Thermal Data for Lithium Sulfate and Binary Eutectics Lithium Sulfate–Lithium Chloride, Lithium Sulfate–Sodium Chloride, and Lithium Sulfate–Potassium Chloride

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With drop calorimetry, heat of transition, heat of fusion, and heat capacities are measured for lithium sulfate, and heats of fusion and heat capacities are determined for the binary eutectics lithium sulfate-lithium chloride, lithium sulfate-sodium chloride, and lithium sulfate-potassium chloride. Melting and transition temperatures are measured by differential thermal analysis. Heat of fusion values are 1.76 kcal mol^{-1} for Li_2SO_4, 5.72 for Li_2SO_4–LiCl, 7.48 for Li_2SO_4–NaCl, and 6.77 for Li_2SO_4–KCl. Heat of solid-solid transition for Li_2SO_4 is 5.98 kcal mol^{-1}. Heat capacities for the liquid salts and for the high-temperature Li_2SO_4 solid phase are independent of temperature, whereas those for the low-temperature Li_2SO_4 phase and for the solid eutectics vary linearly with temperature.

A drop calorimetric technique has been previously described (*4*) for the determination of thermal data for salt mixtures. That technique has been used in the present investigation to obtain heat of transition, heat of fusion, and heat capacities for Li_2SO_4 and to obtain heat of fusion and heat capacity data for the binary eutectics Li_2SO_4–LiCl, Li_2SO_4–NaCl, and Li_2SO_4–KCl. Temperatures and heats of transition and fusion, as well as heat capacity data for Li_2SO_4, have been published (*7–10*). A large range of values has been reported for both the transition and fusion temperatures. Li_2SO_4–LiCl is a true binary system, whereas the Li_2SO_4–NaCl and Li_2SO_4–KCl binary mixtures are stable diagonals in the ternary reciprocal systems Li,Na//SO_4,Cl and Li,K//SO_4,Cl, respectively. Melting points, transition temperatures, and eutectic compositions have been determined for the binary systems by differential thermal analysis, and comparisons are made with previously reported data. Heats of fusion and heat capacities for the salt mixtures have not been previously determined.

Experimental

Materials. The samples used in these determinations were prepared by use of analytical reagent-grade chemicals, vacuum dried for 16 hr at 120°C. The eutectic mixtures were prepared by melting the necessary amounts of the individual salts together in a platinum crucible. The samples were cooled, ground, and placed in a sealed platinum capsule. The sample preparation was conducted in a controlled-atmosphere dry room. Moisture content is maintained at approximately 0.25% RH (~50 ppm H_2O at 22°C) by circulating the room air through beds of molecular sieves.

Apparatus. The drop calorimetry apparatus and techniques have been previously described in detail (*4*). A Marshall Model No. 1024 tubular furnace was fitted with a quartz tube in which the sealed platinum sample capsule was suspended. The calorimeter consisted of a copper and quartz dry chamber placed in a water-filled Dewar vacuum flask. Samples were equilibrated in the furnace and then dropped into the calorimeter. Calorimeter temperature was monitored until a maximum value was reached. Enthalpy data were calculated in the manner described in detail in a previous publication (*4*).

Melting and transition temperatures and eutectic compositions were determined with a Stone differential thermal analysis system, Model DTA-202, coupled with a Hewlett-Packard Model 7100B two-pen strip chart recorder. The DTA sample holder was a Model SH-11BR employing ring type, Platinel II thermocouples. Salt samples weighed approximately 4 mg, and calcined alumina was used as the reference material. The extrapolated onset temperature was chosen as the melting point. The eutectic composition was that mixture which gave DTA curves showing a single well-defined endotherm on melting. A 10°C/min heating rate was used for all DTA work. Sample pans were of platinum.

Results and Discussion

For Li_2SO_4 a solid-solid transition was determined to occur at 575.6 ± 1.1°C, and the melting at 853.4 ± 1.9°C. Both of these temperatures were within the range of values reported in the literature: 572–586°C for the solid-solid transition and 818–860°C for melting. If one deletes the value of 818°C which was published in 1878 (*3*), the range of melting point data reported becomes 843–860°C.

In Table I the results of eutectic composition determinations and melting-point measurements for the three salt mixtures are shown as are literature values. The present results for all three systems are in general agreement with those reported by Bergman and other Russian authors (*1, 2, 5, 6*).

The results of the enthalpy determinations for Li_2SO_4 are shown in Table II. They are presented in graphical form in Figure 1. Table III summarizes thermal data calculated from our enthalpy measurements, as well as results reported by Voskresenskaya and Banashek (*10*) which were also obtained by use of drop calorimetry.

Table I. Comparison of Eutectic Composition and Eutectic Melting-Point Data for Li_2SO_4–LiCl, Li_2SO_4–NaCl, and Li_2SO_4–KCl Systems

	Eutectic composition, mol % Li_2SO_4		Eutectic melting point, °C		
Salt system	This work	Lit values	This work	Lit values	Ref
Li_2SO_4–LiCl	36.8 ± 0.2	35.6–36.5	481.6 ± 1.0	478–484	*1, 2, 5, 6*
Li_2SO_4–NaCl	58.1 ± 0.2	58.7	489.4 ± 0.9	499	*2*
Li_2SO_4–KCl	50.7 ± 0.2	51.5	455.0 ± 0.6	456	*2*

Table II. Enthalpy Results at Various Temperatures for Li_2SO_4

Transition point, 575.6 ± 1.1°C; melting point, 853.4 ± 1.9°C

Temp, °C	Enthalpy, cal g^{-1}
214.9	49.3
237.2	55.8
267.6	63.9
296.7	73.1
346.7	88.6
396.4	102.3
447.3	119.7
499.5	138.4
600.5	230.2
642.6	247.4
700.3	266.8
749.0	292.2
799.3	307.7
829.6	322.4
871.5	354.9
878.4	357.8
895.0	366.5
904.5	369.6
906.1	369.4

Table III. Thermal Data Determined for Li_2SO_4

Property	This work	Voskresenskaya and Banashek (*10*)
t_{trans}, °C	575.6	586
ΔH_{trans}, kcal mol^{-1}	5.98	6.53
ΔS_{trans}, cal K^{-1} mol^{-1}	7.05	7.60
t_m, °C	853.4	860
ΔH_{fus}, kcal mol^{-1}	1.76	1.83
ΔS_{fus}, cal K^{-1} mol^{-1}	1.56	1.62
C_p(l), cal mol^{-1} °C^{-1}	48.2	48.4
(temp range)	(t_m to 906°C)	(t_m to 1027°C)
$C_p(\beta)$, cal mol^{-1} °C^{-1}	44.0	52.3
(t_{trans} to t_m)		
$C_p(\alpha)$, cal mol^{-1} °C^{-1}	$14.72 + 0.0308T$	$33.34 + 0.1564T -$
(temp range)	(215°C to t_{trans})	$899.3 \times 10^3\ T^{-2}$
		(20°C to t_{trans})
$C_p(\alpha)$ @ 500K (226.8°C)	30.1	37.5
@ 600K (326.8°C)	33.2	40.2
@ 700K (426.8°C)	36.3	42.4
@ 800K (526.8°C)	39.4	44.4

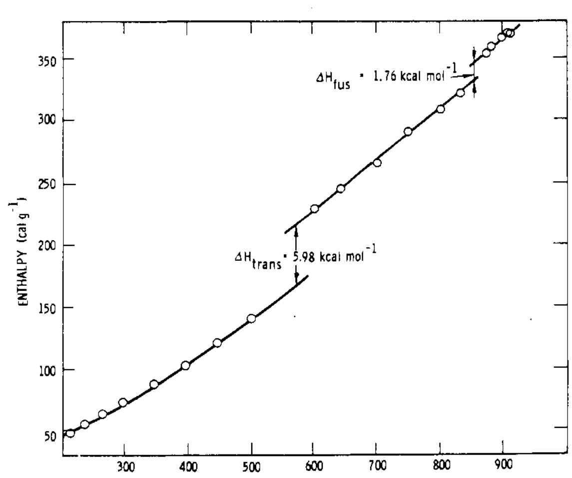

Figure 1. Enthalpy vs. temperature for Li_2SO_4

Table IV. Enthalpy Results at Various Temperatures for Li_2SO_4–LiCl Eutectic

Melting point, 481.6 ± 1.0°C

Temp, °C	Enthalpy, cal g^{-1}
240.6	67.1
282.0	80.6
320.4	93.6
359.0	105.3
399.5	122.0
439.7	136.3
460.0	144.7
499.6	246.7
522.1	253.8
539.3	262.9
558.5	270.2
580.7	278.1
600.5	286.0
601.3	286.0

Table V. Enthalpy Results at Various Temperatures for Li_2SO_4–NaCl Eutectic

Melting point, 489.4 ± 0.9°C

Temp, °C	Enthalpy, cal g^{-1}
239.5	56.8
261.1	62.9
280.1	69.3
300.4	73.9
319.7	79.3
339.3	86.5
359.6	92.5
379.6	98.8
399.8	105.9
419.6	110.6
440.1	118.4
459.9	126.3
480.4	135.7
518.8	233.8
540.1	240.1
558.0	247.0
581.1	255.6
599.6	262.2
600.6	262.6
601.3	264.6

Table VI. Enthalpy Results at Various Temperatures for Li_2SO_4–KCl Eutectic

Melting point, 455.0 ± 0.6°C

Temp, °C	Enthalpy, cal g^{-1}
240.8	50.9
281.0	60.7
320.5	71.3
359.4	81.3
401.1	94.0
432.9	102.3
482.6	192.7
500.5	196.8
519.0	202.8
540.9	210.8
560.4	218.1
581.6	223.9
599.6	232.4
601.8	231.3

Table VII. Thermodynamic Values Determined from Enthalpy Measurements for Li_2SO_4-LiCl, Li_2SO_4-NaCl, and Li_2SO_4-KCl Eutectics

	Li_2SO_4-LiCl	Li_2SO_4-NaCl	Li_2SO_4-KCl
Mean mol wt	66.49	88.68	92.78
t_m, °C	481.6	489.4	455.0
ΔH_{fus}, kcal mol^{-1}	5.72	7.48	6.77
ΔS_{fus}, cal K^{-1} mol^{-1}	7.58	9.81	9.30
θ_c, °C mol^{-1} kg^{-1}	13.2	13.7	14.4
c_p(l), cal mol^{-1} °C^{-1} (t_m to 601°C)	26.1	32.6	31.3
c_p(s), cal mol^{-1} °C^{-1} (240°C to t_m)	0.6 + 0.0277T	0.0 + 0.447T	10.5 + 0.0238T

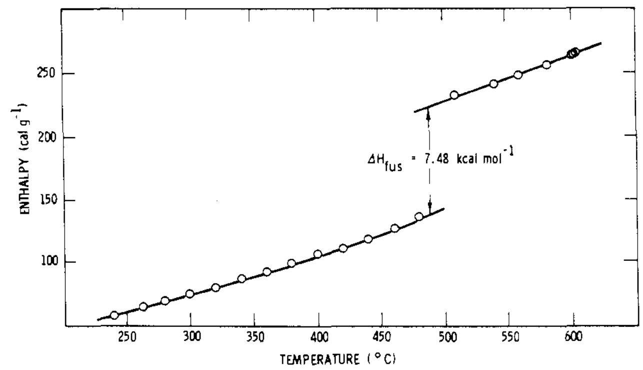

Figure 3. Enthalpy vs. temperature for Li_2SO_4-NaCl eutectic

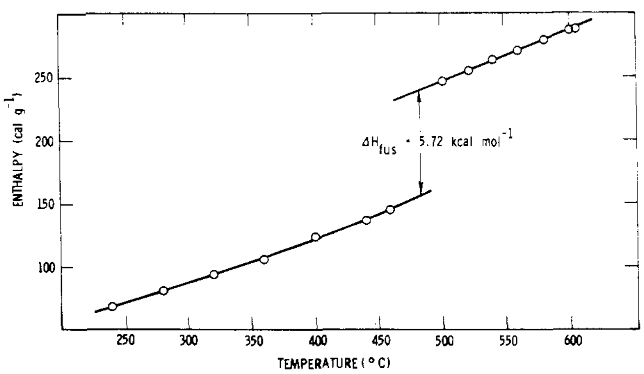

Figure 2. Enthalpy vs. temperature for Li_2SO_4-LiCl eutectic

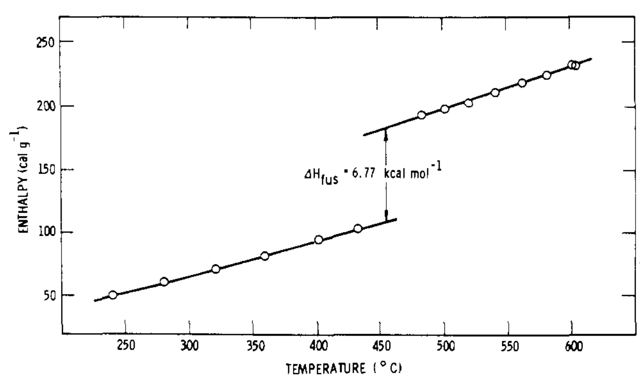

Figure 4. Enthalpy vs. temperature for Li_2SO_4-KCl eutectic

Heat capacities for the liquid, the high-temperature solid (β), and the low-temperature solid (α) are reported for the temperature ranges shown in Table III. In some cases, the agreement is quite close between the two sets of values, e.g., C_p(l) and ΔH_{fus}. In other cases, poor agreement was obtained, e.g., $C_p(\beta)$ and $C_p(\alpha)$. Reasons for these variations are not apparent, although differences in purity of materials could be a cause. In both investigations heat capacities were temperature independent for the liquid and the high-temperature solid (β), but temperature dependent for the low-temperature solid (α). Riccardi (*8*) determined the heat of fusion of Li_2SO_4 to be 1.98 kcal mol^{-1}, using cryoscopic methods.

The enthalpy-temperature results for the eutectic mixtures are shown in tabular form in Tables IV–VI and graphically in Figures 2–4. Table VII summarizes the thermodynamic values determined from these data. The mean molecular weights of the eutectic mixtures are based on the compositions shown in Table I. Entropies of fusion and cryoscopic constants are calculated values based on the experimentally determined heats of fusion and melting points. Heat capacities are valid only for the temperature range shown in Table VII. The heat capacities of the liquid salt mixtures are independent of temperature, but the solid heat capacities vary linearly with temperature. The values reported are accurate to ±1% for heats of fusion and heat of transition and to ±4% for heat capacities. These accuracies are based on error analyses using a method previously described (*4*).

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Nomenclature

t_{trans} = solid–solid transition temperature, °C
ΔH_{trans} = heat of transition, kcal mol^{-1}
ΔS_{trans} = entropy of transition, cal K^{-1} mol^{-1}
t_m = melting temperature, °C
ΔH_{fus} = heat of fusion, kcal mol^{-1}
ΔS_{fus} = entropy of fusion, cal K^{-1} mol^{-1}
C_p(l) = heat capacity of liquid, cal mol^{-1} °C^{-1}
$C_p(\beta)$ = heat capacity of high-temperature solid phase, cal mol^{-1} °C^{-1}
$C_p(\alpha)$ = heat capacity of low-temperature solid phase, cal mol^{-1} °C^{-1}
T = absolute temperature, K
θ_c = cryoscopic constant, °C mol^{-1} kg
C_p(s) = heat capacity of solid, cal mol^{-1} °C^{-1}

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