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VAPORIZATION STUDY OF THE Tl_2S SYSTEM

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ABSTRACT

The vaporization of thallium sulphide has been studied by different techniques. The resulting pressure temperature equation is

$$\log P(\text{kPa}) = (11.0 \pm 0.2) - (11.4 \pm 0.3) 10^3/T$$

The standard sublimation enthalpy $\Delta H^0_{298} = 230 \pm 15$ kJ mole^{-1} has been derived. An estimation of the standard entropy of solid Tl_2S ($S^0_{298} = 134 \pm 16$ J K^{-1} mole^{-1}) is also reported.

INTRODUCTION

Thallium sulphide is widely employed as a semi-conductor at high temperatures [1] but at the moment its vaporization behaviour is not well known. Two different sets of data are reported in the literature. Klanberg et al. [2] and Isakova et al. [3], both employing the transpiration method, found vapour pressure data in fair agreement between them but very different to those measured at lower temperatures by Shakhtakhtinskii [4] using the Knudsen method

In view of this discrepancy and in order to investigate the vaporization process and the vapour composition of this compound, we have studied this system by three different techniques.

EXPERIMENTAL

The Tl_2S sample, 98% pure, was supplied by Alfa Inorganics Ventron. Before determination of its vapour pressure by torsion and Knudsen effusion methods, part of the sample was analyzed using a Bendix ToF mass spectrometer (model 3015) coupled with a high temperature Knudsen source in order to study the vaporization process and the vapour composition. On heating the sample at about 500 K an initial vaporization of sulphur was observed, probably due to impurities in the sample. On further heating, at about 650 K the ions observed by the ionization of the vapour

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were Tl_2S^+, TlS^+, Tl^+, S^+ and SO_2^+ but the corresponding appearance potentials and the substantial constancy of the ion intensity ratios in the temperature range studied showed that $Tl_2S_{(g)}$ is practically the only species present in the vapour phase. The intensity of the Tl_2S ion measured at 45 eV in the temperature range 626–674 K is plotted as $\log(I^+_{Tl_2S}T)$ vs. $1/T$ in Fig. 1. Least-squares treatment of the data gives the equation

$$\log(I^+_{Tl_2S}T) = (22.16 \pm 0.32) - (11628 \pm 206)/T$$

where the associated errors are standard deviations. The absolute vapour pressure values were determined by the torsion method from measurement of the torsion angle α of the effusion cell at each experimental temperature, employing the well-known equation [5]

$$P(\text{kPa}) = \frac{2k\alpha}{(a_1 l_1 f_1 + a_2 l_2 f_2)L} = k^0\alpha$$

where k is the constant of the tungsten torsion wire, a_1 and a_2 are the areas of the effusion holes, l_1 and l_2 are the respective distances from the rotating axis, f_1 and f_2 are the corresponding geometrical factors [6], and L is the torsion wire length. The constants of the employed cells are reported in Table 1. The experimental assembly has been described elsewhere [7].

In order to test if the thermodynamic equilibrium condition, temperature measurements and geometric factors of the used cell are reliable, the absolute vapour pressure of pure zinc as standard element was measured, and the corresponding vaporization enthalpies determined by second- and third-law treatment of the vapour data were compared with the selected value of Hultgren et al. [8]. The comparison showed a very good agreement.

The $Tl_2S_{(g)}$ pressure data, measured in three runs in the temperature range

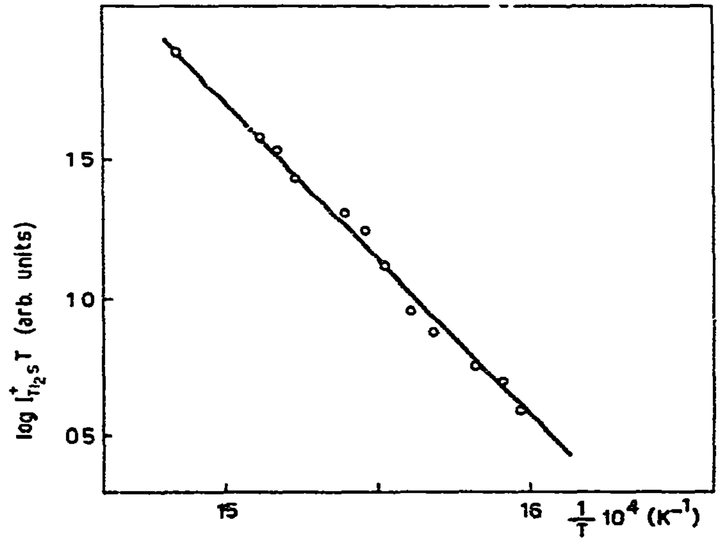

Fig 1 Temperature dependence of $I^+_{Tl_2S}$ ion intensity measured by the mass spectrometer.

TABLE 1

Constants of the employed cells

Torsion cell	Effusion hole (cm^2)		Moment arm (cm)		Correction factor	
	a_1 ($\times 10^{-2}$)	a_2 ($\times 10^{-2}$)	l_1	l_2	f_1	f_2
A	0.95	0.95	0.86	0.85	0.926	0.916
B	1.25	1.25	0.89	0.86	0.591	0.792

768–883 K, are reported in Table 2. For each run a pressure–temperature equation was derived by least-squares treatment and consequently, weighting the slope, the intercept and the corresponding errors proportionally to the number of experimental measurements, the following equation was selected

$$\log P_{(Tl_2S)}(\mathrm{kPa}) = (10.99 \pm 0.11) - (11391 \pm 92)/T \qquad (1)$$

This equation is drawn in Fig. 2.

Some vapour pressure data were also determined by the Knudsen effusion technique, measuring at different experimental temperatures the mass-loss of the Tl_2S sample filled in a Knudsen cell. Determination of the absolute vapour pressure was performed using the equation [9]

$$P(\mathrm{kPa}) = 2.29 m (T/M)^{1/2} (s\Delta t)^{-1} K'$$

where m is the mass of the vapour effused from the cell in time Δt, S is the effusion hole area, M is the molecular weight, T is the experimental temperature, and K' is Clausing's correction factor [10].

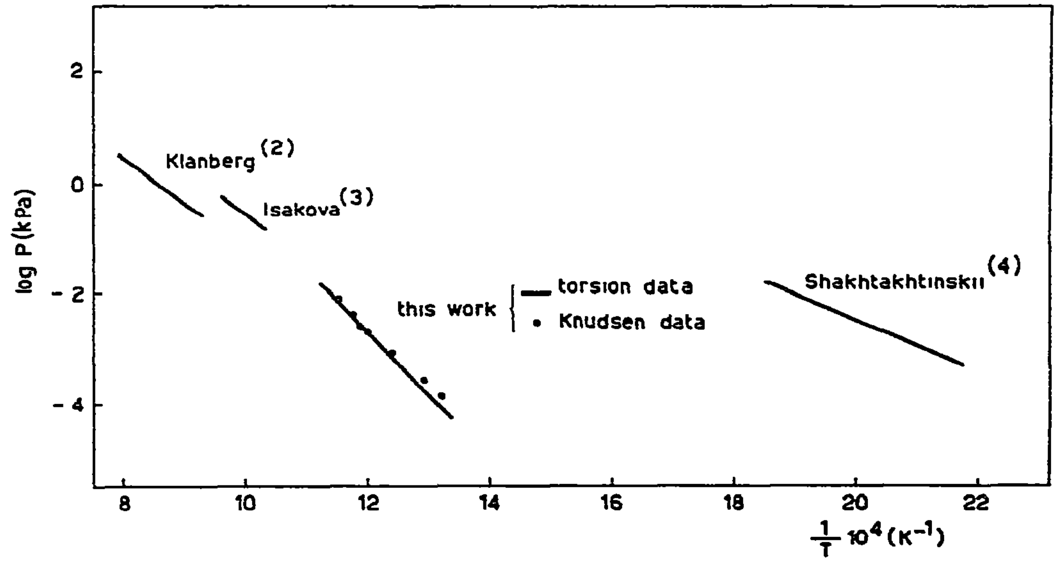

Fig. 2 Comparison of the vapour pressure data for the Tl_2S system.

TABLE 2

Tl_2S vapour pressure measured by torsion method

Cell	T (K)	P (kPa)	ΔH^0_{298} (kJ mole^{-1})	ΔS^0_{298} (J K^{-1} mole^{-1})
A	827	1.53×10^{-3}	218	123
	833	1.76×10^{-3}	218	124
	834	1.88×10^{-3}	217	123
	837	2.22×10^{-3}	217	123
	841	2.43×10^{-3}	217	123
	843	2.66×10^{-3}	217	123
	847	2.86×10^{-3}	217	124
	849	3.20×10^{-3}	217	124
	851	3.28×10^{-3}	217	124
	855	3.85×10^{-3}	217	124
	858	4.23×10^{-3}	217	124
	859	4.53×10^{-3}	217	124
	863	5.20×10^{-3}	216	124
	867	5.83×10^{-3}	216	123
	868	6.55×10^{-3}	216	124
	871	7.17×10^{-3}	216	124
	873	7.87×10^{-3}	216	124
A	811	7.69×10^{-4}	218	123
	826	1.31×10^{-3}	218	124
	829	1.53×10^{-3}	218	123
	831	1.76×10^{-3}	217	123
	841	2.43×10^{-3}	217	123
	845	2.86×10^{-3}	217	123
	850	3.52×10^{-3}	216	123
	852	3.85×10^{-3}	216	123
	856	4.33×10^{-3}	216	123
	860	4.85×10^{-3}	216	123
	861	5.20×10^{-3}	216	123
	863	5.44×10^{-3}	216	123
	865	6.11×10^{-3}	216	123
	867	6.70×10^{-3}	216	123
	869	6.85×10^{-3}	216	123
	873	7.51×10^{-3}	216	123
	875	8.24×10^{-3}	215	123
B	768	1.64×10^{-4}	219	123
	784	3.35×10^{-4}	217	121
	794	4.96×10^{-4}	216	121
	804	7.51×10^{-4}	216	121
	811	1.08×10^{-3}	216	121
	817	1.40×10^{-3}	216	121
	821	1.93×10^{-3}	214	119
	828	2.17×10^{-3}	215	121
	831	2.43×10^{-3}	215	121
	836	2.92×10^{-3}	215	121
	841	3.43×10^{-3}	215	121
	844	3.94×10^{-3}	214	121

TABLE 2 (continued)

Cell	T (K)	P (kPa)	ΔH^0_{298} (kJ mole^{-1})	ΔS^0_{298} (J K^{-1} mole^{-1})
	853	4.96×10^{-3}	214	121
	857	5.83×10^{-3}	214	121
	858	6.39×10^{-3}	214	120
	862	7.34×10^{-3}	214	121
	864	7.86×10^{-3}	214	121
	875	1.13×10^{-2}	213	121
	879	1.28×10^{-2}	213	121
	883	1.50×10^{-2}	213	121

[a] Values derived using $S^0_{298}(Tl_2S_{(s)}) = 159$ J K^{-1} mole^{-1} (see text)

TABLE 3

Vapour pressure data measured by Knudsen technique

T (K)	Time (sec)	Weight loss (mg)	P (kPa)
758	6600	3.33	1.41×10^{-4}
774	6120	5.88	2.73×10^{-4}
807	3600	10.56	8.45×10^{-4}
833	3600	26.40	2.15×10^{-3}
845	1800	16.58	2.72×10^{-3}
852	3600	52.59	4.33×10^{-3}
867	2400	65.76	8.19×10^{-3}

The experimental apparatus used consists essentially of a conventional graphite Knudsen cell (1.2 mm in diameter and $K' = 0.951$) inserted in a molybdenum block. The heating of the assembly is performed by radiation and electron bombardment and the temperature is measured by a calibrated Pt–Pt/Rh(13%) thermocouple or a Leeds–Northrup optical pirometer, depending on the temperature range covered. Also with this technique an assembly calibration was performed vaporizing pure zinc as standard. The Tl_2S pressures measured with this method are summarized in Table 3. Considering the small number of experimental points, no pressure equation was derived from these data; however, the obtained pressure values agree well with the torsion results, as shown in Fig. 2, indicating the reliability of the measurements.

DISCUSSION

Our selected pressure eqn. (1) is compared in Fig. 2 with those reported in the literature [2–4]. As is apparent, our data agree enough with those of Klanberg and

Spandau [2] and Isakova and Nesterov [3]. From the slope of eqn. (1) the vaporization enthalpy $\Delta H^0_{825} = 218 \pm 2$ kJ mole^{-1} was derived; that derived from the slope of the mass-spectrometric equation was $\Delta H^0_{650} = 222 \pm 4$ kJ mole^{-1}. In both cases the associated errors are the only standard deviations. From these values the average standard. sublimation enthalpy $\Delta H^0_{298} = 247 \pm 10$ kJ mole^{-1} (the error is estimated) was derived by using the enthalpic function obtained experimentally by Bencivenni [11] for the gaseous phase and estimated following the procedure suggested by Kubaschewski and Alcock [12] for the condensed phase.

The enthalpic function values are summarized in Table 4. It is interesting to note that the difference in the heat content of the Tl_2S gaseous and condensed phase is comparable with that used by Mills [13] in the evaluation of the standard enthalpy of vaporization.

The third-law ΔH^0_{298} was also derived at each experimental temperature. The necessary free energy functions. $-(G^0_T - H^0_{298})/T$, for the gaseous phase were obtained by Bencivenni [11]. while for the condensed phase they were derived, employing the above reported heat contents, the estimated $Tl_2S_{(s)}$ standard entropy $S^0_{298} = 159$ JK^{-1} mole^{-1} proposed by Mills [13] and the heat of fusion $\Delta H^m_{730} = 12.6$ kJ mole^{-1} reported by Kelley [14]. These values are summarized in Table 4.

The derived ΔH^0_{298} data showed a temperature trend and their mean value $\Delta H^0_{298} = 216$ kJ mole^{-1} is in disagreement with the second-law value. Considering that a possible error source could be connected with the estimated standard entropy of $Tl_2S_{(s)}$. a series of this value was derived by the third-law procedure employing the second-law sublimation enthalpy $\Delta H^0_{298} = 247$ kJ mole^{-1}. The S^0_{298} values so determined do not show any temperature trend and the standard deviations associated with the mean values of each run are very small. Another error source could be the estimated heat capacity of the $Tl_2S_{(s)}$ but this error, minimized in the energy function calculation, would not explain the temperature trend of the third-law ΔH^0_{298} values. Errors in the instrument calibration could also be taken into consideration in order to explain the temperature trend and the difference between the second- and third-law ΔH^0_{298}(sub). but this error should be of a factor ~50 which was not observed in our calibrations.

In view of these considerations and the agreement of the results obtained by different techniques, it may be concluded that the uncertainties associated with the slope and intercept of the pressure–temperature dependence should not be greater than the estimated values reported in the equation

$$\log P(= \text{kPa}) = (11.0 \pm 0.2) - (11.4 \pm 0.3)\ 10^3/T$$

With regard to the Tl_2S standard sublimation enthalpy change, considering that the value $\Delta H^0_{298} = 247$ kJ mole^{-1} is affected by uncertainties related to the estimated heat capacities, and the corresponding value obtained by third-law procedure is in addition affected by an error in the $Tl_2S_{(s)}$ standard entropy, we propose a value of $\Delta H^0_{298} = 230 \pm 15$ kJ mole^{-1} which, although higher than that selected by Mills [13] (209 ± 29 kJ mole^{-1}) is within the limits of the associated uncertainty. Also, concerning the $S^0_{298}(Tl_2S)$ we feel that the estimated value 159 ± 13 J K^{-1}

TABLE 4

Thermodynamic functions of Tl_2S

Tl_2S (gaseous)[a]			Tl_2S (liquid)		
T (K)	$H^0_T - H^0_{298}$ (kJ mole^{-1})	$-(G^0_T - H^0_{298})/T$ (J K^{-1} mole^{-1})	$H^0_T - H^0_{298}$[b] (kJ mole^{-1})	$-(G^0_T - H^0_{298})/T$[c] (J K^{-1} mole^{-1})	$-(G^0_T - H^0_{298})/T$[d] (J K^{-1} mole^{-1})
750	25.9	323	52.4	169	131
800	28.8	327	57.0	174	136
850	31.7	330	61.6	178	140
900	34.6	333	66.2	182	144

[a] Reported by Bencivenni [11]

[b] Estimated using the procedure of Kubaschewski and Alcock [12]

[c] Derived using the estimated $S^0_{298}(Tl_2S_{(s)}) = 159$ J K^{-1} mole^{-1} reported by Mills [13]

[d] Obtained using $S^0_{298}(Tl_2S_{(s)}) = 122$ J K^{-1} mole^{-1} derived from our second-law Tl_2S sublimation $\Delta H^0_{298} = 247$ kJ mole^{-1}

mole^{-1} proposed by Mills can be considered as an upper limit, and we propose 134 ± 16 J K^{-1} mole^{-1} as the most probable.

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