Heats of Fusion of the Monovalent Nitrates by High-Temperature Reaction Calorimetry

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The heat of fusion of the alkali nitrates, silver and thallium nitrate were determined by reaction calorimetry. The measurements were carried out at temperatures somewhat below the melting points of the pure salts by dissolving the solid salts in a concentrated liquid solution in which the same salt served as the solvent. A small correction was applied for the heat of dilution of the liquid solution.

MOST CALORIMETRIC DATA on the heats of fusion of substances melting at elevated temperatures have been obtained by one of two methods: drop calorimetry and integration of high-temperature apparent heat-capacity curves.

In the first mentioned approach, samples of the considered substance are enclosed in capsules and dropped into a room temperature calorimeter from above and below the melting point. The heat of fusion is obtained from the difference in heat content between solid and liquid at the melting temperature.

In the second approach, the apparent heat capacity—i.e., the heat necessary to raise the temperature of the substance 1° C.—is plotted *vs.* temperature. A large peak in the curve will appear at the melting point. The enthalpy of fusion is obtained by integration of the area between this curve and a base line, which connects the heat capacity of the substance below and above the melting temperature.

Both of these methods are subject to sources of significant experimental uncertainty. For example, in the drop method the enthalpy of fusion characteristically represents the difference between two large numbers. In the second method, there may be doubt about how the base line should be drawn.

The present communication describes a method which permits direct, calorimetric determination of the heat of fusion of a small sample at temperatures somewhat below the melting point. This method has been applied to a redetermination of the heats of fusion of the monovalent nitrates.

THEORETICAL

Consider the following process:

$$n_1 A(l) + A_{n_2}B_{n_3}\ \text{(liq. soln.)} = A_{n_1+n_2}B_{n_3}\ \text{(liq. soln.)} \qquad (1)$$

where n denotes number of moles.

The heat effect $[\Delta H(T)]$ associated with this process can be measured at any temperature (T) below the melting point of A and above the liquidus temperature for the liquid solution $A_{n_1+n_2}B_{n_3}$.

Clearly, ΔH may be considered to represent a sum of two terms: the heat of fusion of pure A at the considered temperature, $\Delta H_f(T)$, and the heat of dilution, $\Delta H_d(T)$, associated with the process

$$n_1 A(\text{l}) + A_{n_2}B_{n_3}\text{(liq. soln.)} = A_{n_1+n_2}B_{n_3}\text{(liq. soln.)} \qquad (2)$$

Thus we have

$$\Delta H_f(T) = \Delta H(T) - \Delta H_d(T)$$

In principle both ΔH_f and ΔH_d depend on temperature. However, if we adopt an operating temperature near the melting point of A, and use a small amount of a solute B which mixes with A with a modest heat effect, the term ΔH_d can be made quite small compared with ΔH. Thus, no significant uncertainty is introduced in $\Delta H_f(T)$ if we use values of ΔH_d obtained from heat of mixing data determined above the melting point. In the present series of experiments, ΔH_d was of the order of 1% of ΔH_f.

EXPERIMENTAL

Apparatus and Procedure. We have applied the method outlined above to measure the heats of fusion of the monovalent nitrates at temperatures from 5° to 40° C. below their normal melting points. The measurements have been carried out in the twin reaction calorimeter previously described by Kleppa (*4*). The procedures described earlier were generally used, with the minor modifications dictated by the special nature of the experimental problem.

Suitable amounts of the salt to be studied (component A) and about 10% of another monovalent nitrate (B) were weighed out and melted in a separate furnace. This liquid mixture was placed in the "crucible" of the calorimeter at a temperature somewhat below the melting point of the pure salt A. In the break-off tube of the calorimeter was placed a small weighed, solid sample of the pure solvent. This sample was chosen large enough to give a heat effect of a convenient magnitude (10 to 30 cal.). The solution reaction was initiated by breaking the tip of the break-off tube against the bottom of the crucible. The resulting e.m.f. *vs.* time curve was amplified and recorded as described previously.

After each experiment both a gold-drop and an electrical calibration were performed. The mean of the two values was used to calculate the heat of fusion. The two calibrations agreed within about 1% at the higher temperatures (400° C.) and within about 2% at the lowest temperature

Table I. Heats of Fusion of the Monovalent Nitrates

Salt	Melting Point, ° C.	Temp., ° C.	Number of Expts.	ΔH_f,[a] Cal./Mole	Lit. Values for ΔH_f, Cal./Mole	Method	Ref.
$LiNO_3$	254	249	4	5961 ± 83	6100 ± 2%	Drop	(*2*)
					6060 ± 200	Drop	(*1*)
$NaNO_3$	310	303	8	3696 ± 32	3690 ± 2%	Drop	(*2*)
					3490 ± 7%	C_p	(*8*)
					3596 ± 8	C_p	(*12*)
KNO_3	337	297	4	2413 ± 28	2570 ± 2%	Drop	(*2*)
$RbNO_3$	316	298	8	1105 ± 10	1109 ± 2%	C_p	(*10*)
$CsNO_3$	417	400	4	3213 ± 43	3370 ± 30	C_p	(*9*)
$AgNO_3$	210	202	4	2886 ± 8	2580 ± 1.5%	Drop	(*2*)
					2775 ± 2%	Drop	(*3*)
					2960 ± 60[b]	C_p	(*7*)
$TlNO_3$	206.5	202	6	2264 ± 36	2107 ± 85	Drop	(*11*)

[a] Reported uncertainties are mean deviations. [b] A least squares fit of data given (*3*) was made with EFINS 1620 computer. When two outliers were excluded, ΔH_f at the reported melting point was 2857 cal./mole.

(202° C.). In most cases the electrical calibration data were slightly larger than the gold-drop values.

Materials. The lithium, sodium, and potassium nitrates (Mallinckrodt Analytical Reagents) were used without further purification. The cesium and rubidium nitrates were purchased (Millmaster Chemical Corp.) as "99.9% pure" and were recrystallized twice from distilled water before use. The silver nitrate was prepared by dissolving "fine silver" (Goldsmith Bros.) in HNO_3, and was recrystallized once. The thallium nitrate was prepared by dissolving 99.99% thallium metal (American Smelting and Refining Co.) in HNO_3. After two recrystallizations, no thallic hydroxide was detected on addition of ammonia. All salts were dried at 130° C. before weighing. Calculations of the heats of dilution were made from heat of mixing data previously published by Kleppa (*5, 6*) *et al.*

RESULTS

Heats of fusion determined in the course of the present research are recorded in Table I along with corresponding data taken from earlier calorimetric work. Most of the experimental results were obtained at temperatures only a few degrees below the normal melting point. For sodium and potassium nitrate the measurements covered a somewhat wider range in temperature, down to about 50° C. below the melting point. In the case of potassium nitrate, we were unable to detect any change in the heat of fusion within this range. For sodium nitrate, a ΔC_p of about 1 cal./° C./mole was indicated.

DISCUSSION

On the whole, these new values of the heats of fusion of the nitrates are comparable in quality with corresponding calorimetric data recorded in the literature. In some cases, notably for potassium, cesium, silver, and thallium nitrate our values are believed to represent improvements on these earlier data.

In the present article, we have refrained from comparing our results with corresponding heat of fusion data derived from cryoscopic work. Usually one finds reasonable agreement between the results obtained by these two methods. However, in most cases, the reported cryoscopic measurements are not sufficiently accurate to justify their use in making a choice between two calorimetric values.

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