Journal of Alloys and Compounds 321 (2001) 164–168
Journal of ALLOYS AND COMPOUNDS
www.elsevier.com/locate/jallcom

Contributions to molten salt chemistry by Ole J. Keppa

Milton Blander
Quest Research, 1004 E. 167th Place, South Holland, IL 60473-3114, USA

Received 5 September 2000; accepted 5 December 2000

Abstract

Ole Kleppa and coworkers have accurately measured the enthalpies of mixing of a large number of binary molten salt systems. These results have also been proven to be useful in the analyses of phase diagrams and in creating a reliable database on free energies of mixing of a large number of systems. He made a general confirmation of a specific result by Hildebrand and Salstrom that excess free energies of mixing of simple binary molten salts could be represented by a simple polynomial, an important result for ionic systems with very long range ionic pair interactions. His measurements of the enthalpies of mixing of all binary alkali nitrates led to an expression which was close to that deduced from a simple model by Førland. This result also catalyzed the Conformal Ionic Solution Theory, the only theory fundamentally valid for molten salts. This theory later led to methods for accurately predicting the solution properties of multicomponent molten salt systems from data on the subsidiary binaries and the pure component salts. His measurements of binary systems with the two components having the same cation and two different anions indicated that deviations from ideality were generally very small. A theoretical extension of this conclusion to silicates and other polymeric slags led to reliable predictions of the solubilities (and sulfide capacities) of ionic compounds. Kleppa's work has had a major influence on molten salt chemistry © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Binary systems; Enthalpies of mixing; Molten salts

1. Introduction

Ole Kleppa and associates have accurately measured the enthalpies of mixing of a large number of binary molten salt systems. These results are an important database. In addition, his results catalyzed the deduction of concepts and theories which are necessary for the representation and prediction of the thermodynamic properties of molten salt solutions. Some of his significant contributions are as follows.

1. He confirmed and extended a specific result by Hildebrand and Salstrom [1–7] that excess free energies of mixing of simple binary molten salt systems could be represented by simple polynomials [8,9].
2. His measurements led to the use of equivalent fractions for the simplification of the representation of excess free energies and excess enthalpies of mixing of molten salt systems with mixtures of cations with different charges (e.g. KCl–$MgCl_2$ [10] and KCl–$CeCl_3$ [11]).
3. Measurements of the enthalpies of mixing of alkali nitrate mixtures led to an expression for the relative magnitude of these enthalpies consistent with a form deduced from a simple model by Førland [12,13].
4. The same measurements led to the development of the Conformal Ionic Solution theory [14], the only theory fundamentally valid for molten salts. This theory not only confirms the intuitive Førland model but also confirmed a collection of intuitive models for the very accurate predictions of the properties of multicomponent reciprocal molten salt systems, e.g. Li^+,K^+/F^-,Cl, and additive ternary systems, e.g. Li^+,Na^+,K^+/F^-, from data on the subsidiary binaries and the pure component salts [15].
5. His measurements of binary systems with two components having the same cations and two different anions [16] demonstrated much more broadly than prior work [17] that deviations from ideal solution behavior were generally very small. This result was important in many thermodynamic predictions in complex molten salt and silicate systems [18–23].

Clearly, the accomplishments of Professor Kleppa were driven by a deep understanding of the properties of molten salts and an infallible intuition. A fraction of his work has enabled the development of several fundamental concepts and theories for the prediction and description of the thermodynamic properties of molten salt solutions and the

PII: S0925-8388(01)00967-7

remainder of his work on molten salts is an important database for future developments. In this paper, I will discuss the contributions 1–5 mentioned above.

2. Representation of deviations from ideality

In order to discuss deviation from ideality of molten salt systems we must define an ideal system. We start with a real molar Gibbs free energy of mixing, enthalpy of mixing and entropy of mixing ΔG_m, ΔH_m and ΔS_m which represents the changes of these three quantities upon mixing of the pure liquid components. The relationship between these three quantities is given by

$$\Delta G_m = \Delta H_m - T\,\Delta S_m \tag{1}$$

An ideal molar entropy of mixing has been defined by Temkin [24] as

$$\Delta S_m^i = R\Big(\sum_c \ln X_c + \sum_a \ln X_a\Big) \tag{2}$$

where c represents the cations; a the anions; and X is an ion fraction (cation fraction or anion fraction). By definition, the ideal enthalpy of mixing is zero so that the ideal free energy of mixing is given by

$$\Delta G_m^i = -T\,\Delta S_m^i \tag{3}$$

The differences between the real and the ideal values of the three thermodynamic quantities in Eq. (1) is defined as the excess free energy, enthalpy and entropy of mixing symbolically exhibited in Eq. (4) below. Thus the real free energy, enthalpy and entropy of mixing can be transformed to excess free energies, enthalpies and entropies

$$\Delta G_m - \Delta G_m^i = \Delta G_m^{ex} = \Delta H_m - T\,\Delta S_m^{ex} \tag{4}$$

where the enthalpy of mixing is the same as the excess enthalpy of mixing. For systems with several different cations and one kind of anion or one kind of cation and several different anions, Eq. (2) reduces to that for a simple solution. Solutions with more than one cation and more than one anion are defined as reciprocal systems which are more complex. The chemical potential, μ_{AX} of a single component AX is the derivative of the total value of $n\Delta G_m$ (where n is the total number of moles of salts) with respect to the number of moles n_{AX}. For an ideal solution

$$\mu_{AX}^{id} = \mu_{AX}^{o} + RT \ln X_A X_X \tag{5}$$

where $X_A X_X$ is the ideal activity of the component, a_{AX}^{id} and μ_{AX}^{o} is the standard chemical potential of the salt AX. The real activity, a, of the component defined by $\mu_{AX} = \mu_{AX}^{o} + RT \ln a$ divided by the ideal activity (id) is the activity coefficient, γ_{AX}

$$a_{AX}/a_{AX}^{id} = \gamma_{AX}$$

where the excess chemical potential is

$$\mu_{AX}^{ex} = RT \ln \gamma_{AX} \tag{6}$$

For relatively simple binary mixtures of organic materials, it is found that a simple quadratic expression for the total excess free energy of mixing is adequate to describe the thermodynamic properties

$$\Delta G_m^{ex} = AX_A X_B = \Delta\mu_m^{ex} \tag{7}$$

For more complex solutions, a higher polynomial may be necessary

$$\Delta G_m^{ex} = AX_A X_B(1 + b(X_A - X_B) + cX_A X_B). \tag{8}$$

Analogous equations can be written for ΔH_m. Such polynomials lead to a quadratic first term for the excess chemical potential change upon mixing

$$\mu_{AX}^{ex} = AX_{BX}^2 + \cdots \tag{9}$$

3. Experimental observations

In a series of publications, Hildebrand and Salstrom [1–7] have demonstrated that $\Delta\mu_{AgBr}^{ex}$ in mixtures of alkali bromides with silver bromide could be well represented by the quadratic term in Eq. (9). This is important since excess free energies of the only other important ionic solutions, those of salts in water, were described by the Debye–Huckel term with a square root of the concentration. The representation of the excess chemical potentials by a polynomial greatly simplifies the representation of solution properties. Hersh, Navrotsky and Kleppa [25] measured enthalpies of mixing of these bromides which were mostly lower (less positive or more negative) than the excess free energies of Hildebrand and Salstrom indicating that the excess entropies were usually negative. In addition, the representation of the enthalpies and entropies of mixing required the use of an equation such as Eq. (8) with all the terms in Eq. (8). In other works on simple binary systems with two univalent cations, including mixtures of alkali halides, sulfates, nitrates, and metaphosphates [26,27], Eq. (8) gave an accurate description of the enthalpies of mixing which were largely negative. Of the enthalpies of mixing of alkaline earth chlorides $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ [28], only the enthalpies of mixing of the last three alkaline earth chlorides were simple enough to represent with the terms of Eq. (7). Mixtures with $MgCl_2$ were not simply represented, probably because it tends to be an ordered assembly of four coordinated magnesium ions connected by chloride ions to form a stable network (parallel to zinc chloride and silica liquids) which leads to positive contributions to ΔH_m from the partial breakup of the very stable network by the addition of more ionic alkaline earth chlorides. Similar effects have been observed in silicates. Thus structural ordering of molten components such as $MgCl_2$, BeF_2, $ZnCl_2$ and SiO_2 can complicate the representation of ΔG_m, ΔH_m and ΔS_m of binary solutions. The strongest ordering of this type is for small divalent (for monovalent anions) or tetravalent (for divalent anions) cations which can be just large enough to accommodate four anions as nearest neighbors.

A different type of ordering can be seen in binary mixtures such as, e.g. KCl–$MgCl_2$, or KCl–MCl_2 where M is a divalent transition metal where Mg^{2+} and M^{2+} tend to form tetrahedral complex ions. The maximal ordering is at the 2:1 KCl–$MgCl_2$ composition. Kleppa and coworkers [10,29–31] have performed measurements of the enthalpies of mixing of such systems with tendencies for minima near the composition of 33 mol.% of the divalent salt. Analogous minima for mixtures of alkali halides with trivalent halide salts with trivalent cations which have relatively large radii [32,33] were observed near 25 mol.% of the trivalent halide. These minima are often difficult to describe in terms of Eq. (8). The use of equivalent fractions substituting for ion or mole fractions in Eq. (8) for these two cases greatly simplified the mathematical description of such systems [34] and is generally used in calculations based on Eq. (8) and other more sophisticated equations. Equivalent fractions, Y_i, for MX–NX_n mixtures is defined as

$$Y_{MX} = \frac{X_{MX}}{X_{MX} + nX_{NX_n}} \quad \text{and} \quad Y_{NX_3} = \frac{nX_{NX_n}}{X_{MX} + nX_{MX_n}}$$

The quantitative measurements of Kleppa and coworkers were the key information for this important tool in theoretical solution thermodynamics. However, equivalent fractions can not be used universally. What really happens is that most binary MX–NX_2, mixtures have a minimum where the major solution species are NX_4^{2-} complexes at a 2:1 composition and many MX–NX_3 binaries have a major species of NX_6^{3-} at a 3:1 composition. For divalents with a large radii (e.g. Sr, Ba) and for trivalents with small radii (e.g. Al^{3+}) the use of equivalent fractions do not apply since the coordination numbers are very different (e.g. Ba^{2+}) often has coordination numbers close to 6 and Al^{3+} has a coordination number of 4 for chloride and larger anions.

Perhaps the most important fundamental results were deduced from the measurements of Kleppa and Kleppa and Hersh [8,9] on 10 mixtures of alkali nitrates. All of the observed enthalpies of mixing were negative and are more negative the greater the differences of the cationic radii of the two alkali metal ions. In all systems, an energetic asymmetry in the enthalpies is present so that the values of ΔH_m is more negative for a given pair of salts in a mixture dilute in the large cation nitrates than in a mixture dilute in the small cation nitrates. The parameter b in Eq. (8) is a measure of this energetic asymmetry and is generally negative when the cation of component 1 is smaller than that of component 2. Measurements of all of the systems can be represented using Eq. (8). The authors, by using the enthalpies of mixing at 50–50 mol.% mixtures of these nitrates ($\Delta H_m^{0.5}$) as a measure of the magnitude of the deviations from ideality, deduced an empirical equation which represented these values of $\Delta H_m^{0.5}$

$$4\,\Delta H_m^{0.5} = U\left(\frac{d_1 - d_2}{d_1 + d_2}\right)^2 \tag{10}$$

where d_i is the sum of the radii of the cation and anion of the component salt i and U is about -140 kcal/mol, which is about the magnitude of the lattice energy of the alkali nitrates. This quantity differs little from the coefficient of a simple but ingenious model by Førland [12,13] who calculated the coulomb energy of mixing of a linear array of cation–anion–cation triplets of salts 1 and 2 to form two triplets each with cations 1 and 2 as a near neighbor on opposite sides of the anion. The change in energy is given by the expression

$$\Delta E_c = -\left(\frac{e^2}{d_1} + \frac{e^2}{d_2}\right)\left(\frac{d_1 - d_2}{d_1 + d_2}\right)^2 \tag{11}$$

where e is the electronic charge and the first term in parentheses on the r.h.s. is close to an average lattice energy of the two salts. The form is similar to the empirical Eq. (10). Lumsden [35] calculated the effect of polarization of the anions between two different cations of different size. The equation deduced is similar to Eq. (11)

$$\Delta E_p = -\alpha e^2\left(\frac{1}{d_1} + \frac{1}{d_2}\right)^4\left(\frac{d_1 - d_2}{d_1 + d_2}\right)^2 \tag{12}$$

where α is the anion polarizability factor. This result suggests that all terms in a pair potential which can be described by a factor containing a term d^{-n} will lead to equations similar to Eqs. (11) and (12).

An extension of Førlands calculation to a hypothetical infinite linear array of charged hard spheres of a solvent salt with alternating charges along the length of the array and one ion of salt 2 [36]. Although this one dimensional model is not realistic, it does give insight into the effect of coulombic ionic interactions of longer range than the next nearest neighbors in Førland's model. The results of the calculation indicate that the energetic asymmetry in the data on alkali nitrates is, at least partially, related to the long range coulomb interactions.

Perhaps the most important development based on the experimental results of Kleppa and Kleppa and Hersh [8,9] is the conformal ionic solution (CIS) theory of Reiss, Katz and Kleppa [14]. This ingenious theory was the first which took into account the long range ionic interactions in molten salts solutions and ultimately helped to verify that

1. One expects that the excess free energies and enthalpies

of mixing of simple molten salts could be well represented by a polynomial.

2. The equations deduced bit by bit by various authors for the description of multicomponent systems, based only on nearest neighbor interactions, were valid for the case in which long range interactions were also taken into account.
3. The theory predicts that the equations for the excess free energies and enthalpies of mixing in binary 50–50 mol.% mixtures in terms of interionic nearest neighbor distances of the two salts are:

$$4\,\Delta G_{\mathrm{m}}^{0.5} = A\left(\frac{d_1 - d_2}{d_1 d_2}\right)^2;$$
$$4\,\Delta H_{\mathrm{m}}^{0.5} = B\left(\frac{d_1 - d_2}{d_1 d_2}\right)^2 \quad (13)$$

which, for all practical purposes, is very close to Eq. (10).

Although the original CIS theory was based on a simple hard sphere pair potential, it was shown that the calculation was much more general [37] and included conformal soft sphere repulsions between the ions and much more complex attractive pair potentials. This paper [37] extended the original second order theory to at least fourth order polynomials for the description of the excess free energies and enthalpies of mixing. Ultimately, the theory was applied to multicomponent systems [15,38] where the results of the calculations were constructed to predict the properties of the multicomponent systems from the properties of the subsidiary binaries and the pure components. By transforming the results of the calculations to real values of the binary and unary terms, the accuracy of the predictions for the multicomponent systems was greatly enhanced. Several works had cobbled together concepts and equations for the predictions of the thermodynamic properties of multicomponent solutions from unary and binary data using crude approximations which only include nearest neighbor interactions. The CIS theory confirmed the validity of these concepts and equations. For reciprocal systems, the equations led to surprisingly accurate predictions of the thermodynamic properties of a large number of systems [34,39,40]. This entire development sprang from the measurements of Kleppa and Kleppa and Hersh and the subsequent involvement of Kleppa in the development of the CIS theory.

Another important observation by Kleppa and coworkers is that binary mixtures of salts with a common cation and two different anions generally have very small enthalpies (and undoubtedly small excess free energies) of mixing and tend to be close to ideality [16]. This result has been important for deducing solubility products and solubilities in reciprocal systems and the solubilities of salts (including halides, phosphates, sulfides, nitrates, etc.) in molten silicates [21–23]. For example, to calculate solubility products and solubilities of a slightly soluble salt, AX in reciprocal systems [18–20,41] we can use, e.g. for the simplest case in which BY is the solvent, a cycle for such dilute solutions which is broken down to three equilibria

$$\mathrm{AX(s)} + \mathrm{BY(l)} \Leftrightarrow \mathrm{BX(s,l)} + \mathrm{AY(s,l)} \quad (14)$$

$$\mathrm{AY(s,l)} \Leftrightarrow \mathrm{AY(soln\ in\ BY(l))} \quad (15)$$

$$\mathrm{BX(s,l)} \Leftrightarrow \mathrm{BX(soln\ in\ BY(l))} \quad (16)$$

At equilibrium, the sum of the free energies for Eqs. (14)–(16) per mole of AX(s) is zero. One can thus deduce an equation for the solubility product, K_{sp}, and for the activity coefficient of AX at infinite dilution with solid as standard state, γ^{*}_{AX}.

$$RT \ln \gamma^{*}_{\mathrm{AX}} = -RT \ln K_{\mathrm{sp}} = -RT \ln a_{\mathrm{AY}} a_{\mathrm{BX}}$$
$$= \Delta G^{\mathrm{o}}_{14} + (G^{*}_{\mathrm{AY}} - G^{\mathrm{o}}_{\mathrm{AY}}) + (G^{*}_{\mathrm{BX}} - G^{\mathrm{o}}_{\mathrm{BX}}) \quad (17)$$

where the last three terms are for the standard molar free energies for reactions (14)–(16) and where G^* is the standard free energy (or chemical potential) defined at infinite dilution. If the first free energy term, $\Delta G^{\mathrm{o}}_{14}$, is large and positive, i.e. AX and BY are the stable pair of salts, this term will dominate the summation. The standard free energy changes for the dissolution processes in Eqs. (15) and (16) are generally not very large. For Eq. (16), which is for mixing two salts with a common cation and two different anions, deviations from ideality are generally small as observed by Kleppa and coworkers [16], and the choice of zero for this term is often a good approximation. For this case, the solubility product for AX is a very small number and the activity coefficient of AX(s) is a large number indicating that AX(s) exhibits very large positive deviations from ideality. Analogous equations for this cycle have been used for calculations of solubility products and solubilities for fundamentally and technologically important systems [18–20]. The solubility of salts, e.g. MX, in molten silicates, e.g. MX–SiO_2 which contain anionic species ranging from SiO_4^{4-} to very large polymeric anions designated as $(SiO_2)_nO^{2-}$. Adapting Flory's theory for the thermodynamic properties of a simple molecule mixed with polymers to a mixture of simple anions with polymeric anions and assuming that the non-entropic mixing term in Flory's theory is ideal (zero) which in effect says that the entropic term in Flory's theory is the only significant term, led to equations that accurately predicted, e.g. sulphide and phosphate solubilities [21–23]. This appears to broaden the observation of Kleppa and coworkers.

4. Conclusions

We see that the works of Kleppa and coworkers have been a major contribution to molten salt chemistry. They have helped to develop concepts and theories which allow one to predict the thermodynamic properties of multicomponent systems from those of binary and unary systems. In addition, they have created a prodigious database of enthalpies of mixing of binary systems which, when coupled with other data (even as little as a phase diagram) allows one to fully and usefully describe the total thermodynamic properties of binary systems and use such data in predicting the properties of multicomponent systems.

References

[1] E.J. Salstrom, J.H. Hildebrand, J. Am. Chem. Soc. 52 (1930) 4641–4650.
[2] E.J. Salstrom, J.H. Hildebrand, J. Am. Chem. Soc. 52 (1930) 4650–4655.
[3] J.H. Hildebrand, E.J. Salstrom, J. Am. Chem. Soc. 54 (1932) 4252–4258.
[4] E.J. Salstrom, J. Am. Chem. Soc. 53 (1931) 1794–1799.
[5] E.J. Salstrom, J. Am. Chem. Soc. 53 (1931) 3385–3389.
[6] E.J. Salstrom, J. Am. Chem. Soc. 55 (1933) 1029–1030.
[7] E.J. Salstrom, J. Am. Chem. Soc. 56 (1934) 1272–1275.
[8] O.J. Kleppa, J. Phys. Chem. 64 (1960) 1937.
[9] O.J. Kleppa, L.S. Hirsh, J. Chem. Phys. 34 (1961) 351.
[10] O.J. Kleppa, F.G. McCarty, J. Phys. Chem. 70 (1966) 1249.
[11] G.N. Papatheodorou, O.J. Kleppa, J. Phys. Chem. 78 (1974) 178.
[12] T. Førland, J. Phys. Chem. 59 (1955) 152–156.
[13] T. Førland, Norg. Tek. Vitenskapsakad. 2 (4) (1957).
[14] H. Reiss, J.L. Katz, O.J. Kleppa, J. Chem. Phys. 36 (1962) 144–148.
[15] M. Blander, S.J. Yosim, J. Chem. Phys. 39 (1963) 2610–2616.
[16] O.J. Kleppa, Molten Salt Chemistry. An Introduction and Selected Applications, in: G. Mamantov, R. Marassi (Eds.), D. Reidel, Dordrecht, 1987, pp. 17–62.
[17] H. Flood, T. Førland, K. Motzfeldt, Acta Chem. Scand. 6 (1952) 257.
[18] M. Blander, Thermodynamic properties of molten salt solutions, in: M. Blander (Ed.), Molten Salt Chemistry, Interscience (Wiley), NY, 1964, pp. 127–237.
[19] G.H. Kucera, M.-L. Saboungi, Metall. Trans. 7B (1976) 213–215.
[20] M.-L. Saboungi, J. Marr, M. Blander, J. Electrochem. Soc. 125 (1978) 1567–1573.
[21] R.G. Reddy, M. Blander, Metall. Trans. 18B (1987) 591–596.
[22] R.G. Reddy, M. Blander, Metall. Trans. 20B (1989) 137–140.
[23] B. Chen, R.G. Reddy, M. Blander, 3rd International Conference on Molten Slags and Fluxes, TMS-AIME, Warrendale, PA, 1988, pp. 270–272.
[24] M. Temkin, Acta Physicochim. URSS 20 (1945) 411–420.
[25] L.S. Hersh, A. Navrotsky, O.J. Kleppa, J. Chem. Phys. 42 (1965) 3752.
[26] L.S. Hersh, O.J. Kleppa, J. Chem. Phys. 42 (1964) 1309.
[27] J.L. Holm, O.J. Kleppa, J. Chem. Phys. 49 (1968) 2425.
[28] G.N. Papatheodorou, O.J. Kleppa, J. Chem. Phys. 47 (1967) 2014.
[29] G.N. Papatheodorou, O.J. Kleppa, J. Inorg. Nucl. Chem. 32 (1970) 889.
[30] G.N. Papatheodorou, O.J. Kleppa, J. Inorg. Nucl. Chem. 33 (1971) 1249.
[31] G.N. Papatheodorou, O.J. Kleppa, Z. Anorg. Allg. Chem. 401 (1973) 132.
[32] G.N. Papatheodorou, O.J. Kleppa, J. Phys. Chem. 78 (1974) 178.
[33] K.C. Hong, O.J. Kleppa, J. Phys. Chem. 83 (1979) 2589.
[34] M.L. Saboungi, M. Blander, J. Am. Ceram. Soc. 58 (1975) 1–7.
[35] J. Lumsden, Dis. Faraday Soc. 32 (1961) 138.
[36] M. Blander, J. Chem. Phys. 34 (1961) 432.
[37] M. Blander, J. Chem. Phys. 37 (1962) 172.
[38] M.-L. Saboungi, M. Blander, J. Chem. Phys. 63 (1975) 212–220.
[39] M. Blander, L.E. Topol, Inorg. Chem. 5 (1966) 1641–1645.
[40] M.L. Saboungi, M. Blander, High Temp. Sci. 6 (1974) 37–51.
[41] H. Flood, T. Førland, K. Grjotheim, Z. Anorg. Allgem. Chem. 276 (1954) 289–315.