

Enthalpies of Mixing in Binary Liquid Alkali Carbonate Mixtures

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The enthalpies of mixing in the binary liquid alkali carbonate mixtures have been determined by direct high temperature calorimetry. The measurements were performed over wide ranges of composition at temperatures from 1130 to 1180 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

$$4\Delta H_{0.5}^M = U_0^{++} + 33.7 \Delta\alpha \delta_{12} - 3970 \delta_{12}^2, \text{ kJ mol}^{-1}$$

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.

During the last 15 years a large number of binary molten salt systems have been studied by means of direct high temperature calorimetry. So far, however, the study by Østvold and Kleppa¹ of the liquid alkali sulfate mixtures is the only extensive investigation of systems 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.

Mixtures of molten alkali carbonates, which have the same A_2X charge structure constitute an important and interesting group of solutions, both from a theoretical point of view and because of their technological applications. One

of the authors (Andersen^{2,3}) has for some time been engaged in a study of the thermodynamic properties of molten alkali carbonates. The present determination of the enthalpies of mixing represents an important contribution to these investigations.

Prior to the present work only a few and not very accurate measurements of the thermodynamic excess properties in $Li_2CO_3 - Na_2CO_3$, $Li_2CO_3 - K_2CO_3$, and $Na_2CO_3 - K_2CO_3$ have been carried out. The enthalpies of mixing in the equimolar mixtures of these systems were determined by Barner and Andersen⁴ and by Broers and Ballegoy.⁵ The latter also studied two other compositions in addition to the equimolar mixtures as well as some ternary mixtures. In both of these earlier investigations a rather primitive direct calorimetric technique was used. A detailed discussion has been given by Andersen.³

Lumsden⁶ calculated excess chemical potentials in the systems $Li_2CO_3 - Na_2CO_3$ and $Li_2CO_3 - K_2CO_3$ from the phase diagrams of Janz and Lorenz⁷ and the thermochemical data of Janz *et al.*⁸ Furthermore, Lumsden concluded from calculations based on the CO_2 equilibrium pressures in the systems $CaCO_3 - Na_2CO_3$, $CaCO_3 - K_2CO_3$, and $CaCO_3 - NaKCO_3$ determined by Førland²³ that Na_2CO_3 and K_2CO_3 form ideal liquid solutions.

So far no thermodynamic investigations have been carried out on mixtures containing the heavier alkali metal ions Rb^+ and Cs^+ .

EXPERIMENTAL

Apparatus. All the calorimetric experiments were carried out in a single unit Calvet-type microcalorimeter suitable for work at tem-

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peratures 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.⁹

Due to the corrosive nature of molten alkali carbonates, these cannot, unlike most other salts which have been studied previously, be handled in fused silica containers and by the usual "break-off" technique. Experience has shown that the attack on Palau (20 % Pd - 80 % Au) in "acid" alkali carbonate melts, that is, in melts kept under a relatively high CO_2 pressure, may be considered as negligible.^{3,10} Therefore, this alloy was chosen as the only material in contact with the carbonate melts during the mixing experiments. These were carried out in an atmosphere of pure dry CO_2 .

The experimental arrangements inside the calorimeter proper are shown schematically in Fig. 1. The plunger as well as the dipper-crucible could be manipulated from outside the calorimeter proper.

Chemicals. The chemicals used in the present work were: Li_2CO_3 , Na_2CO_3 , and K_2CO_3 , Baker Chemical Co., Analytical Reagent; Rb_2CO_3 and Cs_2CO_3 , Kawecki Chemical Co., $\geq 99.8\%$.

Semiquantitative spectrographic analysis showed that the metallic impurities in the rubidium carbonate were 0.006 % Na, 0.07 % K, 0.06 % Cs, and others less than 0.01 %; in the cesium carbonate the impurities were 0.08 % Na, 0.01 % K, 0.04 % Rb, and others less than 0.002 %.

The alkali carbonates were dried in a vacuum

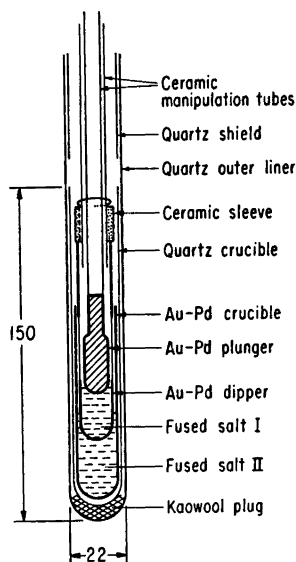


Fig. 1. Schematic diagram of experimental arrangements used for calorimetric measurements.

furnace at about 450 K for a period of 24 h or more. Since some of the alkali carbonates are very hygroscopic, the pick up of water during the weighing process was measured in separate experiments. Under the procedures used this was found to be less than 0.1 % for all salts and could be neglected.

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. Except for Li_2CO_3 - Cs_2CO_3 and Na_2CO_3 - Cs_2CO_3 , which were investigated at 1135 ± 1 K, all systems were studied at 1178 ± 1 K. Under these conditions the weight loss of the most volatile salt, Rb_2CO_3 , as determined in blank experiments, was about 0.3 % while that of Cs_2CO_3 was 0.12 %. The weight loss of Li_2CO_3 was of the same order of magnitude as that of Cs_2CO_3 . In spite of the relatively small vaporization losses, the attack by the vapours on the fused silica liner and shield was considerable, and the lower parts of these parts of the apparatus had to be rebuilt after ten to fifteen runs.

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 50 to 100 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.¹¹ Corrections were made for the heat pick-up of the gold pieces during the fall. These were determined in separate experiments and represented 1.7 % at 1135 K and 2.0 % at 1178 K.

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 dc amplifier and recorded on a Leeds & Northrup 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 K_2CO_3 - Rb_2CO_3 , K_2CO_3 - Cs_2CO_3 , and Rb_2CO_3 - Cs_2CO_3 systems, which have very small enthalpies of mixing, this relative error was much larger.

RESULTS

All the ten binary alkali carbonates were investigated, and the concentration dependence of the enthalpy of mixing was studied for all the lithium and sodium containing systems. For the three remaining systems (K_2CO_3 - Rb_2CO_3 , K_2CO_3 - Cs_2CO_3 , and Rb_2CO_3 - Cs_2CO_3) the heat effects were very small and only average values for mixtures close to the equimolar composition were determined.

The experimental results are tabulated in Table 1. In Figs. 2 and 3 the enthalpy interaction parameter, $\Delta H^M/N_1N_2$, is plotted *versus* the mol fraction of the salt with the smaller cation.

An attempt was made to fit the experimental data for the seven systems shown in Figs. 2 and 3 by the least-squares method to expressions of the form

$$\Delta H^M/N_1N_2 = a + bN_1 + cN_1N_2 \quad (1)$$

Except for Li_2CO_3 - K_2CO_3 , Li_2CO_3 - Rb_2CO_3 , and Li_2CO_3 - Cs_2CO_3 the straight lines gave the best fits. However, since the uncertainties in the enthalpy data for these three systems are relatively large, they are also represented by straight lines. In Table 2 we give the coefficients a and b as well as the enthalpies of mixing at the 50-50 composition.

The temperature dependence of the enthalpy of mixing was tested only for the Li_2CO_3 - Cs_2CO_3 system, through a single measurement at the equimolar composition at 1198 K. The result showed that the enthalpy of mixing is about 8% less negative at this temperature than at 1135 K.

DISCUSSION

The enthalpies of mixing are interpreted in light of the conformal solution theories for fused salts developed by Reiss, Katz, and Kleppa (RKK),¹² by Blander,¹³ and by Davis and Rice (DR).¹⁴

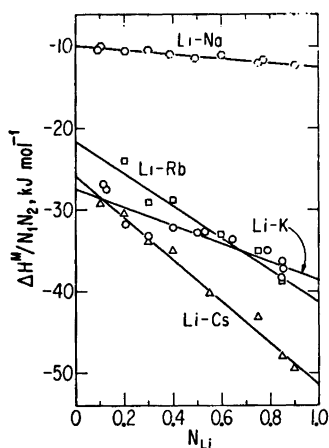
We have chosen to represent the enthalpy of mixing for a given binary system by $4\Delta H^M_{0.5}$, *i.e.*, by the calculated value of the interaction parameter, $\Delta H^M/N_1N_2$, at the equimolar composition. To these values we have applied a correction by estimating the values of U_0^{++} ,

Table 1. Molar enthalpies of mixing of binary liquid alkali carbonate mixtures. N_1 is the mol fraction of the salt with the smaller cation. $\lambda^M = \Delta H^M/N_1N_2$.

Mol fraction N_1	Total mol	ΔH^M kJ mol ⁻¹	λ^M kJ mol ⁻¹
Li_2CO_3-Na_2CO_3 (1178 K)			
0.1003	0.06502	-0.906	-10.038
0.2023	0.06502	-1.710	-10.594
0.2956	0.08346	-2.184	-10.489
0.3882	0.07253	-2.607	-10.975
0.4898	0.09487	-2.864	-11.460
0.6015	0.09248	-2.665	-11.117
0.7479	0.09969	-2.286	-12.125
0.7717	0.09522	-2.054	-11.656
0.8985	0.09008	-1.116	-12.240
Li_2CO_3-K_2CO_3 (1178 K)			
0.1134	0.06262	-2.711	-26.966
0.1243	0.06581	-2.995	-27.514
0.2047	0.05878	-5.203	-31.957
0.3012	0.07062	-7.024	-33.372
0.4001	0.07829	-7.750	-32.288
0.4996	0.07876	-8.229	-32.916
0.5343	0.09001	-8.158	-32.786
0.6457	0.07736	-7.705	-33.681
0.7915	0.10488	-5.781	-35.028
0.8459	0.10207	-5.006	-38.401
0.8489	0.09987	-4.661	-36.334
0.8546	0.10678	-4.630	-37.263
Li_2CO_3-Rb_2CO_3 (1178 K)			
0.2004	0.06597	-3.849	-24.022
0.3014	0.06776	-6.142	-29.171
0.3978	0.06764	-6.916	-28.871
0.4995	0.09191	-8.326	-33.305
0.5958	0.07184	-7.925	-32.908
0.7498	0.10813	-6.573	-35.037
0.8502	0.10940	-4.937	-38.764
Li_2CO_3-Cs_2CO_3 (1135 K)			
0.1000	0.04870	-2.636	-29.289
0.2001	0.04773	-4.879	-30.482
0.3002	0.04651	-7.146	-34.016
0.4002	0.05836	-8.414	-35.052
0.5507	0.08233	-9.966	-40.278
0.7509	0.09194	-8.088	-43.240
0.8498	0.08423	-6.134	-48.057
0.9001	0.08239	-4.460	-49.600
Na_2CO_3-K_2CO_3 (1178 K)			
0.1643	0.05879	-0.697	-5.079
0.2627	0.05655	-1.071	-5.531
0.2693	0.05807	-1.076	-5.468
0.3986	0.06681	-1.323	-5.519
0.5995	0.06560	-1.347	-5.611
0.8301	0.06682	-0.846	-6.000
0.8365	0.06725	-0.855	-6.255

Table 1. Continued.

$\text{Na}_2\text{CO}_3 - \text{Rb}_2\text{CO}_3$ (1178 K)			
0.1970	0.05538	-1.281	-8.096
0.1996	0.05523	-1.352	-8.464
0.3002	0.06601	-1.739	-8.276
0.4360	0.06181	-2.059	-8.372
0.4954	0.07341	-2.134	-8.535
0.4990	0.09195	-2.141	-8.564
0.6994	0.08837	-1.806	-8.590
0.8000	0.07450	-1.351	-8.443
0.8651	0.07985	-0.983	-8.422
$\text{Na}_2\text{CO}_3 - \text{Cs}_2\text{CO}_3$ (1135 K)			
0.1985	0.03297	-1.389	-8.729
0.3594	0.06057	-2.031	-8.819
0.5524	0.07220	-2.124	-8.590
0.7499	0.07946	-1.622	-8.649
0.8500	0.08457	-1.070	-8.395
$\text{K}_2\text{CO}_3 - \text{Rb}_2\text{CO}_3$ (1178 K)			
0.699	0.0807	< 0.002	< 0.010
$\text{K}_2\text{CO}_3 - \text{Cs}_2\text{CO}_3$ (1178 K)			
0.4987	0.06184	0.0719	0.288
0.6967	0.06951	0.0567	0.268
0.8017	0.06128	0.0726	0.457
$\text{Rb}_2\text{CO}_3 - \text{Cs}_2\text{CO}_3$ (1178 K)			
0.3007	0.04943	0.0387	0.188
0.5009	0.05373	0.0473	0.185

Fig. 2. Plots of $\Delta H^M/N_1N_2$ versus N_{Li} for $\text{Li}_2\text{CO}_3 - \text{Alk}_2\text{CO}_3$ mixtures.

the change on mixing in the London - van der Waals dispersion energy between next nearest neighbour cations. The method of estimating U_0^{++} is the same as previously used by Hersh

and Kleppa.¹⁵ 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 $0.75 I$. We have made use of the ionic radii of the alkali metals given by Melnichak and Kleppa.¹⁶ The same method and values were used also by Østvold and Kleppa.¹ The relevant interatomic distances were calculated from the ionic radii of the ions. For the carbonate anion we adopted the thermochemical radius, $r(\text{CO}_3^{2-}) = 1.85 \text{ \AA}$, as given by Kapustin-skii.¹⁷ The importance of the choice of ionic radii will be discussed later. The polarizabilities are those reported by Tessman *et al.*¹⁸ Table 3 shows the ionic radii, polarizabilities, and ionization potentials used in the calculations. In Fig. 4 the corrected interaction parameter, $4\Delta H^M_{0.5} - U_0^{++}$, is plotted versus the square of the distance parameter, δ_{12} ($\delta_{12} = (d_1 - d_2)/d_1d_2$ where d_1 and d_2 are characteristic inter-ionic distances in the two salts). It will be noticed that the points representing the $\text{Li}_2\text{CO}_3 - \text{Na}_2\text{CO}_3$, $\text{Li}_2\text{CO}_3 - \text{K}_2\text{CO}_3$, and $\text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3$ 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

$$\Delta H^M/N_1N_2 = U_0 + U_1\delta_{12} + U_2\delta_{12}^2 \quad (2)$$

According to the DR theory the leading term in U_1 , for a given common anion family, should

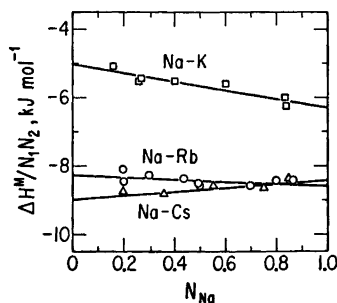
Fig. 3. Plots of $\Delta H^M/N_1N_2$ versus N_{Na} for $\text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3$, $\text{Na}_2\text{CO}_3 - \text{Rb}_2\text{CO}_3$, and $\text{Na}_2\text{CO}_3 - \text{Cs}_2\text{CO}_3$ mixtures.

Table 2. Integral enthalpies of mixing for binary alkali carbonates ($\Delta H^M = N_1 N_2 (a + b N_1)$ kJ mol⁻¹; N_1 is mol fraction of salt with the smaller cation).

System	Temp., K	a	b	$4\Delta H_{0.5}^M$	S.D.
Li-Na	1178	-9.90	-2.59	-11.19	0.25
Li-K	1178	-27.56	-11.00	-33.06	1.49
Li-Rb	1178	-21.67	-19.58	-31.46	1.48
Li-Cs	1135	-25.94	-25.30	-38.59	1.03
Na-K	1178	-5.03	-1.27	-5.66	0.16
Na-Rb	1178	-8.26	-0.32	-8.42	0.14
Na-Cs	1135	-8.89	+0.47	-8.66	0.11
K-Rb	1178			≤ 0.01	
K-Cs	1178			+0.34	
Rb-Cs	1178			+0.19	

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. (2) as follows:

$$\Delta H^M / N_1 N_2 = U_0^{++} + A(\alpha_1 - \alpha_2)\delta_{12} + B\delta_{12}^2 \quad (3a)$$

or for $N_1 = N_2 = 0.5$

$$(4\Delta H_{0.5}^M - U_0^{++}) / (\alpha_1 - \alpha_2)\delta_{12} = A + B\delta_{12} / (\alpha_1 - \alpha_2) \quad (3b)$$

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

A plot of the left hand side of eqn. (3b) versus $\delta_{12} / (\alpha_1 - \alpha_2)$ is presented in Fig. 5, and indicates that the alkali carbonate family is in fact very well represented by this equation. A least square treatment of all the data yields the following values

$$A = +33.7 \text{ kJ } \text{\AA}^{-2} \text{ mol}^{-1}$$

$$B = -3970 \text{ kJ } \text{\AA}^2 \text{ mol}^{-1}$$

Table 3. 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	7263
Na ⁺	0.96	0.95	0.41	4544
K ⁺	1.34	1.33	1.33	3059
Rb ⁺	1.49	1.48	1.98	2644
Cs ⁺	1.68	1.69	3.34	2259

^a Melnichak and Kleppa,¹⁶ ^b Pauling,¹⁹ ^c Tessman *et al.*,¹⁸ ^d *Handbook of Chemistry and Physics*.²⁴

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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 radii¹⁹ for the alkali metal ions instead of the Melnichak radii we obtain the following constants

$$A' = +69.5 \text{ kJ } \text{\AA}^{-2} \text{ mol}^{-1}$$

$$B' = -5150 \text{ kJ } \text{\AA}^2 \text{ mol}^{-1}$$

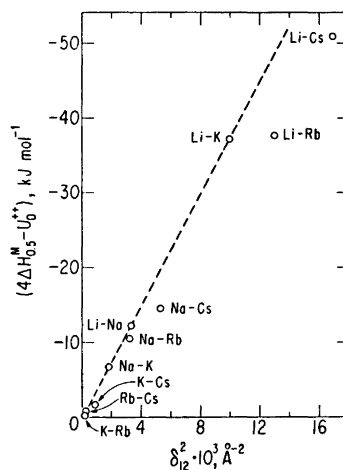


Fig. 4. Dependence of the corrected enthalpy interaction parameter, $4\Delta H_{0.5}^M - U_0^{++}$, on the size parameter δ_{12}^2 in alkali carbonate mixtures.

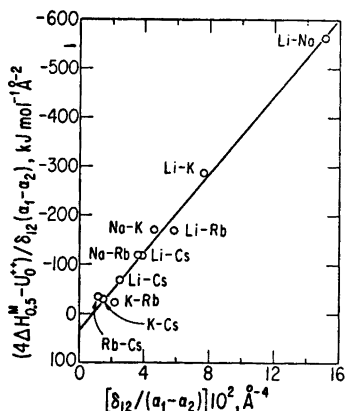


Fig. 5. Dependence of the quantity $(4\Delta H_{0.5}^M - U_0^{++})/\delta_{12}(\alpha_1 - \alpha_2)$ on the parameter $\delta_{12}/(\alpha_1 - \alpha_2)$ in mixtures of molten alkali carbonates. Melnichak's radii for the alkali metal ions are used.

A plot of the left hand side of eqn. (3b) 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. 6. Except for the Li^+ -ion, where the Pauling radius is 0.60 \AA and the Melnichak radius 0.57 \AA , the two set of ionic radii differ by only 0.01 \AA or less. In fact very little is known about the interionic distances in the molten alkali carbonates, and it does not seem possible to choose between the two sets of cationic radii. Furthermore, the choice of the thermochem-

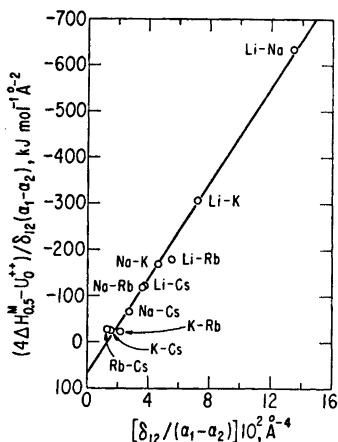


Fig. 6. Dependence of the quantity $(4\Delta H_{0.5}^M - U_0^{++})/\delta_{12}(\alpha_1 - \alpha_2)$ on the parameter $\delta_{12}/(\alpha_1 - \alpha_2)$ in mixtures of molten alkali carbonates. Pauling's radii for the alkali metal ions are used.

ical radius for the CO_3^{2-} -ion also is open to serious question. It was argued by Zarzycki²⁰ that the larger alkali cations may tend to occupy sites near the corners of the carbonate triangle, while the smaller cations may be located closer to the centre of the carbonate anion. Fortunately, small changes in $r(\text{CO}_3^{2-})$ cause relatively small changes in δ_{12} , δ_{12}^2 , and U_0^{++} . Therefore the fundamental conclusions in this discussion are not influenced by this choice.

As pointed out in the introduction the only family of charge type $\text{A}_2\text{X}-\text{B}_2\text{X}$ which has been thoroughly investigated calorimetrically is the alkali sulfate family. Østvold and Kleppa studied these mixtures using essentially the same calorimetric equipment as we have used in the present investigation. They obtained the following values for the constants in eqn. (3b), based on the Melnichak radii for the alkali metal ions and $r(\text{SO}_4^{2-}) = 2.30 \text{ \AA}$

$$A = +68.6 \text{ kJ \AA}^{-2} \text{ mol}^{-1}$$

$$B = -5900 \text{ kJ \AA}^2 \text{ mol}^{-1}$$

Clearly, when we take the different anion radii into account the enthalpy of mixing data for the carbonate and the sulfate families show considerable similarity.

Dantzer and Kleppa²¹ 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,¹⁶ sulfates and carbonates it is evident that significant positive values of A are obtained. In these families it seems that the cation-anion dispersion interactions may

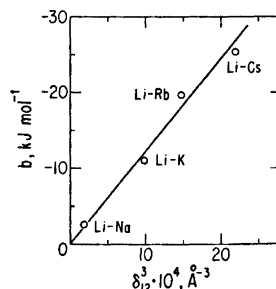


Fig. 7. Dependence of the asymmetry parameter b on the size parameter δ_{12}^3 for the mixtures of lithium carbonate with the other alkali carbonates.

Table 4. Enthalpies of mixing in binary molten alkali carbonates of equimolar composition. The temperatures of investigation are given in parentheses in degrees Kelvin.

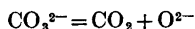
	$4\Delta H_{0s}^M$, kJ mol ⁻¹ Li-Na	Li-K	Na-K
This work	-11.19(1178)	-33.06(1178)	-5.66(1178)
Broers and Ballegoy ⁵	-11.7(≈1200)	-33.5(≈1200)	-5.86(≈1200)
Barner and Andersen ⁴	-14.6(1153)	-35.1(1189)	-7.37(1189)
Lumsden ⁶	-10.0 ^a	-31.0 ^a	0.0 ^a (1202)

^a Indirectly calculated (see Introduction).

give rise to relatively large positive contributions to the enthalpy interaction parameters. These contributions vary linearly with the size parameters 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. 4.

The data in Table 2 show that the lithium containing carbonate mixtures exhibit quite large values of the asymmetry parameter b , which numerically increase sharply in the sequence Li-Na < Li-K < Li-Rb < Li-Cs. According to Blander's calculation¹³ 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 carbonate mixtures as illustrated in Fig. 7. A similar dependence of b on δ_{12}^3 is found also for the lithium sulfate mixtures. However, for the latter the slope is $-22\ 100$ kJ Å³ mol⁻¹ while for the carbonate mixtures it is $-12\ 300$ kJ Å³ mol⁻¹. The tendency of increasing negative slope with increasing anionic size is also evident in the lithium containing alkali halide systems. Calculations based on the data reviewed by Melnichak¹⁶ give the slopes (-2000), -4200 , -5200 , and -9600 kJ Å³ mol⁻¹ for the fluoride, chloride, bromide, and iodide systems, respectively. A similar behaviour is not found in the sodium containing systems.

Influence of the carbonate dissociation. At the high temperatures used in the present investigation the thermal decomposition of the carbonate ions may have to be considered



This dissociation is to some extent prevented by carrying out the experiments in an atmos-

phere of pure CO₂. The carbonate dissociation depends on the cations present in the melt and the dissociation constant decreases in the sequence Li > LiNa > LiK > Na > NaK > K where the double cation symbol refers to the 50-50 mixtures.

When the two salts are mixed, the association process $\text{CO}_2 + \text{O}^{2-} \rightarrow \text{CO}_3^{2-}$ will take place to a limited extent, thus giving rise to a positive contribution to the observed enthalpy. The dissociation constants as well as crude data for the enthalpies of dissociation for Li₂CO₃, Na₂CO₃, K₂CO₃ and their mixtures are given by Andersen.^{2,3*} However, since the accuracy of the data is relatively small and no information is available for Rb₂CO₃ and Cs₂CO₃, we have chosen to present the uncorrected enthalpies of mixing only.

Temperature dependence for the enthalpy of mixing. The single measurement on the equi-

* The dissociation constants, K_d , for the process $\text{CO}_3^{2-} = \text{CO}_2 + \text{O}^{2-}$ in Li₂CO₃, Na₂CO₃, and K₂CO₃ at 1178 K are 4.53×10^{-8} , 5.59×10^{-8} , and 1.94×10^{-8} , respectively. ($K_d \approx [N(\text{O}^{2-})/N(\text{CO}_3^{2-})] [p(\text{CO}_2)/p^\ominus]$ where the standard pressure, p^\ominus , is 101.325 kPa). The respective standard enthalpies of dissociation are 190.8, 298.7, and 341.8 kJ mol⁻¹.

Example of estimate: Since $p(\text{CO}_2)$ is equal to the standard pressure and $N(\text{CO}_3^{2-}) \approx 1$, it follows, that the change in the amount of O²⁻-ions, Δn , during the mixing process, e.g., when half a mol each of Li₂CO₃ and K₂CO₃ are mixed is: $\Delta n \approx K_d(\text{Li}_2\text{CO}_3) - \frac{1}{2}K_d(\text{Li}_2\text{CO}_3) - \frac{1}{2}K_d(\text{K}_2\text{CO}_3) = -2.26 \times 10^{-3}$ mol. Therefore, our estimate of the enthalpy of association is: $\Delta H_{\text{ass}} \approx -(2.26 \times 10^{-3}) \times (190\ 800 + 341\ 800)/2 = -600$ J which is about 7% of the calorimetrically determined enthalpy of mixing.

The corresponding values estimated for the LiNa- and NaK-systems are -500 and -1 J, respectively. The values for the LiRb- and LiCs-systems are probably of the same order of magnitude as that for the LiK-system, while those for the systems which do not contain Li are of the order -1 J.

molar Li_2CO_3 – Cs_2CO_3 mixture at 1198 K indicates that the enthalpy of mixing becomes less exothermic with increasing temperature. The change in heat capacity upon mixing, ΔC_p , is calculated to be of the order $+12 \text{ J K}^{-1} \text{ mol}^{-1}$. The positive value of ΔC_p is in accordance with the results of Østvold and Kleppa¹ for the (Li–Na)₂SO₄ system and of Hong and Kleppa²² for the (Li–K)F system. Hong and Kleppa attempt to explain the numerically smaller values in the enthalpy of mixing at the higher temperatures in terms of the thermal expansion of the salts. They propose the following simple approximate relation between ΔC_p and ΔH^M

$$\Delta C_p = -\frac{2}{3}\Delta H^M\gamma_1 \quad (4)$$

where γ_1 is the volume coefficient of expansion of component 1. This gives the right sign and the right order of magnitude of ΔC_p for the (Li–K)F system. However, for the (Li–Cs)₂CO₃ system the calculated maximum value of ΔC_p is only $1.5 \text{ J K}^{-1} \text{ mol}^{-1}$, i.e., nearly one order of magnitude lower than the experimental value. However, the latter value probably is not very accurate since only one measurement was carried out at 1198 K. Also the increased dissociation of the carbonate ions and the increased volatility of the salts at the higher temperature were not taken into account.

Comparison with earlier data. In Table 4 we compare our new results with earlier data, when such data are available. The earlier data are limited to the 50–50 composition. The agreement with the results of Broers and Ballegoy is quite good. However, Broers and Ballegoy concluded from their results that the experimental uncertainties did not allow a closer analysis of the asymmetry in the ΔH^M curves.

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