When a solution of potassium pentachlorohydroxy ruthenate IV is treated with strong reducing agents such as zinc or lead, the deep brown colour changes successively to yellow, green, blue, and finally deposits the metal itself. The yellow solution contains trivalent ruthenium (Howe, 1927; Charonnat, 1931), but for a time a controversy existed over the green and blue substances, which were thought to contain respectively bivalent and monovalent ruthenium. According to Latimer (1940) the question has been definitely settled by the work of Crowell and Yost (1928), who showed that the blue solution contained the element in the bivalent state, whilst the green colour was due to a mixture of the trivalent and bivalent states. Recently, however, Grube and Nann (1939), as a result of the study of the electrolytic reduction of ruthenium trichloride in hydrochloric acid, claimed that the reduction proceeded to the bivalent state in concentrated acid, but in dilute acid the univalent state resulted. The reduction steps were identified by potentiometric titration with hydrogen peroxide. Univalent ruthenium was found to undergo disproportionation: $2\text{Ru}^+ \rightarrow \text{Ru}^{++} + \text{Ru}$; and the potential of the reaction $\text{Ru}^+ - e^- \rightarrow \text{Ru}^{++}$ was found to be in the range 0·03 to 0·05 volt. The published titration curves, however, do not show well-marked inflexions; the potentials from which the curves were obtained were almost instantaneous and not equilibrium values, and an irreversible oxidant was used. Additional evidence in substantiation of univalent ruthenium is therefore desirable.

The present investigation deals with the determination of the potential of the bivalent/trivalent ruthenium couple in hydrochloric acid with a view to checking the existence of the univalent state.

The mixed oxidant/reductant solution was prepared by the reduction of potassium pentachlorohydroxy ruthenate IV in hydrochloric acid with pure lead foil in an oxygen-free atmosphere of carbon dioxide. The resulting deep blue solution contained 15–20% of bivalent ruthenium, whilst the remainder was trivalent. Although the lack of equimolarity in this solution involved a large correction to obtain the standard potential, the large excess of the trivalent state automatically eliminated the possibility of any of the alleged monovalent state being present. The reduced solution to which varying amounts of acid were added was allowed to come to equilibrium with a smooth gold electrode in an atmosphere of carbon dioxide. As soon as the potential reading was taken the concentration of bivalent ruthenium was determined by addition of a known volume of the solution to oxygen-free ferric alum solution. In this way an equivalent amount of ferrous salt was formed.

$$\text{Ru}^{++} + \text{Fe}^{+++} \rightarrow \text{Ru}^{+++} + \text{Fe}^{++}$$

From the present work it is known that the potential of the Ru$^\II$/Ru$^\III$ system is of the order of 0·1 volt, whilst from the previous paper (This Series,
Part III) the potential of the Ru$^{III}$/Ru$^{IV}$ system is approximately 0.9 volt, hence the ferric salt can only oxidise to the trivalent state. The partly reduced iron solution was then oxidised potentiometrically with potassium permanganate, the first step being due to oxidation of the ferrous ion. The total ruthenium in the solution was estimated by oxidation to the quadrivalent state with a slight excess of chlorine, followed by potentiometric titration with stannous chloride. The potential of the stannous/stannic system (0.13 volt; Latimer, 1940) is such that the reduction $2\text{Ru}^{IV} + \text{Sn}^{++} \rightarrow 2\text{Ru}^{III} + \text{Sn}^{4+}$ proceeds to completion without the formation of any bivalent ruthenium compound, or the separation of ruthenium metal. The difference in the total ruthenium concentration and the bivalent ruthenium concentration then gives the concentration of trivalent ruthenium.

The observed potentials were corrected to the standard equimolar potential by the usual equation. Since the activities of the oxidant and reductant were unknown, the observed concentrations were substituted.

The reduction of ruthenium tribromide in hydrobromic acid could be effected with either silver or lead, but the reduced solution was coloured green. Even when the reduction was carried out with zinc to the point where most of the metal was deposited, the colour remained green. It was concluded that the green colour was not due to admixture of the bivalent and trivalent states, but that the ionic species of bivalent ruthenium is not the simple hydrated Ru$^{++}$ but hydrated (RuBr$^+$) and (RuCl)$^+$. The determination of the potential of the green solution was not successful as a brown deposit formed on the electrode, whilst a satisfactory method could not be found for the estimation of the bivalent ruthenium. The potential of the trivalent/quadrivalent ruthenium couple in hydrobromic acid (approx. 0.7 volt) is almost the same as the ferrous ferric system. The reaction $\text{Ru}^{III} + \text{Fe(CN)}_6^{3-} \rightarrow \text{Ru}^{II} + \text{Fe(CN)}_6^{4-}$, although theoretically feasible, proved to be unsuitable.

The potential of the chloride system was found to be almost independent of the acid concentration from 1.5 N to 6.8 N hydrochloric acid. Measurements in the lower acid concentrations could not be obtained owing to the separation of ruthenium on the electrode

$$3\text{Ru}^{++} \rightarrow \text{Ru} + 2\text{Ru}^{+++}$$

From the independence of the potential on the ionic strength, it can be concluded that increasing ionic strength has the same effect on the activities of both the oxidant and the reductant, and hence that they probably carry the same charge. Since the lowest valencies of the metal are involved, the system is almost certainly cationic, and the equivalence of charge must be due to covalent bonding of part of the halogen. In Part III of this series evidence was put forward for the existence of ruthenium trichloride in dilute solution as either the hydrated ion (RuCl)$^{++}$ or (RuCl$_2$)$^+$, and from the behaviour of ruthenium tribromide towards reducing agents it is suggested that the reductant ion is (RuCl)$^+$. It is considered, therefore, that the redox reaction of the couple is

$$(\text{RuCl}_2)^+ + e^- \rightarrow (\text{RuCl})^+ + \text{Cl}^-.$$
It is concluded from the present study that the univalent ruthenium ion has no existence in solution.

**EXPERIMENTAL.**

**Oxidant and Reductant Solutions.**

An M/50 solution of potassium pentachlorohydroxy ruthenate IV in hydrochloric acid (2 N) was saturated with oxygen-free carbon dioxide and thin strips of lead foil added. After about thirty minutes the deep brown solution had become yellow and the reaction had almost stopped by the deposition of ruthenium on the lead. The solution was decanted on to fresh lead, and sealed in carbon dioxide until after 20–30 minutes a deep royal blue solution had formed. This was filtered from lead chloride and ruthenium metal through a sintered glass filter into a storage vessel, fitted with a burette, so that known volumes could be withdrawn without exposure to oxygen. Since the acid concentration had changed during the reduction by reaction with the lead, the acidity was determined by titration with sodium hydroxide and methyl orange indicator. The total ruthenium in the solution was estimated by dilution of a known volume with dilute hydrochloric acid and oxidation with a slight excess of chlorine water. The excess was then boiled out, and the solution potentiometrically titrated with standard stannous chloride. The excess of chlorine was such that any loss as ruthenium tetroxide could be regarded as negligible. The solution was found to be M/800 with respect to ruthenium.

**Apparatus.**

The redox apparatus was the same as that used in previous determinations (Dwyer, McKenzie and Nyholm, 1946). The saturated calomel electrode, taken as 0.2443 volt at 25° C., was connected to the cell through a saturated potassium chloride salt bridge. During the potential determinations the apparatus was sealed with apeizon wax and kept under a slight pressure of carbon dioxide.

**Procedure.**

An oxygen-free solution (30 ml.) of hydrochloric acid of the required concentration was saturated with carbon dioxide in the redox vessel, the reduced ruthenium solution (10 ml.) added quickly, and the apparatus sealed. After approximately 24 hours equilibrium had been attained, and the potential was measured with a Leeds and Northrup valve potentiometer. The system was unpoised and the ordinary potentiometer was unreliable. A portion of the solution (30 ml.) was immediately withdrawn through a stream of carbon dioxide and added to oxygen-free standard ferric alum solution. Potentiometric titration with potassium permanganate then gave the concentration of bivalent ruthenium at the equilibrium point.

The potential values at the various acid concentrations are shown in Table I.

**Table I. The Potential of the Ru(III)/Ru(II) System in Hydrochloric Acid.**

<table>
<thead>
<tr>
<th>Acid Concentration Normality,</th>
<th>E, Observed (Volt.)</th>
<th>[Ru(II)] × 10^–3</th>
<th>[Ru(III)] × 10^–3</th>
<th>E, Observed Corrected (Volt.)</th>
<th>E_R (Volt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.53</td>
<td>0.128</td>
<td>0.279</td>
<td>0.97</td>
<td>0.160</td>
<td>0.084</td>
</tr>
<tr>
<td>2.6</td>
<td>0.130</td>
<td>0.301</td>
<td>0.95</td>
<td>0.160</td>
<td>0.084</td>
</tr>
<tr>
<td>2.6</td>
<td>0.132</td>
<td>0.305</td>
<td>0.945</td>
<td>0.161</td>
<td>0.083</td>
</tr>
<tr>
<td>3.64</td>
<td>0.121</td>
<td>0.27</td>
<td>0.98</td>
<td>0.154</td>
<td>0.090</td>
</tr>
<tr>
<td>5.22</td>
<td>0.131</td>
<td>0.27</td>
<td>0.98</td>
<td>0.164</td>
<td>0.080</td>
</tr>
<tr>
<td>6.8</td>
<td>0.127</td>
<td>0.28</td>
<td>0.97</td>
<td>0.157</td>
<td>0.087</td>
</tr>
</tbody>
</table>
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Summary.
The potential of the bivalent/trivalent ruthenium couple in hydrochloric acid was found to be 0.084 volt ± 0.005 volt in the hydrochloric acid range of concentrations from 1.53 N to 6.8 N. It is considered that the system is cationic with the ionic species (RuCl₂)⁺ and (RuCl)⁺ for the oxidant and reductant respectively. From the potential values and the behaviour of the system in low acid concentrations, it is concluded that Grube and Nann's alleged univalent ruthenium is really bivalent ruthenium.

References.
Dwyer, McKenzie and Nyholm, 1946. This Journal, 78, 260.
Grube and Nann, 1939. Ibid., 45, 871.

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