Thermodynamic properties of α-platinum dichloride

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The heat capacity of crystalline α-platinum dichloride was measured for the first time in the temperature intervals from 11 to 300 K (vacuum adiabatic microcalorimeter) and from 300 to 620 K (differential scanning calorimetry). In the 300—620 K temperature interval, the $C°_p$ values for α-$PtCl_2$ (cr) coincide with the heat capacity of $CrCl_2$ (cr) within the limits of experimental error, which made it possible to estimate the heat capacity of α-$PtCl_2$ (cr) at higher temperatures. The approximating equation of the temperature dependence of the heat capacity in the interval from 298 to 900 K $C°_p(\pm 0.8) = 63.5 + 21.4 \cdot 10^{-3}T + 0.883 \cdot 10^5/T^2$ (J mol^{-1} K^{-1}) was derived using the experimental values, as well as the literature data on the heat capacity of $CrCl_2$ (cr). For the standard conditions, the $C°_{p,298.15}$ and $S°_{298.15}$ values are 70.92±0.08 and 100.9±0.33 J mol^{-1} K, respectively; $H°_{298.15} - H°_0$ = 14 120±42 J mol^{-1}.

Key words: low-temperature calorimetry, differential scanning calorimetry, platinum dichloride, heat capacity, entropy, enthalpy.

The purpose of this work is to measure the heat capacity of crystalline α-platinum dichloride in the temperature interval from 11 to 620 K and to calculate the entropy and the enthalpy difference using the results obtained. No experimental data on the heat capacity of crystalline platinum chlorides have been reported so far.

Experimental

Synthesis of α-$PtCl_2$. The synthesis is based on the data[1] that α-$PtCl_2$ is formed by heating of β-$PtCl_2$ at 773 K in an evacuated ampule for 2 days. A weighed sample (0.5—0.8 g) of β-$PtCl_2$, which was synthesized using a standard procedure[2] by thermal decomposition of $H_2PtCl_6 \cdot 6H_2O$ in a chlorine flow (P_{Cl_2} = 1 atm), was loaded into a quartz ampule 15—18 mL in volume. The ampule was evacuated at room temperature for 1 h, sealed, and heated in a gradient furnace. The substance transfer (~2/3 of the sample over a period of 10 days) occurred from the "hot" (873 K) to "cold" zone (773 K). The product precipitated represented dark violet dendrites 0.5—1.0 cm in size.

The substance synthesized was identified by elemental, X-ray phase, and spectral analyses and by IR spectroscopy.

Elemental analysis was based on a method of platinum and chlorine determination by separation of the metal from chlorine by the reduction

$$PtCl_x \text{ (cr)} + x/2\ H_2 \text{ (g)} = Pt \text{ (cr)} + x\ HCl \text{ (g)}$$

with simultaneous uptake of hydrogen chloride by water. The optimal conditions for the reduction reaction to occur were preliminarily determined using a Paulik—Paulik—Erdey derivatograph. The quantitative reduction of platinum dichloride was shown to start above 340 K, and the rate maximum was observed at 403 K.

The reduction was carried out as follows. A weighed sample of the substance (0.08—0.15 g) was loaded into a quartz beaker, whose weight was brought to a constant value, and the beaker was mounted in a quartz reactor. The system was purged with hydrogen for 10 min. Then, using a special heater, the temperature in the sample zone was gradually increased with a rate of 50 K h^{-1} to 473 K, and the reaction was carried out for 40 min. Hydrogen chloride that formed was absorbed at the reactor outlet in two consecutively connected vessels filled with distilled water. The apparatus was cooled to room temperature in hydrogen flow, the quartz beaker was taken out and calcined to 1073 K to remove the adsorbed hydrogen. The amount of platinum formed was determined by the difference in weights. Weighing was carried out on an analytical balance with an accuracy of ±0.00005 g. The error in platinum determination was 0.2—0.5%, depending on the sample weight. The content of chloride ions was determined by potentiometric titration with a 0.05 *M* $AgNO_3$ solution under standard conditions with a relative error of ±0.5%. Found (%): Pt, 73.26; Cl, 26.67. $PtCl_2$. Calculated (%): Pt, 73,34; Cl, 26.66.

X-ray diffraction study of α-platinum dichloride was carried out on a DRON-2 diffractometer with filtered copper radiation (Cu-Kα radiation, Ni filter). The interplanar spacings coincided satisfactorily with the values published[1] for α-$PtCl_2$. All reflections in the X-ray diffraction pattern were indexed in the monoclinic unit cell with the parameters a = 13.49 Å, b = 3.18 Å, c = 6.85 Å, β = 107.75°, and Z = 4. These values agree well with the results (space group $C2/m$, unit cell parameters a = 13.258 Å, b = 3.194 Å, c = 6.802 Å, β = 107.75°, Z = 4) obtained in single-crystal X-ray diffraction study.[1]

IR spectra were recorded on a Perkin—Elmer 325 instrument in the region 200—400 cm^{-1} using CsI windows. Samples were prepared as suspensions in anhydrous Nujol. Two strong absorption bands were observed at 326 and 344 cm^{-1}, which agreed with the published data.[3]

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Spectral analysis of the sample studied showed the presence of Pd ($3 \cdot 10^{-2}$ wt.%) and Rh ($1 \cdot 10^{-2}$ wt.%) admixtures. No Ir, Ru, Os, Fe, and Ni admixtures were found within the analysis accuracy (10^{-3}—10^{-4} wt.%).

Experimental procedure. The heat capacity of α-$PtCl_2$ was measured in a vacuum adiabatic microcalorimeter.[4] A nickel ampule for the substance had a useful volume of ~10 cm^3, and the sample weight was 1.0368 g. The heat capacity (thermal value) of the empty ampule was determined in the 10.7—311.30 K interval at 99 experimental points. The smoothed $(C_p)_{empty} = f(T)$ values calculated using these data were then used to determine the heat capacity of the substance. To check this procedure, the heat capacity of benzoic acid (BnOH) was determined at 32 experimental points in the interval from 14 to 273 K. The results obtained agree satisfactorily with the standard data[5] (1% for temperatures from 11 to 30 K and 0.2% for the interval 30—273 K).

The heat capacity of α-platinum dichloride under constant pressure was determined in the temperature interval from 10.7 to 311.30 K in 96 calorimetric experiments. The average deviation of the experimental values from the smoothed $C_p(T)$ curve was 0.8% at 11—30 K and only 0.14% at 30—300 K.

At medium temperatures (300—620 K), the heat capacity of α-$PtCl_2$ (cr) was measured using a differential scanning calorimeter (Setaram). The sample weight was 0.1560 g. The limiting error of the method in heat capacity determination was ±10%.[6]

Results and Discussion

The experimental values of the heat capacity of α-$PtCl_2$ are presented in Table 1. Table 2 lists the smoothed values of the heat capacity, enthalpy differences ($H°_T - H°_0$), and entropies ($S°_T$) of α-$PtCl_2$ (cr) at the temperatures recommended for the tables of smoothed values. The contributions of the thermodynamic values at temperatures from 0 to 11 K were calculated assuming that the heat capacity in this interval is proportional to T^3. Under these conditions, $S°(11\text{ K}) = 0.75$ J mol^{-1} K^{-1}, or ~0.8% of the entropy value at 298.15 K.

For the standard conditions, $C°_{p,298.15}$ and $S°_{298.15}$ are 70.92±0.08 and 100.9±0.33 J mol^{-1} K^{-1}, respectively; $H°_{298.15} - H°_0 = 14120±42$ J mol^{-1}. It was accepted in the calculations that 1 g-mole of α-$PtCl_2$ was 265.996 g.

The errors of the calculated enthalpy differences and the entropies were estimated with allowance for the deviation of the experimental points from the smoothed curve and the calibration accuracy of the empty calorimeter assuming that the $C°_p(T)$ curve had no anomalies below 11 K. The entropies and enthalpy differences of α-$PtCl_2$ under standard conditions were obtained by numerical integration of the $C°_p(T)/T$ and $C°_p(T)$ functions.

The heat capacity values of α-$PtCl_2$ obtained by differential scanning calorimetry in the 300—620 K interval are given in Table 3.

The experimental data in the whole temperature range (10.7—620 K) are shown in Fig. 1. The results obtained by low-temperature calorimetry and DSC are well consistent. Figure 1 also presents the previously published data on the heat capacity of $CrCl_2$ (cr). Based on the results obtained in this work and on the published data, we calculated coefficients for the equation approximating the temperature dependence of the heat capacity of crystalline α-$PtCl_2$ in the temperature interval from 298 to 900 K.

Table 1. Experimental heat capacity values for α-$PtCl_2$ in the temperature interval from 11 to 300 K

T/K	$C°_p$/J mol^{-1} K^{-1}	T/K	$C°_p$/J mol^{-1} K^{-1}
10.74	2.063	82.91	36.13
11.21	2.238	83.26	36.30
11.80	2.460	85.56	37.02
12.28	2.720	86.97	37.59
12.79	2.950	90.54	38.81
13.31	3.297	93.32	39.70
13.79	3.515	98.04	41.29
14.29	3.807	101.84	42.51
14.84	4.105	105.84	43.81
15.60	4.347	114.38	46.32
16.64	4.891	118.00	47.28
17.68	5.481	122.25	48.41
18.69	6.025	128.02	49.91
19.68	6.563	131.67	50.71
20.71	7.071	133.27	51.13
21.78	7.657	138.78	52.43
23,19	8.410	145.43	53.85
24.44	9.079	149.72	54.77
25.57	9.665	155.56	55.90
26.62	10.25	160.44	56.82
27.89	10.88	165.16	57.66
29.90	12.05	170.22	58.49
31.80	13.07	176.47	59.45
33.84	14.23	182.00	60.29
36.00	15.39	192.70	61.67
39.25	17.05	197.86	62.38
40.75	17.97	202.99	62.97
44.13	19.63	208.07	63.51
45.52	20.26	213.46	64.14
48.90	21.85	220.72	64.85
50.11	22.47	226.07	65.44
53.15	23.72	231.18	65.77
56.81	25.11	234.95	66.45
61.28	26.74	239.38	66.61
61.91	27.782	246.46	67.15
65.72	28.65	251.95	67.57
66.07	29.52	264.25	68.49
69.36	30.11	269.63	68.87
69.89	31.27	276.45	69.62
70.67	31.40	279.50	69.87
71.98	31.88	283.24	70.08
72.93	32.10	288.22	70.42
73.68	32.24	294.03	70.75
74.36	33.35	299.57	71.09
75.02	33.11	299.65	71.13
75.85	33.50	300.62	70.79
77.98	33.66	305.72	71.29
80.68	35.32	311.30	71.59

Table 2. Thermodynamic characteristics of α-$PtCl_2$

T/K	$C°_p$	$S°_T$	$H°_T - H°_0$ /J mol^{-1}
	J mol^{-1} K^{-1}		
11	2.163	6.109	0.741
12	2.615	8.494	0.950
13	3.092	11.38	1.176
14	3.586	14.69	1.423
15	4.096	18.53	1.955
16	4.602	22.89	1.971
18	5.690	33.18	2.573
20	6.736	45.61	3.226
25	9.372	85.77	5.021
30	12.07	139.4	6.958
35	14.82	206.6	9.025
40	17.51	287.5	11.18
45	20.03	381.4	13.39
50	22.36	487.4	15.62
55	24.63	605.0	17.86
60	26.88	733.9	20.10
65	29.14	873.6	22.34
70	31.14	1025	24.58
75	33.17	1185	26.790
80	35.21	1356	29.00
90	38.61	1725	33.34
100	41.92	2128	37.58
110	45.020	2563	41.73
120	47.823	3027	45.77
130	50.375	3519	49.71
140	52.677	4034	53.51
150	54.810	4573	57.03
160	56.735	5129	60.83
170	58.450	5707	64.31
180	59.999	62970	67.70
190	61.379	6904	70.96
200	62.592	7527	74.14
210	63.764	8159	77.24
220	64.810	8799	80.25
230	65.731	9452	83.14
240	66.610	10110	85.94
250	67.404	10790	88.70
260	68.199	11460	91.34
270	68.994	12150	93.93
273.15	69.287	12410	94.73
280	69.873	12840	96.44
290	70.500	13540	98.91
298.15	70.919	14120	100.9
300	71.002	14250	101.3

$$C°_p(\pm 0.8) = 63.5 + 21.4 \cdot 10^{-3}T + 0.883 \cdot 10^5/T^2 \text{ (J mol}^{-1}\text{ deg}^{-1}).$$

When estimating the heat capacity of α-$PtCl_2$ in the 620—900 K temperature interval, we based on the fact that the heat capacities of transition metal dichlorides ($CrCl_2$, $TiCl_2$, $ZrCl_2$, and $FeCl_2$) are close to each other and their temperature runs are parallel according to available literature data.[7] In the region 300—620 K, the C_p values of α-$PtCl_2$ are most similar to the published data on the heat capacity of chromium dichloride.[7]

Table 3. Experimental heat capacity values for α-$PtCl_2$ in the temperature interval from 300 to 620 K

T/K	$C°_p$/J mol^{-1} K^{-1}	T/K	$C°_p$/J mol^{-1} K^{-1}
301.1	70.3	460.1	73.6
340.4	68.8	499.8	74.6
340.8	69.4	539.6	75.3
380.6	75.0	579.3	75.0
420.3	75.0	619.1	76.4
420.3	73.8		

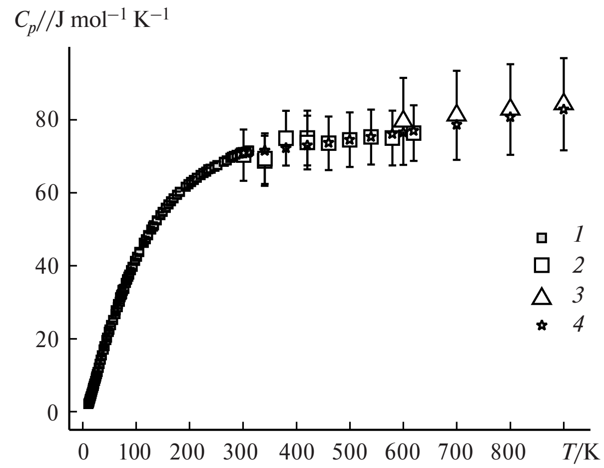

Fig. 1. Temperature dependences of the heat capacities of platinum and chromium dichlorides: our experimental data on the heat capacity of α-$PtCl_2$ obtained in vacuum adiabatic microcalorimeter (*1*) and in differential scanning calorimeter (*2*); published data on the heat capacity of $CrCl_2$ (*3*); heat capacity of α-$PtCl_2$ calculated by the approximating equation (*4*).

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