CCCXLI.—*The Potential of the Iridi–Iridochloride Electrode.*

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IN a previous communication (Terrey, J., 1928, 202), it was shown as a result of information obtained from measurements of the potential of the platino–platinicyanide electrode, that the so-called platinicyanides, $\mathrm{MPt^{III}(CN)_4}$, previously supposed to contain tervalent platinum, should be regarded as containing the platinum in the bi- and quadri-valent states. They are therefore to be written as $\mathrm{M_2Pt^{IV}(CN)_4Pt^{II}(CN)_4}$, and as such are brought into line with the platino–platinichlorides.

The irido–iridichlorides are assumed to be analogous to the ferro–ferrichlorides and it was considered interesting to test this point by measurements of the potential of the iridi–iridochloride electrode.

A definite and reproducible *P.D.* is slowly set up when an iridium electrode is put into a solution of sodium iridichloride and sodium iridochloride. If the irido–iridi-salts are similar in type to the ferro–ferri-salts, the electrode reaction will be expressed by $\overset{--}{\mathrm{IrCl}}_6 + e \longrightarrow \overset{---}{\mathrm{IrCl}}_6$, and the cell reaction is $\mathrm{Hg + NaCl + Na_2IrCl_6 \longrightarrow HgCl + Na_3IrCl_6}$.

The current passes from left to right in the cell

$$\overset{-}{\mathrm{Hg}}|\mathrm{Hg_2Cl_2 + NaCl}|\mathrm{NaCl + Na_2IrCl_6 + Na_3IrCl_6}|\overset{+}{\mathrm{Ir}}.$$

N-Sodium chloride was used as electrolyte, and the total concentration was thus kept approximately constant, so the activities of the iridi- and irido-chloride ions are replaceable by their concentrations. The *E.M.F.* of the cell is then given by

$$E = E_0 + RT/F \,.\, \log_e i/o,$$

where i = concentration of iridichloride,
o = ,, ,, iridochloride.

To test this formula, measurements of the *E.M.F.* were made with varying i/o ratios. Experiments 1—5 and 9—15 were made with o kept constant at $0{\cdot}984 \times 10^{-3}N$, and 6—8 with i constant at $0{\cdot}874 \times 10^{-3}N$.

EXPERIMENTAL.

Sodium iridichloride was obtained by the method of Berzelius by leading a stream of pure dry chlorine over a mixture of finely divided iridium and sodium chloride at a gentle red heat. The uncombined metal was filtered off, after solution of the reaction mixture in the minimum quantity of hot water, and the deep brownish-red liquid evaporated to a small bulk while being kept saturated with chlorine gas. Sodium iridichloride separated as long black needles after spontaneous evaporation of the mother-liquor on a watch-glass. The crystals were dried between filter-paper and ground to a reddish powder (Found: Ir, 34·5. Calc.: Ir, 34·6%).

Sodium iridochloride was prepared by reduction of a sodium iridichloride solution, prepared as above and saturated with chlorine gas, by neutral sodium oxalate as recommended by Delépine (*Compt. rend.*, 1908, **146**, 1267). The large crystals of deepest green (almost black) were dried and crushed to a dirty green powder. The salt crystallises with twelve molecules of water (Found: $Na_3IrCl_6,12H_2O$, 95·0; NaCl, 2·9%). The 2·1% unaccounted for was suspected to be due to the presence of water in the incompletely dried salt. This was verified by completely dehydrating a weighed amount of salt. Most of the water of crystallisation was removed over concentrated sulphuric acid in a desiccator, and the rest was easily taken off at 160°. The small amount of sodium chloride present was immaterial, since a solution of this salt was to be used as the electrolyte.

Solutions.—The iridochloride was weighed anhydrous and made up into a stock solution in *N*-sodium chloride. Solutions 1—5 and 9—18 were prepared by adding 10—15 c.c. of this solution to a weighed quantity of iridichloride, and making the whole up to 50 c.c. with *N*-sodium chloride. Solutions 7 and 8 were made from stock solutions of both iridi- and irido-chlorides diluted to 50 c.c. with *N*-sodium chloride. Solution 6 was made by adding 6·00 c.c. of iridichloride stock solution to a weighed quantity of iridochloride and diluting the mixture to 25 c.c. with *N*-sodium chloride.

Electrodes.—Five types were used: (*a*) platinised glass; (*b*) platinum–iridium points; (*c*) iridium points; (*d*) iridised iridium foil welded to platinum–iridium wire; and (*e*) iridised glass. The last two were the most satisfactory.

(*a*) Platinised glass was early abandoned owing to the steady fall found in *P.D.*, possibly due to interchange between the platinum of the electrodes and the iridium of the solution, which would be facilitated by the large surface of platinum available.

Electrodes (*b*) and (*c*) proved rather troublesome, as the null point was at times difficult to measure and the electrode took a long time to attain equilibrium: solution 15 took 4 days to rise from 0·769 to 0·777 volt.

(*d*) Solutions 1—5 were measured with electrodes of this type, made by using the foil as the cathode during the electrolysis of sodium iridichloride with a low *C.D.*

(*e*) Experiments 6—12 were made with electrodes of this type.

Cell.—The usual pattern of half-cell was used. The electrode was measured against a normal calomel electrode containing sodium chloride instead of potassium chloride.

The apparatus consisted of a Leeds-Northrup type K potentiometer, a Cambridge Instrument Company moving-coil galvanometer, and a Cambridge standard Weston cell. Measurements were made at 25°, the temperature being controlled by an air thermostat.

Results.

The time taken to reach equilibrium was about 48 hours for the best electrodes, and the *P.D.* then remained constant within 0·001 volt for many hours. The measurements for each *i*/*o* ratio were made on a pair of cells. The agreement was generally within 0·001—0·002 volt, but in some cases it was not so good. In all cases the higher value of the *E.M.F.* was taken for the calculations, and values were rounded off to the third decimal place.

Examination of the values of E_0 in Table I shows that an approximately constant value is obtained, although this varies somewhat with the nature of the electrode. The agreement is sufficient to show, however, that the irido–iridichlorides are correctly represented as being of the " ferro–ferri " type.

TABLE I.

Expt. No.	Type of electrode.	*i*, mols./litre × 10^3.	*o*, mols./litre × 10^3.	*i*/*o*.	Max. *E.M.F.* of cell (volt).	*E.M.F.* of electrode (*E*).	$RT/F \times \log i/o$.	E_0.
1	*d*	2·132	0·984	2·166	0·728	1·001	0·020	0·981
2		2·296	0·984	2·333	0·732	1·005	0·022	0·983
3		4·736	0·984	4·815	0·743	1·016	0·040	0·976
4		6·707	0·984	6·818	0·753	1·026	0·049	0·977
5		8·757	0·984	8·900	0·764	1·037	0·057	0·980
6	*e*	0·874	8·330	0·105	0·638	0·911	0·058	0·969
7		0·874	2·990	0·292	0·677	0·950	0·027	0·977
8		0·874	0·944	0·926	0·695	0·968	0·002	0·970
9		1·771	0·984	1·799	0·706	0·979	0·015	0·964
10		5·163	0·984	5·247	0·738	1·011	0·042	0·969
11		5·571	0·984	5·663	0·740	1·013	0·044	0·969
12		11·06	0·984	11·24	0·757	1·030	0·062	0·968
13	*c*	5·970	0·984	6·067	0·748	1·021	0·046	0·975
14		9·857	0·984	10·017	0·755	1·028	0·060	0·968
15		18·482	0·984	18·782	0·777	1·050	0·082	0·968
16	*b*	1·008	0·960	1·049	0·691	0·964	0·001	0·963
17		2·016	0·960	2·100	0·718	0·991	0·019	0·972

The *E.M.F.* of the electrode *E*, given in col. 7, was obtained from the observed maximum *E.M.F.* of the cell (col. 6) by adding the value, + 0·273 volt, of the calomel electrode.

The Effect of Temperature on the Electrode.—The results of measurements at different temperatures are in Table II. The *E.M.F.* varies linearly with the temperature, the coefficient being markedly negative. Col. 7 gives the mean value of dE/dT over a range of not more than 20° in the neighbourhood of 25°, for five different cells, and these values of dE/dT were used to calculate the heat Q evolved in the cell reaction at 25° and at constant pressure (see col. 8).

TABLE II.

Expt. No.	i/o.	$E_{t°}$.	t.	$E_{25°}$.	$E_{29°}$.	$-dE/dT$.	Q.	Q'.
1	2·166	0·747	13°	0·728	—	0·00158	27,800	(3,500)
3	4·815	0·764	8·5	0·743	—	0·00130	26,100	5,200
4	6·818	0·759	19·5	0·753	0·748	0·00120	25,600	5,700
5	8·900	0·777	13·5	0·764	—	0·00113	25,400	5,900
7	0·292	0·688	16	0·675	—	0·00144	25,500	5,800

Since the reaction in both cells can be written

$$\mathrm{Hg} + \overset{-}{\mathrm{Cl}} + \overset{--}{\mathrm{IrCl}_6} \longrightarrow \mathrm{HgCl} + \overset{---}{\mathrm{IrCl}_6},$$

and if the heat of formation of calomel be taken as 31,300 cals., the values for the heat of formation (Q', in cals./mol.) of iridichloride from iridochloride are as given in the last column. The value in the first series being ignored, the mean value for the heat of oxidation is 5,600 cals.

Summary.

The potential of the iridi–iridochloride electrode was measured and the *E.M.F.* shown to vary according to the equation $E = E_0 + RT/F \, . \log_e i/o$.

The temperature coefficient of the cell was determined. From the Gibbs–Helmholtz equation the heat of oxidation of iridochloride was calculated as 5,600 cals.

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