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The degree of ionisation increases with the increase of dilution of the solution the conductivity is increases due to increasing the number of ions. (ii) Effect of dilution on specific conductance : Specific conductance decreases with the increase of dilution of the solution due to the presence of no. of ions in 1cm3 solution decreases. (iii) Effect of dilution on equivalent/molar conductivity : The equivalent/molar conductivity increases with dilution. This is due to the fact that degree of ionisation increases with dilution. υ When the whole of the electrolyte has ionised, further addition of the water bring a small change in the value of equivalent/molar conductance. This stage is called infinite dilution. υ The ratio of equivalent conductivity at any dilution to equivalent conductivity at infinite dilution is called conductivity ratio or degree of dissociation of solute $- ∞ λ α = λ$ Ex : The equivalent conductivity of H2 SO4 at infinite dilution is 384 $Ω–1$ cm2 eq–1. If 49 g H2 SO4 per litre is present in solution and specific resistance is 18.4 $Ω$ then calculate the degree of dissociation. Sol : Equivalent of H2 SO4 = 49 49 = 1N specific conductance = 1 specific resistance = 1 18.4 $⇒$ eq. 1000 1000 1 55 N 18.4 $× κ × λ = = =$ Degree of dissociation $(α)$ = C eq. eq. 55 384 $∞ λ = λ$ = 0.14 $⇒$ $α$ % = 14% 5 . KOHLRAUSCH LAW : This law states that the equivalent conductivity of any electrolyte at infinite dilution eq. ( ) $∞$ $λ$ is the sum of ionic conductances of the cation and anion given by the electrolytes at infinite dilution. eq a c $∞ ∞$ $∞$ $λ$ = $λ$ + $λ$ consider a salt NaCl, its equivalent conductivity at infinite dilution is the sum of two terms i.e. eq Na Cl $+ − ∞ ∞ ∞ λ = λ + λ$ These terms are known as ionic mobilities of anion and cation. For Ax By type solution :- eq c a 1 1 Z Z $∞ ∞ ∞ + − λ = λ + λ$ here c = cation & a = anion and Z+ , Z− are the charges on the cation and anion respectively. Ex : At infinite dilution the equivalent conductance of Al+3 and SO4 – 2 ion are 189 and 160 $Ω–1$ cm2 eq–1 respectively. Calculate the equivalent and molar conductivity at infinite dilute of Al2 (SO4) 3 . Sol : ( ) 3 2 2 4 4 3 eq. Al SO Al SO 1 1 3 2 $+ − ∞ ∞ ∞ ⌈ ⌉⌊ ⌋ λ = λ + λ$ = 1 1 189 160 3 2 $× + ×$ = 143 $Ω–1$ cm2 eq–1 Molar conductivity = $λeq × V. F.$ = 143 × 6 = 858 $Ω–1$ cm2 mol–1 Application : This law can be used to (a) Determine the equivalent conductivities of weak electrolytes at infinite dilution. (b) Determination of degree of dissociation, since $α$, the degree of dissociation of an electrolyte at the dilution V is given by $α = ∞ λ λ$ where $λ∞ = λ∞$ a $+ λ∞$ c 6 . FARADAY'S LAWS OF ELECTROLYSIS : Michael Faraday deduced two important law : (a) Faraday's first law of elecrolysis : This law states that "The amount of a substance deposited or dissolved at an electrode is directly proportional to the charge passing through the electrolytes. If a current of I amperes is passed for t seconds, the quantity of charge Q in coulombs. If W, gram of substances is deposited by Q coulombs of electricity, then $W ∝ Q ∝ It$ $W = Z$ $It = \frac{E}{96500} It$ Where Z is constant of proportionality and is known as electrochemical equivalent. υ When Q = 1 coulomb, W = Z thus electro chemical equivalent may be defined as the weight in grams of an element liberated by the passage of 1 coulomb of electricity. Ex : How many cc of chlorine will be deposited by 100 amp. current flowing for 5 hours through melted NaCl. Sol : $Q = It$ = 100 × 5 × 60 × 60 = 18 × 105 $W = ZQ = \frac{E}{96500} × 18 × 105$ = $\frac{18E}{96500} × 105$ = 18 35.5 3 10 965 $× ×$ = 662.2 g $Θ$ Volume of 71 g Cl2 at NTP = 22.4 L $∴$ volume of 662.2 g Cl2 at NTP = $\frac{22.4}{71} ×$ 662.2 = 208.9 L Ex : The time required to coat a metal surface of 80 cm2 with 0.005mm thick layer of silver (density = 10.5 g cm–3) with the passage of 3A current through silver nitrate solution is − Sol : $Θ$

Volume of layer of silver = 0.005 × 10–1 × 80 = 0.04 cm3 ∴ Mass = Density × volume = 10.5 × 0.04 = 0.42 g So $E = \frac{w}{96500} \times It$ ⟹ $\frac{0.42}{108} = \frac{96500}{96500} \times 3 \times t$ $t = \frac{0.42 \times 96500}{108 \times 3}$ = 125.09 seconds. (b) Faraday's second law : This law states that the amounts of different substances deposited at electrodes by passage of the same quantity of electricity are proportional to their chemical equivalent(E).
$W \propto E$
If W1 and W2 be the amounts of two different substances deposited at electrodes and E1 and E2 be the equivalent weights then - $\frac{W_1}{W_2} = \frac{E_1}{E_2}$ combining the two laws $W \propto It$ $E = \frac{ItE}{F}$ Where $\frac{1}{F}$ is proportionality constant and F is called faraday.
when It = F then W = E
Hence faraday (F) is the quantity of charge in coulombs required to deposit one g equivalent of any substance. υ
The Faraday (F) is also the quantity of charge carried by one mole of electrones.
F = e × N = 1.6 × 10–19 × 6.023 × 1023 = 96500 coulombs. Ex : The same current if passed through solution of silver nitrate and cupric salt connected in series. If the weight of silver deposited is 1.08 g. Calculate the weight of copper deposited Sol : According to faradays second law $\frac{W_1}{W_2} = \frac{E_1}{E_2}$ ⟹ $\frac{1.08}{W_2} = \frac{108}{31.75}$ ⟹ W2 = 0.3175 g 7 . ELECTRO CHEMICAL CELL/GALVANAIC CELL/ VOLTAIC CELL : Example – Daniel Cell υ
A cell in which the chemical energy is transformed into electrical energy. υ
The chemical reaction occuring in a galvanic cell is always a redox reaction. υ
During the chemical process, the reduction in free energy will obtain as a result in the form of electrical energy.
Galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It is also known as voltaic cell. It may be represented as shown in fig. Zinc rod immersed in ZnSO4 behaves as anode and copper rod immersed in CuSO4 behaves as cathode. Oxidation takes place at anode : Zn(s) ⟶ Zn2+ + 2e– (loss of electron : oxidation) Reduction takes place at cathode : Cu2+ + 2e– ⟶ Cu(s) (gain of electron ; reduction) Over all process : Zn (s) + Cu2+ ⟶ Cu (s) + Zn2+
In galvanic cell like Daniell cell ; electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit ; zinc dissolves as Zn2+ ; Cu2+ ion in the cathode cell picks up two electron and become deposited at cathode. υ Salt bridge : 1.
It allows to flow of current by completing the circuit. 2.
It maintains electrical neutrality of electrolytes in two half cells. υ
Characteristics of electrolyte used in salt bridge : 1. The electrolyte should be inert 2. The cations and anions of the electrolyte used should be of the same ionic mobility. θ
ELECTROLYTIC CELL :
This cell converts electric energy into chemical energy. The entire assembly except that of the external battery is known as the electrolytic cell. +ve ion –ve ion Cathode (–) Electrolyte Anode (+) e – + – e – Electrolytic cell Cell reaction : Zn + Cu+2 ⟶ Zn+2 + Cu Representation of Galvanic cell. Zn/Zn+2 // Cu+2/ Cu (C1) (C2) Anode Cathode salt bridge θ REPRESENTATION OF ELECTROCHEMICAL CELL : Ex : (i) Zn (s) | Zn2+ (aq) || Cu2+ (aq.) / Cu (s) (ii) Pt/H2 (g) (1 atm)|H+ (aq) || Cu2+ (aq.) | Cu (s). Inert electrolyte KCl, KNO3 , NH4 Cl etc. with Gelatin or Agar-Agar ↓↓↓ → → Zn CuSO4 K + Zn+2 Cl — e — e I — ZnSO4 Salt Bridge Zn → Zn+2 + 2e— (Oxidation) Anode –ve terminal Cu+2 + 2e— → Cu (Reduction) Cathode +ve terminal Cu Cu +2 1. First of all, the anode is written. 2. After anode, the electrolyte of the anode should be written with its concentration in the bracket. 3.
A slash (/) is put between anode and electrolyte to denote the surface barrier between the two as they exists in different phases. 4.
Then we denote salt bridge by two vertical parallel lines. (II). 5.

Then, we write the electrolyte of cathode (negative electrode) followed by its concentration in bracket. 6. Finally, after a slash, we write the cathode. 7. In case of gas, the gas is to be indicated after the electrode in case of anode and before the electrode in case of cathode. Ex. Pt, H_2 /H+ or H+ / H_2 , Pt υ Electrode potential : When a strip of metal is brought in contact with the solution containing its own ions then the strip of metal gets positively charged or negatively charged and results into a potential being developed between the metallic strip and its solution which is known as electrode potential. At anode $M \rightarrow M^{+n} + ne^-$ (Oxidation Potential) At cathode $M^{+n} + ne^- \rightarrow M$ (Reduction Potential) υ The value of electrode potential depends upon : (1) the nature of electrode (2) the concentration of solution (3) the temperature υ Standard electrode potential (E^0) : If the concentration of ions is unity, temperature is 25°C and pressure is 1 atm (standard conditions), the potential of the electrode is called standard electrode potential. υ The given value of electrode potential be regarded as reduction potential unless it is specifically mentioned that it is an oxidation potential. υ Electro motive force of cell or cell voltage : The difference in the electrode potentials of the two electrodes of the cell is termed as electro motive force [EMF] or cell voltage. E_{cell} = E_{red} (cathode) − E_{red} (anode) or E_{cell} = $E_{oxi.}$(anode) − $E_{oxi.}$(Cathode) or E_{cell} = $E_{oxi.}$(anode) + E_{red}(cathode) 8 . ELECTRO CHEMICAL SERIES : Standard Aqueous Electrode potentials at 298K 'THE ELECTROCHEMICAL SERIES' Element Electrode Reduction Reaction Standard electrode Reduction potential E^0 , Volts Li Li+ + e $\rightarrow$ Li − 3.05 K K+ + e− $\rightarrow$ K − 2.93 Ba Ba+2 + 2e− $\rightarrow$ Ba − 2.90 Ca Ca+2 + 2e− $\rightarrow$ Ca − 2.87 Na Na+ + e− $\rightarrow$ Na − 2.71 Mg Mg+2 + 2e− $\rightarrow$ Mg − 2.37 Al Al+3 + 3e− $\rightarrow$ Al − 1.66 M n Mn+2 + 2e− $\rightarrow$ Mn − 1.18 Zn Zn+2 + 2e− $\rightarrow$ Zn − 0.76 Cr Cr+3 + 3e− $\rightarrow$ Cr − 0.74 Fe Fe+2 + 2e− $\rightarrow$ Fe − 0.44 Cd Cd+2 + 2e− $\rightarrow$ Cd − 0.40 Ni Ni+2 + 2e− $\rightarrow$ Ni − 0.25 Sn Sn+2 + 2e− $\rightarrow$ Sn − 0.14 Pb Pb+2 + 2e− $\rightarrow$ Pb − 0.13