SOLUTION THEORIES FOR HIGH TEMPERATURE IONIC AND METALLIC LIQUIDS

Milton Blander
QUEST Research
1004 E. 167th Place
South Holland IL 60473

ABSTRACT

Theoretical advances permit one to predict the thermodynamic properties of many high temperature multicomponent liquid solutions from the often known properties of the lower order (binary and sometimes ternary) systems. Predictions made *a priori* for solutions in molten salts, silicates and metals appear to be potentially useful in science and technology. We will review these theories with emphasis on the most useful work. For example, a novel representation of the Wagner interaction parameters deduced from statistical mechanics allows one to predict these parameters at all temperatures from a measurement at a single temperature. A theory for sulfide capacities leads to predictions of these quantities *a priori* with accuracy being apparently limited only by the uncertainties in the input data. Using a modification of quasichemical theory, predictions of the properties of multicomponent molten silicates can be made from the properties of the subsidiary binaries when alumina is in dilute solution and ternary data are needed for cases in which alumina is at high concentration. The coordination cluster theory allows one to represent dilute solutions of solutes such as oxygen and sulfur in multicomponent alloys at different temperatures and compositions with data on the subsidiary binary systems with only one parameter for each ternary system. Thus, predictions can be made at all temperatures from measurements at one temperature. Theories of molten salts can be used to predict the phase diagrams and activities of components in large multicomponent systems.

INTRODUCTION

Concepts and theories for high temperature solutions of molten salts, silicates and metals developed in the last 50 years enable one to accurately predict the thermodynamic properties of multicomponent solutions from those of the generally well known binary (or sometimes ternary) systems. The availability of data on many binary and ternary systems allows one to make such predictions for a broad range of high temperature solutions. In this paper, I discuss simple examples of theories which have proven to be useful for technologies and science. These theories greatly minimize the data necessary for predicting properties of complex multi-component solutions of molten salts, silicates and metals.

A simple framework for understanding what we need to know in order to make technologically useful predictions is based on well known thermodynamic principles. In technologies and sciences where molten salts, slags magmas or molten metals are used or studied, one must often calculate the extent of a chemical reaction or of phase changes. To do this, one must first write an equilibrium constant, K, for the reaction in terms of the standard free energy change of the reaction, ΔG^o

$$\Delta G^o = -RT\ln K \qquad (1)$$

The equilibrium constant is generally a function of temperature, T, as well as of the concentrations, X, and activity coefficients, γ, of the individual reactants and products

$$K = K(T, X, \gamma) \qquad (2)$$

In order to calculate the concentrations, X, and hence the extent of a reaction, one requires a knowledge of ΔG^o, the standard free energy change for the reaction, and of the activity coefficients, γ. The standard free energy for the reaction is obtained from calorimetric and other types of equilibrium data on pure compounds. A very large database exists for the determination of this quantity.[1-4] With values of ΔG^o, one thus requires only values of the activity coefficients in order to calculate the extent of a chemical reaction. What is an activity coefficient? In order to go further, we need to define this quantity which is introduced only for the purpose of representing chemical potentials (μ) in a mathematically simple way. Chemical potentials approach minus infinity as one approaches infinite dilution of any component. The concept of activities and activity coefficients provide a convenient formalism for avoiding such infinities.

The chemical potential, μ, is a measure of the reactability of a substance and can be used to define an activity, a, of a substance

$$\mu = \mu^o + RT \ln a \tag{3}$$

where μ^o is the chemical potential of the pure liquid component. For a reaction at equilibrium, the difference between the chemical potentials of the products and the reactants is zero. Thus for a reaction

$$bB + cC + \cdots \Leftrightarrow mM + nN + \cdots \tag{4}$$

$$\Delta G = \Delta\mu^o + RT \ln K = \Delta\mu^o + RT \ln \frac{\Pi a_M^m a_N^n \cdots}{\Pi a_B^b a_C^c \cdots} \tag{5}$$

Activity coefficients represent the deviations of solution properties from those of a hypothetical ideal solution. Thus, in order to define activity coefficients, we have to first define an ideal solution. The definition of an ideal solution for metals and additive molten salts which have either a common cation or common anion is very simple. For example, for a mixture of metals or additive molten salt systems, eg., AX-BX-CX, the ideal molar free energy of mixing, ΔG_m is given by

$$\Delta G_m^{ideal} = RT \Sigma_i X_i \ln X_i \tag{6}$$

where X_i is the atom fraction or mole fraction and $\mu_i^o + RT \ln X_i$ is the chemical potential of component i. The definition of an ideal reciprocal molten salt solution is more complex because there are two ions in any one component. For a reciprocal molten salt solution of many cations and anions, an ideal solution is defined by

$$\Delta G_m^{ideal} = RT(\Sigma_c X_c \ln X_c + \Sigma_a X_a \ln X_a) \tag{7}$$

where X_c is the cation fraction and X_a is the anion fraction. For example, for two cations A^+ and B^+ the cation fraction of A^+ is given by

$$X_{A^+} = \frac{n_{A^+}}{n_{A^+} + n_{B^+}}$$

where n_c is the number of moles of the cation c. A similar expression is used for the anion fractions. The ideal chemical potential for a salt AX mixed with BY is given by

$$\mu_{AX} = \mu_{AX}^o + RT \ln X_A X_X \tag{8}$$

X_A and X_X are cation and anion fractions respectively. The activity defined in Eq.(3) is equal to X_i for an ideal solution of metals and $X_a X_c$ for an ideal reciprocal molten salt solution. Thus, if one mixes 0.5 mole of each of two metals to form one mole of an ideal solution, the activity of each metal is 1/2. The same is true if we mix 0.5 mole of each of two salts with a common anion (or cation) 0.5AX+0.5BX (or 0.5AX+0.5AY). However, if one mixes 0.5AX with 0.5BY, the ideal activities of AX and BY would both be 0.25. In addition, the activities of AY and BX are both also 0.25. Such reciprocal molten salt systems often exhibit very large deviations from ideal solution behavior and different constituents exhibit both positive and negative deviations from ideality.

More complex salts with ions of different valences exhibit more complex properties in solution. For example, a salt A_mX_n in an ideal molten salt solution has an activity given by

$$a_{A_mX_n} = X_A^m X_X^n \tag{9}$$

Most real systems do not exhibit ideal solution behavior and in order to represent such systems we define an activity coefficient, γ_i, for the component i such that the activity coefficient is the ratio of the real activity to the ideal activity

$$\frac{a_i}{a_i^{ideal}} = \gamma_i \tag{10}$$

When γ_i is greater than one, the component i exhibits positive deviations from ideal behavior and when γ_i is smaller than one, component i exhibits negative deviations from ideal behavior. In most (but not all) binary solutions, both components tend to exhibit either positive or negative deviations from ideal solution behavior. As mentioned above, reciprocal molten salt systems are more complex. In a system containing two cations (A^+ and B^+) and two anions (X^- and Y^-) one considers reactions such as

$$AX + BY \Leftrightarrow AY + BX \tag{11}$$

If the standard free energy change for reaction (11) is positive, then the two stable constituents AX and BY both tend to exhibit positive deviations from ideal behavior whereas the unstable pair of salts, AY and BX will both tend to exhibit negative deviations from ideal solution behavior. Deviations of the free energies of mixing from the ideal free energies of mixing are defined as an excess free energy of mixing, ΔG_m^E, and the differences between the real and ideal chemical potential of a component (RTln γ) is defined as the excess chemical potential.

DILUTE RECIPROCAL SOLUTIONS

A simple, useful and revealing calculation can be made for reciprocal systems involving a cycle first suggested by Flood, Fϕrland and Grjotheim.[5] Consider the simple example of the dissolution of a slightly soluble solid salt, AX(s) to form a saturated dilute solution in a molten liquid BY(l). The dissolution can be broken up into three steps

$$AX(s) + BY(l) \Leftrightarrow AY(s,l) + BX(s,l) \tag{12}$$

$$AY(s,l) \Leftrightarrow AY(so\ln.-BY(l)) \tag{13}$$

$$BX(s,l) \Leftrightarrow BX(so\ln.-BY(l)) \tag{14}$$

At equilibrium, the sum of the free energies for equations (12)-(14) per mole of AX(s) is zero. From this, one can deduce an equation for the solubility product, K_{sp}, and for the activity coefficient of AX(s), γ_{AX}.

$$\begin{aligned} -RT\ln K_{sp} &= RT\ln \gamma_{AX} = -RT\ln a_{AY}a_{BX} \\ &= \Delta G_{12}^o + (G_{AY}^o - G_{AY}^*) + (G_{BX}^o - G_{BX}^*) \end{aligned} \tag{15}$$

where the terms in the second line are the changes in the standard molar free energies for the processes exhibited in Eqs. (12)-(14) and where G^* is the standard free energy (or chemical potential) defined at infinite dilution. If the first term in the second line is large and positive, i.e. AX and BY are the stable pair of salts, this term will predominate the summation. The standard free energy changes for the dissolution processes in Eqs. (13) and (14) are generally not very large. For Eq. (14), which is for mixing two salts with a common cation and two different anions, deviations from ideality are generally small[6], and the choice of zero for this term is often a good approximation. For this case, the solubility product for AX is a small number and the activity coefficient of AX(s) is a large number indicating that AX(s) exhibits very large positive deviations from ideality. Conversely, the dissolution of the salt AY in the solvent BX would generally lead to very negative deviations from ideal solution behavior. In general, members of the stable pair of salts tend to exhibit positive deviations from ideality and members of the unstable pair of salts tend to exhibit negative deviations. Eqs. (12)-(14) convert a problem in a ternary system (there are four ions with the constraint of electroneutrality indicating three independent components) to those in the two binaries in Eqs.(13) and (14) by the use of data on the four pure constituents. This process underlines the basic goals of most of the theories in this paper which is to predict the properties of multicomponent systems from those of the lower order (preferably binary) systems. Calculations of solubilities and solubility products have been made using this cycle[5] for fundamental studies[7] and for systems of technological significance[8,9]. In these references, the solvents were sometimes more complex than a simple salt such as BY(l) and in references 8 and 9, the ionic charges of the anions and cations were not all the same. These references illustrate methods of adapting these concepts to complex systems.

When ΔG^o is very large in reciprocal salt systems dilute in two components, dilute ions A^+ and X^- tend to associate to form complex species by reactions such as

$$A^+ + X^- \Leftrightarrow AX \tag{16}$$

$$AX + X^- \Leftrightarrow AX_2^- \tag{17}$$

$$AX + A^+ \Leftrightarrow A_2X^+ \tag{18}$$

with equilibrium constants K_{11}, K_{12}, K_{21} etc. and where the associated species are, of course, solvated by the solvent ions, with the cations filling in the coordination shell about the X^- anion and the anions filling in the coordination shell of the A^+ cations. Since the activity of AY (BX) in Eq. (15) is proportional to the ion fraction of the "free" uncomplexed A^+ cations (X^- anions) in the dilute solution in the solvent, BY, this association to form complexes, when significant, can lead to an increase in the solubility of a salt such as AX which is larger than that one would calculate from the solubility product. By considering a mass balance equation for A^+, for example,

$$X_A^{total} = X_A^{free} + X_{AX} + X_{AX_2} + 2X_{A_2X} + \cdots \qquad (19)$$

one can deduce an equation for determining the equilibrium constants defined as

$$K_{11} = \frac{X_{AX}}{X_A^{free} X_X^{free}} \qquad (20)$$

$$K_{12} = \frac{X_{AX_2}}{X_{AX} X_X^{free}} \qquad (21)$$

$$K_{21} = \frac{X_{A_2X}}{X_A^{free} X_{AX}} \quad \text{etc.} \qquad (22)$$

If we focus on the activity of a dilute solution of AY in the solvent, the change in the value of the activity of this component with the addition of BX at concentrations where no AX(s) precipitates can be used to deduce K_{11}, K_{12}, K_{21} etc. For simplicity, in dilute solutions of AY we can deduce an equation from Eq. (19) for the ratio of the activity of AY with added BX to that with no added BX which is an activity coefficient, γ_{AY}^*, defined as unity at infinite dilution of BX.

$$-\ln \gamma_{AY}^* = K_{11}X_X + (K_{11}K_{12} - K_{11}^2)X_X^2 + \cdots \qquad (23)$$

where K_{11} is the limiting slope of a plot of $-\ln \gamma_{AY}^*$ versus X_X and where X_X is essentially the value of the "free" X when the A^+ cation is much more dilute than the X^- anion. Electromotive force measurements of K_{11} are given in the last column of Table I.[7]

Table I. Measured values of K_{11} and ΔA_{11}(kcal mol^{-1}) for the association of Ag^+ and Cl^- ions in molten nitrates for Z=5.[7]

System	T(°K)	ΔA_{11}	K_{11}
$Ag^+,K^+/Cl^-,NO_3^-$	623	5.85	553
	643	5.89	498
	658	5.93	460
	675	5.87	396
	696	5.88	348
	709	5.86	315
$Ag^+,Na^+/Cl^-,NO_3^-$	604	4.83	277
	637	4.84	226
	658	4.88	205
	675	4.81	176
	696	4.83	160
	711	4.81	146
	773	4.82	110
$Ag^+,Na^+,K^+/Cl^-,NO_3^-$	506	5.40	1050
	551	5.33	644
	658	5.38	302
	752	5.40	180
	801	5.28	133

A statistical mechanical theory leads to equations for such associations[7]

$$K_{11} = Z(\beta_{11} - 1) \qquad (24)$$

$$K_{11}K_{12} = \frac{Z(Z-1)}{2}(\beta_{11}\beta_{12} - 2\beta_{11} + 1) \qquad (25)$$

$$K_{11}K_{21} = \frac{Z(Z-1)}{2}(\beta_{11}\beta_{21} - 2\beta_{11} + 1) \qquad (26)$$

where $\beta_{ij} = \exp(-\Delta A_{ij}/RT)$ where ΔA_{ij} is the bond free energy for reactions such as those in Eqs. (16)-(18), and Z is a coordination number. In Table I we present values of ΔA_{11} at different temperatures for Z=5. Within the uncertainties in the measurements, the values of ΔA_{11} are independent of temperature at Z=5 as well as at other possible values of the coordination number (not shown), e.g., 4 and 6. This means that Eq. 24 (and, though they're not illustrated, also equations (25) and (26)) can accurately predict the temperature coefficients of the association constants so that measurements at one temperature may be used to predict these association constants at all temperatures. This result was shown to be valid for some of the higher order species.[7] In molten salt chemistry, these interactions are described as associations with equilibrium constants. In the metallurgical literature, analogous thermodynamic constants are called Wagner interaction parameters which are the negative of an association constant. As will be discussed below, equations equivalent to (but more general than) Eqs. (24)-(26) describe the temperature dependence of the Wagner interaction parameters (i.e., the ΔA_{ij} are independent of temperature) so that one can predict values at all temperatures from a single measurement.

THE COORDINATION CLUSTER THEORY

A generalization of the concepts for association has been applied to alloys[10-13] and molten salts[14] and leads to an accurate prediction of the activity coefficients of a dilute solute in a binary or multicomponent solvent[15] with minimal data from the binaries and one datum in each ternary. In this section we focus on the solubilities of oxygen and sulfur in binary alloys to illustrate the predictive power of the theory. The theory has a much broader range of usefulness including molten salts and silicates.

Let us consider a solute C dissolved in a binary solvent AB. The dissolution of C can be described in terms of the equilibrium

$$C + (Z-i)A + iB \Leftrightarrow C(A_{Z-i}B_i) \qquad (27)$$

where i can range from 0 to Z, Z is the coordination number of C and $C(A_{Z-i}B_i)$ is a coordination cluster in the solution. The equilibrium constant is given by

$$K_i = \frac{a_i}{a_C a_A^{Z-i} a_B^i} \qquad (28)$$

where a_i is the activity of the species formed in Eq.(27). There is an equivalent equation for molten salt systems. In dilute solutions of C, these species will obey Henry's law so that we can set $a_i = X_i$ (with a standard state defined at infinite dilution), where X_i is the mole fraction of the species. Since $X_C = \Sigma X_i$ where X_C is the total concentration of C atoms in solution, we can use statistical mechanical principles to deduce an equation for the concentration and temperature dependence of the activity coefficients of C in terms of the activity coefficients of the solvent components, γ_A and γ_B, values of the activity coefficients of C in pure A and pure B, $\gamma_{C(A)}$ and $\gamma_{C(B)}$ and a parameter $g_i^E = i(Z-i)h$ which represents the deviation from additivity of the energetic interaction between C and (Z-i)A and iB atoms in the coordination shell of C. In other words, the interaction energy of C with its coordination shell differs from the sum of similar interactions of C in pure A and pure B by the quantity g_i^E. The equation deduced for the activity coefficient of C is

$$\gamma_C^{-1} = \Sigma_i \frac{Z!}{(Z-i)!i!}\left(\frac{X_A\gamma_A^t}{\gamma_{C(A)}^{1/z}}\right)^{Z-i}\left(\frac{X_B\gamma_B^t}{\gamma_{C(B)}^{1/z}}\right)^{i} e^{-g_i^E} \qquad (29)$$

where h is the one energy parameter in the equation relating all the Z values of g_i^E. The parameter t is taken as 1/Z for a substitutional alloy and 1/3 for an interstitial alloy. For h=0, Eq. (29) reduces to the equations of Alcock and Richardson[16] and Jacob and Alcock[17]. For the case of an ideal solution of the solvent A-B, Eq.(29) reduces to the equation of Wagner.[18] Thus, Eq. (29) is a generalization of prior theories. The choice of one value of h for interstitial solutions of O or S in a number of binary alloys led to accurate representations of all the data at all the measured compositions and temperatures for all systems where data was available.[12,13] This meant that with thermodynamic data on the individual binary systems (i.e., A-O, B-O, A-B) and one datum in the ternary, one could predict the activity coefficients at all temperatures and compositions. Particularly note in Figures 1,4,5,7 and 8 of Ref. (12), that the theories of Alcock and Richardson and Jacob and Alcock[16,17] did not accurately represent the data for the Cu-Ni-O, Ag-Cu-O, Ag-Cu-S, Ag-Pb-O and Ag-Pb-S systems and in Fig. 3 of Ref. (12) the theory of Wagner[18] did not accurately represent the Ag-Sn-S system. The extension of the coordination cluster theory to multicomponent solvents[15] should enable one to predict solution properties of a solute such as C in a multicomponent solvent from analogous data on all the pertinent binary and ternary solvents. This theory for multicomponent solvents has not been fully tested.

The coordination cluster theory reduces to an equation equivalent to Eq. (23) in dilute solutions of e.g., B

$$-\ln\frac{\gamma_C}{\gamma_C^*} = K_{11}X_B + (K_{11}K_{12} - \tfrac{1}{2}K_{11}^2)X_B^2 + \cdots \qquad (30)$$

where K_{11} has the same form as Eq. (24) and where the temperature dependence of K_{11} can be predicted from a single measurement at one temperature. Modern books on metallurgical thermodynamics should include Eqs. (24) and (25) as a means of extrapolating measured values of the Wagner interaction parameters to different temperatures.

CONFORMAL IONIC SOLUTION THEORY (CONCENTRATED SOLUTIONS)[19-23]

The conformal ionic solution theory is a statistical mechanical perturbation theory for ionic systems. It permits one to reliably predict the thermodynamic properties of multicomponent systems from those of the pure constituents and the subsidiary binary systems. Even though the equations used are only from a second order perturbation theory for reciprocal systems, calculations from these equations exhibit surprising accuracy for systems in which the quantity ΔG^o for Eq.(11), with all four constituents as liquids, is not large enough to result in an immiscibility gap. The theory for ternary additive systems has been calculated up to fourth order[25] and provides accurate predictions in most systems in which the binary systems are not highly ordered. To simplify the discussion and make the concepts clear, I will focus on the simplest systems with only monovalent ions including ternary reciprocal systems and ternary additive systems (i.e., AX-BX-CX). The same concepts apply to higher order multicomponent systems and to systems having ions with different charges.[24,25] The conformal ionic solution theory is important not only because it is useful but also because it is the only theory valid for ionic systems with largely coulomb interactions, and was used to prove that equations deduced intuitively from standard solution concepts based on short range interactions were valid for ionic systems with long range interactions. There has not been an analogous proof for metallic systems.

We begin with a focus on reciprocal systems $A^+,B^+/X^-,Y^-$. Dilute solutions are often not simple because of the complexity of species and the non-additivity of pair bond interactions which mathematically requires very high order terms. Experience with concentrated solutions indicates that there is considerable cancellation of higher order terms at high concentrations. This is fortunate since the effects of non-additivity of pair bond interactions (i.e., bond energies for a given atom pair are a function of their environment). and the complexity inherent in trying to describe large complex groupings do not seem to be important in a description of concentrated solutions.

For this system there are four ions and four possible constituent salts, AX, AY, BX, and BY. With the constraint of electroneutrality, this is a ternary system with only three of the four constituents being independent components. The choice of the three components changes the equation deduced from the theory. Up to second order terms, the molar free energy of mixing for the reciprocal system with the three components AX, AY, and BY is given by the expression

$$\begin{aligned}\Delta G_m = RT(&X_A \ln X_A + X_B \ln X_B + X_X \ln X_X \\ &+X_Y \ln X_Y) + X_B X_X \Delta G^o + X_A \Delta G_A^E + X_B \Delta G_B^E \\ &+X_X \Delta G_X^E + X_Y \Delta G_Y^E - X_A X_B X_X X_Y \frac{(\Delta G^o)^2}{2ZRT}\end{aligned} \tag{31}$$

where the first term (including the four logarithmic expressions in parentheses) is the ideal total free energy of mixing and the last six terms are the total molar excess free energy of mixing, ΔG_m^E. The second term contains the product of the ion fractions of the two ions of the constituent, BX, which is not a component. The sign of this term is positive if ΔG^o is the standard free energy change for Eq.(11) with all constituents being liquid. The sign of this term is also positive if AY is not chosen as a component and will be negative if either one of the other two salts, AX or BY are not chosen as a component. The next four terms are the weighted sums of the excess free energy of mixing of the four binary systems AX-AY, BX-BY, AX-BX, and AY-BY with binary excess free energies ΔG_A^E, ΔG_B^E, ΔG_X^E and ΔG_Y^E respectively. Although the theory which led to Eq. (31) is only second order, the accuracy of calculations is improved if higher order expressions for the binary excess free energies of mixing are used such as e.g.,

$$\begin{aligned}\Delta G_X^E &= RT(X_A \ln \gamma_A + X_B \ln \gamma_B) \\ &= X_A X_B (b_X + c_X (X_A - X_B) + d_X X_A X_B)\end{aligned} \tag{32}$$

for the binary system AX-BX, where X_A and X_B are cation fractions. There are analogous expressions for the binary excess free energies for the other three binary subsystems of the ternary reciprocal system. One can calculate expressions for the chemical potentials of the four constitiuents by partial differentiation of Eq. (31) multiplied by the total number of moles of salt.

The last term in Eq. (31) is the first correction term for non random mixing of the ions in which the pairs of ions of the stable pair (AX and BY if ΔG^o is positive for Eq. (11)) tend to associate and form larger than random numbers of nearest neighbor pairs. This term, though it is not very large in a large number of cases, is significant for the calculation of phase diagrams and is very important for predicting whether there will or will not be a miscibility gap. When ΔG^{o} is large enough for the system to exhibit a miscibility gap, the theory is less accurate than it is at lower values of ΔG^{o}. For systems with no miscibility gaps, the calculations have proven to be remarkably accurate in almost all cases. As examples of calculations of phase diagrams and their comparisons with measurements, references 20-22, 25 and 26 contain a large number of successful calculations which indicate the power of the equations to make calculations where there are no experimental results and to find errors in the measurements. Extensions of the theory to higher order reciprocal systems and to systems with ions with very different charges have been made.[24,25] Success with the phase diagrams also indicates that calculations of the chemical potentials of the constituents can be reliable. A significant extension of a quasichemical theory for reciprocal systems has provided a calculation of many of the higher order terms which promises to extend the range of values of ΔG^{o} where one might obtain accurate representations of activities and of phase diagrams.[26] This theory is now under investigation to define it's limits.

Additive ternary systems contain salts with either three different cations and one kind of anion or three different anions and one kind of cation. Conformal ionic solution theory has been applied to such ternary systems and has been successful in making predictions for ternary systems from those of the binaries.[23] Although this is significant from a fundamental point of view, there are a number of empirical interpolation methods too numerous to report here which are about as successful. We will cover this topic very briefly. Results of the calculation lead to an expression up to fourth order for the free energy of mixing of a ternary system, AX-BX-CX, which can be calculated solely from the properties of the subsidiary binary systems.

$$\Delta G_m^E = \sum_{i<}\sum_{j} b_{ij}X_iX_j + \sum_{i\neq}\sum_{j} c_{ij}X_i^2X_j + \sum_{i<}\sum_{j} d_{ij}X_i^2X_j^2 + BX_AX_BX_C + \sum_{i\neq j<k} C_iX_i^2X_jX_k \quad (33)$$

where the values of a_{ij}, b_{ij} and c_{ij} are coefficients of Eq. (32) for the three binary subsystems of the ternary and B and C_i are related to these coefficients by the equations

$$B = (c_{AB}^{1/3} + c_{AC}^{1/3})(c_{BA}^{1/3} + c_{BC}^{1/3})(c_{AC}^{1/3} + c_{BC}^{1/3}) \quad (34)$$

$$C_i = 2(c_{ij}c_{ik})^{1/2} \quad (35)$$

where there are three values of C_i in this ternary system and where the coefficients $c_{ij} = -c_{ji}$. Although these equations are fundamentally significant and potentially useful, they are little used because of a prior preference for empirical methods of predicting ternary and multicomponent additive systems.

THEORIES FOR MOLTEN SILICATE SOLUTIONS

Because of the complexity of the subject, I will not be able to fully cover the method of prediction of the thermodynamic properties of silicates. An accurate prediction of the thermodynamic properties of silicate slags has eluded most investigators because of the ordered nature of silicates. One thermodynamic characteristic of highly ordered liquids is that the excess free energy of mixing tends to be "V" shaped and the molar entropy of mixing tends to be "m" shaped (similar to a McDonald's sign). These shapes can not be represented by the usual polynomial representation of these quantities and it was important to create a set of equations which could represent these shapes. Equations for the classical quasichemical solution theory have these properties but the original model had to be greatly modified in order to represent silicates.[28-31] The most important results are:

1. The complex properties of binary systems were very well represented by at most six energy parameters in a polynomial for the concentration and temperature dependence of the change of the bond energies for the process A-A + B-B = 2AB in a binary system A-B.
2. The equations represent the properties well enough to accurately interpolate and extrapolate outside the range of the measurements used to analyze binary systems. Strong evidence for this is that the input data could be reproduced accurately by back calculation with the theoretical equations using the binary energy parameters deduced by an analysis of the known data which included phase diagrams (with many compounds, miscibility gaps, liquidus temperatures, invariant points etc.), measured activities (from volatility, equilibrium and e.m.f. data) etc. Using the binary energy parameters deduced for each binary system analyzed and a simple combining rule one obtains accurate predictions of the properties of ternary systems from the subsidiary binaries. Calculated ternary phase diagrams and activities were generally in very good agreement with measurements. Readers should study references 28-31.
4. When alumina is present, one can predict the properties of multicomponent systems from the

subsidiary ternaries. To perform calculations for silicates, the carefully calculated self-consistent data in reference 32 is preferred.

In addition, a theory for the calculation of the solubility of sulfur (as sulphides) in molten silicates leads to predictions of the solubilities of sulfides (and of sulfide capacities) *a priori* with an accuracy which appears to be limited only by the accuracy of the input data.[33-35] The theoretical formalism can also be applied to the prediction of the solubilities of phosphates and all molten or gaseous salts including, e.g., halides, carbonates, sulfates etc. For sulfides, one considers the equilibrium

$$M_nO(l)+0.5S_2(g) \Leftrightarrow M_nS(l)+0.5O_2(g) \qquad (36)$$

with an equilibrium constant

$$K_M = \left(\frac{p_{O_2}}{p_{S_2}}\right)^{\frac{1}{2}} \frac{a_{M_nS}}{a_{M_nO}} \qquad (37)$$

where M is an ion with a valence of 2/n where n is a stoichiometric number. Sulfide capacity is defined by the equation

$$C_S = (wt\%S)\left(\frac{p_{O_2}}{p_{S_2}}\right)^{\frac{1}{2}} \qquad (38)$$

For dilute solutions of sulfur at mole fractions of silica between 0.33 and 1, the sulfide capacity can be calculated by the expression

$$C_S = 100W_SK_Ma_{MO}\frac{X_{SiO_2}}{W_{AV}}\left(\frac{\Phi_S}{a_{M_nS}}\right) \qquad (39)$$

where $\Phi_S = n_S/n_{Si}$, W_{AV} is the average molecular weight of the solvent, X_{SiO2} is the mole fraction of silica and W_S is the atomic weight of sulfur. From polymer theory, the ratio Φ_S/a_{MS} is given by

$$\ln\left(\Phi_S\Big/a_{M_nS}\right) = \left(\frac{1}{m}-1\right) \qquad (40)$$

where m is an average chain length. Since the calculations are relatively insensitive to the value of m, one can assume that all the M ions (up to valence 2) will break Si-O-Si bonds. Pure silica has two such bonds per silicon and it takes one divalent (n=1) or two monovalent (n=2) to break one bond. Thus, for the case of two divalent ions of M per silicon, m=1. For one or fewer divalent M ions per silicon m=∞. Between $X_{SiO2} = 0.33$ and 0.5 the value of m is given by

$$m = \frac{n_M}{n_{Si}-n_M} \qquad (41)$$

where n_i is the number of moles of i in solution. This relatively crude approximation is adequate for accurate calculations of C_S. At silica concentrations less than 0.33 C_S is given by

$$C_S = 100W_SK_Ma_{M_nO}\left[\frac{1-2X_{SiO_2}}{W_{AV}}\right] \qquad (42)$$

Using the modified quasichemical theory discussed above one can calculate the activity of M_nO and K_M can be calculated from thermodynamic data on the reactants and products in Eq.(3) or from one measurement of C_S in any other system. The resultant calculations represent measurements well within the uncertainties in the input data.[33-35] This method has been extended to multicomponent systems[35] and can be applied to phosphates, halides, sulfates, carbonates etc.

CONCLUSIONS

There has been considerable progress in the last 50 years on predicting thermodynamic solution properties of molten salts, silicates and metals. There are still major gaps in our ability to predict (especially for metals) and work is underway for needed improvements (especially for silicates).

REFERENCES

1. M. W. Chase Jr., JANAF Thermochemical Tables, Third Edition, Am. Chem. Soc., Am. Inst.Phys., N.B.S.,Washington, D. C. (1986) Parts I and II

2. O. Knacke, O. Kubaschewski, and K. Hesselmann, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin (1991)

3. Ihsan Barin, Thermochemical Data of Pure Substances, VCH, Basel (1992) Parts I and II

4. L. B. Pankratz, Thermodynamic Properties of Elements and Oxides,U.S. Bureau of Mines Bulletin 672, U.S. Government Printing Office, Washington D.C. (1982); Thermo-dynamic Properties of Halides , U.S. Bureau of Mines Bulletin 674, U.S. Gov't. Printing Office, Washington, D.C. (1984); L. B. Pankratz, J. M. Stuve, and N. A. Gokcen, Thermodynamic Data for Mineral Technology, U.S. Bureau of Mines Bulletin 677, U.S. Gov't. Printing Office, Washington, D.C. (1984)

5. H. Flood, T. Fϕrland, and K. Grjotheim, Z. Anorg. Allgem. Chem. **276** 289 (1954)

6. O. J. Kleppa, Molten Salt Chemistry, An Introduction and Selected Applications, eds. G. Mamantov and R. Marassi, D. Reidel Pub. Co., Dordrecht, Holland (1987) pp 17-62

7. M. Blander, "Thermodynamic Properties of Molten Salt Solutions", in Molten Salt Chemistry, ed. M. Blander, Interscience (Wiley), N. Y. (1964) pp. 127-237

8. G. H. Kucera and M.-L. Saboungi, Metall. Trans., **7B** 213 (1976)

9. M.-L. Saboungi, J. Marr and M. Blander, J. Electrochem. Soc., **125** 1567 (1978)

10. M. Blander and M.-L. Saboungi, Chemical Metallurgy-A Tribute to Carl Wagner, ed. N.A. Gokcen,TMS-AIME, Warrendale, PA (1981) pp. 223-231

11. M. Blander, M.-L. Saboungi and P. Cerisier, Metall. Trans., **10B** 613 (1979)

12. M.-L. Saboungi, P. Cerisier and M. Blander, Metall. Trans., **13B** 429 (1982)

13. M.-L. Saboungi and M. Blander, J. Electrochem. Soc., **124** 6 (1977)

14. M. Blander and M.-L. Saboungi, Acta Chem. Scand., **A34** 671 (1980)

15. M.-L. Saboungi, D. Caveny, I. Bloom and M. Blander, Metall. Trans., **18A** 1779 (1987)

16. C. B. Alcock and F. D. Richardson, Acta Met., **6** 385 (1958); ibid. **8** 882 (1960)

17. K. T. Jacob and C. B. Alcock, ActaMet., **20** 221 (1972)

18. C. Wagner, Acta Met., **21** 1297 (1973)

19. M. Blander and S. J. Yosim, J. Chem. Phys. **39** 2610 (1963)

20. M. Blander and L. E. Topol, Inorg. Chem., **5** 1641 (1966)

21. M.-L. Saboungi and M. Blander, High Temp. Sci., **6** 37 (1974)

22. M. -L. Saboungi, H. Schnyders, M. S. Foster and M. Blander, J. Phys. Chem., **78** 1091 (1974)

23. M.-L. Saboungi and M. Blander, J. Chem. Phys., **63** 212 (1975)

24. M.-L. Saboungi, J. Chem. Phys., **73** 5800 (1980)

25. M.-L. Saboungi and M. Blander, J. Am. Ceram. Soc., **58** 1 (1975)

26. Y. Dessureault and A. D. Pelton, J. Chim. Phys., **88** 1811 (1991)

27. H. Reiss, J. L. Katz and O. J. Kleppa, J. Chem. Phys., **36** 144 (1962)

28. A. D. Pelton and M. Blander, Proc. Second Int'l. Symp. on Metall. Slags and Fluxes, eds. H. A. Fine and D. R. Gaskell, TMS-AIME, Warrendale, PA (1984) p 281

29. M. Blander and A. D. Pelton, ibid, (1984) p 295

30. A. D. Pelton and M. Blander, Metall. Trans., **17** 805 (1986)

31. M. Blander and A. D. Pelton, Geochim. Cosmochim. Acta, **51** 85 (1987)

32. R. G. Berman, T. H. Brown and H. J. Greenwood, Atomic Energy of Canada Ltd. TR-377 (1985) 62 pp

33. R. G. Reddy and M. Blander, Metall. Trans., **18B** 591-596 (1987)

34. R. G. Reddy and M. Blander Metall. Trans., **20B** 137-140 (1989)

35. B. Chen, R. G. Reddy and M. Blander, 3rd International Conference on Molten Slags and Fluxes, 27-29 June, 1988, Univ. of Strathclyde, Glasgow (1988) pps. 270-272