

# ELECTROCHEMISTRY

## PART IV: THERMODYNAMICS OF ELECTROCHEMICAL CELLS

### Definition of Cells:

A cell is a device or mechanism in which chemical reactions can be used to produce electrical energy, conversely, electrical energy can be used to carry out chemical reactions that do not proceed spontaneously. It consists of two electrodes immersed partly into ionic solution and connected by an external metallic conductor. Chemical reactions occur at the surface of the electrodes and as a result, transfer of charge usually in the forms of electrons occurs to or from neutral molecules or ions. An electrode can act as a source or as a sink of electrons.

### Type of Cells:

The electrochemical cells may be classified into two types:

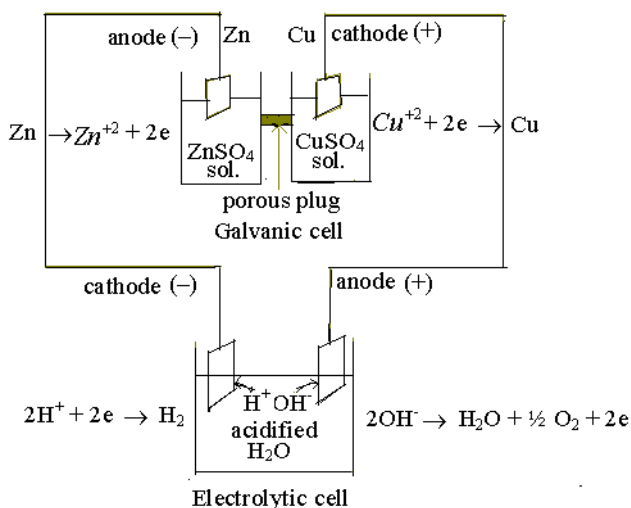
- (a) **Electrolytic Cells:** Electrical energy from an external source is used to bring about chemical change at the electrodes. Charging of Pb-storage cell or electrical purification of metals is of this type of cells:
- (b) **Galvanic Cells:** Free energy of a spontaneous redox reaction is converted into electrical energy. Daniel cell, dry cell are the examples of this type of cells.

### Sign Convention:

In galvanic cell, there is surplus of electrons at anode due to oxidation reaction while there is deficit of electrons at cathode due to reduction reaction. The electrons pass from the anode to the cathode to sustain the chemical reaction. Thus, anode is given (-ve) sign and cathode (+ve) sign.

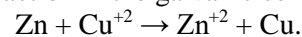
But in electrolyte cell, anode is (+ve) electrode since anions are discharged here and cathode is (-ve) electrode as cations are discharged at the electrode.

However, in both cells, oxidation occurs at the anode and reduction at cathode. We can connect these two types of cells giving full illustration of the above facts.

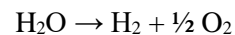


cell	anode		cathode	
	Sign	type of reaction	Sign	type of reaction
Galvanic cell	(-)	oxidation	(+)	reduction
Electrolytic cell	(+)	oxidation	(-)	reduction

Reaction in the galvanic cell

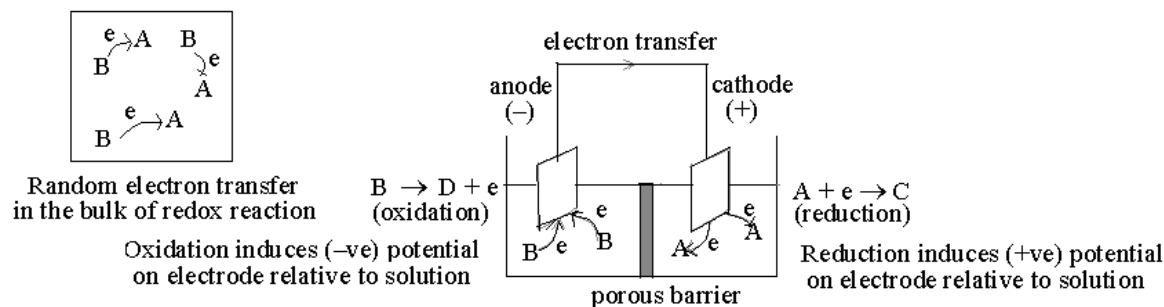


Reaction at the electrolyte cell



### Mechanism of Galvanic Cell:

Let the redox reaction occurring in the galvanic cell be represented by  $A + B \rightarrow C + D$ .



The overall reaction can be regarded as composed of oxidation or de-electronation step  $B \rightarrow D + e$ . and reduction or electronation step  $A + e \rightarrow C$ .

If the reaction is performed in a beaker by mixing A and B reagents then electron released by B in the oxidation step is transferred to a neighbouring species A. In the mixture, the electron transfer will be random and thus it occurs without doing any useful work.

But the same reaction can be done by separating the species A and B by a porous barrier and connected them by an electric circuit making contact with the solutions via two electrodes – one is acting as source of electrons while the other as sink of electrons. When these two electrodes are connected by a wire, electrons dumped by B can be transferred to A.

Directional nature of electron flow in the galvanic cell produces electrical energy and thus chemical energy of the reaction is directly converted into electrical energy.

### Representation of Galvanic Cell:

The above pictorial representation of the Daniel cell is written in symbolic form as given below:



Vertical lines indicate phase boundaries. (–ve) electrode (i.e. anode) is written at the left and (+ve) electrode (i.e. cathode) is in the right. Conc. or activity is written within bracket. Double vertical lines are used for no liquid junction either by inserting salt bridge or porous plug.

### Reversible and Irreversible Galvanic Cells:

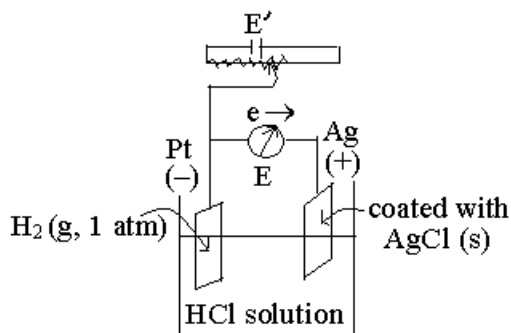
#### Reversible cell:

In the reversible cells, the following conditions are maintained.

- The chemical reaction of the cell stops when an exactly equal opposing emf is applied.
- The chemical reaction of the cell is reversed and the current flows in opposite direction when the opposing emf is slightly greater than that of the cell.

Let us consider a cell in which the reaction occurs as,  $\text{H}_2 (\text{g}) + 2\text{AgCl} (\text{s}) \rightarrow 2\text{Ag} (\text{s}) + 2\text{HCl} (\text{aq})$ .

The cell is represented as



The cell is connected in opposition to a battery of variable potential ( $E'$ ) and variability is controlled by rheostat.

Let the potential of the cell is  $E$ .

- Now if cell potential ( $E$ ) = external potential ( $E'$ ), there is no reaction and no current-flow in the circuit.
- If  $E'$  be decreased infinitesimally such that  $E > E'$ , the cell reaction  $\text{H}_2 (\text{g}) + 2\text{AgCl} (\text{s}) \rightarrow 2\text{Ag} (\text{s}) + 2\text{HCl} (\text{aq})$  continues and infinitesimally small current flows from the cell

(iii) If  $E'$  is increased infinitesimally i.e.  $E < E'$ , the reaction is reversed and infinitesimally small current flows from the battery to the cell. The non-spontaneous reaction  $2\text{Ag} (\text{s}) + 2\text{HCl} (\text{aq}) \rightarrow \text{H}_2 (\text{g}) + 2\text{AgCl} (\text{s})$  occurs and the cell will act as electrolyte cell. If same amount of electricity is passed, it is possible to bring the reaction back to its initial state, i.e. reaction can be reversed. Reversible thermodynamics is applicable only to the reversible cells.

#### Irreversible Cell:

Any other cell which does not obey the above conditions is termed as irreversible. A cell consisting of zinc and copper electrodes dipped into the solution of sulphuric acid is **irreversible**.

The cell is represented as  $\text{Zn (s)} \mid \text{H}_2\text{SO}_4 (\text{aq}) \mid \text{Cu (s)}$ . The cell reaction could not be reversed by controlling the external potential ( $E'$ ).

When  $E > E'$ , the cell reaction is  $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$  and the  $\text{H}_2$  gas is liberated along the Cu electrode (cathode).

When  $E < E'$ , the cell reaction is  $\text{Cu} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2$  and  $\text{H}_2$  gas is evolved along the Zn electrode.

The cell reaction is not reversed.

Further, reaction  $\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{+2} + \text{H}_2$  continues to occur whether the circuit of the cell is closed or open.

As the thermodynamical conditions of reversibility are not maintained, so the principles of reversible thermodynamics are not applied to the irreversible cells.

#### Reversible Electrodes:

The electrodes that constitute the reversible cells are called reversible electrodes. Some examples of this type of electrodes are:  $Zn^{+2} | Zn, Cu^{+2} | Cu$  (1<sup>st</sup> type);  $Cl^- | AgCl(s) | Ag, Cl^- | Hg_2Cl_2(s) | Hg$  (2<sup>nd</sup> type);  $(Fe^{+3}, Fe^{+2}) | Pt, (Ce^{+4}, Ce^{+3}) | Pt$  (3<sup>rd</sup> type electrodes).

#### Condition of Reversible electrodes:

To have reversibility at an electrode, all reactants and products of the electrode half cell must be present at the electrode. For example, Zn when dipped partially into  $ZnSO_4$  solution, it constitutes reversible electrode. The half cell reaction is  $Zn^{+2} + 2e \rightarrow Zn$  (reduction reaction). Both the reactant ( $Zn^{+2}$ ) and product (Zn) are present forming an interface. But if Zn is partially dipped into NaCl solution, it will not be reversible electrode.

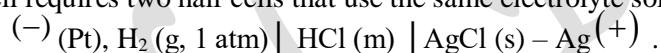
#### Irreversibility in Daniel Cell:

The Daniel cell,  $(-) Zn | ZnSO_4 (c_1) || CuSO_4 (c_2) | Cu (+)$

is also not a truly reversible cell as when the reaction is reversed under the condition  $E < E'$ , the electrode reactions are reversed but the transport of ions at the liquid junction is not reversed. When  $E > E'$ , the reaction at the left half cell is  $Zn \rightarrow Zn^{+2} + 2e$  and at the right half cell,  $Cu^{+2} + 2e \rightarrow Cu$ . At the junction,  $Zn^{+2}$  ions move from the left to right half cell and  $SO_4^{2-}$  ions move from right to left half cell.

But when  $E < E'$ , the cell acts as electrolyte cell and at the left half cell,  $Zn^{+2} + 2e \rightarrow Zn$  i.e. Zn is plating out while at the right half cell, Cu dissolves as  $Cu \rightarrow Cu^{+2} + 2e$ . The electrode reaction is reversed. But at the junction,  $Cu^{+2}$  ions move from right half cell to left half cell and  $SO_4^{2-}$  moves from left half cell to right half cell and the process is not reversed in the liquid junction. However, when very small amount electricity is drawn or passed, the change in the electrodes and at the junction is negligible and so the cell is regarded as reversible cell.

A truly reversible galvanic cell requires two half cells that use the same electrolyte solution as shown below:



**Question:** Daniel cell is a (A) reversible electrochemical cell (B) irreversible electrochemical cell  
(C) reversible electrolytic cell (D) irreversible electrolytic cell

**Answer:** (B)

[Hyderabad Central Univ. Adm. to M Sc 2014]

#### EMF of a Cell and its Measurement:

**Definition of EMF:** The potential difference of a cell is measured between two electrodes, and when there is no current is drawn from the cell, it is called electromotive force (emf). Thus, the emf of a cell ( $E_{cell}$ ) is the limiting value of the electric potential difference between two electrodes as current (I) drawn tends to zero.

$$E_{cell} = (E_{RHE} - E_{LHE}), \text{ as } I \rightarrow 0,$$

where  $E_{RHE}$  is reduction potential of right electrode and  $E_{LHE}$  is reduction potential of the left electrode.

This difference of potentials which causes a current to flow from the electrode of higher potential to the one of lower potential is the electromotive force (emf). However it is not force but it is the energy supplied by the cell divided by the electric charge transported through the cell.  $E_{cell}$  is the property that we determine and relate it with other properties of the cell.

In practice, it is possible to measure  $E_{cell}$  by an instrument, called potentiometer in which the current drawn from the cell is negligible.

#### Limitations of Voltmeter for emf measurement:

- Voltmeter draws some current from the cell, causing thereby a change in the emf due to formation of reaction products at the electrodes. The change in conc. of the reacting components around the electrodes changes the emf of the cell.
- With appreciable current flow, part of the emf will have to be utilized to overcome the internal resistance of the cell and hence potential measured by the voltmeter will not be total cell emf.

$$\text{When voltmeter is used, the emf of the cell, } E_{cell} = I(R + r) = IR + Ir = \Delta\phi + Ir,$$

where R is the external resistance here that of voltmeter and r is the internal resistance of the cell.

Voltmeter measures the potential difference ( $\Delta\phi$ ). Thus when voltmeter is used, the emf ( $E_{\text{cell}}$ ) is found less.

Only when  $I \rightarrow 0$ ,  $E_{\text{cell}} = \Delta\phi$ .

(c) Moreover,  $E_{\text{cell}}$  is the reversible emf of the cell and thus when finite current flows, the cell reaction can not occur reversibly.

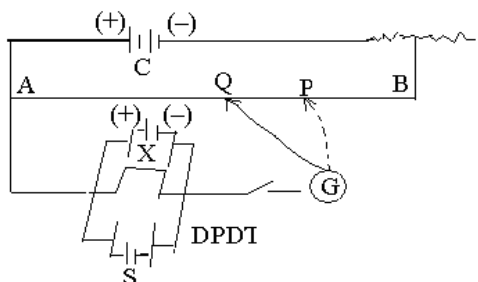
For that reason, voltmeter is not used to measure the cell potential ( $E_{\text{cell}}$ ).

However, we may use electronic or vacuum tube voltmeter where  $R$  is very large and current drawn is negligible (less than or around  $10^{-5}$  amp).

### Measurement of emf:

Poggendorf first used an instrument called potentiometer that compensates the cell potential by coupling an external battery so that either no current or negligibly small current is drawn from the cell. Potentiometer is composed of a slide wire AB of uniform cross sectional area and high resistance. A storage battery (C) of constant emf larger than that of the cell to be measured is connected in series with the terminals of AB. The cell (X) of unknown emf is connected to A with poles in the same direction as that of C (i.e. in opposition). The other terminal of the cell is connected through galvanometer (G) to the sliding wire by a double-pole-double-through (DPDT) key. The position of the terminal is moved along the sliding contact and the rheostat is adjusted until at P, there is no current flows through G. At this point, potential difference between A and P due to the battery C is just balanced by the emf of the cell ( $E_X$ ). Next, a standard cell (S) with known emf ( $E_S$ ) is connected to the sliding wire by means of DPDT. The null-point, Q on the sliding wire is again determined. Fall in potential along AQ is exactly compensated by the emf of the standard cell ( $E_S$ ).

Since the cross sectional area of the wire is uniform, so we have



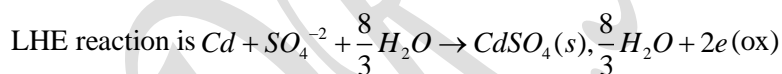
$$\frac{E_X}{E_S} = \frac{\text{pot. diff. between A and P}}{\text{pot. diff. between A and Q}} = \frac{\text{resist. of AP}}{\text{resist. of AQ}} = \frac{\text{length of AP}}{\text{length of AQ}}$$

$$\text{or, } E_X = E_S \times \frac{AP}{AQ}. \text{ Knowing } E_S, E_X \text{ can be calculated.}$$

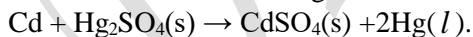
If the galvanometer is sufficient sensitive to balance the potential (without current-flow), precision is extended up to  $1 \times 10^{-5}$  volt for small value of emf down to  $1 \times 10^{-7}$  volt.

### Standard Weston Cadmium Cell:

This cell is most widely used as standard cell and it is represented as

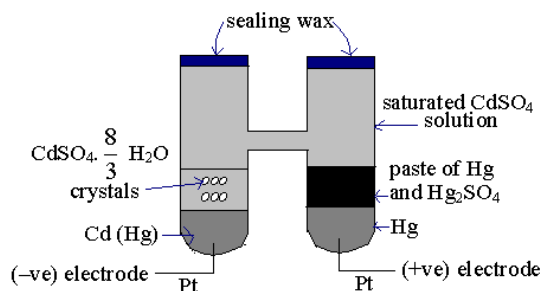


Adding two electrode reactions, we get the net cell reaction as



The cell is prepared in a H-shaped vessel. One arm containing 12.5% Cd amalgam acts as (-ve) electrode and other arm containing Hg in contact with a paste of Hg and  $Hg_2SO_4$  acts as (+ve) electrode. The whole of the vessel is then filled up with

saturated solution of  $CdSO_4$ . Few crystals of  $CdSO_4 \cdot \frac{8}{3} H_2O$  are added over the (-ve) electrode.



The vessel is sealed off. The electrodes are connected to the external circuit through Pt wire sealed at the bottom of the two electrodes. Its emf is measured by comparison with potential difference across a standard known resistance carrying an absolutely known current (e.g., Ag - Coulometer).

### Reasons for using it as standard cell:

- (a) It is physically and chemically stable for a long period of time. It is reversible.  
(b) It is capable of giving a constant and reproducible emf.  
(c) Its temperature - coefficient is also quite small.  $E_{t^{\circ}C} / V = 1.01830 - 4.06 \times 10^{-5} (t - 20) - 9.5 \times 10^{-7} (t - 20)^2$ .

Thus, emf at 20°C is,  $E_{20^{\circ}C} = 1.01830$  V and temperature coefficient is  $dE/dT = -4.06 \times 10^{-5} VK^{-1}$ .

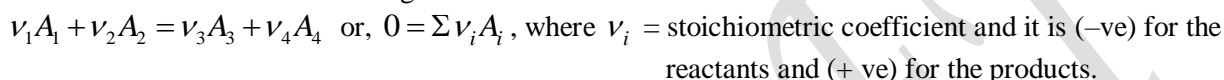
**Problem:** Calculate the emf of Weston Cadmium cell at 25 °C if its temperature variation is given as

$$E_{t^{\circ}C} / V = 1.01830 - 4.06 \times 10^{-5} (t - 20) - 9.5 \times 10^{-7} (t - 20)^2.$$

**Solution:**  $E_{25^{\circ}C} = 1.01830 - 4.06 \times 10^{-5} (25 - 20) - 9.5 \times 10^{-7} (25 - 20)^2 V = 1.01807$  V.

### Thermodynamics of Galvanic Cells:

Let us consider the following chemical reaction that occurs in a Galvanic cell



The free energy change due to the reaction at constant temperature (T) and pressure (P) is  $\Delta G_{T,P} = \sum \nu_i \mu_i$ .

Since the reaction in the cell occurs spontaneously, the free energy (G) of the reaction decreases and this decrease in free energy is transformed into electrical energy (which is non-mechanical energy). Thus, the important relation between the change in chemical energy ( $\Delta G$ ) with electrical energy ( $nFE$ ) is given by

$$-\Delta G_{T,P} = nFE_{cell}. \text{ This relation is valid for reversible isothermal isobaric process only.}$$

Here,  $n$  = number of gm equivalent chemical change occurs and  $E_{cell}$  is the emf of the cell or it is the potential difference of reversible cell when it is in open circuit.  $F$  = faraday of electricity = 96500 C mol<sup>-1</sup>.

This relation makes a bridge between thermodynamics and electrochemistry.

Since  $E_{cell}$  can be determined of a cell by potentiometer,  $\Delta G_{T,P}$  of the cell reaction can be calculated.

#### Intensive nature of $E_{cell}$ :

Again,  $E_{cell} = -(\Delta G_{T,P} / nF)$ .  $E_{cell}$  is an intensive property as  $\Delta G$  and  $n$  are both extensive in nature.

It means that  $E_{cell}$  does not depend on the amount of the materials present in the cell, so it is same whether the cell is big or small. It also does not depend on the mode of writing the equation of the cell reaction.

#### Emf and spontaneity of a cell reaction:

We have the relation,  $-\Delta G_{T,P} = nFE_{cell}$ . For a process (either physical or chemical) to proceed spontaneously,  $\Delta G_{T,P} < 0$ , hence for a cell reaction to go spontaneously,  $E_{cell} > 0$ .

So, the criteria of spontaneity and equilibrium of a cell reaction is specified in terms of cell potential ( $E_{cell}$ ) as:

$\Delta G$	$E_{cell}$	cell reaction
(-ve)	(+ve)	spontaneous
(+ve)	(-ve)	non-spontaneous
0	0	equilibrium

**Expression of  $\Delta S$  of cell reaction:**

$$\text{Again, } \Delta S = - \left[ \frac{\partial(\Delta G)}{\partial T} \right]_P \text{ or, } \Delta S = - \left[ -nF \left( \frac{\partial E_{cell}}{\partial T} \right)_P \right] \text{ or, } \Delta S = nF \left( \frac{\partial E_{cell}}{\partial T} \right)_P, \text{ where } \left( \frac{\partial E_{cell}}{\partial T} \right)_P \text{ is the}$$

temperature-coefficient of the cell emf. This relation can be used to calculate  $\Delta S$  of the cell reaction.

**Expression of  $\Delta H$  of cell reaction:**

$$\text{Gibbs Helmholtz equation gives } \Delta G = \Delta H - T\Delta S \text{ or, } \Delta H = \Delta G + T\Delta S.$$

Putting the expression of  $\Delta G$  and  $\Delta S$ , we get the enthalpy of the cell reaction as

$$\Delta H = -nFE_{cell} + T \times nF \left( \frac{\partial E_{cell}}{\partial T} \right)_P \text{ or, } \Delta H = nF \left[ T \left( \frac{\partial E_{cell}}{\partial T} \right)_P - E_{cell} \right]$$

This electrical measurement of enthalpy of a cell reaction gives more accurate value than the other methods used for determination of  $\Delta H$  (such as calorimetric method, equilibrium constant determination at different temperatures using van't Hoff equation, etc).

**Temperature-dependency of Cell Potential:**

$$\text{We have already deduced that } \Delta S = nF \left( \frac{\partial E_{cell}}{\partial T} \right)_P \text{ or, } \left( \frac{\partial E_{cell}}{\partial T} \right)_P = \frac{\Delta S}{nF}.$$

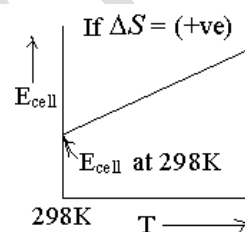
If the cell does not contain a gaseous electrode,  $\Delta S$  is small, less than 50 J/K and it remains almost constant.

If the cell does not contain a gaseous electrode,  $\Delta S$  is small, less than 50 J/K and it remains almost constant.

Separating the variables and integrating assuming  $\Delta S$  independent of T, we get

$$\int_{E_{298K}}^{E_T} dE_{cell} = \frac{\Delta S}{nF} \int_{298K}^T dT \text{ or, } E_T = E_{298K} + \frac{\Delta S}{nF} (T - 298). \text{ When } E_{cell} \text{ is plotted against T, it gives a linear plot}$$

as shown above.



**Problem:** The emf of the cell,  $(-)\text{Cd} \left| \text{CdCl}_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}(s) \right| \text{sat. CdCl}_2 \text{ sol.} \left| \text{AgCl}(s) \right| \text{Ag}^{(+)}$  at 25°C is 0.67533V

and temperature coefficient is  $-6.5 \times 10^{-4} \text{V K}^{-1}$ . Calculate the values of  $\Delta G$ ,  $\Delta S$  and  $\Delta H$  at 25 °C for reaction  $\text{Cd}(s) + 2\text{AgCl}(s) = 2\text{Ag} + \text{CdCl}_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}(s)$

**Answer:** For the reaction,  $n = 2$ .  $\Delta G = -130.313 \text{ kJ mol}^{-1}$ ,  $\Delta S = -125 \text{ JK}^{-1} \text{ mol}^{-1}$  and  $\Delta H = -167.580 \text{ kJ mol}^{-1}$ .

**Problem:** The statement that is correct for both electrochemical (galvanic) cells and electrolytic cells is

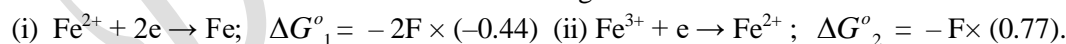
- (A)  $\Delta G = -nFE$  (B) Free energy decreases in both the cells (C) The cell potentials are temperature-independent (D) Chemical energy is converted into electrical energy in both cells. [IIT-JAM 2004]

**Answer:** (A).

**Problem:** Given that  $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}$  and  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77\text{V}$ , the  $E^\circ_{\text{Fe}^{3+}/\text{Fe}}$  is

- (A) 1.21 V (B) 0.33 V (C) -0.036 V (D) 0.036 V [IIT-JAM 2005], [NET, 2014 (II)]

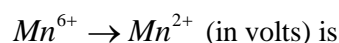
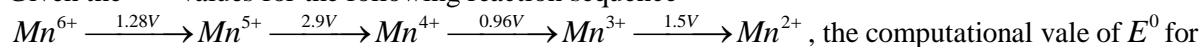
**Answer:** The electrode reaction with their  $\Delta G^\circ$  values are given bellow.



Now adding (i) and (ii), we get  $\text{Fe}^{3+} + 3e \rightarrow \text{Fe}$ ;  $\Delta G^\circ = \Delta G^\circ_1 + \Delta G^\circ_2 = 2F \times (0.44) - F(0.77)$

or,  $\Delta G^\circ = 0.11 F = -3FE^\circ_{\text{Fe}^{3+}/\text{Fe}}$  or,  $E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -0.036 \text{V}$ . Thus the correct option is (C).

**Problem:** Given the  $E^0$  values for the following reaction sequence



[GATE, 2015]

**Ans.** 1.66 V

### Nernst Equation of Cell Potential:

The Nernst equation is derived more easily from van't Hoff reaction isotherm of chemical reaction. Let the chemical reaction occurring within the cell is  $\nu_1 A_1 + \nu_2 A_2 = \nu_3 A_3 + \nu_4 A_4$  or,  $0 = \sum \nu_i A_i$ , where  $\nu$ 's are the stoichiometric coefficients and A's are the reacting components present in the cell and  $\nu_i = (-ve)$  for the reactants and (+ve) for the products.

The van't Hoff reaction isotherm of the reaction is  $\Delta G = \Delta G^0 + RT \ln Q_a$ , where  $\Delta G^0 =$  standard free energy of the reaction and  $Q_a =$  arbitrarily chosen activity quotient of the products and reactants and it is expressed for the

above reaction as  $Q_a = \frac{a_3^{\nu_3} \times a_4^{\nu_4}}{a_1^{\nu_1} \times a_2^{\nu_2}} = \prod a_i^{\nu_i}$ . These  $a$ 's are the arbitrarily chosen activities of the reacting

components. Again,  $\Delta G^0 = -RT \ln K_a$ , where  $K_a =$  activity equilibrium constant of the reaction and

$$K_a = \left( \frac{a_3^{\nu_3} \times a_4^{\nu_4}}{a_1^{\nu_1} \times a_2^{\nu_2}} \right)_{\text{equilibrium}}, \text{ where these activities are for the reacting components at equilibrium of the reaction.}$$

But these thermodynamic terms are connected with electrochemical terms through the relations as given below:

$\Delta G = -nFE_{\text{cell}}$  and  $\Delta G^0 = -nFE_{\text{cell}}^0$ . These relations are valid for isothermal isobaric and reversible processes.

In the relation,  $E_{\text{cell}}^0 =$  standard emf of the cell when all the reacting components are at unit activity.

Inserting these relations in van't Hoff reaction isotherm, we get  $-nFE_{\text{cell}} = -nFE_{\text{cell}}^0 + RT \ln Q_a$

or,  $E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln Q_a$  or,  $E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303RT}{nF} \log Q_a$ . This is Nernst equation for cell potential.

The term  $\frac{2.303RT}{F}$  occurs very frequently in the equation. The value of this term at 25 °C is given as

$$\frac{2.303RT}{F} = \frac{2.303 \times 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{96500 \text{ C mol}^{-1}} = 0.059 \text{ V}. \text{ Thus Nernst equation at 25 °C is}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n} \log Q_a \text{ and } \Delta G^0 = -RT \ln K_a = -nFE_{\text{cell}}^0 \text{ or, } E_{\text{cell}}^0 = \frac{2.303RT}{nF} \log K_a \text{ and at 25 °C, the}$$

expression of standard cell potential is  $E_{\text{cell}}^0 = \frac{0.059}{n} \log K_a$ .

### Nernst Equation of Electrode Potential:

Electrode potential or half-cell potential can also be expressed by Nernst equation.

Let us take the example of Daniel cell,  $(-)\text{Zn} | \text{ZnSO}_4 (a_{\text{Zn}^{2+}}) || \text{CuSO}_4 (a_{\text{Cu}^{2+}}) | \text{Cu}^{(+)}$ .

The cell reaction is given by  $\text{Zn} + \text{CuSO}_4(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{Cu}$  or,  $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$ .

Splitting the cell reaction into two half cell reactions, we can write

At the anode oxidation reaction is  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e$  and at cathode reduction reaction is  $\text{Cu}^{2+} + 2e \rightarrow \text{Cu}$ .

Adding the two half cell reactions, we get the net cell reaction.

Thus net cell reaction = Oxidation reaction at the anode + Reduction reaction at the cathode.

Thus the cell potential

However  $E_{\text{reduction}} = -E_{\text{oxidation}}$ , so  $E_{\text{Zn}(\text{s})|\text{Zn}^{2+}} = -E_{\text{Zn}^{2+}|\text{Zn}}$ . Now the convention is to express electrode potential as

reduction potential, so  $E_{\text{cell}} = E_{\text{Cu}^{2+}|\text{Cu}} - E_{\text{Zn}^{2+}|\text{Zn}}$  i.e.,  $E_{\text{cell}} = E_{\text{RHE}} - E_{\text{LHE}}$  and  $E_{\text{cell}}^0 = E_{\text{Cu}^{2+}|\text{Cu}}^0 - E_{\text{Zn}^{2+}|\text{Zn}}^0$ .

Thus we can write  $\left( E_{\text{Cu}^{2+}|\text{Cu}(\text{s})} - E_{\text{Zn}^{2+}|\text{Zn}(\text{s})} \right) = \left( E_{\text{Cu}^{2+}|\text{Cu}(\text{s})}^0 - E_{\text{Zn}^{2+}|\text{Zn}(\text{s})}^0 \right) - \left( \frac{0.059}{2} \log \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right)$  since  $a_{\text{solid}} = 1$ .

Splitting the two potentials,  $E_{\text{Cu}^{2+}|\text{Cu}(\text{s})} = E_{\text{Cu}^{2+}|\text{Cu}(\text{s})}^0 + \frac{0.059}{2} \log a_{\text{Cu}^{2+}}$  and  $E_{\text{Zn}^{2+}|\text{Zn}(\text{s})} = E_{\text{Zn}^{2+}|\text{Zn}(\text{s})}^0 + \frac{0.059}{2} \log a_{\text{Zn}^{2+}}$ .

The potentials are reduction potentials and we shall continue to write the electrode reduction potentials only. In general, for electrode,  $X^{+n}(\text{solution})|X(s)$ , the reaction of which is  $X^{+n} + ne \rightarrow X(s)$  (reduction). The

electrode potential,  $E_{X^{+n}|X(s)} = E_{X^{+n}|X(s)}^0 - \frac{2.303RT}{nF} \log \frac{a_{X(s)}}{a_{X^{+n}(sol)}}$  or,  $E_{X^{+n}|X(s)} = E_{X^{+n}|X(s)}^0 + \frac{0.059}{n} \log a_{X^{+n}}$

at 25 °C and  $a_{solid} = 1$ . At other temperature,  $E_{X^{+n}|X(s)} = E_{X^{+n}|X(s)}^0 + \frac{RT}{nF} \ln a_{X^{+n}}$ .

**Calculation of equilibrium constant of the cell reaction:** Standard cell potential helps to calculate the equilibrium constant of the cell reaction by using the relation, Thus for Daniel cell,

$$E_{cell}^0 = E_{Cu^{2+}|Cu}^0 - E_{Zn^{2+}|Zn}^0 = 0.337 - (-0.761) = 1.098 \text{ V} . E_{cell}^0 = \frac{0.059}{n} \log K_a \text{ or, } \log K_a = \frac{n \times E_{cell}^0}{0.059}$$

Putting,  $n = 2$ ,  $E_{cell}^0 = 1.098 \text{ V}$ , we get  $\log K_a = 37.22$  and  $K_a = 1.66 \times 10^{37}$  at 25 °C.

This shows that the reaction in the cell is almost complete.

**Problem:** Which is the correct Nernst equation for the redox reaction  $O + ne \rightleftharpoons R$ ?

$$(1) E = E^0 - \frac{RT}{nF} \ln \frac{[O]}{[R]} \quad (2) \frac{[O]}{[R]} = e^{\frac{nF}{RT}(E-E^0)} \quad (3) \frac{[O]}{[R]} = e^{-\frac{nF}{RT}(E-E^0)} \quad (4) \frac{[O]}{[R]} = e^{\frac{RT}{nF}(E-E^0)}$$

**Ans.** Correct option is (3).

[NET (CSIR – UGC), 2013]

**Problem:** If the ratio of composition of oxidized and reduced species in electrochemical cell, is given, as

$[O]/[R] = e^2$ , the correct potential difference will be

$$(1) E - E^0 = + \frac{2RT}{nF} \quad (2) E - E^0 = - \frac{2RT}{nF} \quad (3) E - E^0 = \frac{RT}{nF} \quad (4) E - E^0 = - \frac{RT}{nF}$$

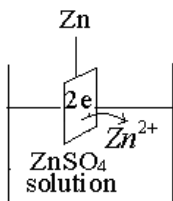
**Ans.** The correct option is (1).

[NET (CSIR – UGC), 2011(I)]

### Origin of Electrode Potential and its Determination:

When an electrode is partially dipped into an electrolyte solution containing the reacting components of the half cell reaction, there occurs a charge separation between the metallic electrode and electrolyte solution. Due to this charge separation, potential difference develops at the phase boundary. This potential difference is called electrode potential.

Let us illustrate with the electrode,  $Zn|Zn^{2+}$ . Zn metal is partially dipped into  $ZnSO_4$  solution. Minute amount of



Zn undergoes dissolution forming  $Zn^{2+}$  by the process  $Zn \rightarrow Zn^{2+} + 2e$ .

When a few atoms of Zn dissolves, the solution becomes positively charged due to excess  $Zn^{2+}$  ion while the electrons that are liberated, remain stick with the Zn metal and it becomes negatively charged. Thus, there develops a charge separation between Zn metal and  $ZnSO_4$  solution at the interface between these two phases. This process of dissolution of Zn into  $Zn^{2+}$  will stop since positively charged  $ZnSO_4$  solution will prevent further dissolution of Zn.

Very quickly equilibrium is set up for the electrode reaction,  $Zn \rightarrow Zn^{2+} + 2e$ .

At this stage, the potential difference between Zn metal and  $ZnSO_4$  solution is called potential of  $Zn|Zn^{2+}$  electrode.

It is not possible to measure a single electrode potential experimentally as an electrode reaction can not take place independently. Neither the oxidation nor the reduction reaction can occur by itself. Thus we need two electrodes to measure the cell potential by potentiometer and the cell potential is the difference of two electrode potentials forming the cell. That is,  $E_{cell} = E_{RHE} - E_{LHE}$ . Thus, the difference of two electrode potentials is obtained. Now, to get the potential of one electrode, other electrode is taken a reference electrode whose potential is known. Frequently, the reference electrode is taken normal  $H_2$  electrode and its potential is assigned to zero by convention at all temperatures.

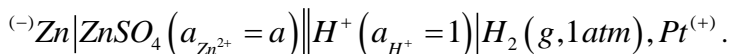


Normal H<sub>2</sub> electrode is prepared by bubbling H<sub>2</sub> gas at 1 atm pressure around platinised platinum foil dipped partially into an acid solution of  $a_{H^+} = 1$ . This electrode potential is represented

as  $E_{H^+(a_{H^+}=1)||H_2(g,1atm)} = 0$  (by convention at all temperatures).

Since all the reacting components of the electrode are at unit activity, it is also called primary standard electrode, and its potential,  $E_{H^+|H_2}^0$  is zero.

Now if we like to determine the potential of  $Zn^{2+}|Zn$  electrode, we shall prepare a cell in which this electrode is coupled with normal H<sub>2</sub> electrode.



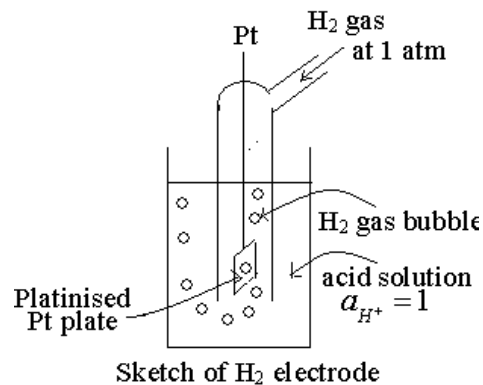
The cell potential,  $E_{cell} = E_{H^+|H_2}^0 - E_{Zn^{2+}|Zn}$  or,  $E_{cell} = -E_{Zn^{2+}|Zn}$  since  $E_{H^+|H_2}^0 = 0$ .  $E_{cell}$  is determined by potentiometer and thus the potential of single electrode,  $Zn^{2+}|Zn$  can be determined. This potential is with reference to normal H<sub>2</sub> electrode whose potential is assigned to zero by convention.

**Problem:** The standard emf of the cell,  $Pt, H_2(g)|HCl(soln)|AgCl(s), Ag(s)$

- (1) increases with T (2) decreases with T (3) remains unchanged with T (4) decreases with [HCl]

[NET(CSIR – UGC), 2015 (II)]

**Answer: (2).** Hints:  $\Delta S = (-)$  for the cell reaction and so,  $E_{cell}$  decreases with rise in temperature.



Standard Reduction Electrode Potentials in Aqueous Solution at 25°C	Standard Potential
Cathode (Reduction) Half-Reaction	$E^0$ (volts)
$Li^+(aq) + e \rightarrow Li(s)$	-3.04
$K^+(aq) + e \rightarrow K(s)$	-2.92
$Ca^{2+}(aq) + 2e \rightarrow Ca(s)$	-2.76
$Na^+(aq) + e \rightarrow Na(s)$	-2.71
$Mg^{2+}(aq) + 2e \rightarrow Mg(s)$	-2.38
$Al^{3+}(aq) + 3e \rightarrow Al(s)$	-1.66
$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$	-0.76
$Cr^{3+}(aq) + 3e \rightarrow Cr(s)$	-0.74
$Fe^{2+}(aq) + 2e \rightarrow Fe(s)$	-0.41
$Cd^{2+}(aq) + 2e \rightarrow Cd(s)$	-0.40
$Ni^{2+}(aq) + 2e \rightarrow Ni(s)$	-0.23
$Sn^{2+}(aq) + 2e \rightarrow Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e \rightarrow Pb(s)$	-0.13
$Fe^{3+}(aq) + 3e \rightarrow Fe(s)$	-0.04
$2H^+(aq) + 2e \rightarrow H_2(g)$	0.00

$\text{Sn}^{4+}(\text{aq}) + 2\text{e} \rightarrow \text{Sn}^{2+}(\text{aq})$	0.15
$\text{Cu}^{2+}(\text{aq}) + \text{e} \rightarrow \text{Cu}^{+}(\text{aq})$	0.16
$\text{ClO}_4^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e} \rightarrow \text{ClO}_3^{-}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$	0.17
$\text{AgCl}(\text{s}) + \text{e} \rightarrow \text{Ag}(\text{s}) + \text{Cl}^{-}(\text{aq})$	0.22
$\text{Cu}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Cu}(\text{s})$	0.34
$\text{ClO}_3^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e} \rightarrow \text{ClO}_2^{-}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$	0.35
$\text{IO}^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e} \rightarrow \text{I}^{-}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$	0.49
$\text{Cu}^{+}(\text{aq}) + \text{e} \rightarrow \text{Cu}(\text{s})$	0.52
$\text{I}_2(\text{s}) + 2\text{e} \rightarrow 2\text{I}^{-}(\text{aq})$	0.54
$\text{ClO}_2^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e} \rightarrow \text{ClO}^{-}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$	0.59
$\text{Fe}^{3+}(\text{aq}) + \text{e} \rightarrow \text{Fe}^{2+}(\text{aq})$	0.77
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e} \rightarrow 2\text{Hg}(\text{l})$	0.80
$\text{Ag}^{+}(\text{aq}) + \text{e} \rightarrow \text{Ag}(\text{s})$	0.80
$\text{Hg}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Hg}(\text{l})$	0.85
$\text{ClO}^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e} \rightarrow \text{Cl}^{-}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$	0.90
$2\text{Hg}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Hg}_2^{2+}(\text{aq})$	0.90
$\text{NO}_3^{-}(\text{aq}) + 4\text{H}^{+}(\text{aq}) + 3\text{e} \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	0.96
$\text{Br}_2(\text{l}) + 2\text{e} \rightarrow 2\text{Br}^{-}(\text{aq})$	1.07
$\text{O}_2(\text{g}) + 4\text{H}^{+}(\text{aq}) + 4\text{e} \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^{+}(\text{aq}) + 6\text{e} \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	1.33
$\text{Cl}_2(\text{g}) + 2\text{e} \rightarrow 2\text{Cl}^{-}(\text{aq})$	1.36
$\text{Ce}^{4+}(\text{aq}) + \text{e} \rightarrow \text{Ce}^{3+}(\text{aq})$	1.44
$\text{MnO}_4^{-}(\text{aq}) + 8\text{H}^{+}(\text{aq}) + 5\text{e} \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	1.49
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^{+}(\text{aq}) + 2\text{e} \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.78
$\text{Co}^{3+}(\text{aq}) + \text{e} \rightarrow \text{Co}^{2+}(\text{aq})$	1.82
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{e} \rightarrow 2\text{SO}_4^{2-}(\text{aq})$	2.01
$\text{O}_3(\text{g}) + 2\text{H}^{+}(\text{aq}) + 2\text{e} \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	2.07
$\text{F}_2(\text{g}) + 2\text{e} \rightarrow 2\text{F}^{-}(\text{aq})$	2.87

## Different Type of Reversible Electrodes or Half-Cells:

A reversible galvanic cell consists of two reversible electrodes or half-cells. One is (-ve) electrode in which electrons are generated due to oxidation reaction and other is (+ve) electrode in which electrons are consumed by its reduction reaction. These processes within cell cause transport of electrons from (-ve) electrode (anode) to the (+ve) electrode (cathode) through the outer circuit.

There are three types of different electrodes used to constitute a cell. The electrodes are discussed in details – such as electrode representation, electrode reaction, electrode potential and their applications.

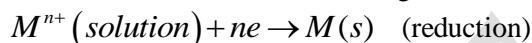
### (A) Type I electrodes: An element in contact with its ions in solution:

It may have various forms.

#### (1) Metal – metal ion electrode $[M^{n+}(\text{solution})|M(s)]$

This is an important type of electrodes and is widely used to prepare a half-cell.

The metal is in electrochemical equilibrium with a solution containing  $M^{n+}$  ions. The half-cell reaction is



The examples are  $Zn^{2+}(\text{soln}) + 2e \rightarrow Zn(s)$ ,  $Cu^{2+}(\text{soln}) + 2e \rightarrow Cu(s)$ ,  $Ag^+(\text{soln}) + e \rightarrow Ag(s)$ , etc.

The potential of the electrode  $E_{M^{n+}|M} = E_{M^{n+}|M}^0 - \frac{RT}{nF} \ln \left( \frac{1}{a_{M^{n+}}} \right)$  or,  $E_{M^{n+}|M} = E_{M^{n+}|M}^0 + \frac{0.059}{n} \log a_{M^{n+}}$  at 25 °C.

[since  $a_M = 1$ ]. For  $Zn^{2+}|Zn$  electrode, the potential is  $E_{Zn^{2+}|Zn} = E_{Zn^{2+}|Zn}^0 + \frac{0.059}{2} \log a_{Zn^{2+}}$ .

**Determination of electrode potential:** The potential of the electrode can be determined by coupling this electrode with normal  $H_2$  electrode or any other reference electrode such as saturated calomel electrode whose potential is known. The potential of the cell is measured by a potentiometer.  $E_{\text{cell}} = E_{M^{n+}|M} - E_{\text{ref}}$ .

**Application of the electrode:** Determining the potential of the electrode, it is possible to find the activity and hence conc. of the metal ion in solution. Even micro molar ( $10^{-6}$  M) conc. of metal ion in solution can be determined very accurately. The valence of the metal ion can also be determined from the electrode potential.

**Limitation:** The metals that react with the solvent can not be used. Group IA and group IIA metals (such as Na, Ca, etc) react with water; Zn reacts in acidic solution. For certain metals, air is to be replaced from the cell by  $N_2$  gas to prevent oxidation of the metal by dissolved  $O_2$ .

#### (2) Amalgam Electrodes: $[M^{n+}(\text{solution})|M(Hg)]$

**Description of the amalgam electrode:** An amalgam is a solution of a metal in liquid Hg. In this electrode, the metal in amalgam is in equilibrium with its ions in solution. Hg remains as inert solvent and does not participate in the electrode process.

**Electrode reaction:** The reaction at the electrode is  $M^{n+} + ne \rightleftharpoons M(Hg)$ . (reduction)

**Examples of the electrodes:**  $Na^+(\text{solution})|Na(Hg)$ ,  $Cd^{2+}(\text{solution})|Cd(Hg)$ ,  $Ag^+(\text{solution})|Ag(Hg)$ ,  $Ca^{2+}(\text{solution})|Ca(Hg)$ , etc.

**Potential of the electrode:** The potential of the electrode at 25 °C is given as  $E_{am} = E_{M^{n+}|M}^0 - \frac{0.059}{n} \log \frac{a_{M(Hg)}}{a_{M^{n+}(\text{soln})}}$

or,  $E_{am} = \left[ E_{M^{n+}|M}^0 - \frac{0.059}{n} \log a_{M(Hg)} \right] + \frac{0.059}{n} \log a_{M^{n+}(\text{soln})} = E_{am}^0 + \frac{0.059}{n} \log a_{M^{n+}(\text{soln})}$ , where  $E_{am}^0$  is constant

when conc. of  $M(Hg)$  remains fixed.

**Preference over pure metal electrodes:** Metals more reactive than Hg act in the electrodes same way as the pure metals but activity is lowered. Thus, it is sometimes preferred to pure metal – metal ion electrode. Na, Ca metals can be used in aqueous solution of the ions in the form of amalgam of the metal. The equilibrium is quickly attained; activity of the metal is moderated by dilution. The effect of impurity present in the metal is minimized due to dilution.

**Determination of  $E_{am}^0$ :** Standard amalgam electrode potential can be easily determined by coupling the electrode with metal / metal ion electrode. One cell, for example, is prepared as  $(-)\text{Cd}|\text{CdSO}_4(\text{sol})|\text{Cd}(\text{Hg})^{(+)}$ .

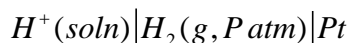
$$E_{\text{cell}} = E_{\text{RHE}} - E_{\text{LHE}} = \left( E_{\text{am}}^0 + \frac{0.059}{2} \log a_{\text{Cd}^{2+}} \right) - \left( E_{\text{Cd}^{2+}|\text{Cd}}^0 + \frac{0.059}{2} \log a_{\text{Cd}^{2+}} \right) = E_{\text{am}}^0 - E_{\text{Cd}^{2+}|\text{Cd}}^0.$$

$E_{\text{cell}}$  is determined by potentiometer and  $E_{\text{Cd}^{2+}|\text{Cd}}^0$  is known from the table of standard potential data.

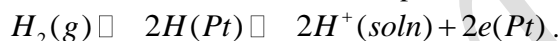
### (3) Gas Electrodes:

**Construction of a gas electrode:** The electrode consists of a gas bubbled at a certain pressure round an inert metal foil or wire placed in a solution containing the ion with which the gas is reversible.

**H<sub>2</sub> gas electrode:** The most important electrode of this type is hydrogen electrode. It is represented as



**Advantage of Pt as inert metal:** The Pt contains a coat of electrolytically deposited colloidal Pt particles (platinum black). It catalyses the forward and backward reaction  $2\text{H}^+(\text{soln}) + 2e \rightleftharpoons \text{H}_2(\text{g}, P \text{ atm})$ , so the equilibrium is rapidly established. The H<sub>2</sub> gas is chemisorbed as H-atoms on the platinum surface:



**Normal H<sub>2</sub> electrode:** It is represented as  $\text{H}^+(a_{\text{H}^+} = 1)|\text{H}_2(\text{g}, 1 \text{ atm}), (\text{Pt})$  and it is primary standard with which all other electrodes are compared. Its potential, by convention, is taken zero at all temperatures

**Potential of H<sub>2</sub> electrode:** The potential of the electrode is given as  $E_{\text{H}^+|\text{H}_2} = E_{\text{H}^+|\text{H}_2}^0 - \frac{0.059}{2} \log \frac{a_{\text{H}_2}}{a_{\text{H}^+}^2}$  at 25 °C

but  $a_{\text{H}_2} = P$  in atm which is usually taken as 1 atm, and  $E_{\text{H}^+|\text{H}_2}^0 = 0$ , so  $E_{\text{H}^+|\text{H}_2} = -\frac{0.059}{2} \log \frac{1}{a_{\text{H}^+}^2}$

$$\text{or, } E_{\text{H}^+|\text{H}_2} = -0.059 \text{ pH}.$$

**Application of the electrode:** The electrode may be utilized to determine pH of a solution by setting up the cell



$$E_{\text{cell}} = E_{\text{sat cal}} - E_{\text{H}^+|\text{H}_2} \quad \text{or, } E_{\text{cell}} = 0.2415 + 0.059 \text{ pH}$$

$E_{\text{sat cal}}$  is 0.2415 V at 25 °C and this electrode is reference electrode whose potential remains fixed.  $E_{\text{cell}}$  is determined by potentiometer and so pH of the solution may be calculated.

**Cl<sub>2</sub> electrode:** This is also gas electrode and its representation is  $\text{Cl}^-(\text{soln})|\text{Cl}_2(\text{g}), (\text{Pt})$ .

The electrode reaction is  $\frac{1}{2}\text{Cl}_2 + e \rightarrow \text{Cl}^-$  and its potential is  $E_{\text{Cl}_2|\text{Cl}^-} = E_{\text{Cl}_2|\text{Cl}^-}^0 - 0.059 \log \frac{a_{\text{Cl}^-}}{\sqrt{a_{\text{Cl}_2}}}$ .

**O<sub>2</sub> electrode:** This gas electrode is represented as  $\text{OH}^-(\text{soln})|\text{O}_2(\text{g}), (\text{Pt})$ .

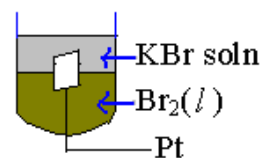
The electrode reaction is  $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e \rightarrow 2\text{OH}^-$  and its potential is  $E_{\text{O}_2|\text{OH}^-} = E_{\text{O}_2|\text{OH}^-}^0 - \frac{0.059}{2} \log \frac{a_{\text{OH}^-}^2}{\sqrt{a_{\text{O}_2}}}$ .

O<sub>2</sub> electrode is not very suitable in practical purposes of measuring pH or pOH of the solution as the equilibrium is not quickly attained.

### (4) Non gas – non metal electrodes:

The members of this type include Br<sub>2</sub> electrode:  $\text{Br}^-(\text{soln})|\text{Br}_2(\text{l}), (\text{Pt})$ ,

the reaction is  $\frac{1}{2}\text{Br}_2(\text{l}) + e \rightarrow \text{Br}^-(\text{soln})$



Schematic representation of Br<sub>2</sub> electrode

I<sub>2</sub> electrode:  $I^-(soln)|I_2(s), (Pt)$ , the reaction is  $\frac{1}{2}I_2(s) + e \rightarrow I^-(soln)$

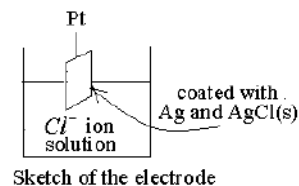
**(B) Type II electrodes:** This type of electrodes consist of either metal – insoluble salt of the metal or metal – insoluble oxide of the metal.

**(1) Metal | insoluble salt of the metal | solution containing common anion of the salt,  $[X^-(soln)|MX(s)|M]$**

**Silver-silver electrode:**

**Preparation of  $Cl^-(soln)|AgCl(s)|Ag$ :** This is most important electrode of this

type. It consists of Ag metal, solid AgCl and a solution that contains  $Cl^-$  (say from KCl or HCl). The electrode contains three phases and it is prepared by electrodeposition of a layer of Ag on a piece Pt foil, followed by electrolytic conversion of part of the Ag to AgCl.



**Electrode reaction:** The Ag metal is in electrochemical equilibrium with the  $Ag^+$  in the solution:  $Ag^+ + e \rightleftharpoons Ag$ . Since the solution is saturated with AgCl and  $Ag^+$  ion is removed from the solution, more AgCl dissolves to maintain the equilibrium,  $AgCl(s) \rightleftharpoons Ag^+(soln) + Cl^-(soln)$ . Combining these two equilibria, we have



**Expression of electrode potential:** According to Nernst equation, the potential at 25 °C is

$$E_{Cl^-(soln)|AgCl(s)|Ag} = E_{Cl^-(soln)|AgCl(s)|Ag}^0 - 0.059 \log a_{Cl^-}, \text{ since } a_{AgCl(s)} = 1 \text{ and } a_{Ag} = 1.$$

The electrode is reversible with  $Cl^-$  ion in solution. Since the solution is in contact with AgCl (s), it is saturated with AgCl and its solubility product,  $K_{sp} = a_{Ag^+} \times a_{Cl^-}$  is maintained. So,  $a_{Cl^-} = K_{sp}/a_{Ag^+}$ . Putting this activity in

the expression of potential of the electrode, we get  $E_{Cl^-(soln)|AgCl(s)|Ag} = E_{Cl^-(soln)|AgCl(s)|Ag}^0 - 0.059 \log (K_{sp}/a_{Ag^+})$

or,  $E_{Cl^-(soln)|AgCl(s)|Ag} = \left[ E_{Cl^-(soln)|AgCl(s)|Ag}^0 - 0.059 \log K_{sp} \right] + 0.059 \log a_{Ag^+}$  at 25 °C.

The term within bracket is constant for the electrode at given temperature.

The electrode can also be viewed as  $Ag^+|Ag$  electrode where Ag metal is in contact with  $Ag^+$  ion in the saturated solution of AgCl and potential of the electrode is given as  $E_{Ag^+|Ag} = E_{Ag^+|Ag}^0 + 0.059 \log a_{Ag^+}$ .

**Determination of solubility product of a sparingly soluble salt:** The two expressions of the electrode potential are same, i.e.,  $E_{Cl^-(soln)|AgCl(s)|Ag} = E_{Ag^+|Ag}$ . Comparing, we get  $E_{Ag^+|Ag}^0 = E_{Cl^-(soln)|AgCl(s)|Ag}^0 - 0.059 \log K_{sp}$ .

At other temperature, the relation is  $E_{Ag^+|Ag}^0 = E_{Cl^-(soln)|AgCl(s)|Ag}^0 - \frac{RT}{F} \ln K_{sp}$ .

The general expression of the relation is  $E_{M^{n+}|M}^0 = E_{X^-(soln)|MX_n(s)|M}^0 - \frac{RT}{nF} \ln K_{sp}$ .

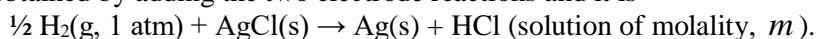
**Problem:** The solubility product of AgBr(s) is  $5 \times 10^{-13}$  at 298 K. If the standard reduction potential of the half cell  $E_{Ag|AgBr(s)|Br^-}^0 = 0.07$  V, the standard reduction potential,  $E_{Ag^+|Ag}^0$  (in volt) is — [GATE, 2015, m = 2]

**Answer: 0.7969 V.**

**Determination of standard electrode potential of  $E_{Cl^-(soln)|AgCl(s)|Ag}^0$ :** This can be done very accurately by the use of the reversible cell,  $(-)(Pt), H_2(g, 1 atm)|HCl(m)|AgCl(s) - Ag^{(+)}$ .

Reaction at LHE:  $\frac{1}{2}H_2(g, 1 atm) \rightarrow H^+ + e$  (oxidation), reaction at RHE:  $AgCl(s) + e \rightarrow Ag(s) + Cl^-$  (reduction).

The net cell reaction is obtained by adding the two electrode reactions and it is



The cell potential,  $E_{cell} = E_{cell}^0 - \frac{RT}{F} \ln a_{HCl}$  (activity of other terms is unity).

$E_{cell}^0$  is standard cell potential and  $E_{cell}^0 = E_{RHE}^0 - E_{LHE}^0 = E_{Cl^-|AgCl(s)|Ag}^0$  as  $E_{H^+|H_2}^0 = 0$  (by convention).

Thus the cell potential,  $E_{cell} = E_{Cl^-|AgCl(s)|Ag}^0 - \frac{RT}{F} \ln a_{HCl} = E_{Cl^-|AgCl(s)|Ag}^0 - \frac{RT}{F} \ln(m^2 \gamma_{\pm}^2)$  as  $a_{HCl} = m^2 \gamma_{\pm}^2$ .

**Relation of mean ionic activity coefficient and cell potential:**  $E_{cell} + \frac{2RT}{F} \ln m = E_{Cl^-|AgCl(s)|Ag}^0 - \frac{2RT}{F} \ln \gamma_{\pm}$ ,

at 25 °C,  $E_{cell} + 0.118 \log m = E_{Cl^-|AgCl(s)|Ag}^0 - 0.118 \log \gamma_{\pm}$  ----- (a)

From Debye-Huckel limiting law,  $\log \gamma_{\pm} = -A z_+ |z_-| \sqrt{i} = -A \sqrt{i} = -A \sqrt{m}$ , where  $A$  is D-H constant and

$A \propto \frac{1}{(DT)^{3/2}}$ . So the potential of the above cell is  $E_{cell} + 0.118 \log m = E_{Cl^-|AgCl(s)|Ag}^0 + 0.118 A \sqrt{m}$

**Plot for determination of  $E_{Cl^-|AgCl(s)|Ag}^0$ :**

Several solutions of different molalities (at lower conc. range) are prepared and cell potentials are determined by potentiometer.

Now, LHS of the equation is plotted against  $\sqrt{m}$ , a straight line is obtained, the extrapolated intercept gives the value of standard

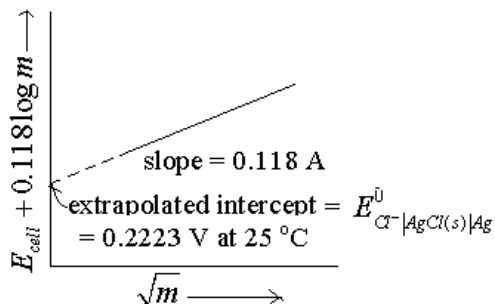
potential of  $Cl^-|AgCl(s)|Ag$  electrode. This plot can also be used to

find the value of D-H constant  $A$  from the slope whose value at

25 °C for aqueous solution is 0.51. When the electrode potential  $E_{Cl^-|AgCl(s)|Ag}^0$  is known, the equation (a)

could be utilized to determine the mean ionic activity coefficient ( $\gamma_{\pm}$ ) of HCl solution of molality,  $m$ .

This emf method is widely used to determine  $\gamma_{\pm}$  of ionic solution of known molality.



**Problem (1):** Solubility product of AgCl,  $K_{sp} = 1.0 \times 10^{-10}$ . Calculate the  $E^0$  for silver – silver chloride electrode immersed in 1.0 (M) KCl at 25 °C. The  $E^0$  for  $Ag^+|Ag$  is 0.799 V.

**Answer:**  $E_{Cl^-|AgCl(s)|Ag}^0 = 0.209$  V.

[Indian Institute of Science, Adm. Test to M Sc, 2003]

**Problem (2):** The solubility product of AgBr(s) is  $5 \times 10^{-13}$  at 298°K. If the standard reduction potential of the half cell,  $E_{Ag|AgBr(s)|Br^-}^0$  is 0.07 V, the standard reduction potential,  $E_{Ag^+|Ag}^0$  (in volts) is -----.

**Answer:**  $E_{Ag^+|Ag}^0 = 0.80$  V.

[GATE, 2015]

**Problem (3):** Two electrodes  $Ag^+|Ag$  and  $Cl^-|AgCl(s)|Ag$  dipped into the solution of aqueous  $AgNO_3$  will have  
(A) Same E and  $E^0$  values (B) Different E and  $E^0$  values (C) Same  $E^0$  values but different E values  
(D) Different  $E^0$  values but same E values.

[IIT-KGP, Adm. to M Sc 2003]

**Answer: (D).**

**Problem (4):** Calculate the solubility product of  $Fe(OH)_3$  at 25 °C. Given,  $Fe \rightarrow Fe^{3+} + 3e$ ;  $E^0 = 0.036$  V

$Fe + 3 OH^- \rightarrow Fe(OH)_3 + 3e$ ;  $E^0 = 0.77$  V.

[Burdwan Univ. 2012]

**Solution:**  $E_{OH^-|Fe(OH)_3|Fe}^0 - \frac{0.059}{3} \log K_{sp} = E_{Fe^{3+}|Fe}^0$ . Putting the values, we get  $-0.77 - \frac{0.059}{3} \log K_{sp} = -0.036$

or,  $K_{sp} = 4.76 \times 10^{-38}$ . [Values of  $E^0$  are given in the problem as oxidation potential]

**Problem (5):** Calculate the solubility product of  $Hg_2Cl_2$  from the following two half-cells:

$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-$ ;  $E_{Cl^-|Hg_2Cl_2(s)|Hg}^0 = 0.2680$  V and

$2Hg^{+2} + 2e \rightarrow 2Hg(l)$ ;  $E_{Hg_2^{+2}|Hg}^0 = 0.80$  V at 25 °C

**Solution:** We have the relation at 25 °C is  $E_{Hg_2^{2+}|Hg}^0 = E_{Cl^-|Hg_2Cl_2(s)|Hg}^0 - \frac{0.059}{2} \log K_{sp}$ . Putting the values,  $0.80 = 0.2680 - \frac{0.059}{2} \log K_{sp}$ . Solving, we get  $K_{sp} = 9.25 \times 10^{-19}$ .

**Problem (6):** The emf at 25 °C of the following cell  $Pt|H_2(g, 1 atm)|HCl(m)|AgCl(s)|Ag$  is 0.4501 volt when  $m = 0.0134 \text{ mol dm}^{-3}$ . Calculate the mean ionic activity coefficient of HCl. (Given,  $E^0 = 0.2223 \text{ volt at } 25^\circ\text{C}$ ). [Viswa Bharati Univ. 1993]

**Solution:** The required relation is  $E_{cell} = E_{cell}^0 - 0.118 \log m - 0.118 \log \gamma_{\pm}$ . Inserting the given data, we get  $0.4501 = 0.2223 - 0.118 \log(0.0134) - 0.118 \log \gamma_{\pm}$ . On solving, we have  $\gamma_{\pm} = 0.649$ .

**Problem (7):** The potential of the cell  $Zn|ZnCl_2(m = 0.01)|AgCl(s) - Ag$  is 1.16 volt. Calculate the activity coefficient of  $ZnCl_2$  solution. Given,  $E_{Zn^{2+}|Zn}^0 = -0.762 \text{ V}$  and  $E_{Cl^-|AgCl(s)|Ag}^0 = 0.2222 \text{ V}$  at 25 °C. [Burdwan Univ. 2004], [Calcutta Univ. 2011]

**Solution:** The cell reaction,  $Zn(s) + 2AgCl(s) \rightarrow 2Ag(s) + ZnCl_2$ . The cell potential,  $E_{cell} = E_{cell}^0 - \frac{0.059}{2} \log a_{ZnCl_2}$ .

But  $E_{cell}^0 = E_{Cl^-|AgCl(s)|Ag}^0 - E_{Zn^{2+}|Zn}^0 = 0.2222 - (-0.762) = 0.984 \text{ V}$  and  $a_{ZnCl_2} = 4m^3 \gamma_{\pm}^3$ .

Putting the values, we get  $1.157 = 0.984 - 0.0295 \log \{4 \times (0.01)^3 \times \gamma_{\pm}^3\}$ . On solving,  $\gamma_{\pm} = 0.699$ .

**Problem (8):** Given that  $E^0(Cl_2|Cl^-) = 1.35 \text{ V}$  and  $K_{sp}(AgCl) = 10^{-10}$  at 25 °C,  $E^0$  corresponding to the electrode reaction  $\frac{1}{2} Cl_2(g) + Ag^+(\text{soln.}) + e \rightarrow AgCl(s)$  is

(1) 0.75 V (2) 1.05 V (3) 1.65 V (4) 1.95 V NET(CSIR – UGC), 2015 (II), m = 4]

**Answer:** Hints: One electrode reaction is  $\frac{1}{2} Cl_2(g) + e \rightarrow Cl^-(\text{soln.})$ ;  $E_{Cl_2|Cl^-}^0 = 1.35 \text{ V}$

and other electrode reaction is  $\frac{1}{2} Cl_2(g) + Ag^+(\text{soln.}) + e \rightarrow AgCl(s)$ ; let the electrode potential is  $x$ .

Subtracting the two, we get the net cell reaction  $AgCl(s) \rightarrow Ag^+ + Cl^-$

The cell potential is  $E_{cell}^0 = E_{Cl_2|Cl^-}^0 - x = 0.059 \log \log(Ag^+ \times Cl^-) = 0.059 \log K_{sp}(AgCl)$ .

Or,  $E_{Cl_2|Cl^-}^0 - x = 0.059 \log \log(Ag^+ \times Cl^-) = 0.059 \log K_{sp}(AgCl)$

Putting the values, we get  $1.35 - x = 0.059 \log 10^{-10}$  or,  $x = 1.95 \text{ V}$ . [Answer (4).]

**Problem (9):** At 25 °C the standard electrode potential for the  $Ag^+|Ag$  electrode is 0.7991 V and the solubility product of AgI is  $8.2 \times 10^{-17}$ . What is the standard electrode potential for  $I^-|AgI(s)|Ag$ . [Burdwan Univ. 2007]

**Answer:**  $E_{I^-|AgI(s)|Ag}^0 = -0.15 \text{ V}$ .

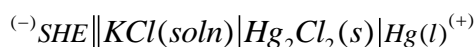
**Calomel electrode:** Another important member of this type is calomel electrode,  $KCl|Hg_2Cl_2(s)|Hg(l)$ .

The electrode reaction is  $Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(\text{soln})$  (reduction reaction).

The electrode potential is  $E_{Cl^-|Hg_2Cl_2(s)|Hg(l)} = E_{Cl^-|Hg_2Cl_2(s)|Hg(l)}^0 - \frac{RT}{2F} \ln a_{Cl^-}^2$ . Other substances are at unit activity.

At 25 °C, the potential is  $E_{Cl^-|Hg_2Cl_2(s)|Hg(l)} = E_{Cl^-|Hg_2Cl_2(s)|Hg(l)}^0 - 0.059 \log a_{Cl^-}$ . But  $E_{Cl^-|Hg_2Cl_2(s)|Hg(l)}^0 = 0.2680 \text{ V}$ .

The electrode is reversible with  $Cl^-$  ion in KCl solution. This electrode is extensively used in laboratory as secondary reference electrode since it can be easily prepared and it attains reversibility rapidly. The potential of the electrode remains constant for long period of time; its value can be obtained by constructing a cell in which standard  $H_2$  electrode is used as one member.

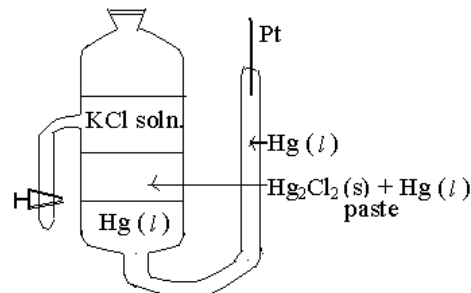


$$E_{cell} = E_{Cl^- | Hg_2Cl_2(s) | Hg(l)} - E_{SHE} = E_{Cl^- | Hg_2Cl_2(s) | Hg(l)} = E_{calomel}, \text{ since } E_{SHE} = 0. \text{ So, } E_{calomel} = E_{cell}.$$

$E_{cell}$  is determined by potentiometer and this gives the value of  $E_{calomel}$ .

$E_{calomel}$  depends on the activity / conc. of KCl solution used in the electrode. Three secondary reference calomel electrodes are normally available depending on the conc. of KCl used.

Conc. of KCl	Saturated	Normal	Decinormal
Electrode potential (V)	0.2415	0.2800	0.3338



**Lead – lead sulphate electrode:** This is another member of this type of electrodes which is used as anode in lead storage cell.

The electrode is represented as  $H_2SO_4(soln) | PbSO_4(s) | Pb$ .

The electrode reaction is  $PbSO_4(s) + 2e \rightarrow Pb(s) + SO_4^{2-}(soln)$ . The potential of the electrode is given as

$$E_{SO_4^{2-}(soln) | PbSO_4(s) | Pb} = E_{SO_4^{2-}(soln) | PbSO_4(s) | Pb}^0 - \frac{RT}{2F} \ln a_{SO_4^{2-}}. \text{ Activities of the other substances are unity.}$$

The standard potential of the electrode,  $E_{SO_4^{2-}(soln) | PbSO_4(s) | Pb}^0 = -0.355 \text{ V}$ .

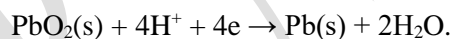
This electrode is reversible with  $SO_4^{2-}$  present in  $H_2SO_4$  solution. All these electrodes are reversible with anion of the electrolyte solution. However, it is possible to prepare this electrode reversible with cation also.

$Sr^{2+} | SrSO_4(s), PbSO_4(s) | Pb$  and the electrode reaction is  $PbSO_4(s) + Sr^{2+} + 2e \rightarrow Pb(s) + SrSO_4(s)$ .

The electrode is reversible with the  $Sr^{2+}$  in solution.

### (2) Metal | insoluble oxide of the metal | $H^+$ or $OH^-$ (soln):

This type of electrode is represented as  $H^+ \text{ or } OH^- | M_2O_n(s) | M(s)$ . The important examples of these electrodes are:  $H^+(soln) | PbO_2(s) | Pb(s)$ ,  $OH^-(soln) | Sb_2O_3(s) | Sb(s)$ . The first electrode is used as cathode in the lead storage cell. The reaction of the electrode,  $H^+(soln) | PbO_2(s) | Pb(s)$  is given as:



$$\text{The potential is written as } E_{H^+ | PbO_2(s) | Pb(s)} = E_{H^+ | PbO_2(s) | Pb(s)}^0 - \frac{RT}{4F} \ln \frac{1}{a_{H^+}^4} = E_{H^+ | PbO_2(s) | Pb(s)}^0 - \frac{RT}{F} \ln \frac{1}{a_{H^+}}.$$

At 25 °C,  $E_{H^+ | PbO_2(s) | Pb(s)}^0 = 1.684 \text{ V}$ . So, the potential of the electrode is  $E_{H^+ | PbO_2(s) | Pb(s)} = 1.684 - 0.059 \text{ pH}$ .

This electrode may also be used to determine pH of the solution (here  $H_2SO_4$ ).

### (3) Type III Electrodes (Redox Electrodes):

Every electrode involves an oxidation – reduction half reaction. But it is convention that the term ‘redox electrodes’ refer only to an electrode whose redox half reaction is between same species of different oxidation states present in the same solution. An inert metal (such as Pt, Au, etc.) is dipped into the solution and it only serves to supply or accept electrons.

**General form of the electrode and its potential:** The general form is  $M^{+n_1}, M^{+n_2} | Pt$ , where  $M^{+n_1}$  is metal ion of higher oxidation state and  $M^{+n_2}$  is of lower oxidation state. The electrode reaction is  $M^{+n_1} + ne \rightarrow M^{+n_2}$  (red), where  $n_1 - n_2 = n$ .

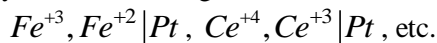


The potential of the electrode is  $E_{M^{+n_1}|M^{+n_2}} = E_{M^{+n_1}|M^{+n_2}}^0 - \frac{RT}{nF} \ln \frac{a_{M^{+n_2}}}{a_{M^{+n_1}}}$ . But the ratio of activities of the two species in the same solution is almost equal to the ratio of conc. of the two species. Thus, the potential at 25 °C is

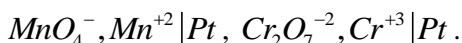
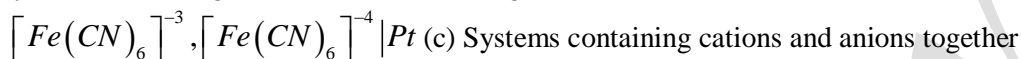
$$E_{M^{+n_1}|M^{+n_2}} = E_{M^{+n_1}|M^{+n_2}}^0 + \frac{0.059}{n} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

**Examples:** This type of electrodes includes the following forms:

(a) Systems containing cations with different charges



(b) Systems containing anions of different charges



**Problem(1):** A platinum electrode is immersed in a solution containing 0.1 (M)  $Fe^{2+}$  and 0.1 (M)  $Fe^{3+}$ .

Its potential is found to be 0.77 V against SHE.

Under standard conditions and considering activity coefficient to be equal to unity the potential of electrode, when the conc. of  $Fe^{3+}$  is increased to 1 (M), is — [GATE, 2014, m = 2]

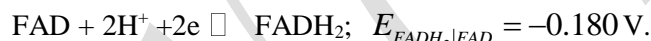
**Solution:**  $E_{Fe^{3+}|Fe^{2+}} = 0.829$  V.

**Problem (2):** According to the Nernst equation, the potential of an electrode changes by 59.2 mV whenever the ratio of the oxidized and reduced species changes by a factor of 10 at 25 °C. What would be the corresponding change in the electrode potential if the experiment is carried out at 30 °C?

(A) 59.2 mV (B) 71.0 mV (C) 60.2 mV (D) None of the above. [TIFR Adm. Test 2015].

**Answer:** (C).

**Problem (3):** 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



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

(A) 0 V (B) 0.24 V (C) (D) 0.12 V (D) none of the above. **Answer:** (B). [TIFR Adm. Test 2014]

**Problem (4):** The potential for the following electrochemical system at 25 °C is



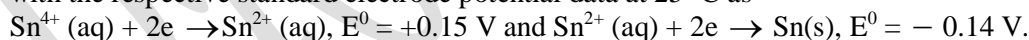
(A) 1.23 V (B) 1.21 V (C) (D) 1.22 V (D) -2.10 V

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

and Standard potential of  $Fe^{2+} + 2e \rightarrow Fe$  is - 0.44V at 25 °C [TIFR Adm. Test 2013]

**Answer:** 1.21 V. So the correct answer is (B).

**Problem (5):** For the cell reaction,  $Sn(s) + Sn^{4+}(aq) \rightleftharpoons 2Sn^{2+}(aq)$ , separate electrode reactions could be written with the respective standard electrode potential data at 25 °C as



When RT/F is given as 25.7 mV, logarithm of the equilibrium constant (ln K) is obtained as

(1) 22.6 (2) 226 (3) 2.26 (4)  $2.26 \times 10^{-1}$ . [CSIR-UGC (NET) 2014 II]

**Answer:** (1)

**Problem (6):** The conc. of  $K^+$  ion inside a biological cell is 20 times higher than outside. The magnitude of potential difference between the two sides is [Given,  $2.303 RT/F = 59 \text{ mV}$ ]

(A) 0 mV (2) 26 mV (3) 77 mV (4) 177 mV. [IIT-JAM 2015]

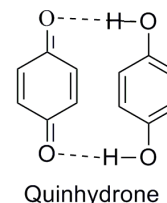
**Answer:** (C)

### Quinhydrone Electrode:

It is an important electrode and is widely used to determine pH of a solution. This is due to simplicity of its set-up in the laboratory.

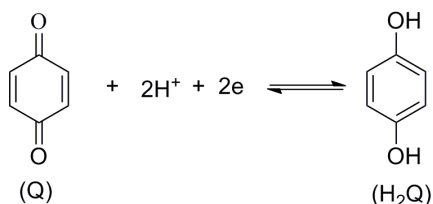
Quinhydrone is a 1:1 molecular compound of quinone (Q) and hydroquinone ( $H_2Q$ ).

It is sparingly soluble in acid solution and decomposes to yield quinone (Q) and hydroquinone ( $H_2Q$ ). An acid solution is saturated with quinhydrone in which an

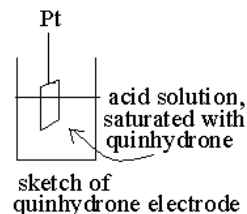


inert electronic electrode of gold or platinum is dipped into the solution.

The electrode is shown as  $H^+ | Q, H_2Q (s) | Pt$  or  $Q, H_2Q$  saturated in acid soln  $| Pt$ .



The electrode reaction is written in brief as  $Q + 2H^+ + 2e \rightleftharpoons H_2Q$  (reduction)



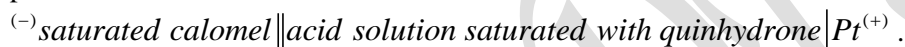
The potential of the electrode is  $E_{H^+|Q, H_2Q(s)|Pt} = E_{H^+|Q, H_2Q(s)|Pt}^0 - \frac{RT}{2F} \ln \frac{a_{H_2Q}}{a_Q \times a_{H^+}^2}$ , where  $E_{H^+|Q, H_2Q(s)|Pt}^0 = 0.6994$  V

and in solution,  $a_{H_2Q} = a_Q$ . Thus, the potential of the electrode at 25 °C,  $E_{H^+|Q, H_2Q(s)|Pt} = 0.6994 - 0.059 pH$ .

The potential depends on the activity of  $H^+$  ion and hence pH of the solution in which quinhydrone is kept saturated in the electrode.

To evaluate  $E_{H^+|Q, H_2Q(s)|Pt}^0$ , the electrode potential is determined at known pH buffer solution and the electrode is

coupled with secondary reference electrode such as saturated calomel electrode. The cell is set up and its potential is determined by potentiometer.



$$E_{cell} = E_{RHE} - E_{LHE} = \left( E_{H^+|Q, H_2Q(s)|Pt}^0 - 0.059 pH \right) - E_{sat.cal} \quad \text{or,} \quad E_{cell} = (0.6994 - 0.059 pH) - 0.2415$$

or,  $E_{cell} = 0.4579 - 0.059 pH$ . Using this relation, pH of the acid solution can be determined. With increase of pH of the solution,  $E_{cell}$  decreases and becomes zero at certain pH. Thus,  $0 = 0.4579 - 0.059 pH$  or,  $pH = 7.76$ .

**Electrode at  $pH \geq 7.76$ :** That is, at  $pH = 7.76$ , the cell potential becomes zero if saturated calomel electrode is used as reference electrode.

Above this pH,  $E_{cell}$  becomes (-ve) and cell set-up is to be reversed. That means calomel electrode will act as (+ve) electrode and quinhydrone electrode as (-ve) electrode.

**Limitation of the electrode:** This electrode is not suitable for solution of  $pH > 8$ , since in this alkaline solution hydroquinone ionizes as  $H_2Q \rightleftharpoons Q^{2-} + 2H^+$  (acts as acid). At this alkaline solution,  $H_2Q$  also gets aerial oxidation. Under this case, linear relationship between  $E_{cell}$  and pH does not hold. Further, this electrode is not used in solution containing oxidizing and reducing agents as they attack quinhydrone.

**Advantages of the electrode:** However, this electrode has several advantages over  $H_2$  electrode. This electrode is very easy to set up, reversibility is quickly attained. A small amount of the solution is needed. Air need not be excluded. This electrode can be used in presence of heavy metal ions and unsaturated organic substances.

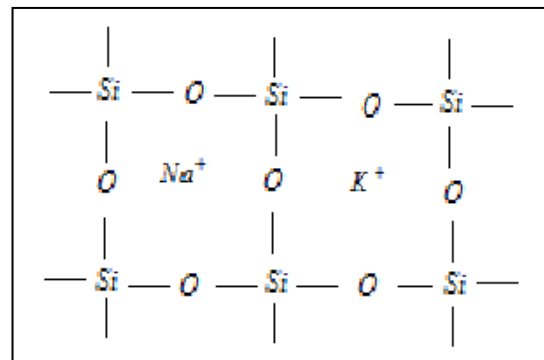
### Glass Electrode:

It is an ion-selective membrane type of electrodes.

**Description of the membrane:** Glass contains a three dimensional net-work of covalently bound Si – O atoms with an overall negative charge. Some cations like  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$  occupy in the spaces of Si – O net-work. These alkali metal ions can move slowly through the glass and so it acts as weak electrical conductor. Thin membrane of the glass reduces its resistance but still the membrane of thickness of 0.005 cm offers a resistance of  $10^7 - 10^9$  ohms.

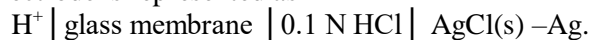
**Preparation of the electrode:** Before use, a freshly prepared glass membrane is immersed in water for a few hours. Monovalent cations such as  $Na^+$  ions at and near the surface of the glass are replaced by  $H^+$  ions from water.

Generally Ag – AgCl(s) and internal filling solution of 0.1 N HCl are taken within the thin membrane glass



container and sealed off. This is also a part of the electrode. In some cases, Hg(l) and Pt terminal are used instead of internal filling solution.

**Mechanism of the electrode:** When a glass electrode is immersed in acid solution, equilibrium is set up between H<sup>+</sup> ions in the solution and H<sup>+</sup> ions in the glass surface. This charge transfer between glass membrane and solution produces a potential difference between the two. This potential difference is known as the potential of the electrode ( $E_{\text{glass}}$ ). The electrode is represented as

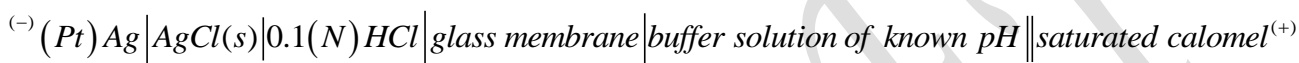


**Potential of the electrode:** When the conc. of internal filling solution (0.1 N HCl) is kept fixed, the potential of the electrode depends on the activity of H<sup>+</sup> ion of the acid solution within which the electrode is dipped.

The potential of the electrode is found as  $E_{\text{glass}} = E_{\text{glass}}^0 + 0.059 \log a_{\text{H}^+}$  at 25 °C

or, 
$$E_{\text{glass}} = E_{\text{glass}}^0 - 0.059 \text{ pH} .$$

$E_{\text{glass}}^0$  is small, called asymmetric potential. It is characteristic constant of each glass electrode. To measure the value of  $E_{\text{glass}}^0$ , the electrode is dipped into a solution of known pH buffer solution and coupled with secondary reference saturated calomel electrode.



The cell potential,  $E_{\text{cell}} = E_{\text{sat.cal}} - E_{\text{glass}}$ . At 25 °C,  $E_{\text{sat.cal}} = 0.2415 \text{ V}$  and  $E_{\text{glass}} = E_{\text{glass}}^0 - 0.059 \text{ pH}$ .

Thus the potential of the cell is 
$$E_{\text{cell}} = (0.2415 - E_{\text{glass}}^0) + 0.059 \text{ pH} .$$

Potentiometer can not measure accurate emf of the cell as galvanometer can not read the extremely small current due to high resistance of glass membrane involved. Electronic voltmeter is used to measure  $E_{\text{cell}}$  as it can read this very small amount of current from the cell. Thus,  $E_{\text{glass}}^0$  can be determined from the expression cited above.

Now, the electrode can be used to determine pH of the unknown solution from the above cell set-up.

Otherwise, cell potential  $E_1$  is determined with buffer solution of known pH<sub>1</sub> and then again the cell potential  $E$  is determined with solution of unknown pH. Then,

$$E - E_1 = 0.059 (\text{pH} - \text{pH}_1)$$

provided, same cell set-up is used in both the cases.

**Advantages of the electrode:** The electrode gives fairly accurate results of pH within error of  $\pm 0.05$ . The range of pH that can be determined is 2 – 10 and it may extend up to 14 by using special type of glasses.

The equilibrium is quickly attained in any solution and is not influenced by the presence of any gas, oxidizing agents or reducing agents and the poison. The electrode is free from salt or protein error. It can be used for long time if carefully handled and stored in distilled water.

**Disadvantages of the electrodes:** The only disadvantage is that, its potential can not be determined by ordinary potentiometer and it requires regular calibration because its asymmetric potential can vary. It is extremely sensitive to electrical interference so wire connections should be properly insulated. It requires careful handling as it is very fragile.

**Problem (1):** Given the oxidation potential  $E_{\text{Cu}^+|\text{Cu}^+}^0 = 0.52 \text{ V}$  and  $E_{\text{Cu}^+|\text{Cu}^{+2}}^0 = 0.16 \text{ V}$  in aqueous solutions, set up the cell according to the reaction  $2\text{Cu}^+ \rightleftharpoons \text{Cu} + \text{Cu}^{+2}$  and estimate the equilibrium constant for reaction. **[Burdwan Univ. 1996]**

**Solution:** The oxidation reaction at the anode,  $\text{Cu}^+ \rightarrow \text{Cu}^{+2} + e$  and reduction reaction at the cathode  $\text{Cu}^+ + e \rightarrow \text{Cu}$ . Combining the two electrode reactions, we get the cell reaction,  $2\text{Cu}^+ \rightleftharpoons \text{Cu} + \text{Cu}^{+2}$ .

On the basis of the reactions, the cell set-up is  $(-) \text{Pt} \mid \text{Cu}^{+2}, \text{Cu}^+ \parallel \text{Cu}^+ \mid \text{Cu}^{(+)}$ .

The standard cell potential is  $E_{\text{cell}}^0 = E_{\text{RHE}}^0 - E_{\text{LHE}}^0 = E_{\text{Cu}^+|\text{Cu}}^0 - E_{\text{Cu}^{+2}|\text{Cu}^+}^0 = (-E_{\text{Cu}^+|\text{Cu}^+}^0) - (-E_{\text{Cu}^+|\text{Cu}^{+2}}^0)$ .

Putting the value of oxidation potential given in the problem, we get

$$E_{\text{cell}}^0 = (-0.52) - (-0.16) = -0.36 \text{ V}$$

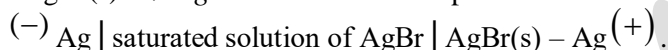
$$\text{But } E_{cell}^0 = \frac{0.059}{n} \log K_a \text{ or, } -0.36 = \frac{0.059}{1} \log K_a \text{ or, } \log K_a = -\frac{0.36}{0.059} = -6.1 \text{ or, } K_a = 7.91 \times 10^{-7}.$$

**Problem (2):** Devise a cell in which the reaction is  $\text{AgBr}(s) \rightleftharpoons \text{Ag}^+ + \text{Br}^-$ .  $E^0$  (red) at 25 °C for  $\text{Br}^- | \text{AgBr}(s)$  and  $\text{Ag}^+ | \text{Ag}$  electrodes are 0.071 V and 0.799 V respectively. Calculate  $K_{sp}$  of AgBr at 25 °C.

[Calcutta Univ. 2013]

**Solution:** LHE reaction is  $\text{Ag} \rightarrow \text{Ag}^+ + e$  (oxidation) and RHE reaction is  $\text{AgBr}(s) + e \rightarrow \text{Ag} + \text{Br}^-$  (reduction).

So the cell reaction is  $\text{AgBr}(s) \rightarrow \text{Ag}^+ + \text{Br}^-$ . Cell set-up on the basis of reaction is given as



At 25 °C, the cell potential is  $E_{cell} = E_{cell}^0 - 0.059 \log(a_{\text{Ag}^+} \times a_{\text{Br}^-})$ , where  $E_{cell}^0 = E_{\text{Br}^- | \text{AgBr}(s) - \text{Ag}}^0 - E_{\text{Ag}^+ | \text{Ag}}^0$ .

AgBr(s) remains in equilibrium with  $\text{Ag}^+$  and  $\text{Br}^-$  in the saturated solution, so  $E_{cell} = 0$  and

$$a_{\text{Ag}^+} \times a_{\text{Br}^-} = K_{sp}. \text{ Putting the values, we get } 0 = \left( E_{\text{Br}^- | \text{AgBr}(s) - \text{Ag}}^0 - E_{\text{Ag}^+ | \text{Ag}}^0 \right) - 0.059 \log K_{sp}$$

$$\text{or, } 0 = (0.071 - 0.799) - 0.059 \log K_{sp} \text{ or, } 0.059 \log K_{sp} = -0.728 \text{ or, } K_{sp} = 4.6 \times 10^{-13}.$$

**Problem (3):** At 298 K, the EMF of the cell  $\text{Pt} | \text{H}_2 (1 \text{ bar}) | \text{H}^+ (\text{soln}) | \text{Cl}^- | \text{Hg}_2\text{Cl}_2(s) | \text{Hg}$  is 0.7530 V.

The potential of the calomel electrode is 0.2802 V. If the liquid junction potential is zero, the pH of the solution is (A) 4.7 (B) 7.4 (C) 8.0 (D) 12.7 [GATE 2011]

**Answer:** (C).

**Problem (4):** The emf of a certain cell is given by  $E = E^0 - (0.059/n) \log X$ . Explain how  $X$  and  $\log X$

will change if the overall cell reaction is multiplied by 2. Will there be any change in  $E$  value due to such an operation? [Burdwan Univ. 1997]

**Answer:** If the overall cell reaction is multiplied by 2,  $X$  becomes  $X^2$  and  $\log X$  becomes  $\log X^2$  or  $2 \log X$ .

But there will be no change in  $E$  value since  $n$  is also changed by  $2n$ .

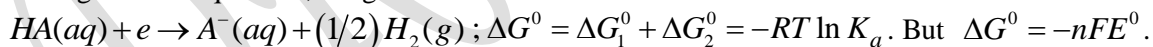
**Problem (5):** The thermodynamic dissociation constant of a weak acid (HA) is  $1.0 \times 10^{-5}$  at 25 °C. Find the standard electrode potential ( $E^0$ ) for the half cell reaction  $\text{HA}(aq) + e \rightarrow \text{A}^-(aq) + (1/2) \text{H}_2(g)$ . [3]

[Burdwan Univ. 1999]

**Answer:**  $\text{HA}(aq) \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq)$ ;  $\Delta G_1^0 = -RT \ln K_a$ , where  $K_a$  is dissociation constant of the acid HA.

Again,  $\text{H}^+(aq) + e \rightleftharpoons (1/2) \text{H}_2(g)$ ;  $\Delta G_2^0 = -nFE_{\text{H}^+ | \text{H}_2}^0 = 0$ , since  $E_{\text{H}^+ | \text{H}_2}^0 = 0$  by convention.

Adding the two equations, we get



$$\text{Hence, } E^0 = \frac{RT}{nF} \ln K_a = 0.059 \log K_a, \text{ since } n = 1 \text{ or, } E^0 = 0.059 \log 1.0 \times 10^{-5} \text{ V} = -0.295 \text{ V}.$$

**Problem (6):** The cell represented by  $\text{Pb} - \text{PbI}_2 | \text{KI}(aq) | \text{AgI} - \text{Ag}$  has an emf of +0.0278 V at 25 °C and

$(\partial E / \partial T) = -1.88 \times 10^{-4} \text{ V/K}$ . Write down the cell reaction and calculate  $\Delta G$  and  $\Delta S$ . It will be

found that all the components appearing in the expression for  $K$  are solids. Why therefore is not

$K = 1$  and  $\Delta G = 0$ ? [1+2+2] [Burdwan Univ. 1999]

**Answer: 1<sup>st</sup> Part:** Adding the anode and cathode reactions, net cell reaction is  $\text{Pb}(s) + 2\text{AgI}(s) \rightarrow \text{PbI}_2(s) + 2\text{Ag}(s)$ .

**2<sup>nd</sup> Part:**  $\Delta G = -40.105 \text{ kJ}$  and  $\Delta S = -36.28 \text{ J/K}$ .

**3<sup>rd</sup> Part:** AgI and  $\text{PbI}_2$  are in their saturated solutions and the reaction occurs between  $\text{Pb}(s)$  and saturated solution of AgI forming  $\text{Ag}(s)$  and  $\text{PbI}_2$  in saturated solution. So  $K \neq 1$  and  $\Delta G^0 \neq 0$ .

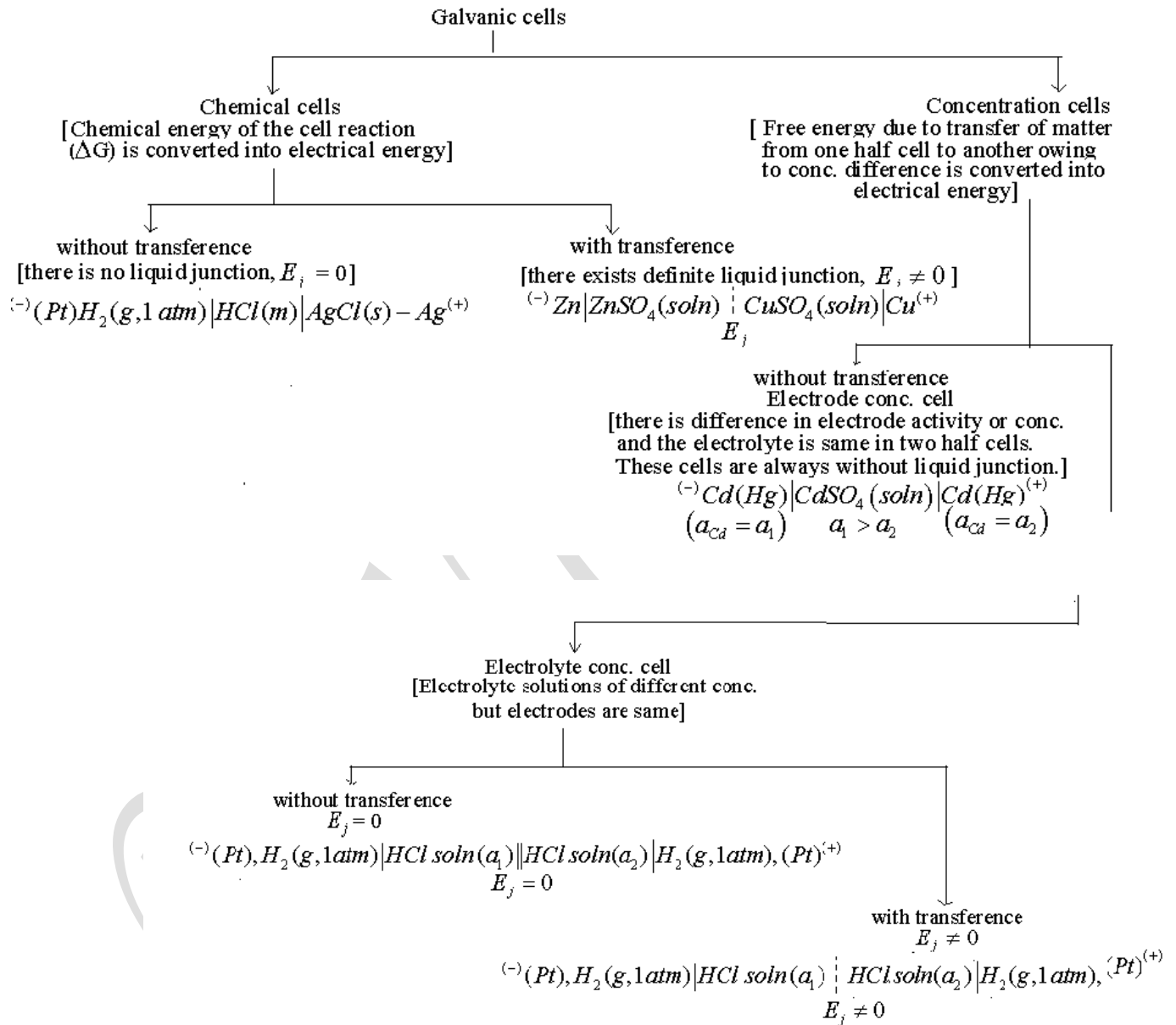
### Classification of Galvanic Cells:

When two solutions of different electrolytes or same electrolyte solutions of different conc. come into contact, there develops a liquid junction potential ( $E_j$ ). Therefore, the cell emf with liquid junction is

$$E_{cell,wlj} = E_{cell,wolj} + E_j,$$

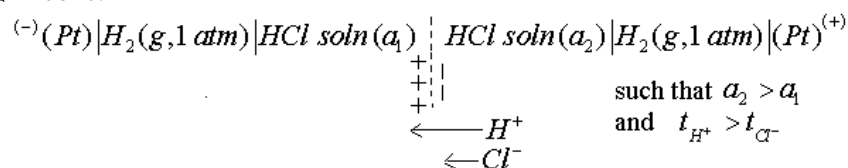
where  $E_{cell,wlj}$  = cell potential with liquid junction,  $E_{cell,wolj}$  = cell potential without liquid junction.

$E_j$  is determined from the difference of the two cell potentials and it can not be directly measured. The galvanic cells could be classified according to the cell with liquid junction or without junction.



### Liquid Junction Potential ( $E_j$ ):

Let us illustrate it by the example of conc. cell with liquid junction of two solutions of same electrolyte differing in conc.



### Origin of development of liquid junction potential:

RHS electrolyte solution is more concentrated than LHS electrolyte solution. So HCl will diffuse from right to left through the junction. But  $H^+$  ion moves faster than  $Cl^-$  ion since  $t_{H^+} > t_{Cl^-}$ . As  $H^+$  takes the lead to cross the junction, lower conc. solution becomes positively charged but higher conc. solution gets negatively charged due to excess  $Cl^-$  ion conc. Thus there occurs a charge separation along the junction.

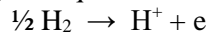
This charge separation retards the speed of  $H^+$  ion but accelerates the speed of  $Cl^-$  ion through the boundary. At equilibrium, the charge separation becomes such that the speed of both the ions are equal and no further charge separation occurs. The potential difference developed at this state due to electrical double layer is the liquid junction potential ( $E_j$ ). This potential depends on the conc. or activity of the two electrolyte solutions forming the junction and the velocity difference of the two ions constituting the electrolyte.

The actual charge separation is very small but the potential difference so produced is appreciable.

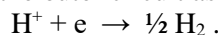
Thus in general, difference of potential resulting at the junction of two solutions is caused by the difference in the rates of diffusion of two ions; the more dilute solution acquires the charge corresponding to that of the faster moving ion.

### Expression of liquid junction potential ( $E_j$ ):

Let one faraday of electricity is drawn from the cell as cited above. So one gram equivalent of  $H_2$  gas dissolves at the LHE forming one gram equivalent  $H^+$  ion,



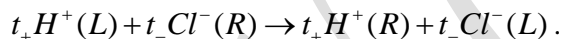
and one gram equivalent  $H^+$  ions is removed from RHE due to flow of one faraday electricity in the outer circuit as



But at the liquid junction,  $t_+$  gram equivalent of  $H^+$  ions move

from LHE to RHE while  $t_-$  gram equivalent  $Cl^-$  ions move

from RHE to LHE and thus one faraday electricity is passed in the inner circuit i.e. at the junction also. This can be expressed by an equation as



The free energy change due to transfer at the junction is given as,

$$\Delta G_j = RT \ln \left( \frac{a_{H^+(R)}^{t_+} \times a_{Cl^-(L)}^{t_-}}{a_{H^+(L)}^{t_+} \times a_{Cl^-(R)}^{t_-}} \right) = RT \left[ t_+ \ln \frac{a_{H^+(R)}}{a_{H^+(L)}} - t_- \ln \frac{a_{Cl^-(R)}}{a_{Cl^-(L)}} \right]$$

Let activity of  $H^+$  ion and  $Cl^-$  ion is taken as the mean activity of  $H^+$  ion and  $Cl^-$  in HCl electrolyte ( $a_{\pm}$ ), then

$$\Delta G_j = RT \left[ t_+ \ln \frac{a_{\pm(R)}}{a_{\pm(L)}} - t_- \ln \frac{a_{\pm(R)}}{a_{\pm(L)}} \right] = (t_+ - t_-) RT \ln \frac{a_{\pm(R)}}{a_{\pm(L)}}. \text{ This free energy change, } \Delta G_j = -nFE_j.$$

Equating, we get  $-nFE_j = (t_+ - t_-) RT \ln \frac{a_{\pm(R)}}{a_{\pm(L)}}$  or,  $E_j = (t_- - t_+) \frac{RT}{nF} \ln \frac{a_{\pm(R)}}{a_{\pm(L)}}$ .

But the activity of HCl,  $a = (a_{\pm})^2$  Thus the expression of liquid junction potential for this cell where  $n = 1$ ,

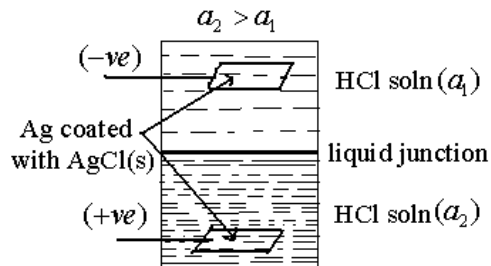
$$E_j = (t_- - t_+) \frac{RT}{2F} \ln \frac{a_2}{a_1} \quad \text{and at } 25^\circ C, \quad E_j = (t_- - t_+) \frac{0.059}{2} \log \left( \frac{a_2}{a_1} \right).$$

$a_1$  and  $a_2$  are the activity of HCl at the LHS and RHS electrolyte solutions respectively.

Converting transport numbers into ionic velocities, we get the expression,  $E_j = \left( \frac{v_- - v_+}{v_- + v_+} \right) \frac{0.059}{2} \log \left( \frac{a_2}{a_1} \right)$ .

Thus in a cell in which  $a_2 > a_1$ , the following liquid junction potentials are developed.

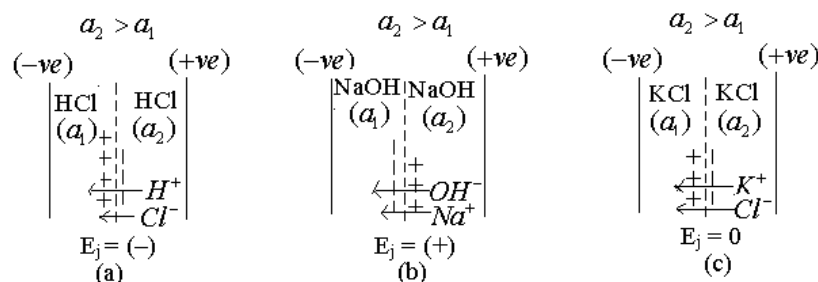
(a) When  $t_+ > t_-$  (i.e. cation is faster than anion) as for junction with HCl solutions,  $E_j = (-ve)$ , the liquid junction potential opposes the cell potential.



(b) When  $t_- > t_+$  (i.e. anion is faster than cation) as for the junction of NaOH solutions,  $E_j = (+ve)$  and liquid junction potential adds to the cell potential.

(c) When  $t_+ = t_-$  (i.e. cation and anion move at equal velocity) as for that KCl and  $\text{NH}_4\text{NO}_3$  solution,  $E_j = 0$ .

The liquid junction potential neither adds nor opposes to the cell potential.



### Salt Bridge:

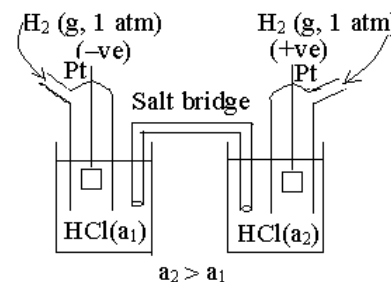
In KCl and  $\text{NH}_4\text{NO}_3$  solutions, both cations and anions have equal velocities, so liquid junction potential ( $E_j$ ) = 0 for solutions differing conc. For that reason, these electrolytes are used in preparing salt bridge. This salt bridge makes an electrical contact between two half-cells and minimizes the liquid junction potential though not eliminates totally. The contribution of liquid junction to the cell potential can be reduced to 1 mV to 2 mV by salt bridge.

#### Preparation of salt bridge:

A hot solution of KCl (or  $\text{NH}_4\text{NO}_3$ ) and agar is filled in an inverted U-shaped delivery tube and the tube is then cooled when a semisolid jelly mass sets in the tube. This is salt bridge used to connect two half-cells of the cell.

#### Mechanism of action of salt bridge:

Strongly conc. solution of KCl in the salt bridge remains in contact with dilute electrolyte solution of the half-cells. The liquid junction potential developed at this junction is quite small. This is because KCl solution is concentrated so the junction potential is determined mainly by the ions of this solution. The mobilities of the isoelectronic ions  $\text{K}^+$  and  $\text{Cl}^-$  in water are nearly equal and so these ions diffuse out of the salt bridge into the dilute electrolyte solution of the half-cell at nearly equal rates and the junction (or diffusion) potential is therefore small. Most cells with salt bridge contain two junctions between conc. KCl solutions and dilute solutions of two half-cells. Thus,  $E_j$  is further reduced by nearly cancellation of oppositely directed junction potentials. The reason for the success of the salt bridge is that  $E_j$  at either end are largely independent of the conc. of the two dilute solutions and so nearly cancels. This explanation is justified by the fact that cell potential determined by the use salt bridge agrees well with the calculated cell potential without liquid junction.



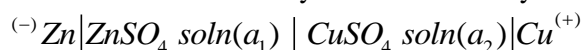
$$E_{cell} = (E_{RHE} + E_j) - (E_{LHE} + E_j) = E_{RHE} - E_{LHE}$$

#### Advantage for the use of agar in the salt bridge:

The semisolid jelly formed by agar within the salt bridge makes certain advantages.

- (1) It prevents the spilling of KCl solution from the tube when it is inverted for contact between two half-cells.
- (2) It prevents siphoning if the electrolyte solution levels differ in the half-cells.
- (3) It slows the ionic diffusion very much so that the junction potential whatever they may be, settles down to reproducible values quickly.

The liquid junction potential for two different electrolyte solutions is very difficult to formulate such as for the cell,

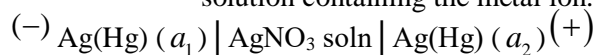


## Concentration Cells

Free energy change ( $\Delta G$ ) due to transport of matter from one half-cell to another is converted into electrical energy.

**(A) Electrode Concentration Cells:** It consists of two identical electrodes of different conc. or pressure dipped into a common electrolyte solution containing ions reversible with the electrodes. It is of two types:

**(1) Amalgam electrode conc. cells:** It is formed by the metal in amalgam differing in activities and dipped into an solution containing the metal ion.

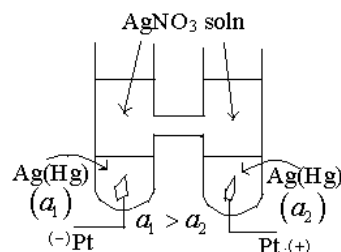


such that  $a_1 > a_2$

Reaction at the LHE,  $\text{Ag(Hg)} \rightarrow \text{Ag}^+ + e$  (oxidation)

Reaction at the RHE,  $\text{Ag}^+ + e \rightarrow \text{Ag(Hg)}$  (reduction)

Net cell reaction is  $\text{Ag(Hg)} \rightarrow \text{Ag(Hg)}$   
 $(a_1) \quad (a_2)$



Free energy change for the cell reaction,  $\Delta G = RT \ln \left( \frac{a_2}{a_1} \right)$ .

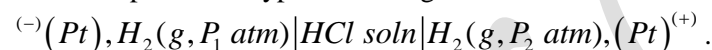
When  $\Delta G$  is converted into electrical energy,  $\Delta G = -nFE_{cell}$ , here  $n = 1$ . So equating, we get the cell potential

$E_{cell} = \frac{RT}{F} \ln \left( \frac{a_1}{a_2} \right)$  or, at 25 °C,  $E_{cell} = 0.059 \log \left( \frac{a_1}{a_2} \right)$ . To make the cell potential (+ve),  $a_1 > a_2$  i.e.

amalgam electrode of higher activity will form anode of the cell and of lower activity will form cathode. The cell will operate spontaneously until  $a_1 = a_2$ . When  $a_1 = a_2$ , the cell stops to produce electricity.

**(2) Gas electrode concentration cells:** It consists of two gas electrodes at different pressures dipped into electrolyte solution containing the ion of the gas.

One example of this type of cell is given here.



The net cell reaction is,  $H_2(g, P_1 \text{ atm}) \rightarrow H_2(g, P_2 \text{ atm})$ .

The free energy change due to this transfer is  $\Delta G = RT \ln \left( \frac{P_2}{P_1} \right)$

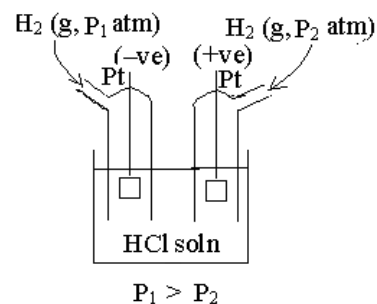
and the electrical energy produced,  $\Delta G = -nFE_{cell}$ .

$n = 2$ , since two gram equivalent of hydrogen gas undergoes in the process.

Thus,  $E_{cell} = -\frac{RT}{2F} \ln \left( \frac{P_2}{P_1} \right)$  or,  $E_{cell} = \frac{RT}{2F} \ln \left( \frac{P_1}{P_2} \right)$ .

At 25 °C, the cell potential is  $E_{cell} = \frac{0.059}{2} \log \left( \frac{P_1}{P_2} \right)$  or,  $E_{cell} = 0.059 \log \sqrt{\frac{P_1}{P_2}}$ . Higher pressure electrode

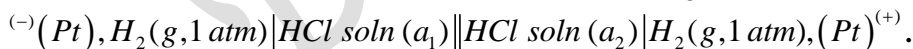
forms anode and the cell will operate till  $P_1 > P_2$ . When  $P_1 = P_2$  the cell ceases to produce electricity.



**(B) Electrolyte Concentration Cells:**

The electrodes on both sides are same but they are dipped into two solutions of same electrolyte differing in conc. It is of two types:

**(1) Electrolyte conc. cells without transference:** The following cell is considered for illustration.



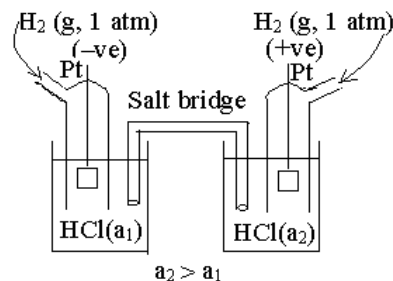
Reaction at the anode:  $\frac{1}{2} H_2(g, 1 \text{ atm}) \rightarrow H^+(L) + e$  (oxidation)

Reaction at the cathode:  $H^+(R) + e \rightarrow \frac{1}{2} H_2(g, 1 \text{ atm})$  (reduction).

Adding the two, we get the net cell reaction,  $H^+(R) \rightarrow H^+(L)$ .

The free energy change due to the process is  $\Delta G = RT \ln \frac{a_{H^+(L)}}{a_{H^+(R)}}$ .

This free energy is converted into electrical energy and  $\Delta G = -FE_{cell,woj}$ .





Equating,  $E_{cell,woj} = \frac{RT}{F} \ln \frac{a_{H^+(R)}}{a_{H^+(L)}}$ . Individual ionic activity ratio can be replaced by their mean activity ratio.

That is,  $\frac{a_{H^+(R)}}{a_{H^+(L)}} = \frac{a_{\pm(R)}}{a_{\pm(L)}} = \sqrt{\frac{a_2}{a_1}}$ , where  $a_1$  and  $a_2$  are the activity of the HCl solutions of LHE and RHE respectively.

Thus the cell potential,  $E_{cell,woj} = \frac{RT}{F} \ln \frac{a_{\pm(R)}}{a_{\pm(L)}} = \frac{RT}{2F} \ln \frac{a_2}{a_1}$ . At 25 °C,  $E_{cell,woj} = \frac{0.059}{2} \log \frac{a_2}{a_1}$ .

**Another cell of this type** is  $(-) Ag - AgCl(s) | HCl \text{ soln } (a_1) || HCl \text{ soln } (a_2) Ag - AgCl(s) (+)$ .

Reaction at LHE,  $Ag + Cl^- (L) \rightarrow AgCl(s) + e$  (oxidation) and at RHE,  $AgCl(s) + e \rightarrow Ag + Cl^- (R)$ .

The net cell reaction is  $Cl^- (L) \rightarrow Cl^- (R)$

Since  $Cl^-$  ion is removed from HCl soln ( $a_1$ ) and produced at HCl soln ( $a_2$ ),  $a_1 > a_2$  to make the process

spontaneous. The cell potential,  $E_{cell,woj} = \frac{RT}{F} \ln \frac{a_{\pm(L)}}{a_{\pm(R)}} = \frac{RT}{2F} \ln \frac{a_1}{a_2}$ .

#### Elimination of liquid junction:

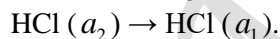
Usually liquid junction potential is tried to be eliminated for the above cell by using salt bridge. However, the liquid junction can be eliminated for the above cell by coupling two chemical cells differing the conc. of two HCl solutions.



LHS cell reaction is  $\frac{1}{2} H_2(g, 1 \text{ atm}) + AgCl(s) \rightarrow Ag(g) + HCl(a_1)$

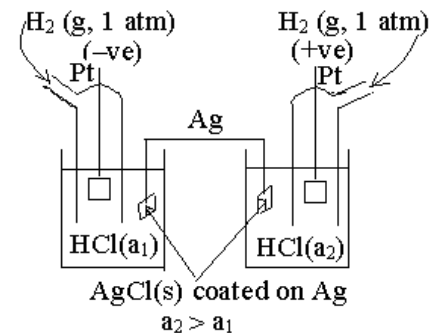
RHS cell reaction is  $Ag(g) + HCl(a_2) \rightarrow \frac{1}{2} H_2(g, 1 \text{ atm}) + AgCl(s)$

Adding the two cell reactions, we get the reaction of the above cell as



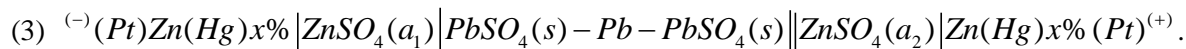
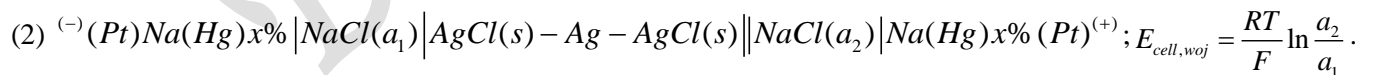
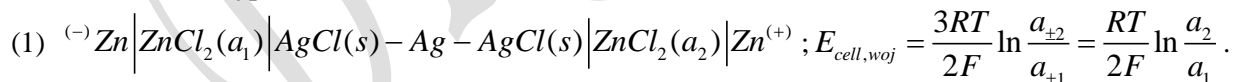
Free energy for the above transfer,  $\Delta G = RT \ln \frac{a_1}{a_2}$ , and  $\Delta G = -FE_{cell}$ .

Equating, we get the cell potential,  $E_{cell} = \frac{RT}{F} \ln \frac{a_2}{a_1}$ .

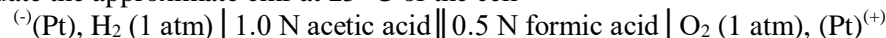


The general expression of cell potential of this type is  $E_{cell,woj} = \frac{\nu RT}{nF} \ln \frac{a_{\pm 2}}{a_{\pm 1}}$ , where  $\nu$  = number of ions produced

from the dissociation of one molecule of the electrolyte,  $n$  = number of faradays of electricity drawn from the cell. Other cells of this type are



**Problem:** Evaluate the approximate emf at 25 °C of the cell



if the dissociation constant of acetic acid and formic acid is  $1.8 \times 10^{-5}$  and  $1.77 \times 10^{-4}$  respectively.

Given, standard reduction potential of  $O_2$  electrode,  $OH^- / O_2 = 0.4$  volt.

**Solution:** Reaction at LHE,  $H_2(1 \text{ atm}) \rightarrow 2H^+ + 2e$  (oxidation) and

reaction at RHE,  $\frac{1}{2} O_2(1 \text{ atm}) + H_2O + 2e \rightarrow 2OH^-$  (reduction).

The net cell reaction,  $\text{H}_2(1 \text{ atm}) + \frac{1}{2} \text{O}_2(1 \text{ atm}) + \text{H}_2\text{O} \rightarrow 2\text{H}^+(\text{L}) + 2\text{OH}^-(\text{R})$ .

The cell potential,  $E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{2F} \ln(a_{\text{H}^+(\text{L})}^2 \times a_{\text{OH}^-(\text{R})}^2) = E_{\text{cell}}^0 - \frac{RT}{F} \ln[a_{\text{H}^+(\text{L})} \times a_{\text{OH}^-(\text{R})}]$ .

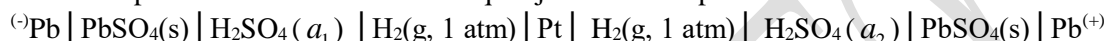
But  $E_{\text{cell}}^0 = E_{\text{O}_2|\text{OH}^-}^0 - E_{\text{H}^+|\text{H}_2}^0 = E_{\text{O}_2|\text{OH}^-}^0 = 0.40\text{V}$ . Activities are approximately equal to the conc. and

so at 25 °C,  $E_{\text{cell}} = 0.40 - 0.059 \log \left[ \sqrt{K_{\text{acetic acid}} \times c_{\text{acetic acid}}} \times \left( \frac{K_w}{\sqrt{K_{\text{formic acid}} \times c_{\text{formic acid}}}} \right) \right]$ ,

$$E_{\text{cell}} = 0.40 - 0.059 \log \left[ \sqrt{1.8 \times 10^{-5} \times 1.0} \times \left( \frac{1.0 \times 10^{-14}}{\sqrt{1.77 \times 10^{-4} \times 0.5}} \right) \right]$$

or,  $E_{\text{cell}} = 0.40 - 0.059 \log \left( \frac{10^{-14}}{\sqrt{5}} \right)$  or, the cell potential is  $E_{\text{cell}} = 1.246\text{V}$ .

**Problem:** Find the expression of the cell without liquid junction as depicted below:



**Solution:** The reaction at the LHS cell is  $\text{Pb} + \text{H}_2\text{SO}_4(\text{L}) \rightarrow \text{PbSO}_4(\text{s}) + \text{H}_2(\text{g}, 1 \text{ atm})$  and the reaction at the RHS cell is  $\text{H}_2(\text{g}) + \text{PbSO}_4(\text{s}) \rightarrow \text{Pb} + \text{H}_2\text{SO}_4(\text{R})$ . Adding the two cell reactions, we get the net cell reaction of the cell without liquid junction,  $\text{H}_2\text{SO}_4(\text{L}) \rightarrow \text{H}_2\text{SO}_4(\text{R})$ .

$$\Delta G = RT \ln \frac{a_2}{a_1} \text{ and this } \Delta G \text{ is converted into electrical energy as } \Delta G = -2FE_{\text{cell,woj}}$$

Equating, we get the potential of the cell without liquid junction as  $E_{\text{cell,woj}} = \frac{RT}{2F} \ln \frac{a_1}{a_2}$

## (2) Electrolyte concentration cell with transference:

Due to diffusion of ions through the junction of the solutions of an electrolyte differing in conc., a potential is developed, called liquid junction potential,  $E_j$ . Thus for the cell



In these type of cells, two liquids meet each other at the junction point. The cell potential is

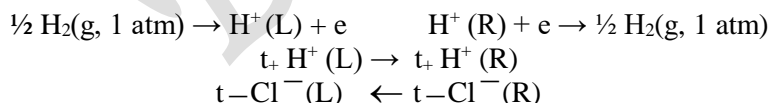
$$E_{\text{cell,wj}} = E_{\text{cell,woj}} + E_j$$

Putting the expression of the two potentials formulated already, we get

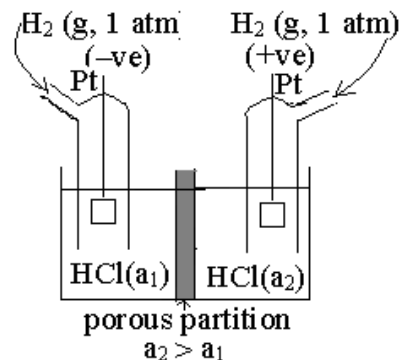
$$E_{\text{cell,wj}} = \frac{RT}{2F} \ln \frac{a_2}{a_1} + \frac{RT}{2F} (t_- - t_+) \ln \frac{a_2}{a_1} = (1 + t_- - t_+) \frac{RT}{2F} \ln \frac{a_2}{a_1} \text{ or, } E_{\text{cell,wj}} = t_- \frac{RT}{F} \ln \frac{a_2}{a_1}$$

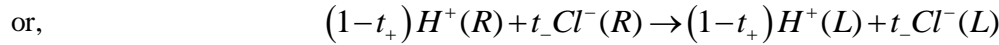
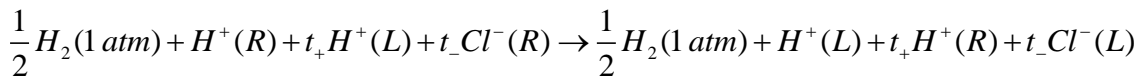
The emf of the cell depends on the transport number of the ion other than one with respect to which the electrodes are reversible.

However, the cell potential can be directly obtained considering the electrode processes and the migration of ions through the junction.



Electrons flow in the external circuit from left to right. Since  $\text{H}^+$  ions are produced in the LHE and  $\text{Cl}^-$  ions are produced in the RHE, the inner circuit is completed by the transference of  $t_-$  gram equivalent  $\text{Cl}^-$  ions from RHE to LHE and  $t_+$  gram equivalent  $\text{H}^+$  ions from LHE to RHE if one faraday of electricity is drawn through the cell. Adding all the processes, we have





Lower conc. HCl solution is in the anode and higher conc. HCl solution is in the cathode for spontaneous process

to occur. The free energy change for the process is  $\Delta G = t_- RT \ln \frac{a_{HCl(L)}}{a_{HCl(R)}} = t_- RT \ln \frac{a_1}{a_2}$  .

The electrical energy produced is  $-nFE_{cell,wj} = t_- RT \ln \frac{a_1}{a_2}$  . Since one faraday electricity is drawn, so  $n = 1$  .

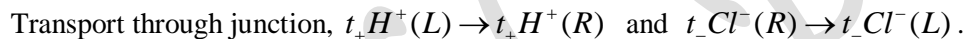
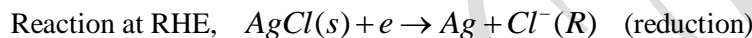
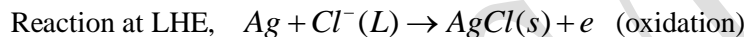
So, potential of the cell with liquid junction is  $E_{cell,wj} = (t_-) \frac{RT}{F} \ln \frac{a_2}{a_1}$  and at 25 °C,  $E_{cell,wj} = 0.059(t_-) \log \frac{a_2}{a_1}$  .

Since two solutions are in contact, there will be actual passage of ions, however small it is. It is thus assumed that the volume of the two solutions are so large that any transfer of ions that occurs produces no change in the conc. of the various species in the solutions.

Other cells of this type are:

**Problem (1):** Find the emf of the cell at 25 °C  $(-)Ag - AgCl(s) | HCl \text{ soln } (a_1) || HCl \text{ soln } (a_2) | AgCl(s) - Ag (+)$

**Solution:** For the passage of one faraday of electricity through the cell, the following processes occur.



The free energy change for the process is  $\Delta G = (t_+) RT \ln \frac{a_{HCl(R)}}{a_{HCl(L)}}$  . This  $\Delta G = -nFE_{cell,wj}$  .

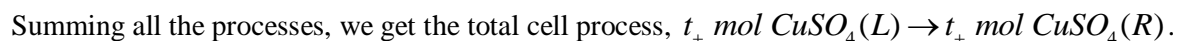
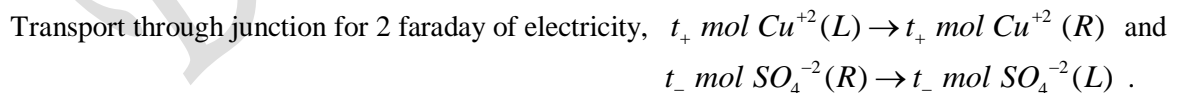
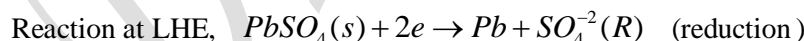
But for the passage of one faraday of electricity,  $n = 1$  . Equating, we get  $E_{cell,wj} = (t_+) \frac{RT}{F} \ln \frac{a_{HCl(L)}}{a_{HCl(R)}}$  .

Since,  $a_{HCl(L)} = a_1$  and  $a_{HCl(R)} = a_2$  , thus at 25 °C, the cell potential is  $E_{cell,wj} = 0.059(t_+) \log \frac{a_1}{a_2}$  .

**Problem (2):** Find the expression of emf of the following cell,



**Solution:** Reaction at LHE,  $Pb + SO_4^{2-}(L) \rightarrow PbSO_4(s) + 2e$  (oxidation)



The free energy for the process,  $\Delta G = (t_+) RT \ln \frac{a_{CuSO_4(R)}}{a_{CuSO_4(L)}}$  =  $(t_+) RT \ln \frac{a_2}{a_1}$  . But  $\Delta G = -2FE_{cell,wj}$  .

Equating, we get cell potential,  $E_{cell,wj} = (t_+) \frac{RT}{2F} \ln \frac{a_1}{a_2}$  , at 25 °C,  $E_{cell,wj} = (t_+) \frac{0.059}{2} \log \frac{a_1}{a_2}$

General expression for potential of the cell,  $M(s) | M_x A_y (a_{\pm 1}) || M_x A_y (a_{\pm 2}) | M(s) ; E_{cell,wj} = t_- \frac{RT}{yF} \ln \frac{a_2}{a_1}$ .

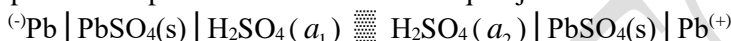
**Problem (3):** Calculate the potential of the cell at 298 K,  
 $(-)Pb(s) | PbSO_4(s) | CuSO_4 (soln) || CuSO_4 (soln) | PbSO_4(s) | Pb(s)(+)$   
 $m = 0.2 \text{ molKg}^{-1} \quad m = 0.02 \text{ molKg}^{-1}$   
 $\gamma_{\pm} = 0.110 \quad \gamma_{\pm} = 0.320$

The transport number of  $Cu^{+2} = 0.370$ . [Calcutta Univ. 2013]

**Solution:**  $E_{cell} = (t_+) \frac{0.059}{2} \log \frac{a_1}{a_2}$ , so  $E_{cell} = (0.370) \frac{0.059}{2} \log \left( \frac{0.2 \times 0.110}{0.02 \times 0.320} \right)^2$ , since  $\frac{a_1}{a_2} = \frac{(m_1 \gamma_{\pm 1})^2}{(m_2 \gamma_{\pm 2})^2}$

or,  $E_{cell} = 0.0117$  volt at 298 K.

**Problem(4):** Find the expression of potential of the cell with liquid junction which is depicted as below:



LHE reaction is  $Pb + SO_4^{+2} (L) \rightarrow PbSO_4(s) + 2e$  and RHE reaction is  $PbSO_4(s) + 2e \rightarrow Pb + SO_4^{+2} (R)$ .

The transport through the junction is  $2t_+ \text{ mol } H^+ (L) \rightarrow 2t_+ \text{ mol } H^+ (R)$  and  $t_- \text{ mol } SO_4^{-2} (R) \rightarrow t_- \text{ mol } SO_4^{-2} (L)$ .

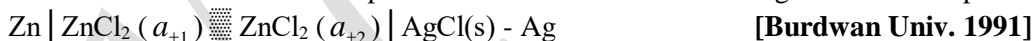
Adding the processes, we get the net cell reaction,  $t_+ H_2SO_4 (L) \rightarrow t_+ H_2SO_4 (R)$ .

$\Delta G = (t_+) RT \ln \frac{a_2}{a_1}$  and the  $\Delta G = -2FE_{cell,wj}$ . Equating, we get  $E_{cell,wj} = (t_+) \frac{RT}{2F} \ln \frac{a_1}{a_2}$ .

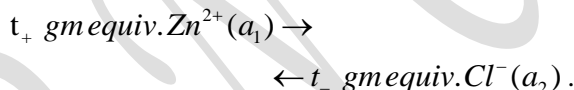
**Problem (5):** Obtain a general expression for the liquid junction potential for a system



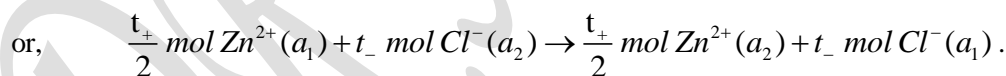
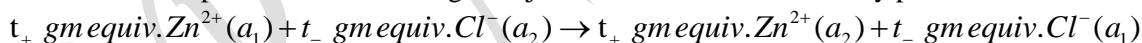
assuming that the mean activity of zinc chloride  $a_2 > a_1$ , and the electrolyte is completely dissociated. Proceed further to obtain an expression of the emf of the following cell with transport



**Solution: 1<sup>st</sup> Part:**



The net transport of the ions through the junction when 1F of electricity passes



The free energy change due to this transport is

$$\Delta G_j = RT \ln \left[ \left( \frac{a_2}{a_1} \right)^{t_+/2} \left( \frac{a_1}{a_2} \right)^{t_-} \right] = RT \left[ \frac{t_+}{2} \ln \left( \frac{a_2}{a_1} \right) - t_- \ln \left( \frac{a_2}{a_1} \right) \right]. \text{ But } \Delta G_j = -FE_j.$$

Thus the liquid junction potential,  $E_j = \left( t_- - \frac{t_+}{2} \right) \frac{RT}{F} \ln \left( \frac{a_2}{a_1} \right)$  or,  $E_j = (2t_- - t_+) \frac{RT}{2F} \ln \left( \frac{a_2}{a_1} \right)$

**2<sup>nd</sup> Part:** For the given cell without transport, we have LHE reaction,  $Zn(s) \rightarrow Zn^{2+} (a_1) + 2e$

and RHE reaction,  $2AgCl(s) + 2e \rightarrow 2Ag(s) + 2Cl^- (a_2)$ . The net reaction for the cell without

transport is  $Zn(s) + 2AgCl(s) \rightarrow Zn^{2+} (a_1) + 2Ag(s) + 2Cl^- (a_2)$ .

The cell potential without transport,  $E_{cell,woj} = E_{cell}^0 + \frac{RT}{2F} \ln \left( \frac{1}{a_1 a_2} \right)$ . Adding, we get

$$E_{cell,wj} = E_{cell,woj} + E_j = E_{cell}^0 + \frac{RT}{2F} \ln \left( \frac{1}{a_1 a_2} \right) + (2t_- - t_+) \frac{RT}{2F} \ln \left( \frac{a_2}{a_1} \right)$$

or,  $E_{cell,wj} = E_{cell}^0 + \frac{3RT}{2F} \ln \left( \frac{1}{a_1^{t_-} a_2^{t_+}} \right)$ . Thus, the potential of the given cell is

$$E_{cell,wj} = E_{cell}^0 - \frac{3RT}{2F} \ln \left( a_2^{t_+} a_1^{t_-} \right) .$$

### Applications of EMF measurements:

Some of the applications have already been discussed in details. However, under this head, again all the possible applications are listed.

#### (1) Determination of valence of an ion:

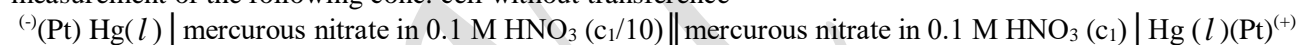
Let us take an electrode  $M^{+n} | M(s)$ , the electrode reaction is  $M^{+n} + ne \rightarrow M(s)$ .

The potential of the electrode at 25 °C is  $E_{M^{+n}|M(s)} = E_{M^{+n}|M(s)}^0 + \frac{0.059}{n} \log a_{M^{+n}}$ . Now the activity of the metal ion in solution is reduced to (1/10)th of the initial value by dilution and let the potential is

$$E'_{M^{+n}|M(s)} = E_{M^{+n}|M(s)}^0 + \frac{0.059}{n} \log \left( a_{M^{+n}} / 10 \right), \text{ so } E_{M^{+n}|M(s)} - E'_{M^{+n}|M(s)} = 0.059/n \text{ or, } n = \frac{0.059}{\left( E_{M^{+n}|M(s)} - E'_{M^{+n}|M(s)} \right)} .$$

The potential of the electrode is determined from the potential of a cell formed by coupling this electrode with a reference electrode of known potential. Thus the valence of the metal ion ( $n$ ) can be determined.

Historically important fact is that the valence of mercurous mercury ion is determined by the emf measurement of the following conc. cell without transference



The emf of the cell,  $E_{cell,woj} = \frac{0.059}{n} \log \left( \frac{c_1}{c_1/10} \right)$  or,  $E_{cell,woj} = \frac{0.059}{n}$ . The cell potential is determined by

the potentiometer and valence of mercurous ion ( $n$ ) is obtained.  $n$  is found to be +2. So the ion is  $Hg_2^{+2}$ .

**Problem:** Consider the metal | metal ion electrode:  $M(s) \rightarrow M^{+n} + ne$ . If the electrode potential changes by 0.03 volts for a ten-fold change in the conc. of  $M^{+n}$ , calculate the value of  $n$ . [Burdwan Univ. 1994]

**Solution:**  $n = 2$

#### (2) Determination of activity coefficient of an electrolyte in solution:

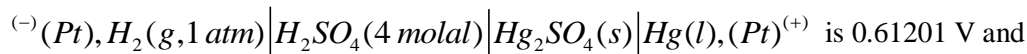
Let us consider the cell,  $^{(-)}(Pt), H_2(g, 1 \text{ atm}) | HCl(m) | AgCl(s) - Ag^{(+)}$ .

The cell potential at 25 °C,  $E_{cell} = E_{cell}^0 - 0.118 \log m - 0.118 \log \gamma_{\pm}$ , where  $E_{cell}^0 = E_{Cl^-|AgCl(s)|Ag}^0 = 0.2222$  volts.

Thus,  $E_{cell} = 0.2222 - 0.118 \log m - 0.118 \log \gamma_{\pm}$ .

Determining the cell potential ( $E_{cell}$ ), the activity coefficient ( $\gamma_{\pm}$ ) of HCl solution of molality ( $m$ ) is measured.

**Problem (1):** At 25 °C, the potential of the cell,



$E_{cell}^0 = 0.61515$  V. Calculate  $\gamma_{\pm}$  of  $H_2SO_4$  solution.

**Solution:** The cell reaction is  $H_2(1 \text{ atm}) + Hg_2SO_4(s) \rightarrow 2Hg(l) + H_2SO_4(soln)$ . The cell potential,

$$E_{cell} = E_{cell}^0 - \frac{0.059}{2} \log a_{H_2SO_4} \text{ or, } \log a_{H_2SO_4} = 2(E_{cell}^0 - E_{cell})/0.059 = 2(0.61515 - 0.61201)/0.059$$

or,  $\log a_{H_2SO_4} = 0.10644$  or,  $a_{H_2SO_4} = 1.2777$ . But  $a_{H_2SO_4} = 4m^3 \gamma_{\pm}^3 = 1.2777$  or,

$m\gamma_{\pm} = (1.2777/4)^{1/3} = 0.6835$ . But molality of  $H_2SO_4$  solution is 4 so,  $\gamma_{\pm} = 0.6835/4 = 0.1708$ .

**Problem (2):** The cell,  $(-)(Pt), H_2(g, 1 atm) | HBr(aq) | AgBr(s) | Ag | (Pt)(+)$  at 25 °C with HBr molality 0.100 mol/kg has  $E_{cell} = 0.2000$  V. Find the activity coefficient of HBr(aq) at this molality.

Given,  $E_{Br^-|AgBr(s)|Ag}^0 = 0.073$  volt at 25 °C. [Burdwan Univ, 2017] [Ans.  $\gamma_{\pm} = 0.84$ ]

### (3) Determination of the thermodynamical properties of the cell reaction:

By measuring the cell potential and temperature coefficient of cell potential, it is possible to calculate  $\Delta G$ ,  $\Delta S$ ,  $\Delta H$  and equilibrium constant ( $K_{eq}$ ) of the cell reaction.

$$(i) \Delta G = -nFE_{cell} \quad (ii) \Delta S = nF \left( \frac{\partial E_{cell}}{\partial T} \right)_p \quad (iii) \Delta H = nF \left[ T \left( \frac{\partial E_{cell}}{\partial T} \right) - E_{cell} \right] \quad \text{and (iv) } E_{cell}^0 = \frac{RT}{nF} \ln K_{eq}.$$

**Problem:** The emf of the cell,  $Cd | CdCl_2(soln) | AgCl(s) - Ag$  is found to be 0.6753 V at 25 °C and 0.6915 V at 0 °C. Calculate  $\Delta G$ ,  $\Delta S$ ,  $\Delta H$  and  $K_{eq}$  of the cell reaction at 25 °C.

Given,  $E_{Cl^-|AgCl(s)|Ag}^0 = 0.222$  volt and  $E_{Cd^{2+}|Cd}^0 = -0.40$  volt at 25 °C.

**Solution:** The cell reaction is  $Cd + 2AgCl(s) \rightarrow CdCl_2(soln) + 2Ag$ ,  $n = 2$  as 2 gm equivalent reaction occurs.

$$\Delta G = -nFE_{cell} \quad \text{or, } \Delta G = -2 \times 96500 \text{ C mol}^{-1} \times 0.6753 \text{ V} \times 10^{-3} \text{ kJ/mol} = -130.33 \text{ kJ mol}^{-1} \text{ at } 25 \text{ }^\circ\text{C}.$$

$$\Delta S = nF \left( \frac{\partial E_{cell}}{\partial T} \right)_p \quad \text{or, } \Delta S = 2 \times 96500 \text{ C mol}^{-1} \left( \frac{0.6753 - 0.6915}{25} \right) \text{ V K}^{-1} = -125.4 \text{ J mol}^{-1} \text{ K}^{-1}.$$

$$\Delta H = \Delta G + T\Delta S = -130.33 \text{ kJ mol}^{-1} + 298 \times (-125.4 \times 10^{-3}) \text{ kJ K}^{-1} \text{ mol}^{-1} = -167.72 \text{ kJ mol}^{-1}.$$

$$E_{cell}^0 = E_{RHE}^0 - E_{LHE}^0 = E_{Cl^-|AgCl(s)|Ag}^0 - E_{Cd^{2+}|Cd}^0 = 0.222 - (-0.40) = 0.622 \text{ volt. But, } E_{cell}^0 = \frac{RT}{nF} \ln K_{eq}.$$

$$\text{Putting the value at } 25 \text{ }^\circ\text{C, } E_{cell}^0 = \frac{0.059}{2} \log K_{eq} \quad \text{or, } \log K_{eq} = \frac{2 \times 0.622}{0.059} = 21.08 \quad \text{or, } K_{eq} = 1.2 \times 10^{21}.$$

### (4) Determination of pH of a solution:

pH of a solution can be determined by the use of the following electrodes at 25 °C:

(a) Hydrogen electrode,  $H^+ | H_2(g, 1 atm)(Pt)$ . Electrode potential,  $E_{H^+|H_2} = -0.059 \text{ pH}$

(b) Quinhydrone electrode,  $H^+ | Q, H_2Q(s), (Au)$ . Electrode potential,  $E_{H^+|Q, H_2Q(s), (Au)} = 0.699 - 0.059 \text{ pH}$ .

(c) Glass electrode,  $H^+ | \text{glass membrane} | 0.1 \text{ N HCl} | AgCl(s) - Ag$ , Potential,  $E_{glass} = E_{glass}^0 - 0.059 \text{ pH}$ .

These electrodes are coupled with a reference electrode of known potential and cell potential is determined by potentiometer or electronic voltmeter. Thus from the value of electrode potential, pH of the solution can be calculated.

**Problem:** The emf of the cell,  $(-)(Pt), Hg(l) | Hg_2Cl_2(s) | HCl(aq) | Q, H_2Q(s), (Au)(+)$  is 0.190 volt.

Calculate the pH of the HCl solution. Given,  $E_{Cl^-|Hg_2Cl_2(s)|Hg}^0 = 0.2676$  V and  $E_{H^+|Q, H_2Q(s)|Au}^0 = 0.6994$  V.

**Solution:** The cell reaction is  $2Hg + Q + 2HCl \rightarrow Hg_2Cl_2(s) + H_2Q$ .

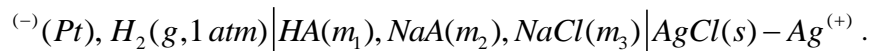
The cell potential is  $E_{cell} = E_{cell}^0 + \frac{0.059}{2} \log a_{HCl}^2$ , the activity of other substances are unity and  $\frac{a_Q}{a_{H_2Q}} = 1$ .

$$\text{Or, } E_{cell} = \left( E_{H^+|Q, H_2Q}^0 - E_{Cl^-|Hg_2Cl_2(s)|Hg}^0 \right) + 0.059 \log a_{HCl} \quad \text{or, } 0.190 = (0.6994 - 0.2676) + 0.059 \times 2 \log a_{\pm}.$$

$$\text{Or, } 0.190 = 0.4318 - 0.118 \text{ pH} \quad \text{or, } \text{pH} = (0.4318 - 0.190)/0.118 \quad \text{or, } \text{pH} = 2.05.$$

**(5) Determination of dissociation constant ( $K_a$ ) of a weak acid (HA):**

The dissociation constant of a weak acid (HA) can be accurately determined by the use of the following cell,



Reaction at LHE,  $\frac{1}{2} H_2 (1 \text{ atm}) \rightarrow H^+ + e$  (oxidation), Reaction at RHE,  $AgCl(s) + e \rightarrow Ag + Cl^-$  (reduction)

Net cell reaction is  $\frac{1}{2} H_2 (1 \text{ atm}) + AgCl(s) \rightarrow Ag(s) + H^+ + Cl^-$ . The potential of the cell is given as

$$E_{cell} = E_{cell}^0 - \frac{RT}{F} \ln(a_{H^+} \times a_{Cl^-}).$$

The activity of all other substances are unity.  $H^+$  ion in the solution comes from

the dissociation of weak acid as  $HA \rightleftharpoons H^+ + A^-$ . The dissociation constant of the acid,  $K_a = \frac{a_{H^+} \times a_{A^-}}{a_{HA}}$

or,  $a_{H^+} = K_a \times \frac{a_{HA}}{a_{A^-}}$ . Replacing  $a_{H^+}$  in the expression of cell potential, we get

$$E_{cell} = E_{cell}^0 - \frac{RT}{F} \ln \left( K_a \times \frac{a_{HA} \times a_{Cl^-}}{a_{A^-}} \right) \text{ and } E_{cell}^0 = E_{Cl^-|AgCl(s)|Ag}^0 - E_{H^+|H_2}^0 = E_{Cl^-|AgCl(s)|Ag}^0, \text{ since } E_{H^+|H_2}^0 = 0.$$

Thus,  $E_{cell} = E_{cell}^0 - \frac{RT}{F} \ln K_a - \frac{RT}{F} \ln \left( \frac{m_{HA} \times m_{Cl^-}}{m_{A^-}} \right) - \frac{RT}{F} \ln \left( \frac{\gamma_{Cl^-}}{\gamma_{A^-}} \right)$ , since  $\gamma_{HA} = 1$  as HA is neutral molecule.

So,  $E_{cell} - E_{cell}^0 + \frac{RT}{F} \ln \left( \frac{m_1 \times m_3}{m_2} \right) = -\frac{RT}{F} \ln K_a - \frac{RT}{F} \ln \left( \frac{\gamma_{Cl^-}}{\gamma_{A^-}} \right)$ . By changing the molality of the different

electrolytes in the solution, cell potential can also be varied. But the general practice is to keep the ratio of acid (HA) and its salt NaA i.e.  $(m_1/m_2)$  constant approximately unity in the series of experiments and to vary the ionic strength ( $i$ ) by using different conc. of NaCl.

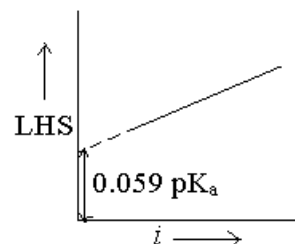
Now LHS may be plotted against the ionic strength ( $i$ ) of the solution. It is

calculated by the use of definition  $i = \frac{1}{2} \sum m_i z_i^2$  and summation is carried over all

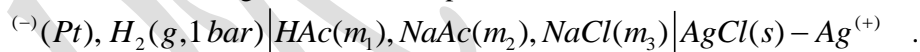
the ions present in the solution. The graph is extrapolated to zero ionic strength

when  $\gamma_{Cl^-}$  and  $\gamma_{A^-}$  each equal to one and  $\ln(\gamma_{Cl^-}/\gamma_{A^-}) = 0$ . The extrapolated

intercept is equal to  $-(RT/F) \ln K_a$  from which very accurate value of  $K_a$  is obtained. At 25 °C, the intercept is  $-0.059 \log K_a = 0.059 pK_a$ .



**Problem:** Consider the following cell at 1 bar  $H_2$  pressure,



(a) Show that  $E_{cell} = E_{cell}^0 - \frac{RT}{F} \ln \left( K_a \times \frac{m_{HAc} \gamma_{HAc} \times m_{Cl^-} \gamma_{Cl^-}}{m_{Ac^-} \gamma_{Ac^-}} \right)$ , where  $K_a$  = dissociation constant of HAc.

(b) The zero-ionic strength limit of  $E_{cell} - E_{cell}^0 + \frac{RT}{F} \ln \left( \frac{m_{HAc} \times m_{Cl^-}}{m_{Ac^-}} \right)$  at 25 °C is 0.2814 volt.

Calculate  $K_a$  of acetic acid at 25 °C

**Solution;** (a) See text given above (b). At zero-ionic strength limit, the value of

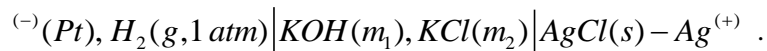
$$E_{cell} - E_{cell}^0 + 0.059 \log \left( \frac{m_{HAc} \times m_{Cl^-}}{m_{Ac^-}} \right) = -0.059 \log K_a \text{ at } 25 \text{ }^\circ\text{C. Thus from the data given}$$

$$-0.059 \log K_a = 0.2814, \text{ or } \log K_a = -\frac{0.2814}{0.059} = -4.7695 \text{ or, } K_a = 1.70 \times 10^{-5}.$$

**(6) Determination of ionic product of water:**

[Burdwan Univ. 2005]

The following cell can be set up to determine the accurate value of ionic product of water.



The cell reaction is  $\frac{1}{2} H_2 (1 \text{ atm}) + AgCl(s) \rightarrow Ag(s) + H^+ + Cl^-$ . The cell potential is given as

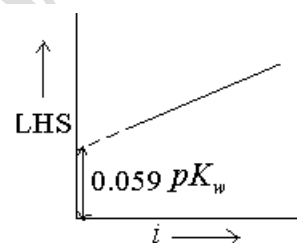
$$E_{cell} = E_{cell}^0 - \frac{RT}{F} \ln(a_{H^+} \times a_{Cl^-}). \text{ But the ionic product of water, } K_w = a_{H^+} \times a_{OH^-} \text{ or, } a_{H^+} = K_w/a_{OH^-}.$$

$$\text{Replacing } a_{H^+} \text{ in the expression of cell potential, we get } E_{cell} = E_{cell}^0 - \frac{RT}{F} \ln\left(K_w \times \frac{a_{Cl^-}}{a_{OH^-}}\right).$$

$$\text{or, } E_{cell} = E_{cell}^0 - \frac{RT}{F} \ln\left(K_w \times \frac{m_{Cl^-} \gamma_{Cl^-}}{m_{OH^-} \gamma_{OH^-}}\right) = E_{cell}^0 - \frac{RT}{F} \ln K_w - \frac{RT}{F} \ln\left(\frac{m_{Cl^-}}{m_{OH^-}}\right) - \frac{RT}{F} \ln \frac{\gamma_{Cl^-}}{\gamma_{OH^-}}$$

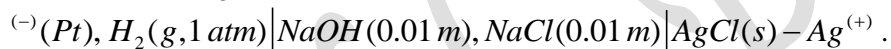
$$\text{or, } E_{cell} - E_{cell}^0 + \frac{RT}{F} \ln\left(\frac{m_2}{m_1}\right) = -\frac{RT}{F} \ln K_w - \frac{RT}{F} \ln \frac{\gamma_{Cl^-}}{\gamma_{OH^-}}.$$

Now for different values of  $m_1$  and  $m_2$ ,  $E_{cell}$  will be different. LHS of the equation can be plotted against the ionic strength ( $i$ ) of the solution mixture. A straight line is obtained and from the extrapolated intercept, the value of  $K_w$  can be calculated.



The intercept =  $0.059 pK_w$  at  $25^\circ C$ .

**Problem:** Consider the following cell at  $25^\circ C$ ,



The potential of the cell is found to be 1.0495 V. Given,  $E_{Cl^-|AgCl(s)|Ag}^0 = 0.2225$  V. Assume that activity coefficient of the ions are unity at this limit conc. of the ions. Calculate  $pK_w$  of water at  $25^\circ C$ .

**Solution:** The cell potential,  $E_{cell} = E_{cell}^0 - 0.059 \log\left(\frac{m_{Cl^-}}{m_{OH^-}}\right) - 0.059 \log K_w - 0.059 \log \frac{\gamma_{Cl^-}}{\gamma_{OH^-}}$  and

$$E_{cell}^0 = E_{Cl^-|AgCl(s)|Ag}^0 - E_{H^+|H_2}^0 = E_{Cl^-|AgCl(s)|Ag}^0 = 0.2225.$$

$$\text{Putting the values, we get } 1.0495 = 0.2225 - 0.059 \log\left(\frac{0.01}{0.01}\right) + 0.059 pK_w, \text{ since } \frac{\gamma_{Cl^-}}{\gamma_{OH^-}} = 1.$$

$$\text{Solving the equation, } pK_w = 14.017.$$

**Problem:** Consider a cell at 1 bar  $H_2$  pressure,  ${}^{(-)}(Pt), H_2 \left| NaOH(m_1), NaCl(m_2) \right| AgCl(s) | Ag | Pt^{(+)}$

$$(i) \text{ Show that } E = E^0 - \frac{RT}{F} \ln(a_{H^+} \times a_{Cl^-}) \text{ and that } E = E^0 - \frac{RT}{F} \ln\left(K_w \times \frac{m_{Cl^-} \gamma_{Cl^-}}{m_{OH^-} \gamma_{OH^-}}\right), \text{ where}$$

$K_w$  is the ionization constant of water. (2+2)

$$(ii) \text{ For this cell at } 25^\circ C, \text{ it is found that } E - E^0 + \frac{RT}{F} \ln\left(\frac{m_{Cl^-}}{m_{OH^-}}\right) \text{ approaches the limit } 0.8279 \text{ V}$$

as the ionic strength goes to zero. Calculate  $K_w$  at  $25^\circ C$ . (2)

[Burdwan Univ. 2007]



**(7) Determination of solubility product of sparingly soluble salt:**

Let us consider the following cell for determination of the solubility product of AgCl at 25 °C,



Reaction at LHE,  $\text{Ag} \rightarrow \text{Ag}^+ + \text{e}$  (oxidation), and reaction at RHE,  $\text{AgCl(s)} + \text{e} \rightarrow \text{Ag} + \text{Cl}^-$  (reduction).

Adding the two, the cell reaction becomes  $\text{AgCl(s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$ . The cell potential is given as,

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{F} \ln \frac{a_{\text{Ag}^+} \times a_{\text{Cl}^-}}{a_{\text{AgCl(s)}}}, \text{ where } E_{\text{cell}}^0 = E_{\text{Cl}^-|\text{AgCl(s)}|\text{Ag}}^0 - E_{\text{Ag}^+|\text{Ag}}^0 \text{ and } a_{\text{AgCl(s)}} = 1.$$

Since  $\text{Ag}^+$  and  $\text{Cl}^-$  remains in equilibrium with  $\text{AgCl(s)}$ , so  $E_{\text{cell}} = 0$  and  $a_{\text{Ag}^+} \times a_{\text{Cl}^-} = K_{\text{sp}}$ .

$$\text{Thus, } 0 = E_{\text{Cl}^-|\text{AgCl(s)}|\text{Ag}}^0 - E_{\text{Ag}^+|\text{Ag}}^0 - \frac{RT}{F} \ln K_{\text{sp}} \text{ or, } E_{\text{Cl}^-|\text{AgCl(s)}|\text{Ag}}^0 - E_{\text{Ag}^+|\text{Ag}}^0 = \frac{RT}{F} \ln K_{\text{sp}} \text{ and at } 25^\circ\text{C},$$

$$E_{\text{Cl}^-|\text{AgCl(s)}|\text{Ag}}^0 - E_{\text{Ag}^+|\text{Ag}}^0 = 0.059 \log K_{\text{sp}}$$

$$\text{For other silver halides, } E_{\text{X}^-|\text{AgX(s)}|\text{Ag}}^0 - E_{\text{Ag}^+|\text{Ag}}^0 = 0.059 \log K_{\text{sp}} (\text{AgX})$$

**Problem:** Solubility product of AgCl,  $K_{\text{sp}} = 1.0 \times 10^{-10}$ . Calculate the  $E^0$  for silver | silver chloride electrode immersed in 1.0 (m) KCl at 25 °C.  $E^0$  for  $\text{Ag}^+ | \text{Ag}$  is 0.799 V.

**Solution:** We have the relation,  $E_{\text{Cl}^-|\text{AgCl(s)}|\text{Ag}}^0 - E_{\text{Ag}^+|\text{Ag}}^0 = 0.059 \log K_{\text{sp}}$ , putting the values, we get

$$E_{\text{Cl}^-|\text{AgCl(s)}|\text{Ag}}^0 = 0.799 + 0.059 \log(1.0 \times 10^{-10}) = 0.209 \text{ volt.}$$

**Problem;** The emf of the cell,  ${}^{(-)}\text{Ag(s)} | \text{AgCl saturated KCl (0.05 mol dm}^{-3}) || \text{AgNO}_3 \text{ (0.1 mol dm}^{-3}) | \text{Ag(s)}^{(+)}$  is 0.431 volt. The mean activity coefficient of KCl is 0.817 and that of  $\text{AgNO}_3$  is 0.723. Calculate the solubility product of AgCl at 25 °C. **[IIT,KGP, Adm. to M Sc 2002]**

**Solution:** Reaction at LHE,  $\text{Ag(s)} \rightarrow \text{Ag}^+(\text{L}) + \text{e}$  (oxidation), reaction at RHE,  $\text{Ag}^+(\text{R}) + \text{e} \rightarrow \text{Ag(s)}$ .

$$\text{Net cell reaction, } \text{Ag}^+(\text{R}) \rightarrow \text{Ag}^+(\text{L}). \text{ Cell potential, } E_{\text{cell}} = -0.059 \log \frac{a_{\text{Ag}^+(\text{L})}}{a_{\text{Ag}^+(\text{R})}} = 0.059 \log \frac{a_{\text{Ag}^+(\text{R})}}{a_{\text{Ag}^+(\text{L})}}.$$

But  $\text{Ag}^+$  ions in the LHE remain in equilibrium with  $\text{Cl}^-$  so,  $a_{\text{Ag}^+(\text{L})} \times a_{\text{Cl}^-(\text{L})} = K_{\text{sp}}$

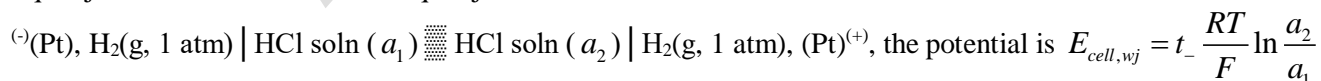
$$\text{or, } a_{\text{Ag}^+(\text{L})} = \frac{K_{\text{sp}}}{a_{\text{Cl}^-(\text{L})}}. \text{ Thus, } E_{\text{cell}} = 0.059 \log \frac{a_{\text{Ag}^+(\text{R})} \times a_{\text{Cl}^-(\text{L})}}{K_{\text{sp}}}$$

$$\text{or, } 0.431 = 0.059 \log \left[ \frac{(0.1 \times 0.723) \times 0.05 \times 0.817}{K_{\text{sp}}} \right] \text{ or, } 0.431 = 0.059 \log \left( \frac{2.953 \times 10^{-3}}{K_{\text{sp}}} \right).$$

$$\text{Solving, we get } K_{\text{sp}} = 1.46 \times 10^{-10}.$$

**(8) Determination of transport number of ion:**

Transport number of an ion is obtained from the electrolyte conc. cell with liquid junction and without liquid junction. For the cell with liquid junction



But when the same cell is set up as without liquid junction



$$\text{is } E_{\text{cell,woj}} = \frac{RT}{F} \ln \frac{a_2}{a_1}. \text{ The cell potentials are determined by potentiometer and } t_{\text{Cl}^-} = E_{\text{cell,wj}} / E_{\text{cell,woj}}.$$

**Problem:** The potential of the following electrolyte conc. cell with transference

$(-)\text{Pb} \mid \text{PbSO}_4(\text{s}) \mid \text{H}_2\text{SO}_4 (m = 1.0) \parallel \text{H}_2\text{SO}_4 (m = 0.1) \mid \text{PbSO}_4(\text{s}) \mid \text{Pb}^{(+)}$  is 0.025 V and the potential of the cell when set up as without transference

$(-)\text{Pb} \mid \text{PbSO}_4(\text{s}) \mid \text{H}_2\text{SO}_4 (a_1) \mid \text{H}_2(\text{g}, 1 \text{ atm}) \mid \text{Pt} \mid \text{H}_2(\text{g}, 1 \text{ atm}) \mid \text{H}_2\text{SO}_4 (a_2) \mid \text{PbSO}_4(\text{s}) \mid \text{Pb}^{(+)}$  is 0.02955 V at 25 °C. Calculate the transference number of  $\text{H}^+$ .

**Solution:**  $E_{\text{cell,wj}} = (t_{\text{H}^+}) \frac{RT}{2F} \ln \frac{a_1}{a_2}$  and  $E_{\text{cell,woj}} = \frac{RT}{2F} \ln \frac{a_1}{a_2}$ . Thus the transport number of  $\text{H}^+$  ion is

calculated from the potential of conc. cell with liquid junction and conc. cell

$$t_{\text{H}^+} = E_{\text{cell,wj}} / E_{\text{cell,woj}} = 0.025 / 0.02955 = 0.846.$$

### (9) Potentiometric titration:

The variation of potential of an electrode with the conc. of ion with which it is in equilibrium, may be used as an indicator in the volumetric analysis. This method is applicable to wide range of titrations provided that an appropriate indicator electrode is available. The potential of indicator electrode depends on the conc. of the ion to be titrated. As it is not possible to determine electrode potential separately, the indicator electrode is used in combination with reference electrode, the potential of which is known and remains constant during the course of titration.

In this text, only three types of potentiometric titrations are discussed based on (a) acid-base neutralization reactions (b) precipitation reactions and (c) redox reactions. Besides these three, potentiometric titration on the basis of complex reactions could also be done very successively.

#### (a) Acid-base titrations:

When an acid is titrated by a base, the reaction is  $\text{HA} + \text{BOH} \rightarrow \text{BA} + \text{H}_2\text{O}$ .

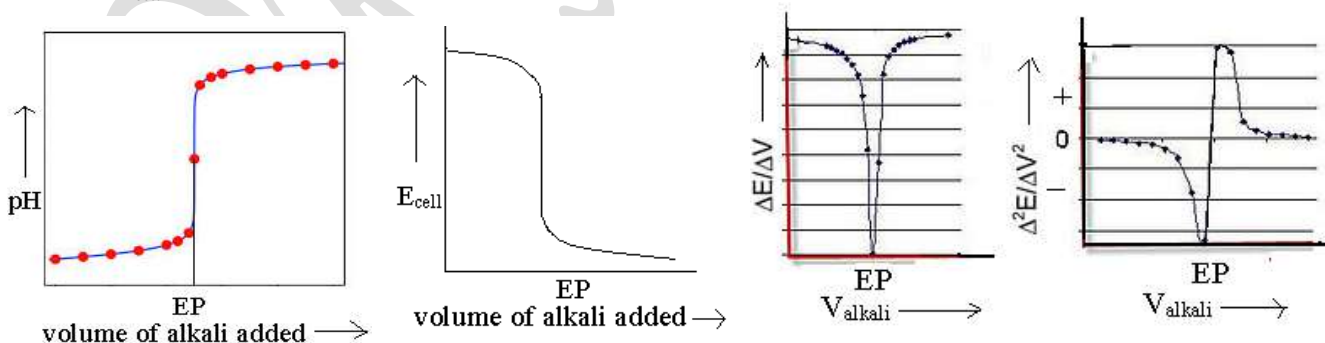
In these titrations,  $[\text{H}^+]$  varies during the progress of titration. The indicator electrode is chosen whose potential depends on the conc. of  $\text{H}^+$  ion in the titre solution. Either quinhydrone or glass electrode is used in these titration.  $\text{H}_2$  – electrode is not generally used due to difficulty to set up in the laboratory. The indicator electrode is coupled with secondary reference electrode, such as saturated calomel electrode. The cell potential is determined time-to-time with the addition of alkali (titrant) from the burette to the acid (titre). The titrant is taken at least ten-times more concentrated than the titre to avoid dilution effect. The cell used is given below:

$(-)$  saturated calomel electrode  $\parallel$  acid solution saturated with quinhydrone  $\mid$  (Pt)  $(+)$

The cell potential at 25 °C is,  $E_{\text{cell}} = E_{\text{H}^+ \mid \text{Q}, \text{H}_2\text{Q}(\text{s}), (\text{Pt})} - E_{\text{sat. cal.}} = (0.699 - 0.059 \text{ pH}) - 0.2415$ ,

$$\text{so, } E_{\text{cell}} = 0.4575 - 0.059 \text{ pH}.$$

With the addition of alkali to the acid solution, pH increases so the cell potential decreases. At the equivalence point, there is a jump of pH so cell potential also decreases sharply. After the equivalence point, there is again small change of  $E_{\text{cell}}$  with the addition of alkali.



The point of the inflexion of the curve (when the curve changes its direction) corresponds to the end point (EP) of the titration. The sharpness of the end point and symmetry of the curve on its two sides depends on the dissociation of the acid and base used and on the basicity of the acid.

Strong acid and base when used in the titration give sharp inflexion of the titration curve. When the curve does not show sharp inflexion, the exact location of the end point is obtained from the differential plot i.e. from the plot of  $\Delta E / \Delta V$  vs. V of the volume of alkali added.

However, if double plot i.e.  $(\Delta^2 E/\Delta V^2)$  vs.  $V$  is used, the inflexion cuts  $V$ -axis and location of EP can be more accurately detected. It is in general that weaker is the acid, less sharp is the inflexion.

**Determination of dissociation constant of weak acid:** It is possible to find approximate value of dissociation constant of weak acid ( $K_a$ ) from the titration curve  $E_{\text{cell}}$  vs.  $V$  of the weak acid (HA) and strong base.

The cell potential at the half neutralization point is obtained from the titration curve.

Let the cell potential at the half neutralization point is  $E_1$ .

Now pH is calculated at this half neutralization of the weak acid using

the relation,  $E_1 = 0.4575 - 0.059 \text{ pH}$ .

According to the Henderson equation,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

At the half neutralization of point,  $[\text{salt}] = [\text{acid}]$  and  $\text{pH} = \text{p}K_a$ . Thus,  $K_a$  of the weak acid can be determined for the acid by using the above relation,

$$\text{p}K_a = \text{pH} = (0.4575 - E_1)/0.059$$

The exact neutralization point is located from the differential plot.

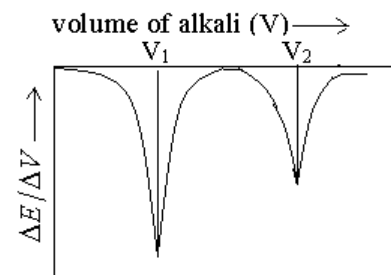
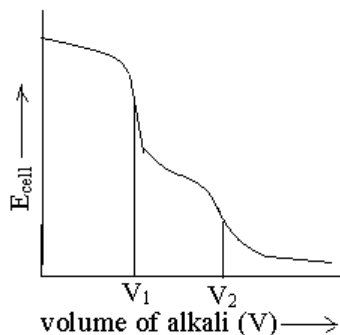
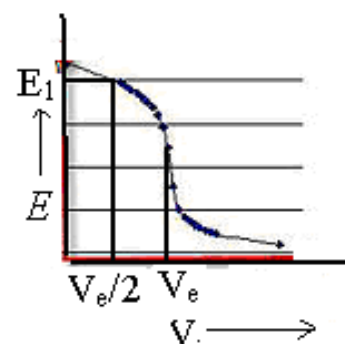
Dibasic acids for which  $K_1 \geq 100K_2$

such as oxalic acid produces two separate inflexions in the titration curve.

By the above process, separate values of  $K_1$  and  $K_2$  can be obtained. A mixture of strong acid and weak acid such HCl and HAc behave same as oxalic acid and from each inflexion; conc. of each acid in the mixture can be estimated. First inflexion corresponds to the neutralization of the strong acid (HCl) and second inflexion corresponds to the weak acid (HAc).

**Question:** Draw the potentiometric titration curve ( $E$  vs.  $V$ ) for the titration of a weak acid by a strong base.

Explain how you would get  $\text{p}K_a$  of the acid from the plot. Also explain the nature of  $\Delta E/\Delta V$  vs.  $V$  curve in this case. [Burdwan Univ. 1999]



### Precipitation reactions:

In this titration, one ion is removed from the solution of titre as precipitate by the addition of the titrant from the burette. The change in conc. of the ion during the course of titration can be followed by measuring the potential of the indicator electrode reversible to the ion.

For the titration of  $\text{AgNO}_3$  solution by  $\text{NaCl}$  solution, the reaction is  $\text{AgNO}_3 + \text{NaCl} \rightarrow \text{AgCl(s)} + \text{NaNO}_3$ .

For the titration, following cell can be set up:

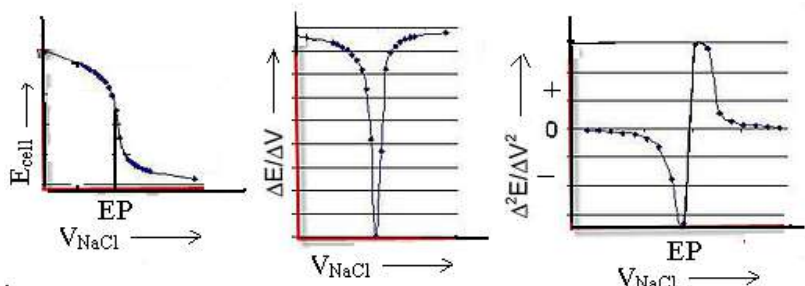


The cell potential at  $25^\circ\text{C}$ ,  $E_{\text{cell}} = E_{\text{Ag}^+|\text{Ag}} - E_{\text{sat cal}} = E_{\text{Ag}^+|\text{Ag}}^0 + 0.059 \log a_{\text{Ag}^+} - 0.2415$ , but  $E_{\text{Ag}^+|\text{Ag}}^0 = 0.799\text{V}$

so,  $E_{\text{cell}} = (0.799 - 0.2415) + 0.059 \log a_{\text{Ag}^+}$  or,  $E_{\text{cell}} = 0.5575 + 0.059 \log a_{\text{Ag}^+}$ .

As the  $\text{NaCl}$  solution is added to  $\text{AgNO}_3$  solution,  $a_{\text{Ag}^+}$  is removed

from the solution in the form of precipitate  $\text{AgCl(s)}$ . The cell potential is decreased as the titration is continued. At the equivalence point, there is sharp decrease of the potential and the end point is located in the titration curve.



### Rough estimate of $K_{sp}$ of $\text{AgCl}(s)$ :

Further, at the end point,  $a_{\text{Ag}^+} = a_{\text{Cl}^-}$  and  $a_{\text{Ag}^+}$  can be calculated from the cell potential at the equivalence point by the use of the relation,  $E_{\text{cell}} = 0.5575 + 0.059 \log a_{\text{Ag}^+}$ .

Thus, the solubility product,  $K_{sp} = a_{\text{Ag}^+} \times a_{\text{Cl}^-}$  or,  $K_{sp} = a_{\text{Ag}^+}^2$ .

**Question:** Write down the cell set-up for potentiometric estimation of chloride ion by  $\text{AgNO}_3$  solution. Give the expression for emf of the cell. [Burdwan Univ. 2011]

**Answer:**  $\text{Cl}^- | \text{AgCl}(s) | \text{Ag}$  can be used as indicator electrode and another secondary reference electrode such as saturated calomel can be used to set up the cell:

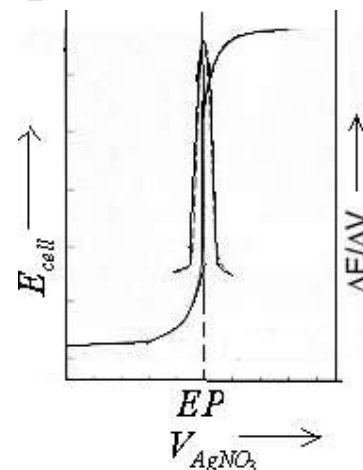
(-) saturated calomel || solution of  $\text{Cl}^-$  ion (titre) |  $\text{AgCl}(s) | \text{Ag}^{(+)}$ .

The cell potential,

$$E_{\text{cell}} = E_{\text{Cl}^- | \text{AgCl}(s) | \text{Ag}} - E_{\text{sat cal}} = E_{\text{Cl}^- | \text{AgCl}(s) | \text{Ag}}^0 - \frac{RT}{F} \ln a_{\text{Cl}^-} - E_{\text{sat cal}}$$

$$\text{or, } E_{\text{cell}} = \left( E_{\text{Cl}^- | \text{AgCl}(s) | \text{Ag}}^0 - E_{\text{sat cal}} \right) - \frac{RT}{F} \ln a_{\text{Cl}^-}.$$

With the addition of  $\text{AgNO}_3$  solution (titrant) from the burette,  $a_{\text{Cl}^-}$  is decreased and  $E_{\text{cell}}$  is increased. At the equivalence point, there occurs a sharp increase of  $E_{\text{cell}}$  from which the end point is located.



### Redox titrations:

Redox titrations are carried out potentiometrically by inserting an inert metal in a solution containing the ion to be titrated. This redox electrode acts as indicator electrode and it is coupled with a reference electrode to form a cell whose potential is determined by potentiometer.

Let us take the example of titration of  $\text{FeSO}_4$  solution by  $\text{Ce}(\text{SO}_4)_2$  solution.

The redox reaction is  $\text{Fe}^{+2} (\text{titre}) + \text{Ce}^{+4} (\text{titrant}) \rightarrow \text{Fe}^{+3} + \text{Ce}^{+3}$

The cell set-up is (-) saturated calomel ||  $\text{Fe}^{+3}, \text{Fe}^{+2}$  in solution |  $(\text{Pt})^{(+)}$

$$\text{The cell potential at } 25^\circ\text{C, } E_{\text{cell}} = E_{(\text{Fe}^{+3}, \text{Fe}^{+2}) | \text{Pt}} - E_{\text{sat cal}} = \left( E_{(\text{Fe}^{+3}, \text{Fe}^{+2}) | \text{Pt}}^0 + 0.059 \log \frac{a_{\text{Fe}^{+3}}}{a_{\text{Fe}^{+2}}} \right) - E_{\text{sat cal}}.$$

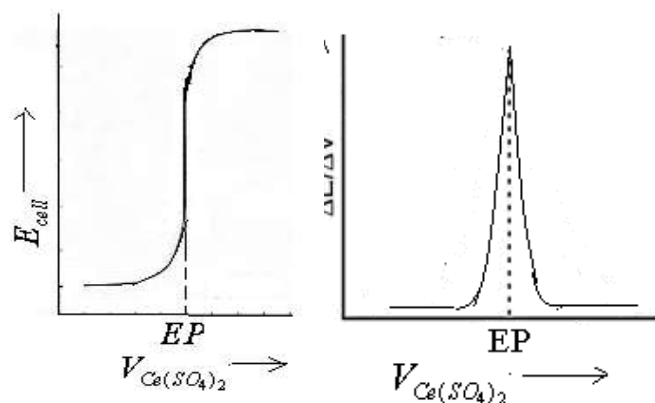
Taking the activity ratio as the conc. ratio of the ions, we have  $E_{\text{cell}} = (0.771 - 0.2415) + 0.059 \log \frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+2}]}$

$$\text{or, } E_{\text{cell}} = 0.5295 + 0.059 \log \frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+2}]}$$

As the titre,  $\text{Ce}(\text{SO}_4)_2$  solution is added to the  $\text{FeSO}_4$  solution,  $[\text{Fe}^{+3}]$  is increased but  $[\text{Fe}^{+2}]$  is decreased resulting the increase of  $[\text{Fe}^{+3}]/[\text{Fe}^{+2}]$  in the titre solution. The cell potential is increased as the titration proceeds and at the end point, there is sharp increase of  $[\text{Fe}^{+3}]/[\text{Fe}^{+2}]$  that produces a sharp increase of cell potential.

After the equivalence point, with further addition of  $\text{Ce}(\text{SO}_4)_2$  solution from the burette, the potential of the indicator electrode is governed by  $(\text{Ce}^{+4}, \text{Ce}^{+3})$  system.

The sharpness of the cell potential at the equivalence point depends on the difference of standard potential of the titre and titrant system. If the standard potentials are close, the end point is not sharp enough and differential plot is required to detect the exact end point.



Potential of the indicator electrode (here  $\text{Fe}^{+3}, \text{Fe}^{+2} | \text{Pt}$ ) at the start of the titration is undefined as  $[\text{Fe}^{+3}]$  is not known.

Before the equivalence point, the potential is  $E_{\text{Fe}^{+3}, \text{Fe}^{+2} | \text{Pt}} = 0.771 + 0.059 \log \left( \frac{f}{1-f} \right)$ ,

where  $f$  is fraction of titration done, At the equivalence point, the potential of the indicator electrode is

$$E_{EP} = \frac{E_{(\text{Fe}^{+3}, \text{Fe}^{+2}) | \text{Pt}}^0 + E_{(\text{Ce}^{+4}, \text{Ce}^{+3}) | \text{Pt}}^0}{2}.$$

The general expression of potential at the equivalence point in the redox titration is  $E_{EP} = \frac{n_1 E_1^0 + n_2 E_2^0}{n_1 + n_2}$ ,

where  $n_1, n_2$  are the number of electrons involved and  $E_1^0, E_2^0$  are the standard electrode potential of the two redox systems respectively.

After the equivalence point, the potential of the indicator electrode is controlled by,  $(\text{Ce}^{+4}, \text{Ce}^{+3})$  system.

$$E_{(\text{Ce}^{+4}, \text{Ce}^{+3}) | \text{Pt}} = E_{(\text{Ce}^{+4}, \text{Ce}^{+3}) | \text{Pt}}^0 + 0.059 \log \frac{[\text{Ce}^{+4}]}{[\text{Ce}^{+3}]} \text{ or, } E_{(\text{Ce}^{+4}, \text{Ce}^{+3}) | \text{Pt}} = 1.44 + 0.059 \log (f - 1),$$

since,  $E_{(\text{Ce}^{+4}, \text{Ce}^{+3}) | \text{Pt}}^0 = 1.44$  at  $25^\circ\text{C}$ .

**Difference from conductometric titration:** Unlike conductometric titration, data points near the equivalence point are important in the potentiometric titration. In the former case, data points away from the equivalence point are important.

**Problem (1):** A 50 ml 0.05 (M) solution of Fe(II) is titrated with 0.05 (M) solution of Ce(IV) in the presence of dilute  $\text{H}_2\text{SO}_4$  at  $25^\circ\text{C}$ . Calculate the equivalence point potential and equilibrium constant  $K$  in terms of  $\log K$ . Given,  $E_{(\text{Fe}^{+3}, \text{Fe}^{+2}) | \text{Pt}}^0 = 0.75 \text{ V}$  and  $E_{(\text{Ce}^{+4}, \text{Ce}^{+3}) | \text{Pt}}^0 = 1.45 \text{ V}$  at  $25^\circ\text{C}$ . [IIT – JAM 2007]

**Solution:** The potential at the equivalence point,  $E_{EP} = \frac{n_1 E_1^0 + n_2 E_2^0}{n_1 + n_2} = \frac{1 \times 0.75 + 1 \times 1.45}{1 + 1} = 1.1 \text{ V}$

The reaction is  $\text{Fe}^{+2} + \text{Ce}^{+4} \rightarrow \text{Fe}^{+3} + \text{Ce}^{+3}$  and the cell set-up is  $(-)\text{Pt} | (\text{Fe}^{+3}, \text{Fe}^{+2}) || (\text{Ce}^{+4}, \text{Ce}^{+3}) | \text{Pt}(+)$ .

$$E_{\text{cell}}^0 = E_{\text{RHE}}^0 - E_{\text{LHE}}^0 = E_{(\text{Ce}^{+4}, \text{Ce}^{+3}) | \text{Pt}}^0 - E_{(\text{Fe}^{+3}, \text{Fe}^{+2}) | \text{Pt}}^0 = (1.45 - 0.75) \text{ V or, } E_{\text{cell}}^0 = 0.60 \text{ V}.$$

Now we have relation,

$$E_{\text{cell}}^0 = \frac{0.059}{1} \log K \text{ or, } \log K = \frac{E_{\text{cell}}^0}{0.059} = \frac{0.60}{0.059} = 10.$$

**Problem (2):** A solution of  $\text{Fe}^{+2}$  is titrated potentiometrically using  $\text{Ce}^{+4}$  solution. Calculate the emf of redox electrode thus formed when (i) 50 % of  $\text{Fe}^{+2}$  is titrated, (ii) 90 % of  $\text{Fe}^{+2}$  is titrated and (iii) 110 % titration is done.

Given:  $\text{Fe}^{+2} \rightarrow \text{Fe}^{+3} + e$ ,  $E^0 = -0.77 \text{ volt}$ ,  $\text{Fe}^{+2} + \text{Ce}^{+4} \rightarrow \text{Fe}^{+3} + \text{Ce}^{+3}$ ;  $K = 10^{14}$ .

[Burdwan Univ. 1986]

**Solution:** The redox electrode is  $E_{(\text{Fe}^{+3}, \text{Fe}^{+2}) | \text{Pt}} = E_{(\text{Fe}^{+3}, \text{Fe}^{+2}) | \text{Pt}}^0 + 0.059 \log \frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+2}]}$ ,

$$\text{but } E_{(\text{Fe}^{+3}, \text{Fe}^{+2}) | \text{Pt}}^0 = -E_{(\text{Fe}^{+2}, \text{Fe}^{+3}) | \text{Pt}}^0 = 0.77 \text{ volt}.$$

(i) When 50 % of  $\text{Fe}^{+2}$  is titrated,  $E_{(\text{Fe}^{+3}, \text{Fe}^{+2}) | \text{Pt}} = E_{(\text{Fe}^{+3}, \text{Fe}^{+2}) | \text{Pt}}^0 + 0.059 \log \frac{0.5}{0.5} = E_{(\text{Fe}^{+3}, \text{Fe}^{+2}) | \text{Pt}}^0 = 0.77 \text{ V}$

(ii) When 90 % of  $\text{Fe}^{+2}$  is titrated,  $E_{(\text{Fe}^{+3}, \text{Fe}^{+2}) | \text{Pt}} = 0.77 + 0.059 \log \frac{0.9}{0.1} = 0.826 \text{ V}$ .

(iii) The equilibrium constant,  $K = \frac{[Fe^{+3}] \times [Ce^{+3}]}{[Fe^{+2}] \times [Ce^{+4}]} = 10^{14}$  or,  $\frac{[Fe^{+3}]}{[Fe^{+2}]} = 10^{14} \times \frac{[Ce^{+4}]}{[Ce^{+3}]} = 10^{14} \times \frac{0.1}{1} = 10^{13}$ .

Since when 110 % titration is done, 10 %  $Ce^{+4}$  remains excess with the 100 %  $Ce^{+3}$  in the solution.

$$E_{(Fe^{+3}, Fe^{+2})|Pt} = 0.77 + 0.059 \log 10^{13} = 0.77 + 0.059 \times 13 = 1.537 \text{ V.}$$

**Problem (3):** Given,  $Ag^+ + e \rightarrow Ag$ ;  $E^0 = 0.50 \text{ V}$  and  $Cu^{2+} + 2e \rightarrow Cu$ ;  $E^0 = 0.34 \text{ V}$ .

A 100 ml solution is 1080 mg with respect to  $Ag^+$  and 635 mg with respect to  $Cu^{2+}$ . If 0.1 mg  $Ag^+$  left in the solution is considered to be the complete deposition of  $Ag^+$ , the cathode potential, so that no copper is deposited during the process is:

(1) 0.16 V (2) 0.84 V (3) 0.31 V (4) -0.16 V. [NET (CSIR-UGC) 2011 (June)]

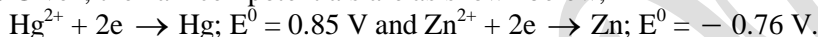
**Problem (4):** In the cell,  $Zn | ZnSO_4 (1.0 \text{ M}) || Fe^{3+} (1.0 \text{ M}), Fe^{2+} (1.0 \text{ M}) | Pt$ , given that standard potential of  $(Fe^{3+}, Fe^{2+}) | Pt = 0.769 \text{ V}$  and  $Zn^{2+} | Zn = -0.76 \text{ V}$ , the standard e.m.f. of the cell is

(1) 0.76 V (2) -1.529 V (3) -0.769 V (4) 1.529 V. [Banaras Hindu Univ. Adm. to M Sc 2012]

**Solution:**  $E_{cell}^0 = E_{(Fe^{3+}, Fe^{2+})|Pt}^0 - E_{Zn^{2+}|Zn}^0 = 0.769 - (-0.76) = 1.529$ , since both the electrodes are in standard state.

The correct answer is (4).

**Problem (5):** Given, the half-cell potentials are as shown below,



The standard cell potential of the cell with spontaneous electrochemical reaction is:

(A) 0.09 V (B) 0.80 V (C) 1.61 V (D) 0.18 [Hyderabad Central Univ. Adm. to M Sc 2015]

**Solution:** The spontaneous reaction is  $Zn + Hg^{2+} \rightarrow Zn^{2+} + Hg$ ;

$$E_{cell}^0 = E_{Hg^{2+}|Hg}^0 - E_{Zn^{2+}|Zn}^0 = 0.85 - (-0.76) = 1.61 \text{ V.} \quad \text{[Answer (C)]}$$

**Problem (6):** Set up the electrochemical cell where the following process takes place,



**Solution:** Let us take the cell,  $(-)Ag - AgCl(s) | ZnCl_2 (a_1) | Zn | ZnCl_2 (a_2) | AgCl(s) - Ag(+)$ .

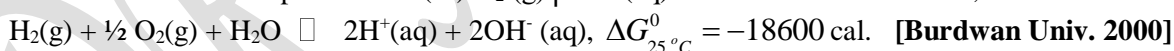
Now let us see whether the cell may comply with the cell reaction given in the problem.

LHS cell reaction is  $2Ag + ZnCl_2 (a_1) \rightarrow 2AgCl(s) + Zn$ , and

RHS cell reaction is  $Zn + 2AgCl(s) \rightarrow 2Ag + ZnCl_2 (a_2)$ . Two cells are coupled in opposition,

Two component cell reactions are added to get the net cell reaction,  $ZnCl_2 (a_1) \rightarrow ZnCl_2 (a_2)$ .

**Problem (7):** Calculate the standard potential of  $(Pt) O_2 (g) | OH^- (aq)$  electrode at 25 °C. Given,



**Solution:** The cell set-up for the reaction is  $(-)Pt, H_2(g) | OH^- (aq) | O_2(g), (Pt)(+)$ .

$$\text{We have } nFE^0 = -\Delta G^0 = 18600 \text{ cal, so } E_{cell}^0 = \frac{18600 \text{ cal}}{2 \times 96500 \text{ C}} = \frac{18600 \times 4.18 \text{ J}}{2 \times 96500 \text{ C}} = 0.403 \text{ V at } 25^\circ \text{C.}$$

$$\text{But } E_{cell}^0 = E_{RHE}^0 - E_{LHE}^0 = E_{O_2|OH^-}^0 - E_{H^+|H_2}^0 \text{ or, } 0.403 = E_{O_2|OH^-}^0 - 0 \text{ or, } E_{O_2|OH^-}^0 = 0.403 \text{ V at } 25^\circ \text{C.}$$

**Problem (8):** Calculate the value of  $(RT/F)$  at 30 °C.

[Burdwan Univ. 2001]

**Solution:** 0.026 volt.

**Problem (9):** Derive the following relation  $\frac{E_2^0}{T_2} - \frac{E_1^0}{T_1} = \frac{\Delta H^0}{nF} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$ , where  $E_1^0$  and  $E_2^0$  are the values of

standard emf ( $E^0$ ) at temperature  $T_1$  and  $T_2$  respectively.

[Burdwan Univ. 2002]

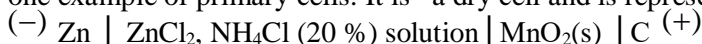
**Solution:** We have  $\Delta G^0 = \Delta H^0 - T\Delta S^0$  or,  $\frac{\Delta G^0}{T} = \frac{\Delta H^0}{T} - \Delta S^0$ . But  $\Delta G^0 = -nFE^0$ . Putting the values at two temperatures and subtracting, we get the above relation, provided  $\Delta H^0$  and  $\Delta S^0$  are temperature independent.

### Commercial Cells:

Some galvanic cells are used as power supply in different commercial purposes. These are called commercial cells. Two types of commercial cells are used.

#### (A) Primary cells or disposal cells:

(1) Laclance cell is one example of primary cells. It is a dry cell and is represented as

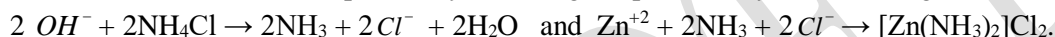


Reaction at LHE (anode):  $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{+2} + 2e$  (oxidation) and

reaction at RHE (cathode):  $2\text{MnO}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2e \rightarrow \text{Mn}_2\text{O}_3 + 2\text{OH}^-$  (reduction).

The net cell reaction is  $\text{Zn}(\text{s}) + 2\text{MnO}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Zn}^{+2} + \text{Mn}_2\text{O}_3(\text{s}) + 2\text{OH}^-$ .

The cell reaction is made towards completion by removing the products by the following side reactions



Since these reactions are not involved directly in the electrode reactions, they do not contribute anything towards the cell potential.

The potential of this cell is 1.5 volt and since the cathode potential is a function of pH, the cell potential falls rapidly on continuous discharge.

#### (2) Lithium – Iodine cell:

It is completely dry cell, no water content is within the cell. It is represented as  $\text{Li} \mid \text{LiI}(\text{s}) \text{ layer} \mid \text{I}_2$

The cell reaction is  $2\text{Li}(\text{s}) + \text{I}_2(\text{s}) \rightarrow 2\text{LiI}(\text{s})$ . The cell potential is 3.5 volts.

It is widely used in Cardiac Pacemaker.

#### (B) Secondary cells or chargeable cells:

Such type of cells can be used again and again by recharging the cell to bring it into the initial state.

To recharge the cell, it is connected with a cell of higher potential than the cell in such a way that the secondary cell acts as the electrolyte cell. So these cells are called storage cells or accumulators.

A good accumulator should satisfy the following conditions:

(a) It should retain the stored electrical energy for a considerable period of time when not in use.

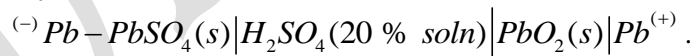
(b) The resistance of these cells should be low, construction should be simple and its cost is also low.

They are called secondary cells because chemical reactions responsible for the energy is induced into the cell by first passing electricity through it.

#### (1) Acid storage cell or lead accumulator:

The cell consists of two electrodes one is  $\text{SO}_4^{-2} \mid \text{PbSO}_4(\text{s}) \mid \text{Pb}$  and other is  $\text{H}^+ \mid \text{PbO}_2(\text{s}) \mid \text{Pb}$ .

The common electrolyte for both the electrodes is 20 %  $\text{H}_2\text{SO}_4$  solution. The cell is represented as



When the cell is used as power supply, the reaction at the anode  $\text{Pb}(\text{s}) + \text{SO}_4^{-2} \rightarrow \text{PbSO}_4(\text{s}) + 2e$  (oxidation)

and at the cathode is  $\text{PbO}_2(\text{s}) + 4\text{H}^+ + \text{SO}_4^{-2} + 2e \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$  (reduction)

The net cell reaction:  $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$ .

When the cell produces electrical energy, forward reaction occurs spontaneously and it is called discharging.  $\text{PbSO}_4(\text{s})$  is formed appreciably at both electrodes and when the reaction attains equilibrium, the cell stops producing electricity. Now the cell is charged by passing electrical energy from external source and non-spontaneous reverse reaction is made to occur. The cell restores its initial condition and Pb is deposited on the original negative electrode,  $\text{PbO}_2(\text{s})$  is formed on the positive electrode and  $\text{H}_2\text{SO}_4$  is regenerated.

The cell potential at 25 °C,  $E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.059}{2} \log a_{\text{H}_2\text{SO}_4}^2 = 2.04 + 0.059 \log a_{\text{H}_2\text{SO}_4}$ .

$$\text{Since, } E_{cell}^0 = E_{H^+|PbO_2(s)|Pb}^0 - E_{SO_4^{2-}|PbSO_4(s)|Pb}^0 = 1.685 - (-0.356) = 2.04 \text{ volt.}$$

The cell potential depends on the activity or conc. of  $H_2SO_4$  in the cell. It is 2.2 volt with no load and 2.0 volt with load.

(2) **Alkali storage cell or Edition accumulator:** This cell consists of  $OH^-|FeO(s) - Fe$  as anode and  $OH^-|Ni_2O_3(s), NiO(s)|Ni$  as cathode. Strong conc. of KOH solution acts as common electrolyte.

The cell is represented as  $(-) Fe|FeO(s)|KOH \text{ conc. soln}|Ni_2O_3(s), NiO(s)|Ni^{(+)}$ .

The cell reaction is  $Fe(s) + Ni_2O_3(s) \xrightleftharpoons[\text{charging}]{\text{discharging}} FeO(s) + 2NiO(s)$ .

Opposite change occurs when spent-up cell is recharged. The oxides really exist in hydrated form.

The cell potential,  $E_{cell} = E_{cell}^0 - \frac{0.059}{2} \log \frac{a_{Fe^{+2}} a_{Ni^{+2}}^2}{a_{Ni^{+3}}^3}$  and  $E_{cell}^0 = E_{OH^-|Ni_2O_3(s), NiO(s)|Ni}^0 - E_{OH^-|FeO(s)|Fe}^0$

$$\text{So, the cell potential, } E_{cell} = 1.32 + 0.059 \log \frac{a_{Ni^{+3}}}{a_{Ni^{+2}} \sqrt{a_{Fe^{+2}}}} = 0.88 - (-0.44) = 1.32 \text{ volt.}$$

Between two accumulators, alkali cell is more durable and it can stand rough handling but more costly. Large number of cells is required to get a particular potential.

(3) **Nickel – Cadmium (Nicad) cell:**

This rechargeable cell is in a jelly-roll arrangement and separated by a layer soaked in moist NaOH or KOH.

The cell is represented as  $(-) Cd|Cd(OH)_2(s)|KOH \text{ soln}|Ni(OH)_3(s), Ni(OH)_2(s)|Ni^{(+)}$ .

The cell reaction is given as  $Cd(s) + 2Ni(OH)_3(s) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$ .

It has larger life than lead storage cell but more expensive to manufacture. It is used in different mobile sets.

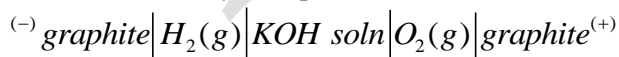
(C) **Fuel Cell:** Converting heat efficiently into electricity is one of the major problems. This is traditionally done by using boilers that drives a turbine which is coupled to a generator. This process is not much efficient and it creates a lot of pollution problem also.

The latest device for the purpose is fuel cell. In these cells, cathode and anode constituents are continuously supplied and the electrical energy is withdrawn indefinitely from the cell as long as outside supply is maintained.

One example is  $H_2 - O_2$  fuel cell.

It consists of three compartments separated from each other by porous electrodes. The  $H_2$  gas is fed in one compartment and  $O_2$  gas is fed into another compartment.

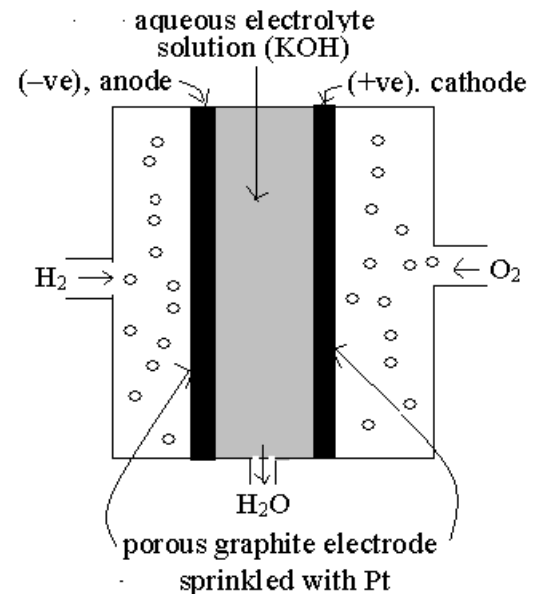
These gases then diffuse slowly through the electrodes and react with an electrolyte kept in the central compartment. The electrodes are made of conducting material such as graphite with sprinkling of Pt that acts as catalyst. The electrolyte is an aqueous solution of a base like KOH solution. The cell may be represented as,



The reaction at LHE,  $H_2(g) \rightarrow 2H^+ + 2e$  (oxidation) and

at RHE,  $\frac{1}{2} O_2(g) + H_2O + 2e \rightarrow 2OH^-$  (reduction).

The net cell reaction is  $H_2(g) + \frac{1}{2} O_2(g) + H_2O \rightarrow 2H^+ + 2OH^-$ ;  $\Delta G^0 = -18600 \text{ cal/mol}$ .





Again,  $\Delta G^0 = -nFE_{cell}^0$ .  $E_{cell}^0 = \frac{\Delta G^0}{-nF} = \frac{-18600 \times 4.2 J}{-2 \times 96500 C} = 0.403 \text{ volt.}$

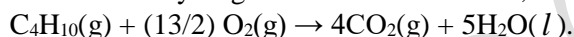
The cell potential,  $E_{cell} = E_{cell}^0 - \frac{0.059}{2} \log(a_{H^+}^2 \times a_{OH^-}^2)$

or,  $E_{cell} = E_{cell}^0 - 0.059 \log(a_{H^+} \times a_{OH^-})$  or,  $E_{cell} = 0.403 - 0.059 \log(10^{-14}) = 1.23 \text{ volt.}$

Although the exchange current of the reaction at the anode is large, the same at the cathode is very small ( $10^{-10} \text{ A/cm}^2$ ) due to slow reduction of  $O_2$ . This restricts the current available from the cell. To increase the available current, the fuel cell uses a catalytic surface with very large surface area as electrode. This increases the available current in spite of low current density.

Fuel cells produce electricity with an efficiency of about 70 % as compared to the thermal plants whose efficiency of about 40 %. The cell was used for providing electricity in the Apollo space programme. The water vapour so produced was condensed to liquid water and it provided drinking water. Other fuel cells use the fuels like C,  $CH_4$ , etc.

**Problem:** Fuel cells provide clean electrical energy to a variety of applications including automobiles and stationary power sources. Normally hydrogen combines with oxygen to give electrical energy and water. If we use butane instead of hydrogen at 1.0 bar and 298 K, the following reaction occurs:



If the change in free energy of the reaction is 2746.06 kJ/mol involving 26 electrons, its open circuit voltage is

- (1) 1.55 V    (2) 1.09 V    (3) 3.15 V    (4) 2.06 V    [NET(CSIR – UGC), 2014 (II), m = 4]

**Solution:**  $\Delta G = -nFE$  or,  $E = -\frac{\Delta G}{nF} = -\frac{(-2726.06 \times 10^3 J mol^{-1})}{26 \times 96500 C mol^{-1}} = 1.0865 \text{ V.}$  So the correct option is (2).

DR N C DEY