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Total vapour pressure of FeI_2 from torsion measurements

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Abstract

The total vapour pressures of iron diiodide were measured by the torsion-effusion method and the temperature dependence is represented by the following equation:

$\log\{p(\mathrm{kPa})\} = (10.80 \pm 0.40) - (9860 \pm 300)/T$

The standard sublimation enthalpy of the reaction: $FeI_2(s) \rightarrow FeI_2(g)$, $\Delta_r H^0(298) = 194 \pm 2$ kJ mol^{-1}, was obtained from second- and third-law treatments of the pressure data considering the partial pressure of $FeI_2(g)$ equal to 0.70 p_{tot}. Comparisons with previous results are made.

Keywords: FeI_2; Vapour pressure; Torsion measurements

1. Introduction

Some of the practical and theoretical importances of vaporization studies of iron(II)iodide were emphasized by Hilpert et al. [1]. Apparently the first vapour pressure data for this compound are those measured by Schäfer and Hönes [2] above both the solid and liquid phases using the transpiration method. The authors assumed that in the temperature range covered (517–686 K) the vaporization is predominantly congruent:

$$FeI_2(s) \rightarrow FeI_2(g) \quad (1)$$

The same authors also determined the following equilibrium constants of the reaction at higher temperature:

$$2FeI_2(s) + I_2(g) \rightarrow 2FeI_3(g) \quad (2)$$

$$2FeI_2(s) + I_2(g) \rightarrow Fe_2I_6(g) \quad (3)$$

where the gaseous iodine derives from the partial decomposition of the iron iodide:

$$FeI_2(s) \rightarrow Fe(s) + I_2(g) \quad (4)$$

a reaction investigated also by other authors [1,3,4]. Schoonmaker et al. [5], by studying mass-spectrometrically the vaporization of $FeI_2(s)$, found that in addition to $FeI_2(g)$ small amounts of $Fe_2I_4(g)$ are also present in the vapour phase and reported some thermodynamic data for the reaction:

$$2FeI_2(s) \rightarrow Fe_2I_4(g) \quad (5)$$

Sime and Gregory [6] measured the total vapour pressures above the iron iodide by the torsion-effusion technique employing two quartz cells with different effusion hole areas and they found a small accommodation coefficient for this compound. Thermodynamic properties of $FeI_2(s)$ [3] and $FeI_2(g)$ and $Fe_2I_4(g)$ [7] were also evaluated from an additional transpiration study of iron and iodide mixtures. Finally, in two interesting mass-spectrometric studies published at nearly the same time, Hilpert et al. [1] and Grade and Rosinger [8] identified the gaseous species above $FeI_2(s)$, measured their partial pressures and determined sets of thermodynamic data for some gaseous equilibria involving the identified species. Unfortunately in both studies: (a) the pressure values were affected by uncertainties due to the ionization cross-sections of the gaseous molecules that were used and to the corrections made for the ion intensity values of fragmentation phenomena; (b) the total vapour pressures calculated from the partial pressures as well as those determined in previous investigations do not agree; (c) the standard molar enthalpy values ascribed

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to the sublimation of iron diiodide to $FeI_2(g)$ (reaction (1)) are in disagreement.

The present study centres on the determination of reliable total vapour pressure data above $FeI_2(s)$ employing the torsion-effusion method, which is independent of the molecular weight of the effusing species.

2. Experimental and discussion

Details of the apparatus used and of the experimental procedure employed have been reported previously [9]. Torsion cells made from different materials (stainless steel, graphite and quartz) having effusion holes with a nominal diameter of 1 mm were used in this study. Their relative instrument constant, that is the ratio of the pressure value existing within the cell used to the corresponding value of the torsion angle measured by the apparatus, was determined by vaporizing pure cadmium and zinc which have well known vapour pressures [10]. The iron diiodide used in this study was supplied by Cerac, and was 99.9% pure.

In order to minimize hydrolysis or oxidation of the sample, the cell was loaded in a dry box. It was then introduced to the torsion apparatus and quickly evacuated. The pressure data are given in Fig. 1. A least squares treatment of the experimental data for each run, yields the coefficients of the linear $\log(p_{tot})$ vs. $1/T$ equation reported in Table 1. From these equations the following one, which is valid over the temperature range 684 to 786 K, was selected:

$$\log\{p(\mathrm{kPa})\} = (10.80 \pm 0.40) - (9860 \pm 300)/T(\mathrm{K})$$

The associated errors were estimated by considering in addition an uncertainty of about ± 1°C in the temperature measurement. This equation is compared with those from the literature in Table 2 and Fig. 2. As can be seen, our total vapour pressures are intermediate between those reported by Grade and Rosinger [8] and those by Hilpert et al. [1] but the slope of our selected $\log\{p(\mathrm{kPa})\}$ vs. $1/T(\mathrm{K})$ equation agrees very well with that of Hilpert et al.

As, over the temperature range considered here, the vapour is essentially made up of $FeI_2(g)$, $Fe_2I_4(g)$ and gaseous iodine in the ratio of their partial pressures (which are practically constant (within 5%) as mass-spectrometrically evaluated) the partial pressures of $FeI_2(g)$ were considered to be equal to $0.70\ p_{tot}$. The $FeI_2(g)$ partial pressures so calculated were employed

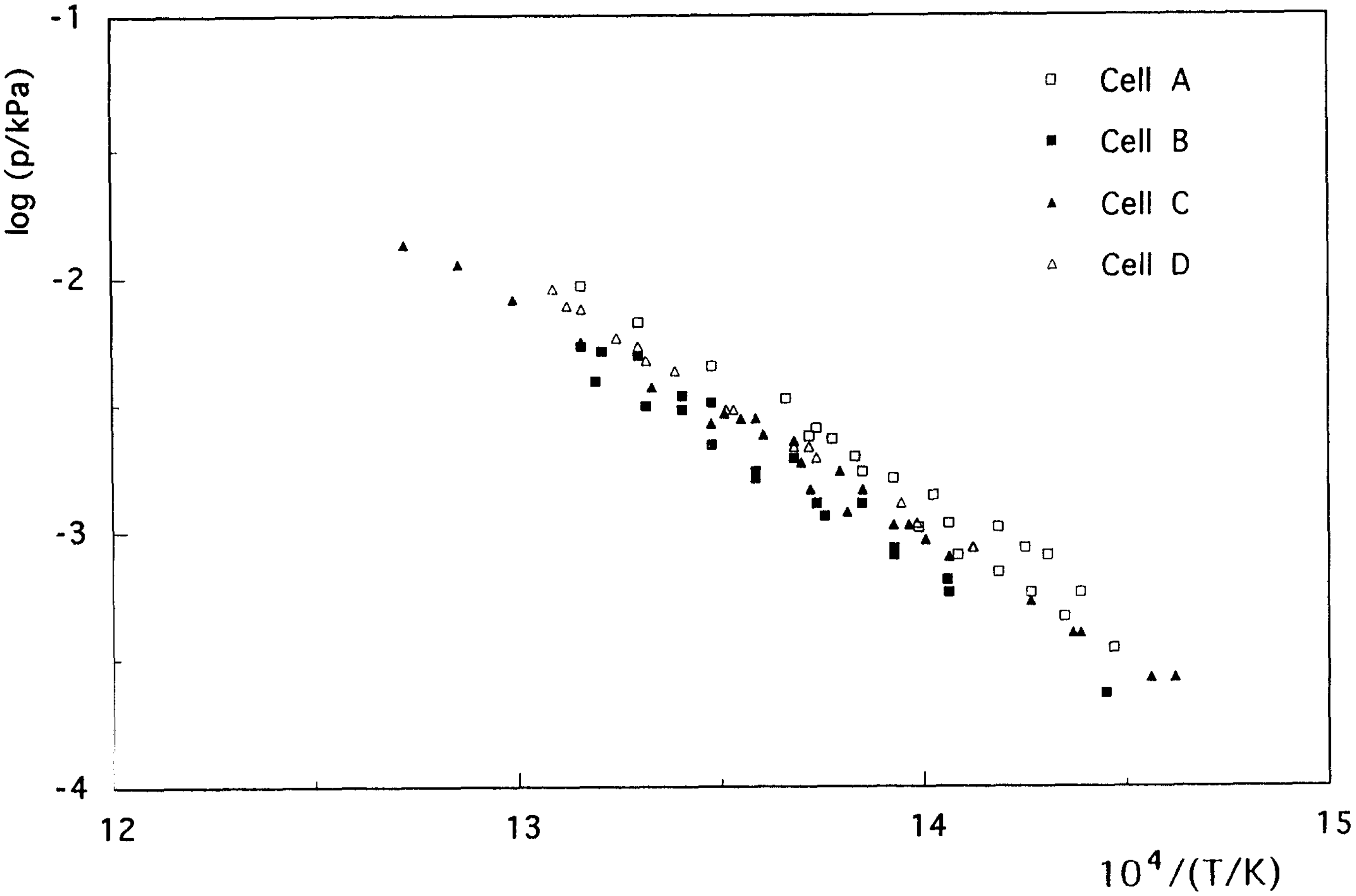

Fig. 1. Experimental total vapour pressure above $FeI_2(s)$.

Table 1
Temperature dependence of the total vapour pressure measured above $FeI_2(s)$ and enthalpies (kJ mol^{-1}) of the sublimation reaction: $FeI_2(s) \rightarrow FeI_2(g)$

Cell	Experiment	No. of points	ΔT (K)	$\log\{p(\text{kPa})\} = A - B/T$		II law		III law
				A^a	B^a	$\Delta_r H^0$ (298)	$\Delta_r H^0$ (298)	$\Delta_r H^0$ (298)
A (graphite)	1	9	695–732	10.38 ± 0.57	9439 ± 404	180.7 ± 7.7	191.7	191.2
	2	6	691–715	10.69 ± 0.49	9770 ± 347	187.0 ± 6.6	197.6	193.4
	3	7	702–760	10.91 ± 0.51	9846 ± 373	188.5 ± 7.1	200.0	191.5
B (graphite)	1	8	692–758	10.50 ± 0.18	9771 ± 131	187.0 ± 2.5	198.3	195.8
	2	6	722–757	10.63 ± 0.72	9754 ± 533	186.7 ± 10.2	198.5	193.5
	3	6	711–760	11.21 ± 0.48	10255 ± 352	196.3 ± 6.7	208.0	194.9
C (steel)	1	7	729–786	10.68 ± 0.31	9841 ± 238	188.4 ± 4.6	200.5	194.2
	2	9	684–736	11.27 ± 0.41	10183 ± 290	194.9 ± 5.6	205.8	193.3
	3	9	687–740	10.96 ± 0.44	9994 ± 320	191.3 ± 6.1	202.3	193.8
D (quartz)	1	5	731–760	11.44 ± 0.34	10311 ± 255	197.4 ± 4.9	209.4	192.7
	2	6	708–762	10.28 ± 0.35	9448 ± 255	180.8 ± 4.9	192.6	192.6
	3	6	708–764	10.76 ± 0.44	9807 ± 322	187.7 ± 6.2	199.2	192.8
			684–786	10.80 ± 40^b	9860 ± 300^b	—	200 ± 6^b	193 ± 2^b

[a] The quoted errors are standard deviations.
[b] Estimated uncertainties.

Table 2
Temperature dependence of total vapour pressures and $FeI_2(g)$ partial pressures above $FeI_2(s)$

Method [Ref.]	ΔT(K)	Total vapour pressure (kPa)	Partial pressure of $FeI_2(g)$ (kPa)
Transpiration [2]	790–850	$\log\{p\} = 12.308 - (10778/T)$	—
Knudsen-effusion [5]	714	$\{p\} = 7.49\ 10^{-4}$	$\{p\} = 6.26\ 10^{-4}$
Torsion-effusion [6]	670–m.p.	$\log\{p\} = 11.73 - (10270/T)$	—
[11][a]	298–*m.p.*	$\log\{p\} = 28.72 - (12180/T) - 5.536 \log T$	—
Transpiration [7]	790–850	—	$\log\{p\} = 18.748 - (9435/T) - 2.969 \log T$
Mass-spectrometry [8]	609–726	$\log\{p\} = 8.139 - (8120/T)$	$\log\{p\} = 8.959 - (8796/T)$
Mass-spectrometry [1]	605–725	$\log\{p\} = 11.133 - (9906/T)$	$\log\{p\} = 11.09 - (9967/T)$
Torsion-effusion	684–786	$\log\{p\} = (10.80 \pm 0.40) - [(9860 \pm 300)/T]$	—

[a] Equation reported by Grade and Rosinger [8].

to determine the molar enthalpy change associated to the sublimation process (1). The thermodynamic functions of iron diiodide in both solid and gaseous phases necessary for the determination of the third-law standard molar enthalpy of this process were taken from Ref. [12]). The average of $\Delta_r H^0(298)$ values obtained in each run are reported in Table 2. From these the final value 193 kJ mol^{-1} was selected as $\Delta_r H^0(298)$ of the reaction (1), with an overall uncertainty of about 2 kJ mol^{-1}. The value agrees with the third-law values found in literature (see Table 3) but is lower than that (200 ± 6 kJ mol^{-1}) calculated from the slope of our selected pressure–temperature equation at the midpoint 730 K and reported at 298 K by using the heat contents given in the same Ref. [12]. Evaluation of the experimental errors associated with pressure and temperature measurements, and a critical analysis of the estimation of $FeI_2(g)$ partial pressure values from the total pressures and of the uncertainties in the thermodynamic functions used in the $\Delta_r H^0(298)$ calculations, cannot account for the difference of about 8 kJ mol^{-1} found between second- and third-law results. However, the third-law values could be considered more reliable than the second-law values. This conclusion is based on the following considerations: (a) the minor scattering of the third-law $\Delta_r H^0(298)$ values calculated in each run; (b) the absence of any evident temperature trends of these values in each experimental run; (c) the second-law $\Delta_r H^0(298)$ values were obtained from the slopes of $\log\{p(\text{kPa})\}$ vs. $1/T(\text{K})$ equations evaluated employing only a few points over relatively small temperature ranges (in fact, in each run only the pressures measured in the first step of the vaporization were taken into account, when, on the sample surface,

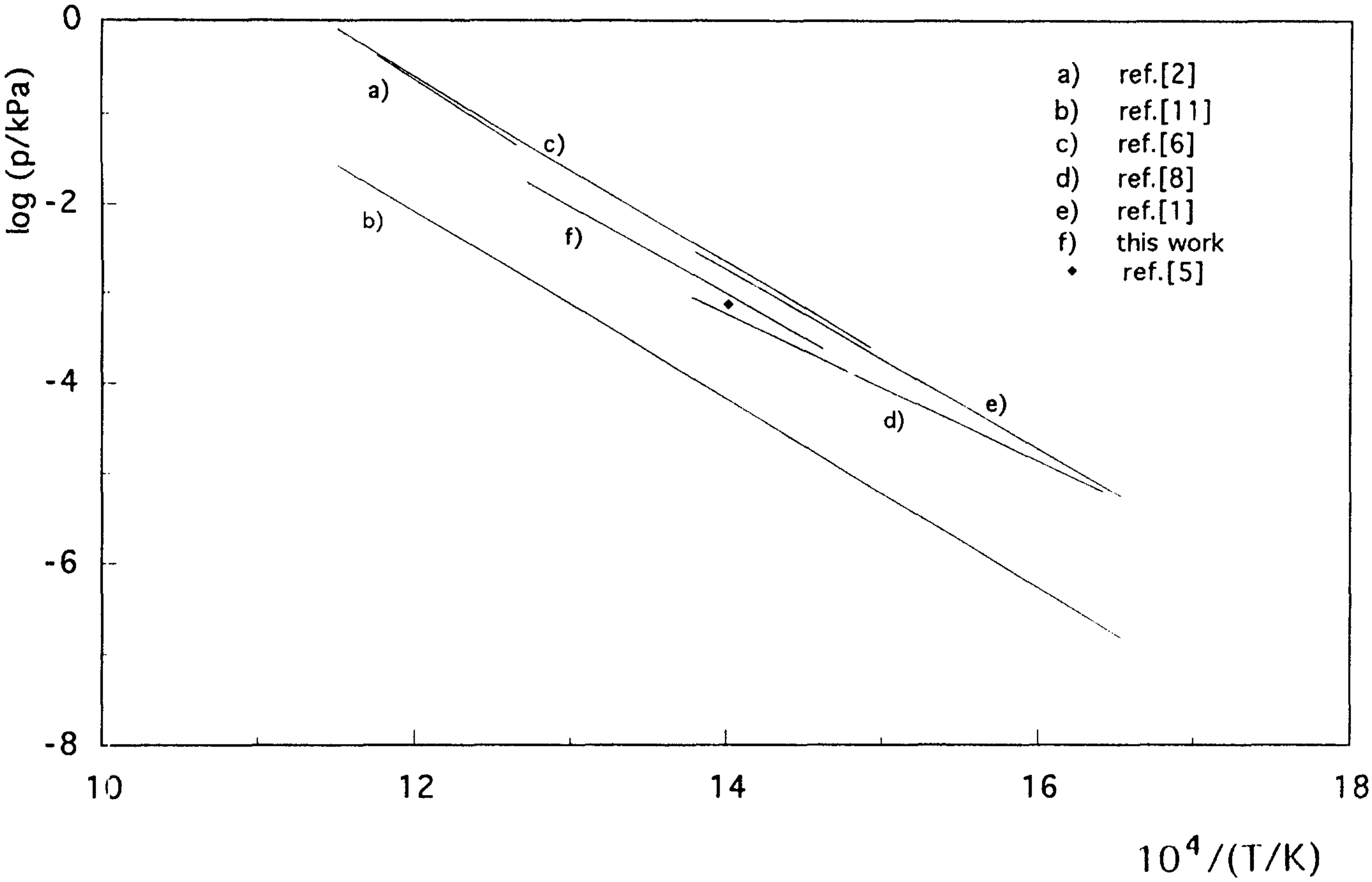

Fig. 2. Comparison of total vapour pressure data above $FeI_2(s)$.

Table 3
Enthalpy changes ($kJ\ mol^{-1}$) associated to the process: $FeI_2(s) \rightarrow FeI_2(g)$

Method [Ref.]	$\bar{T}$(K)	II law		III law	$\Delta_r H^0(298)$
		$\Delta_r H^0(T)$	$\Delta_r H^0(298)$	$\Delta_r H^0(298)$	(selected value)
Transpiration [2]	819	206.5	221.9	—	—
Knudsen-effusion [5] Mass-spectrometry	714	—	—	195.1[a]	—
Torsion-effusion [6] Diaphragm-gage	670–m.p.	196.6	—	—	—
Transpiration [7]	813 750	160.7 162.4	172.9	—	—
Mass-spectrometry [8]	667	—	184.9	195.8	—
Mass-spectrometry [1]	669 670 665	183.4 ± 0.5 193.0 ± 6.1 186.0 ± 3.4	196.6 ± 5.3	192.2 ± 2.8	193.2 ± 2.5
Torsion-effusion (this work)	730	—	200 ± 6	193 ± 2	194 ± 2

[a] Present calculations, using the experimental value $p = 7.49\ 10^{-4}$ (kPa) reported by Schoonmaker et al. [5].

the amount of iron originating from the partial decomposition of $FeI_2(s)$ is negligible). On this basis we propose as standard enthalpy change of reaction (1) a selected value of 194 $kJ\ mol^{-1}$, with an uncertainty of about 2 $kJ\ mol^{-1}$; this is in good agreement with that proposed by Hilpert et al. (193.2 ± 2.8 $kJ\ mol^{-1}$) [1].

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