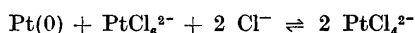


The Equilibrium Between Platinum(0), Platinum(II), and Platinum(IV) in a Chloride Ion Medium at 60°C

OLLE GINSTRUP* and IDO LEDEN

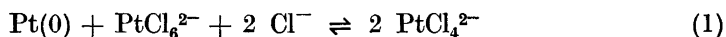
Division of Inorganic and Physical Chemistry, University of Lund, Lund, Sweden

The equilibrium



has been studied at 60°C in aqueous solutions of 3 M chloride or perchlorate. The equilibrium constant was found to be $(20 \pm 3) \times 10^{-3} \text{ M}^{-1}$, when the positive ions of the medium were hydrogen ions, and $(45 \pm 7) \times 10^{-3} \text{ M}^{-1}$ when they were mainly sodium ions. At least one month was needed to obtain equilibrium between the platinum metal and the solutions, which initially consisted of either chloro-complexes of platinum(II) or platinum(IV).

For the redox reaction



no reliable data seem to exist. Latimer¹ gives very few references but has obviously based his data on questionable measurements by Lorentz and Spielmann² for the couple $\text{PtCl}_4^{2-}/\text{Pt}(0)$. Further data for the couple $\text{PtCl}_6^{2-}/\text{PtCl}_4^{2-}$ lead to a very approximate value for the equilibrium constant of reaction (1).

Grube and Reinhardt³ have studied the equilibrium directly by shaking platinum metal with a solution of chloroplatinic acid in 0.4–7.5 M hydrochloric acid. Their methods of analysis and calculation were somewhat crude; *cf.* our discussion.

One experimental difficulty is that the reaction rate is very slow at room temperature. At 60°C the rate is sufficiently fast especially if the amount of platinum metal used is not too small.

The equilibrium constant, K , is defined as

$$K = \frac{[\text{PtCl}_4^{2-}]^2}{[\text{PtCl}_6^{2-}][\text{Cl}^-]^2} \quad (2)$$

* Present address: Department of Analytical Chemistry, University of Umeå, Umeå, Sweden.

During the course of this work another concentration quotient, Q , defined as

$$Q = \frac{[\text{II}]^2}{[\text{IV}][\text{Cl}^-]^2} \quad (3)$$

has been used. [II] denotes the total amount of platinum(II), determined by direct analysis. [IV] represents the total amount of platinum (IV). If the dissociation of PtCl_4^{2-} and PtCl_6^{2-} may be neglected, $K = Q$.

At lower chloride ion concentrations (0.15 M and especially 0.03 M) the data seem to indicate that PtCl_6^{2-} and PtCl_4^{2-} (whose dissociation is known from Elding's work ^{4,5}) dissociate to about the same extent.

The free chloride ion concentration was corrected for complex formation with platinum(II) and platinum(IV); see the experimental section.

EXPERIMENTAL

Chemicals. Hydrochloric acid (Merck's *p.a.*) and perchloric acid (Baker's *p.a.*) were diluted to 3 M stock solutions.

Sodium perchlorate was prepared by neutralising perchloric acid (Baker's *p.a.*) with sodium carbonate (Merck's *p.a.*). The solution was filtered from precipitated flakes before evaporation.

Commercial platinum salts were used without further purification. The following preparations were used: potassium chloroplatinate(II) (Degussa),⁴ potassium chloroplatinate(IV) (Engelhard Ind.), sodium hexachloroplatinate(IV) (Johnson, Matthey & Co Ltd.), and chloroplatinic acid (BDH).

Platinum metal. Platinum black, prepared by precipitation from acid solutions of platinum(IV) with hydrazine sulphate, was used in some early measurements. Later a commercial preparation from Engelhard Ind. was used. Different preparations gave the same results.

Platinum metal was purified as much as possible by repeated agitation with 3 M hydrochloric acid. Large amounts of platinum were dissolved both as platinum(II) and platinum(IV).

Preparation of the reaction tubes. Each test tube was filled with the solution to be studied (about 10 ml) and platinum metal, which had been carefully washed with the same solution, was added. The tube was connected to a gas system and was alternately evacuated and filled with nitrogen. This procedure was repeated three times, after which the tube was sealed by melting.

To expel all oxygen from the solution, evacuation of the tube was continued, until the solution boiled. In a few instances the evaporation caused by this was determined by titrating the solution with respect to chloride or hydrogen ion contents after the tube had been reopened. The solution was free from platinum. The largest change observed was 3 %, so this source of error could be neglected.

Attainment of equilibrium. The tubes were mounted in an air thermostat at $60 \pm 0.5^\circ\text{C}$ and effectively agitated by rotation. The agitation time varied between a few days and a few years. In the early experiments about 50 mg platinum was used in each reaction tube and it took an unreasonably long time to attain equilibrium. In the later experiments about 1 g of platinum metal was used in each tube and equilibrium seemed to be attained within a month.

Effect of light. In the air thermostat a carbon filament lamp was used for heating. An attempt to hasten the reaction with a mercury arc lamp had no effect.

Analysis of the solutions. The solutions were analysed by a coulometric technique.⁶ The accuracy of the analysis was generally far better than the observed spread of the K -values. The uncertainty in the determination of platinum(II) was about $0.01 \mu\text{mole}$ and in the determination of platinum(IV) about $0.02 \mu\text{mole}$. As a rule the sample size was $5 \mu\text{mole}$ (total amount of platinum). Thus, the analytical errors were less than 2 %, providing that 10 to 80 % of the total amount of platinum existed as platinum(II).

It is a remarkable fact that platinum(II) in the solutions was oxidized quite rapidly by air. Normally solutions of platinum(II) are stable in air but the oxidation seems to be catalyzed by platinum black. Therefore, samples were withdrawn from the tube within a few minutes after opening.

Stoichiometric calculations. The free chloride ion concentration in the equilibrium solution was corrected for complex formation between platinum and chloride ion:

$$[\text{Cl}^-]_0 + 4[\text{PtCl}_4^{2-}]_0 + 6[\text{PtCl}_6^{2-}]_0 = [\text{Cl}^-] + \bar{n}_{\text{II}}[\text{II}] + \bar{n}_{\text{IV}}[\text{IV}] \quad (4)$$

Notations:

$[\text{Cl}^-]_0$ chloride ion concentration in the initial solution

$[\text{PtCl}_4^{2-}]_0$ concentration of platinum(II) in the initial solution (weighed)

$[\text{PtCl}_6^{2-}]_0$ concentration of platinum(IV) in the initial solution (weighed)

$[\text{Cl}^-]$ chloride ion concentration in the equilibrium solution

\bar{n}_{II} ligand number for platinum(II) in the equilibrium solution

\bar{n}_{IV} ligand number for platinum(IV) in the equilibrium solution

[II] concentration of platinum(II) analysed in the equilibrium solution

[IV] concentration of platinum(IV) analysed in the equilibrium solution

In most cases \bar{n}_{II} was close to 4 and \bar{n}_{IV} was close to 6. When the chloride ion concentration was 30 mM, \bar{n}_{II} was computed from Elding's ⁵ dissociation constants and \bar{n}_{IV} was set equal to

$$\bar{n}_{\text{IV}} = 2 + \bar{n}_{\text{II}} \quad (5)$$

which would be the case if PtCl_4^{2-} and PtCl_6^{2-} dissociate to the same degree (*cf.* Ginstrup and Leden ⁷).

In most experiments more platinum metal was dissolved than could be accounted for by reaction (1), perhaps because of adsorbed oxygen in the metal or residual air in the solution. A measure of this dissolution was ΔPt , defined by

$$\Delta\text{Pt} = [\text{II}] + 2[\text{IV}] - [\text{PtCl}_4^{2-}]_0 - 2[\text{PtCl}_6^{2-}]_0 \quad (6)$$

ΔPt was usually about 5 mM but values of 20 mM were not uncommon. Some reaction tubes contained platinum(IV) from the start and others platinum(II), so equilibrium was attained from both directions.

The direction of attaining equilibrium might be changed if the dissolution of platinum is too large. The following two cases are the worst possible.

1) Starting with platinum(II). If the foreign oxidation acts entirely on platinum(II) in the solution to give only platinum(IV) and if

$$\Delta\text{Pt} > [\text{IV}]$$

the equilibrium is approached from the quadrivalent side. These measurements have been marked with rings in Fig. 2.

2) Starting with platinum(IV). If the foreign oxidation acts entirely on platinum(0) to dissolve only as platinum(II) and if

$$\Delta\text{Pt} > [\text{II}]$$

the equilibrium is approached from the bivalent side. This case is less probable than the former. In Fig. 2 these measurements have been denoted as starting from the quadrivalent side.

RESULTS

The results have been collected in Figs. 1 and 2. Each point on the graphs represents a completely independent experiment. For $[\text{PtCl}_4^{2-}]$ and $[\text{PtCl}_6^{2-}]$ the analytical concentrations of platinum(II) and platinum(IV) have been used without correction for dissociation. The free chloride ion concentration has been corrected for complex formation according to eqn. (4). This correction is important only at the smallest chloride ion concentrations.

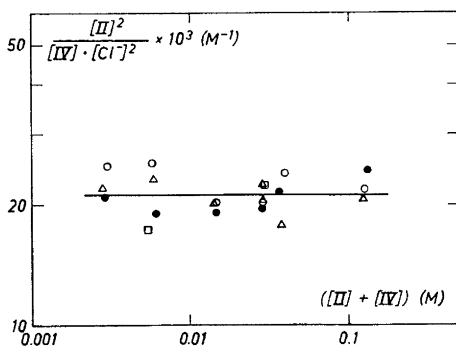


Fig. 1. The concentration quotient Q (eqn. 3) as a function of total amount of platinum at constant chloride ion concentration (0.6 M) and hydrogen ion concentration (3 M). Agitation time: Δ 4 months, \square 9 months, \circ 16 months, \bullet 24 months. The horizontal line is drawn at the average value $21.2 \times 10^{-3} \text{ M}^{-1}$. The scale on both axes is logarithmic.

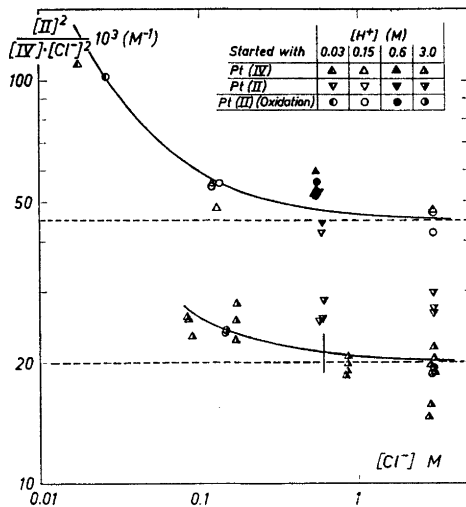


Fig. 2. Q as a function of chloride ion concentration. The bar at 0.6 M chloride concentration represents the 21 points in Fig. 1. The full drawn curves are calculated from Elding's dissociation constants for PtCl_4^{2-} and $K = 20 \times 10^{-3} \text{ M}^{-1}$, respectively $K = 45 \times 10^{-3} \text{ M}^{-1}$. Both axes have logarithmic scales.

Fig. 1 shows the results obtained in the solvent 0.6 M HCl and 2.4 M HClO_4 . All the solutions contained only platinum(IV) when shaking started. The results show that the concentration quotient Q , according to eqn. (3), remains constant within the limits $Q = (21.2 \pm 2.3) \times 10^{-3} \text{ M}^{-1}$, irrespective of the platinum contents of the solution and of the reaction time.

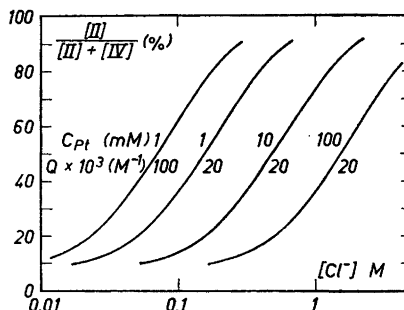
Fig. 2 shows that Q varies somewhat with the chloride ion concentration. This might be due to the dissociation of PtCl_4^{2-} and PtCl_6^{2-} . If the two species dissociate to the same extent (*cf.* Ginstrup and Leden⁷) Q may be rewritten and simplified to

$$Q = \frac{[\text{PtCl}_4^{2-}]^2}{[\text{PtCl}_6^{2-}][\text{Cl}^-]^2} \cdot \frac{[\text{II}]^2}{[\text{PtCl}_4^{2-}]^2} \cdot \frac{[\text{PtCl}_6^{2-}]}{[\text{IV}]} \approx K \cdot \frac{[\text{II}]}{[\text{PtCl}_4^{2-}]} \quad (7)$$

The quotient $[\text{II}]/\text{PtCl}_4^{2-}$ as a function of the chloride ion concentration has been calculated from Elding's⁵ dissociation constants. Fig. 2 shows that the experimental values of Q fit this curve if $K = 20 \times 10^{-3} \text{ M}^{-1}$ when the hydrogen ion concentration was 3 M and if $K = 45 \times 10^{-3} \text{ M}^{-1}$ when the hydrogen ion concentration was 0.03–0.6 M.

As shown by the symbols, equilibrium has been obtained from both directions. The rate of reaction is highly dependent on the amount of platinum metal present. There is some evidence that the reaction becomes slower as

Fig. 3. The fraction of platinum(II) in equilibrium with platinum(IV) and platinum(0) as a function of the chloride ion concentration. The curves have been calculated for a few values of the total amount of platinum and of the conditional equilibrium constant Q . These values have been marked on each curve.



the chloride ion concentration increases, which might also be the reason for the reduction in reproducibility in 3 M chloride.

The surface of the platinum metal changed visibly during the course of an experiment from velvet black through gray to metallic lustre. The grains still contained black powder under a thin shell of glimmering metal. This change indicates that a continuous exchange of platinum between metal and solution is occurring.

DISCUSSION

It seems obvious that the solutions have closely reached an equilibrium state in the time allowed. The evidence for this is:

1. There is a visible exchange of platinum between metal and solution.
2. Within the given limits of uncertainty a steady state has been attained, *i.e.* there is no further change of concentrations with time.
3. The same steady state has been obtained from both sides.
4. The steady state concentrations satisfy a simple law of mass action in a rather wide range of concentrations. (Apparent deviations at low chloride concentrations may have been caused by a plausible degree of dissociation of the chloride complexes).

The values of K for 3 M H^+ and 3 M Na^+ are similar enough for the difference to be caused by the different ionic environment.

From Grube and Reinhardt's³ figures K values between $26 \times 10^{-3} M^{-1}$ and $530 \times 10^{-3} M^{-1}$ were calculated. The reason for their high values could be that they only analysed the sum of platinum(II) and platinum(IV) in the equilibrated solutions, and assumed that the increase of platinum arose from the reaction only. They had no specific analysis method for platinum(II) or platinum(IV) available and made a gravimetric analysis. Our analyses show, however, that a large and unreproducible part of the dissolved platinum derives from foreign oxidation. For this reason Grube and Reinhardt have probably overestimated the concentrations of platinum(II) seriously. In addition, they tried to account for the changes in the solvent by using mean activity coefficients of hydrochloric acid as the activity coefficient of the chloride ion.

Our results show that solutions of tetrachloroplatinates(II) are thermodynamically unstable. Fig. 3 shows the distribution of platinum(II) and platinum(IV) in equilibrium with platinum(0) as a function of the chloride ion concentration of the solution. As parameters, some values have been chosen for the total concentration of platinum and for Q , which might be regarded as a conditional equilibrium constant.

REFERENCES

1. Latimer, W. *Oxidation potentials*, 2nd Ed., Prentice Hall, New York 1952.
2. Lorentz, R. and Spielmann, P. E. *Z. Elektrochem.* **15** (1909) 293.
3. Grube, G. and Reinhardt, H. *Z. Elektrochem.* **37** (1931) 307.
4. Elding, L. I. and Leden, I. *Acta Chem. Scand.* **20** (1966) 706.
5. Drougge, L., Elding, L. I. and Gustafson, L. *Acta Chem. Scand.* **21** (1967) 1647.
6. Ginstrup, O. *To be published.*
7. Ginstrup, O. and Leden, I. *Acta Chem. Scand.* **22** (1968). *In press.*

Received June 23, 1967.