THE VAPOR PRESSURE OF THE GeAs SYSTEM

DANIELA FERRO and VINCENZO PIACENTE *

Istituto di Chimica Fisica, Università degli Studi di Roma, 000185 Rome (Italy)

(Received 23 November 1981)

ABSTRACT

A mass-spectrometric study of the vaporization behavior of gallium arsenide showed that this compound vaporizes according to the equilibrium

$$GeAs_{(s)} \rightleftharpoons Ge_{(s)} + X/2\ As_{2(g)} + (1-X)/4\ As_{4(g)}$$

The vapor pressure was measured by mass-spectrometric and torsion-effusion techniques in the temperature range 703–861 K. The pressure–temperature equation

$$\log P(kPa) = (13.4 \pm 0.2) - (13590 \pm 350)/T$$

and the vaporization enthalpy change, $\Delta H_{782}^0 = 260 \pm 7$ kJ mole^{-1}, were derived.

INTRODUCTION

Some works on the thermodynamic properties of germanium arsenide are reported in the literature [1] but the vaporization behavior of this compound is not studied. Some total vapor pressure data have been previously determined by static method in the high pressure range [2,3] but apparently no data are reported in the literature for the low pressure range.

In view of this deficiency we have deemed it suitable to investigate the vaporization of this compound and in particular to measure its vapor pressure by employing two different techniques.

EXPERIMENTAL AND DISCUSSION

The GeAs sample was kindly supplied by R. Hillel, and its purity was tested by X-ray. The vaporization behavior was studied mass-spectrometrically and the absolute total vapor pressure determined by torsion-effusion technique.

---

* To whom correspondence should be addressed.

Mass-spectrometric results

In this study a time-of-flight mass spectrometer Bendix (model 3015) coupled with a standard graphite Knudsen source having an effusion hole 1 mm in diameter was employed. The temperature of the sample was measured using a calibrated chromel–alumel thermocouple and a Leeds and Northrup optical pyrometer in the high temperature range. Other details regarding the instruments and the generality of the method have been described elsewhere [4]. The calibration of the instrument was performed by a quantitative silver vaporization [5]. On heating the sample, As^+, As_2^+, As_3^+ and As_4^+ were the only ionic species observed in the temperature range (703–810 K) studied up to $m/q = 400$, the resolution limit of our instrument under the actual experimental conditions. Appearance potentials of these ions showed that As_4^+ and As_2^+ are produced by direct ionization of the corresponding neutral species so that the vaporization of the germanium arsenide occurs according to the equation

$$GeAs_{(s)} = Ge_{(s)} + X/2\, As_{2(g)} + (1 - X)/4\, As_{4(g)}$$

From the measured ion intensities the As_2 and As_4 partial pressures are derived following the usual procedure [4], employing a silver calibration in order to determine the instrument constant and the ionization cross-sections proposed by Mann [6], according to the additivity rule. An appreciable contribution to the As_2^+ ion
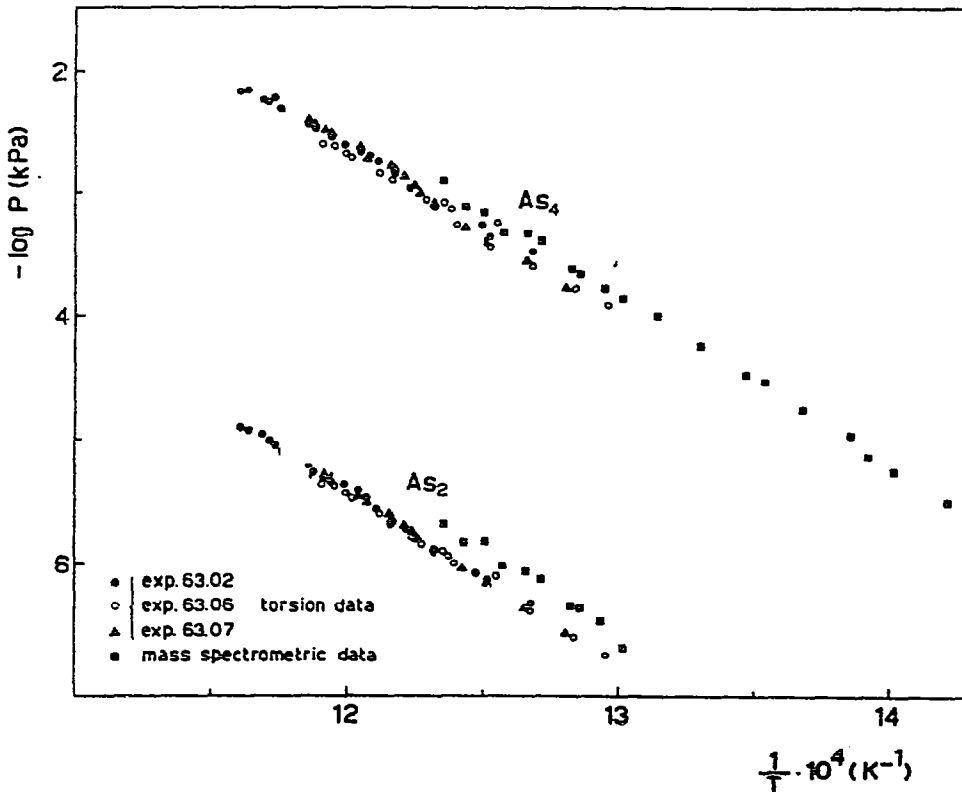

Fig. 1. As_4 and As_2 partial vapor pressures over the GeAs system.

intensity due to the dissociation of $As_{4(g)}$ was observed in the As_2^+ ionization efficiency curve so that, in addition to the contributions of As^+ and As_3^+, the As_4^+ and As_2^+ ion intensities were opportunely corrected by an estimated amount corresponding to about 40% of the measured As_2^+ ion intensity. The As_2 and As_4 pressure values are plotted in Fig. 1. From these data the following total vapor pressure—temperature equation was derived

$$\log P_{tot}(kPa) = (13.94 \pm 0.11) - (13787 \pm 176)/T$$

The standard enthalpy of the dissociative reaction

$$As_{4(g)} \rightleftharpoons 2\,As_{2(g)}$$
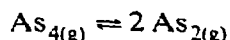
was determined by a third-law treatment of the partial pressure data using the free energy functions reported by Hultgren et al. [7]. The results are reported in Table 1.

The agreement of our average value, $\Delta H_{298}^0 = 283 \pm 1$ kJ mole^{-1} (the error is the only standard deviation), with that selected by Hultgren et al. [7] (288 $\pm$ 25 kJ mole^{-1}) and the substantial absence of temperature trend in the calculated third-law ΔH_{298}^0 values lead us to think that the uncertainties associated with the temperature measurement, the calibration factor and the corrections for the fragmentation processes are minor. Vaporization of germanium was observed by reheating the residue at about 1400 K. The derived absolute vapor pressure values of this element compared with those reported in the literature showed the near unit activity for germanium, thus confirming the assumed vaporization behavior of germanium arsenide.

TABLE 1

Heat of the dissociative reaction $As_{4(g)} \rightleftharpoons 2\,As_{2(g)}$ calculated using mass spectrometric partial pressure measurements

T (K)	P_{As_4} (kPa)	P_{As_2} (kPa)	$-R\ln K_p$ (J K^{-1} mole^{-1})	$-\Delta[(G_T^0 - H_{298}^0)/T]$ (J K^{-1} mole^{-1})	ΔH_{298}^0 (kJ mole^{-1})
752	5.61×10^{-5}	$(\sim 1.58\times10^{-7})$	217.1	151.1	(~ 276.9)
768	1.25×10^{-4}	2.14×10^{-7}	219.6	151.1	284.7
773	1.62×10^{-4}	3.16×10^{-7}	214.4	151.0	282.4
778	2.09×10^{-4}	4.07×10^{-7}	212.3	151.0	282.6
780	2.45×10^{-4}	4.08×10^{-7}	213.6	150.9	284.3
787	3.63×10^{-4}	6.92×10^{-7}	208.1	150.9	282.5
790	4.36×10^{-4}	8.31×10^{-7}	206.6	150.9	282.4
796	4.89×10^{-4}	9.55×10^{-7}	205.2	150.9	283.5
800	6.76×10^{-4}	1.51×10^{-6}	200.3	150.9	281.0
805	7.75×10^{-4}	1.52×10^{-6}	201.4	150.8	283.5
810	1.17×10^{-3}	2.00×10^{-6}	200.3	150.8	284.3
					283 ± 1 [a]

[a] The error is the standard deviation.

Torsion-effusion results

The total vapor pressure of GeAs was also measured by torsion-effusion technique. The method and the experimental apparatus have been described in detail elsewhere [8]. At each experimental temperature the vapor pressure was derived from the torsion angle α of the torsion wire on which the effusion cell is suspended by the equation

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

where K is the torsion constant of the tungsten wire ($\sim 30\ \mu$m in diameter, 30 cm long). a_1 and a_2 are the areas of the twc effusion holes, l_1 and l_2 are the distances from the rotation axis, and f_1 and f_2 are the corresponding geometrical factors [9]. The geometrical constants of the three cells used are reported in Table 2. Calibrations of the assembly and the cells used were checked by vaporization of pure magnesium as standard.

The GeAs was studied in the temperature range 772–861 K. The measured total vapor pressures and the corresponding pressure–temperature equations determined in each run are reported in Table 3. The As_2 and As_4 partial pressures were derived from the total pressure using the equilibrium constants of the dissociative reaction

$$As_{4(g)} \rightleftharpoons 2\,As_{2(g)}$$

selected by Hultgren et al. [7]. The values obtained are plotted in Fig. 1 for comparison with the mass-spectrometric data. Considering the various error sources in the absolute vapor pressure determination, the data should be considered in very good agreement. On this basis the following total pressure temperature equation is proposed

$$\log P_{tot}(\text{kPa}) = (13.4 \pm 0.2) - (13590 \pm 350)/T$$

where the slope and the intercept were obtained by weighting the corresponding values derived from each torsion (Table 3) and mass-spectrometric run proportionally to the number of points. The associated errors represent the semidispersion of

TABLE 2

Constants of the torsion-effusion cells

Cell	Orifice area		Moment arms		Freeman's factor [9]	
	$a_1 \times 10^3$ (cm^2)	$a_2 \times 10^3$ (cm^2)	l_1 (cm)	l_2 (cm)	f_1	f_2
Graphite (A)	7.10±0.05	7.05±0.05	0.86	0.85	0.926	0.916
Graphite (B)	12.28±0.05	13.25±0.05	0.89	0.86	0.591	0.792
Pyrophillite (C)	13.2±0.1	13.3±0.1	0.76	0.77	0.551	0.543

the data and should reflect the estimated uncertainties in the temperature measurements and the calibration constants. From the slope of this equation, the second-law vaporization enthalpy, $\Delta H^0_{782} = 260 \pm 7$ kJ mole^{-1}, was derived.

TABLE 3

Vapor pressure data derived from torsion measurement

Exp.	Cell	T (K)	P_{tot} (kPa)	P_{As_2} (kPa)	P_{As_4} (kPa)
63.02	A	789	3.26×10^{-4}	4.63×10^{-7}	3.33×10^{-4}
		799	4.40×10^{-4}	7.06×10^{-7}	4.44×10^{-4}
		801	5.50×10^{-4}	8.26×10^{-7}	5.55×10^{-4}
		812	7.70×10^{-4}	1.29×10^{-6}	7.76×10^{-4}
		818	1.10×10^{-3}	1.84×10^{-6}	1.11×10^{-3}
		822	1.43×10^{-3}	2.21×10^{-6}	1.44×10^{-3}
		828	1.98×10^{-3}	3.43×10^{-6}	2.00×10^{-3}
		830	2.20×10^{-3}	3.78×10^{-6}	2.22×10^{-3}
		835	2.53×10^{-3}	4.26×10^{-6}	2.55×10^{-3}
		838	2.75×10^{-3}	4.65×10^{-6}	2.77×10^{-3}
		840	3.08×10^{-3}	5.14×10^{-6}	3.10×10^{-3}
		842	3.41×10^{-3}	5.66×10^{-6}	3.44×10^{-3}
		843	3.64×10^{-3}	6.12×10^{-6}	3.66×10^{-3}
		851	4.85×10^{-3}	8.51×10^{-6}	4.89×10^{-3}
		852	5.17×10^{-3}	9.20×10^{-6}	5.21×10^{-3}
		853	5.39×10^{-3}	9.84×10^{-6}	5.43×10^{-3}
		855	5.72×10^{-3}	1.06×10^{-5}	5.77×10^{-3}
		859	6.60×10^{-3}	1.19×10^{-5}	6.65×10^{-3}
		861	6.71×10^{-3}	1.26×10^{-5}	6.76×10^{-3}

$\log P_{tot}(\text{kPa}) = (12.95 \pm 0.18) - (13002 \pm 149)/T$

Exp.	Cell	T (K)	P_{tot} (kPa)	P_{As_2} (kPa)	P_{As_4} (kPa)
63.05	C	781	1.65×10^{-4}	2.61×10^{-7}	1.67×10^{-4}
		790	2.76×10^{-4}	4.25×10^{-7}	2.78×10^{-4}
		800	3.86×10^{-4}	6.61×10^{-7}	3.89×10^{-4}
		805	5.52×10^{-4}	9.08×10^{-7}	5.56×10^{-4}
		811	7.72×10^{-4}	1.29×10^{-6}	7.78×10^{-4}
		815	9.92×10^{-4}	1.60×10^{-6}	1.00×10^{-3}
		817	1.10×10^{-3}	1.77×10^{-6}	1.11×10^{-3}
		819	1.32×10^{-3}	2.01×10^{-6}	1.33×10^{-3}
		822	1.49×10^{-3}	2.25×10^{-6}	1.50×10^{-3}
		823	1.60×10^{-3}	2.45×10^{-6}	1.61×10^{-3}
		828	1.87×10^{-3}	3.04×10^{-6}	1.89×10^{-3}
		830	2.32×10^{-3}	3.54×10^{-6}	2.33×10^{-3}
		837	2.98×10^{-3}	4.83×10^{-6}	3.00×10^{-3}
		838	3.15×10^{-3}	5.20×10^{-6}	3.17×10^{-3}
		842	3.31×10^{-3}	5.46×10^{-6}	3.33×10^{-3}
		843	3.97×10^{-3}	6.40×10^{-6}	4.00×10^{-3}
		850	4.19×10^{-3}	7.91×10^{-6}	4.73×10^{-3}

$\log P_{tot}(\text{kPa}) = (14.61 \pm 0.29) - (14370 \pm 325)/T$

TABLE 3 (continued)

Exp.	Cell	T (K)	P_{tot} (kPa)	P_{As_2} (kPa)	P_{As_4} (kPa)
63.06	B	772	1.25×10^{-4}	1.80×10^{-7}	1.26×10^{-4}
		780	1.66×10^{-4}	2.49×10^{-7}	1.68×10^{-4}
		789	2.50×10^{-4}	4.04×10^{-7}	2.52×10^{-4}
		799	3.74×10^{-4}	7.13×10^{-7}	3.77×10^{-4}
		807	5.84×10^{-4}	9.77×10^{-7}	5.88×10^{-4}
		808	7.49×10^{-4}	1.16×10^{-6}	7.55×10^{-4}
		810	8.31×10^{-4}	1.28×10^{-6}	8.37×10^{-4}
		815	9.03×10^{-4}	1.46×10^{-6}	9.10×10^{-4}
		817	9.99×10^{-4}	1.66×10^{-6}	1.01×10^{-3}
		822	1.25×10^{-3}	2.06×10^{-6}	1.26×10^{-3}
		825	1.41×10^{-3}	2.52×10^{-6}	1.42×10^{-3}
		832	1.91×10^{-3}	3.37×10^{-6}	1.93×10^{-3}
		834	2.08×10^{-3}	3.68×10^{-6}	2.09×10^{-3}
		837	2.33×10^{-3}	4.28×10^{-6}	2.35×10^{-3}
		840	2.50×10^{-3}	4.63×10^{-6}	2.52×10^{-3}

$\log P_{tot}(\text{kPa}) = (12.73 \pm 0.25) - (12872 \pm 202)/T$

For comparison, our pressure equation together with the available literature data are plotted in Fig. 2. This comparison shows that our vapor pressure values are lower than the data of Ugai et al. [2] and Hillel [3] by about a factor of 10 while the corresponding vaporization enthalpies are in good agreement. A possible source of error in our pressure measurements could arise from the fact that as long as the vaporization of GeAs proceeds according to the decomposition reaction [1], a Ge enrichment of the sample surface occurs with a subsequent small lowering of the arsenic vaporization rate. To avoid this we have retained as significant for the equilibrium constants calculation only the $As_{4(g)}$ and $As_{2(g)}$ pressure data measured in the initial part of the vaporization runs.

Furthermore, reproducibility of data was found on increasing and decreasing temperatures in the initial parts. Another well-known source of error in the absolute pressures obtained in the mass-spectrometric determinations is the uncertainty associated with molecular cross-sections, fragmentation contributions, etc. The fact that the mass-spectrometric pressure values are in excellent agreement with those determined by the torsion-effusion techniques and the fact that the dissociation energy of $As_{4(g)}$ to $As_{2(g)}$ checked employing our pressure data is in agreement with the literature data, lead to the exclusion of gross errors in our pressure values which, we think, should be reliable within a factor two.
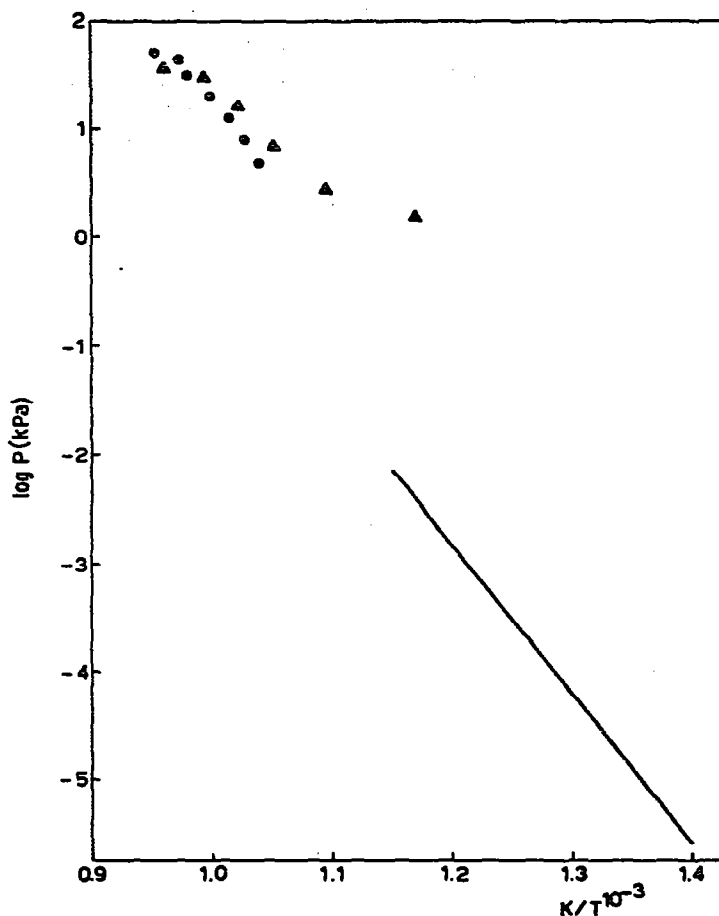
Fig. 2. Total vapor pressure over the GeAs system: present data (————): Ugai's data (●): Hillel's data (▲).

REFERENCES

1 For example, V. Blachnik and A. Schneider, Z. Anorg. Chem., 372 (1970) 314. E.G. Goucharov, N.F. Gladyhev and Ya. A. Ugai, Russ. J. Inorg. Chem., 22 (1977) 1059. T. Wadsten, Thermochim. Acta, 21 (1977) 285.
2 Ya. A. Ugai, N.F. Gladyshev and E.G. Gouchazov, Russ. J. Inorg. Chem., 23 (4) (1978) 589.
3 R. Hillel, private communication.
4 R. Bowles, in D. Price and S.E. Williams (Eds.), Time-of-Flight Mass Spectrometry, Pergamon, Oxford, 1969, pp. 211–226.
5 R.T. Grymley, in J.L. Margrave (Ed.), The Characterization of High Temperature Vapours, N.J., 1967, pp. 195–243.

6 B.J. Mann, Recent Developments in Mass Spectrometry, Proc. Tokyo Conf., Tokyo, 1970, p. 814.

7 R. Hultgren, R.L. Orr and K.K. Kelley, Supplement to Selected Values of Thermodynamic Propertie of Metals and Alloys, Department of Mineral Technology, University of California, 1967.

8 V. Piacente and G. De Maria, Ric. Sci., 39 (1969) 549.

9 R.D. Freeman and A.W. Searcy, J. Chem. Phys., 22 (1954) 762.