Heats of Fusion and Heat Capacities of Lithium Chloride–Potassium Chloride Eutectic and Potassium Nitrate

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Heats of fusion and heat capacities have been measured for the lithium chloride–potassium chloride eutectic and for potassium nitrate using drop calorimetry. Values for heats of fusion are 3.10 ± 0.02 and 2.39 ± 0.02 kcal mol^{-1} for LiCl-KCl and KNO_3, respectively. Heat capacities for LiCl-KCl were determined to be 17.3 ± 0.6 cal mol^{-1} deg^{-1} for the liquid from 352° to 580°C and 12.3 ± 0.2 cal mol^{-1} deg^{-1} from 240° up to the melting point of 352°C. For KNO_3, heat capacities above and below the 337°C melting point are reported as 32.4 ± 0.5 and 31.5 ± 0.2 cal mol^{-1} deg^{-1}, respectively over the temperature range 239–390°C. Cryoscopic constants and entropies of fusion are calculated. Comparison is made with literature values. The method described is believed to give accuracies of ±1% for heat of fusion and ±4% for heat capacity.

A need for heats of fusion and heat capacities of salt mixtures has recently arisen in this laboratory, and although thermal data are readily available in the literature for many single salts, similar data for salt mixtures are relatively scarce. Consequently, a drop calorimeter has been assembled for determination of desired data. To establish the accuracy of this technique, thermal data were determined and compared with available experimental data on materials previously investigated by other workers—specifically, potassium nitrate and the lithium chloride–potassium chloride eutectic. This paper, the first of a series which will report determinations of thermal data for salt mixtures, describes the experimental technique and reports experimental heats of fusion and heat capacities for KNO_3 and the LiCl-KCl eutectic as well as the calculated entropies of fusion and cryscopic constants of these salts.

Experimental

Materials. The samples used in these determinations consisted of analytical reagent KNO_3, vacuum dried for 16 hr at 120°C and LiCl-KCl eutectic (Anderson Physical Laboratories, Inc.) prepared according to the method of Laitinen et al. *(11)* to remove H_2O, oxide and hydroxyl ions, and heavy metal impurities. The eutectic composition of 59.0 ± 0.5 mol % LiCl–41.0 ± 0.5 mol % KCl was verified using differential thermal analysis. Copper used as a heat reference was from J. T. Baker Co. and was 99.92% pure. Melting points of the salts were 337° ± 1°C for KNO_3 and 352° ± 1°C for LiCl-KCl.

Apparatus. The apparatus and technique were similar to those described by Janz *(5)*. The furnace and calorimeter arrangement is shown in Figure 1. A Marshall Model No. 1024 tubular furnace (A) was fitted with a 2.5-mm-thick copper tube (B) for a more uniform heat distribution. A 30-mm-i.d. quartz tube (C) extending approximately 13 cm below and 6.5 cm above the furnace was fitted inside the copper. A ceramic cap (D) covered the top of the quartz tube. Furnace temperature was controlled with a Honeywell Model R7161J Versatronik SCR Trigger Controller and monitored with a calibrated Chromel-Alumel thermocouple (E) in conjunction with a Dymec Model 2401A DVM. The bottom end of the quartz tube rested on a Transite plate (F) except during the actual drop, when the furnace assembly was swung over the calorimeter.

The calorimeter consisted of a 7.0 cm i.d. × 19.0 cm deep wide-mouthed Dewar vacuum flask (G) filled with 420.0 grams of water. The dry chamber (H) into which the capsule was dropped was made from a 30-mm-i.d. quartz tube (I) 18.0 cm long attached by deKhotinsky cement to a 7-cm-long copper cup (J). The dry chamber was supported in the Dewar by a Styrofoam stopper (K), and a foam rubber shock absorber (L) was placed between the bottom of the copper cup and the vacuum flask. Except during the actual drop, a Styrofoam cap (M) covered the top opening of the dry chamber. A reciprocating stirrer (N) fabricated from four horizontal perforated Plexiglas disks separated by approximately 4 cm and attached to an eccentric wheel driven at 17 rpm by an electric motor was used to agitate the water in the calorimeter. Water temperature was measured by a Parr Model 1651 Calorimetric Thermometer (O), held in place by a small glass tube (P) attached to the quartz (I) with deKhotinsky cement.

Samples were sealed by heliarc welding under inert atmosphere in 15-ml platinum capsules (R). The capsules were molded to fit tightly in the copper cup (J) to ensure good thermal contact. A small Pt strip in the form of a loop was welded onto the top of the capsule. By means of this loop the capsule was suspended through two holes in the ceramic cap (D) using two 28-gage copper or steel wires (S) connected to either end of a 1-cm-

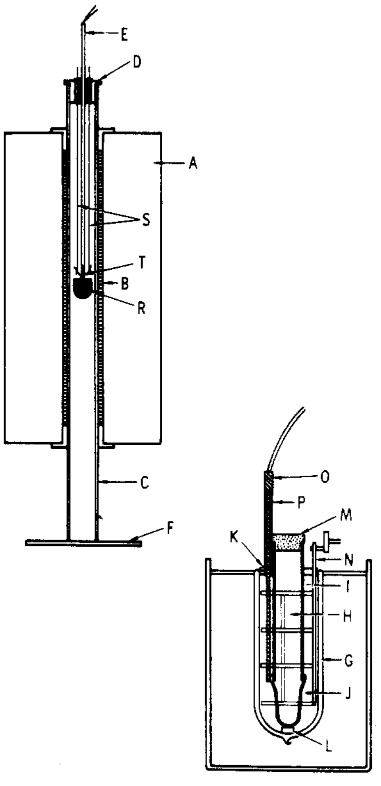

Figure 1. Diagram of furnace and calorimeter
A, furnace; B, copper tube; C, quartz tube; D, ceramic cap; E, Chromel-Alumel thermocouple; F, Transite plate; G, Dewar vacuum flask; H, dry chamber; I, quartz tube; J, copper cup; K, Styrofoam stopper; L, foam rubber; M, Styrofoam cap; N, stirrer; O, Parr Calorimetric Thermometer probe; P, glass tube; R, platinum capsule; S, copper wire; T, fuse wire.

long, 33-gage fuse wire (T). The other ends of the suspension wires passed through the ceramic cap and were attached to the leads from a Parr Ignition Unit (Parr Instrument Co.).

Procedure. Enthalpy determinations were made over the temperature range 239-390°C for KNO_3. For the LiCl KCl eutectic, enthalpy was determined at temperatures ranging from 240° to 580°C. Samples were usually equilibrated in the furnace for 1.5-4 hr prior to the drop. However, at temperatures only slightly above the melting temperature of the sample, equilibrium times of 16 hr or longer were used. Water (420.0 grams) was placed in the calorimeter and allowed to equilibrate for 15 min prior to initial temperature readings. Water temperature was adjusted so that the heat transferred from the hot capsule would raise the water temperature from a value below to a value above room temperature. Approximately 10-20 min after equilibration of the water, the cap was removed from the dry chamber, the furnace was swung over the calorimeter, the capsule dropped, the furnace returned to its original position, and the cap replaced. This operation took less than 5 sec. The capsule was dropped by igniting the fuse wire by means of the Parr Ignition Unit. The heat generated by this ignition is very small (~2.3 cal). Small errors of this type become insignificant since they are present for both the reference and the sample.

Calorimeter temperature was monitored following a drop until a maximum value was reached. A typical temperature-time curve is shown in Figure 2. The t_m shown in Figure 2 is the time when area A is equal to area B. To a very close approximation this is the time when the temperature is equal to $0.63\ (T_2 - T_1) + T_1$.

The temperature rise of the water (calorimeter) resulting from the heat transferred from the hot capsule may be calculated using Equation 1, which includes a radiation correction term *(1)*.

$$\Delta T_c = T_2 - T_1 + \{(T_1 - T_o)[(T_1 - T_e)(t_m - t_1) + (T_2 - T_e)(t_2 - t_m)]/(t_1 - t_0)(T_e - 0.63\ T_1 - 0.37\ T_0)\} \quad (1)$$

Heat loss for the cooling reference capsule was calculated from the known thermal properties of copper *(8)* and platinum *(9)* according to

$$\Delta H_r = \text{moles Cu}\ \{5.41(T_f - T_2) + 0.75 \times 10^{-3} \times [(T_f + 273.15)^2 - (T_2 + 273.15)^2]\} + \text{moles Pt}\ \{5.74(T_f - T_2) + 0.67 \times 10^{-3}[(T_f + 273.15)^2 - (T_2 + 273.15)^2] - 0.10 \times 10^5[1/(T_f + 273.15) - 1/(T_2 + 273.15)]\} \quad (2)$$

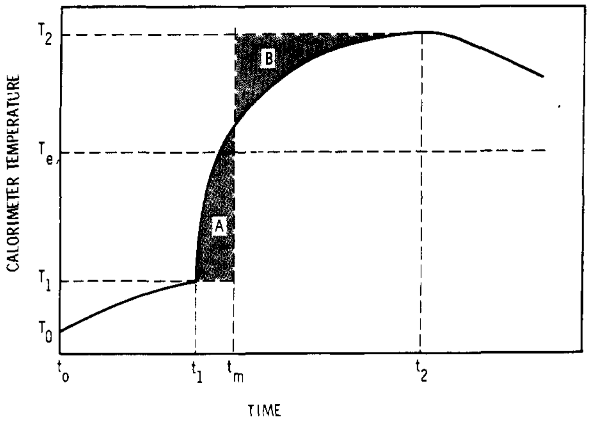

Figure 2. Calorimeter temperature vs. time

The heat equivalent of the calorimeter which was calculated for any given drop of the reference capsule according to

$$E = \Delta H_r / \Delta T_c \quad (3)$$

varied slightly, but significantly with furnace temperature (449.5 cal °C^{-1} at 580°C and 465.3 cal °C^{-1} at 240°C). Consequently, heat equivalent was expressed as a linear function of furnace temperature

$$E = 476.4 - 0.0464\ T_f \quad (4)$$

It follows from Equations 1 and 4 that the heat lost by the sample capsule will be given by

$$\Delta H_c = (476.4 - 0.0464\ T_f) \left\{ T_2 - T_1 + \frac{(T_1 - T_o)[(T_1 - T_e)\ (t_m - t_1) + (T_2 - T_e)(t_2 - t_m)]}{(t_1 - t_o)(T_e - 0.63\ T_1 - 0.37\ T_o)} \right\} \quad (5)$$

The heat loss resulting from cooling of the platinum sample capsule itself was calculated from the weight and the heat capacity of platinum *(9)* as follows:

$$\Delta H_{\mathrm{Pt}} = \frac{W_{\mathrm{Pt}}}{195.1} \left\{ 5.74\ (T_f - T_2) + 6.7 \times 10^{-4} [(T_f + 273.15)^2 - (T_2 + 273.15)^2] - 1.0 \times 10^4 \left(\frac{1}{T_f + 273.15} - \frac{1}{T_2 + 273.15} \right) \right\} \quad (6)$$

The enthalpy of the sample material, corrected to an arbitrary final temperature of 25°C, is calculated as

$$\Delta H_s = (\Delta H_c - \Delta H_{\mathrm{Pt}})(T_f - 25.000)/(T_f - T_2) \quad (7)$$

Regression analysis was used to fit both linear and quadratic equations relating enthalpy to furnace temperature. Best-fit equations were selected; one for temperatures above the melting point (T_m) and one for temperatures below T_m. Heat of fusion was determined from the sample weight (W_s) and from the difference in enthalpy values at T_m as calculated from the two equations. The heat capacities of the liquid and the solid were determined by differentiating the respective enthalpy-temperature equations with respect to temperature.

Finally, entropy of fusion and cryoscopic constant were calculated from the molar heat of fusion:

$$\Delta S_{\mathrm{fus}} = (\Delta H_{\mathrm{fus}} \times 10^3)/(T_m + 273.15) \quad (8)$$

$$\theta_c = \mathrm{R}(T_m + 273.15)^2 M_s / \Delta H_{\mathrm{fus}} \times 10^6 \quad (9)$$

Results and Discussion

The results of the enthalpy determinations are shown in Table I for the LiCl-KCl eutectic and in Table II for KNO_3. These results are shown in graphical form in Figures 3 and 4. The thermodynamic values determined from these data are shown in Table III. The molecular weight of the LiCl-KCl eutectic is the calculated mean molecular weight based on the eutectic composition 59 mol % LiCl-41 mol % KCl *(11)*.

The error values established for the thermodynamic values were estimated by simulation from assumed individual errors for each measured input variable in the calculation. For this simulation, the input variables were assumed to be normally distributed about the midpoints of the stated error range with standard deviations chosen

Table I. Enthalpy Results at Various Temperatures for the LiCl-KCl Eutectic

Melting point, 352°C

Temp, °C	Enthalpy, cal g^{-1}
239.7	45.0
241.2	46.0
260.0	49.4
260.1	49.7
269.7	51.1
279.6	54.7
280.1	54.1
290.6	55.5
300.1	57.7
302.2	58.3
319.7	62.1
321.8	63.7
329.1	65.0
339.6	66.9
350.7	70.0
359.6	127.4
361.1	127.8
364.1	130.3
369.3	132.1
371.0	131.3
372.1	131.9
379.9	134.3
380.7	134.1
388.6	137.3
390.0	137.1
399.1	139.7
399.7	140.3
400.5	141.2
450.6	157.1
496.1	168.9
549.3	187.4
579.1	197.9

Table II. Enthalpy Results at Various Temperatures for Potassium Nitrate

Melting point, 337°C

Temp, °C	Enthalpy, cal g^{-1}
239.1	68.4
239.8	69.0
259.7	74.6
260.0	74.3
280.1	80.9
280.6	81.6
299.7	86.9
300.3	87.1
319.5	93.6
319.5	93.6
348.0	125.8
350.6	126.4
359.5	129.7
361.9	130.6
364.5	132.1
373.4	133.4
379.9	136.4
381.1	136.6
387.6	139.2
388.3	138.7
389.8	138.8

Table III. Thermodynamic Values Determined from Enthalpy Measurements for the LiCl-KCl Eutectic and for KNO_3

	LiCl-KCl eutectic	KNO_3
Mol wt	55.28	101.11
T_m, °C	352	337
ΔH_{fus}, kcal mol^{-1}	3.10 ± 0.02	2.39 ± 0.02
ΔS_{fus}, cal °C^{-1} mol^{-1}	4.96 ± 0.03	3.93 ± 0.04
θ_c, °C mol^{-1} kg	13.9 ± 0.1	31.1 ± 0.3
C_p (l), cal mol^{-1} °C^{-1}	17.3 ± 0.6	32.4 ± 0.5
C_p (s), cal mol^{-1} °C^{-1}	12.3 ± 0.2	31.5 ± 0.2

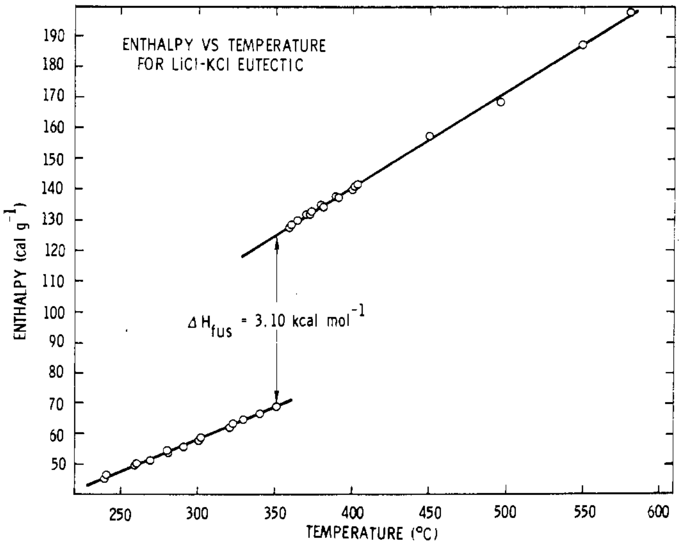

Figure 3. Enthalpy vs. temperature for the LiCl–KCl eutectic

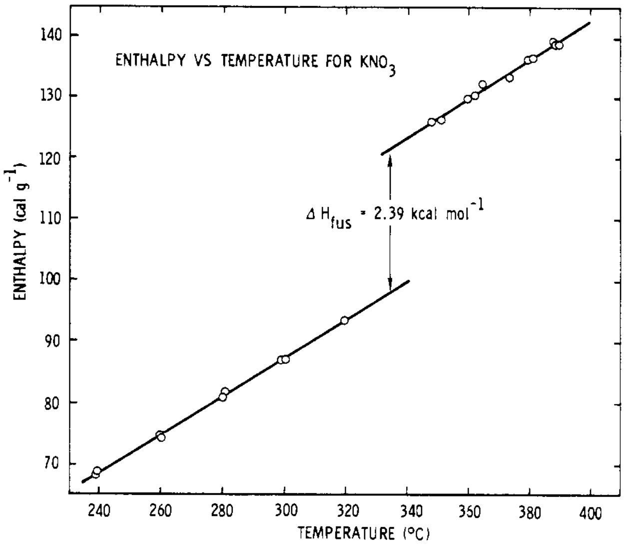

Figure 4. Enthalpy vs. temperature for KNO_3

equal to one sixth of the error range. The error range is shown in Table IV. The simulation was carried out by sampling from the distribution of each input variable and making the final thermodynamic calculations using these sample values as input variables. This process was repeated 100 times and the standard deviation of the 100 calculations was determined. The stated error limits on the final reported values are ±1 std dev.

On the basis of this error analysis, the final determinations are believed to be accurate to ±1% for heats of fusion and to ±4% for heat capacities. These accuracies are similar to those reported by other workers *(3, 5)* using similar drop calorimetric techniques.

The data for LiCl–KCl determined in this work are compared with literature values in Table V. Agreement is good between our results and those of Janz et al. *(16)*.

Table IV. Estimated Error Range for the Measured Variables

Variable	Estimated error range
T_o	±0.003°C
T_1	±0.003°C
T_2	±0.003°C
T_e	±0.2°C
t_o	±0.0 min
t_1	−0, +0.25 min
t_2	±1.0 min
t_m	±0.5 min
T_f	±1.0°C
W_{Pt}	−0.001, +0.25 gram
W_s	±0.001 gram
T_m	±1.0°C
M_s	±0.0

Table V. Comparison of Heat of Fusion Values for LiCl-KCl Eutectic

Heat of fusion, kcal mol^{-1}	Ref.
3.10 ± 0.02	This work
3.20 ± 0.06	Janz et al. *(16)*
3.6	Powers and Blalock *(13)*

Table VI. Comparison of Values for KNO_3

Property determined	Value	Ref.
Heat of fusion, kcal mol^{-1}	2.300 ± 0.005	*(15)*
	2.357	*(2)*
	2.39 ± 0.02	This work
	2.40 ± ~4%	*(4)*
	2.413 ± 0.028	*(10)*
	2.57 ± <2%	*(6)*
	2.63	*(14)*
	2.80	*(7)*
	2.84	*(18)*
	2.91	*(12)*
Heat capacity (l), cal mol^{-1} °C^{-1}	32.4 ± 0.5	This work
	33.6 ± >2%	*(6)*
Heat capacity (s), cal mol^{-1} °C^{-1}	29.5 ± >2%	*(6)*
	31.5 ± 0.2	This work

The discrepancy between the literature values is discussed by Janz. Considerably more data are available for KNO_3 and comparisons of our results with these data are shown in Table VI. Our value for heat of fusion agrees well with the more recently reported numbers of Doucet and Vallet *(2)*, Franzosini and Sinistri *(4)*, and Kleppa and McCarty *(10)*. In addition, at our request, the National Bureau of Standards critically evaluated the literature values and reported as their best estimate based on this survey a value of 2.400 ± 0.050 kcal mol^{-1} *(17)*. This is in excellent agreement with our result of 2.39 ± 0.01 kcal mol^{-1}. Error values shown in Tables V and VI are those reported by the authors.

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Nomenclature

E = heat equivalent of the calorimeter, cal °C^{-1}
ΔH_c = heat lost by sample capsule and contents during cooling from T_f to T_2, cal
ΔH_{fus} = heat of fusion, kcal mol^{-1}
ΔH_{Pt} = heat lost by platinum sample capsule during cooling from T_f to T_2, cal
ΔH_r = heat lost by reference capsule and contents during cooling from T_f to T_2, cal
ΔH_s = heat lost by salt sample during cooling from T_f to T_2, cal
M_s = gram molecular weight of salt
R = gas constant, 1.987 cal mol^{-1} deg^{-1}
ΔS_{fus} = entropy of fusion, cal °K^{-1} mol^{-1}
ΔT_c = corrected temperature rise of the calorimeter due to the heat transferred from the capsule, °C
T_e = equilibrium or room temperature, °C
T_f = capsule temperature in the furnace, °C
T_m = melting temperature, °C
T_o = temperature of the calorimeter 10–20 min prior to the drop, °C
T_1 = temperature of calorimeter at time of drop, °C
T_2 = maximum temperature reached by the calorimeter, °C
t_m = time when area A = area B (Figure 2) and is approximately equal to the time when the temperature is $0.63\,(T_2 - T_1) + T_1$, min
t_o = time of T_o and can be arbitrarily set as 0, min
t_1 = time of drop, min
t_2 = time when T_2 occurs, min
W_{Pt} = weight of platinum sample capsule, grams
W_s = weight of salt sample, grams
θ_c = cryoscopic constant, °C mol^{-1} kg

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