

The Redox System Platinum(0)/Platinum(II)/ Platinum(IV) with Chloro and Bromo Ligands

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The equilibrium constants for the reactions $\text{PtX}_6^{2-} + \text{Pt}(0) + 2\text{X}^- \rightleftharpoons 2\text{PtX}_4^{2-}$ with $\text{X} = \text{Cl}$ or Br , and the standard emf's of the liquid junction free cells $\text{Ag}, \text{AgX} | \text{Solvent}, \text{PtX}_6^{2-}, \text{PtX}_4^{2-} | \text{Ir}$ have been measured at 25 and 60°C. All determinations (except otherwise noted) were performed in solvents made by mixing 3 M solutions of perchloric acid, hydrochloric (or hydrobromic) acid, sodium perchlorate, and sodium halide. From these measurements standard potentials for the couples $\text{PtX}_4^{2-}/\text{Pt}$ and $\text{PtX}_6^{2-}/\text{Pt}$ have been calculated. The standard potentials of the couples Pt^{2+}/Pt and Pt^{4+}/Pt could be calculated after estimation of the total stability constants. The influence of the composition of the solvent and the choice of reference electrode is examined in some detail.

The reactions under study in this work are summarized in Table 1. The first three reactions have been the subject of three previous papers. The heterogeneous equilibrium (1A) has been measured¹ for the chloride system at 60°C. The platinum redox emf has been measured² for the chloride system at 60°C. The hydrogen electrode measurements³ embrace the chloride and bromide systems at both 25°C and 60°C.

In this work, the platinum measurements are extended to the bromide system and to the temperatures 25°C and 60°C. All data, including the previous measurements,^{1,2} have been more thoroughly treated than before.^{1,2} Constants for a number of platinum equilibria have been calculated.

METHODS

All measurements (unless otherwise noted) have been carried out in solvents (ionic media) of 3 M total ionic strength. The halide ion concentration has been varied between 0.03 and 3 M (the anion balance has been established by adding perchlorate ions to 3 M) and the hydrogen ion concentration has also

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Table 1. The defining eqns. for *A* the reactions studied in this paper, *B* the equilibrium constants or standard emf's and *C* the activity coefficients involved. X stands for Cl or Br.

| Eqn. | A Reaction | B Equilibrium constant or standard emf referred to the actual solvent | C Equilibrium constant or standard emf referred to a specified solvent and the corresponding activity coefficients |
|------|--|---|---|
| 1 | $\text{Pt}(s) + \text{PtX}_6^{2-} + 2\text{X}^- \rightleftharpoons 2\text{PtX}_4^{2-}$ | $K = \frac{[\text{PtX}_4^{2-}]^2}{[\text{PtX}_6^{2-}] \cdot [\text{X}^-]^2}$ | $K_{\text{solvent}} = K \cdot \frac{y_{\text{PtX}_4^{2-}}}{y_{\text{PtX}_6^{2-}}} \cdot \frac{y_{\text{PtX}_4^{2-}}}{y_{\text{X}^-}}$ |
| 2 | $\text{PtX}_6^{2-} + 2\text{Ag}(s) \rightleftharpoons \text{PtX}_4^{2-} + 2\text{AgX}(s)$ | $E_2^\circ = E_2^\circ - \frac{RT}{2F} \ln \frac{[\text{PtX}_6^{2-}]}{[\text{PtX}_4^{2-}]}$ | $E_{2,\text{solvent}}^\circ = E_2^\circ - \frac{RT}{2F} \ln \frac{y_{\text{PtX}_6^{2-}}}{y_{\text{PtX}_4^{2-}}}$ |
| 3 | $2\text{AgX}(s) + \text{H}_2 \rightleftharpoons 2\text{Ag}(s) + 2\text{H}^+ + 2\text{X}^-$ | $E_3^\circ = E_3^\circ + \frac{RT}{F} \ln [\text{H}^+] \cdot [\text{X}^-]$ | $E_{3,\text{solvent}}^\circ = E_3^\circ + \frac{RT}{F} \ln y_{\text{H}^+} \cdot y_{\text{X}^-}$ |
| 4 | $\text{Pt}^{2+} + 4\text{X}^- \rightleftharpoons \text{PtX}_4^{2-}$ | $\beta_4^{\text{II}} = \frac{[\text{PtX}_4^{2-}]}{[\text{Pt}^{2+}] \cdot [\text{X}^-]^4}$ | $\beta_{4,\text{solvent}}^{\text{II}} = \beta_4^{\text{II}} \cdot \frac{y_{\text{PtX}_4^{2-}}}{y_{\text{Pt}^{2+}} \cdot y_{\text{X}^-}^4}$ |
| 5 | $\text{PtX}_4^{2-} + 2\text{Ag}(s) \rightleftharpoons \text{Pt}(s) + 2\text{AgX}(s) + 2\text{X}^-$ | $E_5^\circ = E_2^\circ - \frac{RT}{2F} \ln K$ | $E_{5,\text{solvent}}^\circ = E_5^\circ - \frac{RT}{2F} \ln \frac{y_{\text{PtX}_4^{2-}}}{y_{\text{X}^-}}$ |
| 6 | $\text{Pt}^{2+} + \text{H}_2 \rightleftharpoons \text{Pt}(s) + 2\text{H}^+$ | $E_6^\circ = E_5^\circ + E_3^\circ + \frac{RT}{2F} \ln \beta_4^{\text{II}}$ | $E_{6,\text{solvent}}^\circ = E_6^\circ - \frac{RT}{2F} \ln \frac{y_{\text{Pt}^{2+}}}{y_{\text{H}^+}}$ |
| 7 | $\text{PtX}_6^{2-} + 4\text{Ag}(s) \rightleftharpoons \text{Pt}(s) + 4\text{AgX}(s) + 2\text{X}^-$ | $E_7^\circ = E_2^\circ - \frac{RT}{4F} \ln K$ | $E_{7,\text{solvent}}^\circ = E_7^\circ - \frac{RT}{4F} \ln \frac{y_{\text{PtX}_6^{2-}}}{y_{\text{X}^-}}$ |
| 8 | $\text{PtX}_6^{2-} + \text{H}_2 \rightleftharpoons \text{PtX}_4^{2-} + 2\text{H}^+ + 2\text{X}^-$ | $E_8^\circ = E_2^\circ + E_3^\circ$ | $E_{8,\text{solvent}}^\circ = E_8^\circ + \frac{RT}{F} \ln y_{\text{H}^+} \cdot y_{\text{X}^-} - \frac{RT}{2F} \ln \frac{y_{\text{PtX}_6^{2-}}}{y_{\text{PtX}_4^{2-}}}$ |
| 9 | $\text{Pt}^{4+} + 6\text{X}^- \rightleftharpoons \text{PtX}_6^{2-}$ | $\beta_6^{\text{IV}} = \frac{[\text{PtX}_6^{2-}]}{[\text{Pt}^{4+}] \cdot [\text{X}^-]^6}$ | $\beta_{6,\text{solvent}}^{\text{IV}} = \beta_6^{\text{IV}} \cdot \frac{y_{\text{PtX}_6^{2-}}}{y_{\text{Pt}^{4+}} \cdot y_{\text{X}^-}^6}$ |
| 10 | $\text{Pt}^{4+} + 2\text{H}_2 = \text{Pt}(s) + 4\text{H}^+$ | $E_{10}^\circ = E_7^\circ + E_3^\circ + \frac{RT}{4F} \ln \beta_6^{\text{IV}}$ | $E_{10,\text{solvent}}^\circ = E_{10}^\circ - \frac{RT}{4F} \ln \frac{y_{\text{Pt}^{4+}}}{y_{\text{H}^+}}$ |

been varied between 0.03 and 3 M with sodium ions as a complement. At the lowest chloride ion concentration used, 30 mM, the chloroplatinates are partly dissociated. The influence of the dissociation may be corrected for (*cf.* p. 1531) and the measurements in the solvents with higher chloride ion concentrations and the bromide measurements are free from this ambiguity. The

hydrogen ion concentration was kept high, at least 30 mM to suppress protolysis of the halogenoquo complexes.

Equilibrium with Pt(0). (Reaction (1A)). The experiments were performed as described in a previous paper.¹ The sealed reaction tubes were rotated in an air thermostat (at $60 \pm 0.5^\circ\text{C}$) or in a water thermostat (at $25 \pm 0.1^\circ\text{C}$). Each tube contained about 1 g platinum metal and 10 ml solution. The total concentration of platinum salts was in the range 2–60 mM. After an adequate agitating time, the tubes were opened and analyzed coulometrically^{1,45} for the equilibrium concentrations of platinum(II) and platinum(IV). The original halide ion concentration of the solutions was corrected as earlier.¹ As in the previous measurements,¹ the equilibrium was approached from both sides.

Emf measurements. (Reaction (2A)). The electrodes and the cell were the same as in the earlier experiments.^{2,3} The cell was thermostated with a water stream of temperature $25 \pm 0.1^\circ\text{C}$ or $60 \pm 0.1^\circ\text{C}$. At 60°C , the cell was mounted inside an air thermostat¹ of temperature $60 \pm 0.5^\circ\text{C}$. Appropriate amounts of platinum(II) and platinum(IV) salts were weighed in. The total concentration of platinum was in the vicinity of 10 mM. The emf was measured with a digital voltmeter (Solartron LM 1440) or a differential voltmeter (HP 3420 B) to a precision of $10 \mu\text{V}$.

EXPERIMENTAL

Chemicals. Reagent grade chemicals were generally used without further purification. Perchloric acid was from BDH (catalogue number 10176) or Baker (9652). Hydrochloric acid was from BDH (10125) or Merck (319). Hydrobromic acid was from Baker (6010) or Merck (307). Sodium perchlorate was of own make¹ or from Fluka (71850) or Merck (6564). Sodium chloride was from Fisher (S-271) or Merck (6404). Sodium bromide was from Baker (0271). Platinum black was obtained from Engelhard Ind. It was purified by washing with 3 M HCl or HBr.¹

From these reagents, 3 M stock solutions were prepared with quartz-distilled water. The stock solutions were analyzed by argentometric or acidimetric titrations within 0.3 % (sodium perchlorate and sodium halide solutions after passage through a cation exchanger). The measuring solvents were made up by mixing appropriate volumes of these stock solutions.

Weighed amounts of platinum salts were dissolved in the various solvents. Sources of platinum(II) were: potassium chloroplatinate(II) K_2PtCl_4 (Degussa or Heraeus) and potassium bromoplatinate(II) $\text{K}_2\text{PtBr}_4 \cdot 2\text{H}_2\text{O}$ (Engelhard Ind., Degussa or Johnson and Matthey). Sources of platinum(IV) were: potassium chloroplatinate(IV) K_2PtCl_6 (Engelhard Ind.), potassium bromoplatinate(IV) K_2PtBr_6 (Heraeus or Johnson and Matthey) and "chloroplatinic acid" $\text{H}_2\text{PtCl}_6 \cdot \text{XH}_2\text{O}$ (BDH or Hopkins and Williams).

In the bromide series, potassium chloroplatinate(II) was used alternately with potassium bromoplatinate(II), since the latter compound is difficult to obtain in pure form. Due to the stronger complexation,⁴ the chloride in the platinate(II) was exchanged by bromide.

Most of the platinum solutions were analyzed on their contents of platinum(II) and platinum(IV) with a coulometric technique.^{1,45}

No differences could be detected between different preparations of the same chemical.

CALCULATIONS

Choice of standard state. In this work, the activity of a reacting species is commonly chosen to be equal to its concentration. This means, that the standard state of the species is a hypothetical solution of the species of unit

concentration, and the species shall have the same properties as if it had the concentration given in the solvent used.

For the hydrogen and halide ions, the actual concentrations in the solvent may be directly recalculated to 1 M. The platinum species studied are not parts of the solvents so the concentrations of these species should be extrapolated to zero to be strict. An extrapolation of this kind is shown in Fig. 1, Ref. 1. It can be seen that the presence of quite high concentrations of platinum salts have negligible influence on the equilibrium constant. In the platinum emf measurements the total concentration of platinum species was about 10 mM, so no extrapolation was considered necessary, but the concentrations of the platinum species were directly recalculated to 1 M. This definition of the standard state is the same as eqn. (5) of Ref. 3. For a definition of the standard emf in a specified solvent as used in Table 1, column C, see Ref. 3.

Equations used. The standard emf E_2° was calculated according to eqn. (2B). The logarithm of the equilibrium constant K was calculated according to eqn. (1B). They were found to vary slightly with the composition of the solvent. A good fit was obtained with the empirical eqn. (11).

$$A = \frac{[\text{H}^+][\text{ClO}_4^-]}{C_{\text{tot}}^2} A_{\text{HClO}_4} + \frac{[\text{H}^+][\text{X}^-]}{C_{\text{tot}}^2} A_{\text{HX}} + \\ + \frac{[\text{Na}^+][\text{ClO}_4^-]}{C_{\text{tot}}^2} A_{\text{NaClO}_4} + \frac{[\text{Na}^+][\text{X}^-]}{C_{\text{tot}}^2} A_{\text{NaX}} \quad (11)$$

A stands for the standard emf or logarithm of the equilibrium constant. A_{HClO_4} , A_{HX} , A_{NaClO_4} , and A_{NaX} are "corner values" corresponding to the values of the standard emf (or the logarithm of the equilibrium constant) in the "corner solvents" perchloric acid, hydrochloric (or hydrobromic) acid, sodium perchlorate, and sodium halide, respectively. C_{tot} is the total equivalent concentration as defined in Ref. 3, eqn. (1).

An equation analogous to eqn. (11) has been used previously in Ref. 3, eqn. (7). It is useful for describing an experimental quantity as a linear interpolation between the corresponding quantities of the "corner points".

In Table 1 the quantities of eqns. (1B–3B) are defined in terms of measured equilibrium concentrations and cell emf's. The quantities of eqns. (4B) and (9B) are obtained from other sources. For the remaining reactions formulas are given in Table 1 for calculation of the standard emf's.

Details of calculation. All concentrations were calculated and analyzed at room temperature. The volume expansion to 60°C has been neglected.

All the standard emf's (or logarithms of equilibrium constants) of a series were fitted to eqn. (11) by means of a computer programme, Letagrop Vrid.⁵⁻⁷ The programme determined the four "corner points" so that the error square sum $U = \sum (A_{\text{calc}} - A_{\text{meas}})^2$ was minimized. The programme also computed the standard deviation in each of these "corner points" and in the whole material.⁵

The bromide measurements at 60°C were statistically examined. Both the terms $(\log K_{\text{calc}} - \log K_{\text{meas}})$ for the agitating series and the terms $(E_{\text{calc}}^\circ - E_{\text{meas}}^\circ)$ for the emf series were tested by the Kolmogorov-Smirnov⁸ test and were found to follow the normal distribution on the 1% level. This means, that the standard deviations calculated

were good estimates for the real ones. Since the number of measurements was satisfactorily great, the confidence level approached the theoretical.

When two quantities were combined to yield a third quantity, the error of the calculated quantity was computed as the square root of the sum of the squares of the errors of the two underlying quantities. In eqns. (5B), (6B), (7B), and (10B), the error in the last term has to be multiplied by a submultiple of $(RT/F)\ln 10$.

Corrections of the concentrations of PtX_4^{2-} , PtX_6^{2-} , and X^- . During the agitating experiments, some platinum black dissolved through a foreign oxidation. Correction has been made for a corresponding decrease in the free halide ion concentration due to complex formation with the dissolved platinum.¹

Corrections due to dissociation of PtX_4^{2-} and PtX_6^{2-} ^{1,2} have been carried out only in the chloride system at 60°C. In the other measurements, the halide ion concentration was never below 0.1 M. The bromoplatinates are less dissociated than the chloroplatinates.^{4,10}

The final results given refer to $K_6^{IV} = 12 \times 10^{-3}$ M and $K_4^{II} = 21 \times 10^{-3}$ M.¹¹ A variation of K_6^{IV} between 0 and 30×10^{-3} M gave a variation of the corner point values well within their standard deviations. The influence of the appearance of Fig. 2, Ref. 1, was moderate.

The dissociation constant K_6^{IV} has been calculated from the emf measurements.² However, there was a calculation error. With Elding's recent¹¹ dissociation constant for $PtCl_4^{2-}$ a new calculation gave 12×10^{-3} M with the limits of error $(5 - 20) \times 10^{-3}$ M.

The determination of the dissociation constants from potentiometric redox measurements has been treated in some detail by Kravtsov *et al.*¹²

Table 2. Summary of the platinum and hydrogen³ measurements and some calculated quantities. *n* stands for the number of measurements of each corner point (see text). Δ is the error taken as twice the standard deviation calculated by the computer programme.

| System | Temp °C | Solvent (corner point) | Measured quantities | | | | | | | | | Calculated quantities | | | | | | | |
|----------|------------|------------------------------|-----------------------|---------|----------|------------------|------------|-------------|------------------------------------|------------|-------------|-----------------------|-------------|------------|-------------|------------|-------------|--|--|
| | | | Agitating experiments | | | Emf measurements | | | Hydrogen electrode measurements | | | | | | | | | | |
| | | | n | 3+log K | Δ | n | E_2^0/mV | Δ/mV | n | E_3^0/mV | Δ/mV | E_5^0/mV | Δ/mV | E_7^0/mV | Δ/mV | E_8^0/mV | Δ/mV | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | | |
| chloride | 25 | HClO ₄ | 6.8 | 1.88 | 0.26 | 3.0 | 503.9 | 2.00 | 12.2 | 186.3 | 0.22 | 537.0 | 7.9 | 520.5 | 4.3 | 690.2 | 2.01 | | |
| | | HX | 3.1 | 1.86 | 0.42 | 4.8 | 502.5 | 1.60 | 6.3 | 201.8 | 0.34 | 536.2 | 12.5 | 519.4 | 6.4 | 704.3 | 1.64 | | |
| | | NaClO ₄ | 4.1 | 2.20* | 0.29 | 2.8 | 512.3 | 2.20 | 9.3 | 205.5 | 0.26 | 536.0 | 8.8 | 524.1 | 4.8 | 717.8 | 2.22 | | |
| | | NaX | 1.0 | 2.20* | 0.29 | 2.4 | 511.2 | 2.40 | 6.1 | 213.4 | 0.32 | 534.9 | 8.8 | 523.0 | 4.9 | 724.6 | 2.42 | | |
| | | Total | 15 | | 0.60 | 13 | | 3.06 | 34 | | 0.69 | | | | | | | | |
| chloride | 60 | HClO ₄ | 34.0 | 1.30 | 0.07 | 9.7 | 523.1 | 0.62 | 3.0 | 158.6 | 0.90 | 579.2 | 2.4 | 551.2 | 1.3 | 681.7 | 1.09 | | |
| | | HX | 17.2 | 1.32 | 0.11 | 2.9 | 523.1 | 1.24 | 2.7 | 180.8 | 0.94 | 578.6 | 3.8 | 550.8 | 2.2 | 703.9 | 1.56 | | |
| | | NaClO ₄ | 20.4 | 1.64 | 0.09 | 3.6 | 528.9* | 0.88 | 5.4 | 175.9 | 0.62 | 574.8 | 3.0 | 551.9 | 1.7 | 704.8 | 1.08 | | |
| | | NaX | 10.3 | 1.59 | 0.13 | 0.9 | 528.9* | 0.88 | 1.9 | 190.7 | 1.18 | 575.5 | 4.3 | 552.2 | 2.3 | 719.6 | 1.47 | | |
| | | Total | 82 | | 0.34 | 17 | | 1.78 | 13 | | 1.32 | | | | | | | | |
| bromide | 25 | HClO ₄ | 10.7 | 0.14 | 0.05 | 6.7 | 542.2 | 0.64 | 7.0 | 28.6 | 0.44 | 626.8 | 1.6 | 584.5 | 1.0 | 570.8 | 0.78 | | |
| | | HX | 7.6 | 0.12 | 0.06 | 8.6 | 540.9 | 0.64 | 9.9 | 36.8 | 0.38 | 626.1 | 1.8 | 583.5 | 1.1 | 577.7 | 0.74 | | |
| | | NaClO ₄ | 7.8 | 0.30* | 0.05 | 6.3 | 548.3 | 0.64 | 4.6 | 50.8 | 0.54 | 628.2 | 1.5 | 588.2 | 0.9 | 599.1 | 0.84 | | |
| | | NaX | 1.9 | 0.30* | 0.05 | 12.3 | 547.5 | 0.48 | 9.5 | 51.1 | 0.38 | 627.4 | 1.4 | 587.4 | 0.8 | 598.6 | 0.61 | | |
| | | Total | 28 | | 0.14 | 34 | | 1.46 | 31 | | 1.14 | | | | | | | | |
| bromide | 60 | HClO ₄ | 10.1 | 0.30 | 0.07 | 6.7 | 557.2 | 0.56 | 6.0 | 3.5 | 0.66 | 646.4 | 2.3 | 601.8 | 1.2 | 560.7 | 0.87 | | |
| | | HX | 8.6 | 0.23 | 0.07 | 8.6 | 556.3 | 0.54 | 8.1 | 17.1 | 0.56 | 647.8 | 2.3 | 602.0 | 1.3 | 573.4 | 0.78 | | |
| | | NaClO ₄ | 14.8 | 0.41 | 0.06 | 6.3 | 563.7 | 0.54 | 6.6 | 24.2 | 0.64 | 649.2 | 1.9 | 606.5 | 1.1 | 587.9 | 0.84 | | |
| | | NaX | 6.5 | 0.39 | 0.09 | 11.3 | 562.2 | 0.44 | 7.3 | 30.2 | 0.60 | 648.4 | 3.1 | 605.3 | 1.6 | 592.4 | 0.74 | | |
| | | Total | 40 | | 0.18 | 33 | | 1.26 | 28 | | 1.58 | | | | | | | | |

* few measurements to separate these two corner points.

RESULTS

Survey of the measurements. All results of the measurements in 3 M media have been condensed in Table 2. The previously published^{1,2} results for the chloride system at 60°C have been recalculated and are included in Table 2. The measurements on hydrogen electrodes³ have also been included. Finally, Table 2 contains the calculated quantities E_5° , E_7° , and E_8° . The number of measurements (n) in Table 2 are non-integer numbers. This is because the total number of measurements within a series was divided between the "corner points" as in a previous paper.³

The errors given in Table 2 are twice the standard deviation delivered by the computer. For reasons given above, the real value of a constant is within the limits (calculated constant \pm error) with a confidence level approaching the theoretical, 95 %. It might be remarked that this reasoning is purely statistical and does not take systematic (unknown) errors into account.

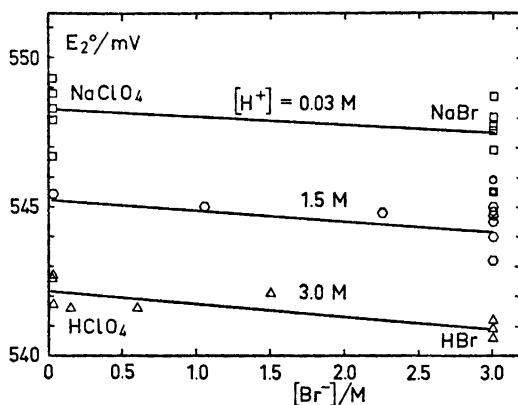


Fig. 1. Standard emf according to eqn. (2B) as a function of the bromide ion concentration. Temperature 25°C. The hydrogen ion concentration can be read from the point notations: \square , 0.03–0.15 M. \circ , 0.6 M. $\langle \rangle$, 1.5 M. \triangle , 3.0 M. The straight lines are calculated from eqn. (9)¹¹ with the corner values of Table 2.

One of the emf measuring series, the bromide system at 25°C, is shown in detail in Fig. 1. The straight lines illustrate the good fit between eqn. (11) and the measurements. These lines are calculated with the corner values of Table 2, column 8, and with three values of the hydrogen ion concentration used in the measurements.

In a few measuring series the quotient $[\text{PtBr}_6^{2-}]/[\text{PtBr}_4^{2-}]$ was varied. Nernst's law was found to be satisfied over an even greater interval than before.²

Fig. 2 gives emf measurements at varying total ionic strength of the solutions. The solutions contained bromoplatin(IV), bromoplatinate(II), and hydrobromic acid to a total ionic strength of 60 mM. Higher total ionic strengths were obtained by adding concentrated perchloric acid. The variations are seen to be small.

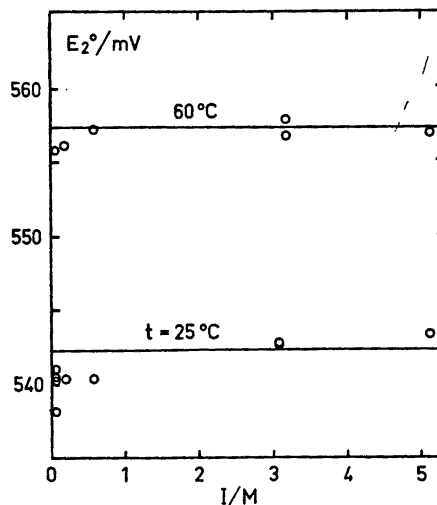


Fig. 2. Standard emf according to eqn. (2B) as a function of the ionic strength of the solution. The solution contained 5 mM PtBr_6^{2-} , 5 mM PtBr_4^{2-} , 30 mM HBr, and (except at the lowest ionic strength) HClO_4 to increase the ionic strength.

Attainment of equilibria. The establishment of a stable emf was faster in the bromide measurements than in the chloride measurements² at 60°C. The chloride measurements at 25°C were very time-consuming. The same trend will be found in the spread of the final emf values (*cf.* Table 2, column 9).

With respect to the *agitating experiments* the exchange with the metallic precipitate was faster in the bromide series than in the chloride.¹ After only a week, the metallic platinum was brightly shining. In the bromide measurements at 60°C, equilibrium seemed to be reached when the first tubes were opened, after 10 days, but the measurements were extended to 12 months. In the bromide measurements at 25°C the same equilibrium constant was found after 2, 6, and 12 months.

The equilibration was very slow in the chloride system at 25°C. Test tubes were opened after 4, 8, and 13 months. No systematic difference could be detected between the series of age 8 and 13 months, so equilibrium was judged to be attained. The values found from the test tubes of age 4 months invariably deviated from the equilibrium values towards the start condition of the solutions. These values were discarded.

The spread of the determined equilibrium constants was greater in the chloride measurements than in the bromide measurements (*cf.* Table 2, column 6).

INFLUENCE OF THE IONIC MEDIUM

Fig. 1 illustrates the change of the standard emf E_2° (eqn. (2B)) in the bromide system when the composition of the solvent was changed at constant total concentration. The linear slopes observed are

$$\frac{\partial E_2^\circ}{\partial [\text{Br}^-]} = -0.3 \text{ mV M}^{-1} \text{ and } \frac{\partial E_2^\circ}{\partial [\text{H}^+]} = -2 \text{ mV M}^{-1}$$

These slopes are typical for the standard emf E_2° , as can be easily verified from the corner values of Table 2, column, 8 both for the chloride and bromide system at both 25°C and 60°C. As has been pointed out before ^{2,3} these advantageously small slopes are due to the fact that the only dissolved species in the net cell reaction are PtX_6^{-2} and PtX_4^{2-} , occurring on either side of the reaction formula (*cf.* eqns. (2A) and (2B)). The medium effects may be formally expressed by the quotient of the activity coefficient $y_{\text{PtX}_6^{2-}}/y_{\text{PtX}_4^{2-}}$ (see eqn. (2C)).

For the sake of argument, let us study the cell $\text{Pt}(\text{H}_2)|\text{Solvent}, \text{PtX}_6^{2-}|\text{PtX}_4^{2-}|\text{Ir}$. The standard emf's of column 17 of Table 2 would result. The variations with the composition of the solvent amount to 30 mV and it would be very hard to draw any conclusions regarding the validity of Nernst's law, *i.e.* if the proposed cell reaction was actually determining the emf. Even if the values E_3° (column 11, Table 2) were at hand (this is most often not the case), so that the standard emf E_2° could be calculated, the errors would accumulate and the conclusions be doubtful. This example illustrates the importance of choosing a suitable reference electrode.³

The balance obtained of the medium effects is still more evident, when the total ionic strength of the solvent is changed. Compare Fig. 2 of this work with Fig. 4 of Ref. 3! This balance is also valid for the equilibrium constant K . An examination of the values of column 5 of Table 2 shows medium effects, expressed as emf's of

$$\frac{RT}{2F} \frac{\partial \ln K}{\partial [\text{X}^-]} = -0.5 \text{ mV M}^{-1} \text{ and}$$

$$\frac{RT}{2F} \frac{\partial \ln K}{\partial [\text{H}^+]} = -5 \text{ mV M}^{-1} \text{ as an average}$$

These slopes are close to the slopes of the standard emf E_2° . A discussion in terms of activity coefficients (eqns. (1C) and (2C)) gives the result that the medium effects of one ion PtX_4^{2-} is well counterbalanced by medium effects of two ions X^- .

Similarly, the calculated standard emf E_5° (eqns. (5B) and (5C)) does only vary a few mV, when the solvent is varied from edge to edge (Table 2, column 13). The balance of the medium effects is obtained between two singly charged anions X^- and one doubly charged anion PtX_4^{2-} . In the same manner, the values of the standard emf E_7° varies but slightly (Table 2, column 15). This reasoning implies, that the stability constant β_4^{II} , involving six ionic species of different charge types, ought to be sensitive to medium effects (eqn. (4C)).

It must be remarked, that the concept of activity coefficients is purely formal. It gives an account of the fact, that the species of the reaction under study are influenced by the surrounding solvent atmosphere, but it is not possible to split the effect between the different ionic species. Anyway, it is easy to treat the ions individually, and the results are generally reasonable, as shown above.

Throughout this work the measurements have been described by major chemical effects, obeying equilibrium equations, and minor rest effects, labelled "medium effects". It is, however, possible that these minor effects are also chemical. For example, the platinum measurements depend on the hydrogen ion concentration. By introducing a new species HPtX_6^- with a stability constant of 0.2 M^{-1} (both for the chloride and bromide systems), the medium effect can be entirely eliminated. It is difficult to reach a positive conclusion regarding this strong acid. In the hydrogen electrode measurements chemical explanations will be still more difficult, so the minor effects have been treated as medium effects in this work.

ESTIMATION OF THE STANDARD POTENTIALS E_6° AND E_{10}°

These standard potentials are hypothetical only, since the hydrated ions Pt^{2+} and Pt^{4+} are subject to hydrolysis, but they are useful for a quantitative description of the system.

Since values for the total stability constants β_4^{II} and β_6^{IV} are available only in the solvent 0.5 M perchloric acid, all data given under this heading refer to that solvent. The values used and the results obtained are summarized in Table 3.

Table 3. Calculation of the standard potential E_6° of the couple Pt^{2+}/Pt and E_{10}° of the couple Pt^{4+}/Pt . Solvent: 0.5 M perchloric acid.

| System | Temp. °C | E_3°/mV | $\frac{\beta_4^{\text{II}}}{\text{M}^{-4}}$ | E_5°/mV | E_6°/mV | $\frac{\beta_6^{\text{IV}}}{\text{M}^{-6}}$ | E_7°/mV | E_{10}°/mV |
|----------|-------------|-----------------------|---|-----------------------|-----------------------|---|-----------------------|--------------------------|
| Chloride | 25 | 234 | 6×10^{13} | 537 | 1178 | | | |
| Bromide | 25 | 78 | 2×10^{16} | 627 | 1186 | 10^{33} | 585 | 1152 |
| Chloride | 60 | 211 | 1×10^{13} | 577 | 1218 | | | |
| Bromide | 60 | 63 | 2×10^{15} | 658 | 1217 | | | |

Values of the standard emf E_3° in 0.5 M perchloric acid have been estimated from literature.^{3,13-17} The only direct measurements are by Murdoch and Barton¹³ on hydrochloric acid-perchloric acid mixture at 25°C. These and measurements at higher perchloric acid concentrations^{3,13,14} are lower than similar measurements in pure hydrochloric¹⁵ or hydrobromic^{16,17} acid, and the values in Table 3 are estimated from measurements in 0.5 M hydrochloric or hydrobromic acid.

The standard potential E_6° of the couple Pt^{2+}/Pt . The values of E_5° are mean values from Table 2, column 13. It seems reasonable that the change of the 3 M solvents to 0.5 M perchloric acid gives rise to negligible medium effects.

Elding^{11,18,19} has measured the three first stepwise constants for the dissociation of PtCl_4^{2-} at both 25°C and 60°C. He observed the quotient between the stepwise constants to be about 10 and estimated the value of the last dissociation constant and could then calculate the total stability constant β_4^{II} .

Elding's measurements of the first dissociation constants of the bromide system²⁰ are less accurate, presumably due to disproportionation of PtBr_4^{2-} .

Martin and Dunning⁴ have measured the stability constant for the replacement of the four chloride ions in tetrachloroplatinate(II) by bromide ions by a radiometric procedure in 0.318 M NaClO₄ and found the value 395 at 25°C. From this value and Elding's¹¹ value for β_4^{II} in the chloride system, β_4^{II} for the bromide system has been calculated.¹¹ The result is in general agreement with Elding's²⁰ measurements. From the observed temperature dependence,²⁰ a value for β_4^{II} in the bromide system at 60°C has been estimated. The agreement between the calculated values of E_6° is good. The limit of error is probably determined by β_4^{II} and is estimated as 1.18 ± 0.03 V at 25°C and 1.22 ± 0.05 V at 60°C (2σ). This compares favourably with Latimer's²¹ value of 1.2 V at zero ionic strength, founded on rough measurements²² and estimates.

The standard potential E_{10}° of the couple Pt^{4+}/Pt . Elding and Gustafson²³ have measured the constants for three of the stepwise dissociations of PtBr_6^{2-} at 25°C in 0.5 M HClO₄. The values are: $K_6^{\text{IV}} = (5.3 \pm 0.3) \times 10^{-4}$ M; $K_5^{\text{IV}} = (0.97 \pm 0.15) \times 10^{-4}$ M; $K_4^{\text{IV}} = (0.9 \pm 0.1) \times 10^{-5}$ M. The limits of error given are estimates of 1σ .

The quotient between K_6^{IV} and K_5^{IV} is 5 and between K_5^{IV} and K_4^{IV} 10. Under the assumption that the quotient between consecutive stepwise dissociation constants is 5, β_6^{IV} (eqn. (9B)) may be calculated to be 2×10^{30} M⁻⁶. If the quotient is 10, $\beta_6^{\text{IV}} = 2 \times 10^{33}$ M⁻⁶. $\log \beta_6^{\text{VI}}$ may be estimated as 33 ± 5 (2σ).

The standard potential E_{10}° is calculated (eqn. (10B)); see Table 3. The limits of error are given by the error in β_6^{IV} : $E_{10}^\circ = 1150 \pm 70$ mV (2σ).

A direct comparison can be made between the β_6^{IV} values of the bromide and chloride systems (*cf.* eqn. (10B));

$$\log \frac{\beta_{6\text{Br}}^{\text{IV}}}{\beta_{6\text{Cl}}^{\text{IV}}} = (521 - 585 + 234 - 78) \times 4/59.2 = 5.3 \pm 0.5 \quad (2\sigma)$$

COMPARISON WITH LITERATURE VALUES

Measurements on the couple $\text{PtX}_6^{2-}/\text{PtX}_4^{2-}$. Many measurements on this couple were found and are compiled in Table 4. All authors but one have given their final result as a standard potential *versus* the normal hydrogen electrode (NHE). The results may be read in column 12.

It is immediately seen that the different values seriously disagree. Latimer's²¹ value is especially far away from the others. Several reasons for the disagreement are obvious. Temperature and solvent are unlike. Liquid junction potentials are large in cases where the reference electrode and the rest of the cell contained different solutions. Grube and Reinhardt³¹ have used a reference electrode at 18°C, while the remaining part of the measuring cell was at 60°C. Some authors have tried to recalculate their results to zero ionic strength. Column 9 allows a more stringent comparison to be done. In this column primary values were picked out which have been obtained with the same solvent in the whole cell and with calomel reference electrodes. The agreement is seen to be good. The values of column 10 have been recalculated *versus* the silver/silver chloride electrode and agree well with our results.

Table 4. Survey of measurements found in literature on the couple PtX_8^{2-}/PtX_6^{2-} .

| System | T_{meas} °C | Reference | Electrode | [X ⁻]/M | Solvent | Reference electrode | Standard emf of cells without liquid junction Solvent | E°/mV vs Hg_2Cl_2 vs AgCl | Stated value of the standard potential Stated at ionic strength | | | |
|----------|----------------------------|-------------------------------|--|-----------------------------------|-----------------------------------|---------------------------|---|---|--|---------------|-----|-----|
| | | | | | | | 8 | 9 | 10 | 11 | 12 | |
| Chloride | 25 | Miller et al. ²⁴ | Platinized glass | 0.005-1 | 0.005-1 M NaCl | Hg_2Cl_2 , 1 M NaCl | 1 M NaCl | 461.3 | 506.9 | 0 | 721 | |
| | 35 | Smith ²⁵ | Platinized glass | 0.1 | 0.1 M KCl | Hg_2Cl_2 , 0.1 M KCl | 0.1 M KCl | 457.3 | 506.3 | | | |
| | 50 | Stelling ²⁶ | Pt-sheet | 2.5 | 2.5 M HCl | Hg_2Cl_2 , 1 M KCl 25°C | | | | 0 | 740 | |
| | 20 | Grinberg et al. ²⁷ | Pt-sheet, Au-sheet Pt-glass, Ir-sheet | 1 | 1 M NaCl | Hg_2Cl_2 , sat. KCl | | | | 1 M | 756 | |
| | 25 | " | " | 1 | " | " | | | | " | 758 | |
| | 30 | " | " | 1 | " | " | | | | " | 764 | |
| | 35 | " | " | 1 | " | " | | | | " | 767 | |
| | 40 | " | " | 1 | " | " | | | | " | 770 | |
| | 25 | " | " | 1 | 1 M HCl | " | | | | 1 M | 726 | |
| | 25 | Kravtsov et al. ²⁸ | Pt-sheet | 0.01-1 | 3 M H_2SO_4 | Hg_2Cl_2 , sat. NaCl | | | | 3 M H_2SO_4 | 708 | |
| | 35 | Yamamoto et al. ²⁹ | Graphite rod | 0.04-1 | 0.1-1 M HCl | Hg_2Cl_2 , 1 M HCl | | | | | 730 | |
| | 35 | " | " | 1 | 1 M HCl | Hg_2Cl_2 , 1 M HCl | | 1 M HCl | 459.2 | 508.2 | 730 | |
| 70 | " | " | 1 | " | " | | | | | 747 | | |
| 90 | " | " | 1 | " | " | | | | | 757 | | |
| 60 | Grube et al. ³¹ | Pt-sheet, Ir-sheet | 0.4-7.5 | 0.4-7.5 M HCl | Hg_2Cl_2 , sat. KCl 18°C | | | | | 0 | 745 | |
| - | Latimer ²¹ | " | | | | | | | | | 680 | |
| 25 | This work | Pt-sheet, Ir-glass | 0.03-3 | 3 M(H, Na)(Cl, ClO ₄) | AgCl, solvent | | | table 2, column 8 | 0 | 0 | 726 | |
| 60 | " | " | 0.03-3 | " | " | | | " | " | 0 | 718 | |
| Bromide | 25 | Grinberg et al. ²⁷ | Pt-sheet, Au-sheet | 1 | 1 M NaBr | Hg_2Cl_2 , sat. KCl | | | | 1 M | 643 | |
| | 25 | Kravtsov et al. ²⁸ | Pt-wire | 1 | 1 M NaBr, 3 M H_2SO_4 | " | | | | 3 M H_2SO_4 | 581 | |
| | - | Latimer ²¹ | " | | | | | | | | 590 | |
| | 25 | This work | Pt-sheet, Ir-glass | 0.03-3 | 3 M(H, Na)(Br, ClO ₄) | AgBr, solvent | | | table 2, column 8 | 0 | 0 | 613 |
| | 60 | This work | " | 0.03-3 | " | " | | | " | " | 0 | 608 |

The difference between the calomel and silver/silver chloride electrodes has been calculated from their E° values from Ives and Janz' book.³³ The difference is independent of the chloride ion concentration.

Rough values of the standard potential E_8° have been calculated from the measurements of this work. It has been assumed that the standard emf $E_{2,aq}^{\circ}$

Table 5. Survey of literature values for the standard potentials of the couples $\text{PtX}_4^{2-}/\text{Pt}$, $\text{PtX}_6^{2-}/\text{Pt}$ (and $\text{PtX}_6^{2-}/\text{PtX}_4^{2-}$).

| System | Temp. °C | Reference | Solvent | Standard potentials at infinite dilution (mV vs NHE) | | |
|----------|-------------|-----------|-----------------------------------|--|---------------------------------------|---------------------------------------|
| | | | | $\frac{\text{PtX}_6^{2-}}{\text{PtX}_4^{2-}}$ | $\frac{\text{PtX}_4^{2-}}{\text{Pt}}$ | $\frac{\text{PtX}_6^{2-}}{\text{Pt}}$ |
| Chloride | 25 | 22 | Sat. K_2PtCl_4 | | 720 | |
| | 60 | 31 | 0.4–7.5 M HCl | 745 | 785 | 765 |
| | 18 | 34 | 1 M NaNO_3 , var. KCl | | 716 ^a | |
| | 35 | 30 | 1 M HCl | 730 | 749 | |
| | 70 | 30 | 1 M HCl | 747 | 768 | |
| | 90 | 30 | 1 M HCl | 757 | 778 | |
| | — | 21 | | 680 | 730 | |
| | — | 35 | | 770 | 750 | 760 |
| | 25 | This work | 3 M (H, Na) (Cl, ClO_4) | 726 | 758 | 744 |
| | 60 | This work | 3 M (H, Na) (Cl, ClO_4) | 718 | 767 | 747 |
| Bromide | 18 | 34 | 1 M NaNO_3 , var. KBr | | 608* | |
| | — | 21 | | 590 | 580 | |
| | — | 35 | | 640 | 670 | 660 |
| | 25 | This work | 3 M (H, Na) (Br, ClO_4) | 613 | 698 | 657 |
| | 60 | This work | 3 M (H, Na) (Br, ClO_4) | 608 | 697 | 653 |

^a Calculated directly from the measurements in the reference.

at infinite dilution equals the values found in perchloric acid (*cf.* Fig. 2). After addition of $E_{3,\text{aq}}^\circ$ values³ (that is, standard potentials for the silver/silver halide electrodes), the values given in Table 4, column 12, resulted.

Measurements on the couples $\text{PtX}_4^{2-}/\text{Pt}$ and $\text{PtX}_6^{2-}/\text{Pt}$. Only a few measurements on these couples were found^{22,30,31,34} and are compiled in Table 5 together with data chosen by Latimer²¹ and by Goldberg and Hepler³⁵ in a recent review and together with results from this work. All data are given at infinite dilution in water and with the normal hydrogen electrode as a reference.

The earlier experimental foundation for these standard potentials is rather meagre. Latimer²¹ has used only the very rough measurements of Lorenz and Spielmann.²² Grube and Reinhardt³¹ have used the same approach as in this work, but their experimental tools and calculations were rather crude.²

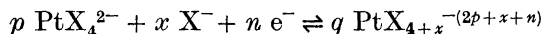
The method of Yamamoto *et al.*³⁰ is interesting. They titrated a solution containing PtCl_6^{2-} with tin(II) potentiometrically and obtained a titration curve with two S-formed regions. The first region was described as the reduction of platinum(IV) to platinum(II). The other region would describe the reaction of platinum(II) to platinum(0). The standard potentials calculated both agree well with the results of this work (*cf.* Table 5). This seems promising since it indicates that there might exist a possibility of establishing a rapid equilibrium platinum(II)-platinum(0) which is normally very slow. The reason might be that Yamamoto and co-workers measured their emf's when the reduced platinum was still very finely divided and active enough to produce almost immediate equilibration with platinum(II) in the solution.

In a series of investigations^{34,36-38} Grinberg and his coworkers have attempted to measure the concentration of the hydrated ion Pt^{2+} directly with "active" platinized platinum electrodes. From these measurements, they calculated the total stability constants for platinum(II) with many ligands after introduction of Latimers²¹ standard potential for the couple Pt^{2+}/Pt .

Most probably, their measurements are strongly influenced by other redox couples in the solution, for example $\text{PtX}_4^{2-}/\text{PtX}_6^{2-}$. As shown in this work, this couple has the ability to establish a defined emf even for small concentrations of PtX_6^{2-} , whereas the exchange with the metallic platinum is very slow.

Grinberg *et al.*³⁹ have carried out dissolution experiments on a neutron activated platinum sheet. The exchange rate found was much smaller than the exchange rate of the $\text{PtX}_4^{2-}/\text{PtX}_6^{2-}$ couple.^{28,40,41} In addition, a great deal of the radioactivity in Grinberg's solutions may be due to ^{199}Au .⁴²

The present author has further analyzed the primary emf values of Grinberg and coworkers.^{34,36,37} A general platinum electrode redox reaction has been used:



The standard potential and its standard deviation (1σ) have been calculated for chemically possible values of the stoichiometric coefficients x , n , and q . The stoichiometric coefficient p has been taken equal to unity. The concentration of the platinum species $\text{PtX}_{4+x}^{-(2p+x+n)}$ has been assumed to be proportional to the concentration of the species PtX_4^{2-} . The results of calculations on the PtCl_4^{2-} measurements,³⁴ which are typical, are shown in Table 6. The spread is seen to be severe. There is no electrode reaction giving

Table 6. Treatment of Grinberg's³⁴ measurements of the proposed couple $\text{PtCl}_4^{2-}/\text{Pt}$. The numbers in the body of the table are calculated standard potentials (mV) together with their standard deviations (1σ). In the calculations, different values of the stoichiometric coefficients q , n , and x have been used.

| q | n | -4 | -3 | -2 | x -1 | 0 | 1 | 2 |
|-----|-----|-----------|----------|----------|-----------|----------|----------|-----------------------|
| 0 | -4 | 691 ± 48 | 685 ± 44 | 680 ± 40 | 674 ± 36 | 668 ± 32 | 662 ± 29 | 656 ± 26 |
| 0 | -3 | 688 ± 54 | 681 ± 48 | 673 ± 43 | 665 ± 37 | 658 ± 33 | 650 ± 28 | 642 ± 25 |
| 0 | -2 | 683 ± 65 | 671 ± 56 | 660 ± 48 | 648 ± 41 | 637 ± 34 | 625 ± 30 | 614 ± 28 |
| 0 | -1 | 666 ± 99 | 643 ± 82 | 620 ± 66 | 597 ± 53 | 574 ± 45 | 551 ± 44 | 528 ± 51 |
| 0 | 1 | 733 ± 42 | 756 ± 31 | 779 ± 29 | 802 ± 39 | 825 ± 54 | 848 ± 71 | 871 ± 89 |
| 0 | 2 | 716 ± 16 | 728 ± 18 | 739 ± 24 | 751 ± 32 | 762 ± 40 | 774 ± 50 | 785 ± 59 |
| | | a | | | | | | |
| 1 | -4 | 723 ± 50 | 717 ± 46 | 711 ± 41 | 705 ± 37 | 699 ± 33 | 694 ± 28 | 688 ± 25 |
| 1 | -3 | 730 ± 57 | 723 ± 50 | 715 ± 44 | 707 ± 38 | 699 ± 33 | 692 ± 27 | 684 ± 22 |
| 1 | -2 | 746 ± 69 | 734 ± 60 | 723 ± 50 | 711 ± 41 | 699 ± 33 | 688 ± 25 | 676 ± 18 ^b |
| 1 | -1 | 792 ± 107 | 769 ± 88 | 746 ± 69 | 723 ± 50 | 699 ± 33 | 676 ± 18 | 653 ± 19 |
| 1 | 1 | 607 ± 51 | 630 ± 33 | 653 ± 19 | 676 ± 18 | 699 ± 33 | 723 ± 50 | 746 ± 69 |
| 1 | 2 | 653 ± 19 | 665 ± 16 | 676 ± 18 | 688 ± 25 | 699 ± 33 | 711 ± 41 | 723 ± 50 |

^a Grinberg's proposed reaction: $\text{PtX}_4^{2-} + 2\text{e}^- \rightleftharpoons \text{Pt} + 4\text{X}^-$.

^b The chemically more probable reaction: $\text{PtX}_4^{2-} + 2\text{X}^- \rightleftharpoons \text{PtX}_6^{2-} + 2\text{e}^-$.

significantly lower standard deviation of the standard potential than any other. A simple F-test shows that the standard deviation must be greater than 30 mV to make it possible to reject that electrode reaction with 95 % confidence, as compared with the electrode reactions having the smallest standard deviations (16 mV). There are 23 such reactions.

The calculated standard potentials for the $\text{PtX}_6^{2-}/\text{PtX}_4^{2-}$ cell reactions^{34,36-37} are about 90 mV lower than the literature values. This gives the not unlikely value 10^{-3} for the quotient $[\text{PtX}_6^{2-}]/[\text{PtX}_4^{2-}]$. The same reasons as above apply to the measurements of Lorenz and Spielmann.²²

CONCLUSIONS

It has been shown, that consistent equilibrium values are obtained by using solvents of constant ionic strength, cells without liquid junction, and a suitable reference electrode. The values given in Tables 2 and 3 are regarded as the final results of this work. The data given can be used in other similar solvents. This is evident from Fig. 2 and the good agreement between the few primary literature values to be found in Table 4, column 10, and the data of Table 2, column 8.

The extrapolation of measurement from one solvent to another similar solvent is thus possible, with one particular exception: pure water. At low concentrations, the measurements are not reliable and the medium effects are large. Thus, the estimated values in Table 4, column 12, and in Table 5 are given for comparison purposes only.

Martin⁴ and Dunning have measured the exchange of Cl^- against Br^- in PtCl_4^{2-} and found a quotient of 395 (*cf.* p. 1536). The same quotient may be calculated from the E_3° and E_5° values of this work and the value, 170, is in fair agreement. Thus, the chloride and bromide measurements are consistent.

With the same methods as in this work, good values of β_4^{II} may be determined for other systems. At the same time β_6^{IV} values are obtained. These are founded on the crude value of β_6^{IV} for PtBr_6^{2-} and are accordingly uncertain. Quotients between β_6^{IV} -values are, however, more reliable.

It is not possible to find any evidence for dimeric platinum complexes from the rather crude measurements. This is in accord with a paper of Martin *et al.*⁴⁴ At 50 mM total concentration of bromoplatinate(II), the concentration of $\text{Pt}_2\text{Br}_6^{2-}$ was less than 2 % of the total concentration.

The measurements have shown that the chloroplatinate(II) ion is not thermodynamically stable but disproportionates to platinum black and chloroplatinate(IV) ions to an extent dependent upon the equilibrium constant K , the chloride ion concentration, and the total concentration of platinum. This is illustrated in Fig. 3, Ref. 1. The bromoplatinate(II) ion is still more liable to disproportionation, since the equilibrium constant K is about $2 \times 10^{-3} \text{ M}^{-1}$. The disappearance of the bromoplatinate(II) is also enhanced by the higher reaction rates, compared with the chloride system. Nevertheless, solutions of bromoplatinate(II) can be conditionally stable, if catalysts, particularly platinum black, are absent.

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