Thermochimica Acta, 185 (1991) 219–226
Elsevier Science Publishers B.V., Amsterdam

High temperature heat capacities of the tin(II) halides measured by differential scanning calorimetry

Peter J. Gardner and Steve R. Preston

Department of Chemistry, Royal Holloway and Bedford New College, University of London, Egham Hill, Egham, Surrey, TW20 0EX (UK)

(Received 27 November 1990)

Abstract

The high temperature heat capacities of the tin(II) halides (SnX_2; X = Cl, Br, I) have been determined by differential scanning calorimetry over the temperature range 370–800 K. This temperature range includes the melting transitions for which the temperatures and enthalpy changes are reported.

INTRODUCTION

The tin(II) halides are used widely as additives in modern high-pressure metal halide 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 range of temperature must be known.

The high temperature heat capacities of the tin(II) halides in the condensed phase above 298 K, and particularly in the liquid phase, are not well established. This paper reports the heat capacities of the condensed and liquid phases, together with the enthalpies and temperatures of fusion, in the temperature range 370–800 K. Our experimental method was differential scanning calorimetry. With careful operation and calibration [2] this method will yield results with an accuracy of ±2% between 300 and 1000 K.

EXPERIMENTAL

Materials

Tin(II) chloride was prepared from the dihydrate. The sample used in this work was part of a batch of material prepared by O'Brien and Mucklejohn [3]. The bromide was from APL Engineered Materials (formerly Anderson Physics Laboratories, Inc.) and was used without further purification. Tin(II) iodide was prepared from $SnCl_2$ and KI using a method described by

0040-6031/91/$03.50

TABLE 1

Analytical data for the tin(II) halides

	Specification	Halide content [a] (mass %)
$SnCl_2$	99±1%; O < 4 ppm; H_2O < 2 ppm [3]	37.2 (37.40)
$SnBr_2$	99.999%; O <100 ppm [b]; Sn = 42.46±0.21%	57.0 (57.38)
SnI_2		67.8 (68.13)

[a] Calculated values in parentheses.

[b] APL specification.

Brauer [4] and was purified by successive vacuum distillation. The samples were supplied in sealed glass ampoules under argon by courtesy of GE Thorn Lamps Ltd. Each was analysed in solution for halide by a potentiometric titration using a reversible silver/silver halide indicator electrode; they were initially mixed with water in the presence of excess sulphite (5 g) to inhibit halogen loss on acidification. The mixture was then slowly acidified by the drop-wise addition of concentrated nitric acid. This procedure digests the halide with minimal halogen loss. The analytical results are collected in Table 1.

The halides (40.15 mg $SnCl_2$, 48.56 mg $SnBr_2$, 53.90 mg SnI_2) 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 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 [5]. For heat capacity studies, the scan speed was 10 K min^{-1} and the sensitivity was 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 [6] from 400 to 1200 K are known. The results obtained by this procedure for molybdenum metal, a recommended heat capacity test material [7], have been quoted in a previous publication [5]. The mean deviation between the experimental points from 400 to 800 K and a regression line for the reference values is ±0.76%.

The results for the transition enthalpies and temperatures reported below were obtained with a scan speed of 5 K min^{-1} and a sensitivity setting of 1 mcal sec^{-1}. Unlike the determination of heat capacity where each data point is calculated relative to a sapphire standard, the enthalpies of transition derive from the integration of a power–time curve and are an absolute measurement. Consequently, the accuracy of the measurement depends, *inter alia*, on the accuracy of electrical standards within the instrument. In

TABLE 2

Transition enthalpies and temperatures 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] (%)
In	429.8 ±0.2	3253± 49	−0.67
	(429.77±0.01 [8])	(3275± 7 [9])	
Sn	505.2 ±0.2	7080±106	−0.94
	(505.10±0.01 [10])	(7147± 22 [10])	
Zn	692.6 ±0.14	6870±100	−2.22
	(692.74±0.01 [11])	(7026± 40 [11])	
Al	933.7 ±0.2	10480±157	−2.60
	(933.47 [12])	(10760± 70 [12])	

[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 not less than 99.99+% and were given an acid wash prior to drying and encapulsation under argon.

[b] Each material was scanned five times and the quoted value is a mean. The precision, expressed as a standard deviation of the mean, was less than ±0.4% in each case. This is unrealistically small and the quoted precision is ±1.5%, an average figure obtained from the tin dihalide studies where each sample was scanned more than ten times.

[c] $\Delta = 100(\Delta H_{\text{expt}} - \Delta H_{\text{lit}})/\Delta H_{\text{lit}}$.

order to calibrate the instrument, enthalpies of fusion of pure samples of In, Sn, Zn and Al were determined using similar experimental conditions as for the tin dihalide studies. The results are collected in Table 2.

From the results in Table 2, it is clear that transition temperatures are reproduced to a satisfactory accuracy but that transition enthalpies are around 1% low at 500 K, rising to around 3% low at 900 K. Accordingly the transition enthalpies reported below for the tin halides were corrected by an amount linearly interpolated between 500 and 900 K at the melting point.

The effect of scan speed on transition temperatures and enthalpies of Sn, Pb and Al was investigated; the effect on temperature has been investigated many times [13] by other workers but the effect on fusion enthalpy has been much less frequently studied. The results are given in Table 3.

TABLE 3

Effect of scan speed on transition enthalpy and temperature [a]

Material	$\Delta H(T_t)$ (J mol^{-1}) (T_t (K))		
	2.5 K min^{-1}	5 K min^{-1}	10 K min^{-1}
Sn	6980±110 (505.0±0.1)	7080±100 (505.2±0.2)	7160±70 (506.1±0.2)
Pb	4590±130 (600.3±0.1)	4620±110 (600.6±0.1)	4680±80 (600.9±0.2)
Al	10430± 90 (933.1±0.1)	10480± 50 (933.7±0.2)	10500±30 (934.2±0.2)

[a] Five scans were recorded at each scan speed and the uncertainty interval is ±1 standard deviation of the mean.

RESULTS AND DISCUSSION

The tin(II) halides undergo a single transition in our experimental temperature range (370–800 K), in each case associated with melting. The transition temperatures and enthalpies are compared with literature results [14] in Table 4.

The heat capacities were regressed to linear expressions and the regression and correlation coefficients are collected in Table 5. Figure 1 shows the raw experimental heat capacities for the tin(II) halides. The agreement between the work reported here and that reported by Russian authors for the chloride [15], bromide [16] and iodide [17] is good. The agreement is least satisfactory for the bromide where some discontinuity between our results and the literature results [16] is apparent (see Fig. 2).

Unknown heat capacities are commonly estimated from known values for similar materials by empirical scaling procedures based on molecular mass. The hazards of this procedure are clear from this work in that at 500 K, the heat capacity for SnI_2 is less than both the corresponding values for $SnCl_2$ and $SnBr_2$; at 200 K, values for SnI_2 fall in between those of $SnBr_2$ and $SnCl_2$.

Kubaschewski and Alcock [18] describe an empirical procedure for the estimation of C_p at 298 K for predominantly ionic inorganic solids based on the additivity of ionic contributions. Results from the application of this

TABLE 4

Transition temperatures and enthalpies of fusion of the tin(II) halides. The uncertainty intervals are ±1 standard deviation of the mean

	n [a]	T (K)	$\Delta H(T)$ (kJ mol^{-1})	Literature [14]
$SnCl_2$	10	519.80±0.18	14.10±0.14	520(14.5±0.2)
$SnBr_2$	8	507.07±0.23	14.30±0.14	504(17.1±1.7)
SnI_2	14	593.25±0.12	12.10±0.22	593(18.0±1.7)

[a] n is the number of scans.

TABLE 5

Regression and correlation (r^2) coefficients for C_p(J K^{-1} mol^{-1}) = $a + bT$

Phase	Range (K)	a [a]	b [a]	r^2
$SnCl_2$(s)	350–500	64.70 ±0.27	0.04486±0.00064	98.6
$SnCl_2$(l)	520–800	73.67 ±0.23	0.04051±0.00034	99.4
$SnBr_2$(s)	350–500	63.89_5 ±0.46	0.04933±0.00107	97.5
$SnBr_2$(l)	520–800	70.18 ±0.33	0.05004±0.00049	99.0
SnI_2(s)	350–590	67.23 ±0.22	0.03528±0.00047	98.5
SnI_2(l)	600–800	70.10 ±0.59	0.03924±0.00083	97.0

[a] Uncertainty intervals are ±1 standard deviation of the regression coefficients.

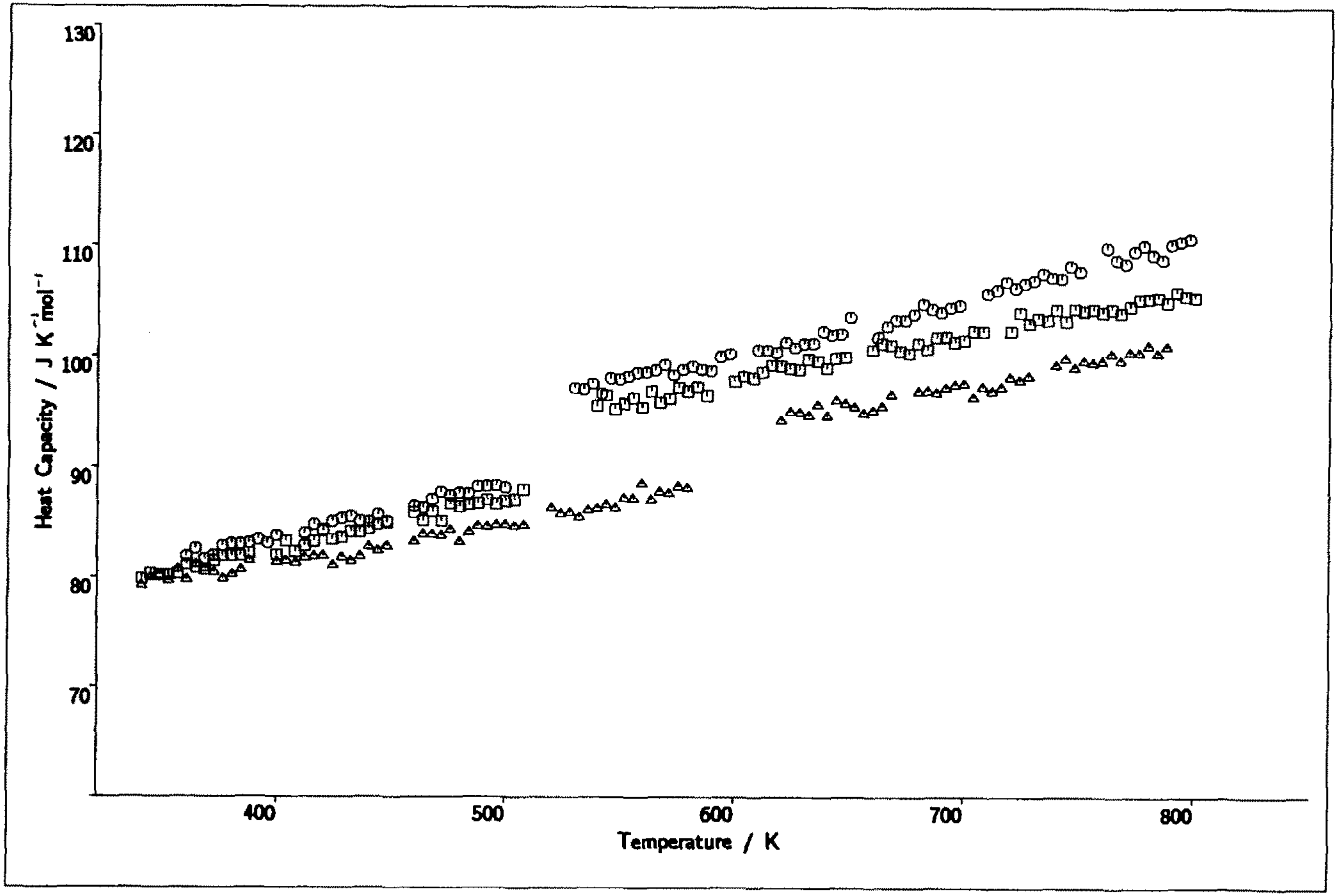

Fig. 1. Heat capacities for the tin(II) halides (s and l); raw data at 4 K intervals (half of the data points are omitted for clarity. $SnCl_2$, □; $SnBr_2$, ○; SnI_2, △).

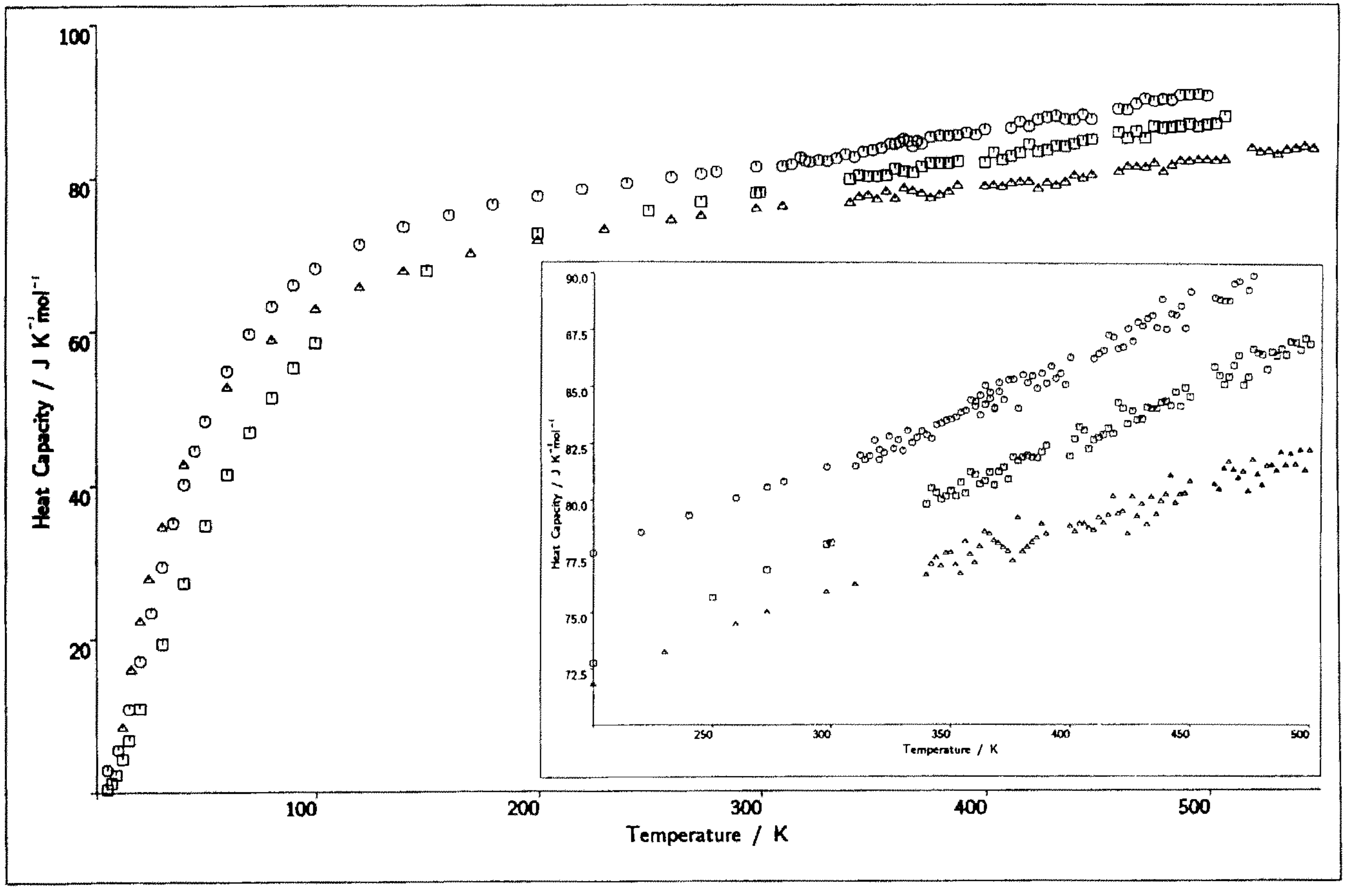

Fig. 2. Comparison of smoothed heat capacity results from the literature [15–17] to 300 K and the raw data reported here from 340 to 500 K. For clarity ($C_p(SnBr_2)+2.5$; ○) and ($C_p(SnI_2)-2.5$; △) J K^{-1} mol^{-1} are plotted, whereas, $C_p(SnCl_2)$ (□) is unscaled. Inset: The region between 200 and 500 K on an expanded scale. Note the relatively poor continuity for $SnBr_2$.

TABLE 6

The heat capacities of the solid tin(II) halides at 298.15 K (J K^{-1} mol^{-1}) from an estimation procedure [18], from this work and from the literature [15–17]

Material	C_p(est.)	C_p(lit.)	C_p(this work)
$SnCl_2(s)$	72.8	78.05	78.07
$SnBr_2(s)$	75.3	78.97	78.60
$SnI_2(s)$	76.1	78.45	77.75

method to the tin(II) halides are compared with experimental values from the literature and with extrapolated values from this work in Table 6.

The literature values and the work reported here agree satisfactorily but the estimated values, particularly for the chloride, show marked deviation.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Dr. Mucklejohn and Mr. O'Brien (GE Thorn Lamps Ltd., UK), Dr. Ditmars (National Institute of Standards and Technology, USA) and Dr. Head (RHBNC, UK) for helpful discussion and the gift of materials.

REFERENCES

1 M.A. Cayless and A.M. Marsden, Lamps and Lighting, 3rd edn., Edward Arnold, London, 1983.
2 J.E. Callanan and S.A. Sullivan, Rev. Sci. Inst., 57 (1986) 2584.
3 N.W. O'Brien and S.A. Mucklejohn, J. Chem. Thermodyn., 19 (1987) 1065.
4 G. Brauer, Handbook of Preparative Inorganic Chemistry, Vol I, Academic Press, New York, 1963, p. 734.
5 P.J. Gardner and S.R. Preston, Thermochim. Acta, 175 (1991) 129.
6 G.T. Furukawa, T.B. Douglas, R.E. McCoskey and D.C. Ginnings, J. Res. Nat. Bur. Stand., 57 (1956) 67.
7 D.A. Ditmars, A. Cezairliyan, S. Ishihara and T.B. Douglas, Standard Reference Materials: Enthalpy and heat capacity standard reference material, Molybdenum SRM 781, from 273 to 2800 K, NBS Special publication 260-55, September 1977.
8 F. Grønvold, J. Therm. Anal., 13 (1978) 419.
9 D.A. Ditmars, reported at 11th I.U.P.A.C. Conference on Chemical Thermodynamics, Como, Italy, Aug 26–31, 1990.
10 Certificate of Analysis, Standard Reference Material 2220, National Inst. of Standards and Technology, Gaithersburg, MD 20899, USA.
11 D.A. Ditmars, J. Chem. Thermodyn., 22 (1990) 639.
12 D.A. Ditmars, Chemical Thermodynamics Division, National Inst. of Standards and Technology (see ref. 10), personal communication, November 1990.
13 G.W.H. Höhne, H.K. Cammenga, W. Eysel, E. Gmelin and W. Hemminger, Thermochim. Acta, 160 (1990) 1.
14 T.N. Sevest'yanova and N.V. Karpenko, Russ. J. Phys. Chem., 45 (7) (1971) 1044.

15 I.E. Paukov, Yu.G. Stenin and G.I. Frolova, Zh. Fiz. Khim., 53 (1979) 2636.
16 G.A. Berezovskii, Yu.G. Stenin and I.E. Paukov, Zh. Fiz. Khim., 54 (1980) 1871.
17 M.P. Anisimov, N.N. Zhamskaya and I.E. Paukov, Zh. Fiz. Khim., 48 (1974) 1878.
18 O. Kubaschewski and C.B. Alcock, Metallugical Thermochemistry, 5th edn., Pergamon, Oxford, 1979.