Electrochemical cell and Applications

of EMF MEASUREMENTS

Electrochemical cell-

- **An electrochemical cell is a device capable of either generating electrical energy from chemical reactions (Chemical energy) or using electrical energy to cause chemical reactions.**

Electrical energy ⇄ Chemical energy

- Electrochemical cell are two types-

(1) Electrolytic cell: which convert electrical energy to chemical reactions.

e.g. electrolysis of aqueous solution NaCl by passing electricity.

(2) Galvanic cells or Voltaic cell: which generate an electric current by using chemical reactions.

e.g. Daniel cell

Parts of Electrochemical cell-

- **Vessel:** which contains all electrochemical system.
- **Electrolyte:** in the form of electrolytic solutions into which two electrodes are submerged.
- **Electrodes:** usually metal strips/wires connected by an electrically conducting wire.
- **Anode:** electrode where oxidation takes place.
- **Cathode:** electrode where reduction takes place.
- **Salt Bridge:** U-shaped tube that contains a gel permeated with a solution of an inert electrolyte. Present in galvanic cell for maintaining electro neutrality of two half cell's electrolytic solutions.

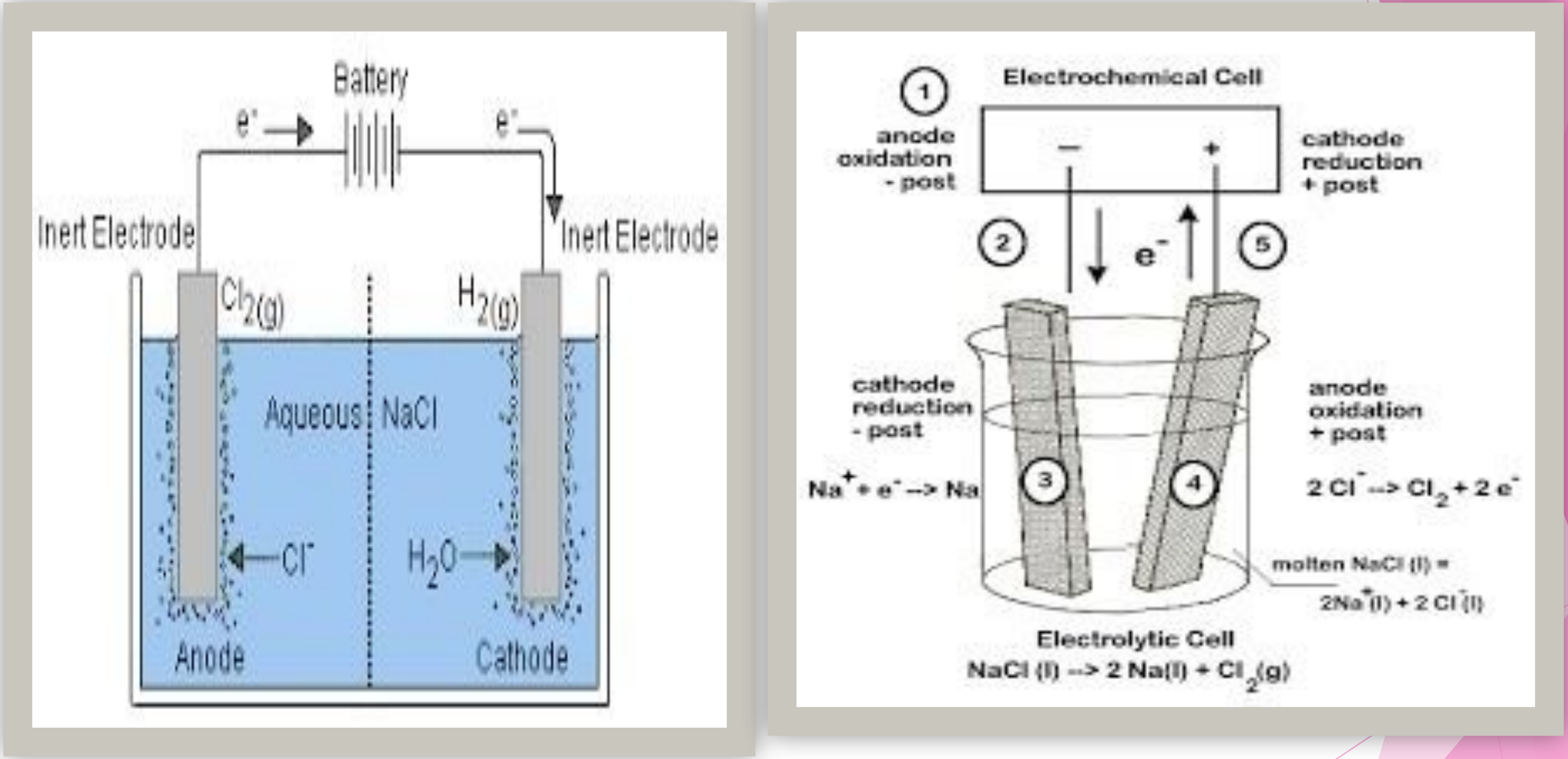

Figure: Electrolytic cell

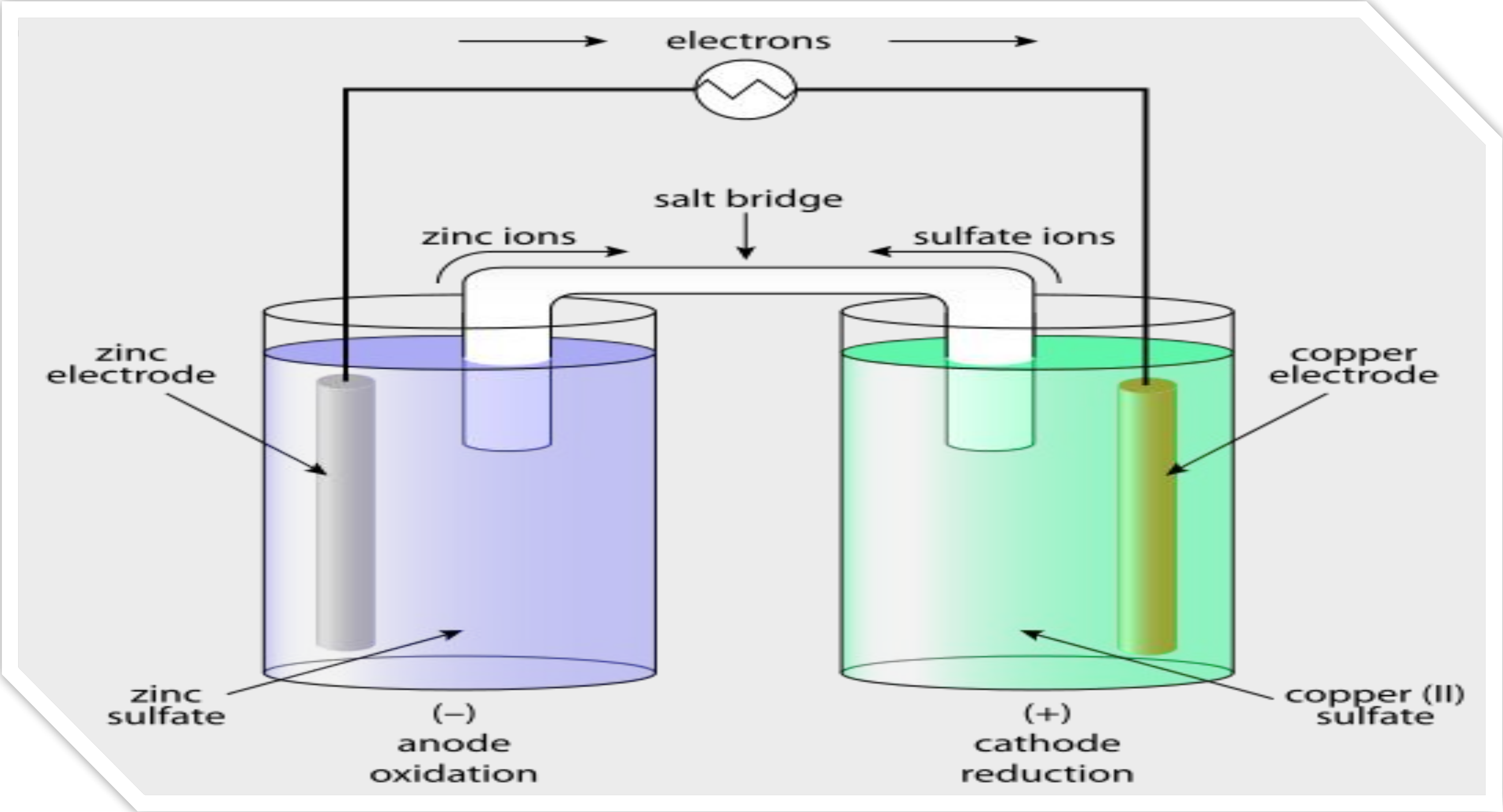

Figure: Galvanic cell

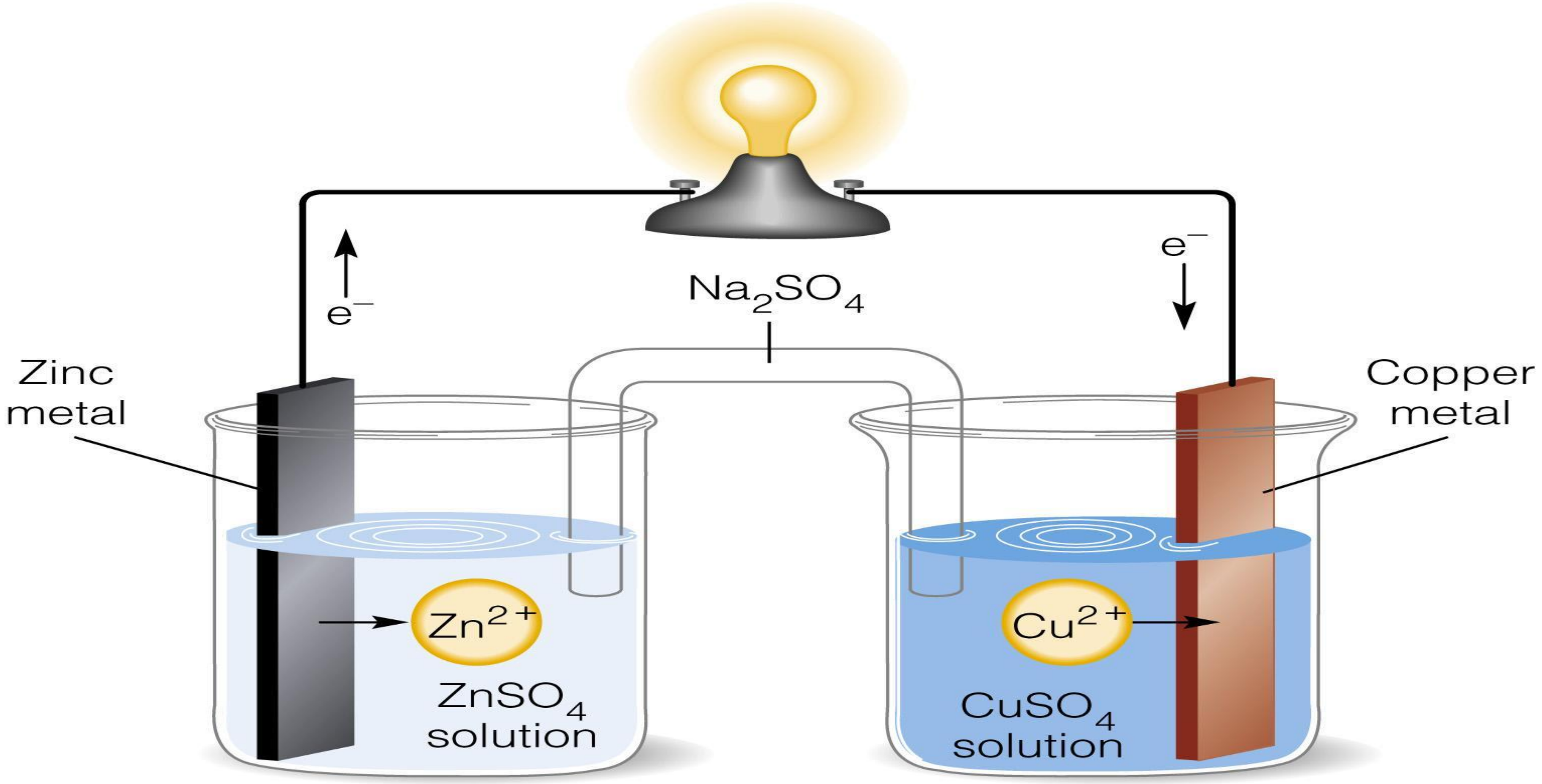

Figure: Chemical reactions in Daniel cell

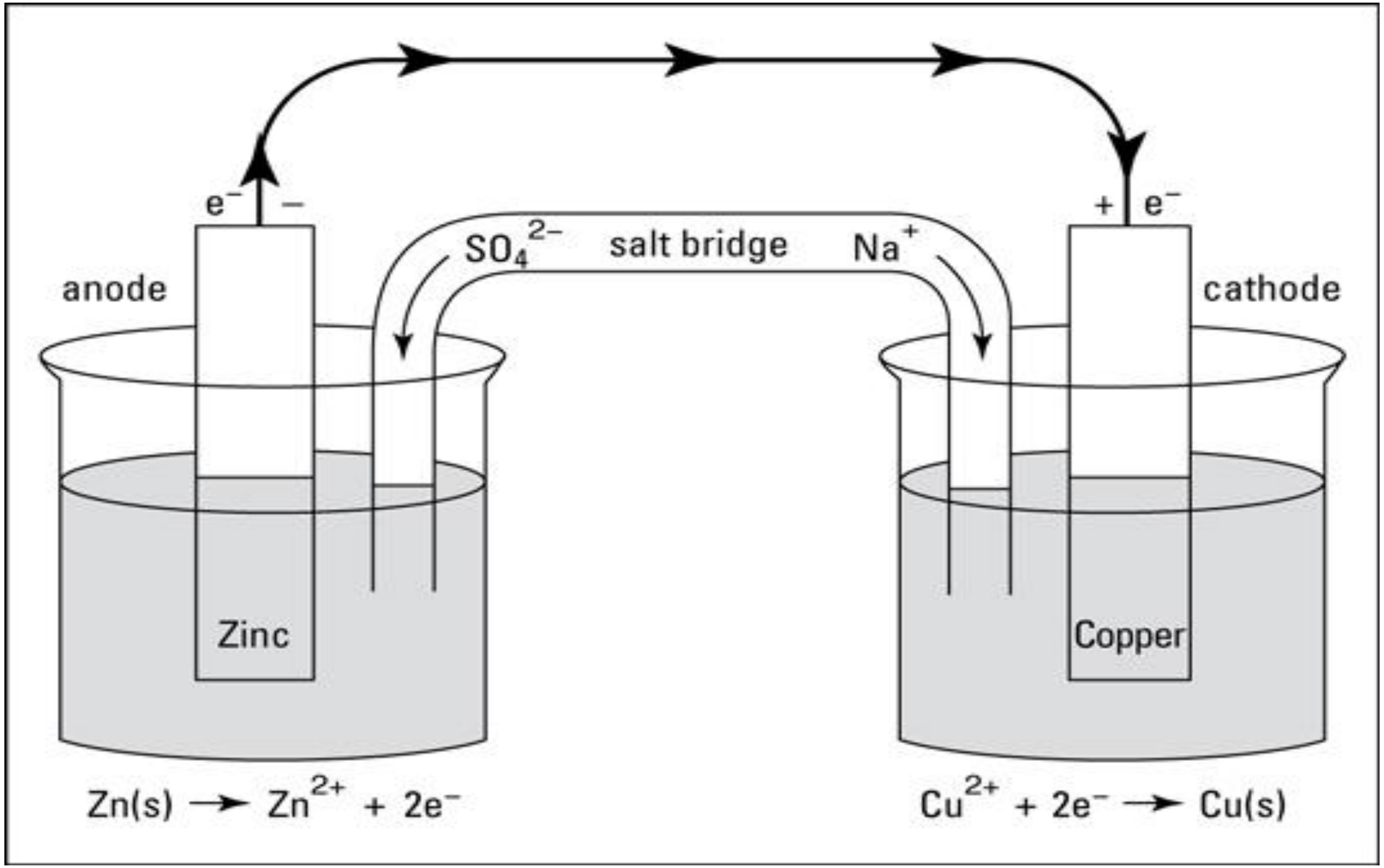

Figure: Chemical reactions in Daniel cell

Galvanic cell:

- A galvanic cell is also referred to as a voltaic cell. The common household battery is an example of a galvanic cell.
- Galvanic cell composed of two half cells or two electrode-

  (i) Left hand electrode or Anode:

  Zn electrode submerged in $ZnSO_4$ aqueous solution

  (ii) Right hand electrode or Cathode:

  Cu electrode submerged in $CuSO_4$ aqueous solution
- The electricity or EMF is generated due to half cell reactions taking place at different cell
- The combination of two half reactions whose addition gives the overall cell reaction or net cell reaction:

- At anode (Left hand electrode):

  $Zn_{(s)} \rightleftarrows Zn^{2+} + 2e^-$ ---(oxidation half reaction)

- At cathode (Right hand electrode):

  $Cu^{2+} + 2e^- \rightleftarrows Cu_{(s)}$ ---(reduction half reaction)

- Net overall cell reaction can be obtained by adding oxidation and reduction half cell reactions

  $Zn_{(s)} + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu_{(s)}$

- EMF of this galvanic cell is given by Nernst equation as follows:

$$\mathrm{E} = E^0 + \frac{RT}{nF} ln \frac{[Cu^{+2}]}{[Zn^{+2}]}$$ ---- Eq. no. (1)

$$\mathrm{E} = E^0 + \frac{2.303RT}{nF} log_{10} \frac{[Cu^{+2}]}{[Zn^{+2}]}$$ ---- Eq. no. (2)

Where, E^0 = Standard EMF of Galvanic cell = 1.10 V

On putting the values of Temperature (T) = 25^0C (298.15K), Value of gas constant, R= 8.31 J/K/mol, Faraday, F= 96500 Coulomb

$$E = E^0 + \frac{0.0591}{2} log_{10} \frac{[Cu^{+2}]}{[Zn^{+2}]} \qquad \text{---- Eq. no. (3)}$$

Cell notation for Electrochemical cell:

This is the way of representation of electrochemical cell by combination of symbols.

- A galvanic cell is generally represented by putting a vertical line between species which are in direct contact e.g. metal and electrolyte solution
- Species which are not in direct contact are represented by putting a double vertical line between them e.g. the two electrolytes connected by a salt bridge.
- Anode is denoted on the left and the cathode on the right

Cell notation for Galvanic cell:

$$Zn_{(s)} \mid ZnSO_{4\ (aqueous\ soln.)} \parallel CuSO_{4\ (aqueous\ soln.)} \mid Cu_{(s)}$$

Electromotive Force (EMF)-

- The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts.
- By latest consideration, the cell potential is the difference between the electrode potentials (reduction potentials) of the cathode and anode.
- It is called the cell electromotive force (EMF) of the cell when no current is drawn through the cell.
- So, EMF of cell is determined by techniques or devices which draw no current

  From the cell during measurements.
- By observing cell notation , $E_{cell} = E_{right} - E_{left}$ or $E_{cell} = E_{cathode} - E_{anode}$
- According to latest convention of IUPAC all the electrode potential all expressed in terms of reduction potential with respect to standard hydrogen electrode (S.H.E.)

- When all the standard electrode potential (in terms of reduction potential) are arranged from higher to lower value then this is termed as Electrochemical series.
- Electrochemical series is given on next page.
- There are so many applications of this Electrochemical series.
- Out of these applications, some one can calculate standard EMF (E_0) of a particular cell alternatively.
- For example the standard EMF of Galvanic cell

Anode- $Zn_{(s)} \rightleftarrows Zn^{2+} + 2e^-$ (E^0_{el} = - 0.76 Volt)

Cathode- $Cu^{2+} + 2e^- \rightleftarrows Cu_{(s)}$ (E^0_{el} = 0.34 Volt)

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = 0.34 - (-0.76) = 1.10 \text{ Volt}$$

Table 1 The standard electrode potentials at 298 K

Ions are present as aqueous species and H_2O as liquid; gases and solids are shown by g and s.

Reaction (Oxidised form + ne^-	→ Reduced form)	E°/V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2 + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	$\rightarrow H_2(g)$	0.00
$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	–0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	–0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$	–0.25
$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	–0.44
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	–0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	–0.76
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-(aq)$	–0.83
$Al^{3+} + 3e^-$	$\rightarrow Al(s)$	–1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$	–2.36
$Na^+ + e^-$	$\rightarrow Na(s)$	–2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	–2.87
$K^+ + e^-$	$\rightarrow K(s)$	–2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	–3.05

Increasing strength of oxidising agent

Increasing strength of reducing agent

1. A negative E° means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
2. A positive E° means that the redox couple is a weaker reducing agent than the H^+/H_2 couple

Figure: Electrochemical Series

- **Example 1:** Find the standard electrode potential of the cell using electrochemical series; $Cu_{(s)} | Cu^{2+} || Cl^{-} | AgCl_{(s)} | Ag_{(s)}$ and predict the direction of electron flow when the two electrodes are connected.

- **Solution.** The reactions corresponding to this cell will be:

$Cu(s) \rightarrow Cu^{2+}_{(aq)} + 2e^{-}$ Anode reaction (oxidation)

$AgCl_{(s)} + e^{-} \rightarrow Ag_{(s)} + Cl^{-}_{(aq)}$ Cathode reaction (reduction)

Net Reaction can be obtained by adding anode and cathode reaction

$$Cu_{(s)} + 2AgCl_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2Cl^{-}_{(aq)} + 2Ag_{(s)}$$

Value of $E^0_{cathode}$ and E^0_{anode} can be obtained by using electrochemical series.

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = (0.22 – 0.34) \text{ Volt} = -0.12 \text{ V}$$

Applications of EMF Measurements-

(i) Determination of Equilibrium Constant

- By measurement of the standard Emf of the cell, E°, some one enable to evaluate the equilibrium constant for the electrode reaction.
- The relation between the standard free energy change(**G^0**) and the equilibrium constant(K) is:

$$G^0 = -RT \ln K \qquad \text{---- Eq. no. (4)}$$

- Standard free energy is related to the standard electrode potential by relation:

$$G^0 = -\,n\,FE^0 \qquad \text{----- Eq. no. (5)}$$

From Eq. no. (1) and (2)

$$E^0 = (RT/nF) \ln K \qquad \text{----- Eq. no. (6)}$$

$$E^0 = (2.303RT/nF) \log_{10} K$$

at T =298K, R= 8.13J/K/mol, F=96500 Coulomb Eq. no. (3) becomes

$$E^0 = (0.0591/n) \log_{10} K \qquad \text{----- Eq. no. (7)}$$

For determining equilibrium constant (K) of particular type of equilibrium reaction some one has:

- To design a electrochemical cell in which net cell reaction is same as equilibrium reaction.
- To determine EMF of above cell.
- To calculate equilibrium constant by Eq. no. (7)

(ii) Determination of Solubility Products-

- Solubility product of sparingly soluble salt $MX_{(s)}$ viz. AgCl etc. can be determined.
- Sparingly soluble salt is type of equilibrium constant.
- Let us suppose a sparingly soluble salt $MX_{(s)}$ in equilibrium with its ions in a saturated solution

$$MX_{(s)} \rightleftharpoons M^{+}{}_{(aq.)} + X^{-}{}_{(aq.)}$$

$$K_{SP} = a_{M}{}^{+} \cdot a_{x}{}^{-}$$

- The above cell reaction is the cell reaction for following cell

$$M, M^{+} X^{-}{}_{(\text{saturated soln})} \mid MX_{(s)}, M$$

The half cell reaction are:

At Right hand electrode $\quad MX_{(S)} + e^{-} \rightleftharpoons M + X^{-}{}_{(\text{aqueous})}$

At Left hand electrode $\quad M \rightleftharpoons M^{+}{}_{(\text{aqueous})} + e^{-}$

Overall reaction $\quad MX_{(S)} \rightleftharpoons M^{+}{}_{(\text{aqueous})} + X^{-}{}_{(\text{aqueous})}$

$$E^0_{cell} = E^0_{right} - E^0_{left} \qquad \text{------- Eq. no. (8)}$$

- By considering K_{SP} as equilibrium constant and using eq. no.(4), (5), (6)

$$nFE^0_{cell} = 2.303RT \log_{10} K_{SP}$$

$$\log_{10} K_{SP} = nFE^0_{cell} / 2.303\ RT$$

At $25\,^0$ C $\qquad \log_{10} K_{SP} = nE^0_{cell} / 0.0591 \qquad$ ------- Eq. no. (9)

E^0_{cell} can be determined by using eq. no. (8) and electrochemical series.

So, by using eq. no. (9) some one can determine K_{SP}

(iii) Determination of pH-

- For this half cell (Hydrogen electrode) is setup with the test solution as electrolyte.
- EMF of the cell depends on the concentration of H^+ or pH of solution.
- Principle behind this method is to determine the activity of H^+ or the concentration of H^+.

  Since, $pH = -\log H^+$

- Conc./ activity of H^+ can be determined by setting a cell in which one of the electrodes is reversible to hydrogen ions.
- In practice the EMF OF hydrogen electrode is combined with another reference

  electrode such as standard hydrogen electrode (SHE)

  or a saturated calomel electrode (SCE) or any other reference electrode. ..

- By using S.H.E. cell notation of considered cell can be given as follows:

$$Pt|\ H_{2\ (1atm)}\ |\ H^{+}_{\ (1M)}||\ H^{+}_{\ (unknown)}|\ H_{2\ (1atm)}\ |\ Pt$$

- For single hydrogen electrode Pt/H_2 (1atm) /H^+, the electrode reaction is:

$$H^{+} + e^{-} \rightarrow \tfrac{1}{2} H_{2\,(g)}$$

$$E_{right} = E^{0}_{SHE} + \frac{RT}{nF} ln \frac{[H^{+}]}{[P_{H2}]^{1/2}}$$

$$E_{right} = E^{0}_{SHE} + \frac{2.303RT}{nF} log_{10} \frac{[H^{+}]}{[P_{H2}]^{1/2}}$$

- Since, $E^{0}_{SHE} = 0$ and $P_{H2}^{1/2} = 1$

$$E_{right} = 0.0591 \log_{10} [H^{+}]$$

$$E_{right} = -\ 0.0591\ pH \qquad \text{---- Eq. no. (10)}$$

-

- Since, EMF (E_{cell}) of cell constructed for pH determination can be given by

$$E_{cell} = E_{right} - E_{left}$$

- E_{left} is S.H.E. whose Electrode potential is arbitrarily assigned equal to zero by IUPAC.

- So, $$E_{cell} = E_{right} - 0$$

$$E_{cell} = E_{right} \qquad \text{---- Eq. no. (11)}$$

- From eq. no. (11) and (12)

$$E_{cell} = -\,0.0591\ \mathrm{pH}$$

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

- E_{cell} m is determined by no current drawing based measurement (viz. potentiometer) and hence pH can be determined.

- Exercise 1

The standard EMF of the Daniel cell involving the cell reaction $Zn_{(s)}$ + Cu^{2+} ⇌ Zn^{2+} + $Cu_{(s)}$ is 1.10 Volts. Calculate the equilibrium constant of the cell reaction at 25^0C

- Exercise 2

Calculate equilibrium constant for the following electrochemical cell

Zn/Zn^{2+} //Fe^{3+}, Fe^{2+} /Pt ; Whose standard EMF is 1 .534V, the overall cell reaction is Fe^{3+} + 1/2Zn = Fe^{2+} + 1/2 Zn^{2+}

- Exercise 3

Find the standard electrode potential of the cell using electrochemical series; $Cu_{(s)}$ | Cu^{2+} | Cl^- || $AgCl_{(s)}$ | $Ag_{(s)}$ and predict the direction of electron flow when the two electrodes are connected.

References-

- P C Jain , M. Jain, Engineering Chemistry, Dhanpat Rai Publications.
- S. S. Dara, A Text Book of Engineering Chemistry, S. Chand & Company.
- Shashi Chawla, Engineering Chemistry, Dhanpat Rai Publications.
- https://quizlet.com/312668465/galvanic-cells-flash-cards/

THANK YOU