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Electrochemistry: Electrochemical cell, Conductance & Ionic Equilibria

Key Terminologies:

Basic Terms: Electrochemistry [2.9.1], Faraday's Law of Electrolysis [2.9.2], Electrochemical Cell [2.9.3], Galvanic Cell [2.9.5], Electrolytic Cell [2.9.6], Reversible & Irreversible Cell [2.9.7], Electrode Potential [2.9.8], Standard Electrode Potential [2.9.9], Electrochemical Series [2.9.10], Cell Diagram [2.9.11], Salt Bridge [2.9.12], EMF of Cell [2.9.13], Gibb's Free Energy of Cell [2.9.14], Standard Hydrogen Electrode [2.9.15], Calomel Electrode [2.9.15], Nernst Equation [2.9.16], Resistance [2.9.26], Conductance [2.9.27], Specific Conductance [2.9.28], Equivalent Conductance [2.9.29], Molar Conductance [2.9.30], Ionic Mobility [2.9.33], Kohlrausch's Law [2.9.36], Ionic conductance [2.9.37], Conductometric Titrations [2.9.43], Arrhenius Theory of Electrolytic Dissociation [2.9.45], Ostwald's Dilution Law [2.9.46], Degree of Dissociation [2.9.49], Common Ion Effect [2.9.50], Solubility Product [2.9.52], pH of Solution [2.9.53], Buffer Solution [2.9.55], Acid-Base Indicator [2.9.59], Equivalence Point [2.9.59], pH range [2.9.59], Hydrolysis [2.9.62], Hydrolysis Constant [2.9.63], Water Dissociation Constant [2.9.64], Degree of Hydrolysis [2.9.65], Acid Dissociation Constant [2.9.66], Base Dissociation Constant [2.9.67]

Standard Terms: EMF & Equilibrium Constant [2.9.17], Concentration Cell [2.9.18], Electrode Concentration Cell [2.9.18], Electrolyte Concentration Cell [2.9.18], Potentiometric Titrations [2.9.21], Battery [2.9.22], Primary Battery [2.9.22], Secondary Battery [2.9.22], Polarization [2.9.23], Overvoltage [2.9.24], Asymmetric Effect [2.9.33], Viscous Effect [2.9.33], Electrophoretic Effect [2.9.33], Debye-Huckel-Onsager Theory [2.9.34], Ionic Atmosphere [2.9.35], Transport Number [2.9.41], Hittorf's Method [2.9.42], Moving Boundary Method [2.9.42], pH measurement by Hydrogen Electrode [2.9.54], pH measurement by Quinhydrone Electrode [2.9.54], pH measurement by Glass Electrode [2.9.54], Buffer Action [2.9.56], Henderson-Hasselbalch Equation [2.9.57], Buffer Capacity [2.9.58]

Advanced Terms: Cell with Transference [2.9.19], Cell without Transference [2.9.19], Liquid Junction Potential [2.9.20], Dry Cell [2.9.22], Mercury Cell [2.9.22], Lead Storage Battery [2.9.22], Fuel Cell [2.9.22], Concentration Polarization [2.9.23], Corrosion [2.9.25], Debye-Falkenhagen Effect [2.9.39], Wien Effect [2.9.40], Ghosh's Equation [2.9.48], Ostwald's Theory Of Indicators [2.9.61], Quinoid Theory of Indicators [2.9.61], Tafel Equation [2.9.70]

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Key Conceptual Points

Subunit 9A: Electrochemical Cell

2.9.1. **Electrochemistry** is the study of production of electricity from the energy released during a spontaneous chemical reaction and the use of electrical energy to bring about non-spontaneous chemical transformations.

2.9.2. **FARADAY'S LAWS OF ELECTROLYSIS:** Michael Faraday studied the quantitative aspect of electrolysis. In 1834, he formulated two laws which are known as **Faraday's Laws of Electrolysis**. $1 \text{ F} = 96485 \text{ C mol}^{-1}$.

First Law: The amount of a given product liberated at an electrode during electrolysis is directly proportional to the quantity of electricity which passes through the electrolyte solution.

$$Q = I \times t$$

Second Law: When the same quantity of electricity passes through solutions of different electrolytes, the amounts of the substances liberated at the electrodes are directly proportional to their chemical equivalents.

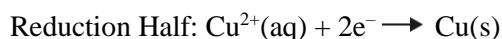
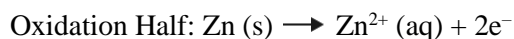
$$m = Z \times I \times t$$

2.9.3. **Electrochemical Cell:** A spontaneous chemical process is the one which can take place on its own and in such a process the Gibbs energy of the system decreases. It is this energy that gets converted to electrical energy. The reverse process is also possible in which we can make non-spontaneous processes occur by supplying external energy in the form of electrical energy. These inter conversions are carried out in equipment called Electrochemical Cell.

2.9.4. **Classification of Electrochemical cells:** Electrochemical cells are of two types

- (i) **Galvanic Cell:** Converts chemical energy into electrical energy.
- (ii) **Electrolytic Cell:** Converts electrical energy into chemical energy.

2.9.5. **Daniel Cell as Galvanic Cell:** Cell energy is extracted from a spontaneous chemical process or reaction and it is converted to electric current. For example, Daniel Cell is a Galvanic Cell in which Zinc and Copper are used for the redox reaction to take place.



Zn is the reducing agent and Cu^{2+} is the oxidising agent. The half cells are also known as Electrodes. The oxidation half is known as Anode and the reduction half is called Cathode. Electrons flow from anode to cathode in the external circuit. Anode is assigned negative polarity and cathode is assigned positive polarity. In Daniel Cell, Zn acts as the anode and Cu acts as the cathode.

2.9.6. **Electrolytic Cell:** These electrodes are dipped in an electrolytic solution containing cations and anions. On supplying current the ions move towards electrodes of opposite polarity and simultaneous reduction and oxidation takes place.

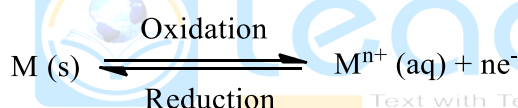
Preferential Discharge of ions: Where there are more than one cation or anion the process of discharge becomes competitive in nature. Discharge of any ion requires energy and in case of several ions being present the discharge of that ion will take place first which requires the energy.

2.9.7. Reversible & Irreversible Cell: A reversible cell is made up to two reversible electrodes. A galvanic cell is reversible, if it satisfies the conditions for thermodynamic reversibility i.e.,

- (i) the driving force and the opposing force be infinitesimally different from each other
- (ii) it should be possible to reverse any change taking place by applying a force infinitesimally greater or smaller than one acting

***Irreversible Cell:** A cell is said to be irreversible if it does not satisfy one of the conditions of reversibility.

2.9.8. Electrode Potential: It may be defined as the tendency of an element, when it is placed in contact with its own ions to either loss or gain electrons and in turn become positively or negatively charged. The electrode potential will be named as oxidation or reduction potential depending upon whether oxidation or reduction has taken place.



Characteristics: (i) Both oxidation and reduction potentials are equal in magnitude but opposite in sign. (ii) It is not a thermodynamic property, so values of E are not additive.

2.9.9. Standard Electrode Potential [E^0]: It may be defined as the electrode potential of an electrode determined relative to standard hydrogen electrode under standard conditions. The standard conditions taken are:

- (i) 1M concentration of each ion in the solution.
- (ii) A temperature of 298 K.
- (iii) 1 bar pressure for each gas.

2.9.10. Electrochemical Series: The half-cell potential values are standard values and are represented as the standard reduction potential values as shown in the table at the end which is also called Electrochemical Series.

Standard Reduction Potential Table:

$\text{H}_4\text{XeO}_6 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{XeO}_3 + 3\text{H}_2\text{O}$	+3.0	$\text{Hg}_2\text{SO}_4 + 2\text{e}^- \rightarrow 2\text{Hg} + \text{SO}_4^{2-}$	+0.62
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.87	$\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	+0.60
$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$	+2.07	$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	+0.56
$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}$	+2.05	$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.54
$\text{Ag}^{2+} + \text{e}^- \rightarrow \text{Ag}^+$	+1.98	$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	+0.52
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	+1.81	$\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$	+0.53
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.78	$\text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{Ni}(\text{OH})_2 + \text{OH}^-$	+0.49
$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}$	+1.69	$\text{Ag}_2\text{CrO}_4 + 2\text{e}^- \rightarrow 2\text{Ag} + \text{CrO}_4^{2-}$	+0.45
$\text{Pb}^{4+} + 2\text{e}^- \rightarrow \text{Pb}^{2+}$	+1.67	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	+0.40
$2\text{HClO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}_2 + 2\text{H}_2\text{O}$	+1.63	$\text{ClO}_4^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{ClO}_3^- + 2\text{OH}^-$	+0.36
$\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$	+1.61	$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \rightarrow [\text{Fe}(\text{CN})_6]^{4-}$	+0.36
$2\text{HBrO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Br}_2 + 2\text{H}_2\text{O}$	+1.60	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.51	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	+0.27
$\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+}$	+1.51	$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	+0.22
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.40	$\text{Bi} + 3\text{e}^- \rightarrow \text{Bi}$	+0.20
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.36	$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	+0.16
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33	$\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$	+0.15
$\text{O}_3 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{O}_2 + 2\text{OH}^-$	+1.24	$\text{AgBr} + \text{e}^- \rightarrow \text{Ag} + \text{Br}^-$	+0.07
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.23	$\text{Ti}^{4+} + \text{e}^- \rightarrow \text{Ti}^{3+}$	0.00
$\text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{ClO}_3^- + \text{H}_2\text{O}$	+1.23	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0, by definition
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23	$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.04
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.09	$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^-$	-0.08
$\text{Pu}^{4+} + \text{e}^- \rightarrow \text{Pu}^{3+}$	+0.97	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	+0.96	$\text{In}^+ + \text{e}^- \rightarrow \text{In}$	-0.14
$2\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	+0.92	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$	+0.89	$\text{AgI} + \text{e}^- \rightarrow \text{Ag} + \text{I}^-$	-0.15
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	+0.86	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23
$\text{NO}_3^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	+0.80	$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$	-0.28
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.80	$\text{In}^{3+} + 3\text{e}^- \rightarrow \text{In}$	-0.34
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	+0.79	$\text{Tl}^+ + \text{e}^- \rightarrow \text{Tl}$	-0.34
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+0.77	$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.36
$\text{BrO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Br}^- + 2\text{OH}^-$	+0.76	$\text{V}^{2+} + 2\text{e}^- \rightarrow \text{V}$	-1.19
$\text{Ti}^{3+} + \text{e}^- \rightarrow \text{Ti}^{2+}$	-0.37	$\text{Ti}^{2+} + 2\text{e}^- \rightarrow \text{Ti}$	-1.63
$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.40	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{In}^{2+} + \text{e}^- \rightarrow \text{In}^+$	-0.40	$\text{U}^{3+} + 3\text{e}^- \rightarrow \text{U}$	-1.79
$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.41	$\text{Sc}^{3+} + 3\text{e}^- \rightarrow \text{Sc}$	-2.09
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.36
$\text{In}^{3+} + 2\text{e}^- \rightarrow \text{In}^+$	-0.44	$\text{Ce}^{3+} + 3\text{e}^- \rightarrow \text{Ce}$	-2.48
$\text{S} + 2\text{e}^- \rightarrow \text{S}^{2-}$	-0.48		

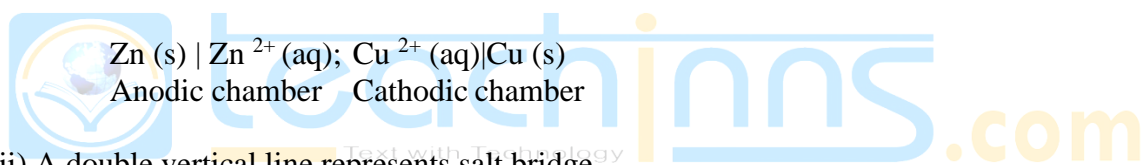
$\text{In}^{3+} + \text{e}^- \rightarrow \text{In}^{2+}$	-0.49	$\text{La}^{3+} + 3\text{e}^- \rightarrow \text{La}$	-2.52
$\text{U}^{4+} + \text{e}^- \rightarrow \text{U}^{3+}$	-0.61	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.74	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.87
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76	$\text{Sr}^{2+} + 2\text{e}^- \rightarrow \text{Sr}$	-2.89
$\text{Cd}(\text{OH})_2 + 2\text{e}^- \rightarrow \text{Cd} + 2\text{OH}^-$	-0.81	$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	-2.91
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83	$\text{Ra}^{2+} + 2\text{e}^- \rightarrow \text{Ra}$	-2.92
$\text{Cr}^{2+} + 2\text{e}^- \rightarrow \text{Cr}$	-0.91	$\text{Cs}^+ + \text{e}^- \rightarrow \text{Cs}$	-2.92
$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18	$\text{Rb}^+ + \text{e}^- \rightarrow \text{Rb}$	-2.93
		$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.93
		$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05

2.9.11. Cell Diagram: The following conventions or notations are applied for writing the cell diagram in accordance with IUPAC recommendations. The Daniel cell is represented as follows:



(i) Anode half-cell is written on the lefthand side while cathode half-cell on right hand side.

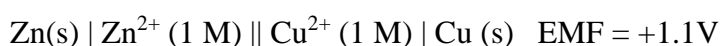
(ii) A single vertical line separates the metal from aqueous solution of its own ions.



(iii) A double vertical line represents salt bridge.

(iv) The molar concentration (C) is placed in brackets after the formula of the corresponding ion.

(v) The value of e.m.f. of the cell is written on the extreme right of the cell. For example,



If an inert electrode like platinum is involved in the construction of the cell, it may be written along with the working electrode in bracket say for example, when a zinc anode is connected to a hydrogen electrode.



2.9.12. Salt Bridge: Salt bridge is used to maintain the charge balance and to complete the circuit by facilitating the flow of ions through it. It contains a gel in which an inert electrolyte like Na_2SO_4 or KNO_3 etc are mixed. Negative ions flow to the anode and positive ions flow to the cathode through the salt bridge and charge balance is maintained and cell keeps on functioning.

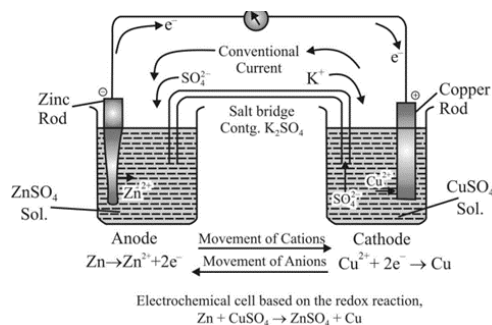


Fig.1: Salt Bridge in an Electrochemical cell

2.9.13. Electromotive Force [EMF] of a Cell: The difference between the electrode potentials of two half cells is called cell potential. It is known as electromotive force (EMF) of the cell if no current is drawn from the cell.

$$E_{\text{cell}} = E_{\text{cathode}} + E_{\text{anode}}$$

For this equation we take oxidation potential of anode and reduction potential of cathode. Since anode is put on left and cathode on right, it follows therefore,

$$E_{\text{cell}} = E_{\text{R.H.E}} - E_{\text{L.H.E}}$$

For a Daniel cell, therefore,

$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0 \\ &= 0.337 - (-0.763) = +0.11 \end{aligned}$$

2.9.14. Spontaneity of Cell reaction: For a spontaneous cell reaction ΔG should be negative and cell potential should be positive in the below equation.

$$\Delta G = -nFE_{\text{CELL}}$$

Where, ΔG = free energy change in a cell reaction, n = number of electrons involved in the reaction, F = Faraday Constant of electric potential, E_{cell} = EMF of cell.

***Relationships of Thermodynamic Variables with EMF of a Cell:**

Relation Between Gibbs' Free energy & EMF of the Cell:

If we take standard value of cell potential in the above equation, we will obtain standard value of ΔG as well.

$$\Delta G^0 = -nFE^0$$

Relation between Entropy & EMF of the Cell:

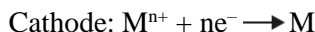
$$\Delta S^0 = nF \left(\frac{\partial E}{\partial T} \right)_P$$

Relation Between Enthalpy & EMF of the Cell:

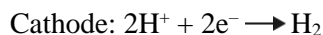
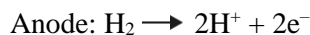
$$\Delta H^0 = -nFE^0 + nF \left(\frac{\partial E}{\partial T} \right)_P$$

2.9.15. Types of Electrodes:

1. Metal-Metal Ion Electrodes: A metal rod/plate is dipped in an electrolyte solution containing metal ions. There is a potential difference between these two phases and this electrode can act as a cathode or anode both.

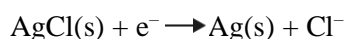


2. Gas Electrodes: Electrode gases like H_2 , Cl_2 etc are used with their respective ions. For example, H_2 gas is used with a dilute solution of HCl (H^+ ions). The metal should be inert so that it does not react with the acid.



The hydrogen electrode is also used as the standard to measure other electrode potentials. Its own potential is set to 0 V as a reference. When it is used as a reference the concentration of dilute HCl is taken as 1 M and the electrode is called “**Standard Hydrogen Electrode (SHE)**”.

3. Metal- insoluble Electrode: We use salts of some metals which are sparingly soluble with the metal itself as electrodes. For example, if we use $AgCl$ with Ag there is a potential gap between these two phases which can be identified in the following reaction:



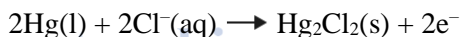
This electrode is made by dipping a silver rod in a solution containing $AgCl(s)$ and Cl^{-} ions.

4. Calomel Electrode: Mercury is used with two other phases; one is a calomel paste (Hg_2Cl_2) and electrolyte containing Cl^{-} ions.

Cathode:

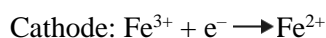
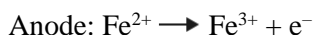


Anode:

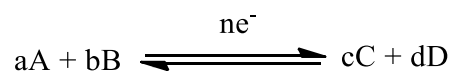


This electrode is also used as another standard to measure other potentials. Its standard form is also called Standard Calomel Electrode (SCE).

5. Redox Electrode: In these electrodes two different oxidation states of the same metal are used in the same half-cell. For example, Fe^{2+} and Fe^{3+} are dissolved in the same container and an inert electrode of platinum is used for the electron transfer. Following reactions can take place:



2.9.16. Nernst Equation: It relates electrode potential with the concentration of ions. Thus, the reduction potential increases with the increase in the concentration of ions. For a general electrochemical reaction of the type,



The Nernst Equation is

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{RT}{nF} \ln([C]^c[D]^d/[A]^a[B]^b)$$

At standard condition, that means $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$, $T = 298 \text{ K}$, $F = 96485 \text{ Cmol}^{-1}$

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{n} \ln([C]^c[D]^d/[A]^a[B]^b)$$

2.9.17. Relation between Equilibrium Constant & EMF:

$$\log K_{eq} = nE_{cell}^0/0.0591 \text{ \& } E_{Cell}^0 = [RT/nF] \ln K_{eq}$$

2.9.18. Concentration Cells: If two electrodes of the same metal are dipped separately into two solutions of the same electrolyte having different concentrations and the solutions are connected through salt bridge, such cells are known as concentration cells. For example,

(i) **Electrode Concentration Cell:**



$$E_{cell} = - \frac{RT}{nF} \ln(a_2/a_1) ; a_1 > a_2$$

(ii) **Electrolyte Concentration Cell:**



$$E_{cell} = \frac{RT}{nF} \ln(C_2\gamma_2/C_1\gamma_1)$$

2.9.19. Cell with Transference and Cell without Transference: The Electrolyte Concentration Cells without Transference are those which have two electrodes of the same kind are placed in two solutions of different concentrations or activities which are connected by a salt-bridge.

$$E_{cell} = (RT/nF) \ln(a_2/a_1) = (RT/nF) \ln(m_2\gamma_2/m_1\gamma_1)$$

Where, a = activity of electrolyte, n = number electrons involved in the cell reaction, γ = activity co-efficients

****The concentration cells with transference or transport** are those which have two same kind of electrodes immersed in two solutions of the same electrolyte of different concentrations are brought in direct contact with each other through a permeable partition to ions for exchanging.

$$E_{cell} = - 2t_- (RT/F) \ln(a'_1/a'_2)$$

Where, t_- = transport number of anion, a' = mean activity

2.9.20. Liquid Junction Potential (LJP):

$$E_J = [(u_+ - u_-)/(u_+ + u_-)](RT/F) \ln(a'_1/a'_2)$$

$$= (t_+ - t_-)(RT/F) \ln(a'_1/a'_2)$$

$$= (t_+ - t_-) (RT/F) \ln(m_2\gamma''_2/m_1\gamma''_1)$$

Where, t_+ , t_- = transport number of cation and anion, γ'' = mean activity co-efficient, u_+ , u_- = ionic mobility of cation and anion

2.9.21. Potentiometric titrations: In a potentiometric titration, a suitable electrode immersed in the solution to be titrated acts as the 'indicator'. The **indicator electrode** is paired with a reference electrode and the two electrodes are connected to an electronic voltmeter. The emf of the indicator electrode changes gradually with the change of concentration of ions caused by the addition of titrant from the burette. The equivalence point is indicated by a sharp change in electrode potential. Since the reference electrode potential has a constant value, any change in the indicator electrode potential is reflected by a similar change in the cell potential. Therefore, the equivalence point can be found by plotting a graph between the cell emf and the volume of titrant added from the burette. A sharp rise of the curve shows the equivalence point and the corresponding volume on the graph is the volume of the solution used for the titration.

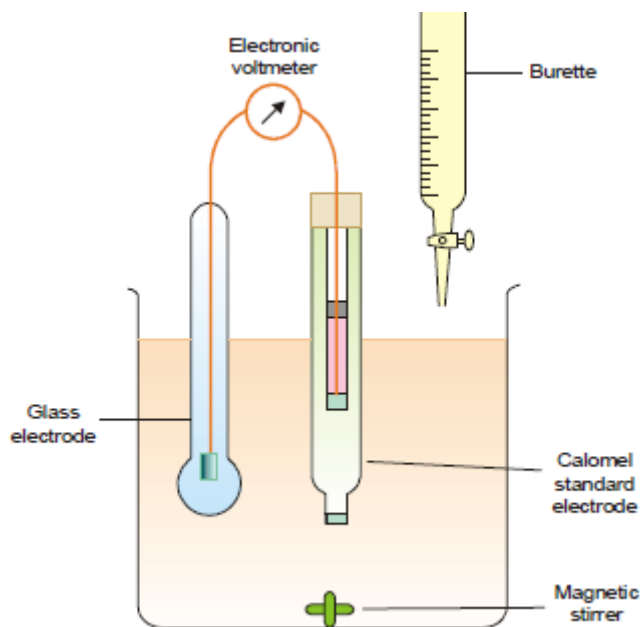
The potentiometric titrations may be of three types:

- (a) Acid-base titrations
- (b) Oxidation-reduction titrations
- (c) Precipitation titrations

(a) Acid-base Titrations: The apparatus used for potentiometric acid-base titrations is shown in Fig.2. A hydrogen electrode or a glass electrode is immersed in solution of the acid whose strength is to be determined. The glass electrode is coupled with a standard calomel electrode. The cell thus formed is connected to the potentiometer or electronic voltmeter. When alkali is added, pH of the solution changes. The emf of the cell also changes with pH of the solution in accordance with the relation.

$$E = E^{\circ} + 0.0591 \text{ pH}$$

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Fig.2: Potentiometric Acid-Base Titration Apparatus

The standard alkali solution is then added from the burette in small volumes. After each addition, the emf of the cell is recorded. The emf is then plotted against the volume of alkali added. The shape of the curve for the titration of a strong acid against strong alkali (HCl versus NaOH) is shown in Fig.3. The steepest portion of the curve indicates the equivalence point.

However, when the solutions are very dilute, or weak acids or bases, are involved, the steepness of the curve is less marked and it is difficult to judge the end-point. In such a case, we plot the slope of the curve, $\Delta E/\Delta V$ against the volume of alkali used. The maximum of the curve indicates the end-point.

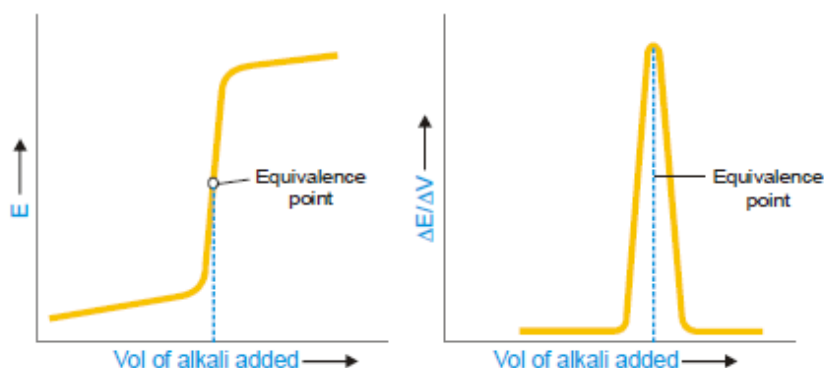


Fig.3: Potentiometric Acid-Base titration curves

(b) Oxidation-reduction Titrations: The titration of ferrous ions (Fe^{2+}) with ceric ions (Ce^{4+}) is an example of oxidation-reduction (or redox) titration. Fe^{2+} ion is oxidised to Fe^{3+} ion, while Ce^{4+} is reduced to Ce^{3+} ion.



This titration can be carried in the apparatus shown in Fig.4. The indicator electrode is a shiny platinum strip dipping in the solution of Fe^{2+} ions, and it is connected to a standard calomel electrode. The Ce^{4+} solution is added from the burette and the cell potential, E , recorded after each addition.

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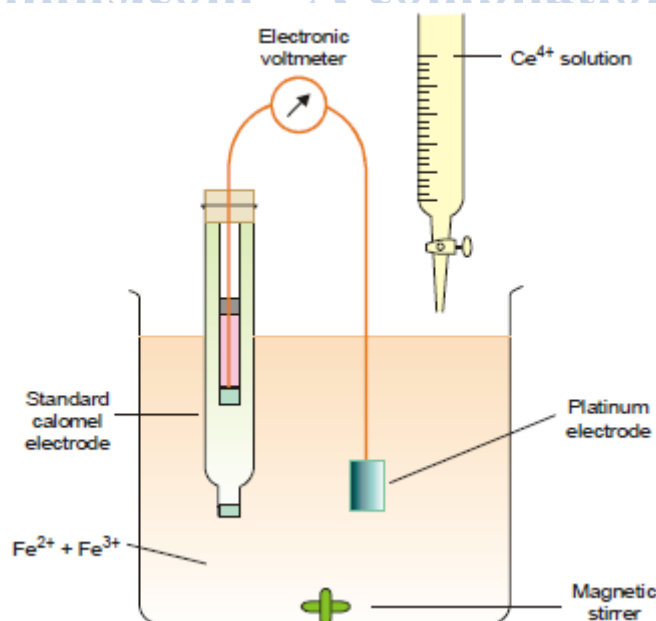


Fig.4: Apparatus for potentiometric titration of Fe^{2+} with Ce^{4+}

The potential of the platinum electrode depends on the ratio $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$. The potential of the Cell, also changes with the change of the ratio $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$. Therefore, the cell potential changes with the addition of Ce^{4+} ions from the burette. Fig.5 shows how the potential of the

cell changes during the titration. At the equivalence point there is a sharp rise of potential which indicates the endpoint. Potentiometric titrations of this type are particularly useful for coloured solutions in which an indicator cannot be employed.

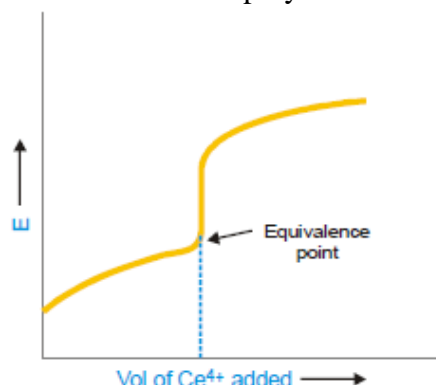


Fig.5: Potentiometric titration curve of Fe^{3+} ions and Ce^{4+} ions

(c) Precipitation Titration: A typical precipitation titration is that of sodium chloride solution against silver nitrate solution. The apparatus set up for the purpose is shown in Fig.6. A silver electrode dipping in the unknown sodium chloride solution is coupled with a calomel electrode through a salt bridge. However, if the Calomel electrode was in direct contact with a solution containing excess silver ions, chloride would seep through the sintered base and react to form an insoluble layer of silver chloride. Any change in the cell potential is due to changes in concentration of Ag^+ ions around the silver electrode.

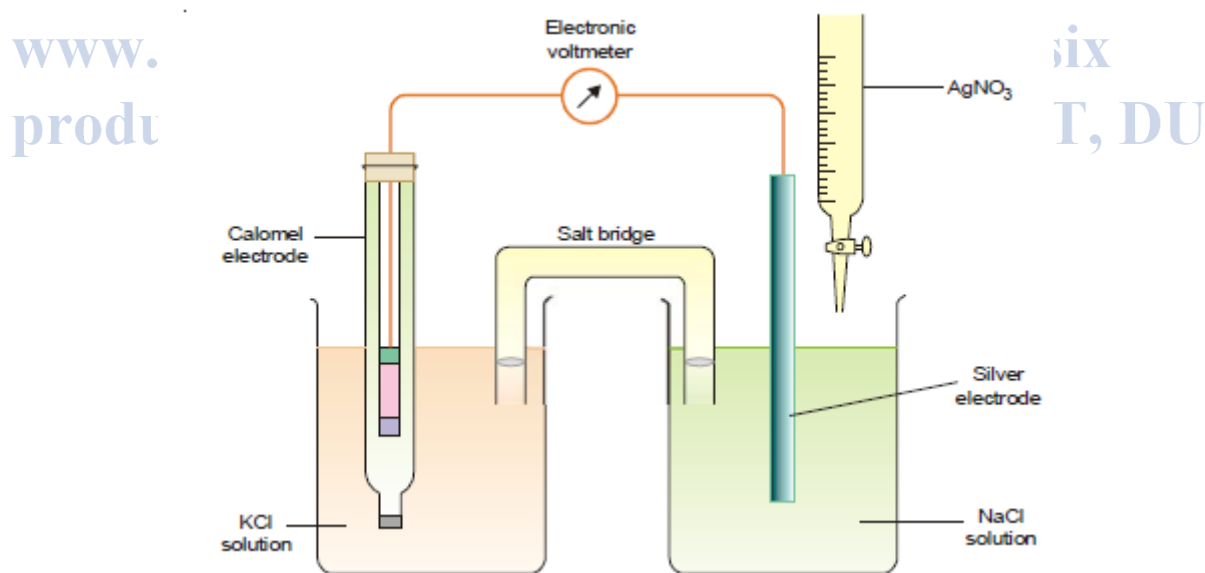


Fig.6: Potentiometric titration of sodium chloride against silver nitrate solution

Initially the concentration of Ag^+ ions will be zero. But as silver nitrate is added from the burette, silver chloride is precipitated. Now the solution will contain a small concentration of Ag^+ ions formed by the slight dissociation of silver chloride. This concentration will increase slightly as Cl^- ions are removed in order to maintain the solubility product $\text{KSP} = [\text{Ag}^+][\text{Cl}^-]$. After the equivalence point, the concentration of Ag^+ ions and, therefore the silver electrode

potential will rise very sharply owing to the presence of excess of Ag^+ ions. The volume of AgNO_3 solution used to reach the equivalence point as shown in Fig.7.

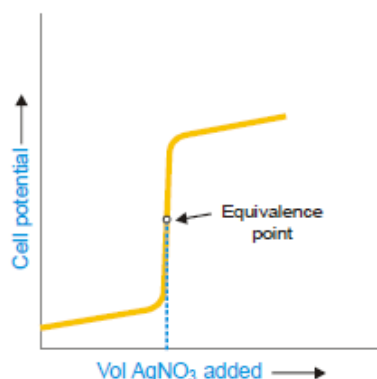


Fig.7: Potentiometric Titration curve for precipitation reaction

2.9.22. **Batteries:** When Galvanic cells are connected in series to obtain a higher voltage the arrangement is called Battery.

(i) **Primary Battery:** Primary cells are those which can be used so long the active materials are present. Once they get consumed the cell will stop functioning and cannot be re-used. Examples are Dry Cell and Mercury cell.

***Dry Cell:**

Anode: Zn container

Cathode: Carbon (graphite) rod surrounded by powdered MnO_2 and carbon.

Electrolyte: NH_4Cl and ZnCl_2

Cell Reaction:

Anode: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

Cathode: $\text{MnO}_2 + \text{NH}_4^+ + \text{e}^- \rightarrow \text{MnO}(\text{OH}) + \text{NH}_3$

The standard potential of this cell is 1.5 V and it falls as the cell gets discharged continuously and once used it cannot be recharged.

***Mercury Cell:**

These are used in small equipment like watches, hearing aids.

Anode: Zn – Hg Amalgam

Cathode: Paste of HgO and carbon

Electrolyte: Paste of KOH and ZnO

Anode: $\text{Zn}(\text{Hg}) + 2\text{OH}^- \rightarrow \text{ZnO}(\text{s}) + \text{H}_2\text{O} + 2\text{e}^-$

Cathode: $\text{HgO}(\text{s}) + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg}(\text{l}) + 2\text{OH}^-$

Overall Reaction: $\text{Zn}(\text{Hg}) + \text{HgO}(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{Hg}(\text{l})$

The cell potential is approximately 1.35V and remains constant during its life.

(ii) **Secondary Batteries:** Secondary cells are those which can be recharged again and again for multiple uses. e.g. lead storage battery and Ni – Cd battery.

***Lead Storage Battery:**

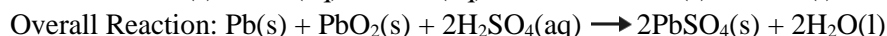
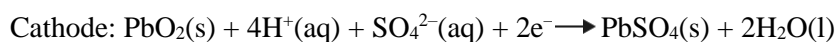
Anode: Lead (Pb)

Cathode: Grid of lead packed with lead oxide (PbO_2)

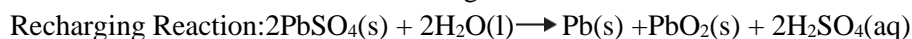
Electrolyte: 38% solution of H_2SO_4

Discharging Reactions

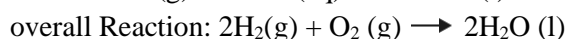
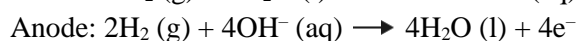
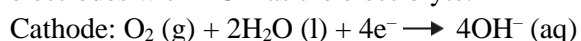
Anode: $\text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$



To recharge the cell, it is connected with a cell of higher potential and this cell behaves as an electrolytic cell and the reactions are reversed. Pb(s) and PbO₂(s) are regenerated at the respective electrodes. These cells deliver an almost consistent voltage.



***Fuel Cell:** A fuel cell differs from an ordinary battery in the sense that the reactants are not contained inside the cell but are externally supplied from an external reservoir. Fuel cell is used in space vehicles and in this cell the two gases are supplied from external storages. In this cell carbon rods are used as electrodes with KOH as the electrolyte.



2.9.23. Polarization: An electrolysis cell which uses voltage in excess of the theoretical reversible value is called a **polarized cell**. The potential in excess of the theoretical value which has to be applied for electrolysis at an appreciable rate is called **polarization potential**. This phenomenon of the departure from the theoretical potential is called **polarization**.

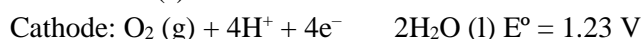
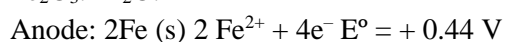
****Concentration Polarization:** The phenomenon of the departure of the electrode potential from its reversible value as a result of the change of concentration in the vicinity of an electrode during electrolysis in a cell is called Concentration Polarization.

2.9.24. Overvoltage: The overvoltage or overpotential is the polarization potential which arises due to irreversibility in electrode processes if the product is a gas during electrolysis.

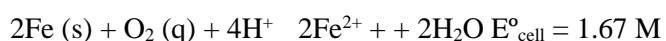
*The overvoltage depends on:

1. The nature and the physical state of the electrode used.
2. The Physical state of the substance deposited. If the latter is a gas, the overvoltage is high. If it is a metal, that would be small.
3. The temperature and the current density at which the overvoltage is measured.

2.9.25. Corrosion: It involves a redox reaction and formation of an electrochemical cell on the surface of iron or any other metal. At one location oxidation of iron takes place (anode) and at another location reduction of oxygen to form water takes place (cathode). First Fe gets oxidised to Fe²⁺ and then in the presence of oxygen it forms Fe³⁺ which then reacts with water to form rust which is represented by Fe₂O₃.xH₂O.



Overall Reaction:



Rusting of iron can be avoided by painting it or by coating it with some other metals like Zinc. The latter process is known as Galvanisation. As the tendency of Zn to get oxidised is more than iron it gets oxidised in preference and iron is protected. This method of protecting one metal by the other is also called Cathodic Protection.

Subunit 9B: Electrolytic Conductance

2.9.26. **Resistance:** Resistance refers to the opposition to the flow of current. For a conductor of uniform cross section(a) and length(l); Resistance R ,

$$R \propto l/a ; R = \rho \frac{l}{a}$$

Where, ρ = resistivity or specific resistance.

2.9.27. **Conductance:** The reciprocal of the resistance is called conductance. It is denoted by C .

$$C = 1/R$$

Conductors allow electric current to pass through them. Examples are metals, aqueous solutions of acids, bases and salts etc. Insulators do not allow the electric current to pass through them. Examples are pure water, urea, sugar etc. Unit of conductance is ohm^{-1} or mho or Siemen(S).

2.9.28. **Specific Conductance:** Specific conductance (k) can be defined as reciprocal of specific resistance. Conductance is basically the ease of current flow through a liquid conductor. Specific conductance is defined by the conductance of a solution of the dissolved electrolyte and the whole solution is being placed between two electrodes of 1 sq. cm area and 1 cm. Unit of conductance will simply be reciprocal of unit of resistance i.e., $1/\text{ohm} = \text{ohm}^{-1}$ = mount of specific conductance = $1/\text{ohm.cm} = \text{mho.cm}^{-1}$.

2.9.29. **Equivalent conductance:** From the expression of conductance, we know that

$$\begin{aligned} \Lambda &= \frac{1}{R} \\ &= \frac{1}{\rho \frac{l}{a}} \\ &= \frac{a}{\rho l} \\ &= \frac{1}{\rho} \frac{a}{l} \\ &= \frac{V}{\kappa l^2}; \end{aligned}$$

Where, V = volume of the solution = area x length = $a \times l$

Equivalent conductance is defined by the conductance of a solution containing 1 gm-equivalent of the dissolved electrolytes and the whole solution is being placed between two electrodes of 1 sq. cm area and 1 cm apart. Thus, equivalent conductance

$$\Lambda = kV$$

(as $l = 1 \text{ cm}^2$)

Now, say c gm-equivalent dissolved in 1000 cc of solution. So, 1 gm-equivalent will be present in $1000/C$ cc solution.

So, equivalent conductance

$$(\Lambda) = \frac{1000\kappa}{c}$$

Unit of equivalent conductance =

$$\frac{\text{mho.cm}^{-1}}{\text{gm-equivalent.cc}} = \frac{\text{mho.cm}^{-1}}{\text{gm-equivalent.cm}^3} = \text{mho.cm}^2.\text{gm-equivalent}^{-1}$$

2.9.30. Molar conductance: Molar conductance is defined by the conductance of a solution containing 1 gm-mole of the dissolved electrolyte and the whole solution is being placed between two electrode 1 cm apart. Molar conductance can be expressed by,

$$\Lambda_m = kV_m$$

(V_m = volume of a solution containing 1 gm-mole dissolved electrolyte)

Now, say C gm-mole dissolved in 1000 cc of solution. So, 1 gm-mole will be present in $1000/C_m$ cc solution. So, molar conductance

$$\Lambda_m = 1000k/C_m$$

2.9.31. Relation between equivalent conductance and molar conductance: Let us consider an electrolyte (molecular weight M) having weight W gm taken in between two electrodes (in the cubic core); p and q are the valency and number of cations are respectively.

Now, equivalent weight of the electrolyte is; $E = M/pq$

C gm equivalent = $W/E = Wpq/m$

$$\begin{aligned} \text{Now, equivalent conductance} &= \Lambda = \frac{1000\kappa}{c} \\ &= \frac{1000\kappa}{\frac{W \times pq}{M}} \\ &= \frac{1000\kappa}{M \text{ gram mole} \times pq} \\ &= \frac{\Lambda_m}{pq} \end{aligned}$$

$$\Lambda_m = \Lambda \times pq$$

2.9.32. Effect of temperature on equivalent conductance: In general, equivalent conductance should increase with temperature as with increased temperature, the dissociation of electrolyte and ionic mobility of ions increase. Conductance and temperature are correlated by this equation:

$$\Lambda^\circ_T = \Lambda^\circ_{298K} [1 + \alpha(T - 298)]$$

Where, Λ°_T and Λ°_{298K} are the equivalent conductance at $T^\circ\text{C}$ and 25°C (298K) respectively; ' α ' is the temperature coefficient.

2.9.33. Effect of concentration on equivalent conductance of Strong Electrolytes: Conductance of an electrolyte depends on the number of ions present in the solution and **the speed of the ions which is known as ionic mobility**. As strong electrolyte already completely dissociated in solution hence number of ions do not change with dilution. Therefore, the conductance of a strong electrolyte depends upon only the ionic mobility of the ions present in solution.

(a) Asymmetric Effect or Relaxation Effect: In a concentrated solution, the density of ions is high as the attraction between ions are high. According to Debye and Huckel, at high concentration a particular type of ion is surrounded by the opposite charged ions and thus an ionic cloud is being created. A cationic cloud formed on an anion and vice versa. These ionic clouds are generally spherical when no electric fields are present. But in presence of an external electrical field these ionic spheres get distorted. As the extend of ionic cloud distortion increases the ionic mobility decreases. This is commonly known as **relaxation effect**. As dilution increases, the extend of this distortion decreases or the attraction between ions decreases; as a result, the ionic mobility or the conductance of the solution increases. With increase in concentration, the equivalent conductance of any electrolyte decreases but the pattern of the graph is different for strong and weak electrolyte. Conductance generally depends upon the number of ions and speed of ions (ionic mobility). Strong electrolytes are completely dissociated in solution and hence decrease in concentration or increase in dilution will increase the ionic mobility only. Hence the with dilution equivalent conductance will increase slightly in a regular straight line. **At infinite dilution this value will reach at its maximum which is termed as limiting equivalent conductance (Λ_0)**. Example of strong electrolytes are NaCl, KCl, K_2SO_4 , HCl, H_2SO_4 , HNO_3 , NaOH, KOH etc.

(b) Viscous Force: When a cation of radius r_+ moves with a velocity u_+ relative to the solvent, then according to Stokes law the frictional resistance offered by the solvent is

$$F = -6\pi\eta r_+ u_+$$

At infinite dilution the retarding forces originating from interionic interaction disappear. Only retarding force that acts at infinite dilution is the viscous force. The steady state is attained only due to the balance of electrical force and the viscous force. Then,

$$F = -6\pi\eta r_+ u_+ = Z_+ E e 10^7$$

So, ionic mobility is given by,

$$U_+ = u_+/E = Z_+ e 10^7 / 6\pi\eta r_+ = K_1 / \eta r_+$$

Where, $K_1 = Z_+ e 10^7 / 6\pi$

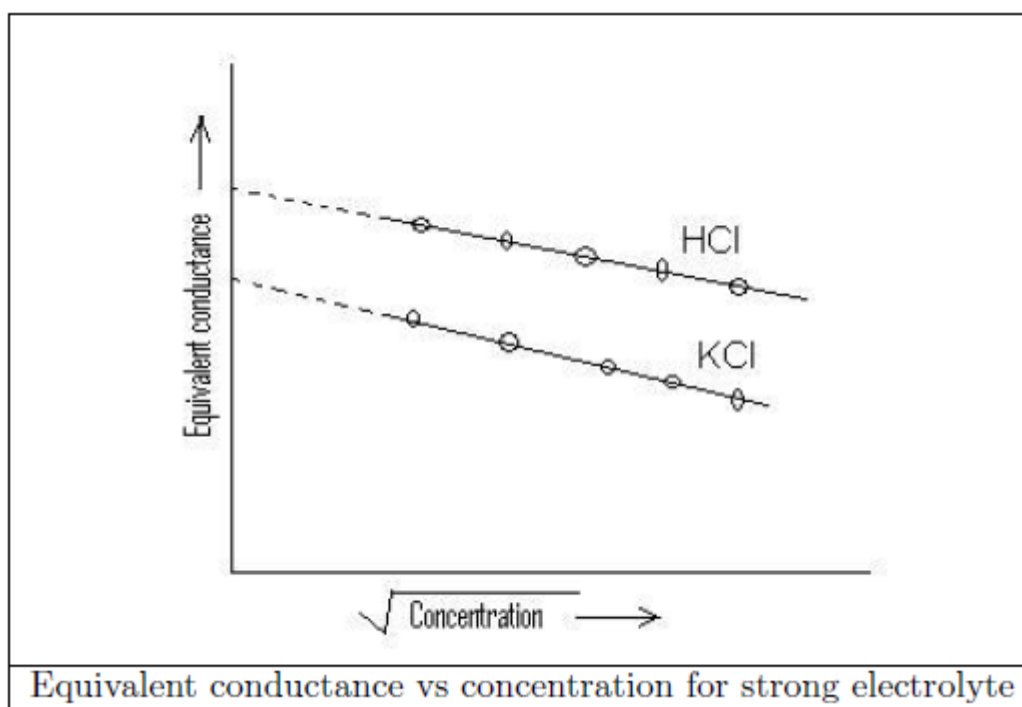
At infinite dilution such a condition of steady state is maintained since the magnitude of other retarding forces can be neglected. At infinite dilution, equivalent conductance can be represented by $\Lambda_0 = F(U_+ + U_-)$, where u_+ and u_- are the ionic mobilities of cation and anion respectively. Now,

$$\Lambda_0 = K_1 F (1/r_+ + 1/r_-) / \eta$$

For ions of large size, the solvation can be neglected; hence, r_+ and r_- can be regarded constant in any solvent. However, this consideration is not valid for ions of high charge and low radius. Therefore, for ions of large size, $\Lambda_0 \eta$ is constant. This is called **Walden value**. This rule suggests that the factors which lower the value of viscosity coefficient must increase the value of Λ_0 . This is supported by the fact that on increasing temperature η decreases while Λ_0 increases.

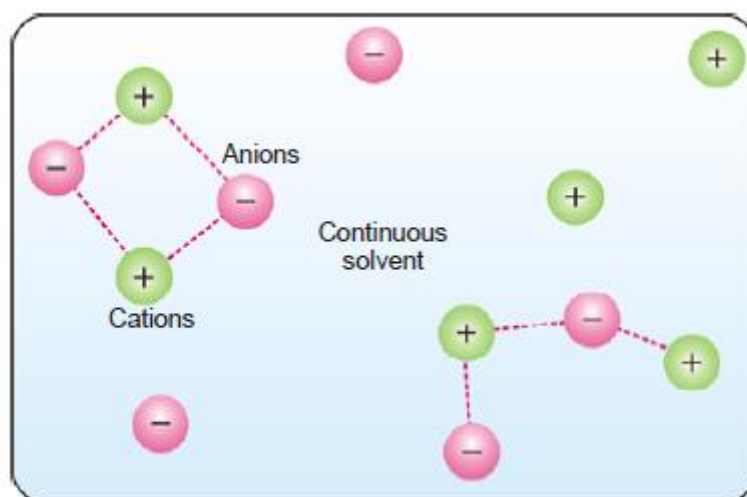
(c) Electrophoretic effect: Migration of ion through the solvent imparts momentum to the adjacent solvent molecules and hence streaming of solvent is associated with the movement of ions. In the deformed ion atmosphere density of negative charge is greater behind the cation than in front. So, the

streaming of solvent is more in the direction opposite to that of the central ion as greater number of anions remaining behind the cation impart greater momentum to the solvent than do the central ion. Consequently, the relative velocity of the central ion with respect to the solvent becomes greater than the speed of the ion had there been no streaming of the solvent. The increase in relative speed increases the viscous drag. The streaming of the solvent with the migration of ion is called electrophoresis and its regarding effect on the speed of an ion is called electrophoretic effect. Like asymmetric effect, electrophoretic effect is also proportional to \sqrt{C} and inversely proportional to Dielectric Constant.



2.9.34. Debye-Huckel-Onsagar Equation: In 1923 Debye and Huckel and in 1926 Onsagar put forward the **modern theory of strong electrolytes** in which account is taken of the electrostatic forces between the ions. Without going into its mathematical details, a brief outline of the main ideas of the theory is given below:

- (1) **The strong electrolyte is completely ionised at all dilutions.** The present position as it has emerged from the study of Raman spectra, X-ray analysis of crystals, Distribution coefficients and vapour pressures is that there is a very small amount of unionised substance also present and therefore, instead of saying 'completely ionised' we should say 'almost completely ionised'.
- (2) **Since oppositely charged ions attract each other, it suggests that anions and cations are not uniformly distributed in the solution of an electrolyte but that the cations tend to be found in the vicinity of anions and vice-versa** (Fig. below). Though the solution is on the whole neutral, there is in the vicinity of any given ion a predominance of ions of opposite charge which we call as **counter ions**. The ions are all the time on the move in all directions but on the average, more *counter ions* than like *ions* pass by any given ion. This spherical haze of opposite charge is called **ionic atmosphere**.
- (3) Decrease in equivalent conductance with increase in concentration is due to fall in mobilities of the ions due to greater inter-ionic effect and *vice-versa*.
- (4) The ratio $\lambda_v / \lambda_\infty$ does not correctly give the degree of dissociation α for strong electrolytes but only the conductance or conductance coefficient f_c .
- (5) In spite of almost complete ionisation, λ_v is much less than λ_∞ .



The relationship between concentration of any electrolyte and its equivalent conductance is given by **Debye-Huckel-Onsager equation**,

$$\Lambda_{eqv.} = \Lambda_0 - [A + B\Lambda_0]\sqrt{C}$$

where 'A' and 'B' are constants and its value depends upon stoichiometry of the electrolyte of interest, 'C' is the concentration of the electrolyte in gm-eqv./L.

$$A = 82.4/(DT)^{1/2}\eta \quad B = (8.2 \times 10^5)/(DT)^{1/2}$$

Where, D = dielectric constant, T = temperature, η = Viscosity.

Originally Debye-Huckel-Onsager equation is

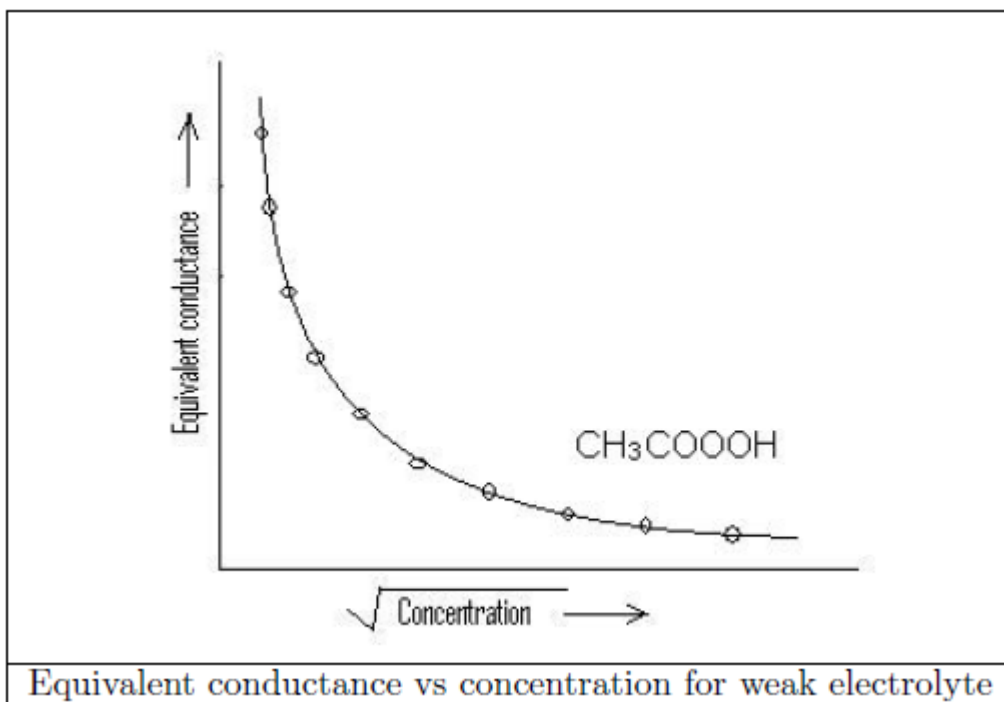
$$\Lambda_{eqv.} = \Lambda_0 - [29.15(Z_+ + Z_-)/(DT)^{1/2}\eta + (9.9 \times 10^5)/(DT)^{1/2}\Lambda_0\omega]\sqrt{\{C(Z_+ + Z_-)\}}$$

In simple case of a (1:1) electrolyte, Z_+ and Z_- are unity and $\omega = (2 - \sqrt{2})$, then the equation becomes

$$\Lambda_{eqv.} = \Lambda_0 - [82.4/(DT)^{1/2}\eta + (8.2 \times 10^5)/(DT)^{1/2}\Lambda_0\omega]\sqrt{\{C(Z_+ + Z_-)\}}$$

2.9.35. Effect of concentration on equivalent conductance of Strong Electrolytes: Weak electrolytes are partially dissociated in solution and hence with increase in dilution or decrease in concentration both the dissociation of electrolytes and the number of ions increases. These two combined effects increase equivalent conductance exponentially and becomes almost equal parallel to y-axis. Thus, at infinite dilution, the equivalent conductance of a weak electrolyte cannot be determined. But from Kohlrausch's law, indirectly we can calculate that. So, for weak electrolyte when equivalent conductance reaches maximum at almost complete dissociation, i.e.; dissociation constant (α) is close to unity. α can be expressed as a ratio of equivalent conductance at a certain concentration of an electrolyte (Λ) with equivalent conductance at infinite dilution (Λ_0) of same electrolyte.

We think, the weightage of text is only 10 percent, the rest 90 percent of weightage lies within our remaining five services: solution of 1250 previous years questions and 1000 model questions (unit and subunit wise) with proper explanation, on-line MOCK test series, last minute suggestions and daily updates because it will make your preparation innovative, scientific and complete. Access these five services from our website: www.teachinns.com and qualify not only the eligibility of assistant professorship but also junior research fellowship.



2.9.36. **KOHLRAUSCH'S LAW:** From a study of the equivalent conductance's of different electrolytes at infinite dilution (λ_∞), Kohlrausch discovered that each ion contributes to the conductance of the solution. In 1875, he enunciated a generalisation which is called the **Kohlrausch's Law**. It states that the **equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductance of the component ions**. The law may be expressed mathematically as:

$$\lambda_\infty = \lambda_a + \lambda_c$$

where λ_a is the equivalent conductance of the anion and λ_c that of the cation.

For example, the equivalent conductance of NaCl at infinite dilution at 25°C is found to be 126.45. The equivalent conductance of Na^+ and Cl^- ion is 50.11 ohm^{-1} and 76.34 ohm^{-1} respectively. Thus,

$$\lambda_\infty(\text{NaCl}) = \lambda_{\text{Cl}^-} + \lambda_{\text{Na}^+}$$

$$\text{or, } 126.45 = 50.11 + 76.34$$

This is in conformity with the Kohlrausch's Law.

2.9.37. **Transport number and Ionic conductance:** Transport number can be defined as fraction of current transported by a particular type of ion in a solution of electrolyte.

So, transport number for cation

$$t_+ = I_+/I$$

and transport number for anion

$$t_- = I_-/I$$

where I_+ is the amount of current carried by cation and I_- is the amount of current carried by anion. Current carried by any type of ion depends upon speed of ions (u), charge of the ions (c) and valency of ion (z). Thus,

$$I_+ \propto u_+ c_+ z_+$$

$$I_- \propto u_- c_- z_-$$

$$t_+ = \frac{u_+ c_+ z_+}{(u_+ c_+ z_+) + (u_- c_- z_-)}$$

$$t_- = \frac{u_- c_- z_-}{(u_+ c_+ z_+) + (u_- c_- z_-)}$$

$$t_+ = \frac{u_+}{(u_+) + (u_-)}$$

$$t_- = \frac{u_-}{(u_+) + (u_-)}$$

Let us consider at infinite dilution the ionic conductance of cation is λ_c and ionic conductance of anion is λ_a . Now as ionic conductance varies directly proportional to speed of that particular type of ion

$$u_+ \propto \lambda_c \text{ and } u_- \propto \lambda_a$$

Thus,

$$t_+ = \frac{\lambda_c}{(\lambda_c + \lambda_a)} \text{ and } t_- = \frac{\lambda_a}{(\lambda_c + \lambda_a)}$$

$$\text{or, } t_+ = \frac{\lambda_c}{\Lambda_0} \text{ and } t_- = \frac{\lambda_a}{\Lambda_0}$$

So, transport number of a particular type of ion can be expressed as fraction of conductance at infinite dilution offered by that particular type of ion.

2.9.38. Mobility of H^+ and OH^- ions in aqueous solution: The ionic mobility and hence the conductance value of both H^+ and OH^- ion is very high. The conductance value of H^+ and OH^- ions are $350 \text{ mho cm}^2 \text{ mole}^{-1}$ and $200 \text{ mho cm}^2 \text{ mole}^{-1}$ respectively. Earlier it was considered that high charge density of both the ion is responsible for this abnormal high conductance. But in aqueous solution the H^+ ion basically exists as a hydroxonium ion H_3O^+ . The high mobility can be explained by the fact that from hydroxonium ion the H^+ ion migrates to neighbouring water molecule and thus the proton molecule is transported from one molecule to other molecule of water. Thus, in presence of an external field water molecule migrates from one molecule to another molecule. A proton does not travel an entire distance up to the electrode rather it only travels the distance between two water molecules. This mechanism is known as Grotthuss-type mechanism. Hydroxyl ion are getting transported in similar manner. The major difference is that in proton transfer proton transported from hydroxonium ion to water molecule but in case for hydroxide ion transport proton transported from water to adjacent hydroxide ion.

2.9.39. Debye-Falkenhagen Effect: Debye and Falkenhagen examined the conductance behaviour of a solution of a strong electrolyte by applying alternating currents of different frequencies. They predicted that if the frequency of A. C. current is high so that the time of oscillation is small in comparison with the relaxation time of the ionic atmosphere, the asymmetry effect will be virtually absent. In other words, the ionic atmosphere around the central ion will remain symmetric. The retarding effect due to asymmetry may, therefore, be entirely absent and conductance may be higher. The conductance of a solution, therefore, should vary with the frequency of A. C. current used. The higher the frequency, the higher conductance, evidently. This effect is also known as **dispersion of conductance**, has been verified experimentally. The conductance remains independent of the frequency of alternating current up to 10 cycles per second. But with further increase in frequency, the conductance starts increasing towards a certain limiting value indicating complete absence of asymmetry effect.

2.9.40. Wien Effect: Speed of an ion in an electric field varies with the applied potential gradient. Thus, under a potential gradient of about 2×10^4 volt per cm, an ion may have a speed of about 100 cm per sec. The ion, therefore, should pass several times through the thickness of the ionic atmosphere during the time of relaxation. The moving ion, therefore, will be almost free from the effect of the oppositely charged ionic atmosphere. The ion will be moving so fast that there will be no time for the ionic atmosphere to be formed. The asymmetry and electrophoretic effects, under these circumstances, may be negligibly small or even absent. Thus, the conductance of a strong electrolyte in aqueous solution increases to a certain limiting value with increase in potential gradient applied. This observation has been verified experimentally by Wien much before the development of the theory of strong electrolytes and is known as **Wien effect**.

2.9.41. Transport Number: During electrolysis the current is carried by the anions and the cations. The fraction of the total current carried by the cation or the anion is termed its **Transport number** or **Hittorf's number**. If v_+ represents the speed of migration of the cation and v_- that of the anion,

$$\text{the transport number of cation} = \frac{v_+}{v_+ + v_-}$$

$$\text{the transport number of anion} = \frac{v_-}{v_+ + v_-}$$

The transport number of the cation is represented by t and that of the anion by t_- .

$$\text{Thus} \quad t_+ = \frac{v_+}{v_+ + v_-} \quad \text{and} \quad t_- = \frac{v_-}{v_+ + v_-}$$

$$\text{or} \quad \frac{t_+}{t_-} = \frac{v_+}{v_-} \quad \text{and} \quad t_+ + t_- = 1$$

If the speed ratio v_+/v_- be denoted by r , we have,

$$r = \frac{t_+}{t_-} = \frac{t_+}{1 - t_+}$$

and

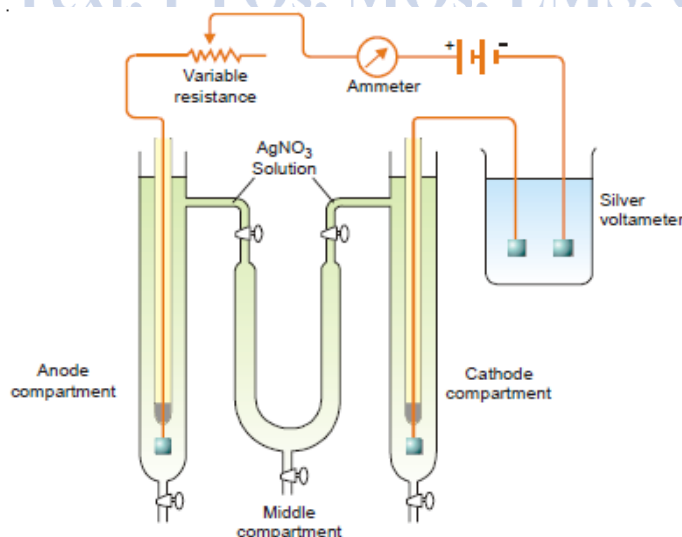
$$t_- = \frac{1}{1 + r}$$

2.9.42.DETERMINATION OF TRANSPORT NUMBER: There are two methods for determination of the transport number of an ion:

- (1) Hittorf's method
- (2) Moving Boundary method

1. Hittorf's Method: This method of determining transport number is based on **Hittorf's Rule**. According to this rule, **the loss of concentration around any electrode is proportional to the speed of the ion moving away from that electrode**. The transport number of an ion is calculated from the changes in concentration found experimentally around the electrodes. The apparatus used in this method consists of two vertical glass tubes joined together through a U-tube in the middle. All the three tubes are provided with stopcocks at the bottom. The U-tube is also provided with stopcocks at the tops of the two limbs. By closing these stopcocks, the communication between the solutions in the cathode and anode limbs can be stopped. The silver anode is sealed in a glass-tube and the cathode is a piece of freshly silvered foil. The apparatus is filled with a solution of silver nitrate and a steady current of about 0.01 ampere is passed for two to three hours. It is an important precaution that the current is passed only for a short time so that too large a change in concentration does not take place. The apparatus is connected with a silver or copper coulometer as shown in diagram below, which shows the circuit for the experiment.

When the current has been passed for about three hours, the stopcocks at the top of the U-tube are closed. The whole of the liquid in the anode compartment is carefully drained into a weighed flask and its weight determined. Its silver content is determined by titrating against a standard solution of potassium thiocyanate. The weight of silver deposited in the silver coulometer is also noted. If a copper coulometer is used in place of silver coulometer, the weight of silver equivalent to the copper deposited is calculated by multiplying it with 108/31.5. There should be no change in the concentration of the solution in the U-tube if the experiment has been successfully performed. If the above experiment has been performed by using silver electrodes, in this case nitrate ions attack the silver anode. Consequently, there is an increase in concentration of Ag^+ ions rather than decrease. The same experiment can also be performed by using platinum electrodes to avoid the attack of anions at the anode.



Hittorf's Experimental Set Up

Two different cases may arise :

Case 1. When electrodes are unattackable (Pt electrodes are used).

After passing electric current :

Let the weight of anodic solution taken out = a g

weight of AgNO_3 present in it by titration = b g

weight of water = $(a - b)$ g

Before passing electric current :

Let weight of AgNO_3 in $(a - b)$ g of water before passing electric current be = c g

\therefore Fall in concentration

$$= (c - b) \text{ g of AgNO}_3 = \frac{(c - b)}{170} \text{ g eqvt of AgNO}_3$$

$$= \frac{(c - b)}{170} \text{ g eqvt of Ag} = d \text{ (say)}$$

Let the weight of silver deposited in silver coulometer be

$$= w_1 \text{ g}$$

$$= \frac{w_1}{108} \text{ g eqvt of Ag}$$

$$= W \text{ (say) g eqvt of Ag}$$

$$\text{Transport number of } \text{Ag}^+ \text{ ion } (t_{\text{Ag}^+}) = \frac{\text{Fall in concentration around anode in g eqvt}}{\text{Amt. of Ag deposited in g eqvt}} = \frac{d}{W}$$

$$\text{and Transport number of } \text{NO}_3^- \text{ ion } (t_{\text{NO}_3^-}) = 1 - \frac{d}{W}$$

Case 2. When electrodes are attackable (Ag electrodes are used).

Increase in conc. of anodic solution = $(b - c)$ g of AgNO_3

$$= \frac{(b - c)}{170} \times 108 \text{ g of Ag}$$

$$= \frac{(b - c)}{170} \text{ g eqvt of Ag}$$

$$= e \text{ (say)}$$

If no Ag^+ ions had migrated from the anode, the increase in concentration of Ag^+ ions would have been equal to W .

\therefore Fall in concentration due to migration of Ag^+ ion = $W - e$

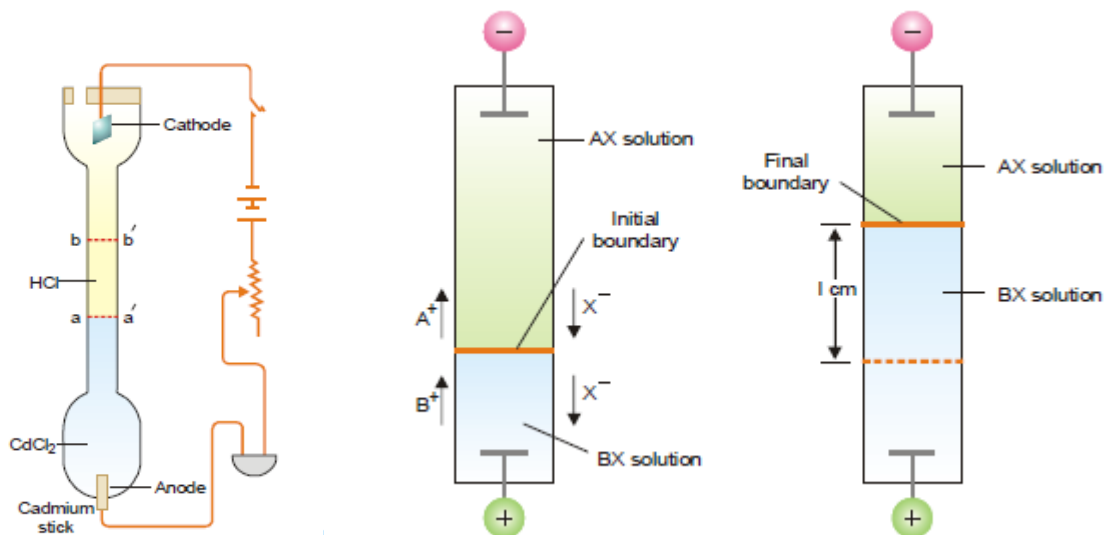
$$\text{Hence, transport number of } \text{Ag}^+ \text{ ion } (t_{\text{Ag}^+}) = \frac{W - e}{W}$$

$$\text{and transport number of } \text{NO}_3^- \text{ ion } (t_{\text{NO}_3^-}) = 1 - \frac{W - e}{W}$$

2. Moving Boundary Method: The moving boundary method is based on the direct observation of migration of ions under the influence of applied potential. This method is very accurate and has been used in recent years for precision measurements. The apparatus used consists of a long vertical tube fitted with two electrodes at the two ends shown in diagram below. The tube is filled with a solution of cadmium chloride (CdCl_2) at the lower end and hydrochloric acid at the upper end in a way that there is a sharp boundary between the two (due to difference in their refractive indices). The platinum cathode dipped in HCl solution is inserted at the top and the anode (cadmium stick) is introduced at the bottom. On passing electric current through the apparatus, hydrogen gas is evolved at the cathode and H^+ ions move toward the anode. The H^+ ions are replaced by Cd^{2+} ions and hence the boundary line moves in

the upward direction. By noting the length through which the boundary moves and the quantity of electricity passed through the cell, the transport number of H^+ ion can be calculated.

In general, if the transport number of a cation A^+ is to be determined, the electrolyte AX solutions taken in the upper part of the apparatus and a layer of another electrolyte BX having the common anion X^- is introduced in the lower part of the apparatus. The electrolyte BX is selected so that the velocity of B^+ ion is less than that of A^+ ion. In such a case, the situation is described in figure below.



Moving Boundary Method Experimental Set up

Let c be the original concentration of A^+ ions in gram-equivalents per ml of the solution.

If the distance through which boundary moves = l cm, and the area of cross-section of the tube = s sq cm.

Then the number of equivalents of A^+ moving upward = $s \times l \times c$

Let the number of Faradays of current passed = n

The fraction of current carried by A^+ ions = $n \times t_{A^+}$

Hence

$$n \times t_{A^+} = s \times l \times c$$

and

$$t_{A^+} = \frac{s \times l \times c}{n} \quad \dots (1)$$

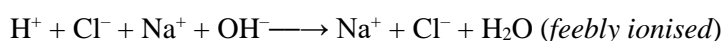
where $n = Q/F$, Q being the quantity of current passed and F stands for Faraday (= 96,500 coulombs).

The above expression can now be written as

$$t_{A^+} = \frac{s \times l \times F \times c}{Q} \quad \dots (2)$$

2.9.43. Conductometric titration: Titrations in which conductance measurements are made use of in determining the end-point of acid-alkali reactions, some displacement reactions or precipitation reactions are called Conductometric titrations. In these titrations, advantage is taken of the fact that the conductance of a solution at a constant temperature depends upon the number of ions present in it and their mobility. For this purpose, the titrant is added from a burette into a measured volume of the solution to be titrated which is taken in a conductance cell and the conductance readings corresponding to the various additions are plotted against the volume of the titrant. In this way two linear curves are obtained, the point of intersection of which is the end-point. Several phenomena like hydrolysis of reactants or products or partial solubility of a precipitated product give rise, however to a curvature in the curves. The shapes of curves obtained in certain types of titration are discussed below:

(1) Titration of a Strong acid against a Strong base: Consider the reaction in which hydrochloric acid solution is titrated against a solution of sodium hydroxide. Take 20 ml of the acid solution in the conductance cell placed in a thermostat and determine its conductance. Now add 1 ml sodium hydroxide solution from the burette at a time. After each addition, determine the conductance of the solution after thorough mixing and plot the conductance of the solution against the volume of the alkali added. It will be observed that the points lie on two lines which are almost straight. The point of intersection of the interpolated lines will be the endpoint and the volume of alkali corresponding to this point is the volume of alkali required to neutralise 20 ml of the acid (Fig.1). The reason for this is that before the addition of alkali, the conductance of the solution is due to presence of H^+ and Cl^- ions. Since hydrogen ions possess the greatest mobility of any ion, the greater part of the conductance is due to it. As alkali solution is added, the hydrogen ions are removed by combination with the hydroxyl ions forming feebly ionised water molecules and their places are taken up by comparatively slow-moving Na^+ ions.



As a result of this, the conductance of the solution decreases and continues to fall with every subsequent addition of alkali till the end-point is reached. After the equivalence point, the further addition of sodium hydroxide solution results in an increase of conductance since the hydroxyl ions are no longer removed in the chemical reaction in the form of feebly ionised water. The point of minimum conductance, therefore, coincides with the end-point of the titration. In order to get accurate results, the volume change during titration should be as little as possible. The titrant should, therefore, be about 10 times as strong as the acid solution in the conductance cell in order to keep the volume change small. If this is not so, a correction to the readings has to be applied viz, actual conductance = $[(v+V)/V] \times \text{observed conductance}$; where v is the volume of the titrant and V is the original volume of the solution to be titrated.

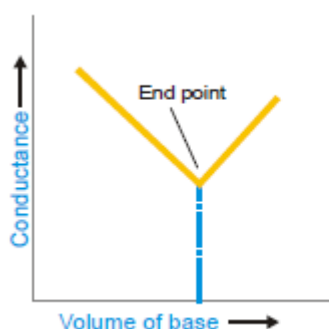


Fig.1: Conductometric Titration curve

Strong Acid vs Strong Base

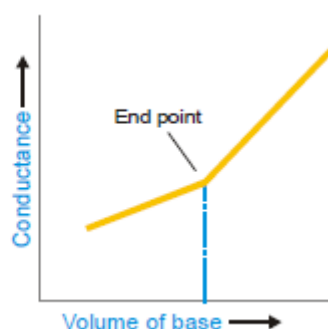
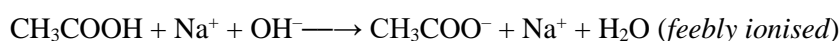


Fig.2: Conductometric Titration curve

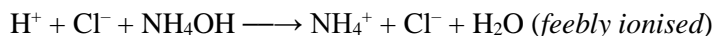
Weak Acid vs Strong Base

(2) Titration of a Weak acid against a Strong alkali: When a weak acid like acetic acid is titrated against a strong alkali like sodium hydroxide, we get a curve of the type shown in Fig.2. The initial conductance of the solution is low because of the poor dissociation of the weak acid. On adding alkali, highly ionised sodium acetate is formed. The acetate ions at first tend to suppress the ionisation of acetic acid still further due to *Common Ion Effect* but after a while the conductance begins to increase because the conducting power of highly ionised salt exceeds that of the weak acid.



Immediately after the end point, further addition of sodium hydroxide introduces the fast-moving hydroxyl ions. Thus, the *conductance value shows a sharp increase*. The point of intersection of the two curves, gives the end-point.

(3) Titration of a Strong acid against a Weak base: The curve obtained for the titration of a strong acid against a weak base is shown in Fig.3. In this case, the conductance of the solution will first decrease due to the fixing up of the fast-moving⁺ ions and their replacement by slow moving NH_4^+ ions.



After the end-point has been reached, the addition of ammonium hydroxide will not cause any appreciable change in conductance value as it is a weak electrolyte and its conductance is very small compared with that of the acid or its salt. The shape of this part of the curve will, therefore, be as shown in the figure.

(4) Titration of a Weak acid against a Weak base: The conductometric method is particularly suitable as such titrations do not give a sharpened-point with indicators. Consider the titration of acetic acid with ammonium hydroxide. The complete titration curve is shown in Fig.4. The initial conductance of the solution in this case is also low due to the poor dissociation of the weak acid. But it starts increasing as the salt $\text{CH}_3\text{COONH}_4$ is formed. After the equivalence point, the conductivity remains almost constant because the free base NH_4OH is a weak electrolyte. The end-point is quite sharp.

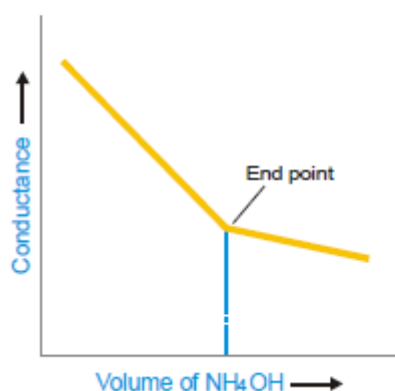


Fig.3: Conductometric Titration curve

Strong Acid vs Weak Base

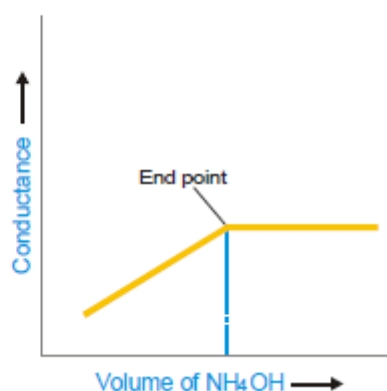
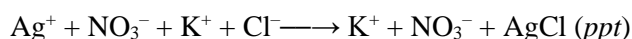


Fig.4: Conductometric Titration curve

CH_3COOH vs NH_4OH

(5) Precipitation reactions: The end-point in precipitation reactions can be accurately determined by conductometric titration. The accuracy is further increased by working with fairly dilute solutions and addition of alcohol which reduces the solubility of the precipitate and prevents adsorption. In the titration of potassium chloride against silver nitrate, for example, the change in conductance on the addition of silver nitrate is not much since the mobility of the potassium ion and the silver ion is of the same order. Thus, the curve is nearly horizontal.



After the end-point, there is a sharp increase in conductance due to an increase in the number of free ions in the solution.

We think, the weightage of text is only 10 percent, the rest 90 percent of weightage lies within our remaining five services: solution of 1250 previous years questions and 1000 model questions (unit and subunit wise) with proper explanation, on-line MOCK test series, last minute suggestions and daily updates because it will make your preparation innovative, scientific and complete. Access these five services from our website: www.teachinns.com and qualify not only the eligibility of assistant professorship but also junior research fellowship.

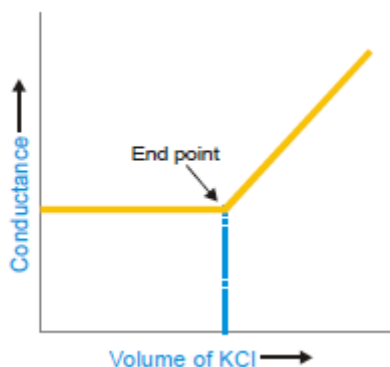


Fig.5: Conductometric Titration curve

AgNO_3 vs KCl

2.9.44. Advantage of Conductometric Titrations:

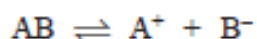
- (1) Coloured solutions where no indicator is found to work satisfactorily can be successfully titrated by this method.
- (2) This method is useful for the titration of weak acids against weak bases which do not give sharp change of colour with indicators in ordinary volumetric analysis.
- (3) More accurate results are obtained because the end -point is determined graphically.

Subunit 9C: Ionic Equilibrium

2.9.45. Arrhenius Theory of Electrolytic dissociation: an electrolyte dissociates into ions in water solutions. These ions are in a state of equilibrium with the undissociated molecules. This equilibrium is called the **Ionic equilibrium**.

2.9.46. Ostwald's Dilution Law: Ostwald noted that the Law of Mass Action can be applied to the ionic equilibrium as in the case of chemical equilibrium.

Let us consider a binary electrolyte AB which dissociates in solution to form the ions A^+ and B^- .



Let C moles per litre be the concentration of the electrolyte and α (alpha) its degree of dissociation. The concentration terms at equilibrium may be written as :

$$\begin{aligned} [\text{AB}] &= C(1 - \alpha) \text{ mol litre}^{-1} \\ [\text{A}^+] &= C\alpha \text{ mol litre}^{-1} \\ [\text{B}^-] &= C\alpha \text{ mol litre}^{-1} \end{aligned}$$

Applying the Law of Mass Action :

$$\text{Rate of dissociation} = k_1 \times C(1 - \alpha)$$

$$\text{Rate of combination} = k_2 \times C\alpha \times C\alpha$$

At equilibrium :

$$\begin{aligned}
 k_1 \times C(1-\alpha) &= k_2 \times C\alpha \times C\alpha \\
 \text{or} \quad \frac{C\alpha \times C\alpha}{C(1-\alpha)} &= \frac{k_1}{k_2} = K_c \\
 \text{or} \quad K_c &= \frac{\alpha^2 C}{(1-\alpha)} \text{ mol litre}^{-1} \quad \dots(1)
 \end{aligned}$$

The equilibrium constant K_c is called the **Dissociation constant or Ionization constant**. It has a constant value at a constant temperature.

If one mole of an electrolyte be dissolved in V litre of the solution, then

$$C = \frac{1}{V}$$

V is known as the **Dilution** or the solution. Thus the expression (1) becomes

$$K_c = \frac{\alpha^2}{(1-\alpha)V} \quad \dots(2)$$

This expression which correlates the variation of the degree of dissociation of an electrolyte with dilution, is known as **Ostwald's Dilution Law**.

2.9.47. Ostwald's Theory on Weak & Strong Electrolyte: For weak electrolytes, the value of α is very small as compared to 1, so that in most of the calculation we can take $1 - \alpha \approx 1$. Thus, the Ostwald's Dilution Law expression becomes



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$$K_c = \frac{\alpha^2}{V}$$

It implies that the degree of dissociation of a weak electrolyte is proportional to the square root of the dilution i.e.,

$$\begin{aligned}
 \alpha &\propto \sqrt{K_c V} \\
 \alpha &= K' \sqrt{V}
 \end{aligned}$$

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For strong electrolytes, the value of α is large and it cannot be neglected in comparison with 1. Thus, we have to use the original expression of Ostwald dilution law. That is,

$$K_c = \frac{\alpha^2}{(1-\alpha)V} \quad \text{or} \quad \alpha^2 = K_c V - \alpha K_c V$$

which gives a quadratic equation

$$\alpha^2 + \alpha K_c V - K_c V = 0$$

from this equation the value of ' α ' can be evaluated.

2.9.48. Ghosh's Formula for Strong electrolytes: In 1918 J.C. Ghosh revived Southerland's theory of strong electrolytes. He assumed that though the electrolyte is completely ionized, all the ions are not free to move owing to the influence of electric charges and it is only the *mobile ions* which contribute to the conductance of the solution. The value α represents the "active" proportion of the electrolyte and can be determined by purely electrical data, the Law of Mass Action playing no part whatsoever. His formula is

$$\sqrt[3]{V} \log \alpha = K$$

2.9.49. Degree of Dissociation: The fraction of the amount of the electrolyte in solution present as free ions is called the Degree of dissociation. If the degree of dissociation is represented by x , we can write

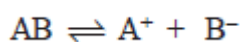
$$x = \text{amount dissociated (mol/L)} / \text{initial concentration (mol/L)}$$

The value of x can be calculated by applying the Law of Mass Action to the ionic equilibrium stated above,

$$K = [A^+][B^-] / [AB]$$

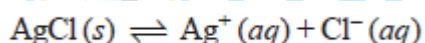
If the value of the equilibrium constant, K , is given, the value of x can be calculated.

2.9.50. THE COMMON-ION EFFECT: When a soluble salt (say A^+C^-) is added to a solution of another salt (A^+B^-) containing a common ion (A^+), the dissociation of AB is suppressed.



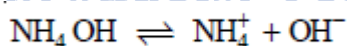
By the addition of the salt (AC), the concentration of A^+ increases. Therefore, according to LeChatelier's principle, the equilibrium will shift to the left, thereby decreasing the concentration of A^+ ions. Or that, the degree of dissociation of AB will be reduced. **The reduction of the degree of dissociation of a salt by the addition of a common-ion is called the Common-ion effect.** Let us consider a few examples to illustrate the common-ion effect.

Example 1. In a saturated solution of silver chloride, we have the equilibrium



When sodium chloride is added to the solution, the concentration of Cl^- ions will increase. The equilibrium shown above will be shifted to the left to form more of solid $AgCl$. Thus, the solubility of $AgCl$, a typical sparingly soluble salt, will decrease.

Example 2. When solid NH_4Cl is added to NH_4OH solution, the equilibrium



shifts to the left. Thereby the equilibrium concentration of OH^- decreases. This procedure of reducing the concentration of OH^- ions is used in qualitative analysis.

2.9.51. FACTORS WHICH INFLUENCE THE DEGREE OF DISSOCIATION: The *degree of dissociation* of an electrolyte in solution depends upon the following factors:

(1) Nature of Solute: The nature of solute is the chief factor which determines its degree of dissociation in solution. Strong acids and strong bases, and the salts obtained by their interaction are almost completely dissociated in solution. On the other hand, weak acids and weak bases and their salts are feebly dissociated.

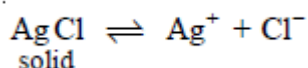
(2) Nature of the solvent: The nature of the solvent affects dissociation to a marked degree. It weakens the electrostatic forces of attraction between the two ions and separates them. This effect of the solvent is measured by its '*dielectric constant*'. The **dielectric constant** of a solvent may be defined as its capacity to weaken the force of attraction between the electrical charges immersed in that solvent.

The dielectric constant of any solvent is evaluated considering that of vacuum as unity. It is 4.1 in case of ether, 25 in case of ethyl alcohol and 80 in case of water. The higher the value of the dielectric constant the greater is the dissociation of the electrolyte dissolved in it because the electrostatic forces vary inversely as the dielectric constant of the medium. Water, which has a high value of dielectric constant is, therefore, a strong dissociating solvent. The electrostatic forces of attraction between the ions are considerably weakened when electrolytes are dissolved in it and as a result, the ions begin to move freely and there is an increase in the conductance of the solution.

(3) **Concentration:** The extent of dissociation of an electrolyte is inversely proportional to the concentration of its solution. The less concentrated the solution, the greater will be the dissociation of the electrolyte. This is obviously due to the fact that in a dilute solution the ratio of solvent molecules to the solute molecules are large and the greater number of solvent molecules will separate more molecules of the solute into ions.

(4) **Temperature:** The dissociation of an electrolyte in solution also depends on temperature. The higher the temperature greater is the dissociation. At high temperature the increased molecular velocities overcome the forces of attraction between the ions and consequently the dissociation is great.

2.9.52. **SOLUBILITY PRODUCT:** When an ionic solid substance dissolves in water, it dissociates to give separate cations and anions. As the concentration of the ions in solution increases, they collide and reform the solid phase. Ultimately, a dynamic equilibrium is established between the solid phase and the cations and anions in solution. For example, for a sparingly soluble salt, say AgCl, we can write the equilibrium equations as follows:



At equilibrium the solute continues to dissolve at a rate that exactly matches the reverse process, the return of solute from the solution. Now the solution is said to be saturated. **A Saturated solution is a solution in which the dissolved and undissolved solute are in equilibrium.** A saturated solution represents the limit of a solute's ability to dissolve in a given solvent. This is a measure of the "solubility" of the solute. **The Solubility (S) of a substance in a solvent is the concentration in the saturated solution.** Solubility of a solute may be represented in grams per 100 ml of solution. It can also be expressed in moles per litre. **Molar Solubility is defined as the number of moles of the substance per one litre (l) of the solution.** The value of solubility of a substance depends on the solvent and the temperature. Applying the Law of Mass Action to the above equilibrium for AgCl, we have

$$K = [\text{Ag}^+][\text{Cl}^-]/[\text{AgCl}]$$

The amount of AgCl in contact with saturated solution does not change with time and the factor [AgCl] remains the same. Thus, the equilibrium expression becomes

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

where [Ag⁺] and [Cl⁻] are expressed in mol/L. The equilibrium constant in the new context is called the **Solubility Product Constant** (or simply the **Solubility Product**) and is denoted by K_{sp} . The value of K_{sp} for a particular solubility equilibrium is constant at a given temperature. The product [Ag⁺][Cl⁻] in the K_{sp} expression above is also called **Ionic Product**.

#When two reacting solutions are mixed, calculate the concentration of each ion in the solution in which precipitation is produced? The ionic product, Q , is then calculated. We know that K_{sp} is the ionic product when the ions are in contact with the solid substance. Therefore, the precipitation will occur for any higher ion concentrations. In other words, the precipitation will take place if $Q > K_{sp}$. If $Q < K_{sp}$, no precipitation will occur.

2.9.53. **THE pH OF SOLUTIONS:** A knowledge of the concentration of hydrogen ions (more specifically hydronium ions) is of the greatest importance in chemistry. The pH concept is very convenient for expressing hydrogen ion concentration. It was introduced by Sorensen in 1909. Hydrogen ion concentrations are typically quite small numbers. Therefore, chemists report the hydrogen ion concentration of a solution in terms of pH. It is defined as **the negative of the base-10 logarithm (log) of the H⁺ concentration**. Mathematically it may be expressed as

$$\text{pH} = -\log [\text{H}^+]$$

where [H⁺] is the concentration of hydrogen ions in moles per litre.

2.9.54. **Potentiometric determination of pH of an electrolytic solution:** This is the most accurate and reliable method for finding pH of a solution. It is based upon the principle that many redox electrodes such as Hydrogen electrode, Quinhydrone electrode or Glass electrode are reversible to H⁺

ions in the solution and their electrode potentials thus, depend on the concentration of H^+ or H_3O^+ ion; so, on pH of the aqueous solutions.

(1) **By using Hydrogen Electrode:**

$$pH = [E_{\text{cell}} - E_{\text{calomel}}]/0.0591 = [E_{\text{cell}} - 0.2415]/0.0591$$

(2) **By using Quinhydrone Electrode:**

$$pH = [E_{\text{QHE}}^0 - E_{\text{calomel}} - E_{\text{cell}}]/0.0591 = [0.4581 - E_{\text{cell}}]/0.0591$$

(3) **By using Glass Electrode:**

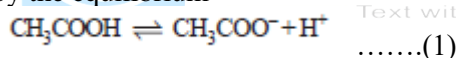
$$pH = [E_{\text{cell}} + E_{\text{glass}}^0 - E_{\text{calomel}}]/0.0591 = [E_{\text{cell}} + E_{\text{glass}}^0 - 0.2415]/0.0591$$

2.9.55. BUFFER SOLUTION: It is often necessary to maintain a certain pH of a solution in laboratory and industrial processes. This is achieved with the help of buffer solutions, buffer systems or simply buffers. **A buffer solution is one which maintains its pH fairly constant even upon the addition of small amounts of acid or base.** In other words, a buffer solution resists (or buffers) a change in its pH. That is, we can add a small amount of an acid or base to a buffer solution and the pH will change very little. Two common types of buffer solutions are:

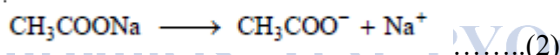
(1) a weak acid together with a salt of the same acid with a strong base. These are called **Acid buffers** *e.g.*, $CH_3COOH + CH_3COONa$. ($pH = 4.74$)

(2) a weak base and its salt with a strong acid. These are called **Basic buffers**. *e.g.*, $NH_4OH + NH_4Cl$.

2.9.56. Buffer Action: We have already stated that a buffer solution containing equimolar amounts (0.10 M) of acetic acid and sodium acetate has pH 4.74. Now we proceed to discuss how the addition of a small amount of HCl or NaOH to the buffer solution affects its pH. The pH of the buffer is governed by the equilibrium



The buffer solution has a large excess of CH_3COO^- ions produced by complete ionisation of sodium acetate,



(1) **Addition of Acid [HCl]:** Upon the addition of HCl, the increase of H^+ ions is counteracted by association with the excess of acetate ions to form unionised CH_3COOH . Thus, the added H^+ ions are neutralised and the pH of the buffer solution remains virtually unchanged. However, owing to the increased concentration of CH_3COOH , the equilibrium (1) shifts slightly to the right to increase H^+ ions. This explains the marginal increase of pH of the buffer solution on addition of HCl (Fig. below).

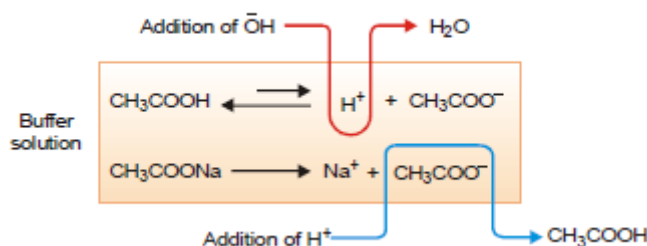
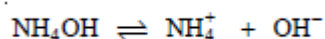


Fig.1: Buffer Action of Acid Buffer

(2) **Addition of Base [NaOH]:** When NaOH is added to the buffer solution, the additional OH^- ions combine with H^+ ions of the buffer to form water molecules. As a result, the equilibrium (1) shifts forthright to produce more and more H^+ ions till practically all the excess OH^- ions are neutralised and the original buffer pH restored. However, a new equilibrium system is set up in which $[CH_3COOH]$ is lower than it was in the original buffer. Consequently $[H^+]$ is also slightly less and pH slightly higher than the buffer pH values (Fig.1). Operation of a Basic buffer as NH_4OH/NH_4Cl can also be explained

on the same lines as of an acid buffer (Fig.2) upon addition of HCl the H^+ ions combine with OH^- ions of the buffer to form water molecules. The equilibrium,



is shifted to the right till all the additional H^+ ions are neutralised and the original buffer pH restored. When NaOH is added to the buffer solution, OH^- ions associate with excess of NH_4^+ ions to form dissociated NH_4OH . Thus, the pH of the buffer is maintained approximately constant.

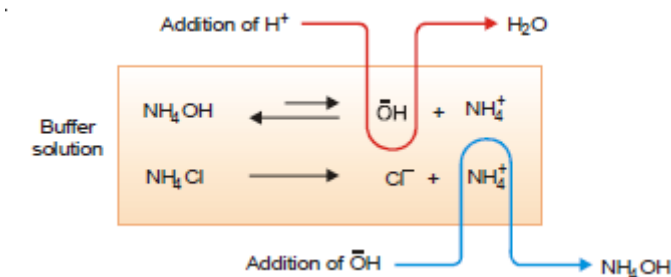
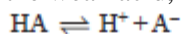


Fig.2: Buffer Action of Basic Buffer

2.9.57. Calculation of pH of BUFFER SOLUTIONS: The pH of an acid buffer can be calculated from the dissociation constant, K_a , of the weak acid and the concentrations of the acid and the salt used. The dissociation expression of the weak acid, HA, may be represented as



and
$$K_a = \frac{[H^+][A^-]}{[HA]}$$

or
$$[H^+] = K_a \times \frac{[HA]}{[A^-]} \quad \dots(1)$$

The weak acid is only slightly dissociated and its dissociation is further depressed by the addition of the salt (Na^+A^-) which provides A^- ions (Common ion effect). As a result, the equilibrium concentration of the unionised acid is nearly equal to the initial concentration of the acid. The equilibrium concentration $[A^-]$ is presumed to be equal to the initial concentration of the salt added since it is completely dissociated. Thus, we can write the equation (1) as

$$[H^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]} \quad \dots(2)$$

where [acid] is the initial concentration of the added acid and [salt] that of the salt used. Taking negative logs of both sides of the equation (2), we have

$$-\log[H^+] = -\log K_a - \log \frac{[\text{acid}]}{[\text{salt}]} \quad \dots(3)$$

But $-\log[H^+] = \text{pH}$ and $\log K_a = \text{p}K_a$

Thus from (3) we have

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

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

This relationship is called the **Henderson-Hasselbalch equation** or simply **Henderson equation**. In a similar way, the Henderson-Hasselbalch equation for a basic buffer can be derived. This can be stated as:

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

2.9.58. Buffer Capacity: The Buffer Capacity is defined as the amount [number of moles] of the acid or base which when added to 1 Litre of the given buffer solution change its pH by unity. It is also termed as "Magnitude of Buffer Action" because addition of a very small amount of acid or base would be enough to cause a very large remarkable change in pH of the solution.

$$\text{Buffer Capacity } (\beta) = \frac{\text{no. of moles of acid or alkali}^{\text{added}}}{\text{Change in pH}} = \frac{d[B]}{dpH} = - \frac{d[A]}{dpH}$$

Where, $d[A]$ = small change in acid concentration, $d[B]$ = small change in base concentration

*Buffer index (β) is always positive, because

(I) on addition of a base to a buffer solution, its pH is increased. That means $d[B]$ and dpH both positive; so also β .

(II) on addition of an acid to buffer solution, its pH decreased. That means $d[A]$ is positive but dpH is negative, overall β again becomes positive.

For a given concentrations of acid or base and its salt present in the buffer solution; the buffer capacity will be maximum when the ratio of the salt to the weak acid or weak base is (1:1), i.e., if the buffer solution is prepared by equimolar amount of an acid or base and its corresponding salt.

2.9.59. ACID-BASE INDICATORS: In an acid-base titration the base solution can be added gradually from a burette into an acid solution contained in a receiver flask. When the amount of the base added equals the amount of the acid in the flask, the **equivalence point** or the **end-point** is reached. The end-point of a titration is shown by colour change of an indicator previously added to the acid solution in the receiver flask. **An acid-base indicator is an organic dye that signals the end-point by a visual change in colour.** Phenolphthalein and methyl orange are two common examples of acid-base indicators. Phenolphthalein is pink in base solution and colourless in acid solution. Thus, when added to the acid solution in the receiver flask, it shows no colour. As the added base is in slight excess, it becomes pink. Thus, phenolphthalein signals the end-point by a colour change from colourless to pink. Similarly, methyl orange indicates the end-point by a colour change from red (in acid) to yellow (in base).

#pH range of indicators

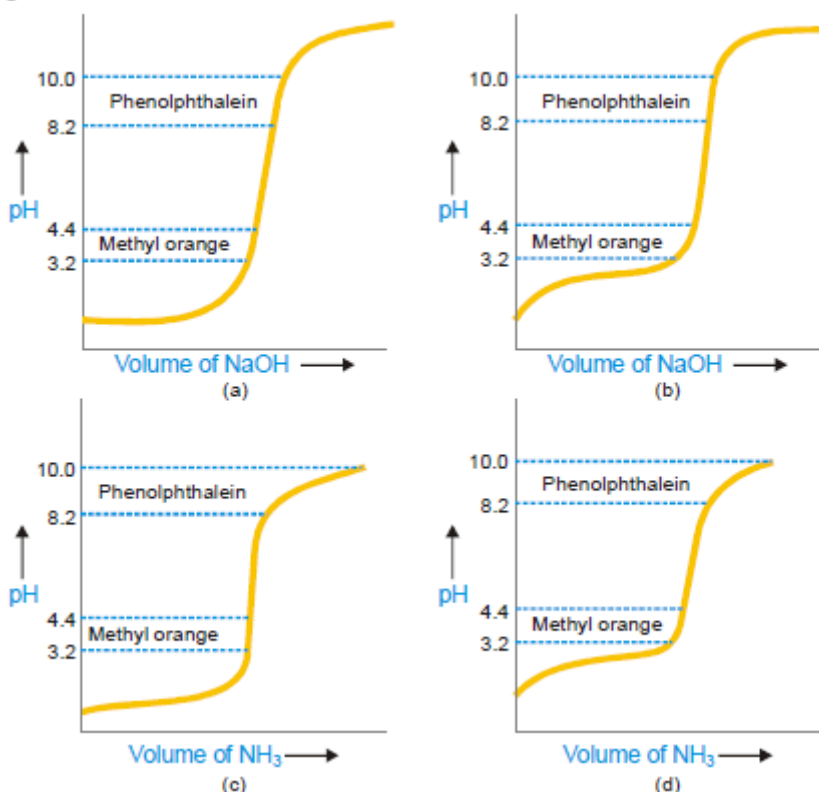
Most indicators do not change colour at a particular pH. They do so over a range of pH from two to three units. This is called the **pH range** which is different for various indicators.

Indicator	Colour change (acid-base)	pH range
Methyl orange	red-orange	3.1–4.4
Methyl red	red-yellow	4.4–6.0
Litmus	red-blue	5.0–8.0
Bromothymol blue	yellow-blue	6.0–7.6
Phenolphthalein	colourless-pink	8.3–10.0

2.9.60. CHOICE OF A SUITABLE INDICATOR: The choice of a suitable indicator for a particular acid-base titration depends on the nature of the acid and the base involved in the titration. We may have the titration of:

- a strong acid with a strong base
- a weak acid with a strong base
- a strong acid with a weak base
- a weak acid with weak base

Which indicator is suitable for a given titration, can be found by examining the titration curve of that titration. We have already discussed that a suitable indicator is one which has a small pH range that falls wholly on the upright portion of the titration curve. All the pH curves given in below diagrams refer to addition of 0.1 M monoacid base to 25 ml of 0.1 M of monobasic acid. The equivalence point in all cases is at pH 7 when all the acid has been neutralised by the base to form a salt. If the titration is performed so that acid is added to the base, the pH curve is the mirror image of that shown.



To find a suitable indicator from a study of the pH curves for: (a) a strong acid and strong base; (b) weak acid and strong base; (c) strong acid and weak base; (d) a weak acid and weak base.

2.9.61. THEORIES OF ACID-BASE INDICATORS: An acid-base indicator is an organic substance used for the detection of equivalence point or neutral point in an acid-base titration. An indicator has one colour in acid solution and entirely different in basic solution. The end-point of the titration is shown by a colour change of the indicator. Two theories have been put forward to explain the indicator action in acid-base titrations:

- (i) Ostwald's theory
- (ii) Quinonoid theory

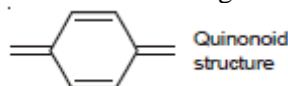
We will discuss these with reference to two commonly used indicators, namely, methyl orange and phenolphthalein.

(i) Ostwald's theory: According to this theory

- (1) an acid-base indicator is a weak organic acid (HIn) or a weak organic base (InOH), where the letter 'In' stands for a complex orange group. Methyl orange and phenolphthalein are both weak acids.
- (2) the unionised indicator, ' HIn ', has a colour different from the $[\text{In}^-]$ ions produced by the ionisation of the indicator in aqueous solution.
- (3) the degree of ionisation of the indicator determines the visible colour of the indicator solution.

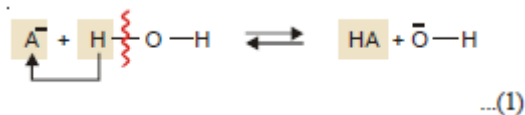
(ii) Quinonoid theory: The Ostwald's theory takes care of the quantitative aspect of indicator action adequately. The Quinonoid theory, on the other hand, tells us the cause of colour change of an indicator in acid-base solutions. It lays down that:

- (1) the unionised HIn molecule and the anion $[\text{In}^-]$ are tautomeric forms of the indicator which is an organic dye.
- (2) one tautomeric form possesses the quinonoid structural unit and is called the **quinonoid form**. It has a deep colour. The other form has a lesser colouring group, say, $-\text{N}=\text{N}-$ and or simply benzene rings and is called the benzenoid form. This form has a light colour or no colour.

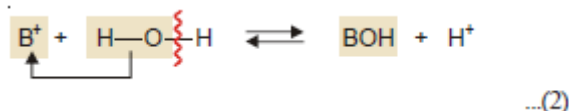


(3) the colour change of the indicator occurs when one tautomeric form is transformed into the other due to change of pH of the solution.

2.9.62. Hydrolysis: The salt of a weak acid, HA and a strong base, dissolves in water to form the anion⁻. The A⁻ anion tends to react with water by drawing a proton (H⁺) from its molecule to form the unionised molecule.



Similarly, the salt of a weak base, BOH, and a strong acid dissolves in water to form the cation B⁺. The cation B⁺ reacts with water by accepting OH⁻ ions from its molecule.



The reaction of an anion or cation with water accompanied by cleavage of O–H bond is called Hydrolysis.

2.9.63. Hydrolysis Constant [K_h]: Hydrolysis is a reversible reaction. The equilibrium constant derived by application of Law of Mass action to a hydrolysis (or hydrolytic) reaction is called the Hydrolysis constant or Hydrolytic **constant**. The hydrolysis constant is represented by K_h .

*The general hydrolysis reaction of a salt of weak acid (HA) and strong acid can be written as



This leads to the equilibrium constant expression

$$K_h = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-][\text{H}_2\text{O}]}$$

The concentration of water, [H₂O], is very large and is regarded as practically constant. Thus, the hydrolysis constant expression assumes the form

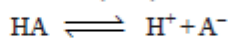
$$K_h = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

2.9.64. Relation between K_h , K_w and K_a :

We know that the ionic product of water, K_w , is expressed as

$$K_w = [\text{H}^+][\text{OH}^-]$$

For the dissociation of a weak acid, HA,



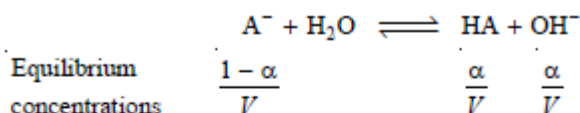
acid dissociation constant, K_a , is expressed as

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\frac{K_w}{K_a} = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} = K_h$$

$$\frac{K_w}{K_a} = K_h$$

2.9.65. Relation between Hydrolysis constant and Degree of hydrolysis: The degree of hydrolysis is the fraction of the salt which has undergone hydrolysis when equilibrium is established. It is generally represented by α . Suppose we start with one mole of the salt dissolved in V litres of solution. Then the equilibrium concentrations are:



Hence the hydrolysis constant K_h is given by

$$K_h = \frac{[HA][OH^-]}{[A^-]} = \frac{\alpha/V \times \alpha/V}{1-\alpha/V} = \frac{\alpha^2}{(1-\alpha)V}$$

If α is small, $(1-\alpha)$ may be taken as equal to one. Then,

$$\begin{aligned}
 K_h &= \frac{\alpha^2}{V} \\
 \text{or} \quad \alpha^2 &= K_h V = \frac{K_w}{K_a} V \\
 \therefore \alpha &= \sqrt{\frac{K_w V}{K_a}} \\
 &= \sqrt{\frac{K_w}{K_a C}}
 \end{aligned}$$

where C is the initial concentration of the salt. Knowing the values of K_w , K_a and C , the degree of hydrolysis can be calculated.

2.9.66. Relation Between pH and Acid Dissociation Constant: The pH of an aqueous solution of weak acid and strong base can be derived as follows,

$$[OH^-] = \frac{\alpha}{V} = \alpha C$$

$$\text{and} \quad [H^+] = \frac{K_w}{[OH^-]}$$

$$\therefore [H^+] = \frac{K_w}{\alpha C}$$

$$\text{But} \quad \alpha = \sqrt{\frac{K_w}{K_a C}}$$

$$\therefore [H^+] = \frac{K_w}{C} \sqrt{\frac{K_a C}{K_w}} = \sqrt{\frac{K_w K_a}{C}}$$

Taking logarithms and reversing the sign throughout

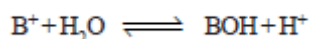
$$-\log[H^+] = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log C$$

$$\text{pH} = \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log C$$

$$= 7 + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log C$$

It is evident that pH of the solution will always be greater than 7. Thus, **aqueous solution of salt of weak acid and strong base will be always alkaline.**

2.9.67. Relation Between pH and Base Dissociation Constant: The hydrolysis of a salt of a weak base BOH (*e.g.*, NH_4OH) and a strong acid may be represented by the equation:



Applying the Law of Mass Action to the above hydrolysis reaction, the hydrolysis constant, K_h , is given by

$$K_h = \frac{[H^+][BOH]}{[B^+][H_2O]}$$

Since $[H_2O]$ is very large, it is taken to be constant and the hydrolysis constant expression is reduced to

$$K_h = \frac{[H^+][BOH]}{[B^+]}$$

#Relation between K_h , K_w and K_b : We know that the ionic product of water K_w is expressed as,

$$K_w = [H^+][OH^-]$$

For the dissociation of a weak base, BOH,



The dissociation constant, K_b , can be expressed as,

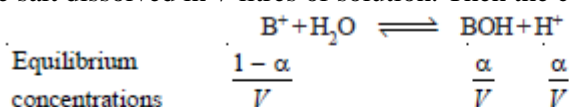
$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$\frac{K_w}{K_b} = \frac{[H^+][BOH]}{[B^+]} = K_h$$

$$\frac{K_w}{K_b} = K_h$$

Thus, the hydrolysis constant, K_h , varies inversely as the dissociation constant, K_b , of the base. Therefore, **weaker the base greater will be the hydrolysis constant of the salt.**

##Relation between Hydrolysis constant and degree of hydrolysis: Suppose we start with one mole of the salt dissolved in V litres of solution. Then the concentrations when equilibrium is attained, are,



Applying the Law of Mass Action, the hydrolysis constant, K_h is given by the expression

$$K_h = \frac{[H^+][BOH]}{[B^+]} = \frac{\alpha/V \times \alpha/V}{(1-\alpha)/V} = \frac{\alpha^2}{(1-\alpha)V}$$

When α is small, $(1-\alpha)$ may be considered as equal to one. Then we have

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$$K_h = \frac{\alpha^2}{V}$$

or $K_h \times V = \alpha^2$

or $\alpha = \sqrt{K_h \times V}$

From (4) we have

$$K_h = \frac{K_w}{K_b}$$

$$\therefore \alpha = \sqrt{\frac{K_w}{K_b} \times V}$$

$$= \sqrt{\frac{K_w}{K_b \times C}}$$

where C is the initial concentration of the salt.

Derivation of pH. From the above discussion it is clear that

$$[H^+] = \frac{\alpha}{V} = \alpha \times C$$

Substituting the value of α from equation (5), we have

$$[H^+] = \frac{1}{V} \sqrt{\frac{K_w \times V}{K_b}} = \sqrt{\frac{K_w}{K_b V}} = \sqrt{\frac{K_w \times C}{K_b}}$$

Taking logarithms and reversing the signs

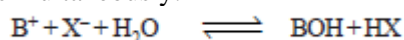
$$-\log[H^+] = -\frac{1}{2} \log K_w - \frac{1}{2} \log C + \frac{1}{2} pK_b$$

$$\text{Or, pH} = \frac{1}{2} pK_w + \frac{1}{2} pK_b - \frac{1}{2} \log C$$

$$\text{Or, pH} = 7 + \frac{1}{2} pK_b - \frac{1}{2} \log C$$

In this case it is evident that pH will always be less than 7. Thus, **the solution of a salt of weak base and strong acid will always be acidic.**

2.9.68. Mathematical Expression for Hydrolysis of salt of weak acid and weak base: In this type of salt, both the anion of weak acid (X^-) and the cation of weak base (B^+) undergo hydrolysis simultaneously.



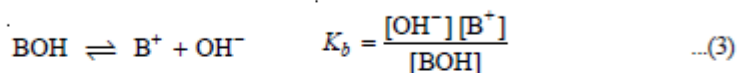
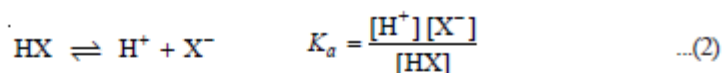
#Determination of Hydrolysis constant: Applying Law of Mass Action to the above hydrolysis reaction we have the hydrolysis constant, K_h .

$$K_h = \frac{[BOH][HX]}{[B^+][X^-][H_2O]}$$

$[H_2O]$ is very large and is taken to be constant. The hydrolysis constant expression, therefore, becomes

$$K_h = \frac{[BOH][HX]}{[B^+][X^-]} \quad \dots(1)$$

##Relation between K_h , K_w , K_a and K_b : Applying Law of Mass Action to the ionisation of weak acid, HX, weak base, BOH, and water, we can write

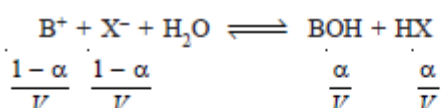


$$K_w = [\text{H}^+][\text{OH}^-] \quad \dots(4)$$

Dividing (4) by (3) and (2), we have

$$\begin{aligned} \frac{K_w}{K_a \times K_b} &= \frac{[\text{H}^+][\text{OH}^-][\text{HX}][\text{BOH}]}{[\text{X}^-][\text{H}^+][\text{B}^+][\text{OH}^-]} \\ &= \frac{[\text{HX}][\text{BOH}]}{[\text{X}^-][\text{B}^+]} \\ \frac{K_w}{K_a \times K_b} &= K_h \quad \dots(5) \end{aligned}$$

###Relation between Hydrolysis constant and Degree of Hydrolysis: Let us start with 1 mole of the salt of a weak acid and weak base. If α is the degree of hydrolysis (fraction hydrolysed), the equilibrium concentrations are:



Substituting these in the hydrolysis constant expression (1)

$$K_h = \frac{\alpha/V \times \alpha/V}{1 - \alpha/V \times 1 - \alpha/V}$$

or
$$K_h = \frac{\alpha^2}{(1 - \alpha)^2}$$

When α is small, $(1 - \alpha)$ may be taken as equal to one. Thus we have

$$K_h = \alpha^2$$

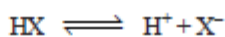
or
$$\alpha = \sqrt{K_h}$$

From equation (5)
$$K_h = K_w / K_a \times K_b$$

$$\therefore \alpha = \sqrt{\frac{K_w}{K_a \times K_b}} \quad \dots(6)$$

####Derivation of pH: Hydrogen ion concentration of the solution of a salt of weak acid and weakbase can be derived from the dissociation equilibrium of the weak acid, HX.

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$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$$

$$\therefore [\text{H}^+] = \frac{K_a [\text{HX}]}{[\text{X}^-]}$$

From the hydrolysis reaction of the salt, we know that

$$[\text{HX}] = \frac{\alpha}{V} \quad \text{and} \quad [\text{X}^-] = \frac{1 - \alpha}{V}$$

Substituting these values we have

$$[\text{H}^+] = \frac{K_a \times \frac{\alpha}{V}}{\frac{1 - \alpha}{V}} = K_a \left(\frac{\alpha}{1 - \alpha} \right)$$

Ignoring α as compared to unity,

$$[\text{H}^+] = K_a \times \alpha$$

Substituting the value of α from equation (6),

$$[\text{H}^+] = K_a \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{K_w K_a}{K_b}}$$

Taking logarithms and reversing the sign throughout

$$-\log[\text{H}^+] = -\frac{1}{2} \log K_w - \frac{1}{2} \log K_a + \frac{1}{2} \log K_b$$

or

$$\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

If

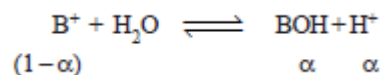
$$\text{p}K_a = \text{p}K_b$$

i.e., the dissociation constant of the acid is equal to that of the base,

$$\text{pH} = \frac{1}{2} \text{p}K_w = 7$$

Thus, the solution will be neutral despite the fact that hydrolysis has taken place. Since the dissociation constant of acetic acid is almost the same as that of ammonium hydroxide, the solution of ammonium acetate is neutral i.e., it has a pH of 7. If $\text{p}K_a > \text{p}K_b$ i.e., the acid is relatively weaker than the base, the solution will be alkaline as pH is more than 7. If $\text{p}K_a < \text{p}K_b$ i.e., the acid is relatively stronger, the solution will be acidic as pH will be less than 7.

2.9.69. Conductometric Measurement of Degree of Hydrolysis: The degree of hydrolysis, α , of a salt can be determined by conductance measurements. Let us consider a solution containing the salt of a weak base and a strong acid. The hydrolysis reaction can be written as



If it be assumed that the base is so weak that it is not dissociated at all, it will contribute nothing to conductance of the solution. The equivalent conductance of the salt, therefore, consists of:

(a) that due to $(1 - \alpha)$ equivalents of the salt.

(b) that due to α equivalents of the acid produced by hydrolysis.

$$\begin{aligned}\Lambda &= (1 - \alpha) \Lambda_{\text{salt}} + \alpha \Lambda_{\text{acid}} \\ \Lambda - \Lambda_{\text{salt}} &= \alpha (\Lambda_{\text{acid}} - \Lambda_{\text{salt}}) \\ \alpha &= \frac{\Lambda - \Lambda_{\text{salt}}}{(\Lambda_{\text{acid}} - \Lambda_{\text{salt}})}\end{aligned}$$

Λ is found by conductance measurements. Λ_{acid} is taken as the value for strong acid at infinite dilution. Λ_{acid} is determined by adding excess of weak base to the solution to suppress hydrolysis so that the resulting experimentally determined value of Λ can be taken as that of the unhydrolyzed salt.

2.9.70. Tafel Equation: The overvoltage E_{ov} depends upon the current passing and an empirical formula has been introduced to attribute that; it is called Tafel equation. J is the current density, and i/A where i is the current and A is the area of the electrode. 'R' is approximately equal to $2RT/nF$ and 'P' is of the order of 1 volt for H_2 generated on C, Ag or Hg, and of the order of 0.5 volt for O_2 discharged on Pb, C, Ag and other metals.

$$E_{\text{ov}} = P + R \ln J$$

Sometimes, P = arbitrary constant and R always equal to $2RT/nF$.

It can be written in another form

$$\eta_i = (RT/\alpha F) \ln(J_i/J_o)$$

where, α = Transfer coefficient

2.9.72. Relation between Ionic Strength & Mean Activity Coefficient: Ionic Strength of a solution is expressed as

$$I = \frac{1}{2} \sum c_i Z_i^2$$

Where, I = ionic Strength, C_i = Concentration of the solution, Z_i = Charge on corresponding ions

Mean activity coefficient is related to ionic strength of the solution as follows

$$\log \gamma_{\pm} = -2.303A|Z_- Z_+| \sqrt{I}$$

Where, A = Constant

Previous Year Questions Analysis with Explanation

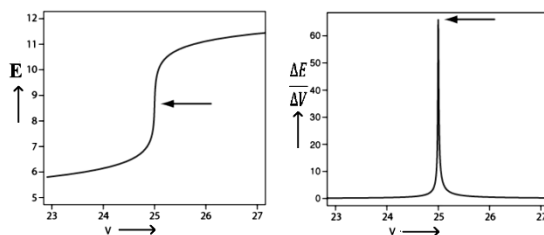
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Q. In a potentiometric titration, the end point is characterized by

- (a) $\frac{dE}{dV} = 0, \frac{d^2E}{dV^2} = 0$ (b) $\frac{dE}{dV} \neq 0, \frac{d^2E}{dV^2} = 0$ (c) $\frac{dE}{dV} = 0, \frac{d^2E}{dV^2} \neq 0$ (d) $\frac{dE}{dV} \neq 0, \frac{d^2E}{dV^2} \neq 0$

where E is the emf of the titration cell and V is the volume of the titrant added

Ans.

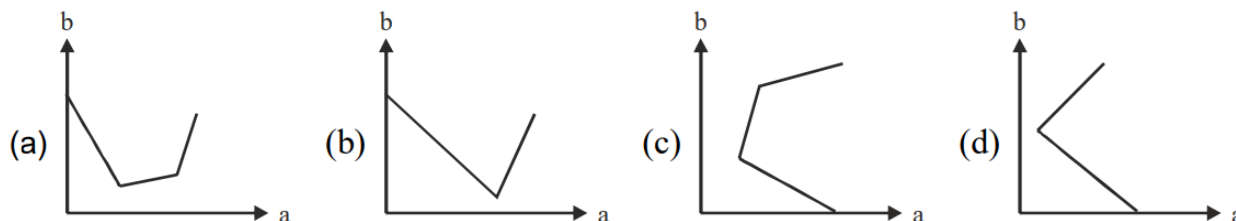


Nature of potentiometric first differentiate with a end point $\frac{dE}{dV} \neq 0, \frac{d^2E}{dV^2} = 0$.

curve is sigmoidal and sharp peak, for which at

Correct option is (b). [Key point 2.9.21]

Q. On titrating conductometric ally a NaOH solution with a mixture of HCl and $\text{CH}_3\text{CO}_2\text{H}$ solutions, plot of the volume of mixed acid added (b) in y-axis against the conductance (a) in x-axis is expected to look like



Ans. The initial conductivity is high it is due to HCl which by common ion effect suppress the ionization of CH_3COOH . Upon titration; decrease in conductivity occurs due to replacement of H^+ ion with mobility 350 by Na^+ ion with mobility 43, till all the H^+ ions from HCl are neutralized. CH_3COOH will thus ionize and react with NaOH. Thus, we will have two breaks.

Correct option is (c). [Key point 2.9.49]

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Q. The standard electrode potential E^0 at a fixed temperature and in a given medium is dependent on

- (a) only the electrode composition
- (b) the electrode composition and the extent of the reaction
- (c) the extent of the electrode reaction only
- (d) the electrode reaction and the electrode composition

Ans. The standard electrode potential E^0 is fixed at a particular T. Due the deviation from ideality and change in electrode concentration, electrode potential changes as per Nernst equation.

Correct option is (d). [Key point 2.9.16]

Q. Two aqueous 1:1 electrolyte systems A and B are at different temperatures T_A and T_B and C_A and C_B concentrations, respectively. Their Debye lengths will be equal if

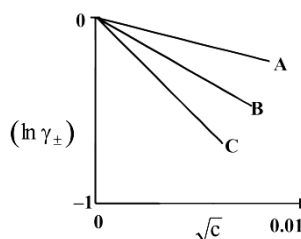
- (a) $T_A = 2T_B$ and $C_A = 2C_B$
- (b) $T_A = 2T_B$ and $C_A = C_B/2$
- (c) $T_A = \sqrt{2}T_B$ and $C_A = 2C_B$
- (d) $T_A = 2T_B$ and $C_A = \sqrt{2}C_B$

Ans. Debye – Huckel screening length,

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{e^2 N_A \sum c_i Z_i^2}}; \text{ i.e., } \frac{1}{\kappa_A} = \sqrt{\frac{T_A}{C_A}} \text{ and } \frac{1}{\kappa_B} = \sqrt{\frac{T_B}{C_B}}. \text{ So, now, the condition, } \kappa_A = \kappa_B \text{ will achieve when } T_A = 2T_B \text{ and } C_A = 2C_B.$$

Correct option is (a). [Key point 2.9.34]

Q. Aqueous solutions of NaCl, CaCl₂ and LaCl₃ show the following plots of logarithms of mean ionic activity coefficient ($\ln \gamma_{\pm}$) vs molar concentration (c)



The correct option is then

	NaCl	CaCl ₂	LaCl ₃
(a)	C	B	A
(b)	A	B	C
(c)	A	C	B
(d)	C	A	B

Ans. As we know, $\log \gamma_{\pm} = -2.303A|Z_-Z_+|\sqrt{I}$

Correct option is (b). [Key point 2.9.71]

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Q. The ionic mobilities of NH_4^+ and HCO_3^- $6 \times 10^{-4} \text{ V}^{-1}\text{s}^{-1}$ and $5 \times 10^{-4} \text{ V}^{-1}\text{s}^{-1}$, respectively. The transport numbers of NH_4^+ and HCO_3^- are, respectively

- (a) 0.545 and 0.455 (b) 0.455 and 0.545
(c) 0.090 and 0.910 (d) 0.910 and 0.090

$$\text{Ans. } t_{\text{NH}_4^+} = \frac{u_+}{u_+ + u_-} = \frac{6 \times 10^{-4}}{6 \times 10^{-4} + 5 \times 10^{-4}} = \frac{6}{11} = 0.545$$

$$t_{\text{HCO}_3^-} = \frac{u_-}{u_+ + u_-} = \frac{5 \times 10^{-4}}{6 \times 10^{-4} + 5 \times 10^{-4}} = \frac{5}{11} = 0.455$$

Correct option is (a). [Key point 2.9.41]

Q. The ionic strength of a solution containing 0.008 M AlCl_3 and 0.005 M KCl is

- (a) 0.134 M (b) 0.053 M (c) 0.106 M (d) 0.086 M

$$\text{Ans. } I = \frac{1}{2} \sum c_i Z_i^2$$

$$\text{For } \text{AlCl}_3, I = \frac{1}{2} [(0.008 \times 3^2) + (0.024 \times 1^2) + (0.005 \times 1^2) + (0.005 \times 1^2)] = 0.053$$

Correct option is (b). [Key point 2.9.71]

Q. If the specific conductance's of a sparingly soluble (1:1) salt ($\text{MW} = 200 \text{ g mol}^{-1}$) in its saturated aqueous solution at 25°C and that of water are $1.5 \times 10^{-3} \text{ ohm}^{-1}\text{dm}^{-1}$ and $1.5 \times 10^{-5} \text{ ohm}^{-1}\text{dm}^{-1}$, respectively, and the ionic conductance's for its cation and anion at infinite dilution are 0.485 and $1.0 \text{ ohm}^{-1}\text{dm}^2\text{mol}^{-1}$, respectively, the solubility (in gL^{-1}) of the salt in water at 25°C is

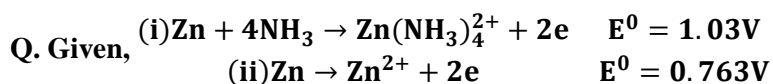
- (a) 1×10^{-6} (b) 1×10^{-3} (c) 2×10^{-1} (d) 2×10^{-4}

$$\text{Ans. } K_{\text{salt}} = K_{\text{solution}} - K_{\text{water}} = 1.5 \times 0.99 \times 10^{-3}$$

$$\text{Now, solubility, } s = \frac{K_{\text{salt}}}{\Lambda_{\text{salt}}} = \frac{1.5 \times 0.99 \times 10^{-3}}{(0.485 + 1)} = 1 \times 10^{-3} \text{ mol. dm}^{-3} = 2 \times 10^{-3} \text{ gm. L}^{-1};$$

Correct option is (c). [Key point 2.9.52]

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The formation constant of the complex $\text{Zn}(\text{NH}_3)_4^{2+}$ is approximately

$$\frac{2.303RT}{F} = 0.0591$$

- (a) 1×10^5 (b) 1×10^7 (c) 1×10^9 (d) 1×10^{12}

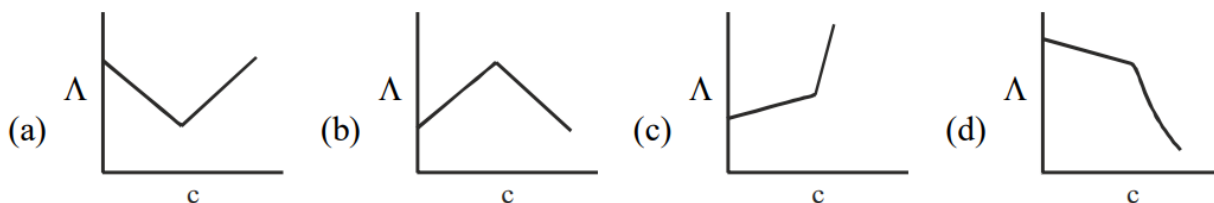
Ans. For the formation of the complex we need to reverse the reaction (ii).

So, $E_{\text{cell}}^0 = 1.03 - 0.763 = 0.267$.

Now, $E_{\text{cell}}^0 = \frac{0.0591}{2} K_{\text{eq}}; \Rightarrow K_{\text{eq}} = 10^{\frac{0.267 \times 2}{0.0591}} \cong 10^9$.

Correct option is (c). [Key point 2.9.17]

Q. The molar conductivity (Λ) vs. concentration (c) plot of sodium dodecylsulfate in water is expected to look like



Ans. The effect of concentration of electrolyte is given by,

$$\log CMC = -a \log c_i - b$$

For surfactant molecule, with increasing concentration, molar conductance decreases linearly till the CMC point. After that, it decreases exponentially.

Correct option is (d). [Key point 2.9.33]

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Q. The electrochemical cell potential (E), after the reactants and products reach equilibrium, is (E^0 is the standard cell potential and n is the number of electrons involved)

- (a) $E = E^0 + nF/RT$ (b) $E = E^0 - RT/nF$ (c) $E = E^0$ (d) $E = 0$

Ans. At equilibrium, the reaction quotient becomes 1.

Thereafter, Nernst equation reduced to $E = E^0$.

Correct option is (c). [Key point 2.9.17]

Q. The specific conductance of a solution is $0.176\Omega^{-1}\text{cm}^{-1}$. If the cell constant is 0.255 cm^{-1} , the conductance (Ω^{-1}) of that solution is

- (a) 1.449 (b) 0.690 (c) 0.045 (d) 0.431

Ans. We know that, $\kappa = G \left(\frac{l}{A} \right)$; $G = \frac{(l/A)}{\kappa} = \frac{0.255}{0.176} = 1.449$.

Correct option is (a). [Key point 2.9.28]

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Q. The equivalent conductance at infinite dilution of a strong electrolyte (Λ^0) can be obtained from the plot of

- (a) Λ vs. C (b) Λ vs. \sqrt{C} (c) Λ vs. C^2 (d) Λ vs. $\frac{1}{C}$

Ans. For a strong electrolyte, Λ^0 can be obtained from the plot of Λ vs. \sqrt{C} .

Correct option is (b). [Key point 2.9.33]

Q. In the specific conductance of an electrolyte solution is $0.2\Omega^{-1}$ and cell constant is 0.25 cm^{-1} , the conductance of the solution is

- (a) $1.25\Omega^{-1}$ (b) $1.0\Omega^{-1}$ (c) $0.8\Omega^{-1}$ (d) $2.0\Omega^{-1}$

Ans. We know that, $\kappa = G \left(\frac{l}{A} \right)$; $G = \frac{(l/A)}{\kappa} = \frac{0.2}{0.25} = 0.8$

Correct option is (c). [Key point 2.9.28]

Q. The predicated electromotive force (emf) of the electrochemical cell

$Fe(s)|Fe^{+2}(aq, 0.001M)||Cd^{+2}(aq, 0.001M)|Cd(s)$ is

$$\left(E_{Fe^{+2}/Fe}^0 = -0.447V \text{ and } E_{Cd^{+2}/Cd}^0 = -0.403V \right)$$

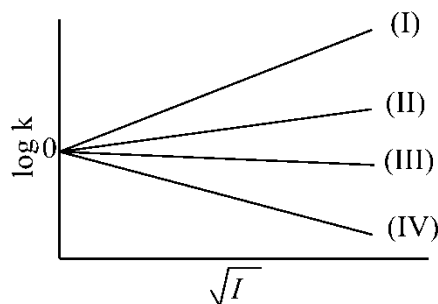
- (a) -0.850 V (b) +0.447 V (c) +0.8580 V (d) -0.044 V

Ans. $E_{cell} = E_{cell}^0 - \frac{0.059}{2} \log \left(\frac{0.001}{0.001} \right)$; i.e., $E_{cell} = E_{cell}^0 = -0.403 + 0.447 = 0.447$

Correct option is (b). [Key point 2.9.17]

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Q. The plot of the rate constant vs. ionic strength of the reaction ($A^{2+} + B^-$) follows the line (refer to the figure).



- (a) (I) (b) (II) (c) (III) (d) (IV)

Ans. Slope = $2AZ_AZ_B = -4A = -ve$ (salt effect).

Correct option is (d). [Key point 2.9.72]

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Q. The standard cell potential for the reaction $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ is +1.10 V. The Gibbs's free energy change during the reaction is ($F = 96500$ coulomb mol^{-1})

- (a) -21.2 KJ mol^{-1} (b) $+212$ KJ mol^{-1}
(c) -212 KJ mol^{-1} (d) -212 KJ mol^{-1}

Ans. $\Delta G^0 = -nFE^0 = -2 \times 96500 \times 1.1 = -212.3$ kJ mol^{-1}

Correct option is (b). [Key point 2.9.14]

Q. The standard cell potential of cell, $Pt|H_2(g)|HBr(aq)|AgBr(s)|Ag(s)$ was measured over a range of temperature, and the data was fitted as $E^0(volt) = 0.01 - 1 \times 10^{-4}(T - 298) - 2 \times 10^{-6}(T - 298)^2$ the standard reaction entropy ($JK^{-1} mol^{-1}$) and enthalpy ($KJmol^{-1}$) at 298 K are

- (a) -9.65 and -3.85 (b) -3.84 and -9.65
(c) -18.3 and -7.68 (d) -7.68 and -18.3

Ans.

$$\Delta S^0 = nF \left(\frac{\partial E}{\partial T} \right)_p = 2 \times 96500 \{ -10^{-4} - 4 \times 10^{-6}(298 - 298) \} = -9.65 \text{ JK}^{-1} \text{ mol}^{-1}.$$

$$\begin{aligned} \Delta H^0 &= -nFE^0 + nF \left(\frac{\partial E}{\partial T} \right)_p \\ &= -96500 \times [0.01 - 1 \times 10^{-4}(298 - 298) - 2 \times 10^{-6}(298 - 298)^2 + 298 \times 9.65] \\ &= -3.85 \text{ KJmol}^{-1} \end{aligned}$$

Correct option is (a). [Key point 2.9.14]

Q. A solution of Fe^{+3} is titrated potentiometrically using Ce^{+3} solution at 25°C . The emf (in V) of the redox system thus formed when, (i) 50% of Fe^{+3} and (ii) 80% of Fe^{+3} are titrated, would respectively be (Given $E_{\text{Fe}^{+3}/\text{Fe}^{+2}}^0 = 0.77\text{V}$, $\log_{10} 2 = 0.301$)

(a) 0.734 and 0.77

(b) 0.77 and 0.385

(c) 0.77 and 0.734

(d) 0.385 and 0.367

Ans.

At 50%

$$E_{\text{Fe}^{+3}/\text{Fe}^{+2}} = E_{\text{Fe}^{+3}/\text{Fe}^{+2}}^0 - \frac{0.0591}{1} \log \left(\frac{0.5}{0.5} \right) = 0.77$$

At 80%

$$E_{\text{Fe}^{+3}/\text{Fe}^{+2}} = E_{\text{Fe}^{+3}/\text{Fe}^{+2}}^0 - \frac{0.0591}{1} \log \left(\frac{0.8}{0.2} \right) = 0.734$$

Correct option is (c).

[Key point 2.9.17]

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Q. The correct statement among the following

(a) Salt bridge is required for the mixing of the solutions in the two half cells

(b) Salt bridge allows current to flow between the half cells without mixing the solutions

(c) Salt bridge enhances the rate of the reaction

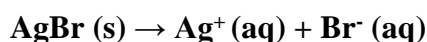
(d) Salt bridge consists of a non-electrolyte in a gel

Ans. Saltbridge allows current to flow between half cells without mixing the solutions in two counters.

Correct answer is (b).

[Key point 2.9.12]

Q. The standard free energy of the reaction



Is closest to $[E^0(\text{AgBr/Ag, Br}^-) = 0.07\text{ V}; E^0(\text{Ag/Ag}^+) = 0.80\text{ V}; F = 96500\text{ Cmol}^{-1}]$

(a) 7 kJmol^{-1}

(b) 70 Jmol^{-1}

(c) 70 kJmol^{-1}

(d) 7 Jmol^{-1}

Ans. $E_{\text{cell}}^0 = E_{\text{Br}^-/\text{AgBr/Ag}}^0 - E_{\text{Ag}^+/\text{Ag}}^0 = 0.07 - 0.80 = -0.73\text{ V}$

We know, $\Delta G^0 = -nFE_{\text{cell}}^0 = -1 \times 96500 \times (-0.73) = 70445\text{ Jmol}^{-1} = 70.4\text{ kJmol}^{-1}$

Correct answer is (c).

[Key point 2.9.14]

Q. Conductivities of water and saturated solution of a sparingly soluble salt AB_2 are 7 and $21 \mu\text{Sm}^{-1}$, respectively. Given $\lambda_{A^{2+}}^0 = 12.72 \text{ mS m}^2 \text{ mol}^{-1}$ and $\lambda_{B^-}^0 = 7.64 \text{ mS m}^2 \text{ mol}^{-1}$, solubility of AB_2 , in the mol m^{-3} , is

- (a) 5×10^{-4} (b) 5×10^{-3} (c) 5×10^{-5} (d) 5×10^{-6}

Ans. $K_{\text{saturated solution}} = k_{\text{water}} + k(AB_2)$

Or, $k(AB_2) = 21 - 7 = 14 \mu\text{Sm}^{-1} = 14 \times 10^{-6} \text{ Sm}^{-1}$



$$\Lambda^0(AB_2) = \lambda_{A^{2+}}^0 + 2\lambda_{B^-}^0 = 12.72 + 2 \times 7.64 = 28 \text{ mS m}^2 \text{ mol}^{-1} = 28 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$$

$$\text{Now, } \Lambda^0(AB_2) = k(AB_2)/1000 \times S(AB_2)$$

Pitting the values,

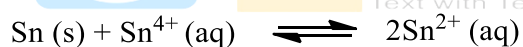
$$28 \times 10^{-3} = (14 \times 10^{-6})/10^3 \times S(AB_2)$$

$$\text{Or, } S(AB_2) = 5 \times 10^{-4} \text{ mol m}^{-3}$$

Correct answer is (a).

[Key point 2.9.36]

Q. The equilibrium constant of the following reaction



At 300K is close to [Given: $E^0(\text{Sn}^{4+}/\text{Sn}^{2+}) = +0.15 \text{ V}$; $E^0(\text{Sn}^{2+}/\text{Sn}) = -0.15 \text{ V}$; $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$; $F = 96500 \text{ Cmol}^{-1}$]

- (a) $10^{6.08}$ (b) $10^{8.08}$ (c) $10^{10.08}$ (d) $10^{12.08}$

Ans. The relation between EMF and equilibrium constant is

$$E_{\text{cell}}^0 = [RT/nF] \ln K_{\text{eq}}$$

$$\text{Or, } E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 - E_{\text{Sn}^{2+}/\text{Sn}}^0 = [(2.303 \times 8.314 \times 300)/(2 \times 96500)] \ln K_{\text{eq}}$$

Putting the values of E^0 ,

$$0.15 - (-0.15) = 0.0297 \ln K_{\text{eq}}$$

$$\text{Or, } K_{\text{eq}} = 10^{10.08}$$

Correct answer is (b).

[Key point 2.9.17]

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Q. The mobility of a divalent cation in water is $8 \times 10^{-8} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$. The effective radius of the ion is [viscosity of water = 1 cP, $e = 1.6 \times 10^{-19} \text{ C}$] [NET 2019 June]

- (a) 106 pm (b) 212 pm (c) 424 pm (d) 318 pm

Ans. We know, $\mu = Ze/6\pi\eta r$

$$\text{Or, } r = Ze/6\pi\eta\mu = (2 \times 1.6 \times 10^{-19}) / (6 \times 3.14 \times 10^{-3} \times 8 \times 10^{-8}) = 212.3 \times 10^{-12} \text{ m} = 212.3 \text{ pm}$$

As 1 PaS = 10 poise = 10^3 cP

Correct answer is **Option (b)**. [Key point 2.9.33]

Q. If the overpotential of an electrolysis process is increased from 0.5V to 0.6V, then the ratio of current densities $[\ln(J_{0.6}/J_{0.5})]$ of the electrolysis will be equal to [given transfer coefficient = 0.5]

- (a) $0.5F/RT$ (b) $0.05F/RT$ (c) $0.1F/RT$ (d) $0.01F/RT$ [NET 2019 June]

Ans. According to Tafel Equation,

$$\eta_i = (RT/\alpha F) \ln(J_i/J_o)$$

$$\text{Now, } \eta_{0.5} = (RT/\alpha F) \ln(J_{0.5}/J_o) \dots \dots \dots (i)$$

$$\eta_{0.6} = (RT/\alpha F) \ln(J_{0.6}/J_o) \dots \dots \dots (ii)$$

now, (ii) – (i),

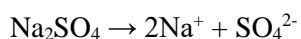
$$\ln(J_{0.6}/J_{0.5}) = (\alpha F/RT)(\eta_{0.6} - \eta_{0.5}) = (0.5F/RT)(0.6 - 0.5) = 0.05F/RT$$

Correct answer is **Option (b)**. [Key point 2.9.70]

Q. The chemical potential (μ) of a 2 molar Na_2SO_4 solution is expressed in terms of mean ionic activity co-efficient (γ_{\pm}) as

- (a) $\mu^0 + 5RT \ln 2 + 3RT \ln \gamma_{\pm}$ (b) $\mu^0 + 3RT \ln 2 + 3RT \ln \gamma_{\pm}$ [NET 2019 June]
(c) $\mu^0 + 3RT \ln \gamma_{\pm}$ (d) $\mu^0 + 4RT \ln \gamma_{\pm}$

Ans. We know, $\mu_i = \mu^0 + RT \ln a_i$



$$m \quad \quad \quad 0 \quad \quad \quad 0$$

$$0 \quad \quad \quad 2m \quad \quad m$$

$$a_i = (\gamma_{\pm})^{(2+1)}(2m)^2(m)^1 = (\gamma_{\pm})^3 m^3 = (\gamma_{\pm})^3 2^5 \quad \text{as } m = 2$$

$$\mu_i = \mu^0 + RT \ln [(\gamma_{\pm})^3 2^5] = \mu^0 + RT \ln [(\gamma_{\pm})^3 + 5RT \ln 2]$$

Correct answer is **Option (a)**. [Key point 2.9.72]

Model Questions

1. The non metallic cation is in
 - a. PCl_3
 - b. VOCl
 - c. NH_4Cl
 - d. CrO_2Cl_2
2. The element which does not exist in liquid state at room temperature are
 - a. Na
 - b. Ga
 - c. Br
 - d. Hg
3. Melting point is maximum for
 - a. LiCl
 - b. NaCl
 - c. KCl
 - d. RbCl
4. The first ionization potential of Al is smaller than that of Mg because
 - a. The atomic size of Al < Mg
 - b. The atomic size of Al > Mg
 - c. The atomic number of Al > Mg
 - d. Al has one unpaired electron in p orbital
5. There is no S – S bond in-
 - a. $\text{S}_2\text{O}_4^{2-}$
 - b. $\text{S}_2\text{O}_5^{2-}$
 - c. $\text{S}_2\text{O}_3^{2-}$
 - d. $\text{S}_2\text{O}_7^{2-}$
6. The bond length in O_2 , O_2^+ and O_2^- species follow the order-
 - a. $\text{O}_2^- < \text{O}_2 < \text{O}_2^+$
 - b. $\text{O}_2^- < \text{O}_2^+ < \text{O}_2$
 - c. $\text{O}_2^+ < \text{O}_2 < \text{O}_2^-$
 - d. $\text{O}_2 < \text{O}_2^+ < \text{O}_2^-$
7. The structure of ClO_3F is –
 - a. Linear
 - b. Square planar
 - c. Trigonal planar
 - d. Tetrahedral

8. Which of the following species have bond order of three?

- I. N_2
- II. NO^-
- III. NO^+
- IV. C_2^-

Select the correct answer using the codes given below

- a. I and II
- b. I, II and III
- c. I, II and IV
- d. I, II and IV

9. Choose the correct order of Bond energies in the following series –

- a. $\text{C}=\text{O} > \text{O}=\text{O} > \text{C}-\text{O}$
- b. $\text{C}=\text{O} > \text{C}-\text{O} > \text{O}=\text{O}$
- c. $\text{C}-\text{O} > \text{O}=\text{O} > \text{C}=\text{O}$
- d. $\text{O}=\text{O} > \text{C}-\text{O} > \text{C}=\text{O}$

10. Which of the following does not apply to the phrase ‘anti-bonding orbital’?

- a. Involves an energy higher than that of the atomic orbital
- b. Involves an energy on conductive to increased stability
- c. A designation related to molecular orbital or bond
- d. An expression used when an electron is removed from atoms

11. Intermolecular forces in solid hydrogen are –

- a. Vander Waals forces
- b. Covalent forces
- c. Hydrogen bonds
- d. None of these

12. total Van der Waals forces are proportional to the distance between nucleus of non bonding atoms –

- a. r^6
- b. $1/r^6$
- c. r^5
- d. $1/r^5$

13. Which of the following combination can be regarded as soft acids?

- a. BF_3 and Sn^{4+}
- b. Cu^+ and Cd^{2+}
- c. SCN^- and H^-
- d. Na^+ and NH_3

14. Which of the following species is the strongest Bronsted-Lowry base in water?

- a. NH_3
- b. F^-
- c. NH_2^-
- d. CO_3^{2-}

15. Which of the following is a soft base?

- a. CH_3COO^-
- b. H^-
- c. NO_3^-
- d. CO_3^{2-}

Answer

SL. No.	Answer
1.	c
2.	a
3.	b
4.	d
5.	d
6.	c
7.	d
8.	d
9.	d
10.	d
11.	A
12.	B
13.	B
14.	C
15.	B

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1. **Text: Unit wise separate pdf**
2. **PYQs: Previous Years Questions**
3. **MQs: Model Questions**
4. **LMS: Last Minute Suggestion**
5. **OMT: Online MOCK Test**
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