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Abstract

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ON THE INSTABILITY CONSTANTS OF PALLADIUM COMPLEXES. COMPOUNDS OF THE TYPE $K_2[PdX_4]$

There are few data in the literature on the instability constants of Pd(II) complexes. Latimer (^{1}) calculated the overall instability constants for the ions $[PdCl_4]^{2-}$ and $[PdBr_4]^{2-}$ from thermochemical data. For $[PdCl_4]^{2-}$ he gives the value $K = 5 \cdot 10^{-13}$ (pK 12.3), and for $[PdBr_4]^{2-}$ the value $K = 8 \cdot 10^{-14}$ (pK 13.1). In addition, the instability constant for $(PdCl_4)^{2-}$ was found from potentiometric data by Templeton (^{2}) (pK 13.3), and from spectrophotometric data by O. Lyubaneva (^{3}) (pK 12.2) and K. Fernelius (^{4}) (pK 15.7). The considerable difference between the constant obtained by Fernelius and the data of other authors is noteworthy.

A. A. Grinberg and M. I. Gel’fman (^{5,6}) obtained values of the overall instability constants of a series of Pt(II) compounds by a potentiometric method using a platinum electrode. In the present work an analogous procedure was applied to determine the overall instability constants of the ions $[PdCl_4]^{2-}$, $[PdBr_4]^{2-}$, $[PdJ_4]^{2-}$, and $[Pd(SCN)_4]^{2-}$. The systems $K_2[PdCl_4] + KCl$; $K_2[PdBr_4] + KBr$; $K_2[PdJ_4] + KJ$; $K_2[Pd(SCN)_4] + KSCN$ were studied at various concentrations of the complex and the halide.

The concentration of Pd^{2+} ions was determined from measurements of the e.m.f. of the cell:

$$\overset{+}{\mathrm{Pd}} \mid K_2[PdX_4],\ KX \parallel KCl,\ Hg_2Cl_3 \mid \overset{-}{\mathrm{Hg}}.$$

With a smooth palladium electrode it was not possible to obtain reproducible results. However, the problem was solved by using, as the electrode, spongy palladium situated at the bottom of the vessel containing the solution under study. An electrode made of a short platinum wire, electrolytically coated with palladium, was immersed in the spongy palladium. The spongy palladium was obtained from a solution of palladium chloride by reduction with hydrazine salts. The metal was repeatedly and thoroughly washed with hot water, dried at 110°, and kept for several days in a vacuum desiccator for complete removal of absorbed gases.

The measurements were carried out by a compensation circuit at 18-20° in a nitrogen atmosphere. Potassium chloro-, bromo-, and rhodanopalladites were prepared by the usual method, and their composition was checked by analysis. Potassium iodopalladite was obtained in solution by adding to a solution of potassium iodide a definite weighed portion of $K_2[PdCl_4]$. This amount of $K_2[PdCl_4]$ determined the concentration of the complex formed. The concentration of chlorine, bromine, iodine, and rhodanide ions was produced by dissolving weighed portions of the salts KCl, KBr, KJ, and KSCN. In the case of KJ, a correction was introduced for the amount of KJ consumed in the formation of iodopalladite. A constant ionic strength equal to unity was maintained in the solutions studied by addition of KNO_3. The e.m.f. measurement was made from the moment of dissolution of the complex until the equilibrium potential was established. Equilibrium in the case of the chloride and bromide systems was established within 5-8 days, in the case of the rhodanide system within 5 days, and in the case of the iodide system within 2-3 days. Constancy of the e.m.f. was confirmed by the establishment of the same potential after anodic polarization of the electrode. Polarization was carried out for 30-60 sec, the electrode not being removed from the solution, and the potential shifted by 50-100 mV. From the equilibrium value of the emf, the potential of the palladium electrode in the given solution was calculated. The concentration of $[Pd^{2+}]$ ions in the solution was calculated from the Nernst equation. The normal potential of the system $Pd^{2+} + 2e \rightleftarrows Pd$ was taken as 0.987 V (^{1}). The experimental results are compared in Tables 1-4.

Table 1

Finding the values of the instability-index K_{inst} of $[PdCl_4]^{2-}$

Conc. $K_2[PdCl_4]$, mol/l	Conc. KCl, mol/l	$E = E_{\text{Pd}} - E_{\text{cal}}$, mV	E_{Pd}, mV	$-\lg[Pd^{2+}]$	pK_c	Conc. $K_2[PdCl_4]$, mol/l	Conc. KCl, mol/l	$E = E_{\text{Pd}} - E_{\text{cal}}$, mV	E_{Pd}, mV	$-\lg[Pd^{2+}]$	pK_c
0.01	1.0	315	563	14.6	12.6	0.005	1.0	310	558	14.8	12.5
0.01	0.1	440	688	10.3	12.3	0.005	0.1	444	692	10.2	11.9
0.005	1.0	319	567	14.5	12.2	0.001	1.0	293	541	15.4	12.4
0.005	1.0	313	561	14.7	12.4	0.001	0.1	417	665	11.1	12.1
0.005	1.0	323	571	14.3	12.1						

$$pK_c = 12.2 \pm 0.5$$

Table 2

Finding the values of the instability-index K_{inst} of $[PdBr_4]^{2-}$

Conc. $K_2[PdBr_4]$, mol/l	Conc. KBr, mol/l	$E = E_{Pd} - E_{cal}$, mV	E_{Pd}, mV	$-\lg[Pd^{2+}]$	pK_c
0.001	1.0	195	443	18.8	15.8
0.001	0.1	310	558	14.8	15.8
0.0025	1.0	203	451	18.5	15.9
0.0025	1.0	192	440	18.9	16.3
0.0025	1.0	196	444	18.8	16.2
0.0025	1.0	208	456	18.3	15.7
0.0025	0.5	240	488	17.2	15.8
0.0025	0.5	249	497	17.0	15.6
0.0025	0.1	305	553	15.0	16.4
0.0001	0.1	305	553	15.0	16.0

$$pK_c = 16.1 \pm 0.5$$

Table 3

Finding the values of the instability-index K_{inst} of $[PdJ_4]^{2-}$

Conc. $K_2[PdJ_4]$, mol/l	Conc. KJ at equilibrium, mol/l	$E = E_{Pd} - E_{cal}$, mV	E_{Pd}, mV	$-\lg[Pd^{2+}]$	pK_c
0.001	1.0	−79	169	28.2	25.2
0.001	1.0	−84	164	28.4	25.4
0.001	0.5	−60	188	27.5	25.4
0.0005	1.0	−74	174	28.0	24.7
0.0005	1.0	−97	151	29.0	25.7
0.0005	1.0	−58	190	27.4	24.2
0.0005	0.5	−34	214	26.7	24.6
0.0005	0.5	−39	209	26.8	24.7

$$pK_c = 24.9 \pm 0.7$$

Table 4

Finding the values of the index $K_{\text{inst}}[Pd(SCN)_4]^{2-}$

Conc. $K_2[Pd(SCN)_4]$, mol/l	Conc. KSCN, mol/l	$E = E_{Pd} - E_{cal}$, mV	E_{Pd}, mV	$-\lg[Pd^{2+}]$	pK_c
0.003	1.0	−130	118	30.0	27.5
0.003	0.1	−27	221	36.3	27.9
0.001	1.0	−149	101	30.6	27.6
0.001	0.1	−46	202	27.0	28.0

$$pK_c = 27.6 \pm 0.2$$

From the data presented in Tables 1-4 it is evident that the values we found for the instability constants of the ion $[PdCl_4]^{2-}$ are in satisfactory agreement both with Latimer' s calculated data and with the experimental data of O. Lobaneva and Templeton. The value obtained by us for the ion $[PdBr_4]^{2-}$ differs from the calculated value (Latimer (1)) by approximately three orders of magnitude.

Comparison of the data presented with previously obtained constants for complexes of divalent platinum shows that the thermodynamic stability of platinum and palladium complexes increases with increasing atomic weight of the coordinated halogen. At the same time, we can see that the overall instability constants of the ions $[PdCl_4]^{2-}$, $[PdBr_4]^{2-}$, and $[PdJ_4]^{2-}$ are 4-5 orders of magnitude greater than the corresponding constants for Pt(II) and Hg(II) derivatives, i.e., that the palladium complexes mentioned are thermodynamically less stable in comparison with analogous compounds of divalent platinum and divalent mercury. At the same time, we know that, with respect to kinetic lability, the Pd(II) acido complexes occupy an intermediate position between the labile mercury and the relatively inert platinum acido complexes. The greater stability of the ion $[Pd(SCN)_4]^{2-}$ is somewhat surprising. According to our data, this ion is more robust than the ions $[Hg(SCN)_4]^{2-}$ and $[Pt(SCN)_4]^{2-}$. This circumstance indicates the need for further investigation of the stability and structure of the ion $[Pd(SCN)_4]^{2-}$.

It should be noted that, along with the indicated solutions, measurements of potentials were carried out in the system $K_2[Pd(CN)_4] + KCN$. In such solutions, establishment of an equilibrium potential is not observed, which is probably connected with the gradual dissolution of palladium black in the presence of CN^- ions. However, the order of magnitude of the potentials shows that cyanopalladite possesses greater thermodynamic stability in comparison with all the studied complexes of the type $[PdX_4]^{2-}$.

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