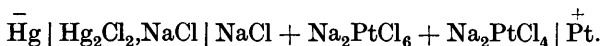## XCII.—*The Platini-Platino-chloride Electrode. A New Type of Chlorine Electrode.*

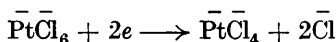By Virginia F. Miller and Henry Terrey.

An inert electrode in a solution of sodium chloroplatinate and sodium chloroplatinite acquires a definite potential. The mechanism of the electrode differs from that of the usual oxidation-reduction type in that there is no change in valency. Measured against a calomel electrode, the platinum of the platini-platino electrode is positive to the mercury. The cell reaction is expressed by

$$2Hg + Na_2PtCl_6 \longrightarrow 2HgCl + Na_2PtCl_4 \quad . \quad . \quad (1)$$

the current passing from left to right inside the cell :

$$\overset{-}{Hg} \mid Hg_2Cl_2,NaCl \mid NaCl + Na_2PtCl_6 + Na_2PtCl_4 \mid \overset{+}{Pt}.$$

The electrode reaction is

$$\overline{Pt}\overline{Cl}_6 + 2e \longrightarrow \overline{Pt}\overline{Cl}_4 + 2\overline{Cl}$$

and the *E.M.F.* is given by

$$E = E_0 + RT/2F \cdot \log [\overline{Pt}\overline{Cl}_6]/[\overline{Pt}\overline{Cl}_4][\overline{Cl}]^2,$$

or, more exactly, by

$$E = E_0 + RT/2F \cdot \log a_i/a_o a^2_{Cl} \quad . \quad . \quad . \quad . \quad (2)$$

where a_i, a_o, and a_{Cl} are the activities of the chloroplatinate, the chloroplatinite, and the sodium chloride, respectively.

To test the above relationship, two series of measurements were carried out. In the first, the chloride concentration was kept constant and the $i : o$ ratio varied. In the second, this ratio was constant and the chloride concentration varied. (Here, i and o represent the total concentrations of chloroplatinate and chloro-platinite, respectively.)

The values of E_0 calculated according to the above expression for the two series of measurements are given in Table I (full data in Tables II and III). Since the concentration of sodium chloride is much higher than those of the platinum salts, the ratio of the activities of the latter was assumed to be equal to the ratio of their concentrations, i.e., $a_i/a_o = i/o$. The activity of the chlorine ion was taken to be the same as in the corresponding sodium chloride solution.

TABLE I.

Series I.			Series II.		
$i : o$ ratio.	NaCl (mols./litre).	E_0 (volts).	$i : o$ ratio.	NaCl (mols./litre).	E_0 (volts).
0·5804	1	0·7191	1·4642	1·0000	0·7202
0·9199	,,	0·7217	,,	0·7000	0·7184
1·4642	,,	0·7202	,,	0·5000	0·7176
2·0441	,,	0·7211	,,	0·2000	0·7173
2·9282	,,	0·7206	,,	0·1000	0·7165
5·3773	,,	0·7210	,,	0·0500	0·7143
11·8033	,,	0·7213	,,	0·0100	0·7060
29·5633	,,	0·7211	,,	0·0048	0·6985

It will be seen that with constant sodium chloride concentration a satisfactorily constant value for E_0 is obtained. The value, however, changes slightly with change in the sodium chloride environment. This suggests that the ratio of the activities of the chloro-platinate and -platinite ions is not independent of the surroundings and that this ratio should be expressed as a function of the sodium chloride concentration, i.e., $a_i/a_o = K . i/o$, where K is a function of the ionic strength of the sodium chloride * solution. When K is constant, this leads to the expression

$$E = (E_0 + RT/2F . \log K) + RT/2F . \log (i/o) - RT/F . \log a_{Cl}. \quad . \quad . \quad . \quad (3)$$

the given values of E_0 in Series I being really values of

$$(E_0 + RT/2F . \log K),$$

where K corresponds to M-sodium chloride solution.

* At low concentrations of sodium chloride it would possibly be preferable to use the total ionic strength of the solution instead of that of the sodium chloride alone.

If the values of E in Series II are plotted against a_{Cl}, a straight line is obtained for the first six values. A straight line would result if log K were itself a linear function of log a_{Cl}, i.e., if log $K = \alpha + \beta$ log a_{Cl}, where α and β are constants.

Making this assumption, we have

$$E = E_0 + RT/2F.(\beta - 2)\log a_{Cl} + RT/2F.\log i/o + RT/2F.\log \alpha$$

or $E = (E_0 + C) + RT/2F.(\beta - 2)\log a_{Cl} + RT/2F.\log i/o$ (4)

where C is an undetermined constant which cannot be evaluated until the nature of K is known. As will be seen later, this expression gives a satisfactorily constant value for $(E_0 + C)$.

Experimental.

The sodium chloroplatinate was obtained by dissolving platinic chloride in sodium chloride and crystallising the hexahydrate. The chloroplatinite was made by converting platinum tetrachloride into dichloride by heating at 350° and dissolving the residue in hydrochloric acid. This solution was neutralised with barium carbonate, and on evaporation gave dark red crystals of $BaPtCl_4,3H_2O$, contaminated with a little barium chloride. Treatment of this salt with sodium sulphate gave the corresponding sodium salt; owing to its high solubility it was impossible to purify it by crystallisation (Found : H_2O, 12·11; NaCl, 8·01; Na_2PtCl_4, 79·88%). Since, however, sodium chloride was used as the electrolyte, the removal of the small amount present as impurity was unnecessary. In making up the solutions the sodium chloroplatinite was weighed anhydrous. Except for solutions 6, 7, and 8 of the first series and for the more concentrated platinum solutions, the electrode mixtures were made by adding 3—10 c.c. of a stock solution to the required amount of sodium chloride and then diluting to 25 c.c. Solutions 6, 7, and 8 were made by taking weighed amounts of the two salts.

The Cell.—The electrode vessels were of the type commonly used for single electrodes, with a tap sealed in the connecting tube to prevent diffusion. The electrode was measured against a normal calomel electrode containing sodium chloride instead of potassium chloride. Platinised glass was found to be the most suitable form of electrode, equilibrium being established after about 24 hours. The cells were measured at 25°, an air thermostat being used to control the temperature. The measuring apparatus consisted of a Pye potentiometer, a Cambridge Instrument Company moving-coil galvanometer, and a Cambridge standard cadmium cell.

Results.

After attainment of equilibrium, readings varied by less than 0·1 millivolt over a period of several hours, except in the case of the 0·2N-sodium chloride solution, where the variation from the mean over 6 hours was 0·6 millivolt. The values were tested for reproducibility. For solution 8 of the first series, the first sample gave a mean value of 0·5057, with no variation in the readings in 8 hours after attainment of equilibrium; the second sample gave a mean value of 0·5057, the readings varying from 0·5056 to 0·5058.

The effect of change in the values of i and o with a constant ratio between them was as follows, the sodium chloride concentration being N.

i (mol./litre).	o (mol./litre).	$i : o$.	$E.M.F.$ of cell.
(a) 0·005548	0·009559	0·580	0·4549
(b) 0·0005548	0·0009559	0·580	0·4532

A solution with concentrations one-tenth of those in (b) did not give constant readings.

Table II gives the results of the first series of readings in N-sodium chloride solution. The value used for the calomel electrode potential was 0·2731 volt. Table III gives the results of the second series of measurements, in which a liquid potential was introduced between the connecting liquid and the electrode solution, diminishing the $E.M.F.$ measured. This potential was calculated from the relationship

$$E_L F = (n_k - n_a)RT \log C_1\alpha_1/C_2\alpha_2$$

where E_L is the liquid potential, n_k and n_a are the transport numbers of the kation and anion, respectively, and α_1 and α_2 are the activity coefficients of the sodium chloride solutions.

The calculation of β in equation (4) was carried out by taking the values of E found in experiments 2 and 6 (Table III), whence, by subtraction,

$$(E_2 - E_6) = RT/2F \cdot (\beta - 2)[\log (a_{Cl})_6 - \log (a_{Cl})_2]$$

and hence $\beta = 0·1317$.

The Effect of Temperature on the E.M.F. of the Electrode.

The potentials of solutions 6 and 7 of the first series were measured at 21°, 25°, and 30°, with the following results :

$i : o$.	$E.M.F.$ (volt) of electrode.		
	21°	25°	30°
(6) 5·3773	0·7532	0·7537	0·7537
(7) 11·8033	0·7627	0·7641	0·7642

TABLE II.

Cell $\overline{\text{Hg}}$ | Hg_2Cl_2, N-NaCl | N-NaCl + Na_2PtCl_6 + $\text{Na}_2\overset{+}{\text{PtCl}_4}$ | Pt. Temperature 25°.

($a_{\text{Cl}} = 0\cdot650$.)

No.	$i \times 10^3$ (mols./litre).	$o \times 10^3$ (mols./litre).	$\dfrac{i}{o}$	E.M.F. cell.	E.M.F. electrode, E.	$\dfrac{RT}{2F}(\beta-2)\log a_{\text{Cl}}$	$\dfrac{RT}{2F}\log\dfrac{i}{o}$	$E_0 + C$.
1	0·5548	0·9559	0·5804	0·4532	0·7232	0·01035	−0·0070	0·7199
2	0·9187	0·9987	0·9199	0·4617	0·7317	0·01035	−0·0011	0·7225
3	1·4623	0·9987	1·4642	0·4662	0·7362	0·01035	0·0049	0·7209
4	2·041	0·9987	2·0441	0·4714	0·7414	0·01035	0·0092	0·7218
5	2·9243	0·9986	2·9282	0·4751	0·7455	0·01035	0·0138	0·7213
6	5·3703	0·9987	5·3773	0·4837	0·7537	0·01035	0·02163	0·7218
7	11·789	0·9987	11·8033	0·4941	0·7641	0·01035	0·0317	0·7220
8	29·524	0·9987	29·5633	0·5057	0·7757	0·01035	0·0436	0·7218

Mean 0·7215

TABLE III.

$i : o = \text{constant} = 1\cdot4642.$ Temperature 25°.

Cell $\overline{\text{Hg}}$ | Hg_2Cl_2, N-NaCl | xNaCl + 0·001462 Na_2PtCl_6 + 0·0009987 $\text{Na}_2\overset{+}{\text{PtCl}_4}$ | Pt.

NaCl (mols./litre).	a_{NaCl}.	a_{Cl}.	E.M.F. cell.	E.M.F. electrode, E_1.	Liquid potential, E_2.	$E_1 + E_2$ (E).	$\dfrac{RT}{2F}(\beta-2)\log a_{\text{Cl}}$	$\dfrac{RT}{2F}\log\dfrac{i}{o}$	$E_0 + C$.
1·0000	0·650	0·650	0·46615	0·7362	0·0000	0·7362	0·01035	0·0049	0·7209
0·7000	0·673	0·471	0·47099	0·7410	0·0016	0·7426	0·0181	0·0049	0·7196
0·5000	0·689	0·344	0·47665	0·7467	0·0032	0·7499	0·0256	0·0049	0·7194
0·2000	0·752	0·150	0·49353	0·7635	0·0073	0·7707	0·0455	0·0049	0·7203
0·1000	0·798	0·0798	0·50580	0·7758	0·0105	0·7863	0·0602	0·0049	0·7213
0·0500	0·842	0·0421	0·51694	0·7869	0·0137	0·8006	0·0761	0·0049	0·7196
0·0100	0·922	0·00922	0·5400	0·8100	0·0213	0·8313	0·1126	0·0049	[0·7138]
0·00479	0·940	0·00450	0·5473	0·8173	0·0250	0·8423	0·1298	0·0049	[0·7076]

Mean 0·7202

*In the first series $dE/dT = 0.000033$; in the second $dE/dT = 0.000084$. At 25° the $E.M.F.$ of the cell is 0.4837 and 0.4941 in the two series. Applying the Gibbs–Helmholtz equation, $nFE - Q = nFT dE/dT$ (where Q is the heat evolved in the cell-reaction at constant temperature and pressure), to these data we obtain

$$Q = 21,830 \text{ cals. from 1st series}$$
$$21,610 \quad ,, \quad ,, \text{ 2nd } ,,$$

The heat of formation of $2HgCl = 62,600$ cals. and thus the heat of formation of Na_2PtCl_6 from Na_2PtCl_4 and Cl_2 is seen from the equation (1) for the cell-reaction to be 40,770 cals. (1st series), 40,990 cals. (2nd series). We may compare this value with that of Thomsen from direct heat measurement, $viz.$, 42,000 cals.

Summary.

The potential of the platini-platino-chloride electrode has been measured. The $E.M.F.$ varies according to the equation

$$E = (E_0 + C) + RT/2F \cdot (\beta - 2) \log a_{Cl} + RT/2F \cdot \log i/o$$

where β and C are constants.

The temperature coefficient of the cell was determined. From the Gibbs–Helmholtz equation the heat of formation of sodium chloroplatinate from the chloroplatinite and chlorine was calculated as 40,880 cals.