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Sublimation enthalpy of solid P_4S_3 derived from vapour pressure measurements

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Abstract

The standard sublimation enthalpy of solid phosphorus trisulphide, P_4S_3, was determined by measuring its vapour pressure. The pressure measurements were carried out by employing transpiration, torsion and Knudsen-effusion methods.

From the results obtained, the pressure–temperature equation $\log p$ (kPa) = $(9.34 \pm 0.25) - (4420 \pm 100)/T$ was derived and a standard sublimation enthalpy, $\Delta H^{\ominus}_{298}$, of 102 ± 4 kJ mol^{-1} was proposed as the average of the values obtained by second- and third-law treatment of the vapour pressure data.

INTRODUCTION

Phosphorous trisulphide sublimes congruently [1]. The vapour pressure of this compound was measured in the high-pressure range by Forthmann and Schneider [2] and by Bouix and Vincent [1], both over liquid phase. Apparently no vapour pressure data are published for lower temperatures. As part of our research programme undertaken to investigate the vaporisation behaviour of sulphides [3–8], the sublimation of solid P_4S_3 was studied by measuring the vapour pressure of this compound as a function of temperature using three methods: transpiration, torsion and Knudsen-effusion. In all the experiments, the pressure ranges covered were lower than those covered in previous works [1,2].

EXPERIMENTAL RESULTS AND DISCUSSION

The phosphorus trisulphide used in this study was 99.9% pure (Aldrich Chemie). The methods and techniques used have been described previously, the transpiration method in ref. 9, the torsion method in ref. 10 and the Knudsen-effusion method in ref. 11.

The experimental data and the corresponding vapour pressure values obtained by the transpiration method are reported in Table 1. Pure helium was employed as the carrier gas.

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TABLE 1

Vapour pressure and third-law standard sublimation enthalpy values of solid P_4S_3 obtained from the transpiration method

T (K)	Mass (mg)	Δt (min)	Flow of carrier gas (ml min^{-1})	$-R\ln p$ (J mol^{-1} K^{-1})	$-\Delta(G_T^\ominus - H_{298}^\ominus)/T$ (J mol^{-1} K^{-1})	$\Delta H_{298}^\ominus$ (kJ mol^{-1})
387	33	1274	50	81.1	188.1	104.2
394.5	43	1200	50	78.3	187.4	104.8
401.5	79	1340	50	74.3	186.7	104.8
403.5	46	875	40	73.3	186.5	104.8
412	5	38	70	70.4	185.6	105.5
414.5	83	930	40	68.9	185.3	105.3
416	6	30	70	66.8	185.2	104.8
420	14	120	40	66.6	184.8	105.6
420	14	100	40	65.3	184.8	105.0
421.5	10	53	50	64.6	184.6	105.5
421	9	40	60	64.7	184.6	105.0
422	12	45	70	64.5	184.6	105.1
425	33	90	50	59.1	184.1	103.5
					Average	104.9 ± 0.6

The Knudsen data were obtained in two runs using two different cells: graphite (run 1) and pyrophyllite (run 2), both with effusion holes of about 1 mm in diameter. In order to determine the instrument constants necessary for the pressure calculation from the measured torsion angles, the vapour pressure of very pure mercury [12] was employed as a standard. The vapour pressures of P_4S_3 measured with this technique are reported in Table 2. Table 3 lists the pressure measured by the Knudsen method. Pure mercury was also used as a standard for calibration of the Knudsen cell.

The pressure–temperature equations reported in Table 4 were obtained by a least-squares treatment of the vapour pressure data measured in each run. Figure 1 compares the plots of these equations, together with the literature results. Considering our equations, and weighting their slopes and intercepts in proportion to the number of experimental points, the equation was derived

$$\log p\ (\mathrm{kPa}) = (9.34 \pm 0.25) - (4420 \pm 100)/T \tag{1}$$

where the associated errors are estimated. From the slope of the linear equations of each experiment, the second-law sublimation enthalpy of P_4S_3 at the mid-point P_4S_3 temperature was determined and is reported in Table 4. At each experimental temperature, the third-law treatment of the vapour pressure value gives a standard sublimation enthalpy value for this compound. The free energy functions of solid P_4S_3 necessary for this calculation were those of Mills [13] and those of the gaseous phase were from Bouix and Vincent [1]. The $\Delta H_{298}^\ominus$ values thus obtained are reported in Tables 1–3, and

TABLE 2

Vapour pressure and third-law standard sublimation enthalpy values of solid P_4S_3 obtained from the torsion method

T (K)	α (deg.)	$-R\ln p$ (J mol^{-1} K^{-1})	$-\Delta(G_T^\ominus - H_{298}^\ominus)/T$ (J mol^{-1} K^{-1})	$\Delta H_{298}^\ominus$ (kJ mol^{-1})
Run 1				
350	1.5	99.9	191.2	101.9
355.5	2.5	95.7	190.8	101.8
358	3	94.2	190.6	101.9
361	3.5	93	190.3	102.3
363	4	91.9	190.1	102.4
366.5	5.5	89.2	189.8	102.3
368	6	88.4	189.7	102.3
371	8	86.1	189.4	101.8
373	9.5	84.6	189.2	102.1
375	11.5	83.1	189.1	102.1
377	12.5	82.3	188.9	102.2
380	15	80.8	188.6	102.4
382	18	79.2	188.4	102.3
384	21	78.1	188.3	102.3
386	24	76.9	188.1	102.3
387	25.5	76.4	188.1	102.3
389	30	75	187.9	102.3
392.5	35.5	73.7	187.6	102.5
395.5	42	72.3	187.4	102.7
398	46.5	71.4	187.1	103.2
400	52.5	70	186.9	102.9
			Average	102.3 ± 0.3
Run 2				
351.5	1.5	99.9	191.1	102.3
355	2	97.7	190.9	102.4
358	2.5	95.7	190.6	102.5
362	3	94.1	190.2	102.9
364	3.5	93	190	103
366	4.5	90.9	189.9	102.8
368	5.5	89.1	189.7	102.6
370	6.5	87.8	189.5	102.6
373	9	85.2	189.2	102.3
376.5	11	83.4	188.9	102.6
379	13	82.1	188.7	102.6
380	14.5	81.1	188.6	102.5
383	18.5	79	188.4	102.4
385.5	23	77.3	188.2	102.4
387	26	76.2	188.1	102.3
390	30	75	187.8	102.5
392	34	74.1	187.6	102.6

TABLE 2 (continued)

T (K)	α (deg.)	$-R\ln p$ (J mol^{-1} K^{-1})	$-\Delta(G^{\ominus}_T - H^{\ominus}_{298})/T$ (J mol^{-1} K^{-1})	$\Delta H^{\ominus}_{298}$ (kJ mol^{-1})
394	38	73.1	187.4	102.7
396	43	72.3	187.2	102.8
398.5	48	71.2	187	102.9
400	52	70.4	186.9	102.9
402	56	69.9	186.6	103.1
			Average	102.6 ± 0.2

TABLE 3

Vapour pressure and third-law standard sublimation enthalpy values of solid P_4S_3 obtained from the Knudsen method

T (K)	Mass (mg)	Δt (s)	$-R\ln p$ (J mol^{-1} K^{-1})	$-\Delta(G^{\ominus}_T - H^{\ominus}_{298})/T$ (J mol K^{-1})	$\Delta H^{\ominus}_{298}$ (kJ mol^{-1})
335	96.43	162900	109.10	192.59	101.0
342	55.95	57000	104.89	191.58	101.4
347	15.76	10800	101.44	191.54	101.7
352	95.41	47100	98.76	191.12	102.0
353	18.94	7200	96.46	191.08	101.5
353	23.84	10800	98.00	191.08	102.0
370	26.01	3720	88.23	189.54	102.8
372	69.00	7320	85.75	189.33	102.3
373	26.82	3060	86.32	189.24	102.8
378	112.13	7800	82.11	188.82	102.4
380	52.36	3720	82.30	188.61	102.9
382	36.57	1800	79.24	188.45	102.3
391.5	39.31	1200	75.22	187.65	102.9
				Average	102.1 ± 0.6

TABLE 4

Vapour pressure and sublimation enthalpy of values of solid P_4S_3

Method	ΔT (K)	$\log p$ (kPa) $= A - B/T$		Sublimation enthalpy (kJ mol^{1})		
		A [a]	B [a]	2nd law		3rd law
				$\Delta H^{\ominus}_T$	$\Delta H^{\ominus}_{298}$	$\Delta H^{\ominus}_{298}$
Transpiration	387–425	9.03 ± 0.65	4383 ± 269	83.9 ± 5.2	98.8 ± 5.2	104.9 ± 0.6
Torsion (run 1)	350–400	9.38 ± 0.14	4407 ± 52	84.4 ± 1	98.4 ± 1	102.3 ± 0.4
Torsion (run 2)	351–402	9.90 ± 0.18	4622 ± 70	88.5 ± 1	102.4 ± 1	102.6 ± 0.3
Knudsen	335–391	8.64 ± 0.23	4142 ± 84	79.3 ± 1.6	93.0 ± 1.6	102.1 ± 0.6

[a] The errors are standard deviations.

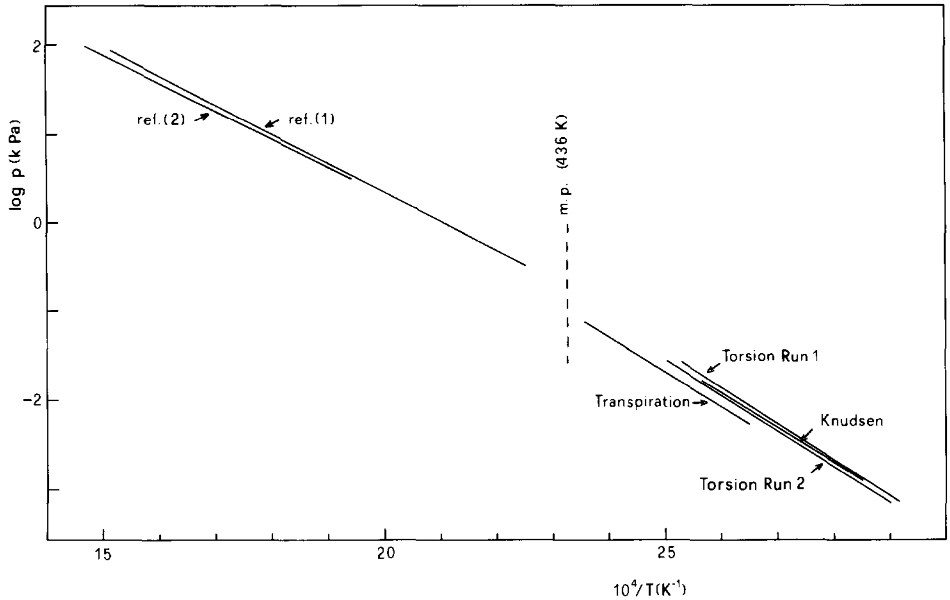

Fig. 1. Comparison of temperature–pressure equations with those reported in literature.

the average value derived in each experiment is reported in Table 4, which also gives the standard sublimation enthalpies calculated from the second-law $\Delta H_T^\ominus$ values reported at 298 K, using the enthalpic functions taken from the literature [1,13] and taking into account the solid transformation at 312 K [14].

The values are in agreement. The $\Delta H_{298}^\ominus$ value obtained from the second-law treatment of Knudsen data is lower than that calculated from the third-law elaboration of the same pressure data. Considering the presence of a small temperature trend in the third-law $\Delta H_{298}^\ominus$ values, we believe that the Knudsen vapour pressures measured at the lowest temperatures are not reliable; therefore, the $\Delta H_T^\ominus$ derived from the slope of the Knudsen equation was not taken into consideration.

From these results, an average $\Delta H_{298}^\ominus$ value of 102 ± 4 kJ mol^{-1} as the standard sublimation enthalpy of P_4S_3 is proposed, with the estimated uncertainty also taking into account the small experimental temperature range covered.

REFERENCES

1 J. Bouix and H. Vincent, J. Therm. Anal., 12 (1977) 371.
2 R. Forthmann and A. Schneider, Z. Phys. Chem., 49 (1966) 22.
3 D. Ferro, V. Piacente and P. Scardala, J. Mater. Sci. Lett., 7 (1988) 1301.
4 D. Ferro, V. Piacente and P. Scardala, J. Less-Common Met., 147 (1989) 1.
5 D. Ferro, V. Piacente and P. Scardala, J. Chem. Thermodyn., 21 (1989) 483.
6 V. Piacente, P. Scardala and D. Ferro, J. Mater. Sci. Lett., 9 (1990) 365.

7 G. Bardi, V. Piacente and G. Trionfetti, J. Mater. Sci. Lett., 9 (1990) 970–971.
8 R. Gigli, V. Piacente and P. Scardala, J. Mat. Sci. Lett., 9 (1990) 1148.
9 P. Scardala, V. Piacente and D. Ferro, J. Less-Common Met., 162 (1990) 11.
10 V. Piacente, P. Scardala, D. Ferro and R. Gigli, J. Chem. Eng. Data, 30 (1985) 372.
11 V. Piacente, T. Pompili, P. Scardala and D. Ferro, J. Chem. Thermodyn., 23 (1991) 379.
12 R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley and D.D. Wagman, Selected Values of the Elements, American Society for Metals, Metals Parc, OH, 1973.
13 K.C. Mills, Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides, Butterworths, London, 1974.
14 A.C. Clever, E.F. Westrum and W.A. Corden, J. Phys. Chem., 69 (1965) 1214.