THE ELECTROCHEMISTRY OF CORROSION

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INTRODUCTION

The surfaces of all metals (except for gold) in air are covered with oxide films. When such a metal is immersed in an aqueous solution, the oxide film tends to dissolve. If the solution is acidic, the oxide film may dissolve completely leaving a bare metal surface, which is said to be in the active state. In near-neutral solutions, the solubility of the oxide will be much lower than in acid solution and the extent of dissolution will tend to be smaller. The underlying metal may then become exposed initially only at localised points where owing to some discontinuity in the metal, e.g. the presence of an inclusion or a grain boundary, the oxide film may be thinner or more prone to dissolution than elsewhere. If the near-neutral solution contains inhibiting anions, this dissolution of the oxide film may be suppressed and the oxide film stabilised to form a passivating oxide film which can effectively prevent the corrosion of the metal, which is then in the passive state.

When the oxide-free surface of a metal becomes exposed to the solution, positively charged metal ions tend to pass from the metal into the solution, leaving electrons behind on the metal, i.e.

$$\underset{\textit{atom in metal surface}}{M} \rightarrow \underset{\textit{ion in solution}}{M^{n+}} + \underset{\textit{electron(s) in metal}}{ne^{-}} \qquad (1)$$

The accumulation of negative charge on the metal due to the residual electrons leads to an increase in the potential difference between the metal and the solution. This potential difference is called the electrode potential or, simply, the potential of the metal, which thus becomes more negative. This change in the potential tends to retard the dissolution of metal ions but to encourage the deposition of dissolved metal ions from the solution onto the metal, i.e. the reverse of reaction (1). Continuation of the dissolution and deposition of metal ions would result in the metal reaching a stable potential such that the rate of dissolution becomes equal to the rate of deposition. This potential is termed the reversible potential E_r and its value depends on the concentration of dissolved metal ions and the standard reversible potential E^o for unit activity of dissolved metal ions, $a_M{}^{n+}$, i.e.

$$M^{n+} + ne^{-} \leftrightarrows M \tag{2}$$

$$E_{r,M^{n+}/M} = E^{o}{}_{M^{n+}/M} + \frac{RT}{nF} \ln a_{M^{n+}} \tag{3}$$

where R is the gas constant, T the absolute temperature, F the Faraday and n the number of electrons transferred per ion. Once the potential reaches the reversible potential, no further net dissolution of metal occurs. The net amount of metal which dissolves during this process is generally very small.

The potential of a metal in a solution does not usually reach the reversible potential but remains more positive because electrons can be removed from the metal by alternative reactions. In acid solutions, electrons can react with hydrogen ions, adsorbed on the metal surface from the solution, to produce hydrogen gas.

$$\underset{\textit{adsorbed on metal surface}}{2H^{+}} + \underset{\textit{in metal}}{2e^{-}} \rightarrow \underset{\textit{gas}}{H_2} \tag{4}$$

The occurrence of reaction (4) permits the continued passage of an equivalent quantity of metal ions into solution, leading to corrosion of the metal. Reaction (4) is also reversible and has a reversible potential given by

$$E_{r,H^{+}/H_2} = E^{o}{}_{H^{+}/H_2} - \frac{RT}{F} \ln \frac{p_{H_2}^{\frac{1}{2}}}{a_{H^{+}}} \tag{5}$$

where p_{H_2} is the partial pressure (fugacity) of hydrogen gas. If the partial pressure of hydrogen is allowed to build up, then the reversible potential of reaction (4) could be attained. No further net reaction of hydrogen ions would occur and so the net dissolution of metal ions would effectively cease. Normally hydrogen escapes from the system, so that the potential remains more negative than the reversible potential and corrosion continues.

In neutral solutions, the concentration of hydrogen ions is too low to allow reaction (4) to proceed at a significant rate, but electrons in the metal can react with oxygen molecules, adsorbed on the metal surface from air dissolved in the solution, to produce hydroxyl ions

$$\underset{\text{adsorbed on metal surface}}{O_2 + 2H_2O} \quad \underset{\text{in metal}}{+4e^-} \quad \rightarrow \quad \underset{\text{in solution}}{4OH^-} \tag{6}$$

Again, the potential of the metal remains more negative than the reversible potential for reaction (6)

$$E_{r,O_2/OH^-} = E^o_{O_2/OH^-} - \frac{RT}{4F} \ln \frac{a_{OH^-}{}^4}{p_{O_2}} \tag{7}$$

Thus corrosion can proceed by the coupling of reactions (1) and (6).

In electrochemical terminology, an electrode at which an oxidation reaction occurs is called an anode. The process of oxidation involves a loss of electrons by the reacting species, as occurs in the metal dissolution reaction (1). Thus an area of a corroding metal where metal dissolution occurs is an anode and metal dissolution is the anodic reaction of corrosion. An electrode at which a reduction reaction occurs is called a cathode. Reduction involves a gain in electrons, as occurs in reactions (4) and (6). The reduction of hydrogen ions and oxygen are thus the cathodic reactions of corrosion and the area of a corroding metal where these reactions occur is a cathode.

POTENTIALS AND POLARISATION

Since the corrosion reactions involve the transfer of electrons and ions between the metal and the solution the rates are equivalent to electric currents. The rates of these reactions depend on the potential difference between the metal and the solution, i.e. the potential of the metal. As the potential of the metal becomes more positive, the rates of anodic reactions increase and the rates of cathodic reactions decrease. The converse effect on the reaction rates occurs as the potential of the metal becomes more negative. From the relationships between the potential of a metal and the currents flowing (equivalent to rates of the corrosion reactions) the corrosion behaviour can be understood. The relationships between potential and current (termed polarisation curves) can be determined as shown schematically in Fig 1. The potential in the test solution of the metal under study, the working electrode, is measured against that of a reference electrode by means of a voltmeter. The reference electrode is chosen to give a stable and reproducible potential in the solution. The reference electrode most commonly used is the saturated calomel electrode, which consists of mercury covered with a paste of mercurous chloride and mercury in a chloride solution. The potential depends on the concentration of chloride ions and a saturated solution of potassium chloride is used because this minimises the junction potential between the test solution and the solution in the reference electrode in the measuring cell.

Metal/Test solution/KCI (satd), Hg_2CI_2 (solid)/Hg. Contact between the test solution and the saturated potassium chloride solution of the calomel electrode is usually made through a porous ceramic plug, which minimises the mutual contamination of the two solutions. The potential difference across this cell gives the potential of the metal in the test solution against the saturated calomel electrode (SCE) and is quoted as such. The primary standard of electrode potential is the standard hydrogen electrode (hydrogen gas at 1 atm pressure (unit fugacity) over platinised platinum in a solution containing hydrogen ions at unit activity) which is arbitrarily defined as having a potential of zero volts at all temperatures?, i.e. $E^{o}{}_{H^+/H_2}$ in equation (5) is zero. This is not commonly used as a practical electrode, but potentials are often quoted on this scale, e.g. the potential of the saturated calomel electrode is +0.24 volt against the standard hydrogen electrode (SHE). Another reference electrode used for measuring potentials of corroding metals is the silver/silver chloride electrode, which consists of a silver wire coated with silver chloride in a chloride solution. This electrode is commonly used in seawater. For measuring potentials of metals in soils, the copper/copper sulphate electrode may be used. This consists of a copper rod in a saturated solution of copper sulphate. This electrode can be made very robust, with a wooden plug saturated with the copper sulphate solution to make contact with the test environment.

The potential-current relationship of the working electrode may be determined by either of two main methods. In the galvanostatic method, a fixed current is applied from a constant-current power source connected between the working electrode and a counter electrode, which is usually made of some inert material such as platinum. The change in potential induced in the working electrode by the passage of current is measured against the reference electrode.

In order to minimise the inclusion in the measured potential of any potential drop occurring in the solution due to its resistance, i.e. an IR drop, the reference electrode is brought into contact with the test solution through a tube which ends in a fine capillary known as a Luggin capillary. This is placed close to the surface of the working electrode, though no closer than twice the external diameter of the capillary to avoid screening of the electrode from the flow of current. In the potentiostatic method, as illustrated in Fig 1, the potential of the working electrode is controlled at a fixed value with a potentiostat. This instrument uses a feed-back circuit to pass appropriate currents to the working electrode so that its potential measured against the reference electrode is maintained at the desired value, regardless of variations in current corresponding to changes in the rates of the corrosion reactions. The potentiostatic method of polarisation has the advantage that it can follow more closely the behaviour of metals during the formation and breakdown of passivating films, where the behaviour primarily depends on the potential of the metal, and very large changes in currents can occur at constant potential.

POLARISATION BEHAVIOUR OF CORRODING METALS

A corroding metal in a solution takes up a potential, the corrosion potential, such that the rate of the anodic reaction of metal dissolution is equal to the rate of the cathodic reactions of hydrogen and/or oxygen reduction. If the potential of the corroding metal is displaced slightly from the corrosion potential, E_{corr}, either by galvanostatic or potentiostatic polarisation, then the potential E is initially a linear function of the current density i (the current per unit area). This linear relationship holds for a potential displacement of up to about 10 mV. The slope of the linear polarisation curve dE/di is termed the polarisation resistance R_p. The polarisation resistance is inversely proportional to the rate of corrosion expressed as the equivalent corrosion current density i_{corr}, i.e.

$$i_{corr} = B / R_p \qquad (8)$$

where B is a constant. Measurements of the polarisation resistance provide a valuable means of rapidly determining the instantaneous rate of corrosion of a metal, as used in several commercial instruments. The value of the constant B can be determined from weight loss measurements or from electrochemical data.

As the displacement of the potential of the metal from the corrosion potential is increased beyond about 10 mV, the polarisation curve increasingly deviates from the linear relationship between potential and current until a region is reached when the potential exhibits a linear dependence on the logarithm of the current density as shown in Fig 2. This behaviour is characteristic of the occurrence of a single electrochemical reaction on the metal surface, indicating that the displacement of potential is so great that one of the corrosion reactions, either anodic or cathodic depending on the direction of potential change, has been retarded until its rate is negligible compared to the rate of the reaction being accelerated. Then the relationship between the observed potential E and current density i is given by

$$E - E_r = i_o + b \log i \tag{9}$$

The difference between the observed potential and the reversible potential E_r is the over-potential. The term i_o is the exchange current density, i.e. the current density of the opposing reactions at the reversible potential. The constant b which is the slope dE/d log i of the polarisation curve is termed the Tafel slope and is related to the kinetics of the corrosion reaction. For the cathodic reactions of hydrogen ion reduction or oxygen reduction, the value of B is generally about 120 mV. For metal dissolution reactions from active surfaces, values of b are generally smaller and in the range 30 to 70 mV.

Polarisation curves similar to that of Fig 2 are generally observed for both the anodic dissolution of metal and the cathodic reduction of hydrogen ions in acid solutions. Figure 3 shows schematically the juxtaposition of the anodic and polarisation curves (full lines) for a metal corroding in an acid. This diagram also shows the relationship of the polarisation curves to the reversible potentials and exchange current densities of the metal dissolution and hydrogen ion reduction reactions. The observed Tafel regions of the polarisation curves extrapolated to the corrosion potential E_{corr}, intersect there to give the value of the corrosion current density i_{corr}. Further extrapolation leads to the reversible potentials and exchange currents of the reactions, the values of which determine the relative position of the observed polarisation curves. The values of the reversible potentials represent the extreme values which the potentials of the anodic and cathodic areas can reach. If the concentration of hydrogen ions in the acid is increased, then according to equation (5) the reversible potential becomes more positive. The exchange current also increases, but the Tafel slope of the polarisation curve remains unchanged. Thus the polarisation curve of the hydrogen ion reduction reaction is displaced parallel to itself, from AB to CD, to initiate at the more positive reversible potential and large exchange current density, as shown in Fig 4. According to equation (3), the anodic reaction is not affected by the change in pH. Thus the increase in hydrogen ion concentration causes the anodic and cathodic polarisation curves now to intersect at D instead of B, so that the corrosion potential becomes more positive and the current at the intersection, the corrosion current increases. Diagrams such as Fig 4, which represent schematically the polarisation curves of the anodic and cathodic reactions in relation to the corrosion potential and current are known as Evans Diagrams. These are valuable for understanding and predicting qualitatively the influence of changes in the polarisation curves on the corrosion potentials and currents, and conversely the effects of changes in corrosion potential and current on the polarisation curves.

The cathodic and anodic reactions of corrosion will now be considered in more detail.

CATHODIC REACTIONS

In the cathodic reduction of hydrogen ions or oxygen molecules, these species must be adsorbed on the metal surface in order to react. Thus the hydrogen ions or oxygen molecules must be transported from the bulk solution up to the metal/solution interface. This transport occurs by the processes of diffusion and convection, and in the case of hydrogen ions electromigration. As the potential of the metal is made more negative in the Tafel region, the rate of reduction of hydrogen ions and oxygen molecules may increase to such an extent that it exceeds the rate at which these species can be transported to the metal surface. Then the rate of transport of the reducible species controls the rate of reduction. The cathodic current density attains a limiting value equivalent to the rate of transport and independent of potential, as illustrated in Figs 5 and 6. This is termed the limiting diffusion current density and its magnitude increases with increasing concentration of the reducible species (Fig 5) and increasing movement of the solution (Fig 6). As the potential becomes even more negative, the rate of reduction of water to produce hydrogen

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (10)$$

increases until it may exceed the diffusion limited rates of reduction of hydrogen ions or oxygen. The observed current density then increases e.g. along the line JKC in Fig 5, due to the reduction of water. In this potential region the diffusion limited currents of reduction of hydrogen ions or oxygen continue to contribute to the total observed currents.

In acid solutions the limiting diffusion current density for reduction of hydrogen ions becomes significant in relation to corrosion at hydrogen ion concentrations of 0.01 M (i.e. pH 2) and below. The concentration of dissolved oxygen in air saturated aqueous solutions at ambient temperature is about 0.002 M and so the rate of transport of oxygen often limits the cathodic reduction current and the corrosion rate. The effect on the corrosion currents or rates is illustrated in Figs 5 and 6, which could represent the corrosion of steel in neutral chloride solutions. If the anodic polarisation curve intersects the cathodic polarisation curves in the region of the limiting diffusion currents, the corrosion currents are equal to the limiting diffusion currents and hence increase with increasing flow velocity (Fig 6) and concentration (Fig 5), the corrosion potentials becoming more positive. If there is a change in the position and/or Tafel slope of the anodic polarisation curve, e.g. due to a change in solution composition or for a different metal, the intersections of the anodic curves with the limiting current density regions of the cathodic curves lead to the same corrosion currents, though the corrosion potentials change. Thus under these conditions the corrosion rates depend only on the rate of reduction of the cathodic reactant and the corrosion is said to be under cathodic control.

ANODIC REACTIONS

On anodic polarisation of a metal, as the potential is made more positive in the Tafel region, as in Fig 3, the current for metal dissolution may reach a maximum value and then decrease abruptly to a small value, as indicated schematically in Fig 7. This behaviour is best observed by potentiostatic polarisation, and is due to the reaction of the metal surface with water to form an oxide, e.g.

$$xM \;+\; y\,H_{2O} \;\rightarrow\; M_xO_y \;+\; 2yH^+ \;+\; 2ye^- \qquad (11)$$

$$E_{r,M_xO_y/M} \;+\; E^o{}_{M_xO_y/M} \;+\; \frac{RT}{F}\ln a_{H^+} \qquad (12)$$

The oxide gradually spreads over the surface to form a thin film. The passage of metal ions through an oxide film takes place very slowly and so the current due to metal ions leaving the metal becomes very small when the surface is completely covered with an oxide film. The metal is thus protected against corrosion by a passivating oxide film. The formation of the passivating oxide film is observed to begin near the peak B of the polarisation curve AB and the potential of the peak is referred to as the critical (primary) passivation potential, E_{pp}. The initial passivation potential depends on the pH value of the solution becoming about 60 mV more negative for a unit increase in pH value. The critical passivation potential also depends slightly on the composition of the solution, particularly with respect to the presence of anions which may favour or hinder passivation. Another important parameter of the passivation process is the critical passivation current density (i_{crit}) which is required to attain the critical passivation potential. The critical passivation current density generally decreases considerably as the pH increases, reflecting the increasing stability of the oxide films with respect to dissolution. The critical passivation current density is also dependent on the nature of the anions in the solution, according to whether these tend to stabilise the oxide film. The value of the critical passivation current density gives a measure of the ease of passivation; the smaller the current, the easier is passivation.

When the metal surface is completely covered with a passivating oxide film, the oxide film thickness increases to an equilibrium value and the current of metal ions passing through the film becomes independent of potential. The most negative potential at which this state is attained is called the Flade potential, E_F. This represents the most negative limit of stability of the passive state, and is usually determined by allowing the potential to become more negative from the passive state, so that the transition to the active state is observed. The Flade potential is generally close to the critical passivation potential and depends on the composition of the solution in a similar way. The passive current density i_p which passes through the passivating film is a measure of the protectiveness of the film. The passive current density decreases as the pH is made more alkaline and may also depend on the anion content of the solution.

As the potential of a metal in the passive state is made more positive, the passive current density i_p remains reasonably constant until eventually the current begins to increase with potential. Such increase in current may be due to localised breakdown of the passivating oxide film by anions, particularly chloride ions. These anions induce localised dissolution of the passivating oxide film at weak points, usually associated with some discontinuity such as a grain boundary, dislocation or inclusion in the metal, leading to exposure of the underlying metal which can dissolve, giving rise to an increase in the anodic current. Continued dissolution can lead to the formation of pits. The breakdown of the oxide by anions with the initiation of pitting occurs at a critical potential called the critical breakdown or pitting potential E_b, and the current then increases rapidly with potential, as along DE. The value of E_b depends on the concentrations in the solution of inhibitive anions (which stabilise the passivating oxide film) and aggressive anions (which break down the oxide film). If the ratio of inhibitive to aggressive anions is sufficiently high, the breakdown of the film by the anions may be completely suppressed and no critical breakdown potential is observed. As the ratio of inhibitive to aggressive anions decreases, the breakdown potential is observed to become more negative.

If the composition of the solution is such that breakdown of the film by aggressive anions does not occur, then for some metals an increase in anodic current may be observed to occur with positive displacement of potential e.g. along FG, when oxidation of the metal occurs to produce a soluble ion. Thus on chromium containing alloys, such as stainless steels, the chromium may be oxidised at rather positive potentials to form dichromate ions, which are soluble

$$2\,Cr + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 12e^- \qquad (13)$$

This process is known as transpassive dissolution and becomes important as a corrosion reaction only in strongly oxidising solutions, e.g. concentrated nitric acid. As the potential is made even more positive, the rate of transpassive dissolution may decrease due to the onset at G of secondary passivity, the nature of which is not fully understood. Further increase in potential leads to the breakdown of water, and the anodic current increases with potential along HI due to the evolution of oxygen

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (14)$$

The formation of a passivating oxide film on metal surfaces is an important aspect of corrosion protection. Figure 8 illustrates schematically the anodic and cathodic polarisation curves of a system where passivation is possible e.g. stainless steel in dilute acid solution. If the solution is oxygen-free, the cathodic reaction will be reduction of hydrogen ions with a cathodic polarisation curve UV which intersects with the anodic polarisation curve ABCDE at V, corresponding to corrosion in the active state. The reversible potential U for the hydrogen ion/hydrogen equilibrium is more negative than the critical passivation potential B, and so in this system the potential could not go more positive than U and so passivation could not occur. However, the standard electrode potential for the oxygen/hydroxyl ion equilibrium, equation (7), is 1.24 V more positive than that of the hydrogen ion/hydrogen equilibrium, equation (5). Thus dissolved oxygen is a more powerful oxidising agent than the hydrogen ion, and is more capable of polarising metals into the passive region. However, the reduction of oxygen must occur with such a high current that the equivalent anodic current exceeds the critical current density for passivation, i_{crit} in order to induce transition from the active to the passive state. Thus if a high concentration of oxygen is present, and the solution is flowing, the cathodic polarisation curve will be HIJK. The limiting diffusion current density of the oxygen reduction reaction is greater than the critical passivation density and so the active-passive transition can take place. The anodic and cathodic polarisation curves then intersect at I. This provides a stable corrosion potential in the passive region and the metal will be protected. If only a small quantity of oxygen is present, the polarisation curve will be according to LMNP. If the steel is initially in the active state, the polarisation curves intersect at P and so corrosion proceeds with the corresponding corrosion current. The reduction of oxygen cannot in this case provide sufficient current to bring the potential of the metal to the critical passivation potential. However if the metal is already in the passive state, then the polarisation curves intersect at M. Thus this quantity of oxygen can maintain the passive state. If however the potential of the system falls below N, the anodic current density of dissolution exceeds the limiting current density of oxygen reduction and the potential falls to P and corrosion proceeds in the active state. If a small concentration of chloride ions is present in the solution, then a breakdown potential will be induced at D and the dissolution current will increase along DE. Since the corrosion potential represented by the intersection point I is more negative than the breakdown potential D, then the oxide film remains stable. If the chloride ion concentration is increased so that the breakdown potential is displaced to a more negative potential R, then since the corrosion potential I more positive than R, breakdown will occur and the dissolution current will increase along RS. Thus the protection of a metal by a passivating film depends on the maintenance of the potential at a value between the Flade potential and the breakdown (or transpassive) potential and requires appropriate combinations of concentrations of oxygen, hydrogen ions, and inhibitive and aggressive anions in the solution.

THE ELECTROCHEMICAL NATURE OF THE METAL

For different metals, the cathodic polarisation curves for reduction of hydrogen ions or oxygen molecules do not change greatly. The reversible potentials for these reactions will not change, but the exchange currents and the Tafel slopes of the polarisation curves may differ somewhat. However, the anodic polarisation curves are very dependent on the nature of the metal. The tendency of a metal to form metals ions in the solution is related to its standard electrode potential for the metal/metal ion reaction, equations (2) and (3), which represents the thermodynamic driving force for the dissolution reaction to occur. Values of standard electrode potentials for a number of common metals are given in Table 1. The more negative the standard electrode potential, the greater the tendency to form metal ions and hence to corrode. The reversible potential at the appropriate concentration of metal ions in the solution represents the most negative potential that the metal can attain. However due to the polarisation of the anodic reaction the corrosion potential is more positive than the reversible potential. The corrosion of the metal may be affected by the formation of an oxide film, and the tendency to form such a film is related to the standard electrode potential for the reaction, equations (11) and (12). The values for these standard electrode potentials given in Table 1 generally run parallel with the standard electrode potentials for the metal/metal ion reactions. These standard potentials give the potentials at which an oxide can be formed, but a protective oxide film is not necessarily produced at these potentials, either because (a) the oxide may be soluble in the solution, (b) because for kinetic reasons the oxide needs an additional potential to form at a significant rate, or (c) the oxide film is not stable due to breakdown by aggressive ions e.g. chloride. Thus if the corrosion potentials of the metals in 0.5 M NaCI solution, given in Table 1, are compared with the standard electrode potentials for the formation of metal ions and oxides, the order of the metals is somewhat different. Titanium has the most positive corrosion potential despite its very negative thermodynamic potential for metal ion formation. This is because it forms a very protective oxide film at very negative potentials, and the film is resistant to breakdown by chloride ions.

For chromium and aluminium, there are considerable ennoblements of potential due to the formation of oxide films, but these are partially broken down by chloride ions giving rise to localised corrosion. On the other metals, protective oxide films are not formed due to the effects of chloride ions, or film solubility. The corrosion rate in chloride solution is then controlled mainly by the value of the reversible potential for the metal/metal ion reaction in relation to the cathodic polarisation curve for oxygen and water reduction. This is illustrated in Fig 9, which indicates that the anodic polarisation curves of copper, iron and zinc intersect the cathodic reduction curve of oxygen, so that the corrosion potentials become more negative and the corrosion currents increase in the order, copper < iron < zinc.

For each metal, the thermodynamic data for the reactions involving the metal, its ions, and its oxides can be usefully presented as a potential pH diagram, known as a Pourbaix diagram after its originator. Figure 10 shows a simplified Pourbaix diagram for iron in aqueous solutions in which no complex ions are formed and the oxides or iron are the only stable solid phases. The diagram is calculated for concentrations of dissolved iron of 10^{-6} M and for a temperature of 25 ^{o}C. In the diagram the horizontal lines represent the reversible (or equilibrium) potentials for reactions which are independent of pH i.e. Fe^{2+}/Fe, Fe^{3+}/Fe^{2+}. The vertical line represents an equilibrium with no change in valency i.e. Fe^{3+}/Fe_2O_3. The sloping lines represent equilibria which involve a change in valency and are pH dependent e.g. Fe_3O_4/Fe. The diagram thus shows the zones of thermodynamic stability of the various ions (in solution) and the solid oxides of iron in relation to the standard reversible potentials of the H^+/H_2 or O_2/OH^- reactions, indicated as dashed lines. If the potential–pH condition is such that the thermodynamically stable form of iron is an ion in solution i.e. Fe^{2+}, Fe^{3+} or $HFeO_2^-$, then iron will corrode to produce this ion. If the thermodynamically stable form of iron is the metal, then the state of immunity exists, and the metal cannot corrode. A corroding metal can be brought into the state of immunity by polarising it cathodically to make its potential more negative such that it falls within the immunity zone. This is the process of cathodic protection. If the thermodynamically most stable state of iron is an oxide then it is possible for a protective oxide film to form on the metal surface so that the iron is in the passive state. However, as discussed above, the passivating film may not be protective, and so corrosion may occur in the passive state. Conversely a passivating oxide film may be more protective than appears from the potential –pH diagram. Thus iron can be passivated in sulphuric acid at pH 0 by making its potential more positive than +0.6 V, because a metastable oxide film is produced which possesses a low rate of dissolution.

Pourbaix diagrams are available for all the metals and are useful in understanding and predicting the tendency to corrode. However, the only condition which can be predicted with some certainty is the zone of immunity. In the zones of corrosion and passivity, the kinetic factors controlling the rate of formation and dissolution of surface films are generally more important than the thermodynamic stability of the ions or oxides of the metal in determining whether significant corrosion occurs.

BIBLIOGRAPHY

Electrochemical Principles of Corrosion. A Guide for Engineers.
L L Shreir, Dept. of Industry, 1982.
Elementary Electrochemistry, A R Denaro, Butterworths, 1971 (2nd ed).
Basic Electrochemistry, J M West, Van Nostrand – Reinhold, 1973.

Table 1

Comparison of standard electrode potentials and corrosion potentials in 0.5 M NaCI solution of some common metals

Metal	Standard Electrode Potential for M^{n+}/M	Standard Potential for M_xO_y/M at pH 6	Corrosion Potential in Aerated 0.5 M NaCI Solution pH ~6
	V (SHE)	V (SHE)	V (SHE)
Magnesium	-2.37	-1.27	-1.40
Aluminium	-1.63	-1.84	-0.57
Titanium	-1.66	-1.62	+0.18
Zinc	-0.76	-0.77	-0.78
Chromium	-0.74	-0.93	-0.11
Iron	-0.44	-0.45	-0.44
Copper	+0.34	+0.12	+0.06