THE HIGH TEMPERATURE HEAT CAPACITIES OF INDIUM(I) BROMIDE AND INDIUM(III) BROMIDE BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The high temperature heat capacities of indium(I) bromide (crystal and liquid) and indium(III) bromide (crystal) in the temperature range 333–700 K were determined. A chemical reaction during the melting of indium(I) bromide, possibly disproportionation to give indium metal and indium(III) bromide, was also investigated.

INTRODUCTION

Inorganic halides are widely used as additives within the envelopes of the current generation of high-pressure discharge lamps [1], and indium(I) bromide has been considered in this context [2]. The effect of the addition is to improve significantly the spectral distribution and colour rendition of the lamp. Databases of thermodynamic and transport data for these inorganic halides are being compiled for use in modelling the discharge. Some recent experimental work on the vaporization thermodynamics of indium(I) halides has been reported [3]. In the processing of these results an estimated temperature-independent constant value for the molar heat capacity of liquid indium(I) bromide was used, there being no literature data.

This paper reports the heat capacities of InBr (solid and liquid) and $InBr_3$ (crystal) in the temperature range 333–700 K using differential scanning calorimetry (DSC) and discusses the possible disproportionation of InBr on melting.

EXPERIMENTAL

Materials

The indium(I) bromide (APL Engineered Materials, Inc., formerly Anderson Physics Laboratories, Inc.) was supplied in glass ampoules sealed under

TABLE 1

Analytical data for the indium bromides

	Specification	Content (mass%)	
		In	Br
InBr	99.9995%, O <100 ppm [a]	58.98, 58.52 [3]	41.00
InBr$_3$	99.999% [b]	–	67.59

[a] APL Engineered Materials, Inc.
[b] Aldrich.

argon by courtesy of Thorn Lighting Ltd., Light Sources Division. The material was synthesized from the elements and the synthesis and analysis have been described in detail [3]. In addition, each material was analyzed in solution for bromide by a potentiometric titration using a reversible silver/silver bromide indicator electrode; both materials were initially digested in nitric acid in the presence of sulphite to inhibit halogen loss. The analytical results are collected in Table 1.

The bromides (24.49 mg InBr, 22.24 mg InBr$_3$) were sealed under argon in special 0.2 mm thick gold sample pans. Separate experiments revealed that the rupture temperature for sealed empty pans was ca. 800 K.

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 point of standard materials [4]. For heat capacity studies, the scan speed was 10 K min^{-1} and the sensitivity was 1 mcal s^{-1}. The instrument operates in a comparative mode, the unknown heat capacity being determined relative to a sapphire standard, for which reliable heat capacity values [5] between 400 and 1200 K are known.

Results were obtained by this procedure for molybdenum metal, a recommended heat capacity test material [6]. The mean deviation between the experimental points and a regression line for the reference values is ±0.76% between 400 and 800 K and the results have been illustrated graphically [4].

Raman spectroscopy

Raman spectra were obtained on solid samples sealed in melting-point tubes. A Coderg PH1 spectrometer was used equipped with a Coherent Radiation Ltd. (CRL) model 52 argon ion laser operating at either 514.5 nm (green) or 600 nm, using a CRL CR-599 dye laser (Rhodamine G) pumped at 4 W by the argon ion laser operating on all lines. The slit width was

between 1 and 6 cm^{-1} and spectra were recorded from 20 to 300 cm^{-1} from the exciting line.

RESULTS AND DISCUSSION

There are conflicting literature reports for the melting temperature of indium(I) bromide covering the range 493–558 K [3,7–13]. The melting temperature measured here (554 K) is close to that reported by Walter et al. [7] (553 K) and Brumleve et al. [3] (553 K). Indium(I) bromide does not appear to melt reversibly and this may explain the large divergence in the literature melting points. Initially, three endothermic signals were noted in our experimental range (333–700 K): at 478, 519 and 554 K. The largest feature is at 554 K (assumed melting) and the smaller features were not characterized. Cooling and recycling over the same range revealed small but significant changes in the onset temperatures and magnitude of the endotherms. Continued repetition of the thermal cycle caused further marked changes but finally, after eight cycles, a stable composition was obtained which gave reproducible transition features. These changes are summarized in Table 2.

We were unable to identify the cause of these changes but partial disproportionation (eqn. (1)) appears likely

$$3InBr \rightleftharpoons 2In + InBr_3 \tag{1}$$

There is reliable evidence [7,8] for the occurrence of this disproportionation equilibrium in melts, although at 558 K (just in excess of our nominal melting point and where In is liquid and $InBr_3$ is solid), the equilibrium constant is small (2.2×10^{-5} [13]). The phase diagram for the In(I)Br/ In(III)Br_3 system [7] suggests congruent melting of In(I)Br at 553 K and

TABLE 2

Onset temperatures (T, K) and magnitudes (I, kJ mol^{-1}) of endotherms noted during successive cycling of In^IBr over the temperature range 333–700 K at 5 K min^{-1}

Cycle no.	Peak 1		Peak 2		Peak 3		Peak 4	
	T	I	T	I	T	I	T	I
1	478.1	0.8	519.3	8.1	554.1	16.4	–	–
2	475.9	0.8	519.1	8.0	554.3	16.2	–	–
3	461.3	0.9	503.6	9.7	554.1	12.5	–	–
4	459.2	1.1	497.9	12.3	554.2	3.2	–	–
5	452.4	1.6	474.7	16.1	–	–	651.4	1.2
6	452.3	5.2	474.3	10.7	–	–	651.3	1.2
7	452.8	13.8	474.5	6.7	–	–	651.2	1.3
8	453.1	13.1	474.1	6.4	–	–	651.3	1.2
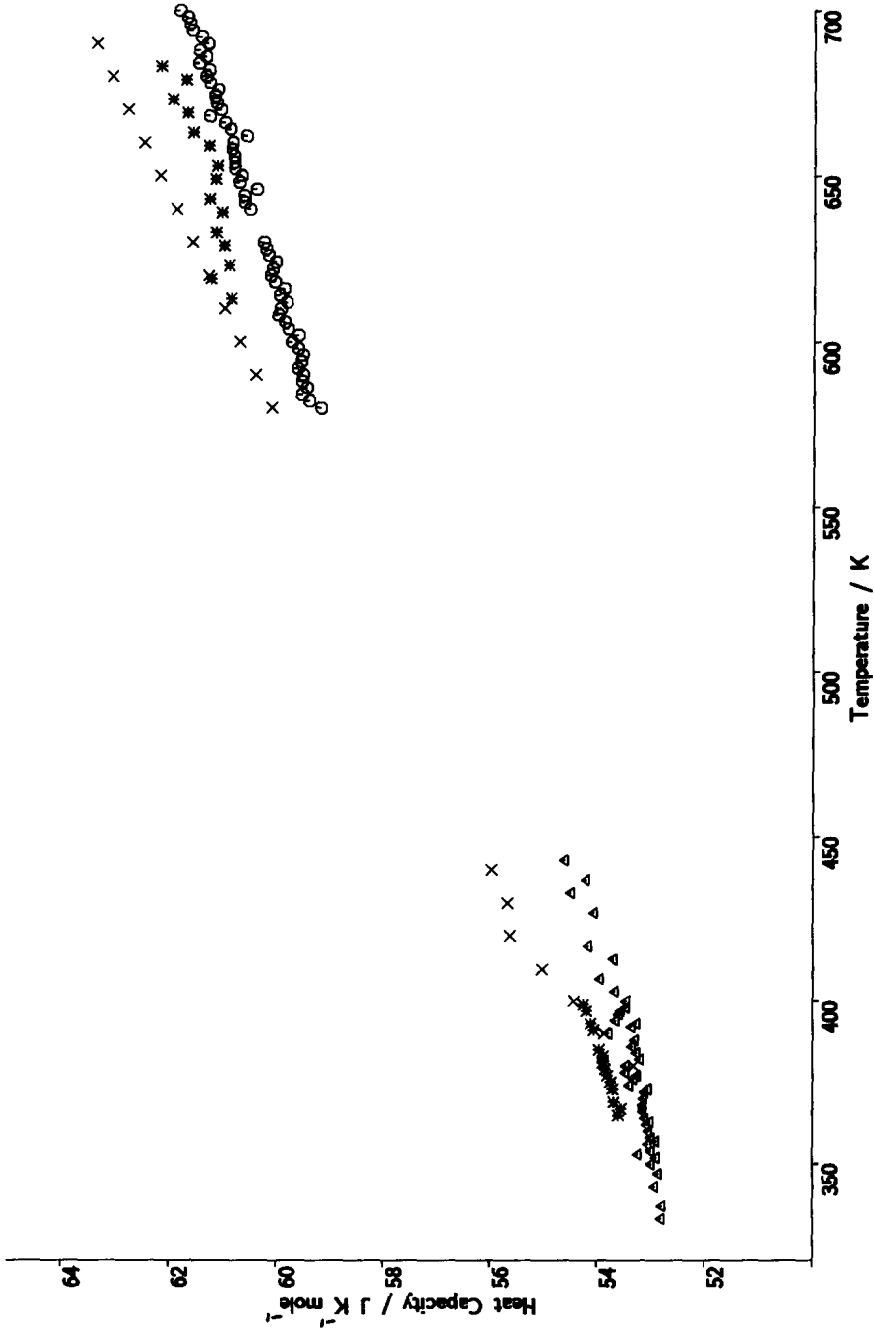
Fig. 1. Heat capacities for (△) solid and (○) liquid InBr. (∗) Stable composition; (×) calculated results (see text). The points (△, ○) were obtained during melting cycles 1 and 2 (see Table 2).
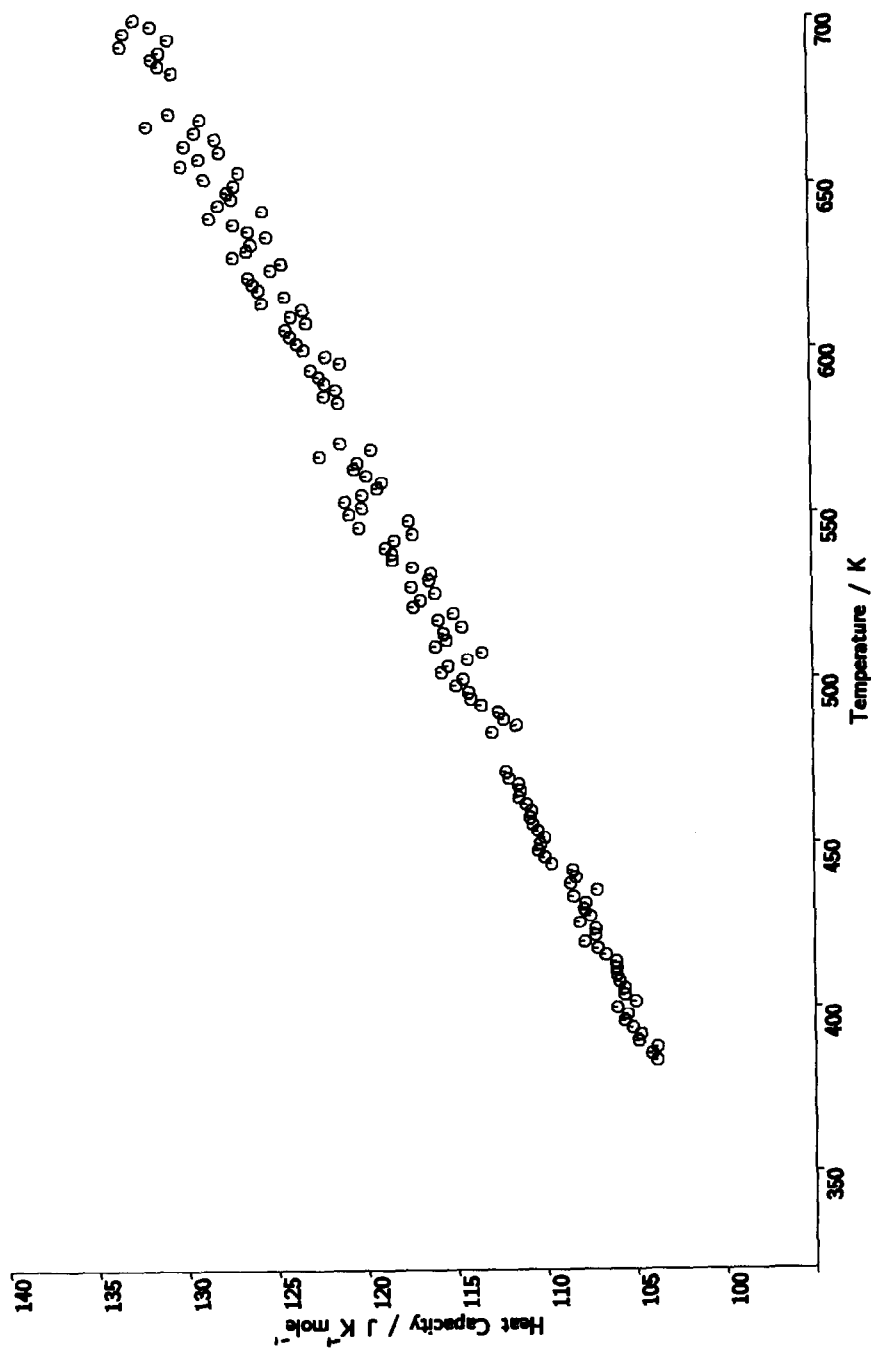
Fig. 2. Heat capacities for InBr₃ (crystal).

although other sub-bromides (In_2Br_3, In_4Br_7 and $InBr_2$) occur at high $In^{III}Br_3$ mole fractions, none has a melting point in excess of InBr. It appears likely that the effects we observe in scanning calorimetry are due to disproportionation (eqn. (1)), but phase separation within the sealed pan possibly displaces the reaction from its equilibrium position.

In order to obtain reliable heat capacities for the solid and liquid phases of $In^I Br$ we adopted the following protocol. Measurements were completed on a fresh sample in the range 333–443 K where InBr is solid. The sample was then taken through the melting point and measurements made from 580 to 700 K on the liquid. The sample was cooled and determinations at several points repeated (from 360 to 400 K) in the solid range. Finally, the sample was remelted and measurements at several points were repeated (from 630 to 680 K) in the liquid range. A statistical test showed that there was no significant difference between the repeated and original measurements. The results were regressed to yield the following expressions, where eqn. (2) is valid over the range 333–443 K and eqn. (3) over the range 580–700 K.

$$C_p(\text{InBr, c}) \ (\text{J K}^{-1} \text{ mol}^{-1}) = (48.80 \pm 0.21) + (0.01177 \pm 0.00056)T \qquad (2)$$

$$C_p(\text{InBr, l}) \ (\text{J K}^{-1} \text{ mol}^{-1}) = (47.93 \pm 0.12) + (0.01964 \pm 0.00018)T \qquad (3)$$

Correlation coefficients for eqns. (2) and (3) were 96.7% and 99.8%, respectively, and the uncertainty intervals are to within a single standard deviation of the regression coefficients.

To assess the likely effect of disproportionation on our results, the sample was remelted eight times until a reproducible DSC trace was obtained. Then heat capacity values in the InBr solid range (360–400 K) were determined, followed by results in the liquid range (630–680 K). These results are identified as the "stable composition" in Fig. 1 and are clearly higher than the results for the authentic solid and liquid phases. It is of interest to determine how much higher these results would be if disproportionation was complete; for this calculation we require the heat capacities of In (crystal (c) and liquid (l)) [14] and $InBr_3$(c). There are no literature data for $InBr_3$ and we undertook heat capacity measurements for the solid between 360 and 700 K, for which

$$C_p(\text{InBr}_3, \text{ c}) \ (\text{J K}^{-1} \text{ mol}^{-1}) = (69.69 \pm 0.30) + (0.0893 \pm 0.0006)T \qquad (4)$$

with $r^2 = 99.5\%$. Consequently, we may calculate C_p for $[2\text{In(c)} + \text{InBr}_3(\text{c})]/3$ (360–430 K) and for $[2\text{In(l)} + \text{InBr}_3(\text{c})]/3$ (430–700 K); the melting temperature of $InBr_3$ (709 K) is outside our experimental range. The results described above are identified as "calculated" in Fig. 1 and they are significantly higher than the "stable composition" results. The results for $InBr_3$ are shown in Fig. 2.

Confirmation of the suggestion that only slight disproportionation had occurred came from Raman spectroscopy. A sample of InBr that had been

maintained at 623 K for 1 h gave a Raman spectrum identical to that of a pure sample, which agreed well with a literature spectrum [15]. If significant conversion to $InBr_3$ had occurred, a strong band at 172 cm^{-1} from the $InBr_3$ spectrum would have been apparent; this was not observed.

In summary, it is overwhelmingly likely that, although some chemical change occurs on melting, our heat capacity results for the solid and liquid phases of InBr are realistic. Furthermore, the effect on the results of disproportionation, if this was the chemical change noted, was insignificant.

ACKNOWLEDGEMENT

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