Chapter 11 Electrochemical Cells, Batteries, and Fuel Cells

►Emersion of metal electrode in an aqueous solution of metal cation

→Equilibrium is established which leads to negative charge (electrons) formation on the electrode.

►Electrode + solution = Half-cell

►Two half-cells form electrochemical cell:

Equilibrium is determined when the electrochemical potential (ECP) of a species is the same in all parts of the cell.

ECP=chemical potential+ electrical potential

►ECP can be changed by applying external electrical potential to the cell→Spontaneous change in cell reaction can be reversed.

►Electrochemical cell determines:

equilibrium constant and mean activity coefficient of a solute.

Used as power supplier-battery.

When reactants are continuously supplied-fuel cell.

11.1 Effect of electrical potential on the chemical potential of charged species

Consider Zn electrode partially immersed in aqueous solution of $ZnSO_4$ (Figure 1).

$$Z_n(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad (1)$$

$$Annode\ reaction: Oxidation$$
$$Charge\ separation\ arises\ through\ dissociation\ equilibrium.$$

→Negative charge builds up (charging) on the Zn electrode and positive charge builds up (charging) in the solution with equal amount.

→Causes a difference in electrical potential between the electrode and solution.

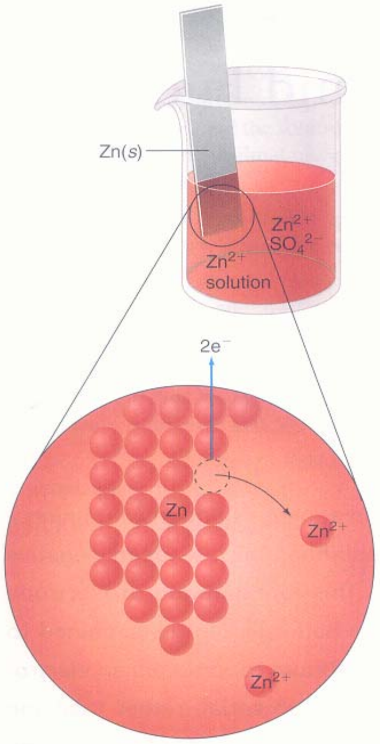

FIGURE 11.1

When a Zn electrode is immersed in water, a very small amount of the Zn goes into solution as $Zn^{2+}(aq)$, leaving two electrons behind on the Zn electrode per ion formed. Although the charge buildup on the electrode and in the solution is very small, it leads to a difference on the order of 1 V in the electrical potential of the solution and the electrode.

(Figure 1)

At equilibrium, <10^{-14} mole of Zn (s) dissociate ($Zn^{2+}+2e^-$) in one liter of solution→This minute amount of charge transfer creates ca 1 V difference of electrical potential (전위차=전압) between the electrode and solution.

Such small electrical potential does not affect chemical potential of neutral atom or molecule, but does the charged species.

Reversible work to transfer dn mole of charge from a phase at φ_1 *to a phase at* φ_2 *(All others are the same)*:

$$dw_{rev} = (\varphi_2 - \varphi_1)\,dQ = (\varphi_2 - \varphi_1)(-z\,F\,dn) \qquad (2)$$

φ = *Electrical potential*
dQ = *Amount of charge transferred through the potential*
z = *charge in unit of electron charge* $(+1, -1, +2, -2 \ldots)$
F = *Faraday constant* (= *Absolute magnitude of charge associated with one mole of singly charged species*)
= 96,485 *Coulombs/mole* (*C/mole*)

Note $Q = z_+ n_+ = z_- n_-$ $(n_+ = n\nu_+)$: *Cation and anion carry the same total charge.*
$Na^2SO_4 \rightarrow 2Na^+ + SO_4^{-2} \rightarrow 1*2 = 2*1$

Since the work is nonexpansion work
$dw_{rev} = dG =$ *difference in ECP between the two phases* (Going from phase 1 to 2)

$$dG = \widetilde{\mu}_2\,dn - \widetilde{\mu}_1\,dn \qquad (3)$$

ECP is the sum of chemical potential and electrical potential on a charged particle:

$$\widetilde{\mu} = \mu + z\varphi F \qquad (4)$$

Rewrite (4) for φ_1 and φ_2 (*Note* $\mu_1 = \mu_2$) and subtracting one from the other gives;

$$\widetilde{\mu}_2 - \widetilde{\mu}_1 = +z(\varphi_2 - \varphi_1)F \quad \text{or}$$

$$\widetilde{\mu}_2 = \widetilde{\mu}_1 + z(\varphi_2 - \varphi_1)F \qquad (5)$$

►Difference in electrical potentials provide difference in ECP.
Only $(\varphi_2 - \varphi_1)$ (not separately) can be measured.
So, let

$$\varphi_1 = 0,$$

Then

$$\widetilde{\mu}_2 = \widetilde{\mu}_1 + z\varphi_2 F \qquad (6)\ \text{(Basis for electrochemical rxn)}$$

Charged particle flows along decreasing ECP. So, negatively charged particle (z<0) flows toward a more positive Φ, and positively charged particle (z>0) toward a more positive Φ. ECP is easily changed by changing Φ.

As an object moves in the direction that the force accelerates it, its potential energy decreases. The gravitational potential energy of an object at higher altitude decreases as it falls and is translated to kinetic energy.

At equilibrium in electrochemical environment:

$$\Delta G_R = \sum_i \nu_i \tilde{\mu}_i = 0 \qquad (7)$$

$(Note\ \Delta G_R = \sum_i \nu_i \mu_i = 0$ for $nonelectrolyte)$

Note

1) $\tilde{\mu}_i$ *varies far greater extent than* μ_i since $z_i \varphi F$ *changes larger than* μ_i, *either* + or − .

2) ΔG_R *could be* + (*Spontaneous diection* ←) or − (*Spontaneous direction* →)

3) *Change in* φ *can change the sign of* ΔG, *hence the direction of spontaneous reaction.*

11.2 Conventions and standard states in electrochemistry

Daniel cell: → Zn^{2+}/Zn and Cu^{2+}/Cu

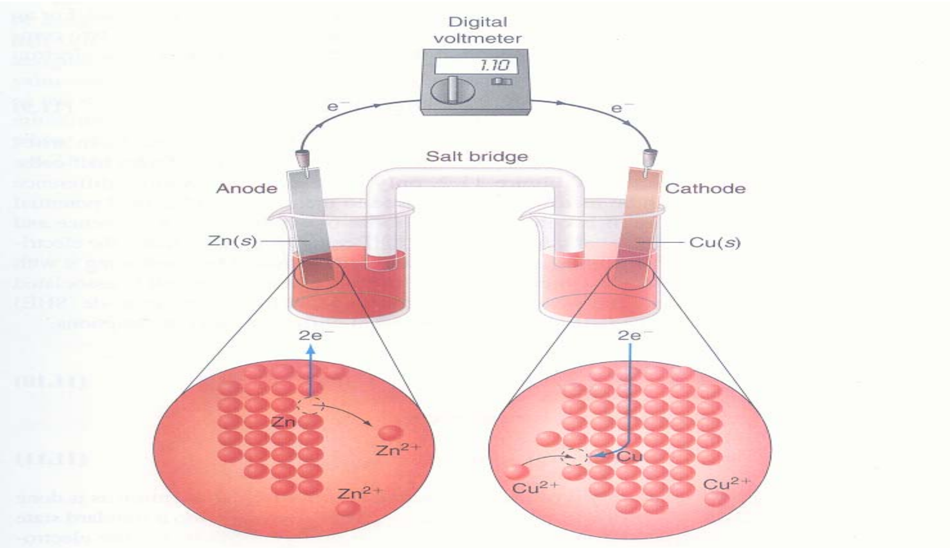

FIGURE 11.2

Schematic diagram of the Daniell cell. Zn^{2+}/Zn and Cu^{2+}/Cu half-cells are connected through a salt bridge in the internal circuit. A voltmeter is shown in the external circuit. The inset shows the atomic level processes that occur at each electrode.

Figure 2 (Daniel Cell)

► Left half-cell = $Zn^{2+}/Zn\ half-cell$: Anode (Oxidation)

Zn electrode is immersed in ZnSO4 solution.

(ZnSO4 is completely dissociated to Zn^{2+} and SO4^{2-})

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$$

► Right half-cell = $Cu^{2+}/Cu\ half-cell$: Cathode (Reduction)
Cu electrode is immersed in $CuSO_4$ solution.
($CuSO_4$ is completely dissociated to Cu^{2+} and $SO4^{2-}$)

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \qquad (17)\cdot$$

►Two half cells are connected by KCl salt bridge (ion conductor):
Salt bridge
i) electrolytes suspended in gel.
ii) transfers ions but does not mix up the two solutions.
iii) keeps both solutions neutral during the electrochemical reaction.

►Electric current flows by connecting the two electrodes w/ Pt wire.

$$\overset{Current}{I = \frac{dQ}{dt} = zF\frac{dn}{dt}}$$

Since equilibrium is established btn electrode and solution in each half cell, difference in electrical potential exists between the electrode and solution in each of the half-cells.

Can this electrical potential be directly measured?-No.
Place one Pt wire (inert probe) to Zn electrode.
Place a second Pt wire in $ZnSO_4$ solution.
Connect the two wires to a voltmeter→The measured voltage is the difference in electrical potential btn the two Pt wires. ∵ However, difference in φ can only be measured between one phase and a second phase of identical composition (Pt wire connected to the Zn electrode and Pt electrode-solution probe) → φ in the solution can not be directly measured (A). (The difference in φ across a resister is measured is measured by connecting the metal wire at each end of the resister with metal probes connected to the terminals of a voltmeter)

►Based on (A), we choose the standard state as;

i) φ = 0 for all ions in the solution

→ $\overline{\mu} = \mu_i$ (ions in solution) (8)

μ_i is calculated by Debye-Hückel limiting law.

→ $n_1 d\mu_1 + n_2 d\mu_2 = 0$

ii) Chemical potential of electron in metal electrode≡0 →

$$\widetilde{\mu}_e = \mu + z\varphi F = -\varphi F \qquad (z = -1 \text{ for } electron) \qquad (9)$$

We still can only measure the elecrrical potential difference (not the absolute one) between the two half-cells using the setup of Figure 2. ►By adopting a reference half-cell having zero electrical potential (SHE), we get the electrical potential for any half-cell.

The standard hydrogen electrode (SHE)(See Figure 11.3) .

$$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g) \qquad (10)$$

(Generally written as reduction)

The equilibrium is described by (7) as

$$\frac{1}{2}\mu_{H_2(g)} - \mu_{H^+(aq)} - \widetilde{\mu}_{e^-} = 0$$

$$\rightarrow \quad \mu_{H^+(aq)} + \widetilde{\mu}_{e^-} = \frac{1}{2}\mu_{H_2(g)} \qquad (11)$$

(Note: $\varphi_{(ion)}$ *in solution* $= 0$ and $\mu_e = 0$, $\varphi_{H_2} = 0$ *being used*)

Separation of $\mu_{H^+}(aq)$, $\mu_{H_2}(g)$ into standard state and activity dependent terms gives, and sub (9) into (11):

$$\mu^{\circ}_{H^+} + RT\ln a_{H^+} - F\varphi_{H^+/H_2} = \frac{1}{2}\mu^{\circ}_{H_2} + \frac{1}{2}RT\ln f_{H_2} \qquad (12)$$

or

$$\varphi_{H^+/H_2} = \frac{\mu^{\circ}_{H^+} - \frac{1}{2}\mu^{\circ}_{H_2}}{F} - \frac{RT}{F}\ln\frac{f^{1/2}_{H_2}}{a_{H^+}} \qquad (13)$$

Adopt Henry's standard state for $H^+(aq)$ (Good for solute-dilute):
As $c_i \to 0$, $\gamma_i \to 1$, and $a_i \to c_i$
$a_i = (c_i/c_i)\gamma_i = 1$ for $c_{H+} = 1.00M$ (called unit activity) (a)
H_2 pressure=1 atm → P=f (@low pressure) (b)
(a) + (b) = Conditions for SHE
Also $\mu_{H2}^{o} = 0$.

Under these conditions, (13) becomes;

$$\varphi_{H^+/H_2} = \frac{\mu^{\circ}_{H^+}}{F} \qquad (14)$$

We know from Ch 10

$$\Delta G_f^{\circ}(H^+, aq) = \mu^{\circ}_{H^+} = 0 \qquad \left(\frac{dG}{dn_i} = \mu_i.\ \Delta G = \mu \text{ for } 1\ mole\ of\ H^+\right)$$

So,

$$\varphi_{H^+/H_2} = 0 \qquad (15)$$

The electrical potential of SHE half-cell is 0.00 volts.

►The SHE is a convenient reference electrode against which the potential of all other half-cells can be measured (Half-cell potentials other than SHE cannot be directly measured).
►With SHE, the entire potential is assigned to the Zn/Zn^{2+} half-cell if $H^+(aq)$ and $H_2(g)$ have activity of one. (Figure 4)
►The Henry's standard state based on molarity is used for the standard state of activity of H+(aq): $a_i \to c_i$, $\gamma_i \to 1$ as $c_i \to 0$.
►For fast achievement of equilibrium (Eq 10) the reaction is carried out over a Pt catalyst (See Figure 3).

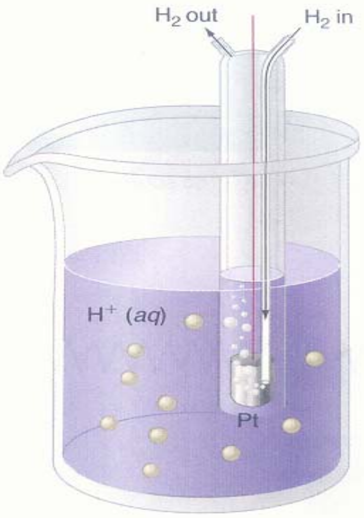

FIGURE 11.3

The standard hydrogen electrode (SHE) consists of a solution of an acid such as HCl, H_2 gas, and a catalyst that allows the equilibrium in the half-cell reaction to be established rapidly. The activities of H_2 and H^+ are equal to one.

Figure 3

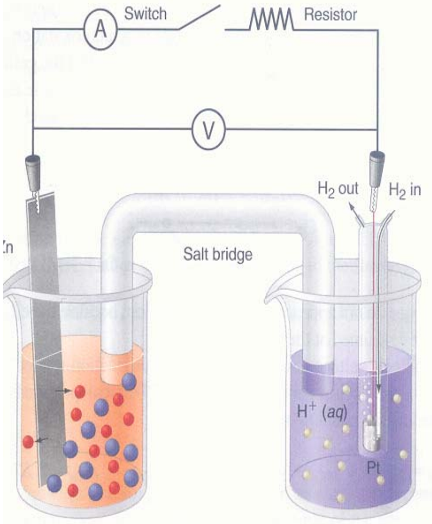

FIGURE 11.4

In a cell consisting of an arbitrary half-cell and the standard hydrogen electrode, the entire cell voltage is assigned to the arbitrary half-cell.

Figure 4