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Enthalpy of sublimation of platinum tetrafluoride

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The saturated vapour of platinum tetrafluoride was studied by Knudsen-cell mass spectrometry. The only gaseous species found was $PtF_4(g)$. The molar sublimation enthalpy: $\Delta_{sub}H^\circ_m(PtF_4, 298.15\ K) = (207 \pm 16)\ kJ \cdot mol^{-1}$ was obtained.

1. Introduction

The present work is part of a systematic study of the thermodynamic properties of gaseous platinum fluorides.(1, 2) It was the purpose of this paper to determine the sublimation enthalpy of platinum tetrafluoride by means of Knudsen-cell mass spectrometry. The value obtained was to be compared with the literature values of $\Delta_f H^\circ_m(PtF_4, g)$,(1) and $\Delta_f H^\circ_m(PtF_4, s)$.(3)

2. Experimental

A MI-1201 ($\pi/2$, 200 mm) mass spectrometer, supplied with an electron-impact ion source described in reference 4, was used. Platinum effusion cells were employed for evaporation. The ratio of total inner surface and effusion-orifice areas was about 500. To prevent hydrolysis the cell was loaded with the sample in a dry box. Less than 5 min was necessary for transferring the sample from the box to the spectrometer (the time of contact with air). Most experiments were conducted with a two-chamber Knudsen cell. A substance with a known vapour pressure was placed in one of the chambers, the other being loaded with the substance under investigation. Both chambers were kept at the same temperature. Since the vapour pressure of the substance chosen as a standard was less than that of platinum tetrafluoride, the effusion orifice over the cell loaded with the standard was larger than that of the sample one $\{A(\mathrm{std})/A(PtF_4)$ was between 4 and $8\}$.

The synthesis of platinum tetrafluoride was carried out by thermolysis of the compound $[BrF_2]_2[PtF_6]$, obtained by interaction of H_2PtF_6 dried in glassy-carbon beakers at 393 K over a 4 h period with distilled BrF_3, the reaction temperature being raised from 393 to 413 K, *i.e.* up to the beginning of incongruent

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fusion of $[BrF_2]_2[PtF_6]$.(5) The viscous dark-brown fusion cake having been obtained, BrF_3 was split out at 450 K *in vacuo* (approximately 0.1 Pa). The product was ground, placed in a glassy-carbon boat, and finally separated from bromine traces by fluorine flowing for 60 min over it at 430 to 470 K. The yield of platinum tetrafluoride was 96 mass per cent in terms of the initial platinum content.

Chemical analysis of the product was made as follows: platinum—gravimetrically, after reducing with hydrazine hydrate; fluorine—potentiometrically, after separation of platinum black in the filtrate by means of the ion-selective electrode OP-711 "F". Found for the product: Pt, (71.80±0.06) mass per cent; F, (27.90±0.28) mass per cent; calculated for platinum tetrafluoride: Pt, 71.97; F, 28.03.

All procedures with platinum fluorides were performed in a box dried with P_2O_5 and purged with N_2. The prepared PtF_4 had a light-brown colour.

Caesium iodide used as a standard was commercially available and ultra-pure grade; the mass fraction of impurities was not greater than 10^{-5}.

3. Results

The samples were sublimed in the temperature range 620 to 720 K. The mass spectrum of positive ions from PtF_4 saturated vapour is listed in table 1. The spectrum remained practically unchanged in the temperature range studied and coincided with that already known in the literature for PtF_4(g) alone. No F_2^+, F^+, or PtF_k^+ ($k > 4$) ions were detected. On the basis of the results the platinum tetrafluoride sublimation was assumed to be congruent without decomposition; the unique component of the vapour is the PtF_4 molecule.

TABLE 1. Mass spectrum of saturated vapour over solid PtF_4; $U_{ion} = 50$ to 70 V, $T = 620$ to 720 K

	Pt^+	PtF^+	PtF_2^+	PtF_3^+	PtF_4^+
PtF_4(g)	0.2±0.5	0.26±0.05	0.57±0.05	1	0.50±0.04

The ratio of PtF_4 and CsI(7) standard partial pressures was determined in three independent measurements with two-chamber effusion cells. The value being determined was the ratio $I(^{195}PtF_3^+)/I(CsI^+)$. The volatilities of platinum tetrafluoride and caesium iodide are comparable, and the m/e values for $^{195}PtF_3^+$ and CsI^+ ions are close, the latter point accounting for the choice of standard. The ratio of PtF_4 and CsI pressures was found by the expression:

$$p(PtF_4)/p(CsI) = \alpha(Pt)I(^{195}PtF_3^+)\sigma(CsI)K(PtF_4)/I(CsI^+)\sigma(PtF_4)K(CsI),$$

p, I, σ, and K denoting the partial pressure, ion current at ionizing potential of 50 to 70 V, total ionization cross-section, and mass-spectrum coefficient of a species, and $\alpha(Pt)$ the isotopic distribution coefficient for Pt. The $K(PtF_4)$ and $K(CsI)$ values were taken from table 1 and reference 8, whereas $\sigma(PtF_4)$ and $\sigma(CsI)$ were calculated by the additive scheme using atomic cross-sections.(9) The ratios $p(PtF_4)/p(CsI)$ obtained were treated by the second- and third-law methods. A plot of $\ln\{p(PtF_4)/p(CsI)\}$ against $1/T$ gave the second-law value for the difference between the sublimation enthalpies of platinum tetrafluoride and caesium iodide:

$$\mathrm{PtF_4(s)} = \mathrm{PtF_4(g)}, \tag{1}$$

$$\mathrm{CsI(s)} = \mathrm{CsI(g)}, \tag{2}$$

$$\Delta\Delta H_{\mathrm{m}}^{\circ}(3) = \Delta H_{\mathrm{m}}^{\circ}(1) - \Delta H_{\mathrm{m}}^{\circ}(2). \tag{3}$$

Using $\ln\{p(\mathrm{PtF_4})/p(\mathrm{CsI})\}$ and the difference of $\Delta\Phi(T, 298.15\ \mathrm{K})$ for reactions (1) and (2) one obtained the same value by the third-law procedure. The experimental and calculated values are collected in table 2.

There are no literature thermodynamic functions of $\mathrm{PtF_4(s)}$. The third-law calculations as well as the conversion of the second-law results to the temperature of 298.15 K were made using the functions for $\mathrm{ZrF_4(g)}$ and $\mathrm{ZrF_4(s)}$.(10) Thermodynamic functions for CsI(s) and CsI(g), and the sublimation enthalpy for CsI were taken from reference 7. From the results presented in table 2 at 298.15 K

TABLE 2. Experimental results used in determining the sublimation enthalpy of platinum tetrafluoride: n denotes the number of measurements and s the standard deviation when $n > 1$

T/K	n	$\ln\dfrac{I(^{195}\mathrm{PtF_3^+})}{I(\mathrm{CsI^+})}$	s	$\dfrac{\Delta H_{\mathrm{m}}^{\circ}(298.15\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$	T/K	n	$\ln\dfrac{I(^{195}\mathrm{PtF_3^+})}{I(\mathrm{CsI^+})}$	s	$\dfrac{\Delta H_{\mathrm{m}}^{\circ}(298.15\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}}$
623	1	3.81		208.1	673	2	4.41	0.75	206.7
629	1	4.03		207.8	674	1	3.81		209.9
632	1	3.91		208.1	675	1	3.72		210.3
633	3	4.54	0.73	205.3	678	2	3.84	0.02	209.9
636	1	4.71		204.2	679	1	4.14		207.2
640	1	3.83		209.2	680	1	3.07		209.2
646	1	3.74		209.7	683	1	5.89		210.6
648	4	3.77	0.16	209.3	684	1	3.97		209.2
649	1	3.68		210.2	685	1	4.52		206.4
651	1	4.64		204.7	686	3	4.01	0.11	209.3
653	1	5.22		202.0	687	2	4.78	0.28	204.8
656	3	4.09	0.68	208.0	689	5	4.65	0.44	205.2
657	2	4.34	1.02	206.6	690	1	4.03		208.9
658	1	3.68		210.4	693	2	4.68	0.89	205.0
661	3	4.58	0.79	205.2	697	1	4.61		205.8
663	1	5.05		202.8	699	2	4.34	0.62	206.6
664	1	5.10		202.7	706	1	3.97		209.4
665	4	4.72	0.61	204.7	708	1	3.95		209.9
667	2	3.58	0.02	211.2	715	1	3.77		211.4
670	1	3.93		209.1					

At $T = 298.15\ \mathrm{K}$: $\Delta H_{\mathrm{m}}^{\circ}(1) = (206.5 \pm 6.5)\ \mathrm{kJ\cdot mol^{-1}}$, (the third law),
$= (208 \pm 26)\ \mathrm{kJ\cdot mol^{-1}}$, (the second law).
At $T = 668\ \mathrm{K}$: $\Delta H_{\mathrm{m}}^{\circ}(1) = (215 \pm 26)\ \mathrm{kJ\cdot mol^{-1}}$, (the second law).
$\Delta S_{\mathrm{m}}^{\circ}(1) = (198 \pm 20)\ \mathrm{kJ\cdot K^{-1}\cdot mol^{-1}}$, (the second law),
$= 198\ \mathrm{kJ\cdot K^{-1}\cdot mol^{-1}}$. (the third law).
$\sigma(\mathrm{PtF_4})/\sigma(\mathrm{CsI}) = 0.61$; $K(\mathrm{CsI})/K(\mathrm{PtF_4}) = 1.9$.

$K(\mathrm{CsI}) = \{I(\mathrm{Cs^+}) + I(\mathrm{CsI^+})\}/I(\mathrm{CsI^+})$,
$K(\mathrm{PtF_4}) = \{I(\mathrm{PtF_4^+}) + I(\mathrm{PtF_3^+}) + I(\mathrm{PtF_2^+}) + I(\mathrm{PtF^+}) + I(\mathrm{Pt^+})\}/I(\mathrm{PtF_4^+})$.

CsI_m^+ ($m = 0$ or 1) and PtF_n^+ ($n = 0$ to 4) are produced, respectively, from CsI and $\mathrm{PtF_4}$ molecules by electron impact.

one can find: $\Delta H^\circ_m(1) = (206.5 \pm 6.5)\,\mathrm{kJ \cdot mol^{-1}}$ (the third law); $\Delta H_m(1) = (208 \pm 26)\,\mathrm{kJ \cdot mol^{-1}}$ (the second law). The temperature dependence of the saturated vapour pressure is described by the equation:

$$\ln\{p(\mathrm{PtF_4})/\mathrm{Pa}\} = -(25.2 \pm 1.6) \times 10^3(\mathrm{K}/T) + 33.1 \pm 1.2.$$

4. Discussion

The value of $(207 \pm 16)\,\mathrm{kJ \cdot mol^{-1}}$ is proposed for $\Delta H^\circ_m(1)$ at $T = 298.15$ K. The uncertainty was chosen on the basis of the result obtained by the third law. It consists of the following components: (i) the error of reproducibility ($\delta_1 = 6.5\,\mathrm{kJ \cdot mol^{-1}}$); (ii) the error introduced by ionization cross-section estimation ($\delta_2 = 2.4\,\mathrm{kJ \cdot mol^{-1}}$); (iii) the error of CsI sublimation enthalpy determination ($\delta_3 = 3.0\,\mathrm{kJ \cdot mol^{-1}}$);(7) and, finally, (iv) the error associated with the application of $\mathrm{ZrF_4}$ functions ($\delta_4 = 10\,\mathrm{kJ \cdot mol^{-1}}$). The last error is defined as follows. The thermodynamic functions of sublimation of the two tetrafluorides: $\mathrm{MnF_4}$,(7) and $\mathrm{ZrF_4}$,(10) having vapour pressures close to that of $\mathrm{PtF_4}$, are available in the literature. The functions for $\mathrm{ZrF_4}$,(10) were calculated from the experimental values; in addition, the enthalpy of sublimation of $\mathrm{PtF_4}$ defined in accordance with the second law is in good agreement with the value of $\Delta S^\circ_m(1)$ determined using the thermodynamic functions of $\mathrm{ZrF_4}$.(10) The application of $\mathrm{MnF_4}$ thermodynamic functions(7) at $T = 298.15$ K results in the value of $\Delta H^\circ_m(1)$ differing by $10\,\mathrm{kJ \cdot mol^{-1}}$ from that given in table 2. Thus, the thermodynamic functions of $\mathrm{ZrF_4}$ are used to calculate the equilibrium (1), while the value of $10\,\mathrm{kJ \cdot mol^{-1}}$ is taken as δ_4.

The ratio $I(^{195}\mathrm{PtF_3^+})/I(\mathrm{CsI^+})$ was observed to reduce gradually with time, the temperature remaining constant. The variation $\Delta[RT \ln\{I(^{195}\mathrm{PtF_3^+})/I(\mathrm{CsI^+})\}]$ did not exceed $5.8\,\mathrm{kJ \cdot mol^{-1}}$; however, it caused considerable error in the value obtained according to the second law. The variation of the ratio is likely to have been brought about by $\mathrm{PtF_4}$ thermodynamic-activity decrease and the formation of an intermediate phase in $(\mathrm{Pt} + \mathrm{PtF_4})$ (sublimation was performed from platinum effusion cells). To take into account the error related to the $\mathrm{PtF_4}$ activity decrease, the error $\delta_5 = 5.8\,\mathrm{kJ \cdot mol^{-1}}$ was introduced. The overall error was calculated by the expression: $\delta = \pm(\Sigma^5_{i=1}\delta_i^2)^{1/2} = \pm 16\,\mathrm{kJ \cdot mol^{-1}}$.

Values of $\Delta_f H^\circ_m(\mathrm{PtF_4}, \mathrm{g}, 298.15\,\mathrm{K}) = -(524 \pm 25)\,\mathrm{kJ \cdot mol^{-1}}$,(1) and $\Delta_f H^\circ_m(\mathrm{PtF_4}, \mathrm{s}, 298.15\,\mathrm{K}) = -681\,\mathrm{kJ \cdot mol^{-1}}$,(3) are available in the literature. In reference 3 the molar formation enthalpy of $\mathrm{PtF_4}$ is given without specifying the relevant error. We have estimated this to be $25\,\mathrm{kJ \cdot mol^{-1}}$. The difference $\{\Delta_f H^\circ_m(\mathrm{PtF_4}, \mathrm{g}) - \Delta_f H^\circ_m(\mathrm{PtF_4}, \mathrm{s})\} = (157 \pm 35)\,\mathrm{kJ \cdot mol^{-1}}$ is, within the limits of the error estimated, in agreement with the value $(207 \pm 16)\,\mathrm{kJ \cdot mol^{-1}}$ obtained in the present work. However, the values of $\Delta_f H^\circ_m$ for $\mathrm{PtF_4(s)}$ and $\mathrm{PtF_4(g)}$ are highly inaccurate. The main errors are caused by (i) inaccuracy of the $\Delta_f H^\circ_m(\mathrm{MnF_3{-}F})$ value,(11) the latter being the key one in determining $\Delta_f H^\circ_m(\mathrm{PtF_4}, \mathrm{g}, 298.15\,\mathrm{K})$ and having in it the factor 4; (ii) the lack of experimentally found thermodynamic functions for $\mathrm{PtF_4(g)}$ and $\mathrm{PtF_4(s)}$; and (iii) the low reliability of $\Delta_f H^\circ_m(\mathrm{PtF_4}, \mathrm{s}, 298.15\,\mathrm{K})$ (the error is absent).

In our opinion it is impossible at present to define $\Delta_f H^\circ_m(\text{PtF}_4, \text{g})$ or $\Delta_f H^\circ_m(\text{PtF}_4, \text{s})$ from equation (1) with an accuracy exceeding that given in the literature.

The authors of reference 6 have pointed to the process of PtF_4 thermal decomposition proceeding *via* the reaction: $\text{PtF}_4(\text{s}) = \text{Pt}(\text{s}) + 2\text{F}_2(\text{g})$, the corresponding pressure of F_2 being equal to 10^5 Pa at $T = 833$ K. No fluorine evolution was observed in our experiments. The application of a decomposition pressure value given in reference 6 to the calculation of the molar enthalpy of formation of $\text{PtF}_4(\text{s})$ results in the value: $\Delta_f H^\circ_m(\text{PtF}_4, \text{s}) = -64.5 \text{ kJ} \cdot \text{mol}^{-1}$ at $T = 298.15$ K. This value sharply conflicts with that given in reference 3.

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