Doon Public School Bhuj

Chapter- ELECTROCHEMISTRY (UNIT - III)

SYLLABUS:-

Redox reaction, conductance in electrolytic solutions, specific & molar conductivity. Variation of conductivity with concentration, Kohlrausch's Law, electrolysis & laws of electrolysis(elementary ideas)dry cell, electrolytic cells & Galvanic cells, Lead accumulator, EMF of cell, standard electrode potential, Nernst equation and its application to Chemical cell, fuel cell; Corrosion.

SUMMARY OF THE CHAPTER:-

ELECTROCHEMISTRY is that branch of Chemistry which deals with the study of relationship between the chemical energy & electrical energy & the conversion of one form to another.

REDOX REACTIONS:-

Oxidation is the process which involves loss of electrons & reduction is a process in which it involves gain of electrons. The reactions which involve both that reaction simultaneously are called as REDOX REACTION.

ELECTROCHEMICAL CELLS:-

The devices in which electrical energy is produced as a chemical reaction (Redox reaction).

Ex: Daniel Cell

ELETROLYTIC CELL:-

The devices in which the chemical reaction takes place by electrical energy.

CONDUCTORS:-

The substances which allow the passage of electric current through them. They can divide into two groups:

- ✔ Metallic Conductor.
- ✔ Electrolytic conductor: They may be strong electrolyte or week electrolyte.

Ohm's Law:-

$I \propto V$ or $V \propto I$

Or $V=IR$

Or $I=V/R$

CONDUCTANCE OR CUNDUCTIVITY:-

It is reciprocal of resistance.

$C=1/R$

SPECIFIC CONDUCTANCE:-

It is the conductance between opposite faces of 1 cm cube of a conductor (K Kappa).

K=Cl/A

EQUIVALENT CONDUCTANCE:-

It is the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in a solution.

MOLAR CONDUCTANCE:-

It is the conducting power of all the ions produced by dissolving 1 gm mole of an electrolyte in the solution. Conductance can be measured by using Wheatstone bridge.

KOHLRAUSCH LAW:-

At infinite dilution, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ions present.

ELECTROCHEMICAL CELL/ GALVANIC CELL/ VOLTANIC CELL:-

The devices in which Redox reaction produces electricity, called electrochemical cell. In these cells:

- ✔ Oxidation occurs at anode.
- ✔ Reduction occurs at cathode.
- ✔ Anode is negative while cathode is positive.
- ✔ Electron flows in external circuit from anode to cathode.

ELECTRODE POTENTIAL:-

The electrical potential set up between electrode & its solution is called electrode potential.

CELL POTENCIAL/ ELECTROMOTIVE FORCE:-

The difference between electrode potential of two electrodes in an electrochemical cell is called cell potential.

E^o cell = $E^o_{cathode} - E^o_{anode}$

$= E^o_{right} - E^o_{left}$

MEASUREMENT OF ELECTRODE POTENTIAL:-

The potential individual half cell cannot be measured. We can only measure the difference between the two half cell potentials of the cell. For this standard hydrogen electrode is used as one electrode whose electrode potential is zero. This S.H.E can be used as anode or cathode.

NERNST EQUATION:-

It gives the relationship between electrode potential & concentration of metal ions in the solution (electrolysis).

NERNST EQUATION FOR A CELL REACTION:-

$aA + bB \xrightarrow{heat} cC + dD$

$$E = E^o \text{ cell} - \frac{2.303\,RT}{nF} * \log \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

EMF & EQUILIBRISM CONSTANT:-

In a DANIEL CELL (Zn/Cu cell) as time passes the concentration of Zn++ ions increases & Cu++ ions decreases. After some time concentration of Zn++ & Cu++ becomes constant & Voltammeter gives zero reading. In this situation NERNST eq. may be written as

E^o cell = 2.303RT/nF * log Kc [Zn_2+/Cu_2^+ = Constant Kc]

=0.059 log Kc/n

EMF & Gibbs free energy change

$\Delta G^o = - nFE^o$ cell

FARADAY'S LAW OF ELECTROLYSIS:-

First Law: The amount of substance librated at the electrode during electrolysis is directly proportional to the Quantity of electricity passed.

W = Z*C*t

Second Law: If some of electricity is passed through different electrolyte, the amounts of substances liberated at electrode are directly proportional to their chemical equivalents.

PRODUCT OF ELECTROLYSIS:-

The product of electrolysis depends on the standard electrode potential of the species in the cell.

Ex: The electrolysis of molten NaCl gives Na^+ at cathode & Cl^- at anode. But aqueous NaCl solutions have Na^+, Cl^-, OH^- & H^+. On electrolysis it gives H_2 at cathode due to higher value of E^o is preferred. At anode Cl_2 gas is produced due to over potential of Oxygen.

MERCURY CELL:-

It consist of zinc mercury amalgam as anode, a paste of H_2O & carbon as cathode. The electrolyte is a paste of KOH & ZnO.

LEAD STORAGE BATTERIES:-

This cell is uses lead as anode & a grid of lead dioxide as cathode. Dil. Sulphuric acid (38 % by mass) used as an electrolyte.

FUEL CELL:-

Those cells which produces electrical energy by the combustion of fuels such as hydrogen, CO_2, CH_4, etc.

CORROSION:-

The process of eating away of metals when exposed to moist air. It is mainly Oxidation of metals in presence of other impurities. Corrosion is an electrochemical process.

Corrosion can be prevented by following methods:

- ✔ Barrier protection.
- ✔ Sacrificial protection – Galvanization.
- ✔ Electrical protection.
- ✔ By using anti-rust solution, etc.

ELECTROCHEMISTRY QUESTIONS

VERY SHORT ANSWERS TYPE QUESTION (1 Marks Each):

Q1. Why conductivity of a solution does decreases with dilution?

Ans. On dilution the number of ions per unit volume decreases thus conductivity decreases.

Q2. If 0.5 ampere current flows through a wire for 2 hours.Calculate number of electrons through the wire.

Ans. Q = 1(ampere)*2*60*60(sec.) = 3600 C

96500 C is equivalent of 1 mole = $6.02X10^{23}$ electrons

3600 C is equivalent of 1mole = $6.02X10^{23}$ *3600/96500

= $2.246X10^{22}$ electrons.

Q3. How much charge is required in the reduction of one mole of Al^{3+} to Al?

Ans. The reaction is $Al^{3+} + 3e^{-} \longrightarrow Al$

∴ Quantity of charge required = 3F = 3*96500= 289500 C

Q4. Write importance of salt bridge in a Galvanic cell?

Ans. 1. To complete the inner circuit &

2. To maintain electrical neutrality.

Q5. What is meant by cell constant?

Ans. It is the ratio of distance between electrodes & area of cross - section.

Q6. Why an aqueous NaCl on electrolysis gives H_2 gas at cathode & not sodium?

Ans. Standard reduction potential of mater is greater than that of sodium.

Q7. What is the role of $ZnCl_2$ in a dry cell?

Ans. $Zncl_2$ combines with NH_3 to forms a complex salt otherwise due to pressure of NH_3 cell may crack.

Q8. Write two advantages of H_2-O_2 fuel cell.

Ans. 1. Do not cause any type of pollution &

2. They have high efficiency (60% - 70%).

Q9. How much electricity (Faraday) is required to produce 20 gm of Ca from calcium Chloride?

Ans. $Ca^{2+} + 2e^{-} \longrightarrow Ca$

For 1 mole ca (40 gm Ca require) = 2F

20 gm ca require = 1F

Q10. Suggest two materials other than hydrogen that can be used as fuel in fuel cells?

Ans. Methane & Methanol.

SHOR ANSWER TYPE QUESTION (2 Marks Each):

Q1. Why does a Galvanic cell become dead after some time?

Ans. As the reaction in cell precedes the concentration of ions in one half cell increases while in other half cell decreases hence electrode potential also changes. When concentration become equal the E.M.F become zero.

Q2. Calculate the E.M.F of the following cell:

$Ni(s) + 2\ Ag^{+}(0.002m) \longrightarrow Ni^{2+}\ (0.160m) + 2Ag(s)$

Given E^{o} cell = 1.05V

Ans. From NERNST eq: E^{o} cell = E^{o} cell - 0.0591/n * log $[Ni^{2+}]/ [Ag^{+}]^2$

OR

E^{o} cell = 1.05 – 0.0591/2 * log $0.160/ (0.002)^2$

= 1.05 – 0.14V = 0.91V

Q3. Write the chemistry of recharging the lead storage battery.

Ans. During recharging, electrical energy is supplied to the cell from an external source at this time cell operates like an electrolyte cell. Overall reaction on recharging is as ender:-

$2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{--}$

Q4. Calculate standard cell potential of the following cell:-

$2Cr + 3Cd^{2+} \longrightarrow 2Cr^{3+} + 3Cd$

Given $E^o\ Cr^{3+}/Cr = -0.74V$, $E^o\ Cd^{2+}/Cd = -0.40V$

Ans. E^o cell = E cathode – E anode = - 0.40 – (-0.74) =+0.34v

We know that $\Delta G^o = -nF\ E^o$ cell

$= -6ml * 96500 * 0.34 = -196.86$ Ks/ml

$-\ \Delta G^o = 2.303\ RT \log K$

$196860 = 2.303 \times 8.314 \times 298 \log K$

$\text{Log } K = 34.5014$

Or K = Anti log of 34.5014 = 3.192×10^{34}

Q5. The conductivity of 0.20 m solution of KCl at 298 K is 0.02485 cm^{-1}. Calculate its molar conductivity.

Ans. m = K*1000/molarities

=0.0248*1000/0.20

= 124.5 cm^2mole

Q6. Explain what standard Hydrogen electrode is.

Ans. It is a reference electrode. It consists of platinum foil which is dipped in 1m HCl solution. Pure H_2 is passed in the solution at 1 atm pressure. Its electrode potential is zero. It can be used as anode & cathode.

Q7.m for NaCl, HCl & Na Ac are 126.4, 425.9 & 91.05 $cm^2\ mol^{-1}$ respectively. Calculate ^o_m for H Ac.

Ans. $\Delta\ ^o m$ (H Ac) = $\Delta^o m$ (HCl) + $\Delta\ ^o m$ (NaAc) - Δ^o m(NaCl)

= 425.9 + 91 – 126.4

= 390.55 $cm^2\ mol^-$

Q8. The E^o cell for Daniel cell is 1.1 V. Calculate the standard Gibbs energy for the reaction:

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

Ans. Of $\Delta G = -nF\ E^o$ cell (n=2)

Of = $-2*1.1v*96500\ C\ mol^{-1}$

$= -212300\ J\ mol^{-1} = -21.230$ KJ/ml

Q9. Account for the following:-

a) Alkaline medium inhibits the rusting.

b) Iron does not rusted even if zinc coating is broken down at any point in a galvanized pipe.

Ans. a) This is due to the alkalinity prevent the availability of H^+ ions.

b) In GI pipes Zinc coating acts as anode & exposed iron acts as cathode. If zinc undergoes corrosion protecting iron from rusting.

Q10. Can we store copper sulphate solution in zinc pot?

$E^o\ Zn^{2+}/Zn = -0.76$ V, $E^o\ Cn^{++}/Cn = 0.34$ V

Ans. As per the cell formed the E^o cell units be

E^o cell = $E^o\ Cu^{2+}/Cu - E^o\ Zn^{++}/Zn$

$= 0.34 – (-0.76) = 1.1V$

Since E^o cell is positive thus reaction will takes place & we cannot store it in Zinc pot.

SHORT ANSWER TYPE QUESTION:

Q1. What is Fuel Cell? Write It's Advantages.

Ans. Fuel cells are those cells which produces electrical energy by the combustion of fuels such as hydrogen, CO_2, CH_4, etc. $H_2 – O_2$ fuel cells are used in Apollo Space Programme.

Advantages:

a) It is pollution free.

b) Home high efficiency.

c) It is a continuous source of energy.

Q2. In the button cell following reaction takes place.

$Zn(s) + Ag_2O + H_2O \longrightarrow Zn^{2+}(aq) + 2Ag(s) + OH^-(aq)$

Determine E^o & ΔG^o for the reaction.

Given $Zn \longrightarrow Zn^{2+} + 2e$, $E^o = -0.76$ V, $Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-$. $E^o = 0.344$V

Ans. Zn is oxidized & Ag_2O is reduced.

E^o cell = E^o Ag_2O/Ag - E^o Zn^{++}/Zn

= 0.344 – (- 0.76)

= 1.104 V

$\Delta G^o = - nF E^o$ cell

= -2*96500*1.104

= $-2.13*10^5$ J

Q3. Define conductivity & molar conductivity for the electrolytes. Discuss their variation with concentration.

Ans. For conductivity & molar conductivity refers to Gist of the lesson.

Both changes with the concentration of electrolyte.

The conductivity always decreases with decrease in concentration of weak & strong electrolyte.

The molar conductivity increases with decrease in concentration or on dilution.

Q4. Calculate ΔG^o & the equilibrium constant for the reaction takes place in a cell.

Zn (s) | Zn^{++} (1m) || Cu^{2+} (1m) | Cu(s)

Given: E^o $Zn^{2+}/n = -0.76$ V, E^o $Cu^{2+}/Cu = 0.344$ V, F = 96500 C/mol^- 1

Ans. 1) ΔG^o can be calculated as under.

$\Delta G^o = - nF E^o$ cell (n = 2)

2) For equation constant

$\Delta G^o = -2.303\ RT \log Kc$

Q5. Write difference between Metallic & Electrolyte Conduction.

Ans.

a) No Chemical change takes place in the conductor.	a) Chemical changes take place in electrolyte.
b) Only electrons move.	b) Matter moves in the form of ions.
c) At high temperature conductance decreases.	d) At high temperature conductivity increases.
d) Shows high conductance.	d) Have relatively smaller conductance.

LONG ANSWER TYPE QUESTION (5 Marks Each):-

Q1. a) Suggest a way to determine the molar conductivity value of water.

b) Define Kohlrausch's law.

c) What is electrochemical series? Explain its importance.

Ans. a) The molar conductance of the water can be obtained from the knowledge of molar conductance at infinite dilution of sodium hydroxide, HCl & NaCl.

$\Delta^o m\ H_2O = \Delta^o m\ NaOH + \Delta^o m\ HCl - \Delta^o m\ NaCl$

b) Kohlrausch's Law: The molar conductivity of an electrolyte at infinity solution is the sum of the individual contribution of the anion & cation of the electrolyte.

c) Electrochemical series: the arrangement of metals & non metals in increasing order of their standard electrode potentials is called electrochemical series.

At the top of the series Li is placed it's electrode potential is – 3.05 V. It's negative value shows that the reductions of Li^+ ion is least probable, whereas Li can easily lose electron to become Li^+ ion, Oxidation is most probable.

Fluorine is at the bottom of the series which can be reduced most easily because it's electrode potential value is + 2.87 V (Oxidation is least probable).

Q2. a) Predict the product of electrolysis aq. $AgNo_3$ with silver electrode:

Given $E^o\ Ag^+/Ag = +0.80$ V

b) Write NERNST equation for electrode reaction.

$m^{n+} + ne^- \longrightarrow m$

c) Explain the mechanism of rusting of iron.

Ans. a) $AgNO_3\ (s) \longrightarrow Ag^+ + NO_3^-$

At cathode – Ag^+ ion has lower potential than H^+ ion therefore Ag^+ ion will be deposited as Ag in preference to H^+ ion.

At anode – As Ag anode attacked by NO_3^- ions thus Ag of anode will dissolve to form Ag^+ ion in the solution.

b) For the given electrode reaction the nearest eq. will be

$E\ m^{n+}/m = E^o\ m^{n+}/m - 2.303\ RT/nF^* \log [m]/ [m^{n+}]$

c) Rusting Of Ion:

Rusting is an electrochemical reaction in which iron is oxidized by losing electron to other electronegative element like O_2, S, etc.

The non uniform surface of iron in presence of moist O_2, CO_2 or impurity act as a small electric cell. A film of moisture with Co_2 acts as an electrolytic solution. Pure iron acts as anode & impure portion act as cathode. Reaction takes place at anode is:

$[Fe\ (s) \rightarrow Fe^{2+} + 2e^-]X2$

At cathode: $H^+ + e^- \rightarrow H$

$4H + \text{dissolved } O_2 \longrightarrow 2H_2O$

Over all reaction at cathode $O_2 \longrightarrow 2H_2O$

Over all cell reaction is:

$2Fe + 4H^+ + O_2 \longrightarrow 2Fe^{+2} + 2H_2O$

$4Fe^{2+} + O_2 + 4H_2O \longrightarrow 2Fe_2O_3 + 8H^+$

$Fe_2O_3 + x\ H_2O \longrightarrow Fe_2O_3.xH_2O$

Q3. a) Explain cathodic protection from rusting.

b) Explain method of measurement of conductance of a solution.

c) Explain law of electrolysis.

Ans. a) Cathodic Protection of Iron:-

This is an example of electrical protection. In this process a plate of more reactive metal (Zn, Mg) is connected with iron pipe or tank through metal wire. The iron acts as cathode & the more reactive metal act as an Anode. The reaction metal sacrificed to protect the iron.

b) The value of conductance of any solution can be calculated with the help of Wheatstone bridge.(fig.3.5 NCERT text book). It consist of two fixed resistance R_3 & R_4, a variable resistance R_1 & conductivity cell R_2 when all are balance then :

$R_1/R_2 = R_3/R_4$ Or $R_2 = R_1 * R_4/R_3$

c) Laws of electrolysis: Given in the summary of the lesson.