CALORIMETRIC DETERMINATION OF THE THERMODYNAMIC PROPERTIES OF THE ALKALI METAL SALTS $NaNO_3$, KNO_3, $Na_2Cr_2O_7$, $K_2Cr_2O_7$ AND THEIR BINARY EUTECTIC SOLUTIONS

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ABSTRACT

This work is part of a more general project in thermal energy storage by means of the solid–liquid phase transformation. The phase diagrams were checked and slightly modified. A drop calorimeter was used to measure the enthalpies over a small temperature range near the melting points, so enabling the determination of the heats of fusion and the specific heats of the solid and liquid phases over these ranges.

For $NaNO_3$, KNO_3, $Na_2Cr_2O_7$, $K_2Cr_2O_7$, $NaNO_3$–KNO_3, $NaNO_3$—$Na_2Cr_2O_7$, $NaNO_3$–$K_2Cr_2O_7$, KNO_3—$K_2Cr_2O_7$ and $Na_2Cr_2O_7$—$K_2Cr_2O_7$, the enthalpies in the solid and liquid states and the heats of fusion were found to be, respectively, in cal mole^{-1}: 9300, 12800, 3500 at 581 K; 10300, 12500, 2200 at 611 K; 23600, 29600, 6000 at 625 K; 25000, 34400, 9400 at 666 K; 5700, 8200, 2500 at 495 K; 10300, 13800, 3500 at 535 K; 8700, 11300, 2600 at 495 K; 11100, 13500, 2400 at 537 K; 20300, 23600, 3300 at 573 K. The results for the heats of fusion of the solutions are compared with values obtained by means of simple methods of estimation.

INTRODUCTION

This work was performed as part of a more general project in thermal energy storage by means of the solid—liquid phase transformation. Energy storage by this means has been proposed for use over temperatures ranging from below ambient to 800—900°C, with inorganic salts being favored as storage media over much of this range. There is, however, a surprising dearth of experimentally determined data for the required thermodynamic properties, namely temperature of fusion, heat of fusion and specific heat, particularly in the case of eutectic mixtures, which offer the advantage of a relatively lower temperature of operation. Estimated values are therefore frequently used for the preliminary selection of energy storage salt systems. Acquisition of experimental data is thus very desirable, both for the accumulation of data and for testing the validity of the various methods of estimation.

The alkali metal nitrates and dichromates $NaNO_3$, KNO_3, $Na_2Cr_2O_7$ and $K_2Cr_2O_7$ and their binary eutectic solutions were studied. The phase diagrams [1] were checked and slightly modified, as reported elsewhere [2]. In

the present work a drop calorimeter was used to measure the enthalpies over small ranges of temperature near the melting points, so enabling the determination of the heats of fusion and the specific heats of the solid and liquid phases over these ranges.

EXPERIMENTAL

The calorimeter, based on one by Oelsen [3], consists of a thermos vessel surrounded by polyurethane insulation and containing a measured quantity of water. A small glass stirrer and a thermopile (two chromel—alumel couples in series) are provided. Immersed in the water is a flat-bottomed copper tube attached with teflon tape to a quartz guide tube passing through the insulation covering the calorimeter. The sample, in a flat-bottomed crucible (SiO_2 or Al_2O_3), is heated to the desired temperature in a furnace located directly above the calorimeter, then lowered rapidly via the guide tube, until it rests on the flat bottom of the copper tube, the guide tube then being immediately plugged against heat loss. The copper tube provides good thermal contact between the hot crucible and the water but eliminates localized boiling. The initial sample temperature is measured by a fine chromel—alumel thermocouple in a short, thin-walled quartz sheath immersed in the sample, the wires passing along the thin wire suspending the crucible. A potentiometer was used for all temperature measurements except a few in which a single thermocouple was used for the water temperature; in those cases a digital nano-voltmeter was employed.

In order to reduce heat losses to the walls of the calorimeter, sample size was adjusted so that the temperature increase of the water never exceeded 8—9 K. Accordingly, salt samples were from 10 to 30 g, with 400 g of water in the calorimeter.

Calorimeter calibration

In the case where no phase change is involved, the equation for the heat balance in the calorimeter can be written

$$m_s \int_{T_1}^{T_3} \frac{Cp^{(s)}}{M_s} \, dT + \sum m_i \int_{T_1}^{T_3} \frac{Cp^{(i)}}{M_i} \, dT + m_w(T_3 - T_2) + Y = 0 \tag{1}$$

where m_s = weight of sample (g), M_s = gram molecular weight of sample, m_i = weight of crucible, thermocouple, etc. (g), M_i = gram molecular weight of crucible, thermocouple, etc., m_w = weight of water in calorimeter (g), $Cp^{(s)}$ = specific heat of sample (cal mole^{-1} K^{-1}), $Cp^{(i)}$ = specific heat of crucible, thermocouple, etc. (cal mole^{-1} K^{-1}), T_1 = initial temperature of sample (K), T_2 = initial temperature of water (K), T_3 = final temperature of water and sample (K), and the specific heat of water is taken as being equal to 1 cal g^{-1} K^{-1}.

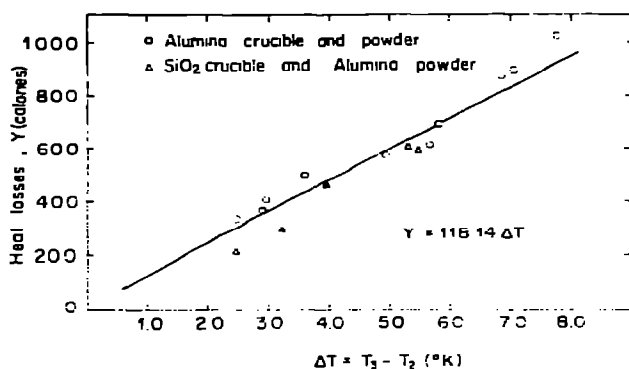In the case of a phase change within the temperature interval $(T_1—T_3)$,

Fig. 1. Calibration curve of calorimeter.

eqn. (1) becomes

$$m_s \left[\int_{T_1}^{T_{tr}} \frac{Cp_{(\alpha)}^{(s)}}{M_s} \, dT + \frac{\Delta H_{tr}}{M_s} + \int_{T_{tr}}^{T_3} \frac{Cp_{(\beta)}^{(s)}}{M_s} \, dT \right] + \sum M_i \int_{T_1}^{T_3} \frac{Cp^{(i)}}{M_i} \, dT$$

$$+ m_w (T_3 - T_2) + Y = 0 \qquad (2)$$

where T_{tr} = temperature of the phase transformation (K), $Cp_{(\alpha)}^{(s)}$, $Cp_{(\beta)}^{(s)}$ = specific heat of sample in α and β phases, respectively, (cal mole^{-1} K^{-1}) and ΔH_{tr} = heat of transformation (cal mole^{-1}). The term Y is a characteristic of the calorimeter and can be determined if a sample and container of known specific heat are used. It represents the losses to the walls of the calorimeter and is obviously a function of the increase in temperature of the water, but this function is complex. A calibration curve must therefore be established for the range of (T_3-T_2) to be used, expressing Y as a function of (T_3-T_2).

In the present work, alumina powder (Al$_2$O$_3$, reagent grade), held in alumina or silica crucibles, was used for the calibration. This choice was aimed at duplicating as far as possible the heat transfer conditions encountered in the actual measurements. Published values of Cp [4] were inserted in eqn. (1), taking Cp for the very fine thermocouple and its sheath as that for vitreous silica. Regression analysis of the results shown in Fig. 1 yielded the analytic expression of the variation of Y as a function of $\Delta T = (T_3 - T_2)$

$$Y(\text{cal}) = 118.14 \, \Delta T \qquad (3)$$

with a standard deviation of 65 cal.

RESULTS

The left-hand term in each of eqns. (1) and (2) is, of course, the enthalpy of the sample. It is the difference between two enthalpy values, that at tem-
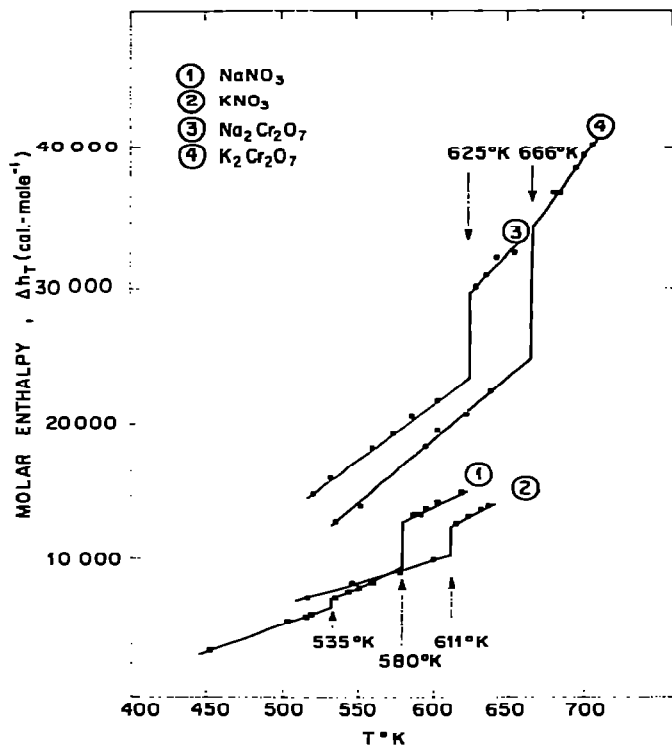
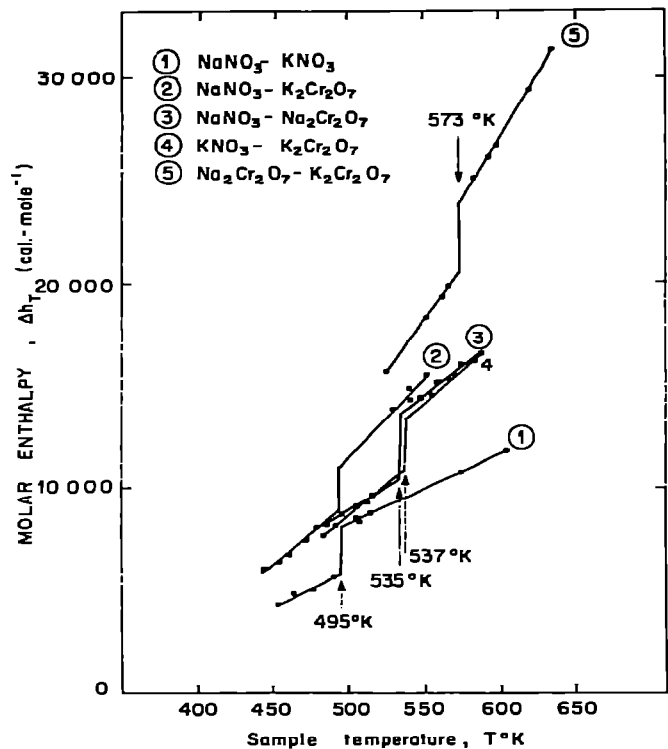Fig. 2. Variation of molar enthalpy of pure salts as a function of temperature.

Fig. 3. Variation of molar enthalpy of binary eutectic solutions as a function of temperature.

perature T_1 and that at temperature T_3, and so represents the enthalpy of the sample at T_1 referred to T_3 rather than to 298 K. Put in terms of molar enthalpy, this means that we obtain $H_T - H_{T_3}$ rather than the usual $H_T - H_{298}$, but, because T_3 is close to 298 K, the error is negligibly small. We shall denote $H_T - H_{T_3}$ by Δh_T in future discussion.

The results obtained for the salts $NaNO_3$, KNO_3, $Na_2Cr_2O_7$, $K_2Cr_2O_7$ and their binary eutectic solutions in the solid and liquid states are summarized in Figs. 2 and 3 and Table 1. The specific heat, Cp, is assumed to be constant over the small temperature range covered in each case. Hence Δh_T can be

TABLE 1

Results obtained for pure salts and their binary eutectic solutions in solid and liquid states

Material	Mole weight (g)	T_F (K)	Δh_T (cal mole^{-1}) = $Cp \times T$ (K) + b			S.D.
			Cp (cal mole^{-1} K^{-1})	b		
$NaNO_3$	85	581	50.7 ± 7.6	-16680	(l)	204
			48.3 ± 3.8	-18733	(β)	85
			40.2 ± 1.3	-14777	(α)	69
			(450—650 K)			
KNO_3	101	610	55.6 ± 8.8	-21529	(l)	145
			32.1 ± 3.1	-9320	(s)	197
			(500—675 K)			
$Na_2Cr_2O_7$	262	625	106 ± 28	-36567	(l)	523
			82.3 ± 2.5	-27874	(s)	111
			(500—670 K)			
$K_2Cr_2O_7$	294	666	141.7 ± 5	-59978	(l)	103
			96.3 ± 4	-39148	(s)	360
			(575—720 K)			
$NaNO_3-KNO_3$ (0.503—0.497) *	93	495	33.9 ± 0.5	-8628	(l)	48
			31.6 ± 7.2	-9961	(s)	204
			(450—560 K)			
$NaNO_3-K_2Cr_2O_7$ (0.775—0.225) *	132	495	72.2 ± 21	-24433	(l)	341
			54.5 ± 5.7	-18284	(s)	162
			(440—575 K)			
$NaNO_3-Na_2Cr_2O_7$ (0.73—0.27) *	132	535	51.5 ± 7.5	-13698	(l)	216
			43.0 ± 1.2	-12681	(s)	
			(450—575 K)			
$KNO_3-K_2Cr_2O_7$ (0.81—0.19) *	138	537	63.2 ± 0.5	-20473	(l)	13
			63.2 ± 2.1	-22911	(s)	93
			(450—600 K)			
$Na_2Cr_2O_7-K_2Cr_2O_7$ (0.5596—0.4404) *	276	573	125.7 ± 2.8	-48441	(l)	119
			97.7 ± 3.4	-35668	(s)	110
			(500—675 K)			

* Composition in molar fraction.

TABLE 2

Thermodynamic properties of pure salts (NaNO$_3$, KNO$_3$, Na$_2$Cr$_2$O$_7$ and K$_2$Cr$_2$O$_7$)

Salt	$Cp^{(\alpha)}$ (cal mole^{-1} K^{-1})		$Cp^{(\beta)}$ (cal mole^{-1} K^{-1})		$Cp^{(l)}$ (cal mole^{-1} K^{-1})
	Present work	Lit.	Present work	Lit.	Present work
NaNO$_3$	450—550 K 40	298—550 K 6.34 + 53.3 × 10^{-3} T [6] 39.6 [7]	48 T_{tr} = 535 K ΔH_{tr} = 380 cal	550—580 K 35.7 [6] 44.6 [7]	580—650 K 51
KNO$_3$			500—611 K 32	401—611 K 28.8 [6]	611—675 K 56
Na$_2$Cr$_2$O$_7$			500—625 K 82	533—583 K 70 [8]	625—670 K 106
K$_2$Cr$_2$O$_7$			575—666 K 96	<671 K 36.7 + 54.8 × 10^{-3} T [8]	666— 142

expressed as a function of T as follows

$$\Delta h_T = Cp \times T + b \qquad (4)$$

Values for Cp and b were obtained by regression analysis using the least squares method.

The temperatures of the liquid—solid and solid—solid transformations were determined earlier by the cooling curve method [2]. The molar heats of fusion, ΔH_F, and of transition, ΔH_{tr}, were derived from the Δh_T values at the transformation temperatures, and are reported in Tables 2 and 3.

TABLE 3

Measured and estimated values of enthalpies of fusion, ΔH_F, of binary eutectic solutions

Eutectic solution	T_F (K)	ΔH_F (cal mole^{-1})			
		Measured	Method 1	Method 2	Method 3
NaNO$_3$—KNO$_3$ (0.503—0.497) *	495	2500	2800	1800	n = 2 3000
NaNO$_3$—Na$_2$Cr$_2$O$_7$ (0.73—0.27) *	535	3500	4100	3500	n = 2.27 3600
NaNO$_3$—K$_2$Cr$_2$O$_7$ (0.775—0.225) *	495	2600	4800	3900	n = 2.225 3300
KNO$_3$—K$_2$Cr$_2$O$_7$ (0.81—0.19) *	537	2400	3500	1050	n = 2.19 3500
Na$_2$Cr$_2$O$_7$—K$_2$Cr$_2$O$_7$ (0.5596—0.4404) *	573	3300	6700	4200	n = 3 5200

* Composition in molar fraction.

Lit.	$\Delta h_{T_F}^{(s)}$ (cal mole^{-1})		$\Delta h_{T_F}^{(l)}$ (cal mole^{-1})		ΔH_F (cal mole^{-1})	
	Present work	Lit.	Present work	Lit.	Present work	Lit.
580—700 K			$T_F = 580$ K			
37 [6]	9300	9200 [6]	12 800	12 700 [6]	3500	3500 [6]
31.2 [7]		9000 [7]		12 500 [7]		3520 [7]
611—700 K			$T_F = 611$ K			
30 [6]	10 300	9980 [6]	12 500	12 800 [6]	2200	2800 [6]
	23 600		$T_F = 625$ K		6000	
			29 600			
720 K	$T_F = 666$ K		$T_F = 671$ K			
98 [8]	25 000		34 400		9400	8500 [8]

DISCUSSION

(1) The standard deviations obtained from the regressions indicate that a linear correlation between Δh_T and T over the temperature range of the measurements is acceptable.

(2) The results for the pure salts $NaNO_3$, KNO_3, $Na_2Cr_2O_7$ and $K_2Cr_2O_7$ are in general agreement with those found in the literature. In addition, in the case of $NaNO_3$, supporting evidence was found for the $\alpha = \beta$ transition identified by Janz et al. [7]. We·found a transition temperature of 585 K and ΔH_{tr} equal to approximately 380 cal mole^{-1}.

(3) No experimental enthalpy values exist in the literature for the binary eutectic solutions, hence no comparisons can be made. However, some discrepencies with published phase diagrams were noted, and modifications to the eutectic compositions and temperatures were proposed in earlier publications [2].

(4) The results can be compared with values estimated from data for the pure salts by the three methods commonly used.

Simple molar addition

$$\Delta H_F^{(1-2)} = X_1 \Delta H_F^{(1)} + X_2 \Delta H_F^{(2)} \tag{5}$$

where $\Delta H_F^{(i)}$ = heat of fusion of i, and X_i = mole fraction of i.

Modified molar addition

The modified form of eqn. (5) takes into account the lower melting point of the solution and the differences between the specific heats of the solid

and liquid phases [5]

$$\Delta H_F^{(1-2)} = X_1 \Delta H_F^{(1)} + X_2 \Delta H_F^{(2)} + X_1 \int_{T_E}^{T_F^{(1)}} (Cp_{(s)}^{(1)} - Cp_{(l)}^{(1)})\, dT$$

$$+ \int_{T_E}^{T_F^{(2)}} (Cp_{(s)}^{(2)} - Cp_{(L)}^{(2)})\, dT \tag{6}$$

where $Cp_{(\alpha)}^{(i)}$ = specific heat of pure salt (i) in (α) phase, $T_F^{(i)}$ = fusion temperature of salt (i), and T_E = eutectic temperature of eutectic solution (1—2).

Entropy of fusion

The entropy of fusion, ΔS_F, can also be used to estimate $\Delta H_F^{(1-2)}$

$$\Delta H_F^{(1-2)} = 3n T_E \tag{7}$$

where n is the equivalence number of the solution and ΔS_F is taken as being equal to 3.

Values estimated by the three methods are included in Table 3, but with no clear trend, the results are too few for valid comment on any comparison. However, it can be remarked that all three methods demonstrate a certain usefulness for a first approximation of the data required for energy storage purposes. In particular, method 2, by its formulation, should yield good approximations when the specific heats of the constituents in the solid and liquid states are not too different, i.e. $(Cp_{(s)}^{(i)} - Cp_{(l)}^{(i)})$ is small, and when the temperatures of fusion, $T_F^{(i)}$, are not too much higher than the eutectic temperature, T_E.

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