

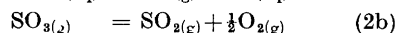
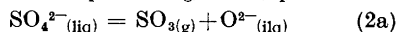
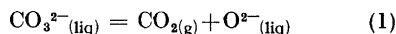
Enthalpies of Mixing in Liquid Mixtures of Lithium Sulphate and Sodium Sulphate

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The thermochemistry of the binary mixtures formed by fused salts of the common anion type AlK_1X-AlK_2X , X^- being one of the halides, F^- , Cl^- , Br^- , or I^- , have been the subject of intensive investigations^{1,2} for the period of the last ten years. However, of systems with a common oxyanion like NO_3^- , CO_3^{2-} , SO_4^{2-} , only enthalpies of mixing of the nitrates³ have been measured.

The nitrates are low melting salts and do not constitute any serious problem from the experimental point of view. The higher melting carbonates and sulphates, however, are much more difficult to handle in the molten state. They melt in the temperature range 800–1000°C, and may disproportionate according to one of the following equations:



The thermochemistry of the molten carbonates and sulphates is of interest since they may be used as heat transport media. Because of their acid-base properties they cannot be kept in silica containers like the nitrates. However, a special technique and experimental arrangement developed by Holm and Kleppa¹ for studying the thermochemistry of mixtures of molten fluorides, also made it possible to study mixtures of molten alkali sulphates.

The calorimeter and the experimental arrangements were the same as described in Fig. 1 in the paper by Holm and Kleppa,¹ except for the graphite sleeve which was removed, and the graphite plunger which was replaced by a platinum plunger. The experimental set-up is shown in Fig. 1.

The following chemicals were used: Na_2SO_4 , anhydrous powder, Analytical Reagent, J. T. Baker, was dried for several hours at 120°C. $Li_2SO_4 \cdot H_2O$, Fisher Certi-

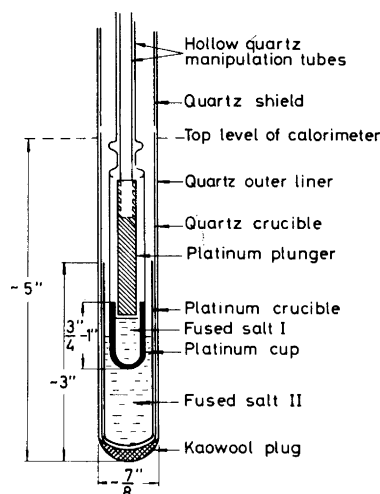


Fig. 1. Semi-schematic illustration of experimental arrangements inside the calorimeter proper.

fied Reagent, was dried for at least 2 h at about 140°C and was then considered free from water.

Table 1. Enthalpies of mixing in liquid mixtures of lithium sulphate with sodium sulphate.

Composition $X_{Li_2SO_4}$	ΔH^M , Cal/mole	$\Delta H^M/(1-X)X$
0.0800	-121	-1644
0.1520	-213	-1652
0.1972	-285	-1800
0.2584	-365	-1905
0.3068	-406	-1909
0.3740	-467	-1994
0.4865	-541	-2166
0.6017	-525	-2247
0.7085	-473	-2291
0.7964	-365	-2250
0.8072	-348	-2236
0.8495	-281	-2199
0.9001	-192	-2133
0.9051	-183	-2150

In the system $Li_2SO_4-Na_2SO_4$ 14 mixtures were examined. The results are given in Table 1 and plotted in Fig. 2. The

Table 2. Summary of enthalpy of mixing data for $(\text{Li}^+ - \text{Na}^+)X^-$ mixtures.
 $\Delta H^M = X_{\text{Li}}(1 - X_{\text{Li}})(a + bX_{\text{Li}} + cX_{\text{Li}}^2)$ cal.

System	Temp(°C)	a	b	c	Ref.
$(\text{Li}^+ - \text{Na}^+)\text{F}^-$	1008	-1900	- 60	0	(1)
$(\text{Li}^+ - \text{Na}^+)\text{Cl}^-$	740	-1120	(0)	(0)	(2)
$(\text{Li}^+ - \text{Na}^+)\text{Br}^-$	690	- 710	- 140	0	(2)
$(\text{Li}^+ - \text{Na}^+)\text{NO}_3^-$	345	- 464	- 11.5	0	(3)
$(\text{Li}^+ - \text{Na}^+)_2\text{SO}_4^{2-}$	900	-1388	-2390	+1683	this work
$1/4 (\text{Li}^+ - \text{Na}^+)\text{SO}_4^{2-}$		- 395	- 600	+ 420	

enthalpies of mixing divided by the product of the mole fractions $X(1-X)$ were fitted through a least square treatment to $\Delta H^M = X(1-X)(-1388 - 2390X + 1683X^2)$ X being the mole fraction of lithium sulphate.

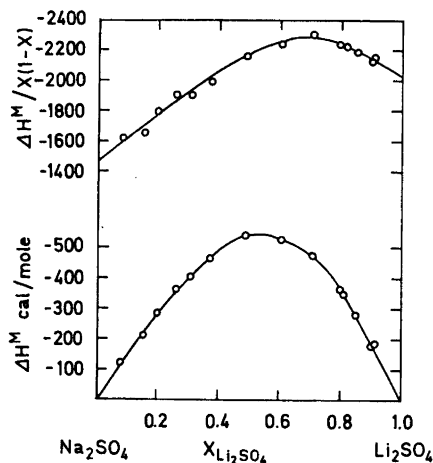


Fig. 2. Enthalpies of mixing in sodium sulphate-lithium sulphate liquid mixtures at 900°C.

In Table 2 enthalpies of mixing expressed as $\Delta H^M = X_{\text{Li}}(1 - X_{\text{Li}})(a + bX_{\text{Li}} + cX_{\text{Li}}^2)$ are compared for mixtures of different anions. As can be seen the value of a increases from -1900 in the fluoride system to -347 in the sulphate system with increasing size of the anion.

The radii given for the two oxyanions NO_3^- and SO_4^{2-} are the thermochemical radii.

	a, cal	$r(X^-)$, Å
F^-	-1900	1.36
Cl^-	-1120	1.81
Br^-	- 710	1.95
NO_3^-	- 464	1.89
SO_4^{2-}	- 347	2.30

The most interesting feature of the $(\text{Li}^+ - \text{Na}^+)_2\text{SO}_4^{2-}$ system is the large asymmetry in the enthalpy of mixing data which is shown by the value of b , ($b = -600$ cal). This large asymmetry is probably due to a change in the nearest neighbour interactions. A mixture with a high lithium sulphate content seems to be more favorable from an electrostatic point of view than a mixture with a high content of sodium sulphate. This could be due to preferred cation sites around the sulphate anion in the mixture, as suggested by several authors, among them Zarzycki.⁴

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