Thermodynamic characteristics of thermal dissociation of platinum trichloride

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Single crystals of platinum trichloride were grown for the first time. The IR spectrum of single-crystal $PtCl_3$ was recorded. The pressure of thermal dissociation of $PtCl_3$ was measured by the static method with a quartz membrane-gauge zero-pressure manometer. An approximating equation for the dissociation pressure *vs.* temperature ($540\ K \le T \le 775\ K$) for the reaction $2\ PtCl_3(s) \rightarrow 2\ PtCl_2(s) + Cl_2(g)$ was found. The enthalpy ($123.1\pm1.7\ kJ\ mol^{-1}$) and entropy ($183.6\pm2.8\ J\ mol^{-1}\ K^{-1}$) for the dissociation of $PtCl_3(s)$ were calculated at 298.15 K.

Key words: platinum trichloride, synthesis; dissociation; enthalpy; entropy.

Modern technologies, such as affinage and processing of secondary platinum raw materials based on the use of gaseous chlorine, to be optimized need reliable thermodynamic data for substances formed in a Pt—Cl system. Few published thermodynamic characteristics of platinum chlorides are contradictory.[1—6] These data have been critically reviewed.[7]

We have previously[8] shown that the dissociation of $PtCl_4$ produces $PtCl_3$, $PtCl_2$, and Pt; the heat of formation of $PtCl_4(s)$ calculated from the tensimetric experiments ($246.3\pm1.3\ kJ\ mol^{-1}$) agrees well with the calorimetric data ($245.6\pm1.9\ kJ\ mol^{-1}$). In this study we determined the thermodynamic characteristics of dissociation of crystalline platinum trichloride.

Experimental

Two batches of platinum trichloride samples, synthesized and purified by different methods, were used. The samples of the first batch were synthesized directly in a membrane-gauge chamber of a manometer as the final product of the first step of $PtCl_4$ dissociation, being a finely dispersed powder of $PtCl_3$ (synthesis and identification of the starting platinum tetrachloride have been described previously[8]). The samples of the second batch as black-green single-crystal needles of length 4—5 mm were prepared in a sealed quartz tube with a temperature drop $773 \rightarrow 748$ K in excess pure Cl_2 ($p_{Cl_2} = 14$ atm) by chemical transportation of powdered $PtCl_3$ synthesized by a standard method.[9] The substance was slowly transported: after 12 days, the amount of the sublimed product was 40% of the weight of the starting substance. The resulting product was identified by elemental analysis, X-ray diffraction analysis, and IR spectroscopy. Found (%): Pt, 64.67; Cl, 35.50. $PtCl_3$. Calculated (%): Pt, 64.72; Cl, 35.28. The conventional method[9] for synthesizing $PtCl_3$ by the thermal decomposition of $PtCl_4$ in a Cl_2 flow at 663 K gives a chlorine to platinum ratio of ~2.7. The divergence is likely due to the fact that the standard synthesis occurs under essentially nonequilibrium conditions and, hence, platinum tetrachloride partially decomposes to $PtCl_2$. The interplane distances of the resulting $PtCl_3$ samples coincide with the d_α values calculated from the structural data.[6]

IR spectrum of $PtCl_3$, ν/cm^{-1}: 255 v.s, 302 s, 323 s, 362 m. No published data on the IR spectrum of $PtCl_3$ were found.

The dissociation pressure was measured by the static method using quartz membrane-gauge zero-pressure spoon-type manometers[10] on a setup described previously.[8] The limiting error of temperature measurements estimated by calibration against mercury, naphthalene, and argon was at most ±1 K at 900 K and increased to ±2 K at 1200 K; the accuracy of temperature maintenance was ±0.1 K; the maximum error in the pressure measurement caused by the diaphragm sensitivity and by the errors in the corrections for the "reversible" and "irreversible" zero drifts of the pressure gauge varied from one experiment to another, being 0.2—2 Torr. The pressure was measured in the isothermal and nonisothermal regimes of temperature maintenance.[8] Since equilibration of $PtCl_3$ dissociation was rather slow (24—200 h and more), we succeeded to attain the equilibrium only from the side of lower pressures.

Calculation of the concentration of platinum-containing components of the gas phase for the studied temperature range using published data on the thermodynamics of gaseous platinum chlorides[5,11,12] showed that the total vapor pressure of these substances did not exceed $9 \cdot 10^{-5}$ atm. Therefore, taking into account that a noticeable homogeneous region[13] is absent for platinum tri- and dichlorides, we accepted in experimental data processing that platinum trichloride dissociates *via* the reaction

$$2\ PtCl_3(s) \rightarrow 2\ PtCl_2(s) + Cl_2(g).$$

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2032—2034, October, 2004.

Table 1. Entropy ($S°_{298.15}$/J mol^{-1} K^{-1}) and heat capacity ($C_p°$/J mol^{-1} K^{-1})* of platinum and platinum chlorides

Substance	$S°_{298.15}$	a	b	c	T/K
Pt(cr)	41.55±0.21[15]	28.49[16]	$5.27 \cdot 10^{-3}$	$0.25 \cdot 10^5$	298—900
$PtCl_2$(s)	100.876[17]	63.5[17]	$21.4 \cdot 10^{-3}$	$0.883 \cdot 10^5$	298—900
$PtCl_3$(s)	141.235[18]	121.34[18]	—	—	298—900

* In the form $C_p°(T) = a + bT + c/T^2$.

The calculations were carried out by a known procedure[14] using the objective function

$$\varphi = \sum_{i=1}^{N} \frac{(p_i^{\text{exp}} - p_i^{\text{calc}})^2}{\Delta p_i^2 + \left(\dfrac{\partial p}{\partial T}\right)^2 \cdot \Delta T_i^2},$$

where N is the number of experimental points; p_i^{exp} is the experimental pressure; p_i^{calc} is the pressure calculated by the accepted physicochemical model; Δp_i and ΔT_i are the maximum errors of pressure and temperature measurements, respectively.

The errors of the desired values were calculated taking into account the Student coefficients for a 95% confidence interval. The thermodynamic values used in calculations are presented in Table 1.

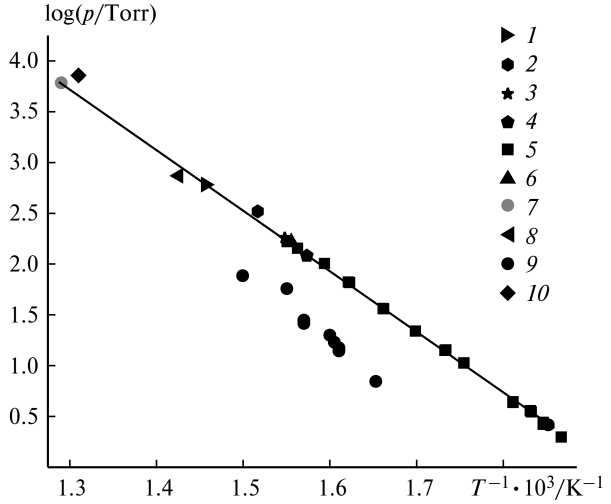

Fig. 1. Pressure of platinum trichloride dissociation in the coordinates log$p = f(T)$ according to our and published data: entries *1* (*1*), *2* (*2*), *3* (*3*), *4* (*4*), *5* (*5*), and *6* (*6*); Eq. (1) (*7*); Refs 1 (*8*), 4 (*9*), and 6 (*10*).

Results and Discussion

Six different experiments were carried out (25 points in an interval of 540 K ≤ T ≤ 775 K; the ratio of the sample weight to the membrane-gauge chamber volume was varied from 0.01 to 0.002 g cm^{-3}). In entries *1—5*, we used samples prepared directly in a membrane-gauge chamber as the product of the first step of $PtCl_4$ dissociation, and single crystals of platinum trichloride were used in entry *6*. A very slow equilibration time in the case of single-crystal samples should be noted. In this experiment, the single equilibrium point was obtained as follows. At 643 K, a time dependence of the pressure was measured

$$p = 165.6 - 200/\tau^{1/4},$$

where τ is the time of temperature maintenance. For $\tau = \infty$, the pressure turned out to be 166 Torr, which is by 18% higher than the last experimentally measured value (for τ = 500 h).

The obtained experimental data are presented in Fig. 1. It is seen that the dissociation pressure is independent of the ratio of the weighed sample to the membrane-gauge chamber volume and of the prehistory of samples. Deviations from one experiment to another are random, which indirectly confirms the validity of the physicochemical model chosen and indicates that the experiments contain no serious systematic errors.

The results of calculation are presented in the form of the equation

$$\log(p_{Cl_2}/\text{Torr}) \pm 2\sigma = 31.1936 - 7569.7/T + 64490/T^2 - 6.4112\log T + 0.0998 \cdot 10^{-2} \cdot T, \quad (1)$$

where $\sigma^2 = 2165/T^2 - 7.139/T + 1.3599 \cdot 10^{-2}$ (540 K ≤ T ≤ 775 K).

The published data on the pressure of $PtCl_3$ dissociation are also presented in Fig. 1. The data in the studies[1,6] are very close to our results. The values obtained in the work[4] are substantially lower. This divergence is caused by the fact that the previous experiments[4] were carried out with a permanent temperature increase and, hence, nonequilibrium pressures were measured.

Using the data in Table 1, we obtained for the first time the thermodynamic functions of the dissociation of platinum trichloride: $\Delta H°_{298.15}$ = 123.1±1.7 kJ mol^{-1}; $\Delta S°_{298.15}$ = 183.6±2.8 J mol^{-1} K^{-1}.

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Received January 19, 2004;
in revised form May 17, 2004