FUNDAMENTALS OF THE POTENTIAL-pH DIAGRAM AND ITS APPLICATIONS IN CORROSION STUDIES

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Prediction of corrosion behaviour of a metal under different environmental conditions has been described with the help of thermodynamics. This is represented in the potential pH diagram as drawn for copper and magnesium. The factors which limit the practical application of such a diagram has been described.

Recent work of Pourbaix[1] and his associates has shown that the corrosion phenomenon of metals in aqueous solutions can be represented diagrammatically in a condensed form. Later a short approach to this has been shown by Vernik[2]. It is a major advance in the field of corrosion. In the present paper, an attempt has been made to classify the construction, interpretation and application of the potential pH diagram developed by Pourbaix.

The diagram is a graphical representation of the possible chemical and electrochemical reactions calculated from the thermodynamic values of the reactants and reaction products. Before describing the corrosion phenomenon it is necessary to understand the difference between a chemical and electrochemical reaction.

In a chemical reaction, only neutral molecules and positively or negatively charged ions take part, with the exclusion of electrons[1] e.g.
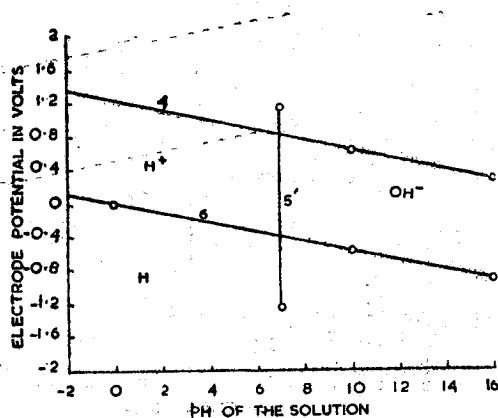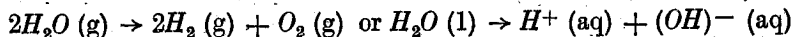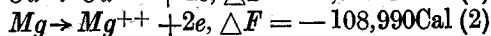
$$2H_2O \text{ (g)} \rightarrow 2H_2 \text{ (g)} + O_2 \text{ (g)} \text{ or } H_2O \text{ (1)} \rightarrow H^+ \text{ (aq)} + (OH)^- \text{ (aq)}$$


Fig. 1—Potential (pH) diagram for water illustrating the equilibrium of $H+$, OH^- and gaseous hydrogen.

An electrochemical reaction has been defined to be a reaction involving, besides molecules and ions, electrons arising from a metal or other substance by metallic conduction. Oxidation is that reaction which proceed in the direction corresponding to the liberation of electrons, such as,

$$Cu \rightarrow Cu^{++} + 2e, \triangle F = 15,530 \text{ Cal} \quad (1)$$
$$Mg \rightarrow Mg^{++} + 2e, \triangle F = -108,990 \text{Cal} \quad (2)$$

where $\triangle F$ = change in free energy.

On the other hand, in case of reductions, the reaction proceeds in the direction corresponding to the absorption of electrons, e.g.,
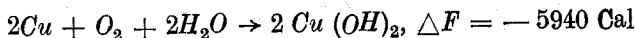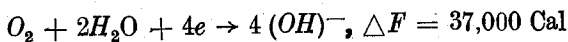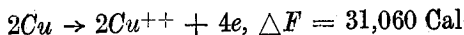
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$$O_2 + 2H_2O + 4e^- \rightarrow 4 (OH)^- \text{ (aq)} \tag{3}$$
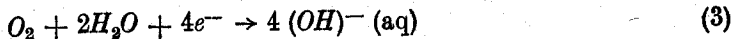
$$\triangle F = - 37,000 \text{ Cal.}$$

The free energy of the reactions like (3) can be calculated from the free energy of formation of H_2O [— 56,690 Cal.] and that of $(OH)^-$ [— 37,595 Cal.] The free energy of the various reactions are now available from the work of Pourbaix[1] and Latimer[3].

Reactions like (1), (2) or (3) frequently appear in the construction of the diagram and it is to be understood that when such a reaction like (1), (2) is presented, it represents only the reaction at the anodic sites and a reaction like (3) must have been occuring at some other site simultaneously. When corrosion occurs the free energy of reactions like (1) and (3) will combine to give a net negative free energy of the total reaction.

Thus

$$2Cu \rightarrow 2Cu^{++} + 4e, \triangle F = 31,060 \text{ Cal}$$

$$O_2 + 2H_2O + 4e \rightarrow 4 (OH)^-, \triangle F = 37,000 \text{ Cal}$$

$$2Cu + O_2 + 2H_2O \rightarrow 2 Cu (OH)_2, \triangle F = - 5940 \text{ Cal}$$

So copper will corrode in presence of oxygen and water and is not immune in this state.

But in water, in the absence of oxygen, the situation is different. The anodic reaction $Cu \rightarrow Cu^{++} + 2e, \triangle F = + 15,530$ Calorie can only be associated with cathodic reaction $2H^+ + 2e = H_2$ (g); if $\triangle F = 0$; the free energy change for the total reaction is positive, hence the copper will not corrode in water at pH value zero, whereas magnesium will corrode spontaneously. This is apparent from Fig. 2 and Fig. 3, where

for copper $\triangle F = nF (y_2 - y_1) =$ positive

for magnesium $\triangle F = nF (y_2' - y_1) =$ negative

In natural condition; water has neither $pH = 0$ (in which case only $\triangle F = 0$ for the reaction $2H^+ + 2e \rightarrow H_2$) nor the metal dipped in water has a concentration of one gm mol per litre. Adoption of the following familiar equation will help to proceed further.
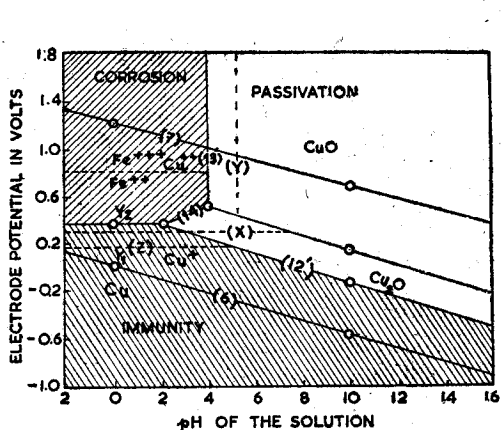

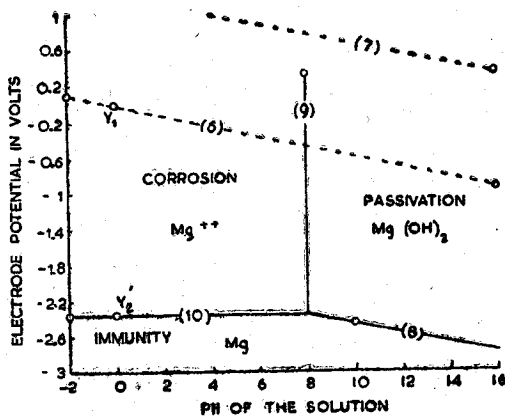Fig. 2—Potential (pH) diagram of copper illustrating the stable regions of Cu, Cu^{++}, CuO and Cu_2O.

Fig. 3—Potential (pH) diagram of magnesium illustrating the relative stability of Mg, Mg^{++} and MgO.

$$E = E_0 + \frac{RT}{nF} \; Ln \; \frac{\text{activity of oxidised state}}{\text{activity of reduced state}} \qquad (4)$$

and $\quad \triangle F = + \; n \; F.E.$

where $\triangle F = $ Free energy change of the reaction.

$\quad\quad E = $ Reversible electrode potential.

$\quad\quad T = $ Absolute temperature.

$\quad\quad n = $ Number of electrons liberated or absorbed in the reaction.

$\quad\quad R = $ Universal gas constant.

For copper to cupric ion in the standard state :

$$\triangle F = 15530 = 2 \cdot 96500 \; E_0 \times \text{[Conversion factor for volt Coulomb Watt, to Calorie]}$$

or $$E_0 = \frac{15530 \times 4 \cdot 18}{2 \times 96500} = + \cdot 34 \; \text{Volt.}$$

This shows the calculation of the oxidation potential of a metal from its free energy of formation or vice-versa

For the reaction, $\quad H_2 \rightarrow 2H^+ + 2e$

$$E = E_0 + \frac{RT}{2F} \; Ln \; \frac{(aH^+)^2}{\{pH_2 \; (g)\}} \;, \quad \text{if } pH_2 \; (g) = 1$$

We have $E = \cdot 059 \log (aH^+)$

$\quad\quad\quad = - \cdot 059 \cdot pH; \quad \text{for } pH = 7$

$\quad\quad\quad = - \cdot 413 \; \text{Volt}$

or $\quad\quad \triangle F = - 9534 \; \text{Cal/gm ion.}$

For the cathodic reduction

$$2H^+ + 2e = H_2; \; E = 0 \cdot 413 \text{ and } \triangle F = + 9534 \; \text{Cal.}$$

For the anodic oxidation of copper $\quad Cu \rightarrow Cu^{++} + 2e$

$$E = .34 + \frac{RT}{2F} \; Ln \; \frac{(a \; Cu^{++})}{a \; Cu}$$

$$= \cdot 34 + \frac{\cdot 059}{2} \log (a \; Cu^{++})$$

So for corrosion of copper to occur in pure water

$$+ \cdot 34 + \frac{\cdot 059}{2} \log a \; Cu^{++} \leqslant - 0 \cdot 413,$$

or $$a \; Cu^{++} \leqslant 10^{-25 \cdot 5} \; \text{gm per litre.}$$

So in pure water copper will dissolve to a negligible extent of $10^{-25 \cdot 5}$ gm per litre only, whereas base metals will corrode spontaneously. The above discussion also shows that for higher partial pressure of hydrogen less of metal will corrode.

CONSTRUCTION OF DIAGRAM

These thermodynamic considerations can be represented systematically in details in a potential—pH diagram of the metal in aqueous solution. To draw the diagram the possible reactions between the metal, H^+, and $(OH)^-$ are to be written first. e.g.,
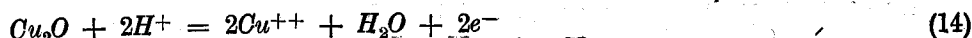
For water

$$H_2O = H^+ + (OH)^- \tag{5}$$

$$H_2 = 2H^+ + 2e^- \tag{6}$$

$$2H_2O = O_2 + 4H^+ + 4e^- \tag{7}$$

For magnesium

$$M_g + H_2O = M_gO + 2H^+ + 2e^- \tag{8}$$

$$M_g^{++} + H_2O = M_gO + 2H^+ \tag{9}$$

$$M_g = M_g^{++} + 2e \tag{10}$$

For copper

$$Cu = Cu^{++} + 2e \tag{11}$$

$$2Cu + H_2O = Cu_2O + 2H^+ + 2e^- \tag{12}$$

$$Cu^{++} + H_2O = CuO + 2H^+ \tag{13}$$

$$Cu_2O + 2H^+ = 2Cu^{++} + H_2O + 2e^- \tag{14}$$

After writing the equations, the following derived equations from equation (4) are to be used for the electrochemical reaction $aA + CH_2O = bB + mH^+ + ne$

$$E = E^0 - \frac{\cdot 0591 \, m}{n} \, pH + \frac{0 \cdot 0591}{n} \, \log \frac{(B) \, b}{(A) \, a} \tag{15}$$

and
$$E^0 = \frac{bB - aA}{23060 \cdot n} = \frac{\Sigma \nu \mu^0}{23060 \cdot n} = \frac{\Sigma \nu \mu^0}{\dfrac{96500 \cdot n}{4 \cdot 18}}$$

where μ^0 is the standard chemical potential.

$\nu =$ Number of species taking part in a reaction. (a, b, c. etc.).

For chemical reactions:

If μ be the chemical potential of the various reacting substances M.

We have, $\mu = \mu^0 + RT \, Ln(M)$

where $R =$ is the ideal gas constant

$T =$ is the absolute temperature.

For equilibrium of a chemical reaction :

$$\Sigma \nu \mu^0 = 0$$

or

$$\Sigma \nu \mu^0 + RT \ \Sigma \nu \log (M) = 0$$

or

$$\Sigma \nu \mu^0 + 4 \cdot 575 \ T \ \Sigma \nu \log (M) = 0$$

or

$$\Sigma \nu \log (M) = - \ \frac{\Sigma \nu \mu^0}{4 \cdot 575 \ T} = \log K$$

At   25 °C $$\Sigma \nu \log (M) = \log K = - \frac{\Sigma \nu \mu^0}{1363}$$

For the reaction $aA + H_2O = bB + mH^+$

$$\log \frac{(B)b}{(A)a} = - \ \frac{\Sigma \nu \mu^0}{1363} + m \ p\text{H} \tag{16}$$

The values of $\Sigma \nu \mu^0$ can be obtained readily. Putting these values in equation (15) we obtain for copper, for the reaction

$$Cu \ \rightarrow \ Cu^{++} + \ 2e$$

$$E = \frac{\overset{[Cu^{++}]*}{15530}}{\dfrac{96500}{4 \cdot 18} \cdot 2} + \frac{\cdot 0591}{2} \ \log (Cu^{++})$$

$$= \cdot 34 + .0295 \log (Cu^{++}) \tag{17}$$

For the reaction $2Cu + H_2O = Cu_2O + 2H^+ + 2e$

$$E_0 = \frac{- \overset{[Cu_2O]}{34980} + \overset{[H_2O]}{56690}}{23060 \cdot 2} - \frac{2 \cdot 0591}{2} \ p\text{H}$$

$$E_0 = 0 \cdot 471 - 0 \cdot 0591 \ p\text{H} \tag{18}$$

Using equation (16) for the chemical reactions :

$$H_2O = H^+ + (OH)^-$$
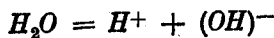
$$\log (OH)^- = - \frac{- \overset{[OH^-]}{37595} + \overset{[H_2O]}{56690}}{1363} + p\text{H}$$

$$= - 14 + p\text{H} \tag{19}$$

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*The symbol on the bracket represents the species for which μ^0 has been used.

and for the reaction

$$Cu^{++} + H_2O = CuO + 2H^+$$
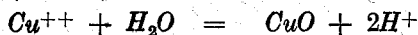
$$\log \frac{CuO}{(Cu^{++})} = \frac{-\overset{[CuO]}{30400} + \overset{[H_2O]}{56690} - \overset{[Cu^{++}]}{15530}}{1363} + 2\,p\text{H}$$

$$\log (Cu^{++}) = 7\cdot89 - 2\,p\text{H} \tag{20}$$

From equation (15) we obtain lines parallel to the $p\text{H}$ axis [in equation (17) by inserting some definite value of concentration of copper ion] and inclined lines [equation (18)]. From equation (16) we obtain lines perpendicular to the $p\text{H}$ axis, if we put the activity of both the substance, equal or unity, [Equations (19) and (20)].

The position of a line changes when activity changes from unity. If copper in contact with $0\cdot01$ molar solution of Cu^{++} is considered, the activity of the solution is $0\cdot01$ and the position of the line will be given by

$$E = 0\cdot34 + 0\cdot0295 \log (0\cdot01)$$

$$= 0\cdot34 - 0\cdot0590$$

$$= 0\cdot281 \text{ Volts. Derived from equation (17).}$$

This is represented by the line x in the Fig. 2. Similarly when $0\cdot01$ molar solution of Cu^{++} ions are in contact with CuO, the position of line [equation (20)] in Fig. 2, will be shifted and determined by the equation :

$$\log (0\cdot01) = 7\cdot89 - 2\,p\text{H}$$

or

$$-2 = 7\cdot89 - 2\,p\text{H}$$

$$p\text{H} = \frac{9\cdot89}{2} = 4\cdot945$$

This is represented by the line y.

However, for the alloy systems, Lumsden[4] has attempted to get the activity of the constituents from the mole fraction of the constituents ; but Pourbaix[5] himself suggested not to use his diagram in the case of alloys for interpretation of their corrosion behaviour. When the oxidation reduction systems such as $Cu^+ \rightleftharpoons Cu^{++} + e$ or $Fe^{++} \rightleftharpoons Fe^{++} + e$ ions are involved, these being an electrochemical reaction, equation (15) is to be used,

So for the reaction $\qquad Cu^+ \rightleftharpoons Cu^{++} + e$

$$E = \frac{15530 - 12000}{\dfrac{96500}{4\cdot 18}\cdot 1} + \cdot 0591 \log\left(\frac{Cu^{++}}{Cu^+}\right)$$

$$E = \cdot 153 + \cdot 0591 \log\left(\frac{Cu^{++}}{Cu^+}\right)$$

We get the line z in the Fig. 2 by taking the activity of both the ions to be equal. Similarly for the electrochemical reaction $Fe^{++} = Fe^{+++} + e$

$$E = \frac{-2530 + 20300}{\dfrac{96500}{4\cdot 18}} + 0\cdot 0591 \log\left(\frac{Fe^{+++}}{Fe^{++}}\right)$$

$$= 0\cdot 771 + 0\cdot 0591 \log\left(\frac{Fe^{+++}}{Fe^{++}}\right)$$

This equation shows that Fe^{+++}/Fe^{++} line in potential pH diagram for a strong ($\sim$ fraction of Normal) solution of $FeCl_3$ is much above the Cu^{++}/Cu line, and thus it explains copper dissolution in this solution. Similarly the behaviour of chromic acid can be explained. Pourbaix[6] also verified his theoretical predictions of immunity, corrosion and passivation for iron with passivating agents such as chromates, permanganates, and polarizing the corrosion samples anodically or cathodically.

DISCUSSIONS

The diagram shows directly that when the metal oxidation line (equation 17) lies above the line represented (equation 6) in water diagram, the metal is immune and when it is below [e.g. $Mg = Mg^{++} + 2e$ equation (10)] the metal will corrode spontaneously These diagrams have been drawn for all the metals in aqueous solution[1], and from a glance of this diagram we can follow the corrosion characteristics of the metal in aqueous, acidic or alkaline solution.

However, the rate of corrosion cannot be determined from the potential pH diagram as it depends on the nature of the passive film formed, the exchange current density of the anodic and cathodic reactions, and their polarization behaviour[7].

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