TGT Science

# Electrochemistry

It is study of production of electricity from energy which is released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformation.

**Some Basic Definitions**

**Oxidation:** Loss of electron $Zn \longrightarrow Zn^{+2} + 2e^-$

**Reduction**: Gain of electron $Cu^{+2} + 2e^- \longrightarrow Cu$

**Electrolyte:** A solution that contains ions is called electrolyte. Electrolyte is an ionic conductor.

**Electrode:** Surface at which oxidation or reduction takes place.

**Redox Reaction:** An oxidation-reduction (redox) reaction

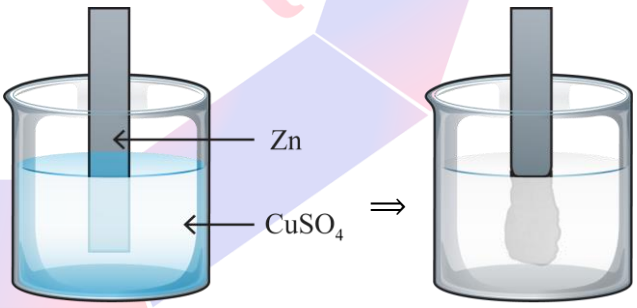
$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$$

**Placing a Zn rod in $CuSO_4$ solution:**

- $CuSO_4$ solution is blue in colour. But if we place a Zn rod in $CuSO_4$ solution, colour fades out. This is because of reduction of

  $Cu^{+2} \longrightarrow Cu$
- $Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$
- Above is a spontaneous reaction.

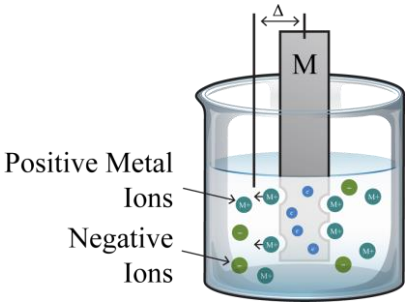
  It does not require any external work.



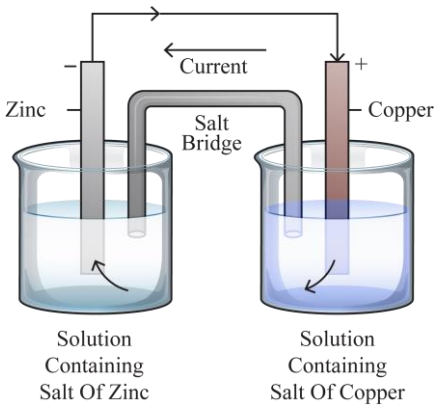

The solutions colour changes from blue to colorless

**Electrode Potential:** Potential difference between metal and metal ion in which electrode is dipped is called electrode potential.

- Electrode potential of Zn → Zn | $ZnSO_4$
- Electrode potential of Cu → Cu | $CuSO_4$



**Galvanic or voltaic cell:** A galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy.




- Spontaneous then $\Delta G$ = –ve
- In this device $\Delta G$ of spontaneous redox reaction is converted into electrical work (which may be used for running a motor, fan, heater etc.)

**Construction:** It consist of two metallic electrodes dipping in electrolytic solution. The solution in two compartment is connected through an inverted u-shaped tube containing a mixture of agar-gar jelly and an electrolyte like KCl, $KNO_3$ etc. This tube is called salt bridge.

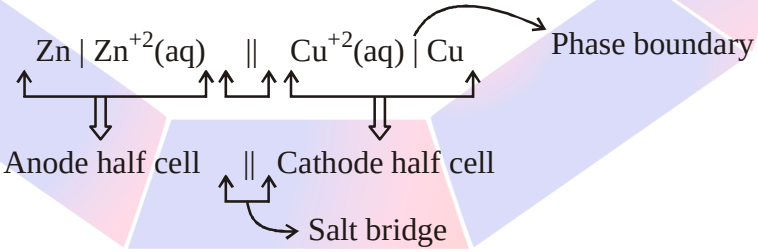
- Salt bridge is necessary because.
  - (a) It connects the solution of two half cells. Thus completes the cell circuit.
  - (b) It prevents diffusion of solutions from one compartment to other.
- In representation of cell, salt bridge is represented by ||.
- In galvanic cell: Oxidation at anode [negative plate]

Reduction at cathode [positive plate]

**Daniel cell:** Among the galvanic cells when cell is designed in such a manner to make the use of spontaneous reaction between Zn and Cu ion to produce an electric current, that cell is called Daniel cell.

**Reaction:** $Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{+2}(aq)$

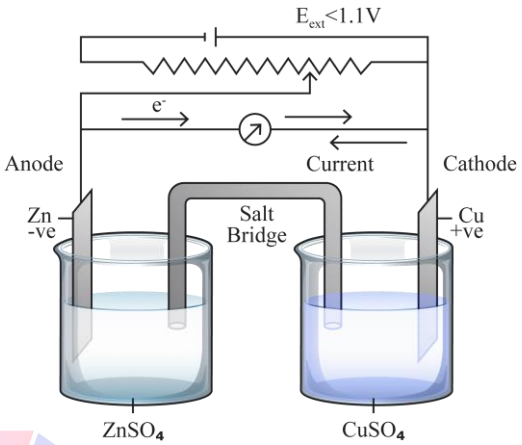
**Cell representation:**




- **Zn:** Anode (oxidation) and **Cu:** Cathode (reduction)
- The two half-cell reactions are:
  - (a) $Cu^{+2} + 2e^- \rightarrow Cu(s)$ [Reduction half reaction: Occurs at cathode]
  - (b) $Zn(s) \rightarrow Zn^{2+} + 2e^-$ [Oxidation half reaction: Occurs at anode]

# ELECTROCHEMICAL CELL

## (i) Galvanic cell

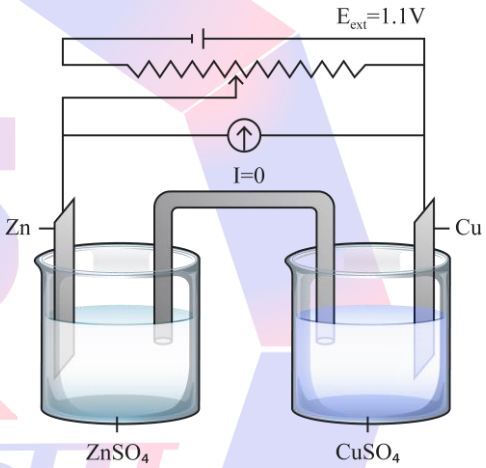



- Chemical energy → Electrical energy
- **ΔG = –ve spontaneous reaction**
- Power is produced
- When $E_{ext} < 1.1$ V

(i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.

(ii) Zn dissolves at anode and copper deposits at cathode

## (ii) Reversible

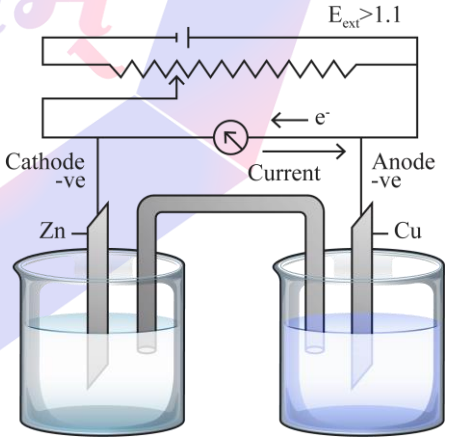



- No net reaction
- When $E_{ext} < 1.1$ V

(i) No flow of electrons or current.

(ii) No chemical reaction.

## (iii) Electrolytic cell




- Electrical energy → chemical energy
- **Non** spontaneous reaction [ΔG = +ve]
- **Power** is consumed.
- When $E_{ext} > 1.1$ V

(i) Electrons flow from Cu to Zn and current flows from Zn to Cu.

(ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

- Functioning of Daniel cell when external voltage ($E_{ext}$) opposing the cell potential is applied.

**[Note:** (i) When the concentration of all the species involved in a half cell is unity then the electrode potential is known as Standard Electrode Potential.

(ii) IUPAC Convention: Standard Reduction Potential (SRP) is SEP.

(iii) Cell Potential: the potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts.]

- $E_{cell} = E_{cathode} - E_{anode} = E_{right} - E_{left}$ $\quad [\text{Cell} : \underset{\text{Cell}}{\text{Anode half}} \;\|\; \underset{\text{Cell}}{\text{Cathode half}}]$

(a) For a reaction $Zn(s) + Cu^{+2}(aq) \rightarrow Cu(s) + Zn^{+2}(aq)$

Cell: $Zn \mid Zn^{+2}(aq) \parallel Cu^{+2}(aq) \mid Cu(s)$

$E_{cell} = E_{Cu^{+2}\mid Cu} - E_{Zn^{+2}\mid Zn}$

(b) For a reaction $Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{+2}(aq) + 2Ag(s)$

- Half-cell reactions:

  Cathode (reduction): $2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)$

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

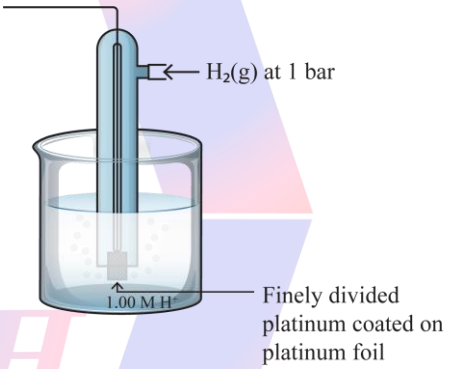
- Cell representation: Cu(s) | Cu+2(aq) || Ag+(aq) | Ag(s)

$$E_{cell} = E_{right} - E_{left} = E_{Ag^{+}\mid Ag} - E_{Cu^{+2}\mid Cu}$$

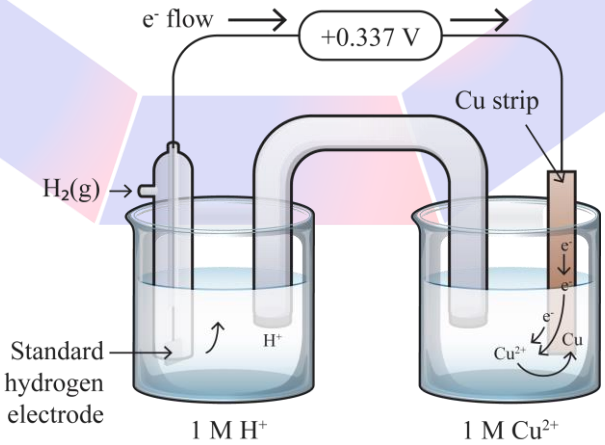
## Standard Hydrogen Electrode

- Representation of half-cell for standard hydrogen electrode: $Pt(s) \mid H_2(g)\ (1\ bar) \mid H^{+}(aq)$
- According to convention, a half cell called standard hydrogen electrode is assigned a zero potential at all temperatures corresponding to the reaction

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




## Measurement of Electrode Potential




- Construct a cell by taking standard hydrogen electrode as anode (reference half-cell) and other half-cell as cathode, gives the reduction potential of another half-cell.

  Standard Hydrogen Electrode [$Pt(s) \mid H_2(g)\ (1\ bar) \mid H^{+}(aq)\ (1\ M)$] || another half-cell.

- If the concentrations of the oxidized and the reduced forms of species in the right-hand half-cell are unity. Then the cell potential is equal to standard electrode potential ($E°_R$) of the given half-cell. $E^o = E^o_R - E_L = E^o_R - 0 = E^o_R$

- **To calculate: (i) $E^o_{Cu^{+2}/Cu}$, make a cell Pt(s) | $H_2$(g) (1 bar) | $H^+$(aq) 1 M || $Cu^{+2}$(aq) 1 M | Cu**

**EMF of this cell = 0.34 V**

$$E^o_{cell} = E^o_{Cu^{+2}/Cu} - E^o_{SHE}$$

$$0.34\ V = E^o_{Cu^{+2}/Cu} - 0 \text{ then } \boxed{E^o_{Cu^{+2}/Cu} = 0.34\ V}$$

**(ii) Similarly, $E^o_{Zn^{+2}/Zn}$ can be calculated by following cell.**

**Pt(s) | $H_2$(g) (1 bar) | $H^+$(aq) 1 M || $Zn^{+2}$(aq) 1 M | Zn**

$$E^o_{cell} = E^o_{Zn^{+2}/Zn} - E^o_{SHE} = E^o_{Zn^{+2}/Zn} - 0$$

$$\text{then } \boxed{E^o_{Zn^{+2}/Zn} = -0.76\ V}$$

- In first case, +ve value of SEP indicates that $Cu^{+2}$ get reduced more easily than $H^+$, means we can say that $H_2$ gas can reduce $Cu^{+2}$ ion.
- In second case, –ve value of SEP indicates that Zn get oxidized by $H^+$ ion.

**EMF of Daniel Cell**

**Cell:** Zn(s) | $Zn^{+2}$(aq) (1 M) || $Cu^{+2}$(aq) (1 M) | Cu(s)

$$E^o_{cell} = E^o_{Cu^{+2}/Cu} - E^o_{Zn^{+2}/Zn} = 0.34\ V - (-0.76\ V) = 1.10\ V$$

**Inert Electrode:** Metals like platinum or gold are used as inert electrode. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for conduction of electrons.

For example: Hydrogen Electrode: Pt(s) | $H_2$(g) | $H^+$(aq)

Bromine Electrode: Pt(s) | $Br_2$(aq) | $Br^-$(aq)

**Nernst equation:** It gives relation between electrode potential, temperature, and concentration of metals ions.

For reaction $M^{n+}(aq) + ne^- \longrightarrow M(s)$

n → No. of electrons

- $E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$
- $E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$

R = Gas constant = 8.314 $JK^{-1}$ $mol^{-1}$

F = Faraday's constant = 96487 C $mol^{-1}$

T = 298 K and [M] = 1 = [Solid]

- In Daniel cell: Electrode potential for any given concentration of Cu+2/Zn+2.

For Cathode: $E^{o}_{Cu^{+2}/Cu} = E^{o}_{Cu^{+2}/Cu} - \frac{0.059}{2}\log\frac{1}{[Cu^{+2}(aq)]}$

For Anode: $E^{o}_{Zn^{+2}/Zn} = E^{o}_{Zn^{+2}/Zn} - \frac{0.059}{2}\log\frac{1}{[Zn^{+2}(aq)]}$

Cell Potential $E_{cell} = E^{o}_{Cu^{+2}/Cu} - E^{o}_{Zn^{+2}/Zn}$

$= \left[E^{o}_{Cu^{+2}/Cu} - E^{o}_{Zn^{+2}/Zn}\right] - \frac{0.059}{2}\log\frac{[Zn^{+2}(aq)]}{[Cu^{+2}(aq)]}$

**Q. For the cell Zn(s) | $Zn^{+2}$ (2M) || $Cu^{+2}$ (0.5 M) | Cu(s)**

**(i) Write the equation for each half cell.**

**(ii) Calculate cell potential at 25°C**

**Given:** $\mathbf{E^{o}_{Zn^{+2}/Zn} = -0.76\ V}$

$\mathbf{E^{o}_{Cu^{+2}/Cu} = +0.34\ V}$

**Ans.** (i) Anode: $Zn(s) \longrightarrow \underset{[2M]}{Zn^{+2}(aq)} + 2e^{-}$

Cathode: $\underset{(0.5\ M)}{Cu^{+2}(aq)} + 2e^{-} \longrightarrow Cu(s)$

(ii) $E^{o}_{cell} = E^{o}_{Cu^{+2}/Cu} - E^{o}_{Zn^{+2}/Zn} = 0.34\ V - (-0.76\ V) = 1.10\ V$

$E_{cell} = E^{o}_{cell} - \frac{0.059}{2}\log\frac{[Zn^{+2}]}{[Cu^{+2}]} \Rightarrow 1.10\ V - \frac{0.059}{2}\log\frac{2}{0.5}$

$E_{cell} = 1.10\ V - \frac{0.059}{2} \times 0.602\ V = 1.10\ V - 0.0178\ V = 1.0822\ V$

**Q. A Zn rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at its dilution at 298 K. Calculate the electrode potential.**

$\mathbf{E^{o}_{Zn^{+2}/Zn} = -0.76\ V}$

**Ans.** Reaction $Zn^{+2} + 2e^{-} \rightarrow Zn$

By using Nernst equation, we get

$E^{o}_{Zn^{+2}/Zn} = E^{o}_{Zn^{+2}/Zn} - \frac{0.059}{2}\log\frac{1}{[Zn^{+2}]}$

$$\Rightarrow \quad [Zn^{+2}] = \frac{95}{100} \times 0.1 = 0.095\ M$$

$$E^{o}_{Zn^{+2}/Zn} = -0.76 - \frac{0.059}{2} \log \frac{1}{0.095} = -0.7901\ V$$

**Q. Calculate the emf of the following cell a 298 K.**

**$2Cr(s) + 3Fe^{+2}$ (0.1 M) $\rightarrow 2Cr^{+3}$ (0.01 M) + 3Fe(s)**

**Given:** $\mathbf{E^{o}_{Cr^{+3}/Cr} = -0.74\ V}$

$\mathbf{E^{o}_{Fe^{+2}/Fe} = -0.44\ V}$

**Ans.** Half-cell reaction

At anode: $[Cr \rightarrow Cr^{3+} + 3e^{-}] \times 2$

At cathode: $[Fe^{+2} + 2e^{-} \rightarrow Fe] \times 3$

$$E^{o}_{cell} = E^{o}_{Fe^{+2}/Fe} - E^{o}_{Cr^{+3}/Cr} \text{ then } \boxed{n = 6}$$

$$= -0.44\ V - (-0.74\ V) = 0.3\ V$$

$$E = E^{o} - \frac{0.059}{n} \log \frac{[Cr^{+3}]^2}{[Fe^{+2}]^3}$$

$$E_{cell} = 0.3\ V - \frac{0.059}{6} \log \frac{(0.01)^2}{(0.1)^3} \quad \text{then} \quad \boxed{E_{cell} = 0.31\ V}$$

**Q. Calculate the emf of the following cell at 25°C**

**Ag(s) | $Ag^{+}$ ($10^{-3}$ M) || $Cu^{2+}$ ($10^{-1}$ M) | Cu(s)**

**Given** $\mathbf{E^{o}_{cell} = +0.46\ V}$ **and** $\mathbf{\log 10^{n} = n}$

**Ans.**

$$\mathbf{E}_{cell} = E^{o}_{cell} - \frac{0.059}{2} \log \frac{[Ag^{+}]^2}{[Cu^{+2}]}$$

$$E_{cell} = 0.46\ V - \frac{0.059}{2} \log \frac{(10^{-3})^2}{(10^{-1})}$$

$$E_{cell} = 0.608\ V$$

(i) $[Ag(s) \longrightarrow Ag^{+}(aq) + e^{-}] \times 2$

(ii) $Cu^{+2}(aq) + 2e^{-} \longrightarrow Cu(s)$

$$2Ag(s) + Cu^{+2} \longrightarrow Cu + 2Ag^{+}$$

$\boxed{n = 2}$

**Q.** **Calculate the emf of the following cell at 298 K (25°C)**

**$Fe(s) \mid Fe^{2+}(0.001\ M) \parallel H^+(0.01\ M) \mid H_2(g)\ (1\ bar) \mid Pt(s)$**

**Given:** $E^o_{cell} = 0.44\ V$ **or** $(E^o_{Fe^{+2}/Fe} = -0.44\ V$ **and** $E^o_{H^+/H_2} = 0\ V)$

**Ans.** $E^o_{cell} = E^o_{H^+/H_2} - E^o_{Fe^{+2}/Fe} = 0.44\ V$

$$E_{cell} = E^o - \frac{0.059}{2}\log\frac{[Fe^{+2}]}{[H^+]^2} = 0.44\ V - \frac{0.059}{2}\log\frac{(10^{-3})}{(10^2)^2}$$

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$$E_{cell} = 0.44 - \frac{0.059}{2} = 0.4104\ V$$

1. $Fe(s) \longrightarrow Fe^{+2}(aq) + 2e^-$
2. $\left[H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)\right] \times 2$

$$Fe(s) + 2H^+(aq) \longrightarrow Fe^{+2}(aq) + H_2$$

$\boxed{n = 2}$

**Equilibrium constant from Nernst Equation**

For a general reaction $aA + bB \longrightarrow cC + dD$

Nernst equation can be written as

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln Q$$

At equilibrium $E_{cell} = 0 \implies 0 = E^o_{cell} - \frac{RT}{nF}\ln K_c$

$\left[Q \rightarrow \text{Reaction Quotient}\right.$

$\left.Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}\right]$

And $Q = K_c$ = equilibrium constant

$$\boxed{E^o_{cell} = \frac{2.303\,RT}{nF}\log K_c}$$

At 25°C $T = 298\ K$

$F = 96487\ C\ mol^{-1}$

$R = 8.314\ JK^{-1}\ mol^{-1}$

$$\boxed{E^o_{cell} = \frac{0.059}{n}\log K_c}$$

**Example:** For Daniel cell $Cu^{2+} + Zn \longrightarrow Cu + Zn^{+2}$ $E^o_{cell} = 1.1\ V$

Then $n = 2$ = No. of electron transferred

$$1.1\ V = \frac{0.059}{2}\log K_c$$

$$\log K_c = 37.388 \implies K_c = 2 \times 10^{37}$$

**Relation between $E_{cell}$ and Gibbs energy of reaction**

$$\boxed{\Delta G = -nF\,E_{cell}}$$

[Electrical work done in one second is equal to electrical potential multiplied by total charge ($E_{cell} \times nF$)]

- Work done by galvanic cell is equal to decrease in Gibbs energy.
- If concentration of all the reacting species is unity, then $E_{cell} = E^o_{cell}$

$$\boxed{\Delta G^\circ = -nF\,E^o_{cell}}$$

- By measuring $E^o_{cell}$, we can calculate $\Delta G^\circ$ and equilibrium constant ($\Delta G^\circ = -RT \ln K$)

**Example:** For Daniel cell $E^o_{cell} = 1.1$ V then value of $\Delta G^\circ$ =? If F = 96500 C $mol^{-1}$

$\rightarrow$ $\boxed{n = 2}$

$$\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.1$$

$$\Delta G^\circ = -212300 \text{ J mol}^{-1}$$

**Q. Calculate $\Delta G^\circ$ and log $K_c$ for the following reaction:**

$$\mathbf{Cd^{2+}(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Cd(s)}$$

**Given:** $\mathbf{E^o_{Cd^{2+}/Cd} = -0.403\ V}$

$\mathbf{E^o_{Zn^{2+}/Zn} = -0.763\ V}$

**Ans.** $E^o_{cell} = E^o_{Cd^{2+}/Cd} - E^o_{Zn^{2+}/Zn} = (-0.403) - (0.763) = 0.36$ V

$n = 2$ = No. of moles of electron used

$F = 96500$ C $mol^{-1}$

(1) $\Delta G^\circ = -nE^\circ F = -2 \times 96500 \times 0.36$ V $= 69480$ J $mol^{-1}$

(2) $E^o_{cell} = \dfrac{0.059}{n} \log k_c$

then $\log k_c = \dfrac{n\,E^o_{cell}}{0.059} = \dfrac{2 \times 0.36}{0.059} = 12.18$

**Q. A copper silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell.**

**Given:** $\mathbf{E^o_{Ag^+/Ag} = 0.80\ V,\ E^o_{Cu^{+2}/Cu} = 0.34\ V}$

**Ans.** Cell Reaction: $Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

$$E^{o}_{cell} = E^{o}_{Ag^+/Ag} - E^{o}_{Cu^{+2}/Cu} = 0.80\ V - 0.34\ V = 0.46\ V$$

By using Nernst equation

$$E_{cell} = E^{o}_{cell} - \frac{0.059}{n} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$n$ = 2 = No. of electron taking part ($E_{cell}$ = 0.422 V)

$$0.422\ V = 0.46\ V - \frac{0.059}{2} \log \frac{0.1}{[Ag^+]^2} \qquad ([Cu^{+2}] = 0.1\ M)$$

$$\log \frac{0.1}{[Ag^+]^2} = 1.288$$

$$\Rightarrow \quad \frac{0.1}{[Ag^+]^2} = \text{antilog } 1.288 = 19.41$$

$$\frac{0.1}{19.41} = [Ag^+]^2 = 0.00515$$

$$[Ag^+] = 0.0717 = 7.17 \times 10^{-2}\ M$$

**Q. (i) Write the formulation for the galvanic cell in which the reaction takes place. Identify the cathode and the anode reactions in it.**

$$\mathbf{Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{+2}(aq) + 2Ag(s)}$$

**Ans.** At anode: $Cu(s) \longrightarrow Cu^{+2}(aq) + 2e^-$

At cathode: $2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$

(ii) Write the Nernst equation and calculate the emf of the following cell.

$Sn(s) \mid Sn^{2+}\ (0.04\ M) \parallel H^+\ (0.02\ M) \mid H_2(g) \mid Pt(s)\ (1\ bar)$

Given: $E^{o}_{Sn^{+2}/Sn} = -0.14\ V$

**Ans.** At anode: $Sn(s) \longrightarrow Sn^{+2}(aq) + 2e^-$ $\boxed{n = 2}$

At cathode: $2H^+(aq) + 2e^- \longrightarrow H_2(g)$

Net reaction: $Sn(s) + 2H^+(aq) \longrightarrow Sn^{2+}(aq) + H_2(g)$

$$E^{o}_{cell} = E^{o}_{H^+/H_2} - E^{o}_{Sn^{+2}/Sn}$$

$$= 0\ V - (-0.14\ V)$$

$$= 0.14\ V$$

$$E_{cell} = E^{o}_{cell} - \frac{0.059}{n} \log \frac{[Sn^{+2}]}{[H^+]^2}$$

$$= 0.14\ V - \frac{0.059}{2} \log \frac{0.04}{(0.02)^2}$$

$$= 0.14\ \text{V} - \frac{0.059}{2}\log\left(\frac{4}{100}\right)\left(\frac{100}{2}\right)^2$$

$$\mathbf{E_{cell} = 0.0809\ V}$$

**Table of SEP at 298 K**

| Reaction (Oxidised form + ne → Reduced form) | | $E^\ominus$/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 ↓

- For $F_2$ gas SEP is highest in table indicating that $F_2$ has maximum tendency to get reduced to $F^-$ : $F_2$ is the strongest oxidizing agent.
- Li has lowest SEP indicating that $Li^+$ is a weakest oxidizing agent and Li metal is the most powerful reducing agent

- As value of SRP decreases for metal ion $\Rightarrow$ Reducing power of metal increases

**Example:** Arrange following metals in an increasing order of their reducing power.

SEP of metals are:

(i) $K^+ / K = -2.93$ V (ii) $Ag^+ / Ag = 0.80$ V

(iii) $Cu^{2+} / Cu = 0.34$ V (iv) $Mg^{2+} / Mg = -2.37$ V

(v) $Cr^{+2} / Cr = -0.74$ V (vi) $Fe^{+2} / Fe = -0.44$ V

- Reducing power of metal $\propto \frac{1}{\text{Reduction potential}}$
- Order of reducing power: Ag < Cu < Fe < Cr < Mg < K

**Electrochemical Series:** If SRP values of different electrodes are arranged in a series in increasing order, then series is called electrochemical series.

Top (i) $Li^+ + e^- \longrightarrow Li^+$

$\downarrow$

(ii) $2H^+ + 2e^- \longrightarrow H_2$

$\downarrow$

Bottom (iii) $F_2 + 2e^- \longrightarrow F^-$

**Application of Series:**

(i) SRP $\downarrow$ $\Rightarrow$ Reducing power $\uparrow$

$\Rightarrow$ Oxidizing power $\downarrow$

For Daniel cell

(ii) Anode: Oxidation $\rightarrow$ Electrode higher up in series

Cathode: Reduction $\rightarrow$ Lower in series with respect to anode

Anode : Zn

Cathode : Cu

(iii) Metals which are higher up in series can displace metals in lower in series from their salt solution.

$CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu$ $\quad E^o_{Zn^{2+}/Zn} = -0.76$ V

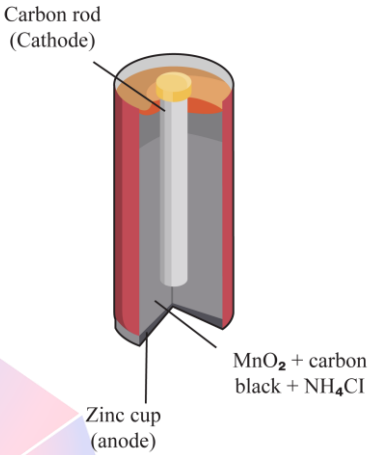
$ZnSO_4 + Cu \longrightarrow$ No reaction $\quad E^o_{Cu^{2+}/Cu} = 0.34$ V

(iv) Metals placed above than hydrogen can release $H_2$ gas on reaction with dilute acid solution.

$Mg + 2HCl \longrightarrow MgCl_2 + H_2$

$Cu + HCl \longrightarrow$ No reaction

**Batteries:** A battery contains one or more than one cell connected in series. It is basically a galvanic cell where the chemical energy of redox reaction is converted into electrical energy. There are mainly 2 types of batteries.




(a) **Primary Batteries:** In primary batteries the reaction occurs only once and after use over a time period battery becomes dead and cannot be reused again.

**Leclanche cell: [Dry cell]**

Anode —: Zinc container

Cathode —: Carbon rod [Surrounded by $MnO_2$ + carbon]

- The space between electrodes is filled by a moist paste of $NH_4Cl$ and $Zn\ Cl_2$.

Anode Reaction: $Zn(s) \longrightarrow Zn^{+2} + 2e^-$

Cathode Reaction: $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

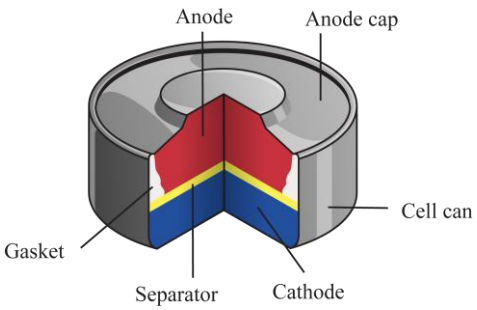
Overall Reaction: $Zn(s) + 2NH_4^+ + 2MnO_2 \longrightarrow Mn_2O_3(s) + H_2O(l) + \left[Zn(NH_3)_2\right]^{2+}$

- By using Nernst equation $E_{cell} = E^o_{cell} - \dfrac{2.303\ RT}{nf}\ \log\dfrac{\left[Zn(NH_3)_2\right]^{2+}}{\left[NH_4^+\right]^2}$

- Due to the presence of ions $\left(\left[Zn(NH_3)_2\right]^{2+}\right)$ in the overall reaction, its voltage decreases with time.

- **Use:** Commonly used in transistors and clocks.

**Mercury cell**




Anode: Zn – Mg amalgam

Cathode: Paste of HgO and carbon

Electrolyte: Past of ZnO + KOH

Anode Reaction:

$Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

Cathode Reaction: $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

Overall Reaction: $Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

- The voltage of a mercury cell remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

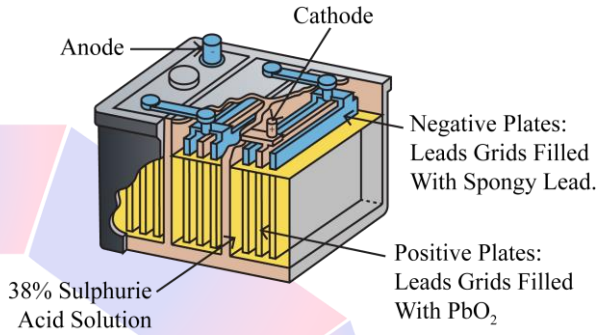
(b) **Secondary Batteries:** A secondary cell after use can be recharged by passing current through it in opposite direction so that it can be used again. A secondary cell can undergo a large no. if discharging and charging cycles.

**Lead storage Battery:** It is a most important secondary cell, common, used in automobiles in invertors.

Anode: Lead [Pb]

Cathode: A grid of lead with $PbO_2$.

Electrolyte: 38% $H_2SO_4$ solution (by mass)




Anode Reaction: $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

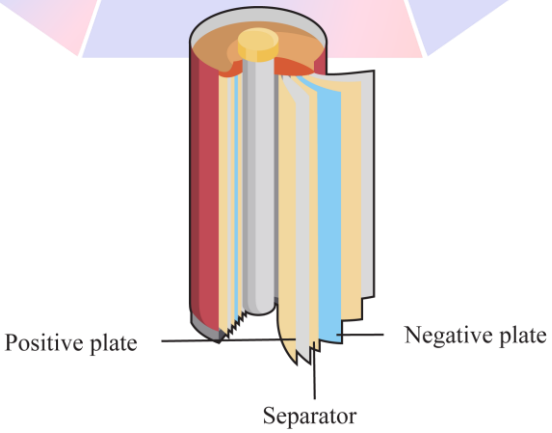
Cathode Reaction: $PbO_2(s) + SO_4^{2-}(aq) \xrightarrow[+2e^-]{+4H^+} PbSO_4(s) + 2H_2O(l)$

Overall Reaction: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4 + 2H_2O(l)$

**Nickel – Cadmium cell:** Ni – Cd cell is a secondary cell. It has longer life than lead storage cell but more expensive to manufacture.

The overall reaction during discharging is:

$Cd(s) + 2Ni(OH)_3 \longrightarrow CdO(s) + Ni(OH)_2(s) + H_2O(l)$

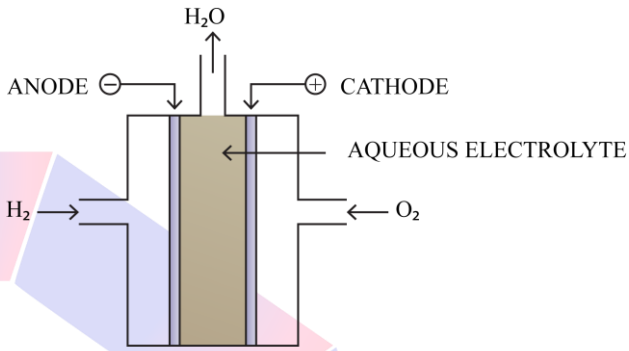


**Fuel cells**

Galvanic cells that are designed to convert the energy of combustion of fuels [like $H_2$, $CH_4$, $CH_3OH$] directly into electrical energy are called fuel cells.

**$H_2$ – $O_2$ Fuel cell**

- It is an important fuel cell which uses the reaction of $H_2$ with $O_2$ to form $H_2O$.
- The cell was used for providing electrical power in the Apollo space program. The water vapor produced during the reaction were condensed and added to the drinking water supply for the astronauts.




- In the cell $H_2$ and $O_2$ are bubbled through porous carbon electrodes into concentrated aq. NaOH solution.
- The catalysts like Pt or Pd are incorporated into the electrons for increasing the rate of electrode reactions.

Cathode Reaction: $O_2(s) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq.)$

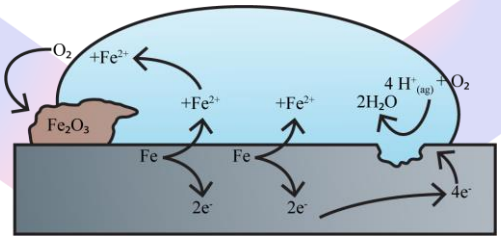
Anode Reaction: $2H_2(g) + 4OH^-(aq.) \longrightarrow 4H_2O(l) + 4e^-$

Overall Reaction: $2H_2(s) + O_2(g) \longrightarrow 2H_2O(l)$

Advantages of $H_2$ — $O_2$ cell: – Fuel cell do not cause any pollution unlike thermal plant (Coal, oil burning produces $CO_2$ gas). Efficiency of fuel cell is high than thermal plants.

**Corrosion:** It is basically an electrochemical phenomenon in which a metal oxide or other salt of metal forms a coating on the metal surface.

For example: Rusting of iron.




Oxidation: $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$

Atmospheric Oxidation: $2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s) + 4H^+(aq)$

**The Rasayanam!**

# Electrochemistry | Practice set-1 | TGT Chemistry

1. The Edison storage cell is represented as:
   $Fe(s) + FeO(s)|\, KOH(aq)|\, Ni_2O_3(s)|\, Ni_2O_3(s)|\, Ni(s)$
   The half reactions are $Ni_2O_3(s) + H_2O(l) + 2e^- \rightarrow 2NiO(s) + 2OH^-;\ E° = +0.40\ V$
   $FeO(s) + H_2O(l) + 2e^- \rightarrow Fe(s) + 2OH^-;\ E° = -0.87\ V$
   Choose the incorrect statement
   a) $E_{anode}$ increases with increase in concentration of $OH^-$
   b) $E_{cathode}$ decreases with increase in concentration of $OH^-$
   c) $E^{\circ}_{cell} = 1.27\ V$
   d) $E_{cell}$ increases with increase in concentration of FeO

2. Standard reduction potentials of the half reactions are given below:
   $F_2(g) + 2e^- \longrightarrow 2F^-(aq);\quad E° = +2.85\ V$
   $Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq);\quad E° = +1.36\ V$
   $Br_2(l) + 2e^- \longrightarrow 2Br^-(aq);\quad E° = +1.06\ V$
   $I_2(s) + 2e^- \longrightarrow 2I^-(aq);\quad E° = +0.53\ V$
   The strongest oxidizing and reducing agents respectively are:
   a) $F_2$ and $I^-$ b) $Br_2$ and $Cl^-$ c) $Cl_2$ and $Br^-$ d) $Cl_2$ and $I_2$

3. The standard reduction potential for $Fe^{2+}|Fe$ and $Sn^{2+}|Sn$ electrodes are $-0.44\ V$ and $-0.14\ V$ respectively. For the cell reaction, $Fe^{2+} + Sn \longrightarrow Fe + Sn^{2+}$, the standard e.m.f. is:
   a) + 0.30 V b)0.58 V c)+ 0.58 V d)− 0.30 V

4. The emf of the cell, $(E_{Zn^{2+}/Zn} = -0.76\ V)$
   $Zn\ /\ Zn^{2+}\ (1\ M)\ ||\ Cu^{2+}\ (1\ M)\ |\ Cu$
   $(E_{Cu^{2+}/Cu} = +0.34\ V)$ will be
   a) +1.10 V b)-1.10 V c)+0.42 V d)-0.42 V

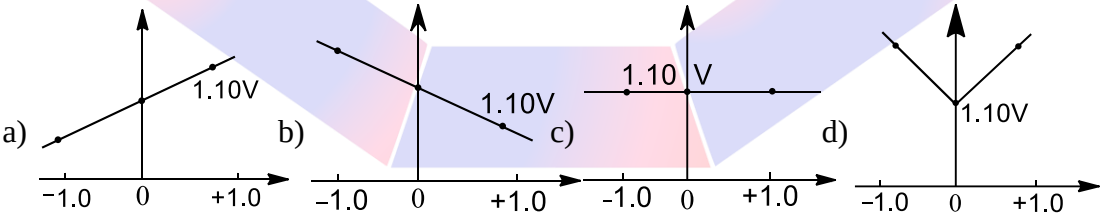
5. Consider the reaction, $M^{n+}(aq) + ne \longrightarrow M^0(s)$. The standard reduction potential values of the metals $M_1, M_2$ and $M_3$ are $-0.34$ V, $-3.05$ V and $-1.66$ V respectively. The order of their reducing power will be:
   a) $M_1 > M_2 > M_3$ b) $M_3 > M_2 > M_1$ c) $M_1 > M_3 > M_2$ d) $M_2 > M_3 > M_1$

6. In an electrolytic cell, the cathode and Anode are respectively represented as:
   a) Positive electrode, negative electrode
   b) Negative electrode, positive electrode
   c) Both positive and negative electrode
   d) None of the above

7. The cell reaction is spontaneous, when
   a) $E^\circ_{red}$ is negative b) $E^\circ_{red}$ is positive c) $\Delta G^\circ$ is zero d) $\Delta G^\circ$ is positive

8. The emf of the cell $Mg|\,Mg^{2+}(0.01\ M)||\,Sn^{2+}(0.1\ M)|Sn$ at 298 K is (Given, $E^\circ_{Mg^{2+},Mg} = -2.34$ V, $-2.34$ V, $E^\circ_{Sn^{2+},Sn} = -0.14$ V)
   a) 2.23 V b) 1.86 V c) 1.56 V d) 3.26 V

9. Which graph correctly correlates $E_{Cell}$ as a function of concentrations for the cell (for different values of $M$ and $M'$)?
   $Zn(s) + Cu^{2+}(M) \longrightarrow Zn^{2+}(M') + Cu(s)$;
   $E^\circ_{Cell} = 1.10\ V$
   $X-$ axis : $\log_{10}\frac{[Zn^{2+}]}{[Cu^{2+}]}$, $Y-$ axis : $E_{Cell}$



10. In electrolysis, oxidation takes place at:
    a) Anode
    b) Cathode
    c) The anode as well as cathode
    d) The surface of electrolyte solution

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1.d | 2.a | 3.d | 4.a | 5.d | 6.b | 7.b | 8.a | 9.b | 10. a |

# Practice Set-2 Electrochemistry TGT Science

1. The $E°_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are $-0.41, +1.57, +0.77$ and $+1.97$ V respectively. For which one of these metals, the change in oxidation state from +2 to +3 is easiest?

   a) Fe b) Mn c) Co d) Cr

2. The standard reduction electrode potential values of the elements $A, B$ and $C$ are + 0.68, –2.50 and – 0.50 V respectively. The order of their reducing power is:

   a) $A > B > C$ b) $A > C > B$ c) $C > B > A$ d) $B > C > A$

3. The passage of electricity in the Daniell cell when Zn and Cu electrodes are connected:

   a) From Cu to Zn inside the cell

   b) From Cu to Zn outside the cell

   c) From Zn to Cu outside the cell

   d) None of the above

4. Ni / $Ni^{2+}$ [1.0 M] || $Au^{3+}$ [1.0 M] / Au where $E^{\circ}$ for $Ni^{2+}$ /Ni is $-0.250$ V; and $E^{\circ}$ for $Au^{3+}$ / Au is 0.150 V. The emf of the cell is

   a) +1.25 V b)-1.75 V c)+1.75 V d)+0.4 V

5. The approximate e.m.f. of a dry cell is:

   a) 2.0 V b)1.2 V c)6 V d)1.5 V

6. $E_1, E_2$, and $E_3$ are the emfs of the following three galvanic cells respectively
   I. Zn (s) | $Zn^{2+}$ (0.1 M) || $Cu^{2+}$ (1 M) | Cu (s)
   II. Zn (s) | $Zn^{2+}$ (1 M) || $Cu^{2+}$ (1 M) | Cu (s)
   III. Zn (s) | $Zn^{2+}$ (1 M) || $Cu^{2+}$ (0.1 M) | Cu (s)
   Which one of the following is true?
   a) $E_2 > E_1 > E_3$ b) $E_1 > E_2 > E_3$ c) $E_3 > E_1 > E_2$ d) $E_3 > E_2 > E_1$

7. In a galvanic cell, which is wrong?
   a) Anode has negative polarity
   b) Cathode has positive polarity
   c) Reduction takes place at anode
   d) Reduction takes place at cathode

8. The rusting of iron takes place as follows
   $2H^+ + 2e^- + \frac{1}{2} O_2 \longrightarrow H_2O\ (l);$
   $E^\circ = +1.23\ V$
   $Fe^{2+} + 2e^- \longrightarrow Fe\ (s); \quad E^\circ = -0.44\ V$
   Calculate $\Delta G^\circ$ for the net process.
   a) -322 kJ $mol^{-1}$ b) -161 kJ $mol^{-1}$ c) -152 kJ $mol^{-1}$ d) -76 kJ $mol^{-1}$

9. The value of equilibrium constant for a feasible cell reaction is:
   a) < 1 b) Zero c) = 1 d) > 1

10. At 25°C, the standard e.m.f. of cell having reactions involving a two-electron change is found to be 0.295 V. The equilibrium constant of the reaction is:
    a) $29.5 \times 10^{-2}$ b) 10 c) $10^{10}$ d) $29.5 \times 10^{10}$

Answer Key

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1. (d) | 2.(d) | 3.(b) | 4.(d) | 5. (d) | 6. (d) | 7. (c) | 8. (a) | 9. (d) | 10. (c) |

## Electrochemistry Practice Set-3 TGT Science

**Contact No. 8285162819, 9911689985**

1. $E^{\circ}$ for $Fe^{2+} + 2e^{-} \rightarrow Fe$ is -0.44 V and $E^{\circ}$ for $Zn^{2+} + 2e^{-} \rightarrow Zn$ is -0.76 V thus
   a) Zn is more electropositive than Fe
   b)Zn is more electronegative than Fe
   c) Fe is more electropositive than Zn
   d)None of the above

2. $I_2(s)|\, I^{-}(0.1\ M)$ half-cell is connected to a $H^{+}(aq)|\, H_2(1\ bar)|$ Pt half-cell and emf is found to be 0.7714 V. If $E^{\circ}_{I_2/I^{-}} = 0.535$ V, find the pH of $H^{+}/H_2$ half-cell
   a) 1 b)2 c)3 d)5

3. The $E^{\circ}_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are -0.41 V, +1.57 V, +0.77 V and +1.97 V respectively. For which one of these metals the change in oxidation state from +2 to +3 is easiest?
   a) Cr b)Mn c)Fe d)Co

4. Standard reduction potentials of the two electrodes $Co^{2+}/Co$ and $Fe^{2+}/Fe$ are -2.28 V and -0.44 V respectively?
   a) -0.16 V
   b) -0.72 V
   c) +0.72 V
   d) +0.16 V

5. $E^{\circ}_{Cu} = 0.34\,V\,, E^{\circ}_{Zn} = 0.76\,V$. ADaniel cell contains 0.1 M $ZnSO_4$ solution and 0.01 M $CuSO_4$ solution at its electrodes. EMF of the cell is

a) 1.10 V b)1.04 V c)1.16 V d)1.07 V

6. The $E^{\circ}$of $Fe^{2+}$ / Fe and $Sn^{2+}$ /Sn are -0.44 V and -0.14 V respectively. If cell reaction is

$Fe + Sn^{2+} \rightarrow Fe^{2+} + Sn$

then emf of the cell is

a) +0.30 V b)-0.58 V c)+0.58 V d)-0.30 V

7. The cell reaction of the galvanic cell

$Cu\,(s)\,|\,Cu^{2+}\,(aq)\,||\,Hg^{2+}\,(aq)\,|\,Hg\,(l)$ is

a) $Hg + Cu^{2+} \longrightarrow Hg^{2+} + Cu$ b)$Hg + Cu^{2+} \longrightarrow Cu^{+} + Hg^{+}$

c) $Cu + Hg \rightarrow CuHg$ d)$Cu + Hg^{2+} \longrightarrow Cu^{2+} + Hg$

8. The reduction electrode potential, $E$ of 0.1 M solution of $M^{+}$ ions $(E_{RP} = -2.36\,V)$ is

a) -4.82 V b)-2.41 V c)+2.41 V d)None of these

9. The equilibrium constant for the reaction given below at 298 K is:

$Zn(s) + Fe^{2+}(aq0.01M) \longrightarrow Zn^{2+}(0.1M) + Fe(s);$

$E_{cell}$ = 0.2905 V at 298 K

a) $e^{0.32/0.0295}$ b)$10^{0.595/0.76}$ c)$10^{0.0250/0.32}$ d)$10^{0.32/0.0295}$

10. The e. m. f. of the cell $Zn\,|\,Zn^{2+}\,(1\,M)||\,Cu^{2+}|Cu(1M)$ is 1.1 volt. If the standard reduction potential of $Zn^{2+}|\,Zn$ is $-0.78$ volt, what is the oxidation potential of $Cu\,|\,Cu^{2+}$?

a) + 1.86 V b)0.32 V c)$-$ 0.32 V d)$-1.86$ V

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1-a | 2-c | 3-a | 4-a | 5-d | 6-a | 7-d | 8-b | 9-d | 10-c |