

Enthalpies of Mixing in Binary Liquid Alkali Sulfate Mixtures

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The enthalpies of mixing of the binary liquid alkali sulfate mixtures have been measured in the temperature region 900–1100°C. The results indicate that the enthalpies of mixing at the 50–50 compositions are well represented by the semi-empirical expression

$$4\Delta H_{0.5}^M = U_0^{++} + 16.4\Delta\alpha\delta_{12} - 1400\delta_{12}^2, \text{ kcal/mol}$$

In this expression, $\delta_{12} = (d_1 - d_2)/d_1d_2$, where d_1 and d_2 are characteristic interionic distances in the two salts, U_0^{++} represents a numerical estimate of the positive contribution to the enthalpy of mixing, which arises from the London-van der Waals interaction between next nearest neighbor cations, and $\Delta\alpha$ is the difference in polarizability between the two cations.

During the past decade, the new high-temperature calorimetric techniques developed in this Laboratory have made possible a series of detailed calorimetric studies of simple fused salt mixtures. These investigations were initiated through the work of Kleppa,¹ and of Kleppa and Hersh² on the binary alkali nitrates. Later, these studies were extended by Hersh and Kleppa³ to the binary alkali chlorides and bromides, and by Holm and Kleppa⁴ to the alkali fluorides. Most recently, Melnichak and Kleppa⁵ also carried out an investigation of the enthalpies of mixing of the binary alkali iodides. These authors discussed the complete set of enthalpies of mixing for the mixed-cation-common-anion fused alkali halide mixtures in terms of the Davis-Rice⁶ theory. They found that the "reduced enthalpy interaction parameter" at the 50–50 composition, $(4\Delta H_{0.5}^M - U_0^{++})/\delta_{12}^2$, varies with the nature of the common anion and changes from about –340 kcal Å²/mol for the fluoride melts through –400 kcal Å²/mol for the chlorides and the bromides to –540 kcal Å²/mol for the iodide mixtures.

A series of calorimetric measurements on the liquid system $\text{Li}_2\text{SO}_4 - \text{Na}_2\text{SO}_4$ were previously carried out in this Laboratory by Holm,⁷ and have now been published. More recently, the same system was also studied in our Laboratory

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by Anderson,⁸ who obtained results which differed somewhat from those of Holm. The present work was initiated in order to attempt to resolve this discrepancy, and also to extend our calorimetric investigations to a more general study of molten sulfate mixtures. The present report represents the first example of an extensive thermochemical investigation of fused salt mixtures of the charge type $A_2X - B_2X$, where A and B are singly charged, alkali metal ions, while X is a doubly charged anion. Other examples of fused salt systems of this charge type are the alkali carbonates, the tungstates, and the molybdates.

EXPERIMENTAL AND MATERIALS

The following chemicals were used in the present work:

Li_2SO_4 : Baker, analyzed reagent 99.9 % $Li_2SO_4 \cdot H_2O$.

Na_2SO_4 : Allied Chemicals, reagent grade anhydrous Na_2SO_4 .

K_2SO_4 : Mallinckrodt, analytical reagent.

Rb_2SO_4 : Made from Rb_2CO_3 (Kawecki Chemical Co., high purity salt 99.9 %) and H_2SO_4 (Baker, analyzed reagent).

Cs_2SO_4 : Made from Cs_2CO_3 (Kawecki Chemical Co., high purity salt 99.9 %) and H_2SO_4 (Baker, analyzed reagent).

Semiquantitative spectrographic analysis showed no metallic impurities beyond 0.05 % in any of the sulfates. The premelted salts assayed 99.9 % Li_2SO_4 , 100.0 % Na_2SO_4 , 99.7 % K_2SO_4 , 99.9 % Rb_2SO_4 , and 99.9 % Cs_2SO_4 , respectively, as determined by the ion-exchange method reported by Melnichak and Kleppa.⁵

The mixing experiments were performed at 910°C [$(Li_2 - Na_2)SO_4$ only] and 1085–1090°C (all systems). The calorimeter temperature was measured with a Pt/Pt, 13 % Rh thermocouple which was standardized against a National Bureau of Standards calibrated Pt/Pt, 10 % Rh couple.

All calorimetric experiments were performed in a single-unit microcalorimeter suitable for work up to 1100°C. Apart from its single (rather than twin) construction, this apparatus is similar to the one used by Hersh and Kleppa³ at temperatures up to 800°C.

The experimental arrangements inside the calorimeter were similar to those used by Holm,⁷ but with the following modifications. The inside platinum cup, which contains one of the two fused salts, was only about 1 mm smaller in diameter than the platinum crucible. Similarly, the platinum plunger, which was used to displace the fused salt in the cup, was only about 1 mm smaller in diameter than the cup. As a result of this, it was possible to explore the full range of liquid compositions. Also the stirring was very effective, and was always complete after three stirring operations (or less).

Each stirring operation gave rise to a small reproducible heat effect, which in most cases represented 0–5 % of the total heat of mixing. However, when the heat of mixing was very small, as in the systems



the stirring correction represented as much as 10–50 % of the total observed heat effect.

Prior to each calorimetric experiment, the fused silica liner with its contents was preheated to a temperature about 50°C above that of the calorimeter proper. This serves to reduce the thermal disturbance which occurs when the loaded liner is introduced into the calorimeter. In typical runs, the experiment was carried out some 1–1½ h after the liner had been introduced.

In each run, a total of about 50 mmol of salt was used. The calibration of the calorimeter was carried out by dropping – from room temperature into the apparatus at working temperature – small pieces of pure 2 mm Pt-wire weighing a total of about 1 g. The evaluation of the resulting endothermic heat effect was based on Kelley's equation for the heat content of platinum.⁹

No difference was found between calibrating into the platinum-covered plunger or calibrating directly into the sulfate melt.

During its fall into the calorimeter, the platinum wire picks up some heat. The magnitude of this effect was determined in separate experiments, by carrying out calibrations

with Pt-wires of different diameters. Extrapolation to zero surface area showed that for 2 mm wires, this pick-up of heat represents 3 % of the heat content at 900°C, and 6 % at 1090°C.

RESULTS

All the ten binary alkali sulfate systems were investigated. The concentration dependence of the enthalpy of mixing was studied for all the lithium sulfate mixtures, and for the mixtures of sodium sulfate with cesium and rubidium sulfate. For the remaining four binary systems, the enthalpy of mixing was determined at the 50-50 composition only. The experimental results of the

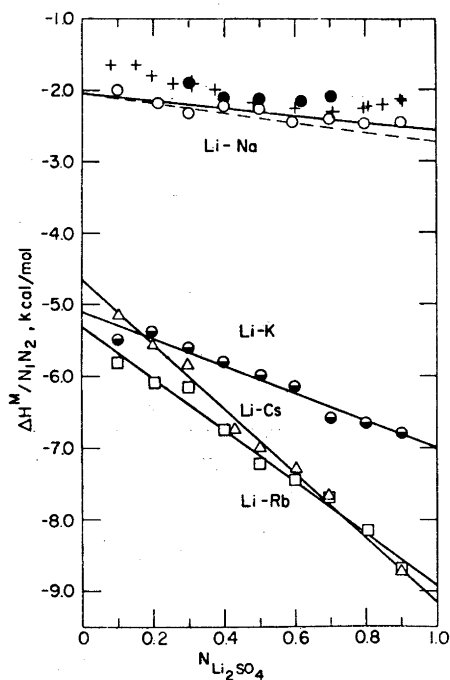


Fig. 1. $\Delta H^M/N_1N_2$ for liquid mixtures of lithium sulfate with the other alkali sulfates. ●, Li_2SO_4 - Na_2SO_4 at 1085°C. ○, Li_2SO_4 - Na_2SO_4 at 910°C. ⊙, Li_2SO_4 - K_2SO_4 at 1085°C. □, Li_2SO_4 - Rb_2SO_4 at 1085°C. △, Li_2SO_4 - Cs_2SO_4 at 1090°C. +, Li_2SO_4 - Na_2SO_4 at 900°C (Holm⁷). - - -, Li_2SO_4 - Na_2SO_4 at 900°C. (Anderson⁸).

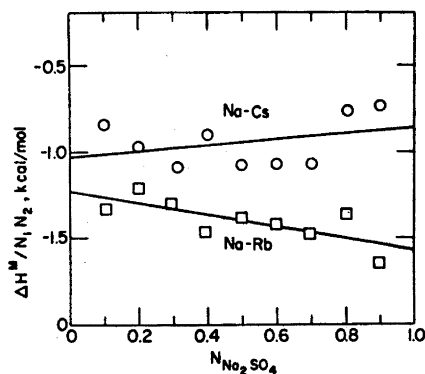


Fig. 2. $\Delta H^M/N_1N_2$ for liquid mixtures of sodium sulfate with rubidium sulfate and cesium sulfate. □, Na_2SO_4 - Rb_2SO_4 at 1080°C. ○, Na_2SO_4 - Cs_2SO_4 at 1080°C.

present investigation are presented in graphical form in Figs. 1 and 2. These figures give the enthalpy interaction parameter, $\Delta H^M/N_1N_2$, plotted versus the mole fraction of the salt with the smaller cation, N_2 . The experimental

values of the interaction parameter, $\Delta H^M/N_1N_2$ were subjected to a least squares treatment in order to fit this quantity to polynomials of the form

$$\Delta H^M/N_1N_2 = a + bN_2 + cN_2(1 - N_2)$$

In each case it was found that the data could best be fitted by a simple straight line ($c=0$). The experimentally determined values of a and b are given in Table 1, along with the values of the interaction parameter at the 50–50

Table 1. Integral enthalpies of mixing for binary alkali sulfates ($\Delta H^M = N_1N_2(a + bN_2)$ kcal/mol; N_2 : mole fraction of smaller ion).

System	°C	a	b	$4\Delta H_{0.5}^M$	S.D.
Li–Na	1085	–1.86		–2.07	
Li–Na	910	–2.05	–0.53	–2.31	0.07
Li–Na ^a	900	–2.03	–0.69	–2.38	0.05
Li–K	1085	–5.12	–1.86	–6.05	0.12
Li–Rb	1080	–5.30	–3.59	–7.10	0.13
Li–Cs	1090	–4.66	–4.48	–6.90	0.13
Na–K	1080			–1.05	
Na–Rb	1080	–1.23	–0.38	–1.40	0.09
Na–Cs	1080	–1.03	+0.17	–0.94	0.15
K–Rb	1080			–0.01	
K–Cs	1080			+0.22	
Rb–Cs	1080			+0.09	

^a Data obtained by Anderson,⁸ The James Franck Institute, University of Chicago 1968.

composition, $4\Delta H_{0.5}^M$. The last column in the table gives the standard deviation of the experimentally determined interaction parameter from the analytical curve. In Fig. 1 we also include the experimental points for Li_2SO_4 – Na_2SO_4 given by Holm,⁷ and a curve which represents the results of Anderson.⁸ As can be seen from this figure, our data for the Li_2SO_4 – Na_2SO_4 mixtures agree very well with those of Anderson,⁸ but show somewhat more negative values than the work of Holm.

The discrepancy represents 20–30 %, both in the lithium-rich and in the sodium-rich regions, but is very much smaller in the middle of the system. The apparatus used by Holm was only slightly different from the one used in the present work, and we have no satisfactory explanation which will account for the discrepancy.

DISCUSSION

The conformational solution theory of Reiss, Katz and Kleppa¹⁰ (RKK) has been fairly successful in rationalizing the solution behavior of simple mixed-cation-common-anion fused salt mixtures. According to the RKK theory, the enthalpies of mixing for a series of related mixed-cation-common-anion fused salt systems should be given by an expression of the type

$$\Delta H^M \cong N_1N_2\Omega \delta_{12}^2 \quad (1)$$

In this expression, N_1 and N_2 are the mol fractions of the two components; δ_{12} is a size parameter, $\delta_{12} = (d_1 - d_2)/d_1 d_2$ (d_1 and d_2 are characteristic interionic distances in the two salts), while Ω is a negative constant which depends only on the coulombic interactions between the ions of the salt mixture. According to the theory, Ω is essentially independent of the nature of the common anion, as long as its charge is unchanged.

Enthalpies of mixing consistent with eqn. (1) were first found by Kleppa and Hersh² for the alkali nitrates, and later, but to a lesser extent, for the alkali chlorides and bromides.³ For the latter systems, better agreement with theory is achieved if one takes into account also the London-van der Waals interaction between next nearest neighbor cations, as originally suggested by Lumsden¹¹ and by Blander.¹² The enthalpies of mixing in these systems were represented by the semi-empirical relations

$$\Delta H^M = N_1 N_2 (U_0^{++} + \Omega \delta_{12}^2) \quad (2)$$

In this expression, U_0^{++} represents an estimate of the London-van der Waals contribution to the enthalpy of mixing.

A more formal theoretical justification for this expression is provided by Davis and Rice,⁶ who modified the coulombic pair potential of RKK by including also short-range dispersion interactions. The Davis-Rice theory is based on the same assumption as the RKK theory, namely that the thermodynamic properties of the mixed system can be accounted for in terms of a model ionic melt. The properties of the melt are:

(1) The pair potential between ions can be written as a sum of coulomb and dispersion interactions.

(2) The short-range repulsive interactions between ions of like charge can be neglected because of local structure and the coulomb repulsion. The pair potential between ions of like charge will have the form

$$u(r_{ij}) = q^2/k r_{ij} + \xi v(r_{ij}), \quad r_{ij} > 0 \quad (3)$$

(3) For ions of opposite charge, the pair potential is

$$\begin{aligned} u(r_{ij}) &= \infty & r_{ij} \leq d \\ u(r_{ij}) &= -q^2/k r_{ij} + \xi v(r_{ij}), & r_{ij} > d \end{aligned} \quad (4)$$

Here q is the electronic charge, k a dielectric constant introduced formally to account for many-body polarization interactions of directly coulombic origin, and d is the cation-anion hard-core separation.

The parameter ξ represents the coupling parameter for the particular short-range interaction under consideration, while $v(r_{ij})$ is defined as

$$v(r_{ij}) = -r_{ij}^{-n}$$

Examples of ξ and n pertinent to ionic interactions are:

(a) Polarization interaction: $n=4$, $\xi = 1/2 q^2 (\alpha_A + \alpha_B)$, where α_A and α_B are the polarizabilities of ion A and ion B, respectively.

(b) London-van der Waals interaction: $n=6$, $\xi \cong 3/2 \alpha_A \alpha_B I_A I_B / (I_A + I_B)$, where I_A and I_B are the characteristic excitation energies of ions A and B, respectively.

According to the Davis-Rice theory, the enthalpies of mixing for a series of simple binary fused salt mixtures which have one component in common will be given by

$$\Delta H^M = N_1 N_2 (U_0 + U_1 \delta_{12} + U_2 \delta_{12}^2) \quad (5)$$

We shall return in some detail to the significance of the terms in this expression below.

The actual value of the coefficient Ω in (2) depends somewhat on the assumed magnitude of U_0 , but was found to be roughly $-340 \text{ kcal } \text{Å}^2/\text{mol}$, $-410 \text{ kcal } \text{Å}^2/\text{mol}$, $-430 \text{ kcal } \text{Å}^2/\text{mol}$, $-540 \text{ kcal } \text{Å}^2/\text{mol}$ for the fluorides, chlorides, bromides, and iodides, respectively.⁵ However, the deviation from the straight line relationship between ΔH^M and δ_{12}^2 , predicted by eqn. (2), was quite pronounced for the fluorides. It was suggested by Holm and Kleppa,⁴ that this might be due to cation-cation core repulsion in the presence of the small fluoride anion and/or to possible contributions to the enthalpy of mixing from the ion-dipole interaction considered theoretically by Davis and Rice. More recent work by Melnichak¹³ indicates that the latter of these effects probably is the more important, since the deviation is proportional to the difference in the polarizability of the two cations, and to the first power in δ_{12} as predicted by the theory of Davis and Rice (see below).

The different values of the coefficient Ω may, according to the theory of Davis and Rice, be due to the change in the cation-anion dispersion interactions on going from one common anion system to another. The polarizability of the anion is changing very considerably from the fluoride ion ($\alpha_F = 0.64 \text{ Å}^3$) to the iodide ion ($\alpha_I = 6.43 \text{ Å}^3$). This may account for the observed trend towards more negative enthalpies of mixing (for a given value of δ_{12}^2) from the fluorides through the chlorides and bromides to the iodides. The data for the alkali sulfate mixtures show a dependence on δ_{12}^2 which is similar to that of the alkali fluorides. This is apparent from Fig. 3 which shows a plot of the "cor-

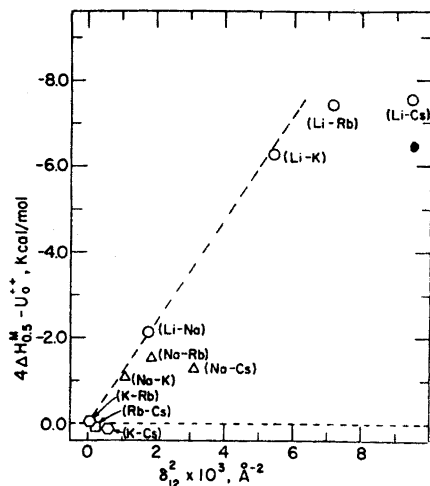


Fig. 3. Dependence of the corrected enthalpy interaction parameter, $4\Delta H_{0.5}^M - U_0^{++}$, on the size parameter δ_{12}^2 . \circ , systems with Li^+ as smaller cation. Δ , systems with Na^+ as smaller cation. \square , systems with K^+ as smaller cation. \square , systems with Rb^+ as smaller cation.

rected enthalpy interaction parameter". $4\Delta H_{0.5^M} - U_0^{++}$, versus δ_{12}^2 for these mixtures. As already mentioned, U_0^{++} represents a numerical estimate of the positive contribution to the enthalpy of mixing which arises from the van der Waals interactions between next nearest neighbor cations. In the present work, we adopted the method of evaluation of U_0^{++} previously used by Hersh and Kleppa,³ taking into account the higher cation to anion ratio of the sulfate melts. However, in the London expression for the dispersion energy, we adopted the uncorrected value of the ionization potential, I , of the alkali ion rather than the value $0.75 I$, used by Mayer,¹⁴ and by Hersh and Kleppa.³ This choice was dictated by more recent work on the dispersion energy, which suggests that the earlier estimates were significantly too low (see Pitzer¹⁵). The interatomic distances used in the present work were calculated from the ionic radii of the ions involved. In Table 2 we list the ionic

Table 2. Ionic radii used in the present work. From Melnichak.¹³ Numbers in parenthesis are the Pauling radii.

Ion	Radius in Å
Li ⁺	0.57 (0.60)
Na ⁺	0.96 (0.95)
K ⁺	1.34 (1.33)
Rb ⁺	1.49 (1.48)
Cs ⁺	1.68 (1.69)
SO ₄ ²⁻	2.30

radii of the alkali cations and of the sulfate anion. The radius of the sulfate anion, $r_{\text{SO}_4} = 2.30$ Å, is the thermochemical radius. For the alkali metal cations we have used the radii of Melnichak.¹³ These were calculated by the method of Pauling,¹⁶ but taking into account the new interatomic distances for the alkali halides and oxides listed by Wyckoff.¹⁷ Except in the case of the lithium ion, where the radius is changed from 0.60 to 0.57 Å, the new radii differ only by 0.01 Å from the old Pauling values. Even so, this change in radius for the lithium ion gives rise to very noticeable changes in the square of the distance parameter, δ_{12}^2 , for these systems.

It was argued by Zarzycki¹⁸ that the larger alkali cations show a tendency to occupy sites near the corners of the sulfate tetrahedron, while the smaller ions occupy sites closer to the center of the sulfate ion. Under these circumstances, the assumption of a constant sulfate anion radius might be questioned. On the other hand, since we want to compare the different sulfate systems with each other (and with the alkali halides), and since the main contribution to the difference in δ_{12}^2 between two solution systems arises from the difference in the cation radii, we believe that the assumption of a constant sulfate radius is acceptable for the purpose of the present discussion.

The following properties of the binary alkali sulfate melts should be noted (see Fig. 3):

(1) The plots of the corrected enthalpy interaction parameter deviate considerably from a linear dependence on δ_{12}^2 . This is particularly evident in the case of $\text{Li}_2\text{SO}_4 - \text{Rb}_2\text{SO}_4$ and $\text{Li}_2\text{SO}_4 - \text{Cs}_2\text{SO}_4$, as well as for $\text{Na}_2\text{SO}_4 - \text{Rb}_2\text{SO}_4$

and $\text{Na}_2\text{SO}_4 - \text{Cs}_2\text{SO}_4$. Actually, Fig. 3 suggests a systematic difference between mixtures formed by lithium sulfate, on the one hand, and those formed by sodium sulfate on the other. Melnichak and Kleppa⁵ noted that a similar systematic difference is found also in the binary alkali halides, the difference increasing in the sequence iodides < bromides < chlorides < fluorides.

(2) The corrected interaction parameter, $4\Delta H_{0.5}^M - U_0^{++}$, approaches zero when $\delta_{12}^2 \rightarrow 0$. It shows small positive values for $\text{K}_2\text{SO}_4 - \text{Rb}_2\text{SO}_4$ and $\text{Rb}_2\text{SO}_4 - \text{Cs}_2\text{SO}_4$, but is much more negative than for the corresponding halides at higher values of δ_{12}^2 .

(3) The interaction parameter, $\Delta H^M/N_1N_2$, is a linear function of composition for all the systems investigated. The energetic asymmetry, b , *i.e.* the slope of $\Delta H^M/N_1N_2$ versus the mole fraction of the smaller cation, is much more negative than for the corresponding halide melts.

According to the theory of Davis and Rice, the enthalpy of mixing for binary mixed-monovalent-cation-common-anion systems should be given by an equation of the form of (5). In the considered sulfate mixtures, the constants U_0 , U_1 , and U_2 will differ from the constants which apply in the halide melts due to the double negative charge on the sulfate ion, and due to the presence of twice as many cations as in one mole of halide. Even so, the functional form of eqn. (5) will be unchanged.

If, in the perturbation theory of Davis and Rice, second nearest neighbor interactions (+ +) are neglected where they occur along with nearest neighbor (+ -) terms in the theoretical expressions, we obtain the following dependence of the coefficients U_0 , U_1 and U_2 on the coupling parameter ξ .

$$U_0 = f[\xi_{12}^{++} - \frac{1}{2}(\xi_1^{++} + \xi_2^{++})] \quad (6a)$$

$$U_1 = f[\xi_1^{+-} - \xi_2^{+-}] \quad (6b)$$

$$U_2 = f[\Omega + f(\xi^{+-})] \quad (6c)$$

Note that U_0 is determined largely by the change in London-van der Waals interaction between next nearest neighbor cations. This term is essentially the interaction term considered by Lumsden¹¹ and independently by Blander,¹² which we have designated by U_0^{++} above (eqn. 2).

The term U_1 is proportional to the difference in cation-anion dispersion interaction in the two components in the mixture. Finally, the term U_2 is determined largely by the change in coulomb interactions, and the major contribution is the RKK term Ω . However, U_2 also contains contributions from cation-anion dispersion interactions which we have gathered together in (6c) in the general term $f(\xi^{+-})$.

If we are justified in adopting the perturbation theory approach in our attempts to refine RKK theory, this in itself implies that this second term $f(\xi^{+-})$ must be small compared to Ω . If this assumption is made explicitly, we see that the principal difference between Davis-Rice theory and RKK theory rests in the terms U_0 and U_1 .

From an analysis of the functional dependence of ξ^{+-} on the properties of the ions we conclude that the leading term in $\xi_1^{+-} - \xi_2^{+-}$ for a common anion system will be proportional to $\alpha_1 - \alpha_2$, the difference in polarizability of the two cations. Making this substitution in (5) we may write

$$\Delta H^M/N_1N_2 = U_0 + A(\alpha_1 - \alpha_2)\delta_{12} + B\delta_{12}^2 \quad (7a)$$

$$\text{or} \quad (4\Delta H^M - U_0)/(\alpha_1 - \alpha_2)\delta_{12} = A + B\delta_{12}/(\alpha_1 - \alpha_2) \quad (7b)$$

where the coefficients A and B are to be determined from experiment.

A plot of the left hand side of eqn. (7b) versus $\delta_{12}/(\alpha_1 - \alpha_2)$ is presented in Fig. 4, and indicates that the alkali sulfate data are in fact very well represented

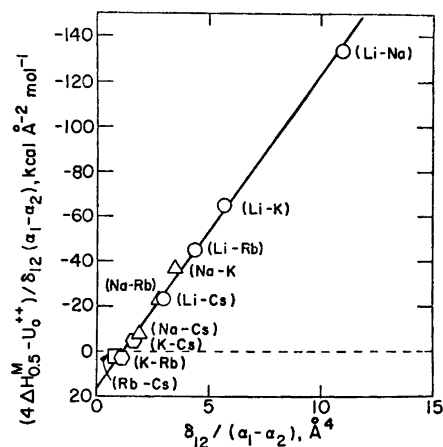


Fig. 4. Dependence of the quantity $(4\Delta H_{0.5}^M - U_0^{++})/\delta_{12}(\alpha_1 - \alpha_2)$ on the parameter $\delta_{12}/(\alpha_1 - \alpha_2)$. O, systems with Li^+ as smaller ion. Δ , systems with Na^+ as smaller ion. \square , systems with K^+ as smaller ion. \square , systems with Rb^+ as smaller ion.

by this equation. A least squares treatment of all the data yields the following values:

$$A = 16.4 \text{ kcal}/\text{\AA}^2 \text{ mol}, \text{ and } B = -1400 \text{ kcal } \text{\AA}^2/\text{mol}.$$

From this analysis we note:

(1) Unlike the situation in the binary alkali chloride, bromide, and iodide systems, the data for the binary alkali sulfates show evidence of cation-anion dispersion interactions, which give rise to positive contributions to the enthalpy interaction parameters. These contributions vary linearly with the size parameter δ_{12} and with $(\alpha_1 - \alpha_2)$, the difference in polarizability of the two cations. A similar term was previously found in the binary alkali fluorides.¹³ This effect accounts for the deviations from linearity in the plot of corrected interaction parameter versus δ_{12}^2 given in Fig. 3. It is of interest to note that the numerical value of the coefficient A , $16.4 \text{ kcal}/\text{\AA}^2 \text{ mol}$, is two times the value for the corresponding fluorides, for which Melnichak finds $A = 8.2 \text{ kcal}/\text{\AA}^2 \text{ mol}$.¹³ However, we believe this numerical correlation must be considered entirely fortuitous.

(2) The slope of the straight line in Fig. 4 gives the numerical value of B . This coefficient, which for the binary alkali sulfates is $-1400 \text{ kcal } \text{\AA}^2/\text{mol}$, is larger than the corresponding coefficients for the binary alkali halide mixtures by a factor of the order of 3. This is roughly the ratio of the Madelung constant for structures of type A_2X (or AX_2) to that for structures of type AX . Hence, the observed ratio is consistent with the basic assumption which underlies the RKK theory, namely that the principal contribution to the enthalpy of mixing in simple binary alkali salt mixtures is coulombic in origin.

It remains to comment briefly on the energetic asymmetries in the alkali sulfate mixtures. Fig. 2 shows that the energetic asymmetries for the sodium sulfate mixtures are very small, and appear to be of opposite sign for $\text{Na}_2\text{SO}_4 - \text{Rb}_2\text{SO}_4$ and $\text{Na}_2\text{SO}_4 - \text{Cs}_2\text{SO}_4$. On the other hand, the lithium sulfate containing mixtures exhibit quite large asymmetries, which numerically increase sharply in the sequence $\text{Li}-\text{Na} < \text{Li}-\text{K} < \text{Li}-\text{Rb} < \text{Li}-\text{Cs}$. According to Blander's calculation of the higher order terms of the RKK theory¹⁹ it may be expected that the asymmetry parameter, b should depend on ionic size through the third power of δ_{12} . Such a behavior is in fact observed for the lithium sulfate containing mixtures, as illustrated in Fig. 5. A similar dependence of b on δ_{12}^3

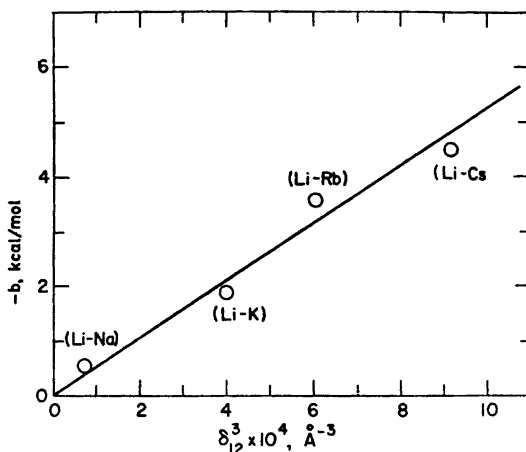


Fig. 5. Dependence of the asymmetry parameter b on the size parameter δ_{12}^3 for the mixtures of lithium sulfate with the other alkali sulfates.

is found also for the corresponding lithium halide mixtures, with the slope of the plot of b versus δ_{12}^3 increasing significantly in the sequence fluoride < chloride < bromide < iodide. Even so the corresponding slope for the sulfates is larger than the halide slopes by a factor which ranges from about 4 for the lithium iodides mixtures to more than 10 for the lithium fluoride containing mixtures.

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REFERENCES

1. Kleppa, O. J. *J. Phys. Chem.* **64** (1960) 1937.
2. Kleppa, O. J. and Hersh, L. S. *J. Chem. Phys.* **34** (1961) 351.
3. Hersh, L. S. and Kleppa, O. J. *J. Chem. Phys.* **42** (1965) 1309.
4. Holm, J. L. and Kleppa, O. J. *J. Chem. Phys.* **49** (1968) 2425.
5. Melnichak, M. E. and Kleppa, O. J. *J. Chem. Phys.* **52** (1970) 1790.

6. Davis, H. T. and Rice, S. A. *J. Chem. Phys.* **41** (1964) 14.
7. Holm, J. L. *Acta Chem. Scand.* **24** (1970) 709.
8. Anderson, P. *Unpublished results*, 1968.
9. Kelley, K. K. *U. S. Bur. Mines, Bull.* No. 584 (1960).
10. Reiss, H., Katz, J. L. and Kleppa, O. J. *J. Chem. Phys.* **36** (1962) 144.
11. Lumsden, J. *Discussions Faraday Soc.* **32** (1961) 138.
12. Blander, M. *J. Chem. Phys.* **36** (1962) 1092.
13. Melnichak, M. E. *Unpublished work*.
14. Mayer, J. E. *J. Chem. Phys.* **1** (1933) 270.
15. Pitzer, K. S. *Inter- and Intramolecular Forces and Molecular Polarizability*, In Prigogine, I., Ed., *Advances in Chemical Physics*, Interscience, New York-London 1959, Vol. II.
16. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca 1960, p. 511.
17. Wyckoff, R. W. G. *Crystal Structures*, 2nd Ed., Interscience, New York-London 1965, Vol. I, p. 242.
18. Zarzycki, J. *Discussions Faraday Soc.* **32** (1961) 38.
19. Blander, M. *J. Chem. Phys.* **37** (1962) 172.

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