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Note

VAPOUR PRESSURE AND SUBLIMATION ENTHALPY OF GeI_4

D. FERRO and S. STRANGES
Dipartimento di Chimica, Università "La Sapienza", Roma (Italy)

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In order to continue a systematic study of the vaporization process of germanium halides [1], this note reports the results obtained on the vaporization of germanium tetraiodide. The vaporization of this compound is congruent and was studied by Jolly and Latimer [2] employing the transpiration method. Chernyaev and coworkers measured the vapour pressure of liquid [3] and solid [4] phases of this compound by the same technique and later Opperman [5], employing the manometric method, determined a new set of pressure data on the liquid phase at high temperature. Apparently no other data are available and this induced us to determine new measurements of the vapour pressure by the torsion effusion method.

The GeI_4 supplied by Ventron was 99% pure, with indium as the principal impurity. The method and the assembly employed are described in a previous work [6]. Six experimental runs were carried out over the average temperature range 323–420 K employing three standard graphite cells with different effusion hole areas. In Fig. 1 the results are drawn as log p vs. $1/T$.

The data, when treated following the "selected points" procedure suggested by Thomson [7], yield the Antoine equation

$$\log p = A - B/(t + C) = 16.15 \pm 0.41 - (9.6 \pm 0.3)10^3/(t + 435)$$

where the temperature t is expressed in degrees Celsius and p is in kilopascals. The "free from error" point used in this calculation, $\log p^0 = 0.52$ kPa, $t^0 = 140\,^\circ C$ was obtained as an extrapolation of our experimental data near to the melting point (146 °C) [5]. The associated errors on the constants A and B were calculated as standard deviations following the procedure suggested by Thomson [7].

The standard sublimation enthalpy, $\Delta_{sub}H^\circ_{298} = 76.5 \pm 5.7$ kJ mol^{-1}, was derived from the constants C and B using the equation

$$\Delta_{sub}H^\circ_T = \frac{2.303\,BRT^2}{C + T - 273}$$

where T is in Kelvin.

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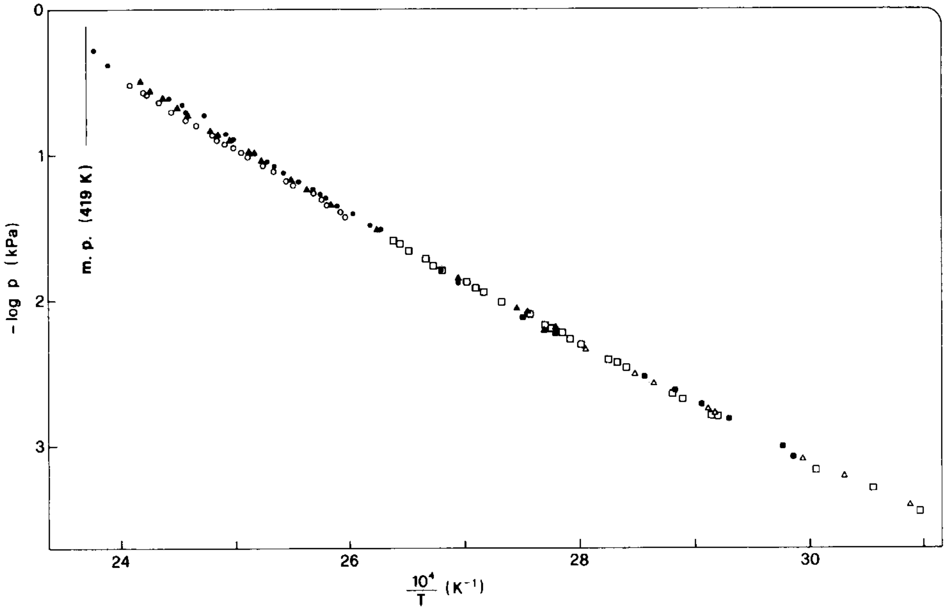

Fig. 1. Vapour pressure of $GeI_4(s)$: cell A (□ run 3, △ run 4, ■ run 1); cell B (▲ run 7); cell C (● run 6, ○ run 2).

The pressure–temperature equations of GeI_4 and the values of $\Delta_{sub}H^\circ_{298}$ obtained in this study and those reported in the literature are summarized for comparison in Table 1. Apparently our value is smaller than those reported in the literature, but we believe that the discrepancy is minor considering the uncertainties in C_p values used by other researchers and the different elaboration of experimental results. On this basis we propose the value of 80 ± 4 kJ mol^{-1} for $\Delta_{sub}H^\circ_{298}$ of solid GeI_4. From the vapour pressure data and this sublimation enthalpy, the free energy function, $(G^\circ_T - H^\circ_{298})/T$, of the solid phase was calculated by the third law method,

TABLE 1

Temperature dependence of the vapour pressure and standard enthalpy of $GeI_4(s)$

Reference	Phase	ΔT (K)	Vapour pressure $\log p$(kPa)	$\Delta_{sub}H^\circ_{298}$ (kJ mol^{-1})
Chernyaev et al. [4]	s	379–407	$10.12-4380/T$	87
Jolly and Latimer [2]	s	352–408	$9.51-4173/T$	82
Chernyaev et al. [3]	l	526–625	$7.12-3110/T$	87 [a]
Opperman [5]	l	423–598	$6.91-3090/T$	84.4 ± 3.0
This work	s	323–420	$16.15 \pm 0.41 - \frac{(9.6+0.3)10^3}{t_s+435}$	76.5 ± 5.7

[a] Calculated using $\Delta_{melt}H^\circ_{298} = 14.94 \pm 1.25$ kJ mol^{-1} reported by Opperman [5].

employing the corresponding free energy function of the gaseous phase derived from the literature [8,9]. For the solid GeI_4 this function is practically constant over the covered temperature range and is equal to 290.

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