Thermochemistry of Simple Fused Salt Mixtures

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Recent developments in high temperature reaction calorimetry have paved the way for an attack on some of the fundamental problems of fused salt solution chemistry. In the present paper a brief survey is given of the information now available on the thermochemistry of simple fused salt mixtures. New data are presented on the binary liquid systems (Na−K)Cl, (Na−K)Br and (Na−K)I, as compared to the previously explored (Na−K)NO_3. Preliminary results are given for some common alkali cation-mixed anion systems where the anions are Cl^-, Br^- and I^-.

During recent years we have been engaged in a study of the properties of binary fused salt mixtures through the use of precision high temperature reaction calorimetry. In the initial phases this work was restricted to temperatures below 500°C. This restriction was imposed by the lack of calorimetric equipment suitable for higher temperatures, and severely limited the type of problem which could be studied effectively. Nevertheless, it provided the experimental basis for a first systematic attack on some of the fundamental problems of fused salt mixtures.

Among the salts which melt below 500°C the alkali nitrates represent a particularly simple group. Although the nitrate ion is not spherically symmetrical, the liquid alkali nitrates are thermally stable and seem to have many features in common with the alkali halides. So far almost all of our work below 500°C has been devoted to studies of liquid mixtures formed by the alkali nitrates.

Quite recently we have succeeded in developing reliable calorimetric equipment and techniques for temperatures up to about 800°C. This opens up a large new field to detailed investigation. Although the experimental difficulties associated with precision calorimetry in this temperature range are much greater than below 500°, we are at present obtaining a great deal of new and significant thermochemical information on simple fused halide systems.

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From a fundamental point of view the simplest types of binary fused salt systems are those which are formed by two components which have the same charge structure and which contain a common ion. The common ion may be an anion, as in NO_3-KNO_3, or a cation as in $NaNO_3-NaCl$. It is characteristic of these mixtures that the changes associated with the mixing processes to a first approximation may be attributed to changes which occur in the second nearest neighbor ionic populations. In the present report we shall confine our attention to these two simplest classes of fused salt solution systems.

COMMON ANION SYSTEMS

In a study of all the binary mixtures formed by the alkali nitrates, it was found [1] that the molar enthalpies of mixing, ΔH^M, to a good first approximation could be represented by a simple semi-empirical relation

$$\Delta H^M = -X(1-X)A\delta^2$$

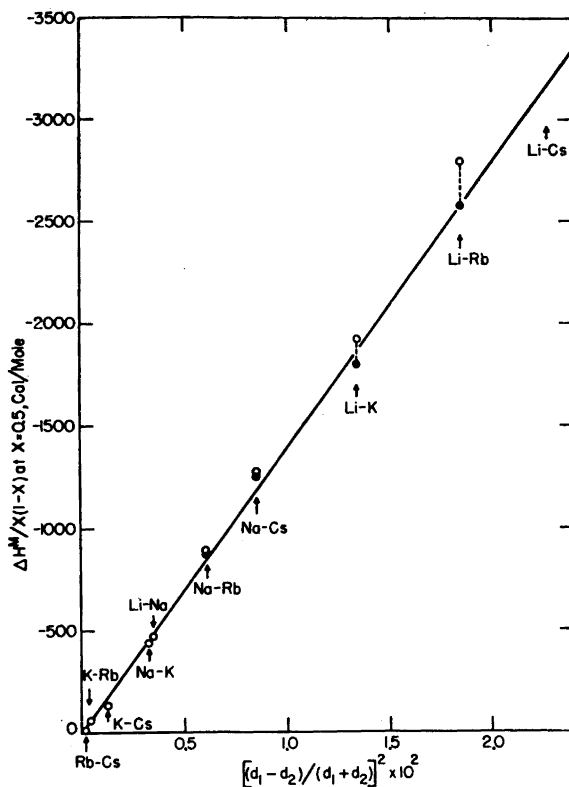In this expression X is the mole fraction, while $\delta = (d_1-d_2)/(d_1 + d_2)$; d_1 and

Fig. 1. The dependence of the magnitude of the enthalpy of mixing of binary alkali nitrates on the parameter $(d_1-d_2)/(d_1 + d_2)$. (See also Ref.[1]).
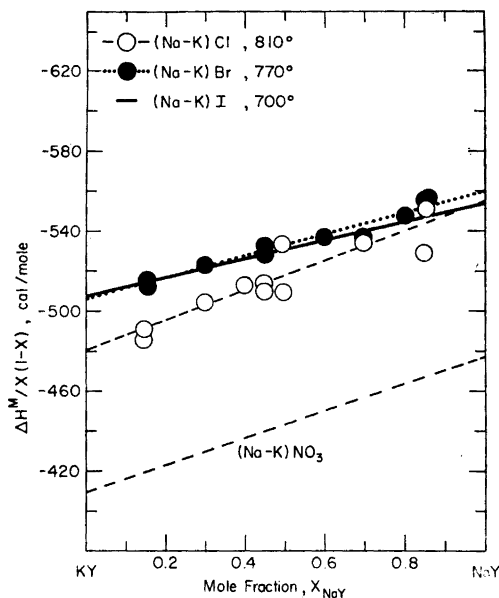
Fig. 2. The dependence of the interaction parameter $(\Delta H^M/X(1-X))$ on composition in liquid sodium-potassium chloride, -bromide, -iodide and -nitrate mixtures.

d_2 are the sum of the radii of the ions $(r_+ + r_-)$ which are present in the two pure salts. Note that all the enthalpies of mixing are negative. The numerical value of the constant, A, was found to be 140 kcal/mole, *i.e.*, of the order of magnitude of the lattice energy of the considered salts. Fig. 1 illustrates to what extent the experimental data obey this relation.

Our recent explorations in the field of common anion systems have been devoted to an extension of this work to the binary alkali halides. These investigations are still in progress. However, we now have reliable data for some systems, and present in Fig. 2 our results for the liquid systems (Na—K)I, (Na—K)Br, and (Na—K)Cl. In this figure we plot the experimental "interaction parameter", $\Delta H^M/X(1-X)$, *versus* composition. For comparison we have included in the figure corresponding information for the previously explored system (Na—K)NO$_3$.

It will be noted that in all cases the interaction parameter appears to vary linearly with composition. Thus we may write

$$\Delta H^M/X(1-X) = a + bX_{Na}$$

The experimental values of a and b obtained from a least squares treatment of the data are recorded in Table 1 along with corresponding values for the nitrates.

The data for the nitrates were obtained at two temperatures, and showed no temperature dependence within experimental error. Therefore, it is assumed that the results for the four systems considered here may be discussed without

Table 1. Summary of enthalpy of mixing data for sodium-potassium fused salt mixtures (in cal/mole).

System	Temperature °C	a	b
(Na – K)Cl	810	– 480	– 74
(Na – K)Br	770	– 506	– 54
(Na – K)I	700	– 507	– 47
(Na – K)NO$_3$	345 – 450	– 408	– 68

regard to the fact that the data actually were obtained at different temperatures.

It is noteworthy that the enthalpy of mixing varies relatively little from one halide system to the other. However, the magnitude is significantly larger for these systems than for the corresponding nitrate mixtures.

In our original interpretation of the results for the alkali nitrates, it was suggested that the main contribution to the negative mixing enthalpy in this type of system probably arises from a reduction in second nearest neighbor Coulomb repulsion between the cations. This view had previously been advanced by Førland [2] and by Blander.[3]

As a result of more recent theoretical and experimental work in this area, it is now believed that at least two additional factors must also be taken into account.

(*a*) There is an additional *negative* contribution to the mixing enthalpy which is due largely to *polarization* of the common anion. It was argued by Lumsden [4] that this effect should be larger than the term resulting from the reduction in cation-cation repulsion. However, this seems very unlikely (see below).

(*b*) There is a positive contribution to the mixing enthalpy which is related to the change in the Van der Waals-London energy on mixing.[4,5] Since, in charge symmetrical systems, the nearest neighbor configurations will be relatively little changed in the mixing process, we are again largely concerned with the second nearest neighbor cation-cation interactions.

It was suggested by Lumsden [6] that, in view of the similarity of size of the nitrate and iodide ions, the Coulombic and Van der Waals contributions to the mixing enthalpy should be of comparable magnitude in fused iodides and in fused nitrates. Therefore, due to the larger polarizability of the iodide ion, we should obtain a significantly larger negative enthalpy of mixing in a binary iodide than in the corresponding nitrate mixture. Fig. 2 shows that for sodium-potassium this is indeed the case. In fact, based on the heat data for these two systems and the polarizabilities for I$^-$ and NO$_3^-$ reported by Tessman, Kahn and Shockley,[7] Hersh and Kleppa [8] have estimated the polarization contribution to the enthalpy of mixing in sodium-potassium nitrate to be about 30 % of the observed values. The corresponding figure for the iodides is of the order of 45 %.

For a given pair of cations, the Coulombic energies will tend to increase slowly with decreasing size of the common anion. On this basis one might

have expected the negative enthalpies of mixing in liquid sodium-potassium halides to increase somewhat in the sequence $I^- < Br^- < Cl^-$. However, Fig. 2 shows that the observed sequence actually is $Cl^- < I^- \sim Br^-$ .This change of sequence may be attributed to the effect of the positive Van der Waals energy, which varies with interionic distance as d^{-6}. As a consequence we must expect that the Van der Waals energy contribution should become increasingly important as the size of the common anion becomes smaller. Lumsden [4] estimated the magnitude of this term from a calculation based on the model of the corresponding solid solutions. It is now known that his values are too large by a factor of the order of 2.5.[9] If we apply this correction we estimate with Lumsden the positive Van der Waals contributions to the inter-action parameter to be about $+ 0.12$ kcal for (Na—K)Cl, $+ 0.08$ kcal for (Na—K)Br and $+ 0.04$ kcal for (Na—K)I. If the observed negative mixing enthalpies are corrected for these positive Van der Waals terms, we will in fact obtain the expected sequence $I^- < Br^- < Cl^-$.

COMMON CATION SYSTEMS

Even at 500°C and below a number of higher melting salts dissolve to a significant extent in the liquid nitrates. In this temperature range, we have been able to survey the properties of solutions of alkali bromides and chlorides in the corresponding nitrates by means of dilution calorimetry. In such experi-ments a concentrated solution of the halide in the nitrate is mixed with the pure liquid nitrate in the calorimeter. Generally, the heat effects associated with these dilutions were very small, and the relative error correspondingly large. The results were evaluated under the simplifying (but reasonable) assumption that the interaction parameter, $a = \Delta H^M / X(1-X)$, is independent of the composition of the liquid mixture.

We present in Fig. 3 a graph of the experimental values of a for chlorides and bromides in the corresponding alkali nitrates, taken from the recent work of Kleppa and Meschel.[10] The interaction parameters are plotted *versus* the radius ratio, $r_{cation}/\bar{r}_{anions}$, where $\bar{r}_{anions}$ is the mean value of the two anion radii.
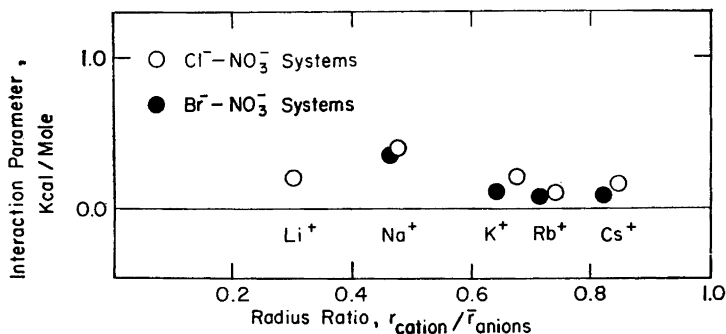

Fig. 3. Interaction parameters *versus* radius ratio for alkali halide-nitrate mixtures. (From Ref.[10]).

Fig. 3 has several interesting features. Note first that the interaction parameters for these systems are all positive, rising slightly from lithium to sodium, and then becoming smaller in the sequence $\mathrm{Na} > \mathrm{K} > \mathrm{Rb} > \mathrm{Cs}$. Note also the extensive analogy between the alkali nitrate-bromide and the alkali nitrate-chloride data.

Kleppa and Meschel have considered the significance of these results. They stress that for the systems in question the size relations between anions and cations are such that the anions are not well separated, either in the pure salts or in the mixtures. They go on to propose that the observed positive enthalpies of mixing possibly may arise from the short range repulsive potential acting between the anion cores. This interpretation is essentially equivalent to the "packing effect" interpretation suggested in a different context by Flood.[11]

By means of our new 800°C calorimeter we have been able to carry out some liquid-liquid mixing experiments for common cation-mixed *halide* systems. As was the case of the dilution experiments mentioned above the heat effects were very small. Only for one system (NaCl—NaBr) have we made a detailed study covering a wide range of compositions. Our experimental results for this system are presented in Fig. 4. It will be noted that the interaction parameter depends relatively little on composition.

For some other common cation-mixed halide systems our results are summarized in Table 2. These values are subject to revision, and should be considered as preliminary only.

It will be noted that there is a considerable degree of analogy between the data for the halide-nitrate systems in Fig. 3 and the new halide-halide values given in Table 2. For example, it appears that the trend towards lower interaction parameter in the sequence $\mathrm{Na} > \mathrm{K} > \mathrm{Rb} > \mathrm{Cs}$ is common to both sets of systems. Also, we see that the increase from lithium to sodium is found in both sets.

Apart from the very small negative value for Cs(Br—Cl), we note that all the interaction parameters for the chloride-bromide systems are positive and
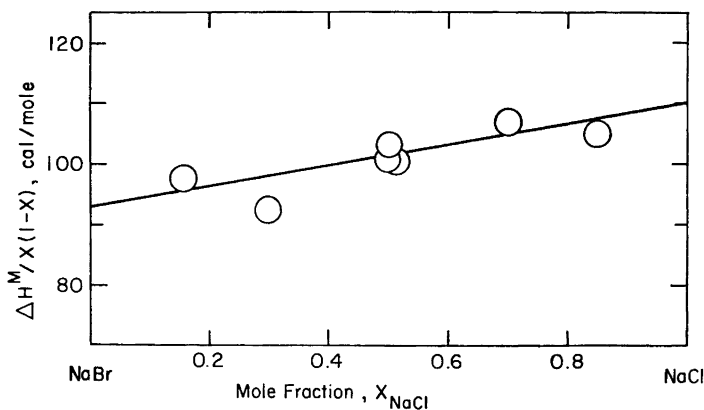

Fig. 4. The dependence of the interaction parameter on composition in liquid sodium chloride-bromide melts.

Table 2. Interaction parameters (a, in kcal/mole) for liquid halide-halide systems from preliminary measurements.

System	Li(Cl−Br)	Na(Cl−Br)	K(Cl−Br)	Rb(Cl−Br)
a	0.05	0.09−0.11	0.06	0.05

System	Cs(Cl−Br)	Rb(Br−I)	Cs(Br−I)	Cs(Cl−I)
a	−0.03	0.12	0.10	0.13

tend to be somewhat smaller than for the corresponding halide-nitrate mixtures. Looking at all the available anion-anion data there is also some evidence that increasing disparity in size between the two anions gives rise to increasing *positive* interaction parameters. This is certainly consistent with the core repulsion interpretation outlined above.

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