

The Coordination Cluster Theory. Application to Ternary Reciprocal Molten Salt Systems *

M. BLANDER and M.-L. SABOUNGI

Chemical Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

The coordination cluster theory (CCT) is extended to ternary reciprocal molten salt solutions of one component (AY) in dilute solution in a binary solvent (AX – BX). Comparison with prior theories of reciprocal systems leads to the identification of the parameters in the CCT theory with quantities which are measurable in the pure constituents and in the four binary subsystems. Predictions of the specific bond free energies for forming associated species between Ag^+ and Cl^- or Br^- ions in sodium and potassium nitrates are made. Although the absolute values of these predicted energies are 15–20% smaller than experimental values, they have the correct relative values for different species in a given solvent and between different solvents for the same species. The CCT theory provides a basis for making predictions of association energies and for correlating and understanding the energetics of association in dilute reciprocal salt solutions.

I. INTRODUCTION

Ion association appears to be an important phenomenon in dilute reciprocal molten salt solutions. Measurements by electromotive force measurements^{1–8} and cryoscopy^{1,9–11} have been used to identify the associated species. The rationalization of the thermodynamic properties of the associated species, especially of the association constants and their temperature dependence, has been investigated by means of several theoretical models.^{1,12,13} However, the energetics of the association process remained unclear in the sense that there was no unified physical theory for the

energy change accompanying the formation of an associated ionic species.

In this paper, we utilize a new theoretical approach, the coordination cluster theory^{14,15} (CCT) to examine the energetics of association in a system consisting of B^+ and Y^- ions in dilute solution in a solvent consisting of A^+ and X^- ions. The CCT was first derived for substitutional and interstitial alloys;^{14,15} the activity coefficient of the solute was shown to be a function of the thermodynamic properties of the solvent, once the interactions of the solvent atoms in the coordination shell of the solute were modeled.

The extension of the CCT to ionic reciprocal systems is presented; the equation obtained for the activity coefficient of the dilute solute is compared to equations derived from prior theories.^{12,16–18} The identification of the energetic parameters for the ionic association process is made possible by this comparison. The predicted values of the energetics of association in the case of Ag^+ with Cl^- or Br^- in alkali nitrate solvents are compared with available experimental results.

II. APPLICATION OF THE COORDINATION CLUSTER THEORY TO IONIC SYSTEMS

As mentioned earlier, the CCT was developed for metallic systems.^{14,15} The dependence of the activity coefficient of a solute C in dilute solution in a binary solvent A – B, on the composition of the solvent, is described in terms of atomic associations and involves (1) the limiting activity coefficient of C in pure A, $\gamma_{C(A)}$, and in pure B, $\gamma_{C(B)}$; (2) the atom fractions of the solvent components, X_A and X_B ; and (3) the activity coefficients, γ_A and γ_B . The

* This work was performed under the auspices of the Basic Energy Sciences Division of the U.S. Department of Energy.

relation (1) was obtained, where Z is the coordination number of the solute C, t is a geometric parameter ($t \geq 1/Z$), and g_i^E is an excess Gibbs free energy of mixing of i atoms B and $(Z-i)$ atoms A present in the coordination shell of C, i.e., in a typical configuration $C(A_{Z-i}B_i)$.

$$(\gamma_C)^{-1} = \sum_{i=0}^Z \frac{Z!}{i!(Z-i)!} \left(\frac{X_A \gamma_A^t}{\gamma_{C(A)}} \right)^{Z-i} \left(\frac{X_B \gamma_B^t}{\gamma_{C(B)}} \right)^i \times \exp\left(-\frac{g_i^E}{RT}\right) \quad (1)$$

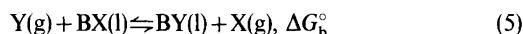
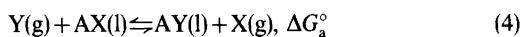
There is no rigorous thermodynamic derivation for g_i^E . Several heuristic approximations for g_i^E have been proposed. A simple equation was used first by Wagner,¹⁹ who implicitly assumed that the A and B atoms form "a regular solution" in the coordination shell, eqn. (2), where h is an energy

$$g_i^E = i(Z-i)h/2 \quad (2)$$

parameter. The "specific bond free energy" for bonding the i th B atom to a C atom, ΔA_i , is related to h through eqn. (3).

$$\Delta A_i = \frac{RT}{Z} \ln[\gamma_{C(B)}/\gamma_{C(A)}] - tRT \ln[\gamma_B/\gamma_A] + (Z-2i+1)h/2 \quad (3)$$

The extension of the above equations to ternary molten salt systems can be directly made for additive systems schematically represented by $(A^+, B^+, C^+/X^-)$ or $(A^+/X^-, Y^-, Z^-)$. For reciprocal systems, e.g., $(A^+, B^+/X^-, Y^-, Z^-)$, the extension is not as straightforward. If $AX-BX$ is considered as a solvent and Y is a hypothetical gaseous solute, one can define the exchange equilibria (4) and (5), where



g refers to gas, l to liquid, and ΔG_a° and ΔG_b° to the standard Gibbs free energy changes of reaction (4) and (5), respectively. The activity coefficient, γ_Y , of the solute Y can be readily derived from eqn. (1): eqn. (6).

$$(\gamma_Y)^{-1} = \sum_{i=0}^Z \frac{Z!}{i!(Z-i)!} \left(\frac{X_A \gamma_{AX}^t}{\gamma_{Y(AX)}} \right)^{Z-i} \left(\frac{X_B \gamma_{BX}^t}{\gamma_{Y(BX)}} \right)^i \times \exp\left[-\frac{g_i^E}{RT}\right] \quad (6)$$

The terms, $\gamma_{Y(AX)}$ and $\gamma_{Y(BX)}$, represent the limiting activity coefficients of Y in pure AX and BX, respectively, γ_{AX} and γ_{BX} represent the activity coefficients of AX and BX in the AX-BX systems, respectively.

The ion fractions of A and B, X_A and X_B , are defined by eqn. (7), where N_A and N_B are the

$$X_A = \frac{N_A}{N_A + N_B} \text{ and } X_B = \frac{N_B}{N_A + N_B} \quad (7)$$

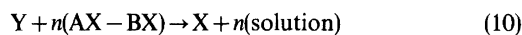
numbers of mol of A and B, respectively. The quantities g_i^E and ΔA_i are defined by equations identical to eqns. (2) and (3), with the subscripts, A, B, C(A) and C(B), replaced with AX, BX, Y(AX) and Y(BX), respectively. The limiting activity coefficients, $\gamma_{Y(AX)}$ and $\gamma_{Y(BX)}$, are related to ΔG_a° and ΔG_b° by eqns. (8) and (9).

$$RT \ln \gamma_{Y(AX)} = \Delta G_a^\circ + RT \ln \gamma_{AY(AX)} \quad (8)$$

$$RT \ln \gamma_{Y(BX)} = \Delta G_b^\circ + RT \ln \gamma_{BY(BX)} \quad (9)$$

where $\gamma_{AY(AX)}$ represents the activity coefficient of AY at infinite dilution in pure AX and $\gamma_{BY(BX)}$ represents the activity coefficient of BY at infinite dilution in pure BX.

The quantity $RT \ln \gamma_Y$ as derived from eqn. (6) can be rationalized as the standard Gibbs free energy change for the process (10), where n is a



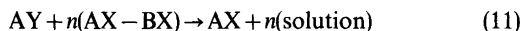
large number of the order of Avogadro's number, and the solution is defined as containing $(n-1)$ mol of X and one mol of Y.

III. DISCUSSION

In this section, we compare the results derived from the CCT for reciprocal ternary molten salt systems with equations obtained from various models and theories. In addition, nonrandom mixing and association in dilute solution are discussed. Finally, the values calculated for the

specific bond free energies from the CCT for selected illustrative systems are compared with experimental data.

a. *Comparison with prior theories and models.* In order to compare the CCT with prior molten salt theories, one has to consider the process (11),



which is the difference between reactions (10) and (4). Consequently, the standard Gibbs free energy change for reaction (11), ΔG_c° , is given by eqn. (12),

$$\Delta G_c^\circ = RT \ln \gamma_Y - \Delta G_a^\circ = RT \ln(\gamma_{AY}/\gamma_{AX}) \quad (12)$$

where γ_{AY} refers to the activity coefficient of AY in the ternary reciprocal system. Thus, one has eqn. (13).

$$RT \ln \gamma_{AY} = RT \ln \gamma_{AX} + RT \ln \gamma_Y - \Delta G_a^\circ \quad (13)$$

By expanding $RT \ln \gamma_Y$ as derived from eqn. (6) in a power series in X_A and X_B up to the second-order in ion fractions, the expression (14) is obtained,

$$\begin{aligned} RT \ln \gamma_{AY} = & -X_B \Delta G^\circ + ZtX_B \ln(\gamma_{AX}/\gamma_{BX}) + \\ & + RT(X_A \ln \gamma_{AY(AX)} + X_B \ln \gamma_{BY(BX)}) + \\ & + Z(Z-1)X_A X_B h/2 - \frac{X_A X_B}{2ZRT} \\ & [\Delta G^\circ + ZtRT \ln(\gamma_{BX}/\gamma_{AX}) + \\ & + RT \ln \gamma_{AY(AX)} - RT \ln \gamma_{BY(BX)}] \end{aligned} \quad (14)$$

where ΔG° is the standard Gibbs free energy change for the reaction (15). Eqn. (14) incor-



$$\Delta G^\circ = \Delta G_a^\circ - \Delta G_b^\circ \quad (16)$$

porates terms present in the corresponding relation derived from the conformal ionic solution (CIS) theory.¹⁶ For solutions dilute in Y^- the activity coefficient of AY deduced from the CIS theory¹⁶ is given by eqn. (17), which contains only

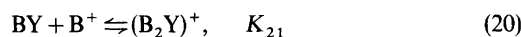
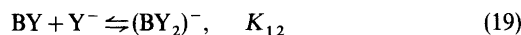
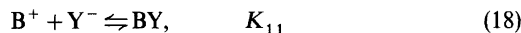
$$\begin{aligned} RT \ln \gamma_{AY} = & -X_B \Delta G^\circ + X_B(X_B - X_A)\lambda_X + \\ & + X_A \lambda_A + X_B \lambda_B + X_A X_B \lambda_Y - X_A X_B \\ & \frac{(\Delta G^\circ)^2}{2ZRT} + \dots \end{aligned} \quad (17)$$

second-order terms. The first term on the right hand side of eqn. (17) has been derived in the pioneer work of Flood, Førland and Grjøtheim;¹⁷ the next four terms were deduced by Førland¹⁸ based on a random mixing model. The coefficient λ_i is an energy parameter for a quadratic representation of the Gibbs excess free energy of mixing of a binary system where i is the common ion, *e.g.*, in the AX-BX system $\Delta G_m^E(AX-BX) = \lambda_X X_A X_B$. Eqn. (17) applies rigorously to those reciprocal systems in which the excess Gibbs free energy of mixing of the binary subsystems can be described by a quadratic representation.

The comparison of eqns. (14) and (17) permits one to identify terms such as h and t and in addition leads to a generalization of the CIS equations.

The first four quantities on the right hand side of eqn. (14) are exactly identical to the first five quantities on the right hand side of eqn. (17) if $\lambda_Y = Z(Z-1)h/2$, if $t=1/Z$, and if the excess Gibbs free energies of three of the binary subsystems can be represented by a quadratic expression in the corresponding ion fractions, *i.e.*, $\Delta G_m^E(AX-BX) = \lambda_X X_A X_B$, $RT \ln \gamma_{AY(AX)} = \lambda_A$ and $RT \ln \gamma_{BY(BX)} = \lambda_B$. However, the equation derived from the CCT for $RT \ln \gamma_{AY}$ is valid for any thermodynamic formulation of the binary subsystems, even when strong associations exist (*i.e.*, large deviations from random mixing). This point is a considerable advantage in comparison with the CIS equations. Even the expanded form of the CCT equation, eqn. (14), contains a more complete description of the nonrandom mixing contribution than does eqn. (17). Additional terms are in the last bracketed term in eqn. (14) and can be obtained from the CIS theory if higher-order terms in the perturbation calculations¹⁶ are considered. The importance of the more complete description of the nonrandom mixing contribution as formulated from the CCT [eqns. (6), (8), (9) and (13)] stems from the fact that one can accurately describe ionic association.

b. *Nonrandom mixing in dilute solutions.* In the limiting case where X_B approaches zero, associations occur between the B^+ and Y^- ions to form various associated species such as in eqns. (18)–(20).



etc. ...

Each species, $(B_i Y_j)^{+(i-j)}$ is characterized by an association constant K_{ij} . The above equilibria should be viewed within the context of the CCT; B^+ refers to the configuration $B(X_Z)$ where Z ions X are the nearest neighbors of B ; BY refers to the configuration $B(X_{Z-1}, Y)$ where $(Z-1)$ ions X and one ion Y occupy the first coordination shell of B ; finally Y^- , $(BY_2)^-$ and $(B_2Y)^+$ designate the configurations $Y(A_Z)$, $B(X_{Z-2}Y_2)$ and $Y(A_{Z-2}B_2)$, respectively.

The association constants K_{11} , K_{12} and K_{21} are related to parameters in the CCT through eqns. (21)–(23),^{13–15} where the quantity β_{ij} is related to

$$K_{11} = Z(\beta_{11} - 1) \quad (21)$$

$$K_{11}K_{21} = \frac{Z(Z-1)}{2}(\beta_{11}\beta_{12} - 2\beta_{11} + 1) \quad (22)$$

$$K_{11}K_{21} = \frac{Z(Z-1)}{2}(\beta_{11}\beta_{21} - 2\beta_{11} + 1) \quad (23)$$

the “specific bond free energy” in dilute solutions in AX , ΔA_{ij}° by eqn. (24).

$$-RT \ln \beta_{ij} = \Delta A_{ij}^\circ \quad (24)$$

When $j=1$, ΔA_{i1}° is given by eqn. (3) where the concentration of B^+ ions is very low, $X_B \approx 0$. Keeping in mind that, in this case, h and t are identified with $2\lambda_Y/Z(Z-1)$ and $1/Z$, respectively, eqn. (3) becomes eqn. (25). Thus, as X_B and X_Y

$$A_{i1} = \frac{RT}{Z} \ln [\gamma_{Y(BX)}/\gamma_{Y(AX)}] - \frac{RT}{Z} \ln [\gamma_{BX}/\gamma_{AX}] + \lambda_Y(Z-2i+1)/Z(Z-1) \quad (25)$$

approach zero and AY is the solute, one has eqn. (26). The quantity ΔA_{i1}° defined as $\lim(\Delta A_{i1})_{X_B \rightarrow 0}$ is

$$\Delta A_{i1}^\circ = \Delta A_{i1}^\circ - 2(i-1)\lambda_Y/Z(Z-1) \quad (26)$$

$$\Delta A_{i1}^\circ = \lambda_Y/Z - (RT/Z) \ln [\gamma_{BX(AX)}\gamma_{Y(AX)}/\gamma_{Y(BX)}] \cong (-\Delta G^\circ + \lambda_Y + \lambda_B - \lambda_A - \lambda_X)/Z \quad (27)$$

given by eqn. (27) where $\gamma_{Y(AX)}$ and $\gamma_{Y(BX)}$ are defined by eqns (8) and (9), respectively, and $\gamma_{BX(AX)}$ is the activity coefficient of BX at infinite dilution in AX and is the limit of the ratio $(\gamma_{BX}/\gamma_{AX})$ as $X_B \rightarrow 0$. The quantity ΔA_{i1}° is constant. If BX is the solute in the binary solvent $AX-AY$ dilute in AY , it can be

shown that:

$$\Delta A_{ij}^\circ = (\Delta A_{i1}^\circ)' - 2(j-1)\lambda_B/Z(Z-1) \quad (28)$$

where $(\Delta A_{i1}^\circ)'$ is given by eqn. (29).

$$\begin{aligned} (\Delta A_{i1}^\circ)' &= (\lambda_B - \Delta G^\circ)/Z - \\ (RT/Z) \ln [\gamma_{AY(AX)}\gamma_{BX(AX)}/\gamma_{BY(AY)}] &\cong \\ (-\Delta G^\circ + \lambda_B + \lambda_Y - \lambda_X - \lambda_A)/Z &\cong \Delta A_{i1}^\circ \end{aligned} \quad (29)$$

c. *Comparison with experimental data.* In what follows, measurements of association constants of silver and halide ions in molten nitrates are reviewed for some ternary reciprocal systems.^{1,4–7} Also, the specific bond free energies ΔA_{ij}° are calculated using the CCT [eqns. (26)–(29)] for a value of $Z=4$.

In Table 1, the values of the thermodynamic coefficients needed for calculations in the systems $(Na, Ag/NO_3, Cl)$, $(K, Ag/NO_3, Cl)$, $(Na, Ag/NO_3, Br)$ and $(K, Ag/NO_3, Br)$ are grouped. The interaction coefficients, λ of the four binary subsystems are derived assuming that the excess Gibbs free energy of mixing is a quadratic function of the ion fractions.²⁰ The values for λ_{Ag} are the most uncertain as pointed out by Lumsden.²⁰ Some measurements indicate very negative values whereas other more likely results yield values which are zero or slightly negative. In the calculations, a value of zero has been chosen, although one must be aware of the uncertainty. Finally for $Z=4$, values of $(\Delta G^\circ/Z)$ are given in Table 1 as deduced from measurements.^{21,22} This ratio is, of course, independent of solution effects and by coincidence is the same for $NaNO_3$ and KNO_3 in the bromide systems.

By use of eqns. (26–29), ΔA_{11}° , ΔA_{12}° and ΔA_{21}° are calculated and compared with the experimental values for the associations of Ag^+ with Cl^- and Br^- in $NaNO_3$ and KNO_3 solutions. The calculated values (grouped in Table 2) have the correct relative values, with the values for the chlorides being closer to the experimental data than those for the bromides; the fact that specific bond free energies ΔA_{11}° and ΔA_{12}° are equal stems from the fact that $\lambda_{Ag}=0$. The somewhat large difference between measured and calculated values for ΔA_{ij}° (Table 2) might be related to the perhaps too simple approximation for ΔA_{i1}° in eqn. (27) and for g_i^E in eqn. (2).

Table 1. Thermodynamic parameters for some reciprocal molten salt systems^a (kcal mol⁻¹).

System	λ_A	λ_{Ag}	λ_{NO_3}	λ_Y	$\Delta G^\circ/Z$
(Na,Ag NO ₃ ,Cl)	0.40	0	0.68	0.90	4.4
(K,Ag NO ₃ ,Cl)	0.21	0	-0.60	-2.20	4.8
(Na,Ag NO ₃ ,Br)	0.36	0	0.68	1.05	5.5
(K,Ag NO ₃ ,Br)	0.12	0	-0.60	-1.48	5.5

^a The interaction parameters λ_i are taken from Lumsden.²⁰ The subscript A refers to either Na or K, and the subscript Y refers to either Cl or Br depending on the system. ΔG° refers to the standard Gibbs free energy change for reaction (15) and $Z=4$. (1 kcal=4.184 kJ).

Table 2. Measured and calculated specific bond free energies in some reciprocal molten salt systems (kcal mol⁻¹).

System	$-\Delta A_{11}^\circ$	$-\Delta A_{12}^\circ$	$-\Delta A_{21}^\circ$	Ref.
(Na,Ag NO ₃ ,Cl)	5.10	5.10	(5.0) ^a	4
	4.4 ^b	4.4 ^b	4.5 ^b	
(K,Ag NO ₃ ,Cl)	6.14	6.1	5.8	5
	5.3 ^b	5.3 ^b	4.8 ^b	
(Na,Ag NO ₃ ,Br)	6.74	6.7	6.9	6
	5.5 ^b	5.5 ^b	5.8 ^b	
(K,Ag NO ₃ ,Br)	7.40	7.4	7.1	7
	5.8 ^b	5.8 ^b	5.5 ^b	

^a Parentheses refer to an estimate value. ^b Calculated values for $Z=4$.

However, the *solvent effect* on values of ΔA_{11}° and on differences between ΔA_{21}° or ΔA_{12}° and ΔA_{11}° is predicted by the CCT equations even though the absolute magnitudes are smaller than the experimental values. For example, since the experimental values for λ_{Ag} are zero or slightly negative, the expectation is that $\Delta A_{12}^\circ \approx \Delta A_{11}^\circ$. This expectation is consistent with values in Table 2. Values of λ_Y in the KNO₃ solvents are negative, leading to the expectation that, as observed, $\Delta A_{21}^\circ > \Delta A_{11}^\circ$ in this solvent. On the other hand, values of λ_Y are fairly positive in the NaNO₃ solvents, leading to the expectation that $\Delta A_{21}^\circ < \Delta A_{11}^\circ$, which could be true within the uncertainties in the data.

Thus, however crude the different approximations, they have provided a means for correlating and understanding relative values of interaction energies (specific bond free energies) for association in dilute solutions, as well as a framework for future work. A more accurate representation can be developed in the future as a larger more coherent body of data becomes available for analysis.

IV. CONCLUSION

The coordination cluster theory provides a framework for describing and understanding the energetics of association in dilute reciprocal salt solutions. An approximation of the quantity g_i^E permits one to identify all the energetic terms in the theory with measurable quantities. Relative values of the "specific bond free energies" for different associated species and the relative solvent effects are correctly predicted, and even the absolute values are indicative of the strength of bonding of the species considered. Much better correlations with all data would be obtained if the coordination number were considered to be an adjustable parameter.

In order to fully understand the energetics of association, one must ultimately analyze a larger body of data and introduce approximations for bond energies which are based on more fundamental principles deduced from quantum mechanics, rather than the heuristic approximations used here. Nevertheless, the equations discussed appear to be potentially useful for

making predictions in ternary reciprocal systems based on data in lower order systems (*i.e.*, pure salts and binaries). Further testing of these predictions is needed in order to define their range of applicability and to provide a basis for future theoretical studies of bond energies of solution species.

REFERENCES

1. Blander, M. In Blander, M., Ed., *Molten Salt Chemistry*, Interscience, New York 1964.
2. Saccheto, G. A., Bombi, G. G. and Macca, C. J. *Electroanal. Chem.* 36 (1972) 47.
3. White, S. H., Inman, D. and Jones, B. *Trans. Faraday Soc.* 64 (1968) 2841.
4. Hill, D. G., Braunstein, J. and Blander, M. *J. Phys. Chem.* 64 (1960) 1038.
5. Manning, D. L., Braunstein, J. and Blander, M. *J. Phys. Chem.* 66 (1962) 2069.
6. Manning, D. L., Bansal, R. C., Braunstein, J. and Blander, M. *J. Am. Chem. Soc.* 84 (1962) 2028.
7. Alvarez-Funes, A., Braunstein, J. and Blander, M. *J. Am. Chem. Soc.* 84 (1962) 1538.
8. Vallet, C. and Braunstein, J. *J. Phys. Chem.* 77 (1973) 2672.
9. Saboungi, M.-L., Vallet, C. and Doucet, Y. *J. Phys. Chem.* 77 (1973) 1699.
10. Ratjke, S. H. K. *Complex Formation in Alkali-Aluminium Fluoride Melts*, The Norwegian Institute of Technology, The University of Trondheim, Trondheim 1974.
11. Braunstein, J., Blander, M. and Lindgren, R. M. *J. Am. Chem. Soc.* 84 (1962) 1529.
12. Blander, M. and Braunstein, J. *Ann. N. Y. Acad. Sci.* 79 (1960) 838.
13. Blander, M. *J. Chem. Phys.* 34 (1961) 432.
14. Saboungi, M.-L. and Blander, M. *J. Electrochem. Soc.* 124 (1977) 6.
15. Blander, M., Saboungi, M.-L. and Cerisier, P. *Met. Trans. B* 10 (1979) 613.
16. Blander, M. and Yosim, S. J. *J. Chem. Phys.* 39 (1963) 2610.
17. Flood, H., Førland, T. and Grjotheim, K. *Z. Anorg. Allgem. Chem.* 276 (1954) 289.
18. Førland, T. *Nor. Tek. Vitenskapsakad. Medd.* 2 (1957) No. 4.
19. Wagner, C. *Acta Metall.* 21 (1973) 1297.
20. Lumsden, J. *Thermodynamics of Molten Salt Mixtures*, Academic, New York 1966.
21. Blander, M., Braunstein, J. and Silverman, M. D. *J. Am. Chem. Soc.* 85 (1963) 895.
22. Blander, M. and Luchsinger, E. B. *J. Am. Chem. Soc.* 86 (1964) 319.

Received April 18, 1980.