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Thermodynamic characteristics of thermal dissociation of platinum tetrachloride

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The pressure of thermal dissociation of platinum tetrachloride by the first step $PtCl_4(s) = PtCl_3(s) + 0.5\ Cl_2(g)$ was measured by the static method with a quartz membrane-gauge zero-pressure manometer. An approximating equation for the dissociation pressure *vs.* temperature was found. The enthalpy (52160±880 J mol^{-1}) and entropy (72.1±1.6 J mol^{-1} K^{-1}) of dissociation were calculated. The heat of formation found for platinum tetrachloride (−246.3±1.3 kJ mol^{-1}) at 298.15 K agrees well with the value obtained by the calorimetric method (−245.6±1.9 kJ mol^{-1}).

Key words: platinum tetrachloride, vapor pressure, enthalpy of dissociation, entropy of dissociation, thermochemistry.

Modern technologies of platinum affinage and secondary raw materials processing aimed at extracting noble metals are based on specific features of the behavior of platinum chlorides. One of the most important aspects of the chemistry of compounds in the Pt—Cl system is a problem of the thermodynamic characteristics of chemical processes occurring in this system. However, despite sufficient attention of researchers,[1—6] this problem remains fairly unclear.

The thermal dissociation of crystalline $PtCl_4$ has been investigated in most detail by the isoteniscope method.[1] Two steps associated with the dissociation of crystalline platinum tetra- and dichlorides were found in the temperature dependence of the total equilibrium pressure. The following scheme of dissociation was proposed[1] on the basis of the obtained experimental data:

$$PtCl_4(s) \rightarrow PtCl_3(s) \rightarrow PtCl_2(s) \rightarrow PtCl(s) \rightarrow Pt(s).$$

Other authors[2—5] have the same opinion on the character of thermal dissociation of $PtCl_4$. However, some researchers[6] reject the formation of both platinum mono- and trichloride in this process. Thus, there is no single viewpoint presently about phases formed upon thermal dissociation of platinum tetrachloride.

This work is aimed at studying the first step of platinum tetrachloride dissociation

$$PtCl_4(s) = PtCl_3(s) + 0.5\ Cl_2(g)$$

and determining the thermodynamic characteristics of this process.

Experimental

Starting materials. Platinum tetrachloride was synthesized by two methods. The first (traditional) route is the decomposition of $H_2PtCl_6 \cdot 6H_2O$ in a Cl_2 flow (p_{Cl_2} = 1 atm).[7] The optimum temperature of the synthesis at which the final product has the composition $n_{Cl}/n_{Pt} = 3.94$ and contains a minimum amount of water ($n_{H_2O}/n_{Pt} = 0.01$) is 220 °C (batch *A*). Gaseous chlorine was preliminarily dried by passing over H_2SO_4 and $CaCl_2$. The reaction duration was 8—10 h, and a weighed sample was 300 mg. The second method is the reaction of platinum metal with Cl_2 under excess chlorine pressure (p_{Cl_2} = 50 atm) in a thick-wall quartz tube (outer diameter 8 mm, inner diameter 3 mm). Metallic platinum completely converted to $PtCl_4$ within 5 days at 200 °C. One loading gave ~1 g of $PtCl_4$ (batch *B*).

The synthesized substances were identified by elemental analysis, X-ray diffraction analysis, and IR spectroscopy. For batch *A*, found (%): Pt, 58.28; Cl, 41.67. For batch *B*, found (%): Pt, 57.60; Cl, 42.20. $PtCl_4$. Calculated (%): Pt, 57.81; Cl, 42.19.

Interplane distances for platinum tetrachloride samples synthesized by different methods agree satisfactorily with the earlier obtained values.[8,9] The IR spectra also coincide with the known results.[8,10]

All procedures on substance weighing and transferring to a membrane-gauge chamber were carried out in a dry box (argon, drying agent P_2O_5).

Experimental procedure. The dissociation pressure was measured by the static method with quartz membrane-gauge zero-pressure manometers of the spoon-type. We chosen an anisothermic procedure as the main method of the study. According to this procedure, a thin-wall quartz tube (d = 3 mm, l = 20—30 cm), whose temperature during experiment was maintained at ~20 °C, was sealed through a thick-wall capillary connection (inner diameter ~1 mm) to the main volume of the

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membrane-gauge chamber (20 mL) placed in a non-gradient temperature zone. Such a design makes it possible to multiply remove a portion or the whole amount of gaseous chlorine from the membrane-gauge chamber without interrupting the experiment. For this purpose, a sealed end of the tube was cooled with liquid nitrogen, and a part of the tube containing condensed chlorine was sealed off after a necessary amount of chlorine was accumulated in the tube (which can be concluded by a change in the pressure in the membrane-gauge chamber). Note that freezing of chlorine is accompanied by removal of gaseous admixtures (H_2O, HCl, O_2, N_2, and others) that were introduced with the substance under study, evolved during experiment from quartz, or diffused into the membrane-gauge chamber through quartz. The latter is especially important, because some experiments took several months because of slow equilibration: the time of equilibration ranged from several hours to three months, depending on the temperature, dispersity, and weight of the sample. Therefore, the amount of foreign gases accumulated due to diffusion could be significant. The anisothermal variant of the static method made it possible to perform check experiments when a residual pressure was vanishingly small.

The conventional procedure in which the whole membrane-gauge chamber occurs in the constant temperature zone was used only to refine results on the first step of $PtCl_4$ dissociation.

The dissociation pressure was measured in the temperature-controlled regime at a specified temperature of the oven, and the equilibrium was attained from the side of lower pressures. We failed to attain equilibrium from higher pressures, because this procedure required a much longer exposure time.

The limiting errors of pressure measurement were 1—2 Torr. The random error of temperature measurement was at most ±0.5 °C. To find corrections to indications of a measuring thermocouple, calibrating experiments on determination of the saturated vapor pressure of reference substances (water, naphthalene, mercury, and cadmium) were carried out. These corrections were 1—1.5 °C, depending on temperature.

To remove adsorbed gases, the membrane-gauge zero-pressure manometers were heated in a high vacuum for 3—4 h at 500—700 °C before filling with the substance.

The results of measurements are presented in Fig. 1. In the first tensimetric experiment, a product of batch *A* served as the starting sample. The experiment included several stages. First, the membrane-gauge zero-pressure manometer with a sample was heated to 380 °C (regions I^I—IV^I). Then the instrument was cooled to 200 °C, ballast (residual) gases and chlorine were frozen in a capillary with liquid nitrogen, the capillary was sealed off, and heating of the working chamber of the manometer was started again. The data obtained at this stage are presented by regions IV^{II}—VI^{II}.

Since regions I^I—IV^I were obtained under conditions of a considerable temperature gradient along the capillary, the second check experiment was made. In this case, a sample from batch *B* was used. The conditions of synthesis of this sample allowed us to remove foreign gases almost immediately. A distinct break point is seen in Fig. 1, indicating some excess chlorine and the absence of a significant residual pressure.

Results and Discussion

Based on an analysis of the experimental data, we can interpret the obtained dependences as follows: evolution and thermal expansion of sorbed (residual) gases (H_2O, HCl, O_2, N_2, and others) occur in region I^I; region II^I corresponds to the equilibrium pressure of $PtCl_4$ dissociation (coexisting phases $PtCl_4$(s), $PtCl_3$(s), Cl_2(g), residual gases); III^I is the region of divariant equilibrium of the phases $PtCl_3$(s), Cl_2(g), and residual gases; IV^I and IV^{II} correspond to the equilibrium of the gas phase with $PtCl_3$(s) and $PtCl_2$(s); V^{II} is the region of divariant equilibrium ($PtCl_2$(s), Cl_2(g), and residual gases); VI^{II} is the region of monovariant equilibrium of the phases $PtCl_2$(s), Pt(s), Cl_2(g), and residual gases.

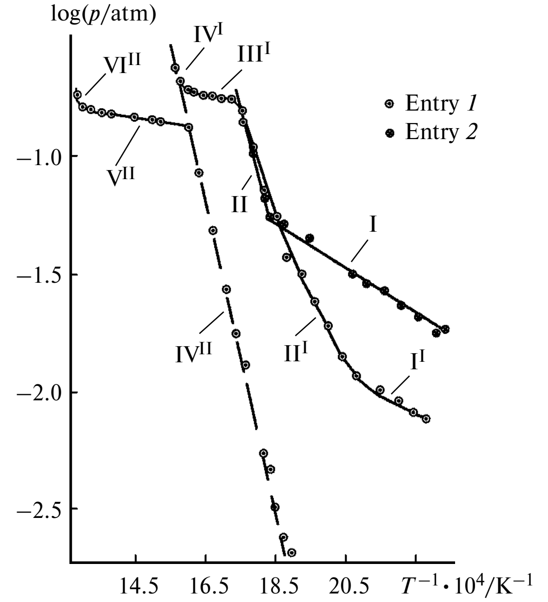

Fig. 1. Temperature plot of the pressure of $PtCl_4$ dissociation in the coordinates log*p* = *f*(*T*) (for regions I, II, I^I—IV^I, and IV^{II}—VI^{II}, see clarification in the text).

The latter region was attributed to this equilibrium due to the absence of chlorine in the substance remained after the last dissociation step completed.[11] Thus, as authors of the study,[6] we did not find a region corresponding to the PtCl phase in the stepwise thermal dissociation of $PtCl_4$(s).

Two regions can be distinguished in the plot log*p* = *f*(1/*T*) for the second experiment: smooth (I) and steep (II), and a pronounced break point is observed. It is most likely that chlorine evolution occurs in region I (it is not clear whether this chlorine is adsorbed, absorbed, or occluded). Region II coinciding with line II^I for the first experiment should be assigned to the thermal dissociation of $PtCl_4$ by the first step.

The data obtained for the regions of monovariant equilibrium IV^{II} and IV^I (coexisting phases $PtCl_3$(s), $PtCl_2$(s), and Cl_2(g)) coincide with the results of studying the dissociation of $PtCl_3$(s).[11] The data of entries *1* and *2* on the pressure of $PtCl_4$ dissociation (p_{dis}) in the first step were processed by the second and third laws of thermodynam-

Table 1. Entropy ($S°_{298}$/J mol^{-1} K^{-1}) and heat capacity of platinum chlorides and chlorine ($C_p°$/J mol^{-1} K^{-1})*

Substance	$S°_{298}$	a	b	c
$PtCl_4(s)$[12]	185.221	146.44	—	—
$PtCl_3(s)$[12]	141.235	121.34	—	—
$Cl_2(g)$[13]	222.978± ±0.033	37.03	$0.6694 \cdot 10^{-3}$	$-2.845 \cdot 10^5$

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

ics. The values of heat capacity and entropy necessary for calculations are presented in Table 1.

In the first experiment, we took into account the pressure of residual gases (p_{res})

$$p_{tot} = p_{dis} + p_{res} = p_0 \cdot \exp(-\Delta H°_{dis}/RT + \Delta S°_{dis}/R) + C_{res} \cdot RT,$$

where p_0 = 1 atm; $\Delta H°_{dis}$ and $\Delta S°_{dis}$ are the enthalpy and entropy of dissociation, and C_{res} is the residual gas concentration.

The results of experimental data processing are presented in Tables 2 and 3. The results of processing by the second and third laws of thermodynamics show a satisfactory agreement. Since the absolute entropies of platinum chlorides used in calculations are based on estimates taken from the handbook,[12] we recommend to prefer the results of processing by the second law of thermodynamics.

Using the heat of formation of $PtCl_3(s)$,[11] we calculated the standard heat of formation of $PtCl_4$, which is equal to −246.3±1.3 kJ mol^{-1}. This value is well consistent with the results obtained by the calorimetric method (−245.6±1.9 kJ mol^{-1})[14] and agrees satisfactorily with the heat of formation of $PtCl_4$ obtained in the work[15] (−248.5 kJ mol^{-1}).

Our and published data on the pressure of $PtCl_4$ dissociation are presented in Fig. 2 showing that the results of entries *1* and *2* are well consistent. The literature values are much lower. This is likely related to the fact that in the work[6] the sample for studying $PtCl_4$ was synthesized by the decomposition of $H_2PtCl_6 \cdot 6H_2O$ in a Cl_2 flow at 360 °C, *i.e.*, under conditions when, according to our data, crystal hexahydrate of chloroplatinic acid decomposes to form $PtCl_3$. Two steps assigned to the dissociation of $PtCl_4$ and $PtCl_2$ were found[6] in the curve of stepwise decomposition of $PtCl_4$. These facts suggest that authors of the work[6] studied, most likely, the dissociation of a product close in composition to $PtCl_3$ rather than $PtCl_4$ and, in addition, under conditions far from equilibrium. A comparison of the results of the work[1] and our data on $PtCl_3$ dissociation shows that these authors missed,[1] most likely, the first step of dissociation.

Table 2. Thermodynamic characteristics of platinum tetrachloride dissociation by the first step

Treatment procedure	$\Delta_{dis}H°_{298}$ /J mol^{-1}	$\Delta_{dis}S°_{298}$ /J mol^{-1} K^{-1}
Second law of thermodynamics	52160±880	72.1±1.6
Third law of thermodynamics	50850±880	68.6±5

Note. $\ln(p/\text{Torr}) = (14.796 - 6068.8/T) \pm 2\delta$, $\delta = 0.0084 - 8.99/T + 2418/T^2$ (483—574 K).

Table 3. Experimental (p_{exp}) and calculated by the second (II) and third (III) laws of thermodynamics pressures (p_{calc}) of platinum tetrachloride dissociation

Entry	T/°C	p_{exp} /Torr	p_{calc}/Torr	
			II	III
1	210.0	9.51	9.33	9.75
1	220.0	11.59	12.06	12.47
1	230.0	15.48	15.41	15.80
1	240.0	19.70	19.510	19.83
1	250.0	25.03	24.467	24.66
1	261.0	29.89	31.07	31.04
1	269.0	36.73	36.73	36.47
1	280.5	46.32	46.32	45.59
1	290.0	55.69	55.69	54.43
1	301.0	68.38	68.38	66.33
2	281.0	47.36	46.78	46.02
2	287.0	51.94	52.58	51.50
2	292.0	57.84	57.84	56.46

Thus, we studied the pressure of platinum tetrachloride dissociation by the first step by two different experimental procedures. The enthalpy and entropy of the pro-

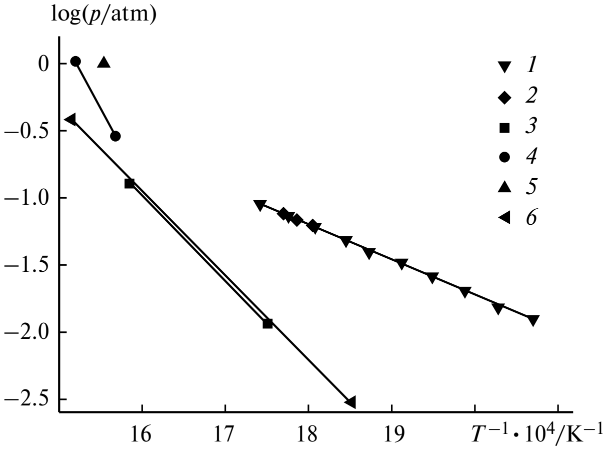

Fig. 2. Temperature plot of the dissociation pressure for the process $PtCl_4(s) = PtCl_3(s) + 0.5\ Cl_2(g)$ in the coordinates $\log p = f(T)$ according to the data of different authors: our data (*1*, *2* (the first and second experiments, respectively)), Ref. 1 (*3*), Ref. 6 (*4*), and Ref. 2 (*5*); our approximation for the process $2\ PtCl_3(s) = 2\ PtCl_2(s) + Cl_2(g)$[11] (*6*).

cess were calculated. A good agreement of the results of processing using the second and third laws of thermodynamics indicates that the chosen physicochemical model is adequate and serious systematic errors are absent from the experiment.

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