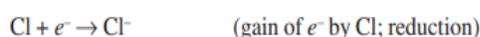
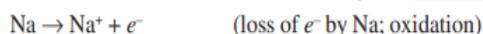


## ELECTROCHEMISTRY

- Electrochemistry may be defined as the branch of chemistry which deals with the quantitative study of inter-relationship between chemical energy and electrical energy and inter-conversion of one form into other relationships between electrical energy taking place in redox reactions.

## OXIDATION AND REDUCTION AS ELECTRON TRANSFER PROCESS

- Process in which an atom or ion loses one or more electrons to the other is called oxidation and the process in which an atom or ion gains one or more electrons is termed as reduction. *Example*



## OXIDATION NUMBER

- The oxidation number is basically the count of electrons that atoms in a molecule can share, lose or gain while forming chemical bonds with other atoms of a different element. Oxidation number is also referred to as oxidation state.

## BALANCING REDOX REACTION

- The redox reaction can be balanced by any of the following methods: (a) Oxidation number method. (b) Ion electron method.
- Balancing redox reactions:** first requires splitting the equation into the two half-reactions of reduction and oxidation. All atoms except oxygen and hydrogen should be balanced first. In acidic conditions, the oxygen atoms should be balanced with water, while hydrogen atoms should be balanced with  $\text{H}^+$ .

## ELECTROLYTIC CONDUCTION

- When a voltage is applied to the electrodes dipped into an electrolytic solution, ions of the electrolyte move and, therefore, electric current flows through the electrolytic solution. The

power of the electrolytes to conduct electric current is termed **conductance or conductivity**.

- Conductivity (k) :**

$$k = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$$

Where, R is Resistance,  $l/A$  = cell constant ( $G^*$ ) and  $\rho$  is resistivity.

- Measurement of Conductance:** The conductance of an electrolyte is measured with the help of a conductivity cell. Conductivity cell is a device which has two parallel platinum electrodes coated with platinum black.

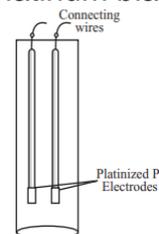


Fig. 13.1: Conductivity Cell

**K (conductivity) = conductance × cell constant**

- Molar Conductivity:** Molar conductivity is the conducting power of all the ions furnished by one mole of an electrolyte in a solution of specified concentration. It is denoted by  $\lambda_m$  and is related to K by the relation.

$$\lambda_m = \frac{1000 K}{M}$$

Where M is the molarity of the solution. Its units are  $\text{S cm}^2 \text{ mol}^{-1}$

- Kohlrausch's Law:** At infinite dilution, the molar conductivity of an electrolyte is the sum of the ionic conductivities of the cations and anions, e.g., for  $\text{A}_x\text{B}_y$ .

$$\Lambda_m^0 (\text{A}_x\text{B}_y) = x\Lambda_{\text{A}^+}^0 + y\Lambda_{\text{B}^-}^0$$

$$\Lambda_{\text{eq}}^0 = \Lambda_{\text{A}^+}^0 + \Lambda_{\text{B}^-}^0$$

## ELECTRO CHEMICAL CELLS

- An electrochemical cell is a device used for the interconversion of electrical and

chemical energy. An electrochemical cell contains two electrodes (cathode and anode) and an electrolyte. These are of two types; based on the nature of conversion of energies.

- **(a) Electrolytic cell:** (Faradaic cell) In electrochemical cells, a battery is used to carry out redox reactions on the electrodes of the cell. Thus, these cells convert electrical energy into chemical energy.
- **(b) Galvanic cell (Voltaic cell):** In galvanic cells an emf is developed as a result of redox reaction occurring on the electrodes. These cells convert chemical energy into electrical energy.

### FARADAY'S LAWS OF ELECTROLYSIS

- **Faraday's First Law of Electrolysis:** It states that the mass of a substance liberated during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte taken as

a solution or as melt.  $w = zIt$

- **Faraday's Second Law of Electrolysis:** It states that "The masses of different ions liberated at the electrodes, when the same amount of electricity is passed through different electrolytes are directly proportional to their chemical equivalents".

$$\frac{w_A}{w_B} = \frac{\text{Equivalent mass of A}}{\text{Equivalent mass of B}}$$

- **Salt Bridge:** A salt bridge is a inverted U tube filled with a concentrated solution of an inert electrolyte like KCl or  $\text{NH}_4\text{NO}_3$  which does not take part in the cell reaction.
- **Electrode Potential:** When an electrode is in contact with the solution of its ions in a half-cell, it has a tendency to lose or gain electrons which is known as electrode potential. It is expressed in volts. It is an intensive property, i.e., independent of the amount of species in the reaction.
- **Standard electrode potential:** The

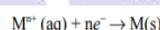
potential difference developed between metal electrode and solution of ions of unit molarity (1M) at 1 atm pressure and  $25^\circ\text{C}$  (298 K) is called standard electrode potential. It is denoted by  $E^\circ$ .

### MEASUREMENT OF ELECTRODE POTENTIAL

- It is not possible to measure single electrode potential. It is because the reaction taking place at the electrodes is oxidation or reduction and these reactions do not take place in isolation. It can be measured with respect to a reference electrode. The electrode used as reference electrode is standard hydrogen electrode (SHE).
- **Electrochemical Series:** Standard potential of a large number of electrodes have been measured and they have been listed in the increasing order of electrode potential in a series called electro chemical series.

### NERNST EQUATION FOR ELECTRODE POTENTIAL

- Nernst equation relates electrode potential to the concentration of ions in the electrolyte. An electrode reaction is always written as reduction reaction.



$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]} = E^\circ - \frac{0.059}{n} V \log \frac{1}{[M^{n+}]}$$

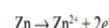
The cell potential of electrochemical reaction :  $aA + bB \xrightarrow{nc^-} cC + dD$  is given by :

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF} \log [Q_c] = E^\circ_{\text{cell}} - \frac{0.059}{n} V \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

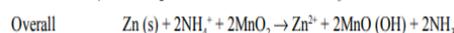
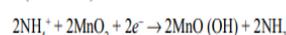
### BATTERIES AND FUEL CELLS

- **Dry cell :**

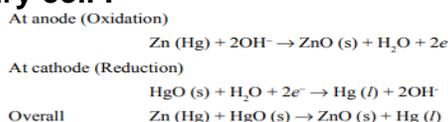
At anode (Oxidation)



At cathode (Reduction)



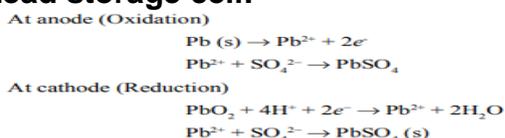
- **Mercury cell :**



$$\Delta G^0 = -nF E_{\text{cell}}^0$$

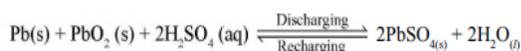
Where,  $\Delta G^0$  = standard Gibbs energy change and  $nF$  is the number of Faradays of charge passed.  $E_{\text{cell}}^0$  is standard cell potential.

- **Lead storage cell:**



$$\Delta G^0 = -2.303 RT \log K_c$$

Overall



- **Relation between  $k$  and  $\Lambda_m$ :**

$$\Lambda_m = \frac{1000 \times k}{C}$$

- **Kohlrausch's law :** (a) In general, if an electrolyte on dissociation give  $v_+$  cations and anions  $v_-$ , then its limiting molar conductivity ( $\Lambda_m^0$ ) is given by

$$\Lambda_m^0 = v_+ \lambda_+^0 + v_- \lambda_-^0$$

Here,  $\lambda_+^0$  and  $\lambda_-^0$  are the limiting molar conductivities of cation and anion respectively and  $v_+$  and  $v_-$  are the number of cations and anions furnished by one formula unit of the electrolyte.

- (b) Degree of dissociation ( $\alpha$ ) is given by :

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0}$$

Here,  $\Lambda_m^c$  is molar conductivity at the concentration  $C$ , and  $\Lambda_m^0$  is limiting molar conductivity of the electrolyte.

- (c) Dissociation constant ( $K$ ) of weak electrolyte

$$K = \frac{C\alpha^2}{1-\alpha} = \frac{C \left( \frac{\Lambda_m^c}{\Lambda_m^0} \right)^2}{1 - \frac{\Lambda_m^c}{\Lambda_m^0}}$$

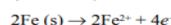
- **Relation between  $E_{\text{cell}}^0$  and equilibrium constant ( $K_c$ ) :**

$$E_{\text{cell}}^0 = \frac{2.303RT}{nF} \log K_c = \frac{0.059}{n} V \log K_c$$

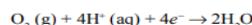
- On dilution of a solution, its conductivity decreases while molar conductivity increases.

- **Corrosion:** Corrosion of metals is an electrochemical phenomenon. In corrosion, metal is oxidized by loss of electrons to oxygen and formation of oxides.

At anode (Oxidation) :



At cathode (Reduction) :



Atmospheric oxidation :



- The conductance is reciprocal of resistance and the conductivity is reciprocal of specific resistance.

## FACTORS AFFECTING CONDUCTIVITY

- There are three main factors that affect the conductivity of a solution: the concentrations of ions, the type of ions, and the temperature of the solution.
- A galvanic cell can be written in symbolic form as Anode |Electrolyte| |Electrolyte| Cathode.
- The emf of a cell is the potential difference between two electrodes in the open circuit.
- When a metal is dipped in its own salt solution then the potential of metal with respect to solution is called electrode potential.

## CELL EMF AND GIBBS ENERGY

Check Yourself

1. The charge required for the reduction of 1 mol of  $\text{MnO}_4^-$  to  $\text{MnO}_2$  is

- (A) 1 F    (B) 3 F    (C) 5 F    (D) 6 F

2.  $\text{NH}_4\text{NC}_3$  is used in salt bridge because

(A) It forms a jelly like material with agar-agar.

(B) It is a weak electrolyte.

(C) It is a good conductor of electricity.

(D) The transport number of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions is almost equal.

3. The reaction,  $3\text{ClO}^- (\text{aq}) \rightarrow \text{ClO}_3 (\text{aq}) + 2\text{Cl}^- (\text{aq})$  is an example of

- (A) Oxidation reaction  
 (B) Reduction reaction  
 (C) Disproportionation reaction  
 (D) Decomposition reaction

4. The emf of the cell:

$\text{Ni} / \text{Ni}^{2+} (1.0 \text{ M}) // \text{Au}^{3+} (1.0 \text{ M}) / \text{Au}$  ( $E^\circ = -0.25 \text{ V}$  for  $\text{Ni}^{2+}/\text{Ni}$ ;  $E^\circ = 1.5 \text{ V}$  for  $\text{Au}^{3+}/\text{Au}$ ) is

- (A) 1.25 V                      (B) -1.25 V  
 (C) 1.75 V                      (D) 2.0 V

5. If  $E^\circ \text{Fe}^{2+}/\text{Fe} = -0.441 \text{ V}$  and  $E^\circ \text{Fe}^{2+}/\text{Fe}^{2+} = 0.771 \text{ V}$ , the standard EMF of the reaction,

$\text{Fe} + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+}$  will be

- (A) 1.212 V                      (B) 0.111 V  
 (C) 0.330 V                      (D) 1.653 V

Check Yourself

1. Express the relation among cell constant, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solution related to its conductivity?

2. The molar conductivity of a 1.5 M solution of an electrolyte is found to be  $138.9 \text{ S cm}^2 \text{ mol}^{-1}$ . Calculate the conductivity of this solution.

3. A zinc rod is dipped in 0.1 M solution of  $\text{ZnSO}_4$ . The salt is 95% dissociated at this dilution at 298 K. calculate the electrode potential.

[  $E^\circ \text{Zn}^{2+} / \text{Zn} = -0.76 \text{ V}$  ]

4. Write the reactions taking place at cathode and anode in lead storage battery when the battery is in use. What happens on charging the battery?

5. The conductivity of 0.20 M solution of KCl at 298 K is  $0.025 \text{ S cm}^{-1}$ . Calculate its molar conductivity.

Test Yourself

**Question:** Express the relation between conductivity and molar conductivity of a solution held in a cell.

$$\lambda_m = \frac{\kappa \times 1000}{C}$$

**Answer:**



## Answers

### Check Yourself

Answer: 1(B); 2(D); 3(C); 4(C); 5(A)

### Stretch Yourself

1. Do it by yourself.

2. **Hint:** Molar conductivity is the conductivity of one molar of electrolyte. Molar conductivity is determined by dividing the conductivity of electrolytes with the concentration of electrolyte.

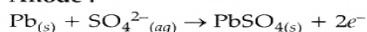
**Formula used:**  $K = \frac{\lambda_m \times 1000}{C}$

$$\begin{aligned}
 \text{Sol. } [Zn^{2+}] &= 0.1 \times \frac{95}{100} = 0.095 \text{ M} \\
 Zn^{2+} + 2e^- &\longrightarrow Zn(s) \\
 E_{Zn^{2+}/Zn} &= E_{Zn^{2+}/Zn} - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]} \\
 &= -0.76 \text{ V} - \frac{0.0591}{2} \log \frac{1}{0.095} \\
 &= -0.76 \text{ V} - \frac{0.0591}{2} (\log 1000 - \log 95) \\
 &= -0.76 \text{ V} - \frac{0.0591 \text{ V}}{2} (3.000 - 1.9777) \\
 &= -0.76 \text{ V} - \frac{0.0591 \text{ V}}{2} \times 1.0223 \\
 &= -0.76 \text{ V} - \frac{0.0604 \text{ V}}{2} \\
 &= -0.76 \text{ V} - 0.0302 \text{ V} = -0.7902 \text{ V}
 \end{aligned}$$

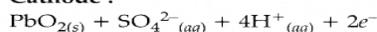
3.

4. The cell reactions when the battery is in use are given below:

**Anode :**



**Cathode :**



i.e., Overall, cell reaction consisting of cathode and anode reactions is :



On charging the battery, the electrode reactions are reverse of those that occur during discharge.

Molar conductivity  $\Lambda_m$

$$= \frac{\text{Conductivity (K)} \times 1000}{\text{Concentration of solution}}$$

5. Hint: