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Sublimation enthalpy of tellurium tetrabromide by the torsion effusion method

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Abstract

The total vapour pressure of $TeBr_4(s)$ was measured in the temperature range 423–485 K by the torsion effusion method. The total pressure as a function of temperature can be represented by the following equation:

$$\log(p/k\text{Pa}) = (11.17 \pm 0.20) - (6104 \pm 100)(\text{K}/T)$$

The equilibrium involved in the vaporization process is described by:

$$(x+y)TeBr_4(s) \rightarrow xTeBr_4(g) + yTeBr_2(g) + yBr_2(g)$$

where $x = 0.06$ and $y = 0.47$.

The reaction enthalpy $\Delta H^0(298) = 119 \pm 4$ kJ mol^{-1} was obtained from the second and third law treatment of the data.

Keywords: Sublimation enthalpy; Tellurium tetrabromide; Torsion effusion method

1. Introduction

During our investigation of the vaporization behaviour of tellurium tetrahalides [1], we measured the vapour pressure of solid $TeBr_4$.

A number of thermodynamic papers on $TeBr_4$ available in the literature report some values of formation enthalpy obtained calorimetrically [2–4]: $\Delta_{\text{form}}H^0(298)$ (kJ mol^{-1}) = −184.5, −208.4, −177.8 respectively, and one was obtained by an electrochemical method [5] $\Delta_{\text{form}}H^0(298)$ (kJ mol^{-1}) = −189.4.

As concerns the sublimation process, the literature experiments on the vapour pressure were carried out by using static tensimetric methods and refer to high-temperature ranges [6,7].

Von Oppermann and co-workers [6] found that the compound vaporizes incongruently following the reactions:

$$TeBr_4(s) \rightarrow TeBr_4(g) \qquad (1)$$

$$TeBr_4(s) \rightarrow TeBr_2(g) + Br_2(g) \qquad (2)$$

The total vapour pressure was measured at temperatures from 553 to 660 K. From the partial pressure values of the gaseous species, the authors calculated the equilibrium constant of the homogeneous reaction:

$$TeBr_4(g) \rightarrow TeBr_2(g) + Br_2(g) \qquad (3)$$

in the temperature range 573–798 K.

Ivashin and Petrov [7] determined the total vapour pressure in the same temperature range, but their results are in disagreement.

We have measured the pressures of the gas above $TeBr_4(s)$ with the torsion effusion method in the range 423–485 K, which is considerably lower than that investigated in Refs. [6] and [7], with the aim of verify the coherence of the previous determinations and the reliability of the equilibria at lower temperature.

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2. Experimental

Tellurium tetrabromide was used as delivered by Alfa (99% pure). In order to avoid air contamination of the sample, the effusion cell was refilled in a dry box and the effusion holes were sealed with naphthalene, which sublimates quickly in vacuum at room temperature.

Details of the torsion apparatus used are reported in a previous paper [8]. Three graphite cells with different diameters of effusion holes were employed (cells A, B and C: 1.0, 0.65 and 0.3 mm, respectively).

For each cell the instrumental constant, in which are collected geometrical factors and the elastic properties of the torsion wire (tungsten 30 μm in diameter), was determined indirectly through the vaporization of metallic cadmium as a standard.

The experimental temperatures were measured by a calibrated chromel to alumel thermocouple inserted in a second cell placed below the torsion one. The expected temperature errors were about ± 1°C at lower temperatures and not more than 0.5°C at higher ones, due to the possible inaccuracy in determining the time at which thermal equilibrium was reached.

The total vapour pressure over $TeBr_4(s)$ was measured in seven runs, with the temperature ranging from 423 to 485 K; the results are reported in Fig. 1. For each experimental run the data were treated by the least squares method, obtaining the equations reported in Table 1. Weighting the slopes and intercepts of the log p vs. $1/T$ equations according to the number of the experimental points, the following equation was selected:

$$\log(p/\mathrm{kPa}) = (11.17 \pm 0.20) - (6104 \pm 100)(K/T) \qquad (4)$$

where the reported uncertainties are estimated considering the temperature as the only source of error.

Table 1
Temperature dependence of the total pressure above $TeBr_4(s)$

Run	ΔT (K)	No. of points	$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K})$	
			A^a	B^a
A	443–479	12	11.12 ± 0.22	6075 ± 101
B	436–468	11	11.13 ± 0.16	6113 ± 74
C	429–475	12	11.11 ± 0.31	6096 ± 140
D	423–482	12	11.37 ± 0.14	6198 ± 63
E	431–485	9	11.98 ± 0.16	5981 ± 58
F	438–483	7	11.58 ± 0.39	6269 ± 178
G	439–379	7	11.94 ± 0.15	5981 ± 68

[a] The errors are standard deviations.

3. Results and discussion

From the slope of the total vapour pressure equation, the enthalpy, related to the sublimation of one mole of gaseous mixture, is obtained as $\Delta_{\mathrm{sub}}H^0(450\ \mathrm{K}) = 117 \pm 2$ kJ mol^{-1} through the Clausius–Clapeyron equation. The reported figure can be associated with the reaction:

$$(x + y)TeBr_4(s) \rightarrow xTeBr_4(g) + yTeBr_2(g) + yBr_2(g) \qquad (5)$$

which is the linear combination of the congruent and incongruent vaporizations:

$$xTeBr_4(s) \rightarrow xTeBr_4(g) \qquad (6)$$

$$yTeBr_4(s) \rightarrow yTeBr_2(g) + yBr_2(g) \qquad (7)$$

providing $x + 2y = 1$ in order to obtain one mole of gases.

The quantities x and y of $TeBr_4$ undergoing the different vaporization processes are calculated by extrapolating the data of partial pressure reported by

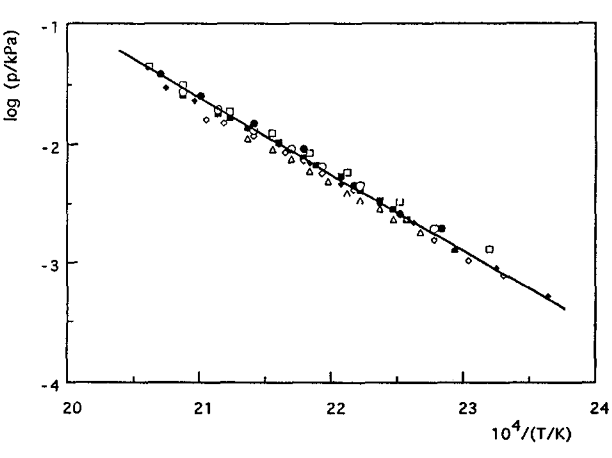

Fig. 1 Experimental vapour pressures of $TeBr_4$. ■: run A; △: run B; ◊: run C; ⧫: run D; □: run E; ●: run F; ○ run G.

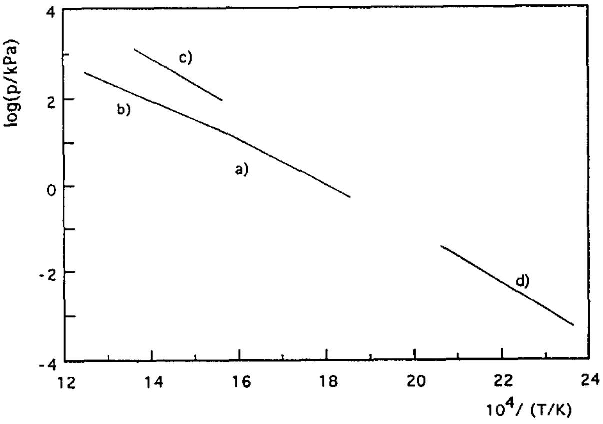

Fig. 2. Comparison of the vapour pressure data of $TeBr_4$: (a) solid phase; (b) liquid phase [6]; (c) liquid phase [7]; (d) our selected equation.

Table 2
Third-law $\Delta_{sub}H^0$ (298) values of the sublimation process ($x+y$) $TeBr_4(s) = xTeBr_4(g) + yTeBr_2(g) + yBr_2(g)$

Run	T(K)	$-R\ln K^0$ ($kJ/K^{-1}\ mol^{-1}$)	$-\Delta$gef ($kJ/K^{-1}\ mol^{-1}$)	$\Delta H^0$298 ($kJ\ mol^{-1}$)
A	443	95.514	157.74	112.19
	445	94.330	157.70	112.15
	447	93.155	157.66	112.12
	450	91.412	157.61	112.06
	453	89.693	157.56	112.00
	457	87.436	157.48	111.93
	459	86.322	157.45	111.89
	463	84.123	157.38	111.81
	468	81.427	157.29	111.72
	471	79.837	157.24	111.66
	473	78.788	157.20	111.62
	479	75.694	157.10	111.51
B	436	99.749	157.86	112.32
	441	96.711	157.77	112.23
	445	94.330	157.70	112.15
	447	93.155	157.66	112.12
	450	91.412	157.61	112.06
	452	90.264	157.57	112.02
	455	88.559	157.52	111.97
	458	86.877	157.47	111.91
	461	85.217	157.41	111.85
	464	83.579	157.36	111.80
	468	81.427	157.29	111.72
C	429	104.120	157.99	112.44
	434	100.980	157.90	112.35
	439	97.918	157.81	112.26
	443	95.515	157.74	112.19
	447	93.155	157.66	112.12
	451	90.837	157.59	112.04
	456	87.996	157.50	111.95
	459	86.322	157.45	111.89
	462	84.669	157.40	111.83
	467	81.961	157.31	111.74
	472	79.311	157.22	111.64
	475	77.748	157.17	111.59
D	423	107.980	158.09	112.55
	430	103.490	157.97	112.43
	436	99.749	157.86	112.32
	442	96.111	157.75	112.21
	447	93.155	157.66	112.12
	453	89.693	157.56	112.00
	458	86.877	157.47	111.91
	463	84.123	157.38	111.81
	468	81.427	157.29	111.72
	473	78.788	157.20	111.62
	477	76.717	157.14	111.55
	482	74.176	157.05	111.45
E	431	102.860	157.95	112.41
	438	98.525	157.83	112.28
	444	94.921	157.72	112.17
	452	99.264	157.57	112.02
	458	86.877	157.47	111.91
	464	83.579	157.36	111.80
	471	79.837	157.24	111.66
	479	75.694	157.10	111.51
	485	72.677	157.00	111.40
F	438	98.525	157.83	112.28
	444	94.921	157.72	112.17
	451	90.837	157.59	112.04
	459	86.322	157.45	111.89
	467	81.961	157.31	111.74
	476	77.231	157.15	111.57
	483	73.674	157.04	111.43
G	439	97.918	157.81	112.26
	450	91.412	157.61	112.06
	456	87.996	157.50	111.95
	461	85.217	157.41	111.85
	467	81.961	157.31	111.74
	473	78.788	157.20	111.62
	479	75.694	157.10	111.51

Von Oppermann et al. [6] to the covered temperature range, through the equations $x = p_{TeBr_4}/P$ and $y = (P - p_{TeBr_4})/2P$, where P is the total pressure.

The extrapolation can be justified by the good agreement between our data and those found by Von Oppermann et al., as is shown in Fig. 2. From this calculation, performed at various temperatures, we obtained the values $x = 0.06$ and $y = 0.47$, which do not vary appreciably in the 298–450 K range, so we have considered these figures as representative of the stoichiometry of the vaporization process.

By using the heat capacities of $TeBr_4(s)$ ($138.5\ J\ K^{-1}\ mol^{-1}$ [5]), $TeBr_4(g)$ ($108.2 - 104.6/T - 3.6 \times 10^5/T^2\ J\ K^{-1}\ mol^{-1}$ [9]), $TeBr_2(g)$ ($58.2 - 50.2/T - 1.6 \times 10^5/T^2\ J\ K^{-1}\ mol^{-1}$ [9]) and $Br_2(g)$ ($36.9\ J\ K^{-1}\ mol^{-1}$ [10]), we have obtained, through the Kirchhoff equation, the standard sublimation enthalpy of the above reaction at 298.15 K as $\Delta_{sub}H^0(298) = 121 \pm 2\ kJ\ mol^{-1}$.

We have also calculated, for each experimental temperature, $\Delta H^0(298)$ using the third law method [11]: $\Delta H^0(298) = -T(R\ln K^0 + \Delta \text{gef})$, where gef $((G^0(T) - H^0(298))/T)$ is the Gibbs energy function and K^0 is the equilibrium constant of Reaction (5). This last is related to the total pressure by the equation $K^0 = 0.415P/P^0$, where P^0 is the pressure of the reference state. The values of gef need for the involved species are calculated from the standard entropy and specific heat reported in Refs. [5], [9] and [10] through the equation

$$\begin{aligned} \text{gef}(T) &= [H^0(T) - TS^0(T) - H^0(298)]/T \\ &= \frac{1}{T}\int_{298}^{T} C_p(T')\mathrm{d}T' - \int_{298}^{T} C_p(T')/T'\mathrm{d}T' - S^0(298) \end{aligned} \tag{8}$$

where T is each experimental temperature and T' is the integration variable.

The figures obtained, reported in Table 2, show a small trend as a function of temperature and their $\Delta H^0(298)$ average (112 ± 1 kJ mol^{-1}) is about 10 kJ mol^{-1} lower than that obtained by the second law method.

An attempt to explain such a discrepancy can be carried out. We start with a comparison between our results and those of Von Oppermann et al. [6]. No match with Ivashin's data [7] can be significantly performed because they are referred to the liquid phase. Since we are interested in Reaction (5), we need to combine Von Oppermann's values $\Delta H^0(298) = 130 \pm 6$ kJ mol^{-1} for Reaction (1) and $\Delta H^0(298) = 105 \pm 3$ kJ mol^{-1} for Reaction (3) in order to obtain the standard enthalpy of Reaction (5) as the linear combination $\Delta H^0(5) = x\Delta H^0(1) + y\Delta H^0(2)$, where $\Delta H^0(2) = \Delta H^0(1) + \Delta H^0(3)$. The resulting value $\Delta H^0(4) = 118 \pm 6$ kJ mol^{-1} is in good agreement with our second-law result (121 ± 2 kJ mol^{-1}).

In this way we can believe that no evident error sources are derived from experimental uncertainties. Moreover, the variation of x and y with temperature is too small to justify a great difference in the final enthalpy and the uncertainties of the C_p used should affect both the second- and third-law ΔH values.

Nevertheless a small error in the temperature measurement could justify the small drift of the log p vs. $1/T$ line and the small trend in the third-law ΔH values.

4. Conclusions

Our study indicates that the vaporization process of $TeBr_4$(s) is represented by equilibrium (5), and consequently the related partial equilibria hold at low temperatures.

From the total vapour pressure measurements over $TeBr_4$(s) the overall sublimation enthalpy is derived at 450 K and 298 K for the incongruent vaporization process.

A series of evaluations and literature comparisons led us to weight opportunely the experimental results of standard enthalpy obtained by the second and third laws, selecting the final value 119 ± 4 kJ mol^{-1} as $\Delta_{\mathrm{sub}}H^0(298)$ for $TeBr_4$. This value is related to the sublimation Reaction (5) with the formation of one mole of gaseous mixture. It is also possible to obtain the enthalpy of sublimation of one mole of $TeBr_4$(s) according to equilibrium (5) as $\Delta_{\mathrm{sub}}H^0(298)/(x+y) = 225 \pm 4$ kJ mol^{-1}.

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