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# Thermodynamics of Mixing in Na–K β-Aluminas

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The activities of the components in the pseudo-binary Na–K β-alumina system have been calculated from equilibrium ion-exchange data. Using data from exchanges with molten nitrate, chloride, and iodide salts, the results indicate that this system shows negative deviations from ideal mixing. A model involving preferential "ion pairing" of Na and K ions gives a good fit to the experimental data. Two maxima in the excess stabilities are found at compositions lying close to those which have been shown to exhibit the lowest ionic conductivities in the system. It is suggested that the "mixed-alkali" effect in Na–K β-alumina is strongly related to the presence of cation order, and that the driving force for order results from reduction of nearest-neighbor cation repulsions. © 1987 Academic Press, Inc.

## I. Introduction

β- and β″-aluminas are technologically important fast ionic conductors. The conductivity and structure of sodium β- and β″-alumina are well documented in the literature (see, for example, (*1, 2*)). Recent work (*3, 4*) has shown these structures are capable of accomodating rapid diffusion of not only monovalent ions, but also divalent and trivalent species. Many studies of "mixed-cation" β-aluminas have also been made. Relative to the pure end members, the mixed-cation β-aluminas generally show a large decrease in their ionic conductivity and an associated increase in activation energy (*5–7*). This phenomenon is analogous to the well-known behavior of mixed-alkali glass systems and has been termed the "mixed-alkali effect" (*8, 9*).

A universally accepted explanation for the mixed-alkali effect in glass and β-alumina systems is still lacking. It seems clear the decrease in conductivity is related to structural and energetic changes of the ions in the mixed cation systems. Ingram *et al.* (*10*) have suggested the origin of the mixed-alkali effect in both glass and β-alumina systems may lie in the formation of "mixed ion pairs." Several researchers have used a weak electrolyte model based on ion-pair formation to model the conductivities of these systems (*6, 11*).

Few investigators have attempted to use thermodynamic techniques to gain insight into the mixed-alkali effect. Many of the proposed models for the origin of the effect can be supported or rejected by consideration of the thermodynamic mixing properties of these systems. For example, models invoking preferential ion pairing, or ion association, between unlike cations would be supported by evidence for negative deviations from ideal mixing, whereas models relying upon microscopic phase separation, or like-ion clustering, would be expected to

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result in positive deviations from ideality. No results on the thermodynamic mixing properties of β-aluminas have been reported previously. However, some data are available for glass systems (*11, 12*). The results for glass systems are somewhat in conflict. Enthalpy of solution experiments on Na–Li borates (*11*), which show a strong mixed-alkali effect, indicate negative deviations from ideal mixing. From an analysis of critical temperatures in pseudo-binary silicate systems, Tomozawa *et al.* (*12*) have claimed evidence for positive deviations from ideality.

In this paper the results of a thermodynamic analysis of the Na–K β-alumina system will be described. Previous studies of the ionic conductivities have found that substantial resistivity increases occur across the binary system (*2, 6*). The initial work on this system (*2*) showed that at a composition close to $X_K = 0.2$ the crystals have a conductivity three orders of magnitude smaller than the pure Na end member at 273 K. A more recent redetermination of the conductivities confirmed the general trend in the conductivities, but found that the minimum occurs close to $X_K = 0.8$ (*6*).

Using available data for the equilibrium ion-exchange characteristics of β-alumina in $NaNO_3$–$KNO_3$ molten salts, the activity–composition relations in the Na–K β-alumina system are reported in this paper. The resultant free energies of mixing are interpreted using thermodynamic mixing models and are compared to the trends in the ionic conductivities across the binary system.

## II. Experimental: Thermodynamic Treatment of Ion-Exchange Data

In the original work of Yao and Kummer (*1*) on the β-aluminas comprehensive equilibrium ion-exchange data were reported for Na–K β-alumina crystals in $NaNO_3$–$KNO_3$ molten salts at 345°C. Higher temperature data for exchange between β-alumina and NaI–KI, and NaCl–KCl melts at 800°C were also presented. The starting composition of the crystals was $Na_{1.22}Al_{11}O_{17.11}$. The partitioning of Na and K between β-alumina and a melt of known composition was determined by gravimetric and chemical analysis. Using a different analytical technique, described elsewhere (*13*), we have confirmed their results for exchange between β-alumina and Na–K nitrate melts.

The experimental data for distribution of Na and K between β-alumina and a molten salts of known composition can be used to evaluate the activities of both ions in the crystal. This technique has been used in previous work (*1, 14*), but is briefly restated here to draw attention to some previous oversights.

The exchange of ions between the melts and β-alumina can be described by the following chemical equilibrium:

$$Na^+_{1.22(\beta)} + 1.22\ KNO_{3(melt)} = K^+_{1.22(\beta)} + 1.22\ NaNO_{3(melt)}. \quad (1)$$

Apart from exchanges using a pure melt, all species in the above equilibrium are impure and have activities less than unity. By using a large excess of melt changes in the melt composition during equilibration can be neglected.

At equilibrium the free energy change of the reaction is zero and therefore,

$$\Delta G = \Delta G^\circ + RT \ln K_{eq.} = 0 \quad (2)$$

where $\Delta G^\circ$ is the standard free energy of reaction (1) at the temperature of the ion exchange and $K_{eq.}$ is the equilibrium constant. For the equilibrium as written in (1) the equilibrium constant is given by

$$K_{eq.} = (a_{K_{1.22(\beta)}})(a_{NaNO_3})^{1.22}/(a_{Na_{1.22(\beta)}})(a_{KNO_3})^{1.22}. \quad (3)$$

It should be noted that as written in the preceding equations the equilibrium con-

stant and the activities of ions in $\beta$-alumina correspond to mixing of 1.22 total cations. In cases where the total number of cations is not unity "ideal," i.e., random, mixing is no longer characterized by $a = X$ but by $a = X^n$, where $n$ represents the total number of sites per formula unit on which mixing can take place. For easy identification and characterization of deviations from ideal mixing, it is more useful to rewrite the chemical equilibrium in terms of one-site mixing. Then nonideal mixing is represented by cases where $a \neq X$. Equation (1) can therefore be written as

$$Na^+_{(\beta)} + KNO_{3(melt)} = K^+_{(\beta)} + NaNO_{3(melt)} \quad (4)$$

where activities refer to "one-site" mixing, i.e., for ideal mixing $a = X$, but note $\Delta G°$ for reaction (4) is not that for 1 mole of $\beta$-alumina but rather for 1/1.22 moles. Subsequent calculation of free energy differences between pure $Na_{1.22}$ $\beta$-alumina and $K_{1.22}$ $\beta$-alumina should therefore be multiplied by 1.22 if Eq. (4) is to be used. This point has been overlooked in previous treatments (*1*).

Using reaction (4) for the reasons given above,

$$\Delta G°/RT = -\ln\{a_{K_{(\beta)}} \cdot a_{NaNO_3})/(a_{Na_{(\beta)}} \cdot a_{KNO_3})\}. \quad (5)$$

The activities in the molten $NaNO_3$–$KNO_3$ system can be calculated from available enthalpy of mixing data for that system (*15*), and, as described by Yao and Kummer, activity coefficients in the Na–K $\beta$-alumina system can be calculated by a method first used by Ekedahl (*14*).

Letting

$$Z = \{(a_{NaNO_3}/a_{KNO_3})/(X_{K_\beta}/X_{Na_\beta})\} \quad (6)$$

then

$$\Delta G°/RT = -\ln Z - \ln \gamma_{K_\beta} + \ln \gamma_{Na_\beta}. \quad (7)$$

Therefore,

$$d\{\Delta G°/RT\} = 0 = -d \ln Z - d \ln \gamma_{K_\beta} + d \ln \gamma_{Na_\beta}. \quad (8)$$

Using the Gibbs-Duhem relation,

$$X_{K_\beta} d \ln \gamma_{K_\beta} + X_{Na_\beta} d \ln \gamma_{Na_\beta} = 0 \quad (9)$$

and from substitution of Eq. (9) in Eq. (8),

$$\ln \gamma_{Na_\beta} = \int_{\ln Z, X_{K_\beta}=0}^{\ln Z, X_{K_\beta}} X_{K_\beta} d \ln Z \quad (10)$$

and

$$\ln \gamma_{K_\beta} = -\int_{\ln Z, X_{Na_\beta}=0}^{\ln Z, X_{Na_\beta}} X_{Na_\beta} d \ln Z. \quad (11)$$

Thus from plots of ln $Z$ versus $X_{K_\beta}$ the activity coefficients of both components in the $\beta$-alumina solid solution can be evaluated by graphical integration. A plot of ln $Z$ versus $X_{K_\beta}$ from Yao and Kummer's data is presented in Fig. 1.

## III. Thermodynamical Modeling

No modeling or discussion of the activity coefficients in the Na–K $\beta$-alumina system have been reported. Activity coefficients and resultant activities, calculated considering one mole of total ions being mixed, are given in Table I. One interesting aspect of the data is that the activity coefficients of both components across the entire system

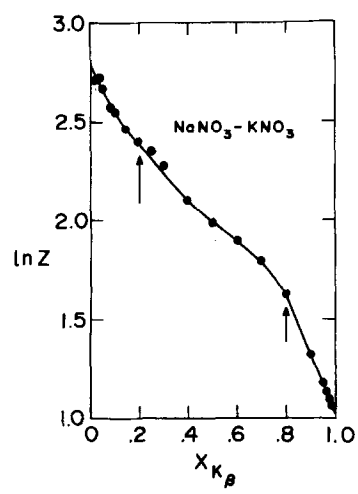


FIG. 1. ln $Z$ versus $X_K$ for the equilibrium between Na–K $\beta$-alumina and Na–K molten nitrate salts at 345°C. Data taken from Ref. (*1*).

TABLE I

THERMODYNAMIC MIXING PARAMETERS FOR Na–K β-ALUMINA AT 345°C

| $X_{K_\beta}$ | $\gamma_{K_\beta}$ | $\gamma_{Na_\beta}$ | $a_{K_\beta}$ | $a_{Na_\beta}$ | $\Delta G_{mix}^{excess}/X_{Na} \cdot X_K$ 1-site (J) | $T\Delta S_{mix}$ 2-site ($JK^{-1}$) | $\Delta G_{mix}^{excess}$ 2-site (J) |
|---|---|---|---|---|---|---|---|
| 0.02 | 0.482 | 0.999 | 0.01 | 0.97 | −4116 | 323 | −266 |
| 0.04 | 0.510 | 0.997 | 0.02 | 0.96 | −4022 | 490 | −534 |
| 0.1 | 0.572 | 0.988 | 0.06 | 0.89 | −3840 | 641 | −1382 |
| 0.2 | 0.653 | 0.965 | 0.13 | 0.77 | −3682 | 456 | −2725 |
| 0.3 | 0.719 | 0.936 | 0.22 | 0.65 | −3583 | 1594 | −2322 |
| 0.4 | 0.776 | 0.891 | 0.31 | 0.53 | −3684 | 2133 | −2237 |
| 0.5 | 0.833 | 0.841 | 0.42 | 0.42 | −3687 | 2294 | −2217 |
| 0.6 | 0.875 | 0.792 | 0.52 | 0.32 | −3742 | 2133 | −2251 |
| 0.7 | 0.904 | 0.746 | 0.63 | 0.22 | −3910 | 1594 | −2391 |
| 0.8 | 0.943 | 0.655 | 0.75 | 0.13 | −4259 | 456 | −2817 |
| 0.9 | 0.981 | 0.526 | 0.88 | 0.05 | −4691 | 641 | −1464 |
| 0.95 | 0.990 | 0.448 | 0.94 | 0.02 | −5419 | 552 | −733 |
| 0.975 | 0.996 | 0.406 | 0.97 | 0.01 | −5654 | 365 | −365 |

are less than unity. The activity-composition relations, shown in Fig. 2, clearly indicate negative deviations from ideal mixing occur in this system. Generally negative deviations are indicative of a tendency toward order between the ions being mixed in the solution. In this case this corresponds to cation order within the conduction planes of the Na–K system.

In almost all crystalline solids mixing between ions of equal valence, on one type of site, results in positive deviations from ideal mixing (*16*). The magnitude of the positive deviations increases with the component volume mismatch (*16*), leading to macroscopic phase separation in systems where the components have substantially different volumes. Most of the instability arises from strain energy. Negative deviations occur in some glass systems (*11*), and in almost all molten salt systems (*17*). Therefore, the thermodynamic characteristics of crystalline Na–K β-aluminas are quite anomalous and are in fact analogous to the thermodynamic behavior of "liquid-like" systems. This result is not surprising because the cations in the fast-conducting β-aluminas do show "liquid-like" behavior in the two-dimensional conduction planes.

The activity data given in Table I can be fitted using a regular solution-type model such that,

$$\Delta G_{mix}^{excess} = RT(X_{Na}\ln \gamma_{Na} + X_K \ln \gamma_K) = W \cdot X_{Na}X_K \quad (12)$$

where $W$ is a regular solution interaction parameter.

In Fig. 3 $\Delta G_{mix}^{excess}/X_{Na} \cdot X_K$ is plotted as a function of $X_{K_\beta}$. As expected from the activity coefficient data, the calculated $W$'s are negative at all concentrations. However, $W$ is not constant across the pseudo-binary system and the data only give a reasonable fit to the regular solution model

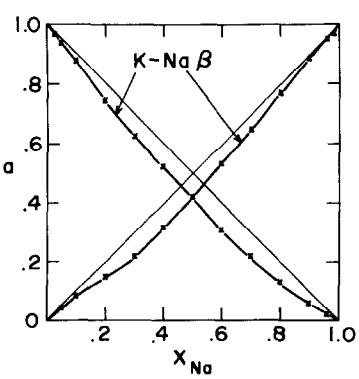


FIG. 2. Activity–composition relations in Na–K β-alumina at 345°C.

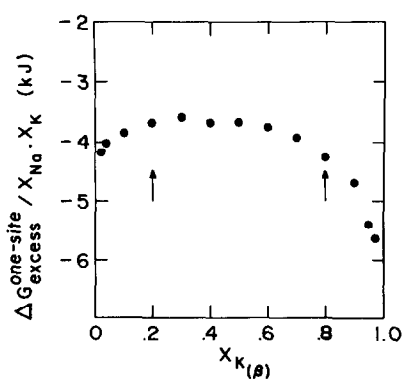


FIG. 3. The regular solution parameter plotted as a function of composition.

between approximately $X_K = 0.3$ and 0.7. Definite anomalies in the mixing behavior occur outside these compositions, with the solid solutions apparently showing even larger stabilizations. These two anomalies are even more apparent in the plot of ln $Z$ versus $X_{K_\beta}$ from which the activity coefficients were calculated, see Fig. 1. The plot consists of three almost linear regions. Between $X_K = 0$ and $X_K \simeq 0.2$ and $X_K \simeq 0.8$ and 1.0 the slope is greater than in the intermediate region. This confirms that the stabilizations in the solid solution are larger outside the range $X_K \simeq 0.2$ to $X_K \simeq 0.8$.

Yao and Kummer also presented data for the distribution of Na and K between $\beta$-alumina and molten NaI–KI and NaCl–KCl salts at 800°C. Using their data the activities of Na and K in $\beta$-alumina have been calculated from the iodide and chloride partitioning using the approach described previously. Activities in the molten salt systems were calculated from the experimental enthalpy of mixing data of Kleppa (*18*) assuming regular behavior. The plots of ln $Z$ versus $X_{K_\beta}$ are shown in Fig. 4. Calculated values of the activities in the $\beta$-aluminas are given in Table II.

From Fig. 4 it is apparent that the variation of ln $Z$ with $X_{K_\beta}$ is similar in the iodide and chloride exchanges. The general trend is also similar to that in Fig. 1 for the nitrate system. The values of the calculated activity coefficients in the Na–K $\beta$ system do vary for each molten salt system, however, negative deviations are observed in each of the three exchanges. Since the data for the iodides and chlorides were collected at 800°C, one would expect the calculated activity coefficients to be closer to unity than those calculated from the nitrate system. This does seem to be the case for the chloride data but less so for the iodide data.

The salient points for the following discussion are for all three systems: (a) negative deviations are calculated for the Na–K $\beta$ systems, and (b) distinct anomalies in the energetics are observed close to $X_K = 0.2$ and $X_K = 0.8$. Because of the greater number of data points available from the nitrate exchanges, and the inherent increased accuracy of the experiment for the lower temperature exchanges, all further calculations were performed using data from that equilibrium.

TABLE II

ACTIVITIES OF Na–K $\beta$-ALUMINA CALCULATED FROM EXCHANGES AT 800°C

| | Chloride exchange | | Iodide exchange | |
|---|---|---|---|---|
| $X_{K_\beta}$ | $a_{Na_\beta}$ | $a_{K_\beta}$ | $a_{Na_\beta}$ | $a_{K_\beta}$ |
| 0.02 | 0.982 | 0.02 | 0.983 | 0.01 |
| 0.04 | 0.965 | 0.04 | 0.964 | 0.02 |
| 0.1 | 0.91 | 0.095 | 0.899 | 0.06 |
| 0.2 | 0.806 | 0.193 | 0.768 | 0.14 |
| 0.3 | 0.71 | 0.284 | 0.643 | 0.242 |
| 0.4 | 0.61 | 0.375 | 0.535 | 0.341 |
| 0.5 | 0.51 | 0.466 | 0.427 | 0.448 |
| 0.6 | 0.405 | 0.564 | 0.325 | 0.56 |
| 0.7 | 0.292 | 0.676 | 0.231 | 0.673 |
| 0.8 | 0.179 | 0.788 | 0.145 | 0.785 |
| 0.9 | 0.08 | 0.904 | 0.064 | 0.902 |
| 0.95 | 0.04 | 0.955 | 0.031 | 0.95 |
| 0.975 | 0.02 | 0.979 | 0.02 | 0.979 |

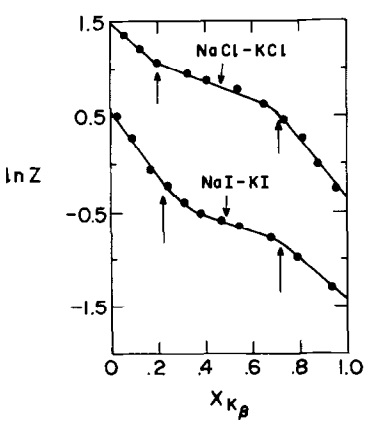


FIG. 4. ln $Z$ versus $X_K$ for Na–K $\beta$-alumina in equilibrium with iodide and chloride melts. Exchange data from Ref. (*1*).

## IV. Mixing Models/Discussion

From the results given in the previous section it is clear that the Na–K β system shows a tendency toward cation order resulting in a negative excess free energy of mixing. Furthermore, compositions lying between $X_K = 0$ and $X_K \simeq 0.2$, and $X_K \simeq 0.8$ and $X_K = 1.0$, show somewhat larger relative stabilizations than the other intermediate compositions. To meaningfully model the mixing behavior reference must be made to the structure of the conduction planes in β-alumina.

High-conductivity, cation-excess sodium β-alumina has the formula $Na_{1.22}Al_{11}O_{17.11}$. In one unit cell each conduction plane contains 1.22 sodium ions distributed among the available sites. Three crystallographically distinct cation sites are available, the Beevers-Ross (BR), midoxygen (mO), and anti-Beevers-Ross (aBR) sites. In Na β-alumina only the BR and mO sites are significantly occupied (*19*). Structural refinements of K β-alumina show similar occupations, with some evidence for a small occupation of aBR sites (*20*). Currently accepted structural models (*19*) for the cationic arrangement in these compounds place 0.78 sodiums occupying BR sites, with the remaining 0.44 ions occupying the mO or "interstitial" sites. The 0.22 "excess" sodium ions are presumed to occupy half of the mO sites forming "ion pairs" with 0.22 of the "stoichiometric" sodium mO ions. The intermediate BR site is unoccupied, see Fig. 5. The excess sodium content is charge-compensated by half as many excess oxygen ions in mO sites.

There has been considerable discussion as to the detailed mechanism of conduction in Na β-alumina (*4, 19*). It is clear that diffusion occurs via an interstitial mechanism and depends largely upon the mobility of the mO "ion pairs" (*4*). Most recent debates have focused on what percentage of

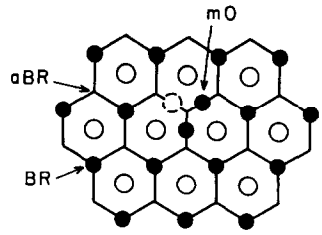


FIG. 5. A schematic of the cation positions in the conduction planes of Na β-alumina showing the formation of interstitial ion pairs. Open circles represent "column" oxygens, filled circles sodium ions in BR and mO sites. Excess oxygen ions, open hatched circle, occupy mO sites, and excess $Na^+$ ions form interstitial "ion pairs."

these ion pairs are mobile. Several workers have used a weak electrolyte model, in which it is assumed that only a small fraction of ion pairs are mobile, to model the conductivities. Evidence has been presented for two types of interstitial pairs: (a) those strongly bound to excess oxygen ions and (b) a smaller percentage of weakly bound ion pairs which have a higher mobility. In previous investigations of the conductivity of Na–K β-aluminas workers have presented some evidence to suggest preferential formation of Na–O–K ion pairs in the interstitial sites (*6, 10*). Because the conduction process occurs via an interstitialcy mechanism, the mobility of the ions in the interstitial sites directly determines the magnitude of the conductivity of the crystals. If stable (Na–O–K) ion pairs are formed this may explain the large decrease in the conductivity and the accompanying increase in the activation energies.

The activity data in Table I have been remodeled using a treatment which accounts for the different structural sites in the conduction planes. Noting that distinct anomalies in the thermodynamic behavior of the Na–K system occurred at mole fractions close to 0.2 and 0.8, the most obvious model is one based on preferential interstitial (Na–O–K) ion-pair formation. If Na–K pair formation does occur in all the intersti-

tial sites, regardless of any subsequent definition of bound or free pairs, the maximum ion-pair formation would occur at $X_K = 0.22/1.22 = 0.18$ and 0.82. In our thermodynamic model we have constrained the initial substitution of K into Na $\beta$-alumina to the interstitial sites up to a composition corresponding to the maximum degree of ion-pair formation, i.e., to a mole fraction $X_K = 0.18$. Subsequent substitution is assumed to occur on the BR sites. After all sodium ions on the BR sites are replaced by potassium ions, i.e., at $X_K = 0.82$, further substitution necessarily results in a breaking up of the (Na–O–K) ion pairs and (K–O–K) ion-pair formation.

Using this model configurational entropies of mixing were calculated for the system. Because the model assumes preferential formation of stable (Na–O–K) ion pairs at the mO sites, zero configurational entropies of mixing occur not only for the two end members but also at $X_K = 0.18$ and at $X_K = 0.82$. Three maxima in the configurational entropy term occur at $X_K = 0.09$, 0.5, and 0.91, respectively. These correspond to mixing between equal numbers of Na–K and Na–Na ion pairs on the mO sites, equal numbers of Na and K ions on the BR sites, and equal numbers of Na–K and K–K ion pairs on the mO sites, respectively. Mathematically the configurational term is given by

$$\Delta S_{\text{mix}}^{\text{conf.}} = -0.18R(X_p \ln X_p + X_{\text{Na-K}} \ln X_{\text{Na-K}}) - 0.64R(X_{\text{NaBR}} \ln X_{\text{NaBR}} + X_{\text{KBR}} \ln X_{\text{KBR}}) \quad (13)$$

where $X_p$ represents the mole fraction of either the Na–Na or K–K ion pairs on the interstitial sites, and $X_{\text{NaBR}}$ and $X_{\text{KBR}}$ represent the mole fraction of Na and K ions on the BR sites. Therefore, the first term results from mixing between unlike ion pairs on the available ion-pair sites and the second term represents the entropy from mixing of ions on the BR sites. The variation of $\Delta S$ with composition is shown in Fig. 6.

Excess free energy, or enthalpy of mixing terms can now be calculated relative to this new model by

$$\Delta G_{\text{mix}}^{\text{excess}} = \Delta G^{\text{mix}} - T\Delta S_{\text{mix}}^{\text{excess}} = \Delta H_{\text{mix}}^{\text{excess}}. \quad (14)$$

The calculated values of $\Delta G^{\text{mix}}$ and $\Delta G_{\text{mix}}^{\text{excess}}$ ($= \Delta H_{\text{mix}}^{\text{excess}}$) are given in Table I. The variation of the calculated excess free energies of mixing are plotted as a function of composition in Fig. 7. The fit of the data to the model is excellent. As illustrated by Fig. 7 there is a linear increase in the enthalpic stability of the solutions up to $X_K \simeq 0.2$. This corresponds to the linear increase in the number of the (Na–K) ion pairs which reaches a maximum at $X_K \simeq 0.2$. Similarly there is a linear decrease in the excess stability corresponding to the breaking up of (Na–K) ion pairs by substitution of potassium. According to our model between $X_K = 0.18$ and 0.82 ionic substitution occurs on the BR sites and the stable (Na–K) ion pairs remain unaffected. The energetics of mixing of Na and K on the BR sites are clearly illustrated by Fig. 7. Apparently mixing on these sites results in a relative decrease in the stability of the solution as a whole. Thus BR mixing gives rise to positive deviations from ideal mixing. However, because of the inherent enthalpic

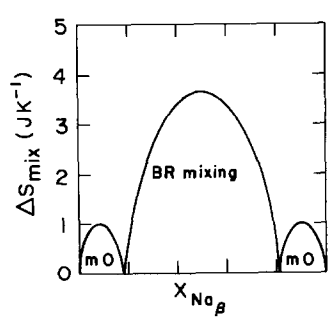


FIG. 6. Configurational entropies in Na–K $\beta$-alumina calculated assuming interstitial ion pairing between Na and K (see text).

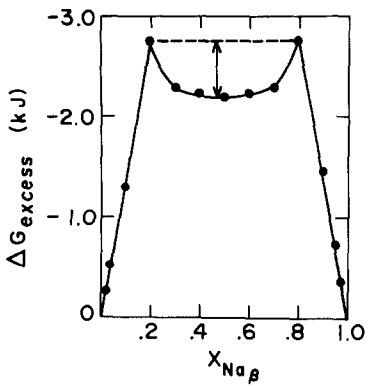


FIG. 7. Excess free energies at 345°C calculated using the ion-pair model.

stability of the previously formed (Na–K) ion pairs, the total enthalpy of mixing of the solution remains negative.

The mixing of the ions on the BR sites is more characteristic of the behavior expected in "normal" crystalline materials. That is, as a result of the "size difference" between the ions being mixed destabilizations occur. We can define an enthalpic interaction parameter, $W_{BR}$, for the BR site mixing with,

$$X_{NaBR} \cdot X_{KBR} \cdot W_{BR} = \Delta H^{mix}_{BR}. \quad (15)$$

The energetics of BR mixing conform to regular solution behavior with $W_{BR} = 3587$ J, for mixing on 1 BR site/formula unit.

Using correlations between the mixing energetics and component volume mismatch developed by Davies and Navrotsky (*16*) we can estimate the magnitude of the interaction parameter expected from mixing on the BR sites. A term $\Delta V[= V_2 - V_1/\frac{1}{2}(V_1 + V_2)]$ represents the effective mismatch between the volumes of the two end members. Because mixing in this system takes place only in the conduction planes of the structure, the effective volumes of the conduction planes in Na and K β-alumina have been used to estimate the expected interaction parameter. Using the available data for the volumes of the two unit cells and subtracting the volume of the "inert" spinel blocks (estimated width being $[c_{Na_\beta} - 2d_{Na^+_{(VIII)}}]$ Å = 8.905 Å, where $c_{Na_\beta}$ is the length of the unit cell in Na β-alumina, $d$ is the ionic diameter of Na (*21*), and the factor of two accounts for the two conduction planes/cell); the $\Delta V$ term is calculated to be 0.08415. For a system in which univalent ions are being mixed the correlations predict a $W$ of 1.8 kJ (*16*). Bearing in mind all the uncertainties inherent in this calculation this agreement is reasonable.

The similarity between the variation of the excess free energy data presented in Fig. 7 and the variation of the activation energies and conductivities in this system are striking. Our model predicts that the most energetically stable compositions in this system lie close to $X_K = 0.2$ and 0.8. In the original determination of the ionic conductivities (2) a minimum in $\ln \sigma$ and a maximum in the activation energy was observed at $X_K = 0.8$, with evidence for a second minimum and maximum, respectively, at $X_K = 0.2$. A more recent determination of the conductivities (*6*) found one minimum at $X_K \simeq 0.8$. We suggest there may be two maxima in the activation energy and two associated minima in the conductivities at $X_K = 0.2$ and at $X_K = 0.8$ corresponding to the compositions with the maximum enthalpic stability. Direct comparison with the conductivity results is difficult due to the lack of agreement between the previous determinations. However, we feel our results do give considerable insight into the behavior of the Na–K β-alumina system.

We can now make predictions regarding the low-temperature stability of this system. It is well known that the mixed-alkali effect increases with decreasing temperature and becomes less pronounced at high temperature. This behavior is consistent with an ordered ion-pair model. At high temperature the $T\Delta S$ term becomes increasingly significant with respect to any excess enthalpy of mixing and systems tend

toward ideal behavior. The results from the NaCl–KCl exchanges illustrate this effect in the Na–K $\beta$-aluminas. Though it should be noted that significant negative deviations are still apparent at 800°C. With decreasing temperature the contribution of $T\Delta S$ to the free energy of mixing decreases and enthalpic stabilizations play an effectively larger role. Thus, the effect of ion pairing upon the total free-energy of mixing, and therefore upon the activities, becomes increasingly important.

The low-temperature phase diagram of this system can be calculated from our expression for the total free energy,

$$\Delta G^{\text{mix}} = -\Delta H_{\text{IP}} \cdot X_{\text{Na-K}} + W_{\text{BR}} \cdot X_{\text{Na}_{\text{BR}}} \cdot X_{\text{K}_{\text{BR}}} - T\Delta S_{\text{mix}}^{\text{model}} \quad (16)$$

where $\Delta H_{\text{IP}}$ (= −2771 J) represents the stability of 0.18 ion pairs and $W_{\text{BR}}$ (= +2296 J) is the interaction parameter for mixing on the 0.64 BR sites. Excess heat capacity terms have been neglected.

At absolute zero the free energy of mixing curve corresponds to that for the excess enthalpy. The occurrence of a double minimum in the free energy will result in a two-phase region corresponding to $Na_{0.82}K_{0.18}$ and $K_{0.82}Na_{0.18}$. All compositions between $X_K = 0.18$ and 0.82 can lower their free energies by phase separation into a two-phase mixture with each phase having complete Na–K ion pairing in mO sites, and either full Na or K occupation of BR sites. The predicted critical temperature is 240 K. Below this temperature we predict that "phase separation" should occur, above 240 K all compositions should be one phase mixtures but should still show maximum enthalpic stability at $X_K \simeq 0.2$ and 0.8.

Finally, because the behavior of the Na–K $\beta$-alumina energetics has been interpreted in this paper by assuming Na–K ion pairing, we conclude by addressing the driving force for the order. The thermodynamic behavior is similar to that encountered in molten salt systems. Several models for the ordering of cations in those systems have been presented. In many cases the theoretical treatments have allowed quantitative correlations between the deviations from ideality, and ionic size and polarizability differences (*17*). Using a simple Coulombic approach, it has been shown that in a system in which complete relaxation of bond lengths is possible the electrostatic repulsions between nearest-neighbor cations are reduced if the ions are of different "size," i.e., if the cation–anion bond lengths are different (*22*). For a one-dimensional $-A-X-B-$ arrangement Forland showed the $A$–$B$ cation repulsions are decreased if $A$ and $B$ are arranged in an ordered fashion. The reduction in the Coulombic energy is given by

$$e^2(1/d_{AX} + 1/d_{BX})[(d_{AX} - d_{BX})/(d_{AX} + d_{BX})]^2/2. \quad (17)$$

The driving force for order increases with increasing $A$–$B$ size differences. Therefore, this simple model gives insight into the possible driving force for $A$–$B$ order in molten systems. The model is only effective in cases where the $A$–$X$ and $B$–$X$ bond lengths can relax to those they would adopt in the pure end-members. In solid solution systems the constraints of a "rigid lattice" prevent complete relaxation and generally destabilizations result from strain. It seems reasonable that in fast-ionically conducting systems substantial bond-length relaxation is possible, and that this in turn allows the operation of the Forland mechanism to give a driving force for cation order.

## V. Conclusions

Thermodynamic analysis of the Na–K $\beta$-alumina system has found evidence for ordering between the cations. The ion-pair model, in which preferential Na–K order in mO sites is assumed, gives a good fit to the experimental activity data. Two minima are

found in the calculated excess enthalpies of mixing, these occur at compositions close to those at which minima are observed in the ionic conductivities. We suggest that the mixed alkali effect in this system is strongly related to the presence of cation order, and propose that the driving force results from reduction of nearest-neighbor cation repulsions. In a forthcoming publication we will report similar correlations between excess thermodynamic stability and the mixed alkali effect in the Na–Ag, Na–Li, and Na–Tl β-alumina systems.

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