

Applied Chemistry Modules

4. Module-4: Electrochemistry & Corrosion

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1. Oxidation & Reduction

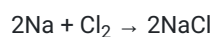
Oxidation is a process which involves loss of electrons.



Reduction is a process which involves gain of electrons.



Reaction which involves both oxidation and reduction is called redox reaction.



2. Conductors, Insulators & Semiconductors

Substances which allow the passage of electricity through them are called conductors.

Eg:- Metals, Graphite, Electrolytes etc.

Substances which do not allow the passage of electricity through them are called insulators.

Eg:- Plastics, glass, rubber etc.

Substances having conductivity intermediate between insulators and conductors are called semiconductors.

Eg:- Germanium doped with Arsenic

Silicon doped with Phosphorus etc.

Metallic & Electrolytic conductors

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Metallic conductors	Electrolytic conductors
Conduction is due to the flow of electrons	Conduction is due to the movement of ions
No chemical change during conduction	Chemical change happens during conduction
No transfer of matter	Transfer of matter happens towards electrodes
Conduction decreases with temperature	Conduction increases with temperature

Ex: Metals, Graphite etc	Ex: NaCl, KCl etc
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3. Electrolytes & Non-Electrolytes

Substances which conduct electricity either in molten state or in aqueous solutions are called electrolytes.

Ex: Molten NaCl, KCl solution etc

Substances which do not conduct electricity either in molten state or in aqueous solutions are called non-electrolytes.

Ex: Sugar, Urea etc.

Strong & Weak electrolytes

The electrolytes which are almost completely dissociated into ions in solution are called strong electrolytes.

Eg:- HCl , KCl , NaOH , KOH etc.

The electrolytes which do not ionize completely in solution are called weak electrolytes.

Eg:- CH_3COOH , NH_4OH , H_2CO_3 etc

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4. Electrolysis & Electrolytic cell

It is the process of decomposition of an electrolyte by the passage of electricity through it. The device used to carry out the electrolysis is called *electrolytic cell*.

5. Faradays laws of electrolysis

First law of electrolysis

According to this law, the mass of substance deposited or liberated at an electrode as a result of electrolysis is directly proportional to the quantity of electricity passed through the electrolyte.

$$m \propto Q$$

$$m = z Q$$

$$m = z It \text{ (since, } Q=It \text{)}$$

m = mass of substance produced at the electrode

I = strength of current in Amperes

t = time in seconds

z = electrochemical equivalent (ece) of the substance deposited at the electrode

Electrochemical equivalent is the mass of substance produced at the electrode by passing a current of One Ampere for one second through the electrolyte.

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Second law of electrolysis

When same quantity of electricity is passed through solutions of different electrolytes, the masses of substances deposited at the respective electrodes are directly proportional to their equivalent masses (equivalent weights)

$$m_1/m_2 = E_1/E_2$$

where m_1 and m_2 are the masses of substances deposited at the electrodes, E_1 and E_2 are equivalent weights of the substances respectively.

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Faraday(F).

One Faraday is the electricity carried by one mole of electrons (ie charge carried by 6.02×10^{23} electrons)

$$1 F = 96500 C$$

Problem-1

Estimate the mass of the copper metal produced during passage of 5A current through copper sulphate solution for 100minutes. Atomic mass of copper is 63.5.

Problem-2

In a certain electrolysis 0.561gm of zinc is deposited in a cell containing $ZnSO_4$ solution. Calculate the mass of copper deposited in another cell containing $CuSO_4$ solution in series. Atomic weights of Zn and Cu are 65.4 and 63.5 respectively.

6. Applications of electrolysis

Electroplating

It is the process of producing thin coating of a metal on the surface of another metal by electrolysis.

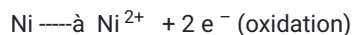
The object to be electroplated is taken as the cathode and the metal to be deposited on the object is made the anode. The electrolyte is a solution of soluble salt of the superior metal. When electric current is passed through the electrolyte solution, metal at the anode goes into the solution and gets deposited in the form of a thin layer on the object (cathode).

Generally superior metals like gold, silver, nickel etc are deposited over inferior metals like iron, copper etc.

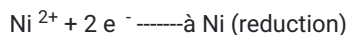
Electroplating is mainly used to protect a metal from corrosion, to improve its physical appearance, to modify its hardness etc.

Ex: Electroplating of nickel on an object (mild steel spoon) _____

In this process, a Nickel plate is taken as anode and steel spoon is taken as cathode. The electrolyte is a solution of Nickel sulphate. On passing electric current through the electrolyte solution, Nickel from the anode undergoes oxidation to form Nickel ions ____



The Ni^{2+} ions then undergo reduction at the cathode and get deposited as a thin coating of Nickel metal on the cathode (steel spoon)



Electrolytic refining

It is the process of converting impure metal to pure metal with the help of electrolysis.

Copper is refined using an electrolytic method. Anodes are of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode.



7. Electrochemical cell (Galvanic cell or Voltaic cell)

It is the device used to convert chemical energy produced during redox reaction into electrical energy.

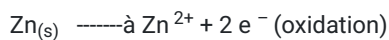
Daniel Cell

Revision Notes and Important Questions of Electrochemistry for IIT JEE 2019

Daniel cell consists of two half cells-Zinc half cell (anode half-cell) and Copper half cell (cathode half-cell).

In the zinc half-cell, a zinc rod is dipped into ZnSO_4 solution and in the copper half-cell, a copper rod is dipped into CuSO_4 solution. These two electrodes are then connected to a voltmeter through a wire. When the circuit is completed, the electric current starts flow through the external circuit.

At anode



At cathode



The overall reaction (net reaction) is



Types of Galvanic cells

a) Primary cells

These are the cells which cannot be recharged.

In primary cell, the redox reaction occur only once and the cell become inactive after completion of the reaction

Ex:- Daniel cell, Dry cell, Mercury cell etc.

b) Secondary cells

These are the cells which can be recharged. ie, the electrode reactions can be reversed by passing electric current from an external source.

Ex:- Lead storage battery, Nickel-Cadmium cell (Nicad cell) etc.

c) Fuel cells

Fuel cells are Galvanic cells in which energy produced by the oxidation of fuels is directly converted into electrical energy.

Ex:- Hydrogen – Oxygen fuel cell.

Fuel cells are mainly used in space vehicles, military vehicles, submarines etc.

8. Electrode potential(E)

The tendency of an electrode to lose or gain electrons when it is in contact with a solution of its own ions is called electrode potential. The tendency to lose electrons is called oxidation potential whereas the tendency to gain electrons is called reduction potential.

Standard electrode potential (E°).

If the electrode is suspended in a solution of 1M concentration at 298K, the electrode potential is called standard electrode potential.

Cell potential (Cell voltage or EMF of the cell).

The difference in reduction potentials of two half cells of a cell is known as Electro Motive Force (EMF) of the cell or cell potential.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

Problem 1

Calculate the standard emf (std cell potential) of the Daniel cell. The standard electrode potentials of Cu and Zn are 0.34 V and -0.76 V respectively.

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\text{Cu}} - E^\circ_{\text{Zn}} \\ &= 0.34 - (-0.76) = 0.34 + 0.76 \\ &= 1.1 \text{ V} \end{aligned}$$

Problem: 2

Reduction potentials of Zn and Ag electrodes are -0.76 V and 0.8 V respectively. Compute the emf if a cell is constructed using these electrodes

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\text{Ag}} - E^\circ_{\text{Zn}} \\ &= 0.8 - (-0.76) = 0.8 + 0.76 \text{ V} \\ &= 1.56 \text{ V} \end{aligned}$$

9. Electrochemical series (activity series)

The arrangement of elements in the order of increasing values of standard reduction potentials is called electrochemical series.

Applications of electrochemical series

Following are the important applications of electrochemical series.

1. Electrochemical series helps to calculate the standard EMF of a Galvanic cell from the standard electrode potential values.
2. Electrochemical series helps to compare the reactivity of metals.
3. It helps to predict the spontaneity of any redox reaction. If EMF of the cell is positive, it is spontaneous, otherwise not.
4. It helps to compare the reducing and oxidizing powers of various elements used as the electrodes.

10. Corrosion

It is the slow destruction of a metal due to its reaction with the gases in air and moisture present in the atmosphere.

Factors affecting corrosion

1. Presence of impurities in the atmosphere

The presence of gases like CO_2 , H_2S , SO_2 etc in the atmosphere increases the speed of corrosion.

2. Temperature

Rate of corrosion increases with increase of temperature.

3. Air and moisture

Presence of moisture (humidity) in the air increases the rate of corrosion.

4. Presence of impurities in the metal

The rate of corrosion increases with the quantity of impurities in the metal. Impure metals undergo corrosion easily than pure metals.

5. Influence of pH

In acidic medium, the pH will be less than 7 and the corrosion will be more compared to neutral medium and basic medium.

6. Presence of electrolyte

Corrosion is faster in the presence of electrolytes.

Methods to prevent corrosion

1. Barrier protection (protective coatings)

In this method, a protective coating is applied on the surface of the metal so that a barrier is made between the metal surface and the atmosphere. Protective coatings may be:

Metallic coating (Ex:- Coating of zinc over iron)

Nonmetallic coating (Ex:- Chromate coating or Oxide coating)

2.Cathodic Protection

In this method, a reactive metal plate such as Zinc or Magnesium is connected to the metal to be protected from corrosion.

Ex:-Iron pipes are protected from corrosion by connecting them with metals like Zinc, Magnesium etc. In this case, Zinc or Magnesium undergoes oxidation and corroded instead of iron pipe. The iron pipe becomes cathode and protected from corrosion.

3. Galvanization

The process of coating iron objects with zinc is called galvanization. As a result of galvanization, the metal iron is protected from corrosion.

4. Anti rust solutions

It is the method in which alkaline phosphate or alkaline chromate solutions are used. So that metal chromate or metal phosphate coatings are formed on the surface of the metallic objects. Such coatings act as a protective coating, which helps to prevent corrosion.