

Enthalpies of Mixing in Binary Liquid Alkali Hydroxide Mixtures

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The enthalpies of mixing in the binary liquid alkali hydroxide mixtures have been determined by direct high temperature calorimetry. The measurements were performed over wide ranges of composition at 773 K.

The results are discussed and interpreted in terms of the conformal solution theory for fused salts of Reiss, Katz, and Kleppa as modified by Blander and by Davis and Rice. The enthalpies of mixing at the 50:50 compositions are well represented by the semiempirical expression

$$4\Delta H_{0.5}^M = U_0^{++} + (17.8/\text{\AA}^2)\Delta\alpha\delta_{12} - (1250/\text{\AA}^{-2})\delta_{12}^2, \text{ kJ mol}^{-1}$$

In this expression, $\delta_{12} = (d_1 - d_2)/d_1 d_2$, 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 neighbour cations; $\Delta\alpha$ is the difference in polarizability between the two cations.

A large number of binary molten salt systems have been studied by means of direct high temperature heat of mixing calorimetry. Thus, among the monovalent symmetrical salts with a common anion, AX-BX, extensive studies have now been carried out on the alkali halides and on the alkali nitrates. So far, no comparable thorough study has been made of the binary alkali hydroxides, which are of interest both from a practical and theoretical point of view. For example, it is well known that

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the ionic radius of OH^- is roughly comparable to that of F^- . However, the former ion has much greater polarizability, and also has a permanent dipole moment. Hence a comparison of the liquid hydroxides with the liquid fluorides is of special interest.

To our knowledge the only direct calorimetric measurements carried out on molten alkali hydroxides are those of Aghai-Khafri *et al.*¹ However, these authors studied only the NaOH–KOH system and only in very dilute solutions. Prior to this, Lumsden² had calculated excess chemical potentials in this system from the phase diagram of Reshetnikov and Vilutis,³ using the thermochemical data given by Douglas and Dever,⁴ and by Kelley.⁵

EXPERIMENTAL

Apparatus. All the calorimetric experiments were carried out in a single unit Calvet-type microcalorimeter suitable for work at temperatures up to about 1400 K. Apart from its single (rather than twin) construction and the higher operating temperature, the calorimeter is similar to that previously described by Kleppa.⁶

Due to the corrosive nature of molten alkali hydroxides, these cannot, unlike most other salts which have been studied previously, be handled in fused silica containers and by the usual “break-off” technique. Separate tests showed that the attack on Palau (20% Pd and 80% Au) by alkali hydroxide melts kept in an inert atmosphere was negligible. Therefore, this alloy was chosen as the only material in contact with the hydroxide melts during the mixing experiments. These were carried out in an atmosphere of pure dry argon.

Table 1. Supplier and purity of chemicals.

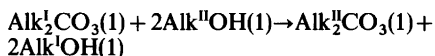
Chemicals	Supplier Purity	Content of Alk ₂ CO ₃ in mol %	Impurities by spectroscopic analysis in weight %
LiOH	Baker Chemical Co. Analytical Reagent	0.32	NaOH + KOH 0.07 Others ≤ 0.003
NaOH	Baker Chemical Co. Analytical Reagent	0.36	KOH 0.002 Others ≤ 0.003
KOH	Baker Chemical Co. Analytical Reagent	0.15	NaOH + RbOH 0.11 Others ≤ 0.015
RbOH	Kawecki Berylco Industries, Inc. High purity	0.30	KOH 0.42, CsOH 0.22 Others ≤ 0.10
CsOH	Kawecki Berylco Industries, Inc. High purity	0.24	NaOH + KOH + RbOH 0.09 Others ≤ 0.06

The experimental arrangements inside the calorimeter proper are the same as those previously used by Andersen and Kleppa.⁷ Both the plunger and the dipper-crucible could be manipulated from outside the calorimeter proper.

Chemicals. The chemicals used in the present work and their purities are shown in Table 1.

The alkali hydroxides, which as received contained up to 12 weight % of water, were dried by heating them slowly in an atmosphere of dry argon up to 700–800 K over a period of 24 h. Silver was found to be a reasonably satisfactory container material. Because of the instability of LiOH (probably due to the reaction $2\text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2\text{O}$) and the volatility of RbOH and CsOH care was taken to avoid prolonged heating at elevated temperatures.

The carbonate contents determined by means of a CO₂-evolution technique were 0.15–0.36 mol percent, and they were hence of the same order of magnitude in all the hydroxides. Therefore enthalpy contributions due to reciprocal reactions of the type



could be neglected.

The alkali hydroxides are extremely hygroscopic. In order to avoid the pick-up of H₂O and CO₂ the filling and weighing processes were carried out in a dry box in an atmosphere of dry argon.

Procedure. Immediately before insertion into the calorimeter, the fused silica liner with its content was preheated for a period of 15 min about 50 K above the operating temperature of the calorimeter.

In typical runs the total time elapsed prior to mixing was about 2 h. All systems were studied at the temperature 773 ± 1 K.

Due to the instability and volatility of the hydroxides at more elevated temperatures we did not study the temperature dependence of the enthalpies of mixing.

The mixing of the two salts was achieved by vertical manipulation of the plunger and dipper. After the initial mixing process three additional stirring operations were carried out at one minute intervals to assure complete mixing. Each stirring operation gave rise to a small reproducible heat effect, which had to be corrected for in some of the experiments.

In each run a total of 80 to 250 mmol of salt was used. The calibration of the calorimeter was achieved by dropping weighed pieces of 2 mm gold wire from room temperature into the calorimeter. The evaluation of the resulting endothermic heat effects was based on Kelley's equation for the heat content of gold.⁵ At 773 K the weight losses because of vaporization and decomposition of the hydroxides were small, less than 0.2 %, and could be neglected. Also, the correction which is made for the heat pick-up of the gold pieces during the fall into the calorimeter was very small; from data given by Melnichak⁸ this correction was estimated to be 0.1 % or less.

The temperature-sensing device of the calorimeter consists of a 54+54 junction Pt-Pt/13%Rh thermopile, the output of which is amplified by means of a Leeds & Northrup D.C. amplifier and recorded on a Type H-Azar recorder. The emf *versus* time curves were integrated by means of an

Ott precision planimeter. In this way the area between the curve and the "base line", which is proportional to the total heat effect, could be determined with a precision of about $\pm 0.3\%$. The error due to uncertainty in drawing the base line was in most experiments estimated to be about $\pm 1\%$. However, in some experiments, especially those on the KOH-RbOH, KOH-CsOH, and RbOH-CsOH systems, which have very small enthalpies of mixing, this relative error was much larger.

RESULTS

All the ten binary alkali hydroxide systems were investigated. The concentration dependence of the enthalpy of mixing was studied for all the lithium and sodium containing systems. For the three remaining systems (KOH-RbOH, KOH-CsOH, and RbOH-CsOH) the heat effects were small and

Table 2. Molar enthalpies of mixing of binary liquid alkali hydroxide mixtures. x_1 is the mol fraction of the salt with the smaller cation.

Mol fraction x_1	Total, mol	$\Delta H^M / \text{kJ mol}^{-1}$	$(\Delta H^M / x_1 x_2) / \text{kJ mol}^{-1}$
LiOH-NaOH			
0.1499	0.19565	-0.843	-6.617
0.1505	0.17573	-0.885	-6.921
0.2503	0.22867	-1.243	-6.625
0.2513	0.24393	-1.353	-7.193
0.3607	0.17295	-1.627	-7.055
0.4010	0.20050	-1.678	-6.987
0.5512	0.22328	-1.718	-6.944
0.8010	0.25397	-1.087	-6.820
0.8464	0.17349	-0.937	-7.207
0.9002	0.27949	-0.636	-7.077
LiOH-KOH			
0.05045	0.10112	-0.558	-11.651
0.1000	0.13188	-1.135	-12.609
0.1508	0.13267	-1.704	-13.304
0.1996	0.16809	-2.274	-14.232
0.2999	0.15755	-3.266	-15.556
0.3001	0.15234	-3.074	-14.637
0.4000	0.14742	-3.574	-14.890
0.5002	0.16926	-4.324	-17.295
0.5503	0.18262	-4.283	-17.308
0.5999	0.17121	-4.075	-16.979
0.7000	0.21776	-3.758	-17.896
0.8003	0.22927	-2.950	-18.457
0.8483	0.16875	-2.438	-18.942
0.9000	0.21886	-1.756	-19.514
0.9202	0.24742	-1.437	-19.562

LiOH-RbOH			
0.05004	0.10112	-0.492	-10.345
0.1000	0.12370	-1.048	-11.644
0.1997	0.07887	-1.758	-10.997
0.2514	0.13841	-2.366	-12.572
0.3001	0.15930	-2.879	-13.705
0.4000	0.15984	-3.382	-14.093
0.5501	0.18421	-4.093	-16.538
0.6500	0.18502	-4.088	-17.970
0.7521	0.19726	-3.404	-18.252
0.9201	0.24090	-1.488	-20.247

LiOH-CsOH			
0.05194	0.10894	-0.412	-8.369
0.2000	0.08560	-1.781	-11.130
0.3000	0.11309	-2.416	-11.507
0.4001	0.16377	-3.450	-14.376
0.4505	0.13329	-3.661	-14.788
0.5806	0.16209	-3.561	-14.624
0.9000	0.23144	-1.850	-20.559
0.9500	0.26970	-1.038	-21.851

NaOH-KOH			
0.1998	0.12685	-0.4193	-2.622
0.1999	0.12631	-0.3901	-2.439
0.2003	0.14481	-0.3611	-2.255
0.2517	0.12357	-0.4937	-2.621
0.4997	0.18120	-0.6072	-2.429
0.6009	0.16501	-0.5113	-2.132
0.8800	0.17567	-0.2263	-2.143
0.8801	0.15160	-0.2298	-2.176
0.9004	0.21219	-0.1825	-2.035
0.9001	0.18303	-0.2048	-2.278

NaOH-RbOH			
0.2000	0.13486	-0.6211	-3.882
0.4010	0.12907	-0.8663	-3.606
0.8801	0.17088	-0.3623	-3.433
0.9001	0.17512	-0.3178	-3.533

NaOH-CsOH			
0.2506	0.11301	-0.5934	-3.160
0.4002	0.13298	-0.7974	-3.322
0.7998	0.15368	-0.4651	-2.905
0.8959	0.16969	-0.2890	-3.099
0.9002	0.15683	-0.2964	-3.299

KOH-RbOH			
0.2998	0.13034	0.0468	0.223
0.7502	0.14087	0.0323	0.172

KOH-CsOH			
0.2001	0.10837	0.1633	1.020
0.9000	0.13470	0.1249	1.389

RbOH-CsOH			
0.3499	0.11198	0.0541	0.238
0.8500	0.11285	0.0322	0.252

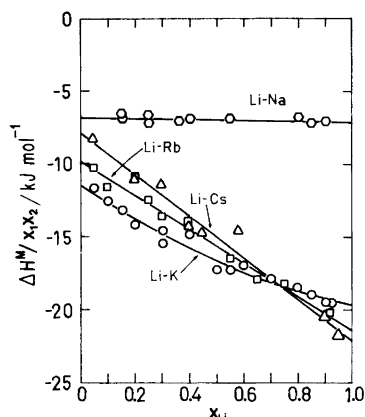


Fig. 1. Plots of $\Delta H^M/x_1x_2$ versus x_{Li} for LiOH-AlkOH mixtures.

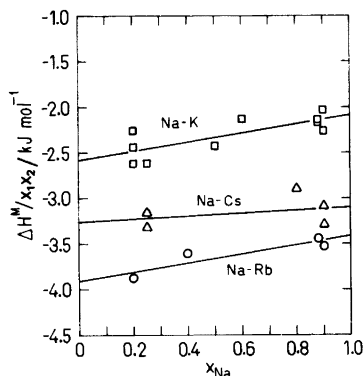


Fig. 2. Plots of $\Delta H^M/x_1x_2$ versus x_{Na} for NaOH-KOH, NaOH-RbOH, and NaOH-CsOH mixtures.

values for two mixtures only in each system were determined.

The experimental results are tabulated in Table 2. In Figs. 1 and 2 the enthalpy interaction parameter, $\Delta H^M/x_1x_2$, is plotted versus the mol fraction of the salt with the smaller cation.

By means of the least squares method the experimental data for the seven systems shown in Figs. 1 and 2 were fitted to linear expressions of the form

$$\Delta H^M/x_1x_2 = a + bx_1 \quad (1)$$

For LiOH-KOH a curve of second degree

$$\Delta H^M/x_1x_2 = a + bx_1 + cx_1x_2 \quad (2)$$

was found to give a much better fit. In Table 3 we give the values of the coefficients a , b and c as well as the enthalpies of mixing at the 50:50 composition.

DISCUSSION

The enthalpies of mixing are interpreted in light of the conformational solution theories for fused salts developed by Reiss, Katz, and Kleppa (RKK),⁹ by Blander,¹⁰ and by Davis and Rice (DR).¹¹

We have chosen to represent the enthalpy of mixing for a given binary system by $4\Delta H_{0.5}^M$, i.e., by the calculated value of the interaction parameter, $\Delta H^M/x_1x_2$, at the equimolar composition. To these values we have applied a correction by estimating the values of U_0^{++} , the change on mixing in the London-van der Waals dispersion energy between next nearest neighbour cations. The method of

Table 3. Integral enthalpies of mixing for binary alkali hydroxides at 773 K ($\Delta H^M = x_1x_2(a + bx_1 + cx_1x_2)$ kJ mol⁻¹; x_1 is mol fraction of salt with the smaller cation).

System	a	b	c	$4\Delta H_{0.5}^M$	S.D.
LiOH-NaOH	-6.80	-0.30		-6.95	0.20
LiOH-KOH	-11.43	-8.28	-4.34	-16.66	0.47
	(-12.13)	(-8.31)		(-16.29)	0.55
LiOH-RbOH	-9.79	-11.61		-15.60	0.58
LiOH-CsOH	-7.81	-14.28		-14.95	0.82
NaOH-KOH	-2.58	+0.49		-2.34	0.14
NaOH-RbOH	-3.91	+0.49		-3.66	0.11
NaOH-CsOH	-3.26	+0.16		-3.18	0.19
KOH-RbOH				+0.20	
KOH-CsOH				+1.21	
RbOH-CsOH				+0.25	

estimating U_0^{++} is the same as previously used by Hersh and Kleppa.¹² However, in the present work we have in the London expression adopted the uncorrected values of the ionization potential of the alkali ions, I , rather than the value $0.75I$. This choice was dictated by more recent work on the dispersion energy, which generally suggests that the earlier estimate was significantly too low (see, e.g., Pitzer²⁵). We have made use of the ionic radii of the alkali metals given by Melnichak and Kleppa.¹³ The same method and values were used also by Østvold and Kleppa¹⁴ and by Andersen and Kleppa.⁷ The relevant interatomic distances were calculated from the ionic radii of the ions. For the hydroxide anion we adopted the thermochemical radius, $r(\text{OH}^-) = 1.40 \text{ \AA}$, as given by Kapustinskii.¹⁵ The importance of the choice of ionic radii will be discussed later. The polarizabilities are those reported by Tessman *et al.*¹⁶ Table 4 shows the ionic radii, polarizabilities, and ionization potentials used in the calculations. In Fig. 3 the corrected interaction parameter, $4\Delta H_{0.5}^M - U_0^{++}$, is plotted *versus* the square of the distance parameter, δ_{12} ($\delta_{12} = (d_1 - d_2)/d_1 d_2$ where d_1 and d_2 are characteristic interionic distances in the two salts; $d = r_+ + r_-$). It will be noted that the points representing the LiOH-NaOH, LiOH-KOH and NaOH-KOH systems fall close to a straight line through the origin, while most of the points which represent the rubidium or cesium containing systems fall below this line.

The ionic conformal solution theory of Reiss, Katz, and Kleppa as modified by the perturbation theory of Davis and Rice, predicts that the enthalpies of mixing for families of related fused salt solutions should be of the form

$$\Delta H^M/x_1 x_2 = U_0 + U_1 \delta_{12} + U_2 \delta_{12}^2 \quad (3)$$

Table 4. Ionic radii, polarizabilities, and ionization potentials for the alkali metal ions.

Ion	r^a Å	r^b Å	α^c Å ³	I^d kJ mol ⁻¹
Li ⁺	0.57	0.60	0.03	7296
Na ⁺	0.96	0.95	0.41	4563
K ⁺	1.34	1.33	1.33	3069
Rb ⁺	1.49	1.48	1.98	2653
Cs ⁺	1.68	1.69	3.34	2422

^a Melnichak and Kleppa.¹³ ^b Pauling.¹⁷ ^c Tessman *et al.*¹⁶ ^d "Handbook of Chemistry and Physics".²⁴

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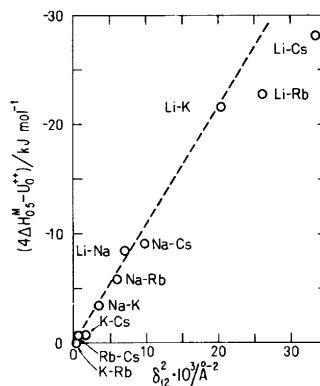


Fig. 3. Dependence of the corrected enthalpy interaction parameter, $4\Delta H_{0.5}^M - U_0^{++}$, on the size parameter δ_{12}^2 in alkali hydroxide mixtures.

According to the DR theory the leading term in U_1 , for a given common anion family, should be proportional to $\Delta\alpha = \alpha_1 - \alpha_2$, i.e., the difference between the polarizabilities of the two cations. Taking this into account and substituting U_0^{++} for U_0 we may write eqn. (3) as follows:

$$\Delta H^M/x_1 x_2 = U_0^{++} + A(\alpha_1 - \alpha_2)\delta_{12} + B\delta_{12}^2 \quad (4a)$$

or for $x_1 = x_2 = 0.5$

$$(4\Delta H_{0.5}^M - U_0^{++})/(\alpha_1 - \alpha_2)\delta_{12} = A + B\delta_{12}/(\alpha_1 - \alpha_2) \quad (4b)$$

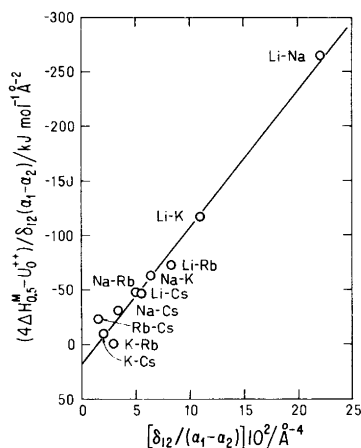


Fig. 4. Dependence of the quantity $(4\Delta H_{0.5}^M - U_0^{++})/\delta_{12}(\alpha_1 - \alpha_2)$ on the parameter $\delta_{12}/(\alpha_1 - \alpha_2)$ in mixtures of molten alkali hydroxides. Melnichak's radii for the alkali metal ions are used.

In these expressions A and B are unknown coefficients to be determined from experiments.

A plot of the left hand side of eqn. (4b) versus $\delta_{12}/(\alpha_1 - \alpha_2)$ is given in Fig. 4, and indicates that the alkali hydroxide family is in fact very well represented by this equation. A least squares treatment of all the data yields the following values

$$A = +17.8 \text{ kJ } \text{\AA}^{-2} \text{ mol}^{-1}$$

$$B = -1250 \text{ kJ } \text{\AA}^2 \text{ mol}^{-1}$$

According to Davis and Rice the quantity B should mainly reflect the sum of the coulombic energy of mixing predicted by the RKK theory plus a term which arises from nearest neighbour dispersion interactions.

The numerical values of A and B depend greatly on the actual choice of the interionic distances. For example, if we use the original Pauling radii¹⁷ for the alkali metal ions instead of the Melnichak radii we obtain the following constants

$$A' = +36.3 \text{ kJ } \text{\AA}^{-2} \text{ mol}^{-1}$$

$$B' = -1650 \text{ kJ } \text{\AA}^2 \text{ mol}^{-1}$$

A plot of the left hand side of eqn. (4b) versus $\delta_{12}/(\alpha_1 - \alpha_2)$, where U_0^{++} and δ_{12} are calculated by use of the Pauling radii, is shown in Fig. 5. Except for the Li^+ -ion, where the Pauling radius is 0.60 \text{\AA} and the Melnichak radius 0.57 \text{\AA}, the two set of ionic radii differ only by 0.01 \text{\AA} or less. Actually

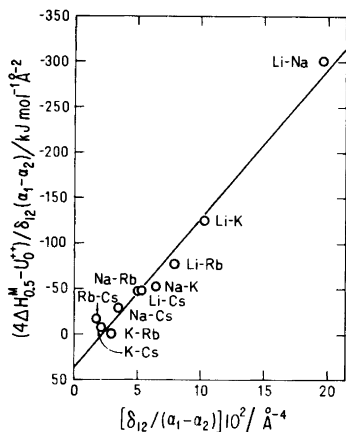


Fig. 5. Dependence of the quantity $(4\Delta H_{0.5}^M - U_0^{++})/\delta_{12}(\alpha_1 - \alpha_2)$ on the parameter $\delta_{12}/(\alpha_1 - \alpha_2)$ in mixtures of molten alkali hydroxides. Pauling's radii for the alkali metal ions are used.

very little is known about the interionic distances in the molten alkali hydroxides, and it does not seem possible to choose between the two sets of cationic radii. Furthermore, the choice of the thermochemical radius for the OH^- -ion also is open to question. Fortunately, small changes in $r(\text{OH}^-)$ cause relatively small changes in $\delta_{12}, \delta_{12}^2$, and U_0^{++} . Therefore, the fundamental conclusions in this discussion are not influenced by this choice.

Dantzer and Kleppa¹⁸ have expressed doubt whether the small non-zero values of the constant A in the nitrate, chloride, and bromide families are physically significant. However, for the fluorides,¹³ sulfates,¹⁴ carbonates,⁷ and hydroxides it is evident that significant positive values of A are obtained. In these families it seems that the cation-anion dispersion interactions may give rise to relatively large positive contributions to the enthalpy interaction parameters. These contributions vary linearly with the size parameter δ_{12} and with $(\alpha_1 - \alpha_2)$. This effect might account for the deviations from linearity in the plot of corrected interaction parameter versus δ_{12}^2 given in Fig. 3.

The data in Table 3 show that the lithium containing hydroxide mixtures exhibit quite large values of the asymmetry parameter b , which numerically increases sharply in the sequence $\text{Li-Na} < \text{Li-K} < \text{Li-Rb} < \text{Li-Cs}$. According to Blander's calculation¹⁰ of the higher order terms of the RKK theory it may be expected that this parameter should depend on ionic size through the third power of δ_{12} . Such a behaviour is in fact found for the lithium containing hydroxide mixtures as

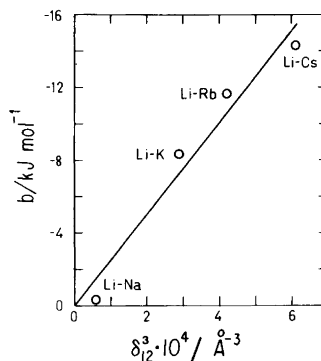


Fig. 6. Dependence of the asymmetry parameter b on the size parameter δ_{12}^3 for the mixtures of lithium hydroxide with the other alkali hydroxides. For the Li-K system the constant b from the linear plot has been used.

illustrated in Fig. 6. A similar dependence of b on δ_{12}^3 is found also for the lithium mixtures of other anion families.

Comparison with earlier data. Aghai-Khafri *et al.*¹ obtained the following values for the limiting partial molar excess enthalpies of potassium hydroxide in liquid sodium hydroxide and of sodium hydroxide in liquid potassium hydroxide, respectively.

$$H^{E,\infty}(\text{KOH}) = -2430 \pm 210 \text{ J mol}^{-1} *$$

$$(-2090 \pm 140 \text{ J mol}^{-1})$$

$$H^{E,\infty}(\text{NaOH}) = -3050 \pm 170 \text{ J mol}^{-1} *$$

$$(-2580 \pm 140 \text{ J mol}^{-1})$$

The data given in the parentheses are those obtained from the results of the present investigation. The agreement between the two sets of data is good when the very considerable experimental difficulties are taken into account.

From the NaOH branches of the liquidus and solidus curves of the phase diagram of Reshetnikov and Vilutis,³ Lumsden² calculated a Gibbs excess energy interaction parameter of about -1260 J mol^{-1} . This is about one-half of the corresponding values of the enthalpy interaction parameter obtained in the present work, and points toward small negative excess entropies. This is consistent with what is found in many simple fused salt mixtures.

The thermochemical radius of the hydroxide ion

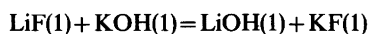
* According to least squares calculations carried out by the present authors $H^{E,\infty}(\text{KOH}) = -2410 \pm 350 \text{ J mol}^{-1}$ and $H^{E,\infty}(\text{NaOH}) = -2790 \pm 240 \text{ J mol}^{-1}$.

Table 5. Enthalpies of mixing in equimolar mixtures of liquid alkali hydroxides and fluorides ($4\Delta H_{0.5}^M/\text{kJ mol}^{-1}$).

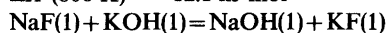
Alkali metals	Hydroxides ^a	Fluorides ^b
Li-Na	-6.95	-8.08
Li-K	-16.66	-19.45
Li-Rb	-15.60	-20.29
Li-Cs	-14.95	-16.15
Na-K	-2.34	-0.38
Na-Rb	-3.66	+0.38
Na-Cs	-3.18	(+3.55) ^c
K-Rb	+0.20	+0.36
K-Cs	+1.21	(+2.05) ^c
Rb-Cs	+0.25	-

^a This investigation. ^b Holm and Kleppa²² and Holm.²³ ^c Calculated from phase diagram data.

($r_{\text{OH}^-} = 1.40 \text{ \AA}$) is very close to the ionic radius of the fluoride ion ($r_{\text{F}^-} = 1.36 \text{ \AA}$). To a first approximation one therefore should expect the enthalpies of mixing of the alkali hydroxide mixtures to be comparable to those of the corresponding fluorides. The similarities of the alkali hydroxides and fluorides are also reflected in the small enthalpy changes of the following reciprocal reactions:



$$\Delta H^\theta(800 \text{ K}) = -12.1 \text{ kJ mol}^{-1} *$$



$$\Delta H^\theta(800 \text{ K}) = -3.1 \text{ kJ mol}^{-1} *$$

Table 5 shows results from the present investigation compared with data on the fluorides obtained by Holm and Kleppa²² and by Holm.²³ The consistency between the two sets of data is fairly good. Even so, there are some interesting systematic differences. Thus we note that the enthalpies of mixing of the lithium hydroxide containing systems consistently are less negative than those of the corresponding fluorides.

It is possible that these differences may be explained by the high ionic potential of the small Li^+ -ion, which would tend to limit the rotational freedom of the OH^- -ions in the melts, and perhaps even give rise to some formation of Li^+OH^- ion pairs. If the OH^- -ion is free to rotate (or rather "tumble"), the higher polarizability of the OH^- -ion ($\alpha_{\text{OH}^-} = 1.2 \text{ \AA}^3$)¹⁶ compared to the F^- -ion ($\alpha_{\text{F}^-} = 0.64 \text{ \AA}^3$),¹⁶ presumably would give rise to somewhat more negative mixing enthalpies in the hydroxides than in the fluorides. This is consistent with the new enthalpy data for the mixtures involving sodium and the larger alkali cations. Hence it is possible that the enthalpy of mixing data may reflect a structural difference between the liquid hydroxides and the liquid fluorides, which should be most pronounced for the lithium salts. This possible structural difference may also be involved in making the melting points lower in the hydroxides than in the fluorides. In this context, it is of interest to note that the highest melting alkali hydroxide is LiOH (m.p. 744 K), while the highest melting fluoride is NaF (m.p. 1269 K).

* The thermochemical data used are those tabulated in JANAF.²⁴ The fluorides are in a hypothetical state below their normal melting points.

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