335.   *Electrometric Studies of the Precipitation of Hydroxides.   Part XII. The Reaction of Sodium Hydroxide on Platinic Chloride in Solution, and a Note on the Reaction of Potassium Cyanide on Platinic Chloride.*

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KOHLRAUSCH (*Wied. Ann.*, 1897, **63**, 433) attributed the acidity and high conductivity of platinic chloride solutions to the existence of the complex acid, $H_2PtCl_4(OH)_2$, and Miolati (*Z. anorg. Chem.*, 1900, **22**, 445) considered that he had confirmed this suggestion by conductometric titration with alkali.   Actually, his curves indicate a rapid fall in conductivity to a minimum with approximately one equivalent of alkali; thereafter the conductivity increased but the increase became more pronounced when two equivalents had reacted. Moreover, the specific conductivity of the platinic chloride solution at the beginning of one titration was much higher than at the beginning of another, although the concentrations were identical.   The present work shows that platinic chloride on dissolving in water continues to hydrolyse, giving free hydrochloric acid for some hours, and this, as revealed by conductometric and glass-electrode titrations, is accompanied by the formation of an increasingly basic complex in the solution.

The following table gives the variation at $25°$ in specific conductivity with time of $0·001377M$-platinic chloride solution.

Time (hours)	$\frac{1}{4}$	$\frac{1}{2}$	1	$1\frac{3}{4}$	$2\frac{3}{4}$	$4\frac{1}{2}$	20	24
$\kappa \times 10^3$ (mhos)	1·092	1·117	1·166	1·242	1·327	1·398	1·489	1·515

It being assumed that the gradual increase in conductivity was caused by the hydrolytic reaction $PtCl_4 + xH_2O \longrightarrow Pt(OH)_xCl_{4-x} + xHCl$, and that the basic chloride is of negligible conductivity, calculation shows that, immediately the solution was prepared by diluting 2 c.c. of $0.0413M$-platinic chloride to 60 c.c., x was equal to approximately 2, and became equal to 3 after 24 hours. This interpretation is borne out by the conductometric curves, I, II, and III, in the Fig. They refer to titrations of 60 c.c. of $0.001377M$-platinic chloride with $0.02N$-sodium hydroxide at 25°, I being that of an immediate titration, II that of a solution which had stood at 25° for 4 hours before titration, and III the curve given by a solution after it had previously stood for 24 hours. Curve IV refers to a series of solutions corresponding to various stages of the titrations, but which had been kept in the thermostat at 25° for some days until constant results were given. The initial slopes of I, II, and III are very nearly those which

NaOH, Equivalents (I,II,III,IV).
KCN, Equivalents (A and B).
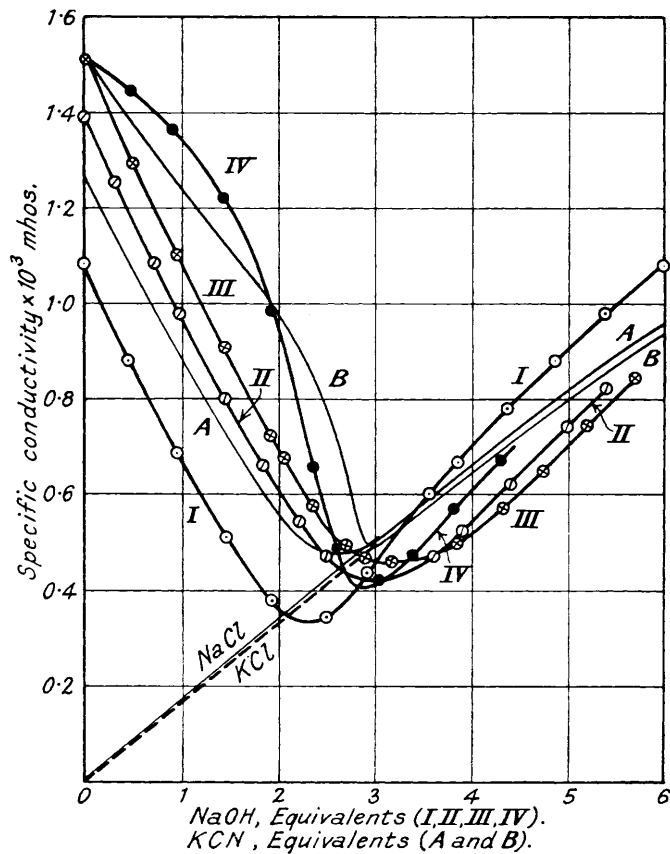
would have been given by the hydrochloric acid liberated by the hydrolysis in the solutions. The higher specific conductivities represented by IV suggest that, on the removal of some acid by neutralisation with the alkali, the basic portion, in consequence, underwent a little further hydrolysis. No precipitation occurred during these titrations.

A glass-electrode titration of the solution that had stood for 24 hours showed an initial p_H of 2.45. Hence, if this were due to hydrochloric acid, it would indicate that $x = 2.9$ instead of 3 (above). The titration curve was typical of the neutralisation of a strong acid by a strong base and was sharply inflected with 2.8 equivalents of alkali. Solutions that had not stood so long gave somewhat higher p_H values and earlier end-points. The p_H values of the alkaline solutions produced thereafter were such as would have been caused if the basic platinic chloride underwent no further decomposition, and that this was the case is also borne out by the slopes acquired by the final sections of the conductometric curves.

In the Fig. the conductivity due to the sodium chloride that was formed is given by the line marked NaCl. It will be seen that the minima in curves I, II, III, and IV fall below this line,

from which it would appear that, not only had the basic salt, then present, no conductivity, but in all probability it had combined with sodium chloride to form a substance having a small conductivity. Miolati (*loc. cit.*) has shown that platinum migrates to the anode during the electrolysis of solutions of platinic chloride. It is likely, therefore, that the basic portion is negatively charged and that the platinic chloride solutions may be represented thus :

$$PtCl_4 + xH_2O \rightleftharpoons xHCl + Pt(OH)_xCl_{(4-x)} \rightleftharpoons (x-y)HCl + yH^{\cdot} + Pt(OH)_xCl'^y_{(4-x+y)},$$
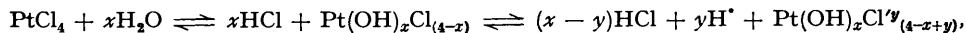
so that on neutralisation with sodium hydroxide some sodium chloride is formed together with a pseudo-salt containing the basic platinic chloride in the negative part.

Although platinocyanides are well-defined salts, no stable platinicyanides appear to exist. The possibility of the formation of the potassium salt by the action of potassium cyanide on platinic chloride solution has been investigated electrometrically. Curve A is that of a direct titration of 60 c.c. of 0·001377M-platinic chloride with 0·025M-potassium cyanide, and B represents the conductivities obtained on a series of similar platinic chloride solutions, containing varying amounts of potassium cyanide, after sufficient time had been allowed for the attainment of equilibrium. The line marked KCl gives the conductivity set up by the potassium chloride formed. The minimum was given in the immediate titration with between 2 and 3 mols. of potassium cyanide, whereas the aged solutions gave a minimum at 3 mols. From the position of the point of intersection of the KCl line, it follows that the initial reaction consisted of the conversion of the hydrolysed hydrochloric acid (*ca.* 3 mols.) into potassium chloride, with the liberation of free hydrogen cyanide which had no effect on the conductivity of the solution. This was proved by means of the glass electrode. Thus, after ageing, an inflexion in the titration curve of the solution was given with exactly 3 mols. of potassium cyanide, and the curve afterwards obtained showed that the hydrogen-ion concentration was buffered by equilibria between the free hydrogen cyanide and cyanide ions. In the conductometric curves A and B, the final branches corresponded closely with the potassium chloride first formed and the excess of potassium cyanide added. A glass electro-titration in the reverse manner, *i.e.*, of potassium cyanide with platinic chloride, led to the same conclusions. The first section was buffered in the region of $p_{K_{HCN}} = 9·32$ and the inflexion occurred when the ratio of the potassium cyanide to the platinic chloride added was slightly smaller than 3 : 1. There is thus no evidence of the formation of a platinic cyanide, either simple or complex.

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