

# Electrochemical Properties of the Platinum Metals

## A NEW APPROACH TO STUDIES OF CORROSION RESISTANCE AND CATHODIC PROTECTION

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It is often possible to understand, and indeed to predict, experimental results or practical applications in the field of electrochemistry and corrosion by bearing in mind the fundamental principle that any change is impossible unless it tends to the realisation of a state of thermodynamic equilibrium. One of the authors has described in earlier publications (1, 2) a method for the calculation of equilibrium conditions in reactions between metals and dilute aqueous solutions, and the means whereby such equilibria can be represented graphically so as to present a considerable body of information in a small space. The method employed is based upon the concept of "solution potential" introduced by Nernst, but shows the importance of determining the pH of the solution as well as potential in the study of chemical and electrochemical oxidation-reduction phenomena.

The conditions of thermodynamic equilibrium of all the reactions that can occur when a metal is in contact with an aqueous solution at a given temperature are expressed on potential-pH diagrams in which the equilibrium potential is plotted against pH for each reaction. As will be shown later, any solid, liquid, gaseous or dissolved substance having a definite chemical potential is thermodynamically stable in the presence of an aqueous solution only in conditions corresponding to certain definite domains in a potential-pH diagram. The limits of these domains depend on the concentrations and pressures of the substances present.

*For a number of years Dr. Pourbaix has been well known for his original method of treatment, based on thermodynamic equations, of the changes occurring when a metal is immersed in an aqueous solution. His graphical method, which compresses a great deal of information into a relatively simple diagram, has helped to elucidate a number of problems concerning corrosion, cathodic protection and other electrochemical phenomena. This article summarises the general basis of treatment and describes the work recently completed in his laboratories on the platinum metals.*

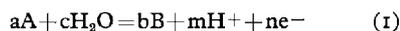
These diagrams must be regarded only as rough approximations, and the conclusions to which they lead must be accepted with reserve, but they do none the less provide an interpretation of observed facts sufficiently accurate for many purposes and they indicate profitable lines for further experiment. They show the conditions in which the occurrence of given oxidation and reduction reactions is possible from the energetic standpoint, and enable one to predict and interpret many phenomena in the fields of corrosion, of cathodic protection, of electrodeposition and of other branches of electrochemistry.

It is unfortunately impossible in a summary such as this to give details of the method by

which these diagrams are constructed, but a full exposition of the subject may be found in the senior author's book *Thermodynamics of Dilute Aqueous Solutions* (1) and in "Lectures on Electrochemical Corrosion", given at the University of Brussels (3).

## Construction of Potential-pH Diagrams

The reactions involved in a metal-water system are written in such a form that if substance A is changed into substance B, the only other species appearing in the equation are water molecules, hydrogen ions and electrons:



When the laws of equilibrium are applied to reactions written in this way, equilibrium conditions are obtained that are automatically expressed as a function of the same two independent variables:

The pH, which determines the influence of the  $H^+$  ions

The potential E, which determines the influence of electrons.

Provided that only dilute solutions are considered, the concentration of water remains constant and need not be explicitly considered in setting up equilibrium conditions for different systems. The only other variables in the expression for equilibrium conditions are the concentrations of components A and B when these occur in the dissolved or liquid state.

In the limited space available here it must be accepted that for the general equation (1), the equilibrium conditions are expressed by the equation:

$$E = E^\circ - \frac{0.0591m}{n} \text{pH} + \frac{0.0591}{n} [b \log(B) - a \log(A)] \quad (2)$$

where

E = equilibrium potential

$E^\circ$  = standard equilibrium potential, a quantity which can be calculated from the

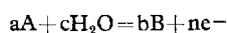
thermodynamic properties of the reaction components.

(A) and (B) represent the concentrations of the components A and B.

From the general equation (1) four types of reaction can be obtained, and equation (2) representing the equilibrium conditions can be altered accordingly. These four types come under the two main headings, oxidising and non-oxidising reactions:

(a) Oxidising reactions (i.e. reactions involving electrons) which also involve hydrogen ions. These are represented by equation (1) and the equilibrium conditions by equation (2).

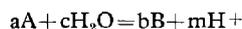
(b) Oxidising reactions not involving hydrogen ions, in which case  $m=0$  in equation (1) and thus



and, from equation (2)

$$E = E^\circ + \frac{0.0591}{n} [b \log(B) - a \log(A)] \quad (3)$$

(c) Non-oxidising reactions involving hydrogen ions, where  $n=0$  in equation (1) and thus



In this case the reaction is independent of E and it can be shown (4) that the equilibrium conditions are given by:

$$a \log(A) - b \log(B) = \log K - m \text{pH} \quad (4)$$

where

K = equilibrium constant. Log K can be calculated from the thermodynamic properties of the components.

(d) Non-oxidising reactions which do not involve hydrogen ions, in which case  $m=0$  and  $n=0$  in equation (1) and thus



Since these reactions are independent of both potential and pH, their equilibrium equation cannot be

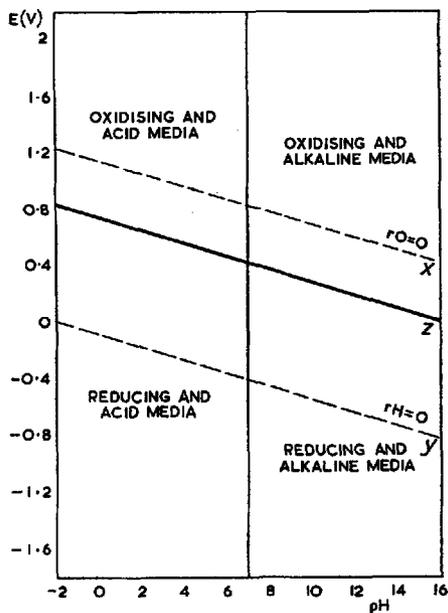


Fig. 1 Potential-pH diagram of water at 25°C and one atmosphere pressure

plotted on a potential-pH diagram. Such reactions will not often be met with, however, in studying metal-water systems.

In addition to the above variations in the equation for equilibrium it should be remembered that the equilibrium conditions are only affected by the concentrations of the reactants when they are in the dissolved or liquid state. Where solid reactants are involved their concentration terms are omitted from the equation.

The lines representing the equilibrium conditions of each reaction are obtained by substituting the relevant values of  $E^\circ$  or  $K$  in equations (2), (3) or (4) for given concentrations of reactant and product (if these are in the liquid phase) and plotting the corresponding values of  $E$  and  $pH$ .

The form of potential-pH diagrams is best considered by reference to a simple example, that of water, which is shown in Fig. 1. The dotted line  $x$  refers to the conditions of equilibrium of the reaction:

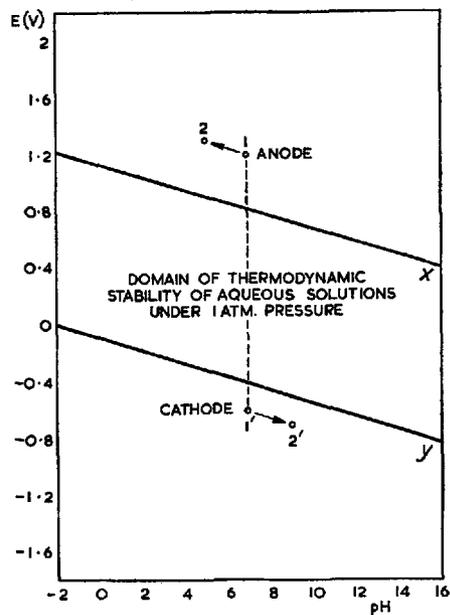
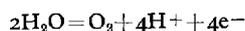
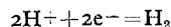


Fig. 2 Conditions of thermodynamic stability and decomposition of water at 25°C and one atmosphere pressure

and the line  $y$  to:



At equilibrium the pressure of oxygen and hydrogen in the respective reactions is equal to one atmosphere. The area shown in Fig. 2, enclosed by the two lines  $x$  and  $y$ , represents the domain of thermodynamic stability of water at 25°C and one atmosphere; outside the two lines  $x$  and  $y$  this pressure is greater than one atmosphere, hence oxygen and hydrogen tend to be evolved and the water is no longer stable.

The decomposition of water can be brought about both chemically and electrochemically. Chemical oxidising and reducing agents with potentials in the range above  $x$  or below  $y$  respectively, are capable of decomposing water. Similarly electrolysis using anodes and cathodes maintained at the desired potential will decompose water into hydrogen and oxygen. In electrolysing a neutral aqueous solution the points representing the anode and cathode will lie at, e.g. 1 and 1' of Fig. 1 if the solution is perfectly stirred so that the anodic and cathodic  $pH$ 's are the same, and

at  $z$  and  $z'$  in the normal case where the anolyte becomes acid and the catholyte becomes alkaline.

The potential of a solution gives a measure of its oxidising or reducing power and it can be shown that at the line  $z$  in Fig. 1 solutions are neutral with respect to oxidation-reduction reactions in the same way as solutions of pH 7 are neutral to acid-base reactions. Solutions with potentials lying above  $z$  are oxidising and those with potentials below  $z$  are reducing.

In constructing potential-pH diagrams for a metal-water system the metal reactions are superposed on the diagram for water and thus the behaviour of a metal in all types of solution whether oxidising, reducing, acid or alkaline can be determined.

### Corrosion Studies

Using certain hypotheses (5) the potential-pH diagram of a metal-water system can be converted to a diagram showing the general circumstances under which the metal is:

- (a) in a state of immunity or of cathodic protection, the metal being then incorrodible because the potential is too low for the corrosion reaction to be thermodynamically possible,
- (b) in a state of corrosion, in which case the metal tends to be dissolved in the aqueous solution, or
- (c) in a state of passivation where the metal is covered by a film of oxide which is generally, though not always, protective.

These states relate to the following domains on the potential-pH diagram: (a) domain of thermodynamic stability of the metal, (b) domain of thermodynamic stability of a metal ion and (c) domain of thermodynamic stability of a metal oxide. In the case (b) corrosion is normally considered to occur if the concentration of metal ions in solution is greater than  $10^{-6}$  g ion/litre, hence the line representing equilibrium between the metal

or metal oxide and a solution of metal ions of concentration  $10^{-6}$  g ion/litre is the line dividing the domains of corrosion and non-corrosion.

### Applications in Electrochemistry

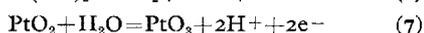
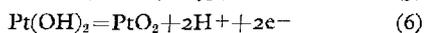
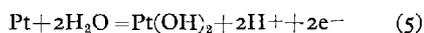
As well as the application to corrosion studies considered above, these diagrams may be applied to the numerous fields of electrochemical reactions which occur in electrolysis, electrodeposition, general chemistry and analytical chemistry. It is important not to forget, however, that the diagrams are theoretical and not valid except within the limits of certain hypotheses; they cannot be used except with prudence, and they should be considered essentially as guides for experimental studies.

Recently the work has been completed in the laboratories of the Centre Belge d'Etude de la Corrosion (Cebelcor) on the treatment of the platinum group metals by this method. Their general electrochemical properties, and in particular their corrosion resistance properties, will now be considered in the light of the above discussion.

## PLATINUM

A potential-pH diagram for the platinum-water system at  $25^{\circ}\text{C}$  was obtained (6) by a consideration of the following six reactions:

### Heterogeneous reactions involving two solid components—electrochemical reactions



Substituting the relevant values of  $E^{\circ}$  in the expression in equation (2) and remembering that since, in these cases, the components A and B are solids the equilibrium is not dependent on their concentration, the following values for equilibrium potential E are obtained:

For equation (5):  $E = 0.980 - 0.0591\text{pH}$

For equation (6):  $E = 1.045 - 0.0591\text{pH}$

For equation (7):  $E = 2.000 - 0.0591\text{pH}$

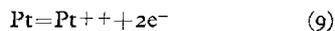
### Heterogeneous reactions involving one solid component—chemical reaction



By substitution in equation (4):

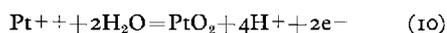
$$\log(\text{Pt}^{++}) = -7.06 - 2\text{pH}$$

### Electrochemical Reactions



Substituting in equation (3):

$$E = 1.188 + 0.0295 \log(\text{Pt}^{++})$$



where

$$E = 0.837 - 0.1182\text{pH} - 0.0295 \log(\text{Pt}^{++})$$

Fig. 3 shows the potential-pH diagram and Fig. 4 the corresponding corrosion diagram obtained from the above equations. The ions  $\text{Pt}(\text{OH})^{+++}$ ,  $\text{PtO}^{+++}$ ,  $\text{PtO}_4^{--}$  and  $\text{PtO}_3^{--}$  are shown in the diagram in their approximate positions but no quantitative treatment was possible due to the lack of thermodynamic data. The oxides  $\text{PtO}_2 \cdot x\text{H}_2\text{O}$  and  $\text{PtO}_3 \cdot x\text{H}_2\text{O}$  are given in the hydrated form, but the exact amount of hydration is

unknown and thus their thermodynamic properties are known only very approximately. This leads to doubt as to the exact position of the lines corresponding to equations (6) and (7).

It must be emphasised here that Fig. 3 is valid only in the absence of substances which form complex ions with platinum. This limitation, which applies to all these diagrams, is, of course, very important in the case of the platinum metals which have a great tendency to form complex ions. In general the presence of complexing substances will increase the corrosion because of the greater tendency for the metal to go into solution.

### Corrosion Properties of Platinum

Fig. 4, deduced from Fig. 3, shows the theoretical conditions for the corrosion, immunity and passivation of platinum. Platinum is seen to be a very noble metal since its domain of stability covers most of the domain of stability of water. With the exception of certain strongly oxidising conditions

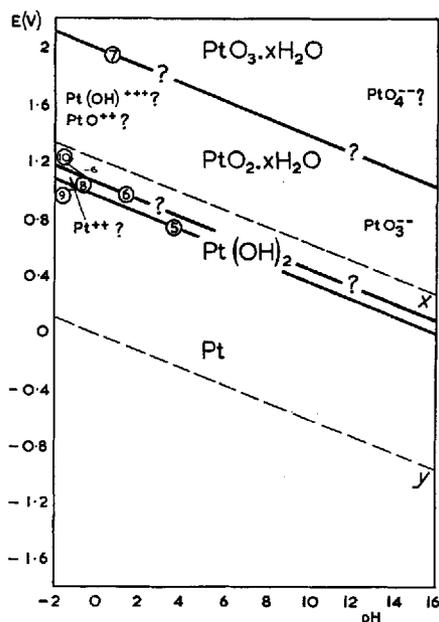


Fig. 3 Potential-pH diagram for the platinum-water system at 25°C

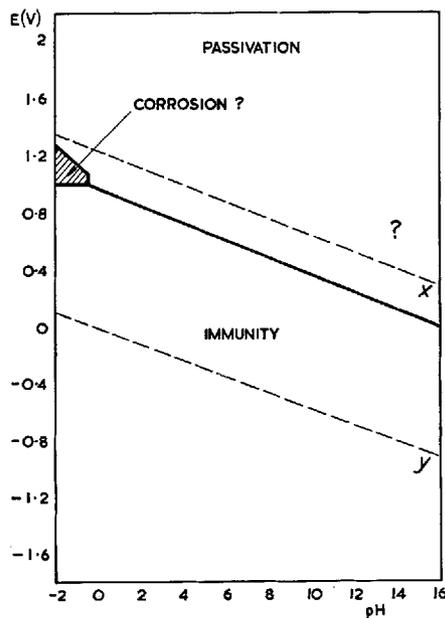


Fig. 4 Theoretical conditions for the corrosion, immunity and passivation of platinum at 25°C

corresponding to the part of Fig. 3 situated above the lines 9 and 5 metallic platinum is stable in the presence of aqueous solutions of any pH, provided they contain no complexing substances. At temperatures around 25°C it remains unaltered in the presence of water or of aqueous solutions of caustic alkalis. It is unattacked by acids and attacked only with difficulty by oxidising agents.

The predictions of Fig. 4 are borne out in practice, where it is found that the non-complexing acids, sulphuric and nitric, do not attack platinum. Ferric chloride and hydrogen peroxide solutions also appear to be without any action. The best known reagent for dissolving platinum, aqua regia, acts by means of a combination of oxidising and complexing actions. Hydrochloric acid, which does not attack platinum on its own, will attack it when it contains chlorine in solution, because it then combines oxidising and complexing actions. According to C. Marie (7), platinum is oxidised at ordinary temperatures by the following reagents:  $K_2S_2O_8$ ,  $K_2Cr_2O_7$ ,  $KClO_3$ , concentrated  $HNO_3$ ,  $K_3Fe(CN)_6$  and  $KMnO_4$ . The oxidation products are  $PtO_2$ , with eventual formation of some  $Pt(OH)_2$  and  $Pt^{++}$  ions.

When used as an anode (upper part of Fig. 4) platinum normally remains unattacked, notably in solutions of sulphuric, nitric and hydrochloric acids and caustic alkali. It is, however, as would be expected from a consideration of Fig. 3, covered with a film of  $PtO_2$  or  $PtO_3$  which is normally protective. If the platinum is used in the form of platinum black, however, the oxide formed is not protective and separates off in the form of a brown skin, the platinum suffering anodic attack.

Platinum cathodes normally absorb large quantities of hydrogen which, according to D. T. Hurd (8), is, for the most part, occluded in fissures and faults in the metallic structure. A. Thiel and W. Hammerschmidt (9) found that a platinum cathode absorbed about 35 times its own volume of hydrogen at ordinary temperature.

## Cathodic Protection

Since the primary step in the corrosion of a metal in aqueous solution is oxidation to its ions, which is only possible above the equilibrium potential, a metallic surface can be corroded only if its potential lies above the potential characteristic of equilibrium between the metal and its ions for the concentration of ions in solution. Corrosion can thus be inhibited by reducing the potential of a metal surface to such a value that the corrosion reaction is thermodynamically impossible. The basis of cathodic protection lies in effecting this reduction of potential by electrical means. The metal is made the cathode in an electrolytic cell in which the corrosive media acts as the electrolyte. Platinum is frequently used as the anode in cathodic protection because, as has been shown above, it is not corroded even at the high potentials at which an anode must be maintained. An important use of cathodic protection occurs in ships and marine installations where platinum anodes have been used with great success.

## Electrodeposition of Platinum

Fig. 3 indicates that metallic platinum is stable in aqueous solution at low potentials, hence it can be deduced that elemental platinum will be formed by the reduction of aqueous solutions of its salts. Such reduction may be achieved electrolytically and platinum is electro-deposited on a commercial scale from electrolytes comprising solutions of complex salts such as sodium hexahydroxyplatinate or diamminodinitrosoplatinum.

## Platinum Electrodes for the Measurement of pH

Platinum is stable under the conditions of potential and pH corresponding to the equilibrium of the reaction



indicated in Fig. 3 by line x. This reaction can be accomplished practically reversibly on

the surface of platinum which has a great facility for absorbing hydrogen. Because of this, platinum can, as is well known, be used for the construction of hydrogen electrodes for the measurement of pH, particularly since it can be employed in a finely divided form previously saturated with hydrogen by cathodic treatment. The potential of this electrode depends on pH and on hydrogen pressure according to the following equation, at 25°C:

$$E = 0.000 - 0.0591pH - 0.0295 \log P_{H_2}$$

When the hydrogen pressure is one atmosphere this relation can be simplified to

$$E = - 0.0591pH.$$

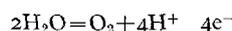
### Stability and Formation of the Oxides of Platinum

It is also possible, by consideration of the potential-pH diagram in Fig. 3, to deduce certain properties of the oxides of platinum.

Hydrated platinous oxide,  $Pt(OH)_2$ , would be expected to be stable, as in fact it is, in water and in non-complexing aqueous solutions provided that they are not oxidising or strongly reducing. As indicated by its position in Fig. 3, it would be expected to act both as an oxidising and reducing agent; it does, in fact, oxidise hydrogen, hydriodic acid, sulphurous acid, and arsenious acid to water,

iodine, sulphuric acid, and arsenic acid respectively while itself being reduced to platinum and, on the other hand, reduces hydrogen peroxide, ozone, and permanganate to water, oxygen, and manganese dioxide respectively while itself being oxidised to the hydrated form of platinic oxide,  $PtO_2 \cdot xH_2O$ .

Platinic oxide,  $PtO_2$ , would be expected to be stable in the presence of oxygen at one atmosphere pressure since its limit of stability is indicated by the line corresponding to the equilibrium conditions of the reaction:



It should be, and is, stable in the presence of water, unaffected by acid and neutral solutions, and a moderately energetic oxidising agent.

Platinum trioxide,  $PtO_3$ , is unstable and tends to decompose into platinic oxide and oxygen as would be expected. It is an extremely powerful oxidising agent capable of oxidising water to oxygen as can be predicted from the figure since it can be seen that water is unstable at the potentials at which  $PtO_3$  exists.

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*The second part of this article, to appear in the July issue of "Platinum Metals Review", will deal with the electrochemical properties of the metals iridium, palladium, rhodium and ruthenium.*

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