

reaction, hence,

$$\Delta G = -nFE$$

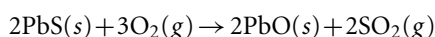
where

ΔG = free energy change (joules)

E = standard potential of the reaction (volts).

Illustrative Example 2.2

- (1) Calculate the standard enthalpy change for the following reaction at 298 K:



Solution:

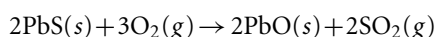
Given that the standard enthalpies of formation are:

$$\Delta H_{298}^{\circ} \text{PbS} = -94.5 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_{298}^{\circ} \text{PbO}(s) = -220.5 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_{298}^{\circ} \text{SO}_2(g) = -298 \text{ kJ} \cdot \text{mol}^{-1}$$

Rewrite the equation:



$$2(-94.5) \quad 3(0) \quad 2(-220.5) \quad 2(-298.0)$$

The standard enthalpy of formation of an element is taken as zero at 298 K.

Using equation:

$$\Delta H = H_2 - H_1, \text{ where } H_2 = \text{total enthalpy of formation of products and } H_1 \text{ is for the reactants}$$

$$\begin{aligned} \Delta H &= [2(-220.5) + 2(-298)] - [2(-94.5) + 0] \\ &= -848.0 \text{ kJ} \end{aligned}$$

- (2) For the equilibrium $\text{ZnO}(s) + \text{C}(s) \rightleftharpoons \text{Zn}(s) + \text{CO}(g)$

- (a) Deduce the direction in which the reaction would be feasible at 300 and 1200 K, when all reactants and products are in their standard states (i.e. unit activities).

- (b) Deduct K_p for the reaction using the relationship $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ for the reaction.

Given enthalpies and entropies of reaction:

$$\Delta H_{300} = +65 \text{ kJmol}^{-1}$$

$$\Delta S_{300} = +13.7 \text{ JK}^{-1} \text{mol}^{-1}$$

$$\Delta H_{1200} = +180.9 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S_{1200} = +288.6 \text{ JK}^{-1} \text{mol}^{-1}$$

Solution:

- (a) For reaction at 300 K:

$$\begin{aligned} (1) \quad \Delta G^{\circ} &= 65000 - (300 \times 13.7) \\ &= 60890 \text{ J} \cdot \text{mol}^{-1} \end{aligned}$$

For reaction at 1200 K:

$$\begin{aligned} (2) \quad \Delta G^{\circ} &= 180900 - (1200 \times 288.6) \\ &= -165420 \text{ J} \cdot \text{mol}^{-1} \end{aligned}$$

As ΔG° is negative for the reaction at 1200 K, the reaction proceeds from left to right in the forward direction at 1200 K. The forward reaction is not feasible at 300 K to produce 1 bar of CO_2 from 1 bar of CO: but it would form much lower CO_2 pressures spontaneously. Such low CO_2 pressures would not be sufficient to 'push back the atmosphere' and so effectively no Zn would be produced.

- (b) Calculation of K_p .

The equilibrium constant (K) is given by

$$\Delta G = \Delta G^{\circ} + RT \ln \left(\frac{a_C^c a_D^d}{a_A^a a_B^b} \right) \quad (2.19)$$

but the term in parenthesis is not K , but is any arbitrary non-equilibrium activity for which ΔG is the free energy change if such a reaction was carried out.

At equilibrium $\Delta G=0$, and then $a_C^c a_D^d / a_A^a a_B^b = K$ equilibrium constant = $\Delta G^\circ + RT \ln K$.

$$\text{So, } \Delta G^\circ = -RT \ln K \quad (2.20)$$

Equation (2.19) can be rewritten as:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_C P_D}{P_A P_B} \right)$$

where P is partial pressure (actual) assuming A, B, C and D are gases. The above equation connecting ΔG and K is a form of van't Hoff isotherm.

Now calculate K_p

$$\ln K_p = -\frac{\Delta G^\circ}{RT}$$

At 1200 K,

$$\begin{aligned} \log_{10} K_p &= \frac{-165420}{2.303 \times 8.314 \times 1200} \\ &= 7.197 \end{aligned}$$

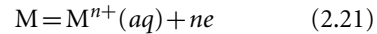
So, $K_p = 1.574 \times 10^7$.

Similarly at 300 K, $K_p = 2.512 \times 10^{-11}$. The value of K_p at 1200 shows that the reaction proceeds fast (left to right) compared to the reaction at 300 K, which proceeds at a negligible rate. At 1200 K, bright red hot, reaction kinetics are fast and it is safe to interpret a large K value as a meaning that reaction is fast. But the reaction $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ has a very large K value at room temperature, yet is negligibly slow (unless sparked), due to the very slow kinetics at room temperature. K is a thermodynamic factor, but kinetics may allow only a negligible rate.

2.7 REVERSIBLE ELECTRODE POTENTIAL

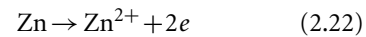
When a metal is immersed in an electrolyte, a dynamic equilibrium is established across the

interface with a potential difference between the metal and electrolyte. The atoms of the metal, M , ionize producing aquo-ions, $M^{n+}(aq)$, and electrons, ne , according to



where M represents metal atoms. The metal is left with a negative charge and its positively charged metal ions, $M^{n+}(aq)$, in the electrolyte are attracted back towards the metal surface. Thus, a potential difference and dynamic equilibrium between the metal and the solution is established. The atoms of the metal continue to ionize until the displacement of electrical charges produced balances the tendency of the metallic atoms to ionize into the electrolyte.

Consider, for example, a piece of zinc metal in water. Zinc dissolves producing positively charged zinc ions (cations):



The zinc ions in the solution remain very close to the metal surface. The zinc metal becomes negatively charged as the positive ions leave its surface. The excess electrons on the zinc surface orient themselves opposite to a layer of zinc ions of equal and opposite charge on the water side of the zinc/water interface. Such a process leads to the formation of an electrical double layer of about 1 nm (10^{-7} cm) thickness along the metal/solution interface (Fig. 2.9).

Figure 2.9A shows the metal/solution interface at the moment of immersion and the formation of double layer is shown in Figs 2.9B and C. The double layer shown in Figs 2.9B and C is formed as a result of attraction between the negative ions (anions) and positive ions (cations) on one hand, and repulsion between similarly charged ion, anions or cations on the other hand. As a result of the above interactions, cations diffuse amongst the anions until an equilibrium is established between the metal and solution, and between the bulk of the solution and the layer adjacent to the metal surface. The plane passing through the ions absorbed on the metal surface is called the *Inner Helmholtz*

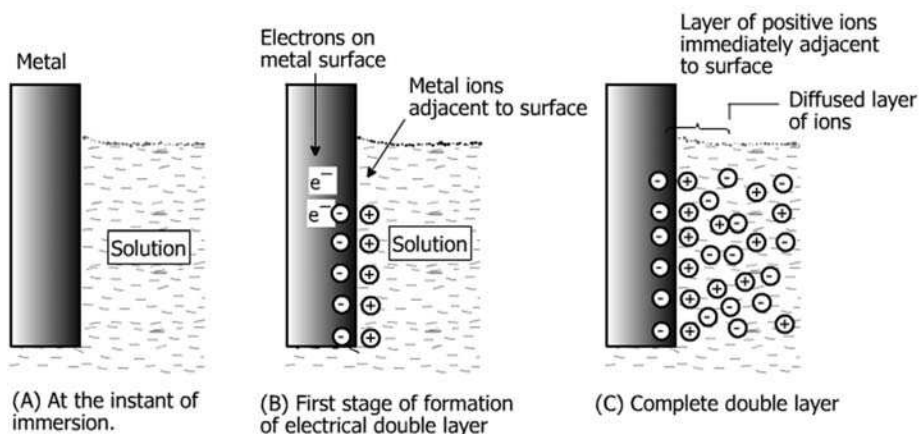
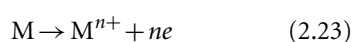


Figure 2.9 Representation of electrical double layer at a metal/solution interface

plane, whereas the plane passing through the center of solvated cation is called the *Outer Helmholtz plane*, which also marks the beginning of a diffuse layer when an excess of charges is neutralized (Fig. 2.9C). At this stage, it is sufficient to understand the meaning of double layer to know the electrode potential. Returning to equation (2.21), it should be noted that under the equilibrium conditions in the system, the rate of ionization on the metal surface:



becomes equal to the rate of discharge across the double layer:

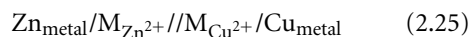


In other words, the rate of forward reaction (equation (2.23)) becomes equal to the rate of backward reaction (equation (2.24)) on the metal electrode. This is described as an exchange current.

The double layer described above is responsible for the establishment of potential difference between the metal and solution, and this potential difference is referred to as '*Absolute Electrode Potential*.' More details will be given in Chapter 3.

2.7.1 EXAMPLES OF REVERSIBLE CELLS

Figure 2.2 shows a Daniel cell which is a good example of a reversible cell. A Daniel cell can be presented as follows:

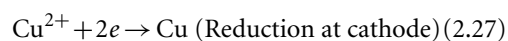


where:

$M_{Zn^{2+}}$ = 1.0 mol of zinc salt, as for example $ZnSO_4$ per liter

$M_{Cu^{2+}}$ = 1.0 mol of $CuSO_4$ per liter.

When writing down a cell, it is common practice to put the anode on the left-hand side and the cathode on the right-hand side. The anode is the electrode where oxidation reaction takes place, and the cathode is the electrode where reduction reaction takes place. Accordingly, the reactions in a Daniel cell can be written as:



An emf of 1.10 V is produced in a Daniel cell. This potential is equal to the difference in potentials between the anode and the cathode. It is called the '*Reversible Cell Potential*' (E_{rev}) or '*Equilibrium Potential*' (E_{eq}).

2.7.2 DIFFERENCE BETWEEN REVERSIBLE POTENTIAL AND STANDARD POTENTIAL

If a metal is immersed in a solution of its own ions, such as zinc in ZnSO₄ solution, or copper in CuSO₄ solution, the potential obtained is called the *reversible potential* (E_{rev}).

If, on the other hand, the substances taking part in the process are in their standard states, such that the activities of the metallic ions are equal to unity or gases are at 1 bar pressure, the potentials obtained are called 'Standard Electrode Potentials' (Table 2.1). A standard potential refers to the potential of pure metal measured with reference to a hydrogen reference electrode. The details of reference electrodes are provided later in this chapter.

Table 2.1 Standard reduction potentials, 25°C (Modified from Uhlig)

Electrode reaction	E° (V)
Au ³⁺ + 3e = Au	1.50
Pt ²⁺ + 2e = Pt	ca 1.2
Hg ²⁺ + 2e = Hg	0.854
Pd ²⁺ + 2e = Pd	0.987
Ag ⁺ + e = Ag	0.800
Hg ₂ ²⁺ + 2e = 2Hg	0.789
Cu ⁺ + e = Cu	0.521
Cu ²⁺ + 2e = Cu	0.337
2H ⁺ + 2e = H ₂	0.000
Pb ²⁺ + 2e = Pb	-0.126
Sn ²⁺ + 2e = Sn	-0.136
Mo ³⁺ + 3e = Mo	ca -0.2
Ni ²⁺ + 2e = Ni	-0.250
Co ²⁺ + 2e = Co	-0.277
Tl ⁺ + e = Tl	-0.336
In ³⁺ + 3e = In	-0.342
Cd ²⁺ + 2e = Cd	-0.403
Fe ²⁺ + 2e = Fe	-0.440
Ga ³⁺ + 3e = Ga	-0.53
Cr ³⁺ + 3e = Cr	-0.74
Zn ²⁺ + 2e = Zn	-0.763
Nb ³⁺ + 3e = Nb	ca -1.1
Mn ²⁺ + 2e = Mn	-1.18

Electrode reaction	E° (V)
Zr ⁴⁺ + 4e = Zr	-1.53
Ti ²⁺ + 2e = Ti	-1.63
Al ³⁺ + 3e = Al	-1.66
Hf ⁴⁺ + 4e = Hf	-1.70
U ³⁺ + 3e = U	-1.80
Be ²⁺ + 2e = Be	-1.85
Mg ²⁺ + 2e = Mg	-2.37
Na ⁺ + e = Na	-2.71
Ca ²⁺ + 2e = Ca	-2.87
K ⁺ + e = K	-2.93
Li ⁺ + e = Li	-3.05
FeO ₄ ²⁻ + 8H ⁺ + 3e = Fe ³⁺ + 4H ₂ O	1.9
Co ³⁺ + e = Co ²⁺	1.82
PbO ₂ + SO ₄ ²⁻ + 4H ⁺ + 2e = PbSO ₄ + 2H ₂ O	1.685
NiO ₂ + 4H ⁺ + 2e = Ni ²⁺ + 2H ₂ O	1.68
Mn ³⁺ + e = Mn ²⁺	1.51
PbO ₂ + 4H ⁺ + 2e = Pb ²⁺ + 2H ₂ O	1.455
Cl ₂ + 2e = 2Cl ⁻	1.3595
Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e = 2Cr ³⁺ + 7H ₂ O	1.33
O ₂ + 4H ⁺ + 4e = 2H ₂ O	1.229
Br ₂ (l) + 2e = 2Br ⁻	1.0652
Fe ³⁺ + e = Fe ²⁺	0.771
O ₂ + 2H ⁺ + 2e = H ₂ O ₂	0.682
I ₂ + 2e = 2I ⁻	0.5355
O ₂ + 2H ₂ O + 4e = 4OH ⁻	0.401
Hg ₂ Cl ₂ + 2e = 2Hg + 2Cl ⁻	0.2676
AgCl + e = Ag + Cl ⁻	0.222
SO ₄ ²⁻ + 4H ⁺ + 2e = H ₂ SO ₃ + H ₂ O	0.17
Cu ²⁺ + e → Cu ⁺	0.153
Sn ⁴⁺ + 2e = Sn ²⁺	0.15
AgBr + e = Ag + Br ⁻	0.095
Cu(NH ₃) ₂ ⁺ + e = Cu + 2NH ₃	-0.12
Ag(CN) ₂ ⁻ + e = Ag + 2CN	-0.31
PbSO ₄ + 2e = Pb + SO ₄ ²⁻	-0.356
HPbO ₂ ⁻ + H ₂ O + e = Pb + 3OH ⁻	-0.54
2H ₂ O + 2e = H ₂ + 2OH ⁻	-0.828
Zn(NH ₃) ₄ ²⁺ + 2e = Zn + 4NH ₃	-1.03

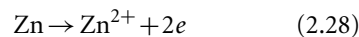
2.7.3 HALF CELLS

The term half cell is frequently used in electrochemistry. To illustrate the formation of

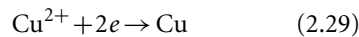
half cells, consider a Daniel cell, shown in Fig. 2.2. In the cell shown, zinc rod is immersed in one molar solution of zinc sulfate, and copper rod in one molar solution of copper sulfate. The two solutions, zinc sulfate and copper sulfate, are separated by a porous pot, which prevents them from mixing but allows electrical contact. As shown in the figure, Zn in ZnSO₄ (1.0 M) forms one half cell and Cu in CuSO₄ (1.0 M) forms another half cell. Each half cell has its own potential.

2.7.4 REACTIONS IN THE CELL

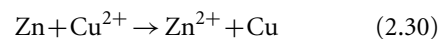
In Daniel cell, zinc dissolves and a potential is set up between the zinc ions and zinc metal in the zinc half cell. In the copper half cell, copper ions are deposited on the copper metal and a potential is set up. Once the half cells are in equilibrium, no further deposition or dissolution would occur. If, now, the two half cells are joined by a conductor, as shown in Fig. 2.2, electrons would flow from zinc (anode) to copper (cathode). As a result of electron flow, the equilibrium in the half cells is distributed, and, therefore zinc will dissolve further according to the anodic reaction (oxidation),



and copper ions will discharge from copper sulfate solution in order to remove the excess electrons according to the cathodic reaction (reduction of Cu²⁺ ions to Cu metal):



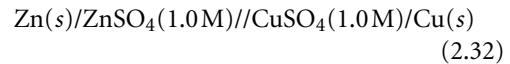
The overall reaction of the cell is the sum of the above two half cell reactions:



The emf of the cell is the algebraic sum of the potentials of the half cells or 'Standard Electrode Potential:'

$$E_{\text{cell}} = E_{\text{Zn/Zn}^{2+}} + E_{\text{Cu}^{2+}/\text{Cu}} \quad (2.31)$$

The above cell (Daniel cell) can also be represented as:



2.7.5 STANDARD HYDROGEN POTENTIAL (SHE) AND MEASUREMENT OF SINGLE ELECTRODE POTENTIALS

Absolute single electrode potential is a characteristic property of a metal. All metals have characteristic electrode potentials. Absolute single electrode potentials cannot be measured directly. They can be measured with respect to a standard electrode such as standard hydrogen electrode (SHE). The standard hydrogen electrode is a widely used standard electrode. It is arbitrarily assumed to have zero potential at all temperatures by definition. Thus, it provides a zero reference point for electrode potentials. The construction of the standard hydrogen electrode is shown in Fig. 2.10. As shown in the figure,

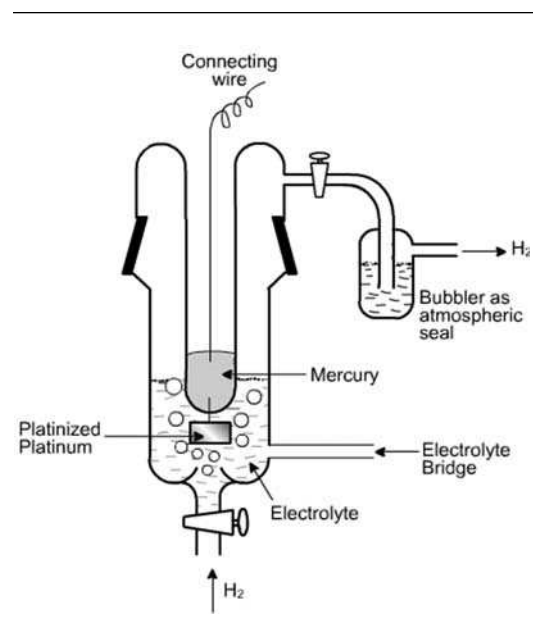
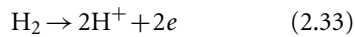
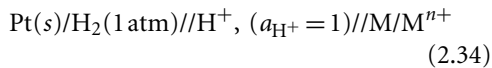


Figure 2.10 Hydrogen electrode

a platinum electrode is dipped in a solution containing hydrogen ions at unit activity. To obtain hydrogen ions at unit activity, a solution of one mol per liter HCl can be used. To obtain unit activity of hydrogen gas, hydrogen is passed at one atmospheric pressure over platinum plate in the solution. The SHE is expressed as

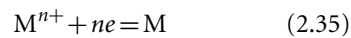


The most acceptable method of obtaining standard electrode potentials is by comparing the electrode potential of metals with the standard hydrogen electrode. Since the SHE has zero electrode potential at all temperatures by definition, the electrode potential of a metal is numerically equal to the emf of the cell formed by SHE and the metal electrode. In other words, the emf of the cell represents the electrode potential of the half cell formed by the metal with respect to the standard hydrogen electrode. In such a cell, reaction on the hydrogen electrode is oxidation and reaction on the other electrode is reduction. Such a cell can be expressed as:

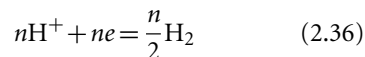


The activity or concentration of the M^{n+} ion solution needs to be specified, as cell potential will vary with it.

The electrode reaction for such a cell can be written as (considering reduction reactions as convention):

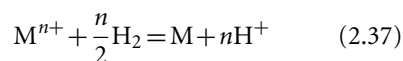


for metal electrodes, and



for the standard hydrogen electrode (SHE).

The cell reaction is obtained by taking the difference of equations (2.35) and (2.36) above:



Reaction (2.37) is the complete reaction for the cell expressed in equation (2.34) above, where

one of the electrodes is SHE and the other is the metal electrode of which we want to measure the single electrode potential. The emf of the cell expressed in equation (2.34) is given by:

$$E_{\text{cell}} = E_{\text{M}^{n+}/\text{M}} - E_{\text{H}^+/\text{H}_2}^{\circ} \quad (2.38)$$

where $E_{\text{H}^+/\text{H}_2}^{\circ}$ (SHE), the electrode potential of standard hydrogen electrode and is assumed equal to zero at all temperatures by convention. Therefore, equation (2.38) becomes:

$$E_{\text{cell}} = E_{\text{M}^{n+}/\text{M}} \quad (2.39)$$

2.7.6 THE POTENTIAL (EMF) OF A CELL

The emf of any cell is, therefore given by

$$E_{\text{cell}} = [E_{\text{Right}} - E^{\circ}(\text{SHE})]_{\text{Right}} - [E_{\text{Left}} - E^{\circ}(\text{SHE})]_{\text{Left}} \quad (2.40)$$

and

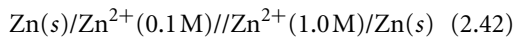
$$E_{\text{cell}} = E_{\text{Right}} - E_{\text{Left}} \quad (2.41)$$

As the potential of SHE cancels, no matter what value it is, the emf of the cell, E_{cell} , is not affected. The cell potential (emf) is positive if the left-hand electrode is negative and the right-hand electrode, positive. Consequently, oxidation would occur on the left-hand electrode, and reduction on the right-hand electrode.

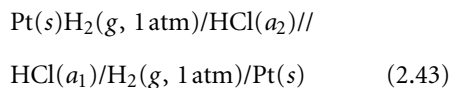
2.8 CONCENTRATION CELL

In a concentration cell, the emf results from transportation of an electrolyte (anion, cation or both) from the more concentrated solution to the more dilute solution. Here the metal is in contact with two half cells having the same electrolyte at two different concentrations. Such a cell is represented, for example, by two zinc

electrodes immersed in zinc sulfate solutions at different concentrations:



Another example of a concentration cell is two standard hydrogen electrodes immersed into two HCl solutions of different concentrations:



In the above cell, HCl is in two different concentrations. The activity (molality \times activity coefficient) a_1 is greater than activity a_2 ; $a_1 > a_2$. Several types of concentration cells are encountered in corrosion. For example, a concentration cell is formed if one end of a pipe is exposed to soil and the other end to air. The end of the pipe in air is exposed to a high concentration of oxygen than the end of the pipe in the soil. The formation of a concentration cell leads to differential aeration corrosion in buried structures in the soil.

2.9 LIQUID JUNCTION POTENTIAL

For accurate measurement of emf, two conditions must be satisfied:

- (a) The cell reaction must be reversible and
- (b) no current must be drawn from the cell.

The boundary between two electrolytic solutions with different concentrations is a source of *irreversibility* in measuring the emf of the cells. The potential difference developed at the boundary is called '*Liquid Junction Potential*.'

The potential difference is caused by the migration of ions from one electrolyte to another electrolyte. Let us take the case of concentrated HCl forming a junction with dilute HCl. Both H^+ and Cl^- ions diffuse from concentrated HCl to dilute HCl. The hydrogen ion moves faster and, therefore, the dilute solution becomes positively charged due to ingress of H^+ ions from the stronger acid solution and the more concentrated

solution thus acquires a relative negative charge. The consequent potential difference across the double layer, which is a positively charged layer in the dilute solution side and a negatively charged layer in the concentrated solution, may effect the emf of the cell seriously in certain cases. It is generally believed that the difference in potential is caused by the difference in the rate of diffusion of oppositely charged ions. In the above example, the charge acquired by a dilute solution is that of the faster moving ion (H^+); chloride ions (Cl^-) diffuse much slower. The magnitude of the liquid junction potential may affect the reversible potential positively or negatively depending on the mobilities of the ions. The most common method of removing liquid junction potential is to insert a KCl salt bridge between the electrolytes. Porous barriers are also used. The introduction of salt bridge minimizes the liquid junction potential. The KCl contained in the bridge, allows the migration of K^+ and Cl^- ions which carry most of the current and migrate with the same mobility.

The potential of zinc is more negative, hence it is considered as an anode ($\text{Zn} \rightarrow \text{Zn}^{2+} + 2e$) and the potential of nickel is less negative than zinc, hence it is considered as a cathode ($\text{Ni}^{2+} + 2e \rightarrow \text{Ni}$). The sign of the potential is changed for zinc as it oxidizes. From the potential obtained (+0.51 V), it is clear that the reaction will proceed spontaneously.

2.10 APPLICATION OF FREE ENERGY TO CORROSION CELLS

It is known that corrosion reactions produce electrical energy. The amount of work done by a cell is equal to the quantity of electrical energy which it generates under constant pressure, temperature and concentration of the reaction. In an electrochemical reaction, electrical energy available is equal to the product of potential of the cell and the quantity of electricity involved (volts \times amperes \times time). That is, Electrical energy = $E \times Q$. This is equal to the net work done by the cell. From Faraday's law, Q is

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one Faraday (F) for each gram equivalent of the reactants. For n gram equivalent of the reactants, Q is equal to nF . Work can only be performed if the free energy of the cell is decreased, as shown in Section 2.6.2:

$$\Delta G = -nFE \quad (2.44)$$

where

ΔG = change in Gibbs free energy of a cell in joules per mole

n = number of electrons involved in the reaction

E = emf of the cell in volts.

If all substances are in their standard states (i.e. at unit activity) the expression (2.44) becomes:

$$\Delta G^\circ = -nFE^\circ \quad (2.45)$$

Illustrative Example 2.3

For the cell $[\text{Cu}/\text{Cu}^{2+}(1.0\text{M})]/[\text{Zn}^{2+}(1.0\text{M})/\text{Zn}]$, and the cell reaction $\text{Cu} + \text{Zn}^{2+} \rightarrow \text{Cu}^{2+} + \text{Zn}$:

$$\text{If } \Delta G_{298^\circ\text{K}}^\circ = -147.5 \frac{\text{kJ}}{\text{mol}^{-1}} \text{ for } \text{Zn}^{2+}$$

$$\text{and } \Delta G_{298^\circ\text{K}}^\circ = 63.35 \frac{\text{kJ}}{\text{mol}^{-1}} \text{ for } \text{Cu}^{2+}$$

Solution of the Problem:

$$\Delta G_{\text{Reaction}}^\circ = \sum n_i \Delta G(i) - \sum n_j \Delta G(j)$$

where

i = products

j = reactants

n = number of moles

$$\therefore \Delta G_{\text{Reaction}}^\circ = 2 [63.35 + 0 - (-147.5 + 0)]$$

So,

$$\Delta G_{\text{Reaction}}^\circ = 425.1 \frac{\text{kJ}}{\text{mol}}$$

Since,

$$\begin{aligned} \Delta G_{\text{Reaction}}^\circ &= -nFE \\ &= -2 \times 96500 \times E \end{aligned}$$

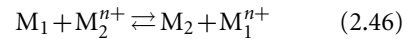
Hence,

$$E_{\text{Reaction}}^\circ = -0.002 \text{ V}$$

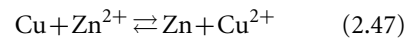
Reaction does not take place simultaneously.

2.1.1 NERNST EQUATION

The Nernst equation expresses the emf of a cell in terms of activities of products and reactants taking place in the cell reaction. Consider a general cell reaction:



M_1 and M_2 represent metal electrodes, such as Cu and Zn, in a cell, and the above reaction (2.46) can be written as:



The free energy change (ΔG) of a reaction is given by the difference in the molar free energy of products and reactants as shown in Section 2.6.

$$\Delta G = \sum n_i \Delta G(i) - \sum n_j \Delta G(j) \quad (2.48)$$

Therefore, the free energy change for the reaction (2.46) can be expressed as:

$$\Delta G^\circ = (G_{\text{M}_2}^\circ + G_{\text{M}_1^{n+}}^\circ) - (G_{\text{M}_1}^\circ + G_{\text{M}_2^{n+}}^\circ) \quad (2.49)$$

If the substances are in their standard states the above expression becomes:

$$\Delta G^\circ = (G_{\text{M}_2}^\circ + G_{\text{M}_1^{n+}}^\circ) - (G_{\text{M}_1}^\circ + G_{\text{M}_2^{n+}}^\circ) \quad (2.50)$$

Free energies of any metal, such as M_1 at its standard state and any arbitrary state are related through the following equation:

$$G_{\text{M}_1} - G_{\text{M}_1}^\circ = RT \ln a_{\text{M}_1} \quad (2.51)$$

where a_{M_1} is the activity of metal M_1 , R is the universal gas constant, and equal to 8.314 joules/degree/mole, and T is absolute