

Bahir Dar University

College of Science

Chemistry Department

Chemical Kinetics and Electrochemistry (Chem. 3051)

Unit Two

Electrochemical Cell

Introduction

Key terms

Before taking up the study of the electrochemical cells, we should be familiar with a few common terms.

Current is the flow of electrons through a wire or any conductor.

Electrode is the material : a metallic rod/bar/strip which conducts electrons into and out of a solution.

Anode is the electrode at which oxidation occurs. It sends electrons into the outer circuit. It has negative charge and is shown as (–) in cell diagrams.

Cathode is the electrode at which electrons are received from the outer circuit. It has a positive charge and is shown as (+) in cell diagrams.

Electrolyte is the salt solutions in a cell.

Half-cell. Each half of an electrochemical cell, where oxidation occurs and the half where reduction occurs, is called the half cell.

Introduction ...

What are half reactions ?

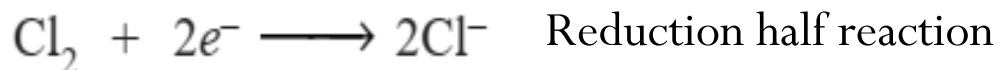
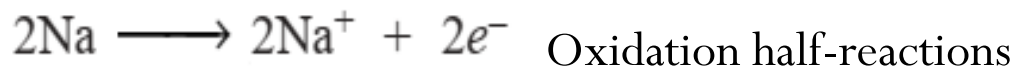
Let us consider a reaction $2\text{Na} + \text{Cl}_2 \longrightarrow 2\text{Na}^+ + 2\text{Cl}^-$

- It occurs by the transfer of electrons from Na to Cl. Na loses an electron and is said to be oxidized to Na^+ ion.
- At the same time, Cl gains an electron and is reduced to Cl^- ion.
- Such a reaction which is brought about by loss of electrons (oxidation) and gain of electrons (reduction) *simultaneously*, is called an *oxidation-reduction reaction or redox reaction*.
- The redox reaction can be considered as made up of two half reactions.

For example, the redox reaction



is composed of two half-reactions :



Introduction ...

Cell potential or electromotive force (emf)

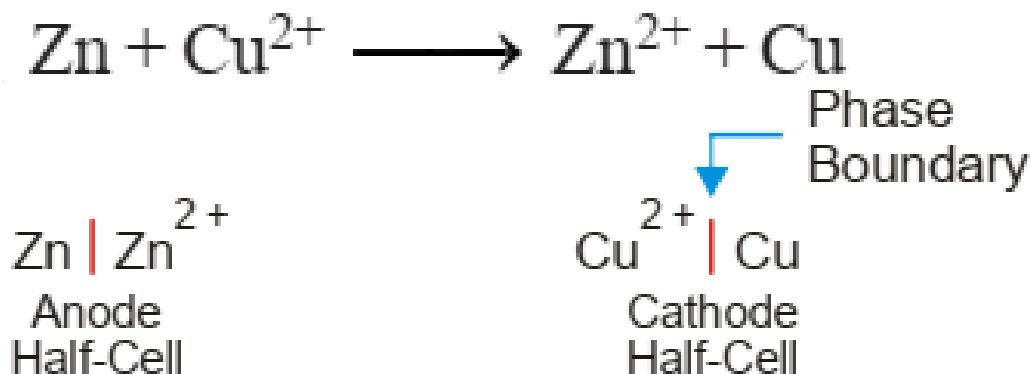
- When, electrons are released at the anode and it becomes negatively charged.
- The negative **electrode pushes** electrons through the external circuit by *electrical repulsions*. The metal (M) electrode gets positive charge due to the discharge of M^{n+} ions on it. Thus electrons from the outer circuit are *attracted into this electrode*.
- The flow of current through the circuit is determined by *the ‘push’, of electrons at the anode and ‘attraction’ of electrons at the cathode*.
- These two forces constitute the ‘driving force’ or ‘electrical pressure’ that sends electrons through the circuit. This driving force is called the **electromotive force** or **cell potential**.
- The emf of cell potential is measured in units of volts (V) and is also referred to as **cell voltage**.

Introduction ...

Cell diagram or Representation of a Cell

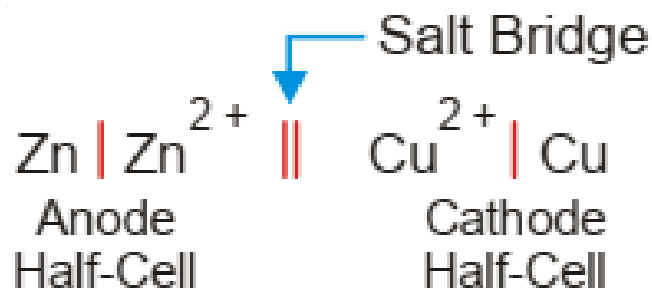
- A cell diagram is an abbreviated symbolic representation of an **electrochemical cell**. For this purpose, we will consider that a cell consists of two half-cells. Each half-cell is again made of a metal electrode contact with metal ions in solution.
- 1) a **single vertical line** (|) represents a phase boundary between metal electrode and ion solution (electrolyte).

Thus the two half-cells in a the reaction below are indicated as



Introduction ...

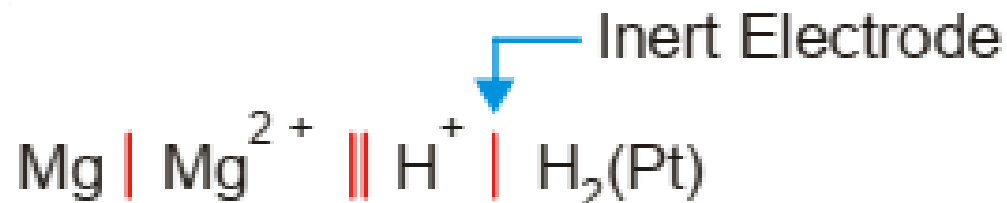
- 2) A **double vertical line** (||) represents the salt bridge, porous partition or any other **means** of permitting ion flow while preventing the electrolyte from mixing.
- 3) **Anode half-cell is written on the left and cathode half-cell on the right.**
- 4) In the **complete cell diagram**, the two half-cells are separated by a **double vertical line (salt bridge) in between**. The zinc-copper cell can now be written as



Introduction ...

- 5) The symbol for an **inert electrode**, like the platinum electrode is often enclosed in a bracket.

For example,



- 6) The value of emf of a cell is written on the right of the cell diagram.
Thus a zinc-copper cell has emf 1.1V and is represented as



Calculating the emf of a cell

- The *emf* of a cell can be calculated from the half-cell potentials of the two cells (anode and cathode) by using the following formula:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_R - E_L \end{aligned}$$

where E_R and E_L are the reduction potentials of the right-hand and left-hand electrodes respectively.

- These are found by connecting the half-cell *with a standard hydrogen electrode* whose reduction potential has been arbitrarily fixed as zero.

Electrochemical cells

- A device which produces an **electrical current** from a chemical reaction (**redox reaction**) is called an **electrochemical cell**.
- When a bar of zinc is dipped in a solution of copper sulphate, copper metal is deposited on the bar which is called **Daniel cell**.

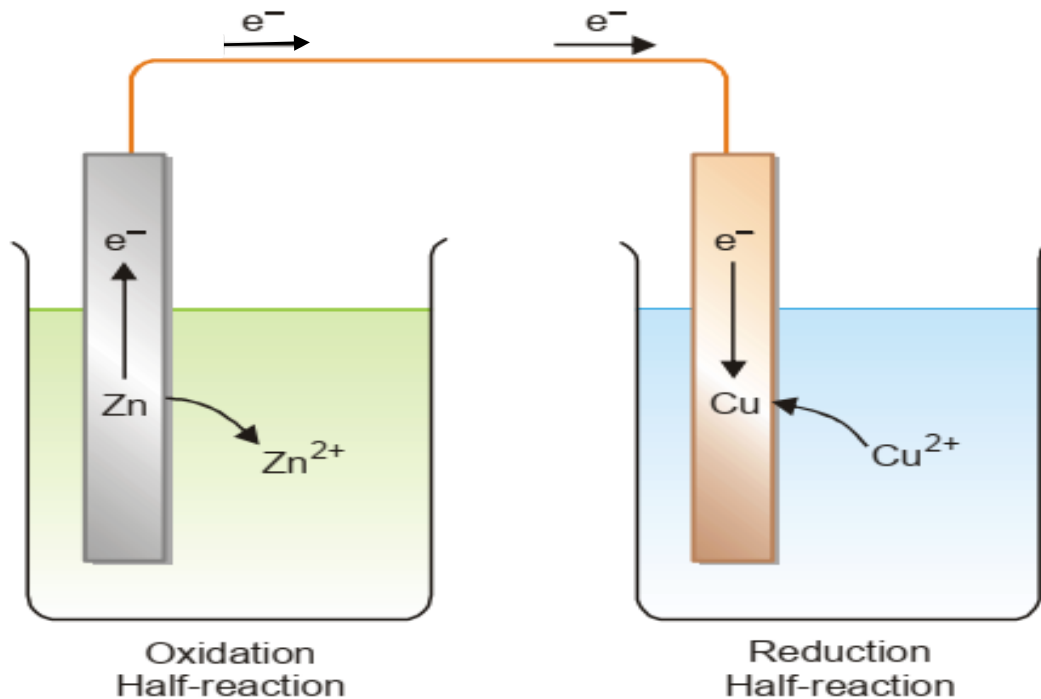


Figure 2.1; Separate half-reactions cause flow of electrons (current) in the wire connecting them.

- Here the **two half-reactions** occur in separate compartments which are connected by a wire (as shown in Fig. 2.1).
- The electrons produced in the left compartment flow through the wire to the other compartment. However the current will flow for an instant and then stop.

The net reaction is: $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$

This is a redox reaction and the two half-reactions are :



- In this change, Zn is oxidized to give Zn^{2+} ions and Cu^{2+} ions are reduced to Cu atoms. The electrons released in the first half-reaction are used up by the second half-reaction.

- The solutions in the two compartments may be connected, say, by a **salt bridge**.
- The salt bridge is a U-tube filled with an electrolyte such as *NaCl, KCl, or K_2SO_4* .
- *It provides a passage of ions* from one compartment to the other compartment without extensive mixing of the two solutions.
- With this ion flow, the circuit is complete and electrons pass freely through the wire *to keep the net charge zero* in the two compartments.

Reversible electrodes

- A familiar example of a reversible electrode is the Daniel cell (Fig. 2.2 a). We know that electrons flow from **zinc electrode to copper** electrode.

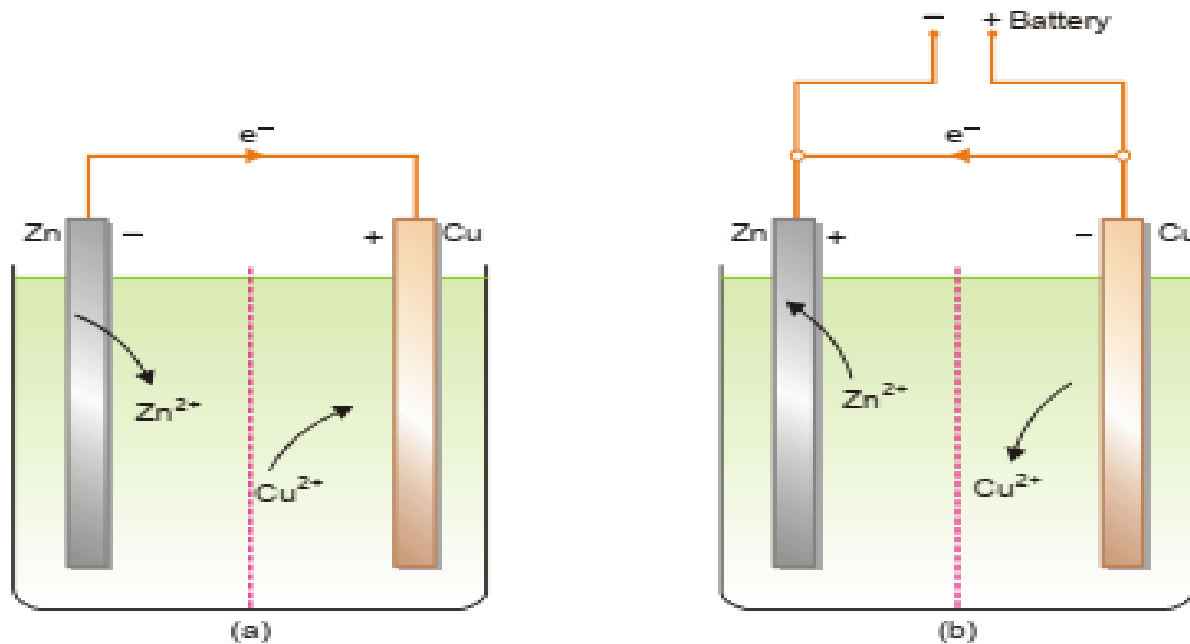
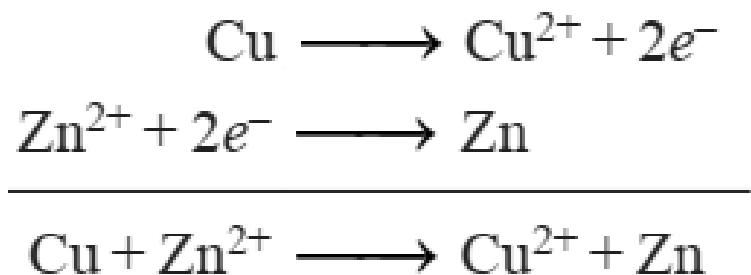


Figure 2.2: Reversible Daniel cell : (a) Zn-Cu cell in which current flows from left to right; (b) Cu-Zn cell in which current flows from right to left on application of external emf (battery).

- However, when the two electrodes are connected to an external battery that opposes the **cell electromotive force (emf)**, the above reaction is reversed (Fig. 2.2 b). Cu from the copper electrode dissolves to form Cu^{2+} ion and Zn^{2+} ion is discharged on the zinc electrode to give Zn atom.
- The overall reaction taking place in the cell may be written as



❖ **A reversible cell** may be defined as : **a cell that operates by reversal** of the cell current and direction of cell reaction by infinitesimal change of emf on either side of the balance point.

Thermodynamics of electrochemical cells

Relation between emf and free energy

- When a cell produces a current, the current can be used to do work—for instance *to run a motor*.
- Thermodynamic principles can be employed to derive a relation between *electrical energy and the maximum amount of work, W_{\max}* obtainable from the cell.
- The maximum amount of work obtainable from the cell is the *product of charge flowing per mole and maximum potential difference, E* , through which the charge is transferred.

$$W_{\max} = -nFE \dots\dots\dots 1$$

where n is the number of moles of electrons transferred and is equal to the valence of the ion participating in the cell reaction.

F stands for Faraday constant and is equal to *96,500 coulombs* and

E is the emf to the cell

- According to thermodynamics, the maximum work that can be derived from a chemical reaction is equal to the free energy (ΔG) for the reaction.

$$W_{\max} = \Delta G \quad \dots\dots\dots 2$$

- Therefore by combining equation 1 and 2, we can write

$$\Delta G = -nFE \quad \dots\dots\dots 3$$

According to Gibbs-Helmholtz equation, the decrease in free energy of a system at constant pressure is given by the expression

$$-\Delta G = -\Delta H - T \left(\frac{\partial(\Delta G)}{\partial T} \right)_p \dots\dots\dots 4$$

where $-\Delta H$ is the decrease in heat content of the system or heat of the reaction at constant pressure

Substituting the value of ΔG from (3)

$$nFE = -\Delta H - T \left(\frac{\partial(-nFE)}{\partial T} \right)_p$$

$$nFE = -\Delta H + nFT \left(\frac{\partial E}{\partial T} \right)_p$$

$$E = \frac{-\Delta H}{nF} + T \left(\frac{\partial E}{\partial T} \right)_p \dots\dots\dots 5$$

If the heat of the reaction (or free energy change) and the temperature coefficient of a cell are known, we can calculate the emf, E , of the cell. For example, in case of a Daniel cell $(\partial E/\partial T)_p$ is nearly zero, $n = 2$ and $\Delta H = -50,100$ Cals.

Since $1 \text{ Cal} = 4.185 \text{ Volt-Coulomb}$,

$$E = \frac{-\Delta H}{nF} = \frac{-4.185 \times (-50,100)}{2 \times 96,500} \\ = 1.09 \text{ V}$$

Thus the emf of Daniel cell is 1.09 volts. Conversely, if the emf of a reversible cell and its temperature coefficient $(\partial E/\partial T)_p$ are known, ΔH (or ΔG) can be calculated. The heats of reaction calculated from emf measurements are nearly the same as derived from thermal measurements.

Determination of standard electrode potential

- The **standard electrode potential** of an electrode can be defined as the potential difference that arises between the electrode and the electrolyte **under standard conditions** (Temp' = 298K, pressure = 1 atm, unity concentration of reacting species).

The Nernst equation

- In 1889 Walter Nernst derived a mathematical relationship which enable us to calculate the **half-cell potential**, E , from the **standard electrode potential**, E° , and the **temperature** of the cell. This relation known as the *Nernst equation and can be stated as;*

$$E = E^\circ - \frac{2.303RT}{nF} \log K \quad \dots(1)$$

where

E° = standard electrode potential

R = gas constant

T = Kelvin temperature

n = number of electrons transferred in the half-reaction

F = Faraday of electricity

K = equilibrium constant for the half-cell reaction as in equilibrium law

Calculation of Half-cell potential

For an oxidation half-cell reaction when the metal electrode M gives M^{n+} ion,



the Nernst equation takes the form

$$E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{[M^{n+}]^m}{[M]^n} \quad \text{Where, m and n are their coefficients} \quad \dots(2)$$

- Since the concentration of solid metal [M] is equal to one. Therefore the above equation can be written as:

$$E = E^{\circ} - \frac{2.303RT}{nF} \log[M^{n+}] \quad \dots(3)$$

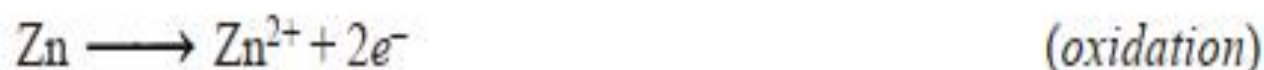
Substituting the values of R, F and T at 25°C, the quantity $2.303 RT/F$ comes to be 0.0591. Thus the Nernst equation (3) can be written in its simplified form as

$$E = E^{\circ} - \frac{0.0591}{n} \log[M^{n+}]$$

SOLVED PROBLEM. What is the potential of a half-cell consisting of zinc electrode in 0.01M ZnSO_4 solution at 25°C , $E^\circ = 0.763 \text{ V}$.

SOLUTION

The half-cell reaction is



The Nernst equation for the oxidation half-cell reaction is

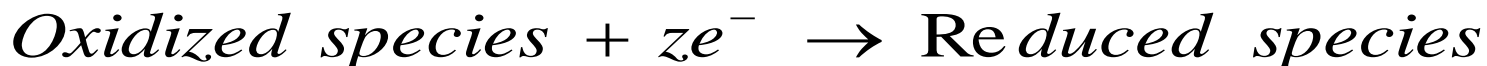
$$E = E^\circ - \frac{0.0591}{n} \log[\text{Zn}^{2+}]$$

The number of electrons transferred $n = 2$ and $E^\circ = 0.763 \text{ V}$.

Substituting these values in the Nernst equation we have

$$\begin{aligned} E &= 0.763 - \frac{0.0591}{2} \log(0.01) \\ &= 0.763 - \frac{0.0591}{2} (-2) \\ &= 0.763 + 0.0591 = \mathbf{0.8221 \text{ V}} \end{aligned}$$

Calculation of emf of Redox reaction



- The relationship between concentration and potential is given by the Nernst equation:

$$E_{\text{cell}} = E^0 + \frac{RT}{nF} \log \left(\frac{[\textit{oxidised species}]}{[\textit{reduced species}]} \right)$$

Where R is the gas constant, T is the absolute temperature, n is the number of electrons, F is Faraday constant, E^0 is the standard electrode potential.

Consider cell reaction: $\text{Zn} + 2\text{Ag}^+ \rightleftharpoons \text{Zn}^{2+} + 2\text{Ag}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log K$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

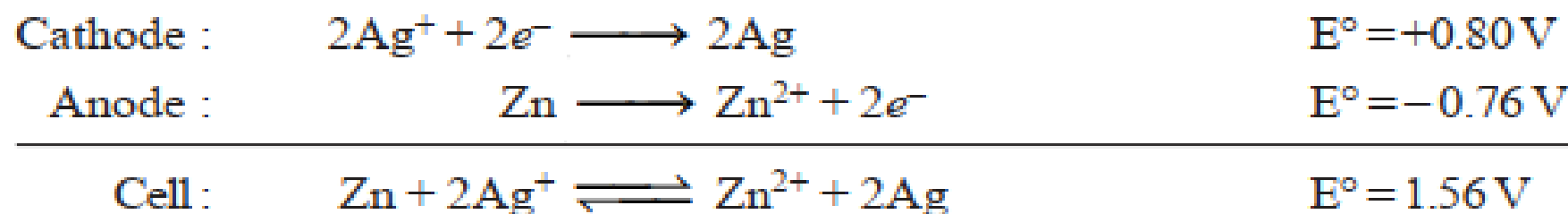
SOLVED PROBLEM. Calculate the emf of the cell.



The standard potential of Ag/Ag^+ half-cell is +0.80 V and Zn/Zn^{2+} is -0.76 V.

SOLUTION

Step 1. Write the half-cell reactions of the anode and the cathode. Then add the anode and cathode half reactions to obtain the cell reaction and the value of E_{cell}° .



Step 2. K for the cell reaction $= \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$

substitute the given values in the Nernst equation and solving for E_{cell} , we have

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^\circ - \frac{0.0591}{n} \log K \\
 &= 1.56 - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \\
 &= 1.56 - \frac{0.0591}{2} \log \frac{[10^{-3}]}{[10^{-1}]^2} \\
 &= 1.56 - 0.02955 (\log 10^{-1}) \\
 &= 1.56 + 0.02955 \\
 &= \mathbf{1.58955 \text{ V}}
 \end{aligned}$$

Calculation of Equilibrium constant for the cell reaction

The Nernst equation for a cell is

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log K$$

At equilibrium, the cell reaction is balanced and the potential is zero. The Nernst equation may, now, be written as

$$0 = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log K$$

or

$$\log K = \frac{n E^{\circ}_{\text{cell}}}{0.0591}$$

SOLVED PROBLEM. Calculate the equilibrium constant for the reaction between silver nitrate and metallic zinc.

SOLUTION

Step 1. Write the equation for the reaction



Step 2. Substitute values in the Nernst equation at equilibrium

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log K$$

$$0 = 1.56 - 0.03 \log K$$

$$-1.56 = -0.03 \log K$$

$$\log K = \frac{-1.56}{-0.03} = 52$$

$$K = 1 \times 10^{52}$$

Classes of electrochemical cells

The **two** primary types of electrochemical cells are

1. Galvanic cell

2. Electrolytic cell

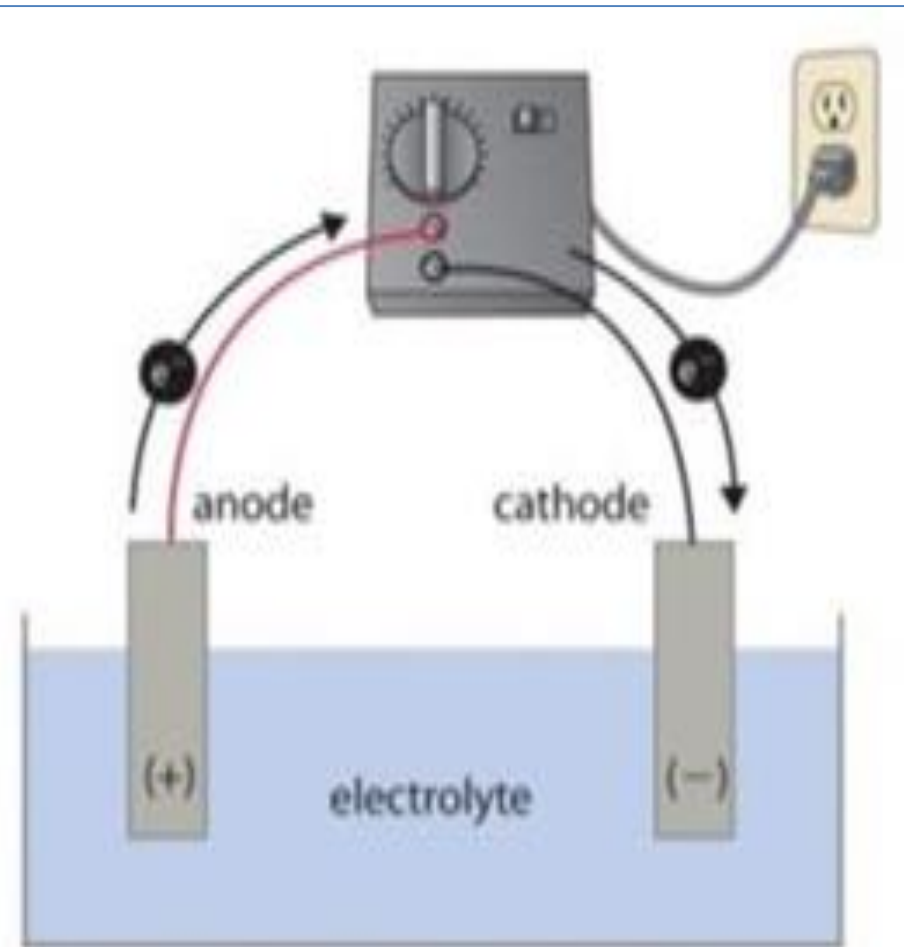
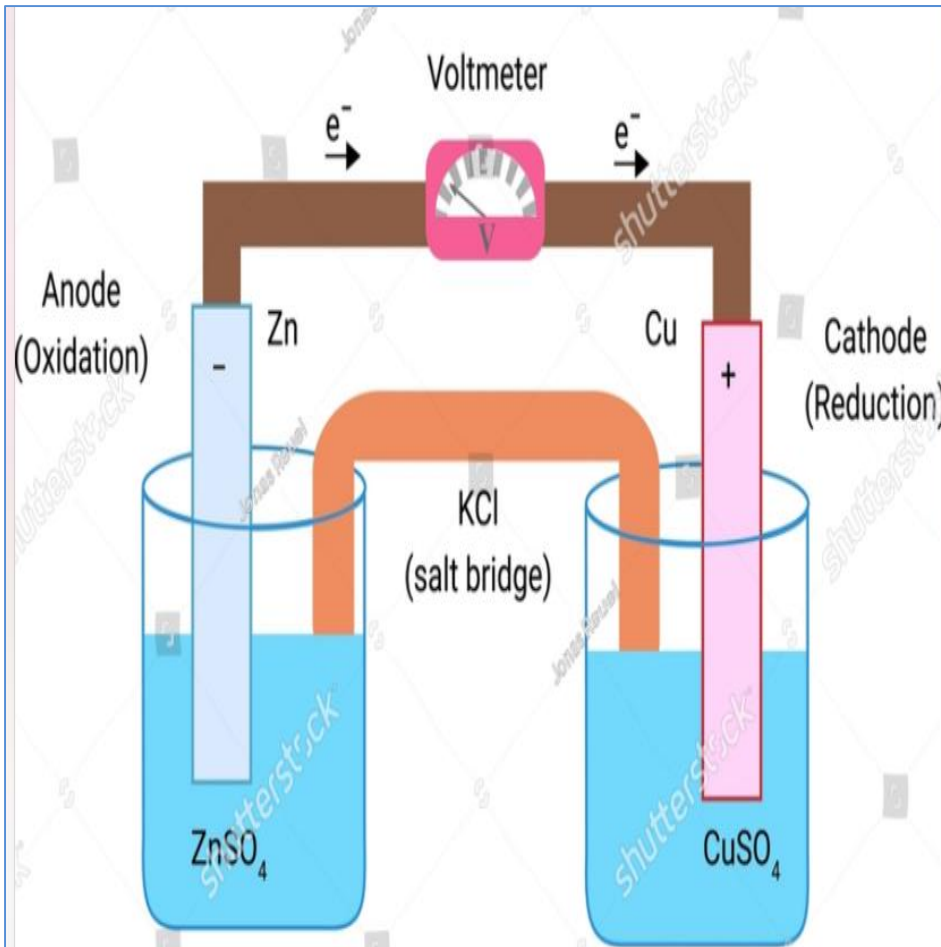


Figure 2.3 illustration of galvanic and electrolytic cells

The key differences between Galvanic cells and electrolytic cells.

Galvanic Cells	Electrolytic Cells
Spontaneous redox reactions convert the chemical energy to an electric energy	Non-spontaneous redox reactions convert the electric energy to a chemical energy
Electric energy is generated by redox reactions	Electric energy brings about the chemical reaction with the help of an external source
The cathode is the positive electrode and anode is the negative electrode	The anode is the positive electrode and cathode is the negative electrode
The process of oxidation takes place at the anode and the reduction process occurs at the cathode	Here, the oxidation process occurs at the anode while the reduction process takes place at the cathode
Half cells are set up in different containers and are connected through salt bridges	Electrodes are kept in the same container in a molten or solution electrolyte
Application lies in Batteries	Application lies in purifying copper and electroplating

Similarities between Galvanic and Electrolytic Cells

Both Galvanic and Electrolytic cells contain:

- **Two electrodes:** the anode where oxidation occurs and the cathode where reduction occurs (note that Cathode does not mean +, and Anode does not mean -)
- **Volt meter:** measures the electric current. In galvanic cells, this shows how much voltage is produced and in electrolytic cells, this shows how much voltage is applied to the system.
- **Electrolyte**
 - ❖ conducting medium
 - ❖ has contact with electrodes
 - ❖ usually in aqueous solution of ionic compounds
- Salt bridge

Liquid junction potential

- A liquid junction potential is developed when a cell contains two electrolytic solutions of different concentration in contact with one another.
- The more concentrated solution possesses a tendency to diffuse into the comparatively less concentrated one.
- Large concentration difference between the liquid phases results in high liquid junction potential.
- The rate of diffusion of an ion at the junction of the two solutions is proportional to its speed.
- If the cations (positively charged ions) move faster from concentrated solution to diluted solution than anions (negatively charged ions), the (+)ve ions will diffuse ahead of the (-)ve ions in the dilute solution.
- Thus the dilute solution will be (+)vely charged with respect to concentrated solution.

- Similarly, if the anion (negatively charged ions) moves faster, it will diffuse rapidly than (+)ve ion and the dilute solution will be (-)vely charged.
- In both cases, an electrical double layer is formed at the junction of solutions resulting potential difference. This potential difference developed at the junction of two solutions is known as liquid junction potential (EL) or diffusion potential, the magnitude which depends upon the relative speed of the ions.
- The electrical separation and potential difference thus arises will continue to increase until the rates of diffusion of (-)ve and (+)ve ions are equalized by electrical forces.
- If two ions are moving with the same speed there will be no liquid junction potential.

Expression for Liquid Junction Potential

- When different concentrations of same electrolytic solutions are in contact, liquid junction potential can be measured.
- Let us consider the simplest case in which the junction is formed between two solutions of the same uni-univalent electrolyte with activities a_1 and a_2 .



- Adopting the usual convention for a (+)ve emf, the left hand electrode is the source of electrons so that current flows through the interior of the cell from left to right.
- If one Faraday of electricity is passed in the cell, n gram ion of cation (i.e. K^+ ion) migrates from left to right i.e., from solution of activity a_1 to a_2 .
- Likely, n gm ion of anion (i.e., Cl^- ion) migrates from right to left.

n_a and n_c are the transference numbers of anions and cations respectively. If transference number is assumed to be independent of concentration, then the *free energy change* during the passage of one faraday of electricity may be calculated.

The free energy change for (+)ve ion in the left compartment

$$= n_c RT \ln \frac{(a_+)_2}{(a_+)_1} \dots\dots\dots (1)$$

The free energy change for (-)ve ion in the right compartment

$$= n_a RT \ln \frac{(a_-)_1}{(a_-)_2} \dots\dots\dots (2)$$

Thus the total free energy change (ΔG) is

$$\Delta G = n_c RT \ln \frac{(a_+)_2}{(a_+)_1} + n_a RT \ln \frac{(a_-)_1}{(a_-)_2} \dots\dots\dots (3)$$

Let E_L be the liquid junction potential. The electrical work done $= -nE_L F$

$$\therefore \Delta G = -E_L F \quad (n=1) \dots\dots\dots (4)$$

From equation (3) and (4)

$$-E_L F = n_c RT \ln \frac{(a_+)_2}{(a_+)_1} + n_a RT \ln \frac{(a_-)_1}{(a_-)_2}$$

$$\Rightarrow E_L = -\frac{n_c RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} - \frac{n_a RT}{F} \ln \frac{(a_-)_1}{(a_-)_2}$$

$$\therefore E_L = -n_c \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} + n_a \frac{RT}{F} \ln \frac{(a_-)_2}{(a_-)_1} \dots\dots\dots (5)$$

- Here a_1 and a_2 are the mean activities of the electrolyte in the two solutions.
By making further approximation of writing;

$$\frac{(a_-)_2}{(a_-)_1} = \frac{a_2}{a_1} \text{ and } \frac{(a_+)_2}{(a_+)_1} = \frac{a_2}{a_1}$$

Hence, equation (5) reduces to $E_L = -n_c \frac{RT}{F} \ln \frac{a_2}{a_1} + n_a \frac{RT}{F} \ln \frac{a_2}{a_1}$

$$\therefore E_L = (-n_c + n_a) \frac{RT}{F} \ln \frac{a_2}{a_1} \dots\dots\dots (6)$$

Since $n_a + n_c = 1$

$$\therefore n_a = (1 - n_c)$$

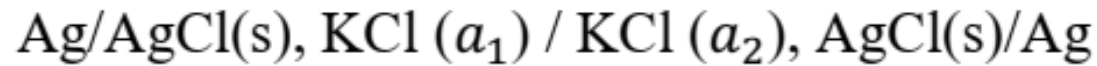
Equation (6) may be written as

$$E_L = (-n_c + 1 - n_c) \frac{RT}{F} \ln \frac{a_2}{a_1}$$

$$\therefore E_L = (1 - 2n_c) \frac{RT}{F} \ln \frac{a_2}{a_1} \dots\dots\dots (7)$$

It is clear from equation (6) that the sign of liquid junction potential depends upon the relative values of transference number of anion and cation.

If the liquid junction potential under consideration forms part of the concentration cell,



the emf of the cell (E_t) is given by

$$E_t = -2n_c \frac{RT}{F} \ln \frac{a_2}{a_1} \dots\dots\dots (8)$$

Dividing equation (7) by (8), we have

$$\frac{E_L}{E_t} = \frac{(1 - 2n_c)}{-2n_c}$$

$$\therefore E_L = \frac{(2n_c - 1)}{2n_c} E_t \dots\dots\dots (9)$$

This is the expression for liquid junction potential (diffusion potential).

Measurement of pH

- For measuring pH a half-cell is set up with the test solution as electrolyte. The *cell potential of the cell depends on the concentration of H^+ ions or pH of the solution.*
- The *cell potential* of the half-cell is determined *by coupling* it with another *standard electrode and measuring* the *cell potential* of the complete cell.
- The commonly used standard (reference) electrodes are :
 - a) The standard hydrogen electrode (SHE)
 - b) The standard calomel electrode (SCE)
 - c) Silver-silver electrode

a. Using standard Hydrogen electrode

- A standard hydrogen electrode is coupled with another hydrogen electrode which contains the solution of unknown pH. In both half-cells hydrogen gas is used at 1 atm pressure and 25°C. The cell potential of the complete cell is recorded experimentally.
- The cell reaction can be presented as:

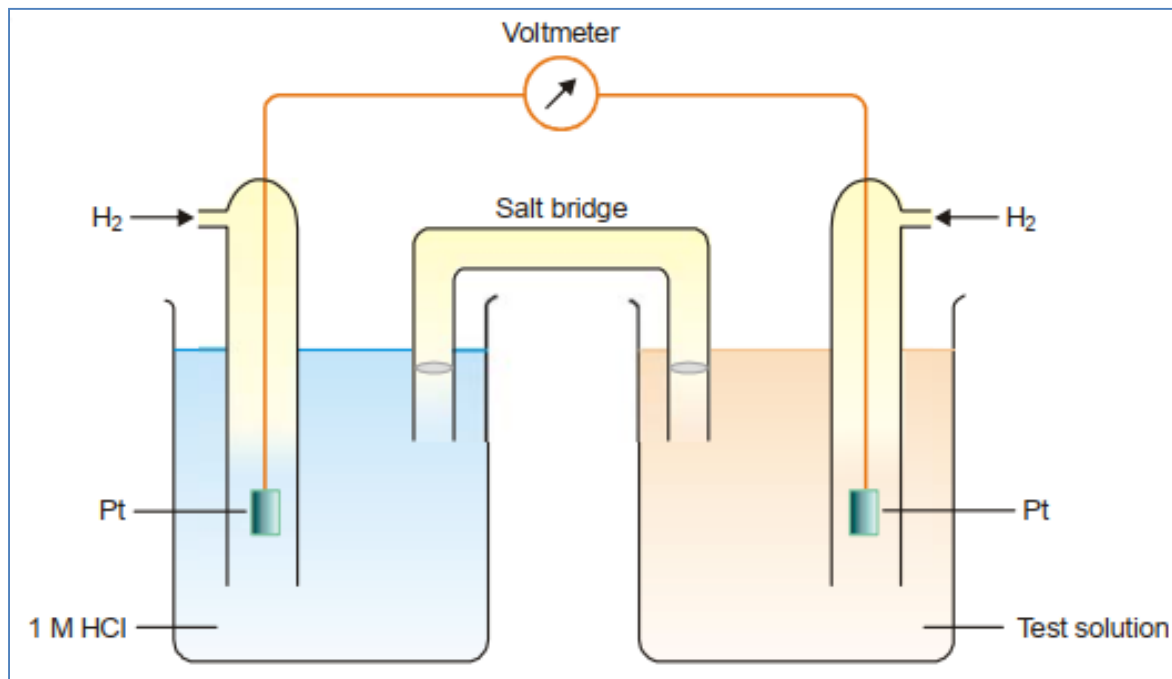


Figure 2.4 Determination of pH with Hydrogen electrode.

Calculations. The second electrode reaction is



The electrode potential of the second half-cell is given by the Nernst equation

$$E = E^\circ + \frac{2.303RT}{nF} \log \frac{[\text{H}^+]}{\text{H}_2^{1/2}}$$

Since $\text{H}_2^{1/2} = 1$ and $E^\circ = 0$, we have

$$E = \frac{2.303RT}{nF} \log[\text{H}^+] = \frac{2.303RT}{nF} \log[\text{H}^+]$$

Substituting the values of R , T and n (charge number of H^+) and F (Faraday constant), the expression becomes

$$E = 0.0591 \log [\text{H}^+]$$

or

$$E = -0.0591 \text{ pH} \quad \dots(\text{A})$$

$$\text{pH} = \frac{-E_{\text{cell}}}{0.0591}$$

b. Using standard calomel electrode (SCE) instead of SHE

- The hydrogen electrode is relatively difficult to set up and operate under standard conditions. It is far easier to use the calomel electrode (mercury(I) chloride, Hg_2Cl_2) as a secondary reference electrode.
- A hydrogen electrode containing solution of unknown pH is paired with a standard calomel electrode with emf value 0.2415 volt. The complete cell reaction may be represented as; $\text{Pt}, \text{H}_2(1 \text{ atm}) \mid \text{H}^+(\text{Unknown}) \parallel \text{KCl}(\text{Sat Solution}) \mid \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$

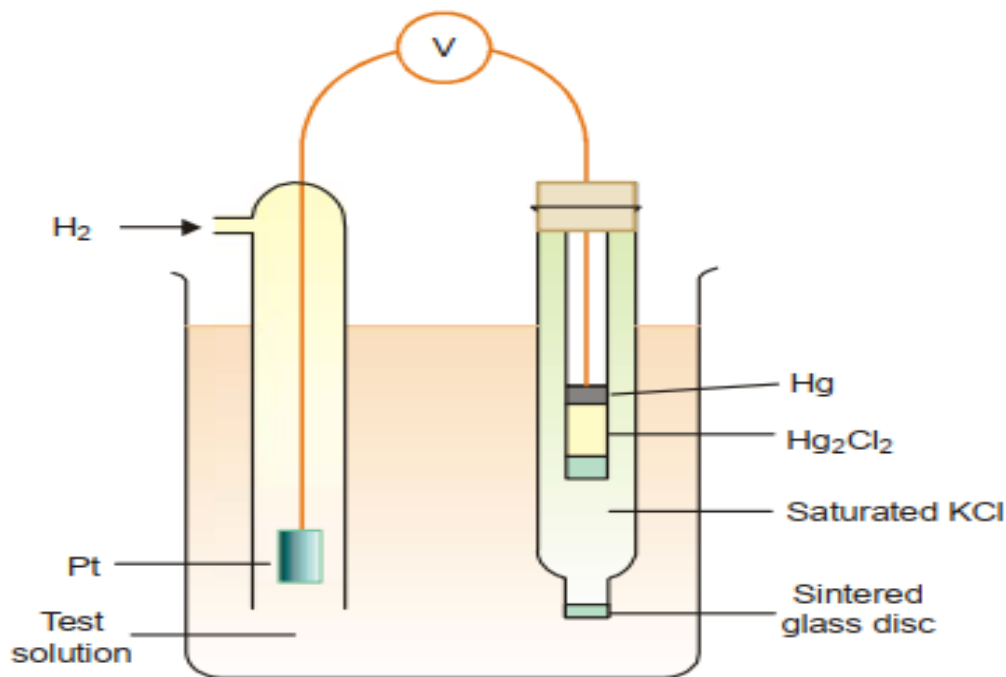


Figure 2.5; A calomel electrode coupled with unknown hydrogen electrode

By noting the emf of the cell with the help of a voltmeter, the pH of the unknown solution can be calculated as follows :

The emf of the cell will be given by the expression

$$\begin{aligned} E_{\text{cell}} &= E_{\text{right}} - E_{\text{left}} \\ &= 0.2415 - (-0.0591 \times \text{pH}) \end{aligned} \quad \dots(\text{from eq A})$$

$$E_{\text{cell}} = 0.2415 + 0.0591 \times \text{pH}$$

or

$$\text{pH} = \frac{E_{\text{cell}} - 0.2415}{0.0591}$$

Membrane potentials

- If two different concentrated electrolyte solutions are separated by a membrane, a potential difference will be set up between the two solutions if the membrane is permeable to some ions and impermeable to others.
- For example consider two KCl solutions separated by a membrane permeable to k^+ but impermeable to Cl^- .
- If solution α is more concentrated than solution β , k^+ ions will diffuse through the membrane from solution α to β this will cause solution β to become positively charged relative to solution α and it produce *higher electric potential* (voltage) *difference which is called the membrane potential*.
- Actually, the amount of k^+ that has to diffuse through the membrane to produce the potential difference is chemically insignificant. As k^+ diffuse through the membrane, the electrical potential difference that is set up across the membrane retards the diffusion of more k^+ , and *eventually an equilibrium is reached*.

At equilibrium

$$\mu_i(\alpha) = \mu_i(\beta)$$

Where μ is chemical potential

ϕ is electrical potential

z_i is charge number

And
$$\mu_i = \mu'_i + z_i F \phi_i$$

μ'_i is transformed potential

➤ This can be rewrite as: $\mu'_i(\alpha) + z_i F \phi(\alpha) = \mu'_i(\beta) + z_i F \phi(\beta)$

➤ The transformed chemical potential depends on the activity a_i like the chemical potential does, and so we have

$$\mu'_i = \mu_i'^{\circ} + RT \ln a_i$$

➤ Substituting this relation in equation above we obtained;

$$\mu_i'^{\circ}(\alpha) + RT \ln a_i(\alpha) + z_i F \phi(\alpha) = \mu_i'^{\circ}(\beta) + RT \ln a_i(\beta) + z_i F \phi(\beta)$$

- Since the solvent is the same on both sides of the membrane and the electric potentials have to be the same in the definition of the standard states for the transformed chemical potential of i,

$$\mu_i'^{\circ}(\alpha) = \mu_i'^{\circ}(\beta)$$

- The above equation becomes;

$$RT \ln a_i(\alpha) + z_i F \phi(\alpha) = RT \ln a_i(\beta) + z_i F \phi(\beta)$$

- Thus; $\Delta\phi = \phi(\beta) - \phi(\alpha) = -\frac{RT}{z_i F} \ln \frac{a_i(\beta)}{a_i(\alpha)}$
- Where $\Delta\phi$ is referred to as membrane potential.

Example *Calculation of a membrane potential*

The membrane potential for a resting nerve cell is given by $\Delta\phi = \phi_{\text{int}} - \phi_{\text{ext}} = -70 \text{ mV}$ where ϕ_{int} is the potential internal to the cell and ϕ_{ext} is the potential external to the cell. Given the fact that the concentration of K^+ inside a resting nerve cell is about 35 times that outside the cell, what membrane potential is expected?

Solution

$$\Delta\phi = -\frac{RT}{z_i F} \ln \frac{\text{inside}}{\text{outside}}$$
$$= -\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{96485 \text{ C mol}^{-1}} \ln 35$$
$$= -91 \text{ mV}$$

Examples of electrochemical cells

- Electrochemical cells are used for various purposes in our daily life. Some examples of these cells or batteries are:
 1. Dry cell standardized as 1.5V **cell** which is used to power many electrical appliances such as TV remotes and clocks.
 2. Nickel Cadmium (Nicad, or Cadnica cell)
 3. Many commercially important batteries (such as the [lead-acid battery](#))
 4. **Lithium-ion batteries** are used in a wide range of tools such as for solar power storage systems, mobile phones, tablets, laptops, etc.
 5. Fuel cells which are an important class of electrochemical cells that serve as a source of clean energy in several remote locations.

Example; 1 The emf of the following cell at 25°C is 0.445V.



Calculate the pH of the unknown solution, $E_{\text{cell}} = 0.2415$.

SOLUTION

$$E_{\text{cell}} = 0.445 \text{ V (given)}$$

$$E_{\text{cell}}^{\circ} = E_{\text{Right}}^{\circ} - E_{\text{left}}^{\circ} = 0.2415 - 0 = 0.2415 \text{ V}$$

Using the relation

$$\text{pH} = \frac{E_{\text{cell}} - 0.2415}{0.0591}$$

∴

$$\begin{aligned} \text{pH} &= \frac{0.445 - 0.2415}{0.0591} = \frac{0.2035}{0.0591} \\ &= 3.44 \end{aligned}$$