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Sublimation study of the tin sulphides SnS_2, Sn_2S_3 and SnS

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Abstract

The vaporization of $SnS_2(s)$ occurs following the equilibria

$$SnS_2(s) \longrightarrow \tfrac{1}{2}Sn_2S_3(s)+\tfrac{1}{4}S_2(g)$$

$$Sn_2S_3(s) \longrightarrow 2SnS(s)+\tfrac{1}{2}S_2(g)$$

$$SnS(s) \longrightarrow SnS(g)$$

The vapour pressures over the condensed phases were measured by the simultaneous torsion–Knudsen effusion technique. The pressures of $S_2(g)$ over $SnS_2(s)$ and $Sn_2S_3(s)$ and of $SnS(g)$ over $SnS(s)$ are expressed respectively by

$$\log p\ (\mathrm{kPa})=(12.41\pm0.40)-(11.3\pm0.3)\times10^3/T, \qquad \Delta H^\circ_{298}=54.5\pm1.0\ \mathrm{kJ\ mol^{-1}}$$

$$\log p\ (\mathrm{kPa})=(11.81\pm0.50)-(11.2\pm0.4)\times10^3/T, \qquad \Delta H^\circ_{298}=112.0\pm2.0\ \mathrm{kJ\ mol^{-1}}$$

$$\log p\ (\mathrm{kPa})=(9.40\pm0.10)-(10.7\pm0.1)\times10^3/T, \qquad \Delta H^\circ_{298}=220.0\pm2.0\ \mathrm{kJ\ mol^{-1}}$$

where the standard enthalpies are derived by second- and third-law treatment of the results. From these data the standard heats of formation of $SnS_2(s)$ and $Sn_2S_3(s)$ were calculated to be -148 ± 2 kJ mol^{-1} and -253 ± 2 kJ mol^{-1} respectively.

1. Introduction

The vaporization of tin monosulphide predominantly occurs according to the reaction

$$SnS(s) \longrightarrow SnS(g) \tag{1}$$

A very small amount of the dimer form $Sn_2S_2(g)$ was also found spectrometrically by Colin and Drowart [1] in the vapour phase. Several authors have studied the vaporization of this compound by measuring the vapour pressure by different techniques, *e.g.* boiling point [2], transpiration in the conventional way [3–5] or coupled to a quadrupole mass spectrometer [6], Knudsen method [4, 7, 8] and mass spectrometry [1]. All the reported vapour pressure data are in agreement within a factor of 2. A set of pressures measured over SnS(s) by using an open crucible [9] is decidedly low, and this is probably due to the assumption of a vaporization coefficient for SnS equal to unity, which is incorrect according to Wiedemeier and Csillag [8].

In the case of tin disulphide, contrary to Al-Alamy *et al.* [10] who report that $SnS_2(s)$ vaporizes to produce SnS(s) as residue, it has been found [11]

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that $SnS_2(s)$ vaporizes according to the reaction

$$SnS_2(s) \longrightarrow \tfrac{1}{2}Sn_2S_3(s) + \tfrac{1}{4}S_2(g) \qquad (2)$$

The sulphur pressures over $SnS_2(s)$ were measured by Wiedemeier and Csillag [11], Gerasimov *et al.* [12] and Karakhanova *et al.* [13]; however, the reported results are not in good agreement.

A pressure–temperature equation is also reported by Sevryukov [14], but the pressures are considerably lower than those found by other authors [11–13].

Finally, concerning the vaporization behaviour of $Sn_2S_3(s)$, some authors reported that this compound decomposes to $Sn_3S_4(s)$ [13, 15] or $Sn_4S_5(s)$ [12]; however, differential thermal analysis, high temperature X-ray diffraction [16] and a thermogravimetric study [17] did not provide any evidence of the existence of these intermediate phases. An accurate Knudsen effusion study of the decomposition of $Sn_2S_3(s)$, carried out with a mass spectrometer and a vacuum microbalance [17], proved that this compound decomposes according to the reaction

$$Sn_2S_3(s) \longrightarrow 2SnS(s) + \tfrac{1}{2}S_2(g) \qquad (3)$$

The sulphur pressures over $Sn_2S_3(s)$ were measured by dew point [13] and Knudsen [17] methods.

As part of our research programme on the vaporization process of metal sulphides [18–24] we have studied the vaporization of SnS_2 by employing two different techniques.

2. Experimental details

The tin monosulphide and disulphide used in this study were supplied by Strem Chemicals Inc. and Aldrich Chemical Inc. respectively, both having a purity of about 99.8%, the main impurity being sulphur. The pressure measurements were carried out mainly by the torsion method. Some pressure values were also simultaneously determined by the Knudsen method employing a torsion effusion–weight loss assembly described in detail in a previous paper [25]. Four torsion cells were used, each with a different size of effusion holes. The calibration constants necessary for torsion and Knudsen vapour pressure calculations were determined by vaporizing pure lead as reference material [26] and their values are reported in Table 1.

A preliminary run was carried out in order to have qualitative information of the overall vaporization behaviour of tin disulphide (Fig. 1). The vaporization of this compound is characterized by a first step in which the vapour pressure shows reproducible values. When about 5% of the original sample is vaporized, the pressure decreases and the new values lie on a new $\log p$ *vs.* $1/T$ line. A similar behaviour occurs at higher temperatures when an additional 10% of the sample is vaporized.

The vapour in the first and second steps of the vaporization is essentially constituted by $S_2(g)$, as inferred from the fact that the pressure values

TABLE 1

Instrumental constants of the torsion–Knudsen assembly

Cell (material)	Nominal diameter (mm)	K_{torsion} (kPa rad^{-1})	K_{Knudsen} (kPa min K$^{-1/2}$ mg$^{-1/2}$)
A (graphite)	2.10	7.4×10^{-3}[a]	3.0×10^{-3}
B (pyrophyllite)	1.80 1.80	10.7×10^{-3} 14.8×10^{-3}[a]	4.4×10^{-3} 4.4×10^{-3}
C (graphite)	0.40 0.40	20.5×10^{-2} 24.8×10^{-2}[a]	6.1×10^{-2} 6.1×10^{-2}
D (pyrophyllite)	0.30	39.4×10^{-2}	

[a] Changed the torsion wire.

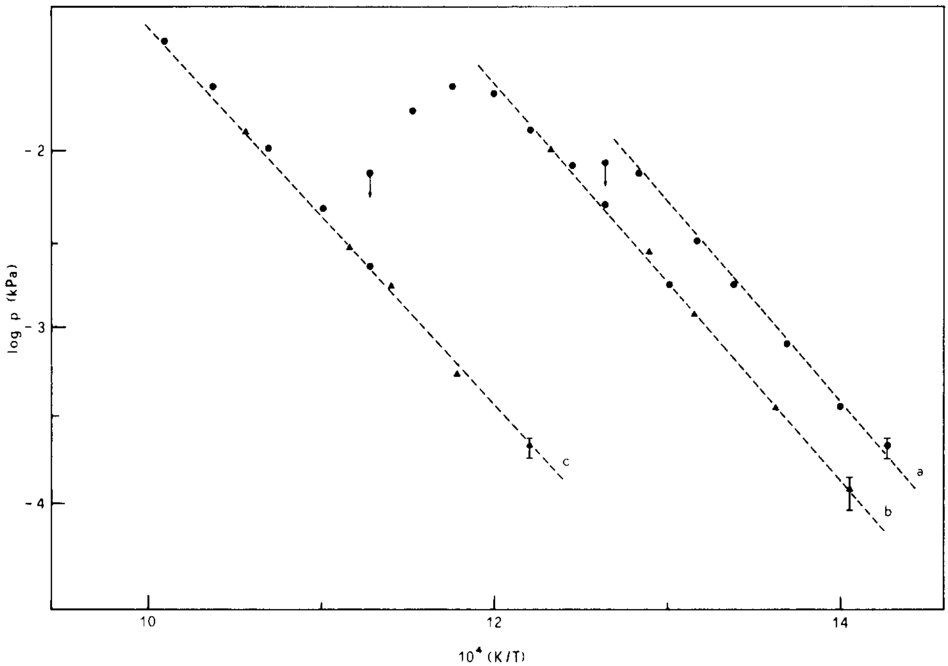

Fig. 1. Preliminary run showing the vaporization of tin disulphide: ▲, pressure values measured on decreasing the temperature. The dashed lines a, b and c represent eqns. (4), (5) and (8) respectively (see text).

calculated by the Knudsen effusion method employing as molecular weight of the effused vapour that of $S_2(g)$ agree very well with those measured simultaneously by torsion effusion (see Table 2). On this basis the vaporization behaviour of $SnS_2(s)$ may be described by the consecutive reactions (2), (3) and (1). In Table 3 and Fig. 2 are reported the vapour pressures measured

TABLE 2

Comparison of torsion and Knudsen data

Run	Surface of sample	T (K)	Vapour pressure (10^{-4} kPa)	
			Torsion	Knudsen[a]
39	SnS_2	725.5	6.2	6.1
		736	10.5	10.5
		740.5	13.6	13.7
	Sn_2S_3	759.5	14.6	14.6
		767	19.7	20.0
41	SnS_2	734	10.3	10.6
		742	15.6	15.6
	Sn_2S_3	747	8.2	8.2
		767	17.5	17.8
45	SnS_2	796	197.0	191.0
	Sn_2S_3	822	160.0	158.0
		848.5	422.0	410.0

[a] Calculated considering S_2(g) the only gaseous species in the vapour phase.

by the torsion method in the first step of vaporization of SnS_2(s) when the amount of Sn_2S_3 on the sample surface is negligible. Unfortunately, a limited number of points were measured by the Knudsen effusion technique, because at low temperature the weight loss rate is not easily measurable, being at the limit of the instrument sensitivity, while at higher temperatures the composition of the condensed surface may change appreciably in the course of weight loss rate measurement in isothermal conditions. For this reason the vapour pressures measured with this last method are only taken as a check of the torsion ones. Three runs in the overall temperature range 689–806 K were carried out by using different effusion cells. The linear least-squares treatment of the data points gives for each run a corresponding log p *vs.* $1/T$ equation. The equations so obtained are summarized in Table 4. From these, the following equation representative of the temperature dependence of the sulphur pressure over SnS_2(s) was selected:

$$\log p\ (\text{kPa}) = (12.41 \pm 0.40) - (11.3 \pm 0.3) \times 10^3/T \qquad (4)$$

The errors in the slope and intercept of this equation and of the subsequent selected pressure–temperature equations are estimated considering as the only uncertainty source that associated with the temperature measurement.

From the slope of eqn. (4) the enthalpy associated with reaction (2) at the mean experimental temperature, $\Delta H^\circ_{747} = 54.0 \pm 1.4$ kJ mol^{-1}, was derived. The heat capacities of SnS_2(s) and Sn_2S_3(s) reported by Wiedemeier *et al.* [27] and for S_2(g) those selected by Hultgren *et al.* [26] showed that this enthalpy does not change appreciably up to 298 K. This standard enthalpy was also calculated by third-law treatment of the vapour pressure at each experimental temperature. The necessary free-energy functions for this cal-

TABLE 3

Vapour pressure of SnS_2 and third-law standard enthalpy of the process $SnS_2(s) \rightarrow \frac{1}{2}Sn_2S_3(s) + \frac{1}{4}S_2(g)$

Run (cell)	T (K)	α (10^{-2} rad)	p (10^{-4} kPa)	$-R\ln K_p$ (J mol^{-1} K^{-1})	$-\Delta[(G^\circ_T - H^\circ_{298})/T]$ (J mol^{-1} K^{-1})	ΔH°_{298} (kJ mol^{-1})
39	689	0.94	1.01	28.7	50.6	54.7
(B)	696	1.14	1.22	28.2	50.6	54.8
	704.5	2.04	2.13	27.0	50.6	54.7
	710.5	2.76	2.94	26.4	50.6	54.7
	719.5	4.36	4.66	25.4	50.6	54.7
	725.5	5.77	6.18	24.9	50.5	54.7
	727.5	6.98	7.50	24.5	50.5	54.6
	736	9.90	10.54	23.7	50.5	54.6
	740.5	12.51	13.58	23.4	50.5	54.7
	745	13.66	14.59	23.2	50.5	54.9
					Average	54.7 ± 0.1
41	693	0.87	1.22	28.2	50.6	54.6
(B)	702	1.44	2.13	27.2	50.6	54.6
	703.5	1.74	2.53	26.8	50.6	54.5
	710	2.32	3.34	26.2	50.6	54.5
	714	2.62	3.85	25.9	50.6	54.6
	719	3.79	5.67	25.1	50.6	54.4
	722.5	4.36	6.48	24.9	50.6	54.5
	727	5.81	8.61	24.3	50.5	54.4
	734	6.98	10.33	23.9	50.5	54.7
	737	8.73	12.97	23.6	50.5	54.4
	742	10.47	15.60	23.0	50.5	54.5
	743	11.64	17.12	22.8	50.5	54.4
					Average	54.5 ± 0.1
45	751	1.16	23.71	22.2	50.0	54.6
(C)	759.5	1.74	35.87	21.3	50.5	54.5
	786.5	6.11	124.62	18.7	50.4	54.4
	796	9.60	197.58	17.8	50.4	54.3
	802.5	10.77	221.90	17.4	50.3	54.4
	806.5	12.40	254.32	17.2	50.3	54.5
					Average	54.4 ± 0.1

culation were taken from the literature [26, 27]. These enthalpies are reported in Table 3 and their average value, $\Delta H^\circ_{298} = 54.6 \pm 0.1$ kJ mol^{-1}, is practically equal to that determined by the second-law method.

Considering the vaporization process of SnS_2 (reaction (2)), continuing the vaporization, the surface of the sample is practically constituted by only Sn_2S_3. The vapour pressure data taken at this stage of the vaporization are reported in Table 5 and drawn in Fig. 3. The experimental results were treated in the same way as those obtained in the first step with $SnS_2(s)$. From the pressure–temperature equations reported in Table 4 the equation

$$\log p\ (\mathrm{kPa}) = (11.81 \pm 0.50) - (11.2 \pm 0.4) \times 10^3/T \qquad (5)$$

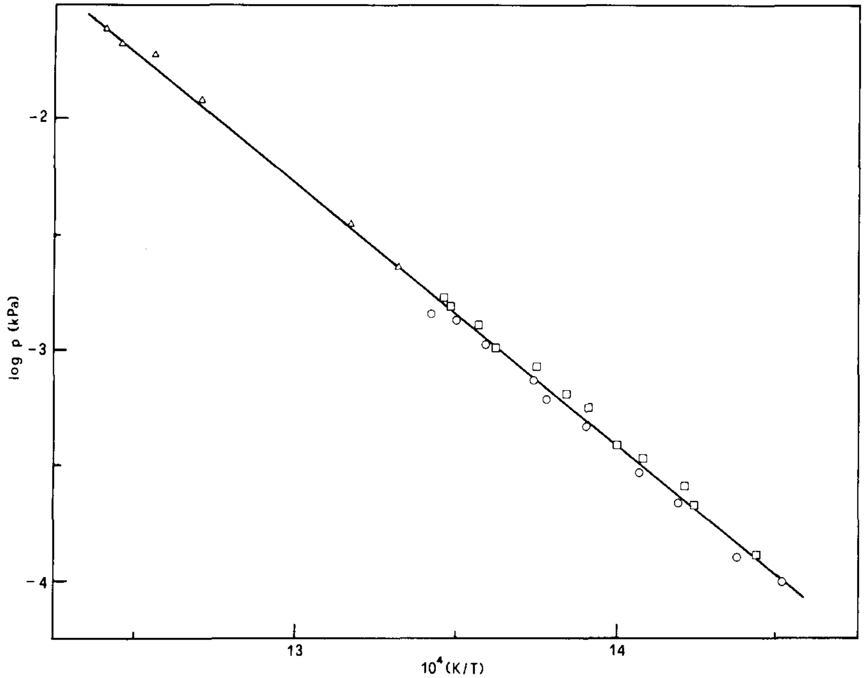

Fig. 2. Vapour pressure of SnS_2(s): ○, run 39; □, run 41; △, run 45.

TABLE 4

Pressure–temperature equations determined during the vaporization of SnS_2, Sn_2S_3 and SnS

System	Run	Cell	Number of points	ΔT (K)	$\log p$ (kPa) $= A - B/T$	
					A	B
SnS_2[a]	39	B	10	689–745	12.23±0.31	11196±219
	41	B	12	693–743	12.46±0.32	11313±232
	45	C	6	751–806.5	12.63±0.40	11446±314
Sn_2S_3[b]	39	A	8	724–775.5	11.93±0.97	11239±726
	41	A	9	699–767	11.25±0.49	10708±360
	45	B	15	776–862	12.09±0.20	11425±163
SnS[b]	39	A	6	795–863	9.19±0.14	10380±114
	40	B	7	952.5–1047	9.29±0.26	10484±255
	44	B	16	878.5–1039	9.70±0.20	10941±189
	45	B	16	913–1044	9.71±0.11	10935±109
SnS[a]	43	A	10	816–940	9.43±0.04	10770±32
	46	B	15	906–1043.5	9.38±0.07	10740±66
	47	A	11	793–932	9.16±0.05	10528±40

The quoted errors are standard deviations.

[a] Pure.

[b] Residue of vaporization of SnS_2.

TABLE 5

Vapour pressure of Sn_2S_3 (residue of SnS_2 vaporization) and third-law standard enthalpy of the process $Sn_2S_3(s) \rightarrow 2Sn_2S_3(s) + \frac{1}{2}S_2(g)$

Run (cell)	T (K)	α (10^{-2} rad)	p (10^{-4} kPa)	$-R\ln K_p$ (J mol^{-1} K^{-1})	$-\Delta[(G^\circ_T - H^\circ_{298})/T]$ (J mol^{-1} K^{-1})	ΔH°_{298} (kJ mol^{-1})
39	724	1.45	2.13	54.4	103.0	114.0
(B)	727.5	2.26	3.34	52.5	103.0	113.1
	740.5	3.79	5.67	50.3	103.0	113.5
	752	7.28	10.84	47.7	103.0	113.3
	759.5	9.90	14.59	46.3	103.0	113.4
	764	12.74	18.85	45.4	103.0	113.3
	767	13.28	19.66	45.2	103.0	113.7
	775.5	14.84	22.09	44.6	103.0	114.5
					Average	113.6 ± 0.5
41	699	0.57	0.81	58.1	103.0	112.6
(B)	713.5	1.09	1.62	55.6	103.0	113.2
	717	1.09	1.62	55.6	103.0	113.7
	729.5	2.07	4.25	51.4	103.0	112.6
	732	2.61	3.85	51.8	103.0	113.3
	744	5.53	8.21	48.7	103.0	112.9
	747	5.53	8.21	48.7	103.0	113.3
	757	8.15	12.16	47.1	103.0	113.6
	767	11.92	17.53	45.6	103.0	113.9
					Average	113.2 ± 0.4
45	776	0.87	21.58	44.8	103.0	114.7
(C)	788	1.45	35.87	42.7	103.1	114.9
	792	2.04	50.76	41.2	103.1	114.3
	798	2.62	63.35	40.2	103.1	114.4
	803	3.17	78.63	39.5	103.1	114.5
	812.5	4.07	101.32	38.3	103.1	114.9
	817	4.90	121.59	37.5	103.1	114.9
	822	6.46	160.09	36.4	103.1	114.6
	829	8.15	201.63	35.4	103.1	114.8
	835	10.47	260.40	34.5	103.1	114.9
	841.5	13.51	335.38	33.3	103.1	114.8
	848.5	17.04	422.52	32.3	103.1	114.9
	853	20.45	507.63	31.6	103.1	114.9
	858	24.60	609.97	30.8	103.1	114.9
	862	27.00	669.75	30.5	103.1	115.1
					Average	114.7 ± 0.2

was selected as the most representative of the temperature dependence of the sulphur pressure over $Sn_2S_3(s)$ in the overall temperature range 700–860 K. From the second- and third-law treatments of the results the standard enthalpies associated with reaction (3), $\Delta H^\circ_{298} = 108 \pm 4$ kJ mol^{-1} and 114.0 ± 0.5 kJ mol^{-1} respectively, were calculated. In addition to the free-energy functions and the heat capacities of $Sn_2S_3(s)$ and $S_2(g)$ used previously, those of SnS(s) were also taken from the same literature source [27].

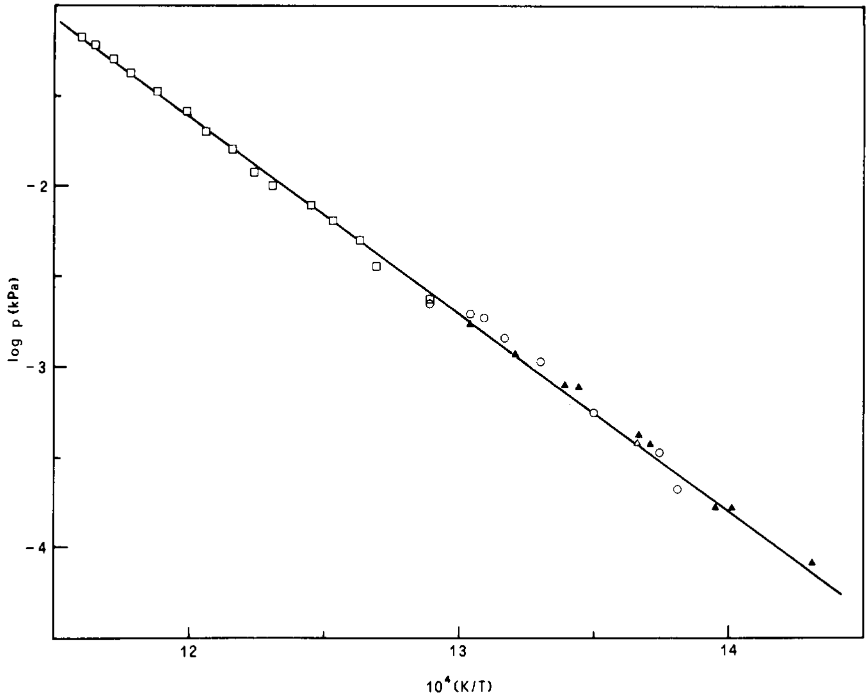

Fig. 3. Vapour pressure of Sn_2S_3(s): ○, run 39; ▲, run 41; □, run 45.

On continuing the vaporization, the vapour pressure above the residue decreases again. When its surface is practically covered by only SnS(s) and the vapour is constituted by only SnS(g), the temperature dependence of its pressure is represented by the equation

$$\log p \text{ (kPa)} = (9.57 \pm 0.30) - (10.8 \pm 0.3) \times 10^3/T \qquad (6)$$

This equation, drawn as a continuous line in Fig. 4 with the experimental points, was selected from those reported in Table 3. In particular, two sets of vapour pressures (runs 40 and 44) were obtained by fast heating SnS_2 samples without measuring the vapour pressures over SnS_2 and the intermediate compound Sn_2S_3; measurements were started when about 30% of the original weight was vaporized.

The usual third-law treatment of the vapour pressure data gives the standard sublimation enthalpies of SnS(s) reported in Table 6. The necessary free-energy functions of SnS(g) were taken from ref. 28. The average value $\Delta_{\text{sub}}H^\circ_{298} = 218.4 \pm 0.5$ kJ mol^{-1} is in very good agreement with that obtained from the slope of the selected equation (6), $\Delta_{\text{sub}}H^\circ_{920} = 206 \pm 6$ kJ mol^{-1} corrected at 298 K, $\Delta_{\text{sub}}H^\circ_{298} = 220 \pm 6$ kJ mol^{-1}, by using the heat capacities reported in the literature [27, 28].

In order to check the consistency of the pressure values measured during the different vaporization steps of SnS_2(s), some vaporization runs of pure

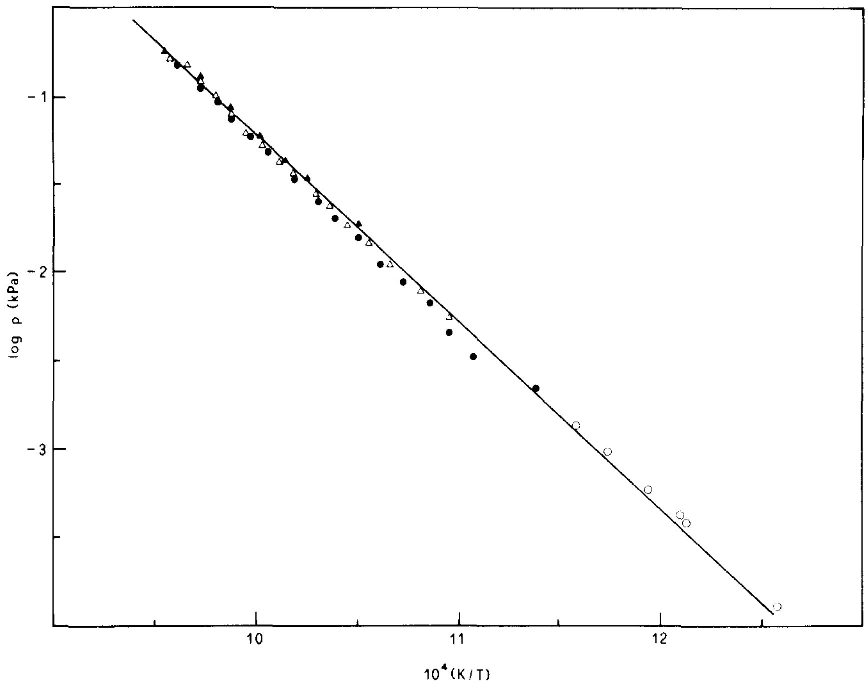

Fig. 4. Vapour pressure of SnS(s): ○, run 39; ▲, run 40; ●, run 44; △, run 45.

SnS(s) were also carried out. The results are reported in Table 7 and Fig. 5.

The temperature–pressure equation

$$\log p \text{ (kPa)} = (9.33 \pm 0.10) - (10.7 \pm 0.1) \times 10^3/T \quad (7)$$

was selected in the usual way. This equation agrees within experimental uncertainties with that found over the residue of the vaporization of SnS_2(s), which proves that when about 20%–30% of SnS_2(s) is vaporized, the surface of the residue is practically constituted by only SnS.

On this basis we propose as representative of the temperature dependence of the vapour pressure over SnS(s) the selected equation

$$\log p \text{ (kPa)} = (9.40 \pm 0.10) - (10.7 \pm 0.1) \times 10^3/T \quad (8)$$

This third-law elaboration of the vapour pressure values measured over pure SnS(s) gives a sublimation enthalpy $\Delta_{sub}H^{o}_{298} = 220.7 \pm 0.5$ kJ mol^{-1} in good agreement with that derived by the second law ($\Delta_{sub}H^{o}_{905} = 205 \pm 2$ kJ mol^{-1}), $\Delta_{sub}H^{o}_{298} = 218 \pm 2$ kJ mol^{-1}.

3. Conclusions

Our selected temperature–pressure equations determined over SnS_2(s), Sn_2S_3(s) and SnS(s) are reported in Table 8 with those found in the literature

TABLE 6

Vapour pressure of SnS (residue of SnS_2 vaporization) and third-law standard sublimation enthalpy of the process $SnS(s) \rightarrow SnS(g)$

Run (cell)	T (K)	α (10^{-2} rad)	p (10^{-4} kPa)	$-R\ln K_p$ (J mol^{-1} K^{-1})	$-\Delta[(G^\circ_T - H^\circ_{298})/T]$ (J mol^{-1} K^{-1})	$\Delta_{sub}H^\circ_{298}$ (kJ mol^{-1})
39	795	0.87	1.30	112.8	159.8	216.7
(B)	824	2.62	3.95	103.6	159.3	216.7
	826.5	2.91	4.36	102.8	159.3	216.6
	837.5	4.07	6.08	99.9	159.1	217.0
	852	6.68	9.93	95.9	158.9	217.1
	863	9.30	13.98	93.1	158.8	217.3
					Average	216.9 ± 0.3
40	952.5	4.94	193.02	71.4	157.4	218.0
(D)	975.5	8.87	351.29	66.2	157.1	217.9
	989	15.60	440.00	64.3	156.9	218.5
	998	15.40	608.00	61.6	156.9	218.1
	1013.5	22.40	882.54	58.6	156.7	218.2
	1027.5	33.70	1335.60	55.1	156.3	217.3
	1047	45.80	1802.60	52.6	156.1	218.5
					Average	218.1 ± 0.4
44	878.5	0.57	22.70	89.0	159.3	218.2
(D)	903	0.87	34.35	85.6	158.2	220.1
	913	1.17	46.30	83.1	158.0	220.1
	921	1.74	68.49	79.8	157.9	219.0
	931.5	2.26	90.28	77.5	157.7	219.2
	941.5	2.91	113.68	75.6	157.6	219.6
	952	4.07	160.60	72.8	157.4	219.2
	962	5.24	206.90	70.6	157.3	219.3
	970.5	6.52	260.40	68.7	156.2	218.3
	981.5	8.78	351.29	66.2	157.0	219.1
	994	12.43	496.28	63.3	156.8	218.8
	1003	15.29	610.48	61.6	156.7	219.0
	1012	19.49	768.65	59.8	156.6	218.9
	1019	24.43	967.65	57.8	156.4	218.3
	1028.5	32.29	1275.50	55.5	156.3	217.9
	1039	38.60	1533.60	54.0	156.2	218.3
					Average	218.7 ± 0.8
45	913	1.45	56.94	81.4	158.0	218.6
(D)	925	2.04	80.45	78.5	157.8	218.6
	938	2.85	113.68	75.6	157.6	218.8
	948	3.79	149.85	73.3	157.5	218.8
	957	4.84	193.02	71.2	157.4	218.7
	965.5	6.09	243.07	69.3	157.2	218.7
	972	7.28	285.53	68.0	157.2	218.8
	982	9.60	376.42	65.7	157.0	218.6
	989	11.32	442.28	64.3	156.9	218.8
	996.5	13.63	544.11	62.6	156.8	218.6
	1004.5	16.28	639.25	61.3	156.7	218.5
	1013	20.37	804.72	59.3	156.8	218.9
	1020.5	26.31	1036.80	57.2	156.4	218.0
	1028	32.29	1275.50	55.5	156.3	217.8
	1036	38.42	1533.60	54.0	156.2	217.7
	1044	42.76	1681.50	53.2	156.1	218.5
					Average	218.5 ± 0.4

TABLE 7

Vapour pressure of SnS and third-law standard sublimation enthalpy of the pure SnS according to SnS(s) → SnS(g)

Run (cell)	T (K)	α (10^{-2} rad)	p (10^{-4} kPa)	$-R\ln K_p$ (J mol^{-1} K^{-1})	$-\Delta[(G^\circ_T-H^\circ_{298})/T]$ (J mol^{-1} K^{-1})	$\Delta_{sub}H^\circ_{298}$ (kJ mol^{-1})
43	816	2.32	1.72	110.5	159.5	220.3
(A)	825	3.19	2.43	107.8	159.3	220.4
	834	4.36	3.24	105.1	158.2	219.6
	848	7.28	5.47	100.9	159.0	220.4
	862	11.64	8.61	97.1	158.8	220.5
	878.5	19.49	14.59	92.7	158.5	220.7
	893	31.12	23.20	88.8	158.3	220.7
	910	52.36	39.41	84.4	158.1	220.7
	926	84.35	62.52	80.6	157.8	220.8
	940	122.17	92.41	77.4	157.6	220.9
					Average	220.5 ± 0.3
46	906	0.87	34.35	85.6	158.1	220.8
(D)	916	1.13	45.29	83.3	158.0	221.0
	925.5	1.45	56.94	81.4	157.8	221.4
	932	1.74	68.49	79.8	157.8	221.4
	945	2.60	103.65	76.4	157.6	221.1
	955	3.42	136.68	74.1	157.4	221.1
	965.5	4.62	184.41	71.6	157.3	220.9
	977	6.23	248.75	69.1	157.2	221.1
	986.5	7.65	306.00	67.4	156.9	221.9
	994	9.43	376.42	65.7	156.8	221.1
	1004.5	12.43	496.28	63.3	156.7	221.0
	1025	20.37	804.82	59.3	156.4	221.1
	1034	24.23	967.65	57.8	156.2	221.3
	1043.5	29.82	1190.40	56.1	156.1	221.4
					Average	221.2 ± 0.3
47	793	1.01	0.71	117.2	159.8	219.6
(A)	813	2.18	1.62	110.8	159.5	219.8
	828	3.79	2.84	106.3	159.3	219
	842	6.11	4.56	102.4	159.1	220.4
	856.5	9.90	7.29	98.4	158.9	220.4
	871	15.17	11.65	94.6	158.6	220.5
	886	25.88	19.25	90.4	158.4	220.1
	898	37.52	27.86	87.3	158.2	220.5
	912	55.85	42.25	83.9	158.0	220.6
	924	78.54	58.26	81.2	157.8	220.8
	932	110.53	82.38	78.3	157.8	220.0
					Average	220.3 ± 0.4

for comparison. Our results are in better agreement with those obtained by Wiedemeier and Csillag. Contrary to what was reported by those authors [11, 17], no obvious influence of the effusion hole diameter of the used cells on the vapour pressure values above SnS_2(s) and Sn_2S_3(s) was observed in our experiments.

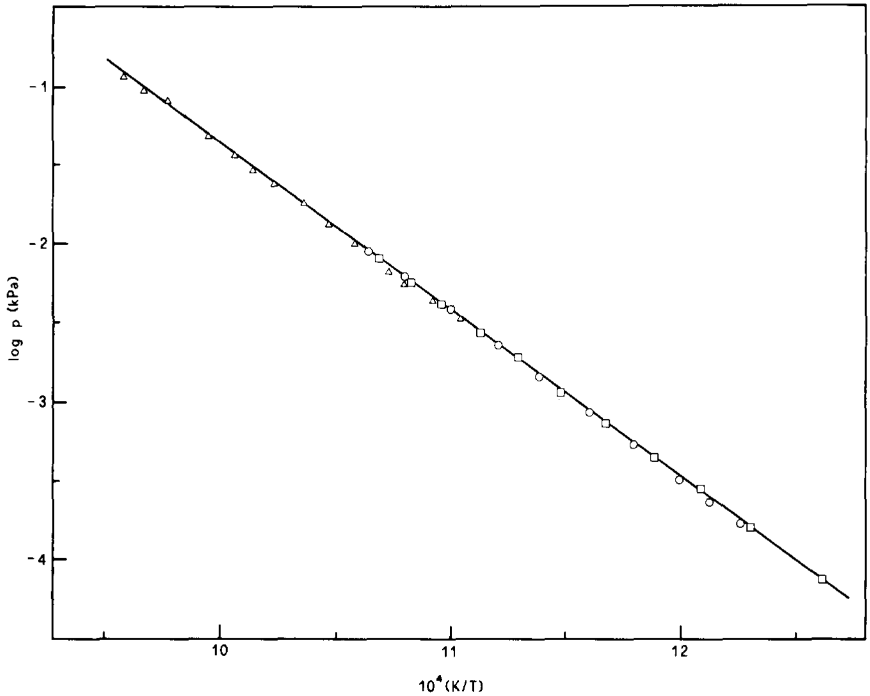

Fig. 5. Vapour pressure of pure SnS(s): ○, run 43; △, run 46; □, run 47.

In conclusion, this study has shown that the vaporization of $SnS_2(s)$ occurs in three steps connected with the change in chemical composition of the surface of the sample according to the consecutive equilibria (2), (3) and (1).

The $S_2(g)$ pressure above $SnS_2(s)$ and $Sn_2S_3(s)$ can be well expressed by the selected equations (4) and (5) respectively and the SnS(g) pressure above SnS(s) by eqn. (8). Second- and third-law treatment of the results gives the following average standard enthalpies associated with reactions (2), (3) and (1):

$\Delta H^\circ_{298}(\text{reaction (2)}) = 54.5 \pm 1.0\ \text{kJ mol}^{-1}$

$\Delta H^\circ_{298}(\text{reaction (3)}) = 112.0 \pm 2.0\ \text{kJ mol}^{-1}$

$\Delta_{\text{sub}} H^\circ_{298}(\text{reaction (1)}) = 220.0 \pm 2.0\ \text{kJ mol}^{-1}$

The heat of formation of $Sn_2S_3(s)$ has been calculated by combining ΔH°_{298} of reaction (3) selected here, the heat of formation of SnS(s) $(-102.9 \pm 0.1\ \text{kJ mol}^{-1})$ [8] and the partial sublimation enthalpy of sulphur to $S_2(g)$ (130.4 kJ mol^{-1}) [28]. The value $\Delta_{\text{form}} H^\circ_{298}(Sn_2S_3) = -253\ \text{kJ mol}^{-1}$, with an error estimated to be less than ± 2 kJ mol^{-1}, is in good agreement with that reported by Wiedemeier and Csillag $(-254.5\ \text{kJ mol}^{-1})$ [17] and with that selected by Mills $(-263 \pm 21\ \text{kJ mol}^{-1})$ [28].

TABLE 8

Comparison of vapour pressures above SnS_2, Sn_2S_3 and SnS

Reference	Compound	Phase	ΔT or T (K)	Method	log p (kPa) $= A - B/T + C \log T$			p value (kPa)
					A	B	C	
Gerasimov *et al.* [12]	SnS_2	s	650, 675, 700, 720	Static				4.3, 12.7 28.7, 48.9
Karakhanova *et al.* [13]	SnS_2	s	773–1020	Dew point	6.00 ± 0.15	4736 ± 200		
Sevryukov [14][a]	SnS_2	s	623–773	?	15.78	19280		
Wiedemeier and Csillag [11]	SnS_2	s	678–798	Knudsen	12.43 ± 0.22	11400 ± 150		
This work	SnS_2	s	689–806	Torsion	12.41 ± 0.40	$(11.3 \pm 0.3) \times 10^3$		
Karakhanova *et al.* [13]	Sn_2S_3	s	779–1009	Dew point	4.16 ± 0.46	3611 ± 200		
Wiedemeier and Csillag [17]	Sn_2S_3	s	688–820	Knudsen	11.95 ± 0.37	11240 ± 280		
This work	Sn_2S_3	s	699–862	Torsion	11.81 ± 0.50	$(11.2 \pm 0.4) \times 10^3$		
Colin and Drowart [1]	SnS	s	815–1005	Mass spectrometry	9.35	10625		
Klushin and Chernykh [2]	SnS	l	1108–1250	Boiling point	8.67	9980		
St. Clair *et al.* [3][b]	SnS	s	1023, 1073, 1123	Transpiration				0.1, 0.3, 1.0
St. Clair *et al.* [3][b]	SnS	l	1173, 1223	Transpiration				2.0, 4.0
Rau [4][c]	SnS	s(α)	700–875	Knudsen	16.512	11194	−2.19	
Rau [4][c]	SnS	s(β)	875–1154	Transpiration	16.722	11160	−2.19	
Rau [4][c]	SnS	l	1154–?	Transpiration	7.529	8566		
Richards [5]	SnS	s	950–1075	Transpiration	9.09	10470		
Nakamura and Fuwa [6]	SnS	s	975–1150	Transpiration–mass spectrometry	10.88	12365		
Benuni and Tseidler [7][d]	SnS	s	890–1084	Knudsen	9.08	10470		
Wiedemeier and Csillag [8]	SnS	s	733–944	Knudsen	9.54 ± 0.23	10878 ± 200		
Hsiao and Schlechten [9]	SnS	s	776–977	Knudsen	7.50	6728		
This work	SnS residue	s	795–1047	Torsion	9.57 ± 0.30	$(10.8 \pm 0.3) \times 10^3$		
This work	SnS pure	s	793–1043	Torsion	9.33 ± 0.10	$(10.7 \pm 0.1) \times 10^3$		

[a] As reported in Chem. Abstr., 53, 16663 g.

[b] Values found in Chem. Abstr., 49, 2966 e.

[c] Solid-to-solid transition, 875 K (as reported by Mills [28]).

[d] As reported by Mills [28].

From our heat of formation of Sn_2S_3(s) and employing ΔH°_{298} selected for reaction (2), the heat of formation of SnS_2(s) has been calculated. Also in this case the value $\Delta_{\mathrm{form}}H^\circ_{298}(SnS_2) = -148 \pm 2$ kJ mol^{-1} agrees with that found by Wiedemeier and Csillag (-149.7 kJ mol^{-1}) [11] and with that selected by Mills (-153 kJ mol^{-1}) [28].

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