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High Temperature Heat Content and Fusion Properties for
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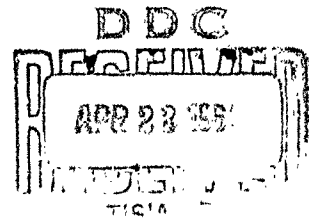
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High Temperature Heat Content and Fusion Properties for
Binary Carbonate Mixtures: Li, K/CO₃ and Na, K/CO₃

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ABSTRACT

The enthalpy changes between temperatures ranging from 150° to 900°C have been measured by drop calorimetry for the equimolar Na, K/CO₃ minimum melting mixture (m. pt. 710°C) and the equimolar Li, K/CO₃ mixture (m. pt. 505°C). Heats of fusion (kcal mol⁻¹) thus determined are: Na, K/CO₃, 4.7; Li, K/CO₃, 8.7, respectively. Entropies of fusion and specific heats are likewise reported. The heat of mixing (kcal mol⁻¹) and the excess entropy of mixing (cal deg⁻¹ mol⁻¹) at 898°C are, respectively, +1.8 and +0.2 for the Na, K/CO₃ mixture, and -0.1 and -1.5 for the Li, K/CO₃ mixture. The thermodynamic relations are discussed.

Introduction

The high temperature heat content and fusion properties for Li₂CO₃, Na₂CO₃, K₂CO₃ and the ternary eutectic mixture have been reported¹ from this laboratory. Thermal data for binary mixtures of the alkali metal carbonates appear nonexistent. This communication reports the results for the temperature range from 150° to 900°C for two binary mixtures, the equimolar minimum melting mixture (m. pt. 710°C) in the Na₂CO₃-K₂CO₃ system, and the equimolar mixture (m. pt. 505°C), in the Li₂CO₃-K₂CO₃ system. Heats and entropies of mixing, calculated from these data, are also reported and discussed in the light of current viewpoints for inorganic ionic melts.

Experimental

The Li₂CO₃, Na₂CO₃, and K₂CO₃ (analytical reagent grade

chemicals) were dried to constant weight under a CO_2 atmosphere at 600°C and stored over P_2O_5 in desiccators until used.

The high-temperature phase-transition calorimeter and its operation were the same as used previously and have been described elsewhere in detail;^{2,3} the calorimetric assembly is capable of measuring entropy changes greater than $1.5^\circ/\text{T}$ cal deg⁻¹ mol⁻¹. The carbonates were contained in thin "ampoules" of Au-Pd alloy (80 wt. % Au) and these ampoules were hermetically sealed in stouter Pt crucibles. Copper, hermetically sealed in platinum, served for calibration of the calorimetric assembly. As noted previously, the water equivalent of the calorimeter showed a slight linear dependence on the initial temperature of the capsule; this source of error was minimized by constructing calibration and sample capsules as similar in heat content as possible.

25° Correction: The enthalpy corrections, for the small temperature difference between the final calorimeter temperature and 25°C , were in all cases less than 1% of the total enthalpy change.

Results

Heat content changes are shown in Figure 1 for the temperature range investigated. The results for the coefficients of molar enthalpy and heat capacity functions, and the solid-state transition and fusion parameters are in Tables 1 and 2, respectively. The standard deviation from the least squares analysis of the data for the two systems (Fig. 1) was 0.1 kcal.

$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$: Reisman⁴ has reported solid-state transitions at 422°C in K_2CO_3 and at 410°C in Li_2CO_3 , while Jaffrey⁵ has noted two transitions in Li_2CO_3 , at 410°C and 465°C , respectively. These transitions were not detectable in the mixture by least-squares analyses of the present work (Fig. 1). The observed results for the fusion transition (Fig. 1, A) are in Table 2.

$\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$: In Na_2CO_3 , two transitions have been reported by Reisman⁴ (355° and 485°C , respectively) and by Jaffrey⁵ (360° and 480°C , respectively), while four polymorphic forms were reported by Khlapora:⁶ α , room temperature to $340^\circ\text{-}350^\circ\text{C}$; β , $340^\circ\text{-}350^\circ$ to $470^\circ\text{-}485^\circ\text{C}$; γ ,

470°-485° to 565°-620°C; and δ , above 560° to 710°C (melting point). In K_2CO_3 , Reisman⁴ noted one transition at 422°C. A least-squares analysis of the data for the mixture (Fig. 1) indicated the results could be expressed, within the limits of accuracy ($\pm 1\%$), by the distinctly separate equations for the solid-state temperature ranges: 160°-355°C, 355°-422°C, 422°-485°C, and 485°-710°C (Table 1). The bracketed values for the solid-state transitions at 355° and 422°C (Table 2 and Fig. 1, E, B) indicate that these are indirect values, calculated from the enthalpy equations. The 485°C transition (Table 2 and Fig. 1, C) was directly observed. The parameters for the fusion transition (Fig. 1, B) are in Table 2.

Discussion

The temperature dependence of the heats of fusion and entropy of fusion are given by:

$$\Delta H_T = \Delta H_{T_m} + \int_T^{T_m} \Delta C_p dT \quad (1)$$

$$\text{and } \Delta S_T = \Delta S_{T_m} + \int_T^{T_m} \frac{\Delta C_p}{T} dT \quad (2)$$

At constant temperature, the expressions for a mixture are:

$$\Delta H_M = X_A \Delta H_A + X_B \Delta H_B + \Delta H_{mix} \quad (3)$$

$$\text{and } \Delta S_M = X_A \Delta S_A + X_B \Delta S_B + \Delta S_{mix}^* + \Delta S_{mix}^E \quad (4)$$

where A and B are the pure components of the binary mixture, the subscript M refers to the mixture, the other symbols have the conventional significance, and ΔS_{mix}^* is simply 1.363 e.u. for a binary mixture.

The difference in heat capacity [$C_{p(\text{solid})} - C_{p(\text{melt})}$] in equation (1) and equation (2) is given by:

$$\Delta C_p = -a' + b'T \quad (5)$$

The coefficients a' and b' are given in Table 3. The C_p equations of the solid mixtures were calculated from the data of the pure components and the appropriate summation, $\sum X_i C_{pi}$; for the liquid mixtures, the

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equations were those experimentally observed. From equations (1), (2), (3), and (4), the heats and excess entropies of mixing for the two binary mixtures were calculated at the melting points of the highest melting component, K_2CO_3 (898°C). The results are in Table 4, together with the values for the ternary eutectic for comparison.

Examination of the values for the heats and excess entropies of mixing relative to the known liquidus-solidus phase equilibria^{4,7} is of interest. Where a solid solution from two ionic salts is formed with cations of the same charge and a common anion, the value of ΔH_{mix} is always positive^{8,9} when a chemical compound is formed, the value of ΔH_{mix} is large and always negative;⁹ for similar binary systems where neither solid solutions nor compounds are formed, the heats of mixing are always negative and not so large.⁸ It is apparent (Table 4) that for the system of known solid solutions,⁴ Na, K/CO₃, ΔH_{mix} is positive as would be predicted from the preceding generalizations; for the other binary systems, ΔH_{mix} is negative and small. The phase diagram shows⁷ that compound, (LiK)CO₃, melts congruently at a rather flat maximum (505°C) and is closely flanked by two eutectic mixtures of 42.7 and 62.0 mol. % Li₂CO₃, both melting in this temperature range (i.e., 498° and 488°C, respectively). The very small heat of mixing observed for the equimolar Li, K/CO₃ mixture undoubtedly reflects these features of the phase equilibrium diagram. Relative to the values for the excess entropies of mixing (Table 4), randomization in melts from the binary solid-solution system (Na, K/CO₃) appears practically ideal. For the Li, K/CO₃ binary and the Li, Na, K/CO₃ ternary mixtures the randomization appears markedly less than would be predicted for ideal mixing in the liquid state.

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Table 1.

Coefficients of Molar Enthalpy and Heat Capacity Functions

$$H_T - H_{298.2} = aT + bT^2 + c; C_p = a + 2 bT$$

<u>Carbonate Mixture</u>		<u>Temp. Range</u>	<u>a</u>	<u>b x 10³</u>	<u>c x 10³</u>
<u>Composition</u>	<u>Phase</u>	<u>(°K)</u>	<u>(cal mol⁻¹)</u>		
Li ₂ CO ₃ -K ₂ CO ₃ (50-50 mol %)	S	457-778	33.82	-	-11.24
	L	778-1200	44.65	-	-10.96
(m. 505°C)					
Na ₂ CO ₃ -K ₂ CO ₃ (50-50 mol %)	S	440-628	34.24	-	-10.98
	S	628-695	43.50	-	-16.71
	S	695-758	65.05	-	-31.64
	S	758-983	47.63	-	-17.82
	L	983-1197	44.26	-	-9.84

Table 2.

Heats of Transition and Heats and Entropies of Fusion

<u>Carbonate Mixture</u>		<u>ΔH_{tr}</u>	<u>ΔH_f</u>	<u>ΔS_f</u>
<u>Composition</u>	<u>Temp. ($^{\circ}\text{C}$)</u>	(cal mol $^{-1}$)	(kcal mol $^{-1}$)	(e.u.)
Li ₂ CO ₃ -K ₂ CO ₃ (50-50 mol %)	505	-	8.7 \pm 0.1	11.2 \pm 0.1
	355	*(88)	-	-
Na ₂ CO ₃ -K ₂ CO ₃ (50-50 mol %)	422	*(55)	-	-
	485	606	-	-
	710	-	4.7 \pm 0.1	4.7 \pm 0.1

*The brackets indicate that these values were too small to gain directly from the graphs and were accordingly calculated from the enthalpy data.

Table 3

Coefficients of the Heat Capacity Difference Function

$$[C_p (\text{solid}) - C_p (\text{liquid}) = a' + b'T]$$

System	-a'	b' x 10 ³
Li ₂ CO ₃ ⁽¹⁾	27.03	29.20
Na ₂ CO ₃ ⁽²⁾	25.85	24.60
K ₂ CO ₃ ⁽³⁾	17.76	15.42
Li ₂ CO ₃ -K ₂ CO ₃	33.1	34.4
Na ₂ CO ₃ -K ₂ CO ₃	31.3	31.2

Table 4.

Heats and Entropies of Mixing

Temp. (°C)	ΔH_m (kcal mol ⁻¹)	ΔS_e (e.u.)
<u>Li₂CO₃-K₂CO₃ (50-50 mol %; m. pt. 505°C)</u>		
898	-0.1 ± 0.1	-1.5 ± 0.1
<u>Na₂CO₃-K₂CO₃ (50-50 mol %; m. pt. 701°C)</u>		
898	+1.8 ± 0.1	+0.2 ± 0.1
<u>Li₂CO₃ (43.5), Na₂CO₃ (31.5), K₂CO₃ (25.0); (m. pt. 397°C)</u>		
898	-0.8 ± 0.2	*-2.8 ± 0.2

*The value of ΔS_e for the ternary is given in reference 1 as +1.3 and appears in error due to the addition rather than subtraction of the ideal entropy of mixing term.

Fig. 1. Heat content changes as a function of temperature for binary carbonate mixtures.

Legend: () Li_2CO_3 (50%), K_2CO_3 (50%);

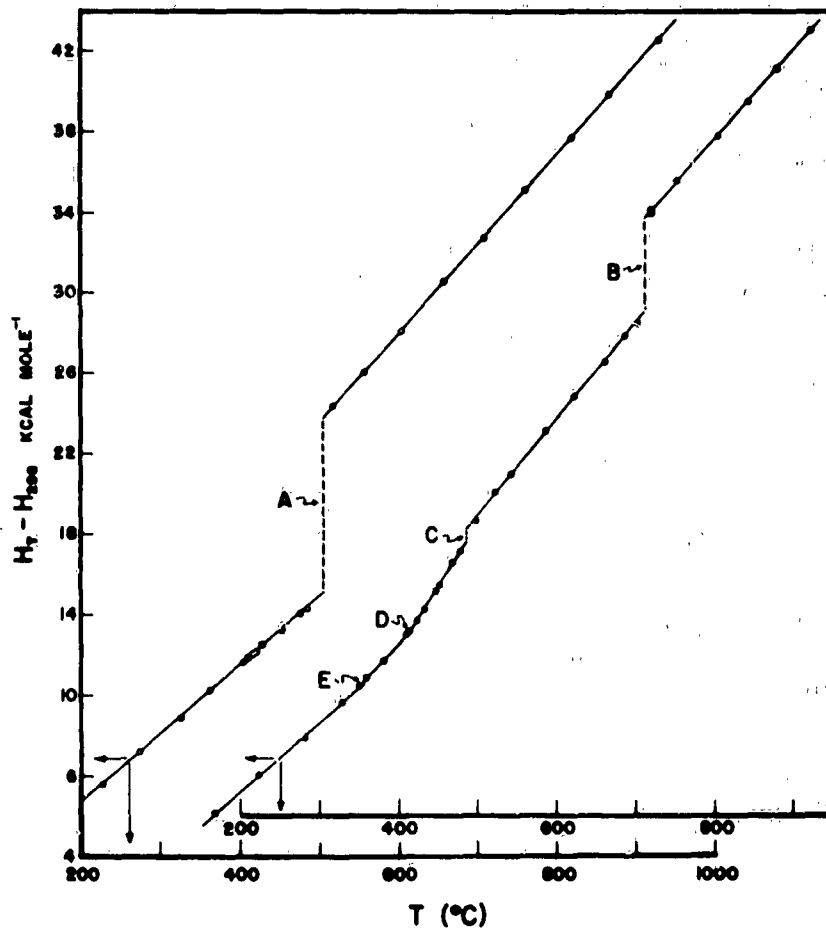
(⊙) Na_2CO_3 (56%), K_2CO_3 (44%);

A: 505°C; ΔH_f , 8700 cal; B: 710°C;

ΔH_f , 4673 cal; C: 485°C, ΔH_{tr} , 606 cal;

D: 422°C, ΔH_{tr} , 55 cal; E: 355°C,

ΔH_{tr} , 88 cal.



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