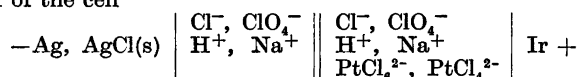


## Emf Measurements on the System Platinum(IV)/Platinum (II) in a Chloride Ion Medium at 60°C

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The redox potential of the couple  $\text{PtCl}_6^{2-}/\text{PtCl}_4^{2-}$  versus a silver-silver chloride electrode has been determined at 60°C by measuring the emf of the cell



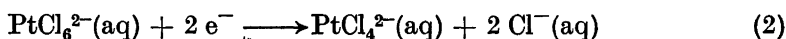
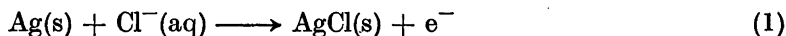
The concentration of hydrogen ions and chloride ions was always the same in the two half cells, which contained perchlorate ions at an ionic strength of 3 M. The standard potential of the cell was found to be 523 mV in 3 M acid and 529 mV when sodium ions were the dominating positive ions. The calculated values of the standard potentials of the couples  $\text{PtCl}_6^{2-}/\text{Pt(0)}$  and  $\text{PtCl}_4^{2-}/\text{Pt(0)}$  and of the dissociation constant for  $\text{PtCl}_6^{2-}$  are collected in Table 1.

The whole cell contained the same solvent, *viz.* an aqueous solution of 3 M electrolyte. A little silver chloride was dissolved in the reference electrode compartment and the other half cell contained approximately 0.01 M platinum salts. Thus diffusion potentials were negligible.

The standard state of the different species was chosen such that their activities were equal to their molarities in the 3 M solvent.

Dissociation of the species  $\text{PtCl}_6^{2-}$  and  $\text{PtCl}_4^{2-}$  may complicate the system. Dissociation is considerable at chloride ion concentrations below 100 mM. Thus, an appreciable part of the perchlorate ions must be exchanged for chloride ions in order to obtain an adequate measuring interval.

The two half cell reactions may be written as:



Since the chloride ion concentration is uniform throughout the whole cell, it disappears from the expression for the emf  $E$ :

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$$E = E^{\circ}_{\text{IV/II}} + \frac{RT}{2F} \ln \frac{a_{\text{PtCl}_6^{4-}}}{a_{\text{PtCl}_4^{2-}}} \quad (3)$$

$E^{\circ}_{\text{IV/II}}$  is the standard potential of the cell in the 3 M solvent used in the cell in question.

Instead of the activity  $a_{\text{PtCl}_4^{2-}}$ , the total concentration of 'platinum(IV) (denoted [IV]) is used throughout this work. Similarly, [II] replaces  $a_{\text{PtCl}_6^{4-}}$ . The last term of eqn. 3 is rewritten and denoted  $E'$ :

$$E' = \frac{RT}{2F} \ln \frac{[\text{IV}]}{[\text{II}]} \quad (4)$$

When Nernst's law in its simplest form is obeyed, the difference

$$E - E' = E^{\circ}_{\text{IV/II}} \quad (5)$$

should remain constant irrespective of variations in the quotient [IV]/[II] or chloride ion concentration.

#### EXPERIMENTAL

*Chemicals.* Commercial platinum salts were employed without further purification. Potassium chloroplatinate(IV) and potassium chloroplatinate(II) were obtained from Engelhard and Degussa, respectively.<sup>1</sup> It was impossible to purify salts of platinum(II) entirely from platinum(IV) and hence all solutions were analysed for platinum(II) and platinum(IV).

Hydrogen hexachloroiridate(IV) acid and Gum Accacia USP Powder were obtained from Fluka and Baker Phillipsburg, respectively.

The same preparations as in a previous work<sup>2</sup> were employed for hydrochloric acid, perchloric acid, and sodium perchlorate.

*Electrodes.* It was found desirable to develop electrodes with as fast and reproducible potential response as possible. Several types of platinum, iridium, gold, graphite, boron carbide, and tin oxide electrodes were tested. "Metallized glass electrodes" according to Newberry<sup>3</sup> and Zakharevskij<sup>4,5</sup> were found to be the best, particularly with an iridium film.

The preparation was as follows. A well cleaned glass rod, diameter 4 mm, length 150 mm, was dipped into a solution of hydrogen hexachloroiridate(IV) and was gently ignited in a Bunsen flame. The treatment was repeated until the layer of iridium became opaque which required about twenty immersions. Around the uppermost part of the rod, a copper wire was wound and tin soldered. Contact was made with an alligator clip.

The solution of hydrogen hexachloroiridate(IV) contained about 5% iridium. To increase the viscosity of the solution it was mixed with a warm aqueous solution of "Gum Accacia".

Even these electrodes gave a rather poor potential response for changes in the composition of the solution. A remarkable observation was that the presence of air caused a decrease in the electrode potential. At the same time the reproducibility declined and the response was slower.

*Reference electrodes.* Silver-silver chloride electrodes according to Brown<sup>6</sup> were used. In some early measurements the reference electrodes were unsatisfactory due to the high solubility of silver chloride in the chloride solutions.<sup>7</sup> The solubility is substantially higher at 60°C than at 25°C. In later measurements the reference vessel was always furnished with excess solid silver chloride.

*Cell.* The measuring vessel and reference vessel were two titration vessels joined by a siphon fitted with a stopcock. The titration vessels were obtained from Ingold, Zürich, and consisted of a plastic cover with 5 standard bores NS 14 and a beaker with a threaded connection to the cover. On the beaker a jacket for thermostated water was fastened. Magnetic stirring was employed.

A vigorous stream of nitrogen which was purified from oxygen with activated copper, precipitated on kieselguhr,<sup>8</sup> removed the air from the measuring vessel. The gas exit was through a bent capillary.

*Thermostat.* A water stream at a temperature of  $60 \pm 0.1^\circ\text{C}$  was pumped through the jackets of the two titration vessels. In addition, the whole cell was mounted inside a large cabinet, where the air was maintained at  $60 \pm 1^\circ\text{C}$ . The gas was prethermostated and moistened by bubbling it through two washing bottles with 3 M solutions in the air thermostat. Then all effects due to condensation or evaporation of the solution were avoided.

*Emf measurements.* The emf's were measured with a digital voltmeter (Solartron LM 1440) to a precision of 0.1 mV. A digital voltmeter is hum sensitive, but there was no hum in the measuring circuit because the air thermostat was constructed of zinc sheet, which acted as a shield. Furthermore the built-in hum filter of the digital voltmeter was also used.

*Determination of the composition of the solutions.* The solvent was obtained by mixing appropriate volumes of stock solutions of 3 M hydrochloric acid, sodium chloride, perchloric acid, and sodium perchlorate.

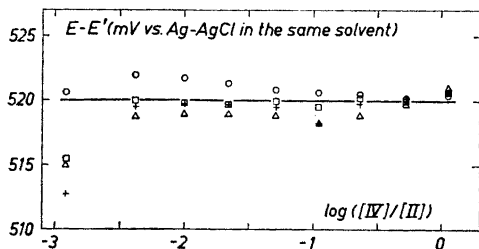
In this solvent weighed amounts of potassium hexachloroplatinate(IV) or potassium tetrachloroplatinate(II) were dissolved to yield about 10 mM platinum. The solution in the platinum half cell was obtained by mixing these two solutions. The total amount of platinum was always about 10 mM, so there was no risk that potassium chloroplatinate(IV) would precipitate.

The weighing and mixing of the platinum salts was controlled by direct analysis of platinum(II) and platinum(IV) by a direct coulometric method.<sup>9</sup> Almost all determinations were reproduced to within 1%.

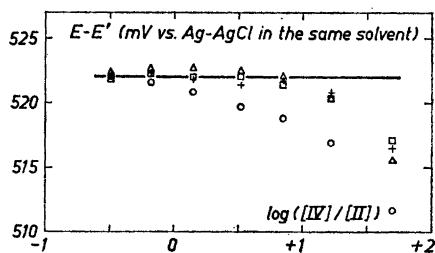
All analyses and preparations were performed at room temperature. At  $60^\circ\text{C}$  all concentrations are smaller due to volume expansion. This has no influence on the emf's, since only the quotient of the two concentrations  $[\text{PtCl}_6^{2-}]$  and  $[\text{PtCl}_4^{2-}]$  is involved (see eqn. 3).

## RESULTS

Fig. 1 shows an example, where increasing volumes of a solution containing platinum(IV) have been added to a solution of platinum(II) in the electrode vessel. The constant value of  $E - E'$  calculated from eqns. (4) and (5) shows that Nernst's law is obeyed within the range



*Fig. 1.* Platinum measurements. The difference  $E - E'$  as a function of the quotient  $[\text{IV}]/[\text{II}]$ . Platinum(IV) has been added to platinum(II).  $[\text{Cl}^-] = 0.6 \text{ M}$ ,  $[\text{ClO}_4^-] = 2.4 \text{ M}$ ,  $[\text{H}^+] = 3 \text{ M}$ . Symbols for different electrodes:  $\circ$ , platinum sheet;  $+$   $\square$   $\triangle$ , three different iridized glass rods.



*Fig. 2.* Platinum(II) added to platinum(IV). Otherwise as in Fig. 1.

$$0.001 < [\text{IV}]/[\text{II}] < 1$$

The results in Fig. 2 were obtained by adding solutions of platinum(II) to an initial solution of platinum(IV) in the titration vessel. It follows that Nernst's law describes the results in the range

$$0.3 < [\text{IV}]/[\text{II}] < 10$$

In these two series, the chloride ion concentration was maintained constant at 0.6 M. The hydrogen ion concentration was 3 M.

It is observed that the solutions studied are generally not in equilibrium with platinum(0). The equilibrium demands a quotient  $[\text{IV}]/[\text{II}] = 0.8$ , when  $[\text{Cl}^-] = 0.6 \text{ M}$  and  $[\text{II}] + [\text{IV}] = 10 \text{ mM}$  (*cf.* Ref. 2).

The cells required 20–90 min to attain their final emf values. Figs. 1 and 2 give  $E^\circ_{\text{IV/II}}$  as 520 mV and 522 mV, respectively, which were obtained from some early measurements, where the reference electrodes were not well controlled, which may be one cause of the discrepancy. Another reason may be that the final potentials of the electrodes were reached from opposite directions in the two series.

Series similar to those given in Figs. 1 and 2 were then repeated for other chloride ion concentrations. The results are shown in Fig. 3, where each point represents an average value from a series in which the quotient  $[\text{IV}]/[\text{II}]$  was varied as above.

The symbols employed are the following:  $\Delta$  denotes that platinum(II) is in excess during the main part of the titration procedure (emf increasing after each addition);  $\nabla$  denotes that platinum(IV) is in excess (decreasing emf);

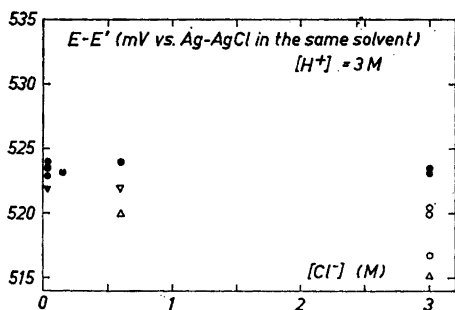


Fig. 3. Platinum measurements. The difference  $E - E'$  as a function of the chloride ion concentration.  $[\text{H}^+] = 3 \text{ M}$ ,  $[\text{ClO}_4^-] + [\text{Cl}^-] = 3 \text{ M}$ . Notations:  $\blacktriangle$   $\Delta$  platinum(II) was titrated with platinum(IV);  $\blacktriangledown$   $\triangledown$  platinum(IV) was titrated with platinum(II);  $\bullet$   $\circ$  only one composition of the solution, with about 5 mM each of platinum(II) and platinum(IV). Filled points: entirely satisfactory measurements. Unfilled points: the reference electrodes or the indicator electrodes were not quite satisfactory.

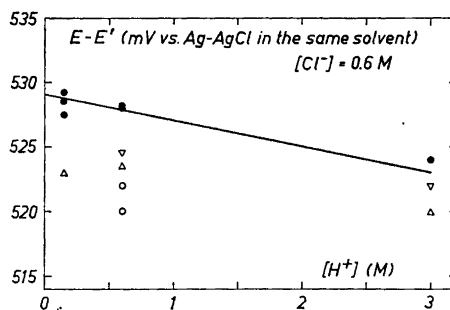


Fig. 4. Platinum measurements. Influence of the hydrogen ion concentration.  $[\text{Cl}^-] = 0.6 \text{ M}$ ,  $[\text{ClO}_4^-] = 2.4 \text{ M}$ ,  $[\text{Na}^+] + [\text{H}^+] = 3 \text{ M}$ . Notations as in Fig. 3.

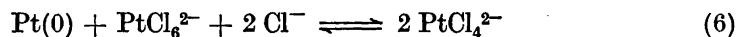
○ denotes that only one value of the quotient  $[\text{IV}]/[\text{II}]$ , in the vicinity of unity, has been measured. Open symbols are used for measurements where the reference electrode has not been at its best or where the final emf has been attained abnormally slowly.

Fig. 3 appears to indicate that  $E-E'$  is independent of the chloride ion concentration as the proposed cell reaction demands for ideal solutions.  $E^\circ_{\text{IV/II}}$  was estimated as 523 mV at the constant concentration of hydrogen ions, 3 M, used in these series.

Fig. 4 contains measurements, where the chloride ion concentration has been maintained constant at 0.6 M and the hydrogen ion concentration has been varied.  $E-E'$  varies somewhat. In 3 M acid it was 523 mV and may be linearly extrapolated to 529 mV in a neutral salt solution.

#### REDOX EQUILIBRIA WITH PLATINUM(0)

The standard potential for the couples  $\text{PtCl}_4^{2-}/\text{Pt}(0)$  and  $\text{PtCl}_6^{2-}/\text{Pt}(0)$  versus a silver-silver chloride electrode in the media used may be computed by combining the standard potential  $E^\circ_{\text{IV/II}}$  obtained above with the equilibrium constant,  $K$  (Ref. 2), for the reaction



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

They have been computed from the eqns.

$$E^\circ_{\text{II}/0} = E^\circ_{\text{IV/II}} - \frac{RT}{2F} \ln K \quad (8)$$

$$E^\circ_{\text{IV}/0} = E^\circ_{\text{IV/II}} - \frac{RT}{4F} \ln K \quad (9)$$

Table 1. Summary of the measurements on the redox system  $\text{PtCl}_6^{2-}/\text{PtCl}_4^{2-}/\text{Pt}(0)$  at ionic strength 3 M. Temperature 60°C. All emf values are given versus the silver-silver chloride electrode.

	$\text{HClO}_4$ <i>a</i>	HCl	$\text{NaClO}_4$ <i>a, b</i>	NaCl <i>b</i>
$E^\circ_{\text{IV/II}}$ (this work) (mV)	$523 \pm 2$	$523 \pm 2$	$529 \pm 2$	$529 \pm 2$
$K$ (Ref. 2; eqn. (7) in this work) ( $\text{M}^{-1}$ )	$(20 \pm 3) \times 10^{-3}$	$(20 \pm 3) \times 10^{-3}$	$(45 \pm 7) \times 10^{-3}$	$(45 \pm 7) \times 10^{-3}$
$E^\circ_{\text{II}/0}$ (mV)	$579 \pm 4$	$579 \pm 4$	$574 \pm 4$	$574 \pm 4$
$E^\circ_{\text{IV}/0}$ (mV)	$551 \pm 3$	$551 \pm 3$	$551 \pm 3$	$551 \pm 3$
$K_6^{\text{IV}}$ (eqn. 11) ( $\text{M}^{-1}$ )	$(29 \pm 5) \times 10^{-3}$			

*a.*  $[\text{Cl}^-]$  at least 30 mM.

*b.*  $[\text{H}^+]$  at least 30 mM in the solutions;  $[\text{H}^+]$  extrapolated to zero.

These standard potentials are collected in Table 1. It appears that the ion  $\text{PtCl}_4^{2-}$  is more affected by the hydrogen ion concentration of the solvent than is the ion  $\text{PtCl}_6^{2-}$ .

#### DISSOCIATION OF $\text{PtCl}_4^{2-}$ AND $\text{PtCl}_6^{2-}$

At the lowest chloride ion concentration used, 0.03 M,  $\text{PtCl}_4^{2-}$  is dissociated to about 50 % (*vide* Elding *et al.*<sup>10</sup>). The difference  $E - E'$  remained constant, however, even at this lowest chloride ion concentration (see Fig. 3). This probably means that  $\text{PtCl}_6^{2-}$  is dissociated to about 50 % also.

A more detailed calculation may be performed by means of eqn. (10)

$$E - E' = E^\circ_{\text{IV/II}} + \frac{RT}{2F} \ln \frac{\gamma_{\text{IV}}}{\gamma_{\text{II}}} - \frac{RT}{F} \ln \frac{[\text{Cl}^-]}{[\text{Cl}^-]_0} \quad (10)$$

Notations:

$$\begin{aligned} \gamma_{\text{IV}} &= [\text{PtCl}_6^{2-}][\text{IV}]^{-1} \\ \gamma_{\text{II}} &= [\text{PtCl}_4^{2-}][\text{II}]^{-1} \end{aligned}$$

$[\text{Cl}^-]_0$ : free chloride ion concentration in the reference half cell and in the measuring vessel before dissociation of the platinum complexes.

$[\text{Cl}^-]$ : the concentration of free chloride ion at equilibrium in the measuring vessel.

In a typical example, the following primary numbers were employed:  $[\text{Cl}^-]_0 = 0.03 \text{ M}$ ;  $[\text{II}] = [\text{IV}] = 5 \text{ mM}$ ;  $E - E' = 523 \pm 2 \text{ mV}$ ;  $E^\circ_{\text{IV/II}} = 523 \pm 2 \text{ mV}$  (from measurements in 0.15, 0.6, and 3 M chloride), where  $\gamma_{\text{II}} = \gamma_{\text{IV}} = 1$ .

By using eqn. (10) and Elding's<sup>10</sup> dissociation constants for platinum(II) an iterated calculation gives:

$$[\text{Cl}^-] = 0.035 \text{ M}; \gamma_{\text{II}} = 0.51 \text{ and } \gamma_{\text{IV}} = 0.55 \pm 0.04$$

If it is assumed that  $\text{PtCl}_6^-$  does not dissociate further, a value for  $K_6^{\text{IV}}$  may be calculated:

$$K_6^{\text{IV}} = \frac{[\text{PtCl}_6^-][\text{Cl}^-]}{[\text{PtCl}_6^{2-}]} = (29 \pm 5) \times 10^{-3} \text{ M} \quad (11)$$

A more detailed account of this method of comparing complex formation of a metal ion at two different valency states may be found in Rosotti and Rosotti's book.<sup>11</sup>

This value of  $K_6^{\text{VI}}$  is in excellent agreement with a recent value of Davidson and Jameson,<sup>12</sup>  $32 \times 10^{-3} \text{ M}$ , measured at 50°C.

#### DISCUSSION

$E - E'$  varies slightly ( $-2 \text{ mV/M}$ ) when the sodium ions of the solvent are exchanged for hydrogen ions (see Fig. 4). The variation is still less when the perchlorate ions of the solvent are exchanged by chloride ions (see Fig. 3). This behaviour seems quite plausible, since the only species involved in the cell reaction are  $\text{PtCl}_6^{2-}$  and  $\text{PtCl}_4^{2-}$  ions. The medium effects upon these ions may be approximately counterbalanced. Since the hydrogen and sodium ions have opposite charge to the platinum anions it is expected that an exchange of sodium ions for hydrogen ions in the solution has larger effects than an exchange of perchlorate ions for chloride ions.

Comparison with earlier measurements will be given in a subsequent paper,<sup>13</sup> which contains some measurements on the platinum system at 25°C and

measurements of the silver-silver chloride electrode *versus* the hydrogen electrode in the same solvents as used in the present work.

Grinberg *et al.*<sup>14-17</sup> have measured potentials of an "active" platinum electrode in solutions of various complex compounds of platinum(II), for example  $\text{PtCl}_4^{2-}$ . They assumed that the potential is governed by the couple platinum(II)/platinum(0)

$$E = E^\circ + \frac{RT}{2F} \ln \frac{[\text{PtCl}_4^{2-}]}{[\text{Cl}^-]^4} \quad (12)$$

Then the total instability constants,  $\beta_4^{-1}$ , of the complexes were calculated after introduction of Latimer's<sup>18</sup> value for the standard potential of the couple  $\text{Pt}^{2+}/\text{Pt}(0)$  (+ 1.2 V *vs.* NHE).

$$E^\circ = 1.2 - \frac{RT}{2F} \ln \beta_4 \quad (13)$$

Such conclusions are doubtful as the measured emf's for varied concentrations of ligand and platinum salt are very far from satisfying eqn. 12. It is probable that the given emf values instead of referring to a questionable equilibrium between Pt(0) and Pt(II) only reflect that unknown occasional amounts of Pt(IV) were present in solution. Also precautions taken against oxidation of Pt(II) by air are not reported. It seems very improbable that an equilibrium between Pt(0), Pt(II), and Pt(IV) had been reached. Fig. 1 shows that the potential of an inert electrode, Pt, Ir, or others, is governed by the Pt(II)–Pt(IV) couple even for traces of platinum(IV) and in solutions, where the dissolved platinum salts are not in equilibrium with Pt(0). This last equilibrium is established very slowly as has been shown in a previous paper.<sup>2</sup>

The problem can possibly be solved for the chloride system by a comparison of the electrode kinetics of the two couples  $\text{PtCl}_6^{2-}/\text{PtCl}_4^{2-}$  and  $\text{PtCl}_4^{2-}/\text{Pt}(0)$ . It is intended to investigate this possibility.

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