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High-temperature heat capacities of tin(II) chloroiodide and tin(II) bromoiodide

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Abstract

The heat capacities at constant pressure for tin(II) choroiodide and tin(II) bromoiodide have been determined for the solid and molten phases in the range 360–800 K by differential scanning calorimetry. The melting temperatures, enthalpies and entropies are reported and are compared with the corresponding data for the parent halides.

INTRODUCTION

There is considerable current interest in the thermodynamic properties of the tin(II) halides and mixed halides [1,2]. They have been used as additives in the current generation of high-pressure metal halide discharge lamps, usually mixed with other halides [3]. For example, the vapour in a typical lamp might contain atomic, molecular and ionic species from combinations of the elements Sn, Na, Cl, I, Hg and Ar, the exact vapour composition depending on the local temperature of the discharge. Knowledge of the thermodynamic and transport properties of these species over a wide range of temperature is necessary for the successful modelling of the lamp discharge [4].

Recent reports of thermodynamic data for tin-containing compounds include a study of the vaporisation equilibrium for SnBrI [1], the total vapour pressure above $SnBr_2$(liquid) [5] and the high-temperature heat capacities of SnX_2 ($X = Cl$, Br and I) [6]. This paper presents results for the heat capacities, and the temperatures, enthalpies and entropies of transition for SnClI and SnBrI in the temperature range 360–800 K; the results are compared with corresponding data for the parent halides, $SnCl_2$, $SnBr_2$ and SnI_2.

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EXPERIMENTAL

Materials

Different syntheses for Sn_2ClBr_3, SnClBr, SnClI and SnBrI have been reported [7,8]: (i) by heating alcoholic solutions of ICl plus excess Sn, (ii) by coprecipitation of SnX_2 and SnY_2 from alcoholic solutions, (iii) by heating equimolar mixtures of the solid salts, and (iv) by shock compression of equimolar mixtures; experimental procedures are not detailed, however. For this work, SnClI and SnBrI were prepared in gram quantities by a modification of method (iii) above. Equimolar mixtures of the pure dihalides were ground together in a dry nitrogen atmosphere and sealed in evacuated glass ampoules. The ampoules were heated to 200 ° C for one hour and then to 270 ° C for a further hour. Analyses for the starting materials have been reported previously [6] and the constitution of the mixed halides was checked by powder X-ray diffraction (XRD). The principal reflections were at identical *d* spacings to those given in the literature [7], and the absence of the high-intensity reflections characteristic of the pure dihalides was noted.

Differential scanning calorimeter

A Perkin–Elmer model DSC-2 with a 3600 data station was used. Samples (approx. 28 mg) were contained in sealed gold sample pans, 0.2 mm in thickness. The sensitivity setting was 1 mcal s^{-1} and the scan speed was 5 K min^{-1} for the calibration check (see Table 1) and 10 K min^{-1} for the heat capacity scans. At the start of the programme, a new sample

TABLE 1

Transition temperatures and enthalpies for some reference materials; literature values are given in parentheses

Material [a]	T_t (K)	$\Delta H_t(T_t)$ [b] (J mol^{-1})	Δ [c] (%)
$(C_6H_5)_2O$	299.9 ± 0.1(300.02 [9])	17200 ± 90(17216 ± 17 [9])	−0.093
In	429.7 ± 0.1(429.77 ± 0.01 [10])	3280 ± 70(3275 ± 7 [11])	+0.15
Sn	505.1 ± 0.2(505.10 ± 0.01 [12])	7180 ± 110(7147 ± 22 [12])	+0.46
Zn	692.7 ± 0.2(692.74 ± 0.01 [13])	7120 ± 100(7026 ± 40 [13])	+1.3
Al	933.5 ± 0.2(933.47 [14])	11020 ± 180(10760 ± 70 [14])	+2.4
Pb	600.7 ± 0.2(600.6 ± 0.5 [15])	4615 ± 130(4772 [15])	See text

[a] The scan speed was 5 K min^{-1} and sample sizes were between 36 and 50 mg. The metals had a nominal purity of 99.99+% and were given an acid wash prior to drying and encapsulation under dry argon.

[b] Each material was scanned five times and the quoted value is the mean; the uncertainty interval is the range.

[c] $\Delta = 100(\Delta H_{exp} - \Delta H_{lit})/\Delta H_{lit}$; $\Delta = -1.49 + 0.00409T$ ($r^2 = 98.5\%$); the result for Pb was not included in the regression.

holder unit (part no. 319-0151) was fitted and commissioned. The temperature and enthalpy scales were checked by measuring the melting temperatures and enthalpies of five standard materials; the results are collected in Table 1.

From the results in Table 1, it is clear that the transition temperatures are reproduced satisfactorily and the transition enthalpies are exact at 350 K but approx. 2.4% high at 930 K; experimental enthalpies were corrected with the linear equation in footnote c of Table 1. Lead is a potentially useful standard and its enthalpy of fusion is well-established [15]. Table 1 includes some results for lead, the sample being cut [14] from the original ingot used by the authors of ref. 15. The mean result, corrected as described above, is significantly lower than the literature result [15]. We can offer no explanation for this.

RESULTS AND DISCUSSION

The literature contains phase diagrams for the systems $SnBr_2/SnCl_2$ [16] and $SnBr_2/SnI_2$ [17], and these indicate compound formation at the stoichiometries Sn_2BrCl_3 and SnBrI respectively. To our knowledge, there is no published phase diagram for the system $SnCl_2/SnI_2$. The mixed halides, SnBrI and SnClI, each undergo a single reversible melting transition in our temperature range (360–800 K). The transition temperatures, enthalpies and entropies are collected in Table 2 and are compared with corresponding values for the parent dihalides.

The experimental heat capacities were regressed to linear expressions in T, and the regression and correlation coefficients are collected in Table 3; some numerical values at fixed temperatures are compared with corresponding values for the pure dihalides in Table 4.

The raw data are presented in Figs. 1 and 2 and regression lines for the pure halides are included for comparison.

TABLE 2

Transition enthalpies, entropies and temperatures for some tin(II) halides and mixed halides

Material	T_t^a (K)	$\Delta H_t(T_t)$ ^{a} (kJ mol^{-1})	$\Delta S_t(T_t)$ ^{a} (J K^{-1} mol^{-1})	Ref.
SnClI [b]	512.3 ±0.1	13.13±0.17	25.63±0.33	This work
SnBrI [b]	521.9 ±0.2	12.45±0.18	23.85±0.34	This work
$SnCl_2$	519.8 ±0.2	14.10±0.14	27.12±0.27	6
$SnBr_2$	507.1 ±0.2	14.30±0.14	28.20±0.28	6
SnI_2	593.2_5 ±0.1	12.10±0.22	20.40±0.37	6

[a] The uncertainty interval is ± one standard deviation of the mean value.

[b] Each of these materials was scanned ten times.

TABLE 3

Regression and correlation (r^2) coefficients for the tin(II) mixed halides, and values of a and b from the equation C_p (J K^{-1} mol^{-1}) = $a + bT$

Phase	Range (K)	a	b	r^2
SnClI(s)	360-500	66.17 ± 0.24	0.04226 ± 0.00057	99.0
SnClI(l)	540-800	74.48 ± 0.20	0.03863 ± 0.00029	99.4
SnBrI(s)	360-510	64.99 ± 0.23	0.04568 ± 0.00052	99.3
SnBrI(l)	550-800	72.27 ± 0.26	0.04324 ± 0.00038	99.2

Tin(II) bromoiodide

From Fig. 1 and the numerical data in Table 4, it is clear that the heat capacities of $SnBr_2$(s) and SnBrI(s) are not significantly different. This may be interpreted as follows. The crystal structures of $SnBr_2$ and SnI_2 are quite different, and that of SnBrI is unknown although a powder pattern has been reported [7]. $SnBr_2$ has orthorhombic symmetry [18] whereas SnI_2 is monoclinic [19] and it is likely that SnBrI will possess one of these two symmetries. The heat capacity of a diamagnetic solid of stoichiometry MX_2 may be assumed to comprise a 'molecular' component arising from covalency in the M-X bonds and a lattice component. For the 'molecular' component, only the vibrational contribution will be active in the solid, rotational and translational motion being quenched (usually). For heavy atom molecules such as $SnBr_2$ and SnI_2, where $h\nu_i < k_B T$ for $T \geq 400$ K, the vibrational contribution approaches its classical limit of $(3n - 6)R$ where n is the number of atoms in the molecular unit and, consequently, is approximately constant irrespective of the halogen. Simple calculation reinforces this point. Assuming the molecular unit is bent (C_{2v}) MX_2 (as in the gaseous tin(II) halides), then the vibrational contribution to C_p at 500 K is 24.3 ± 0.1 J K^{-1} mol^{-1} for $SnBr_2$, SnI_2 and SnBrI, calculated using

TABLE 4

Heat capacities at constant pressure $C_p(T)$ (J K^{-1} mol^{-1}) for solid (298 and 400 K) and liquid (600 and 800 K) tin(II) halides [6] and mixed halides; the error for each datum is approx. ±0.6 J K^{-1} mol^{-1}

Material	Temperature T (K)			
	298 [a]	400	600	800
SnClI(s,l)	78.8	83.1	97.7	105.4
SnBrI(s,l)	78.6	83.3	98.2	106.9
$SnCl_2$(s,l)	78.1	82.6	98.0	106.1
$SnBr_2$(s,l)	78.6	83.6	100.2	110.2
SnI_2(s,l)	77.7	81.3	93.6	101.5

[a] Extrapolated data.

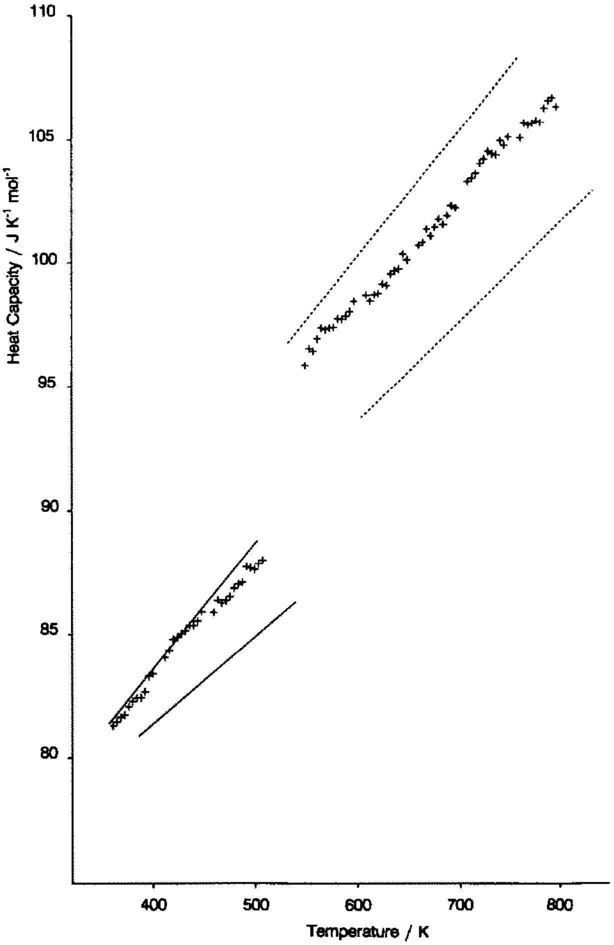

Fig. 1. Heat capacity results for SnBrI in solid (360–510 K, +) and liquid (550–800 K, +). Regression lines for the heat capacities of pure $SnBr_2$ (——— and · · ·, upper lines) and pure SnI_2 (——— and · · ·, lower lines) are included for comparison.

molecular constants selected by Hilpert and co-workers [1,2]; this contribution rises to 24.8 J K^{-1} mol^{-1} at 800 K. Consequently, it is the lattice component which is responsible for (i) the temperature dependence of the heat capacities and (ii) any differences in the heat capacities of these halides. The fact that $C_p(SnBr_2,s) \approx C_p(SnBrI,s)$ between 360 and 500 K suggests that the unit cell dimensions for $SnBr_2$ and SnBrI will be similar and that SnBrI will be orthorhombic.

Assuming that the absolute entropy of the mixed halide may be written as a mole fraction average of the parent halides, i.e.

$$S^{\ominus}[\text{SnBrI,s or l}] = 0.5S^{\ominus}[\text{SnBr}_2\text{,s or l}] + 0.5S^{\ominus}[\text{SnI}_2\text{,s or l}] \qquad (1)$$

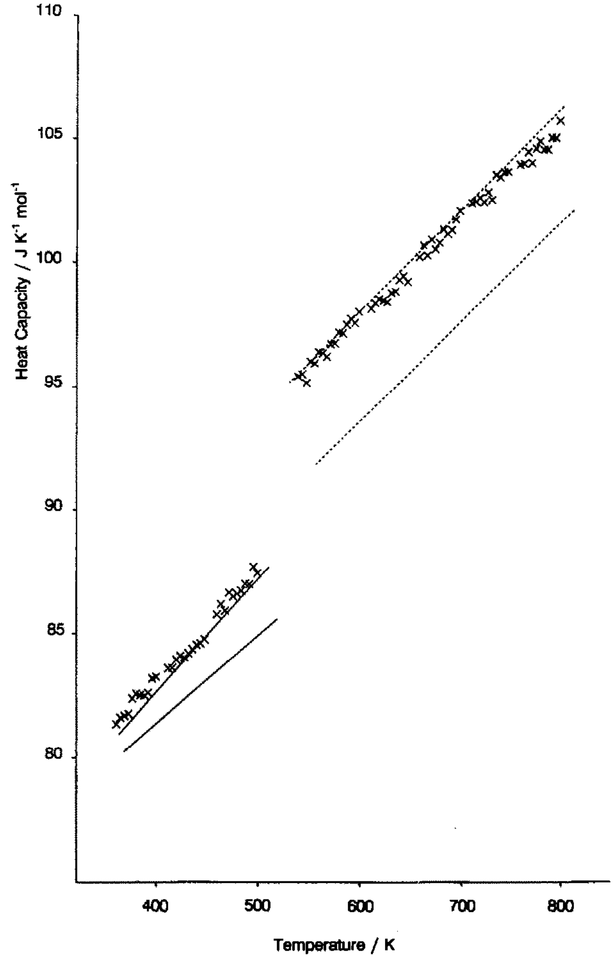

Fig. 2. Heat capacity results for SnClI in solid (360–500 K, ×) and liquid (540–800 K, ×). Regression lines for the heat capacities of pure $SnCl_2$ (——— and · · ·, upper lines) and pure SnI_2 (——— and · · ·, lower lines) are included for comparison.

then the transition entropy for the mixed halide may be expressed as

$$\Delta S_t[SnBrI] = 0.5\Delta S_t[SnBr_2] + 0.5\Delta S_t[SnI_2] \quad (2)$$

Ignoring the different reference temperatures for these values of ΔS_t, eqn. (2) may be used with the results in Table 2 to estimate ΔS_t[SnBrI] as 24.3 ± 0.2 J K^{-1} mol^{-1}. This agrees satisfactorily with the experimental value, 23.85 ± 0.34 J K^{-1} mol^{-1}, and provides support for the assumption contained in eqn. (1). Further, the transition temperature for SnBrI may be estimated from $\Delta H_t(\text{exp})/\Delta S_t(\text{calc})$ as 512 ± 9 K, compared with 521.9 ± 0.2 K obtained experimentally. The phase diagram [17] for the $SnI_2/SnBr_2$ system shows compound formation at 1:1 stoichiometry with a melting temperature of 525 K. The same phase diagram has been simulated [20] using a Redlich–Kister representation for the liquid phase [21] and yields a transition temperature of 526 ± 1 K.

The implications of the assumed eqn. (1) may now be explored. If eqn. (1) is correct then

$$SnBr_2(s) + SnI_2(s) = 2SnBrI(s), \ \Delta S = 0 \qquad (3a)$$

$$SnBr_2(l) + SnI_2(l) = 2SnBrI(l), \ \Delta S = 0 \qquad (3b)$$

The zero entropy change for eqn. (3a) suggests that SnBrI(s) is an ordered solid. For if it were a randomized substitutional solid solution, then ΔS(3a) would be of the order of the ideal entropy of mixing, $-R\Sigma_i x_i \ln x_i$ or $+5.7$ J K^{-1} mol^{-1}, where $i = 2$ and $x_i = 0.5$. There is crystallographic evidence [22] for similar ordering in the mixed lead halides, PbClI, PbBrI and PbClBr which are isostructural with $PbCl_2$. Finally, results from Table 4 may be used in eqns. (3a) and (3b) to test Neumann and Kopp's rule [23] ($\Delta C_p = 0$ for condensed phase reactions); $\Delta C_p(400\ K) = 1.7 \pm 1.5$ J K^{-1} mol^{-1} and $\Delta C_p(600\ K) = 2.6 \pm 1.5$ J K^{-1} mol^{-1}.

Tin(II) chloroiodide

Examination of Fig. 2 shows that the heat capacity of the chloroiodide is not significantly different from the chloride in both the solid and liquid phases. There is crystallographic evidence [7] that $SnCl_2$ and SnClI are isostructural although the unit cell dimensions [8] differ by around 10%. The fact that the heat capacity equality persists into the liquid phase suggests that any short-range order that occurs in the liquid phase arises from Sn–Cl rather than Sn–I bonding. The size difference between Cl and I makes estimation of ΔS_t from an equation similar to eqn. (1) much less soundly based, $\Delta S_t(calc) = 23.7 \pm 0.2$ J K^{-1} mol^{-1}, compared with the observed result, 25.6 ± 0.3 J K^{-1} mol^{-1}. There is no phase diagram for this material to permit a check of the melting temperature of SnClI. Neumann and Kopp's rule is invalid for this mixed halide when tested using equations similar to eqns. (3a) and (3b).

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