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HIGH TEMPERATURE HEAT CAPACITIES OF THALLIUM IODIDE, THULIUM IODIDE AND SODIUM IODIDE BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The heat capacities of thallium iodide (α, β and liquid phases), thulium iodide (crystal) and sodium iodide (crystal) have been determined by differential scanning calorimetry over the temperature range 370–800 K.

INTRODUCTION

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

The heat capacities of inorganic halides in the condensed phase, and, in particular in the liquid phase, are not well established. This paper reports the determination of the heat capacities of TlI (α, β and liquid phases), NaI (crystal) and TmI_3 (crystal) in the temperature range 370–800 K using differential scanning calorimetry. In addition, the transition temperatures and enthalpies for TlI have been measured.

EXPERIMENTAL

Materials

The iodides (APL Engineered Materials, Inc., formerly Anderson Physics Laboratories, Inc.) were supplied in sealed glass ampoules under argon by courtesy of Thorn Lighting Ltd., Light Sources Division. The iodide content of each was analysed in solution by a potentiometric titration using a

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TABLE 1

Analytical data for the iodides

APL specification		Iodide content (mass % of theoretical)
TlI	99.999%; 0 < 200 ppm	99.82
TmI_3	99.96%; H_2O, OH^- < 10 ppm	99.98
NaI	99.999%; H_2O, OH^{-1} < 1 ppm	99.98

reversible silver/silver iodide indicator electrode; TmI_3 and TlI were initially digested in nitric acid in the presence of sulphite to inhibit halogen loss. The analytical results and the APL specification are collected in Table 1.

The iodides (63.2 mg TlI, 13.46 mg NaI and 13.13 mg TmI_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 around 800 K.

Differential scanning calorimetry

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 the following standard materials (the literature and

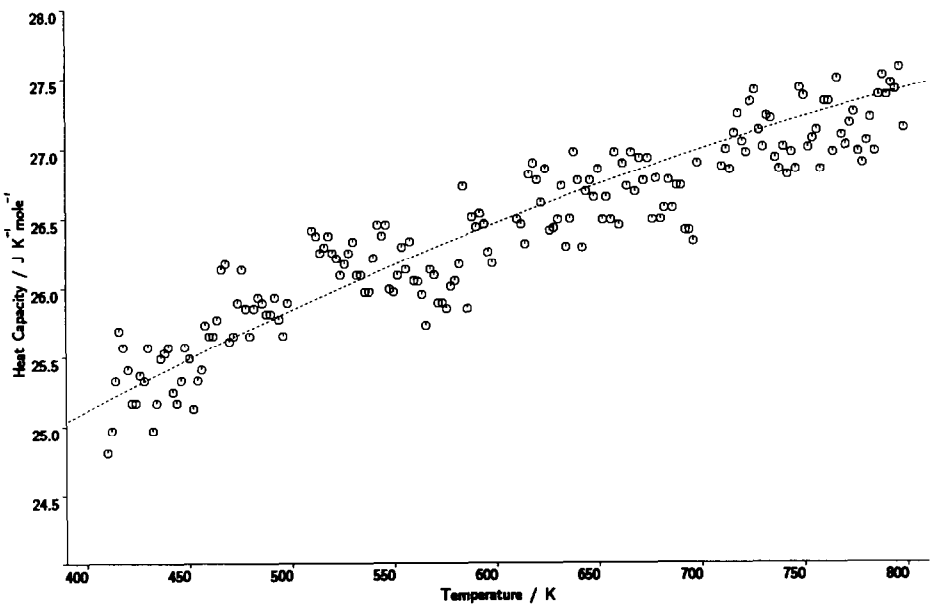

Fig. 1. Heat capacities for molybdenum metal: ⊙, experimental; ------, a regression line from the literature results [3].

found melting temperatures, respectively, are quoted in brackets): *n*-octacosane (335, 334.8 K), *n*-triacontane (339, 338.9 K), naphthalene (355, 355.0 K), indium (429.6, 429.5 K), tin (505.2, 505.3 K) and cadmium (594.2, 594.1 K).

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 capacities [2] from 400 to 1200 K are known

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

Results obtained by this procedure for molybdenum metal, a recommended heat capacity test material [3], are shown in Fig. 1. The mean deviation between the experimental points from 400 to 800 K and a regression line for the reference values is $\pm 0.76\%$.

RESULTS AND DISCUSSION

Thallium iodide

TlI undergoes two transitions in our experimental temperature range (370–800 K): $\alpha \rightarrow \beta$ at 450 K and $\beta \rightarrow$ liquid at 731 K. By cooling the sample very slowly (0.3 K min^{-1}) through the $\alpha \rightarrow \beta$ phase transition temperature (450 K), heat capacities for the supercooled β-phase to 380 K were determined. These points were included in the regression line for the β-phase. The transition temperature and enthalpies are compared with literature results [4] in Table 2.

The principal difference between our results and the literature data is the assignment of the melting temperature; this will effect the calculation of the entropy change of melting. The data were regressed to linear or quadratic expressions and the regression and correlation coefficients are collected in Table 3. The agreement between the work reported here and that of Cubicciotti and Eding [4] is excellent; the main differences are that this work shows curvature in the temperature dependence of the β-phase and a

TABLE 2

Transition temperatures and enthalpies for TlI measured at 5 K min^{-1}

	This work	Literature [4]
$T(\alpha \rightarrow \beta)$ (K)	450 ±1	451 ±1
$\Delta H(\alpha \rightarrow \beta)$ (kJ mol^{-1})	1.10±0.02	0.91
$T(\beta \rightarrow$ liq) (K)	730.8 ±0.5	714.8±0.5
$\Delta H(\beta \rightarrow$ liq) (kJ mol^{-1})	14.74±0.11	14.73

TABLE 3

Regression and correlation (r^2) coefficients for $C_p(\text{J K}^{-1}\text{mol}^{-1}) = a + bT + cT^2$ for thallium(I) iodide: α-phase, 380–444 K; β-phase, 380–724 K [a]; and liquid phase, 750–800 K

Phase	a [b]	b [b]	c [b]	r^2
α, this work	46.4 ± 0.3	0.0186 ± 0.0008	–	94.5
α, lit. [4]	48.4	0.0139	–	–
β, this work	57.2 ± 0.8	−0.0420 ± 0.0029	0.000077 ± 0.000003	99.6
β, lit. [4]	32.3	0.0471	–	–
Liquid, this work	63.7 ± 0.4	0.0105 ± 0.0005	–	91.6
Liquid, lit. [4]	72.0	–	–	–

[a] This range includes data points for a supercooled material from 380 to 450 K.
[b] Uncertainty intervals are ± one standard deviation of the regression coefficients.

linear temperature dependence for the liquid. This permits a modest extrapolation to higher temperatures for the liquid phase. The raw data are shown in Fig. 2.

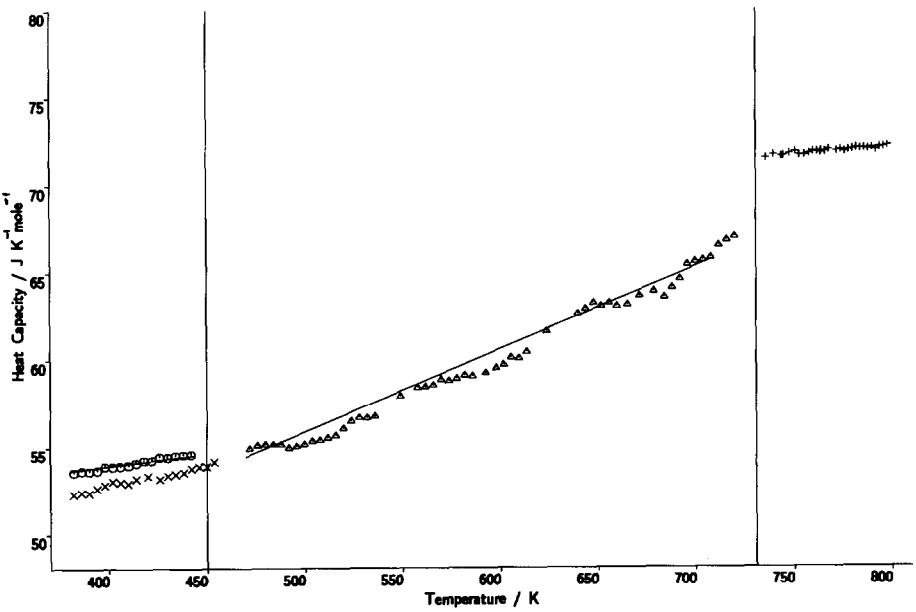

Fig. 2. Heat capacities for thallium(I) iodide: ×, supercooled β-phase; ○, α-phase; △, β-phase; +, liquid phase. The full lines for the α- and β-phases are literature [4] regression lines. The vertical lines indicate the transition temperatures.

Thulium(III) iodide

The melting temperature of TmI_3 is 1394 K which is outside the range of our equipment. No experimental data have been reported for this material

and our results for the solid phase in the range 373–773 K are represented by

$$C_p(\mathrm{TmI_3,\ c})(\mathrm{J\ K^{-1}mol^{-1}}) = (102.72 \pm 0.09) + (0.007353 \pm 0.000158)T \quad (2)$$

The thermal properties of several lanthanide halides have been reviewed [5].

Sodium iodide

Both low [6] and high [7] temperature heat capacity results have been reported for NaI [8]. Our results cover the range 373–773 K and are given by

$$C_p(\mathrm{NaI,\ c})/\mathrm{J\ K^{-1}mol^{-1}} = (44.869_5 \pm 0.081) + (0.02279 \pm 0.00014)T \quad (3)$$

The mean deviation of our raw data from the above regression equation is $\pm 1.07\%$. The high temperature results reported by Gardner et al. [7] include the range 298–934 K and are represented [8] by

$$C_p(\mathrm{NaI,\ c})/\mathrm{J\ K^{-1}mol^{-1}} = 41.953 + 0.02542T + \frac{228000}{T^2} \quad (4)$$

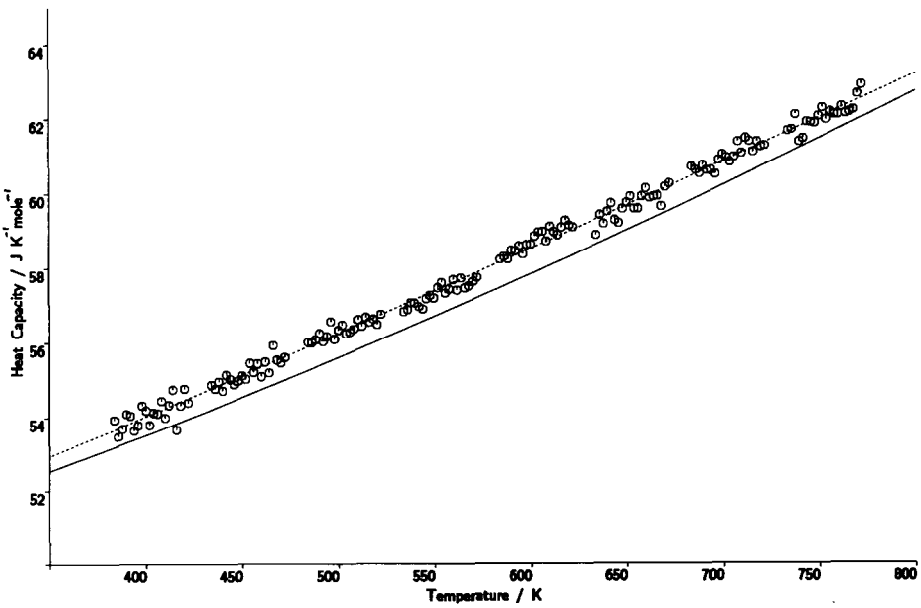

Fig. 3. Heat capacities for sodium iodide: ⊙, raw data; - - - - - -, quadratic regression line for these data; ———, literature [8] regression line.

The deviation of our results given by eqn. (3) from Gardner's regression line, eqn. (4), is 0.5% at 370 K, rising to 1.3% at 540 K and decreasing to 0.8% at 770 K; the mean deviation is +1.07%. Consequently, our results are significantly different from the literature data only in the mid-temperature range (480–610 K), see Fig. 3.

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