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High temperature heat capacities of indium(III) bromide and sodium iodide by differential scanning calorimetry

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Abstract

The heat capacities of indium(III) bromide and sodium iodide have been determined by differential scanning calorimetry over the range 700–1000 K using specially designed high-pressure nickel containers in a commercial differential scanning calorimeter. Enthalpies and temperatures of melting were also recorded.

INTRODUCTION

Inorganic metal halides are widely used as additives within the envelope of the current generation of high-pressure discharge lamps [1]. Their effect is to improve significantly the spectral distribution of the lamp. In order to simulate the discharge spectrum, the identity of the species present and their thermodynamic and transport properties over a wide range of temperature must be known.

The heat capacities of both sodium iodide and indium(III) bromide in the solid phase have been studied previously in this laboratory [2,3]. However, our results were limited to a maximum temperature of ≈ 800 K by the pV effect of the trapped argon gas in the conventional DSC cell fabricated from 0.2 mm thick gold sheet.

This paper reports the heat capacities in the temperature range 700–1000 K which extends both materials into their liquid ranges and, hence, the transition temperatures and enthalpies could also be obtained. The samples were contained in reusable high-pressure nickel DSC cells of our own design. The use of high-pressure containers in DSC work is not new and we have not completed an exhaustive literature survey. Freeberg and Alleman [4] describe reusable cells fabricated in brass, aluminium and stainless steel which operated satisfactorily to 10 atm. The maximum temperature of operation was limited by the use of a Teflon (Du Pont) disc as seal. Schouteten et al. [5] describe a disposable cell in stainless steel (type 316) sealed by resistance welding, thus eliminating the need for a sealing disc.

TABLE 1

Analytical data for NaI and In(III)Br_3 (calculated results in parentheses)

	Specification	Halide content (mass %)
NaI	99.999%; H_2O,OH^- < 1 ppm	84.6 (84.66)
$InBr_3$	99%	67.6 (67.61)

Operating pressures to 80 atm were reported and the possibility of high temperature studies was discussed but no results presented. Goddard et al. [6] describe a disposable stainless steel (EN58B) cell, sealed by arc welding, and usable up to 1200 K; this cell was used for DTA studies, however. Finally, Perkin–Elmer [7] produce a reusable stainless steel cell which has a copper fillet as seal but their literature quotes a maximum operating temperature of 400°C.

EXPERIMENTAL

Materials

The sodium iodide (APL Engineered Materials, Inc, formerly Anderson Physics Laboratories, Inc) was supplied in a sealed glass ampoule under argon by courtesy of GE Thorn Lamps Ltd., Light Sources Division. The indium(III) bromide was supplied by the Aldrich Chemical Company. Each was analysed in solution for halide by a potentiometric titration using a reversible silver/silver halide indicator electrode. The analytical results and the commercial specifications are collected in Table 1.

The metal halides (13.46 mg NaI, 22.24 mg $InBr_3$) were sealed under argon in the specially designed cells described below.

Differential scanning calorimeter

A Perkin–Elmer model DSC-2 equipped with a type 3600 data station was used. The instrumental temperature scale was checked by determining the melting points of standard materials [2]. The enthalpy scale was checked similarly [8]. For heat capacity studies, the scan speed was 10 K min^{-1} at a sensitivity of 1 mcal sec^{-1}. The instrument operates in a comparative mode, the unknown heat capacity being determined relative to a sapphire standard, for which reliable heat capacities [9] from 400 to 1200 K are known.

$$C_p(\alpha - Al_2O_3) = 148.57 - 0.003421T - \frac{20409.6}{T} \quad (J\ K^{-1}\ mol^{-1}) \quad (1)$$

The results obtained by this procedure between 400 and 800 K for molybdenum metal, a recommended heat capacity test material [10], have

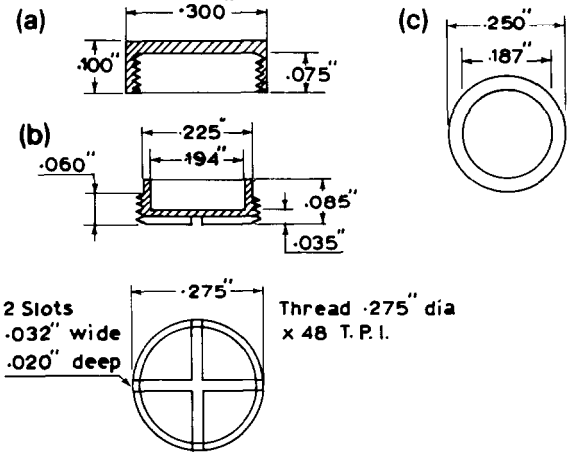

Fig. 1. Diagram of the high-pressure nickel cells (dimensions in inches).

been previously described [2]. For this work, this test procedure was extended to 960 K when the mean absolute deviation between the experimental points from 400 to 960 K and a regression line for the reference values was 0.81%.

High-pressure nickel DSC cells

The two halves of the cell ((a) and (b), Fig. 1) were machined from 10 mm diameter nickel rod (Goodfellow Metals, 99%). Sealing washers (c) were punched from a gold sheet 0.25 mm in thickness. The cells were then cleaned and weighed and made into matched pairs by abrading the flat face of A with emery paper. It was found that they could be matched to within 0.001 g.

In order to seal and reopen the cells, special tools were used. Part (a), Fig. 1, was gripped on its outer diameter in a split bush with a clamp screw; the bush was fitted with a handle. The upper half of the cell ((b), Fig. 1) was located firmly on a vertical post with two keying blades set at 90° to each other and the base (a) was screwed into place, i.e. it was sealed in the inverted position.

The cell was tested by filling with water and heating to 200°C in a TGA rig; at this temperature the internal pressure is about 15 atm and no mass change was noted. Nickel tarnishes perceptibly in air at 570 K and shows a mass increase due to oxidation at 800 K so the DSC sample chamber must be cooled to below this temperature before opening and an inert purge gas is used for routine operation. The thermal response of the cells was checked by measuring the temperature and enthalpy change for the melting of phenoxybenzene, a recommended temperature and enthalpy stan-

TABLE 2

Temperatures and enthalpies of melting for phenoxybenzene [a] in the high-pressure nickel cell

Scan speed (K min^{-1})	T_m (K) [b]	ΔH_m (kJ mol^{-1}) [b]
20	299.8 ± 0.2	17.21 ± 0.04
10	299.7 ± 0.2	17.21 ± 0.03
5	299.6 ± 0.1	17.17 ± 0.03
2.5	299.3 ± 0.1	17.14 ± 0.02

[a] Literature [11] values: $T_m = 300.02$ K, $\Delta H_m = 17.22 \pm 0.02$ kJ mol^{-1}.
[b] Only four results were recorded at each scan speed and the quoted uncertainty interval is the range of the results at each scan speed.

dard [11]. The sample and its calibration were traceable to the Certified Reference Materials Division of the laboratory of the Government Chemist, UK. The results for different scan speeds are collected in Table 2.

Our work uses a scan speed of 5 K min^{-1} for the determination of transition enthalpies and temperatures; at this speed the melting enthalpy of phenoxybenzene is reproduced satisfactorily but the experimental temperature of transition is a little low.

RESULTS AND DISCUSSION

For sodium iodide, we have extended earlier heat capacity results [2] in the solid range (384–772 K) to 920 K. The melting temperature (934 K) and melting enthalpy were measured and results for heat capacity in the liquid range to 1000 K were measured. Figure 2 shows the C_p results for this work compared with previous results [2] from this laboratory. The continuity of the results in the solid phase is excellent.

For indium(III) bromide, the melting temperature (693 K) and the melting enthalpy were measured. Also, the heat capacity in the liquid range from 700 to 850 K was determined. The results are compared with the previous work [3] from this laboratory in Fig. 2. There are no other literature C_p results for this halide. The heat capacities for both systems

TABLE 3

Regression and correlation (r) coefficients for C_p (J K^{-1} mol^{-1}) = $a + bT$

Phase	Range (K)	a [a]	b [a]	r^2
NaI (solid)	384–920 [b]	44.983 ± 0.046	0.022523 ± 0.000068	99.8
NaI (liquid)	950–1000	42.5 ± 2.3	0.0264 ± 0.0024	84
$InBr_3$ (liquid)	700–850	99.3 ± 4.3	0.0527 ± 0.0060	76

[a] Uncertainty intervals are ± one standard deviation of the regression coefficients.
[b] This range includes data points from 384 to 772 K from previous work [2].

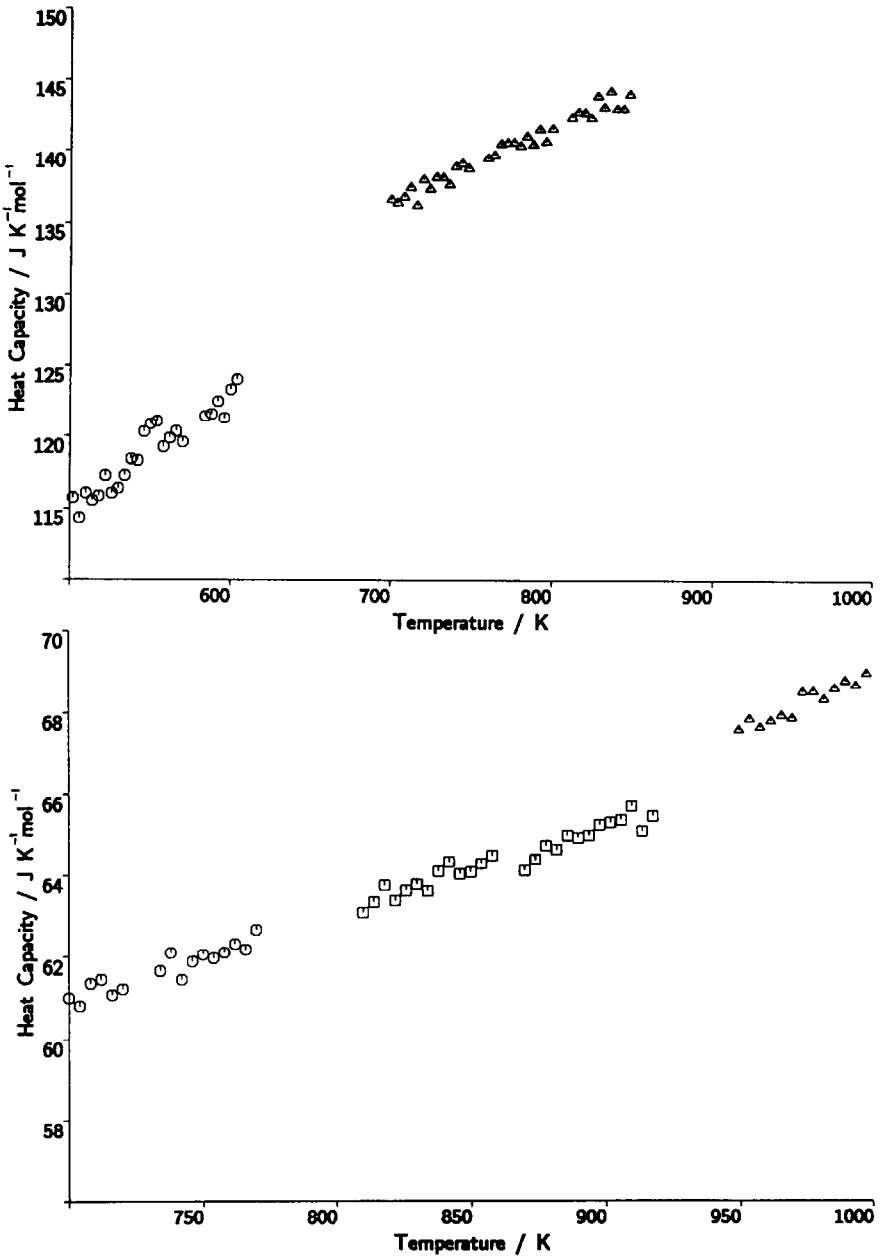

Fig. 2. Lower: heat capacity results (C_p) for sodium iodide at 4 K intervals (half of the experimental points are omitted for clarity). Points (○) to 772 K are from previous work [2]. Points (□), 810–920 K, are new results in the solid range and points (△), 950–1000 K, are in the liquid range. Upper: heat capacity results for $In^{III}Br_3$ at 4 K intervals (half of the experimental points are omitted for clarity). Points (○) are from previous work [3] in the solid range and points (△), 700–850 K, are for the liquid.

TABLE 4

Transition temperatures and enthalpies measured at 5 K min^{-1} (10 measurements of the transition were made in each case)

	T_m (K)	ΔH_m (kJ mol^{-1}) [a]	Literature
NaI (melting)	934.2 ± 0.8 [b]	22.7 ± 0.2	934, 23.74 [12]
$InBr_3$ (melting)	692.8 ± 0.7	26.6 ± 0.7	–

[a] These results include a correction for the calibration of the enthalpy scale of our instrument [8].

[b] Uncertainty intervals are ± one standard deviation of the mean.

were regressed to linear functions and the regression coefficients are given in Table 3. The melting temperatures and enthalpies for both systems are collected in Table 4.

It is surprising to note that this is the first report of the temperature dependence of the liquid phase heat capacity for a material as ubiquitous as sodium iodide.

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