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A VAPORIZATION STUDY OF Al_2Te_3

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ABSTRACT

The vapour pressure over solid Al_2Te_3 has been determined by means of mass-spectrometric, thermobalance, and torsion-effusion techniques in the temperature range 538—760 K. The mass-spectrometric analysis showed that, in the temperature range explored, $Te_2(g)$ is the only species present in the vapour. The pressure—temperature dependence of $Te_2(g)$ was found to be

$$\log P(\text{kPa}) = (5.709 \pm 0.297) - (8270 \pm 152)/T$$

Tellurium seems to vaporize at nearly unit activity and this could be explained by the occurrence of the solid-state reaction $Al_2Te_3(s) = 2/5\ Al_5Te(s) + 13/5\ Te(s)$ and subsequent vaporization of tellurium to $Te_2(g)$. A value of $\Delta H^0_{298}(f) = -270.4 \pm 21$ kJ mole^{-1} for the heat of formation of $Al_5Te(s)$ has been derived.

INTRODUCTION

Binary compounds of IIIB—VIB elements have technological importance as semiconductors. Knowledge of the condensed phase—vapor phase equilibria in these systems is also of interest in relation to the controlled crystal growth processes. The vaporization behaviour of some gallium VIB elements compounds has been investigated previously [1,2] in this laboratory. Apparently, no vaporization study of aluminum telluride has been reported as yet. In this paper we report the results of vapour pressure measurements over samples of solid Al_2Te_3 synthesized by different techniques.

EXPERIMENTAL PROCEDURE AND RESULTS

The sample of Al_2Te_3 purchased from K and K, I.C.N. Pharmaceuticals Inc., had a stated purity of 99% or higher, with Te and Al_2O_3 as the main impurities. To prevent interaction with moisture, handling of the sample during the operations of filling the effusion cells was performed in a dry-box. The vaporization experiments were carried out using the Knudsen mass-spectrometric, thermogravimetric, and torsion-effusion techniques.

Mass spectrometry

The measurements were carried out with a Bendix time-of-flight mass spectrometer, model 3015, coupled with a Knudsen-cell source. The sample was vaporized from a conventional graphite crucible heated by electron bombardment. Details of the apparatus and procedure have been described previously [3]. On heating the sample over the temperature range 538—595 K, only the ions Te_2^+ and Te^+ were observed as products formed from the vapours effusing from the cell and were identified by the usual procedure [4]. Their appearance potentials, 9.0 ± 0.2 and 11.0 ± 0.3 eV, respectively, relative to that of Hg^+ taken as standard [5], indicate that $Te_2(g)$ is the only gaseous species in equilibrium over $Al_2Te_3(s)$ and that Te^+ is in practice formed by fragmentation of $Te_2(g)$.

According to the phase diagram reported by Hansen and Anderko [6], one could conclude that $Al_2Te_3(s)$, in the temperature range explored, vaporizes according to the equation

$$Al_2Te_3(s) = 2/5\ Al_5Te(s) + 13/10\ Te_2(g) \tag{1}$$

The values of $Te_2(g)$ pressures at each temperature were calculated from the ion intensities, I^+, corrected for the isotopic abundance and the fragmentation contributions using the well-known relation $P = I^+T/K$. The value of the instrument sensitivity factor (K) was determined by a quantitative vaporization of silver [7]. The ionization cross-section of Te_2 was estimated from the data of Mann [8] and adopting the additivity postulate. The vapour pressure values so derived are reported in Table 1 and shown in Fig. 1 as a plot of $\log P$ vs. $1/T$. The least-squares fit of these data yielded the equation

$$\log P(\text{kPa}) = (5.864 \pm 0.301) - (8340 \pm 171)/T$$

where the uncertainties are the standard deviations in the intercept and slope. Furthermore, two isothermal vaporization experiments were carried out by heating small amounts of Al_2Te_3 at 564 and 583 K, respectively. In both cases the Te_2^+ ion intensity remained fairly constant during the vapor-

TABLE 1

Pressures of $Te_2(g)$ over $Al_2Te_3(s)$ measured by the mass-spectrometric technique

T (K)	P (kPa)
538	2.477×10^{-10}
550	5.236×10^{-10}
560	9.419×10^{-10}
563	9.419×10^{-10}
564 [a]	1.117×10^{-9}
570	1.714×10^{-9}
574	2.404×10^{-9}
577	2.259×10^{-9}
583 [a]	3.784×10^{-9}
584	3.581×10^{-9}
590	5.546×10^{-9}
595	8.222×10^{-9}

[a] From the quantitative vaporization run.

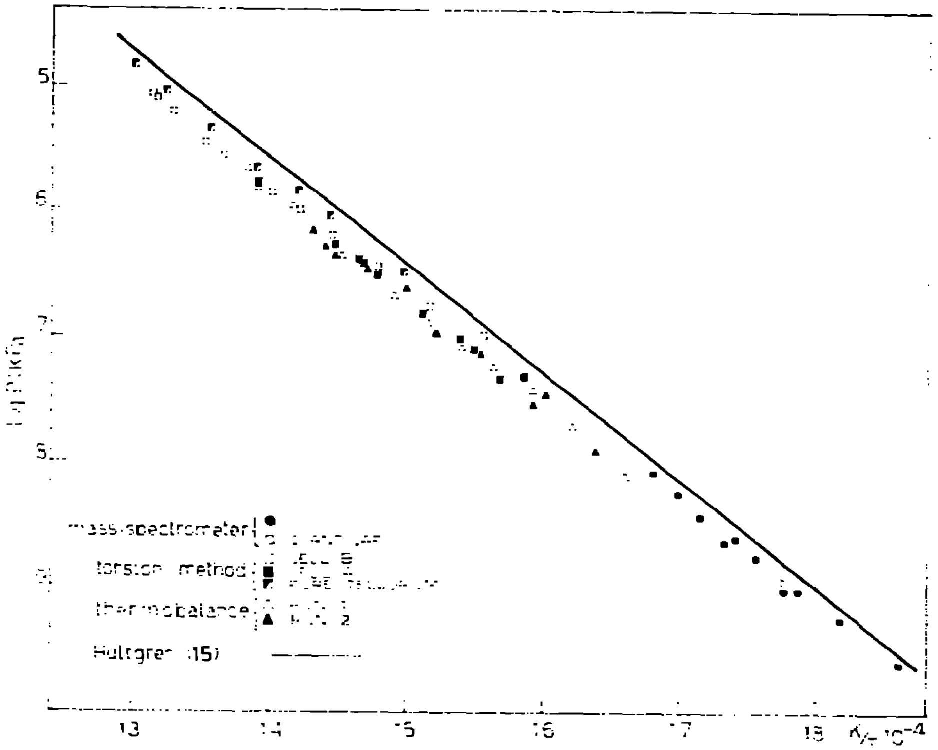

Fig. 1. Plot of log P vs. $1/T$ for solid Al_2Te_3.

ization time and dropped quickly when the samples were reduced to about 20% of the initial weight. On heating the residue up to about 900 K, the vaporization of small amounts of $Te_2(g)$ occurred, but the corresponding pressure values were negligible and not easily reproducible.

Thermogravimetry

Thermogravimetry measurements were carried out using a Setaram Ugyne Eyraud model 1360 thermobalance coupled with a graphite Knudsen cell suspended in the isothermal zone of the furnace. Details of the assembly and of the method were described in a previous work [9]. The vapour pressure values over $Al_2Te_3(s)$ were measured in two different runs over the temperature range 595—706 K using two cells with different diameters of effusion holes. According to the mass-spectrometric results, $Te_2(g)$ was assumed to be the only gaseous species effusing from the cell. At each measured temperature the vapor pressure was calculated from the rate of mass-loss (dm/dt) of the sample by the Knudsen equation [10]

$$P(\text{kPa}) = 2.28\ (T/M)^{1/2}(SK)^{-1}\ dm/dt$$

where M is the molar mass, S the area of the effusion hole of the cell and K the Clausing factor [11]. The results are reported in Table 2 and Fig. 1.

The second-law treatment of the data obtained in both runs gives the following pressure—temperature equations

$$\text{Run 1: } \log P(\text{kPa}) = (5.479 \pm 0.262) - (8133 \pm 170)/T$$
$$\text{Run 2: } \log P(\text{kPa}) = (5.312 \pm 0.321) - (8037 \pm 211)/T$$

TABLE 2

Pressure of $Te_2(g)$ over $Al_2Te_3(s)$ measured by thermogravimetric technique

Run 1 [a]		Run 2 [b]	
T (K)	P (kPa)	T (K)	P (kPa)
595	8.790×10^{-9}	611	1.213×10^{-8}
616	2.158×10^{-8}	622	3.420×10^{-8}
628	3.837×10^{-8}	628	2.911×10^{-8}
639	5.808×10^{-8}	644	7.482×10^{-8}
649	8.395×10^{-8}	657	1.057×10^{-7}
659	1.271×10^{-7}	667	2.312×10^{-7}
671	2.061×10^{-7}	680	3.342×10^{-7}
689	4.207×10^{-7}	691	4.305×10^{-7}
706	1.132×10^{-6}	695	4.943×10^{-7}
		699	6.668×10^{-7}

[a] Cell with effusion hole 0.100 ± 0.005 cm in diameter.
[b] Cell with effusion hole 0.110 ± 0.005 cm in diameter.

Torsion—effusion

The method and the experimental apparatus have been described in detail previously [12,13]. Pressure values of $Te_2(g)$ were derived from the torsion angle, α, of the torsion wire on which the effusion cell is suspended, by the equation

$$P = 2\,\alpha K/(a_1 l_1 f_1 + a_2 l_2 f_2)$$

where K is the torsion constant of the torsion wire, a_1 and a_2 the areas of the effusion holes, l_1 and l_2 the moment arms, and f_1 and f_2 the geometrical correction factors given by Freeman and Searcy [14].

In Table 3 are reported the geometrical constants of the two graphite cells

TABLE 3

Physical constants of the torsion-effusion apparatus [a]

	Cell A (graphite)	Cell B (pyrophillite)
Orifice area cells [b] ($\pm 0.05)10^{-3}cm^2$	(1) 7.85	3.80
	(2) 7.80	3.30
Force correction factors [14]	(1) 0.597	0.371
	(2) 0.584	0.351
Moment arm (cm) ±0.01	(1) 0.825	0.753
	(2) 0.860	0.749

[a] The torsion constant, K, of tungsten wire (length 35.0 ± 0.5 cm; diameter 30 μm) is equal to 0.346 ± 0.003 dyne cm rad^{-1}.
[b] Measured by photographic enlargement.

TABLE 4

Pressures of $Te_2(g)$ over $Al_2Te_3(s)$ measured by the torsion-effusion technique

Cell A		Cell B	
T (K)	*P* (kPa)	*T* (K)	*P* (kPa)
631	4.645×10^{-8}	660	1.625×10^{-7}
638	4.645×10^{-8}	677	3.335×10^{-7}
646	7.745×10^{-8}	692	6.209×10^{-7}
650	9.290×10^{-8}	703	9.226×10^{-7}
661	1.472×10^{-7}	713	1.393×10^{-6}
676	2.944×10^{-7}	719	1.479×10^{-6}
681	3.639×10^{-7}	723	2.198×10^{-6}
683	3.793×10^{-7}	732	2.698×10^{-6}
691	5.117×10^{-7}	740	3.532×10^{-6}
719	1.702×10^{-6}	753	6.109×10^{-6}
719	1.603×10^{-6}	759	7.586×10^{-6}
		760	8.054×10^{-6}

and the torsion wires used. Here again two vaporization runs were carried out in the temperature range 631—760 K. The results are reported in Table 4 and Fig. 1. The least-squares treatment of the data yielded the following equations

Cell A: $\log P(\text{kPa}) = (5.789 \pm 0.179) - (8331 \pm 120)/T$
Cell B: $\log P(\text{kPa}) = (5.984 \pm 0.139) - (8442 \pm 101)/T$

where the associated uncertainties are standard deviations.

As noted in the course of the mass-spectrometric investigations, a rapid decrease of the torsion angle was also observed in the torsion effusion measurements when ~81 ± 2% (by weight) of the sample had evaporated.

CONCLUSIONS

The mass-spectrometric investigation indicated that, in the temperature range studied, $Al_2Te_3(s)$ vaporizes according to the decomposition reaction (1). In the course of the vaporization process the pressure values were sufficiently constant and reproducible until the sample had lost 82 ± 2% of its original weight. At this composition, corresponding in the phase diagram to an intermediate compound of the formula Al_5Te, the vapour pressure of $Te_2(g)$ dropped below the sensitivity of the techniques employed ($\sim 10^{-10}$ kPa). Such behaviour seems to support the proposed vaporization reaction (1) with the formation of a stable $Al_5Te(s)$ phase. However, the existence of this phase is not yet proved, becuase the results of X-ray analysis showed that the residue was in a rather amorphous state and therefore no positive identification could be obtained.

From the vapour pressure equation calculated by utilizing all the data obtained with the three different experimental techniques, the following equation was selected

$$\log P(\text{kPa}) = (5.709 \pm 0.297) - (8270 \pm 152)/T$$

where the intercept and the slope and their associated standard deviations were obtained by proportionally weighting the corresponding values of each set of measurements to the number of points. From this equation, the second-law enthalpy change of the vaporization reaction (1), $\Delta H^0_{298} = 205 \pm 12$ kJ mole^{-1}, could be derived. The estimated error also included the uncertainties connected with the instrument calibration constants and the temperature measurements.

It is interesting to note that tellurium vaporizes at nearly unit activity with a temperature dependence, shown in Fig. 1, very close to that for the pure element reported in the literature [15], and also in agreement with the results of a torsion—effusion vaporization of pure tellurium made for calibration purposes in the course of the present experiments. A possible explanation for this behaviour could be the presence of free tellurium in the sample as a result of a solid-state reaction

$$Al_2Te_3(s) = 2/5\ Al_5Te(s) + 13/5\ Te(s)$$

and subsequent vaporization of tellurium to $Te_2(g)$.

If $Al_5Te(s)$ is formed, its heat of formation could be derived through a thermochemical cycle. Using the heat of formation of Al_2Te_3 selected by Mills [16], $\Delta H^0_{298}(f) = -318.5 \pm 4.2$ kJ mole^{-1}, the sublimation enthalpy of tellurium to $Te_2(g)$, $\Delta H^0_{298}(sub) = 168.0 \pm 0.8$ kJ mole^{-1} [15], and the enthalpy change of reaction (1) reduced to 298 K employing the Neumann—Kop rule and the heat contents reported by Hultgren et al. [15]: $\Delta H^0_{298} = 213 \pm 13$ kJ mole^{-1}, the value $\Delta H^0_{298}(f) = -270 \pm 21$ kJ mole^{-1} was derived for the formation of $Al_5Te(s)$.

By heating the residue at a higher temperature a further release of $Te_2(g)$ was noted, but its pressure was very low and not reproducible. It is possible that the vaporization of $Te_2(g)$ from $Al_5Te(s)$ is kinetically controlled by some diffusion process. Moreover, vapour pressure measurements at temperatures higher than 813 K over $Al_2Te_3(s)$ could not be made with the techniques used because the vapour pressure was too high.

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REFERENCES

1 V. Piacente, G. Bardi, V. Di Paolo and D. Ferro, J. Chem. Thermodyn., 8 (1976) 391, and refs. cited therein.

2 B.M. Nappi, D. Ferro, M. Pelino and V. Piacente, Mater. Chem., 2 (1977) 133.
3 R. Bowles, in D. Price and S.E. Williams (Eds.), Time of Flight Mass Spectrometry, Pergamon, London, 1969, p. 211.
4 W.A. Chupka and M.G. Inghram, J. Phys. Chem., 59 (1955) 100.
5 R.W. Kiser, An Introduction to Mass Spectrometry and Its Applications, Prentice Hall, Englewood Cliffs, New York, 1965.
6 M. Hansen and K. Anderko, Constitution of Binary Alloys, 2nd edn. McGraw Hill, New York, 1958, p. 137.
7 R.T. Grimley, in J.L. Margrave (Ed.), The Characterization of High Temperature Vapors, Wiley, New York, 1967, pp. 195—243.
8 J.B. Mann, in K. Ogata and T. Hayakawa (Eds.), Recent Developments in Mass-Spectrometry, Proc. Conf. Mass Spectroscopy, University Park Press, Tokyo, 1970, pp. 814—820.
9 G. Bardi, R. Gigli, L. Malaspina and V. Piacente, J. Chem. Eng. Data, 18 (1973) 126.
10 M. Knudsen, Ann. Phys., 28 (1909) 75.
11 S. Dushman, Scientific Foundations of Vacuum Technique, Wiley, New York, 1970.
12 V. Piacente and G. DeMaria, Ric. Sci., 39 (1969) 549.
13 R.D. Freeman, in J.L. Margrave (Ed.), The Characterization of High Temperature Vapors, Wiley, New York, 1967, Chap. 7, pp. 152—192.
14 R.D. Freeman and A.W. Searcy, J. Chem. Phys., 22 (1954) 762.
15 R. Hultgren, R.L. Orr, P.D. Anderson and K.K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys, University of California, Berkeley, California, 1971.
16 K.C. Mills, Thermodynamic Data for Inorganic Sulphides, Selenides, and Tellurides, Butterworths, London, 1974, p. 130.