of solution. The ions in the solid-like linear model for the pure salt have no field on them, but in the mixture represented in the inset of Fig. 6 there is an appreciable field intensity on some of the ions which can polarize the ions.

Lumsden[91] has calculated the effect of polarization of the anions by the cations in terms of a one-dimensional model essentially including only nearest-neighbor and next-nearest-neighbor ions. He obtained the relation

$$\Delta\epsilon_p = \frac{\alpha F^2}{2} \propto - \alpha e^2 \left(\frac{1}{d_1} + \frac{1}{d_2}\right)^4 \left(\frac{d_1 - d_2}{d_1 d_2}\right)^2 , \qquad \text{(II.3.9)}$$

where F is the field intensity on an anion between two cations of different size, and α is the polarizability of the anion. Polarization of cations, which may not be small, has been neglected. Equation (9) is the same form as (5) and (8), and $\Delta\epsilon_p$ is negative so that it should be difficult to separate the purely Coulomb interactions from polarization interactions without a valid calculation of the relative magnitude of these two interactions. However, any simple extension such as was made by Lumsden[91] to three dimensions of a one-dimensional model for either the Coulomb or polarization interactions may lead to misleading values for their relative magnitudes.

If the solute in Fig. 6 is salt 2 in the solvent 1 where cation 2 is larger than 1, then the field intensity on the anions adjacent to the solute cation is greater than if the solute is salt 1 and the solvent salt 2. For polarizable anions, this would make the energy of mixing more negative and contribute to the asymmetry effect. If thermal motions are considered, then the tendency of ions to reside longer in regions of high field intensity will also contribute to the asymmetry being in a sense a "positional" polarization. If these simple considerations are valid for a real three-dimensional salt, then at least part of the asymmetry effect is related not only to Coulombic but also to polarization interactions by ions more distant than next-nearest neighbors. In any theory of molten-salt mixtures it appears to be necessary, then, to include long-range interactions, except under very special conditions.

The comparison of the measurements with the concepts discussed is straightforward. As discussed, the parameter λ for a molten salt in (7) is not independent of composition and Kleppa[78] has approximated the effective value of λ as a linear function of composition.

$$\lambda = a' + b'N_1 , \qquad \text{(II.3.10)}$$

so that for values of $-\lambda$ small relative to $Z'RT$, Eq. (7) becomes

$$\Delta H_m = N_1 N_2 (a' + b'N_1) , \qquad \text{(II.3.11)}$$

which is the form of the experimental results in the three systems studied by Kleppa which exhibit the smallest deviations from ideal solution behavior.

For values of $-\lambda$ not too small, Eqs. (7) and (10) lead to

$$\Delta H_m \cong N_1 N_2 \left[a' + b'N_1 - 2N_1 N_2 \frac{(a' + b'N_1)^2}{Z'RT} \right] . \qquad (II.3.12)$$

Comparison with Eq. (II.3.2) shows that c can be identified with $-2\lambda^2/Z'RT$. The precision of the measurements is not high enough to detect a change of c with composition. By using an average value of λ,

$$\bar{\lambda} = a + b/2 ,$$

as a measure of λ, Kleppa showed that a plot of c vs $\bar{\lambda}^2/RT$ for the systems (Na-Rb)NO_3, (Na-Cs)NO_3, (Li-K)NO_3, and (Li-Rb)NO_3 is consistent with a reasonable range of values of Z' of 10 to 12. This is the number of next-nearest neighbors in an NaCl type lattice and is only a small variance with the number of next-nearest neighbors in some molten alkali halides.[87]

Equation (II.3.11) corresponds to the random mixing of the cations on the cation sublattice. The presence of the c term, if λ varies linearly with composition, implied an appreciable non-random mixing of the cations, and c was termed a short-range order parameter by Kleppa.[78]

It should be made clear that although the results of Kleppa have been rationalized in terms of the modified quasi-chemical theory, a fundamental premise of the quasi-chemical theory is that λ is independent of composition. Consequently, the form of the theoretical equations derived, based upon the quasi-chemical theory, although in correspondence with the empirical Eq. (2), requires a sounder theoretical justification.

A justification of the form of the empirical Eq. (2) has been made by the methods in the elegant work of Reiss, Katz, and Kleppa.[110] They used a method, which is essentially an adaptation of the theory of conformal solutions,[88] in which no model is used. The derivation was made for ions behaving as hard-charged spheres with a sum of radii equal to d so that the pair potential

$$u(r) = \infty , \qquad r \leqq d , \qquad (II.3.13a)$$

$$u(r) = \frac{\pm Ze^2}{\kappa r} , \qquad r > d , \qquad (II.3.13b)$$

where r is the distance between the two ions in any given pair, and κ is a dielectric constant which is assumed constant for a set of salts with a common anion. The potential function can be generalized to the form for a monovalent salt

$$u(r) = \pm \frac{1}{d} f(r/d) , \qquad r > d . \qquad (II.3.14)$$

This is a less-stringent condition than (13b). Because of the relative rarity of anion-anion contacts (except in salts as LiI), or cation-cation contacts, the contribution to the configurational integral of configurations in which ions of the same charge are touching (or almost touching) is very small and is neglected. As a consequence, except in these rare configurations, the total contribution to the potential energy of a given configuration due to cation-cation or anion-anion interactions is independent of small differences in the cation size, and only one parameter of length d for the sum of the radii of a cation-anion pair is necessary for the description of a pure salt. For a mixture of salts, two parameters are necessary, d_1 and d_2.

In the derivation of the theory, a single-component reference salt with the single parameter of length d is transformed into either component 1 or 2 by varying d. If $g_i = d/d_i$ where $i = 1$ or 2, then the configuration integral for the pure salt i is

$$Z_i = Z(g_i) = \int \cdots \int \frac{e^{-BU_i}}{(\bar{n}!)^2} (d\tau)^{2\bar{n}} , \qquad \text{(II.3.15)}$$

where U_i is the potential energy of the $2\bar{n}$ ions ($\bar{n}$ cations + $\bar{n}$ anions). Since the cation-anion pair potential is

$$u_i(r) = \frac{1}{d_i} f\left(\frac{r}{d_i}\right) = g_i u(g_i r) , \qquad \text{(II.3.16)}$$

then the total potential

$$U_i = \sum_{\mathrm{A}}^{\bar{n}} \sum_{\mathrm{C}}^{\bar{n}} g_i u_{\mathrm{AC}}(g_i r) + \sum_{\mathrm{A}<}^{\bar{n}} \sum_{\mathrm{A}'}^{\bar{n}} u_{\mathrm{AA}'} + \sum_{\mathrm{C}<}^{\bar{n}} \sum_{\mathrm{C}'}^{\bar{n}} u_{\mathrm{CC}'} , \qquad \text{(II.3.17)}$$

where A represents anions, C cations, and the symbols $\mathrm{A} < \mathrm{A}'$ and $\mathrm{C} < \mathrm{C}'$ signify that the pair potentials are added in a manner so that no pair is counted more than once. The molar Helmholtz free energy,* A_i for pure salt i can be expressed as a series

$$-\frac{A_i}{kT} = \ln Z_i = \ln Z(g_i) = (\ln Z)_{g=1} + (g_i - 1)\left(\frac{\partial \ln Z}{\partial g_i}\right)_{g_i=1} + \frac{(g_1 - 1)^2}{2}\left(\frac{\partial^2 \ln Z}{\partial g_i^2}\right)_{g_i=1} + \ldots , \qquad \text{(II.3.18)}$$

---

*Only the configurational part of the partition function is treated here. In calculations concerning changes upon mixing, the "translational" part drops out and may be neglected. Although the equations that follow were derived for hard sphere ions which interact with a generalized form of the Coulomb potential, the same equations may be derived for more general potential functions. If the core repulsions of a cation-anion pair are of the form $f(g_i r)$ (a special case of this form is the hard-sphere repulsion) and if the other interionic interactions in the system are such that for any given geometric configuration of the ions, the permutations of the two types of cations over all the cation positions do not lead to a change of the contribution of these other interactions to the total potential of the system, then the equations derived will be the same as the equations to be derived [Eqs. (23–27)] with different values of ϕ_{AC} in the integrals which are contained in the coefficients. Types of interaction which would be included in this category are not only Coulomb interactions but also cation charge-anion multipole interactions and, for the cases in which the two cations have relatively small or equal polarizabilities, all other charge-multipole and multipole-multipole interactions. Salt mixtures which conform to this might be termed *conformal ionic mixtures.*

where $Z(g_i)$ has been expanded about $g_i = 1$. Similarly, for a mixture of 1 and 2 the potential energy is given by

$$U_{12} = \sum_{A}^{\bar{n}} \sum_{C_1}^{(N_1\bar{n})} g_1 u_{AC}(g_1 r) + \sum_{A}^{\bar{n}} \sum_{C_2}^{(N_2\bar{n})} g_2 u_{AC}(g_2 r) + \sum_{A}^{\bar{n}} {}_{<} \sum_{A'}^{\bar{n}} u_{AA'}$$

$$+ \sum_{C_1}^{(N_1\bar{n})} {}_{<} \sum_{C_1}^{(N_1\bar{n})} u_{C_1C_1'} + \sum_{C_2}^{(N_2\bar{n})} {}_{<} \sum_{C_2'}^{(N_2\bar{n})} u_{C_2C_2'} + \sum_{C_1}^{(N_1\bar{n})} \sum_{C_2}^{(N_2\bar{n})} u_{C_1C_2} , \qquad \text{(II.3.19)}$$

and Z is given by

$$Z'_{12} = \frac{\bar{n}!}{\bar{n}_1!\,\bar{n}_2!} \int\cdots\int \frac{e^{-BU_{12}}}{(\bar{n}!)^2} (d\tau)^{2\bar{n}} = \frac{\bar{n}!}{\bar{n}_1! n_2!} Z(g_1, g_2) , \qquad \text{(II.3.20)}$$

and the Helmholtz free energy for one mole is

$$-\frac{A_{12}}{kT} = (\ln Z)_{g_1,g_2=1} + (g_1 - 1)\left(\frac{\partial \ln Z}{\partial g_1}\right)_{g_1,g_2=1} + (g_2 - 1)\left(\frac{\partial \ln Z}{\partial g_2}\right)_{g_1,g_2=1}$$

$$+ \frac{(g_1 - 1)^2}{2} \left(\frac{\partial^2 \ln Z}{\partial g_1^2}\right)_{g_1,g_2=1} + \frac{(g_2 - 1)^2}{2} \left(\frac{\partial^2 \ln Z}{\partial g_2^2}\right)_{g_1,g_2=1}$$

$$+ (g_1 - 1)(g_2 - 1)\left(\frac{\partial^2 \ln Z}{\partial g_1 \partial g_2}\right)_{g_1,g_2=1} + \ldots + \sum N_i n \ln N_i . \qquad \text{(II.3.21)}$$

The appropriate derivatives of Eqs. (15) and (20) were used to evaluate the first and second derivatives of ln Z contained in Eqs. (18) and (21). The values of A_1, A_2, and A_{12} thus obtained were used to calculate the total excess Helmholtz free energy of mixing of N_1 moles of component 1 with N_2 moles of component 2 to form one mole of mixture

$$\Delta A_m^E = A_{12} - N_1 A_1 - N_2 A_2 - RT \Sigma N_1 \ln N_1 .$$

The first order terms cancel and the second order terms lead to

$$\Delta A_m^E = N_1 N_2 \frac{d^2}{2ZkT} \left[\bar{n}^3 \epsilon + \bar{n}^3(\bar{n} - 1)\omega - \frac{\alpha^2 \bar{n}^4}{Z}\right] \left(\frac{d_1 - d_2}{d_1 d_2}\right)^2 , \qquad \text{(II.3.22)}$$

where Z, ϵ, ω, and α are related to the integrals characteristic of the "test" salt

$$\alpha = \int\cdots\int \frac{\phi_{AC}}{(\bar{n}!)^2} e^{-BU} (d\tau)^{2\bar{n}} ,$$

$$\epsilon = \int\cdots\int \frac{\phi_{AC}\phi_{AC'}}{(\bar{n}!)^2} e^{-BU} (d\tau)^{2\bar{n}} ,$$

$$\omega = \int \cdots \int \frac{\phi_{AC}\phi_{A'C'}}{(\bar{n}!)^2} e^{-BU} (d\tau)^{2\bar{n}} ,$$

where $\phi_{AC} = u_{AC} + r(\partial u_{AC}/\partial r)$ and a prime on A or C means that the integration is for two different anions or cations. From (22) it was shown that

$$\Delta A_m^E = N_1 N_2 \, \Gamma \, (T,V) \left(\frac{d_1 - d_2}{d_1 d_2} \right)^2 + \ldots , \qquad (II.3.23)$$

$$\Delta G_m^E = N_1 N_2 \, \theta \, (T,p) \left(\frac{d_1 - d_2}{d_1 d_2} \right)^2 + \ldots , \qquad (II.3.24)$$

and

$$\Delta H_m = N_1 N_2 \, \Omega \, (T,p) \left(\frac{d_1 - d_2}{d_1 d_2} \right)^2 + \ldots , \qquad (II.3.25)$$

where Γ, θ, and Ω are functions characteristic of a single "test" salt. The influence of the factor $(d_1 d_2)^2$ on the thermodynamic excess functions is much weaker than the influence of the factor $(d_1 - d_2)^2$. As a consequence, the form of Eqs. (23), (24), and (25) is similar to that implied by Eqs. (8) and (9) and is consistent with the empirical relation (5).

The higher order terms in the theory of Reiss, Katz, and Kleppa were complicated. The higher order terms are simplified by the choice of particular relative values of the perturbation parameters g_1 and g_2 so that $(g_1 - 1) = -(g_2 - 1)$.[17] This condition implies that for each particular mixture a "test" salt is chosen. The calculations lead to the result

$$\Delta A_m^E = N_1 N_2 \, P\delta^2 + N_1 N_2 (N_1 - N_2) Q\delta^3 + [N_1 N_2 R + N_1 N_2 (N_1 - N_2)^2 S]\delta^4 + \ldots , \qquad (II.3.26)$$

where

$$-\frac{P}{kT} = \frac{1}{2} \left(\frac{B^2}{Z^2} - \frac{\bar{n}D}{Z} \right) ,$$

$$-\frac{Q}{kT} = 4 \left(\frac{\bar{n}^2 F}{6Z} \; \frac{\bar{n}^2 BD}{2Z^2} + \frac{B^3}{3Z^3} \right) ,$$

R and S are complicated functions,

$$\delta = \left(\frac{d_1 - d_2}{d_1 + d_2} \right) ,$$

$$B = -B\bar{n}^2 \alpha ,$$

$$D = B^2 \bar{n}^2 [\epsilon + (\bar{n} - 1)\omega] ,$$

$$F = -\frac{B^3 \bar{n}^2}{(\bar{n}!)^2} \int \cdots \int \phi_{AC}\, \phi_{AC'}\, \phi_{AC''}\, e^{-BU}\, (d\tau)^{2\bar{n}}$$
$$+ 3(\bar{n}-1) \int \cdots \int \phi_{AC}\, \phi_{AC'}\, \phi_{A'C''}\, e^{-BU}\, (d\tau)^{2\bar{n}}$$
$$+ (\bar{n}-1)(\bar{n}-2) \int \cdots \int \phi_{AC}\, \phi_{A'C'}\, \phi_{A''C''}\, e^{-BU}\, (d\tau)^{2\bar{n}} \quad ,$$

P, Q, R, and S are characteristic properties of the test salt. In a similar fashion, the heat of mixing may be shown to be

$$\Delta H_m = N_1 N_2 P'\delta^2 + N_1 N_2 (N_1 - N_2) Q'\delta^3 + [N_1 N_2 R' + N_1 N_2 (N_1 - N_2)^2 S']\delta^4 + \ldots , \qquad \text{(II.3.27)}$$

where the prime signifies the proper temperature derivative of the primed quantity. The form of Eq. (27) is seen to be consistent with (2) if $a = P'\delta^2 - Q'\delta^3 + R'\delta^4 + S'\delta^4$, $b = 2Q'\delta^3$, and $c = -4S'\delta^3$. This constitutes proof that the form of Eq. (2) is consistent with rigorous theory. The methods of Reiss, Katz, and Kleppa may thus be used to support in a rigorous manner the form of the empirical Eqs. (2) and (5), as well as the approximate form of Eqs. (8) and (9) which had been derived on an intuitive basis.

Powers, Katz, and Kleppa[74,106] have measured volume changes of mixing of several compositions of each of the binary alkali-nitrate mixtures $(Na\text{-}K)NO_3$, $(Na\text{-}Li)NO_3$, $(Na\text{-}Rb)NO_3$, and $(Na\text{-}Cs)NO_3$. The average values of the quantity $\Delta V^E/N_1 N_2$ are listed below:

Mixture	Temperature (°C)	$\Delta V^E/N_1 N_2$ (cm^3/mole)
$(Na\text{-}K)NO_3$	350	0.26 ± 0.08
	425	0.28 ± 0.08
$(Na\text{-}Li)NO_3$	310	0.26 ± 0.02
$(Na\text{-}Rb)NO_3$	340	0.82 ± 0.10
$(Na\text{-}Cs)NO_3$	425	1.37 ± 0.12

All of these volume changes are positive and obey the approximate equation

$$\Delta V^E = N_1 N_2\, V'\delta^4 ,$$

where $V' \cong 22{,}000$ cm^3/mole. These positive deviations from the additivity of the molar volumes, significantly, are found in mixtures in which the heats of mixing are negative. No satisfactory theory has been proposed for this.

The only data on activities in mixtures of alkali halides with a common anion has been obtained from cryoscopy. Unfortunately such data is not isothermal and uncertainties in the phase diagram and in the heats of fusion as well as the necessity for precise measurement of liquidus temperatures to obtain reasonable values of the excess free energies reduce the value of this source of information. The component LiF in mixtures of LiF-KF, LiF-RbF, and LiF-CsF[3,36] exhibit negative deviations from ideal solution behavior, which are more negative (the activity coefficients are smaller) the larger the difference between the sizes of the two cations. The same is true for the component LiCl in mixtures with KCl, RbCl, and CsCl.[112] This appears to be in accord with the ideas presented in section (II.3). However, the work of Cantor[31] on cryoscopy of NaF in mixtures with KF, RbF, and CsF have indicated that there is a small positive excess free energy which becomes more positive in the order KF < RbF < CsF. Since purely Coulomb or polarization interactions would be expected to always lead to negative deviations from ideal solution behavior, it is clear then that even in mixtures of the highly ionic alkali halides other types of interactions are important. In the next section we will show that these interactions may be, at least in part, related to the dispersion interactions of the solute cations. Some discussion of this for alkali halides has been made.[91]

II.4 Mixtures Containing Polarizable Cations and a Common Anion

In order to separate the various physical interactions which are significant in determining the solution behavior of molten salts, it is advantageous to compare two different mixtures of salts in which the major difference in the solution properties can be related to the differences in the properties of one ion. As an example, mixtures of alkali nitrates with silver or thallous nitrates would be suitable for such a comparison with mixtures containing only alkali nitrates, since the difference in the properties of Ag^+ and Tl^+ ions from those of Na^+ and Rb^+ is largely related to the relatively high polarizabilities of Ag^+ and Tl^+.[*,105]

Kleppa has measured the heats of mixing of $AgNO_3$ and $TlNO_3$ with all of the alkali nitrates except $CsNO_3$.[77,79] By fitting his data to equation (II.3.2), where N_1 is the mole fraction of either $AgNO_3$ or $TlNO_3$, Kleppa obtained the values of the parameters a, b, and c which are listed in Table 2. The observed deviations from ideal solution behavior differ from those of the corresponding mixtures of alkali nitrates with $NaNO_3$ or $RbNO_3$. In addition to the interactions present in mixtures of alkali nitrates, an additional interaction needs to be postulated to rationalize the observed results. This difference has been shown to be in reasonable agreement with a calculation of the London dispersion energy of interaction of next-nearest neighbors.[16] The predominant term of the London dispersion interaction energy between two ions is the dipole-dipole term,

$$U^{kl}_{++} = -S''_6 \, C^{kl}_{++}/d^6 \, , \tag{II.4.1}$$

where S''_6 is a constant probably in the range of 1 to 2 and depends on the structure of the melt, d for a pure salt is the cation-anion distance with the cation-cation distance assumed proportional to d, and d for a mixture is an average cation-anion distance. The paramater C^{kl}_{++} is given by[101]

$$C^{kl}_{++} = \frac{3}{2} \, \frac{\alpha_k \, \alpha_l \, I_k \, I_l}{I_k + I_l} \, , \tag{II.4.2}$$

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[*] It should be noted that although the Pauling radius of Ag^+ ion is 1.26 A, the interionic distances in AgCl and AgBr and the relative molar volumes of liquid $AgNO_3$ and $NaNO_3$ are more consistent with a radius of about 0.95 A which is close to that of Na^+.

where k and l are the two cations, α is the polarizability of an ion, and I has been estimated[101] for the alkali cations, Tl^+ and Ag^+. Values of α and I are listed in Table 3. A calculation of the contributions of this interaction, ΔU_{++}^{AB}, was approximated from the dispersion energy change represented crudely by the process AXA + BXB → 2AXB,

$$\Delta U_{++}^{AB} = 2U_{++}^{AB} - U_{++}^{AA} - U_{++}^{BB} , \qquad \text{(II.4.3)}$$

where the solutes are AX and BX, where $S_6'' \cong 1.8$, and where $2d_{AB} = d_{AA} + d_{BB}$.* Equation (II.4.3) is an approximation to the contribution to $\Delta H_m^{0.5}/N_1 N_2$ so that the relation for molten nitrates (II.3.5) is modified to become

$$\bar{\lambda} \cong 4\Delta H_m^{0.5} = U\delta^2 + \Delta U_{++}^{AB} . \qquad \text{(II.4.4)}$$

The value of $U = -140$ for alkali nitrates includes a small positive contribution from van der Waals' interactions so that a correction is needed which will make ΔU_{++}^{AB} less positive.[16] A cruder but simpler approximation to ΔU_{++}^{AB} may be made in a manner similar to an approximation useful in nonelectrolyte solution theory.[68]

$$\Delta U_{++}^{AB} \cong \left(\sqrt{U_{++}^{AA}} - \sqrt{U_{++}^{BB}}\right)^2 , \qquad \text{(II.4.5)}$$

where the values of C_{++} in Table 3 in conjunction with a value of $S_6'' \cong 1.8$ may be used with Eq. (5) and ionic radii for roughly estimating ΔU_{++}^{AB}. From Table 3 it can be seen that C_{++} will be quite large for Cs^+, Rb^+, and K^+ ions and the positive term, ΔU_{++}^{AB}, in (4) may be large enough to cancel the negative values of $U\delta^2$ for mixtures of, for example, NaF with KF, RbF or CsF. The calculations of Lumsden[91] are in accord with this and this may be used to rationalize the

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*A better approximation for d_{AB} is $[(d_A^2 + d_B^2)/2]^{1/2}$, which differs little from $(d_A + d_B)/2$ when d_A is not very different from d_B. The factor for S_6'' contains a small correction for interactions of longer range than next-nearest neighbors.

Table 3. Polarizability and Potential Parameter Used for Estimating Cation-Cation van der Waals' Interaction

Ion	$\alpha \times 10^{24}$ (cm^3)	$I \times 10^{12}$ (ergs/molecule)
Li^+	0.030	90.9
Na^+	0.182	56.8
K^+	0.844	38.2
Rb^+	1.42	33.0
Cs^+	2.45	39.0
Ag^+	1.72	30.0
Tl^+	3.50	30.0

results of Cantor[31] mentioned at the end of the previous section. However all of these methods are approximate and are useful largely for semiquantitative estimates of solution behavior.

Laity[83] has shown that $\Delta\phi_{\text{diff}}$ is negligible in the cell

$$\mathrm{Ag}\left|\begin{array}{l}\mathrm{AgNO_3}(N_1')\\ \mathrm{NaNO_3}\end{array}\right|\left|\begin{array}{l}\mathrm{AgNO_3}(N_1)\\ \mathrm{NaNO_3}\end{array}\right|\mathrm{Ag}$$

and the emf of this cell is given by

$$\Delta E = RT \ln (a_1/a_1') \; .$$

The measurements are consistent with the expression

$$\mu_1^E = 840 \; N_2^2 \; , \tag{II.4.6}$$

where 1 is $AgNO_3$ and 2 is $NaNO_3$. The results did not exhibit the asymmetry in the heats of mixing found by Kleppa for the same system. Although the total excess entropy is small relative to the total entropy of mixing, it is negative and is not small relative to ΔH_m or ΔG^E;

$$T\Delta S^E = \Delta H_m - \Delta G^E = (-156 \; N_1 - 163) N_1 N_2 \; ,$$

so that although Eq. (6) has the form for regular solutions the excess entropy does not appear to be negligibly small.

There have been many studies of mixtures of silver halides and alkali halides using the formation cell

$$\mathrm{Ag}\left|\begin{array}{l}\mathrm{AgX}\\ \mathrm{M\;X}\end{array}\right|\mathrm{X_2}\;(p = 1\text{ atm})\text{ graphite,}$$

where M is an alkali metal ion and X is a halide. The emf of this cell can be related to the activity of AgX by

$$\mu_1 - \mu_1^0 = -F(E - E^0) = RT \ln a_1 \; , \tag{II.4.7}$$

where 1 is AgX.

The most extensive work on these systems has been the work of Hildebrand and Salstrom who studied mixtures of AgBr with LiBr, NaBr, KBr, and RbBr.[66,116,117] In Fig. 7 are plotted values of μ_1^E for AgBr (component 1) vs N_2^2. Within the experimental precision, μ_1^E is independent of temperature and can be represented by the equation

$$\mu_1^E = \lambda N_2^2 \; . \tag{II.4.8}$$

Values of λ are given in the table below and may be rationalized in terms of Eq. (4) using the data in Table 3. Many studies of mixtures of AgCl with alkali chlorides have been made. Unfortunately, there are significant differences between different measurements on the same systems. The most reliable and consistent studies appear to be those of Salstrom[118] and of Panish[104] on the (Li-Ag)Cl and the (Na-Ag)Cl systems. Although there is scatter in the high-temperature data

Mixture	λ (cal/mole)	Volume Change of 50-50 Mixture (cm^3/mole)
(Li-Ag)Br	1880	−0.13
(Na-Ag)Br	1050	+0.17
(K-Ag)Br	−1480	+0.27
(Rb-Ag)Br	−2580	+0.42
(Li-Ag)Cl	2100	
(Na-Ag)Cl	~800	

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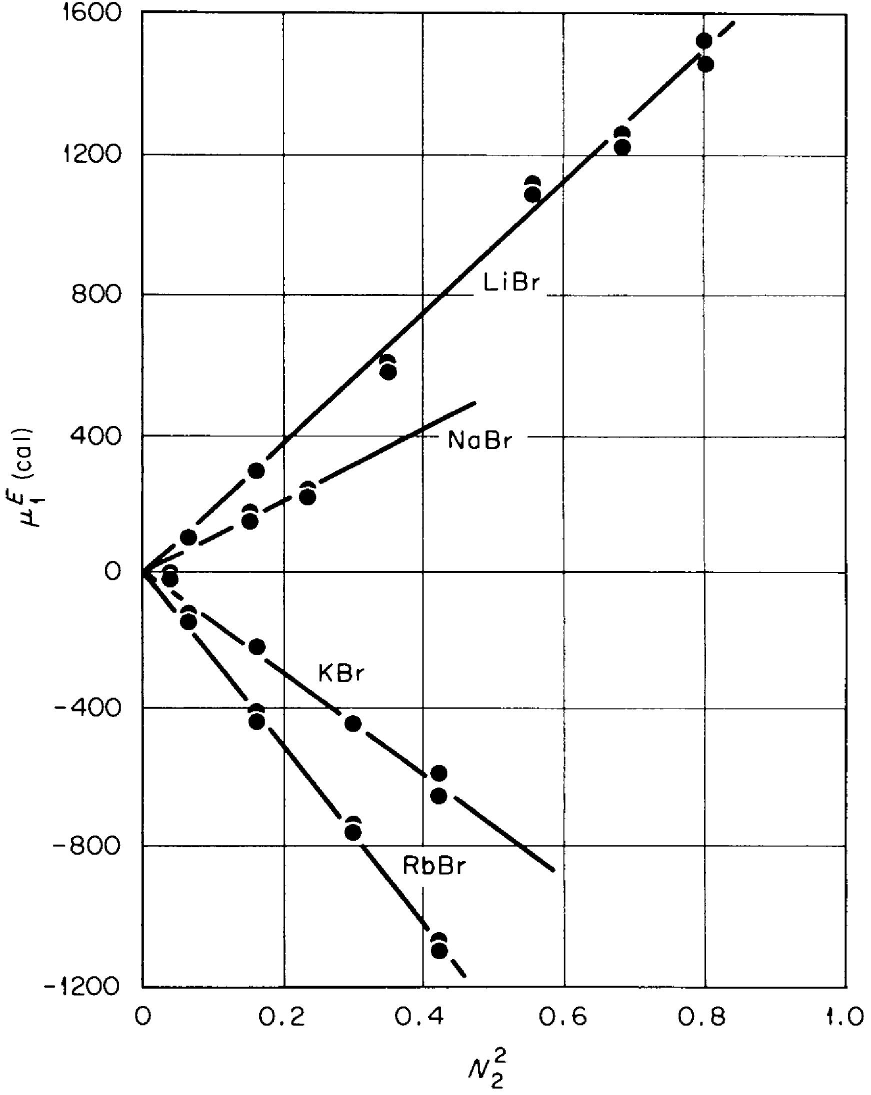

Fig. 7. Values of the Excess Chemical Potential of AgBr (Component 1) in Mixtures with Alkali Bromides.

of Panish, the results of both Salstrom and of Panish on the AgCl-LiCl system lead to positive deviations from ideality, which follow, approximately, Eq. (8) with $\lambda = 2100$ (cal/mole) from 500 to 900°C. Small positive deviations from ideality have been found[104] in the AgCl-NaCl system. There is too much scatter in the results to be able to represent μ_1^E precisely, but crudely $\mu_1^E = 800\ N_2^2$. The work of Stern is consistent with these results.[124]

In all of these chloride systems there is considerable scatter and uncertainty, and it cannot be clearly shown that the data can be best expressed by an expression as Eq. (8) and that λ is truly independent of temperature.

Measurements of AgCl-KCl mixtures by Stern are doubtful.[124] The measurements of Murgulescu and Sternberg indicate that for AgCl-KCl mixtures[102]

$$\mu_1^E = -1555\ N_2^2\ ,$$

and that the excess entropy of mixing was nearly zero. However, the values of E^0 observed by Murgulescu and Sternberg differed from those given by Salstrom, Panish, and Stern by about 9 mv at 500°C.

An interesting comparison with solid solutions is exhibited by Panish.[104] Although the molten salt system AgCl-NaCl exhibited only small positive deviations from ideality, the measured deviations from ideality in the solid solutions were more positive. This illustrates the fact that, aside from other effects, the accommodation of ions of different sizes in a given material leads to a greater positive (or less negative) free-energy change in a crystal than in a liquid.

It was pointed out by Hildebrand and Salstrom[124] that the volume change upon mixing of 50-50 mixtures of the four systems containing AgBr, which are listed on page 32, could not be related to a weakening or strengthening of the interactions of the ions or with the deviations from ideality. As with the results on alkali nitrates for ΔH_m, the values of $\Delta\mu_1^E$ vary in a direction opposite in sign to that of ΔV^E with variations in the cation.

II.5 Binary Mixtures Containing Polyvalent Ions

Although there has been much experimental work on mixtures containing polyvalent ions, very little theoretical discussion based on fundamental physical principles has been published. This section will be devoted to the presentation of thermodynamic data to give the reader an idea of the magnitudes involved and, where enough data exist, to pointing out the correlation of properties of mixtures with the physical properties of the ions. Where it is considered necessary, a discussion of the principles of measurements will be included. In the next section, a discussion of these data and a critique of the description of these data in terms of "complexes" will be made.

Kleppa and Hersh[77] measured the molar heats of mixing of $Ca(NO_3)_2$ with $LiNO_3$, $NaNO_3$, KNO_3, and $RbNO_3$ at 350°C. By using a heat of fusion of $Ca(NO_3)_2$ of 5.7 kcal/mole obtained by extrapolation of their measurements, the limiting heat of solution of liquid $Ca(NO_3)_2$ ($\bar{H}_1^* - H_1^0$ in Table 4) at 350°C obeyed the empirical relation

$$\bar{H}_1^* - H_1^0 = 0.3 - 225[(r_{++}/2) - (r_+/1)]^2/[d_1 + d_2]^2 ,$$

which relates the radii of the divalent and monovalent cations (r_{++} and r_+) to the observed heats of mixing. The heats of solution decrease with increasing radius of the alkali cation. It should be noted that the heat of solution in $LiNO_3$ is positive. No simple representation of the concentration dependence of the molar heat of mixing was made. It was noted, however, that the slope of plots of $\Delta H_m/N_1$[$Ca(NO_3)_2$ is component 1] vs N_1 for mixtures with KNO_3 and $RbNO_3$ had maxima at $N_1 = 0.25$–0.33 (or at equivalent fractions $N_1' = 0.4$–0.5). The results in these two systems probably can not be represented by an equation with as few terms as (II.3.2).

Table 4. Extrapolated Values of the Limiting Heats of Solution of $Ca(NO_3)_2$

Solvent	$\bar{H}_1^* - H_1^0$ (kcal/mole)
$LiNO_3$	+0.25
$NaNO_3$	−0.9
KNO_3	−3.0
$RbNO_3$	-4.3_5

The most extensive comparative studies of binary mixtures containing polyvalent ions have been the cryoscopic measurements of Cantor,[30,31,34] who measured the freezing point lowering of NaF by polyvalent salts. NaF can be considered as a prototype of an ionic salt. In Fig. 8 are plotted the liquidus temperatures of NaF (component 1) in mixtures with the alkaline earth fluorides. The upper line is the calculated liquidus temperature for an ideal solution with the data contained in Table 1. For an ideal solution at the liquidus

$$a_1 = N_1^{\text{ideal}} ,$$

and the activity coefficient in a real solution is given by

$$\gamma_1 = \frac{N_1^{\text{ideal}}}{N_1}$$

at the liquidus, where N_1^{ideal} and N_1 are the compositions of NaF in the ideal and real solutions respectively at the same temperature. A freezing point lower than the ideal value means that $\gamma_1 < 1$ so that the solutions all exhibit negative deviations from ideality. The smaller the radius of the alkaline earth the greater the deviations from ideality.

The Ca^{2+} ion has about the same radius as Na^+, but the NaF-CaF_2 mixture exhibits negative deviations from ideality. This illustrates the effect of charge. Deviations from ideality in the

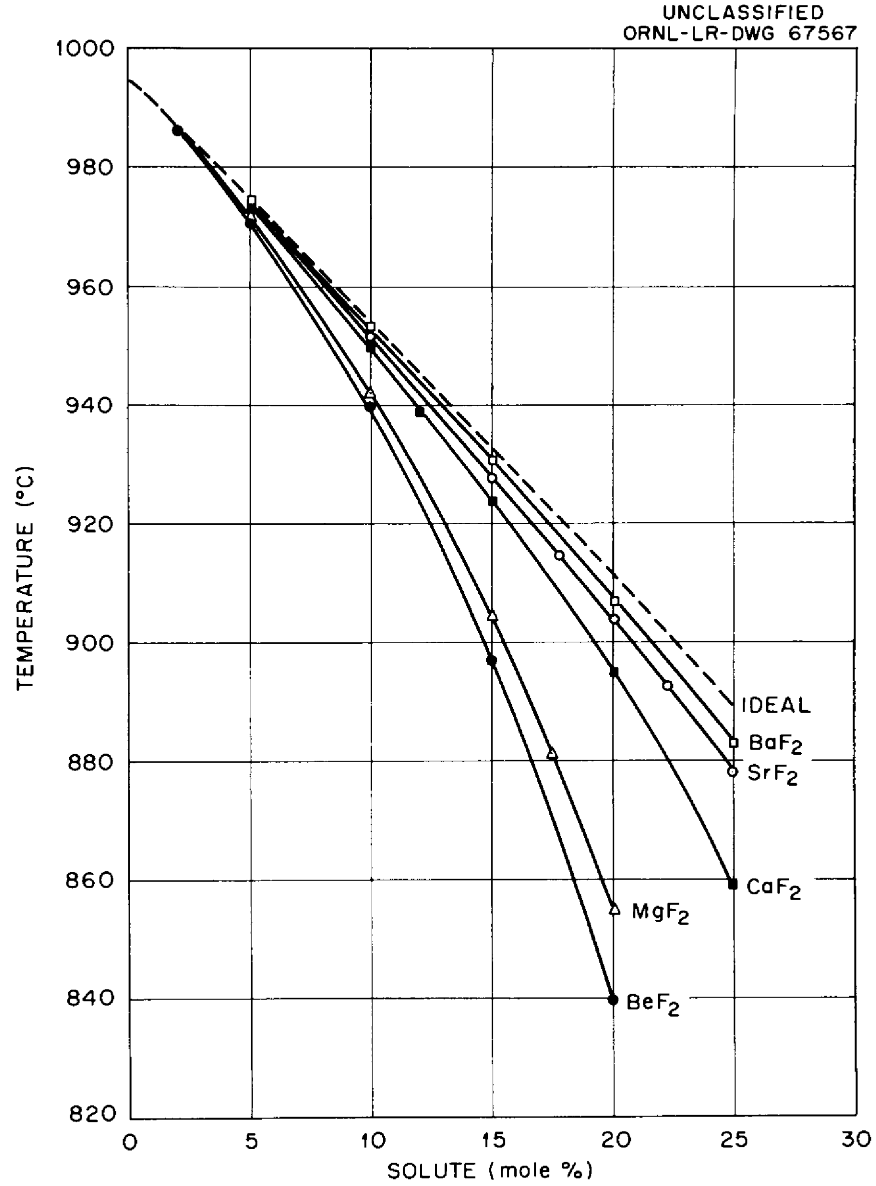

Fig. 8. Liquidus Temperatures of NaF in Mixtures with Alkaline Earth Fluorides.

NaF-BaF$_2$ system are small. Since the Ba^{2+} ion is larger than the Na$^+$ ion, the large size of the divalent ion appears to, at least partially, compensate for the greater charge. The excess free energies of NaF, μ_1^E, at the liquidus temperatures in mixtures with the alkaline earth fluorides are plotted in Fig. 9 vs N_2^2 (where 2 is the solute). (Note that these values of μ_1^E are not isothermal.) For comparison with monovalent cation salts, data with LiF and KF as solutes are also plotted. The Li$^+$ ion is about the same size as the Mg^{2+} ion and both are smaller than the Na$^+$ ion. If the LiF and the MgF$_2$ mixtures are compared with NaF, the deviations from ideality in both appear to be negative, being much more negative in NaF-MgF$_2$ mixtures. On

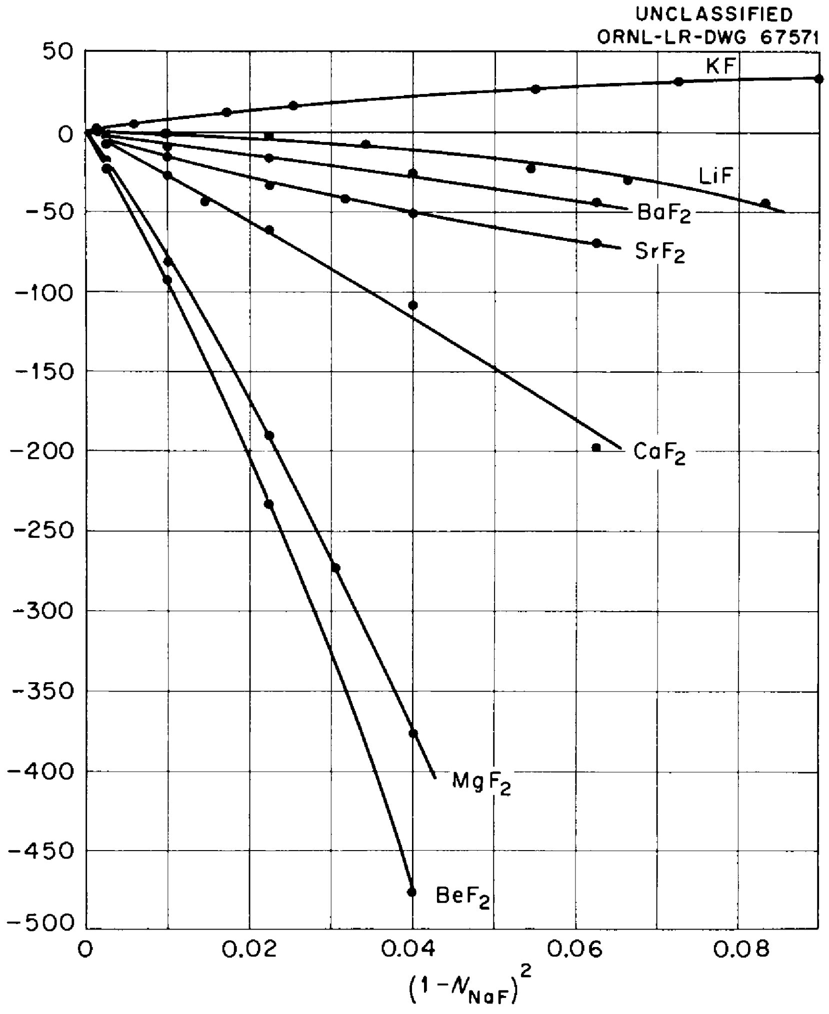

Fig. 9. Excess Chemical Potential of NaF in Mixtures with the Alkaline Earth Fluorides LiF and KF as Calculated from Liquidus Temperatures.

the other hand, the K^+ ion is about the same size as the Ba^{2+} ion, both being larger than the Na^+ ion. The deviations from ideality of the solvent NaF in mixtures with KF and BaF_2 are both small. A further illustration of the influence of charge is shown in Fig. 10, which gives μ_1^E for NaF in mixtures with CaF_2, YF_3, and ThF_4 in which salts the interionic distances are about the same. All of these illustrations show that the deviations from ideal solution behavior are related by a function which appears to be monotonic in the charge of the solute cation, Z, and in $1/d_2$, where d_2 is the sum of the cation and anion radii of the solute. However, other effects such as van der Waals' interactions, ligand-field effects on transition metal ions, etc., will be superimposed on the effects of charge and radius of the ions. Figure 11 gives a parallel plot of μ_1^E at 20 mole % of solute and the lattice energies of the solid solutes MnF_2, FeF_2, CoF_2, NiF_2, and ZnF_2. The measured cation-anion distance in solid MgF_2 is about the same or smaller

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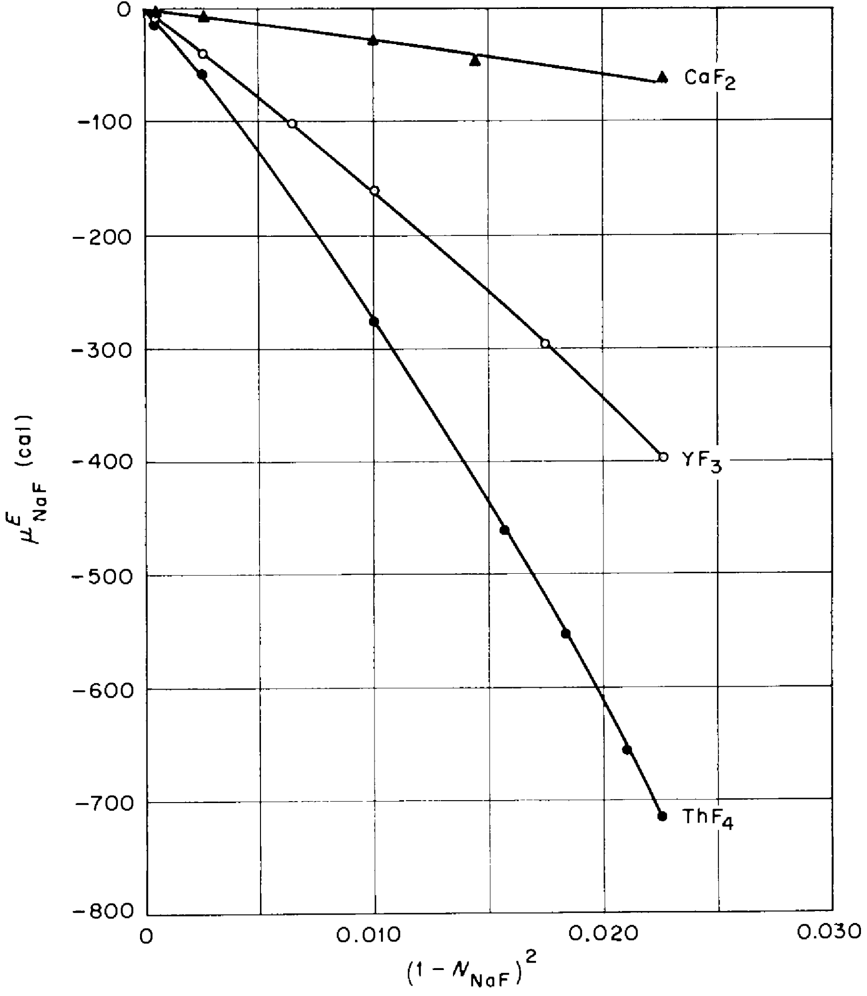

Fig. 10. Excess Chemical Potentials of NaF in Mixtures with CaF_2, YF_3, and ThF_4 as Calculated from Liquidus Temperatures.

than those of these transition metal ions. The greater negative deviations from ideality found for mixtures with the transition metal fluorides are therefore not related solely to the radii of the ions. Since the pattern of the lattice energies with a maximum at NiF_2 or CoF_2 is explained by ligand-field theory for octahedral or to tetrahedral symmetry respectively,[103] then the pattern of μ_1^E and the differences from the NaF-MgF_2 system suggest that the change of the ligand-field effect upon dissolution is related to the deviations from ideality of NaF. Having monovalent ions as next-nearest neighbors in the mixture, as compared to divalent ions as next-nearest neighbors in the pure transition metal fluorides, probably leads to a greater ligand field and a great ligand-field stabilization of the solute component in the mixture than in the pure salt. Whatever the specific structure of the melt and of the ligands about the transition metal ion, it is apparent that the effect of the ligand-field stabilization on the solvent is in the same order as might be expected from ligand-field theory for the solute.

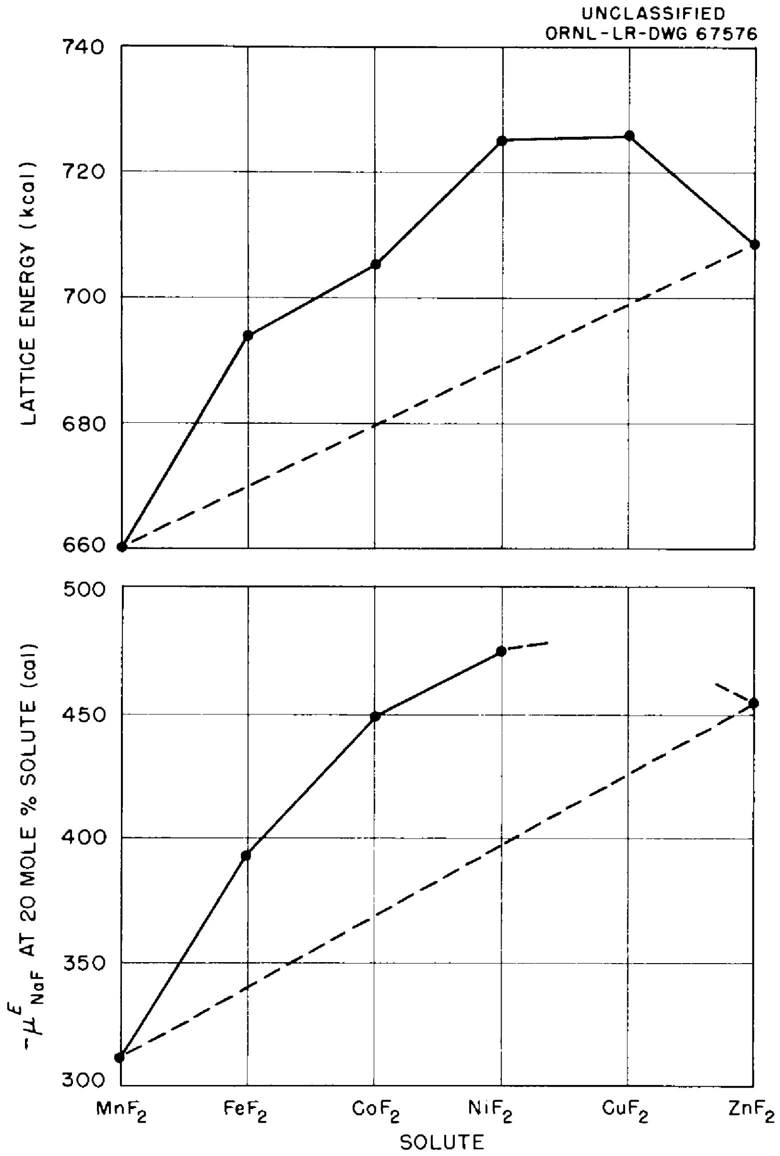

Fig. 11. Parallel Plot of the Lattice Energies of Some Transition Metal Fluorides and the Excess Chemical Potential of NaF in Mixtures with Transition Metal Fluorides.

Cantor[34] has also made cryoscopic measurements on NaF with ZrF_4, HfF_4, ThF_4, and UF_4 as solutes. In Fig. 12 are plotted values of μ_1^E vs N_2^2 at the liquidus for these four mixtures. The deviations from ideality are all more negative than those for the alkaline earth fluorides which further illustrates the effect of charge. The effect of radius appears to be reversed for these tetravalent salts, since Zr^{4+} which has the smallest radius also has the smallest negative deviation from ideality. The cause of this is not clear, although steric hindrance related to anion-anion contacts in the coordination shell adjacent to the tetravalent ion has been suggested as a limiting factor.[34] Thus any tendency by a tetravalent ion to have a high coordination number might

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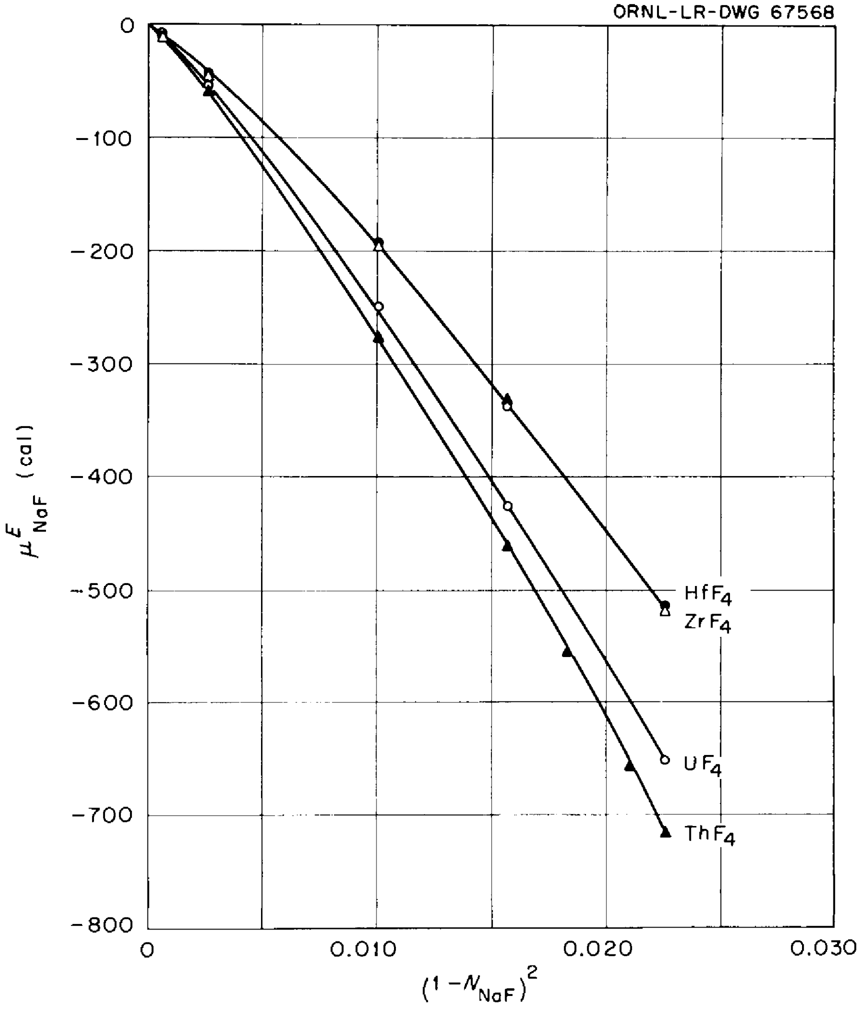

Fig. 12. Excess Chemical Potentials of NaF in Mixtures with ZrF_4, HfF_4, UF_4, and ThF_4 as Calculated from Liquidus Temperatures.

be sterically limited for ions as small as Zr^{4+} and this might limit the magnitude of the deviations from ideal solution behavior.

Another comparative study including polyvalent ions covering a relatively broad range of concentrations was the emf measurements by Yang and Hudson[133] by use of cells of the type

$$M\left|\begin{array}{l}MCl_n\\(LiCl\text{-}KCl\ eutectic)\end{array}\right|Cl_2\ .$$

For M = Pb^{2+}, Cd^{2+}, Zn^{2+}, Mg^{2+}, Be^{2+}, activities were calculated from the relation

$$\mu_1 - \mu_1^0 = -NF(E - E^0) = RT \ln a_1\ .$$

In the five systems measured, the deviations from ideality were always negative ($\gamma_1 < 1$). In Table 5 are given values of (μ_1^E/N_2^2) at 800°K calculated from the measurements in the most dilute solutions of the solute (component 1) with values of E^0 contained in Table 6 for the calculations. Except for $ZnCl_2$, the values of (μ_1^E/N_2^2) are more negative the smaller the radius of the divalent ion. These quantities in addition to the influence of radius are influenced by other factors which are probably significant for polarizable cations such as Zn^{2+}, Cd^{2+}, and Pb^{2+}. It should be noted that the measurements of Takahashi[126] differ from those of Yang and Hudson on mixtures of $PbCl_2$ with the LiCl-KCl eutectic mixtures.

Another series of comparative studies of molten-salt mixtures was made by Lantratov and Alabyshev[85] by using the cell

$$M_I \left| \begin{array}{l} M_I Cl_2 \\ M_{II} Cl_n \end{array} \right| Cl_2 ,$$

where $M_I = Pb^{2+}$, Cd^{2+}, and Zn^{2+} and M_{II} are alkali and alkaline earth metals. They were able to observe the effect of a change in the diluting chloride $M_{II}Cl_n$ on the activity of M_ICl_2. In Fig. 13 values of μ_1^E, at 500°C for $PbCl_2$ in mixtures with LiCl, NaCl, KCl, and $BaCl_2$; at 600°C for $CdCl_2$ in mixtures with NaCl, KCl, and $BaCl_2$; and at 500°C for $ZnCl_2$ in mixtures with NaCl, KCl, and $BaCl_2$, are plotted vs the square of the mole fraction of the other component.

Table 5. Values of (μ_1^E/N_2^2) in Dilute Solutions of Divalent Chlorides in the LiCl-KCl Eutectic Mixture

Solute	(μ_1^E/N_2^2)	N_2
$PbCl_2$	−1,410	0.984
$CdCl_2$	−4,620	0.993
$ZnCl_2$	−8,650	0.984
$MgCl_2$	−8,150	0.986
$BeCl_2$	−14,680	0.998

Table 6. Values of the Parameters in the Equation $E^0 = a + bT(°C)$, Where E^0 is the EMF of the Cell $M/MCl_n/Cl_2$ ($P = 1$ atm)

Salt	a	$b \times 10^4$	References
AgCl	1.0461	−2.92	116
$PbCl_2$	1.5855	−6.25	131
$CdCl_2$	1.7188	−6.29	89
$ZnCl_2$	1.9200	−6.95	131
$MgCl_2$	2.9823	−6.73	89
$BeCl_2$	2.6205	−8.60	133
$PbBr_2$	1.424	−7.4	86, 115

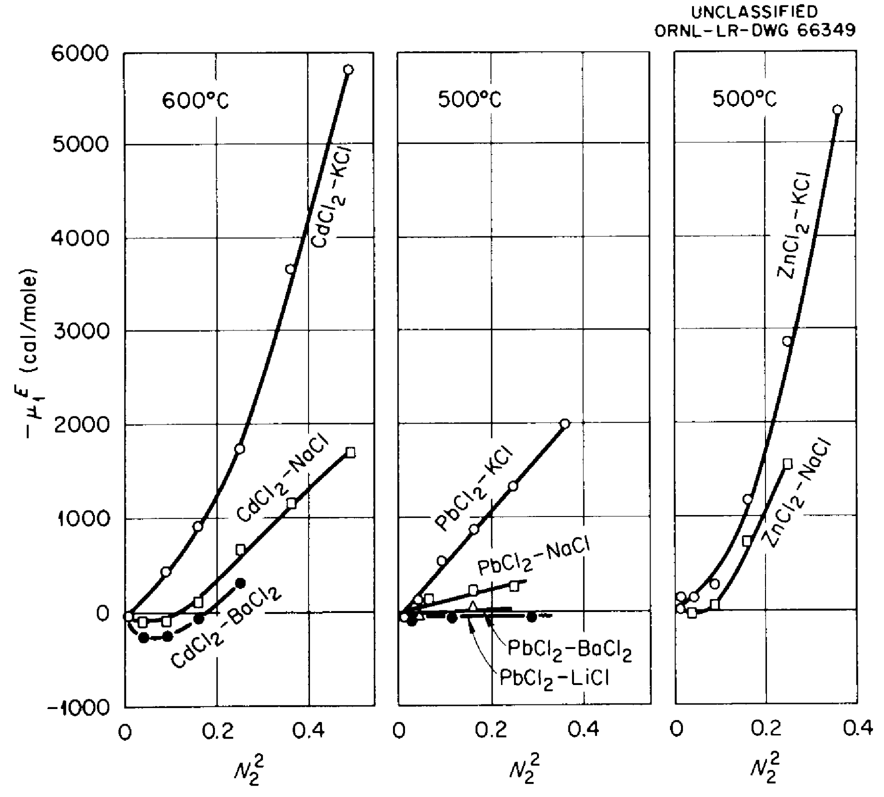

Fig. 13. Excess Chemical Potentials of $CdCl_2$, $PdCl_2$, and $ZnCl_2$ in Mixtures with Other Chlorides as Obtained from EMF Measurements.

The values of E^0 at 600°C used by Lantratov and Alabyshev were 1.4987 v for $ZnCl_2$, 1.3382 for $CdCl_2$, and 1.2215 for $PbCl_2$, which are −4.3, −3.2, and 11.0 mv different from the values calculated by using the data in Table 6. Because of these differences in E^0, the values in μ_1^E must be considered uncertain by about 200 cal. Discrepancies in values of E^0 reported by different workers are common and are probably related to the solubility of metals in their own pure salts. In Table 7 are given values of γ_1 at 600°C and values of the total volume change per mole of mixture, ΔV, at $N_1 = 0.5$. With an increase in the size of the alkali cation in mixtures with alkali chlorides values of γ_1 decrease and values of ΔV increase. These relative variations in the deviations from ideal solution behavior and volume changes are in the same direction as was observed in alkali nitrates and in mixtures of AgBr with alkali bromides. As in the measurements of Yang and Hudson, mixtures of alkali halides with $ZnCl_2$, $CdCl_2$, and $PbCl_2$ exhibit less negative deviations from ideal solution behavior in that order

$$(\gamma_{ZnCl_2} < \gamma_{CdCl_2} < \gamma_{PbCl_2} \text{ and } \mu^E_{ZnCl_2} < \mu^E_{CdCl_2} < \mu^E_{PbCl_2}) .$$

Values of μ_1^E at 589°C from measurements in the $PbBr_2$-KBr[86] system are more negative than those in the $PbCl_2$-KCl system (E^0 values for $PbBr_2$ given in Table 6) but differ appreciably from the measurements of Reid[108] in the same system.

Table 7. Values of γ_1 and Molar Volumes of Mixing in Equimolar Binary Mixtures of Chlorides at 600°C

Diluent	$PbCl_2$		$CdCl_2$		$ZnCl_2$	
	γ_1	ΔV (cm^3/mole)	γ_1	ΔV (cm^3/mole)	γ_1	ΔV (cm^3/mole)
LiCl	1.06[a]	+0.39[b]		−0.053[c]		
NaCl	0.86	+1.19	0.68	+0.20	0.41	−1.38
KCl	0.46	+1.66	0.36	+0.97	0.19	+0.35
$CaCl_2$	1.25					
$BaCl_2$	0.95	−0.43[d]	0.84	−1.85	0.58	−2.63

[a] $N_{LiCl} = 0.466$.

[b] $N_{LiCl} = 0.428$.

[c] $N_{LiCl} = 0.428$.

[d] $N_{BaCl_2} = 0.4$, $T = 650$°C.

Senderoff, Mellors, and Bretz[119] measured the activities of $CeCl_3$ in cells

$$\mathrm{Ce}\left|\begin{array}{l}\mathrm{CeCl_3}\,(N_1)\\ \mathrm{MCl}\,(N_2)\end{array}\right|\mathrm{Cl_2}\,,$$

where M = Na or K. In Fig. 14 are plotted values of μ_1^E vs N_2^2 at 800°C for $CeCl_3$ in mixtures with NaCl and with KCl. At low concentrations the excess entropy of solution appeared to be negative. However, the large scatter in the experimental results indicated in Fig. 14 makes any quantitative conclusions uncertain. It is apparent that the $CeCl_3$ is stabilized considerably by dissolution in both NaCl and KCl with KCl having a larger effect.

Measurements have been made of the activities of the divalent chlorides in $PbCl_2$-KCl mixtures,[67] $PbCl_2$ mixtures with LiCl, NaCl, KCl, and RbCl,[98] $MgCl_2$ mixtures with LiCl, NaCl, KCl, RbCl,[100] $ZnCl_2$-RbCl,[97] and $BeCl_2$-NaCl[98] – and have been reviewed.[96,99] Since these measurements were made by generating chlorine by electrolysis within the cell itself, the state of the chlorine gas is undefined and the E^0 usually differed from those which are given in Table 6. The activity coefficients did follow the expected relative order (that is, for a given divalent chloride they decreased with an increase in size of the alkali cation), but the absolute values are probably unreliable.

The measurements of Laitinen and Liu[82] and of Flengas and Ingraham[47,48] provide another comparative study of the effect of alkali halide solvents on solutes. They used a cell

$$\mathrm{M}\left|\begin{array}{l}\mathrm{MCl}_n\,(N_1)\\ \mathrm{(LiCl\text{-}KCl\ eutectic)}\end{array}\right|\left|\begin{array}{l}\mathrm{PtCl_2}\,(N_2)\\ \mathrm{(LiCl\text{-}KCl\ eutectic)}\end{array}\right|\mathrm{Pt} \qquad \text{(II.5.A)}$$

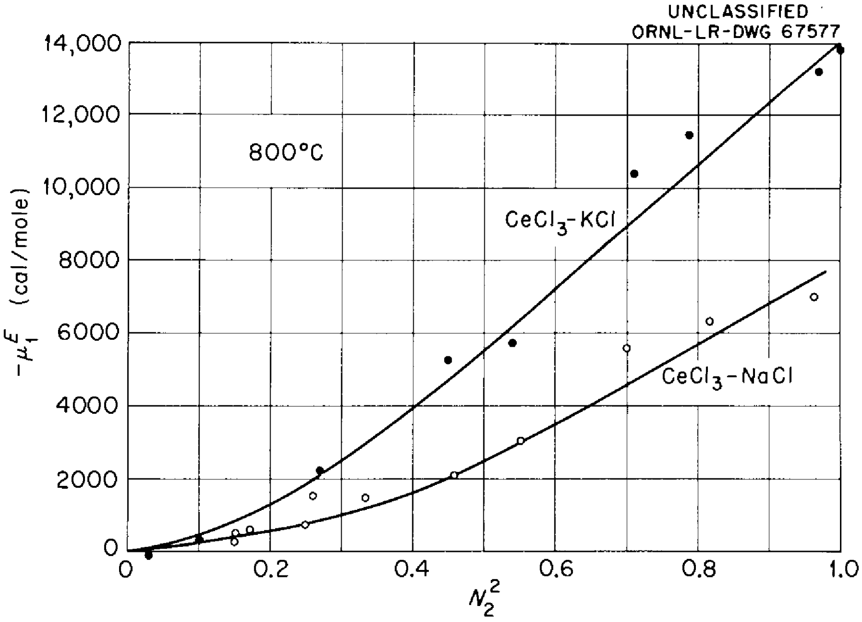

Fig. 14. Excess Chemical Potential of $CeCl_3$ in Mixtures with NaCl and KCl as Obtained from EMF Measurements.

in which the solutes $PtCl_2$ and MCl_n were shown to be dilute enough to obey the Nernst equation,

$$\Delta E_A = \Delta E_A^* - \frac{RT}{F} \ln \frac{(N_1)^{1/n}}{(N_2)^{1/2}} .$$

By adding ΔE_A^* to ΔE_B^*, obtained from the cell

$$\mathrm{Pt}\left|\begin{matrix}\mathrm{PtCl_2}\,(N_2) \\ \mathrm{(LiCl\text{-}KCl\ eutectic)}\end{matrix}\right|\left|\,\mathrm{(LiCl\text{-}KCl\ eutectic)}\,\right|\mathrm{Cl_2}\,, \qquad \text{(II.5.B)}$$

where

$$\Delta E_B = \Delta E_B^* + \frac{RT}{F} \log \frac{1}{(N_2)^{1/2}} ,$$

the standard formation potential is obtained from which the chemical potential of formation of MCl_n may be calculated by using the relation

$$\mu^*_{MCl_n} = -nFE^* = -nF(\Delta E_A^* + \Delta E_B^*) .$$

There are not enough good values of E^0 for the pure liquid solutes at 450°C to make a meaningful comparison of E^* and E^0. Flengas and Ingraham, from the cells

$$\mathrm{M}\left|\begin{matrix}\mathrm{MCl}n \\ \mathrm{NaCl\text{-}KCl\ (50\text{-}50\ mole\ \%)}\end{matrix}\right|\left|\begin{matrix}\mathrm{AgCl} \\ \mathrm{NaCl\text{-}KCl\ (50\text{-}50\ mole\ \%)}\end{matrix}\right|\mathrm{Ag}$$

and

$$\mathrm{Ag}\left|\begin{matrix}\mathrm{AgCl}\\ \mathrm{NaCl\text{-}KCl}\end{matrix}\right\|\ \mathrm{NaCl\text{-}KCl}\ \Big|\ \mathrm{Cl_2}$$

dilute enough in the solute to obey the Nernst relation, obtained values of the standard-formation potential of MCl_n, E^*, in the NaCl-KCl solvent at 700, 800, and 900°C. Values at 700 and 900°C are listed in Table 8.

For a comparison, values of E^* in NaCl-KCl (50-50 mole %) extrapolated to 450°C are given in column 3 of Table 9. Column 4 gives the differences between the values of μ^* in the two solvents. It can be seen that the values of μ^* are always more negative in the NaCl-KCl mixture as expected due to the fact that the effective cation radius in the NaCl-KCl mixtures is greater than in the LiCl-KCl mixtures. Large differences in the two solvents are apparent for the transition metal halides.

In column 4 of Table 8 are listed values of E^0 for the pure liquid at 900°C. Where E^0 was unavailable the standard formation potential for the pure solid is given in parentheses. The values of E^0 are taken from Hamer, Malmberg, and Rubin.[65] It should be noted that the value of E^0 for $ZnCl_2$ is very different from that calculated from Table 6. In view of the discrepancy, both $(\mu^* - \mu^0)$ in Table 8 and values of μ^E cited earlier must be considered questionable for

Table 8. Values of E^*, E^0, and $\mu^* - \mu^0$ in NaCl-KCl (50-50 Mole %) Mixtures

	E^*		E^0,	$\mu^* - \mu^0$,
	700°C	900°C	900°C	900°C
$MnCl_2$	+2.051	+1.967	1.766	−9260
$ZnCl_2$	+1.705	+1.605	1.438	−7200
$CrCl_2$	+1.603	+1.523	~1.307	−9970
TlCl	+1.510			
$CdCl_2$	+1.465		1.279 (700°C)	−8580 (700°C)
$FeCl_2$	+1.365	+1.293	1.084	−9640
$CrCl_3$	+1.270	+1.140	(1.060)[a]	
$PbCl_2$	+1.235	+1.150	1.076	−3420
$SnCl_2$	+1.215	+1.135	~1.255	+5530
$CoCl_2$	+1.169	+1.070	0.939	−6050
CuCl	+1.105	+1.055	0.903	−3510
$NiCl_2$	+0.985			
AgCl	+0.845	+0.795	0.805	230
$CuCl_2$	+0.675	+0.603		

[a] The standard formation potential for the pure solid.

Table 9. Values of E^* (volts) at 450°C in LiCl-KCl and NaCl-KCl Mixtures and Calculated Differences in the Standard Chemical Potentials

MCl_n	E^*(LiCl-KCl)	E^*(NaCl-KCl)[a]	μ^*(NaCl-KCl) − μ^*(LiCl-KCl)
$MgCl_2$	+2.796		
$MnCl_2$	+2.065	2.135	−3230
$AlCl_3$	+2.013		
$ZnCl_2$	+1.782	1.835	−2450
TlCl	+1.587		
$CrCl_2$	+1.641	1.715	−3420
$CdCl_2$	+1.532	1.535	−69
$FeCl_2$	+1.387	1.465	−3600
$PbCl_2$	+1.317	1.352	−1615
$SnCl_2$	+1.298	1.315	−785
$CoCl_2$	+1.207	1.277	−3230
CuCl	+1.067	1.145	−1800
$GaCl_3$	+1.10		
$InCl_3$	+1.051		
$NiCl_2$	+1.011		
AgCl	+0.853	0.905	−1200
$SbCl_3$	+0.886		
$BiCl_3$	+0.804		
$HgCl_2$	+0.7		
$PdCl_2$	+0.430		
$PtCl_2$	+0.216		
AuCl	−0.095		

[a] Values of E^* in NaCl-KCl mixtures are extrapolated from higher temperatures.

$ZnCl_2$. The values of E^0 have, in general, an uncertainty large enough so as to make comparisons of $\mu^* - \mu^0$ semiquantitative. It is clear, however, that the transition metal halides are greatly stabilized by dissolution in alkali halides, the stabilization being greater the larger the radius of the alkali cation.

Reznikov,[111] improving on the method of Treadwell and Cohen,[128] made measurements of the activities of $MgCl_2$ in mixtures with KCl and with NaCl at 750, 850, and 950°C by using the heterogeneous equilibrium

$$MgCl_2 + \frac{1}{2}O_2 \rightleftharpoons MgO + Cl_2 .$$

Reznikov cites evidence that pure MgO is the solid phase in contact with the melt and that the known solid solution of MgO with $MgCl_2$ is unstable at high temperatures. The equilibrium partial pressures of O_2 and Cl_2 for the above reaction were measured for pure liquid $MgCl_2$ and for mixtures of $MgCl_2$ with NaCl and KCl.

$$K = \frac{p^0_{Cl_2}}{\left(p^0_{O_2}\right)^{1/2}} = \frac{p_{Cl_2}}{p^{1/2}_{O_2} a_{MgCl_2}} ,$$

where pure solid MgO and pure $MgCl_2$ are taken as standard states having activities equal to unity, where $p^0_{Cl_2}$ and $p^0_{O_2}$ are the equilibrium partial pressures of Cl_2 and O_2 measured at equilibrium with pure liquid $MgCl_2$ and pure solid MgO, and p_{Cl_2} and p_{O_2} are the partial pressures at equilibrium with a mixture. Reznikov approached the equilibrium from two sides and his results do not differ greatly from, but are probably more reliable than those of Treadwell and Cohen. His values of the activities of $MgCl_2$ are listed below:

T (°C)	$MgCl_2$-KCl Mole % $MgCl_2$ 100	 75	 50	 33.3	$MgCl_2$-NaCl (50 mole % $MgCl_2$)
750	1.0	0.47	0.10	0.010	0.15
850	1.0	0.50	0.11	0.011	0.19
950	1.0	0.54	0.12	0.013	

The activity coefficients in the mixture with NaCl are higher than in the mixture with KCl as expected.

Other measurements using heterogeneous equilibria of the melt with a gas phase include the work of Blood[19] and co-workers on the standard free energy of formation of NiF_2 in NaF-ZrF_4 and LiF-BeF_2 mixtures using the equilibrium

$$Ni + 2HF \rightleftharpoons NiF_2 + H_2 .$$

The equilibrium quotient K_N given by

$$K_N = \frac{N_{NiF_2} P_{H_2}}{P^2_{HF}} ,$$

was constant in dilute solutions indicating that NiF_2 obeyed Henry's law. (HF and H_2 at the temperatures and pressures involved are essentially ideal gases.) The standard free energy (chemical potential) of formation of NiF_2 in its standard state in solution ($\mu^*_{NiF_2}$) could be calculated from the equation

$$\mu^*_{NiF_2} = 2G^0_{HF} - RT \ln K_N .$$

Vapor pressure measurements afford a method of measuring activities in molten-salt mixtures. Unfortunately, the large number of complex compounds found in the vapor often make it difficult to analyze vapor-pressure data. As there is no general discussion of this in standard texts, some of the principles involved in deriving activities from vapor-pressure measurements will be discussed.[83]

The chemical potential of a component in a mixture is related to the fugacity, f, of the component

$$\mu_1 = RT \ln f_1 , \tag{II.5.1}$$

and for the pure liquid $\mu_1^0 = RT \ln f_1^0$;

$$\mu_1 - \mu_1^0 = RT \ln \frac{f_1}{f_1^0} = RT \ln a_1 . \tag{II.5.2}$$

The fugacity is defined in such a way that $f_1/p_1 \to 1$ as $P \to 0$, where p_1 is the partial pressure of the component in the vapor and P is the total pressure.

In investigations of salt vapors it is generally assumed, and will be assumed here, that, except for the formation of associated species or compounds in the vapor, the vapor behaves ideally so that the fugacity of a species in the vapor is equal to the partial pressure of the species.* If only a monomer is present,

$$\mu_1 - \mu_1^0 = RT \ln \frac{p_1}{p_1^0} = RT \ln a_1 . \tag{II.5.3}$$

If a vapor with a monomer vapor molecule represented by M_1 at total pressure, P, associates into several species

$$M_1 \rightleftharpoons \frac{(M_1)_2}{2} \rightleftharpoons \frac{(M_1)_3}{3} \rightleftharpoons \frac{(M_1)_i}{i} ,$$

where $(M_1)_2$ is a dimer, $(M_1)_3$ a trimer, etc., then the total pressure P is (if there is only one component in the vapor)

$$P = (p_1)_1 + (p_1)_2 + (p_1)_3 + \ldots = \Sigma (p_1)_i , \tag{II.5.4}$$

where $(p_1)_i$ is the partial pressure of the associated species $(M_1)_i$. When the vapor is at equilibrium with a mixture (or pure substance)

$$\mu_1(\text{mixture}) = \mu_1(\text{vapor}) .$$

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*Although this assumption may be valid, it has never been investigated. It is probable that at pressures approaching one atmosphere in alkali halides some of the interactions of the dipoles in alkali halide vapors are large enough to have an appreciable effect on the fugacity of the vapor even when the molecules are too far apart to be defined as an associated species.

One total mole of component 1 in the vapor would have the chemical potential (per mole)

$$\mu_1(\text{vapor}) = \frac{(p_1)_1}{P}(\mu)_1 + \frac{(p_1)_2}{2P}(\mu)_2 + \frac{(p_1)_3}{3P}(\mu)_3 + \ldots = \sum \frac{(p_1)_i(\mu)_i}{iP}, \qquad (\text{II}.5.5)$$

where $(\mu)_i$, the chemical potential of the associated species, is given by $(\mu)_i = RT \ln (p_1)_i$ if the non ideality of the vapor is due to the association only, and $(p_1)_i/iP$ is the number of moles of species i in a portion of gas containing a total of one mole of M_1. Because of the equilibrium,

$$(\mu)_1 = \frac{(\mu)_2}{2} = \frac{(\mu)_3}{3} = \frac{(\mu)_i}{i}. \qquad (\text{II}.5.6)$$

Combining Eqs. (5) and (6) we get

$$\mu_1(\text{vapor}) = (\mu)_1 = \frac{(\mu)_i}{i}, \qquad (\text{II}.5.7)$$

so that

$$\mu_1 - \mu_1^0 = RT \ln \frac{(P_1)_1}{(P_1^0)_1} = \frac{RT}{i} \ln \frac{(p_1)_i}{(p_1^0)_i} = RT \ln a_1. \qquad (\text{II}.5.8)$$

In order to measure the activity of the component 1, one need only know the partial pressures at a given temperature of one species containing 1 only which is in equilibrium with a mixture which is in equilibrium with a mixture or with the pure liquid component. At low pressures Eq. (8) is valid for component 1 independently of all other species in the vapor.

The heat of vaporization ΔH_j of species j is given by

$$\frac{d(\mu_j/T)}{d(1/T)} = \frac{Rd \ln p_j}{d(1/T)} = -\Delta H_j. \qquad (\text{II}.5.9)$$

The variation in total pressure with temperature for any mixture or any number of species is

$$\frac{Rd \ln P}{d(1/T)} = R \sum \frac{p_j}{P} \frac{d \ln p_j}{d(1/T)} = -\sum \frac{p_j}{P} \Delta H_j = -\sum X_j \Delta H_j, \qquad (\text{II}.5.10)$$

where X_j is the mole fraction of species j in the vapor, and j can be any species.

Vapor pressures of mixtures have been measured by several methods. The Rodebush and boiling point methods[4,21,33] make a measurement of the total pressure P. In the transport methods[120] the vapor at equilibrium above a liquid is swept away with a known volume of inert gas and analyzed. If only one component of the liquid is vaporized, then the apparent vapor "pressure," P^{Tr}, is

$$\frac{n_1 RT}{V} = P_1^{\mathrm{Tr}} = p_1 + 2(p_1)_2 + 3(p_1)_3 + \ldots = \sum i(p_1)_i, \qquad (\text{II}.5.11\text{a})$$

where P^{Tr} is an apparent "pressure" calculated assuming that the only species is the monomer. For more than one component

$$P_n^{\mathrm{Tr}} = \sum_j \nu_n p_j , \tag{II.5.11b}$$

where P_n^{Tr} is the apparent transport pressure for the nth component and ν_n is the number of molecules of n in species j.

The vapor composition at equilibrium with a given liquid to obtain association constants may be analyzed by using more than one experimental method under a variety of conditions and partial pressures. A complete analysis of the vapor in equilibrium with a mixture requires knowledge of the association constants for all of the species in the vapor. This analysis may be extended to the case where more than one component is vaporized. The precision of partial-pressure measurements decreases very markedly the greater the number of species in the vapor.

The vapor pressure of ZrF_4 in equilibrium with mixtures of ZrF_4 with LiF[121], NaF[120], and with RbF[33,121] have been studied by the transport method[120,121] and by the Rodebush technique.[33] Values of μ_1^E for ZrF_4 at 912°C are given in Fig. 15 with the value of $p^0_{ZrF_4}$ (calculated from the equation given by Cantor for the vapor pressure) at the measured melting point of 912°C;

$$\log p^0_{ZrF_4}\ (\mathrm{mm}) = 12.542 - 11{,}360/T\ (^\circ\mathrm{K})\,. \tag{II.5.12}$$

At high ZrF_4 concentrations the major species in the vapor is ZrF_4. Deviations from ideality are large, and are larger the larger the alkali cation. Some of the values of the vapor pressure used in these calculations were not directly measured but were extrapolated from other temperatures. Although Sense and co-workers report vapor pressures of the alkali fluorides in these mixtures, they do not in any case properly correct for the presence of associated species in the vapors. Cantor and co-workers[33] have reported that in RbF-ZrF_4 mixtures the excess entropies are positive and that the excess enthalpies as obtained from temperature coefficients of vapor pressure data exhibit both positive and negative values. Although these conclusions are more reliable than those obtained from emf data, the temperature coefficients are subject to large errors.

The most thorough study of the vapor pressures of a molten-salt mixture is that of Beusman,[6] who partially studied LiCl-$FeCl_2$ mixtures and studied more completely KCl-$FeCl_2$ mixtures at temperatures from about 850 to 1000°C by using the Rodebush technique for measuring the total pressure and the transport method for measuring the vapor composition.

In the vapor above mixtures of KCl and $FeCl_2$ the presence of the species $FeCl_2$, Fe_2Cl_4, $KFeCl_3$, KCl, and K_2Cl_2 was consistent with his measurements. Calling these species 1, 2, 3, 4, and 5 he could solve for the number of moles of each of these species in a unit volume of vapor and, hence, for the partial pressures at equilibrium with the melt from measurements of the total pressure of salt ($P = n_v RT/V$), and by a chemical analysis of the chemical compounds swept

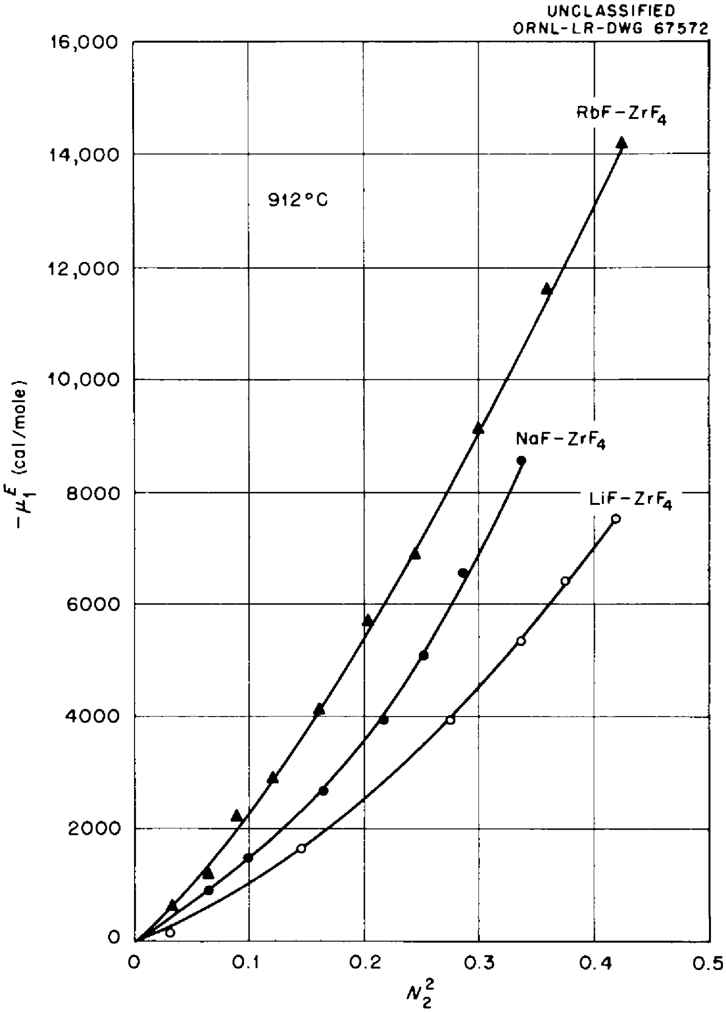

Fig. 15. Excess Chemical Potentials of ZrF_4 in Mixtures with LiF, NaF, and RbF as Obtained from Vapor-Pressure Measurements.

out by a unit volume of gas from above the pure components and from above the mixtures. He solved the simultaneous equations

$$n_v = n_1 + n_2 + n_3 + n_4 + n_5 ,$$

$$n_{Fe} = n_1 + 2n_2 + n_3 ,$$

$$n_K = n_3 + n_4 + 2n_5 ,$$

$$n_1^2 = K_{FeCl_2} n_2 \left(\frac{n_v}{P}\right) ,$$

$$n_4^2 = K_{KCl} n_5 \left(\frac{n_v}{P}\right) ,$$

where n_v is the total number of moles of all species in a unit volume, n_{Fe} and n_K are the number of Fe and K ions in a unit volume, and K_{FeCl_2} and K_{KCl} are the dissociation constants in pressure units for the dimer of the subscript component and were evaluated from data obtained with the pure materials KCl and $FeCl_2$. The presence of a trimer in LiCl vapors made this procedure very imprecise since the calculations, which essentially involve subtracting large numbers, are much more sensitive to errors in the measurements when more species are involved. In Fig. 16 are plotted Beusman's values of μ^E for the two components $FeCl_2$ and KCl at 900°C derived from the values of the partial pressures. It is apparent that values of μ^E are all negative. Calculation of μ^E_{KCl} from $\mu^E_{FeCl_2}$ by integrating the Gibbs-Duhem relation

$$N_1\, d\mu_1^E + N_2\, d\mu_2^E = 0$$

leads to about the same values as were measured.

The deviations from ideality of KCl are somewhat greater than those for $FeCl_2$, and the apparent values of both the excess entropies of mixing and partial molar heat of solution are positive.

Barton and Bloom[4] have measured the vapor pressures of $PbCl_2$-KCl, $CdCl_2$-KCl, and $CdCl_2$-NaCl mixtures at 900°C by using boiling point and transport methods.[113]. At concentrations of

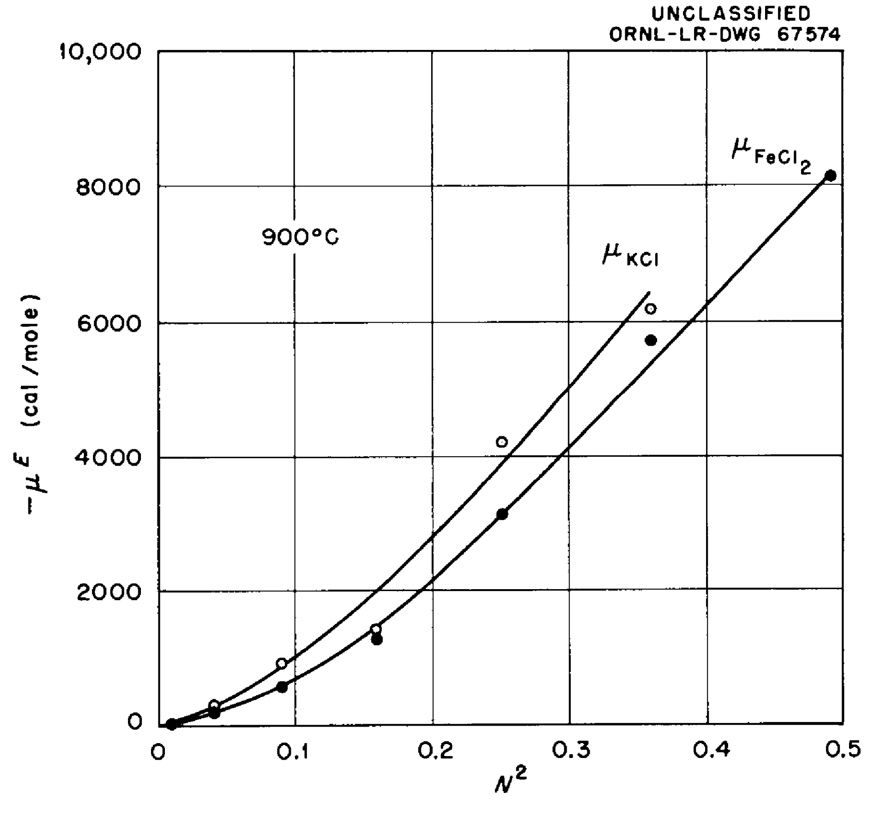

Fig. 16. Excess Chemical Potentials of KCl and $FeCl_2$ in KCl-$FeCl_2$ Mixtures as Obtained from Vapor-Pressure Measurements.

less than 60 mole % alkali halide they could neglect the volatilization of the alkali halides and vapor compounds containing alkali halides. Their results are in fair agreement with the emf measurements of Lantratov and Alabyshev[85] on the $PbCl_2$-KCl system. They found that the apparent deviations from ideal behavior in the $CdCl_2$-KCl system were smaller than in the $CdCl_2$-NaCl system. The measurements in the systems containing $CdCl_2$ are open to question.

II.6 Discussion of Binary Systems with a Common Anion

The results in the previous section exhibit certain very general features for mixtures of salts of a monovalent alkali cation with salts of a polyvalent cation. The most obvious feature is the variation of the thermodynamic properties with cation radius and charge. The deviations from ideal solution behavior of both the alkali ion salt and the salts with polyvalent cations usually become more negative (or less positive) with an increase in the radius of the alkali cation and with an increase of the charge or decrease of the radius of the polyvalent cation. This type of behavior has often been ascribed to "complex ion formation" or to "complexing."[55,62,85,99] This terminology has been used so freely and in so many different senses that some of the "explanations" of solution behavior in terms of "complexes" are merely redundancies of the observed facts and add nothing to the understanding of solution behavior in terms of physical concepts. As a consequence, in this section, a discussion and critique will be given of this concept.

Among the most reasonable and careful considerations of the concept of complex ions are those of Flood and Urnes[55] and Grjotheim.[62] Flood and Urnes, for example, discuss the liquidus curves of RbCl, KCl, and NaCl in mixtures with $MgCl_2$. They reason that a mixture of an alkali halide with an alkali salt of a large divalent anion will exhibit only small deviations from ideality. Evidence for this comes from the apparently negligible deviations from ideality found in the liquidus curves of Na_2SO_4 in mixtures with NaCl and with NaBr.[52] (Note the work of Cantor on the parallel effect of cation radius.) Flood and Urnes propose that the component M_2MgCl_4 containing the $MgCl_4{}^{2-}$ grouping would exhibit small deviations from ideality based on the Temkin definition. Thus at low concentrations of $MgCl_2$,

$$a_{MCl} = \frac{n_{Cl^-}}{n_{Cl^-} + n_{MgCl_4{}^{2-}}} = \frac{n_{MCl} - 2n_{MgCl_2}}{n_{MCl} - n_{MgCl_2}}. \qquad (II.6.1)$$

The procedure of Flood and Urnes is essentially a redefinition of components. They show that the liquidus temperatures[75] (and activities) for KCl and RbCl are in reasonable agreement with Eq. (1). The liquidus temperatures (activities) of NaCl in NaCl-$MgCl_2$ mixtures exhibit positive deviations from the calculations based on Eq. (1). This was ascribed to a partial dissociation of the $MgCl_4{}^{2-}$ ion. Thus, by the redefinition of components, and by the careful choice of systems, reasonable correlations with the data were obtained.

Although such a procedure has the advantage of being simple, there are many criticisms which can be made. The major criticism, perhaps, is that this method can be applied to very few systems and does not lead to quantitative predictions which can be made *a priori*. For example, the liquidus temperatures of NaF in NaF-BeF_2 mixtures are too low to be described by any redefinition of components which is consistent with possible structural concepts. Since the Be^{2+} ions are so small, a coordination of Be^{2+} cannot be expected larger than four and yet a mixture of, for example, NaF and Na_2BeF_4 would have to be described as exhibiting negative deviations from ideal solution behavior. On the other hand, no reasonable choice of a "complex ion" grouping or complex component can be invoked to explain the small deviations from ideality of NaF in NaF-BeF_2 mixtures. Further, although the thermodynamic data may be described by choosing a particular complex component, this does not necessarily imply the existence of the ions of this component in the melt. Except for the very stable (relative to the separate ions) complex ions as NO_3^-, PO_4^{3-}, and SO_4^{2-}, a simple comprehensive description of the solution behavior of mixtures with a common anion cannot generally be made with only one "complex ion" and little can be learned about solution behavior *a priori* from such an approach.

The absence of a simple explanation of the solution behavior of molten-salt mixtures is evident from the analogy between a_{H_2O} in HCl-H_2O mixtures and a_{ZrF_4} in NaF-ZrF_4 mixtures shown in Fig. 17. In water the O-H interaction is very strong so that it is only slightly ionized. At low

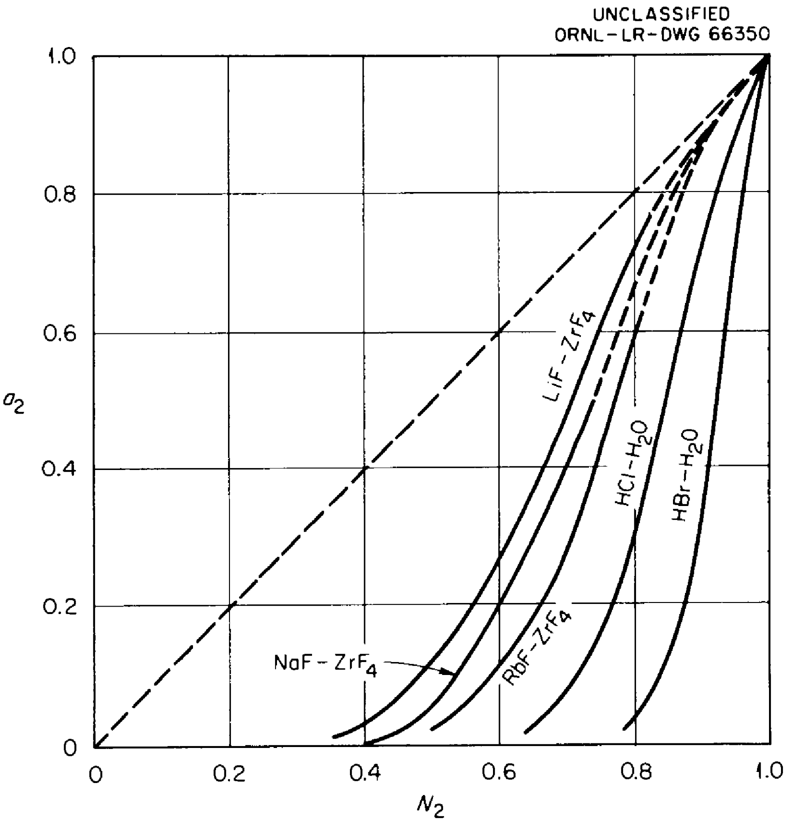

Fig. 17. Plot of the Activity of H_2O in H_2O-HCl and H_2O-HBr Mixtures at 25°C and the Activity of ZrF_4 in ZrF_4-LiF, ZrF_4-NaF, and ZrF_4-RbF Mixtures at 912°C.

concentrations of HCl the solution may be understood in terms of solvated H^+ and Cl^- ions interacting in a dielectric medium. In mixtures with HBr the activity of water is even lower than with HCl. The limiting law at concentrations of HCl greater than the concentration of H^+ from the self ionization of water is

$$\mu_{H_2O} - \mu^0_{H_2O} \cong RT \ln (1 - 2N_{HCl}) , \qquad (II.6.2)$$

since HCl behaves as two particles. If γ_{H_2O} is defined by

$$\mu_{H_2O} - \mu^0_{H_2O} = RT \ln N_{H_2O}\gamma_{H_2O} , \qquad (II.6.3)$$

then at low concentrations

$$\gamma_{H_2O} \cong \frac{1 - 2N_{HCl}}{1 - N_{HCl}} < 1 . \qquad (II.6.4)$$

Interionic interactions of H^+ and Cl^- will cause γ_{H_2O} to differ at higher concentrations from the value given by (II.6.4). Beyond the range of validity of the Debye-Hückel theory, this is unpredictable although there is a persistence of the negative deviations from "ideal" solution behavior.

In NaF-ZrF_4 mixtures, the solvent ZrF_4 may be considered to be more highly ionized than water. Consequently, the self ionization of ZrF_4 and the one particle limiting law will probably hold to higher concentrations than in water so that the deviations from ideality in dilute solutions based on an equation such as (II.6.3) will be smaller in the NaF-ZrF_4 mixture than in HCl-H_2O mixtures. Apparently the smaller (less negative) deviations from ideal solution behavior in the NaF-ZrF_4 mixture as compared to HCl-H_2O mixtures persist at high concentrations. Just as with water, the larger the size of the "foreign" ion (Cl^- and Br^- in H_2O and Li^+, Na^+, and Rb^+ in ZrF_4) the greater the deviations from ideality. This does not explain the observed solution behavior in NaF-ZrF_4 mixtures but merely suggests that any fundamental explanation in concentrated solutions is at least as difficult as in concentrated solutions in water where it is clear that the H^+ and Cl^- ions are solvated but no valid quantitative predictions can be made in terms of structural concepts. Because of these apparent inadequacies of the concept of "complex ions" in describing solution behavior in mixtures containing one type of anion it is in order to discuss and attempt to classify some of the effects and interactions which have been included in the terms "complex ion" or "complexing" in the hope that such a procedure would be more instructive and useful in future attempts at deriving quantitative theories. Most definitions of "complex ions" or of "complexing" fall into two categories.

In the first category a "complex ion" is usually conceived as a microscopic structural entity. A complex ion can be most clearly defined as a grouping of at least one central cation and near-neighbor anions having a particular configuration. If each grouping is isolated from others and shares no anions, then the grouping is a finite complex. NO_3^-, PO_4^{3-}, and SO_4^{2-} ions are finite complexes. If the groupings are all interconnected by shared anions, then infinite complexes are present. By these definitions all pure salts are infinite three-dimensional complexes and very dilute solutions of one salt in another always contain finite complex ions although the configurations of all the finite complexes are not necessarily uniform. X-ray, ultra-violet, infra-red, Raman spectra, and other methods of investigating structure are means for investigating these complex ions.

In the second category the terms "complex ions" or "complexing" are used to describe a tendency to stabilization. This is the least satisfactory use of this terminology, since so many different interactions and concepts are included in this usage that less information is conveyed than by the use of the word stabilization.

For pure materials as for example AgCl, NiF_2 or $HgCl_2$, specific interactions (van der Waals' ligand field and covalent binding) give rise to more negative values of the energy of formation from the isolated ions than might be expected for alkali or alkaline earth halides where Coulomb interactions are relatively more important. In solutions the tendency to "complexing" or toward the stabilization of a component in solution is characterized by negative values of μ^E. Some of the solution effects which influence the values of μ^E are:

(*a*) Coulomb effect. The discussion in section II shows that Coulomb interactions in mixtures of salts containing monovalent ions lead to negative values of μ^E. This effect appears to be present in mixtures containing polyvalent cations. Long-range interactions are very significant in this effect and as a consequence a quantitative description of this effect in terms of finite complexes can only be fortuitously correct.

(*b*) Polarization effect. The field intensity at an ion position will, in general, not be zero because of ionic motions and because of the different sizes and charges of cations. For example, an anion having two cations the same size but of different charge as near neighbors will tend to have a Coulomb field intensity on it. As a consequence, the electrons on the anion and the thermal motions of the anion will be "polarized" so that the negative charges reside a greater fraction of the time near the cation with the higher charge. In a pure molten salt this effect will be expected to be smaller than in a mixture, and the net contribution will lead to a relative stabilization of the mixture (negative contribution to the deviations from ideal solution behavior).

(*c*) van der Waals' interactions. As in mixtures containing monovalent cations these interactions usually will lead to a positive contribution to the deviations from ideal solution behavior for systems containing polarizable cations. To illustrate with a clear-cut example, the systems NaCl-$PbCl_2$ and AgCl-$PbCl_2$ might be compared. In the former the measured deviations from ideal solution behavior of $PbCl_2$ are negative ($\mu^E_{PbCl_2} < 0$), and from the Gibbs-Duhem equation it can be shown that μ^E_{NaCl} is also negative. Measurements in the latter system[116] indicate that μ^E_{AgCl} (and $\mu^E_{PbCl_2}$) is essentially zero at all concentrations. The major differences between these two systems are probably related to the high polarizability of the Ag^+ ion as compared to Na^+ and hence to the contribution to van der Waals' interactions. Quantitative estimates of the magnitude of this effect in such systems are tenuous at present.

(*d*) Ligand field effects.[103] These interactions will tend to stabilize pure salts of transition metal ions and particular configurations of near-neighbor anions will tend to be more probable. Such stabilization, regardless of the specific symmetry of the near-neighbor anions, will tend to be monotonic with the strength of the negative ligand field. For given anions as near neighbors to a particular transition metal ion in a mixture, the negative ligand field will be attenuated by more distant cations with the attenuation tending to be smaller the smaller the charge and the larger the radius of these other cations. The dissolution of a transition metal salt, NiF_2 for example, in an alkali fluoride would lead to a replacement of next-nearest neighbor Ni^{2+} by monovalent alkali cations. This will lead to a stabilization of NiF_2 ($\mu^E_{NiF_2} < 0$), which would be more pronounced the larger the alkali cation. The influence of ligand-field interactions will be limited by steric requirements and in mixtures with alkali metal salts will probably lead to negative contributions to the deviations from ideal solution behavior of both components.

(*e*) Packing and steric effect. To satisfy the tendency toward local electroneutrality it is probable that small highly charged cations will tend to have a larger number of anions as near neighbors than cations of low charge. Any energy changes (stabilization) related to this effect will be sterically limited in accordance with the values of the anion-cation radius ratios.

All of the factors mentioned are included in the concept of "complex ion" of or "complexing" when it is applied to stabilization. Some of these effects may be concomitant with a foreshortening of cation-anion distances (e.g., coulomb, polarization, and/or ligand field) or with a tendency toward specific configurations of anions about cations (e.g., ligand field and/or packing). In all cases, these factors influence the free energy *differences* between pure salts and salts in solution. It may be preferable to refer to the observation of negative values of μ^E as a stabilization, since such a stabilization is not necessarily related to the observation of a "complex ion" as a structural entity. By this usage, no unwarranted implications about the structure of the melt need to be made.

The existence of solid or gaseous compounds which are made from the two salts in a solution cannot be used as evidence that particular "complex ions" are formed in solution. Although many of the factors and interactions which lead to relatively greater stability of gaseous and solid compounds may also give rise to negative deviations from ideal solution behavior, many of the factors influencing the structure of solids or gases have no counterpart in liquids. For example, in solids steric repulsions of the ions are more important than in liquids and have a strong influence on structure; and in gases the entropies of association are generally negative and give rise to a strong influence in favor of forming the simplest compounds. Kinetic definitions of "complex ions" in terms of the lifetime of a grouping or of the relative mobility of ions[20] cannot be clearly related to equilibrium thermodynamic properties or to "complex ions" as a structural entity unless these lifetimes are very long.

Since there is no adequate theory for most binary mixtures, μ^E, for any component in a given mixture containing polyvalent cations, must be estimated empirically by comparison with known systems containing mixtures of the same charge type and the same anion. Keeping in mind the types of interactions which influence the values of μ^E, reasonable estimates may be made by analogy with known systems or by interpolation. The development of a theory, as, for example, by the extension of the perturbation theory of conformal ionic mixtures to mixtures containing cations of different valence, would be an aid in such estimations and might be used to confirm empirical relations such as was proposed by Kleppa.

II.7 Other Systems

Measurements of the activities of lead halides in the mixtures $PbCl_2$-$ZnCl_2$ (ref 131) and $PbBr_2$-$ZnBr_2$ (ref 117) indicated small negative deviations from ideal solution behavior in the former and small positive deviations from ideality in the latter. (Calculations of the activities of $ZnCl_2$ in the first system by use of the Gibbs-Duhem relation were in reasonable agreement with activities calculated from measurements of the partial pressures of $ZnCl_2$ in this system.[126]) In these two systems there is no difference between the mole fraction of a component (N_{PbX_2}) and the product of the ion fractions ($N_{Pb}N_X^2 = N_{Pb} = N_{PbX_2}$) and there is little ambiguity in defining activity coefficients. On the other hand, in a system as $PbCl_2$-$PbBr_2$ there is some ambiguity,[28] since $N_{Pb}N_X^2 = N_X^2 = N_{PbX_2}^2$. In such systems, consequently, the definition of activity coefficients depends on the type of compounds. If the lead halides were very stable molecular compounds and did not react with each other (were not molten salts), then the activity coefficient would be defined by $a_{PbX_2} = N_{PbX_2}\gamma_{PbX_2}$. For ionizing salts (or where the compounds are molecular, and where one might consider the exchange $PbCl_2 + PbBr_2 \rightleftharpoons 2PbClBr$), in order to be consistent with the limiting laws, the activity coefficient is better defined by $a_{PbX_2} = N_{Pb}N_X^2\gamma_{PbX_2}$. On this latter (and more realistic) basis, the activity coefficients, γ_{PbBr_2} in $PbCl_2$-$PbBr_2$ mixtures, are larger than unity.[117] The choice is not always clear-cut as many compounds cannot be strictly classified as either molecular or ionic salts.

Very few other measurements on binary systems that have a common cation have been made. Precise measurements by Toguri, Flood, and Førland[50] on the exchange equilibria

$$Cl_2 + 2MBr \rightleftharpoons 2MCl + Br_2 \qquad \text{(II.7.A)}$$

in LiCl-LiBr, NaCl-NaBr, and KCl-KBr mixtures were used to investigate the activity coefficients of the alkali halides in these mixtures. The equilibrium constant for (A) is

$$K_M = \frac{N_{MCl}^2\gamma_{MCl}^2 p_{Br_2}}{N_{MBr}^2\gamma_{MBr}^2 p_{Cl_2}} = K_M' \frac{\gamma_{MCl}^2}{\gamma_{MBr}^2}, \qquad \text{(II.7.1)}$$

where K_M' is the measured equilibrium quotient. Taking the logarithm of K_M and using as a first approximation for the activity coefficients in any one binary system

$$RT \ln \gamma_{MCl} = \lambda N_{MBr}^2 \quad \text{and} \quad RT \ln \gamma_{MBr} = \lambda N_{MCl}^2,$$

then

$$RT \ln K' = RT \ln K + 2\lambda(N^2_{\mathrm{MBr}} - N^2_{\mathrm{MCl}}) \,. \tag{II.7.2}$$

Plots of $RT \ln K'$ vs $(N^2_{\mathrm{MBr}} - N^2_{\mathrm{MCl}})$ led to the values of λ in Table 10, which indicate small positive deviations from ideality. For these relatively large and polarizable anions, packing or van der Waals' effects have been proposed as possible contributing factors. To contrast this, an analysis of the liquidus temperatures of LiF-LiCl mixtures[64] with the data in Table 1 indicates small negative deviations from ideal solution behavior for both components. Since the F^- ion is smaller and less polarizable than Br^-, it would seem that at least one of these two properties of the ions is significant.

Table 10. Values of λ (cal) from Equilibrium Measurements in Binary Systems with a Common Cation (M)

	Li	Na	K
MBr-MCl	150	350	530
$M_2Cr_2O_7$-M_2CrO_4	0	~300	~500

Similar measurements of the equilibrium

$$M_2Cr_2O_7 \rightleftharpoons M_2CrO_4 + \tfrac{1}{2}Cr_2O_3(\mathrm{solid}) + \tfrac{3}{4}O^2 \tag{II.7.B}$$

in molten mixtures of chromates and dichromates have been made[49] for M = Li^+, Na^+, K^+, or Tl^+. The equilibrium constant, if $CrO_4{}^{2-} = X^{2-}$ and $Cr_2O_7{}^{2-} = Y^{2-}$, is given by

$$K_{\mathrm{M}} = \frac{N_{\mathrm{X}}(p_{O_2})^{3/4}}{N_{\mathrm{Y}}} \, \frac{\gamma_{\mathrm{M_2X}}}{\gamma_{\mathrm{M_2Y}}} = K'_{\mathrm{M}} \, \frac{\gamma_{\mathrm{M_2X}}}{\gamma_{\mathrm{M_2Y}}} \,; \tag{II.7.3}$$

by using the approximation that $RT \ln \gamma_{\mathrm{M_2X}} = \lambda N^2_{\mathrm{M_2Y}}$ and $RT \ln \gamma_{\mathrm{M_2Y}} = \lambda N^2_{\mathrm{M_2X}}$ the values of λ could be obtained from the slope of a plot of $\ln K'_{\mathrm{M}}$ vs $(N^2_{\mathrm{M_2X}} - N^2_{\mathrm{M_2Y}})$. These are given in Table 10 and are seen to be small. When M^+ was an alkali ion the stability of $M_2Cr_2O_7$ relative to M_2CrO_4 increased as the size of the M^+ cation increased and consequently the equilibrium constant K_{M} (and the equilibrium quotient K'_{M}) for reaction (B) decreased with an increase of the size of M^+. This is also true for the equilibrium in reaction (A). These facts are useful for anticipating some of the properties of molten reciprocal salt systems discussed in section III. For example, consider the equilibrium (B) in a mixture of $Na_2Cr_2O_7$ and Na_2CrO_4. The equilibrium constant is given by

$$-RT \ln K_{\mathrm{Na}} = F^0_{\mathrm{Na_2CrO_4}} + \tfrac{1}{2}F^{\square}_{\mathrm{Cr_2O_3}} - F^0_{\mathrm{Na_2Cr_2O_7}} \tag{II.7.4}$$

and is, of course, dependent only on the properties of the pure reactants. If the composition of the mixture is altered so that the Na^+ ion is gradually replaced by K^+ ion, the equilibrium (B) will gradually go more to the left and K'_{Na} will decrease. When very little Na^+ ion is left and the melt is essentially a mixture of $K_2Cr_2O_7$ and K_2CrO_4, the value of K'_{Na} will be equal to the value of K'_K in the mixture containing only the K^+ cation. For this case one obtains from Eq. (3)

$$\begin{aligned} \ln K'_{Na} = \ln K'_K &= \ln K_{Na} - \ln (\gamma_{Na_2X}/\gamma_{Na_2Y}) \\ &= \ln K_K - \ln (\gamma_{K_2X}/\gamma_{K_2Y}) , \end{aligned} \tag{II.7.5}$$

where the activity coefficients are all in a solution containing mainly K^+ ions and very little Na^+ ion. Introducing Eq. (4), one obtains

$$\begin{aligned} \ln (\gamma_{Na_2X}/\gamma_{Na_2Y}) &= \ln (K_{Na}/K_K) + \ln (\gamma_{K_2X}/\gamma_{K_2Y}) \\ &= -\frac{\Delta\mu^0}{RT} + \ln (\gamma_{K_2X}/\gamma_{K_2Y}) , \end{aligned} \tag{II.7.6}$$

where $\Delta\mu^0$ is the free energy change for the reaction of the liquids in (C)

$$Na_2Cr_2O_7 + K_2CrO_4 \rightleftharpoons K_2Cr_2O_7 + Na_2CrO_4 \tag{II.7.C}$$

and the last term in Eq. (6), $\ln (\gamma_{K_2X}/\gamma_{K_2Y})$, can be seen to be small in this case from the data in Table 10. The value of $\Delta\mu^0$ is negative and the ratio of the activity coefficients of the components Na_2CrO_4 and $Na_2Cr_2O_7$ is much greater than unity, and in simple cases such as this, Na_2CrO_4 exhibits positive deviations from ideal solution behavior and $Na_2Cr_2O_7$ exhibits negative deviations from ideal solution behavior. Thus Na_2CrO_4, which is a member of the stable pair in reaction (C), exhibits positive deviations from ideality and $Na_2Cr_2O_7$, which is not a member of the stable pair, exhibits negative deviations from ideal solution behavior. This tendency is present in all reciprocal systems. Flood and Maun[49] have measured $\ln K'$ as a function of the ion fraction of Na^+ in mixtures of Na^+, K^+, CrO_4^{2-}, and $Cr_2O_7^{2-}$ ions. A plot of $\ln K'$ vs N_{Na} given in Fig. 18 can be seen to be nearly linear in the cation fraction. The data fitted the equation

$$\ln K'_{Na,K} = N_{Na} \ln K'_{Na} + N_K \ln K'_K + bN_{Na}N_K , \tag{II.7.7}$$

where b is -0.2 at 662°C. Similar measurements in the Tl^+, K^+, CrO_4^{2-}, $Cr_2O_7^{2-}$ system are plotted in Fig. 18. The quantity b is discussed by Flood and Maun, is related to the properties of binary mixtures made up from the four ions in the system,[49] and is probably small when all the binary systems have small deviations from ideal solution behavior. These properties of reciprocal systems have been used in an ingenious derivation of a zeroth order theory of these systems.[53,54] A more complete description of reciprocal systems is given in section III.

Since linear relations are often useful from a practical point of view, two linear relations which apply to ternary systems having a common anion will be stated.[58] These apply to ternary systems in which the solution properties of two of the components (components 1 and 2) do not differ greatly, mixtures of these two components do not exhibit large deviations from ideal solution behavior,

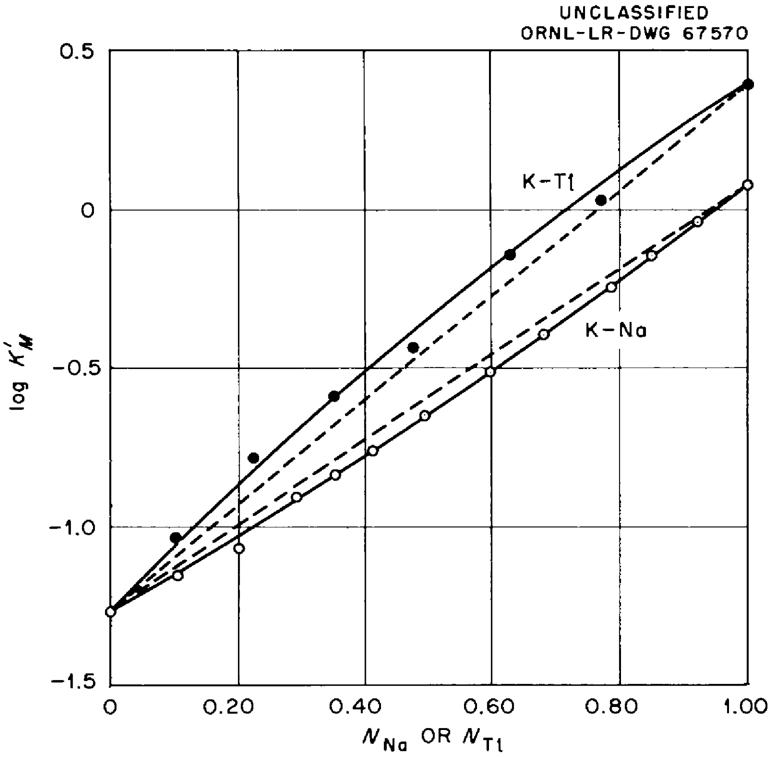

Fig. 18. Measured Values of the Equilibrium Quotient for the Reaction (II.7.B).

and the properties of these two components differ significantly from the third component (component 3). In these cases, some of the properties of the ternary mixtures may be estimated from the properties of binary mixtures composed of the three components.

To illustrate, the measurements of Førland[57,58] on the partial pressures of CO_2 in equilibrium with $CaCO_3$ which is component 3 in mixtures of Na_2CO_3, K_2CO_3, and $CaCO_3$ will be used. The CO_2 is in equilibrium with $CaCO_3$.

$$CaCO_3(\text{solution}) \rightleftharpoons CaO(\text{solid}) + CO_2(\text{gas}).$$

The components Na_2CO_3 and K_2CO_3 have negligible partial pressures of CO_2, and the partial pressure is proportional to the activity of $CaCO_3$ in solution. Førland derived the relation having a form similar to the equation below which at a constant mole fraction of component 3 is

$$\ln \gamma_3 \text{ (in ternary)} = \frac{N_1}{N_1 + N_2} \ln \gamma_3 \text{ (in binary 1-3 mixture)}$$

$$+ \left(\frac{N_2}{N_1 + N_2}\right) \ln \gamma_3 \text{ (in binary 2-3 mixture)} - N_1 N_2 b', \quad \text{(II.7.8)}$$

where b' is related to properties of binary mixtures of 1 and 2 and the last term in (8) is negligible when the properties of 1 and 2 differ little. Although Førland derived this equation (in somewhat different form) under the restrictive assumption of regular solutions, the modified result (Eq. 8) is probably much more general. The form used here has been changed to avoid the ambiguity associated with the concentration scale to be used.

The measurements of p_{CO_2} in mixtures of $CaCO_3$ with Na_2CO_3, with K_2CO_3 and with an equimolar mixture $(Na,K)CO_3$ at a constant mole fraction of $CaCO_3$ was consistent with the equation[58]

$$\ln p_{CO_2}[(Na,K,Ca)CO_3] = \frac{N_{Na}}{N_{Na}+N_K} \ln p_{CO_2}[(Na,Ca)CO_3] + \frac{N_K}{N_{Na}+N_K} \ln p_{CO_2}[(K,Ca)CO_3] , \qquad (II.7.9)$$

which is consistent with Eq. (8). A similar relation for component 1 at constant mole fraction of component 3 is

$$\ln \gamma_1 \text{ (in ternary)} = \ln \gamma_1 \text{ (in binary 1-3 mixture)} + b'''N_2 + b'''N_2^2 , \qquad (II.7.10)$$

where b''' is probably small when components 1 and 2 do not differ greatly in their properties. To illustrate this Christian,[34] in unpublished work on the partial pressure and activities of ZrF_4 at 912°C in mixtures of ZrF_4, UF_4, and NaF containing 54 mole % of NaF, demonstrated that the measurements fitted the equation

$$\ln \gamma_{ZrF_4} = \ln 0.049 + 4.12 N_{UF_4} . \qquad (II.7.11)$$

Further tests in other systems of such linear relations would be of interest.

RECIPROCAL SYSTEMS

III.1 General

Reciprocal systems are mixtures of salts containing at least two cations and two anions. The nature of this class of systems lends itself to theoretical treatment. Perhaps the most obvious, and most naive treatment of this class of systems considers the reciprocal chemical reactions. For example, in the simplest type of reciprocal system A^+, B^+, X^-, Y^-, the reciprocal reaction

$$AY^{(liq)} + BX^{(liq)} \rightleftharpoons AX^{(liq)} + BY^{(liq)} \qquad (III.1.A)$$

is considered. It is easily shown that for the system to conform to Temkin's definition of ideality it is necessary that the free energy change (ΔG^0_A or $\Delta\mu^0_A$) and the enthalpy change (ΔH^0_A) for the equilibrium (A) be zero and that all of the binary systems AX-BX, AX-AY, AY-BY, and BX-BY form ideal solutions. Except for isotopic mixtures all of these conditions are probably not realized in any real systems.

If $\Delta\mu_{\text{A}}^0$ for reaction (A) is negative, then there will be a *tendency* for the components AX and BY to exhibit positive deviations from ideal solution behavior, and if $\Delta\mu_{\text{A}}^0$ is positive there will be a *tendency* for AX and BY to exhibit negative deviations from ideal solution behavior. That these are tendencies and not necessary consequences can be illustrated in a simple manner. The excess free energy (or enthalpy) of dissolution of a small amount of AY to form an "infinitely" dilute solution in BX can be calculated from the sum of $\Delta\mu_{\text{A}}^0$ (or ΔH_{A}^0) with the sum of the excess chemical potentials (or enthalpies) for the processes

$$\text{AX}^{(\text{liq})} \longrightarrow \text{AX}^{(\text{dilute solution})} \; \Delta\mu_{\text{B}} \;, \tag{III.1.B}$$

$$\text{BY}^{(\text{liq})} \longrightarrow \text{BY}^{(\text{dilute solution})} \; \Delta\mu_{\text{C}} \;. \tag{III.1.C}$$

Thus, in dilute enough solutions, the excess chemical potential of solution of AY is $\Delta\mu_{\text{A}}^0 + \Delta\mu_{\text{B}} + \Delta\mu_{\text{C}}$ and hence the sign and magnitude do not depend on $\Delta\mu_{\text{A}}^0$ alone. There is a rough correlation between $\Delta\mu_{\text{A}}^0$ (or ΔH_{A}^0)* and the deviations from ideal solution behavior and the types of behavior which are exhibited in solid-liquid phase equilibria.[5]

In the previous section $\Delta\mu_{\text{B}}$ and $\Delta\mu_{\text{C}}$ have been discussed. The term $\Delta\mu_{\text{A}}^0$ (or ΔH_{A}^0) is related to a variety of types of interactions. When values of $\Delta\mu_{\text{A}}^0$ cannot be obtained from tables, it is sometimes useful to be cognizant of one of the major influences on $\Delta\mu_{\text{A}}^0$, that of coulomb interactions.

For the alkali halides, for example, the largest contribution to $\Delta\mu_{\text{A}}^0$ is the Madelung term

$$-\text{A}e^2\left(\frac{1}{d_{\text{AX}}}+\frac{1}{d_{\text{BY}}}-\frac{1}{d_{\text{AY}}}-\frac{1}{d_{\text{BX}}}\right),$$

where $d_{ij} = r_i + r_j$, where r_i is a cation radius and r_j is an anion radius. It can be shown that if $r_{\text{A}} < r_{\text{B}}$ and $r_{\text{X}} > r_{\text{Y}}$, or $r_{\text{A}} > r_{\text{B}}$ and $r_{\text{X}} < r_{\text{Y}}$ then the Madelung term is positive. This tendency leads to the general *reciprocal Coulomb effect* which is valid for all the alkali halides. This effect is such that in a reciprocal system with two cations and two anions the two stable components (stable pair) as evidenced by $\Delta\mu_{\text{A}}^0$ are the small cation-small anion component and the large cation-large anion component. These two components** would tend to exhibit positive deviations from ideal solution behavior and the other two negative deviations. From a consideration of the Madelung term one would expect positive deviations from ideal solution behavior for the stable pair to increase in the order [NaF-KCl] < [LiF-KCl] < [LiF-CsCl] < [LiF-CsBr]. The last two systems exhibit such large deviations from ideal solution behavior as to have liquid-liquid miscibility gaps which have been observed.[5] The *reciprocal Coulomb effect* probably applies for salts of different valence containing nonpolarizable ions and is in such a direction that in a given system the salts

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*The criteria which are discussed and used by Bergman and associates are the values of $\Delta G(\Delta\mu)$ of the solids at room temperature which in view of their crude correlations are equivalent to $\Delta\mu^0$ or ΔH^0.

**All four components are not independent of each other and only three of the four are true components in the Gibbs sense.

with the smallest or most highly charged cations and smallest or most highly charged anions will tend to be a member of the stable pair.

Obviously, the Coulomb effect is not the only important one and many deviations from the generalization are to be found, especially for systems containing polarizable ions. For example the reaction

$$\mathrm{AgNO_3 + NaCl \rightleftharpoons AgCl + NaNO_3}$$

has a large negative value of $\Delta\mu^0$ or ΔH^0 (about -15 to -17 kcal/mole) which is considerably more than the Coulomb effect and which is probably the result of the large stabilization of AgCl by van der Waals' (London dispersion) interactions[101] of $\mathrm{Ag^+}$ and $\mathrm{Cl^-}$.

By contrast with the binary systems discussed in section II, the interactions are, in general, much larger in reciprocal systems as they are mostly between nearest-neighbor cations and anions rather than next-nearest neighbors and consequently one would expect to find many reciprocal systems with very large deviations from ideal behavior. In the following chapter some of the theories will be discussed which have been advanced for these systems beginning with the simplest approximation and continuing with approximations of increasing complexity.

III.2 The Random Mixing Nearest-Neighbor Approximation[54]

This derivation is based on the Temkin quasi-lattice model. For the simplest member of this class of systems, that containing the two cations $\mathrm{A^+}$ and $\mathrm{B^+}$ and the two anions $\mathrm{X^-}$ and $\mathrm{Y^-}$, the model is an assembly of charges *in vacuo* and consists of two interlocking sublattices, one a lattice of the cations $\mathrm{A^+}$ and $\mathrm{B^+}$ and the other of the anions $\mathrm{X^-}$ and $\mathrm{Y^-}$. The nearest neighbors of the cations are anions and of the anions are cations.

The total entropy of mixing is $\Delta S_T/R = -\Sigma n_i \ln N_i - \Sigma n_j \ln N_j$ and for any component is $\bar{S}_{ij} - S^0_{ij} = -R \ln N_i N_j$, where i and j are cations and anions respectively. All of the ions have the same coordination number Z. The model is restricted so that all of the ions of the same charge are the same size. This restriction eliminates any difference in the long-range Coulombic interactions between either $\mathrm{A^+}$ or $\mathrm{B^+}$ ions or $\mathrm{X^-}$ or $\mathrm{Y^-}$ ions and their respective environments, and limits the model to short range extra-Coulombic effects which are assumed to be nearest-neighbor interactions.* The form of the equations derived will probably apply even to systems with different-size ions.

In Fig. 19 is a two-dimensional representation of the quasi-lattice. If the pair interaction energy of $\mathrm{A^+}$-$\mathrm{Y^-}$ is ϵ_1, of $\mathrm{B^+}$-$\mathrm{X^-}$, ϵ_2, of $\mathrm{A^+}$-$\mathrm{X^-}$, ϵ_3, and of $\mathrm{B^+}$-$\mathrm{Y^-}$, ϵ_4 then

$$\Delta\epsilon = \epsilon_4 + \epsilon_3 - \epsilon_2 - \epsilon_1 = \frac{\Delta E}{\eta}, \tag{III.2.1}$$

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*If random mixing is assumed, or for a dilute solution only one pair need be the same size to eliminate differences in the Coulombic interactions.

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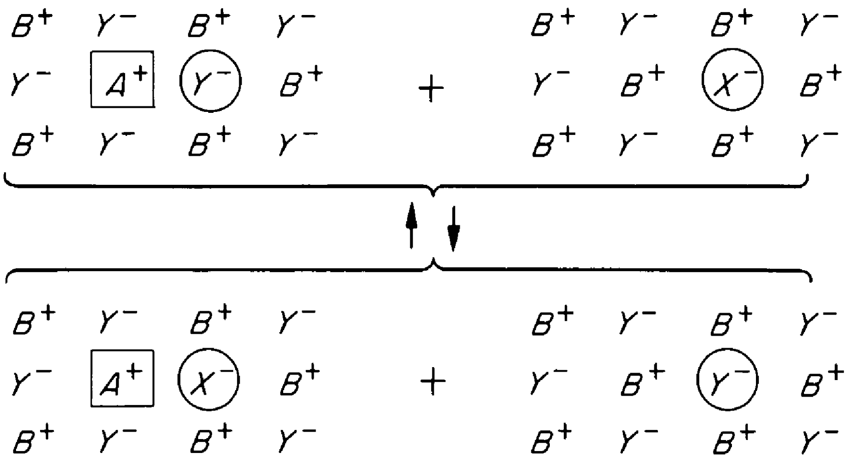

Fig. 19. Two Dimensional Quasi-Lattice Representation of the Process $A^+ + X^- \rightleftharpoons AX$ in the Solvent BY.

where $\Delta\epsilon$ is the energy change for the interchange of the circled X^- and Y^- ions and is the energy of formation of the ion pair A^+-X^-. If there is random mixing of the cations and of the anions on their respective sublattices, then the fraction of positions adjacent to any given cation occupied by a given anion will be equal to the ion fraction of that anion. The assumption is made that the relative energy of each A^+-X^- pair is $\Delta\epsilon$. This is equivalent to the assumption of the noninterference of pair bonds or to the assumption of the additivity of bond energies. Since the total number of positions adjacent to any ion is equal to $\bar{n}_i Z$ or $\bar{n}_j Z$, then the total energy or enthalpy of the solution is

$$E_T = \bar{n}_A Z N_Y(\epsilon_1 + K) + \bar{n}_B Z N_X(\epsilon_2 + K) + \bar{n}_A Z N_X(\epsilon_3 + K) + \bar{n}_B Z N_Y(\epsilon_4 + K) = H_T \ , \qquad \text{(III.2.2)}$$

where ZK is the value of the energy of interactions of the A^+ or the B^+ ions with ions beyond the nearest-neighbor anions. The partial molar enthalpy or energy of solution is

$$\bar{H}_{ij} - H^0_{ij} = \bar{E}_{ij} - E^0_{ij} = \pm (1 - N_i)(1 - N_j)\, Z\Delta E \ , \qquad \text{(III.2.3)}$$

where the − sign is pertinent when ij is AX or BY, and the + sign is pertinent if it is AY or BX. Remembering that $\mu_{ij} = \bar{H}_{ij} - T\bar{S}_{ij}$, then

$$\mu_{ij} - \mu^0_{ij} = \pm (1 - N_i)(1 - N_j)\, Z\Delta E + RT \ln N_i N_j \qquad \text{(III.2.4)}$$

and

$$RT \ln \gamma_{ij} = \pm (1 - N_i)(1 - N_j)\, Z\Delta E \ . \qquad \text{(III.2.5)}$$

The derivation of Eq. (5) is implied by the work of Flood, Førland, and Grjotheim who have, however, emphasized a somewhat more general relation. Equation (5) is strictly valid only for cases in which ΔE is small relative to RT so that one might reasonably be close to random mixing of the ions. The form of Eq. (5) is probably valid in some cases where there is only a small deviation from random mixing and is instructive and important for the qualitative understanding of solution behavior. Flood, Førland, and Grjotheim propose a method for making a crude estimate for $Z\Delta E$ from the heat contents of the pure components. Figure 20 is a two-dimensional quasi-lattice representation of the metathetical reaction (III.1.A) for which the heat change is ΔH^0 per mole.* Since all ions of the same charge are the same size, only extra-Coulombic nearest-neighbor interactions are changed in this reaction. Since the number of nearest neighbors for each of the salts is Zn per mole of salt, then for the reaction $\Delta H^0 = Z\Delta E$, if each pair interaction energy were the same. In real systems the pair interaction energies are probably a function of the number and kinds of anions which are nearest neighbors to a given cation so that ΔE will not be truly constant and will only be roughly approximated by $(\Delta H^0/Z)$.

A relation analogous to (5), but somewhat more general, has been derived by Flood, Førland, and Grjotheim[54]

$$RT \ln \gamma_{ij} = \pm (1 - N_i)(1 - N_j)\, \Delta\mu^0 \,, \qquad \text{(III.2.6)}$$

where $\Delta\mu^0$ is the change of chemical potentials for the metathetical reaction (III.1.A).

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*For many reciprocal salt pairs probably $\Delta S^0 \cong 0$ so that $\Delta H^0 \cong \Delta\mu^0$.

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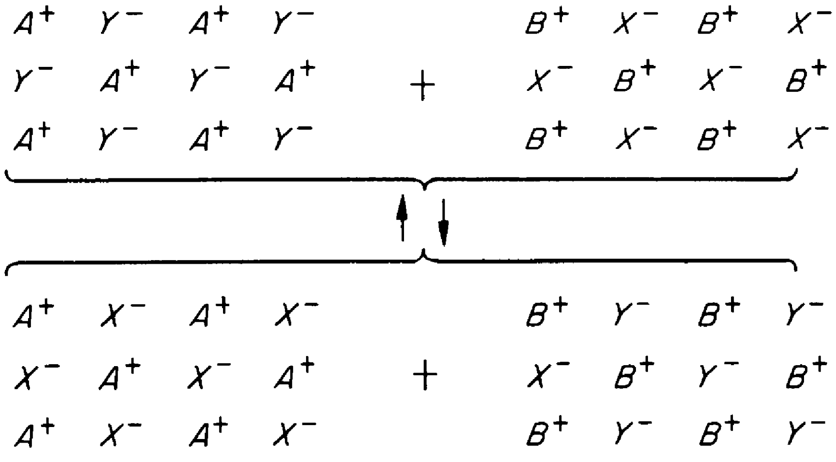

Fig. 20. Two Dimensional Quasi-Lattice Representation of the Metathetical Reaction $AY(liq) + BX(liq) \rightleftharpoons AX(liq) + BY(liq)$.

If the deviations from ideality are large enough, then the solution will tend to separate into two liquid layers. Since the theory is symmetrical in composition, the upper consolute temperature, T_c, below which temperature two liquid phases will form, will be at a composition such that $N_A = N_X = N_B = N_Y = \frac{1}{2}$. It may be calculated from Eq. (5) or (6) by setting the derivative da_{AY}/dN_{AY} equal to zero in mixtures of AY and BX, where $N_A = N_Y = N_{AY} = N_B = N_X$ and N_{AY} is the mole fraction of AY in a mixture made up from the salts AY and BX. The expression for the upper consolute temperature derived from Eq. (5) is

$$T_c = \frac{Z\Delta E}{4R} \simeq \frac{\Delta H^0}{4R} \tag{III.2.7}$$

and from Eq. (6)

$$T_c = \frac{\Delta\mu^0}{4R}. \tag{III.2.8}$$

To illustrate Eqs. (5), (6), (7), and (8) let us consider the dissolution of a mole of liquid AgCl in $NaNO_3$, where the ions Ag^+, Na^+, NO_3^-, and Cl^- correspond to A^+, B^+, X^-, and Y^- respectively. From published data[59,78,114] on the pure salts, $\Delta\mu^0 = +17$ kcal and $\Delta H^0 = +15$ kcal at 455°C. It can be seen from Eqs. (III.1.5) and (III.1.6) that the components AgCl and $NaNO_3$, which are members of the stable pair, should exhibit positive deviations and $AgNO_3$ and NaCl should exhibit negative deviations from the Temkin ideal-solution behavior. The results are similar for the system Ag^+, K^+, NO_3^-, Cl^-. In both these systems the calculated upper consolute temperature is well above the melting point of all the possible components that can make up the system, and two immiscible layers are present in this system. However the measured upper consolute temperature is much lower than that calculated from Eqs. (7) and (8). Similarly in the system Li^+, K^+, Cl^-, F^-, where the stable pair is LiF-KCl, the values of $\Delta\mu^0$ and ΔH^0 at 1000°K are about +17 kcal;[51,59,78] yet two liquid layers have not been detected in the quasi-binary system LiF-KCl,[51] although the calculated consolute temperature is very much higher than the measured liquidus temperatures. Clearly $\Delta\mu^0$ and ΔH^0 are not the sole measure of the deviations from ideality in reciprocal molten-salt systems. In mixtures for a given class of salts, such as alkali halides, they probably serve as a guide to the relative deviations from ideality. For example, the positive deviations from ideality in LiF-KCl quasi-binary mixtures are greater than for the NaF-KCl mixtures. The values of $\Delta\mu^0$ for these two systems are +17 and +8 kcal respectively.[51] An analysis of the quasi-binary liquidus temperatures for LiF-KCl and NaF-KCl in which the stated components exhibit positive deviation from ideal behavior and of the liquidus temperatures for LiCl-KF and NaCl-KF mixtures in which the stated components exhibit negative deviations from ideal behavior has shown that Eq. (5) or (6) only describes the solid-liquid equilibria in a semiquantitative manner.[51] The shortcomings of these two equations stem from a variety of possible reasons. Førland[58] has discussed the influence of those interactions which reciprocal systems have in common with binary systems containing either two cations and one anion or two anions and one cation. As discussed in section II, these interactions are of longer range than nearest-neighbor interactions. Førland has discussed this possibility for the hypothetical case in which this effect can be described in terms of the equations of regular solutions. From the derived relations it can be shown that if the binary systems exhibit negative deviations from ideality, then the correction terms to Eqs. (5) and (6) are in a direction which makes the activity coefficients smaller and which lowers the calculated upper consolute temperature. Although this correction is in the right direction, it is not large enough to lead to a good correspondence of calculations with experiment. As discussed in the following sections it will be shown that two other important effects which have been experimentally demonstrated are present. One effect is related to the nonrandom mixing of the ions which, except for extremely small deviations from ideality, leads to magnitudes and a concentration dependence of the deviations from ideality which are very different from Eqs. (5) and (6). The second effect is the nonadditivity of pair bond interactions.

III.3 Corrections for Nonrandom Mixing: The Symmetric Approximation

For the case in which ΔE is not very small relative to RT, corrections for nonrandom mixing of the ions must be included. Flood, Førland, and Grjotheim have given a preliminary discussion of nonrandom mixing.[54] Explicit calculations based on the nearest-neighbor quasi-lattice model have been made by Blander,[14,18] and Blander and Braunstein.[12]

In the following sections approximations based on the quasi-lattice model will be used to calculate the effect of nonrandom mixing (or associations) on the calculated thermodynamic properties of the model system. These calculations will also be related to conventional association constants for associations of the A^+ and X^- ions to form "complex ions"

$$mA^+ + nX^- \rightleftharpoons A_mX_n^{+(m-n)}$$

and will be used to illustrate some of the properties of these constants. It should be noted that some of the relations derived may also be derived without the use of a quasi-lattice model.[12] The model is useful in defining the parameter Z and in the statistical counting in the theoretical calculations.

In dilute solutions of A^+ and X^- ions in BY most of the associated species (or "complex ions") $A_mX_n^{+(m-n)}$ are isolated from one another by solvent B^+ and Y^- ions and are easily definable. This is in sharp contrast with solutions having only one kind of anion where complex compounds are not easily defined since all cations will have the same anions as near neighbors regardless of the properties of the solution.

The *symmetric approximation*[12] is essentially the quasi-chemical theory of Guggenheim.[63] In this approximation as in the others in section III only nearest-neighbor interactions are taken into account. The assumption is made that the interaction of any given adjacent pair of ions is the same independent of the local environment. A given A^+ ion may interact as many as Z X^- ions and a given X^- ion may interact with as many as Z A^+ ions with the relative energy of each interaction being $\Delta\epsilon$. The total number of the pairs A^+-X^-, B^+-X^-, A^+-Y^-, and B^+-Y^- is $Z(n_A + n_B)\mathcal{N}$. If Y'

is defined as the fraction of positions adjacent to the A^+ ions that are occupied by X^- ions, then the number of pairs of each kind and the total energy of such pairs are given below:

Type of Pair	**Totol Number**	**Total Energy**
A^+-Y^-	$Zn_A(1 - Y')\eta = R_a' - S_a'$	0
B^+-X^-	$Z(n_C - n_A Y')\eta = S_b'$	0
A^+-X^-	$Zn_A Y'\eta = S_a'$	$Zn_A Y'\Delta E$
B^+-Y^-	$Z(n_B - n_C + n_A Y')\eta = R_b' - S_b'$	0

For simplicity the relative energies of the pairs other than A^+-X^- are arbitrarily set at zero. This makes no difference in the final results. R_a' and R_b' are the number of positions adjacent to all the A^+ and B^+ ions respectively; S_a' is the number of positions adjacent to the A^+ ions occupied by X^- ions; and S_b' is the number of positions adjacent to the B^+ ions occupied by X^- ions. The number of ways of distributing these pairs, ω_s', is

$$\omega_s' = \frac{(R_a' + R_b')!}{(R_a' - S_b')!\,S_a'!\,(R_b' - S_b')!\,S_b'!} \,. \tag{III.3.1}$$

As in the quasi-chemical approximation,[63] when ω_s' is summed over all possible values of Y', the value for the total number of configurations is incorrect. A normalizing factor can be calculated to correct this so that the combinatory formula is

$$\Omega_s' = \frac{S_a^\dagger!\,(R_a^\dagger - S_a^\dagger)!\,S_b^\dagger!\,(R_b^\dagger - S_b^\dagger)!\,[(n_A + n_B)\eta]!\,[(n_X + n_Y)\eta]!}{S_a'!\,(R_a' - S_a')!\,S_b'!\,(R_b' - S_b')!\,(n_A\eta)!\,(n_B\eta)!\,(n_X\eta)!\,(n_Y\eta)!} \,, \tag{III.3.2}$$

where the superscript dagger (†) on a symbol signifies the value of that quantity for a random distribution of ions so that $Y^\dagger = N_X$.

The most probable distribution is obtained by maximizing Ω_s' under the condition of constant total energy and constant number of ions involved and is given by

$$\frac{Y}{1 - Y} = \left(\frac{N_X - N_A Y}{1 - N_A - N_X + N_A Y}\right) \beta \,, \tag{III.3.3}$$

where $\beta = \exp(-\Delta E/RT)$, and where the absence of a prime ($'$) on Y (or Ω_s) signifies the value of that quantity in the most probable distribution. The total energy is

$$-\Delta E_T = Zn_A Y \Delta E = -\Delta H_T \,, \tag{III.3.4}$$

and the total entropy of mixing is

$$\Delta S_T = k \ln \Omega_s \,. \tag{III.3.5}$$

The total Helmholtz free energy can be calculated from Eqs. (4) and (5). The following equation is obtained for the partial molar free energy by differentiating the Helmholtz free energy

$$\mu_{AY} - \mu_{AY}^{ST} = RT \ln N_A N_Y \left(\frac{1-Y}{1-N_X}\right)^Z , \tag{III.3.6}$$

where μ_{AY}^{ST} is the chemical potential of AY in its standard state* and

$$\gamma_{AY} \text{ (or } \gamma_{AY}^{*}\text{)} = \left(\frac{1-Y}{1-N_X}\right)^Z . \tag{III.3.7}$$

Because of the symmetry of the problem, Eq. (7) is valid for all of the components by merely redefining Y and ΔE.

In this approximation (as well as the random mixing approximation) the assumption of the noninterference or additivity of pair interactions has been made so that the energy of attachment of an A^+ or an X^- ion to any X^- or A^+ ion respectively is always $\Delta\epsilon$ independent of the number of other ions attached to the A^+ or X^- ions taking part in the attachment. Thus the energy change for the process

$$A_m X_n^{+(m-n)} + A^+ \rightleftharpoons A_{m+1} X_n^{+(m+1-n)}$$

and for

$$A_m X_n^{+(m-n)} + X^- \rightleftharpoons A_m X_{n+1}^{+(m-n-1)}$$

are the same and are independent of the values of m or n. As will be discussed later this places restrictions on the relative values of the successive association constants. The A^+ and X^- ions associate if $\Delta\epsilon < 0$ and $Y > N_X$ and they will be solvated by the B^+ and Y^- ions if $\Delta\epsilon > 0$ and $Y < N_X$. When $\Delta\epsilon = 0$, $Y = N_X$ and the mixture obeys Temkin's definition of ideality.

III.4 Comparison of the Symmetric Approximation with the Random Mixing Approximation

Calculations from Eqs. (III.3.3) and (III.3.7) probably lead to a more realistic description of reciprocal systems than calculations from (III.2.5) and (III.2.6). For a mixture AY-BD, the upper consolute temperature, T_c, can be calculated from the condition

$$(da_{AY}/dN_{AY}) = (dN_A N_Y \gamma_{AY}/dN_{AY}) = 0 .$$

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*Note that in the model $\mu_{AY}^{ST} = \mu_{AY}^{0} = \mu_{AY}^{*}$ if the solvent has an ion in common with AY. The most convenient standard state to use if μ^0 is not the same as μ^* in a real system depends on the concentration of solutes. For example in a solution dilute in A^+ or Y^-, μ_{AY}^{*} is convenient and in the solvent AY, μ_{AY}^{0} is convenient.

The problem is simplified because of the symmetry of the model so that the upper consolute temperature falls at $N_A = N_B = N_X = N_Y = \frac{1}{2}$. The solution is

$$\frac{Z\Delta E}{RT_c} = -2Z \ln \frac{Z-2}{Z} = 4 + \frac{4}{Z} + \frac{16}{3Z^2} + \frac{8}{Z^3} + \dots \qquad \text{(III.4.1)}$$

For very large values of Z, Eq. (1) approximates Eq. (III.2.7).

Z	$Z\Delta E/RT_c$
4	5.5
5	5.1
6	4.9
∞	4.0

As can be seen from the above table, for a given value of $Z\Delta E$, nonrandom mixing gives rise in this case to a *lower* calculated consolute temperature than is calculated under the assumption of random mixing. In Table 11 it can be seen that the consolute temperatures calculated from the symmetric approximation are less unreasonable than those from the random mixing approximation using the same parameters in the calculation. The parameters, $\Delta\mu^0$, are those given by Flood, Fykse, and Urnes.[51] It has been assumed that $\Delta\mu^0 = Z\Delta E$, and a reasonable value of $Z = 4$ has been used in the calculations.

A calculation of γ_{AY} from the two approximations is also given in Table 11 along with values measured at the liquidus temperature at 50 mole %. The symmetric approximation (again for $Z = 4$)

Table 11. Calculated and Measured Parameters at 50 Mole %

AY-BX	LiF-KCl[51]	LiF-NaCl[64]	NaF-KCl[51]
$\Delta\mu^0$ ($\cong Z\Delta E$) (kcal/mole)	17.1	9.1	8.0
Random mixing approximation			
(T_c (°K)	2150	1140	1010
γ_{AY}	7.8	3.2	2.7
Symmetric approximation ($Z = 4$)			
T_c (°K)	1560	830	730
γ_{AY}	4.7	2.8	2.4
Measured temperature (liquidus) (°K)	1045	973	1010
γ_{AY} (from measurements)[a]	3.2	2.6	1.8

[a] γ_{AY} at liquidus temperature where AY is the alkali fluoride.

leads to values of the activity coefficients of LiF and NaF, which are much closer to those derived from the measurements than those calculated from the random mixing approximation. The difference between the experimental results and the calculations from the symmetric approximations is small enough so that the correction for long-range interactions proposed by Førland[58] and mentioned in section III.2 may be large enough to account for the differences.

To illustrate this for a particularly favorable case, in Table 12 are given values of γ_{LiF} [$\gamma_{\mathrm{LiF(meas)}}$] in LiF-KCl mixtures calculated from the liquidus temperatures[51,64] using the heats of fusion in Table 1. Also given are values of γ_{LiF} calculated from the random mixing and the symmetric approximations [$\gamma_{\mathrm{LiF(symm)}}$]. In the last column is given

$$(-\Delta \log \gamma_{\mathrm{LiF}}/N^2_{\mathrm{KCl}}) \left[= \log \frac{\gamma_{\mathrm{LiF(symm)}}}{\gamma_{\mathrm{LiF(meas)}}} \Big/ N^2_{\mathrm{KCl}} \right] ,$$

where, in this case, $N_{\mathrm{K}} = N_{\mathrm{Cl}} = N_{\mathrm{KCl}}$. The form of this quantity ($\Delta \log \gamma_{\mathrm{LiF}}$) is consistent with the form of the relation given by Førland[58] for the correction factor, $\Delta \log \gamma_{\mathrm{AY}}$, which is to be added to $\log \gamma_{\mathrm{AY}}$ in order to account for the influence of interactions of longer range than nearest neighbors when these interactions obey the equations for regular solutions

$$RT\Delta \log \gamma_{\mathrm{AY}} = N^2_{\mathrm{B}} \lambda_{\mathrm{X,Y}} + N^2_{\mathrm{X}} \lambda_{\mathrm{A,B}} + N_{\mathrm{B}} N_{\mathrm{X}} [N_{\mathrm{A}}(\lambda_{\mathrm{Y}} - \lambda_{\mathrm{X}}) + N_{\mathrm{Y}}(\lambda_{\mathrm{A}} - \lambda_{\mathrm{B}})] \ . \qquad \text{(III.4.2)}$$

The terms λ_{X} and λ_{Y} are related to the deviations from ideality in AX-BX and AY-BY systems respectively and λ_{XY} accounts for the same type of long-range interactions as λ_{X} and λ_{Y} but in mixtures containing both X^- and Y^- ions. Similarly λ_{A} and λ_{B} are related to the deviations from ideality in AX-AY and BX-BY systems respectively and in mixtures containing A^+ and B^+ $\lambda_{\mathrm{A,B}}$ refers to the same type of interactions as λ_{A} and λ_{B}. The magnitude of $\lambda_{\mathrm{A,B}}$ and $\lambda_{\mathrm{X,Y}}$ are probably

Table 12. Activity Coefficients of LiF in the LiF-KCl Quasi-Binary

Liquidus Temperature	N_{LiF}	γ_{LiF} From Measurements	γ_{LiF} Symmetric Approximation	γ_{LiF} Random Mixing	$\log \frac{\gamma_{\mathrm{LiF}}(\mathrm{symm})}{\gamma_{\mathrm{LiF}}(\mathrm{meas})} \Big/ N^2_{\mathrm{KCl}}$
1078	0.90	1.10	1.13	1.08	
1068	0.80	1.35	1.45	1.38	0.72
1056	0.65	1.98	2.40	2.71	0.68
1053	0.60	2.30	2.93	3.70	0.67
1045	0.50	3.24	4.72	7.84	0.66
1040	0.46	3.77	5.88	11.17	0.67
1028	0.35	6.28	12.02	34.36	0.67
1020	0.30	8.33	17.97	62.44	0.68
1005	0.25	11.44	29.05	123.6	0.71

closely related (perhaps a weighted average) to λ_A and λ_B and λ_X and λ_Y respectively. These parameters are discussed in section II. In the system discussed here (LiF-KCl) the last term in Eq. (2) is probably small. From the last column of Table 12 a value of $(\lambda_{XY} + \lambda_{AB})$ of -3200 cal/mole is calculated if the last term is neglected. This is reasonable for the interactions of the ions involved (see section II). This unexpectedly good agreement is probably fortuitous in view of the approximate nature of the equations for regular solutions as applied to molten salts and the agreement may not be as good in other systems. However, further detailed investigations of such systems, especially in reciprocal alkali halide mixtures, would be interesting for comparison with these considerations where the symmetric approximation is used for nearest-neighbor interactions and Eq. (III.4.2) is used as a correction factor. This correction factor when included in the calculations of the consolute temperatures, T_c, will lead to much more realistic values than are calculated from Eq. (1).

It should be borne in mind that neither the symmetric approximation nor any other approximation which contains the implicit or explicit assumption of the additivity of pair interactions can be generally valid for all molten salts and that neither can give better than semiquantitative results. This will be discussed in a later section.

If Eq. (III.3.3) is solved for $(1 - Y)$ in terms of $(\beta - 1)$, N_A, and N_D, then

$$(1 - Y) = \frac{-b + \sqrt{b^2 - 4ac}}{2a}$$

and for small values of ac/b^2,

$$(1 - Y) = -\frac{c}{b}\left(1 + \frac{ac}{b^2} + \frac{2a^2c^2}{b^4} + \ldots\right), \tag{III.4.3}$$

where $a = N_A(\beta - 1)$, $b = [1 + (N_B N_X - N_A N_Y)(\beta - 1)]$, $c = -N_Y$. Substituting Eq. (3) in (III.3.7) and taking the logarithm of γ_{AY} one obtains

$$\ln \gamma_{AY} = Z \ln \left(1 + \frac{ac}{b^2} + \frac{2a^2c^2}{b^4} + \ldots\right) - Z \ln b\ . \tag{III.4.4}$$

The meaning of the symmetric approximation is made clear by Eq. (4). Since N_A and N_Y appear in exactly the same way in b and in the product ac, the interchange of particular numerical values of N_A and N_Y will lead to the same value of γ_{AY}. If N_A and N_Y are variables, then the function γ_{AY} is symmetric about the line $N_A = N_Y$. By expanding the logarithms in Eq. (4), one obtains

$$\ln \gamma_{AY} = -ZN_B N_X(\beta - 1) + \frac{Z}{2}[(N_B N_X)^2 + 2N_A N_B N_X N_Y](\beta - 1)^2$$

$$-\frac{Z}{3}[(N_B N_X)^3 + 6(N_B N_X)^2 N_A N_Y + 3N_B N_X(N_A N_Y)^2](\beta - 1)^3 + \ldots . \tag{III.4.5}$$

The remaining terms are sums of products of $(\beta - 1)^p$ and $(N_B N_X)^{p-n}(N_A N_Y)^n$, where $p > 3$ and $p > n \geqq 0$. If $(\beta - 1)$ is small, then only the first term is important and

$$(\beta - 1) = (e^{-\Delta E/RT} - 1) \cong -\frac{\Delta E}{RT} + \dots ,$$

so that Eq. (5) reduces to Eq. (III.2.5), which was calculated from the random mixing approximation. For small enough values of $N_A N_X$ or $N_B N_Y$ the higher terms in Eq. (5) are small relative to the first, so that

$$\ln \gamma_{AY} \cong -N_B N_X Z(\beta - 1) , \qquad \text{(III.4.6)}$$

which has the same form of the concentration dependence as Eq. (III.2.5) but does not contain the implication that there is random mixing of the ions.

III.5 The Asymmetric Approximation

One of the weaknesses of the symmetric approximation is the assumption of the additivity of pair interactions which means that in dilute solutions, for example, the energy for forming the pair AX from A^+ and X^- in the solvent BY is the same as forming AX_2^- from AX and X^- and A_2X^+ from AX and A^+. Measured association constants in dilute aqueous solutions indicate that this is not valid, especially if the central cation is polyvalent.[8] Thus, any generalization of the theory which includes a description of polyvalent cations and other special interactions must include a correction for the fact observed in aqueous and molten-salt solutions and discussed in a later section that species such as, for example, Cd_2Cl^{3+} are not stable in dilute solutions whereas $CdCl_2$ is stable in solution. In the theory which follows only monovalent ions are considered for simplicity. However, most of the relations derived for the association constants in dilute solutions apply to systems containing polyvalent ions as well.

The approximation given in this section is the *asymmetric approximation* which accounts for species as AX_n ($CdCl_2$, $CdCl_3^-$, $AgCl_2^-$, $AgCl_3^{2-}$) and neglects ionic groupings as $A_m X_n$ (Cd_2Cl^{3+}, Ag_2Cl^+). The applicability of this approximation to real systems will depend on the specific nature of the system. The purpose of the approximation is to derive relations which relate the influence of asymmetry of the ionic interactions to the thermodynamic properties of the solution.

In the *asymmetric approximation*[18] the anion portion of the lattice is divided into two regions, *a* and *b*. Region *a* contains all anion positions adjacent to one A^+ ion and $(Z - 1)$ B^+ ions, and region *b* contains all other anion positions. In a solution dilute enough in A^+ to neglect positions adjacent to two A^+ ions, the number of positions in region *a* is $Zn_A \mathfrak{N} = L_A$ and in region *b* is $\mathfrak{N}(n_X + n_Y) - L_A = L_B$. The X^- ions in region *a* are more stable by the energy $\Delta\epsilon$. If $\Delta\epsilon$ is negative, the concentration of X^- ions in region *a* will be greater than in region *b* or, in other words, there will be an association of A^+ and X^- ions. If X' is the concentration in ion fraction units of the X^- ions in region a, then it is also the fraction of positions adjacent to A^+ ions occupied by X^- ions. The A^+ and X^- ions associate when $X' > N_X$ and are solvated when $X' < N_X$. If M'_A and M'_B are the total number of X^- ions in region a and b respectively, then $M'_A = Zn_A X'\mathfrak{N}$ and $M'_B = n_X\mathfrak{N} - M'_A$. The total number of ways of mixing the anions in the anion region of the lattice, and the cations in the cation region of the lattice, Ω'_a, is

$$\Omega'_a = \frac{L'_A!\,L'_B!\,[(n_A + n_B)\mathfrak{N}]!}{(L'_A - M'_A)!\,M'_A!\,(L'_B - M'_B)!\,M'_B!\,(n_A\mathfrak{N})!\,(n_B\mathfrak{N})!} \; . \tag{III.5.1}$$

By using Stirling's approximation for the factorials and maximizing Ω'_a under the condition of constant total energy and constant total number of particles, the most probable distribution is calculated:

$$\frac{X}{1 - X} = \left[\frac{N_X - ZXN_A}{1 - ZN_A(1 - X) - N_X}\right] \beta \; . \tag{III.5.2}$$

The total energy of dilution in the solvent BY is

$$-\Delta E_{Dil} = Zn_A X\Delta E \; , \tag{III.5.3}$$

and the total entropy of mixing is given by

$$\Delta S_T = k \ln \Omega_a \; . \tag{III.5.4}$$

By combining Eqs. (III.5.3) and (III.5.4), the total Helmholtz free energy of dilution can be calculated.

	Total Number	**Total Energy**
L_A	$Zn_A\mathfrak{N}$	0
L_B	$(n_X + n_Y - Zn_A)\mathfrak{N}$	0
M_A	$Zn_A X\mathfrak{N}$	$Zn_A X\Delta E$
M_B	$(n_X - Zn_A X)\mathfrak{N}$	0

Differentiating the total Helmholtz free energy to calculate the chemical potentials of the four salts AX, AY, BX, and BY when the solvent is BY, one obtains

$$\frac{\mu_{AX} - \mu^*_{AX}}{RT} = \ln N_A \left[\frac{N_X - ZN_A X}{1 - ZN_A(1 - X) - N_X}\right] (1 - X)^Z \left[1 + \frac{X}{\beta(1 - X)}\right]^{Z-1} , \tag{III.5.5}$$

$$\frac{\mu_{AY} - \mu^*_{AY}}{RT} = \ln N_A (1 - X)^Z \left[1 + \frac{X}{\beta(1 - X)}\right]^{Z-1} , \tag{III.5.6}$$

$$\frac{\mu_{BX} - \mu^*_{BX}}{RT} = \ln N_B \left[\frac{N_X - ZN_A X}{1 - ZN_A}\right] , \tag{III.5.7}$$

$$\frac{\mu_{\mathrm{BY}}-\mu^0_{\mathrm{BY}}}{RT} = \ln N_{\mathrm{B}} \left[\frac{1-ZN_{\mathrm{A}}(1-X)-N_{\mathrm{X}}}{1-ZN_{\mathrm{A}}}\right] . \qquad \text{(III.5.8)}$$

In the asymmetric approximation a given A^+ ion can have as many as Z X^- ions as nearest neighbors, but a given X^- ion can only have one A^+ ion as a nearest neighbor. Thus only associations to form the groupings $AX_n^{+(1-n)}$ are taken into account and the groupings containing more than one A^+ ion are completely neglected. The energy of attachment of each successive X^- ion to a given A^+ ion is the same so that the energy for the association

$$AX_n^{+(1-n)} + X^- \rightleftharpoons AX_{n+1}^{-n} , \qquad 0 \leqq n \leqq (Z-1) ,$$

is $\Delta\epsilon$ independent of the value of n. This places restrictions on the relative values of the successive association constants as will be shown in the next section.

III.6 Conventional Association Constants

The meaning and interpretation of the *symmetric* and *asymmetric approximations* can be made more evident in terms of conventional association constants in dilute solution. If the ions A^+ and X^- of the two solutes AY and BX in dilute solutions in the solvent BY associate as

$$A^+ + X^- \rightleftharpoons AX$$

$$AX + X^- \rightleftharpoons AX_2^-$$

$$AX_2^- + X^- \rightleftharpoons AX_3^{2-}, \text{ etc.}$$

$$AX + A^+ \rightleftharpoons A_2X^+, \text{ etc.}$$

with the association constants being respectively K_1, K_2, K_3, etc., and K_{12}, etc., then the association constants may be related directly to parameters contained in the two approximations. It has been shown[25] that the thermodynamic association constants may be evaluated from the derivatives of $\ln \gamma^*_{\mathrm{AY}}$ or $\ln \gamma^*_{\mathrm{BX}}$ by the relations which have been derived under the reasonable assumption that in very dilute solutions all species obey Henry's law.

$$\left(\frac{\partial \ln \gamma^*_{\mathrm{AY}}}{\partial R_{\mathrm{BX}}}\right)_{\substack{R_{\mathrm{AY}}=0\\ R_{\mathrm{BX}}=0}} = \left(\frac{\partial \ln \gamma^*_{\mathrm{BX}}}{\partial R_{\mathrm{AY}}}\right)_{\substack{R_{\mathrm{AY}}=0\\ R_{\mathrm{BX}}=0}} = -K_1 , \qquad \text{(III.6.1)}$$

$$\left(\frac{\partial^2 \ln \gamma^*_{\mathrm{AY}}}{\partial R^2_{\mathrm{BX}}}\right)_{\substack{R_{\mathrm{AY}}=0\\ R_{\mathrm{BX}}=0}} = \left(\frac{\partial^2 \ln \gamma^*_{\mathrm{BX}}}{\partial R_{\mathrm{BX}}\,\partial R_{\mathrm{AY}}}\right)_{\substack{R_{\mathrm{AY}}=0\\ R_{\mathrm{BX}}=0}} = K_1^2 - 2K_1K_2 , \qquad \text{(III.6.2)}$$

$$\left(\frac{\partial^2 \ln \gamma^*_{\mathrm{AY}}}{\partial R_{\mathrm{BX}}\,\partial R_{\mathrm{AY}}}\right)_{\substack{R_{\mathrm{AY}}=0\\ R_{\mathrm{BX}}=0}} = \left(\frac{\partial^2 \ln \gamma^*_{\mathrm{BX}}}{\partial R^2_{\mathrm{AY}}}\right)_{\substack{R_{\mathrm{AY}}=0\\ R_{\mathrm{BX}}=0}} = K_1^2 - 2K_1 K_{12}\,, \qquad \text{(III.6.3)}$$

where $R_{ij} = n_{ij}/n_{\mathrm{BY}}$ and where n_{ij} is the number of moles of the solute component ij (AY or BX in this example). The association constants are in mole ratio or mole fraction units which are the most rational units in molten-salt solutions. These relations are not unique for calculating the association constants and many other derivatives of functions of the activity coefficients may be used. It should be noted that there is a single limit of the derivatives of the single-valued functions $\ln \gamma^*_{ij}$ at infinite dilution of all solutes. Therefore these equations define true thermodynamic association constants under conditions where the calculation procedure includes solutions dilute enough so that all species may be reasonably expected to obey Henry's law. By using Eqs. (1), (2), and (3), expressions for association constants have been calculated from the asymmetric and symmetric approximations [Eqs. (III.5.2), (III.5.6), (III.3.3), and (III.3.7)] and are given below:

Association Constant	**Asymmetric Approximation**	**Symmetric Approximation**
K_1	$Z(\beta - 1)$	$Z(\beta - 1)$
K_2	$\left(\frac{Z-1}{2}\right)(\beta - 1)$	$\left(\frac{Z-1}{2}\right)(\beta - 1)$
K_3	$\left(\frac{Z-2}{3}\right)(\beta - 1)$	$\left(\frac{Z-2}{3}\right)(\beta - 1)$
K_n	$\left(\frac{Z-n+1}{n}\right)(\beta - 1)$	$\left(\frac{Z-n+1}{n}\right)(\beta - 1)$
K_{12}	$-\frac{1}{2}$	$\left(\frac{Z-1}{2}\right)(\beta - 1)$

This table makes the differences between the symmetric or quasi-chemical and the asymmetric approximations clear. In both approximations

$$\frac{K_1}{Z} = \frac{2K_2}{Z-1} = \frac{3K_3}{Z-2} = \frac{nK_n}{Z-n+1}\,, \qquad 1 \leqq n \leqq Z\,, \qquad \text{(III.6.4)}$$

which are the statistical ratios of Adams and Bjerrum.[1,9] Thus these approximations are shown to be equivalent to the Adams-Bjerrum ratios[9] in dilute solutions. In the symmetric approximation $K_2 = K_{12}$ but in the asymmetric approximation the effective value of K_{12} is $-\frac{1}{2}$, which is essentially equivalent to zero. Although a negative value of an association constant is meaningless thermodynamically, it can be understood in terms of the model. If all the ions are randomly mixed and the solution is ideal, all the K's are zero. Since in the asymmetric approximation the condition has been introduced that no more than one A^+ ion be a nearest neighbor to any one X^- ion, then there is less than a random number of A^+ ions in positions near an A^+-X^- ion pair. Thus the effective value of K_{12} must be less than zero. This will occur if the A^+ ions repel each other.

It is clear that these two approximations can correspond exactly to real systems only for special cases or in very dilute solutions, where only the first association to form AX is important. However approximate these models are, they are still useful for semiquantitative descriptions of solution behavior. Moreover, as will be shown in the next section, both models lead to a prediction of the temperature coefficient of the first association constant, K_1, for the association of monatomic ions which is correct within the experimental precision of measurements which have been made.

III.7 Comparison of Theory with Experiments in Dilute Solutions

Measurements of $\gamma^*_{AgNO_3}$, the activity coefficients of AgNO$_3$ in the mixture Ag^+, B^+, Cl^-, and NO_3^- dilute in Ag^+ and Cl^-, have been made using the concentration cell

$$\mathrm{Ag}\left|\begin{array}{c}\mathrm{AgNO_3}\\ \mathrm{BNO_3}\end{array}\right\|\begin{array}{c}\mathrm{AgNO_3}\\ \mathrm{BCl}\\ \mathrm{BNO_3}\end{array}\left|\mathrm{Ag}\right. , \qquad \text{(III.7.A)}$$

where B is an alkali metal ion (or a mixture of alkali metal ions). In Fig. 21 are plotted measured values of $-\log \gamma^*_{AgNO_3}$ vs R_{KCl} at 385°C at two values of R_{AgNO_3}. The solvent BNO$_3$ in this case is a 50-50 mole % mixture of NaNO$_3$-KNO$_3$.* The activity coefficients decrease with increasing concentration of KCl, the decrease being smaller the larger the initial concentration of AgNO$_3$. Obviously the concentration dependence of $-\log \gamma^*_{AgNO_3}$ is very badly approximated by (III.2.5) or (III.2.6) and the magnitudes of $-\log \gamma^*_{AgNO_3}$ would require very improbable values of $Z\Delta E$ or $\Delta\mu^0$ (about -300 kcal/mole). This large discrepancy is undoubtedly related to nonrandom mixing of the ions. A comparison of these measurements with calculations based on the asymmetric and symmetric approximations is made in Fig. 21 and shows that the measured concentration dependence of $-\log \gamma^*_{AgNO_3}$ corresponds only roughly to these approximations. At low R_{AgNO_3} both approximations are essentially the same and at the higher chloride concentrations indicate a lower activity coefficient than is measured. This, probably, stems from the fact that in this system

$$K_2 < \left(\frac{Z-1}{2}\right)(\beta - 1) .$$

The activity coefficients at the higher concentrations of AgNO$_3$ lie between the two approximations indicating that $-\tfrac{1}{2} < K_{12} < \left(\frac{Z-1}{2}\right)(\beta - 1)$. The same is true if the solvent is pure NaNO$_3$ or KNO$_3$ with measurements in KNO$_3$ being closer to the asymmetric and in NaNO$_3$ to the symmetric approximation. These comparisons indicate that these two approximations, although much more realistic than the random mixing approximation, can be, at best, semiquantitative. One reason for

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*In these dilute solutions $R_{AgNO_3} = N_{Ag}$ and $R_{KCl} = N_{Cl}$.

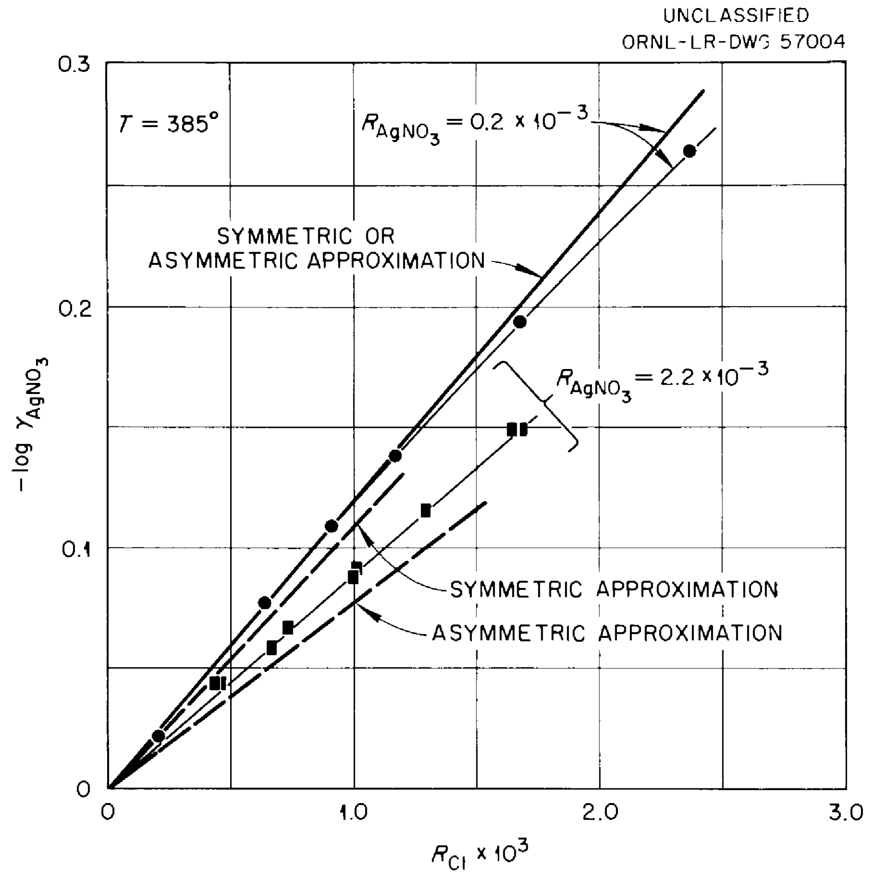

Fig. 21. Comparison of the Concentration Dependence of Measured Values of $-\log \gamma^*_{AgNO_3}$ in $NaNO_3$-KNO_3 (50-50 Mole %) Mixtures with Theoretical Calculations Based on the Symmetric and Asymmetric Approximations.

this is the nonadditivity of pair bond interaction energies in dilute solutions. This means that the relative values of successive association constants do not, in general, correspond to the values given on page 76. In the next section a generalization of theory will be made which will include the possibility of the nonadditivity of pair bond interactions.

The theoretical evaluation of K_1, however, is meaningful for certain systems and in solutions dilute enough in A^+ and X^- so that the most important species is AX, the temperature dependence of the activity coefficients (and of K_1) is predicted by these two approximations. Measurements of $-\log \gamma^*_{AgNO_3}$ in dilute solutions of Ag^+ and Cl^- in the three solvents $NaNO_3$,[70] KNO_3,[23,94] and 50-50 mole % $NaNO_3$-KNO_3[69] mixtures were compared to theory. By comparing the approximation which was closest in concentration dependence to the measured value of $-\log \gamma^*_{AgNO_3}$ at low concentrations of Ag^+ and Cl^- values of K_1 could be evaluated and are given in Table 13. This procedure for evaluating K_1 has been shown to be equivalent to more conventional extrapolation pro-

Table 13. Values of ΔE_1 Obtained from the Comparison of Theory with Experimental Data

T (°K)	$-\Delta E_1$ (kcal)			$K_1 = Z(\beta - 1)^{(a)}$
	$Z = 4$	$Z = 5$	$Z = 6$	
	Asymmetric Approximation, Ag^+, K^+, Cl^-, NO_3^-			
623	6.12	5.85	5.62	553
643	6.17	5.89	5.66	498
658	6.21	5.93	5.69	460
675	6.17	5.87	5.64	396
696	6.18	5.88	5.63	348
709	6.17	5.86	5.62	315
	Symmetric Approximation, Ag^+, Na^+, Cl^-, NO_3^-			
604	5.10	4.83	4.62	277
637	5.12	4.84	4.62	226
658	5.17	4.88	4.65	205
675	5.10	4.81	4.57	176
696	5.13	4.83	4.59	160
711	5.12	4.81	4.56	146
773	5.14	4.82	4.55	110
	Asymmetric Approximation, Ag^+, (Na^+, K^+), Cl^-, NO_3^-			
506	5.6	5.4	5.2	1050
551	5.57	5.33	5.13	644
658	5.67	5.38	5.15	302
752	5.72	5.40	5.13	180
801	5.6_2	5.2_8	5.0_0	133

(a) K_1 in mole fraction units.

cedures[25] if used correctly. To evaluate the parameter $\Delta E(\Delta E_1)$ contained in the theoretical expression for K_1 a value of Z must be assumed where

$$K_1 = Z(\beta - 1) = Z[\exp(-\Delta E_1/RT) - 1] \, . \qquad \text{(III.7.1)}$$

In molten salts a range of values of Z which covers all reasonable possibilities is 4 to 6. In Table 13 are given values of ΔE_1 calculated for values of $Z = 4$, 5, and 6. In any one system and for any one value of Z the values of ΔE_1 thus calculated, within the estimated experimental error, do not vary with temperature. This means that Eq. (1) correctly predicts the temperature coefficient of K_1 in these systems. In the $NaNO_3$-KNO_3 system this prediction is correct over a range of 295°C and for a variation of K_1 by a factor of about 8. At low enough concentrations of Ag^+ and Cl^- so that the only important species is AgCl the variation of $-\log \gamma^*_{AgNO_3}$ with temperature, within the experimental precision, is also correctly predicted. This is illustrated in Fig. 22 which gives a plot of $-\log \gamma^*_{AgNO_3}$ in a dilute solution of Ag^+ and Cl^- in $NaNO_3$ at several temperatures. The dashed lines were calculated from the symmetric approximation using the parameters given in Table 13. Using these essentially constant values of ΔE_1 leads to an excellent correspondence of the calculated and measured values of $-\log \gamma^*_{AgNO_3}$ at low concentrations of Ag^+ and Cl^-.

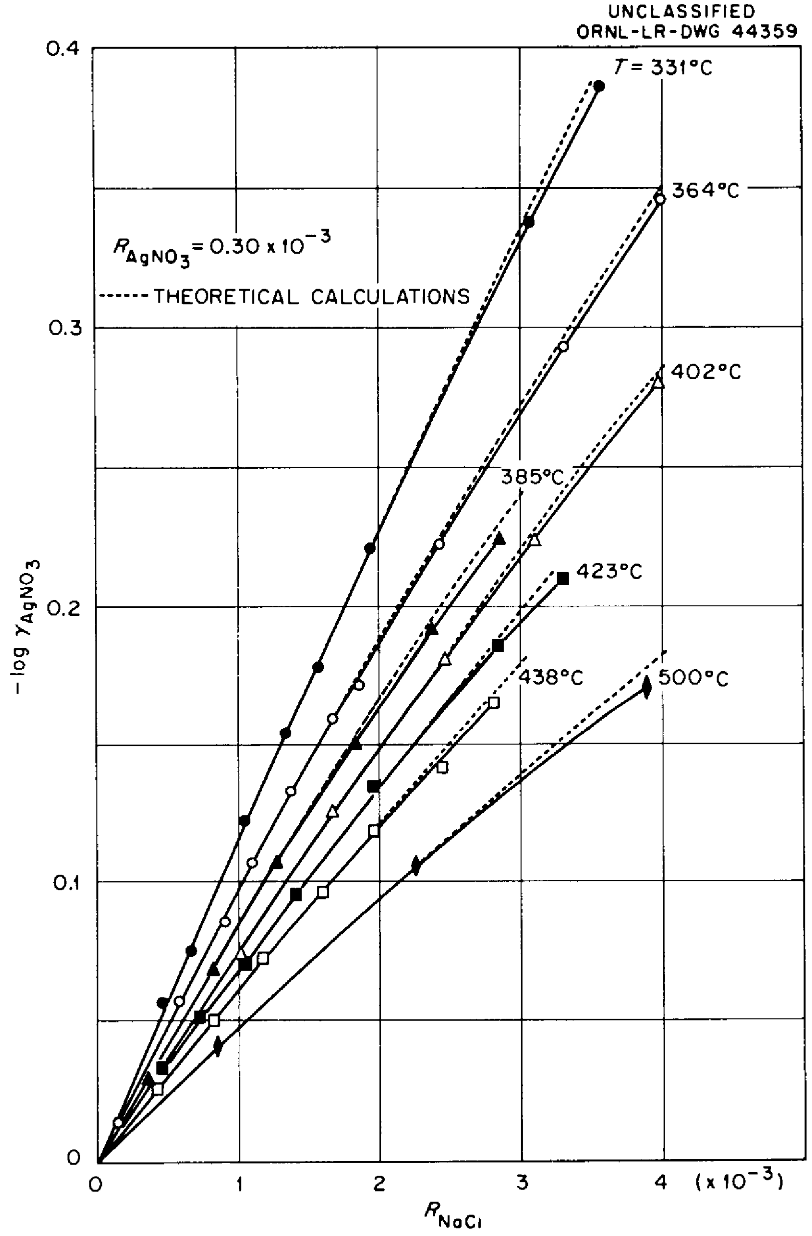

Fig. 22. Comparison of the Temperature Dependence of $-\log \gamma^*_{AgNO_3}$ in $NaNO_3$ with Theoretical Calculations.

The theory, in essence, leads to a prediction of the "configurational" contribution to the entropy of association so that from measurements at one temperature one may also calculate the heat of association, $\Delta H_1'$:

$$\frac{d \ln K_1}{d(1/T)} = \frac{-\Delta H_1'}{R} = \frac{d \ln Z(\beta - 1)}{d(1/T)} . \tag{III.7.2}$$

Since ΔE_1 is independent of temperature,

$$\Delta H_1' \cong \Delta E_1 \left(\frac{\beta}{\beta - 1} \right) , \tag{III.7.3}$$

where it is to be remembered that ΔE_1 can be calculated from measurements at a single temperature. Equation (3) for $\Delta H_1'$ may be confirmed (within the experimental precision and within the range of values of ΔE_1 for the three values of Z) from the values of K_1 given in Table 13. Other reported values of $\Delta H_1'$ which differ from Eq. (3)[38] were calculated from too few points and over too short a range of temperatures to be significant.

III.8 Generalized Quasi-Lattice Calculations[14]

The comparison of both the symmetric and asymmetric approximations with experiments make it evident that less stringent restrictions on the relative energies of association are necessary for a comprehensive theory. In this section a generalized calculation based on the quasi-lattice model will be discussed. The purpose is to calculate more general expressions for some of the higher association constants.

For simplicity, the assumption is made, as in the asymmetric model, that the solution in the solvent BY is so dilute in A^+ ions that one can neglect all groupings of A^+ and X^- ions containing more than one A^+ ion. From a calculation of the partition function for the assembly of A^+, B^+, X^-, and Y^- ions calculations were made of the Helmholtz free energy, the chemical potential for the component AY, and, hence, the activity coefficients of AY, γ^*_{AY}, in terms of the ion fractions of the ions, Z and β_i, where $\beta_i = \exp(-\Delta A_i/RT)$ and ΔA_i is the "specific bond strength" or the "specific Helmholtz free energy change" for the association

$$AX_{i-1}^{(2-i)} + X^- \rightleftharpoons AX_i^{(1-i)} , \qquad 1 \leqq i \leqq Z . \tag{III.8.A}$$

In this approximation $\Delta A_1 \neq \Delta A_2 \neq \Delta A_3 \neq \Delta A_i$ in general. It must be kept in mind that the symbol $AX_i^{(1-i)}$ represents an A^+ ion having i X^- ions and $(Z - i)$ Y^- ions as nearest neighbors. Thus $(\Delta A_i/\mathcal{N})$ is the free energy change for exchanging one X^- ion in the body of solution with a particular Y^- ion adjacent to the A^+ ion in the grouping $AX_{i-1}^{(2-i)}$. The term ΔA_i is related to partition functions for the individual ions involved in the association (A) (which is really an exchange of ions) so that

$$\Delta A_i = -RT \ln \left(\frac{\pi q''_{ki}}{\pi q'_{ki}} \right) , \tag{III.8.1}$$

where $\pi q'_{ki}$ and $\pi q''_{ki}$ represent the product of the partition functions of the individual ions, k, involved in the association process (A) evaluated before and after the association process respectively. If the partition functions are separable so that

$$q_{ki} = \bar{q}_{ki} e^{-E_{ki}/RT} ,$$

where $\bar{q}_k$ represents a partition function for the internal degrees of freedom of the ion of type k, then

$$\Delta A_i = \Delta E_i - T\Delta S_i = (\Sigma E''_{ki} - \Sigma E'_{ki}) - RT \ln \frac{\pi \bar{q}''_{ki}}{\pi \bar{q}'_{ki}} , \qquad \text{(III.8.2)}$$

and the "specific" entropy term, ΔS_i, contains only contributions from the internal degrees of freedom and excludes statistical or combinatory factors for the groupings of ions. For negligible changes in the internal degrees of freedom of the ions involved in the association process $\Delta S_i \cong 0$ and $(d\Delta A_i/dT) = 0$. This is the case for the values of ΔA_1 in the systems cited in Table 13.

The statistical mechanical calculation[14] leads to the equations for some of the successive association constants (in mole fraction units)

(III.8.3)

$$K_1 = Z(\beta_1 - 1) , \qquad \text{(a)}$$

$$K_1 K_2 = \frac{Z(Z-1)}{2!} (\beta_1 \beta_2 - 2\beta_1 + 1) , \qquad \text{(b)}$$

$$K_1 K_{12} = \frac{Z(Z-1)}{2!} (\beta_1 \beta_{12} - 2\beta_1 + 1) , \qquad \text{(c)}$$

$$K_1 K_2 K_3 = \frac{Z(Z-1)(Z-2)}{3!} (\beta_1 \beta_2 \beta_3 - 3\beta_1 \beta_2 + 3\beta_1 - 1) , \qquad \text{(d)}$$

$$K_1 K_2 K_3 K_4 = \frac{Z(Z-1)(Z-2)(Z-3)}{4!} (\beta_1 \beta_2 \beta_3 \beta_4 - 4\beta_1 \beta_2 \beta_3 + 6\beta_1 \beta_2 - 4\beta_1 + 1) . \qquad \text{(e)}$$

Equation (III.8.3a) is the same as the expression for K_1 given in the table on page 76 if $\Delta A_1 = \Delta E_1$. The terms in Z are spatial and statistical factors and the terms in β_i are related to the bond energies. For the case in which $\Delta A_1 = \Delta A_2 = \Delta A_3 = \Delta A_i$ and $\beta_1 = \beta_2 = \beta_3 = \beta_i$, the statistical ratios of Adams and Bjerrum apply.

Some of the relations derived from (III.8.3) exhibit surprising properties. For example by dividing (III.8.3b) by (III.8.3a) one obtains the expression

$$K_2 = [(Z-1)/2] \left[(\beta_2 - 1) + \left(\frac{\beta_2 - \beta_1}{\beta_1 - 1} \right) \right] . \qquad \text{(III.8.4)}$$

It can be seen from (III.8.4) that K_2 depends not only on Z and β_2 but also on β_1. If β_2 is small, this dependence may be relatively significant. If, for example $(2 - 1/\beta_1) > \beta_2 > 1$, then there exists a tendency for the association* of AX with X^- to form AX_2^- and yet the values of K_2 may appear to be negative.** This unusual and apparently contradictory result arises because of the requirement that the conventional association constants, K_i, be almost zero in an almost ideal solution. The standard states for some of the associated species under this requirement which is inherent in the commonly accepted methods of describing associations in solution cannot be understood in a simple way and lead to unusual properties for weak associations. An analogous situation occurs when gas virial coefficients are interpreted in terms of clusters.[71,74]

The assumptions made in the calculation of Eq. (3) are that the ith X^- ion attaching itself to an A^+ ion can do so in $(Z - i + 1)$ equivalent positions. Different relations would be obtained under different assumptions. If, for example, only a linear AX_2^- ion triplet can form, the second X^- ion has a nonzero value of ΔA_2 in only one of the $(Z - 1)$ sites near an AX ion pair which is not already occupied by an X^- ion. For linear AX_2^- then

$$K_1 K_2^l = [Z(Z-1)/2!]\left\{[\beta_1 \beta_2/(Z-1)] + 1 - [Z/(Z-1)]\beta_1\right\} \qquad \text{(III.8.5)}$$

and

$$K_2^l = \tfrac{1}{2}\left[\beta_2 - Z + \left(\frac{\beta_2 - 1}{\beta_1 - 1}\right)\right].$$

The stepwise association constant for formation of linear AX_2^- is K_2^l and would be smaller than K_2 for a nonlinear grouping even with the same values of Z, β_1, and β_2. Thus the comparison of the Eqs. (3b) and (5) demonstrates in this simple case the general principle that *the greater the tendency toward "directionality" in a "bond" the lower will be the association constant, if all other factors are equal.*

Equations (5) and (3a) lead to conclusions differing from those of Bjerrum[7] on the ratios of successive association constants for linear AX_2^-. For values of $\beta_1 = \beta_2 >> 1$ for example, $K_1/K_2^l \cong 2Z$, where Z is a *maximum coordination number.* In Bjerrum's derivation this number is a characteristic coordination number N. For a common case in which $\beta_3 << \beta_2$, N is two and much smaller than Z. The error in the calculation of Bjerrum arises from the fact that when the total possible number of X^- ligands is restricted to N in his derivation, the total number of positions adjacent to a spherical A^+ ion which are available to the first ligand is simultaneously limited to N although the first ligand is actually able to attach itself in any one of Z positions.

The equations discussed in this section can be derived for nearest-neighbor interactions independently of the lattice model. The coordinator number Z in such a derivation would be the ratio of the volume of the first coordination shells adjacent to a mole of A^+ ions to the volume of a mole of solvent anions. Such a derivation would apply to polyvalent cations.

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*If ΔA_i is negative and $\beta_i > 1$, there will be a tendency toward the association of $AX_{i-1}^{(2-i)}$ and X^- to form $AX_i^{(1-i)}$.

**Negative values of K_2 are meaningless thermodynamically, and apparently negative values usually mean a repulsion of the ions involved rather than the assumed association.

III.9 Association Constants in Dilute Solutions

In this section a compilation is given of association constants (in mole fraction units) which have been measured in reciprocal molten-salt systems. Measurements of associations involving the Ag^+ ion have been largely made with cells of the type (III.7.A) and the most reliable measurements for associations involving Tl^+, Pb^{2+}, and Cd^{2+} with halides from cells of the type

$$\mathrm{Ag}\left|\begin{array}{l}\mathrm{AgX(solid)}\\ \mathrm{BX}\\ \mathrm{BNO_3}\end{array}\middle\|\begin{array}{l}\mathrm{A(NO_3)}_n\\ \mathrm{AgX(solid)}\\ \mathrm{BX}\\ \mathrm{BNO_3}\end{array}\right|\mathrm{Ag}\ , \qquad \text{(III.9.A)}$$

using silver–solid-silver halide (AgX) electrodes where A^{+n} is Tl^+, Pb^{2+}, or Cd^{2+}. The emf of cells (III.7.A) and (III.9.A) may be related to the activity and activity coefficients (γ^*) of $AgNO_3$ or BX respectively. To avoid confusion, it should be emphasized that these activity coefficients are defined so as to encompass *all* solution effects including ionic associations ("complex ion" formation). At concentrations where Henry's law is obeyed by all species (probably true at concentrations below 0.5 mole %) it represents only those deviations from ideal solution behavior which are caused by association in solution. This usage is simpler than the usage most often employed in aqueous solutions where deviations from ideal solution behavior are subdivided into "activity coefficient" effects (related to the ionic strength) and an effect due to associations. Thermodynamic association constants may be computed from these measured activity coefficients by an extrapolation method.[24] Some of the association constants cited here have been recalculated from the data in the literature.[24] In cases where errors in calculating association constants may be significantly larger than the errors stated by the original workers and not enough data were available to correct the calculations, the association constants are given in parentheses or omitted. From the tabulated association constants (Tables 14 and 15), values of ΔA_i were calculated from Eqs. (III.8.3) for $Z = 6$ and are given in Table 16 for monatomic ions. For other values of Z, ΔA_i would be somewhat different (for $Z = 4$ the ΔA_i would be more negative by about 0.4 to 0.6 kcal) but the differences between the different values would be about the same. The differences in ΔA_i in Table 16 are related to the association constants (for $K_i >> 1$) by $\Delta A_i' - \Delta A_i'' \cong -RT \ln K_i'/K_i''$.

In every case where measurements were made at more than one temperature for associations involving monatomic ions only, values of ΔA_i for a given association in a given solvent and for $Z = 4$, 5, or 6 were independent of temperature within the experimental uncertainties.* Thus it appears that, for monatomic ions, the temperature variations of K_2 and K_{12} as well as of K_1 may be predicted from Eqs. (III.8.3) by using constant values of ΔA_i, and it appears that the entropy of association is largely the "configurational" entropy calculated from the quasi-lattice model. For

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*There did appear to be trends in the variation of ΔA_i with temperature in some cases. The total variations were smaller than the experimental errors in all cases except for ΔA_1 for the formation of $CdBr^+$ in 50-50 mole % $NaNO_3$-KNO_3, where the variation of ΔA_1 was slightly larger than the estimated experimental errors.

Table 14. Compilation of Association Constants from EMF Measurements (see also Table 13)

T (°K)	Solvent	Associating Ions	K_1	K_2	K_{12}	References
675	$NaNO_3$	$Ag^+ + Br^-$	633	246	280	95
711			500	180	200	
733			430	151	167	
773			325	103	120	
606	$NaNO_3$-KNO_3 (53-47 mole %)	$Ag^+ + Cl^-$	381	145		38
647			302	97		
649		$Ag^+ + Br^-$	1,008	(360)		38
687			781	(199)		
528		$Pb^{2+} + Br^-$	199			39
576			153			
579				67		
529		$Cd^{2+} + Br^-$	1,170	550		39
547			1,030	510		
571			810			
513	$NaNO_3$-KNO_3 (50-50 mole %)	$Tl^+ + Br^-$	31	15		27
519		$Ag^+ + CN^-$	230,000	140,000	80,000	10
559			220,000	105,000	60,000	93
599			190,000	50,000	36,000	
513		$Cd^{2+} + Br^-$	1,520	680	~ 0	25
573			990	450	~ 0	
513		$Cd^{2+} + I^-$	5,330	2,200	~ 0	25
563			3,130	1,300	~ 0	
513		$Pb^{2+} + Br^-$	250	125	~ 0	27
573			170	85	~ 0	92
623	KNO_3	$Ag^+ + Cl^-$	553	215	<40	94
658			460	169	20	
709			315	117	<40	
676		$Ag^+ + Br^-$	932	370	293	2
711			768	285	230	
725			728	273	208	
747			617	228	174	
773			540	195	145	
675		$Ag^+ + I^-$	5,420	2,700	3,555	2
636		$Ag^+ + SO_4^{2-}$	11.6			132
681			12.1			
706			12.7			
722			13.3			
513	$LiNO_3$-KNO_3 (80-20 mole %)	$Cd^{2+} + Br^-$	4,300	1,700		26
513	(65-35 mole %)		3,600	1,600		
444	(50-50 mole %)		7,500	3,300		
513			3,000	1,300		
513	(40-60 mole %)		2,500	1,100		
513	(26-74 mole %)		2,300	1,000		
553	(40-60 mole %)	$Tl^+ + Br^-$	56	30		27

Table 15. Association Constants from Other Measurements

Solvent	T (°K)	Species	K_1	Method
$NaNO_3$[129]	580	$CdCl^+$	190 ± 50	Cryoscopy
		$PbCl^+$	60 ± 20	Cryoscopy
$LiNO_3$-KNO_3[35] (50-50 mole %)	453	$CdCl^+$	(900)[a]	Polarography
		$PbCl^+$	270 ± 80	Polarography
$NaNO_3$-KNO_3[41] (53-47 mole %)	523	$CdCl^+$	(250)	Solubility
	573	$CdCl^+$	(300)	Solubility
	523	$PbCl^+$	(200)	Solubility
	573	$PbCl^+$	(65)	Solubility

[a] Parentheses indicate uncertain data.

associations of Ag^+ with SO_4^{2-} or CN^- values of ΔA_1 decrease with temperature indicating an entropy of association larger than the "configurational" entropy of association. Values of the negative of the "specific bond free energy" (where comparisons can be made) are in the order $SO_4^{2-} < Cl^- < Br^- < I^- < CN^-$ and $Tl^+ < Pb^{2+} < Cd^{2+} < Ag^+$, which is comparable to the order found in water and, in general, the values of $RT \ln K_1$ (K_1 in mole fraction units) are roughly comparable to those found in water. Values of ΔA_i (or ΔE_i) do not correspond precisely to the prediction of Flood, Førland, and Grjotheim (section III.2), but the relative magnitudes can be correlated with the heat (or free energy change) for the reciprocal reaction (III.1.A). For the silver halides for example, the heat changes for a reaction as (III.1.A) are in the same order as ΔA_i and may be correlated largely with non-Coulombic (van der Waals) interactions.[101] Superimposed upon the non-Coulomb interactions is a *reciprocal Coulomb effect* illustrated in the two-dimensional representation in Fig. 23.

The major change in the association of A^+ and X^- is the interchange of nearest-neighbor A^+Y^- and B^+X^- pairs to form A^+X^- and B^+Y^- pairs as illustrated in the lower part of the figure. A calculation of the nearest-neighbor Coulomb energy change (for ions which touch each other) indicates that this contribution to ΔA_1 is $e^2(1/d_{AY} + 1/d_{BX} - 1/d_{BY} - 1/d_{AX})$ and has the sign given below:

Contribution to ΔA_1		
−	$r_A < r_B$	$r_X < r_Y$
−	$r_A > r_B$	$r_X > r_Y$
+	$r_A < r_B$	$r_X > r_Y$
+	$r_A > r_B$	$r_X < r_Y$

Table 16. Average Values of "Specific Bond Free Energies," ΔA_i (kcal/mole), for $Z = 6$ for the Association of Monatomic Ions in Molten Nitrates

Association Ions	Solvent Composition (mole %)			$-\Delta A_1$	$-\Delta A_2$	$-\Delta A_{12}$	References
	$LiNO_3$	$NaNO_3$	KNO_3				
$Ag^+ + Cl^-$	0	100	0	4.59			70
	0	53	47	5.04	4.8		38
	0	50	50	5.12			69
	0	0	100	5.64	5.5		94
$Ag^+ + Br^-$	0	100	0	6.2_3	6.0	6.2	95
	0	53	47	6.6_4	(6.2)		38
	0	0	100	6.8_7	6.7	6.4	2
$Ag^+ + I^-$	0	0	100	9.1_3	9.4	9.8	2
$Tl^+ + Br^-$	40	0	60	2.1			27
	0	50	50	1.8			27
$Cd^{2+} + Cl^-$	0	100	0	4.0			24, 129
$Cd^{2+} + Br^-$	0	53	47	5.5_7	5.6		39
	0	50	50	5.75	5.8		25
	80	0	20	6.64	6.7		26
	65	0	35	6.58	6.6		26
	50	0	50	6.33	6.4		26
	40	0	60	6.16	6.2		26
	26	0	74	6.06	6.1		26
$Cd^{2+} + I^-$	0	50	50	6.99	7.0		25
$Pb^{2+} + Cl^-$	0	100	0	2.8			24, 129
$Pb^{2+} + Br^-$	0	53	47	3.6_9	3.8		39
	0	50	50	3.85			27, 92

with the magnitude being dependent on the relative differences in size. For example, for the association of Ag^+ and Cl^- in KNO_3 this contribution to ΔA_1 is about 2.6 kcal/mole more negative than in $NaNO_3$ and for the association of Ag^+ and Br^- about 1.4 kcal/mole more negative in KNO_3 than in $NaNO_3$. This nearest-neighbor Coulomb contribution to the differences between solvents is in the right direction but is over twice as large as the measured differences in ΔA_1 in these systems given in Table 16. This is probably related largely to the influence of long-range interactions which cannot be assessed for a realistic three-dimensional model but for a one-dimensional model the long-range interactions can be shown to attenuate the effect.[95]

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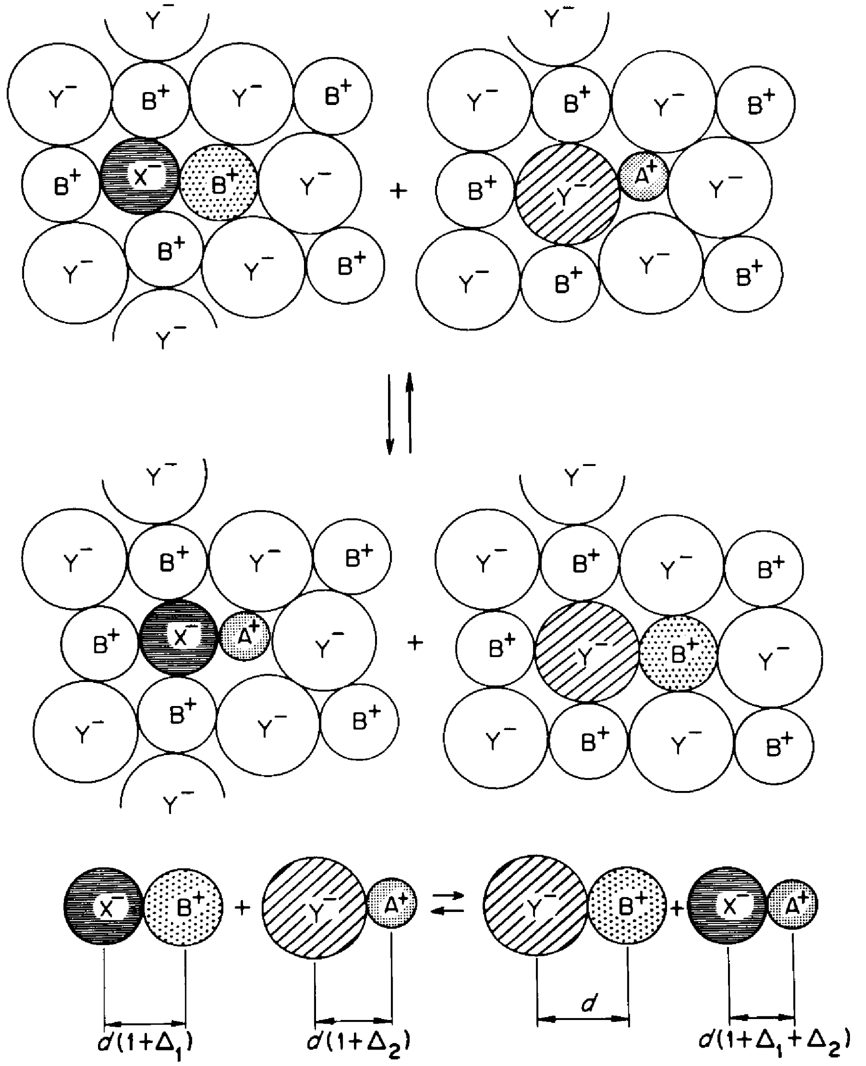

Fig. 23. Two Dimensional Representation to Illustrate the *Reciprocal Coulomb Effect.*

Within the experimental errors the measured constants in mixtures of two nitrates (a and b) obey the linear relations

$$\ln K_1(\text{in mixture}) = N_a \ln K_1(\text{in pure } a) + N_b \ln K_1(\text{in pure } b) \tag{III.9.1}$$

and

$$\Delta A_1(\text{in mixture}) = N_a \Delta A_1(\text{in pure } a) + N_b \Delta A_1(\text{in pure } b)\ . \tag{III.9.2}$$

Surprisingly, values of $-\Delta A_i$ for the formation of $CdBr^+$ and $CdBr_2$ are larger in $LiNO_3$-KNO_3 mixtures the larger the mole fraction of $LiNO_3$ and are larger than in the corresponding $NaNO_3$-KNO_3

mixtures. These particular association constants are, therefore, not related to the radii of the solvent cations by a simple monotonic relationship.

MISCELLANEOUS

Solutions of gases in molten salts are of interest to theoreticians because of their innate simplicity. The rare gases, mainly because they interact relatively weakly with most substances, form the simplest of such solutions. Measurements of the solubility of helium, neon, argon, and xenon have been made in molten fluoride solvents.[13,61] All of the solubilities obeyed Henry's law

$$C_d = K_P(T)P_g \,, \tag{1}$$

where C_d is the concentration of gas in the salt in moles per cm^3 of melt, K_P is a Henry's law constant, and P_g is the gas pressure in atmospheres. A simpler method of expressing solubilities for theoretical treatment is

$$C_d = K_c(T)C_g \,, \tag{2}$$

where C_g is the concentration of gas in the gas phase in moles per cm^3. The use of Eq. (2) and of K_c, which is unitless, eliminates those trivial additive (and usually relatively large) contributions to the entropy of solution which are related to the arbitrary choice of concentration units. Henry's law constants for rare gases are given in Table 17; those for HF in NaF-ZrF$_4$ mixtures (discussed in the following paragraph) are given in Table 18. The solubility of the rare gases increases with an increase of temperature and with a decrease of the size of the gas atom. A calculation of the enthalpy of solution and the standard entropy of solution was made by using the equations

$$\frac{d \ln K_p}{d(1/T)} = -\frac{\Delta H}{R}$$

and

$$\frac{d(RT \ln K_c)}{dT} = \Delta S^0 \,,$$

and is given in Table 19. In all cases, the entropy of solution is a small negative number for the rare gases. If the gas phase concentrations were expressed in pressure units (atmospheres), then values of the standard entropy would be obtained by adding, to the entropies in Table 19, $-R(1 + \ln R'T)$, where R' is the gas constant (cm^3 atm/deg mole), and R is the gas constant in entropy units. The free energy of solution ($\Delta F_c = -RT \ln K_c$) may be estimated roughly by the free energy of formation of holes the size of the rare gas atom

$$-RT \ln \frac{C_d}{C_g} = 18.08 d^2 \sigma = -RT \ln K_c \,,$$

where d is the gas atom radius in Angstroms, and σ is the surface tension. This approximation neglects curvature of the holes and interactions of the gas and liquid.[107]

Table 17. Henry's Law Constants for Noble Gases

Solvent	Gas	T (°C)	Measured	
			$K_P\left(\frac{\text{moles}}{\text{cm}^3\ \text{atm}}\right)\times 10^8$	$K_c \times 10^3$
LiF-NaF-KF (46.5-11.5-42.0 mole %)	He	600	11.3 ± 0.7	8.09
		650	13.7	
		700	17.5 ± 0.2	14.0
		800	23.0 ± 0.7	20.3
	Ne	600	4.36 ± 0.20	3.12
		700	7.51 ± 0.22	6.00
		800	11.18 ± 0.26	9.84
	Ar	600	0.90 ± 0.04	0.645
		700	1.80 ± 0.04	1.43
		800	3.40 ± 0.03	2.99
NaF-ZrF_4 (53-47 mole %)	He	600	21.6 ± 1.0	15.5
		700	29.2 ± 0.7	23.3
		800	42.0 ± 1.3	37.0
	Ne	600	11.3 ± 0.3	8.09
		700	18.4 ± 0.5	14.7
		800	24.7 ± 0.7	21.7
	Ar	600	5.06 ± 0.15	3.62
		700	8.07 ± 0.08	6.44
		800	12.0 ± 0.6	10.6
	Xe	600	1.94	1.39
		700	3.56	2.84
		800	6.32	5.56

By contrast, gases which interact strongly with components of the solvent have much higher solubilities than the rare gases. The solubility of HF in NaF-ZrF_4 mixtures for example is much higher than of the rare gases and increases with an increase in the concentration of NaF indicating that the strong interactions (negative) of HF in solution are with NaF. Measurements of the solubility of water in molten LiCl-KCl mixtures however indicated that the water solubility did not increase significantly (except at 390°C) with increasing concentrations of LiCl with which component water has a relatively strong interaction. The data are given in Table 20. Note that the units are in micromole of H_2O per mole of solution per millimeter pressure. The heats of solution appeared to be −5 and −11 kcal/mole in the 50 and 60% mixtures respectively.

Kinetic measurements have been used to measure equilibrium constants[39,40] for the acid-base reactions,

$$Cr_2O_7^{2-} + NO_3^- \rightleftharpoons NO_2^+(sol) + 2CrO_4^{2-} , \tag{3}$$

$$S_2O_7^{2-} + NO_3^- \rightleftharpoons NO_2^+(sol) + 2SO_4^{2-} , \tag{4}$$

in $NaNO_3$-KNO_3 mixtures (53-47 mole %). (Note that NO_2^+ was assumed. The data fit N_2O_5 equally well.) The limiting step in the reaction was the removal of N_2O_5 by sweeping out its decomposition products in a stream of gas bubbles. Since the evolution of the gas was dependent on rates of diffusion into the gas phase and the rate of bubbling, the kinetics of the reaction were not related to properties of the solution. By an extrapolation procedure the equilibrium constants for (3) and (4) could be deduced and are given in Table 21 and indicate that $S_2O_7^{2-}$ is a stronger "acid" than $Cr_2O_7^{2-}$. The values of K_A were so small that heavy metal ions had to be added to the solution to increase the rate of gas evolution by removing CrO_4^{2-} from solution.

Table 21. Equilibrium Constants[a] for Reactions (3) and (4)

T (°C)	K_A	K_B
235	8.5×10^{-14}	0.026
275	3.8×10^{-12}	0.038

[a] In molality units.

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