

EDUCATALYSTS

Class(12th)

Introduction to Chemical Kinetics

| INTRODUCION

Chemical Kinetics is the branch of chemistry that deals with the rates of reactions

© Factors influencing the rates of reaction © Reaction mechanism

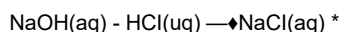
Kinetics studies help us to determine the speed or rate of a chemical reaction and also describe the conditions by which the reaction rates can be altered.

Based on the velocity of chemical reactions, the reactions are classified into three types:

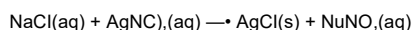
• Very fast (or) instantaneous reaction

The chemical reactions which are completed within the fraction of seconds are called as very fast reactions. Example:

1. Neutralization between strong acids and strong bases.



2. Precipitation reactions



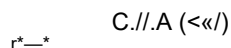
3. Explosive reactions :

Explosion of T.N.T

b. Moderate reactions

The chemical reactions which are completed within hours (or) minutes are called as moderate reactions. Example:

1. Inversion of cane sugar



2. Combustion of hydrogen (or) coal [under normal conditions].

c. Very slow reaction!

The chemical reactions which complete in very long time are called very slow reactions.

Example:

1. Rusting of Iron in presence of air and moisture $4\text{Fe} + 3\text{O}_2 + x\text{H}_2\text{O} \rightarrow 2\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

2. $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$

-KEYNOTE ~ It is not possible to determine

the rates of very fast and very slow reactions by conventional methods. But the rates of reactions with moderate speed can be determined. | RATE OF REACTION

© The decrease in the concentration of the reactant per unit time or increase in the concentration of the product per unit time is called rate of a reaction.

$$\text{Rate} = -\frac{\frac{\text{mol}}{\text{lit.}}}{\text{sec}} = \frac{\text{mol lit}^{-1} \text{ time}^{-1}}{\text{sec}} = \text{mol dm}^{-3} \text{ time}^{-1}$$

Rate is always defined in such a manner so that it is always a positive quantity.

© For a reaction $R \rightarrow P$ Total change in concentration

$$\text{Average rate} = \frac{\Delta[P]}{\Delta t} = \frac{[P]_2 - [P]_1}{t_2 - t_1}$$

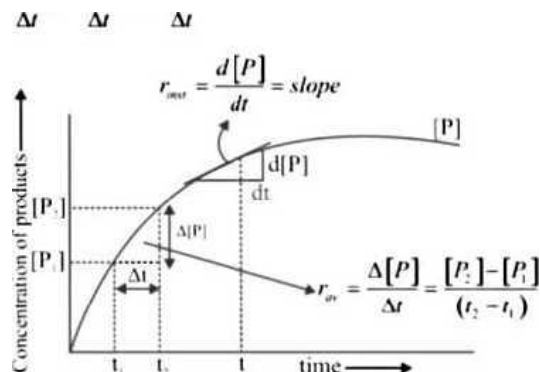


Fig.: Average rate of reaction

Instantaneous rate : rate of reaction at a particular instant.

$$R_{\text{instantaneous}} = \lim_{\Delta t \rightarrow 0} \left[\frac{\Delta c}{\Delta t} \right] = \frac{dc}{dt} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

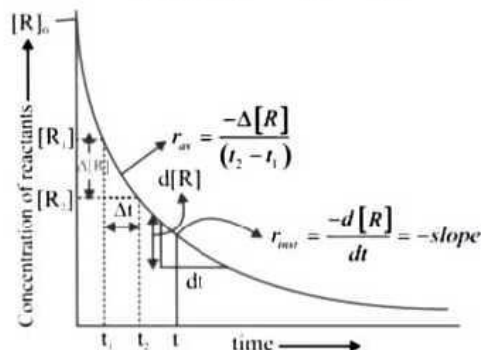


Fig.: Instantaneous rate of reaction Example:

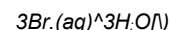
1. $A \rightarrow B$

$$\text{Rate} = \frac{d[B]}{dt} = +\frac{1}{2} \frac{d[A]}{dt}$$

2. $pP + qQ \rightarrow rR + sS$

$$\text{rate} = -\frac{1}{p} \frac{d[P]}{dt} = -\frac{1}{q} \frac{d[Q]}{dt} = +\frac{1}{r} \frac{d[R]}{dt} = +\frac{1}{s} \frac{d[S]}{dt}$$

3. $5\text{Br}(\text{aq}) + \text{BrO}_3(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 5\text{Br}_2(\text{l}) + 3\text{H}_2\text{O}(\text{l})$



$$\frac{1}{6} \frac{\Delta[\text{N}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{NH}_3]}{\Delta t}$$

Relation between reaction rates of different species involved in a reaction

For the reaction : $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$

Rate of reaction of $\text{N}_2 = \frac{1}{6} \frac{\Delta[\text{N}_2]}{\Delta t}$

These rates are not all equal. Therefore by convention the rate of

Rate of reaction of $\text{H}_2 = \frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t}$

Rate of reaction of $\text{NH}_3 = \frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t}$

a reaction is defined as

$$\frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

Rate of reaction

-KEYNOTE - Rate of

reaction value is dependent on the stoichiometric coefficients used in the reaction while rate of any species will be fixed value under given conditions.

- © The rate of a reaction varies exponentially with time of the reaction.
- © The concentration of the reactants in a reaction varies exponentially with time.
- © No reaction takes place with uniform rate throughout the course of the reaction.
- © The rates of chemical reactions differ from one another, since the number and the nature of the bonds are different in the different substances (reactants or products or both)

FACTORS AFFECTING THE RATE OF REACTION

Factors affecting rate of chemical reaction : 1. Nature of reactants

2. Concentration of the reactants
3. Temperature
4. Effect of Catalyst
5. pH of the solution
6. Dielectric constant of the medium.
7. Radiations/light
8. Pressure
9. Electrical & Magnetic field.

1. Nature of the Reactants

(a) Physical state of reactants :

Gaseous state > Liquid state > Solid state Decreasing order of rate of reaction.

(b) Physical size of reactants : As the particle size decreases, rate of reaction increases since surface area increases.

(c) Chemical nature of reactants

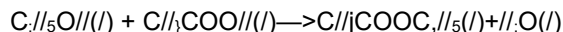
© If more bonds are to be broken, the rate of reaction will be slow.

© Similarly bond strength is more, rate of reaction will be slow. ©

Reactions between ionic substances take place much faster than the

reactions occurring between covalent substances. Because in ionic reactions there is no breaking and forming of bonds.

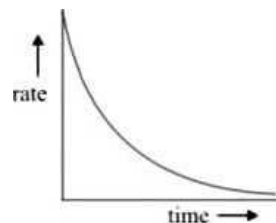
$\text{NaCl(aq)} + \text{AgNO}_3(\text{aq}) \rightarrow \text{AgCl(s)} + \text{NaNO}_3(\text{aq})$ © But covalent molecules involve the breaking (cleavage) and the making (formation) of covalent bonds.



2. Concentration of the reactants

© Except zero order reactions, for all other reactions the rate depends on the concentration of the reactants. © rate \propto (concentration of the reactants)ⁿ or

© 'n' may be any simple value including zero. © For gaseous reactants, rate \propto (pressure of the reactants)ⁿ © Chemical reactions occur due to the collisions between the reacting molecules. Hence greater the number of these molecules in unit volume, greater will be the possibility of their collisions and higher will be the rate of reaction. Eg:- When zinc pieces are added to dilute HCl, chemical reaction takes place slowly liberating gas. But the same reaction is rapid by taking concentrated HCl.



© From this graph it is clear that the rate of reaction gradually decreases with time because of the decrease in the concentration of reacting substances with time.

3. Effect of temperature on the reaction rate

© The rate of a reaction increases with increase in temperature. © In most cases, a rise of 10°C in temperature generally doubles the specific rate of the reaction.

© Increase of temperature increases the number of collisions between the molecules and increases the internal energy of the molecules and hence increases the rate of reaction. © The ratio of two specific rates measured at temperature that differ by 10°C is called the Temperature coefficient, i.e., +10

T.C. = $\frac{\text{Rate at } T+10}{\text{Rate at } T}$ * 2 to 3 (for most of the reactions) © Arrhenius

equation for temperature dependence of a rate constant is $k = A e^{-E_a/RT}$

Train Your Brain

Q. For a reaction $T.C. = 2$. Calculate k_{400} for this reaction.

Ans. $k_{400} = 2 \times 10^{-2} \text{ s}^{-1}$

Arrhenius proposed a theory of reaction rate which states as follows:

- A chemical reaction takes place due to the collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z).
- Every collision does not bring a chemical change. The collisions that actually produce the products are effective collisions. For a collision to be effective the following two barriers are to be effective:
 - Energy barrier-** The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur is known as threshold energy. "The minimum amount of extra energy required by reactant molecules to participate in a reaction is called activation energy (E_a)".
 - Orientation barrier-** Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper direction to make collision effective.

$$k = Ae^{-E_a/RT}$$

A = Arrhenius frequency constant, E_a =

Activation energy.

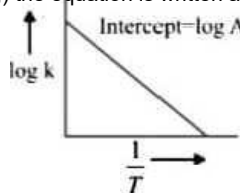
R = Gas constant

T = absolute temperature

For the different temperatures (T) & (T_1), the equation is written as follows:

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\text{Slope} = -\frac{E_a}{2.303R}$$



For Example:

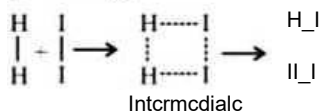


Fig.: Formation of HI through intermediate

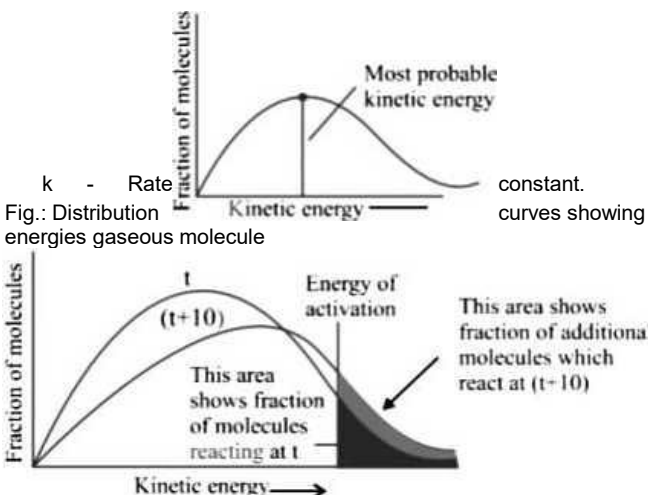
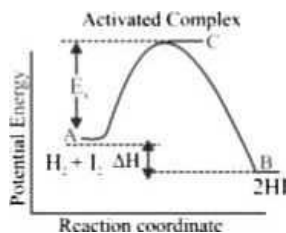


Fig.: Distribution curve showing dependence of rate of reaction

Train Your Brain

Q. For the reaction $CO(g) + Cl_2(g) \rightarrow COCl_2(g)$ under the same concentration conditions of the reactants, the rate of the reaction at $250^\circ C$ is 1500 times as fast as the same reaction at $150^\circ C$. Calculate the activation energy of the reaction. If the frequency factor is $2.0 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ calculate the rate constant of the reaction at $150^\circ C$.

Ans.

$$2.303$$

$$E_a = 32.36 \text{ kcal/mol}$$

$$100$$

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\frac{32360}{2.303 \times 2 \times 423} = 10.301 - 16.609 = -6.308$$

$$k = 4.92 \times 10^{-7} \text{ litres mol}^{-1} \text{ sec}^{-1}$$

Q. The pyrolysis of an organic ester follows a first order process and its rate can be expressed as $k = 78.09 \times 10^{-4} \text{ s}^{-1}$

where k is given in min^{-1} . Calculate the time required for 25 percent reaction to complete at $227^\circ C$. Ans. $t_{25} = 78.09$

$$= -6.06$$

$$500$$

$$6.06$$

$$\log k = 2.303 \times -2.63 : k = 2.344 \times 10^{-4} \text{ min}^{-1}$$

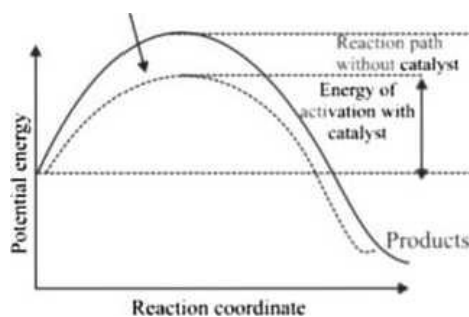
$$\text{when } x = 0.25 : k = r/t \quad 0.75a$$

Fig.: Diagram showing plot of potential energy v/s reaction coordinate.

$$t_{1/4} = \frac{0.693}{k} \log 1.333 = 122.6 \text{ min} \quad 2.344 \times 10^{-6}$$

4. Effect of Catalyst

⊙ A catalyst increases (the rate of the reaction without



Reaction
path with
catalyst

undergoing any chemical change till the end of the reaction.

Energy of activation
without catalyst

Fig.: Effect of catalyst on activation energy

⊙ Catalyst alters

1. Rate of reaction
2. Path of reaction
3. Activation energy
4. Threshold energy
5. Rate constant

⊙ Catalyst does not alter

1. ΔG of reaction
2. Entropy of reactants and energy of products
3. ΔH
4. ΔS
5. K_c

Q In some reactions, the rate of the reaction is directly proportional to the concentration of the catalyst.

Eg : In Acid catalysed hydrolysis reactions of esters, the rate is proportional to the concentration of the acid catalyst.

-KEYNOTE - Catalyst increases the rate of reaction by making an alternate path of low activation energy for reactant molecules.

RATE LAW

Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation. ⊙ Let $nA + mB \rightarrow \text{Products}$

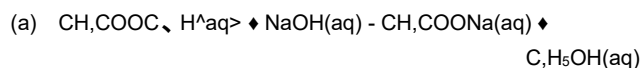
rate, $r \propto [A]^n [B]^m$ Rate equation is obtained

experimentally. **Rate Constant**

⊙ The rate constant of reaction becomes equal to the rate of the reaction when the concentration of all the reactants are unity, hence the rate constant is also known as the specific reaction rate. ⊙ Rate $= k[A]^n [B]^m$
*k' is called rate constant or specific rate or rate per unit concentrations of the reactants.

"Rate"
[unit]

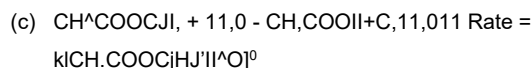
Examples: units of $k = \text{mole}^{-1} \text{L}^n \text{sec}^{-1}$



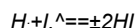
$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{NaOH}]$$



$$\text{Rate} = k[\text{CHCl}_3][\text{Cl}_2]$$



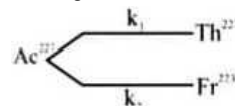
⊙ Rate law equation for reversible reaction



Rate =

$$\text{Rate} = \frac{\text{Rate of forward reaction}}{\text{Rate of backward reaction}}$$

⊙ Rate law equation involving side reactions.



Rate of formation of $\text{Th}^{227} = k_1 [\text{Ac}^{227}]$ Rate of formation of $\text{Fr}^{223} = k_2 [\text{Ac}^{227}]$ Rate $= k_1 + k_2 [\text{Ac}^{227}]$ **Characteristics of Rate constant**

⊙ Rate constant is a measure of (the rate of the reaction. Greater the value of k, faster is the reaction. Similarly, smaller value of rate constant indicates slow reaction.

Q The value of k depends on the nature of the reactants. It is a characteristic constant for a particular reaction at a fixed temperature. Different reactions have different values of k. ⊙ Value of k is a constant for a given reaction, depends only on temperature.

⊙ Units of rate constant depend on the order of reaction.

ORDER OF THE REACTION

Let (here be a reaction: $m_1A + m_2B \rightarrow \text{Products}$). Now, if on the basis of experiment, we find that $\text{Rate} \propto [A]^p [B]^q$

Where p may or may not be equal to m_1 & similarly q may or may not be equal to m_2 .

p is order of reaction with respect to reactant A and q is order of reaction with respect to reactant B and (p + q) is overall order of the reaction

-KEYNOTE -

Order of the reaction can be determined by experimental method only.

For elementary reactions order can be obtained from stoichiometric equation.

But for complex reactions order is to be experimentally calculated.

E.g. $x\text{A} + y\text{B} \rightarrow z\text{C} + \text{products}$ $R = k[\text{A}]^x[\text{B}]^y$

order = $x + y + z$

E.g. Rate = $k[\text{A}]^2[\text{B}]^{-1}$

order = $- + (-1) = -\frac{1}{2}$

Zero order reactions

@ The reaction rate is independent of the concentration of the reactants

Q Some examples of zero order reactions are eg : $(1) \text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$

(II) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

(III) $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$

Q A \rightarrow product

Rate = $k[\text{A}]^0$

@ $k = \frac{-d[\text{A}]}{dt}$

Where C_0 = Initial concentration of reactant C = Concentration of reactant at $t=0$ time x = Concentration of product at t time Q Half-life period ($t_{1/2}$) = $\frac{a}{k}$ Where a = initial concentration

@ Unit of rate constant: $\text{mol L}^{-1} \text{s}^{-1}$

Let us consider a typical first order gas phase reaction $\text{A}(\text{g}) \rightarrow \text{B}(\text{g}) + \text{C}(\text{g})$

Let P_0 be the initial pressure of A and P_t the total pressure of the reaction mixture at time t then

First order reactions

$\text{A} \rightarrow \text{Products}$ $r = k[\text{A}]$

Equation for rate: $-\frac{d[\text{A}]}{dt} = k[\text{A}]$

Equation for rate constant: $2.303 \log \frac{a}{a-x}$

$a-x$

Units for rate constant: sec^{-1} Half life time: $t_{1/2} = \frac{0.693}{k}$

0.695

Second order reactions Q 2A \rightarrow products $r = k[\text{A}]^2$

Wuheny formula: $C_t = C_0 e^{-kt}$

$$k = \frac{2.303}{t} \log \frac{P_0}{(2P_0 - P_t)}$$

Examples :

@ Acid Hydrolysis of ester.

$\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$ @ NH_4NO_3

(aq) $\text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

@ Disintegration of radioactive elements

6.25 $\xrightarrow{t_{1/2}}$

@ Hydrogenation of ethene is an example of first order reaction. $\text{C}_2\text{H}_4(\text{g})$

+ $\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$

Rate = $k[\text{C}_2\text{H}_4]$

@ $\text{Ra} \rightarrow \text{Rn}$

Rate = $k[\text{Ra}]$

Train Your Brain

Q. Calculate $t_{1/2}$: $t_{1/2}$ for a 1st order reaction

$$\ln \frac{a}{a-x} = kt \quad \text{or} \quad \log 2 = \frac{k t_{1/2}}{2.303}$$

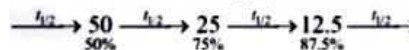
Q. At least how many half-lives should elapse for a 1st order reaction so that the reaction is at least 96.8% completed ? ($\log 2 = 0.3$)

a. 4
93.75%

b. 5

c. 6

A « i. (b) 100



3.125

@ $\text{A} \rightarrow \text{B} + \text{Products}$

$r = M^a H^b$

@ Units for rate constant: lit. mole $^{-1}$ sec $^{-1}$ @ Half lifetime: $t_{1/2}$ (or) $t_{1/2}$

A \rightarrow B \rightarrow products,

a b 0

at time t: a - x b - x

2.303

$t(a-b) \ln(b-x)$

Chemical Kinetics

- Examples:
- (1) $2N_2O \rightarrow 2N_2 + O_2$
 - (2) $2Cl_2O \rightarrow 2Cl_2 + O_2$
 - (3) $Cl_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5O_1H$
 - (4) $2NO \rightarrow 2NO + O_2$
 - (5) $GH_4 + 77 \rightarrow$
 - (6) $2HI \rightarrow H_2 + I_2$

For first order Growth Kinetics

It is used in population growth and bacteria multiplication, $2.303 \log \frac{a}{a-x}$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

When 'a' is initial population and 'a-x' is population after time 't'

nth Order Reactions

Units for rate constant:

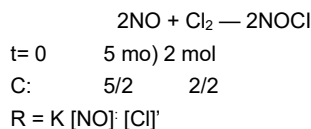
litⁿ . mole¹⁻ⁿ . sec or (atm)ⁿ⁻¹ sec⁻¹ When the order of reaction is n

$$\frac{1}{t} \log \frac{a}{a-x} = k(n-1) \left[\frac{a}{a-x} \right]^n$$

Half life: $t_{1/2}$

Train Your Brain

Q. The reaction $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ is second order in NO and first order in Cl_2 . In a volume of 2 dm³ 5 mole of nitric oxide and 2 mol of Cl_2 were brought together, and the initial rate was 2.4×10^{-3} mole dm⁻³ s⁻¹. What will be the rate when half of the chlorine has reacted? Ans. 4.32×10^{-4} Msec⁻¹



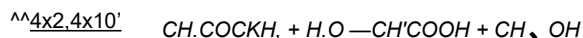
$$2.4 \times 10^{-3}$$

$$= 4 \times 2.4 \times 10^{-3}$$

$$X = 4.32 \times 10^{-4} \text{ w sec}^{-1}$$

$$\# \frac{4 \times 2.4 \times 10^{-3}}{25} \text{ r}^3 T$$

$$25$$



Pseudo Unimolecular reactions

A second order (or of higher order) reactions can be converted into a first order reaction if the other reactant is taken in large excess. Such first order reactions are known as pseudo first order reactions. For $A + B \rightarrow \text{Products}$ (Rate = $k [A]^1 [B]^1$)

$$t(a-b) \log \frac{a(A-x)}{b(A-x)}$$

Now if 'B' is taken in large excess $b \gg a$.

$$\frac{2.303}{bt} \log \frac{a}{a-x} \quad k = \frac{2.303}{bt} \log \frac{a}{a-x}$$

'b' is very large can be taken as constant

$$\Rightarrow kb = \frac{2.303}{t} \log \frac{a}{a-x} \quad \Rightarrow \quad k' = \frac{2.303}{t} \log \frac{a}{a-x}$$

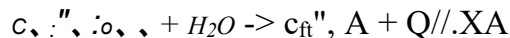
© k is pseudo first order rate constant © k' will

have units of first order. © k will have units of

second order. © Examples of Pseudo 1st order

reactions :

(a) Hydrolysis of cane sugar



(b) Hydrolysis of esters

Train Your Brain

Q. In the reduction of nitric gas with hydrogen, the reaction was found to be 50% complete in 210 seconds when the initial pressure of the mixture was 200 mm. In a second experiment the time of half reaction was 140 seconds when the initial pressure was 300 mm. Calculate the total order of the reaction.

Ans. For a nth order reaction (n l) $\frac{1}{2} \times 2^{n-1}$

$$210 \text{ pO}_2$$

$$UO \sim 1200j$$

$$n = 2$$

-KEYNOTE-

- ♦ If a reactant is present in excess, order w.r.t. this reactant is zero.
- ♦ In the presence of an acid, hydrolysis of ethyl acetate is a pseudo-unimolecular reaction but the actual value of the rate constant depends upon the concentration of H⁺ ions.

Characteristics of First-and Second-Order Reactions of the Type A → Products

	Zero Order	First-Order	Second-Order	n th order
Differential Rate law				
(Integrated Rate law)		$\ln[A]_t = -kt + \ln[A]_0$		
Half-life	$\frac{a}{2k}$	0.693		
	(depends on $[A]_0$)	(Independent of $[A]_0$)	(depends on $[A]_0$)	

MOLECULARITY OF THE REACTIONS

The number of molecules that react in an elementary step is the molecularity of the elementary reaction. Molecularity is defined only for elementary reactions and not for complex reactions. No elementary reactions involving more than three molecules are known, because of very low probability of near-simultaneous collision of more than three molecules.

The rate law for the elementary reaction



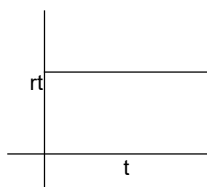
Difference Between Molecularity and order of Reaction

Molecularity of Reaction	Order of Reaction
1. It is defined as the no. of molecules or reactant taking part in the reaction. eg: $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$	1. It is defined as the sum of the powers of concentration terms that appear in rate law. eg: $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$. Rate = $k[\text{NH}_4\text{NO}_2]$
2. It is always a whole number and can neither be zero nor fractional.	2. It may be zero, fractional or even negative w.r.t a particular reaction
3. It is derived from RDS in the mechanism of reaction.	3. It is derived from rate expression.
4. It is theoretical value.	4. It is experimental value.
5. Reactions with molecularity > 4 are rare.	5. Reactions with order 2 or 4 are also rare.
6. Molecularity is independent of pressure and temperature.	6. Order of reaction depends upon pressure and temperature.

METHODS OF DETERMINATION OF ORDER OF REACTION

1. Trial and Error method or Integrated form of rate equation method

Zero order $R \rightarrow P$



First order: $R \rightarrow P$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

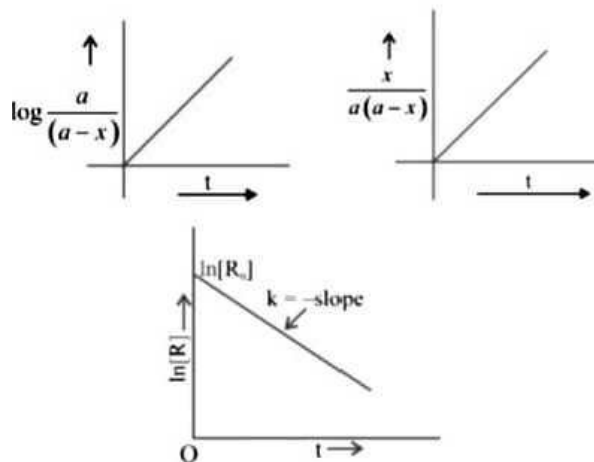


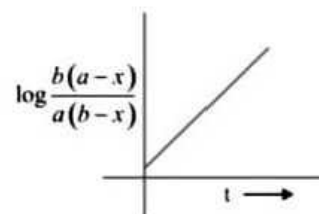
Fig.: A plot between $\ln[R]$ and t for a first order reaction

Second order: $2R \rightarrow P$

$$A = \frac{x}{at(a-x)}$$

Second order $R_1 + R_2 \rightarrow P$

$$\frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$



2. HALF-TIME METHOD

The half lives of each order is unique so by comparing half lives we can determine order of reaction

$$\left(\frac{t_{1/2}}{t_{1/2}'}\right) = \left(\frac{a}{a'}\right)^{n-1}$$

where n = order of reaction

3. Van't Hoff Differential method

For two initial concentrations C₁, C₂, we have

$$-dC_1 = k C_1^{n-1} dt_1 \quad -dC_2 = k C_2^{n-1} dt_2$$

$$\frac{C_1^{1-n}}{1-n} = \frac{C_2^{1-n}}{1-n} + k(t_2 - t_1)$$

4. Ostwald's Isolation method

© This method is useful for reaction which involve a large number of

reactants. In this method, the concentration of all the reactants are taken in large excess except that of one. rate = k(A^aB^bC^c)

[B]^a[C]^b[A]^c

Then value of 'a' can be calculated by previous methods and similarly 'b' and 'c' can also be calculated.

COLLISION THEORY OF REACTION RATES OR KINETIC MOLECULAR THEORY

© The reactant molecules collide with each other and exchange their bonds to convert into products. Without collision there is no reaction. This is called collision theory.

© Collision theory is applicable only for gaseous covalent molecular reactions, not for ionic reactions.

© The rate of the reaction at any given temperature is expected to be proportional to the number of collisions taking place between the reactant molecules in unit time at that temperature. © The actual rate of the reaction is much smaller than the rate calculated from the number of binary collisions of the reacting molecules taking place in unit time.

@ The number of collisions taking place in one second in one litre of an equimolar mixture of H₂ and I₂ (g) at STP is around 10³⁴.

© Collision theory was proposed by Arrhenius. The main principles of collision theory are

Q Collisions must occur between the molecules of reacting gases for a reaction to occur.

Q All collisions do not lead to the formation of products. (Only fruitful collisions lead to formation of products)

© The minimum amount of energy possessed by the colliding molecules to the formation of products or reaction to occur is known as threshold energy.

© The energy possessed by the molecules at STP is known as normal energy or internal energy.

© Normal energy possessed by molecules is always less than threshold

energy.

© The energy to be gained by the molecules during the collision to convert into products is known as activation energy or energy of activation.

© Activation energy = Threshold energy - energy of colliding molecules.

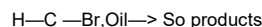
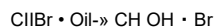
© Activation energy increases, the rate of the reaction decreases. © No. of binary collisions per unit time (Z) is

$$Z = \frac{1}{V} \sum_{i,j} n_i n_j \sigma_{ij} \left(\frac{v_i + v_j}{2} \right)$$

σ_{AB} = collision diameter ;

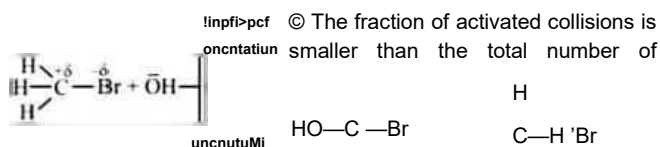
μ = reduced mass

© Specific rate, k = p Z e^{-E_a/RT} or k = A e^{-E_a/RT} © The collisions in which molecules collide with sufficient kinetic energy (called threshold energy) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collisions. Whereas improper orientation makes them simply bounce back and no products are formed. For example, formation of methanol from bromo methane.



100%

Fig.: Diagram showing molecules having proper and improper orientation



Intermediate

collisions.

© Actual rate of reaction is much smaller than the rate of the reaction calculated on the basis of the normal collisions.

Collision Frequency (Z)

Total number of collisions which occur among the reacting molecules per second per unit volume is called collision frequency. Its value is given by $Z = \frac{1}{2} n^2 \sigma v$

v = average velocity

σ = molecular diameter in cm

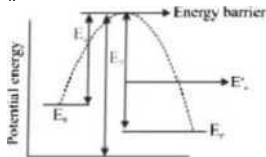
n = number of molecules per cc. ∴ Rate (k) = Z e^{-E_a/RT}

CONCEPT OF ACTIVATION ENERGY

The difference between the energy barrier (i.e., threshold energy) E_a and the energy of normal molecules E_R is called activation energy E_a.

Chemical Kinetin

$$E_a = E_T - E_R$$



Kig.: Reaction Coordinate

$$E_j - E_R - E_a = \text{activation energy of the forward energy } E_j - E_P = E_p = \text{activation energy of the backward energy}$$

TRANSITION STATE

THEORY

According to this theory, the bimolecular reaction between two molecules passes through the formation of activated complex which then decomposes to yield the product AB, shown below

The constant 'A' has unit of time^{-1} and is constant for a given reaction.

-KEYNOTE -

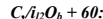
At very high temperature rate becomes equal to frequency factor. i.e., $k = A$.

PHOTOCHEMICAL REACTION

Reactions which take place by the absorption of radiations of suitable wavelength

Photosynthesis of carbohydrates in plants takes place in presence

of chlorophyll and sunlight



The free energy change of a photochemical reaction may not be negative. In the synthesis of carbohydrates and formation of HCl, ΔG is +ve.

OTHER IMPORTANT RELATIONS © Zero order reactions

$$(i) \frac{x_1}{t_1} = \frac{x_2}{t_2}$$

(>>i)

First order reactions:

$$(\frac{1}{t}) \propto \frac{1}{t} \Rightarrow \frac{1}{t} = \frac{1}{t} \cdot \frac{1}{t} = \frac{1}{t^2}$$

$$(ii) \frac{1}{t} \propto \frac{1}{t} \Rightarrow \frac{1}{t} = \frac{1}{t} \cdot \frac{1}{t} = \frac{1}{t^2}$$

$$\frac{1}{t} = \frac{1}{t} \cdot \frac{1}{t} = \frac{1}{t^2}$$

$$t > t_0$$

Second order reactions:

$$(ii) \frac{1}{t} = \frac{1}{t} \cdot \frac{1}{t} = \frac{1}{t^2}$$

$$(iii) \frac{1}{t} = \frac{1}{t} \cdot \frac{1}{t} = \frac{1}{t^2}$$

INTRODUCTION

It deals with

- ⊙ The use of electrical energy for the dissociation of chemical compounds (electrolysis)
- The use of chemical reactions for the production of electrical energy (electrochemical cells)
- ⊙ The use of electrical energy in the study and preparation of chemical substances.
- ⊙ The commercial power generating cells, namely secondary cells (batteries & fuel cells)

The basis of electrochemistry is thus a process in which electrons

are transferred from one system to another. I CELL

Cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge.

Cells are of two types

Electrochemical cell or Galvanic cell or Voltaic cell	Electrolytic cell
A spontaneous chemical reaction generates an electric current.	An electric current drives a non-spontaneous reaction.

-KEYNOTE -

The two types of cells are therefore reverse of each other.

Galvanic Or Voltaic Cell

Working Principle

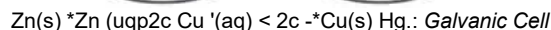
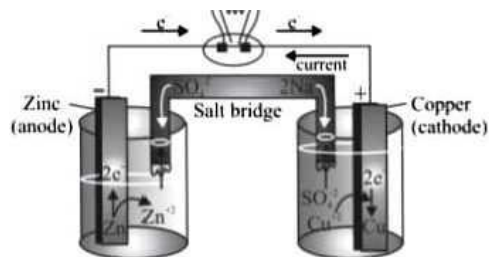
The cell in which chemical energy is converted into electrical energy is called Galvanic cell.

Whenever a metal strip is put in an electrolyte the process of oxidation and reduction takes place simultaneously within the system. Due to this there is a potential difference between the metal phase and the liquid phase.

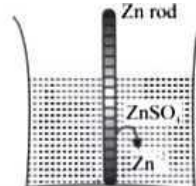
On joining the metal strips through a wire (of negligible resistance) the current flows as long as the potential difference exists between the metal phase and the liquid phase.

Construction of Cell

- ⊙ It has two half-cells, each having a beaker containing a metal strip dipped in its aqueous solution.
- ⊙ The metal strips are called electrodes and are connected by a conducting wire.
- ⊙ Two solutions are connected by a salt bridge.
- ⊙ The oxidation and reduction half reactions occur at separate electrodes and electric current flows through the wire.



Zn rod is placed in ZnSO₄ solution.

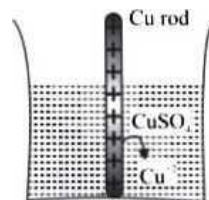


The Zn atom will move in the solution to form Zn²⁺. After some time following equilibrium will be established.



This particular electrode is known as anode :

- ⊙ On anode, oxidation will take place (release of electron). ⊙ Act as source of electrons.
- ⊙ It is of negative polarity.
- ⊙ The electrode potential is represented by $E_{\text{Zn}^{2+}|\text{Zn}}^{\circ}$ (anode) (Cathode)



Some metals (Cu, Ag, Au etc.) are found to have the opposite tendency i.e. when placed in contact with their aqueous ions, the ions from the solution will get deposited on the metal rod. The following equilibrium will be established : $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Cu(s)}$.

This will be known as cathode.

- ⊙ At cathode reduction will take place (gain of electron). ⊙ Act as sink of electron.
- ⊙ Positive polarity will be developed.
- ⊙ Their electrode potential can be represented by $E_{\text{Cu}^{2+}|\text{Cu}}^{\circ}$ (cathode)

Is where oxidation occurs Is where electrons are produced Has a negative sign

Is where reduction occurs Is where electrons are consumed ... Has a positive sign

Selection of electrolyte for Salt Bridge © The electrolyte should be inert.

- © The electrolyte in salt bridge should be such that speed of it's cation equals speed of its anion in electrical field.

Functions of Salt Bridge

- © A salt bridge is a U shaped invened lube that contains a gel permeated with an incri electrolyte.
- © It connects the solution of (wo half cell to complete the circuit. ©

It maintains the electrical neutrality of the solution in order to give continuous flow or generation of current.

Daniel Cell

- © in Daniel cell instead of salt bridge, porous pot (or) porous diaphragm is used.

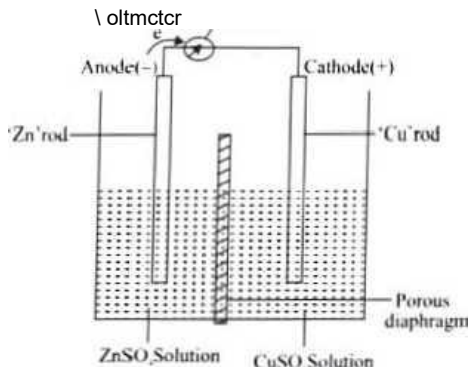


Fig.: Daniel cell having electrodes of Zinc and Copper dipping in the solution of their respective salts

-KEYNOTE -

Daniel cell is also an electrochemical cell.

Shorthand Notation for Galvanic Cells

We require two half cells to produce an electrochemical cell, which can be represented by following few rules:

- The anode half-cell is always written on the left followed on the right by cathode half cell.
- The separation of two phases (state of matter) is shown by a vertical line.
- The various materials present in the same phase are shown together using commas.
- The salt bndge is represented by a double slash (||).
- The significant futures of the substance viz. pressure of a gas. concentration of ions etc. arc indicated in brackets immediately after writing the substance.
- For a gas electrode, the gas is indicated after the electrode for anode and before the electrode in ease of cathode (i.c. Pt. H_2/H .or H/H^+PO

Direction ofc flow

Anode kgl fee JI Cathod(^half-ccll

- $^{(aq. IM^+ || Cl_2(g. 1 atm))Cl^-(aq. IM)}C(s)$
 $Cu(s)^{+}Cu^{+}$ f \ /
Phase boundary Salt bridge

- © If it is Daniel cell

® Zn: $Zn^{+}(c)||Cu^{+}(c); Cu$

- © In ease of a Galvanic cell with a non-metal electrode, inert metal like Pt rod (wire) is introduced in solution which acts as electrode.

A Galvanic cell confining H₂ and Cl₂ gases as electrodes in an HCl solution is rprcsnclcd as.

Pt. H₂(g) (P, atm) | HCl(aq) (C mol / L) | Cl₂(P, atm). Pt

Difference Between Electrochemical Cell And Electrolytic Cell

1 S. No	Electrochemical Cell	Electrolytic Cell	1
1.	It is a combination of two half cells, containing the same or diflcrcnc elcclrodc in the same or diflerent electrolyics.	It is a single cell containing the same electrodes present in the same electrolyte.	
2.	Anode is negative. Cathode is positive.	Anode is posilivc. Cathode is negative.	
3.	It converts chemical energy into electrical energy. produced as a result of redox reaction.	It converts electrical energy into chemical energy. Energy is supplied to the electrolytic solution (o bring about (he redox reaction.	
4.	Cell reaction is spontaneous.	Cell reaction is non-spontaneous.	
5.	Salt bridge is required.	No salt-bridge is required.	
6.	It is source of EMF.	It require EMF.	
7.	It reversible and spontaneous.	It is irreversible and non-spontaneous.	

ELECTRODE POTENTIAL

- © The potential diflcrcncc developed between metal electrode and its ions in solution is known as electrode potential. © Electrode potential depends upon :

- Concentration of the solution.
- Nature of the metal.
- Nature of the electrolyte.
- Pressure, temperature conditions

Electrode Potential

Okidation Potential (O.P.)

- The deurodc potential for oxidation half read ion
- Tendency lo get oxidised
- Grealer l he O.P. then greater will be tendency to get oxidised.

Reduction PotcntiaKR.P.)

- The electrode potential for reduction half reaction
- Tendency to get reduced.
- (ircater the R.P.. greater will be tendency to get reduced.

Standard Electrode Potential (E°)

The potential diflcrcncc developed bclwcen metal electrodes and the solution of its ions al 1 M concntration at 1 bar pressure and 298 K is known as standard electrode potential or standard roduction potential (old name).

Table: Different types of electrode and their reaction in standard condition

	Type of Electrode	Electrode reaction in standard condition	Representation
1..	Metal electrode (Zn electrode, Cu electrode etc)	Reduction: $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn(s)}$ Oxidation: $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	
2..	Hydrogen peroxide electrode	Reduction: $2\text{H}^+ + \text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$ Oxidation: $\text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + \text{O}_2 + 2\text{e}^-$	$\text{H}_2\text{O}_2/\text{H}_2\text{O}$
3..	Redox electrode	Reduction: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	$\text{MnO}_4^-/\text{Mn}^{2+}$
4..	Metal-Metal salt (insoluble electrode)	Reduction: $\text{AgCl(s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^-$ Oxidation: $\text{Ag(s)} + \text{Cl}^- \rightarrow \text{AgCl(s)} + \text{e}^-$	$\text{AgCl(s)}/\text{Ag(s)}$

-KEYNOTE -

Train Your Brain

- According to IUPAC, the given value of electrode potential is regarded as reduction potential unless it is specifically mentioned.
- The reduction potential of an electrode is exactly equal in magnitude but opposite in sign to its oxidation potential.

Electromotive Force (Or Emf) Of The Cell/Cell Potential

The difference in electrical potentials of the two half-cell reactions (oxidation half cell and reduction half cell) is known as emf of the cell or cell potential.

Cell potential $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$ [where, E_{anode} (anode) = oxidation potential of anode & (cathode) = reduction potential of cathode]

Cell potential $E_{\text{cell}} = E_{\text{reduction potential}} - E_{\text{oxidation potential}}$

Cell potential $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

Free Energy Change For Cell Reaction

The free energy change, ΔG (a thermochemical quantity) and the cell potential E (an electrochemical quantity) both measure the driving force of a chemical reaction.

The values of ΔG and E are directly proportional and are related by the equation.

Where n = Number of moles of electron transferred in the reaction.

F Faraday constant = 96485 C/mol e^- = 96500 C/mol e^-

-KEYNOTE -

Cell potential is an intensive property so on multiplying/dividing cell reaction by any number, the value would not change.

1. Write shorthand notation for the following reaction. $\text{Sn}^{2+}(\text{aq}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2\text{Ag(s)}$.

Ans. The cell consists of a platinum wire anode dipping into an Sn^{2+} solution and a silver cathode dipping into an Ag^+ solution therefore $\text{Pt(s)} | \text{Sn}^{2+}(\text{aq}), \text{Sn}^{4+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag(s)}$.

2. Write the electrode reaction and the net cell reaction for the following cells. Which electrode would be the positive terminal in each cell?

- a. $\text{Zn} | \text{Zn}^{2+} || \text{Br}_2 | \text{Pt}$ b. $\text{Cr} | \text{Cr}^{3+} || \text{I}_2 | \text{Pt}$
c. $\text{Pt} | \text{H}_2 | \text{H}^+ || \text{Cu}^{2+} | \text{Cu}$ d. $\text{Cd} | \text{Cd}^{2+} || \text{Cl}^- | \text{AgCl} | \text{Ag}$

- a. Oxidation half cell reaction: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
reduction half cell reaction: $\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$
Net cell reaction: $\text{Zn} + \text{Br}_2 \rightarrow \text{Zn}^{2+} + 2\text{Br}^-$ +ve terminal: Pt
- b. Oxidation half reaction: $\text{Cr} \rightarrow \text{Cr}^{3+} + 3\text{e}^-$
reduction half reaction: $\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$
Net cell reaction: $2\text{Cr} + 3\text{I}_2 \rightarrow 2\text{Cr}^{3+} + 6\text{I}^-$ +ve terminal: Pt
- c. Oxidation half reaction: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$
reduction half reaction: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
Net cell reaction: $\text{H}_2 + \text{Cu}^{2+} \rightarrow \text{Cu} + 2\text{H}^+$ +ve terminal: cathode Pt
- d. Oxidation half reaction: $\text{Cd} \rightarrow \text{Cd}^{2+} + 2\text{e}^-$
reduction half reaction: $[\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-] \times 2$
Net cell reaction: $\text{Cd} + 2\text{AgCl} \rightarrow \text{Cd}^{2+} + 2\text{Ag} + 2\text{Cl}^-$ +ve terminal: cathode Ag

ELECTROCHEMICAL SERIES

- In the electrochemical series, the metals are arranged in the increasing order of reduction potential.
- High reduction potential metal ions undergo reduction first on cathode or it acts as cathode in the electrochemical cell.
- Low reduction potential metal (high negative value) undergo oxidation (or) it acts as anode. It is more reactive (or) more electropositive.
- In the electrochemical series metal placed above can displace the below metal ions from their solution.

Table: Electrochemical Series

Electrode	Reaction	SRP(at 298 K)
•Li	$\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$	-3.05 V
K	$\text{K} \rightarrow \text{K}^+ + \text{e}^-$	-2.93 V
Ca	$\text{Ca} \rightarrow \text{Ca}^{2+} + 2\text{e}^-$	-2.87 V
Na	$\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$	-2.71 V
Mg	$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$	-2.37 V
Al	$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$	-1.66 V
• Electrolytes (H ₂ O)	$\text{H}_2\text{O(l)} + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2\text{(g)} + \text{OH}^-\text{(aq)}$	-0.83 V
•Zn	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	-0.76 V
Cr	$\text{Cr} \rightarrow \text{Cr}^{3+} + 3\text{e}^-$	-0.74 V
•Fe	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$	-0.44 V
Cd	$\text{Cd} \rightarrow \text{Cd}^{2+} + 2\text{e}^-$	-0.40 V
Co	$\text{Co} \rightarrow \text{Co}^{2+} + 2\text{e}^-$	-0.277 V
Ni	$\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$	-0.24 V
Sn	$\text{Sn} \rightarrow \text{Sn}^{2+} + 2\text{e}^-$	-0.14 V
Pb	$\text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}^-$	-0.13 V
	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{(g)}$	0.00 V
Cu	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$	0.34 V
>2	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.54 V
Fc	$\text{Fc} \rightarrow \text{Fc}^+ + \text{e}^-$	0.77 V
Hg	$\text{Hg} \rightarrow \text{Hg}^{2+} + 2\text{e}^-$	0.79 V
Ag	$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$	0.80 V
Hg	$\text{Hg} \rightarrow \text{Hg}_2^{2+} + 2\text{e}^-$	0.85 V
Br ₂	$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.06 V

↑
increasing strength of reducing agent

↓
increasing strength of oxidising agent

© Cell potentials depend on temperature and on the composition of the reaction mixtures.

© It depends upon the concentration of the solute and the partial pressure of the gas, if any.

© The dependence upon the concentration can be derived from thermodynamics.

From thermodynamics

$$\Delta G = \Delta G^\circ + RT \ln Q = -nFE_{\text{cell}} + 2.303 RT \log Q$$

$$2.303 RT$$

Taking T=298K. R = 8.314 J/mol K. F = 96500 C Now we get.

1.23V

1.33V

1.36V

1.51 V

2.87 V

Train Your Brain

Q. Calculate E°_{cell} of (at 298 K).

$\text{Zn(s)} \mid \text{ZnSO}_4(\text{aq}) \parallel \text{CuSO}_4(\text{aq}) \mid \text{Cu(s)}$ given that, $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.76 \text{ V}$; $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$

M

Ans. = (S.R.P)_{cathode} - (S.R.P)_{anode} = $0.34 - (-0.76) = 1.1 \text{ V}$

Q. Given the cell $\text{Ag} \mid \text{AgCl(s)} \mid \text{NaCl (0.05 M)} \parallel \text{AgNO}_3 (0.30 \text{ M}) \mid \text{Ag}$

- Write half reaction occurring at the anode.
- Write half reaction occurring at the cathode.
- Write the net ionic equation of the reaction, d Calculate E°_{cell} , at 25°C .

e. Does the cell reaction go spontaneous as written ? (Given $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}$, $E^\circ_{\text{AgCl}/\text{Ag}} = 0.22 \text{ V}$)

=+ 0.22 volt); $E^\circ_{\text{cell}} = + 0.80 \text{ volt}$)

Ans. (a) LHS electrode is anode and half reaction is oxidation. $\text{Ag} + \text{Cl}^- \longrightarrow \text{AgCl(s)} + \text{e}^- \dots \text{(i)}$

(b) RHS electrode is cathode and half reaction is reduction. $\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag(s)} \dots \text{(ii)}$

(c) From equation (i) and (ii) cell reaction is : $\text{Cl}^- (0.05 \text{ M}) + \text{Ag}^+ (0.30 \text{ M}) \longrightarrow \text{AgCl(s)}$

(d) $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = (0.80 - 0.22) \text{ volt} = 0.58 \text{ volt}$

(c) Yes. the c.m.f value is positive, the reaction will be spontaneous as written in the cell reaction.

Important points about this series

© Metals near the top of the series are strongly electropositive (or weakly electronegative). They lose electrons readily to give cations.

silver displaces gold from gold salt solution as in photography during gold toning process.

- Hydroxides of metals in the upper part of the series are strongly basic and their salts do not undergo hydrolysis. On the other hand, hydroxides of the metals in the lower part of the series are weakly basic and their salts undergo hydrolysis.
- Metals lying above hydrogen are easily rusted. Those situated below are not rusted.
- Metals above hydrogen displace hydrogen from dilute acids.
- More strongly electropositive metals like K, Na, Ca, etc. displace hydrogen from water.
- Iron and other metals above it decompose steam and liberate hydrogen.
- Oxides of iron and other metals below it can be reduced easily.

Oxides of manganese and other metals above it are reduced when heated in a current of hydrogen.

- Oxides of mercury and other metals below it are decomposed on heating.

Train Your Brain

Q. Given that $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.337\text{V}$ and $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = -0.153\text{V}$

then calculate

Ans. (i) $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ AG^o

(ii) $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$ AG^o

after adding $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ AG^o + AG^o = AG^o = -2FE^o = -FE^o

$E^\circ_{\text{cell}} = 2E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$

$= 2 \times 0.337 - (-0.153) = 0.674 - (-0.153) = 0.827\text{V}$

NERNST EQUATION

Nernst equations can be applied to half cell reactions also.

Applications of Nernst equation

$$E_{\text{Red}} = E^\circ_{\text{red}} - \frac{0.059}{n} \log \left[\frac{M(s)}{M^{n+}} \right]$$

$$E_{\text{Red}} = E^\circ_{\text{red}} - \frac{0.059}{n} \log \left[\frac{1}{M^{n+}} \right]$$

$$E_{\text{Red}} = E^\circ_{\text{red}} + \frac{0.059}{n} \log [M^{n+}]$$

Nernst Equation for Electrode Potential

$M^{n+}(\text{aq}) + n\text{e}^- \rightleftharpoons M(\text{s})$

$\text{H}_2(\text{g}) \rightleftharpoons 2\text{H}^+(\text{aq}) + 2\text{e}^-$

2303/RT

$$\log \left[\frac{(H^+)^2}{P_{H_2}} \right]$$

$\Rightarrow E_{\text{Kcd}} =$

Hydrogen Electrode

$$E_{\text{Red}} = E^\circ_{\text{red}} - \frac{2.303 RT}{nF} \log \left(\frac{1}{Zn^{+2}} \right)$$

$$E_{\text{Red}} = E^\circ_{\text{red}} - \frac{0.059}{2} \log \left(\frac{1}{Zn^{+2}} \right)$$

Metal-metal soluble salt electrode $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$

at 298K

Gas electrode - Hydrogen electrode $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

$$E_{\text{Red}} = E^\circ_{\text{red}} - \frac{0.059}{2} \log \left(\frac{P_{H_2}}{[H^+]^2} \right)$$

Redox electrode

$4\text{H}_2\text{O} + \text{Mn}^{2+} \rightarrow \text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^-$

$$E_{\text{ox}} = E^\circ_{\text{ox}} - \frac{0.059}{5} \log \left[\frac{[\text{MnO}_4^-][H^+]^8}{[\text{Mn}^{2+}]} \right]$$

0.059/n

Nernst Equation for cell Potential

$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

n = no. of electrons exchanged during the reaction.

cone, of anode
cone, of cathode

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log Q$$

For example: in the cell $\text{Cu}|\text{Cu}^{2+}||\text{Ag}^+|\text{Ag}$ the cell reaction is $\text{Cu(s)} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 0.059 \log \left[\frac{[\text{Ag}^+]^2}{[\text{Cu}^{2+}]} \right]$$

Calculation of equilibrium constant (K°) from Nernst Equation

$$\Delta G^{\circ} = -nFE^{\circ}$$

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

From thermodynamics, $\Delta G^{\circ} = \Delta G^{\circ} + RT \ln Q$

at chemical equilibrium, $\Delta G^{\circ} = 0$, $E_{\text{cell}}^{\circ} = 0$ — cell will be of no use

$$\text{so, } \Delta G^{\circ} = -RT \ln K_{\text{eq}}$$

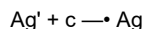
$$\text{at equilibrium, } -nFE^{\circ} = -2.303 RT \log (K^{\circ}) \quad \log K^{\circ} = \frac{2.303 n E^{\circ}}{RT}$$

$$\text{at } 298 \text{ K and } R = 8.314 \text{ J/molK}$$

105X, 1E1

$$K_{\text{eq}} = 10^{nE^{\circ}/0.059}$$

$E^{\circ} = \frac{\text{no. of } e \text{ involved in oxidation / reduction}}{\text{Molar mass}}$ eg.



We know that.

1 mole of $e^- = 1$ Faraday of charge.

i.e. 96500 C of charge deposits E gram metal ($E = \frac{W}{Q}$)

$$1. \quad 96500 \text{ J} = 96500$$

$$\text{So, } W = \frac{JQ}{96500} = \frac{\text{Molar mass}}{96500} \times Q = \frac{W}{96500} \quad (\text{no. of } e \text{ involved})$$

$$W = \frac{L \times 965(X)}{96500} \quad \text{Molar mass}$$

2nd Law: When equal charge is passed through 2 electrolytic cells and these cells are connected in series then mass deposited at electrode will be in the ratio of their electrochemical equivalents or in the ratio of their equivalent masses.

ELECTROLYSIS

- ⊙ Electrolyte is a combination of cations and anions which in fused state can conduct electricity.
- ⊙ This is possible due to the movement of ions from which it is made of.
- ⊙ The process of using an electric current to bring about chemical change is called electrolysis.
- ⊙ Electrolysis is a process of oxidation and reduction due to current flow.
- ⊙ The product obtained during electrolysis depends on following factors:
 - (a) The nature of the electrolyte
 - (b) The concentration of electrolyte
 - (c) The charge density flowing during electrolysis.
 - (d) The nature of the electrode

Faraday's law of Electrolysis

- (i) 1st Law: The mass deposited/released/produced of any substance during electrolysis is proportional to the amount of charge passed into the electrolyte.

$$W \propto Q \quad W = ZQ$$

Where, Z = electrochemical equivalent of the substance, Q = charge

$$\text{Unit of } Z = \frac{\text{Kg/C or g/C}}{\text{coulomb}}$$

- ⊙ Z is defined as mass deposited when 1 C of charge is passed into the solution.

Equivalent mass (E) : Mass of any substance produced when 1 mole of e^- arc passed through the solution during electrolysis.

$$W = ZP = 96500$$

$$\frac{A}{E_2} \quad (0 = \text{same})$$

Train Your Brain

Q. The time required to coat a metal surface of 80 cm^2 with 0.005 mm thick layer of silver (density = 10.5 gm cm^{-3}) with the passage of 3 A current through silver nitrate solution is:

Ans. ... Volume of layer of silver = $0.005 \times 10^{-3} \times 80 = 0.04 \text{ cm}^3$... mass = Density * volume = $10.5 \times 0.04 = 0.42 \text{ gm}$

$$\frac{W}{96500} = \frac{0.42}{96500} \times \frac{3 \times 60 \times 60}{1000}$$

$$\frac{0.42 \times 96500}{108 \times 3} \approx 125.09 \text{ seconds}$$

ELECTROLYTIC CONDUCTANCE

Conductor

Metallic Conductors

1. Charge carriers are e^-
2. No chemical changes
3. No transfer of mass
4. Resistance is because of collision of e^- with fixed metal atoms.
5. Temp $\propto R$
6. Low resistance generally (good conductor).

Electrolytic Conductors

1. Charge carriers are ions (cations/anion)
2. Decomposition of electrolyte takes place.
3. Transfer of mass
4. Resistance is because of collision of ions with solvent molecules & because of interionic force of attraction
5. Temp $\propto R$
6. High resistance generally

Factors Affecting Conductance & Resistance

- © Solute - Solute interactions (Inter - ionic force of attraction): Greater the force of attraction, greater will be the resistance. $\left[\frac{\text{Force} \times \text{Charge}^2}{r^2} \right]$
- © Solute - Solvent interaction (Hydration/Solvation of ions): Greater the solvation, greater will be resistance. Solvation \propto Charge \propto —

size

Sample

Li^+ (Hydrated largest); Cs^+ (Hydrated smallest)

Resistance of $\text{LiCl} >$ resistance of CsCl

3. Solvent-solvent interaction (Viscosity): Greater the viscosity, greater will be resistance.

4. Temperature: $r \propto \frac{1}{T}$

5. Nature of electrolyte :
- Weak electrolyte high resistance
- Strong electrolyte - Low resistance.

Resistance

$$R = \rho \left(\frac{l}{A} \right)$$

ρ - resistivity/specific resistance (constant).

SI unit is $\Omega \cdot \text{m}$

RA

Resistivity of a solution is defined as (the resistance of the solution between two electrodes of 1 cm: area of cross section and 1 cm apart,

or

Resistance of 1 cm³ of solution will be its resistivity.

Conductance

$$G = \frac{1}{R} = \text{mho} = \Omega^{-1}$$

=S (Siemens)

Conductivity/specific conductance:

$$\frac{l}{K} = \frac{\rho \cdot l}{RA} = \frac{\rho \cdot l}{\kappa \cdot A} \Rightarrow \kappa = \frac{\rho \cdot l}{RA} \quad \text{constant unit: } \Omega^{-1} \text{ cm}^{-1}$$

=conductivity of 1 cm³ of solution \propto concentration of ions

$\frac{l}{A}$

$\frac{\rho}{RA}$

κ (no. of ions) no. of charge carriers

- © Since conductivity or resistivity of the solution is dependent on its concentration, so two more type of conductivities are defined for the solution.

Molar conductivity/molar conductance : © Conduct of a solution containing 1 mole of an electrolyte between 2 electrodes which are 1 cm apart.

Let the molarity of the solution be $\times C$

C moles of electrolyte are present in 1 L. of solution.

so molar conductance = $\frac{\kappa}{C}$

Normality

Normality © Its unit is $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

Equivalent conductance : Conductivity of a solution containing 1 g equivalent of the electrolyte.

" equivalent conductivity/conduction.

Normality

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

$$\Rightarrow \frac{\kappa \times 1000}{C} = \frac{\text{Normality}}{\text{Molarity}}$$

© Its units is $\Omega^{-1} \text{ cm}^2$

eq⁻¹.

Train Your Brain

Q. If resistivity of 0.8 M KCl solution is $2.5 \times 10^{-3} \Omega \text{ cm}$ calculate Λ_m of the solution.

$$2.5 \times 10^{-3} \Omega \text{ cm}$$

Variation of conductivity and molar conductivity with concentration

- © Conductivity always decreases with the decrease in concentration both for weak and strong electrolytes.
- © The number of ions per unit volume that carry the current in a solution decreases on dilution.
- © Molar conductivity increases with decrease in concentration. This is because the total volume, V of solution containing one mole of electrolyte also increases.
- © Molar conductivity is the conductance of solution.
- © When concentration approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol Λ° .

Strong Electrolytes

- © For strong electrolytes, Λ increases slowly with dilution and can be represented by the equation $\Lambda = \Lambda^\circ - AC^{1/2}$
- © The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte i.e. the charges on the cations and anions produced on the dissociation of the electrolyte in the solution.
- Example : Thus NaCl , CaCl_2 , MgSO_4 are known as I-I, 2-1, 2-1

☺ All electrolytes of a particular type have the same value for 'A'

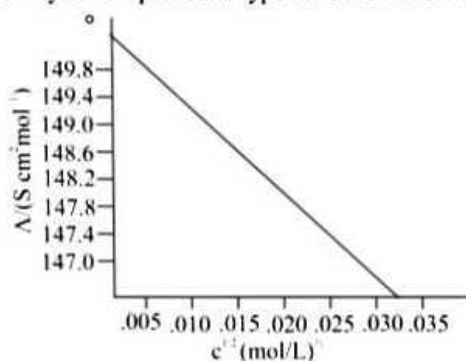


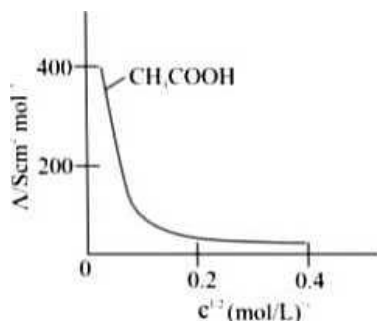
Fig.: Variation of Λ against $c^{1/2}$

Weak electrolytes

☺ Weak electrolytes like acetic acid have lower degree of dissociation at higher concentration and hence for such electrolytes, the change in Λ with dilution is due to increase in the number of ions in total volume of solution that contains 1 mol of electrolyte.

☺ At infinite dilution (i.e. concentration $c \rightarrow 0$) electrolyte dissociates completely ($\alpha = 1$), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately.

Molar conductivity versus $c^{1/2}$ for acetic acid (weak electrolyte)



Effect of Dilution

☺ With dilution " Λ " as well as " Λ_m " of both weak/strong electrolytes increases.

☺ Specific conductivity (κ) decreases with dilution because of decrease in no. of ions per cm^3 of electrolyte.

☺ The molar (or) equivalent conductance of an electrolyte at infinite dilution (or) zero concentration is known as limiting molar conductance (or) limiting equivalent conductance.

○ Λ_0 value for any strong electrolyte is calculated graphically but for weak electrolyte it is determined by Kohlrausch's law.

☺ The magnitude of increase in molar conductance for weak electrolyte is much larger than that for a strong electrolyte because strong electrolytes are almost completely ionised in all concentration and increase in Λ_{eq} (or) Λ_m with dilution is only due to decrease in interionic attractions.

Temperature

The conductivity of all electrolytes increases with increase in temperature.

CONDUCTANCE RATIO (α)

The ratio of the equivalent conductance at any concentration Λ_c to that at infinite dilution (Λ_0) is called conductance ratio (α).

$$\alpha = \frac{\Lambda_c}{\Lambda_0}$$

For weak electrolytes, α = degree of ionisation.

-KEYNOTE - α is high for 0.01 M CH_3COOH solution when compared to that of 0.1 M CH_3COOH , because Λ_c is high in case of 0.01 M CH_3COOH .

DEBYE - HUCKEL - ONSAGER EQUATION

- ☺ In the case of weak electrolytes like CH_3COOH , α is known as degree of dissociation (or) degree of ionisation of electrolyte.
- ☺ The equivalent conductance at large dilution (or) at very low concentration is known as equivalent conductance at infinite dilution (Λ_0 or zero concentration (Λ_0)).
- ☺ The equivalent conductance of an electrolytic solution at any concentration (C) is related to Λ_0 for solutions is given by the following Debye-Huckel - Onsager equation.

$$\Lambda_c = \Lambda_0 - \left[\frac{82.4}{\Lambda_0} \right] C^{1/2}$$

$$\sqrt{C}$$

Where

D = Dielectric constant of water T = Temperature in kelvin scale Λ_c = Equivalent conductance at concentration ' C ' Λ_0 = equivalent conductance at almost zero concentration or infinite dilution.

H = viscosity coefficient of solvent.

In short form this equation is represented as

$$\Lambda_c = \Lambda_0 - b\sqrt{C}$$

Where b is constant and depends on the nature of the solvent and temperature.

KOHLRAUCH'S LAW

☺ Based on κ (specific conductance) value, electrolytes are of two types.

- (i) weak electrolytes: These have low ' κ ' value Eg: weak acids, weak bases.
- (ii) Strong electrolytes: These have high ' κ ' value Eg: strong acids, strong bases. Salt solutions.

☺ The conductance of an electrolyte is due to its ionisation.

☺ The ionisation extent reaches maximum for weak electrolytes as dilution reaches maximum.

-KEYNOTE - ClCH_2COOH has higher ' α ' value than CH_3COOH since ClCH_2COOH is stronger acid than CH_3COOH .

Statement of Kohlrausch's Law

"The equivalent conductance at infinite dilution (Λ_{∞}) of an electrolyte is equal to the algebraic sum of equivalent conductances (or) mobilities of anion (X_{∞}) and cation (A_{∞}) of the electrolyte at infinite dilution"

$$\Lambda_{\infty}(\text{electrolyte}) = \lambda_{\infty}^+ + \lambda_{\infty}^- (\text{ions})$$

$$\Lambda_{\infty} = \frac{1}{n^+} \lambda_{\infty}^+ + \frac{1}{n^-} \lambda_{\infty}^-$$

Train Your Brain

Q. At infinite dilution the equivalent conductance of Al^{3+} and SO_4^{2-} ions are 189 and $160 \text{ cm}^2 \text{ eq}^{-1}$ respectively. Calculate the equivalent and molar conductivity at infinite dilution of $\text{Al}_2(\text{SO}_4)_3$.

$$2 \times 189 + 3 \times 160 = 1437 \text{ cm}^2 \text{ eq}^{-1} \text{ Molar conductivity} = \lambda \times V.F. = 1437 \times 6 =$$

$$8622 \text{ cm}^2 \text{ mol}^{-1}$$

Where n^+ and n^- are charge on each ion furnished by electrolyte. This law is valid at any dilution but is applied only at infinite dilution.

Whereas "molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivities of the cations and the anions each multiplied by the number of ions present in one formula unit of electrolyte" e.g. $\Lambda_{\infty} \text{B}$

$$\Lambda_{\infty} = x \lambda_{\infty}^+ + y \lambda_{\infty}^-$$

$$\text{e.g. (i) } \Lambda_{\infty}^{\text{BaCl}_2} = \lambda_{\infty}^{\text{Ba}^{2+}} + 2 \lambda_{\infty}^{\text{Cl}^-}$$

$$\text{(ii) } \Lambda_{\infty}^{\text{Fe}_2(\text{SO}_4)_3} = 2 \lambda_{\infty}^{\text{Fe}^{3+}} + 3 \lambda_{\infty}^{\text{SO}_4^{2-}}$$

-KEYNOTE-

Ionic conductance is more for hydrated Cs^+ than hydrated Li^+

Applications

© Determination of Λ_{∞} for weak electrolytes

Eg: NH_4OH is a weak electrolyte its Λ_{∞} is calculated as $\Lambda_{\infty}(\text{NH}_4\text{OH}) =$

$\Lambda_{\infty}(\text{NH}_4\text{Cl}) + \Lambda_{\infty}(\text{NaOH}) - \Lambda_{\infty}(\text{NaCl})$ © Degree of ionisation of weak electrolyte

$$\alpha = \frac{\Lambda}{\Lambda_{\infty}}$$

where, Λ = equivalent conductivity at given concentration Λ_{∞} = limiting equivalent conductivity

© Dissociation constant of weak electrolyte $K = c \alpha^2$

$$\alpha = \frac{\Lambda}{\Lambda_{\infty}} \quad \text{molar weight equivalent weight Expression for } K$$

© Calculation of dissociation constant of weak electrolytes.

VARIATION OF K , α & Λ OF SOLUTIONS WITH DILUTION K is a function of concentration of ions in the solution. In case of both strong and weak electrolytes on dilution, the concentration of ions will decrease hence K will decrease.

(K a: C) strong electrolyte

$$\Lambda_{\infty} = \frac{\Lambda}{\alpha} \quad \text{If } r \text{ weak electrolyte}$$

$$\Lambda = \frac{\Lambda_{\infty}}{\alpha} \quad \text{Note: } K = \text{Kappa}$$

K_a = equilibrium constant]

For strong electrolyte : $\Lambda_{\infty} = \text{constant}$

For weak electrolyte : $\Lambda_{\infty} = \frac{m}{c} \quad \text{CELL \& BATTERIES}$

Primary cells:

© (i) It is an electrochemical cell which acts as a source of electrical energy without being previously charged up by an electric current from an external source of current.

(ii) In which electrode reactions cannot be reversed by external source.

Example: Dry cell (Leclanche cells), mercury cells E_{cell} = constant as all substances used are either pure solids or pure liquids.

Secondary cells:

© (i) Electrical energy from an external source is first converted into chemical energy (Electrolysis) and when the source is removed then the cell is made to operate in the reverse direction.

(ii) Secondary cells are those which are rechargeable and can be used again and again.

Example: Lead storage batteries used in automobiles (Cars/ bikes).
Li-ion battery. hydrogen oxygen fuel cell etc. Nickel - cadmium battery

E_{cell} = constant as cell reaction has pure solid/liquid only. Anode: Cd(s)

Cathode : NiO₂(s) Electrolyte : KOH

$Cd + 2OH \rightarrow Cd(OH)_2 + 2e^-$

$2e^- + NiO_2 + 2H_2O \rightarrow Ni(OH)_2 + 2OH^-$ Cd(s) + NiO₂(s) + 2H₂O(l) →

Cd(OH)₂(s) + Ni(OH)₂(s) Lead storage battery

The most important secondary cell is the lead storage battery commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO₂) as cathode. A 38% solution of sulphuric acid is used as an electrolyte. The cell reactions when the battery is in use are given below: Anode: Pb(s) + SO₄²⁻(aq) → PbSO₄(s) + 2e⁻
Cathode: PbO₂(s) + SO₄²⁻(aq) + 4H⁺(aq) + 2e⁻ → PbSO₄(s) + 2H₂O(l)

i. overall cell reaction consisting of cathode and anode reactions is:

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$ On charging the battery the reaction is reversed and PbSO₄(s) on anode and cathode is converted into Pb and PbO₂, respectively. Fuel cells (H₂ - O₂ cell)

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run a turbine to produce electricity. We know that a galvanic cell directly converts chemical energy into electricity and is highly efficient. It is now possible to make such cells in which reactants are fed continuously to the electrodes and products are removed continuously from the electrolyte compartment, (galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells.

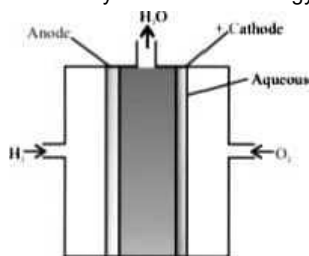
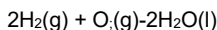


Fig.: Fuel cell using H₂ and O₂ produces electricity One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water. The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:

Cathode: O₂(g) + 2H₂O(l) + 4e⁻ → 4OH⁻(aq) Anode: 2H₂(g) + 4OH⁻(aq) → 4H₂O(l) + 4e⁻ Overall reaction being:



The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70 % compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells. These have been used in automobiles on an experimental basis. Fuel cells are pollution free

and in view of their future importance, a variety of fuel cells have been fabricated and tried.

Dry Cell

A dry cell is one type of electric battery, which is generally used for the home and portable electronic devices. A battery is a device that consists of one or more electrochemical cells, which converts chemical energy into electrical energy.

A dry cell is an electrochemical cell consisting of low moisture immobilized electrolytes in the form of a paste, which restricts it from flowing. Due to this, it is easily transportable.

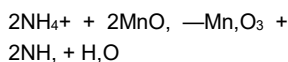
Primary cell

1. Zinc-Carbon cell

Anode

A dry cell consists of a metal container in which a low moisture electrolyte paste covers the graphite rod or a metal electrode. Generally, the metal container will be zinc whose base acts as a negative electrode (anode) and a carbon rod acts as a positive electrode (cathode). It is surrounded by manganese dioxide and low moisture electrolyte like ammonium chloride paste, which will produce a maximum of 1.5V of voltage, and they are not reversible.

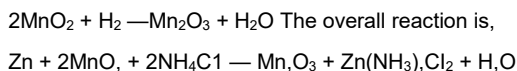
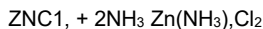
The half cell reaction process has the following steps Step 1: During the process, a reduction reaction occurs within the moistened electrolyte, which comprises manganese dioxide (MnO₂) and ammonium chloride (NH₄Cl) and graphite serves as solid support for the reduction reaction



Step 2: Zinc container serves as an anode and undergoes an oxidation reaction

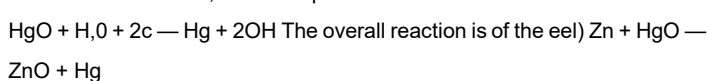
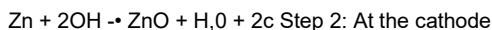


Zinc-carbon cell is the most common dry cell and is also called Leclanché cell. The alkaline battery has almost same half-cell reaction, where KOH or NaOH replaces the ammonium chloride and half-cell reactions are



2. Mercury cell

In the mercury cell, HgO serves as a cathode and zinc metal serves as an anode and the reaction involves the following steps Step 1: At the anode



1 CORROSION

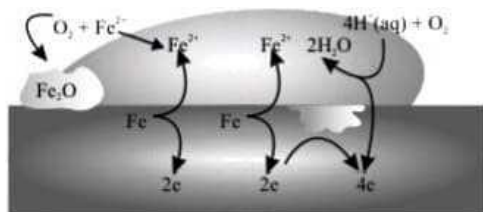
© The natural tendency of conversion of a metal into its mineral

compound form on interaction with the environment (Polluted air, water, associated other metals etc) is known as corrosion. E.g.: Iron converts itself into its oxide (Fe_2O_3 - haematite). Copper converts itself into its carbonate ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$,- Malachite).

Silver converts itself into its sulphide (Ag_2S - Argentum).

- Corrosion of iron by conversion into iron oxide is known as rusting.
- Corrosion of silver by conversion into its sulphide is known as tarnishing.

Mechanism of corrosion



Oxidation : $\text{Fe(s)} \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$

Reduction : $2\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) \rightarrow 2\text{H}_2\text{O(l)}$

Atmospheric Oxidation : $2\text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3(\text{s}) + 4\text{H}^+(\text{aq})$

Electrochemical corrosion

- The process of corrosion may be chemical (or) electrochemical in nature.
- The anodic dissolution of a metal under the conditions of corrosion is known as electrochemical corrosion
 $\text{M} \rightarrow \text{M}^n + \text{n e}^-$
- Corrosion occurs if the environmental conditions of the metal favour the formation of a voltaic cell with the metal acting as anode.
- Electrochemical corrosion is basically of two types as:

- (a) Hydrogen evolution type
- (b) Differential oxygenation type

(i) Hydrogen Evolution type

- This type of corrosion is exhibited by metals which can displace H_2 gas

- Electrolytes $+2\text{V} \rightarrow \text{H}_2(\text{g})$
- $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
- $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$
- $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- $\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-$

from aqueous solution.

- This happens if the electrode potential of the metal under the conditions of corrosion is more negative than that of the hydrogen electrode under the given conditions.
- This type of corrosion depends upon
 - (a) pH of the medium
 - (b) Chemical nature of the metal undergoing corrosion
- Pure zinc does not corrode in salt solutions but in the presence of Cu as impurity. Zn corrodes.
- Zn corrodes in 2M acid but not in neutral salt solution

(ii) Differential Oxygenation type

- This type of corrosion occurs if O_2 concentration is not uniformly distributed on the surface of the metal
- Corrosion of the metal generally occurs at the point where O_2 concentration is less
- The portion of the metal with access to high concentration of O_2 functions as cathode and with access to low concentration of O_2 functions as anode.
Hence, the metal with differential oxygenation acts as a galvanic cell.
Eg : When an iron rod is immersed in NaCl solution the immersed part is corroded due to less oxygenation of the surface of the metal.

Prevention of Corrosion

The main principle underlying the methods of prevention of corrosion is to separate the metal (or) isolate the metal from the environment which is achieved by different ways. They are:

- Alloying (galvanisation)
- To prevent as far as possible the contact of the metal surface with good electrical conducting media.
- Covering by some chemicals like bisphenol.
- Cover the surface by other metals (Sn, Zn etc) that are inert (or) react to save the object.
- Sacrificial electrode of another metal (like Mg, Zn, etc) which corrodes, itself but saves the object.