

Electrochemical Properties of the Platinum Metals

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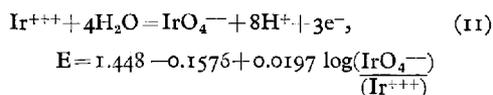
In the first part of their article, published in the April issue of 'Platinum Metals Review', the authors summarised the general basis of their method of treatment, based on thermodynamic equations, of electrochemical phenomena, and then described the characteristics of platinum from this point of view. In this concluding part of their article they deal with the electrochemical properties of other platinum group metals.

It has been shown in the first part of this survey that the construction of potential-pH diagrams to represent equilibrium conditions in reactions between metals and dilute aqueous solution, and the use of these diagrams in the study of various branches of electrochemistry and corrosion, can often give a better understanding of the phenomena involved. The general method of treatment was explained, and the electrochemical properties and corrosion resistance of platinum were considered in the light of this method. Work has recently been completed on the other metals of the platinum group, and these are dealt with similarly in what follows.

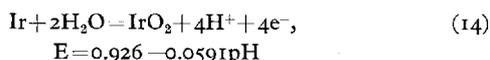
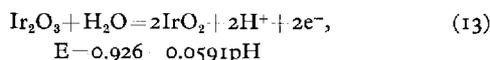
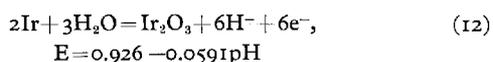
IRIDIUM

The following reactions were considered in constructing a potential-pH diagram of the iridium-water system (10):

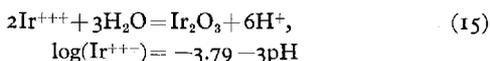
Homogeneous reaction – electrochemical reaction



Heterogeneous reactions involving two solid components – electrochemical reactions



Heterogeneous reactions involving one solid component – chemical reaction



Electrochemical reactions

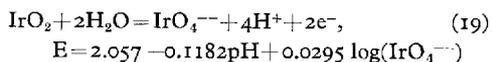
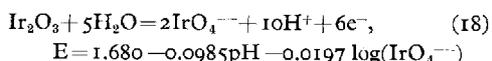
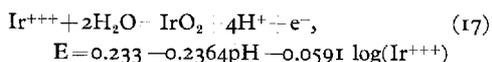
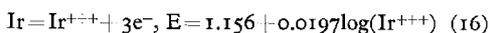


Fig. 5 shows the potential-pH diagram obtained from these equations. Examination of reactions (12), (13) and (14) shows the equilibrium conditions of each to be represented by the same equation. The interpretation of this is that the oxide Ir_2O_3 is thermodynamically unstable with respect to iridium and IrO_2 under all conditions of potential and pH since it has no domain of stability in the diagram. Actually the oxide can be prepared with difficulty in the hydrated form but

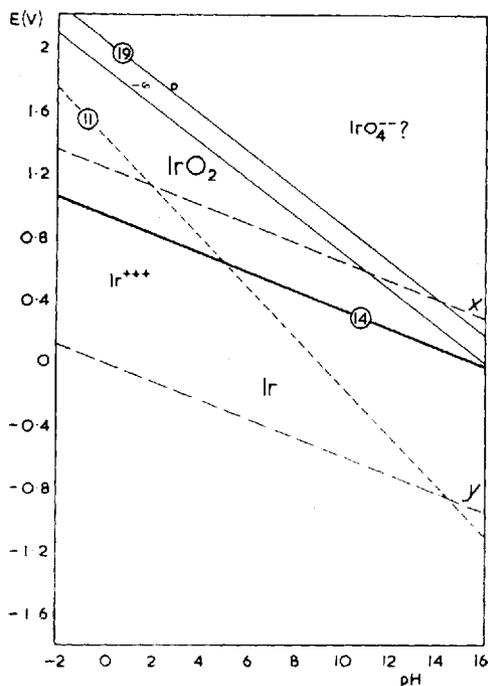


Fig. 5 Potential-pH diagram for the iridium-water system at 25°C

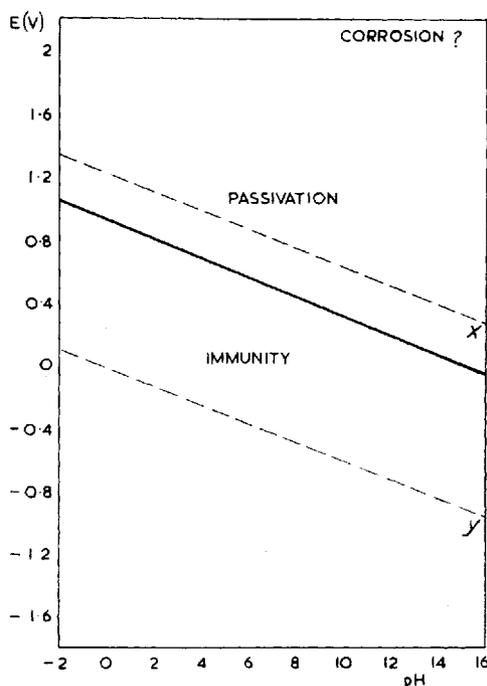


Fig. 6 Theoretical conditions for the corrosion, immunity and passivation of iridium at 25°C

always tends to decompose into IrO_2 and Ir . The other equations, (15) and (18), which involve Ir_2O_3 cannot be plotted on the diagram because this relates only to thermodynamically stable components.

The thermodynamic data for the ionic forms considered, namely Ir^{+++} and IrO_4^{-} , are known only very approximately and it is in fact doubtful whether these ions exist at all in a simple form. Their positions on the diagram have been indicated approximately, but the position of any lines involving these components must be treated with caution.

Corrosion Properties

Fig. 6, derived from Fig. 5, shows iridium to be an extremely noble metal since its region of immunity extends over the greater part of the domain of stability of water. In fact iridium at 25°C is unattacked by water, solutions of caustic alkalis, acids and oxidising agents including aqua regia. It is, together with rhodium, one of the most incorrodible metals and it is necessary to use a fused

mixture of KOH and KNO_3 in order to attack it.

Iridium is normally unattacked when used either as an anode or a cathode, although in the latter case it absorbs hydrogen.

According to Fig. 5 iridium dioxide, IrO_2 , should be insoluble in acid solutions but soluble in oxidising alkaline solutions. In fact, anhydrous IrO_2 is insoluble in acids and bases as well as in aqua regia, although in the hydrated form it is soluble in acids when freshly prepared. From its position it is seen to be the form of iridium stable in the presence of oxygen, and it is an oxidising agent.

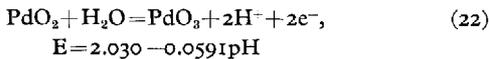
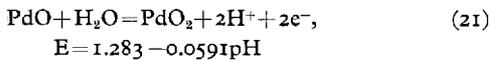
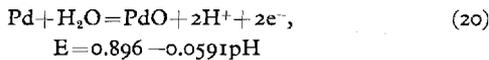
The two positions for the line corresponding to equation (19), labelled o and -6 respectively, relate to different concentrations of IrO_4^{-} in equilibrium with IrO_2 . The o corresponds to unit concentration of ions while -6 corresponds to a concentration of 10^{-6} g ion/litre. It should be noted that the line -6 is the line separating the domains of corrosion and non-corrosion since corrosion

is defined as occurring if the concentration of ions is greater than 10^{-6} . In fact the line is not marked in Fig. 6 since its position is doubtful due to the approximate nature of the thermodynamic data available for IrO_4^- .

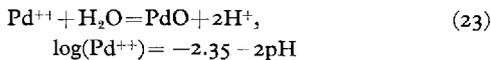
PALLADIUM

The following six reactions were considered in constructing the potential-pH diagram for the palladium-water system (11):

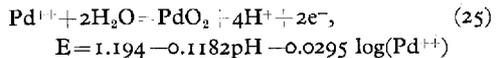
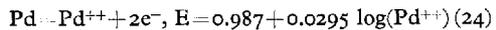
Heterogeneous reactions involving two solid components—electrochemical reactions



Heterogeneous reactions involving one solid component—chemical reaction



Electrochemical reactions



In the equations concerned, PdO and PdO_2 have been considered as $\text{PdO} \cdot \text{H}_2\text{O}$ (or $\text{Pd}(\text{OH})_2$) and $\text{PdO}_2 \cdot 2\text{H}_2\text{O}$ (or $\text{Pd}(\text{OH})_4$).

The diagram obtained from these equations is shown in Fig. 7, and is seen to be similar to that of platinum, the corresponding metal in the heavy triad of platinum metals. The uncertainty in the position of line (22) arises from the imprecision of the thermodynamic data for PdO_3 . The ions PdO_3^{--} and PdO_2^{--} and the palladium hydride, Pd_2H , are shown in their approximate positions but any quantitative treatment is rendered impossible by the lack of data for these components.

Corrosion Properties

Fig. 8, deduced from Fig. 7, indicates the theoretical conditions of corrosion and sta-

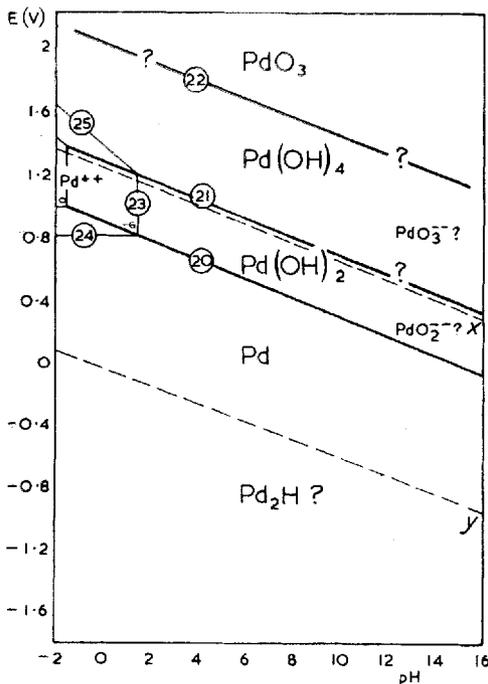


Fig. 7 Potential-pH diagram for the palladium-water system at 25°C

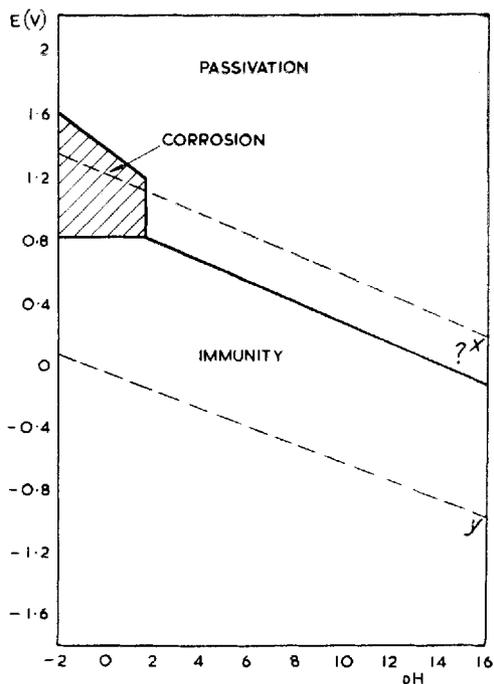


Fig. 8 Theoretical conditions for the corrosion, immunity and passivation of palladium at 25°C

bility to attack of palladium. According to this figure metallic palladium is thermodynamically stable in the presence of aqueous solutions of all pHs with the exception of strong oxidising agents and complexing substances. In practice palladium is unattacked by water, except at high temperatures, and is not tarnished in moist air. Non-oxidising acids, acetic, hydrofluoric, oxalic and sulphuric, are without action at ordinary temperatures. As can be predicted from Figs. 7 and 8, palladium is attacked by strongly oxidising acid solutions: hydrochloric acid which has no action in the absence of an oxidiser, attacks it slowly in the presence of oxygen, more rapidly if it contains chlorine and very rapidly if mixed with nitric acid. Dilute nitric acid attacks palladium only slowly, but the metal is corroded quite rapidly by the concentrated acid.

Palladium is perfectly resistant to attack by alkaline solutions even when these contain oxidising agents. This fact is not in agreement with the hypothetical conditions given in Fig. 7 for the formation of soluble palladites. This discrepancy between theory and practice may be due to the formation on palladium of a protective film (possibly PdO) more stable than the Pd(OH)₂ considered in the figure.

When in use as an electrolytic anode it will be expected from Figs. 7 and 8 that palladium will be corroded in very acid solutions except where the potential is high enough to cause the formation of a protective film of oxide. In fact, palladium anodes dissolve rapidly in concentrated hydrochloric acid solutions but are only slightly attacked by solutions of nitric acid or sodium nitrate. Jirsa (12) when investigating the anodic polarisation of palladium in a 1N solution of caustic soda (pH 13.7) observed several steps in potential corresponding, according to him, to the following successive stages in the oxidation of palladium: Pd → Pd₂O → PdO → PdO₂ → PdO₃ occurring respectively at the potentials: +0.15, +0.4 to 0.5, +0.95 and +1.22 volt.

These results are not in agreement with Fig. 7, but as has been explained, this is subject to certain limitations due to the imprecise nature of the thermodynamic data available for the palladium oxides.

Owing to its exceptional ability to absorb large quantities of hydrogen, palladium exhibits a unique behaviour as an electrolytic cathode. The absorption of hydrogen is accompanied by a change in crystal structure of the metal probably due to the formation of the hydride, Pd₂H. Palladium has one of the lowest hydrogen overpotentials obtained with any metal.

Electrodeposition of Palladium

It follows from Fig. 7 that metallic palladium should be easily obtainable by reduction of solutions of its salts. This can be realised chemically by reduction with hydrogen, metals and inorganic and organic reducing agents. It can also be carried out electrolytically, resulting in the electrodeposition of the metal. This can be effected easily on most of the usual metals.

Palladium Electrode for the Measurement of pH

Since palladium possesses such a low hydrogen overpotential the reaction



can occur practically reversibly on the metal. The reversibility is even greater than that attained using platinum and, like platinum, palladium can be used as a hydrogen electrode for the measurement of pH.

Formation and Stability of the Oxides and Hydroxide of Palladium

Palladium has three oxides: PdO.H₂O or Pd(OH)₂, PdO₂.2H₂O or Pd(OH)₄ and PdO₃. Their conditions of thermodynamic stability are shown in Fig. 7. Palladous hydroxide, Pd(OH)₂, should be soluble in acids, forming palladous ions Pd⁺⁺, and in alkalis forming palladites, PdO₂⁻⁻. In practice it is found that while it is soluble in

acids and alkalis, the solubility is greatly affected by its amount of hydration and by the length of time it has been prepared. As indicated in Fig. 7, palladous hydroxide is stable in the presence of water. It should be and is easily reduced in the cold to metallic palladium by such reagents as formic acid, hydrogen peroxide and hydrogen.

Palladic hydroxide, $\text{Pd}(\text{OH})_2$, is, as would be expected, an energetic oxidising agent, it is unstable in air and decomposes with evolution of oxygen. It is reduced, more energetically than palladous hydroxide, by hydrogen, organic acids and hydrogen peroxide. When freshly prepared it dissolves, with reduction to form palladous ions, in hydrochloric, nitric and sulphuric acids at ordinary temperatures. It is insoluble in dilute solutions of sodium hydroxide, but dissolves in 10N potassium hydroxide giving the palladate ion, PdO_3^{2-} .

Perpalladic oxide, PdO_3 is a strong oxidising agent and is very unstable as would be expected from its position in Fig. 7.

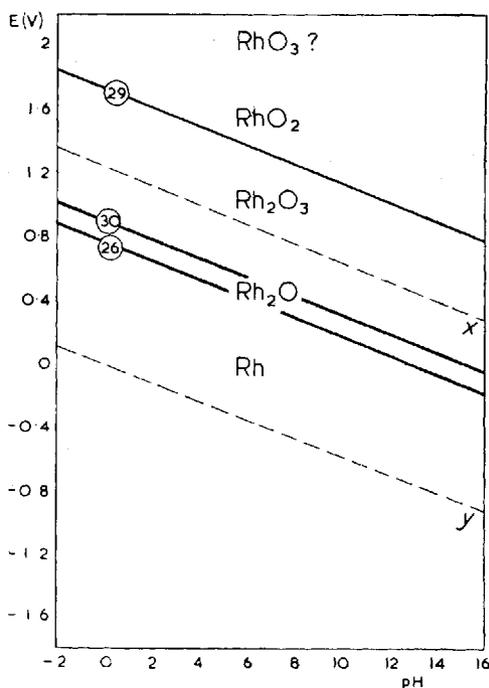
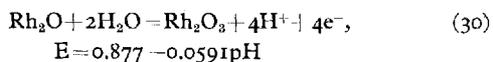
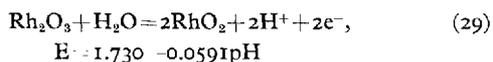
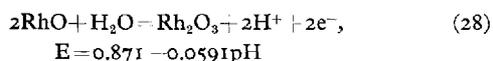
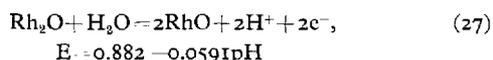
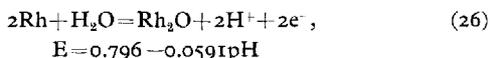


Fig. 9 Potential-pH diagram for the rhodium-water system at 25°C

RHODIUM

The following reactions were considered in constructing a potential-pH diagram for the rhodium-water system (13) in the case where no complexing agents are present:

Heterogeneous reactions involving two solid components—electrochemical reactions



The potential-pH diagram obtained from these equations is shown in Fig. 9. It will be seen from an examination of equations (27),

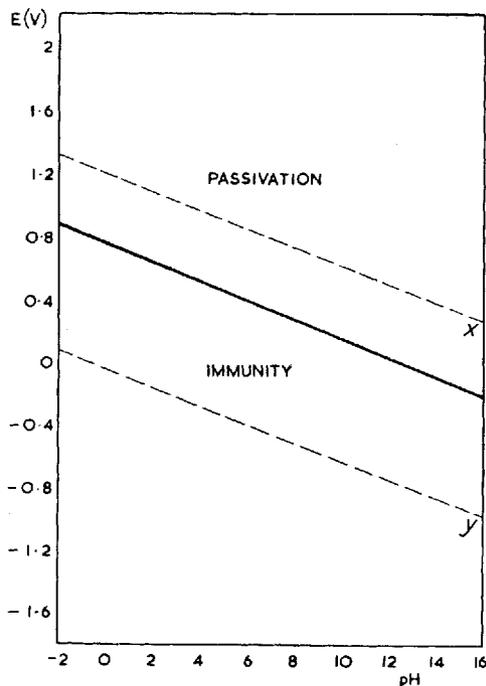


Fig. 10 Theoretical conditions for the corrosion, immunity and passivation of rhodium at 25°C

(28) and (30) that RhO is thermodynamically unstable with respect to Rh₂O and Rh₂O₃ and hence cannot appear on the diagram.

Corrosion Properties

In Fig. 10, deduced from Fig. 9, rhodium is shown to be an extremely noble metal since its domain of stability covers most of the domain of stability of water. This is confirmed in practice where rhodium is found to be stable in the presence of aqueous solutions of all pH's in the absence of complexing agents. At temperatures around 25°C it is unattacked by water, aqueous solutions of caustic alkalis, solutions of acids and oxidising agents including aqua regia. The resistance of rhodium to chemical agents is remarkable and surpasses that of platinum.

The behaviour of rhodium in the massive state appears to be completely in harmony with Fig. 9. However, in the finely divided state, as in rhodium black, rhodium dissolves quite easily in warm concentrated sulphuric acid and in aqua regia.

When used as an anode rhodium is normally unattacked namely in solutions of hydrochloric and sulphuric acids.

Electrodeposition of Rhodium

It follows from Fig. 9 that rhodium is easily obtained in the metallic form by reduction of its solutions. This is carried out electrolytically using solutions of rhodium sulphate or phosphate.

Stability and Formation of Rhodium Oxides

According to Fig. 9, rhodium oxides should be insoluble in all non-complexing solutions; they should be soluble in chlorine containing acids and in alkaline chloride solutions containing a strong oxidising agent.

In fact, Rh₂O is insoluble in acids and in aqua regia; its behaviour in alkaline solutions is unknown. Anhydrous Rh₂O₃ is also insoluble in acids, including aqua regia, and in strongly alkaline solutions provided they

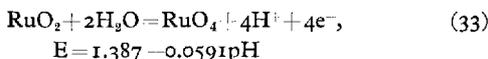
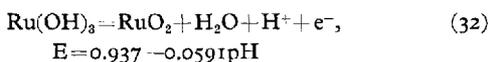
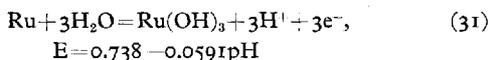
contain no oxidising agent. The hydrated form, Rh₂O₃·5H₂O, is easily soluble in mineral acids and in certain organic acids. The position of Rh₂O₃ in Fig. 9 shows that, except in the presence of complexing alkaline solutions, it tends to be oxidised to the six-valent state. This oxide is the stable form of rhodium in the presence of oxygen and should be considered as an oxidising agent.

Anhydrous RhO₂ is insoluble in acids and alkalis. RhO₂ and its hydrate, RhO₂·2H₂O are, as indicated in Fig. 9, energetic oxidising agents; they oxidise hydrochloric acid to chlorine and react with Na₂O₂ and Na₂S₂P₃ with liberation of oxygen.

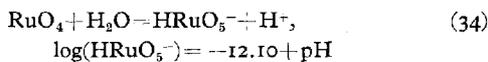
RUTHENIUM

The potential-pH diagram for the ruthenium-water system (14) is far more complicated than those for the other platinum metals considered here, because of the greater number of valency states in which it is able to exist. Consequently the number of reactions to be considered is greater and only the more important ones are given here:

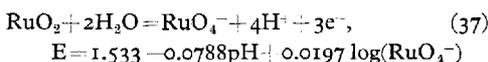
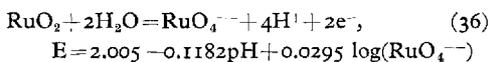
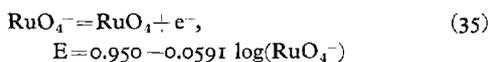
Heterogeneous reactions involving two solid components—electrochemical reactions



Heterogeneous reactions involving one solid component—chemical reaction



Electrochemical reactions



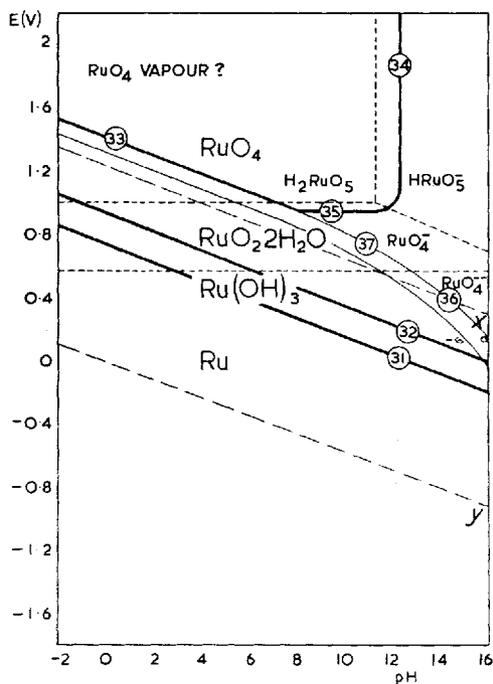


Fig. 11 Potential-pH diagram for the ruthenium-water system at 25°C

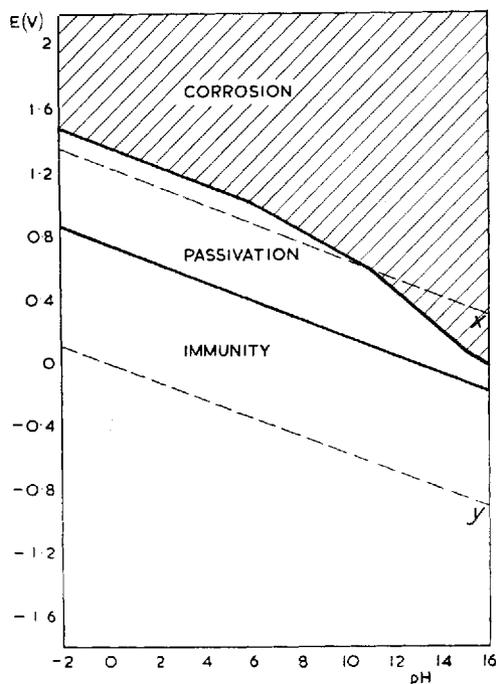


Fig. 12 Theoretical conditions for the corrosion, immunity and passivation of ruthenium at 25°C

The potential-pH diagram derived from these, and other equations, is given in Fig. 11 and the corrosion diagram in Fig. 12.

Corrosion Properties

Ruthenium is shown, in Fig. 12, to be a noble metal since its domain of stability covers a large part of the domain of stability of water. It is, however, together with osmium, decidedly less noble than the other four platinum metals.

Although ruthenium is not attacked by water or non-complexing acids it is easily corroded by oxidising alkaline solutions such as peroxides and alkaline hypochlorites. Ruthenium is passive when used as an anode

in non-complexing solutions. When used as a cathode it absorbs large quantities of hydrogen in common with the other platinum metals.

As can be predicted from Fig. 11, metallic ruthenium should be easily obtained by reduction of aqueous solutions of its salts. This can in fact be carried out both chemically and electrolytically.

The work described above was carried out in the Applied Physical Chemistry Laboratory of the Université Libre, Brussels, with the support of the Union Minière du Haut Katanga and of the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie and dans l'Agriculture.

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