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The Topology of Phase Diagrams of Reciprocal Molten Salt Systems

BY MILTON BLANDER AND L. E. TOPOL

Liquidus temperatures in the reciprocal molten salt system Li,K∥F,Cl are calculated from the conformal ionic solution theory, and the calculated topology of the solid–liquid equilibria is in excellent correspondence with the measurements of Berezina, Bergman, and Bakumskaya. The influence of parameters in the theory on the topology of the solid–liquid phase diagram is discussed. An approximate relation which may be used to predict immiscibility gaps in reciprocal systems is given (eq 16) and is shown to provide a simple and fundamental basis for many of the empirical rules stated by previous workers.

The phase diagrams of a large number of simple molten reciprocal salt systems[1] have been investigated. The topology and characteristics of the solid–liquid equilibria in these systems have been empirically characterized and classified by Russian workers[2] in terms of factors such as the difference in free energies between the stable and unstable solid salt pairs, the polarizabilities of the ions, and electronic structure. In this paper we will apply a recent statistical mechanical theory,[3] the conformal ionic solution theory, to reciprocal salt systems and show that there is a fundamental justification for some of the empirical and less general correlations of the Russian school. Our discussion will be illustrated by calculations of liquidus temperatures in the system Li,K∥F,Cl and it will be demonstrated that the calculations from the theory with the aid of only one unknown parameter, which is adjustable within narrow limits, can reproduce all of the measured topological features of the phase diagram quite accurately. It is believed that this is an extreme test of the theory because the liquidus temperatures and topology of phase diagrams are extremely sensitive, both to small changes in the magnitude of the parameters in the theory and to the form of the equations used. We will discuss how variations in the thermodynamic quantities which enter into the theory influence the calculated phase diagram and show the relationship of these quantities to the features discussed by the Russian workers. The theory cannot be utilized to give detailed predictions of liquidus temperatures *a priori*. We hope to show, however, that topological features of phase diagrams are related to macroscopic thermodynamic quantities in the theory. These quantities, in turn, can be related to microscopic ionic interactions. Thus, it is hoped that this discussion will be a useful guide in predicting topological features and in extracting information from the large number of phase diagrams which have been published. In conclusion, we will apply the theory to the occurrence of miscibility gaps which have been extensively studied and discussed in the Russian literature.[4]

The Theory of Conformal Ionic Solutions.—The theory of conformal ionic solutions has been extended to reciprocal salt systems.[3] The expression derived for the total excess free energy of mixing (ΔG^E_m) of the three salts AC, BC, and BD is[5]

$$\Delta G^E_m = X_A X_D \Delta G^\circ + X_D \Delta G^E_{12} + X_C \Delta G^E_{34} + X_A \Delta G^E_{13} + X_B \Delta G^E_{24} + X_A X_B X_C X_D \Lambda \quad (1)$$

where the X's are ion fractions. For example, the cation fraction of A is $X_A = n_A/(n_A + n_B)$ and the anion fraction of C is $X_C = n_C/(n_C + n_D)$, where the n's are the number of moles of the ions indicated. ΔG° is the standard molar Gibbs free energy change for the metathetical reaction

$$AC(l) + BD(l) \rightleftharpoons AD(l) + BC(l) \quad (2)$$

ΔG^E_{ij} is the excess free energy of mixing of the binary mixture of the salts i and j where AD is salt 1, BD is 2, AC is 3, and BC is 4. Although it has been shown that the terms in ΔG^E_{ij} are general,[3] in this paper we will include only second-order terms so that

$$\Delta G^E_{12} = X_A X_B \lambda_{12} \quad (3a)$$

$$\Delta G^E_{13} = X_C X_D \lambda_{13}, \text{ etc.} \quad (3b)$$

where λ_{ij} is an energy parameter depending solely on

(1) A simple reciprocal salt system is one containing two cations and two anions.

(2) (a) A. G. Bergman, K. A. Evdokimova, and O. F. Bogush, *Izv. Sektora Fiz.-Khim. Analiza, Inst. Obshch. Neorgan. Khim., Akad. Nauk SSSR*, **27**, 419 (1956); (b) J. E. Ricci, "Phase Diagrams of Fused Salts," in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, New York, N. Y., 1964, p 239.

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

(4) (a) I. N. Belyaev, *Usp. Khim.*, **29**, 899 (1960); *Russ. Chem. Rev.*, **29**, 428 (1960); (b) M. L. Sholokhovich, D. S. Lesnykh, G. A. Bukhalova, and A. G. Bergman, *Dokl. Akad. Nauk SSSR*, **103**, 261 (1955).

(5) M. Blander and L. E. Topol, *Electrochim. Acta*, **10**, 1161 (1965). (It should be noted that we have replaced the Helmholtz free energy in this reference by the Gibbs free energy. The difference is not significant in this second-order equation.)

the properties of the binary systems. The term Λ cannot be calculated from theory but is proportional to $(\Delta G^\circ)^2$. This proportionality is particularly important for our calculations and cannot be obtained from a purely thermodynamic formulation. A useful approximation to Λ can be obtained by comparison with the corresponding term in the quasi-lattice theory[5,6]

$$\Lambda = -(\Delta G^\circ)^2/2ZRT \qquad (4)$$

where Z is a "coordination number" which should be between 4 and 6.[7] In the calculations presented here a value of 6 has been chosen for Z.[8] From eq 1 with the aid of the relation

$$RT \ln \gamma_i = \frac{\partial n \Delta G^E_m}{\partial n_i} = \frac{\partial n \Delta G^E_m}{\partial n_+} + \frac{\partial n \Delta G^E_m}{\partial n_-} \qquad (5)$$

the activity coefficients of any component can be calculated. n_+ and n_- denote the number of moles of cations and anions of component i. For example, for BD (component 2) one obtains

$$RT \ln \gamma_2 = X_A X_C \Delta G^\circ + X_A X_C (X_C - X_D)\lambda_{13} +$$
$$X_C(X_A X_D + X_B X_C)\lambda_{24} + X_A(X_A X_D + X_B X_C)\lambda_{12} +$$
$$X_A X_C(X_A - X_B)\lambda_{34} + X_A X_C(X_A X_D +$$
$$X_B X_C - X_B X_D)\Lambda \qquad (6)$$

The parameters in eq 6 can be evaluated from available thermodynamic data, ΔG° from data on the pure salts and λ_{ij} from data on the binary systems. As has been discussed previously,[5] eq 1, 4, and 6 are much more general than is implied by the restrictions of the conformal ionic solution theory.

Calculations in the Li,K‖F,Cl System.—The liquidus temperatures in the Li,K‖F,Cl system measured by Berezina, Bergman, and Bakumskaya[9] are shown in Figure 1. In this section calculations of liquidus temperatures in this system will be made with the use of eq 6 for BD ≡ LiF and with similar equations for the other constituents.

The liquidus temperature, T, is the temperature at which a solid constituent, such as BD, is in equilibrium with a solution in which the component has an activity a_2 related by the equation

$$R \ln a_2 = -L\left(\frac{1}{T} - \frac{1}{T_0}\right) = R \ln X_B X_D \gamma_2 \qquad (7)$$

where L is the heat of fusion and T_0 is the melting point of the pure salt. Since we are not interested in the detailed behavior but rather in the general topology, eq 7 was derived under the simplifying assumption that the heat of fusion is independent of temperature. Thus, for given values of the concentrations, and with the known or calculable thermodynamic parameters
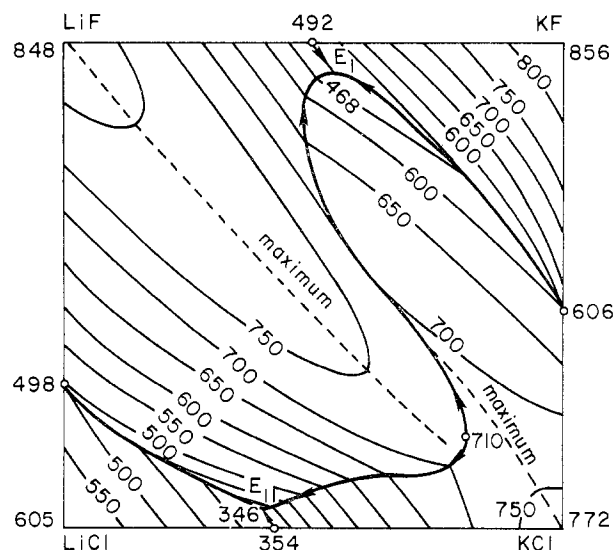
(6) M. Blander and J. Braunstein, *Ann. N. Y. Acad. Sci.*, **79**, 838 (1960).

(7) M. Blander, "Thermodynamic Properties of Molten Salt Solutions," in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, New York, N. Y., 1964, p 127.

(8) The relatively high value 6 is chosen to make the term Λ smaller. This partially compensates for the higher order terms which partly cancel the influence of Λ when $\Delta G^\circ/RT$ becomes large.

(9) S. I. Berezina, A. G. Bergman, and E. L. Bakumskaya, *Zh. Neorgan. Khim.*, **8**, 2140 (1963); *Russ. J. Inorg. Chem.*, **8**, 1118 (1963).

Figure 1.—Liquidus temperatures measured in the Li,K‖F,Cl system.[9]

ΔG°, L, and λ_{ij}, one can calculate the liquidus temperatures, T.

The value of $\Delta G^\circ = 16.3$ kcal/mole was taken from tabulated data[10] for the reaction

$$LiF(l) + KCl(l) \rightleftharpoons LiCl(l) + KF(l) \qquad (8)$$
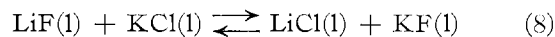
The following values of the melting points and heats of fusion of the four constituents were obtained from accepted literature values:[7,11] for LiF, 1121°K and 6470 cal/mole; for KF, 1129°K and 6750 cal/mole; for LiCl, 878°K and 4760 cal/mole; and for KCl, 1045°K and 6340 cal/mole. Values of λ_{ij} can be calculated from known phase diagrams of the four binary systems.[5,9,12] Since we were primarily interested in the liquidus temperatures, the parameters λ_{ij} chosen were those that gave the best fit of the eutectic temperature and composition under the simplified assumptions that for a given binary system ij

$$RT \ln \gamma_i = \lambda_{ij} N_j^2 \text{ and } RT \ln \gamma_j = \lambda_{ij} N_i^2 \qquad (9)$$

Equations 9 coupled with eq 7 for the two components of the binary systems led to the two equations (10a,b)

$$T(\text{eutectic}) = (\lambda_{ij}(1 - N_i)^2 + L_i)/((L_i/T_{0i}) - R \ln N_i) \qquad (10a)$$

$$= (\lambda_{ij}N_i^2 + L_j)/((L_j/T_{0j}) - R \ln (1 - N_i)) \qquad (10b)$$

from which λ_{ij} could be calculated from the measured value of the eutectic temperature. The calculations from eq 10a,b for each of the four binary systems were done on a computer using the measured eutectic temperature as a fixed point and the eutectic composition and λ_{ij} as variables. This led to calcu-

(10) G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Bewer, McGraw-Hill Book Co., New York, N. Y., 1961, p 674.

(11) A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.*, **64**, 269 (1960).

(12) (a) T. W. Richards and W. B. Meldrum, *J. Am. Chem. Soc.*, **39**, 1816 (1917); (b) I. E. Krauze and A. G. Bergman, *Dokl. Akad. Nauk SSSR*, **35**, 21 (1942); (c) A. G. Bergman and E. P. Dergunov, *ibid.*, **31**, 752 (1941); (d) G. A. Bukhalova and A. G. Bergman, *ibid.*, **66**, 67 (1949).

lated values of X_i (given in Table I) for the composition of each of the binary eutectics. These differ from the measured values of X_i by less than 2 mole %, which is within the experimental uncertainties of the measurements. For λ_{ij}, the calculated values obtained are unique and in reasonable agreement with other available thermodynamic data.[5,7,13] These values of λ_{ij} are also listed in Table I. This procedure is not

TABLE I

	Measured eutectic temp and compn[9]		λ_{ij}, cal/mole	Calcd eutectic compn
LiF–KF	492°	49.5% LiF	−4247	50.8% LiF
LiF–LiCl	498°	30.0% LiF	−365	30.0% LiF
KCl–LiCl	354°	57.5% LiCl	−4133	58.8% LiCl
KCl–KF	606°	45.0% KF	−97.5	43.2% KF

strictly valid for the KCl–KF binary due to the occurrence of solid solutions. This may lead to some minor inconsistencies in our calculations for compositions near this binary system. To derive the liquidus temperatures eq 6 and 7 were combined to yield

$$T[(L_{BD}/T_0) - R \ln X_B X_D] = L_{BD} +$$
$$X_A X_C[\Delta G° + (X_C - X_D)\lambda_{13} + (X_A - X_B)\lambda_{34}] +$$
$$X_C(X_A X_D + X_B X_C)\lambda_{24} + X_A(X_A X_D + X_B X_C)\lambda_{12} +$$
$$X_A X_C(X_A X_D + X_B X_C - X_B X_D)\lambda \quad (11)$$

Equation 11, together with the parameters in the text and in Table I and the values of $\Delta G° = 16.3$ kcal/mole and $Z = 6$, was used in a computer calculation of the liquidus temperatures for the Li,K‖F,Cl system shown in Figure 2. The comparison with the measurements is striking and there is a close correspondence between the topology of the measured and the calculated phase diagrams. From an examination of the equations used we may deduce the factors which give rise to various features and learn how variations in these factors influence the topology.

Discussion

In this section the influence of the thermodynamic parameters in the calculations of phase diagrams will be discussed. In the fundamental thermodynamic equation (7), it is obvious that the heat of fusion and the melting point directly influence the area of the phase field[14] of a given salt. For example, although the activity coefficients of KCl and LiF as calculated from eq 6 are similar at corresponding concentrations, the higher melting point of LiF leads to a much larger area for its phase field in the diagram. In addition, the larger the activity coefficients for any salt in the solution at corresponding concentrations the greater will be the area of its phase field. For example, the melting temperature and heat of fusion of KF are somewhat higher than those of LiF. Although both these factors tend to lead to larger phase fields, the area of the phase field for LiF is larger than that for KF. This is a
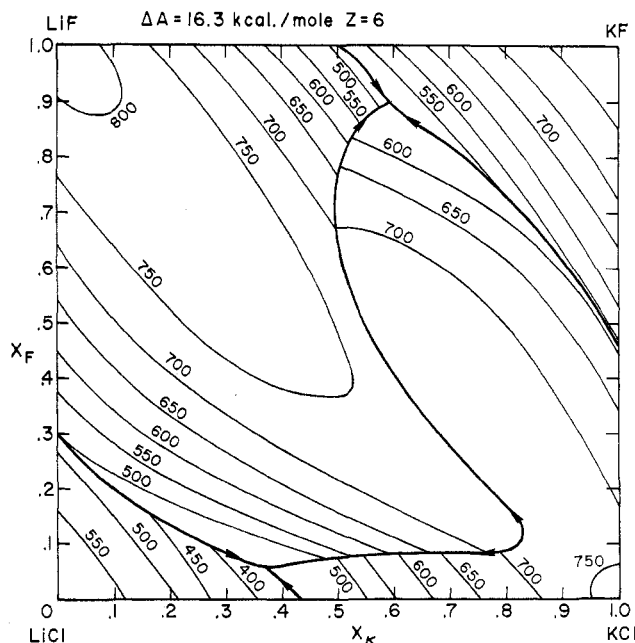
(13) (a) L. S. Hersh and O. J. Kleppa, *J. Chem. Phys.*, **42**, 1309 (1965); (b) R. A. Gilbert, *J. Phys. Chem.*, **67**, 1143 (1963).

(14) The phase field of a given salt in the representations in Figure 1 is defined as the region in the composition diagram from which the given salt is the first salt to precipitate upon cooling.

Figure 2.—Liquidus temperatures calculated for the Li,K‖F,Cl system.

result of the fact that LiF is a member of the stable pair of salts (LiF + KCl) and exhibits positive deviations from ideal solution behavior ($\gamma > 1$), whereas KF is a member of the unstable pair (KF + LiCl) and exhibits negative deviations from ideal solution behavior. Positive deviations cause the liquidus temperatures to be higher for a given composition and lead to intersections at the eutectic valleys at lower concentrations of the given salt than would be the case if the solution were ideal. The opposite is true for negative deviations.

There is an intrusion of the phase field of KCl in the direction of the LiF–KF binary eutectic and one, less obvious, of the field of LiF in the direction of the LiCl–KCl binary eutectic. These intrusions are related to the large negative values of the λ parameters for the LiF–KF and the LiCl–KCl systems.

The shape of the isotherms can also be related to the theory. The bending out of the LiF and KCl isotherms away from the corners representing these pure salts is related to their positive deviations from ideal behavior and the very slight bowing in of the LiCl and KF contours is related to their negative deviations from ideal behavior. (It should be noted that an ideal system would exhibit some bowing out of the isotherms but not nearly as extensive as is shown in Figures 1 and 2.)

We can also examine the influence of variations of the parameters in eq 11 on the phase diagram. For lower $|\Delta G°|$ values, the phase fields of LiF and KCl would get smaller relative to those of LiCl and KF and the bending out away from the corners of the isotherms for LiF and KCl would decrease. If the λ values were not negative, the intrusions of LiF and KCl mentioned above would not be present and, in fact, the theory would predict the presence of two liquid layers. This will be discussed more fully in the next section.

Liquid–Liquid Immiscibility Gaps.—A most interesting feature of some reciprocal systems are liquid–liquid immiscibility gaps. Many correlations have been found between the appearance of immiscibility gaps and various properties of the salts.[4] In this section the calculation of upper consolute temperatures (T_C) from eq 11 will be discussed.[15] For simplicity of presentation the calculation will be limited to the pseudo-binary system for the stable pair here designated as BD–AC. The consolute temperatures calculated along these pseudo-binaries are not necessarily upper consolute temperatures for the system but generally do not differ enough from these quantities to warrant the complications of a more detailed calculation. Along the pseudo-binary $X_B = X_D = X_2$ and $X_A = X_C = X_3$ so that eq 6 becomes

$$RT \ln \gamma_2 = X_3{}^2 \Delta G^\circ + X_3{}^2(\lambda_{13} + \lambda_{34} + \\ 2(1 - X_3)(\lambda_{24} + \lambda_{12} - \lambda_{13} - \lambda_{34})) + \\ X_3{}^2(1 - X_3)(3X_3 - 1)\Lambda \quad (12)$$

where $X_2 + X_3 = 1$. The condition from which the consolute temperature along the pseudo-binary can be calculated is

$$\frac{da_2}{dX_2} = 0 = \frac{dX_2{}^2\gamma_2}{dX_2} = 2X_2\gamma_2 - \frac{X_2{}^2 d\gamma_2}{dX_3} \quad (13)$$

$$\frac{2}{X_2} = \frac{d \ln \gamma_2}{dX_3} \quad (14)$$

Substituting into eq 14 from (12), one finds the result

$$\frac{1}{X_2 X_3} = \frac{\Delta G^\circ}{RT_C} + \frac{1}{2}\left(\frac{\lambda_{12} + \lambda_{24} + \lambda_{13} + \lambda_{34}}{RT_C}\right) + \\ \left(3 X_2 - \frac{1}{2}\right)\left(\frac{\lambda_{24} + \lambda_{12} - \lambda_{13} - \lambda_{34}}{RT_C}\right) + \\ (6X_3 X_2 - 1)\frac{\Lambda}{RT_C} \quad (15)$$

This expression is somewhat unwieldy for general use. Since the theory is approximate for large values of $\Delta G^\circ/RT$, a simplified equation for the consolute temperature which should prove as useful as eq 15 is[16]

$$T_C = \frac{\Delta G^\circ}{5.5R} + \left(\frac{\lambda_{12} + \lambda_{24} + \lambda_{13} + \lambda_{34}}{11R}\right) \quad (16)$$

Equation 16 enables us to make predictions for the occurrence of immiscibility gaps. If the consolute temperature, T_C, is higher than liquidus temperatures along the pseudo-binary for the stable pair of salts, then there should be an immiscibility gap, and if it is

lower, there should not be an immiscibility gap. An immiscibility gap should, of course, be present if T_C is higher than the melting temperature of the highest melting member of the stable pair. Since the theory is approximate and since there are errors in the parameters used, one may make predictions of immiscibility or miscibility with a reasonable degree of certainty only when T_C is much higher or lower than the possible liquidus temperatures. For example, the calculated value of T_C for the Li,K||F,Cl system from eq 16 is 816°, which is higher than the liquidus temperature at $X_{Li} = X_F = {}^1/_2$ but is lower than the melting point of LiF. The uncertainties in using the approximate equation (16) in this borderline case would not warrant any prediction for this system, where, experimentally, the components appear to be completely miscible. A characteristic of such borderline cases is an S shaped liquidus curve as is found in the Li,K||F,Cl system.

From eq 16 we see that we must be cognizant of three factors in predicting immiscibility:

(I) ΔG°: The more positive is ΔG° the higher is T_C. Thus, no immiscibility gap is found in the Li,K||F,Cl system, where ΔG° is 16.3 kcal/mole, whereas an immiscibility gap is found in the Li,K||F,Br system,[2,4] where ΔG° is about 22 kcal/mole.[17] It appears probable that the contribution of the term containing λ_{ij} is about the same in both systems.[7,13,18]

(II) λ_{ij}: The value of ΔG° in the Li,K||F,Cl system (16.3 kcal/mole) is higher than for the Na,Ag||Cl,I system (14.7 kcal/mole).[7,17] However, the negative contribution of λ_{ij} in the first system lowers the calculated value of T_C considerably and no miscibility gap is found. In the latter system the contribution of the λ_{ij} term is small and probably positive[13a] and consequently does not decrease the T_C value calculated from the ΔG° term ($>1330°K$). This T_C value is much greater than the melting point of NaCl (1074°K), the higher melting component, and, thus, an immiscibility gap is predicted and is observed.[2,4]

(III) Liquidus Temperatures: The calculated value of T_C for the Li,K||F,Cl system is higher than T_C calculated for the K,Tl||NO₃,Br system ($\Delta G^\circ \sim 9$ kcal/mole[17]). However, the calculated T_C is lower than the melting point of LiF in the former system, where no immiscibility is found. In the latter system T_C is considerably above the low melting point of TlBr,

(15) The consolute temperature, T_C, is the temperature below which there exists a range of compositions which separate into two immiscible liquids.

(16) Since X_2 at T_C will generally not differ greatly from ${}^1/_2$ we have used the relation $X_2 X_3 \approx {}^1/_4$ and assumed that the term $3(X_2 - {}^1/_2)(\lambda_{24} + \lambda_{12} - \lambda_{13} - \lambda_{34})/RT_C$ is negligible. This is especially valid in many cases where λ_{24} and λ_{13} and also λ_{12} and λ_{34} have the same sign and partly cancel one another. For large values of $\Delta G^\circ/RT$, higher order terms, which are not included in the theory, become significant and partly cancel the effect of the term containing Λ.[6,7] Consequently, for large values of $\Delta G^\circ/RT$, the effective absolute value of the Λ term increases more slowly than is indicated by eq 4. To derive eq 16 we have used the following approximation which appears to be consistent with available data and with theories containing the higher order terms:[6,7] $\Lambda_C/RT_C \approx -3$.

(17) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952. The values of ΔG° calculated from this compilation are for the reactions of the solids at room temperature. The difference between this quantity and ΔG° for the exchange reaction of the pure molten salts should not be large enough to change any of the conclusions obtained here. The correction depends, first, on the magnitude of ΔC_P for the exchange reaction and, second, upon a correction for the difference between the free energies of each salt in the solid and liquid states at the temperature for which ΔG° is calculated. The first correction is generally small (<1 kcal). The second correction may be estimated as follows. For any pure salt which is a solid at the temperature for which ΔG° is calculated a correction of about $+\Delta S_f \Delta T$ is required if the salt is a member of the unstable pair and about $-\Delta S_f \Delta T$ if it is a member of the stable pair. (ΔS_f is the entropy of fusion and ΔT is the difference between the melting point of the salt and the temperature in question.) This correction has been applied to the K, Tl||NO₃, Br system.

(18) (a) O. J. Kleppa and L. S. Hersh, *J. Chem. Phys.*, **36**, 544 (1962); (b) O. J. Kleppa and S. V. Meschel, *J. Phys. Chem.*, **67**, 668 (1963); (c) L. S. Hersh, A. Navrotsky, and O. J. Kleppa, *J. Chem. Phys.*, **42**, 3752 (1965).

the higher melting component of the stable pair, and an immiscibility gap is found.[2,4]

The first factor, $\Delta G°$, has been used in correlations by Russian investigators[2,4] although they utilize $\Delta G°$ and sometimes $\Delta H°$ for the exchange reaction of the solids at room temperature. The other two factors, $\Sigma\lambda_{ij}$ and liquidus temperatures, provide a justification of many of the empirical correlations given by the Russian workers. For example, when the cations are polarizable, it has been observed that an immiscibility gap will occur for smaller values of $\Delta G°$ [2,4] than when the cations are not polarizable. Values of λ_{ij} tend to be more positive (or less negative)[7,13,18] and the melting points of salts are lower when the cations are polarizable. Both factors are in the right direction so as to agree with the observed data. The positive contributions to λ_{ij} which are related to cation polarizabilities have been discussed theoretically[7,18,19] in terms

of the van der Waals (or London) interactions between ions. Thus, one can relate the appearance of immiscibility gaps theoretically to fundamental interactions between the ions. Conversely, the prediction of immiscibility gaps can be made from values of λ_{ij} obtained from a theoretical calculation based on a knowledge of the ionic interactions or from independent measurements of the binary systems.

Conclusion

Many of the significant topological features of phase diagrams including immiscibility gaps can be correlated with the conformal ionic solution theory. Although the theory is approximate, it provides a simple and fundamental basis for many of the empirical rules stated by previous workers.

(19) (a) M. Blander, *J. Chem. Phys.*, **36**, 1092 (1962); (b) J. Lumsden, *Discussions Faraday Soc.*, **32**, 138 (1961).

The Kinetics of Formation and Aquation of Bis(oxalato)bis(dimethyl sulfoxide)chromate(III)

BY KENNETH R. ASHLEY AND RANDALL E. HAMM

The compound potassium *cis*-bis(oxalato)bis(dimethyl sulfoxide)chromate(III) has been prepared, and the visible absorption spectrum in water solution is reported. The kinetics of formation of the compound from *cis*-bis(oxalato)diaquochromate-(III) in DMSO has been investigated. The solvolysis in DMSO is a two-step process with both steps independent of water concentration up to 1.03 M water concentration at 45°. The rate constants for the faster step are 4.61×10^{-4}, 8.20×10^{-4}, 21.9×10^{-4}, and 40.6×10^{-4} sec^{-1} at 30, 35, 40, and 45°, respectively. The activation parameters for this step are $\Delta H^* = 28.5 \pm 1.1$ kcal/mole and $\Delta S^* = 20.1 \pm 3.4$ cal/deg mole. For the slower step the rate constants at 30, 35, 40, 45, 50, and 55° are 1.52×10^{-4}, 3.43×10^{-4}, 7.55×10^{-4}, 16.1×10^{-4}, 34.7×10^{-4}, and 70.3×10^{-4} sec^{-1}, respectively. The activation parameters are $\Delta H^* = 29.7 \pm 0.1$ kcal/mole and $\Delta S^* = 21.9 \pm 0.3$ cal/deg mole. The aquation of the *cis*-bis(oxalato)-bis(dimethyl sulfoxide)chromate(III) was found to be pH independent between pH 1.0 and 4.0 at 55°. A two-step process was also observed for the aquation reaction. The activation parameters for the fast step are $\Delta H^* = 12.3 \pm 0.6$ kcal/mole and $\Delta S^* = -30.2 \pm 1.9$ cal/deg mole. The associated rate constants are 25.1×10^{-4}, 51.0×10^{-4}, and 86.2×10^{-4} sec^{-1} at 35, 45, and 55°, respectively. For the slow step the rate constants are 3.03×10^{-4}, 8.04×10^{-4}, 18.9×10^{-4}, and 45.7×10^{-4} sec^{-1} at 25, 35, 45, and 55°, respectively. The activation parameters are $\Delta H^* = 17.0 \pm 0.8$ kcal/mole and $\Delta S^* = -17.6 \pm 2.6$ cal/deg mole.

Compounds of cobalt and chromium containing dimethyl sulfoxide (DMSO) as a ligand have been reported by various workers.[1] Usually only the spectral characteristics of the compounds were discussed. Schläfer investigated the equilibrium between the ions dichlorotetrakis(dimethyl sulfoxide)chromium(III) and trichlorotris(dimethyl sulfoxide)chromium(III) in DMSO.[2] Tobe and Watts[3] have investigated systems in which the chloro(dimethyl sulfoxide)bis(ethylenedi-

amine)cobalt(III) ion was present. To date, with the exception of Tobe and Watts, no one has investigated the rate of formation of any complex containing DMSO.

In an attempt to find a suitable nonaqueous solvent in which to study the *trans–cis* isomerization of the bis-(oxalato)diaquochromate(III) ion it was observed that DMSO reacted with the complex. This paper reports the results of the investigation of the rate of aquation and the rate of formation of potassium *cis*-bis(oxalato)bis(dimethyl sulfoxide)chromate(III).

Experimental Section

The potassium *trans*-bis(oxalato)diaquochromate(III) was prepared by the method described by Werner.[4] The product

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(2) H. L. Schläfer and H. P. Opitz, *Z. Chem.*, 216 (1962).
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