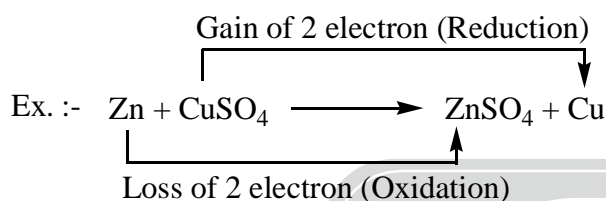


## ELECTROCHEMICAL CELLS

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**Redox Reaction :-** The reaction in which oxidation and reduction takes place simultaneously.



**Oxidation :-** The loss of electron or increase in oxidation number of a substance

**Reduction :-** The gain of electron or decrease in oxidation number of a substance.

**Oxidising Agent or Oxidant :-** The substance which oxidise others and itself gets reduced.

**Reducing Agent or Reductant :-** The substance which reduces others and itself get oxidised.

**Oxidation Number (ON):-** It is the hypothetical charge that an atom would have if all bonds to atoms of different elements were 100% ionic.

It represents the number of electrons lost (if O.N is positive) and gain (if O.N is negative) by an atom of that element in the compound.

**Rules to Determine Oxidation Number :-**

1. All atomic and molecular species have oxidation number of zero

**Ex. :** Mg, H<sub>2</sub>, N<sub>2</sub>, Ca, H

2. All element of group one (except H) in a compound has ON of +1
3. All element of group two in a compound have ON of +2.
4. Al has +3 oxidation number in a compound.
5. For an ion, charge number is equal to oxidation number

**Ex. :** Fe<sup>3+</sup>, ON = +3

Mg<sup>2+</sup>, ON = +2

CO<sub>3</sub><sup>2-</sup>, ON of a anion is -2

6. Flourine has oxidation number of -1
7. Hydrogen will always be +1 except in metal hydrides like NaH, MgH<sub>2</sub>.
8. Oxygen has ON of -2 except in peroxide O<sub>2</sub><sup>2-</sup> (ON = -1), superoxide O<sub>2</sub><sup>-</sup> (ON = -1/2) and OF<sub>2</sub> (ON = +2).

**Ex. :** Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>

$$2x + 7x(-2) = -2$$

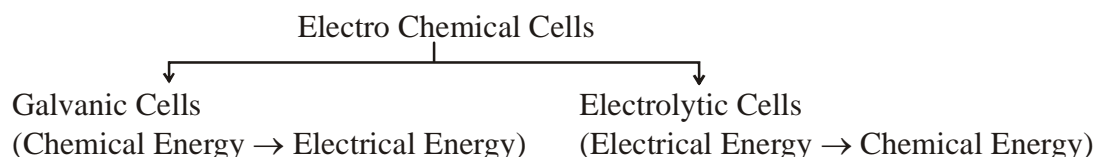
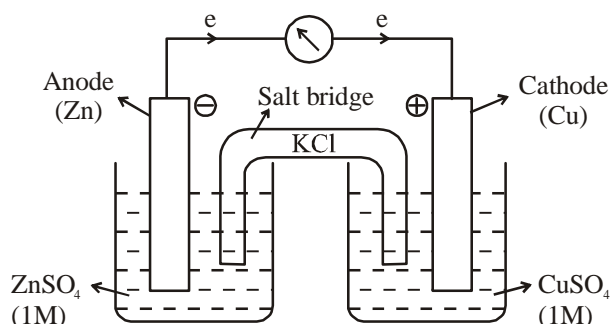
$$2x = 12$$

$$x = +6$$

MnO<sub>4</sub><sup>-</sup>

$$x + 4(-2) = -1$$

$$x = +7$$

**Galvanic Cell :-**

**Anode (Oxidation) :**  $\text{Zn(s)} \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$

**Cathode (Reduction) :**  $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \longrightarrow \text{Cu(s)}$

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

**Salt Bridge :** It is a U-shaped tube containing a solution of an inert electrolyte such as KCl,  $\text{KNO}_3$  or  $\text{NH}_4\text{NO}_3$ .

**Characteristics :** (i) Mobilities of ions should be same  
(ii) Ions should not get oxidised or reduced during the process.

**Function :** (i) Maintain the flow of current  
(ii) Maintain the electrical neutrality of anodic and cathodic compartment

Potential difference develops between electrodes and the electrolyte is called electrode potential.

When half cells are connected by a wire, the difference in the reduction potential of cathode and the reduction potential of anode is called cell potential.

$$E_{\text{cell}} = E_{r(\text{cathode})} - E_{r(\text{anode})}$$

When pressure is 1 bar, temperature is 298K and the concentration of solution is 1M, the cell potential is called standard cell potential ( $E_{\text{cell}}^0$ )

$$E_{\text{cell}}^0 = E_{r(\text{cathode})}^0 - E_{r(\text{anode})}^0$$

$$E_{\text{red}}^0 \uparrow \text{O} \cdot \text{A} \uparrow$$

$$E_{\text{red}}^0 \downarrow \text{R} \cdot \text{A} \uparrow$$

**Reduction Potential :** Tendency to reduce. Higher the reduction potential, more easily the species will reduced

**Ex.:**  $E_{\text{Ag}^+|\text{Ag}}^0 = 0.80\text{V}$        $E_{\text{Cu}^{2+}|\text{Cu}}^0 = 0.34\text{V}$        $E_{\text{Zn}^{2+}|\text{Zn}}^0 = -0.76\text{V}$

**Reduction Tendency :**  $\text{Ag} > \text{Cu} > \text{Zn}$

**Oxidation Potential :** Tendency to oxidise. Lower the reduction potential, more easily the species will oxidise.

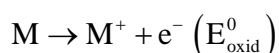
**Oxidation Tendency :**  $\text{Zn} > \text{Cu} > \text{Ag}$

**Strength of Oxidizing Agent :-** Higher the reduction potential, strongest the oxidizing agent.

**O.A. :**  $\text{Ag} > \text{Cu} > \text{Zn}$  .

**Strength of Reducing Agent :-** Lower the reduction potential, strongest the reducing agent

**R.A. :-**  $\text{Zn} > \text{Cu} > \text{Ag}$  .



**Problem:** In which of the following  $\text{CuSO}_4$  can be stored

- (a) Zn pot (b) Ag pot  
(c) Fe pot ( $E^0 = -0.44$ ) (d) Al pot ( $-1.66$  v)

**Soln.**  $\text{CuSO}_4$  can be stored in Ag pot as  $E_{\text{Ag}^+|\text{Ag}}^0 > E_{\text{Cu}^{2+}|\text{Cu}}^0$ .

**Correct option is (b)**

**Problem:** Given that  $\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$        $E^0 = 0.54$  V



Predict which of the following is true

- (a)  $\text{I}^-$  ions will be able to reduce bromine      (b)  $\text{Br}^-$  ions will be able to reduce iodine  
(c) Iodine will be able to reduce bromine      (d) Bromine will be able to reduce iodide ions

**Soln.** Since reduction potential of  $\text{Br}_2 | \text{Br}^-$  is greater than reduction potential of  $\text{I}_2 | \text{I}^-$ , so  $\text{I}^-$  will reduce  $\text{Br}_2$ .

**Correct option is (a)**

**Problem:**  $E_{\text{A}^+/\text{A}}^0 = 0.3$  V       $E_{\text{B}^+/\text{B}}^0 = 0.7$  V       $E_{\text{C}^+/\text{C}}^0 = -0.7$  V

The correct statement is

- (a) B can reduce both A and C      (b) C can oxidise both A and B  
(c) A can oxidise C and reduced B      (d) A can oxidise both B and C

**Soln.** Order of reductional potential :-  $C < A < B$

$\Rightarrow$  order of strength reducing agent :-  $C > A > B$

So, C can reduce both A and B

B can oxidise both A and C

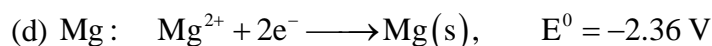
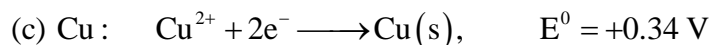
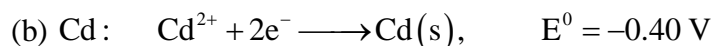
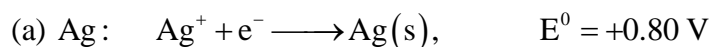
A can oxidise C but will reduce B

**Correct option is (c)**

**Problem:** A 19<sup>th</sup> century iron bridge is protected from corrosion by connecting it to a block of metal (sacrificial anode), which is replaced annually. The corrosion of iron, represented by the chemical equation :



Which of the following metals is best suited as sacrificial anode ?



**Soln.** In rusting oxidation of iron takes place. Sacrificial anode is a metal which can act as anode in place of iron and itself get oxidised and iron gets protected.

Metal with highest oxidation potential is the most suitable metal for sacrificial anode.

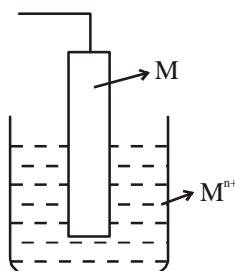
Since Magnesium has lowest reduction potential or highest oxidation potential. So, Mg will be used as sacrificial anode

**Correct option is (d)**

**Types of Half Cell :-**

**1. Metal-Metal ion Half Cell :-** It consists of a metal rod dipped in a solution of metal ion

**Representation :-**  $\text{M}^{n+} | \text{M}$



**If act as cathode :-**  $M^{n+} + ne \rightarrow M(s)$

**If act as anode :-**  $M(s) \rightarrow M^{n+}(aq) + ne^{-}$

**2. Gas-Electrode :-** It consist of a solution containing ions of gas species. In solution, Pt electrode is dipped on which gas was passed over from outside source.

**(i) Hydrogen electrode :-** Representation :-  $H^+ | H_2 | Pt$

In this, hydrogen gas is passed over a platinum electrode which is dipped in HCl solution

**If act as cathode :-**  $H^+ + e^- \rightarrow \frac{1}{2} H_2(g)$

**If act as anode :-**  $\frac{1}{2} H_2 \rightarrow H^+ + e^-$

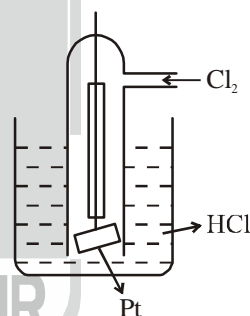
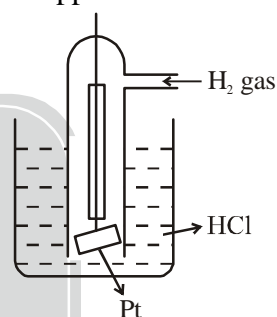
$E_{red}^0 = 0$  {Convention}

**(ii) Chlorine Electrode :-** Representation :-  $Pt | Cl_2(g) | Cl^-$

In this,  $Cl_2$  is passed over a Pt electrode which is dipped in HCl solution

**If act as cathode :-**  $\frac{1}{2} Cl_2 + e^- \rightarrow Cl^-$

**If act as anode :-**  $Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$

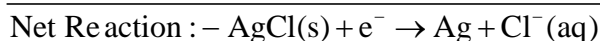
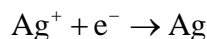
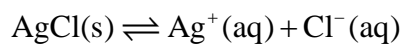


**3 Metal-Metal in soluble salt-anion half cell :-**

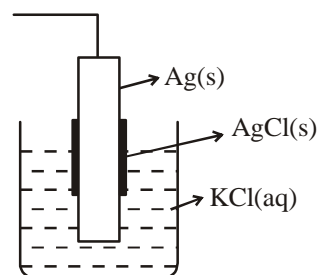
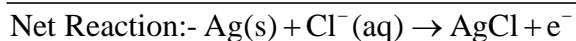
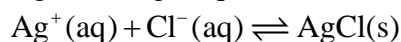
It consist of metal electrode coated with the insoluble salt of metal dipped in a solution containing on ion common to the anion of metal-salt.

**(i)  $Cl^- | AgCl | Ag$  Half Cell :-**

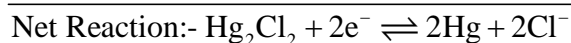
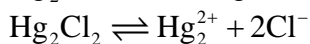
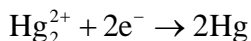
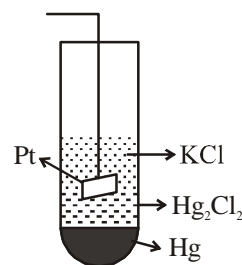
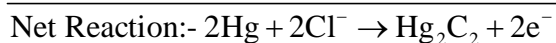
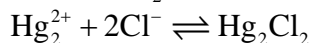
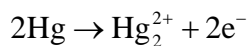
**If act as cathode :-**



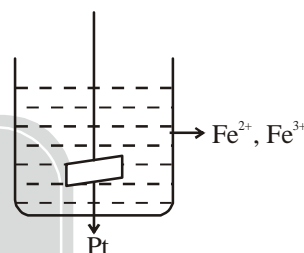
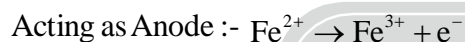
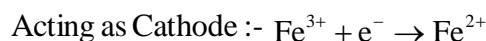
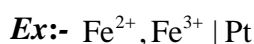
**If act as anode:-**



**(ii) Calomel Electrode :-** Representation :-  $Cl^- | Hg_2Cl_2 | Hg | Pt$

**If act as Cathode :-****If act as Anode :-****4. Oxidation-Reduction Half Cell (Redox Half Cell)**

In this, solution contain metal in more than one oxidation state. This half cell is possible for those metal only which shows more than one oxidation state. Pt is used as electrode.

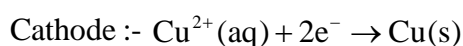
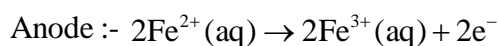
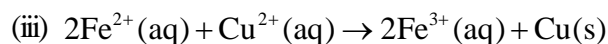
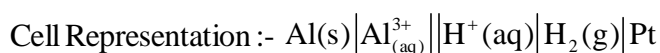
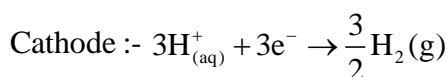
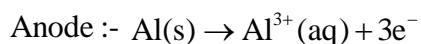
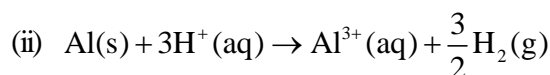
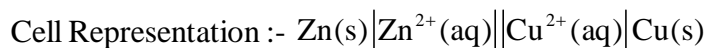
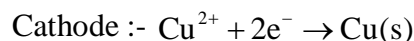
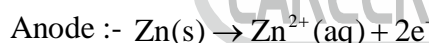
**Cell Representation :-**

Anode || Cathode

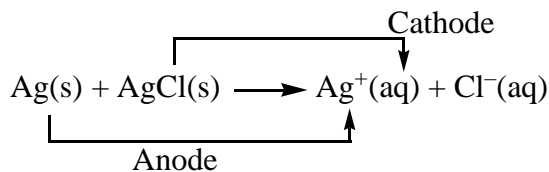
In general,

Pt (Wherever is used)	Metal or Gas	Metal insoluble Salt	Ion or Solution	Salt Bridge	Ion or Solution	Metal insoluble Salt	Metal or Gas	Pt (Wherever is used)
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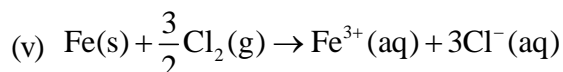
- (i) Salt bridge is represented by || (double dash)
- (ii) Single dash (|) is used to separate different phases
- (iii) Comma (,) is used to separate ions in solution



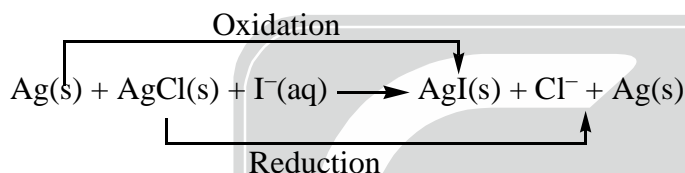
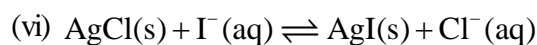
Cell Representation :-  $\text{Pt}|\text{Fe}^{3+}, \text{Fe}^{2+}||\text{Cu}^{2+}(\text{aq})|\text{Cu}(\text{s})$



Cell Representation :-  $\text{Ag}(\text{s})|\text{Ag}^+(\text{aq})||\text{Cl}^-(\text{aq})|\text{AgCl}(\text{s})|\text{Ag}(\text{s})$

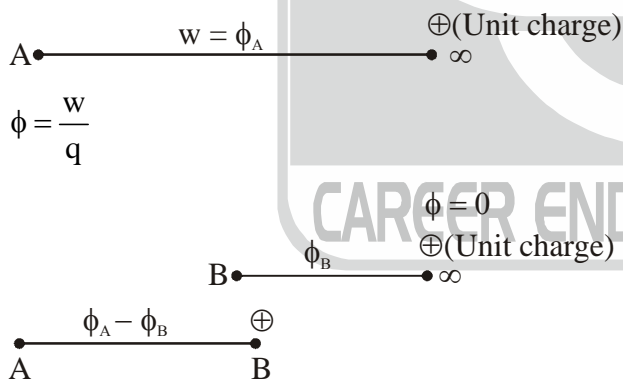


Cell Representation :-  $\text{Fe}|\text{Fe}^{3+}(\text{aq})||\text{Cl}^-|\text{Cl}_2(\text{g})|\text{Pt}$



$\text{Ag}|\text{AgI}|\text{I}^-(\text{aq})||\text{Cl}^-(\text{aq})|\text{AgCl}|\text{Ag}$

**Electric Potential ( $\phi$ )** :- The work done to bring a unit charge from infinity to the point of interest is called electric potential.



$$\frac{w}{q} = \phi_A - \phi_B \Rightarrow \text{Electric potential difference}$$

**Escaping Tendency of Charged Particle :-**

Let 'dn' amount of specie of charge number  $z_i$  is taken from infinity to the point A.

Let electric potential at A is  $\phi$

$$\phi = \frac{w}{q}$$

$$w = \phi q$$

$$\text{or} \quad dw = \phi z_i F dn \quad \dots (1)$$

Let chemical potential at infinity be  $\mu_i$  and at point A be  $\tilde{\mu}_i$

$$\text{Thermodynamically, } dG = \tilde{\mu}_i dn - \bar{\mu}_i dn \quad \dots (2)$$

Equating (1) and (2)

$$\tilde{\mu}_i - \mu_i = \phi Zi F$$

$$\tilde{\mu}_i = \mu_i + \phi Zi F$$

$\mu_i$  = chemical potential at infinity ( $\phi = 0$ )

$\phi$  = Electric potential at point A

$z_i$  = Charge number

$F$  = 1 faraday

$$\begin{array}{ccccc} \tilde{\mu}_i & = & \mu_i & + & \phi Zi F \\ \downarrow & & \downarrow & & \downarrow \\ \text{electrochemical} & & \text{chemical} & & \text{electrical} \\ \text{potential} & & \text{contribution} & & \text{contribution} \end{array}$$

$\mu_i$  will have same value for a species having same composition

(i) **For metals :-**  $z_i = 0$

$$\Rightarrow \tilde{\mu}_i = \mu_i$$

(ii) **For electron :-**  $z_i = -1$

$$\tilde{\mu}_i = \mu_i - \phi F$$

If  $\phi = -ve$  then  $\tilde{\mu}_i \uparrow$  or escaping tendency of  $e^- \uparrow$

If  $\phi = +ve$  then  $\tilde{\mu}_i \downarrow$  or escaping tendency of  $e^- \downarrow$

$\Rightarrow$  If two half cells having +ve and -ve potential will be connected by a wire then electron will move from -ve potential electrode to +ve potential electrode.  
(higher oxidation potential)  $\rightarrow$  (lower oxidation potential)

$$\text{So, } E_{\text{cell}} = E_{\text{oxid(anode)}} - E_{\text{oxid(cathode)}}$$

$$= -E_{\text{red(anode)}} - E_{\text{red(cathode)}}$$

$$E_{\text{cell}} = E_{\text{red(cathode)}} - E_{\text{red(anode)}}$$

**Table: Standard Electrode (Reduction) Potentials,  $T = 25^\circ\text{C}$ :**

Half-cell reaction	$E^\circ/V$	Half-cell representation
$\text{Li}^+ + e^- = \text{Li}$	-3.045	$\text{Li}^+   \text{Li}$
$\text{K}^+ + e^- = \text{K}$	-2.925	$\text{K}^+   \text{K}$
$\text{Na}^+ + e^- = \text{Na}$	-2.714	$\text{Na}^+   \text{Na}$
$\text{Mg}^{2+} + 2e^- = \text{Mg}$	-2.37	$\text{Mg}^{2+}   \text{Mg}$
$\text{H}_2 + 2e^- = \text{H}_2 + 2\text{OH}^-$	-2.25	$\text{H}^-   \text{H}_2   \text{Pt}$
$\text{Al}^{3+} + 3e^- = \text{Al}$	-1.66	$\text{Al}^{3+}   \text{Al}$
$2\text{H}_2\text{O} + 2e^- = \text{H}_2 + 2\text{OH}^-$	-0.828	$\text{OH}^-   \text{H}_2   \text{Pt}$
$\text{Zn}^{2+} + 2e^- = \text{Zn}$	-0.763	$\text{Zn}^{2+}   \text{Zn}$

$\text{Cd}(\text{NH}_3)_4^{2+} + 2\text{e}^- = \text{Cd} + 4\text{NH}_3$	-0.61	$\text{Cd}(\text{NH}_3)_4^{2+}, \text{NH}_3   \text{Cd}$
$2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{C}_2\text{O}_4$	-0.49	$\text{H}_2\text{C}_2\text{O}_4, \text{H}^+   \text{CO}_2   \text{Pt}$
$\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}$	-0.44	$\text{Fe}^{2+}   \text{Fe}$
$\text{Cr}^{3+} + \text{e}^- = \text{Cr}^{2+}$	-0.41	$\text{Cr}^{3+}, \text{Cr}^{2+}   \text{Pt}$
$\text{Cd}^{2+} + 2\text{e}^- = \text{Cd}$	-0.40	$\text{Cd}^{2+}   \text{Cd}$
$\text{Ag}(\text{CN})_2^- + \text{e}^- = \text{Ag} + 2\text{CN}^-$	-0.31	$\text{Ag}(\text{CN})_2^-, \text{CN}^-   \text{Ag}$
$\text{Cu}(\text{OH})_2 + 2\text{e}^- = \text{Cu} + 2\text{OH}^-$	-0.224	$\text{OH}^-, \text{Cu}(\text{OH})_2   \text{Cu}$
$\text{AgI} + \text{e}^- = \text{Ag} + \text{I}^-$	-0.151	$\text{I}^-   \text{AgI}   \text{Ag}$
$\text{Sn}^{2+} + 2\text{e}^- = \text{Sn}$	-0.136	$\text{Sn}^{2+}   \text{Sn}$
$\text{Pb}^{2+} + 2\text{e}^- = \text{Pb}$	-0.126	$\text{Pb}^{2+}   \text{Pb}$
$\text{Cu}(\text{NH}_3)_4^{2+} + 2\text{e}^- = \text{Cu} + 4\text{NH}_3$	-0.12	$\text{Cu}(\text{NH}_3)_4^{2+}, \text{NH}_3   \text{Cu}$
$\text{Fe}^{3+} + 3\text{e}^- = \text{Fe}$	-0.036	$\text{Fe}^{3+}   \text{Fe}$
$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	0.000	$\text{H}^+   \text{H}_2   \text{Pt}$
$\text{AgBr} + \text{e}^- = \text{Ag} + \text{Br}^-$	0.095	$\text{Br}^-   \text{AgBr}   \text{Ag}$
$\text{Cu}^{2+} + \text{e}^- = \text{Cu}^+$	0.153	$\text{Cu}^{2+}, \text{Cu}^+   \text{Pt}$
$\text{Sn}^{4+} + 2\text{e}^- = \text{Sn}^{2+}$	0.15	$\text{Sn}^{4+}, \text{Sn}^{2+}   \text{Pt}$
$\text{AgCl} + \text{e}^- = \text{Ag} + \text{Cl}^-$	0.222	$\text{Cl}^-   \text{AgCl}   \text{Ag}$
$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- = 2\text{Hg} + 2\text{Cl}^-$	0.267	$\text{Cl}^-   \text{Hg}_2\text{Cl}_2   \text{Hg}(\text{Pt})$
$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$	0.337	$\text{Cu}^{2+}   \text{Cu}$
$\text{Ag}(\text{NH}_3)_2^+ + \text{e}^- = \text{Ag} + 2\text{NH}_3$	0.373	$\text{Ag}(\text{NH}_3)_2^+, \text{NH}_3   \text{Ag}$
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$	0.401	$\text{OH}^-   \text{O}_2   \text{Pt}$
$\text{Cu}^+ + \text{e}^- = \text{Cu}$	0.521	$\text{Cu}^+   \text{Cu}$
$\frac{1}{2}\text{I}_2 + \text{e}^- = \text{I}^-$	0.535	$\text{I}_2, \text{I}^-   \text{Pt}$
$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	0.771	$\text{Fe}^{3+}, \text{Fe}^{2+}   \text{Pt}$
$\frac{1}{2}\text{Hg}_2^{2+} + \text{e}^- = \text{Hg}$	0.789	$\text{Hg}_2^{2+}   \text{Hg}(\text{Pt})$
$\text{Ag}^+ + \text{e}^- = \text{Ag}$	0.799	$\text{Ag}^+   \text{Ag}$
$\text{Br}_2(\ell) + 2\text{e}^- = 2\text{Br}^-$	1.086	$\text{Br}^-, \text{Br}_2   \text{Pt}$



$O_2 + 4H^+ + 4e^- = 2H_2O$	1.229	$H^+   O_2   Pt$
$Cr_2O_7^{2-} + 14H^+ + 6e^-$ $\rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cr_2O_7^{2-}, Cr^{3+}, H^+   Pt$
$\frac{1}{2}Cl_2(g) + e^- = Cl^-$	1.359	$Cl^-   Cl_2   Pt$
$Ce^{4+} + e^- = Ce^{3+}$ (1 mol $dm^{-3}H_2SO_4$ )	1.44	$Ce^{4+}, Ce^{3+}   Pt$
$Au^{3+} + 3e^- = Au$	1.455	$Au^{3+}   Au$
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	1.51	$MnO_4^-, Mn^{2+}, H^+   Pt$
$Co^{3+} + e^- = Co^{2+}$	1.82	$Co^{3+}, Co^{2+}   Pt$

### Some Important Relations :

#### (i) Between $E_{cell}$ and $\Delta G$

$$w = \text{charge} \times \text{potential}$$

$$w = q \cdot E_{cell}$$

Work carried out is non-expansion. therefore magnitude of work will be equal to change in gibbs free energy

$$w = \Delta G = q \cdot E_{cell}$$

for 'n' moles of electron

$$q = n \times \text{Charge of 1 mol of electron}$$

$$= n \times (Z_1 F)$$

$$q = -nF$$

$$\Delta G = -nFE_{cell}$$

$$\text{or } \Delta G^0 = -nFE_{cell}^0$$

#### (ii) Relation between $\Delta S$ and $E_{cell}$

$$\left[ \frac{\partial(\Delta G)}{\partial T} \right]_P = -\Delta S$$

$$\text{or } \frac{\partial}{\partial T}(-nFE_{cell}) = -\Delta S$$

$$\text{or } \Delta S = nF \left( \frac{\partial E_{cell}}{\partial T} \right)_P$$

$$\left( \frac{\partial E}{\partial T} \right)_P \rightarrow \text{Temperature coefficient of cell.}$$

#### (iii) Relation between $\Delta H$ and $E_{cell}$

$$\Delta G = \Delta H - T\Delta S$$

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

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

$$\Delta H = nF \left[ T \left( \frac{\partial E}{\partial T} \right)_p - E \right]$$

**Problem:** At 20°C, the standard EMF of a certain cell is +0.2699 V, and at 30°C it is +0.2669V. What can you say about the standard entropy of this reaction? Assume that the standard  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature. **[TIFR-2012]**

- (a)  $\Delta S^\circ = 0$                       (b)  $\Delta S^\circ = +ve$                       (c)  $\Delta S^\circ = -ve$                       (d) Not enough information is given

**Soln.**  $\Delta S = nF \left( \frac{\partial E}{\partial T} \right)_p$

$$\Delta S = nF \left[ \frac{0.2669 - 0.2699}{30 - 20} \right]$$

$$\Rightarrow \Delta S < 0$$

**Correct option is (c)**

**Problem:** The emf of the cell Cd, CdCl<sub>2</sub> · 2.5 H<sub>2</sub>O saturated || AgCl(s), Ag in which the cell reaction is Cd(s) + 2AgCl(s) + aq  $\longrightarrow$  CdCl<sub>2</sub> · 5/2 H<sub>2</sub>O(sat) + 2Ag(s) is 0.6753 volt at 25°C and 0.6915 volt at 0°C. Calculate the free energy change ( $\Delta G$ ), Enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) for the cell reaction at 25°C.

**Soln:** Free energy ( $\Delta G$ ) =  $-nEF = -2 \times 96500 \times 0.6753 = -130.33$  kJ

We have,  $E = -\frac{\Delta H}{2F} + T \left( \frac{\partial E}{\partial T} \right)_p$

$$\left( \frac{\partial E}{\partial T} \right)_p = \left( \frac{0.6195V - 0.6753V}{0 - 25 K} \right) = -0.00065 \text{ V K}^{-1}$$

$$0.6735 = \frac{-\Delta H}{2 \times 96500} + 298(-0.00065)$$

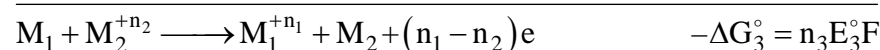
$$\Delta H = -167717 \text{ Joule} = -167.72 \text{ kJ}$$

And  $\Delta S = -\frac{\Delta G - \Delta H}{T} = 123.8 \text{ JK}^{-1}$

**Problem:** Show that the potentials are additive for the process in which half reactions are added to yield an overall reaction but they are not additive when added to yield a third half reaction?



**Soln:**



$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

$$n_3 E_3^\circ F = n_1 E_1^\circ F + n_2 E_2^\circ F$$

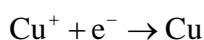
$$E_3^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_3}$$

If  $n_1 \neq n_2 \neq n_3$ , then  $E_{\text{cell}}^0$  are not additives.

$\therefore$  If  $n_1 = n_2 = n_3$  then  $E_3^\circ = E_1^\circ + E_2^\circ$

When two half reactions  $E^0$  are added to give an overall reaction, and the number of moles of electrons involved in each half reaction and the overall reaction is same.

**Problem:** Calculate  $E^0$  for the process

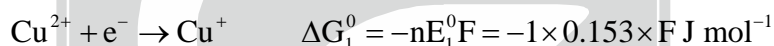


making use of the following  $E^0$  values:



**Soln.** As different number of electrons are involved in reactions (i) and (ii). So, simple subtraction will not give  $E_{\text{cell}}^0$ .

So, we will use  $\Delta G^0$  based method to calculate  $E_{\text{cell}}^0$ .



The reaction  $\text{Cu}^+ + e^- \rightarrow \text{Cu}$  is obtained by subtracting reaction (i) from reaction (ii).

$$\Delta G^0 = \Delta G_2^0 - \Delta G_1^0$$

$$\Delta G^0 = [-2 \times 0.341 \times F - (-1 \times 0.153 \times F)] \text{ J mol}^{-1}$$

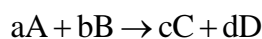
$$-1.F.E^0 = (0.153 - 0.682) F \text{ J mol}^{-1}$$

$$-1.F.E^0 = -0.529 \times F \text{ J mol}^{-1}$$

It follows that,  $E^0 = 0.529 \text{ V}$ .

**(iv) Nernst Equation :-**

$$\Delta G = \Delta G^0 + RT \ln Q$$



$$\Delta G = \Delta G^0 + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$-nFE = -nFE^0 + RT \ln Q; \quad \frac{-nFE}{-nF} = \frac{-nFE^0}{-nF} + \frac{RT}{-nF} \ln Q$$

$$E = E^0 - \frac{RT}{nF} \ln Q; \quad E = E^0 - \frac{2.303RT}{nF} \log Q$$

At 298 K,

$$E = E^0 - \frac{0.0591}{n} \log Q$$

**Problem:** For a cell constructed with a  $\text{Cu}(s)|\text{Cu}^{2+}(\text{aq})$  anode and  $\text{Ag}^+|\text{Ag}(s)$  cathode at  $25.0^\circ\text{C}$ , Calculate the cell potential at  $25.0^\circ\text{C}$  under non-standard conditions:  $[\text{Cu}^{2+}] = 0.300\text{ M}$  and  $[\text{Ag}^+] = 0.0500\text{ M}$ .

(a) 0.44 V                      (b) 0.41 V                      (c) 0.40 V                      (d) 0.34 V                      [TIFR-2010]

**Soln.** Cell reaction :-  $\text{Cu}(s) + 2\text{Ag}^+(\text{aq}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag}(s)$

$$E = E^0 - \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$= (0.8 - 0.34) - \frac{0.0591}{2} \log \frac{0.300}{(0.05)^2}$$

$$= 0.46 - 0.061$$

$$E_{\text{cell}} = 0.398$$

Correct option is (c)

### Application of Nernst Equation

(i) **Relation between  $E_{\text{cell}}^0$  and  $K$  (equilibrium constant) :-**

According to Nernst equation for reaction  $aA + bB \rightarrow cC + dD$

$$E = E^0 - \frac{0.0591}{n} \log Q$$

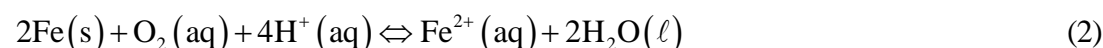
At equilibrium,  $Q = K$  and  $E = 0$

$$E^0 = \frac{0.0591}{n} \log K$$

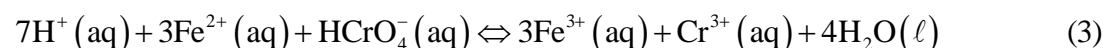
**Problem:** The corrosion of iron in contact with an acidic aqueous solution undergoes the following reaction



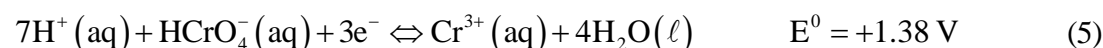
in the anaerobic condition, and the following reaction



in the aerobic condition. during the corrosion, Fe (II) ions are formed in both conditions. If the water is polluted with Cr(IV), the following reaction may take place.



Reaction (3) be broken down to the following redox half-reactions :



The standard potentials of these reactions are with respect to the normal hydrogen electrode. What would be the approximate value of the equilibrium constant of reaction 3 at 298K ? [TIFR-2012]

(a)  $10^{11}$                       (b)  $10^{31}$                       (c)  $10^{-31}$                       (d)  $10^{-11}$

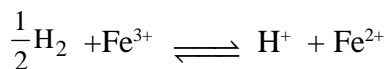
**Soln.**  $E^0 = \frac{0.0591}{n} \log K$

$$(1.38 - 0.77) = \frac{0.0591}{3} \log K$$

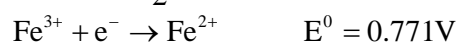
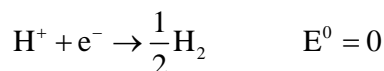
$$\log K = 30.96 \Rightarrow K = 10^{30.96}$$

**Correct option is (b)**

**Problem:** Calculate the equilibrium constant  $K$  for the process



**Soln.** The reactions would have been written as



And  $E^0 = 0.771 \text{V}$ . In this case  $n = 1$  and

$$0.771 = 0.0257 \ln K \text{ or } \ln K = \frac{0.771}{0.0257} = 30.01$$

And therefore,  $K = 1.1 \times 10^{13}$

**Problem:** Calculate the equilibrium constant for the reaction.



**Given:**  $E^0_{\text{Ce}^{+4}/\text{Ce}^{+3}} = 1.44 \text{V}$  and  $E^0_{\text{Fe}^{+3}/\text{Fe}^{+2}} = 0.68 \text{V}$

**Soln:**

$$E^0_{\text{cell}} = \frac{0.059}{2} \log_{10} K_c$$

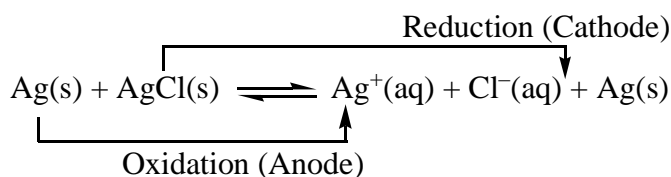
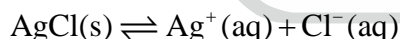
$$E^0_{\text{cell}} = 1.44 - 0.68 = 0.76 \text{V}$$

$$\log_{10} K_c = \frac{0.76}{0.059} = 12.8814$$

$$K_c = 7.6 \times 10^{12}$$

**(ii) Calculation of Solubility Product ( $K_{sp}$ )**

Let take an example of AgCl



For sparingly soluble salt, at equilibrium  $K = K_{sp}$

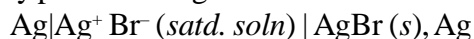
$$E^0_{\text{cell}} = \frac{2.303RT}{nF} \log K_{sp}$$

$$E^0_{\text{Cl}^-|\text{AgCl}|\text{Ag}} - E^0_{\text{Ag}^+|\text{Ag}} = \frac{2.303RT}{nF} \log K_{sp}$$

$$\text{In general, } E^0_{\text{X}^-|\text{MX}|\text{M}} - E^0_{\text{M}^+|\text{M}} = \frac{2.303RT}{nF} \log K_{sp}$$

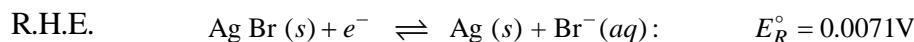
$$\text{At 298 K, } E^0_{\text{X}^-|\text{MX}|\text{M}} - E^0_{\text{M}^+|\text{M}} = \frac{0.0591}{n} \log K_{sp}$$

**Problem:** Calculate the solubility product of AgBr in water at 25°C from the cell



The standard potentials are  $E^\circ_{\text{AgBr,Ag}} = 0.071\text{V}$ ;  $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.799\text{V}$ .

**Soln.** The electrode reactions are:



Hence, for the overall reaction:  $\text{AgBr}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Br}^-(aq)$ ,

$$\begin{aligned} E^\circ &= E^\circ_R - E^\circ_L = -0.728\text{V} \\ &= \frac{0.0591}{1} \log \left\{ \frac{[\text{Ag}^+][\text{Br}^-]}{1} \right\}_{\text{eqilib}} = 0.0591 \log K_{sp} \\ \log K_{sp} &= \frac{E^\circ}{0.0591} = -\frac{0.728}{0.0591}, \quad \text{Hence } K_{sp} = 4.81 \times 10^{-13} \end{aligned}$$

**Problem:** The EMF of the cell:



is 0.45 volt at 25°C. Calculate (i) the solubility product and (ii) the solubility of AgCl. 0.1 M KCl is 85% dissociated and 0.1 M AgNO<sub>3</sub> is 82% dissociated.

**Soln.** Here the salt bridge has NH<sub>4</sub>NO<sub>3</sub>. Since at 25°C, 0.1 M AgNO<sub>3</sub> is 82 per cent dissociated, hence, the Ag<sup>+</sup> ion concentration ( $c_2$ ) on the AgNO<sub>3</sub> side =  $0.1 \times 82/100 = 0.082 \text{ mol dm}^{-3}$ .

Let  $c_1$  be the concentration of Ag<sup>+</sup> ions on the AgCl side due to the solubility of AgCl. Then, assuming that activity coefficients are each equal to unity, the EMF of the cell is given by

$$E = \frac{0.0591}{n} \log \frac{c_2}{c_1} \quad (\text{at } 25^\circ\text{C})$$

Substituting the value of  $E = 0.45 \text{ V}$ ,  $n = 1$  and  $c_2 = 0.082 \text{ mol dm}^{-3}$ , we get

$$0.45 \text{ V} = 0.0591 \text{ V} \log \frac{0.082 \text{ mol dm}^{-3}}{c_1}$$

Hence,  $c_1 = 2.008 \times 10^{-9} \text{ mol dm}^{-3}$

Since at 25°C, 0.1 M KCl is 85 per cent dissociated, hence the Cl<sup>-</sup> ion concentration is given by

$$[\text{Cl}^-] = \frac{0.1 \times 85}{100} = 0.085 \text{ mol dm}^{-3}$$

$$\begin{aligned} \therefore K_{sp} \text{ of AgCl} &= [\text{Ag}^+][\text{Cl}^-] = 2.008 \times 10^{-9} \text{ mol dm}^{-3} \times 0.085 \text{ mol dm}^{-3} \\ &= \mathbf{1.7068 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}} \end{aligned}$$

$$\begin{aligned} \therefore \text{Solubility of AgCl} &= \sqrt{\text{Solubility product of AgCl}} \\ &= \sqrt{1.7068 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}} = 1.308 \times 10^{-5} \text{ mol dm}^{-3} \\ &= 1.308 \times 10^{-5} \text{ mol dm}^{-3} \times 143.5 \text{ g mol}^{-1} = \mathbf{1.875 \times 10^{-3} \text{ g dm}^{-3}} \end{aligned}$$

**Problem:** The EMF of cell  $\text{Ag} | \text{AgI}(s) | 0.05 \text{ M KI} || 0.05 \text{ M AgNO}_3 | \text{Ag}$  is 0.0788 V. Calculate solubility product of AgI.

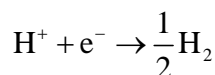
$$E_{\text{cell}} = \frac{0.059}{1} \log_{10} \frac{[\text{Ag}^+]_{\text{RHS}}}{[\text{Ag}^+]_{\text{LHS}}} ; \quad 0.788 = \frac{0.059}{1} \log \frac{[0.05]}{[\text{Ag}^+]_{\text{LHS}}}$$

**Soln:**  $[\text{Ag}^+]_{\text{LHS}} = 2.203 \times 10^{-15}$

$$K_{sp} \text{ of AgI} = [\text{Ag}^+][\text{I}^-] = [2.203 \times 10^{-15}][0.05] = \mathbf{1.10 \times 10^{-16}}$$

**(iii) To Calculate pH of Solution**

Consider hydrogen electrode,



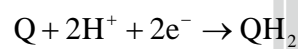
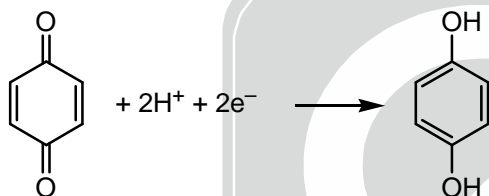
$$E_{\text{H}^+|\text{H}_2} = E_{\text{H}^+|\text{H}_2}^0 - \frac{0.0591}{n} \log \frac{(P_{\text{H}_2})^{1/2}}{[\text{H}^+]}$$

If  $P_{\text{H}_2} = 1$  bar then,

$$E_{\text{H}^+|\text{H}_2} = 0 - 0.0591 \log \frac{1}{[\text{H}^+]}$$

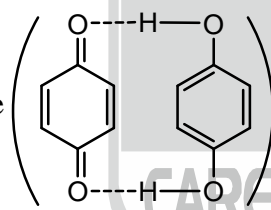
$$E_{\text{H}^+|\text{H}_2} = -0.0591 \{-\log [\text{H}^+]\}$$

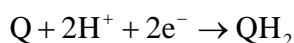
$$E_{\text{H}^+|\text{H}_2} = -0.0591 \text{ pH}$$

→ **Quinhydrone Electrode :-**  $\text{Q}, \text{QH}_2, \text{H}^+ | \text{Au}$ 

Quinone

Hydroquinone

Quinhydrone  is slightly soluble in water releasing quinone and hydroquinone in the same amount.

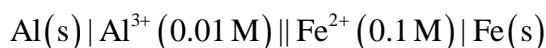


$$E = E^0 - \frac{0.0591}{2} \log \frac{[\text{QH}_2]}{[\text{Q}][\text{H}^+]^2}$$

$$E = E^0 - \frac{0.0591}{2} \{-\log [\text{H}^+]^2\} \quad ([\text{Q}] = [\text{QH}_2])$$

$$E = E^0 - 0.0591 \text{ pH}$$

$$E_{\text{Q}, \text{QH}_2, \text{H}^+ | \text{Au}}^0 = 0.6996 \text{ V}$$

**Problem:** The cell potential for the following electrochemical system at 25°C is:**[TIFR-2013]**

(a) 1.23 V

(b) 1.21 V

(c) 1.22 V

(d) -2.10 V

Given : Standard reduction potential of  $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$  is  $-1.66 \text{ V}$  at 25°C

Standard reduction potential of  $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$  is  $-0.44 \text{ V}$  at  $25^\circ\text{C}$

**Soln.** Net cell reaction :-  $2\text{Al}(\text{s}) + 3\text{Fe}^{2+}(\text{aq}) \longrightarrow 2\text{Al}^{3+}(\text{aq}) + 3\text{Fe}(\text{s})$

$$E = E_{\text{cell}}^0 - \frac{0.0591}{6} \log \frac{[\text{Al}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

$$= [-0.44 - (-1.66)] - \frac{0.0591}{6} \log \frac{(10^{-2})^2}{(10^{-1})^3}$$

$$E = 1.22 - \frac{0.0591}{6} \log 10^{-1}$$

$$E = 1.22 + \frac{0.0591}{6} = 1.229 \approx 1.23 \text{ V}$$

**Correct option is (a)**

**Problem:** According to the Nernst equation, the potential of an electrode changes by  $59.2 \text{ mV}$  whenever the ratio of the oxidized and the reduced species changes by a factor of 10 at  $25^\circ\text{C}$ . What would be the corresponding change in the electrode potential if the experiment is carried out at  $30^\circ\text{C}$  ?

[TIFR-2015]

(a)  $59.2 \text{ mV}$  (b)  $71.0 \text{ mV}$  (c)  $60.2 \text{ mV}$  (d) None of the above

**Soln.**  $\text{M}^{n+} + n\text{e}^- \longrightarrow \text{M}$   
At  $298 \text{ K}$ ,

$$E_1 = E^0 - \frac{0.0591}{n} \log \frac{[\text{Reduced}]}{[\text{Oxidised}]}$$

On changing the ratio by factor 10

$$E_2 = E^0 - \frac{0.0591}{n} \log 10 \frac{[\text{Reduced}]}{[\text{Oxidised}]}$$

$$= E^0 - \frac{0.0591}{n} \log \frac{[\text{Reduced}]}{(\text{Oxidation})} - \frac{0.0591}{n} \log 10$$

$$E_2 = E_1 - \frac{0.0591}{n}$$

$$\text{or } E_2 - E_1 = \frac{59.1}{n} \text{ mV}$$

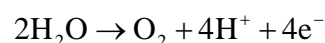
The case taken in the problem has  $n = 1$

$$E_2 - E_1 = 59.1 \text{ mV}$$

**Correct option is (c)**

**Problem:** The standard redox potential of water oxidation to dioxygen is  $-1.23 \text{ V}$ ,

[TIFR-2012]



The redox potential of the same reaction at  $\text{pH} = 7$  would be :

(a)  $-0.41 \text{ V}$  (b)  $-1 \text{ V}$  (c)  $-0.82 \text{ V}$  (d)  $-1.64 \text{ V}$

**Soln.**  $2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad E = -1.23 \text{ V}$



$$E = E^0 - \frac{0.0591}{n} \log [H^+]^4$$

$$E = E^0 + \frac{0.0591}{4} \left\{ -\log [H^+]^4 \right\}$$

$$E = E^0 + 0.0591 \text{ pH}$$

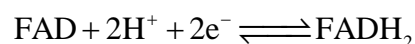
At pH = 7

$$E = E^0 + (0.0591 \times 7) = -1.23 + (0.0591 \times 7)$$

$$E = -0.82 \text{ V}$$

**Correct option is (c)**

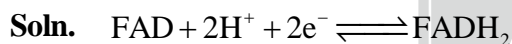
**Problem:** FAD is a redox-active molecule which takes part in many important biological reactions. The redox potential of FAD at pH = 7.0 is given below [TIFR-2014]



$$E_{\text{FADH}_2/\text{FAD}} = -0.180 \text{ V}$$

Calculate the redox potential when the media is acidified to pH 0

- (a) 0 V                      (b) 0.24 V                      (c) 0.12 V                      (d) none of the above



$$E = E^0 - \frac{0.0591}{2} \log \frac{1}{[H^+]^2}$$

$$E = E^0 - \frac{0.0591}{2} \left\{ -\log [H^+]^2 \right\}$$

$$E = E^0 - 0.0591 \text{ pH}$$

At pH = 7

$$E = E^0 - 0.0591 \times 7 = E^0 - 0.4137$$

$$E^0 = -0.180 + 0.4137 = 0.2337 \text{ V}$$

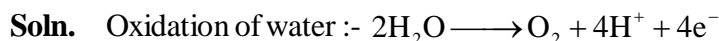
At pH = 0

$$E = E^0 = 0.2337 \text{ V}$$

**Correct option is (b)**

**Problem:** Chemical oxidation of water to produce  $\text{O}_2$  gas is an energy demanding reaction, done routinely by plants using the process called photosynthesis. By how many eV will it be uphill if the water oxidation reaction be carried out at pH = 0 versus at pH = 7.0? [TIFR-2016]

- (a) 0.41 eV                      (b) -1.6 eV  
 (c) -0.41 eV                      (d) cannot be calculated based on the data given.



$$E = E^0 - \frac{0.0591}{4} \log [H^+]^4$$

$$E = E^0 + 0.0591 \text{ pH}$$

At pH = 0

$$E_1 = E^0$$

At pH = 7

$$E_2 = E^0 + 0.0591 \times 7$$

$$E_2 = E_1 + 0.4137$$

$$E_2 - E_1 = 0.4137 \text{ V}$$

By definition, 1eV is the amount of energy gained or lost by an electron moving across an electric potential difference of 1 volt

⇒ 1 volt corresponds to 1 eV

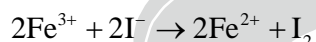
So, 0.4137 V corresponds to 0.4137 eV

**Correct option is (a)**

**Problem:** Given the following  $E^0$  values involving both a one electron and a two electron process,



Find  $E_{\text{cell}}^0$  for the overall Reaction



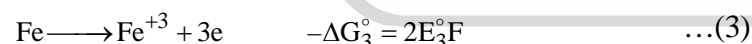
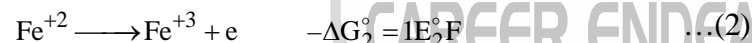
**Soln.**



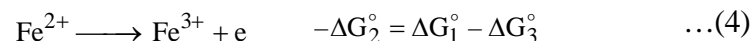
As net cell reaction is obtained by subtraction of equation (2) from (1) and also both equation (1) and (2) have same number of electrons involved.

$$\text{So, } E^0 = 0.771 - 0.536 = 0.235 \text{ V}$$

**Problem:** If  $E_1^0$  is standard electrode potential for  $\text{Fe}/\text{Fe}^{+2}$  and  $E_2^0$  for  $\text{Fe}^{+2}/\text{Fe}^{+3}$  and  $E_3^0$  for  $\text{Fe}/\text{Fe}^{+3}$ . Derive a relation between  $E_1^0$ ,  $E_2^0$  and  $E_3^0$ .



Subtracting equation (1) from (3)

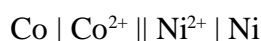


$$E_2^0 F = 3E_3^0 F - 2E_1^0 F$$

$$E_2^0 = \frac{2E_1^0 + E_3^0}{3}$$

$$3E_2^0 = 2E_1^0 + E_3^0$$

**Problem:** Calculate the emf of the cell,



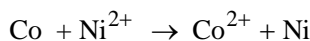
If the concentrations are

$$(a) [\text{Ni}^{2+}] = 1.0 \text{ m} \quad \text{and} \quad [\text{Co}^{2+}] = 0.10 \text{ m}$$

$$(b) [\text{Ni}^{2+}] = 0.010 \text{ m} \quad \text{and} \quad [\text{Co}^{2+}] = 1.0 \text{ m}$$

Given that,  $E_{\text{Ni}^{2+}/\text{Ni}}^0 = -0.257 \text{ V}$  and  $E_{\text{Co}^{2+}/\text{Co}}^0 = -0.280 \text{ V}$

**Soln.** The cell reaction is



Half cell reactions are



The standard emf ( $E^\circ$ ) is thus  $-0.257 - (-0.280) = 0.023 \text{ V}$ , and  $n = 2$ . The cell emf at the first concentrations specified (a) is

$$\begin{aligned} E &= 0.023 - \frac{0.0257}{2} \ln \frac{[\text{Co}^{2+}]}{[\text{Ni}^{2+}]} \\ &= 0.023 - \frac{0.0257}{2} \ln 0.10 = 0.023 + 0.030 = 0.053 \text{ V} \end{aligned}$$

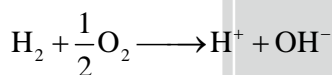
$$\begin{aligned} \text{In (b), } E &= 0.023 - \frac{0.0257}{2} \ln \frac{1.0}{0.010} \\ &= 0.023 - 0.059 = -0.036 \text{ V} \end{aligned}$$

We see that the cell operates in opposite directions in the two cases.

**Problem:** At  $25^\circ\text{C}$ , the free energy of formation of  $\text{H}_2\text{O}(\text{l})$  is  $-56700 \text{ cal mol}^{-1}$  with that of its ionisation to  $(\text{H}^+ + \text{OH}^-)$  is  $19050 \text{ cal mol}^{-1}$ . What is the reversible emf of the cell at  $25^\circ\text{C}$ ?



Addition of above two reactions gives, net cell reaction.



$$\Delta G = -56700 + 19050 = -37650 \text{ cal mol}^{-1} = -158130 \text{ Joule mol}^{-1}$$

$$\therefore \Delta G = -nEF$$

$$\therefore E = -\frac{\Delta G}{nF} = \frac{158130}{2 \times 96500} = 0.819 \text{ V}$$

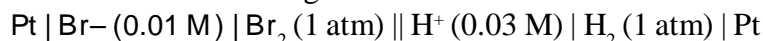
**Problem:** A zinc electrode is dipped in a  $0.1 \text{ M}$  solution of  $\text{ZnSO}_4$  at  $25^\circ\text{C}$ . Assuming that salt is dissociated to 20% at this dilution. Calculate the electrode potential.  $E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76 \text{ V}$



$$\text{Concentration of } [\text{Zn}^{+2}] = \frac{0.1 \times 20}{100} \text{ M}$$

$$\begin{aligned} E_{\text{Zn}/\text{Zn}^{+2}} &= E_{\text{Zn}^{+2}/\text{Zn}}^\circ - \frac{0.059}{2} \log[\text{Zn}^{+2}] \\ &= (-0.76) - \frac{0.059}{2} \log \frac{0.1 \times 20}{100} \\ &= 0.76 - \frac{0.059}{2} \log \frac{1}{50} = \mathbf{0.81 \text{ V}} \end{aligned}$$

**Problem:** Calculate the emf of the following cell at 25°C



Given:  $E_{\text{Br}_2/\text{Br}^-}^\circ = +1.08 \text{ V}$

**Soln.** Cell reaction,  $2\text{Br}^- + 2\text{H}^+ \longrightarrow \text{Br}_2 + \text{H}_2$

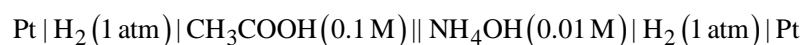
$$E_{\text{cell}} = E_{\text{RHS}}^\circ - E_{\text{LHS}}^\circ \quad [\because E_{\text{Hydrogen}}^\circ = 0]$$

$$= 0 - 1.08 \text{ V} = -1.08 \text{ V}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{2} \log \frac{P_{\text{Br}_2} \times P_{\text{H}_2}}{[\text{Br}^-]^2 [\text{H}^+]^2}$$

$$= -1.08 - \frac{0.059}{2} \log \frac{1}{(0.03)^2 (0.01)^2} = -1.08 - 0.208 = -1.288 \text{ V}$$

**Problem:** Calculate the emf of cell



$K_a$  for  $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$ ,  $K_b$  for  $\text{NH}_4\text{OH} = 1.8 \times 10^{-5}$

**Soln:** At L.H.S.  $\text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COO}^- + \text{H}^+$

$$[\text{H}^+] = C\alpha = C \sqrt{\frac{K_a}{C}} = \sqrt{K_a C} = \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.34 \times 10^{-3} \text{ mol litre}^{-1}$$

At R.H.S.  $\text{NH}_4\text{OH} \longrightarrow \text{NH}_4^+ + \text{OH}^-$

$$[\text{OH}^-] = C\alpha = C \sqrt{\frac{K_b}{C}} = \sqrt{K_b C} = \sqrt{1.8 \times 10^{-5} \times 0.01} = 0.42 \times 10^{-3} \text{ mol litre}^{-1}$$

$$[\text{H}^+][\text{OH}^-] = 10^{-14}$$

$$[\text{H}^+] = \frac{10^{-14}}{0.42 \times 10^{-3}} = 2.359 \times 10^{-11} \text{ mol litre}^{-1}$$

Now, for cell,

At LHE  $\frac{1}{2} \text{H}_2 \longrightarrow \text{H}^+ + \text{e}^-$

At RHE  $\text{H}^+ + \text{e}^- \longrightarrow \frac{1}{2} \text{H}_2$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{1} \log \frac{[\text{H}^+]_{\text{LHE}}}{[\text{H}^+]_{\text{RHE}}}$$

$$= -\frac{0.059}{1} \log \frac{1.34 \times 10^{-3}}{2.35 \times 10^{-3}} = -0.457 \text{ volt}$$

**Problem:** For the cell  $\text{Mg}(\text{s}) | \text{Mg}^{2+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}(\text{s})$ , calculate the equilibrium constant at 25°C and maximum work that can be obtained during operation of cell.

Given:  $E_{\text{Mg}/\text{Mg}^{2+}}^\circ = +2.37 \text{ V}$  and  $E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$

**Soln.**  $\text{Mg} + 2\text{Ag}^+ \longrightarrow \text{Mg}^{2+} + 2\text{Ag}$

$$E_{\text{cell}}^0 = E_{\text{Mg}/\text{Mg}^{2+}}^0 + E_{\text{Ag}^+/\text{Ag}}^0 = 2.37 + 0.80 = 3.17 \text{ V}$$

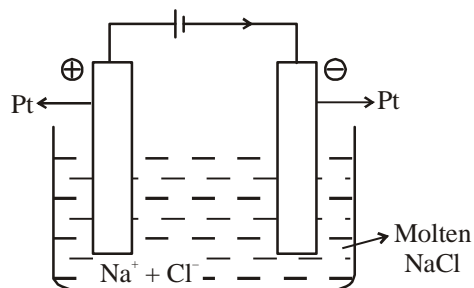
$$\therefore W_{\text{max}} = \Delta G^\circ = -nE^\circ F = 2 \times 3.17 \times 96500 = 6.11 \times 10^5 \text{ Joule} = -6.11 \times 10^2 \text{ kJ}$$

**ELECTROLYTIC CELLS :-** The cell in which non spontaneous chemical reaction is carried out using electrical energy.

Anode :- Oxidation (positive terminal)

Cathode :- Reduction (negative terminal)

### 1. Electrolysis of Molten NaCl :-

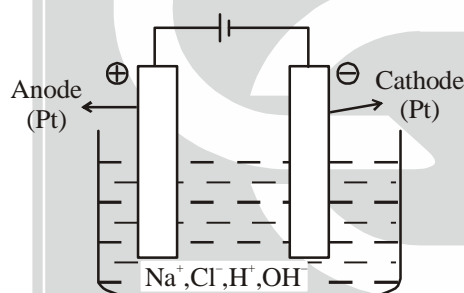


Cathode Reduction :-  $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$

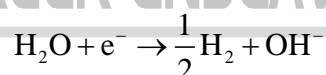
Anode :-  $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$

Net Reaction :-  $\text{Na}^+ + \text{Cl}^- \rightarrow \text{Na} + \frac{1}{2}\text{Cl}_2$

### 2. Electrolysis of Aqueous NaCl :-

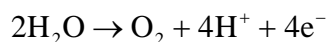


Possible Reactions at cathode :-  $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$



The reaction observed is reduction of water due to high reduction potential.

Possible Reactions at anode :-  $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$



Reaction observed is oxidation of  $\text{Cl}^-$  due to high over potential for oxidation of water even though oxidation potential of water is higher than oxidation potential of  $\text{Cl}^-$ .

**Over Potential / Over Voltage :-** It is the difference between the potential at which gas is actually evolved and the calculate value of potential.

**Over potential :-**  $E_{\text{actual}} - E_{\text{calculated}}$

Value of overpotential depends on

- (i) Nature of ion
- (ii) Nature of electrode

In the above process, pH increases due to formation of NaOH as by product.