

# Heat Capacities of Liquid Sodium and Potassium Nitrates

Ernest W. Dewing

Aluminum Co. of Canada, Ltd., P.O. Box 250, Arvida, Que., Canada

The heat capacities of liquid  $\text{NaNO}_3$  and  $\text{KNO}_3$  are determined in a simple calorimeter by immersing a cold Pt mass and measuring the drop in temperature. The glass of the calorimeter itself contributes only 2% to the total heat capacity. The results for both salts may be expressed by:  $C_p = 33.9 - 0.0156 (T - T_{\text{melting}}) \text{ cal K}^{-1} \text{ mol}^{-1}$ . Integration of this equation and combination with literature values for heat contents yield for liquid  $\text{NaNO}_3$ :  $H_T - H_{298} = -9910 + 42.93 T - 0.0078 T^2 \pm 64 \text{ cal mol}^{-1}$ , and for liquid  $\text{KNO}_3$ :  $H_T - H_{298} = -11,258 + 43.43 T - 0.0078 T^2 \pm 49 \text{ cal mol}^{-1}$ , where the uncertainties are standard deviations of the literature values from these equations.

The recent paper by Clark (3), which gives heat content and heat capacity measurements for  $\text{KNO}_3$ , prompts the publication of this work carried out some years ago. At the time, it was intended to use  $\text{KNO}_3$  and  $\text{NaNO}_3$  as standard substances to calibrate a simple calorimeter designed to measure the heat capacities of low-melting salts, but it became apparent that the literature values were less reliable than calculated values for the calorimeter constants. Even today, they are no better—Clark, for example, claims an accuracy for  $C_p$  (derived by differentiation of heat content data) of 4%.

The temperature change caused by immersing a cold platinum weight into the molten salt was measured to derive the heat capacity; alternatively, by immersing cold solid salt, the heat content of the liquid could be found. The heat capacity of the calorimeter itself was kept small enough that it could be calculated with adequate accuracy. No attempt was made to insulate the calorimeter thermally from the furnace which heated it; heat-transfer corrections were correspondingly large but were not difficult to apply.

## Experimental

The calorimeter (Figure 1) consisted of a thin-walled bulb of about 250-ml capacity blown on the end of a 38-mm o.d. Pyrex tube. A glass propeller-type stirrer on a thin shaft rotated at a few rev/sec; a chromel-alumel thermocouple was immersed directly in the melt. The whole was put into an Inconel strip resistor furnace controlled with a Honeywell time-proportioning controller working on a 3-sec cycle. The Pt weight (43.15 grams) was hung on a Pt wire (of negligible mass); when in the calorimeter, it was above the level of the stirrer to avoid entanglement.

Reagent-grade  $\text{NaNO}_3$  or  $\text{KNO}_3$  was weighed directly into the calorimeter bulb. A run was not started until the thermocouple reading was steady to about  $2 \mu\text{V}$  ( $0.05^\circ$ ) over several minutes. The Pt weight was kept at room temperature (measured with a mercury thermometer) and then lowered as rapidly as possible into the calorimeter. The potentiometer was read at 15-sec intervals for the first 2 min and less frequently thereafter. For heat content determinations, several grams of solid nitrate were briquetted and dropped in instead of the platinum weight.

Table I shows the results of a typical run with  $\text{KNO}_3$ . The minimum temperature of the melt was reached after 45 sec; after 60 sec the temperature was returning exponentially to its initial value, as can be demonstrated by plotting  $\log$  (temperature drop), conveniently in  $\mu\text{V}$  thermocouple reading ( $\phi$ ),

against time (Figure 2). This implies that rate of heat transfer from the furnace is, as expected, proportional to the temperature drop. From the slope of the straight line, the rate of change of temperature owing to heat transfer is expressed as  $\mu\text{V}/\text{sec}/(\mu\text{V} \text{ temperature drop})$ , and this coefficient is then used to calculate the rate of temperature change owing to heat transfer for each point on the initial part of the curve. Integration of these rates gives the total heat-transfer correction to be applied, and the exponential portion of the curve is transformed to a horizontal straight line (Figure 3).

At the end of a series of measurements, the glass of the bulb was cut off and weighed together with the stirrer, and its heat capacity calculated. A typical value was  $2.5 \text{ cal K}^{-1}$  or some 2% of the total measured capacity. Errors in its determination thus had a negligible influence on the final result.

Kelley's (5) values for the heat content of platinum were used.

## Results

Figure 4 shows the heat capacity results for both salts as a function of the temperature minus the melting temperature;  $\text{NaNO}_3$  and  $\text{KNO}_3$  are, on this basis and with the accuracy attained, indistinguishable. The results are in fair agreement with Sokolov and Shmidt (7, 8), especially close to the melting point. There is a marked fall of heat capacity with increasing temperature, and the line drawn is

$$C_p = 33.9 - 0.0156 (T - T_{\text{melting}}) \text{ cal K}^{-1} \text{ mol}^{-1} \quad (1)$$

The standard deviation of the points from the line is  $0.36 \text{ cal/deg/mol}$  or 1.1% of the quantity measured. Integration gives

$$H_T - H_{298} = 42.93 T - 0.0078 T^2 + A \quad (2)$$

for liquid  $\text{NaNO}_3$ , and

$$H_T - H_{298} = 43.43 T - 0.0078 T^2 + B \quad (3)$$

for liquid  $\text{KNO}_3$ , where  $A$  and  $B$  are integration constants which can be fixed from experimental heat contents. Values are given in Table II.

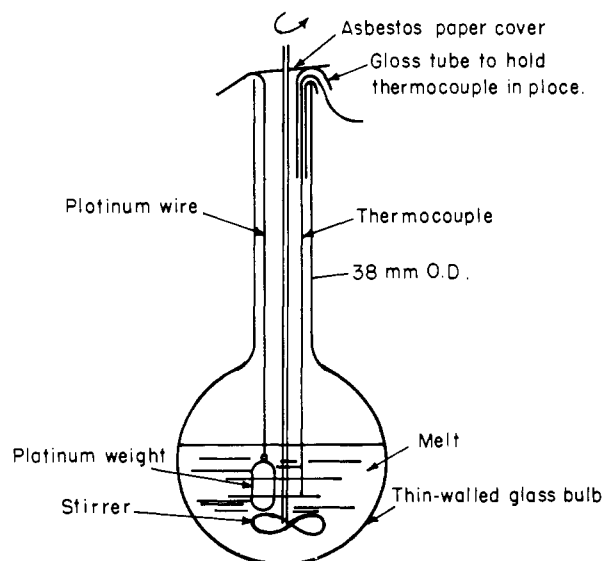
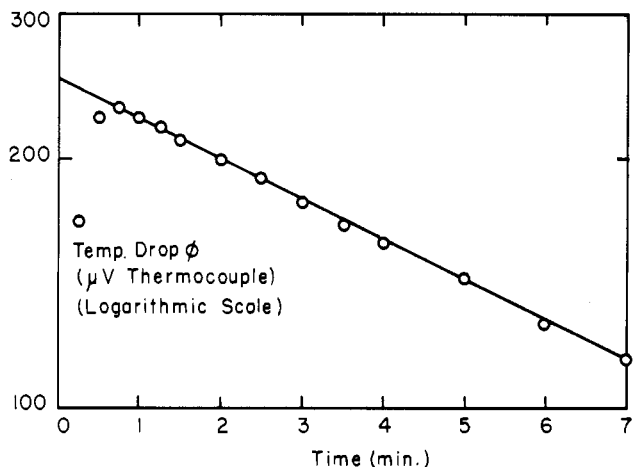


Figure 1. Pyrex calorimeter

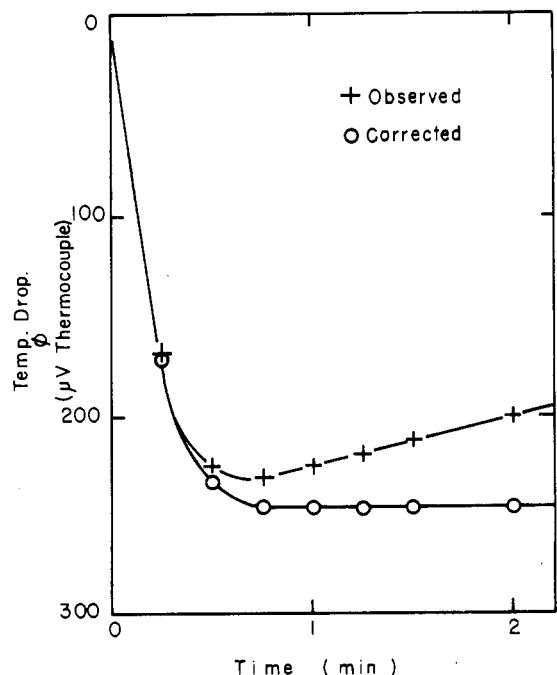
**Table I. Correction of Observed Temperatures for Heat Transfer (Run 6)**

Time, sec	Therm emf, mV	$\phi$ , $\mu V$	$k\phi^a$	$\int k\phi dt$	$\phi + \int k\phi dt$
0	12.945	0	0	0	0
15	12.777	168	0.322	2.4	170.4
30	12.720	225	0.431	8.1	233.1
45	12.714	231	0.443	14.6	245.6
60	12.720	225	0.431	21.2	246.2
75	12.726	219	0.420	27.6	246.6
90	12.733	212	0.406	33.8	245.8
120	12.745	200	0.383	45.6	245.6

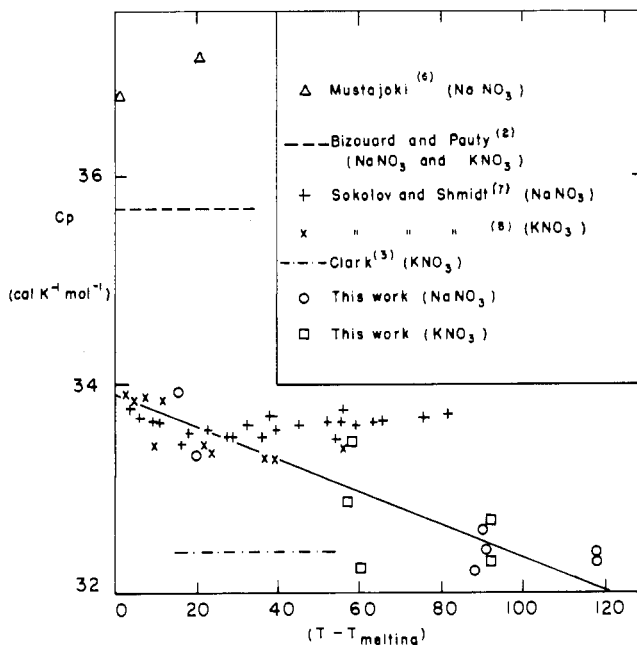
<sup>a</sup> From slope of line in Figure 2;  $k = 1.92 \times 10^{-3} \mu V/\text{sec}/\mu V$  temperature drop.



**Figure 2.** Exponential return of melt temperature toward furnace temperature after immersing Pt weight (Run 6)



**Figure 3.** Correction of observed temperatures for heat transfer



**Figure 4.** Heat capacities of liquid  $\text{NaNO}_3$  and  $\text{KNO}_3$

**Table II. Values of Integration Constants**

Substance	Ref	A or B	SD
$\text{NaNO}_3$	4	$-9,910 \pm 64$ cal/g mol	
	6	$-9,597^a$	
	This work	$-10,040 \pm 304$	
$\text{KNO}_3$	6	$-11,070 \pm 91$	
	7	$-11,118 \pm 209$	
	This work	$-11,015 \pm 380^b$	
	3	$-11,258 \pm 49$	

<sup>a</sup> No standard deviation can be calculated. <sup>b</sup> Standard deviation calculated formally from two values.

### Discussion

For  $\text{KNO}_3$  the four values of the constant  $B$  hardly differ significantly, and the most precise, that of Clark (3), may be accepted. For  $\text{NaNO}_3$ , again the most precise, that of Goodwin and Kalmus (4), can be taken.

There is a big advantage to measuring both heat capacities and heat contents, since they are complementary. Directly measured heat capacities are more accurate than those derived by differentiation of any but the most precise heat content values, and once they are available, even a few experimental heat contents over a narrow temperature range serve to fix the integration constant. In the present case, it is apparent, in view of the small standard deviation of the values of  $B$  derived from Clark's results, that his heat contents and the present heat capacities are entirely compatible. On the other hand, it is not possible for heat contents measured by a simple method like the present one to compete in accuracy with those derived from a much more elaborate apparatus.

For  $\text{KNO}_3$  Clark's (linear) extrapolation of the heat content of the liquid to the melting point gives  $12,378 \text{ cal mol}^{-1}$ ,

whereas the present extrapolation gives  $12,337 \text{ cal mol}^{-1}$ . The difference, 41 cal, represents an uncertainty or, if the present work be accepted, an error in the heat of fusion. It is not large, but since Clark estimated the uncertainty as 20 cal, it is worth noticing.

#### Literature Cited

- (1) Bartholomew, R. F., *J. Phys. Chem.*, **70**, 3442 (1966).
- (2) Bizouard, M., Pauty, F., *Compt. Rend.*, **252**, 514 (1961).

- (3) Clark, R. P., *J. Chem. Eng. Data*, **18**, 67 (1973).
- (4) Goodwin, H. M., Kalmus, H. T., *Phys. Rev.*, **28**, 1 (1909).
- (5) Kolley, K. K., "Contributions to the Data on Theoretical Metallurgy XIII," U.S. Bureau of Mines, Bulletin 584, 1960.
- (6) Mustajoki, A., *Ann. Acad. Sci. Fenn. Ser. A*, **VI**, No. 5 (1957).
- (7) Sokolov, V. A., Shmidt, M. E., *Izv. Sekt. Fiz. Khim. Anal. Inst. Obshch. Neorg. Khim., Akad. Nauk SSSR*, **26**, 123 (1955).
- (8) Sokolov, V. A., Shmidt, M. E., *ibid.*, **27**, 217 (1956).

Received for review September 19, 1973. Accepted April 12, 1975.

## Thermal Conductivity of Anhydrous Borax, Boric Oxide, and Sodium Sulfate

Geoffrey K. Creffield<sup>1</sup> and Anthony J. Wickens

Borax Consolidated Ltd., Borax Research Centre, Cox Lane, Chessington, Surrey KT9 1SJ, England

---

The thermal conductivities of molten borax, boric oxide, and sodium sulfate are determined up to 1270K using the coaxial cylinders technique. The contribution owing to radiant transfer of heat is eliminated by extrapolating the observed results to zero sample thickness, and the true or molecular conductivities are described. In addition, the thermal conductivities of solid borax and boric oxide are determined between 318–553K and 310–503K, respectively, using a Lees' disc technique. The results are described.

---

The measurement of the thermal conductivity of molten borax, boric oxide, and sodium sulfate was conducted to provide much needed fundamental data for use in process heat transfer calculations; these three materials occur in the molten state in processes for the production of anhydrous borax and boric oxide. Data for borax and boric oxide in the solid state down to 298K were required to aid in the design of chill rolls by providing information necessary for heat transfer calculations.

#### Experimental

**Solid products.** The technique employed was based on the Lees' disc method in which the sample is held between two metal discs. Electrical power  $Q$  is supplied to one disc, and the temperature difference,  $\Delta T$ , produced across the sample is measured. Under steady state conditions the thermal conductivity  $K$  can then be calculated from the equation

$$K = \frac{Qx}{A\Delta T} \quad (1)$$

where  $A$  is the area of the sample in contact with the heated disc, and  $x$  is the sample thickness.

In practice a twin plate system (10) was used. The apparatus consisted of two similar specimens (30 mm diameter, 5 mm thick) sandwiched vertically between a thin flat heater disc in the middle and two cold discs on the outside.

Heat losses from the edge of the heater (25 mm diameter, 6 mm thick), kept to a minimum by the use of insulation, were estimated in a separate experiment, and the thermal conductivity results were corrected to allow for this.

The cold sinks were made from solid blocks of aluminum (25 mm diameter, 12.5 mm thick) with thermocouple pockets (3 mm diameter) drilled to within 1 mm of the surfaces.

The sample discs of borax (Borax Consolidated Ltd., Special Quality grade) and boric oxide (prepared by dehydrating Special Quality grade boric acid supplied by Borax Consolidated Ltd.) were prepared by casting the molten salts into nickel moulds. The surfaces of the discs were ground flat using silicon carbide powder. When assembled, thin films of di-*n*-butylphthalate were applied to each side of the sample discs to improve thermal contact.

Power was supplied to the heater disc in small increments, and thermal equilibrium established each time before the temperature difference across each sample was recorded. After allowing for heat losses the conductivity was calculated using Equation 1.

**Molten salts.** An important source of error in all thermal conductivity measurements at high temperatures arises from the radiative transfer of heat, and this results in the observed conductivity being erroneously high. Gardon (3) has pointed out that failure to appreciate the radiation effect has been responsible for the wide variation in reported conductivity data for glasses and for values which appear to increase with sample thickness. Heat transferred per second by radiation is given by the Stefan-Boltzmann equation

$$Q_R = A\epsilon_{io}\sigma(t_i^4 - t_o^4) \quad (2)$$

where  $\epsilon_{io}$  is a radiation interchange factor which involves the absorptivity and emissivity of the containers and the transmission coefficient of the sample. The latter is not always known for molten salt systems, and it is usually more beneficial to attempt to eliminate the radiation effect rather than calculate it.

For a liquid exhibiting radiant transfer of heat, the observed conductivity  $K_T$  may be considered (2) to be

<sup>1</sup> To whom correspondence should be addressed.