

Thermodynamic characteristics of thermal dissociation of platinum dichloride

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The dissociation pressure for the process $\text{PtCl}_2(\text{s}) \rightarrow \text{Pt}(\text{s}) + \text{Cl}_2(\text{g})$ was measured by the static method with diaphragm zero-pressure gauges. The approximating equation for the temperature dependence on the dissociation pressure for the above reaction was found. The enthalpy ($137.7 \pm 0.3 \text{ kJ mol}^{-1}$) and entropy ($163.6 \pm 0.4 \text{ J mol}^{-1} \text{ K}^{-1}$) of $\text{PtCl}_2(\text{s})$ dissociation and enthalpies of formation and absolute entropies of platinum di- and trichlorides at 298.15 K were calculated.

Key words: platinum trichloride, platinum dichloride, dissociation pressure, enthalpy and entropy of dissociation, enthalpy of formation, absolute entropy.

We have previously^{1,2} studied the dissociation of higher platinum chlorides: PtCl_4 and PtCl_3 . In this work, the dissociation of platinum dichloride was studied.

Experimental

Starting substances. Four types of platinum dichloride samples were used in tensimetric studies. They were obtained as follows: (1) by dissociation of platinum tetrachloride *via* the reaction $\text{PtCl}_4(\text{s}) \rightarrow \text{PtCl}_3(\text{s}) \rightarrow \text{PtCl}_2(\text{g})$ immediately in a diaphragm chamber; (2) by dissociation of platinum trichloride *via* the reaction $\text{PtCl}_3(\text{s}) \rightarrow \text{PtCl}_2(\text{s})$ in the diaphragm chamber as well; (3) using a known procedure³ by the decomposition of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in a chlorine flow at 753 K (reaction afforded a finely dispersed olive-green powder (batch 1)); (4) by sublimation of finely dispersed platinum dichloride (batch 1, weighed samples of 0.5–0.7 g) in an evacuated sealed tube (~15 cm³), transfer from the hot (890 K) to cold (800 K) zone. During 10 days, ~2/3 of the starting substance precipitated in the cold zone of the tube. The resulting product was a dark violet substance in the form of dendrites 0.5–1.0 cm (batch 2).

The products synthesized were identified by elemental analysis, X-ray diffraction analysis, and IR spectroscopy. For batch 1, found (%): Pt, 73.42; Cl, 26.47. For batch 2, found (%): Pt, 73.26; Cl, 26.67. PtCl_2 . Calculated (%): Pt, 73.34; Cl, 26.66.

The interplanar distances for the samples of batch 1 agree satisfactorily with those calculated from the structural data⁴ and with the d_{α} values presented previously.⁵ The interplanar distances for the samples of batch 2 are satisfactorily consistent with the values presented in Ref. 6 and do not coincide with those for the product of batch 1. We have earlier found⁷ that the substance of batch 1 was transformed into the substance of batch 2 (according to the set of interplanar distances) upon thermal annealing at 773 K, whereas no backward transition was observed. According to Sheffer's classification, the products of batches 1 and 2 were named the β - and α -modifications of PtCl_2 , respectively.

Experimental procedure. The dissociation pressure was measured by the static method using quartz diaphragm spoon-type zero-membrane gauges on an installation described earlier.^{1,2} The limiting measurement error estimated from calibrations by mercury, naphthalene, and argon did not exceed $\pm 1 \text{ K}$ at 900 K; the accuracy of temperature maintenance was $\pm 0.1 \text{ K}$; the limiting error of pressure measurement caused by sensitivity of the membranes used and errors of corrections for irreversible drift of the zero position of the pressure gauge varied from experiment to experiment, being 0.2–2.0 Torr.

Experiments were carried out in the isothermal and non-isothermal temperature regimes. As in the case of higher platinum chlorides, the PtCl_2 dissociation pressure was equilibrated for a very long time (from 24 to 200 h and more) and, hence, we could approach the equilibrium only from the side of lower pressures.

When processing the experimental data, we believed that the dissociation of platinum dichloride proceeds *via* the reaction



since in the studied temperature and pressure interval the total concentration of platinum chlorides did not exceed $9 \cdot 10^{-5} \text{ atm}$.² Molecular chlorine dissociation can be neglected, because the maximum content of atomic chlorine in our experiments was at most 0.06 Torr.

Calculations were carried out according to a known procedure² using the target function

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

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 limiting errors of pressure and temperature measurement, respectively.

Table 1. Entropy ($S^\circ_{298.15}/\text{J mol}^{-1}\text{K}^{-1}$) and heat capacity of metallic platinum and platinum chlorides ($C_p^\circ/\text{J mol}^{-1}\text{K}^{-1}$)* in the interval $298\text{ K} \leq T \leq 900\text{ K}$

Substance	$S^\circ_{298.15}$	a	b	c
Pt(cr)	41.55 ± 0.25 ⁸	28.49 ⁹	$5.27 \cdot 10^{-3}$	$0.25 \cdot 10^5$
PtCl ₂ (s)	100.9 ± 0.3 ¹⁰	63.5 ¹¹	$21.4 \cdot 10^{-3}$	$0.883 \cdot 10^5$
PtCl ₃ (s)	141.235 ¹²	121.34 ¹²	—	—

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

The use of this target function in data processing provided more reliable estimates of the desired parameters. Errors of the desired values were calculated taking into account Student's coefficients for the 95% confidence interval.

The thermodynamic values used in calculations are given in Table 1.

Results and Discussion

We carried out five experiments and obtained 58 points in the interval $666\text{ K} \leq T \leq 890\text{ K}$; the weighed sample to volume ratio was varied from 0.01 to 0.002.

The starting substances were PtCl₄, PtCl₃, β -PtCl₂, and α -PtCl₂. When higher platinum chlorides were used, PtCl₂ formed directly in the diaphragm chamber during tensimetric study.

The conditions of experiments on studying the thermal dissociation of platinum dichloride are presented in Table 2.

The experimental data are presented in Table 3 and Fig. 1 as the $\log(p/\text{Torr}) = f(1/T)$ plot. It is seen that the dissociation pressure is independent of either the ratio of the weighed sample to the diaphragm chamber volume, or the pre-history of the samples. Thus, the system under study is monovariant, and all the experiments can statistically be processed in combination. The calculations gave the following approximating equation:

$$\log(p/\text{Torr}) \pm 2\sigma = 11.0227 - 6955.1/T, \quad (1)$$

where $\sigma^2 = 1750/T^2 - 4.444/T + 0.2843 \cdot 10^{-2}$ ($666\text{ K} \leq T \leq 890\text{ K}$).

The deviations of the experimental data from those calculated by Eq. (1) are shown in Fig. 2. For all experi-

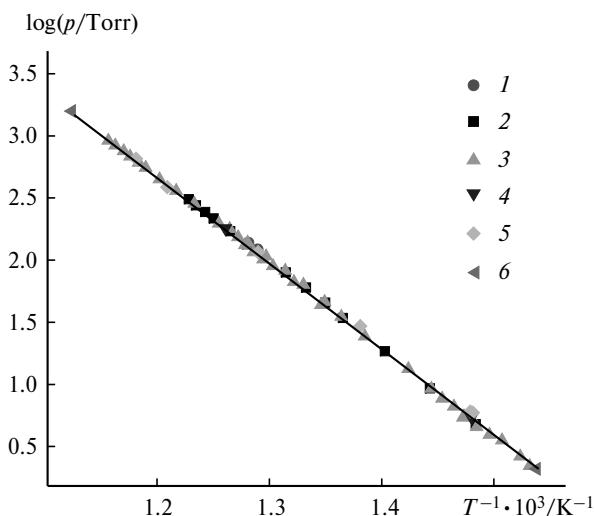
Table 2. Conditions of tensimetric experiments

Entry	Starting substance	Temperature interval/K	Number of points
1	PtCl ₄	775–780	2
2	PtCl ₃	673–814	13
3	β -PtCl ₂	666–870	36
4	β -PtCl ₂	675–793	2
5	α -PtCl ₂	675–846	5

Table 3. Experimental dissociation pressures for platinum dichloride (p_{exp})

Entry	$T/\text{^\circ C}$	$p_{\text{exp}}/\text{Torr}$	Entry	$T/\text{^\circ C}$	$p_{\text{exp}}/\text{Torr}$
1	502.3	122.18	3	567.3	553.80
1	507.3	137.85	3	571.7	609.42
2	400.8	4.79	3	577.2	684.69
2	419.9	9.28	3	581.4	756.33
2	439.7	18.5	3	586.8	839.14
2	459.2	34.33	3	591.5	917.70
2	467.7	45.49	3	379.7	2.21
2	477.2	60.22	3	383.3	2.63
2	487.5	79.81	3	390.3	3.55
2	508.1	134.09	3	395.3	3.93
2	517.3	170.95	3	400.4	4.54
2	526.7	217.16	3	405.6	5.54
2	531.5	243.97	3	409.7	6.63
2	536.9	276.53	3	414.7	7.69
2	541.1	309.08	3	469.8	43.62
3	405.9	5.42	3	483.3	66.87
3	419.2	9.25	3	494.2	89.58
3	429.2	13.33	3	499.3	101.53
3	448.9	24.29	3	504.6	115.91
3	460.0	35.04	3	509.1	132.52
3	468.0	46.09	3	512.9	153.43
3	478.5	63.49	3	523.6	197.50
3	487.8	82.21	4	402.5	5.40
3	497.8	107.36	4	520.0	179.92
3	507.7	138.97	5	402.0	5.92
3	517.6	178.19	5	403.0	6.04
3	537.7	285.75	5	502.0	115.69
3	548.5	361.21	5	554.0	387.57
3	558.7	447.69	5	573.5	655.60

ments, the deviations do not exceed the limiting measurement error and, as a whole, are random, which confirms indirectly that the physicochemical model was cho-

**Fig. 1.** Pressure of platinum dichloride dissociation vs. temperature according to our data: entries 1 (1), 2 (2), 3 (3), 4 (4), and 5 (5) and Eq. (1) (6).

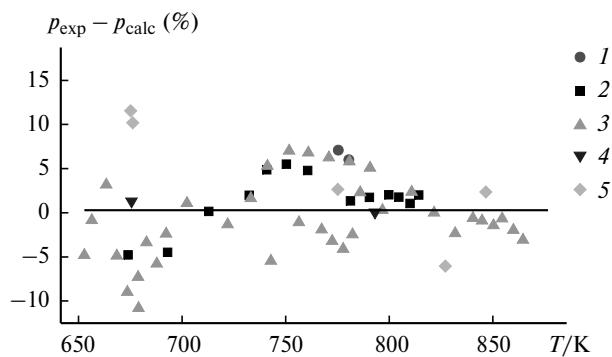


Fig. 2. Deviation of the experimental pressures of platinum dichloride dissociation (p_{exp}) in entries 1–5 (points) from the values calculated (p_{calc}) by Eq. (1) (line).

sen validly and indicates the absence of serious systematic errors in experiments.

The data on dissociation pressure for the β - and α -forms of platinum dichloride are indiscernible within experimental error.

Our and other data on the pressure of PtCl₂ dissociation are shown in Fig. 3. The results of several studies^{13–16} are very close to our data. The data of the work¹⁷ using non-equilibrium experimental conditions (with a continuous temperature increase) are somewhat lower. The results in the work,¹⁸ where the dissociation pressure was measured by the effusion—torsion method, are also lowered compared to our data. At low equilibration rate, as in the case of dissociation of platinum chlorides, effusion procedures should give distorted (underestimated) results.

Based on the data in Table 1, we calculated the enthalpy and entropy of platinum chloride dissociation under standard conditions using the second and third laws of

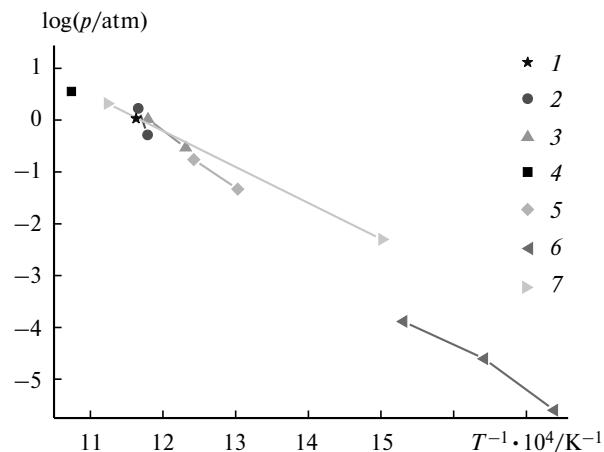


Fig. 3. Pressure of platinum dichloride dissociation vs. temperature according to published and our data: Ref. 13 (1), Ref. 14 (2), Ref. 15 (3), Ref. 16 (4), Ref. 17 (5), and Ref. 18 (6) and Eq. (1) (7).

Table 4. Thermodynamic characteristics of platinum dichloride dissociation

Method of treatment	$\Delta_{\text{dis}}H^\circ_{298} / \text{kJ mol}^{-1}$	$\Delta_{\text{dis}}S^\circ_{298} / \text{J mol}^{-1} \text{K}^{-1}$
Second law of thermodynamics	136.7 ± 0.7	162.8 ± 0.8
Third law of thermodynamics	137.7 ± 0.3	163.6 ± 0.4

thermodynamics (Table 4). It is seen that both types of processing give consistent results.

Nevertheless, we prefer the results of calculation according to the third law of thermodynamics, because the earlier¹⁰ achieved good accuracy in determination of the absolute entropy of PtCl₂ provided a lower error of similar calculations.

In this case, the enthalpy of dissociation taken with an opposite sign is the standard enthalpy of formation of PtCl₂ ($-137.7 \pm 0.3 \text{ kJ mol}^{-1}$). We have previously¹⁹ determined the enthalpy of formation of platinum dichloride by the calorimetric method ($-138.6 \pm 4.6 \text{ kJ mol}^{-1}$). Both values are well consistent. However, since the latter has a higher determination error, we recommend the value calculated from the tensimetric data using the third law of thermodynamics.

Using the thermodynamic characteristics of PtCl₃ dissociation² and $\Delta_f H^\circ_{298}$ and S°_{298} values for PtCl₂, we calculated the standard enthalpy of formation and absolute entropy of platinum trichloride: $-199.2 \pm 1.2 \text{ kJ mol}^{-1}$ and $120.6 \pm 1.4 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The discrepancy between the calorimetric ($-194.2 \pm 1.0 \text{ kJ mol}^{-1}$) and tensimetric ($-199.2 \pm 1.2 \text{ kJ mol}^{-1}$) determinations of the enthalpy of formation of PtCl₃ are beyond the error limit. Probably, one of the reasons for this discrepancy can be the estimation character of the heat capacity values used by us in processing of the tensimetric data on PtCl₃ dissociation. Since the heat of platinum trichloride reduction,¹⁹ which was used for the calculation of its heat of formation, was measured in six calorimetric experiments with good reproducibility, we recommend the heat of formation obtained from calorimetric measurements ($-194.2 \pm 1.0 \text{ kJ mol}^{-1}$). The recommended thermodynamic characteristics for platinum di- and trichlorides are given in Table 5.

Table 5. Thermodynamic characteristics of platinum di- and trichlorides

Compound	$-\Delta_f H^\circ_{298} / \text{kJ mol}^{-1}$	$S^\circ_{298} / \text{J mol}^{-1} \text{ K}^{-1}$
PtCl ₂ (s)	137.7 ± 0.3	100.9 ± 0.3
PtCl ₃ (s)	194.2 ± 1.0	120.6 ± 1.4

Our data on the pressure of platinum dichloride dissociation are, most likely, most reliable to date, because all samples for the study were individual phases according to the results of chemical analysis, X-ray diffraction, and IR spectroscopy. The variant of tensimetric method used in this work, *viz.*, static method for measuring the vapor pressure with a diaphragm zero-pressure gauge, made it possible to obtain equilibrium data. This fact is decisive for the study of such systems as Pt—Cl in which equilibration is very slow. The results of five tensimetric experiments using different methods on studying the dissociation of platinum dichloride in a wide range of temperatures ($666 \text{ K} \leq T \leq 890 \text{ K}$) and pressures (2–1250 Torr) are well consistent. The results of experimental data processing by the second and third laws of thermodynamics coincide, indicating that the chosen physicochemical model is adequate and the experiment has no serious systematic errors.

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