

corrosion of metals and alloys than predicted by emf series. Fortunately, the limitations imposed by emf series are overcome by another series called 'galvanic series' which will be now discussed (Table 2.5).

Table 2.5 Galvanic series in seawater at room temperature

1. Magnesium	38. Stainless steel 310 (active)
2. Mg alloy AZ-31B	39. Stainless steel 301 (active)
3. Mg alloy HK-31A	40. Stainless steel 304 (active)
4. Mg alloy (hot-dip, die cast or plated)	41. Stainless steel 430 (active)
5. Beryllium (hot pressed)	42. Stainless steel 410 (active)
6. Al 7072 clad on 7075	43. Stainless steel 17-7PH (active)
7. Al 2014-T3	44. Tungsten
8. Al 1160-H14	45. Niobium (columbium) 1% Zr
9. Al 7079-T6	46. Brass, yellow, 268
10. Cadmium (plated)	47. Uranium 8% Mo
11. Uranium	48. Brass, naval, 464
12. Al 218 (die cast)	49. Yellow brass
13. Al 5052-0	50. Muntz metal 280
14. Al 5052-H12	51. Brass (plated)
15. Al 5456-0, H353	52. Nickel-silver (18% Ni)
16. Al 5052-H32	53. Stainless steel 316L (active)
17. Al 1100-0	54. Bronze 220
18. Al 3003-H25	55. Copper 110
19. Al 6061-T6	56. Red brass
20. Al A360 (die cast)	57. Stainless steel 347 (active)
21. Al 7075-T6	58. Molybdenum, commercial pure
22. Al 6061-0	59. Copper-nickel 715
23. Indium	60. Admiralty brass
24. Al 2014-0	61. Stainless steel 202 (active)
25. Al 2024-T4	62. Bronze, phosphor 534 (B-1)
26. Al 5052-H16	63. Monel 400
27. Tin (plated)	64. Stainless steel 201 (active)
28. Stainless steel 430 (active)	65. Carpenter 20 (active)
29. Lead	66. Stainless steel 321 (active)
30. Steel 1010	67. Stainless steel 316 (active)
31. Iron (cast)	68. Stainless steel 309 (active)
32. Stainless steel 410 (active)	69. Stainless steel 17-7PH (passive)
33. Copper (plated, cast or wrought)	70. Silicone bronze 655
34. Nickel (plated)	71. Stainless steel 304 (passive)
35. Chromium (plated)	72. Stainless steel 301 (passive)
36. Tantalum	73. Stainless steel 321 (passive)
37. AM350 (active)	74. Stainless steel 201 (passive)
	75. Stainless steel 286 (passive)
	76. Stainless steel 316L (passive)
	77. AM355 (active)
	78. Stainless steel 202 (passive)
	79. Carpenter 20 (passive)
	80. AM355 (passive)
	81. A286 (passive)
	82. Titanium 5A1, 2.5 Sn
	83. Titanium 13 V, 11 Cr, 3 Al (annealed)
	84. Titanium 6 Al, 4 V (solution treated and aged)

(Contd)

Table 2.5 (Contd)

85.	Titanium 6 Al, 4 V (annealed)
86.	Titanium 8 Mn
87.	Titanium 13 V, 11 Cr, 3 Al (solution heat treated and aged)
88.	Titanium 75 A
89.	AM350 (passive)
90.	Silver
91.	Gold
92.	Graphite

The galvanic series is an arrangement of metals and alloys in order of their corrosion potentials in the environment. The potentials of the metals and alloys are measured in the desired environments, with the most noble (positive) at the top and the most active at the bottom. Table 2.5 shows a galvanic series of some commercial metals and alloys in seawater. The potentials are measured in seawater by means of a saturated calomel electrode and all potentials

are expressed with reference to this electrode (Fig. 2.17).

2.13.11 CHARACTERISTICS OF GALVANIC SERIES (TABLE 2.5)

- (1) In the galvanic series, instead of potentials the relative positions of the metals and alloys are indicated.
- (2) The series is based on practical measurement of corrosion potential at equilibrium. The potential of a corroding metal in a given medium can be obtained by connecting the metal or alloy to the negative terminal of a voltmeter and the positive terminal to a reference electrode, generally, the calomel electrode.
- (3) The galvanic series indicates that alloys can be coupled without being corroded. For instance, alloys close to each other in the series can be safely coupled. As shown in the table, monel can be coupled to copper, or bronze, without any risk of galvanic corrosion. However, brass cannot be coupled

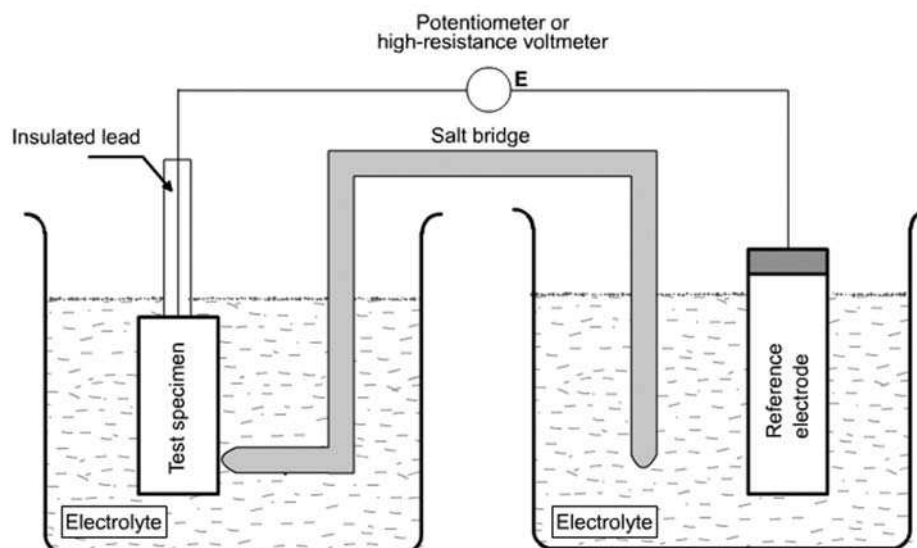


Figure 2.17 Laboratory technique for measuring the single electrode (corrosion) potential E_{corr} of metals and alloys in aqueous environments. Use of salt bridge

with tin, because the two are far away in the table and coupling them may cause serious galvanic corrosion.

- (4) Some alloys exist in two places in the table. For instance, steel (18/8) exists in the passive state as well as in the active state. Steel in the passive state means steel with a film of oxide, which shifts the potential from active to passive. Joining of the two types (active and passive) may lead to serious corrosion. An example of stainless steel in the active state is if it is being continuously scraped.
- (5) Metals and alloys in brackets can be conveniently joined with one another without any risk of corrosion.

Although galvanic series is widely used by designers, nevertheless, it suffers also from certain limitations, such as:

- (1) Each environment requires a different galvanic series, for example, a galvanic series in static seawater cannot be used to predict galvanic corrosion in turbulently flowing seawater.
- (2) Galvanic corrosion also depends on the extent of polarization of the metals in alloys and not only on how close they are in the galvanic series. Predictions based on their position in the galvanic series may not provide enough information on galvanic corrosion. For example, in galvanic corrosion the process of cathodic polarization predominates. For instance, titanium has a tendency to polarize cathodically in seawater. Any less resistant metal attached to titanium will not undergo corrosion as would be expected because of the cathodic polarization of titanium. In engineering applications, alloys rather than pure metals are used, however, the emf series has only a limited value. This series is of extreme importance for design engineers.

In spite of the limitations mentioned above, the galvanic series provides valuable information to engineers and scientists on the galvanic corrosion of metals and alloys in different environments.

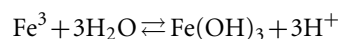
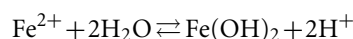
2.14 POURBAIX DIAGRAMS (STABILITY DIAGRAMS)

2.14.1 INTRODUCTION

Potential–pH diagrams are also called Pourbaix diagrams after the name of their originator, Pourbaix (1963), a Belgium electrochemist and corrosion scientist. These diagrams represent the stability of a metal as a function of potential and pH. They are analogues to phase equilibrium diagrams, where the stability of various phases is shown as a function of temperature and percentage composition of the metal. At a particular temperature and composition a stable phase can be easily determined. Similarly, at a particular combination of pH and potential, a stable phase can be determined from the Pourbaix diagram. In such diagrams, the redox potential of the corroding system is plotted on a vertical axis and the pH on a horizontal axis. These diagrams are constructed from calculations based on Nernst equations and solubility data for metal and its species, such as Fe, Fe₂O₃, Fe(OH)₂, Fe₃O₄, etc. in equilibrium. A typical diagram for Fe–H₂O system is shown in Fig. 2.18.

2.14.2 CHARACTERISTICS OF A POURBAIX DIAGRAM

- (1) pH is plotted on the horizontal axis and redox potential E vs SHE on the vertical axis.
- (2) The horizontal lines represent electron transfer reactions. They are pH-independent, but potential-dependent. These lines separate the regions of stability, e.g. Fe and Fe²⁺ in a potential–pH diagram for Fe–H₂O system. Variation of concentration of Fe²⁺ ($10^{-6} - 1$) leads to several parallel lines.
- (3) The vertical lines are potential-independent but pH-dependent and not accompanied by any electron transfer, e.g. lines corresponding to the following reactions:



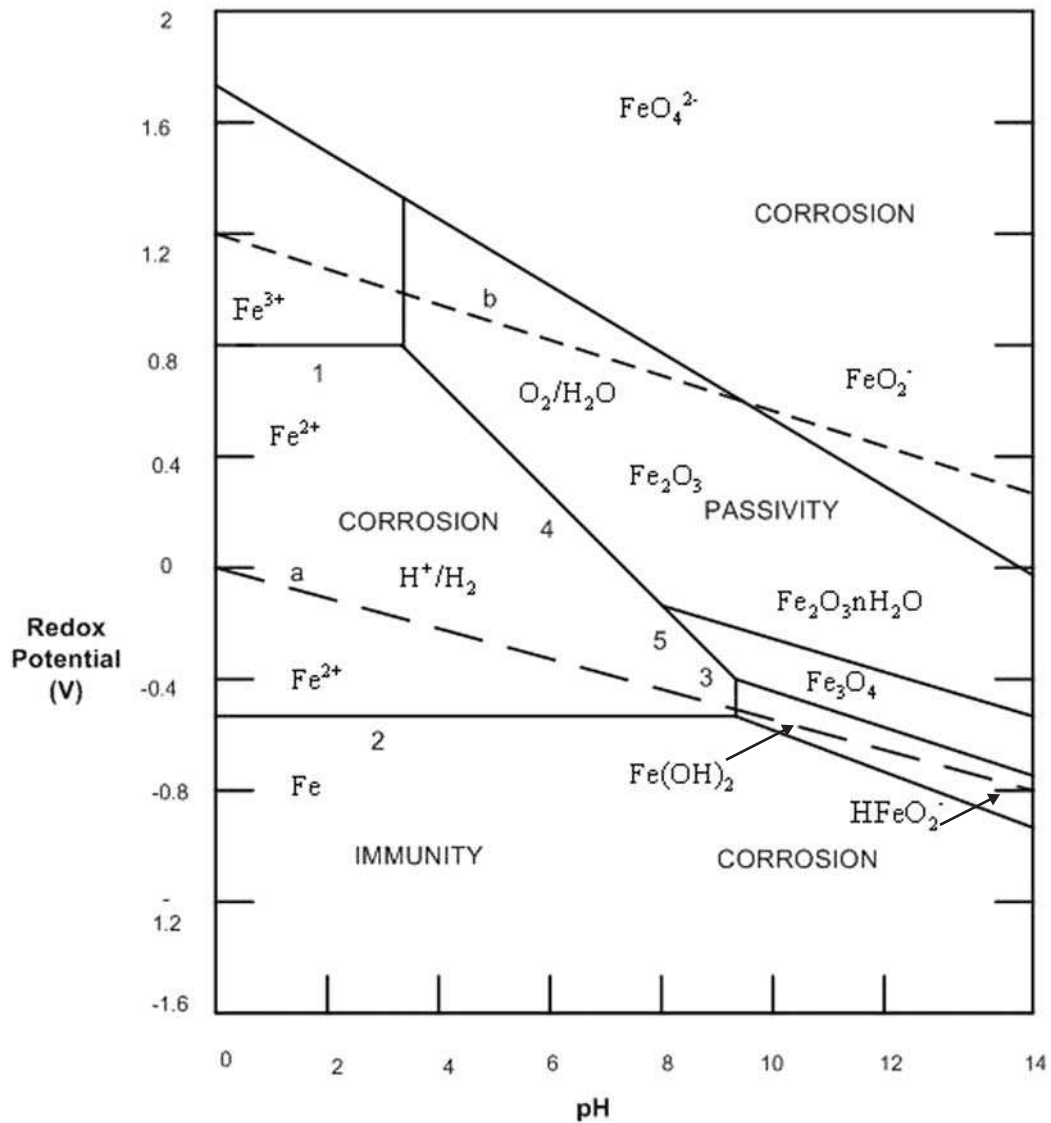
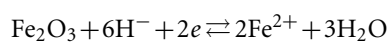


Figure 2.18 Potential-pH diagram for iron

- (4) The sloping, straight lines give the redox potentials of a solution in equilibrium with hydrogen and oxygen, respectively. These equilibria indicate electron transfer as well as pH, e.g.



The above reaction indicates both electron transfer and pH change.

- (5) The concentration of all metal ions is assumed to be 10^{-6} mol per liter of solution. At lower concentration, corrosion should not occur.
- (6) The diagram is computed for the equilibrium conditions at 25°C.
- (7) The upper end of the redox potential axis is the noble end and the lower end, the active end, meaning that the oxidizing power increase with increasing potential.

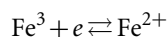
- (8) The hydrogen and oxygen lines are indicated in Pourbaix diagrams by dotted line.

It can be noted that Pourbaix diagrams may be constructed for all elements. The diagrams subdivide the potential–pH plots into regions of immunity, corrosion or passivation. These are very useful in prediction of tendency of metals to corrode. These diagrams, however, has several limitations which will be summarized at the end.

2.14.3 CALCULATIONS INVOLVED IN CONSTRUCTION OF POURBAIX DIAGRAMS

Numerous examples of applying Nernst equation to determine the potential and pH are given in this chapter. These equations are essential tools to calculate the redox potentials in the Pourbaix diagrams. For instance, consider Fig. 2.18, line 1 and let us determine the potential corresponding to reaction occurring in line 1. Here, Fe^{3+} is in equilibrium with Fe^{2+} . Applying Nernst equation, we obtain the reaction

Line 1



$$E = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} + \frac{RT}{f} \ln \left[\frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} \right]$$

(one electron transfer)

$$E = 0.77 + 0.059 \log \left[\frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} \right]$$

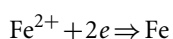
$$\text{where } a = 10^{-6}$$

Take $a = 0.6$ moles.

The log term drops out here as the term a becomes unity. Hence $E = 0.77$ V, and we indicate this value as the potential axis.

Line 2

The equilibrium reaction is



$$E = E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} + \frac{0.059}{2} \log [a_{\text{Fe}^{2+}}]$$

$$E_{\text{Fe}^{2+}/\text{Fe}} = -0.44 + 0.030 \log [a_{\text{Fe}^{2+}}]$$

because $a(\text{Fe}) = 1$

but

$$a = 10^{-6} \text{ mole/liter}$$

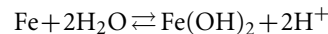
$$E_{\text{Fe}^{2+}/\text{Fe}} = -0.44 + 0.59[-6]$$

$$E = 0.62$$

This value is marked on the potential axis for line 2.

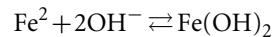
Line 3

The equilibrium reaction is



There is no charge transfer in the above equilibrium system.

or



Here the precipitation of $\text{Fe}(\text{OH})_2$ is shown, and solubility product comes into play (K_{SP}), which can be described by

$$K_{\text{SP}} = [a_{\text{Fe}^{2+}}][a_{\text{OH}^-}]^2 = 10^{-14.71}$$

(Check table of solubility products)

$$\therefore \log [a_{\text{Fe}^{2+}}] + 2 \log [a_{\text{OH}^-}] = -14.71$$

$$\text{but } \log [a_{\text{OH}^-}] = -2 \text{ pH} + 13.29$$

Substituting for $a = 10^{-6}$

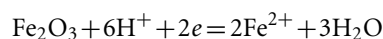
$$-6 = -2 \text{ pH} + 13.29$$

$$\text{pH} = 9.65$$

The corresponding pH value is indicated on the pH axis in the figure.

Line 4

The equilibrium reaction between Fe^{2+} and Fe_2O_3 is



Note that there is some degree of potential-dependence shown by electron transfer as well

some degree of pH-dependence, and the slope is finite as shown by the line. The expression is

$$E = E_{\text{Fe}_2\text{O}_3/\text{Fe}^{2+}}^\circ + \frac{0.0591}{2} \log \frac{[a_{\text{Fe}_2\text{O}_3}]}{[a_{\text{Fe}^{2+}}]^2} + \frac{0.0592}{2} \log [a_{\text{H}^+}]^6$$

Reduced

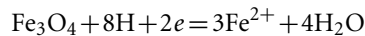
Multiplying $[\frac{0.059}{2}] \log [a_{\text{H}^+}]^6$ by 3, putting $a_{\text{Fe}_2\text{O}_3} = 1$, moving $a_{\text{Fe}^{2+}}$ to numerator, and changing sign in the log term, we get

$$E = 0.73 - 0.059 \log [a_{\text{Fe}^{2+}}] - 0.177 \text{pH}$$

The above expression shows the relativity between the pH and potential. Hence, the slope is now 0.777 which is indicated in the figure.

Line 5

It has also a finite slope and involves equilibrium between Fe^{2+} ions and Fe_3O_4 . The equation for the reaction is



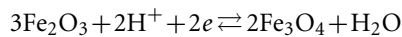
$$E_{\text{Fe}_3\text{O}_4/\text{Fe}^{2+}}^\circ = 0.98$$

Putting $E^\circ = 0.98$ for $\text{Fe}_3\text{O}_4/\text{Fe}^{2+}$ in the Nernst equation for the above reaction and solving

$$E = 0.98 - 0.088 \log (a_{\text{Fe}^{2+}}) - 0.236$$

a slope of -0.236 is obtained, which is indicated in the figure. The slope shows a pH and potential dependence.

Similarly, we can calculate the potentials for other equilibrium reactions involving Fe_2O_3 and Fe_3O_4 . The reaction is given by



$$E^\circ = +0.221 \text{V}_{\text{SHE}}$$

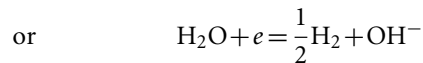
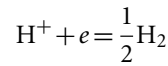
$$E = 0.221 + \frac{0.0551}{2} \log (a_{\text{H}^+})^2$$

$$= 0.221 - 0.059 \text{pH}$$

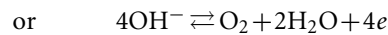
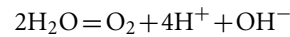
Such calculations can be carried out for different metal-water systems to construct Pourbaix diagrams.

Other lines in the diagram:

- Hydrogen line (a)



- Oxygen line (b)



Below hydrogen line (a) hydrogen is produced by a reduction of H^+ and H_2O , and above oxygen line (b), O_2 is produced by oxidation of H_2O and OH^- . Between the lines *a* and *b* water is stable.

Parallel lines identified by exponent of the activity of Fe^{2+} ions in solution ($a_{\text{Fe}^{2+}} = 10^0, 10^{-2}, 10^{-4}, 10^{-6}$). For instance line 8 corresponds to the formation of Fe_2O_3 from solution of $a_{\text{Fe}^{3+}} > a_{\text{Fe}^{2+}}$. Curves identified as 0, -2 , -4 , -6 , corresponds to $10^0, 10^{-2}, 10^{-4}, 10^{-6}$, respectively (Fig. 2.19).

2.14.4 REGIONS OF IMMUNITY, CORROSION AND PASSIVITY IN POURBAIX DIAGRAMS

Figure 2.20 shows the regions of immunity, corrosion and passivity which are described below.

2.14.4.1 Immunity Region

The region of immunity shown in the Pourbaix diagram for Fe-H₂O indicates that corrosion cannot occur in this region. For instance, at a point *X* in the diagram as the activity of Fe^{2+} would be very low ($\sim 10^{-10}$).

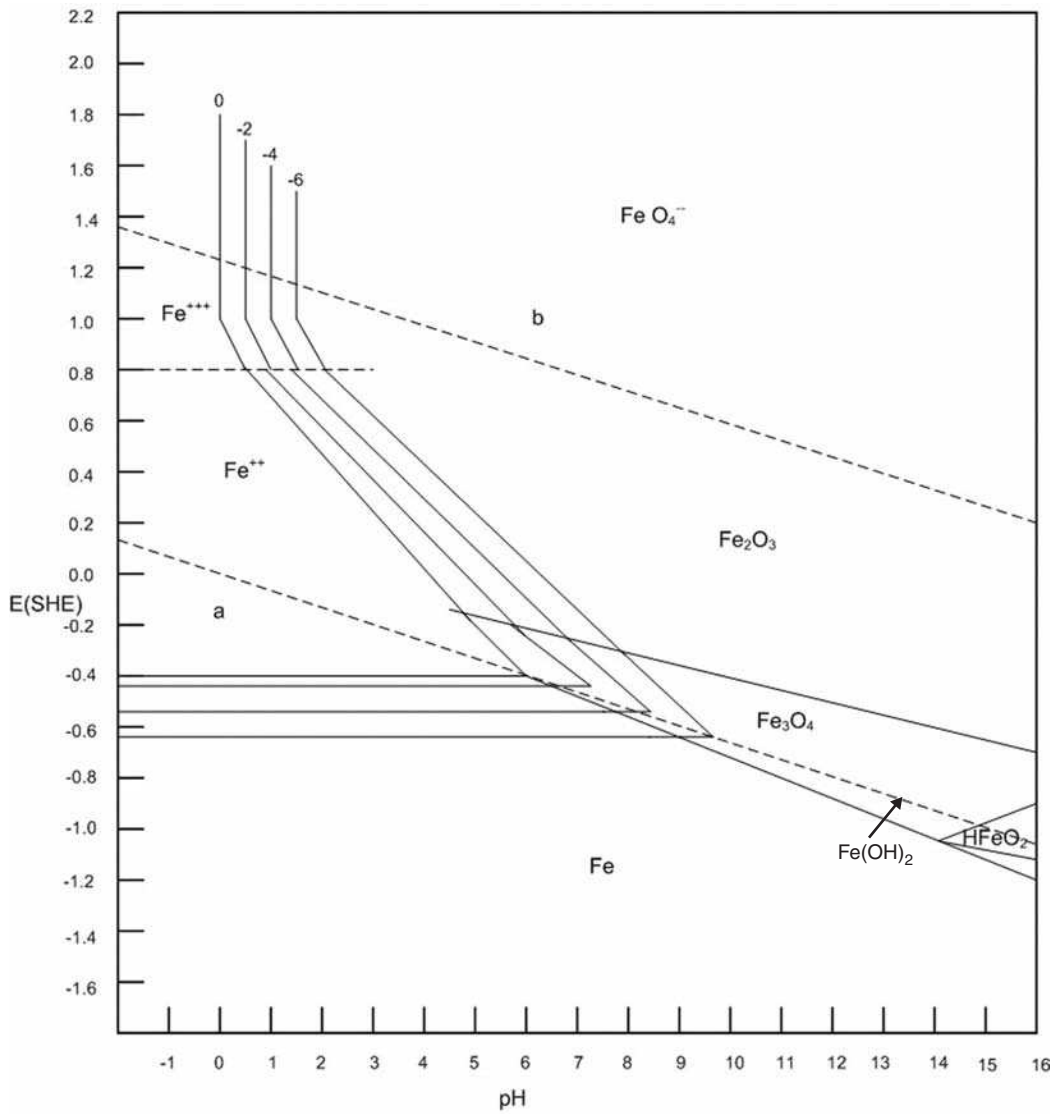


Figure 2.19 Simplified Pourbaix diagram for iron/water system

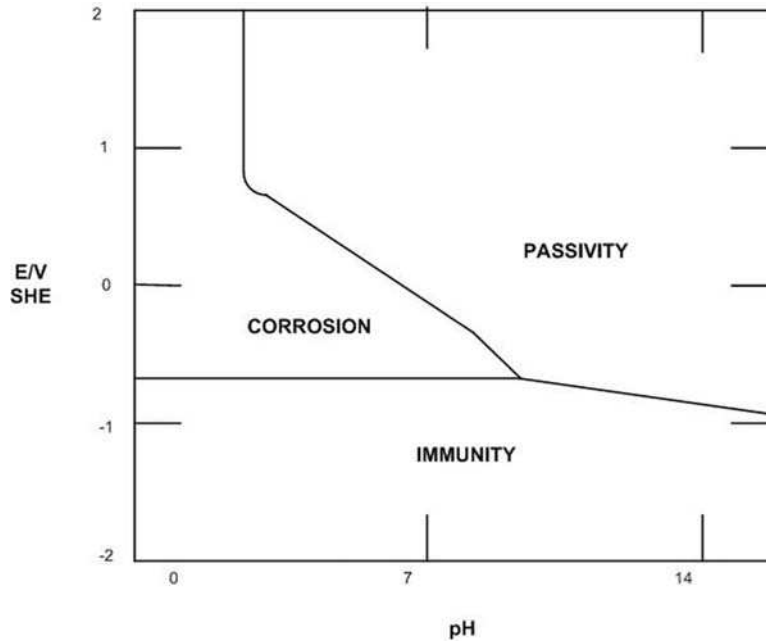


Figure 2.20 Pourbaix diagram for the iron–water system at 25°C showing nominal zones of immunity

2.14.4.2 Corrosion Region

As iron is transformed to soluble species, it is expected that iron would corrode.

2.14.4.3 Region of Passivation

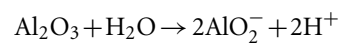
An oxide species in contact with an aqueous solution along a boundary would not allow corrosion to proceed if it is impervious and highly adherent. The thin layer of oxide on the metal surface, such as Fe_3O_2 or Fe_3O_4 is highly protective under the above condition. Metals like aluminum and steel are known to resist corrosion because of development of oxide films in the air.

2.14.5 SOME EXAMPLES OF POURBAIX DIAGRAMS

2.14.5.1 Pourbaix Diagram for Aluminum

A Pourbaix diagram for aluminum and H_2O system is shown in Fig. 2.21. The pH varies

(x -axis) from acidic at low pH to caustic at high pH. Line a is the hydrogen line below which water is no longer stable and decomposes into hydrogen and OH^- (alkalization). Line b is the oxygen line above which water decomposes into hydrogen, oxygen and H^+ (acidification). Water is stable between regions (a) and (b). In acidic conditions Al dissolves as Al^{+3} . In alkaline conditions aluminum dissolves as AlO_2^- .



In neutral solutions (4–8 pH), the hydroxide is insoluble which makes aluminum surface passive. Aluminum dissolves both in acids and bases.

2.14.5.2 Pourbaix Diagram for Copper

A Pourbaix diagram for copper/water system is shown in Fig. 2.22. Copper ($E^\circ = 0.337 \text{ V}$) is more noble than iron ($E_{\text{Fe}}^\circ = -0.444 \text{ V}$), however, it is more stable in water (SHE) than iron. Copper is not passive in acid electrolytes. The oxide of copper, Cu^+ and Cu^{2+} are only

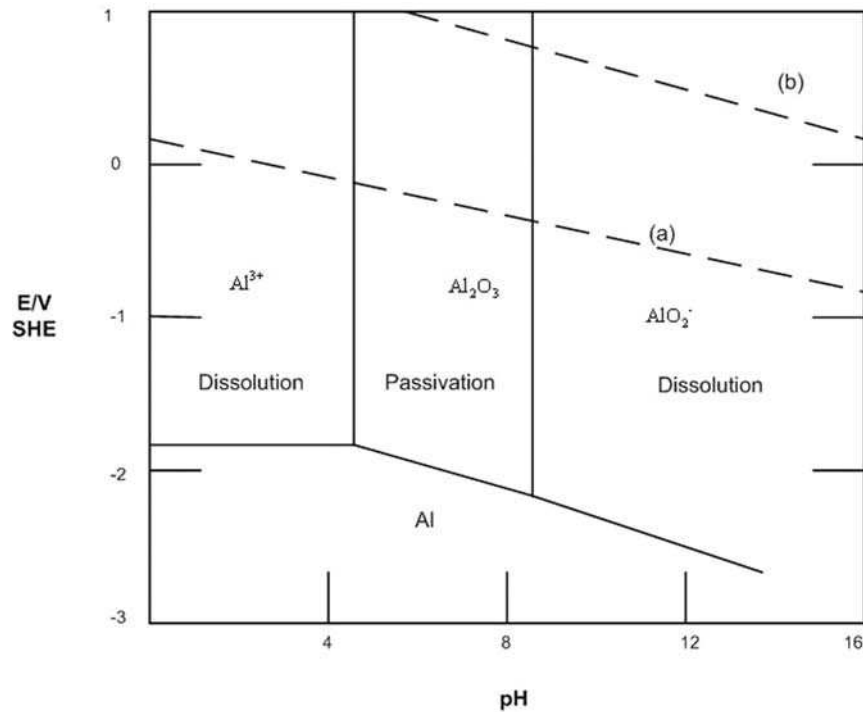


Figure 2.21 Pourbaix diagram for the aluminum–water system at 25°C

protective in weakly acidic and alkaline electrolytes. The region of immunity extends above the line (a) in the diagram which represents oxygen evolution. If the potential of copper is made more noble, it would corrode under mildly acidic and strongly acidic conditions. It would also corrode under strongly alkaline conditions in higher oxidizing potentials.

The scope of the chapter does not permit a broader treatment of Pourbaix diagrams. By identifying the pH and potential ranges, it is possible to control the corrosion of metals in aqueous environment. Aluminum is highly active but it can be used with a minimum risk of corrosion because of its tendency to form protective oxide films which prevent the metal from corrosion. Although titanium is highly active with a very narrow immunity zone towards the bottom of the diagram, it has an excellent tendency for passivation as shown by a highly extended passive zone which extends over the entire range of pH. Titanium, however, corrodes under reducing and highly oxidizing conditions as shown in the lower left region of the pH–potential diagram.

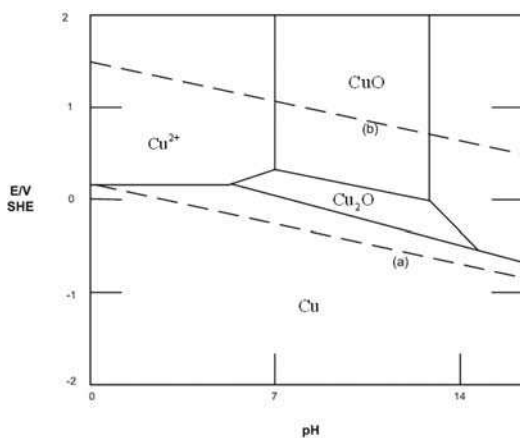


Figure 2.22 Pourbaix diagram for the copper–water system at 25°C

2.14.6 BENEFITS OF POURBAIX DIAGRAMS

Pourbaix diagrams offer a large volume of thermodynamic information in a very efficient and compact format. The information in the diagrams can be beneficially used to control corrosion of pure metals in the aqueous environment. By altering the pH and potential to the regions of immunity and passivation, corrosion can be controlled. For example, on increasing the pH of environment in moving to slightly alkaline regions, the corrosion of iron can be controlled. This can be achieved by water treatment. Similarly, changing the potential of iron to more negative values eliminate corrosion, this technique is called cathodic protection. Also, raising the potentials to more positive values reduces the corrosion by formation of stable films of oxides on the surface of transition metals. Steel in reinforced concrete does not corrode if an alkaline environment is maintained. On the contrary, an alkaline environment for aluminum is a disaster if the pH exceeds 8.0. The above example clearly demonstrate the merits of Pourbaix diagrams in prediction and control of corrosion. However, there are several limitations of these diagrams, which are summarized below:

1. These diagrams are purely based on thermodynamic data and do not provide any information on the reactions. The thermodynamic stability may not be achieved to the kinetics of the reaction. No information is provided in the rates of reaction.
2. Consideration is given only to equilibrium conditions in specified environment and factors, such as temperature and velocity are not considered which may seriously affect the corrosion rate.
3. The activity of species is arbitrarily selected as 10^{-6} g mol which is not realistic.
4. Pourbaix diagrams deal with pure metals which are not of much interest to the engineers.
5. All insoluble products are assumed to be protective which is not true, as porosity, thickness, and adherence to substrate are important factors, which control the protective ability of insoluble corrosion products.

Although the above disadvantages appear to be substantial, the advantages offered by the Pourbaix diagrams far outweigh their limitations.

QUESTIONS

A. MULTIPLE CHOICE QUESTIONS

Select one best answer:

1. The electrode potential of a metal is:
 - The potential which exists at the interface between the metal and the electrolyte
 - The potential between the anodic and cathodic areas of the metal
 - The potential between two metals immersed completely in the same electrolyte
 - The potential of a metal with respect to another metal, which is at a higher concentration
2. The double layer is formed as a result of
 - attractive forces between negative charged metal surface and positive ions only
 - repulsive forces between like positive ions only
 - both attractive and repulsive forces between ions
 - None of the above
3. The most acceptable method of obtaining standard electrode potential is by
 - comparing the electrode potentials of a metal half cell with a hydrogen half cell
 - comparing the electrode potential of a metal immersed in a solution of its ions at any concentration, with the hydrogen half cell

- [] comparing the electrode potential of a metal with any standard electrode, such as Ag–AgCl or Calomel electrode
- [] None of the above
4. A galvanic cell is formed
- [] when two metals are immersed in solutions differing in concentration
- [] when two different metals are immersed in one electrolyte
- [] when two different metals are exposed to air
- [] when two metals are brought close together and electrically insulated from one another
5. In *concentration* cells
- [] the metal is in contact with two half cells having the same electrolyte but at different concentrations
- [] the metal is in contact with two half cells, having the same electrolytes with the same concentration
- [] no liquid junction is present
- [] there is no migration of ions from one electrolyte to another electrolyte
6. If the free energy of a reversible process is negative, it implies that
- [] the cell reaction is spontaneous
- [] the cell reaction is not spontaneous
- [] the cell reaction proceeds from right to left
- [] no reaction takes place at all
7. The value of $(2.303RT)/F$ at 25°C varies with
- [] temperature
- [] the metal being considered
- [] the melting temperature of the metal
- [] None of the above
8. If $E > 0$, the cell reaction
- [] proceeds in forward direction
- [] proceeds in reverse direction
- [] does not proceed
- [] None of the above
9. The most common electrodes used for measurement of corrosion potentials are: (*Mark two correct answers*)
- [] Ag–AgCl
- [] Hg–Hg₂Cl₂
- [] Cu–CuSO₄
- [] Hydrogen electrode
10. A galvanic series is
- [] a list of alloys arranged according to their corrosion potentials in a given environment
- [] a list of metals and alloys according to their corrosion potentials in a given environment
- [] a list of standard electrode potentials of alloys or metals arranged in order of their values
- [] a grouping of metals and alloys based on their ability to get oxidized in a stated environment

B. REVIEW QUESTIONS

1. Distinguish between:
- Metallic conduction and electrolytic conduction.
 - Standard electrode potential and corrosion potential.
 - Anode and cathode.
 - Electronic conduction and ionic conduction.
2. In the sign convention adopted by IUPAC:
- What does the right-hand electrode indicate?
 - What does the left-hand electrode indicate?
 - How the cell potential, E_{cell} , is obtained?
 - What does the positive sign of the cell indicate?

- If $E > 0$, in which direction will the cell reaction proceed, and conversely if $E < 0$, in which direction the reaction would proceed?
- State which of the following statements are true:
 - When two metals, e.g. Zn and Cd, are connected and placed in a solution containing both metal ions, the metal with the lower standard potential would corrode.
 - Conversely, the metal with the higher potential would be deposited.
 - The cell and cell reaction are written in opposite orders, for instance, for the cell $\text{Fe}/\text{Fe}^{2+}(\text{aq})/\text{Cu}^{2+}(\text{aq})/\text{Cu}$, the reaction is

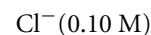
$$\text{Fe}^{2+} + \text{Cu} \rightarrow \text{Cu}^{2+} + \text{Fe}$$
 - The cell potential is obtained by subtracting the electrode potential of the right-hand electrode from the left-hand electrode.
- State the limitations of the emf series and the advantages of galvanic series for an engineer.

C. PROBLEMS

- Devise electrochemical cells in which the following overall reactions can occur:
 - $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu}(\text{s}) + \text{Zn}^{2+}(\text{aq})$
 - $\text{Ce}^{+4}(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Ce}^{3+}(\text{aq}) + \text{Fe}^{3+}(\text{aq})$
 - $\text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
 - $\text{Zn}(\text{s}) + 2\text{Cl}_2(\text{g}) \rightarrow \text{ZnCl}_2(\text{aq})$
- What is the mole fraction of NaCl in a solution containing 1.00 mole of solute in 1.00 kg of H_2O ?
- What is the molarity of a solution in which 1.00 $\times 10^2$ g of NaOH is dissolved in 0.250 kg of H_2O ?
- What is the voltage (E_{cell}) of a cell comprising a zinc half cell (zinc in ZnSO_4) and a copper half cell (Cu in CuSO_4)? The metal concentrations of ZnSO_4 and CuSO_4

are 1 and 0.01, respectively. The activity coefficient for CuSO_4 is 0.047 and for ZnSO_4 is 0.70.

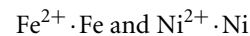
- Calculate E for the half cell in which the reaction $\text{Cu}^{++} (0.1 \text{ m}) + 2e^{-} = \text{Cu}(\text{s})$ takes place at 25°C .
- Calculate the potential for each half cell and the total emf of the cell (E_{cell}) at 25°C :



$$E^{\circ} \text{Pb} = \text{Pb}^{2+} / \text{Pb}^{\circ} = -0.13 \text{ V}$$

$$E^{\circ} \cdot (\text{Cl}_2 - \text{Cl}) = 1.358 \text{ V}$$

- Calculate the emf and the free energy of the cell given below:

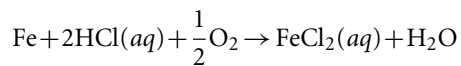


(Obtain data from the literature.)

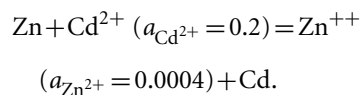
- A piece of copper is immersed in an aqueous solution of KCl with a concentration of 1 kmol/ m^3 . The solubility product of CuCl at 25°C is (1.7×10^{-6}) . Calculate the potential of the copper electrode.
- A test piece of cadmium is placed (a) in flowing seawater, and (b) in stagnant seawater. Predict under which conditions cadmium would corrode. The following information is provided:

pH = 7.0
 Concentration of cadmium ions:
 $\text{Cd}(\text{OH})_2 = 1.2 \times 10^{-14} \text{ kmol}/\text{m}^3$ at 25°C in stagnant condition.
 Concentration of cadmium ions in flowing conditions:
 $= 10^{-6} \text{ kmol}/\text{m}^3$
 $E_{\text{Cd}}^{\circ} = -0.42 \text{ V}$
- Aluminum samples are exposed in Arabian Gulf water. It has been found that aluminum corrodes either as $\text{Al}(\text{OH})_3$ or AlCl_3 in seawater. Show by calculations in which form aluminum corrodes or does it corrode in both forms. The concentration of Al^{+++} in $\text{AlCl}_3 = 10^{-4}$. The solubility product of $\text{Al}(\text{OH})_3$ is 3.7×10^{-15} .
- A piece of zinc measuring $2'' \times 1.5''$ is placed in a 0.002 molar solution of ZnCl_2 . Show whether zinc would corrode in the given medium.

12. A piece of nickel measuring $6'' \times 4''$ is immersed in deaerated water having a pH of 8.0. The solubility product $\text{Ni}(\text{OH})_2$ is 1.6×10^{-16} . Determine the potential of nickel in the given conditions and state whether nickel would corrode or not.
13. Calculate the emf of the following cell at 25°C :
 Fe^{3+} ($a = 0.01$), Fe^{2+} ($a = 0.0001$), Cu^+ ($a = 0.01$)/ Cu .
 Given: E° , $\text{Fe}^{3+}/\text{Fe}^{2+} = -0.771 \text{ V}$ and E° , $\text{Cu}^+/\text{Cu} = 0.5211$.
14. Find the potential of a cell where the reaction $\text{Ni} + \text{Sn}^{2+} \rightarrow \text{Ni}^{2+} + \text{Sn}$, proceeds. The concentration of Ni^{2+} is 1.3 and the concentration of Sn^{2+} is 1.0×10^{-4} . Predict if the reaction would proceed from right to left or left to right.
15. Write a balanced cell reaction and calculate the emf of the following cell:
 Pt/Sn^{2+} ($a = 0.10$), Sn^{4+} ($a = 0.10$), Fe^{3+}/Fe ($a = 0.200$).
16. The following is the reaction when iron corrodes in an acid:



- a) In what direction shall the reaction proceed if the activity of Fe^{2+} is 1, and $a(\text{H}^+) = 1$?
- b) If the temperature is maintained at 25°C , what activity of iron ($a_{\text{Fe}^{2+}}$) would be required to stop the corrosion in acid?
17. Calculate the voltage of the following cell:



18. The potential of an electrode is measured as -0.840 V relative to a 1 N Calomel electrode. What is the electrode potential on a standard hydrogen scale?
19. What pressure would be required to stop corrosion of zinc in deaerated water at 25°C ? The major corrosion product is $\text{Zn}(\text{OH})_2$ and the solubility product is 1.8×10^{-14} at 20°C (Take $\text{pH} = 7$).
20. Calculate the theoretical tendency of cadmium to corrode when it is immersed in a solution of 0.001 M CdCl_2 ($\text{pH} = 2.0$).
21. For the cell $\text{H}_2 (1 \text{ atm}) \cdot \text{HCl} \cdot \text{HgCl} \cdot \text{Hg}$, $E^\circ = 0.2220 \text{ V}$ at 298 K . If $\text{pH} = 1.47$, determine the emf of the cell.
22. Copper corrodes in an acid solution of $\text{pH} = 2$. Hydrogen is bubbled continuously in the solution. Calculate the maximum concentration of Cu^{2+} ions that would result.
23. A cell is composed of a pure copper and pure lead electrode immersed in solutions of their bivalent ions. For a 0.3 molar concentration of Cu^{2+} , the lead electrode is oxidized and shows a potential of 0.507 V . What would be the concentration of Pb ion at 25°C ?

SUGGESTED BOOKS FOR READING

- [1] Davis, J.P. ed. (2000). *Corrosion: Understanding the Basics*. 2nd ed. Ohio: Metals Park, USA.
- [2] Revier, R.W. ed. (2000). *Uhlig's Corrosion Handbook*. New York: John Wiley.
- [3] ASM Handbook (1987). *Corrosion*. Vol. 13, ASM, Ohio: Metals Park, USA.
- [4] Stansbury, E.E. and Buchanan, R.A. (2000). *Fundamentals of Electrochemical Corrosion*. Ohio: ASM, USA.
- [5] Piron, D.L. (1991). *The Electrochemistry of Corrosion*, Texas: NACE, USA.

KEYWORDS

Anode The region of the electrical cell where positive current flows into the electrolyte. Anode is the site where oxidation occurs. In a corrosion cell anode is the region which is dissolving. Cathode is the region of an electrical cell where positive electric current enters from the electrolyte. In a corrosion cell reduction reaction takes place at the cathode.

Electrochemical cell An electrochemical system comprising of an anode and a cathode in a metallic contact and immersed in an electrolyte.

Electrode potential It is the potential of an electrode in an electrolyte as measured against a reference electrode.

Electrolyte It is electrically conductive. It is usually a liquid containing ions that migrate in an electric field.

Free energy From the total heat content of a system (enthalpy), only a part can be converted to useful work. This part of total enthalpy is called free energy, G . Absolute value of free energy (G) cannot be measured, and only changes in free energy (ΔG) are measured.

Galvanic series A table of metals and alloys arranged according to their relative corrosion potential in a given environment.

Half cell An electrode immersed in a suitable electrolyte for measurement of potential.

IR drop Voltage drop caused by current flow in a resistor.

Reference electrode A stable electrode with a known and highly reproducible potential.

Reversible potential (*Equilibrium potential*) It is the potential of an electrode where the forward rate of reaction equals to the reverse rate of reaction.

Standard electrode potential (E°) It is reversible potential of an electrode measured against a standard hydrogen electrode (SHE) consisting of a platinum specimen immersed in a unit activity acid solution through which H_2 gas at 1 atm pressure is bubbled. The potential of the hydrogen electrode (half cell) is taken to be zero.