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Academician A. A. Grinberg and M. I. Gel'fman

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Abstract

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On the Question of the Stability of Complex Compounds of Divalent Platinum

The application of various physicochemical methods to the study of the stability of complex ions in solutions has made it possible to obtain values of instability constants for a very large number of compounds. At the same time, for the most typical complex-forming agents, such as the platinum metals, there are very few data in the literature on instability constants. Even for such widespread and well-studied compounds of divalent platinum as platinates $M_2[PtX_4]$, data on the overall instability constants are lacking.

As early as 1945, one of the authors of this paper ([1]) gave a qualitative series in which the anions are arranged according to their tendency toward complex formation with the divalent platinum ion:

$$NO_3^- < SO_4^{2-} < Cl^- < Br^- < NO_2^-,\ SCN,\ J^- < CN^-.$$

Latimer ([2]), using data on the free energies of formation of ions, calculated values of the overall instability constants for chloro- and bromoplatinites.

$$\frac{[Pt^{2+}][Cl^-]^4}{[PtCl_4^{2-}]} \approx 10^{-16}; \qquad \frac{[Pt^{2+}][Br^-]^4}{[PtBr_4^{2-}]} \approx 3 \cdot 10^{-21}.$$

Noting the closeness of these values to the experimentally obtained instability constants for the corresponding complex mercury compounds, and extending this analogy to other platinites, one of the authors ([3,4]) tentatively predicted the following values of the overall instability constants for iodo- and cyanoplatinite:

$$\frac{[Pt^{2+}][J^-]^4}{[PtJ_4^{2-}]} \approx 10^{-30}; \qquad \frac{[Pt^{2+}][CN^-]^4}{[Pt(CN)_4^{2-}]} \approx 10^{-40}.$$

In the present work an attempt has been made to obtain experimentally the overall instability constants of chloro-, bromo-, iodo-, and cyanoplatinite.

Experimental Part

The concentration of Pt^{2+} ions in solution, necessary for calculating the overall instability constants, was determined by measuring the e.m.f. of cells:

$$\overset{+}{\mathrm{Pt}} \mid \mathrm{K_2[Pt}X_4], \; KX \parallel \mathrm{KCl_{satur.}}, \; \mathrm{Hg_2Cl} \mid \mathrm{Hg}$$
$$C_1 \qquad\qquad C_2$$

The measurements were carried out according to the usual compensation scheme at a temperature of $18 \pm 0.5^{\circ}$. The electrodes were made of platinum foil measuring 10×10 mm^2 and, before the experiment, were platinized in a solution of chloroplatinic acid. To prevent passivation of the electrodes,

measurements were made in a nitrogen atmosphere. The salt bridge connecting the solution under study with the saturated calomel electrode was filled with a $1\,N$ solution of KNO_3. The measurements were carried out at constant ionic strength $\mu = 1$, which was maintained by adding to the solution under study the required amount of $NaNO_3$.

Potassium chloroplatinite was obtained by the method of Gildengershel and Shaginultanov ([5]), by reduction of potassium chloroplatinate with hydrazine sulfate. To obtain potassium bromoplatinite, a solution of potassium chloroplatinite was evaporated with hydrobromic acid to a small volume in a stream of CO_2 ([6]). Potassium iodoplatinite was obtained in solution by adding a definite amount of chloroplatinite to a heated solution of potassium iodide. Cyanoplatinite was obtained by adding chloroplatinite to a hot solution of potassium cyanide, followed by crystallization from a concentrated solution. The composition of all compounds was confirmed by chemical analysis.

A definite concentration of Cl^-, Br^-, J^-, and CN^- ions in solution was created by dissolving the salts KCl, KBr, KJ, and KCN in water. All salts were purified by recrystallization. The e.m.f. measurements were made over time from the moment of dissolution of the complex until establishment of the potential. The experimental data are given in Tables 1–4.

Table 1

Determination of the instability constant of $[PtCl_4]^{2-}$

Conc. $K_2[PtCl_4]$ (mol/l)	Conc. KCl (mol/l)	$E = E_{\mathrm{Pt}} - E_{\mathrm{cal}}$ (mV)	E_{Pt} (mV)	$-\lg[Pt^{2+}]$	pK^c
0.0041	1.0	418	666	18.4	16.0
0.0083	1.0	428	676	18.1	16.0
0.0042	0.5	417	665	18.4	17.2

Conc. $K_2[PtCl_4]$ (mol/l)	Conc. KCl (mol/l)	$E = E_{Pt} - E_{cal}$ (mV)	E_{Pt} (mV)	$-\lg[Pt^{2+}]$	pK^c
0.0096	0.5	435	683	17.8	17.0
0.0183	0.5	434	682	17.8	17.2
0.101	0.5	459	707	17.0	17.2
0.0009	0.2	475	723	16.4	16.2
0.0132	0.2	503	751	15.5	16.4
0.0009	0.1	494	742	15.8	16.8

$$pK^{Cl} = 16.6 \pm 0.6$$

Table 2

Determination of the instability constant of $[PtBr_4]^{2-}$

Conc. $K_2[PtBr_4]$ (mol/l)	Conc. KBr (mol/l)	$E = E_{Pt} - E_{cal}$ (mV)	E_{Pt} (mV)	$-\lg[Pt^{2+}]$	pK^c
0.0037	1.0	313	561	22.0	19.6
0.0085	1.0	295	543	22.7	20.6
0.0677	1.0	303	551	22.4	21.2
0.0020	0.5	332	580	21.4	19.9
0.0040	0.5	323	571	21.7	20.5
0.0055	0.5	325	573	21.6	20.5
0.0040	0.2	370	618	20.0	20.4
0.0027	0.2	370	618	20.0	20.2
0.0680	0.2	407	655	18.8	20.4
0.0006	0.1	380	628	19.7	20.5
0.0011	0.1	410	658	18.7	19.7
0.0054	0.1	388	636	19.4	21.1

$$pK^c = 20.4 \pm 0.8$$

The tables give the e.m.f. values after establishment of equilibrium. In the case of cyanoplatinite, the e.m.f. also increases slowly after establishment of equilibrium, apparently as a result of decomposition of the cyanide; equilibrium was considered to have been established from the moment when the increase was no more than 0.5 mV per hour.

From the equilibrium value of the e.m.f., the value of the platinum-electrode potential E_{Pt} was calculated. The potential of the saturated calomel electrode was taken as equal to 0.248 V. The values of the negative logarithm of the concentration of Pt^{2+} ions were found from the Nernst equation. The value of the standard potential $E^{\circ}_{Pt^{2+}/Pt}$ required for the calculation was taken, according to Latimer ([2]), as equal to 1.2 V.

Starting from the equilibrium concentrations $[Pt^{2+}]$, $[X^{-}]$, and $[PtX_4^{2-}]$, the values of the negative logarithms of the concentration instability constants pK^c were calculated. In the case of iodoplatinite, a correction was introduced into the initial concentration of KJ for the amount of KJ consumed in the formation of iodoplatinite.

Table 3

Determination of the instability constant of $[PtJ_4]^{2-}$

Conc. $K_2[PtJ_4]$, (mol/l)	Conc. KJ, initial (mol/l)	Conc. KJ, equilibrium (mol/l)	$E = E_{\mathrm{Pt}} - E_{\mathrm{cal}}$ (mV)	E_{Pt} (mV)	$-\lg[Pt^{2+}]$	pK^c
0,0066	1,0	0,98	33	281	31,7	29,6
0,0098	1,0	0,96	21	269	32,1	30,1
0,096	1,0	0,62	77	325	30,2	30,0
0,0023	0,5	0,49	63	311	30,7	29,3
0,0082	0,5	0,47	56	304	30,9	30,1
0,0104	0,5	0,46	64	312	30,6	30,0
0,0563	0,5	0,28	108	356	29,1	30,0
0,0153	0,5	0,45	101	349	29,4	29,0
0,0019	0,2	0,19	87	335	29,8	30,0
0,0111	0,2	0,16	130	378	28,3	29,5
0,0008	0,1	0,1	104	352	29,3	30,2
0,0068	0,1	0,07	160	408	27,3	29,7

$$pK^c = 29,6 \pm 0,6$$

Table 4

Determination of the instability constant of $[Pt(CN)_4]^{2-}$

Conc. $K_2[Pt(CN)_4]$ (mol/l)	Conc. KCN (mol/l)	$E = E_{\text{Pt}} - E_{\text{cal}}$ (mV)	E_{Pt} (mV)	$-\lg[Pt^{2+}]$	pK^c
0,0012	0,1	−184	64	39,1	40,2
0,0024	0,1	−186	62	39,2	40,6
0,085	0,1	−149	99	38,0	40,9
0,0006	0,05	−156	92	38,2	40,2
0,0012	0,05	−146	102	37,9	40,2
0,001	0,02	−135	113	37,4	41,2
0,0062	0,02	−128	120	37,2	41,8
0,0742	0,02	−91	157	36,0	41,7
0,0011	0,01	−72	176	35,3	40,3
0,0007	0,01	−117	131	36,8	41,7
0,0027	0,01	−98	150	36,2	41,6
0,0054	0,01	−93	155	36,0	41,7

$$pK^c = 41,0 \pm 0,8$$

Discussion of Results

Consideration of the experimental data presented in Tables 1–4 shows that the obtained values of the overall instability constants of chloroplatinite and bromoplatinite agree well with Latimer' s calculated data. The overall instability constants of iodoplatinite and cyanoplatinite are close to those values that were predicted by one of the authors by analogy with mercury complexes.

Such agreement between the experimental data and theory speaks in favor of the fact that the platinum electrode, widely used as an indifferent electrode because of its passivity, under the indicated conditions can be used as an electrode of the first kind with respect to ions of divalent platinum. As for the mechanism of establishment of the potential, it appears highly unlikely that, with the practically complete absence of free Pt^{2+} ions, they could play an essential role in establishing equilibrium. Apparently, the potential jump arises through the interaction of complex ions with the electrode. The mechanism of this interaction is still unclear. It is possible that in such interaction an essential role is played by B. M. processes of the type

$$[PtX_4]^{2-} + 2e \rightleftarrows [Pt^0X_4]^{4-} \rightleftarrows Pt^0 + 4X^-.$$

Leningrad Technological Institute
named after Lensovet

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Note: Figure translations are in progress. See original paper for figures.