

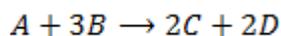
PHYSICAL CHEMISTRY 1.1-CHEMICAL KINETIC

Chemical kinetics is the study of speed or rate of chemical reaction under different conditions and mechanisms of the reaction.

The rate of reaction

Rate of reaction is the change in concentration of reactants and products per unit time.

Consider the following hypothetical reaction:



Rate of reaction can be expressed in terms of disappearance of A or B and rate of formation of C or D. But these rate are not the same i.e. B disappears 3 times as fast as A. Therefore rate of disappearance of B is equal to 3 times rate of disappearance of A.

Rate of disappearance of B = 3 times rate of disappearance of A

Similarity;

Rate of formation of C = 2 times rate of disappearance of A

Rate of formation of D = 2 times rate of disappearance of A

Rate of formation of D = $\frac{2}{3}$ times rate of disappearance of B

The rates of disappearance are negative (since concentration decreases with time) and rate of formation are positive (concentration increase with time). But all result in single positive expression for the rate of reaction.

To remove the effect of stoichiometry, the rate for each species is divided by the co-efficient of the molecules in the balanced equation

$$\text{Rate of reaction} = -\text{Rate of disappearance of B}$$

$$\text{Rate of reaction} = -\frac{1}{3} \text{Rate of disappearance of B}$$

$$\text{Rate of reaction} = \frac{1}{2} \text{Rate of formation of C}$$

$$\text{Rate of reaction} = \frac{1}{2} \text{Rate of formation of D}$$

Example: 01

In the above hypothetical reaction, the initial concentration of A is 1.0M and 1minute later was found to be 0.9982M.

- i) What is rate of reaction in moles per litre per second?
- ii) What is rate of formation of C in $\text{molL}^{-1}\text{sec}^{-1}$?

Solution;

- i) Rate of reaction = -Rate of disappearance of A

$$\begin{aligned} \text{Rate of reaction} &= \frac{-[\Delta A]}{\Delta t} \\ &= \frac{-(0.9982 - 1.0)\text{M}}{60\text{sec}} \\ &= \underline{3 \times 10^{-5} \text{molL}^{-1}\text{sec}^{-1} \text{ or } 3 \times 10^{-5} \text{Msec}^{-1}} \end{aligned}$$

- ii) Rate of reaction = $\frac{1}{2}$ Rate of formation of C

$$\begin{aligned} 3 \times 10^{-5} \times 2 &= \text{Rate of formation of C} \\ &= \underline{6 \times 10^{-5} \text{molL}^{-1}\text{sec}^{-1}} \end{aligned}$$

Example: 2

In the reaction; $2A + B \rightarrow C + 3D$

Reactant A is found to be disappearing at a rate of $2.6 \times 10^{-14} \text{molsec}^{-1}$

- a) What is the rate of reaction?
- b) What is the rate of formation of D?

Solution;

a) Rate of reaction = -Rate of disappearance of A

$$\begin{aligned}\text{Rate of reaction} &= \frac{-[\Delta A]}{\Delta t} \\ &= \underline{2.6 \times 10^{-14} \text{ molsec}^{-1}}\end{aligned}$$

b) Rate of formation of D = $\frac{2}{3}$ × Rate of disappearance of A

$$\begin{aligned}&= \frac{2}{3} \times 2.6 \times 10^{-14} \text{ molsec}^{-1} \\ &= \underline{1.73334 \times 10^{-14} \text{ molsec}^{-1}}\end{aligned}$$

RATE LAW

The law states that “The rate of reaction is direct proportional to the concentration of the reactants each raised to the power of equal to the order of the reaction”

$$\text{Rate} \propto [\text{Reactants}]$$

$$\text{Rate} = K[\text{Reactants}]$$

Where K = Rate constant (Velocity constant)

By definition;

Rate constant is a constant of proportionality in the rate equation which is the measure of the speed with which a reaction is taking place at the given temperature

The units of K depends on the order of reaction

Order of reaction this is the number which shows the manner with which the rate of reaction depends on the concentration of reactants.

Order of reaction can only be obtained experimentally and cannot be deduced from overall balanced equation. OR order of reaction is the sum of power of concentration of the reactants in

the rate law or rate equation.

Consider the example of the reaction; $A + 2B \rightarrow \text{Products}$

The rate law or rate equation is given by; $Rate = K[A]^a[B]^b$

The reaction order with respect to [A] is a and [B] is b and the overall order of reaction is ($a + b$) and that can be a fraction

1. Zero order reaction

Is the reaction in which the rate of the reaction is independent on the concentration of the reactants.

Consider the reaction; $A \rightarrow Products$

$$Rate = K[A]^0$$

$$Rate = K$$

The rate is constant and independent of the concentration of A

Units of rate constant, K

$$K = Rate$$

But $Rate = \frac{[\Delta Concentration]}{\Delta t}$

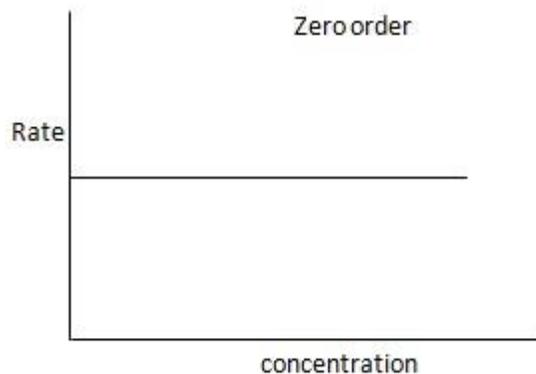
$$K = \frac{[\Delta Contentration]}{\Delta t}$$

$$K = \frac{molL^{-1}}{sec}$$

$$\underline{K = molL^{-1}sec^{-1}}$$

Assignment: Find any two examples of zero order reactions

Graph of rate against concentration A



2. First order reaction

Is reaction in which the rate of reaction is directly proportional to the first power of the concentration of the single reaction reactant.

Consider the reaction; $A \rightarrow \text{Product}$

$$\text{Rate} = K[A]^1$$

$$\text{Rate} = K[A]$$

The units of rate constant, K

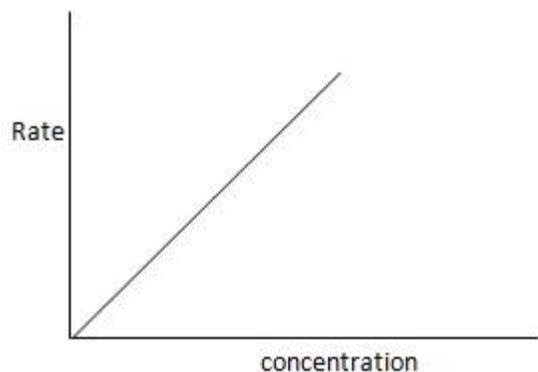
$$\text{Rate} = K[A]$$

$$K = \frac{\text{Rate}}{[A]}$$

$$K = \frac{\text{molL}^{-1}\text{sec}^{-1}}{\text{molL}^{-1}}$$

$$\underline{K = \text{sec}^{-1} \text{ or } (\text{time}^{-1})}$$

Graph of rate against concentration A

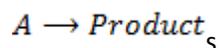


Assignment: Find any 2 reaction of first order reaction

3. Second order reaction

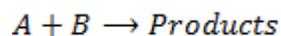
Is the reaction in which rate of reaction is proportional to the second power of concentration of a single reactant or first power of concentration of two reactants (Although rate of reaction

increases with increase in concentration of the reactant, the relationship is not direct)



$$\text{Rate} = K[A]^2$$

Or



$$\text{Rate} = K[A]^1[B]^1$$

Units of rate constant, K

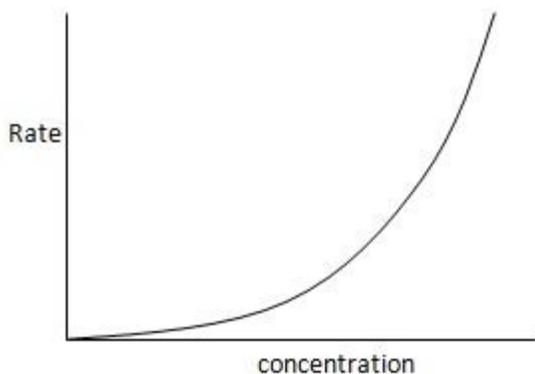
$$\text{Rate} = K[A][B]$$

$$K = \frac{\text{Rate}}{[A][B]}$$

$$K = \frac{\text{molL}^{-1}\text{sec}^{-1}}{\text{molL}^{-1}}$$

$$\underline{K = \text{Lmol}^{-1}\text{sec}^{-1}}$$

Graph of rate against concentration A



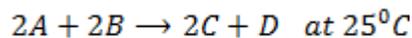
DETERMINATION OF ORDER OF REACTION

This can only be found experimentally.

The order of the reaction can be found by keeping the concentration of one reactant constant and changing the concentration of other at a given temperature.

Example:

- The following data was obtained for the reaction



<i>Experiment</i>	$[A]M$	$[B]M$	<i>Rate</i> ($\text{molL}^{-1}\text{sec}^{-1}$)
1	0.01	0.20	0.1
2	0.02	0.20	0.2
3	0.01	0.40	0.4

- What is the order with respect to;
 - Reactant A
 - Reactant B

iii) Reactant A and B

- b) Calculate the velocity constant and the rate of reaction with concentration A and B are 0.01M and 0.1M respectively.

Solution:

$$\text{Rate} = K[A]^a[B]^b$$

- a) i) The value of a is found when the concentration of B must be kept constant so experiment 1 and 2 are considered;

$$0.1 = K[0.01]^a[0.2]^b \text{ --- (1)}$$

$$0.2 = K[0.02]^a[0.2]^b \text{ --- (2)}$$

Divide equation (1) by (2)

$$\frac{0.1}{0.2} = \frac{K[0.01]^a[0.2]^b}{K[0.02]^a[0.2]^b}$$

$$\frac{1}{2} = \left[\frac{1}{2}\right]^a$$

$$\underline{a = 1}$$

The reaction is first order with respect to reactant A

- ii) The value of b is found when the concentration of A must be kept constant, so experiment 1 and 2 are considered;

$$0.1 = K[0.01]^a[0.2]^b \text{ --- (1)}$$

$$0.4 = K[0.01]^a[0.4]^b \text{ --- (2)}$$

Divide equation (1) by (2)

$$\frac{0.1}{0.4} = \frac{K[0.01]^a[0.2]^b}{K[0.01]^a[0.4]^b}$$

$$\frac{1}{4} = \left[\frac{1}{2}\right]^b$$

$$b = 2$$

The reaction is second order with respect to reactant B

iii) The overall order of reaction;

$$= a + b$$

$$= 1 + 2$$

$$= 3$$

The overall order of the reaction is third order

b) The velocity constant is the average because there are some errors.

Experiment 1:-

$$0.1 = K[0.01]^1[0.2]^2$$

$$K = 250$$

Experiment 2:-

$$0.2 = K[0.02]^1[0.2]^2$$

$$K = 250$$

Experiment 3:-

$$0.4 = K[0.01]^1[0.4]^2$$

$$K = 250$$

$$K = \frac{250+250+250}{3}$$

$$K = 250L^2mol^{-2}sec^{-1}$$

$$R = K[0.01][[0.1]^2]$$

$$R = 0.025molL^{-1}sec^{-1}$$

2. The following data were obtained for; $2x + y \rightarrow z$

Experiment	[x] M	[y] M	Rate (molL ⁻¹ sec ⁻¹)
1	0.2	0.1	7×10^{-4}
2	0.2	0.2	1.4×10^{-3}
3	0.4	0.2	1.4×10^{-3}
4	0.6	0.6	4.2×10^{-3}

Determine the rate law for the above reaction

Solution:

$$Rate = K[x]^a[y]^b$$

The value of a is found when concentration of y is constant.

$$1.4 \times 10^{-3} = [0.2]^a[0.2]^b$$

$$1.4 \times 10^{-3} = [0.4]^a[0.2]^b$$

Divide;

$$1 = [0.5]^a$$

$$a = 0$$

The value of b;

$$7 \times 10^{-4} = [0.2]^a[0.2]^b$$

$$1.4 \times 10^{-3} = [0.2]^a [0.2]^b$$

Divide;

$$\frac{1}{2} = \left(\frac{1}{2}\right)^b$$

$$\underline{b = 1}$$

$$7 \times 10^{-4} = K[0.2]^0 [0.1]^1$$

$$\underline{K = 7 \times 10^{-3}}$$

$$1.4 \times 10^{-3} = K[0.2]^0 [0.2]^1$$

$$\underline{K = 7 \times 10^{-3}}$$

$$1.4 \times 10^{-3} = K[0.4]^0 [0.2]^1$$

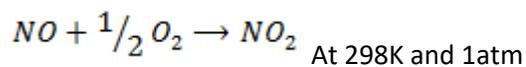
$$\underline{K = 7 \times 10^{-3}}$$

$$4.2 \times 10^{-3} = K[0.6]^0 [0.6]^1$$

$$\underline{K = 7 \times 10^{-3}}$$

$$\therefore \underline{K = 7 \times 10^{-3} \text{ sec}^{-1}}$$

3. The data below was obtained from the reaction;



Experiment	[NO]M	[O ₂] M	Initial rate (molL ⁻¹ sec ⁻¹)

1	4.5×10^{-2}	2.25×10^{-2}	0.8×10^{-2}
2	4.5×10^{-2}	4.5×10^{-2}	1.6×10^{-2}
3	9.0×10^{-2}	9.0×10^{-2}	1.28×10^{-1}
4	3.3×10^{-1}	2.8×10^{-3}	?

Determine:-

- i) Rate law
- ii) Velocity constant
- iii) Rate of reaction in experiment 4

Solution:

$$i) \text{Rate} = K[NO]^a[O_2]^b$$

The value of b:-

$$0.8 \times 10^{-2} = K[4.5 \times 10^{-2}]^a[2.25 \times 10^{-2}]^b \text{ ----- (1)}$$

$$1.6 \times 10^{-2} = K[4.5 \times 10^{-2}]^a[4.5 \times 10^{-2}]^b \text{ ----- (2)}$$

Divide equation 1 by 2

$$\frac{1}{2} = \left[\frac{1}{2}\right]^b$$

$$\underline{b = 1}$$

The value of a:-

$$0.8 \times 10^{-2} = K[4.5 \times 10^{-2}]^a[2.25 \times 10^{-2}]^b$$

$$1.28 \times 10^{-1} = K[9.0 \times 10^{-2}]^a[9.0 \times 10^{-2}]^b$$

$$0.0625 = [0.5]^a 0.25$$

$$\underline{a = 2}$$

ii) Velocity constant, K

$$\text{Rate} = K[\text{NO}]^a[\text{O}_2]^b$$

$$0.8 \times 10^{-2} = K[4.5 \times 10^{-2}]^2[2.25 \times 10^{-2}]^1$$

$$\underline{K = 175.6 \text{ L}^2 \text{ mol}^{-2} \text{ sec}^{-1}}$$

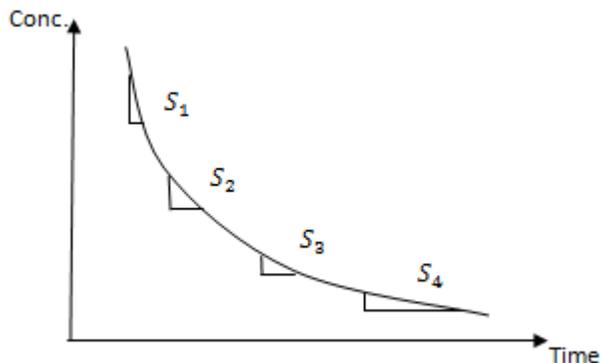
iii) Rate of the reaction in experiment 4

$$\text{Rate} = K[\text{NO}]^a[\text{O}_2]^b$$

$$\text{Rate} = 175.6[3.3 \times 10^{-1}]^2[2.8 \times 10^{-3}]^1$$

$$\underline{\text{Rate} = 0.054 \text{ mol L}^{-1} \text{ sec}^{-1}}$$

Note :- If the rate of reaction is not given directly, it can be found from concentration and time. The graph of concentration against time is always a curve for first and second order reaction



Choose points, draw the tangent and find the slopes

slope = Rate of reaction

Rate = $K[A]^m$ where m = order of reaction

$$S_1 = K[C_1]^m \dots\dots\dots 1$$

$$S_2 = K[C_2]^m \dots\dots\dots 2$$

Using these two equations order of reaction can be obtained. For more than two slopes, introduce log on both sides of rate equation

i.e. $\log R = \log K + m \log[A]$

Therefore a graph of log R against log [A] gives a straight line where m = slope (Order of reaction)

Alternatively:-

$$K = \frac{R}{[A]^m}$$

Assume $m=1$, show $\frac{R}{[A]^1} = \text{Constant } (K)$

$m=2$, show $\frac{R}{[A]^2} = \text{Constant } (K)$

$m=3$, $K = \frac{R}{[A]^3}$

Example:

- For the reaction $A \rightarrow B$ the following data was obtained at 45°C

Time (sec)	0	184	319	400	867	1198	187
$[A] \text{ moldm}^{-3}$	2.33	2.08	1.97	1.79	1.36	1.11	0.7

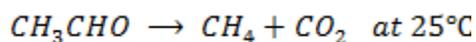
- Plot a graph of [A] against t:

- b) Take tangents to obtain a slope at $[A] = 2, 1.167$ and 1 mol dm^{-3}
- c) The rate law for the above reaction can be

$$R = K [A]^1 \text{ or } R = K[A]^2$$

Use of the result in (b) to find which of the rate law actually holds.

2. The following data was obtained from the reaction;



Rate ($\text{mol dm}^{-3} \text{sec}^{-1}$)	0.02	0.081	0.187	0.318	X
$[\text{CH}_3\text{CHO}] \text{ M}$	0.1	0.2	0.3	0.4	0.15

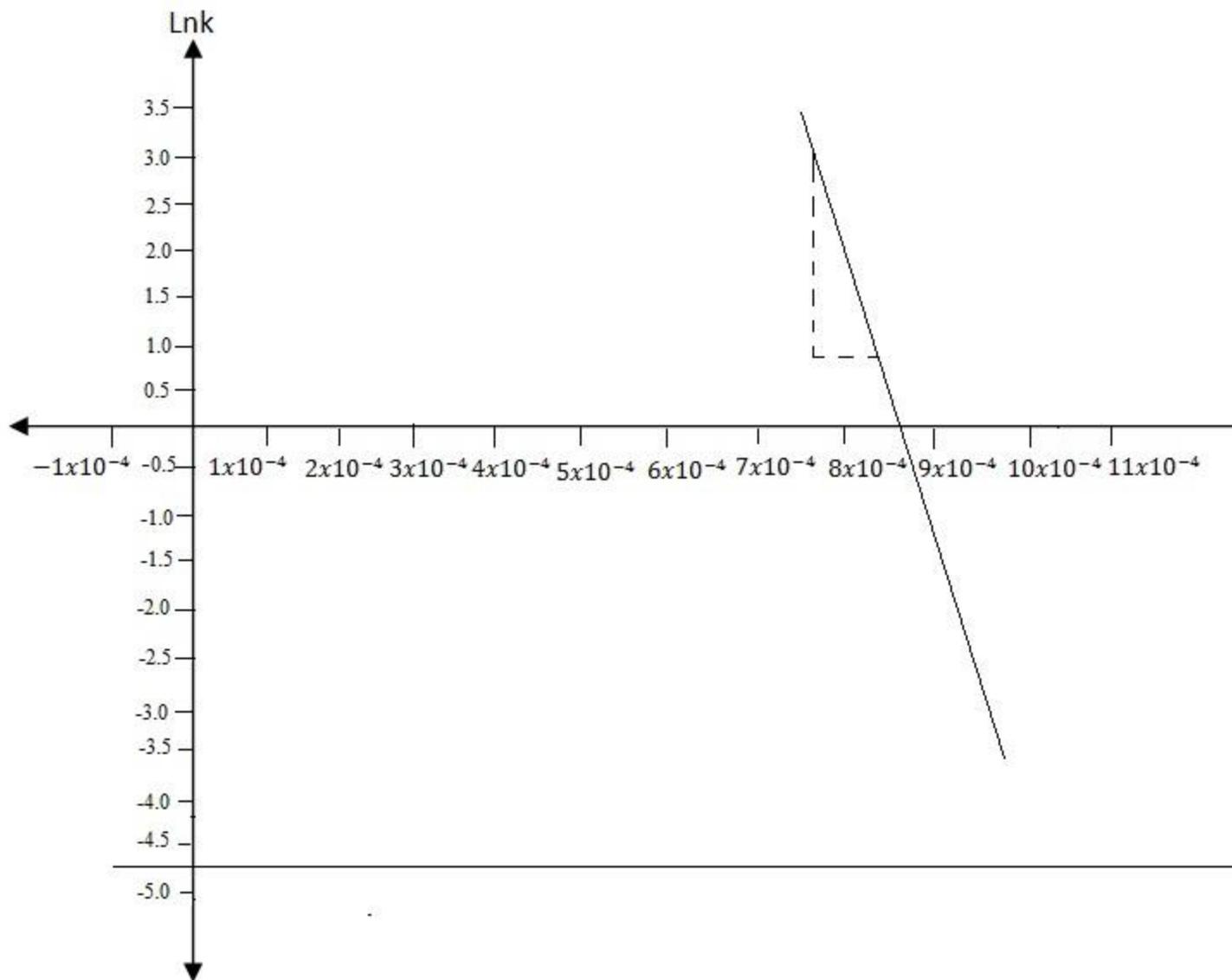
- i. Determine the value of n and K in the equation

$$\text{Rate} = K[\text{CH}_3\text{CHO}]^n$$

- ii. Obtain rate constant and the rate of reaction when concentration of $\text{CH}_3\text{CHO} = 0.15 \text{ mol L}^{-1}$
- iii. Use the above example to explain the fact that the order of reaction must be determined experimentally and not from the co-efficient of balanced equation

Answers

$$\begin{array}{ll} 0.5128 & 9.4966 * 10^{-4} = 0.00094966 \\ -0.9676 & 9.99 * 10^{-4} = 0.00099 \\ 4.5099 & 1.193 * 10^{-3} = 0.001193 = 11.93 * 10^{-4} \end{array}$$



ARRHENIUS EQUATION

From the collision theory, the reaction rate depends the energy and number of collision between molecules and whether the collisions have correct geometry and temperature.

These requirements are summarized by Arrhenius into what is known as the Arrhenius Equation.

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

Where; K =Rate /velocity constant.

R= Universal gas constant

A= Frequency factor (per time)

$e^{-E_a/RT}$ = Fraction of molecules having minimum energy required for the reaction to take place.

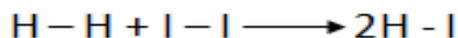
Frequency factor (A) –Express number of collisions occurring and a fraction of them that has the right geometry.

Application of Arrhenius Equation

i) Determination of Activation Energy

Introduce **ln** on both sides of $K = Ae^{-\frac{E_a}{RT}}$

ii) The collision must be energetic enough to break the bond between molecules.



I.e The collision between 2 molecules will not lead to reaction if the kinetic energy cannot provide the necessary activation energy.

As the temperature rises, the number of molecules with energies greater than minimum energy required (ACTIVATION ENERGY) increases.

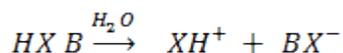
This factor causes the reaction to be sensitive temperature.

PHYSICAL CHEMISTRY 1.2- ACIDS,BASES AND SALTS

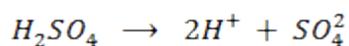
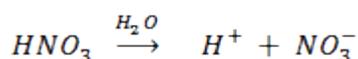
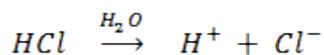
Arrhenius concept of acids and bases .

What is an acid? (according to Arrhenius concept of acids and bases)

- ∅ Arrhenius considered that an acid is a substance which when dissolved in water dissociate to produce H^+ ions as the only positively charged ions i.e.

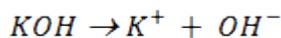
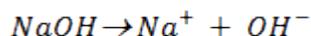


e.g



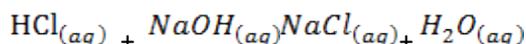
- ∅ -He considered a base to be a substance which produce hydroxyl ions when dissolved in water as the only negatively charge ions i.e

e.g.

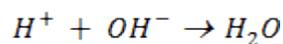


The neutralization of acid with a base yields to a salt and water.

e.g.



Ionic equation



According to Arrhenius, neutralization reaction is all about formation of water.

Weakness of Arrhenius equation

1.

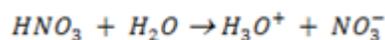
- i) This concept is limited to water. It refers to H^+ and OH^- ions derived from water. A true general concept of acid and base should be appropriate to other solvent like liquid NH_3 and alcohols.

2. ii) The concept does not provide the room for acids and bases which do not contain H^+ ions and HO^- ions.

Bronsted – Lowry concept of acids and bases

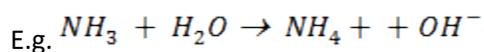
- Bronsted and Lowry proposed a theory of acids and bases applicable to all solvents.
- They proposed that, an acid is any substance that can donate a proton to any other substance.

e.g



Acid Base

- A base is a substance that can accept a proton from any other substance.



Base Acid

- They are called a monoprotic acid an acid which donates only one proton.

e.g. HNO_3 , HCl

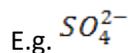
- Diprotic acid can donate two protons.

E.g. H_2SO_4

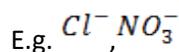
- A polyprotic acid is an acid that can donate more than one proton.

E.g. H_2SO_4 , H_3PO_3 , $H_2C_2O_4$

- A polyprotic base is one which can accept more than one proton.



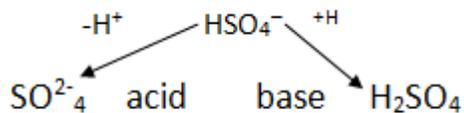
- A monoprotic base is one which can accept only one proton.



NOTE: HCl and Cl^- are acid-base conjugate pair. Another example is HNO_3 and NO_3^-

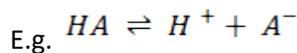
Amphoteric (amphiprotic) acids and bases.

These behave as bronsted – Lowry acids or bases



Conjugate acid base pair

-For every acid, there is a corresponding (conjugate) base to accept a proton



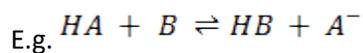
Acid base

(Proton donor) (Proton acceptor)

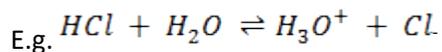
HA and A^- are conjugate pair i.e.

HA is a conjugate acid of A^- and A^- is a conjugate base of HA.

® In a solution, there must be a base to accept a proton



Acid Base Acid Base

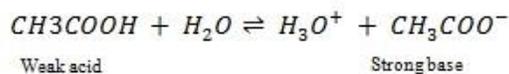


A_1 B_2 A_2 B_1

A_1 , B_1 , and A_2 , B_2 , are acid base conjugate.

NOTE:

From Bronsted–Lowry concept of acid and bases, the stronger the acid, the weaker its conjugate base and the stronger the base, the weaker its conjugate acid.



- CH_3COOH is a weak acid, but its conjugate base i.e. CH_3COO^- is a strong base.

- H_2O is a weak base, but H_3O^+ is strong acid.

Advantage of Bronsted–Lowry concept over Arrhenius

® It can apply to any solvent not necessarily H_2O . Here the definition of bases is much wider.

Weakness:

Since the concept is based on proton transfer, it does not consider other compounds which do not contain hydrogen i.e AlCl_3 , BF_3 , SO_3 .

In contrast to Arrhenius theory, acid and bases are no longer related to salts (by neutralization).

Question 1:

A. Define

- i) Conjugate acid-bases pair.
- ii) Conjugate base.

B. For the following pairs, write down the equation to show the conjugate acid-bases pair.

- i) $\text{HSO}_4^- / \text{H}_2\text{O}$
- ii) $\text{SO}_3^{2-} / \text{H}_2\text{O}$
- iii) $\text{HCO}_3^- / \text{H}_2\text{O}$
- iv) $\text{HCO}_3^- / \text{OH}^-$

Question 2:

a. Write the formula and give the name of the conjugate base for each of the following acids.

- i) HSO_4^-
- ii) HF^-

b. Write the name and formula of the conjugate acids for each of the following bases.

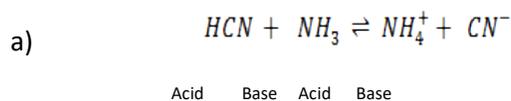
- i) NH_3
- ii) Br^-
- iii) HS^-

Question3:

In each of the following acid-base reaction. Identify the acid and the base on the left and their conjugate partners on the right.

- a) $HCN + NH_3 \rightleftharpoons NH_4^+ + CN^-$
- b) $[Al(H_2O)_6]^{3+} + OH^- \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H_2O$

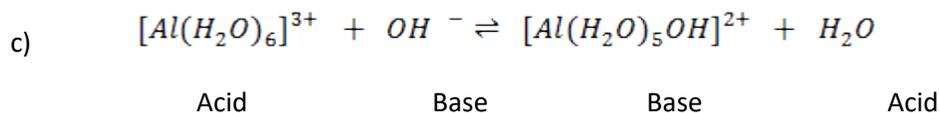
ANSWERS:



HCN, CN^- is a conjugate pair and NH_3 , NH_4^+ is a conjugate pair

b)

HSO_4^- , SO_4^{2-} , is a conjugate pair



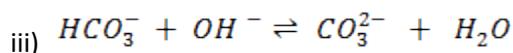
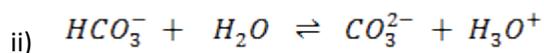
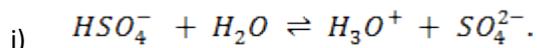
$[Al(H_2O)_6]^{3+}$, $[Al(H_2O)_5OH]^{2+}$ is a conjugate pair.

OH^- and H_2O is a conjugate pair.

Q: Conjugate acid-base pair is a pair which shows that for every proton lost by acid, there is a corresponding base to accept it.

a) Conjugate base.

b)



LEWIS CONCEPT OF ACIDS AND BASES.

- Lewis proposed an even broader concept of acids and bases focusing on electron transfer rather than total transfer.

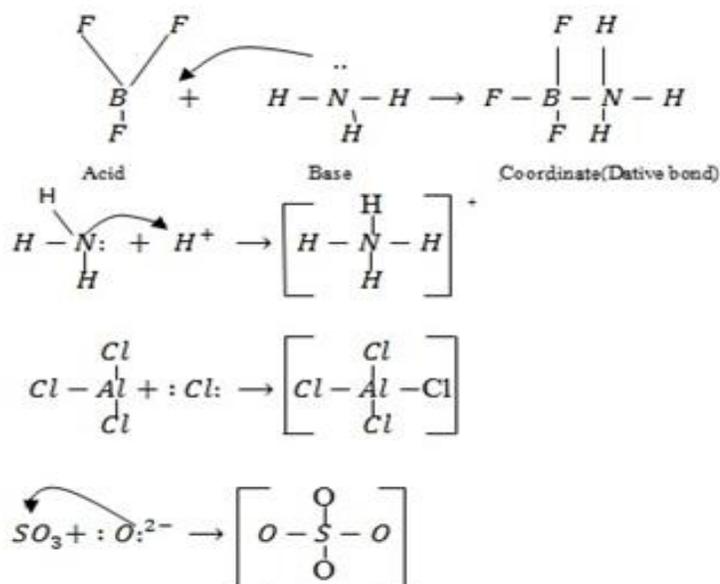
- According to Lewis an acid is a substance that can accept a pair of electrons. Therefore, an acid is an electron pair acceptor.
- A base is a substance that can donate a pair of electrons i.e base is an electrons pair donor.

NOTE

Bronsted–Lowry acids e.g. HCl, H₂SO₄, HNO₃, are not Lewis acid.

Thus, an acid-base reaction can occur when a base provide a pair of electrons to share with an acid resulting into coordinate compound or complex.

Eg



Therefore, ammonia chloride ions (AlCl₃) are Lewis base, while H⁺, BF₃ are Lewis acids.

NOTE: A Bronsted–Lowry base (like NH₃) reacts by donating electron pair to a proton. Therefore Bronsted–Lowry bases are also Lewis bases

Reason:

This is because upon donating a pair of electron, it would have accepted a proton. Therefore, Bronsted – Lowry bases are also Lewis bases.

- i . F⁻ fluoride ion
- ii. Sulphate ion
- iii. NH₄⁺ ammonium ion
- iv. HBr Hydrogen bromid
- v. H₂S Hydrogen sulphide.

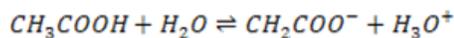
Reason:

These cannot accept a lone pair of electrons hence the Lewis concept of acid is usually used in special cases.

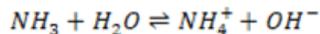
IONIC EQUILIBRIUM OF ACIDS AND BASES.

Most acids and bases are weak i.e does not ionize fully when dissolve in water. Thus a part from water equilibrium, they also establish equilibrium.

e.g.



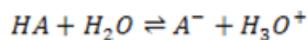
Ammonia which is a typical weak base ionizes as follows:



But the ionization of weak acid/ bases generally occurs to a greater extent than that of water.

STRENGTH OF WEAK ACIDS AND BASES.

The position of equilibrium of a reaction between the acid and water varies from one weak acid to another. The further to the left it lies, the weaker the acid is



The equilibrium constant is written as;

$$K = \frac{[A^-][H_3O^+]}{[HA][H_2O]}$$

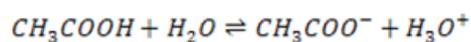
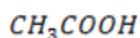
But H₂O is constant at constant temperature.

Putting the constant on the same side

$$K \times [H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

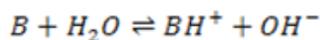
Where K_a = dissociation/ ionization constant of an acid.

for



$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

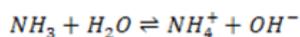
Similarly for weak base, the position of equilibrium varies from base to base. The further to the left it lies, the weaker the base is



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

Where K_b = dissociation/ ionization constant of a base.

For NH_3



$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

The K_a and K_b values are used to determine the strength of acids and bases i.e. K_a and K_b values are quite small for a very weak acid/ base reflecting very little ionization of these acids/ base in solution.

Example:

The K_b value for $C_6H_5NH_2$ is 4.17×10^{-10} , NH_3 is 1.78×10^{-5} . Indicate which base is stronger than the other.

NH_3 is stronger than $C_6H_5NH_2$

The K_b value for $C_6H_5NH_2$ is smaller than $C_6H_5NH_2NH_3$

The strength of weak acids and bases can also be determined from its degree of dissociation (Ostwald's dilution law)

Since K_a and K_b values are inconvenient to handle usually pK_a and pK_b are used.

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

For example;

$$C_6H_5NH_2: \quad pK_b = -\log(4.17 \times 10^{-10})$$

$$pK_b = 9.33$$

$$NH_3: \quad pK_b = -\log(1.78 \times 10^{-5})$$

$$pK_b = 4.75$$

The lower the value for the stronger the acid base respectively and vice versa

THE RELATIONSHIP BETWEEN pK_a AND pK_b FOR A CONJUGATE ACID–BASE PAIR.

Consider the equilibrium.



$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

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

The product of K_a and K_b gives.

$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]}$$

$$K_a \times K_b = [H_3O^+][OH^-]$$

$$K_w = [H_3O^+][OH^-]$$

$$-\log K_a + (-\log K_b) = -\log[H_3O^+] - \log[OH^-]$$

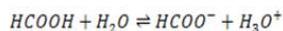
$$pK_a + pK_b = pK_w = 14$$

$pK_a + pK_b = 14$

Example

Formic acid (HCOOH) has a K_a of 1.78×10^{-4} moles. Calculate the $[H_3O^+]$ and the pH of 0.1M. Solution of HCOOH.

Solution



Start	0.1	-	-
Equilibrium	$0.1 - x$	x	x

$$K_a = \frac{[\text{HCOO}^-][\text{H}_3\text{O}^+]}{[\text{HCOOH}]}$$

$$1.78 \times 10^{-4} = \frac{x^2}{0.1 - x}$$

Since K_a value is small, the expression

$$0.1 - x \approx 0.1$$

$$1.78 \times 10^{-4} = \frac{x^2}{0.1}$$

$$x^2 = 1.78 \times 10^{-4} \times 0.1$$

$$x = 4.22 \times 10^{-3}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$= -\log(4.22 \times 10^{-3})$$

$$\text{pH} = 2.37$$

NOTE:

The approximation is done when $[\text{HA}]_0$ is greater than $100 K_a$

$$[\text{HA}]_0 > 100 K_a$$

$$0.1 > 0.0178$$

But if initial concentration $[\text{HA}]_0$ is less than $100 K_a$, then the exact expression formed must be solved.

Calculate $[\text{H}_3\text{O}^+]$ and pH in which has K_a value of moles/ dm^3 .

Solution:

$$\text{HClO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}_2^-$$

Start	0.1	-	-
Equilibrium	$0.1 - x$	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}_2^-]}{[\text{HClO}_2]}$$

$$1.1 \times 10^{-2} = \frac{x^2}{0.1 - x}$$

$$(1.1 \times 10^{-3})(1.1 \times 10^{-2})x - x^2 = 0$$

$$-x^2 - (1.1 \times 10^{-2})x + (1.1 \times 10^{-3}) = 0$$

$$x = 0.028 \text{ M of } [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.028)$$

$$\text{pH} = 1.55$$

Question set 1:

Formic acid (HCOOH) has K_a of (HCOOH) 1.8×10^{-4} moles dm^3 . If you have 0.001 m a solution of the acids. What is the pH of this solution, what is the concentration of HCOOH at equilibrium?

2. If the acid HA is 2% ionized in solution of concentration 0.01m, calculate

- K_a
- $\text{p}K_a$

3. Calculate the degree of ionization $C_6H_5CH_2NH_3^+$, $\text{p}K_b$ is 9.37 in a 0.1M aqueous solution $\alpha = 6.53 \times 10^{-5}$.

4. Calculate pH of a 0.052m acetic acid solution if K_a is $1.8 \times 10^{-5} \text{ M}$

5. For a 0.1M solution of benzoic acid, calculate.

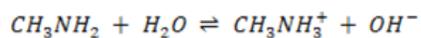
- Concentration of ions and molecules in solution
- The degree of ionization of the acid.

iii) pH of the solution ($K_a = 6.3 \times 10^{-5} \text{ m}$)

6). A hypothetical weak base (MOH) has K_b of $5 \times 10^{-5} M$ for the reaction. $MOH \rightleftharpoons M^+ + OH^-$

Calculate the equilibrium Concentration of MOH, M^+ and OH^- in a $0.15M$ solution MOH.

The weak base methylamine (CH_3NH_2) has K_b of 5×10^{-4} . It reacts with water according to the equation.



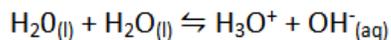
Calculate the equilibrium concentration of OH^- in a $0.25M$ solution of base. What are the pH and pOH of the solution?

Hydroxyl amine (NH_2OH) has a K_b of 6.6×10^{-9} . What are the pH and pOH of $0.051M$ of the base ?

A $0.1m$ solution of chloroacetic acid ($ClCH_2COOH$) has a pH of 1.95. Calculate K_a for the acid.

IONIC PRODUCT OF WATER AND PH.

- Water auto-ionizes i.e transfers a proton from one water molecule to another producing H_3O^+ and OH^-



Base Acid

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

But the concentration of H_2O is much larger than the two ions and is constant at constant temperature. Since the concentration of H_2O is constant it is made part of the constant.

$$K \times [H_2O]^2 = [H_3O^+][OH^-]$$

$$K_w = [H_3O^+][OH^-]$$

Where K_w = ionic product of water constant.

In pure water, $K_w = 1 \times 10^{-14}$ at $25^\circ C$. Since every one H_3O^+ ion formed also one OH^- ion is formed, thus the concentrations are equal.

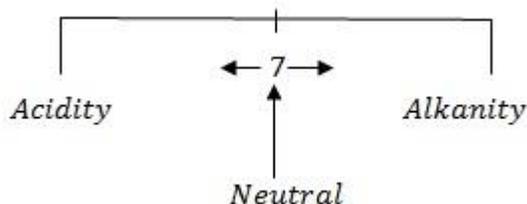
$$[H_3O^+] = [OH^-] = \sqrt{K_w}$$

$$[H_3O^+] = [OH^-] = 1 \times 10^{-7} m$$

Since the concentrations are equal, this implies that pure water is neutral.

pH-Scale

- Is a scale which shows degree of acidity or alkalinity of a solution:



$$\begin{aligned} pH &= -\log [H_3O^+] \\ &= -\log (1 \times 10^{-7}) \\ &= 7 \end{aligned}$$

I.e pH of 7 is neutral point.

pH Is the negative logarithm of base 10 hydrogen ion.

pOH Is the negative logarithm of base 10 of hydroxyl ion concentration.

For pure water

$$pH = 7 \quad pOH = 7$$

$$pH + pOH = 14$$

NOTE:

In acidic solution, the concentration of H_3O^+ is greater than $[OH^-]$.

$$[H_3O^+] > [OH^-]$$

i.e $[H_3O^+] > 1 \times 10^{-7} m$

In basic solution, the concentration of $[OH^-] > [H_3O^+]$

i.e $[OH^-] > 1 \times 10^{-7}$

From

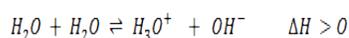
$K_w = [H_3O^+][OH^-]$, Introducing negative log on both sides

$$-\log K_w = -\log[H_3O^+] + (-\log[OH^-])$$

$$pK_w = pH + pOH$$

Variation of $\frac{pH}{T}$ of pure water with temperature.

The formation of H_3O^+ and OH^- ions from water is an endothermic process i.e the forward reaction absorbs heat.



-According to Le Chatelier's principle, when you increase the temp, the forward reaction is favoured, thus concentration of H_3O^+ and OH^- ions will increase but in equal amounts. Thus, the pH will drop but the water will not be acidic the pH scale will also change. It won't remain as 1 to 14 and the neutral point will also shift. The direct effect on increasing temperature is to increase K_w .

The table below shows the effect of temperature on K_w and each value of K_w a new pH must be calculated.

$T \text{ } ^\circ\text{C}$	$K_w \text{ (mol}^2\text{dm}^{-6}\text{)}$	pH
0	0.114×10^{-14}	7.4715
25	1.001×10^{-14}	6.9998
50	5.476×10^{-14}	6.6308
100	51.3×10^{-14}	6.1449

From the table, pH of water fall as temperature increases. This does not mean that water becomes more acidic at higher temperature. This solution is only acidic, If the concentration of $[H_3O^+]$ is great than $1 \times 10^{-7} \text{ M}$.

Example:

- The value of K_w at physiological temperature of a body ($37 \text{ } ^\circ\text{C}$) is $2.4 \times 10^{-14} \text{ M}^2$. What is the pH at neutral point of water at this temperature.

Solution:

$$\sqrt{KW} = [H_3O^+]$$

$$[H_3O^+] = \sqrt{2.4 \times 10^{-14}}$$

$$[H_3O^+] = 1.549 \times 10^{-7} \text{ m}$$

$$pH = -\log [H_3O^+]$$

$$pH = -\log [1.549 \times 10^{-7}]$$

$$\underline{pH = 6.8}$$

2. At 0°C , pK_w is 15. Find pOH at 0°C , if the $[H^+]$ is $3.31 \times 10^{-8} \text{ m}$.

Solution:

$$pH = -\log [H^+]$$

$$pH = -\log (3.31 \times 10^{-8})$$

$$pH = 7.48$$

$$pK_w = pH + pOH$$

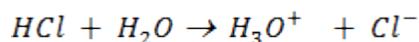
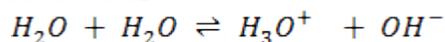
$$pOH = pK_w - PH$$

$$pOH = 14 - 7.48$$

$$\underline{pOH = 6.52}$$

STRONG ACIDS AND BASES.

When an acid is added to water as an aqueous solution of HCl in addition to self ionization of water, the acid also ionizes.



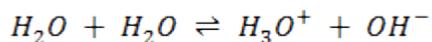
Due to common ion effect of hydroxonium ion as HCl is fully ionized, it suppresses the ionization of water hence $[H_3O^+]$ and $[OH^-]$ ion from water will be less than $1 \times 10^{-7} \text{ M}$.

It is generally acceptable to consider the ionization of HCl to be the sole source of hydroxonium ions. This is also applicable in strong bases for OH^- ions.

Example1:

If 0.001m of NaOH is added to enough amount of 1L of water, what is the concentration of OH^- and H_3O^+ ions?

Solution:



From H_2O x x

From NaOH - 0.001

Equilibrium x $(0.001 + x) \approx 0.001$

$$K_w = [H_3O^+][OH^-]$$

$$1 \times 10^{-14} = [H_3O^+] 0.001$$

$$\underline{[H_3O^+] = 1 \times 10^{-11} \text{ m}}$$

Example2:

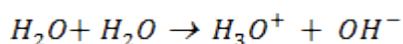
Calculate the concentration of H_3O^+ , Cl^- , and $[OH^-]$ in a 100 cm³ sample of 0.015 m

NOTE:

HCl is the main source of H_3O^+



0.015 0.015



From H_2O x x

From HCl $0.015 + x \approx 0.015$

$$K_w = [H_3O^+][OH^-]$$

$$1 \times 10^{-14} = 0.015 [OH^-]$$

$$[OH^-] = 6.67 \times 10^{-13} \text{ m}$$

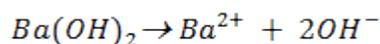
$$[Cl^-] = 0.015m$$

$$[H_3O^+] = 0.015m.$$

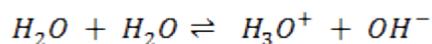
NOTE: Molar concentrations are independent of solution volume i.e $[H_3O^+]$ in 0.015M HCl is the same whether we are describing 1L, 10L or 100cm³ thus the volume of acid is not involved in this calculation.

e.g. Calculate the $[H_3O^+]$, $[OH^-]$ and $[Ba^{2+}]$ in 50 cm³ of 0.01M $Ba(OH)_2$

Solution:



$$0.01M \quad 0.01M \quad 2 \times 0.01 = 0.02M$$



$$\text{From } H_2O \quad \quad \quad x \quad \quad x$$

$$\text{From } Ba(OH)_2 \quad \quad - \quad \quad 0.02$$

$$\text{Equilibrium} \quad \quad x \quad 0.02 + x \approx 0.02$$

$$\text{From:} \quad Kw = [H_3O^+] [OH^-]$$

$$1 \times 10^{-14} = [H_3O^+] 0.02$$

$$[H_3O^+] = 5 \times 10^{-13} m$$

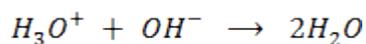
$$[Ba^{2+}] = 0.01m$$

$$[OH^-] = 0.02m$$

NEUTRALIZATION REACTION.

This is the reaction between H_3O^+ from an acid and OH^- ions from a base to form water. Therefore when solutions of acids and bases are mixed together, the chemical reaction must occur in which

$[H_3O^+]$ and $[OH^-]$ combine to form water.

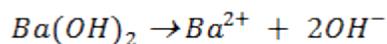


This reaction occur in order to maintain the required value of equilibrium constant K_w . The final solution can be acidic basic or neutral depending on the $[H_3O^+]$ and $[OH^-]$ after neutralization reaction.

Example:

What is the $[H_3O^+]$ obtained by mixing 100cm^3 of 0.015m HCl and 50cm^3 of 0.01m $\text{Ba}(\text{OH})_2$ solution, Is the final solution acidic or basic?

Solution:

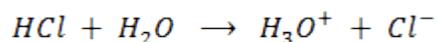


$$0.01\text{m} \quad 0.01\text{m} \quad 0.02\text{m}$$

$$0.02\text{moles} \rightarrow 100\text{cm}^3$$

$$x \rightarrow 50\text{cm}^3$$

$$X = 0.001\text{moles of } \text{OH}^- \text{ (Limiting factor)}$$

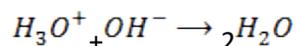


$$0.015 \quad 0.015 \quad 0.015$$

$$0.015\text{moles} \rightarrow 100\text{cm}^3$$

$$X \rightarrow 100\text{cm}^3$$

$$X = 1.5 \times 10^{-3}\text{moles (Factor in excess)}$$



1 1

$$\text{Moles of } \text{H}_3\text{O}^+ \text{ in excess} = (1.5 \times 10^{-3}) - (1 \times 10^{-3})$$

$$= 5 \times 10^{-4}\text{moles}$$

$$5 \times 10^{-4} \text{ moles} \rightarrow 150 \text{ cm}^3$$

$$X \rightarrow 1000 \text{ cm}^3$$

$$X = 3.33 \times 10^{-3} \text{ M of } [H_3O^+]$$

$$K_w = [H_3O^+][OH^-]$$

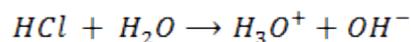
$$1 \times 10^{-14} = 3.33 \times 10^{-3} [OH^-]$$

$$\underline{[OH^-] = 3 \times 10^{-12} \text{ M}}$$

Question:

- 1) What is the pH of a solution obtained by dissolving 312 cm³ of HCl, measured at 30°C at 340 mmHg in 3.25 L of water?

Solution:



From $PV = nRT$

$$n = \frac{PV}{RT}$$

$$n = \frac{45329.6 \times 312 \times 10^{-6}}{8.314 \times 303}$$

$$n = 5.61 \times 10^{-3} \text{ moles of } [H_3O^+]$$

$$[H_3O^+] = \frac{5.61 \times 10^{-3} \text{ moles}}{3.25 \text{ dm}^3}$$

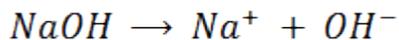
$$[H_3O^+] = 1.7626 \times 10^{-3}$$

$$pH = -\log[H_3O^+]$$

$$pH \equiv 2.76$$

- 2) Calculate the pH of neutralization point when 40cm^3 of 0.1m NaOH is mixed with 60cm^3 of 0.1m HCl.

Solution:

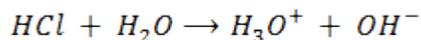


$$0.1 \quad \quad 0.1 \quad \quad 0.1$$

$$0.1\text{moles} \rightarrow 1000\text{cm}^3$$

$$X \rightarrow 40\text{cm}^3$$

$$X = 4 \times 10^{-3}\text{moles} \quad (\text{Limiting factor})$$

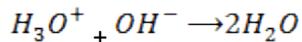


$$0.1 \quad \quad 0.1 \quad \quad 0.1$$

$$0.1\text{moles} \rightarrow 1000\text{cm}^3$$

$$X \rightarrow 60\text{cm}^3$$

$$X = 6 \times 10^{-3}\text{moles of } [\text{H}_3\text{O}^+]$$



$$\text{Moles of } \text{H}_3\text{O}^+ \text{ in excess} \quad (6 \times 10^{-3}) - (4 \times 10^{-3})$$

$$= 2 \times 10^{-3}\text{moles}$$

$$2 \times 10^{-3}\text{moles} \rightarrow 100\text{cm}^3$$

$$X \rightarrow 1000\text{cm}^3$$

$$x = 0.02\text{M of } [\text{H}_3\text{O}^+]$$

$$pH = -\log[H_3O^+]$$

$$pH = -\log(0.02)$$

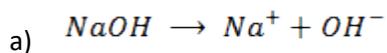
$$\underline{pH = 1.69}$$

3) Calculate the pH of the solution obtained when.

a) 1cm³ of 0.1m NaOH is added to 100cm³ of 0.001m HCl

b) 1cm³ of 0.1m NaOH is added to 100cm³ of 0.1m HCl

Solution:

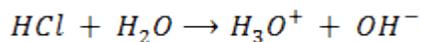


$$0.1M \quad 0.1M \quad 0.1M$$

$$0.1moles \rightarrow 1000cm^3$$

$$X \rightarrow 1cm^3$$

$$X = 1 \times 10^{-4} moles \text{ of } OH^-$$



$$0.001moles \rightarrow 1000cm^3$$

$$X \rightarrow 100cm^3$$

$$X = 1 \times 10^{-4} moles \text{ of } [H_3O^+]$$

$$1 \times 10^{-4} moles \rightarrow 101cm^3$$

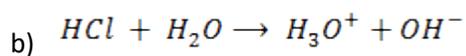
$$X \rightarrow 1000cm^3$$

$$X = 9.9 \times 10^{-4} moles/litre$$

$$pH = -\log[H_3O^+]$$

$$pH = -\log(9.9 \times 10^{-4})$$

$$\underline{pH = 3}$$



$$0.1 \text{ moles} \rightarrow 1000 \text{ cm}^3$$

$$X \rightarrow 1 \text{ cm}^3$$

$$X = 1 \times 10^{-4} \text{ moles of } H_3O^+$$

Again

$$0.1 \text{ moles} \rightarrow 1000 \text{ cm}^3$$

$$X \rightarrow 100 \text{ cm}^3$$

$$X = 0.01 \text{ moles}$$

$$n_T = 0.0001 + 0.01 = 0.0101 \text{ moles}$$

$$0.0101 \text{ moles} \rightarrow 101 \text{ cm}^3$$

$$X \rightarrow 1000 \text{ cm}^3$$

$$X = 0.1$$

$$pH = -\log[H_3O^+]$$

$$= -\log(0.1)$$

$$\underline{pH = 1}$$

BUFFER SOLUTIONS:

A buffer solution is a solution which maintains its pH when small amount of an acid (H^+ or H_3O^+) or alkali (OH^-) is added to it.

OR

Is the one that resist a change in pH when small amount of acid or alkali is added to the solution.

A buffer solution usually consists of a weak acid and one of its salt or a weak base and one of its salts.

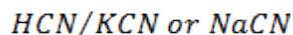
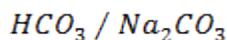
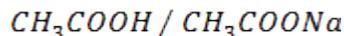
Types of buffer solutions.

i) Acidic buffer solution.

This is the buffer solution which keeps the pH below 7.

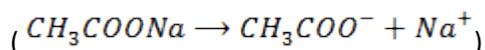
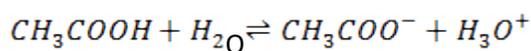
They are formed by mixing a weak acid and its salt (of a strong base)

e.g.



How does the buffer system work?

Consider CH_3COOH / CH_3COONa



Since the salts is strong, it dissociates completely into increases the concentration of CH_3COO^- shifting the equilibrium to the left hand side suppressing the dissociation of acetic acid due to common ion effect. Hence $[CH_3COO^-]$ is equal to the salt concentration and due to the common ion effect, $[CH_3COOH]$ becomes equal to the initial concentration of the acid.

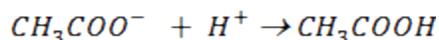
Therefore the solution will contain these important species.

i) A lot of unionized acid

ii) A lot of acetate ions from CH_3COONa

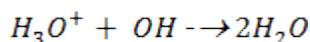
iii) Enough H_3O^+ to make the solution acidic.

When little H^+ are added, the following reaction occurs.



® The acetate ions concentration from the salt are large enough to consume the added hydrogen ions therefore there will be no accumulation of H^+ in the solution.

® If OH^- are added the following reaction occur ;



This decrease $[H_3O^+]$ in the solution, shifting the equilibrium to the right hand side to replace H_3O^+ used to neutralize OH^- added. Therefore no accumulation of OH^- in the solution.

NOTE: Addition of H^+ to acidic buffer increases the acid concentration, but decreases the salt concentration by the same amount of H^+ added.

Addition of OH^- to acidic buffer decreases the acid concentration but increases the $[CH_3COO^-]$ i.e salt by the same amount of OH^- added.

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$[H_3O^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$

$$-\log[H_3O^+] = -\log K_a + \left(-\log \frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$pH = pK_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

Where $[CH_3COO^-] = \text{Salt}$

$[CH_3COOH] = \text{Acid}$

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

According to Henderson Hesselbach

Example:

1. CH_3COOH / CH_3COONa buffer solution containing 1M of acid has a pH of 4.742.
 - a) Determine the salt concentration in buffer given $K_a = 1.8 \times 10^{-5} \text{ moles / dm}^3$.
 - b) To 1 dm³ of a buffer, 0.01M of NaOH, is added. Calculate the pH of the resulting buffer solution.
 - c) Calculate the pH when 0.01 moles HCl are added to 1dm³ of the buffer.
 - d) Calculate the pH of the solution when 0.01moles of NaOH are added to 1dm³ of water sample.
 - e) Calculate the pH of the solution when 0.01moles of HCl are added to 1dm³ of water sample.

ANSWER:

1. Solution
 - a) From Henderson Hesselbach equation.

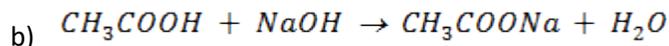
$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$4.742 = -\log (1.8 \times 10^{-5}) + \log [CH_3COONa]$$

$$4.742 = 4.7447 + \log [CH_3COONa]$$

$$\log [CH_3COOH] = -2.72 \times 10^{-3}$$

$$\underline{CH_3COONa) = 0.993M}$$



Less by 0.01 0.01 more by 0.01

$$[CH_3COOH]_{New} = 1 - 0.01$$

$$= 0.99$$

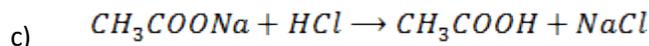
$$[CH_3COONa]_{New} = 0.993 + 0.01$$

$$= 1.003$$

From $pH = pK_a + \log \frac{[Salt]}{[Acid]}$

$$pH = 4.7447 + \log\left(\frac{1.003}{0.99}\right)$$

$$\underline{pH = 4.75}$$



less by 0.01 0.01 more by 0.01

$$[CH_3COONa]_{New} = 0.993 - 0.01$$

$$= 0.983$$

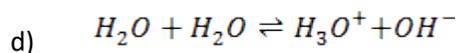
$$[CH_3COOH]_{New} = 1 + 0.01$$

$$= 1.01$$

From $pH = pK_a + \log \frac{[Salt]}{[Acid]}$

$$pH = 4.7447 + \log\left(\frac{0.983}{1.01}\right)$$

$$\underline{pH = 4.73}$$



Initially $x \quad x$

From NaOH $- \quad 0.01$

Equilibrium $x \quad 0.01 - x \approx 0.01$

From $K_w = [H_3O^+][OH^-]$

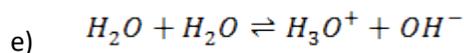
$$1 \times 10^{-14} = 0.01[H_3O^+]$$

$$[H_3O^+] = 1 \times 10^{-12}$$

$$pH = -\log[H_3O^+]$$

$$pH = -\log(1 \times 10^{-12})$$

$$\underline{pH = 12}$$



Initially $x \quad x$

From HCl $0.01 \quad -$

Equilibrium $0.01 + x \approx 0.01 \quad x$

$$pH = -\log[H_3O^+]$$

$$pH = -\log(1 \times 10^{-2})$$

$$\underline{pH = 2}$$

NOTE: Therefore water is not a buffer system

SALT HYDROLYSIS

A salt is a compound which contain metallic or radicle or positive radicle rather than hydrogen (H^+) and acidic or negative or anion radicle rather than hydroxyl ion (OH^-)

Eg:

CH_3COONa , $MgCl_2$, $NaCl$, ZnF_2 , $Ca(NO_3)_2$ and $AlBr_3$, NH_4Cl

CLASSIFICATION OF SALTS

Salts are categorized into four major classes.

These are:

1. i. Normal salt (strong salts).
2. ii. Salts with strong cation and weak anion.
3. iii. Salts with weak cation and strong anion.
- iv. Salts with weak cation and weak Anion.

i) STRONG SALTS

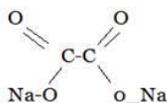
These are salts with strong cation and strong anions.

Eg. $NaCl$, $Ca(NO_3)_2$, $ZnBr_2$, $MgSO_4$ and KBr

ii).SALTS WITH STRONG CATION AN WEAK ANIONS.

These are also known as basic salts mostly are organic salts or salts of carboxylic acid

Eg: CH_3COONa , $HCOOK$, $CH_3-CH_2C-COOK$

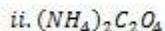
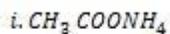


iii) SALTS WITH WEAK CATION AND STRONG ANION

These salts are termed as acidic salts

Eg: NH_4Cl , NH_4F , $(NH_4)_2SO_4$, NH_4NO_3

iv.) SALT WITH WEAK CATION AND WEAK ANION



Salt hydrolysis is the reaction between salt and water to give acid and base it is a reversible reaction of neutralization reaction.

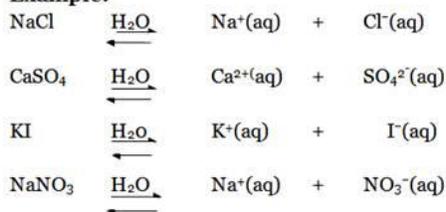
In salt hydrolysis only weak ions react with water to give the respective products.

HYDROLYSIS OF CLASSES OF SALTS

1. Hydrolysis of normal salts

The salts having strong cation and strong anion do not undergo Salt hydrolysis process, rather than ionizing in solution to give free ions.

Example:



2. Hydrolysis of basic salts

The salt having strong cation and weak anion undergo the type of hydrolysis termed as Anionic salt hydrolysis

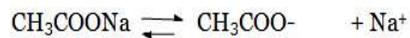
Definition:

Anionic salt hydrolysis is the reaction between water and salt with strong cation and weak anion where by the weak anion react with water to give acid and base.

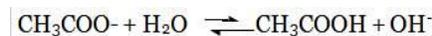
Example



Initially the salt will ionize



Anion will react with H₂O



Example:



Ionization



Anion will react with H₂O



iii) Hydrolysis of salts with weak cation and strong anion. This process is also known as cationic salt hydrolysis

Definition:

Cationic salt hydrolysis is the reaction between water and salt with weak cation and strong anion in which weak cation react with water to give acid and base.

Example:

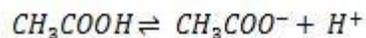


Example



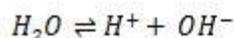
iv) Salt with weak cation and weak anion (weak salt)

This salt undergo both cationic and anionic salt hydrolysis because both weak ions will react with water to give acid and base.



$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \dots \dots \dots (ii)$$

The water dissociation



$$K_w = [H^+][OH^-] \dots \dots \dots (iii)$$

If we divide $\frac{K_w}{K_a}$ (eqn (ii))

$$\frac{K_w}{K_a} = [H^+][OH^-] \times \frac{[CH_3COOH]}{[H^+][CH_3COO^-]}$$

$$\frac{K_w}{K_a} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$\therefore \frac{K_w}{K_a} = K_h \text{ for anionic hydrolysis}$$

Hydrolysis constant for anionic salts hydrolysis

Consider the hydrolysis of CH_3COONa



From hydrolysis equation K_h can be obtained

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-][H_2O]}$$

But $[H_2O] = \text{constant} = 1$

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

HYDROLYSIS CONSTANT (K_h)

Definition:

K_h is the ratio of product of molar concentration of the products to that concentration reactant raised to their power which is equal to the balancing number in a hydrolysis equation.

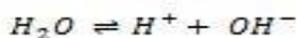
During hydrolysis the weak acid formed and water molecules will also dissociate.

The weak acid dissociation



$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \dots \dots \dots (ii)$$

The water dissociation



$$K_w = [H^+][OH^-] \dots \dots \dots (iii)$$

If we divide $\frac{K_w}{K_a}$ (eqn (ii))

$$\frac{K_w}{K_a} = [H^+][OH^-] \times \frac{[CH_3COOH]}{[H^+][CH_3COO^-]}$$

$$\frac{K_w}{K_a} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$\therefore \frac{K_w}{K_a} = K_h \text{ for anionic hydrolysis}$$

where

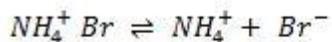
ka = Dissociation constant of acid (CH₃COOH)

kw = Dissociation constant of water

kh = Hydrolysis constant.

Hydrolysis constant for cationic salt hydrolysis

Consider the hydrolysis of NH₄Br

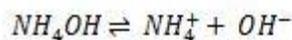


Hydrolysis reaction

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \dots \dots \dots (ii)$$

During hydrolysis the weak base is formed and water molecules will dissociate.

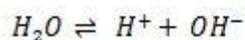
Weak base dissociation



Then

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \dots \dots \dots (iii)$$

Water dissociation



$$K_w = [H^+][OH^-] \dots \dots \dots (iii)$$

Divide eqn (iii) by (iii)

$$\frac{K_w}{K_b} = \frac{[H^+][OH^-][NH_4OH]}{[NH_4^+][OH^-]}$$

$$\frac{K_w}{K_b} = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

$$\frac{K_w}{K_b} = K_h \quad \text{for anionic hydrolysis}$$

where

kb = Dissociation constant of Base

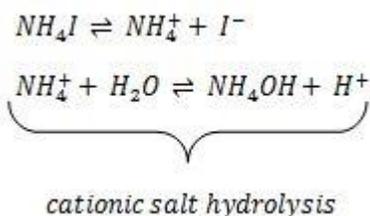
Example

With examples in each briefly write short note on the following

- i) Cationic salt hydrolysis

It is the reaction between water and salt with strong anion and weak cation in which the weak cation react with water to give acid and base.

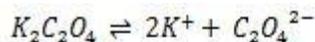
Example



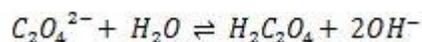
ii) Anionic salt hydrolysis

It is the reaction between water and salt with strong cation and weak anion in which the weak anion react with water to give acid and base.

Example



Then



The above chemical reaction is Anionic salt hydrolysis

(iii) Hydrolysis constant

Hydrolysis constant is the ratio of the products molar concentration to the reactant concentration raised to their powers which is equal to the balancing number in the hydrolysis equation.

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

Normally it is denoted by kh

For anionic salt hydrolysis.

(iv) Acidic salt:

Acidic salt is the type of salt which contain a strong anion and weak cation.

Example:

$(NH_4)_2SO_4$, NH_4Br and NH_4I .

(v) Basic salt

Basic salt is the type of salt which contain a strong cation and a weak anion.

Example:

CH₃COOK, Na₂C₂O₄ and CH₃CH₂COONa.

(vi) Salt hydrolysis :

Salt hydrolysis is the reaction between salt and water to produce base and acid.

Under this process only weak radicals/ions are associated in the reaction.

Example



Example

1. Briefly differentiate cationic salt hydrolysis and anionic salt hydrolysis.

Solution

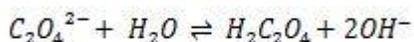
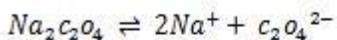
Cationic salt hydrolysis is a reaction between water and salt with weak cation and strong anion where by the weak cation react with water to produce acid and base **while**

anionic salt hydrolysis is a reaction between water and salt with weak anion and strong cation in which the weak anion react with water to produce acid and base.

1. With an example of salt and type of hydrolysis derive the relationship between ka, kw and kh.

Solution

Consider the hydrolysis of Sodium Oxalate.



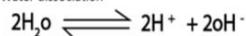
$$\text{Now } Kh = \frac{[H_2C_2O_4][OH^-]^2}{[C_2O_4^{2-}]} \dots \dots \dots (i)$$

During hydrolysis acid formed together with water molecules, ionize in a solution.

Acid ionization.

$$\text{The } K_a = \frac{[H^+]^2 [C_2O_4^{2-}]}{[H_2C_2O_4]} \text{ ----- (ii)}$$

Water dissociation



$$K_w = [OH^-]^2 [H^+]^2$$

$$\frac{K_w}{K_a} = \frac{[OH^-]^2 [H^+]^2 [H_2C_2O_4]}{[H^+]^2 [C_2O_4^{2-}]}$$

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

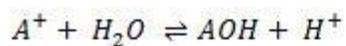
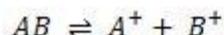
Example

During Hydrolysis the base and water molecule also ionize.

Base ionization

Salt AB undergo cationic salt hydrolysis show that $K_h = \frac{K_w}{K_b}$

solution:

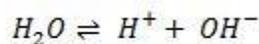


$$\text{Then } K_h = \frac{[H^+][AOH]}{[A^+]} \dots \dots \dots (I)$$



$$\text{Then } K_b = \frac{[A^+][OH^-]}{[AOH]} \dots \dots \dots (II)$$

Water ionization



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

Now $\frac{K_w}{K_b} = \frac{[H^+][OH^-][AOH]}{[A^+][OH^-]}$

$$\frac{K_w}{K_b} = K_h \quad \text{Shown.}$$

Example 4:

Calculate the Hydrolysis constant for the hydrolysis of 0.05 M NH_4NO_3 . if its K_b is 6.67×10^{-6}

Solution

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

$$K_h = \frac{PK_w}{K_b} \quad pK_w = -\log 10^{-14}$$

$$K_w = 10^{-14}$$

$$K_h = \frac{1.0 \times 10^{-14}}{6.67 \times 10^{-6}}$$

$$= 1.499 \times 10^{-9}$$

\therefore The hydrolysis constant is 1.499×10^{-9}

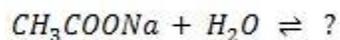
DEGREE OF HYDROLYSIS

Definition:

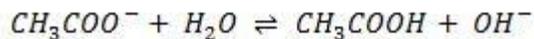
Is the fraction or percentage of the salts that has reacted with water to form acid and base

The degree of Hydrolysis is denoted by h.

Consider the anionic salt hydrolysis below:



Hydrolysis Reaction:



Initially	1	-	-
At equilibrium	1 - h	-	-
Concentrations	(1 - h) c	hc	hc

But

$$(1 - h) \approx 1$$

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$K_h = \frac{hc \cdot hc}{c}$$

$$K_h = h^2c$$

$$h = \sqrt{\frac{K_h}{c}}$$

$$h = \sqrt{K_h \cdot V}$$

But $c = 1/v$.

But

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

Then

$$h = \sqrt{\frac{K_w}{K_a} \cdot V}$$

This is for anionic salt hydrolysis

Where

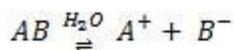
h is the hydrolysis constant

K_w is the water dissociation constant

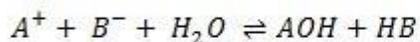
K_a is the acid dissociation constant

THE HYDROLYSIS OF SALT WITH WEAK CATION AND ANION

Consider the salt of weak cation and weak anion as AB. During hydrolysis, the salt will ionize.



weak ions



hydrolysis eqn

$$Kh = \frac{[AOH][HB]}{[A^+][B^-]}$$

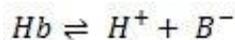
$$[H_2O] = 1 = \text{constant}$$

During the hydrolysis process there is formation of

(i) Weak acid

(ii) Weak base

Ionization of weak acid



$$Ka = \frac{[H^+][B^-]}{[HB]} \dots \dots \dots (i)$$

Ionization of weak base



$$K_b = \frac{[A^+][OH^-]}{[AOH]} \dots \dots \dots (ii)$$

Ionization of water

$$K_w = [H^+][OH^-] \dots\dots\dots(iii)$$

Divide eqn (iii) by (i) and (ii)

$$\frac{K_w}{K_a \cdot K_b} = \frac{[H^+][OH^-] [HB][AOH]}{[H^+][B^-][A^+][OH^-]}$$

$$\frac{K_w}{K_a \cdot K_b} = \frac{[HB][AOH]}{[A^+][B^-]}$$

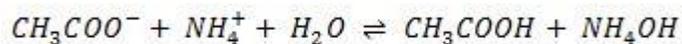
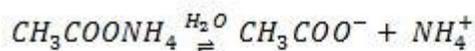
$$\therefore \frac{K_w}{K_a \cdot K_b} = K_h$$

For salt that undergo both cationic and anionic salt hydrolysis (weak salt)

Example

Consider the hydrolysis of ammonium acetate, then derive the relationship between K_h, K_w, K_a and K_b for such hydrolysis.

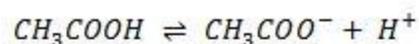
Solution



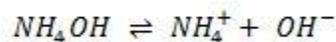
$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$$

$$[H_2O] = 1$$

During the hydrolysis, weak acid and weak base is formed ionization of weak acid



$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$



$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

water ionic product $K_w = [OH^-][H^+]$

$$\begin{aligned} \text{Then } \frac{K_w}{K_a \cdot K_b} &= \frac{[OH^-][H^+][CH_3COOH][NH_4OH]}{[CH_3COO^-][H^+][NH_4^+][OH^-]} \\ &= \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \end{aligned}$$

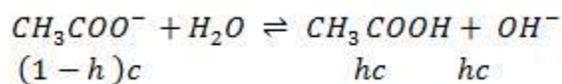
$$\frac{K_w}{K_a \cdot K_b} = K_h$$

The relationship is $K_h = \frac{K_w}{K_a \cdot K_b}$

PH EQUATIONS FOR SALT HYDROLYSIS

a) FOR ANIONIC HYDROLYSIS

Consider the hydrolysis of CH_3COONa



$$K_h = \frac{(CH_3COOH)(OH^-)}{(CH_3COO^-)}$$

$$[OH^-] = \frac{K_h [CH_3COO^-]}{[CH_3COOH]}$$

$$= \frac{K_h c}{hc}$$

$$[OH^-] = \frac{K_h}{h}$$

$$\text{But } h = \sqrt{\frac{K_w \cdot V}{K_a}}$$

$$[OH^-] = \frac{Kh}{\sqrt{\frac{K_w v}{K_a}}}$$

$$[OH^-] = kh \sqrt{\frac{K_a}{K_w V}}$$

$$\text{But } Kh = \frac{kw}{ka}$$

$$[OH^-] = \frac{kw}{ka} \sqrt{\frac{ka}{K_w \cdot v}}$$

But, from water dissociation

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

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

$$\frac{K_w}{[H^+]} = \frac{K_w}{K_a} \sqrt{\frac{K_a}{K_w \cdot v}}$$

$$[H^+] = K_a \sqrt{\frac{K_w \cdot V}{K_a}}$$

$$[H^+]^2 = K_a^2 \cdot \frac{K_w \cdot v}{v_2^2}$$

$$[H^+] = \sqrt{ka \cdot kw \cdot V}$$

$$[H^+] = \sqrt{ka \cdot kw \cdot V}$$

$$[H^+] = (ka^{1/2} \cdot kw^{1/2} \cdot v^{1/2})$$

$$-\log(ka^{1/2} \cdot kw^{1/2} \cdot v^{1/2})$$

$$= \log ka^{1/2} - \log kw^{1/2} - \log v^{1/2}$$

$$pH = \frac{1}{2}pka + \frac{1}{2}pkw - \frac{1}{2}\log v$$

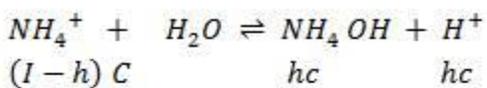
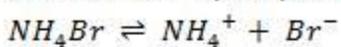
note

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

This is the P^H equation for anionic salt hydrolysis

b) FOR CATIONIC HYDROLYSIS

Consider the hydrolysis of NH_4Br



$$Kh = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

$$[H^+] = \frac{Kh [NH_4^+]}{[NH_4OH]}$$

$$[H^+] = \frac{Kh \cdot C}{hc}$$

$$[H^+] = \frac{Kh}{h}$$

$$\text{But } h = \sqrt{\frac{K_w}{K_b}} \cdot V$$

$$[H^+] = \frac{Kh}{\sqrt{\frac{K_w \cdot V}{K_b}}}$$

$$[H^+] = Kh \sqrt{\frac{K_b}{K_w \cdot V}}$$

$$[H^+]^2 = Kh^2 \cdot \frac{K_b}{K_w \cdot V}$$

$$\text{Also } Kh = \frac{K_w}{K_b}$$

$$[H^+]^2 = \frac{K_w \cancel{K_b}}{K_b \cancel{K_b}} \cdot \frac{K_b}{K_w \cdot V}$$

$$[H^+]^2 = \frac{K_w}{K_b \cdot V}$$

$$[H^+]^2 = \sqrt{\frac{K_w}{K_b \cdot V}}$$

$$[H^+] = k_w^{1/2} \cdot k_b^{-1/2} \cdot v^{-1/2}$$

Then introduce log.

$$\begin{aligned} -\log [H^+] &= -\log (k_w^{1/2} \cdot k_b^{1/2} \cdot V^{-1/2}) \\ &= -\log K_w^{1/2} - \log K_b^{-1/2} - \log V^{-1/2} \\ &= 1/2 - \log k_w - 1/2 - \log k_b - 1/2 - \log V \end{aligned}$$

$$pH = 1/2 pkw - 1/2 pkb + 1/2 \log V$$

This is for the salt undergoing cationic salt hydrolysis

OR

$$PH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log C$$

Example

a) What do you understand by

I. Salt hydrolysis

Is the reaction between water and salt to produce acid and base.

II. Cationic hydrolysis

Is the reaction between water and salt with strong anion and weak cation at which the weak cation react with water to give acid and base.

III. Anionic hydrolysis

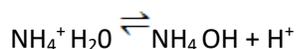
Is the reaction between water and salt with strong cation and weak anion in which the weak anion react with water to produce acid and base.

IV. Conjugate pair

Is the pair of conjugate acid or conjugate base or acid respectively.

b. For cationic hydrolysis show that
$$h = \sqrt{\frac{K_w}{K_b}}$$

Solution. Consider the hydrolysis of NH_4Cl



1 - h h h

At equilibrium (1 - h)c hc hc

$$K_h = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$= \frac{hc}{(1-h)c}$$

But

Assume that $1 - h \approx 1$ (h is very small)

$$K_h = \frac{h^2c}{c}$$

$$\frac{kh}{c} = \frac{h^2c}{c}$$

$$kb/c = h^2$$

$$h = \sqrt{\frac{kh}{c}} = \sqrt{kh \cdot v}$$

$$\text{But } K_h = \frac{kw}{kb}$$

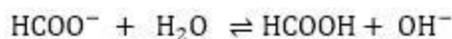
$$\therefore h = \sqrt{\frac{kw \cdot v}{kb}}$$

calculate the conc. of H^+ present in 0.0001M $HCOOH$ ka. $HCOOH = 2.4 \times 10^{-4}$

$$K_w = 10^{-14}$$

Solution





But

$$[\text{H}_3\text{O}^+] = [\text{H}^+] = [\text{HCOOH}]$$

$$[\text{H}_3\text{O}^+] = hc$$

From p^H Eqn.

$$\begin{aligned} p^H &= \frac{1}{2}pka + \frac{1}{2}pkw - \frac{1}{2}\log V \\ &= \frac{1}{2} \times 3.6197 + \frac{1}{2} \times 14 + \frac{1}{2}\log 0.0001 \\ &= 1.8 + 7 + 2 \end{aligned}$$

$$p^H = 10.8$$

$$[\text{H}^+] = \log^{-1}(-10.8)$$

$$= 1.58 \times 10^{-11} \text{M}$$

\therefore The concentration of H_3O^+ is $1.58 \times 10^{-11} \text{M}$

Example 2:

a. Define

p^H is the negative logarithm of hydrogen molar concentration present in the solution.

Acidic salt is the type of salt that consist of strong anion and weak cation.

Basic salt is the type of salt that consist of strong cation and weak anion.

b. Normal salt do not undergo anionic or cationic salt hydrolysis. Briefly account for this statement.

Soln.

Normal salt do not undergo neither anionic nor cationic salt hydrolysis because they have strong acidic and basic radicle and the hydrolysis take place to the weak radicles only. Hence they just ionize in the water only.

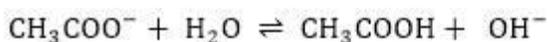
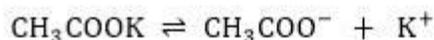
c. Calculate the p^H of the solution with 0.0152M. CH_3COOK if $Ka\text{CH}_3\text{COOH} = 2.18 \times 10^{-8}$ at a particular temperature.

Soln.

From p^H equation.

$$\begin{aligned}
 p^H &= \frac{1}{2}pka + \frac{1}{2}pkw + \frac{1}{2}\log C \\
 &= \frac{1}{2}(-\log 2.18 \times 10^{-8}) + \frac{1}{2}(14) + \frac{1}{2}(\log 0.0152) \\
 &= \frac{1}{2}(-\log 2.18 \times 10^{-8}) + 7 + \frac{1}{2}(\log 0.0152) \\
 &= 9.921 \\
 p^H &= 9.91
 \end{aligned}$$

Alternatively



$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$\frac{10 \times 10^{-14}}{2.18 \times 10^{-8}} = \frac{x^2}{0.0152} \quad \left(\begin{array}{l} \text{Assume } x \text{ is very small} \\ 0.0152 - x = 0.0152 \end{array} \right)$$

$$4.5 \times 10^{-7} = \frac{x^2}{0.0152}$$

$$x^2 = 6.972 \times 10^{-9}$$

$$x = \sqrt{6.972 \times 10^{-9}}$$

$$x = 8.35$$

$$p^{OH^-} = -\log 8.35$$

$$p^{OH^-} = 4.0783$$

$$\text{But } p^H = 14 - p^{OH^-}$$

$$= 14 - 4.0783$$

$$= \underline{9.92}$$

- d. Calculate the p^H of the solution with 0.001M of NH_4NO_3 if $K_b NH_4OH$ is 1.8×10^{-4} .

Soln.

$$\begin{aligned} p^H &= \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log C \\ &= 7 - \frac{1}{2} (-\log 1.8 \times 10^{-4}) - \frac{1}{2} (\log 0.001) \\ &= 7 - 1.8723 + 1.5 \\ &= 8.5 - 1.8723 \\ &= 6.63 \end{aligned}$$

\therefore The p^H of the solution is 6.63

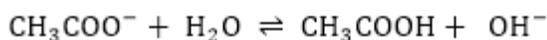
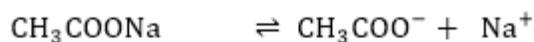
Example 3:

Calculate the hydrolysis constant and the p^H of 0.625M solution of CH_3COONa . K_a of $CH_3C-OOH = 1.754 \times 10^{-5}$ $K_w = 1 \times 10^{-14}$.

Soln.

$$\begin{aligned} K_h &= \frac{K_w}{K_a} \\ &= \frac{1 \times 10^{-14}}{1.754 \times 10^{-5}} \\ &= 5.7 \times 10^{-10} \end{aligned}$$

\therefore The hydrolysis constant is 5.7×10^{-10}



$$\begin{array}{ccc} 0.625 & - & - & - \\ 0.625-x & & x & x \end{array}$$

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$\frac{5.7 \times 10^{-10}}{0.625} = \frac{x^2}{0.625-x} \quad \left(\begin{array}{l} \text{Assume } x \text{ is very small} \\ 0.625-x = 0.625 \end{array} \right)$$

$$x = \sqrt{5.7 \times 10^{-10} \times 0.625}$$

$$x = 1.887 \times 10^{-5}$$

$$[\text{OH}^-] = 1.887 \times 10^{-5}$$

$$p^{\text{OH}} = -\log 1.887 \times 10^{-5}$$

$$p^{\text{H}} = 14 - 4.724$$

$$= 9.27$$

∴ The p^H of the solution is 9.27

E-xample 4.

- a. -What is the p^H of 0.2M solution of NaCN? K_a for HCN = 4 × 10⁻¹⁰ ionic product of -water = 10⁻¹⁴.

Soln.-

$$p^{\text{H}} = \frac{1}{2} pK_a + \frac{1}{2} pK_w + \frac{1}{2} \log C$$

$$= \frac{1}{2} (-\log 4 \times 10^{-10}) + \frac{1}{2} (14) + \frac{1}{2} (\log 0.2)$$

$$= 11.349$$

$$p^{\text{H}} = 11.35$$

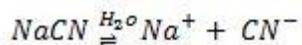
b. -Calculate the p^H of 0.2M NH_4Cl . $K_b = 1.8 \times 10^{-5}$.

S-oln.

$$\begin{aligned}
 p^H &= \frac{1}{2} pK_w - \frac{1}{2} pK_b + \frac{1}{2} \log C \\
 &= \frac{1}{2} (14) - \frac{1}{2} (\log 1.8 \times 10^{-5}) - \frac{1}{2} (\log 0.2) \\
 p^H &= 4.977
 \end{aligned}$$

Example 5.

What is the percentage hydrolysis of NaCN in $N/80$ solution when the dissociation constant for NaCN is 1.3×10^{-9} and $K_w = 1.0 \times 10^{-14}$.



$$80 - X \quad X \quad X$$

$$k_h = \frac{k_w}{k_a}$$

$$\begin{aligned}
 k_h &= \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-9}} \\
 &= 7.69 \times 10^{-6}
 \end{aligned}$$

Also

$$\begin{aligned}
 k_a &= \frac{[Na][CN^-]}{[NaCN]} \\
 x &= \frac{x^2}{80} \\
 &= \sqrt{7.69 \times 10^{-6} \times 80} \\
 &= 0.0248
 \end{aligned}$$

Amount dissociated = 0.0248

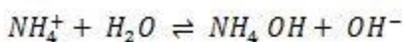
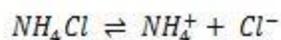
% hydrolysed = $0.0248 \times 100\%$

= 2.48%

The percentage hydrolysis is 2.48%

B. calculate the hydrolysis constant and degree of hydrolysis of NH_4Cl in 0.001m solution $k_b = 1.8 \times 10^{-5}$

Solution.



$$\begin{aligned}
 k_h &= \frac{k_w}{k_b} \\
 &= \frac{10 \times 10^{-14}}{1.8 \times 10^{-5}} \\
 &= 5.55 \times 10^{-10}
 \end{aligned}$$

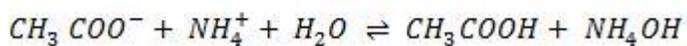
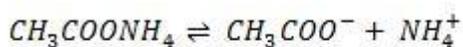
The hydrolysis constant is 5.55×10^{-10}

$$\begin{aligned}
 h &= \sqrt{\frac{k_w \cdot v}{k_b}} \\
 &= \sqrt{\frac{10 \times 10^{-14} \times 1}{1.8 \times 10^{-5} \times 0.001}} \\
 h &= 7.45 \times 10^{-4}
 \end{aligned}$$

The hydrolysis constant is 7.45×10^{-4}

C. calculate the degree of hydrolysis of ammonium acetate if the dissociation constant of ammonium hydroxide is 1.8×10^{-5} that of acetic acid is 1.8×10^{-4} and the ionic product of H_2O is 1×10^{-14} (0.55×10^{-2}).

Solution



Data

$$K_a = 1.8 \times 10^{-5}$$

$$K_b = 1.8 \times 10^{-5}$$

$$K_w = 1 \times 10^{-14}$$

From hydrolysis equation

$$\begin{aligned}
 h &= \sqrt{\frac{k_w \cdot v}{k_a \cdot k_b}} \\
 &= \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}} \\
 &= \sqrt{\frac{1 \times 10^{-14}}{3.2 \times 10^{-10}}} \\
 &= 5.55 \times 10^{-3}
 \end{aligned}$$

Example 6.

What is hydrolysis constant of salt?

Answer

Is the ratio of products concentration to reactant concentration in moles/dm³ raised to their powers which is equal to the balancing number in a hydrolysis equation

Why aqueous solution of sodium carbonate is alkaline derive an expression for the hydrolysis constant and p^H of this solution.

INORGANIC CHEMISTRY 1.1-EXTRACTION OF METALS

Definition: Extraction of metals refers to the process of removing or obtaining metallic elements from their respective ores

What is an ores?

An ores is the mineral from which particular metal can be extracted conveniently and economically. example Haematite (Fe₂O₃), Iron pyrite (FeS₂), galena (PbS), Zinc blende (ZnS), tin- stone or cassiterite (SnO₂)

What are minerals?

- Are naturally occurring metallic compounds found in earth's crust which can be obtained by mining, example Magnetite (Fe₃O₄), Gypsum (CaSO₄·2H₂O), Bauxite (Al₂O₃·2H₂O), Malachite (CuCO₃·Cu(OH)₂), Limestone (CaCO₃) etc.

NB; All minerals are not ores but all ores are minerals

NATURAL OCCURRENCE OF METAL ORES

Metals occur naturally in two states

I. NATIVE OR UNCOMBINED STATE

II. COMBINED STATE

A. NATIVE STATE

The elements are said to occur in the native state when they are found in their elementary form (free metals)

Example; Copper (Cu), Platinum (Pt), Gold (Au), Silver (Ag) and mercury (Hg)

B. COMBINED STATE

The elements are said to occur in combined state when they are found in the form of the compounds. Generally the reactive metals occur as oxides, sulphides, sulphates, silicates, carbonates, chloride, nitrates etc. The elements that occur in combined state include Fe, Cu, Al, Pb, Sn, Ca, Mg, Na, Mn, Cr, Co etc

QUESTION; what are main ores from which tin, copper and aluminium are extracted?

NATURAL OCCURRENCE OF METAL ORES OF TIN, COPPER, AND ALUMINIUM

a) ALUMINIUM

Aluminium is the third element in abundance after silicon and oxygen. It is the most abundant metal in the earth's crust. Aluminium is a reactive metal and hence does not occur as a free metal.

The following are different forms in which aluminium occur in nature;

I. Corundum(Al_2O_3) -Free oxide

II. Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) -Hydrated oxide

III. Silicates ($\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$), KAlSi_3O_8 , $\text{KH}_2\text{Al}_3(\text{SiO}_4)_3$

Kaolin (China clay) Feldspar Mica

IV. Cryolite (Na_3AlF_6)

Aluminium ores have different colours. The colours are due to the presence of other metals which are impurities, example Ruby (red) containing Iron and Titanium, Sapphire (Blue) containing cobalt and Titanium

Bauxite is the most economic ore from which Aluminium is extracted. Deposits of bauxite are exploited in South-East Europe, India, Australia, Brazil, USA, and West Indies

b) TIN (Sn)

Tin does not occur as free element because it is moderately reactive metal. Tin occurs in form of oxide (tin-stone SnO_2) and sulphide (tin-pyrite $\text{Cu}_2\text{S}\cdot\text{FeS}\cdot\text{SnS}_2$). The important ore of tin is cassiterite (tin-stone) this one contains (0.5-10)% of the metal as SnO_2 and the rest are impurities i.e. sulphides of Fe, Cu and tungstates of Fe^{2+} (FeWO_4), Mn^{2+} (MnWO_4), sand, silicious matter, earth matter etc.

The miners call tin-stone as black tin to distinguish it from the white tin which has the name given to metal. Tin deposits occur in Malaysia, Indonesia, Bolivia, China, Burma, Thailand and Nigeria

c) COPPER (Cu)

Copper occurs as free element as well as in combined state. In combined state copper occurs as copper pyrite (CuFeS_2), azurite ($2\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$) and malachite ($\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$). Malachite and azurite are basic carbonates. Deposits of copper occur in Zambia, Democratic Republic of Congo. CuFeS_2 is the chief ore of copper

NB: i) Copper occurs as free metal in late superior in Canada

ii) Copper also occurs naturally in form of oxide (ruby ore – Cu_2O)

iii) Minerals and ores differ from one another due to the fact that minerals contain a low percentage of the metal while the ores contain a large percentage of the metal

iv) The metal cannot be extracted from the mineral; it can be extracted from an ore.

STAGES OF METAL EXTRACTION

There are three major stages of metal extraction

- I. Concentration of ore
- II. Reduction
- III. Refining of purification

I. CONCENTRATION OF ORE

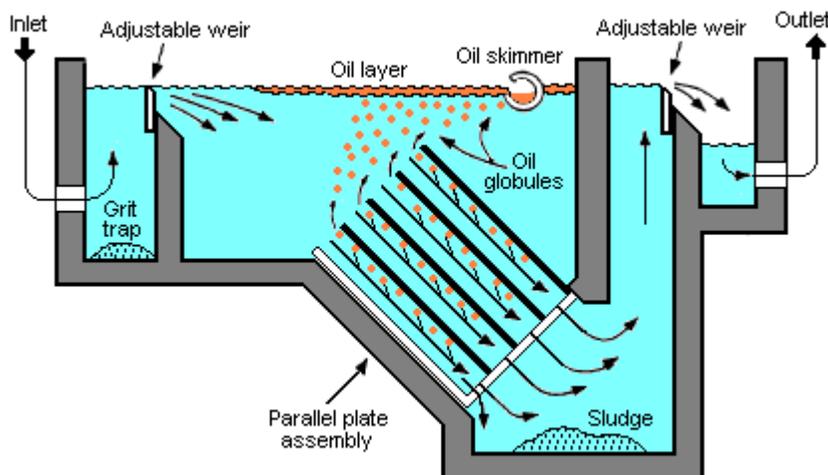
Concentration of ore means increasing the metallic content of the ore by removing the impurities (gangue). The ore which is mined usually contains large amount of rocky impurities such as sand, clay, limestone which are called gangue.

Definition; Gangue is the worthless or useless earthy impurities which are found in an ore.

Before concentration proper separation of ore is carried out, the ore is broken up into lumps which are then ground down to a fine powder which is suitable for the next operation. Concentration of the ore is carried out by any of the following methods depending upon the nature of the ore and gangue.

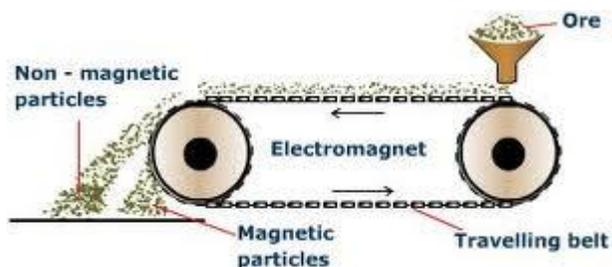
1) GRAVITY SEPARATION (WASHING WITH WATER)

This process is applied where there is well marked difference in the densities of the gangue and the ore. The crushed ore is washed by current water on a sloping table filled with a series of corrugated boards. The table is kept vibrating all the time. The lighter particles of gangue are washed off leaving behind heavier particles of the ore.



2) MAGNETIC SEPARATION

The magnetic impurities present in an ore are separated by a magnet. The powdered ore is allowed to fall on a rubber belt moving around two rollers. One of the rollers is a strong magnet, the ore moves with the belt towards the magnetic roller and then the belts take a turn near the magnet, the magnetic components are attracted by the magnet and form a separate heap. The non-magnetic components (e.g. tin-stone SnO_2) is separated from magnetic component (e.g. Wolframite FeWO_4).

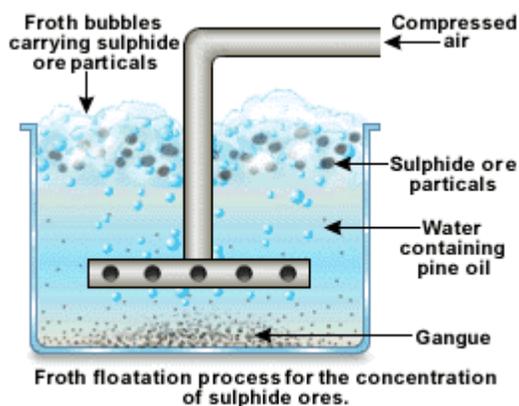


3) FROTH FLOTATION

This method is commonly used for concentration of the low sulphide ores like galena (PbS), copper iron pyrite ($CuFeS_2$ or $Cu_2.Fe_2S$), Zinc blende (ZnS). This method of concentration is based on the different wetting characteristics of the sulphide ore and the gangue particles.

The finely powdered ore is mixed with water in a tank (floatation cell). Some amount of pine oil (froth) and sodium ethyl xanthates collectors are added to it. Air is then blown through the mixture vigorously. The sulphide ore particles which are wetted by the oil rise up to the surface of liquid. The sulphide ore from stable froth which is skimmed off. The gangue particles which are wetted by water sink to the bottom of the tank (floatation cell). The froth with sulphide particles are collected in a separate tank

NB; The role of sodium ethyl xanthate is to collect sulphide ore particles. This compound is attached to sulphide ore particles and makes them water repellent. As a result the sulphide ore particles pass on into froth easily.



4) LEACHING

In this method the ore containing impurities is leached with aqueous solution of a suitable dissolving reagent so that the metal in an ore is converted into simple salt or complex compound while the impurities remain insoluble in the reagent which ore removed by filtration. The metal is then extracted from the simple salt or complex compound formed example impurities in bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) i.e FeO , Fe_2O_3 and SiO_2 can be removed by heating. The crushed bauxite with sodium hydroxide solution (Bayer's process). Aluminium present in the ore is converted into a soluble complex compound (aluminate complex – NaAlO_2) while the impurities (i.e FeO , Fe_2O_3 and SiO_2) remain insoluble and hence are filtered out.

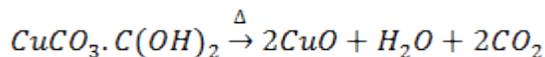
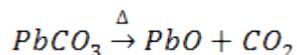
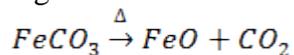
5) CALCINATION OF THE ORE

Calcination of ore refers to the process of heating the concentrated ore strongly in a limited supply of air or in the absence of air. The process of

Calcination brings about the following changes;

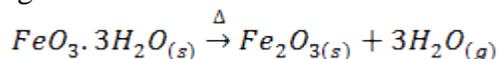
- a) The carbonates ores are decomposed to their representative metal oxide

e.g.

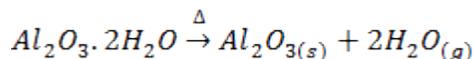


- b) Water of crystallization in the hydrated oxide gets lost in form of water vapour.

eg.



Limorite

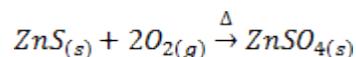
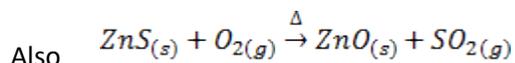
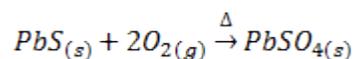
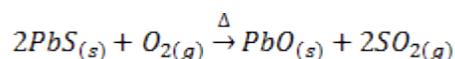


Bauxite

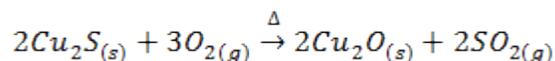
- c) Organic matter, if present in the ore gets lost or expelled and the ore becomes porous

6) ROASTING

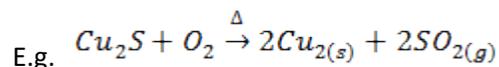
Roasting is the process of heating the concentrated ore strongly in excess air or oxygen below its melting point. Roasting can be done at moderate or high temperature. The roasting is generally for sulphide ores, when roasting takes place at moderate temperature some portion of the sulphide ore like galena (PbS), Zinc blende (ZnS) is converted into metallic oxide and remaining portion is converted into metallic sulphates.



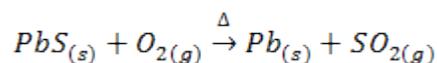
When roasting takes place at high temperature in the presence of oxygen, some sulphide ore give metallic oxide.



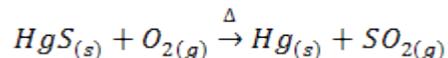
The sulphide ores of some metals like Cu, Pb, Hg, Sb etc when heated strongly in excess of air or oxygen are reduced directly to the metallic elements



Copper glance



Galena



THE DIFFERENCE BETWEEN CALCINATION AND ROASTING

1. Calcination is used for hydrated oxides or carbonates while roasting is for sulphide ores.
2. In calcination the ore is heated strongly in the absence of air or oxygen while in roasting the ore is heated in excess air or oxygen.
3. In calcination the hydrated oxide or carbonate is converted metallic oxide while roasting the sulphides ore is converted into metallic oxide or sulphates or metallic element.

I. REDUCTION

During the extraction of a metal from its ore, the metal ions are reduced to metal atoms by accepting electrons. Thus extraction of a metal from its ore is a reduction process. Reduction of a metal ores by thermal or electrolytic reduction method

In thermal reduction method heat is used in extracting the metal from its ore. In this method a suitable reducing agent may be used example coke, coal, Al, Co, Carbon, Mg, Ca etc

The elements which are extracted by this method are those which are moderately reactive example Zn, Pb, Fe, Sn, Cu etc Reaction takes place either in an electric furnace or blast furnace or suitable container

In electrolytic reduction, electricity is used in extracting the metals from its ore. This method is used in extracting metals which are strongly electropositive (more reactive) like Na, K, Ca, Mg and Al. These metals cannot be reduced by the normal reducing agent like Co or Carbon because their compound (ores) is stable. Even if the metal is formed, carbon reacts with the metal produced to form carbide at high temperature. These reactive metals are extracted by passing through their molten or fused chlorides oxides or hydroxides.

II. PURIFICATION (REFINING) OF IMPURE METALS

Purification is a process of removing impurities from the extracted metal. The metal obtained contain many number of impurities and hence need to be purified. The impurities include other metals, non-metals, unreduced oxides and sulphides of metal slag. The method to be used in purification of a particular metal depends on the nature of the metal to be purified and the impurities to be removed and the purposes for which the metal is to be used

The method used for refining the impure metals can be categorized in four categories

1. PHYSICAL METHODS

a) LIQUAFACATION PROCESS

The process is used for the purification of the metal which melts at lower temperature than each of the impurities associated with it. This method is for purification of Sn, Zn and Pb.

b) FRACTIONAL DISTILLATION

This process is used to purify those metals which are volatile and the impurities in them are non-volatile and vice versa. The vapour of the metal is condensed in a separate vessel while the non-volatile impurities remain behind in the vessel in solid state. Example Purification of Zn where As, Cd, Pb and Fe are impurities.

2. CHEMICAL METHOD

a) OXIDATIVE PROCESS

This process is used to remove metallic and non-metallic elements present as impurities example Mn, Cu, Pb, Sn, Fe, Ag, C, P, S, Si etc. When the oxygen or air is passed through the impure molten metal, the impurities are easily oxidized into their oxides

These oxides;

- i) May form scum on the surface of the metal and hence can easily be removed by skimming
- ii) May be volatile and hence they can escape through the mouth of the furnace
- iii) May form a slag with the lining on their side surface of the furnace and may thus be removed

b) THERMAL DECOMPOSITION METHOD

In this method, the impure metal is converted into a suitable volatile compound which on being heated decomposes to give pure metal, example purification of nickel by Mond's process (carbonyl process)

3. AMALGAMATION PROCESS

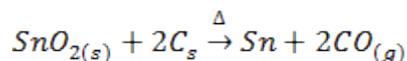
This process is used for extraction of silver and gold. Both silver and gold form amalgam with mercury (example Au/Hg and Ag/Hg). When Au /Hg or Ag/Hg is distilled in an irot retort, mercury being more volatile, distilled off and Au or Ag metal is left behind in the retort.

4.ELECTROLYTIC PROCESS

Purification by electrolytic method gives metal of high purity. In this process, the impure metal is made the anode of the electrolytic cell while the pure metal is made the cathode of the cell. An aqueous solution of suitable sample or complex salt of the metal having some corresponding acid (if necessary) is used as an electrolyte. When the electric current of appropriate strength is passed through the electrolyte, the metal from the impure plate (anode) migrates to the pure plates (cathode) where it is deposited. The soluble impurities go into the solution while the insoluble settle down at the bottom, below the anode. The matter settled below the anode is called anode mud or anode sludge. Sometimes the anode mud contains valuable metals which can be extracted from it. The metal that can be purified by this method include Sn, Pb, Cu, Ag, Ni, Zn, Cr etc

THERMAL REDUCTION OF TIN STONES (SnO₂)

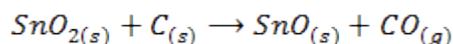
Tin is generally extracted from tin stone (SnO₂). This contains SiO₂ as an impurity (acidic impurity). In order to remove this impurity and reduce tin stone to tin metal, the oxide is mixed with anthracite coal and a basic flux like lime (CaO). The mixture is heated in a reverberatory furnace at 1200°C-1309°C. Then tin stone (SnO₂) is reduced to tin metal (molten tin) and the impurity SiO₂ combine with CaO to form a slag of CaSiO₃ (Calcium Silicate). The molten tin (heavier) forms the lower layer and slag forms the upper layer.



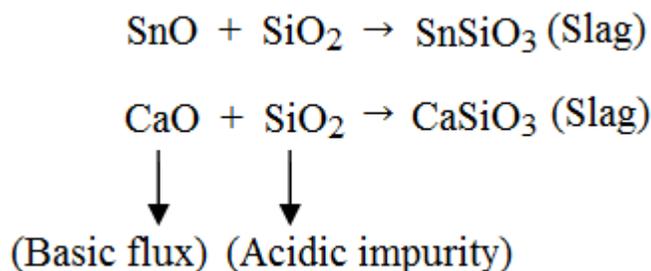
Molten tin

The molten tin is tapped and cast into blocks or ingots. The block contains 70% of metallic tin

Some SnO is also formed during the reduction of SnO₂ to Sn

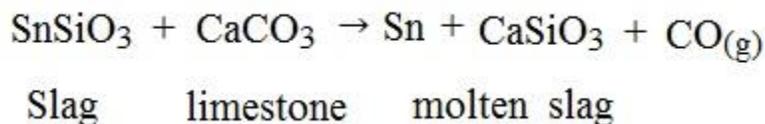


The SnO and CaO react with silica (SiO₂) to form slag of SnSiO₃ and CaSiO₃



The slag of SnSiO₃ and CaSiO₃ being lighter floats on the molten tin metal as an upper layer which is easily removed. Thus SiO₂ (Impurity) is removed in form of a slag. The tin metal can

also be recovered from SnSiO₃ by melting it with limestone (CaCO₃) in a blast furnace or reverberatory furnace.



NB:

I. Flux is a substance which reacts with the gangue (impurities) during smelting to form fusible compound which can easily be removed from molten metal, example CaO and SiO₂. The CaO is basic flux while SiO₂ is an acidic flux.

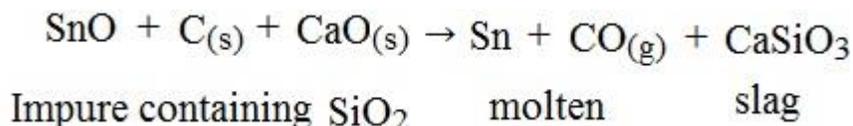
The acidic flux removes the basic impurities example CaO, FeO, MgO etc. The basic flux removes acidic impurities like SiO₂, P₂O₅ etc

II. Slag is a fusible compound obtained by the combination of the flux and gangue present in the ore.



III. The gangue may be acidic (example SiO₂) or basic (example CaO, MgO, FeO etc).

IV. Smelting is the process of conversion of roasted or calcined ore into molten metal using a suitable reducing agent at high temperature in a current of air.



ELECTROLYTIC REDUCTION (ELECTRO METALLURGY)

This method is used for extraction of metals which are very reactive and form very stable compounds for example the oxides, chloride, hydroxides etc of more reactive metal like Na, K, Mg, Ca, Al etc are very stable and hence cannot be reduced to free metals either by carbon or aluminium. However the oxides of the above metal can be reduced by carbon at very high temperature, but as soon as the metal is formed reacts with carbon to form metal carbide. Therefore the metals are obtained by reducing their suitable molten (fused) salts like chlorides, hydroxides etc by electrolytic reduction. The metal is liberated at the cathode. An aqueous electrolyte is not used in electrolytic reduction because the metal obtained at the cathode reacts with water present in the solution

In order to make an electrolytic reduction successful the following condition (criteria) must be satisfied;

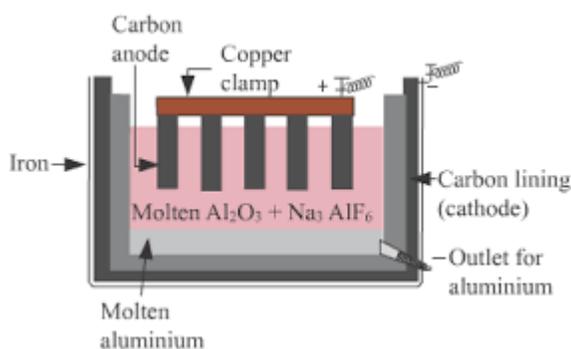
- The liberated metal should not be miscible with the melt (soluble in the melt) for example potassium cannot be obtained by electrolysis of (KCl and CaCl₂) melt, since the liquid potassium is soluble in CaCl₂
- The products obtained as a result of electrolysis may react and hence must be collected separately
- Some other salts may be added to lower the Melting point of compound that melt at very high temperature. The decrease in Melting point makes the process of electrolysis take place at the lower temperature.
- The cell and electrodes should be such of material which are not affected by the electrolyte or the products obtained after electrolysis

ELECTROLYTIC REDUCTION OF ALUMINIUM FROM ALUMINIUM OXIDES(Al₂O₃)

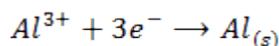
In the electrolytic reduction of aluminum pure Al₂O₃ is mixed with Cryolite (Na₃AlF₆) and then the mixture is melted in an electric furnace. The fused mixture of Al₂O₃ and Na₃AlF₆ is taken in an iron tank lined with carbon from inside. This carbon lining acts as cathode and carbon rods which are dipped into the molten Al₂O₃ and Na₃AlF₆ acts as anode. On passing electric current aluminium metal in the molten state is liberated at the cathode and sinks to the bottom of the cell from which is removed periodically (time to time).

Oxygen from the electrolyte is liberated at the anode. Some of the oxygen combines with the carbon anodes to form carbon monoxide and carbon dioxide. The anodes therefore are gradually worn out.

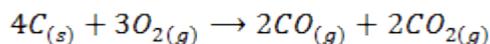
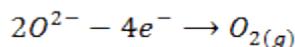
NOTE; The cryolite serves as a solvent and not decomposed



Reaction at the cathode (reduction)



Reaction at the anodes (oxidation)



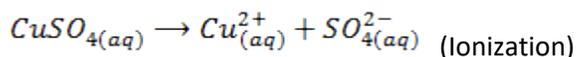
Thus O₂, CO and CO₂ are liberated at the anodes

PURIFICATION OF BLISTER COPPER

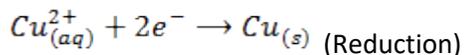
Copper obtained from copper-iron pyrite (CuFeS₂) is called BLISTER COPPER. This copper contained many impurities like Fe, Ni, Zn, Ag, Au etc.

In refining blisters copper, a thick plate of impure copper is made the anode and a thin plate of pure copper is made the cathode. The cathode is coated with graphite and oil which helps in scrapping the copper easily that gets deposited on the cathode 15% CuSO₄ solution containing 5% of H₂SO₄ is used as an electrolyte.

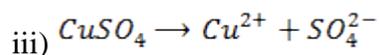
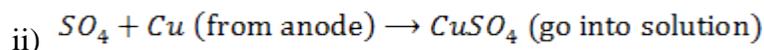
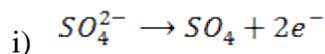
On passing electric current through the electrolyte ionization of CuSO₄ tends to take place



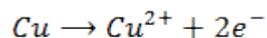
The copper ions (Cu²⁺) obtained move towards the cathode where they accept electrons and become neutral Cu atoms. Thus cathode (pure copper plate) goes on becoming thicker and thicker in size as the electrolysis goes on.

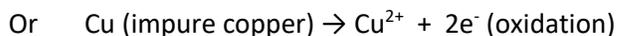


The SO₄²⁻ ions move towards the anode where they lose electrons and become sulphate radicals. These radicals have strong tendency to combine with Cu atoms of copper anode (impure copper plate) to form CuSO₄ which move into the solution which they are again ionized to give Cu²⁺ ions. These Cu²⁺ ions migrate to the cathode where they are deposited as free Cu atoms.



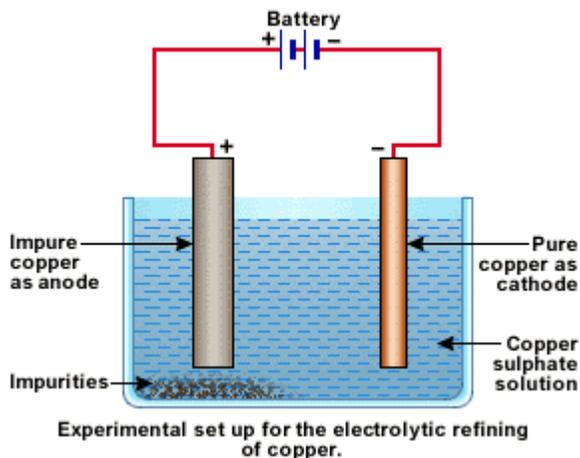
On adding equation (i), (ii) and (iii) we obtain;





The equation above represents the anode reaction (oxidation). This reaction indicates that the anode goes on becoming thinner and thinner in size as the reaction proceeds. From the reaction at the (anode), the pure copper is transferred from impure copper plate to pure plates (cathode).

The soluble impurities like Fe^{2+} , Ni^{2+} , and Zn^{2+} pass into solution as sulphates while the insoluble impurities (example Ag and Au) which are not affected by $\text{H}_2\text{SO}_4\text{-CuSO}_4$ solution settle down below the anode as ANODE MUD or ANODE SLUDGE.



ORGANIC CHEMISTRY 1.1 -POLYMERS

It is obtained from 2 words

- Poly – many
- Merons- units

Polymers are gigantic molecules which form chain of molecules.

A **polymer** is a giant chain like molecule obtained by intermolecular combination of large number of small molecules of the same or different types known as monomers.

E.g: Nylon 6,6

Polyvinylchloride (PVC) $CH_2 = CHCl$ (This is the monomer)

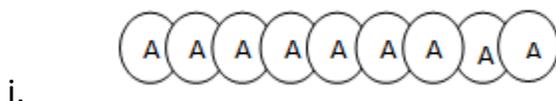
Monomers are small molecules (simple molecules having low molecular masses) which are capable of combining almost indefinitely together to form a polymer.

Structure of polymers

The primary structure of polymers is given by the types of monomers and their arrangement in molecules in the polymer.

If the polymer is made up of one type of monomer, it is known as Homopolymer or simple polymer.

E.g:



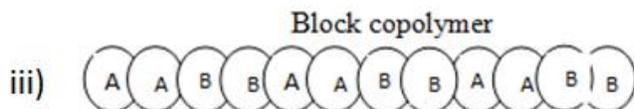
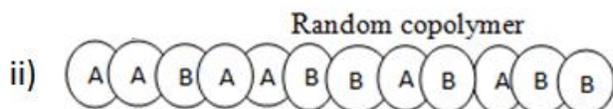
ii. PVC i.e. $CH_2 = CHCl$

If the polymer is made up of two or more different types of monomers known as copolymer

There are 3 types of copolymer depending on order of polymer units

TYPES OF POLYMERS

- Synthetic Polymers.
- Natural / Synthetic rubber.
- Vulcanisation .



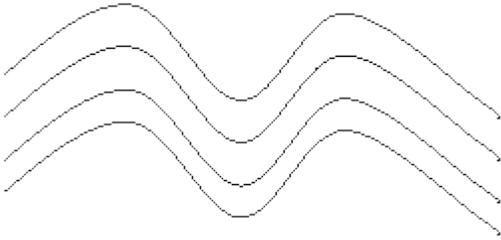
Examples of copolymer include:

- (a) Nylon 6,6
- (b) Polyester

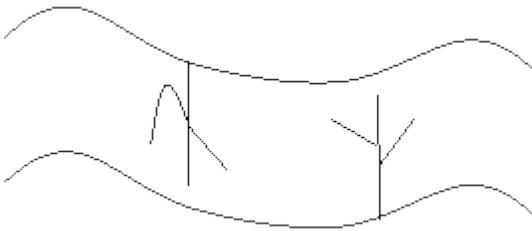
Polymer can be classified into 2 classes on the basis of their structures

- (a) Linear polymer
- (b) Branched chain polymer

Linear chain polymer



Branched chain polymer



Properties:

- i. Linear chain polymer have higher melting point and boiling point than branched polymers

Reason: - Van der Waal forces are stronger in the linear chain polymer.

- ii. Linear polymer have higher density
- iii. Linear polymer also have higher tensile strength

i)Classification based on molecular forces

There are 2 major classes

1. Thermosetting polymer
2. Thermoplastic polymer

THERMOSETTING POLYMER

- These are polymers which cannot be moulded on heating
- When heated they become hard.

Reason: - On heating they undergo further reaction which increases cross linked chain. They cannot be fused i.e infusible.

E.g: Bakelite

THERMOPLASTIC POLYMER

These are polymers which can be moulded on heating.

- They become soft when and when heated become stiff

E.g: PVC

They are linear structures with no cross linkage. Van der Waal will exist between molecules

ii) Classification based on the nature of polymer

There are 2 major classes

1. Natural
2. Artificial or synthetic polymer

Natural
polymers

Example:

- i. Cotton made up of cellulose, starch (made of glucose)
- ii. Bamboo stick
- iii. Paper
- iv. Proteins
- v. DNA, monomer nucleic acid

Artificial polymers

Example:

- a. PVC, monomer $CH_2 = CHCl$ (Chloroethene)
- b. Cellulose

iii) Classification based on the mechanism of polymerization

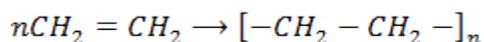
There are 2 major classes of polymer

- a. Addition polymer
- b. Condensation polymer

A.

Addition polymerization

This is due to combination of unsaturated monomers (contain double or triple bond)



Ethene

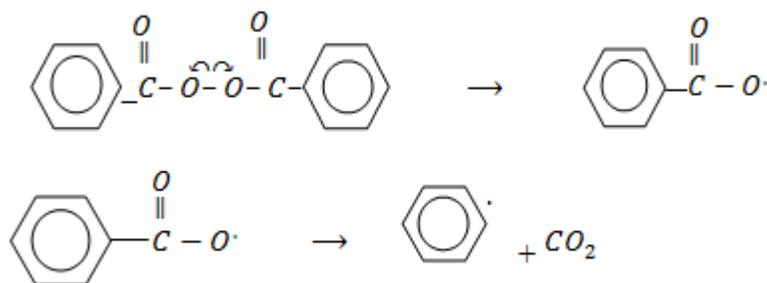
polyethene

Addition polymerization proceeds into 3 possible mechanisms

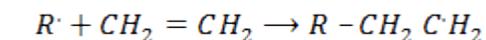
1. -Free radical polymerization
2. -Cationic polymerization
3. -Anionic polymerization

Free radical polymerization

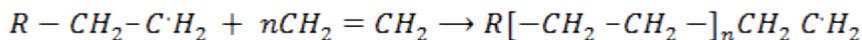
Free radical polymerization is one which the reaction are catalysed by free radical obtained by organic peroxide (R-O-O-R')



Step: 01 Chain initiation step

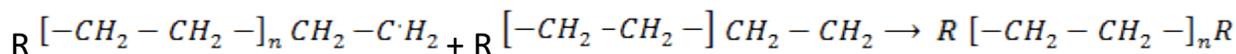


Step : 02 Chain propagation step



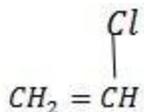
Step: 03 Chain termination step

The reaction stops when two free reactions combine or when the radicals undergo disproportionation

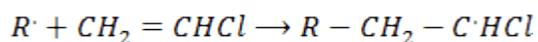


Example

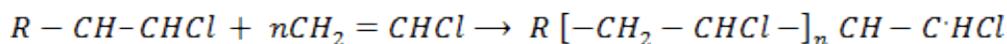
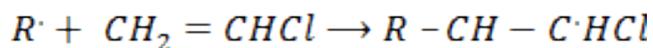
Polymer



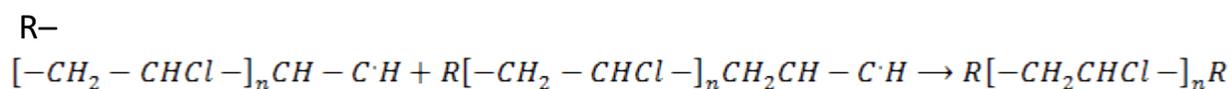
Chain initiation step .



Chain propagation step

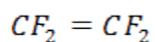
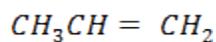


Chain termination step



Polymer

Other polymer can be made from



Cationic polymerization

In this polymerization the initiator is an electrophyl. The electrophyl adds to the alkene causing it to become a cation

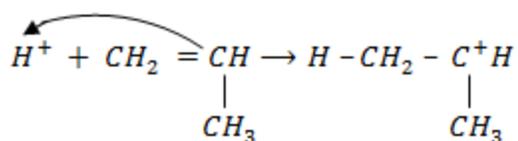
Example of initiators:-

electrophiles H^+ , $-NO_2$

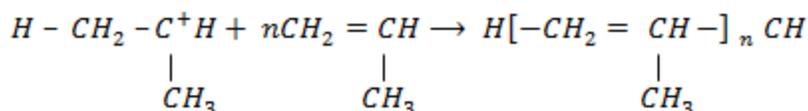
- i. Lewis acid e.g $AlCl_3$, BF_3 , H^+

Mechanism

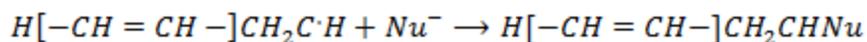
1. 1. Chain initiation step



2. Chain propagation step

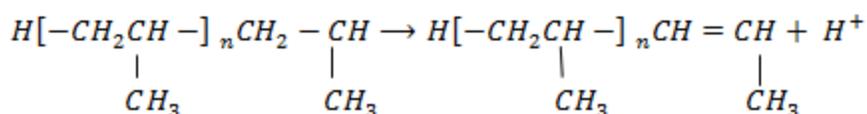


3. Chain termination step



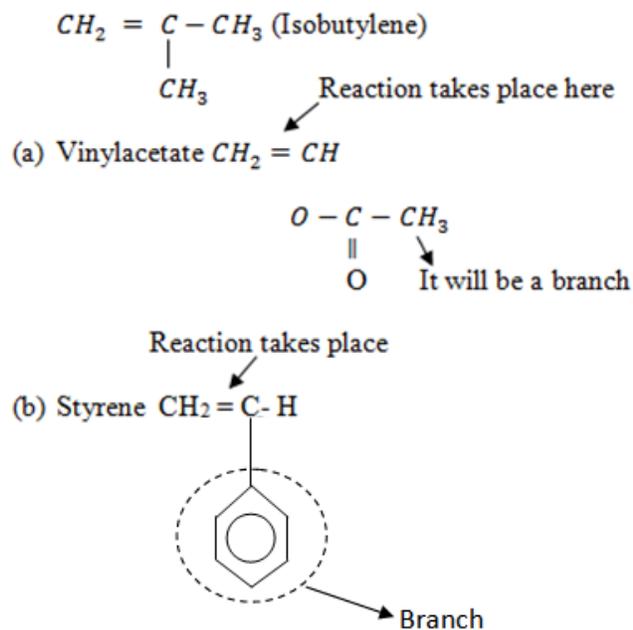
NOTE: Chain termination can either take place by loss of proton or absorption of the nucleophil

By loss of proton



Here we use a strong base to remove the hydrogen

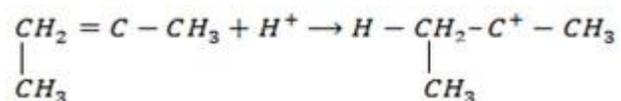
Other monomers which can undergo Cationic polymerization include



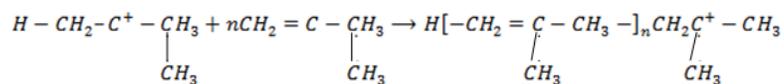
Using Isobutylene

1.

1. Chain initiation step

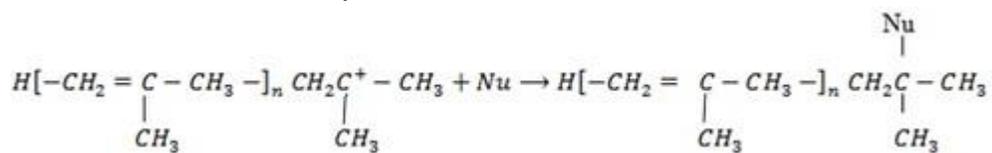


2. Chain propagation step



3.

3. Chain termination step



Anionic polymerization

Mechanism

Initiated by nucleophile that react with alkenes to form anionic propagating site

Example of nucleophile

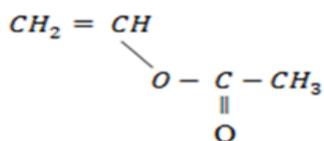
NaNH₂

Butyl lithium BuLi

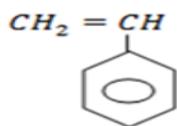
R - O⁻ (Alkoxide)

Grignard reagent

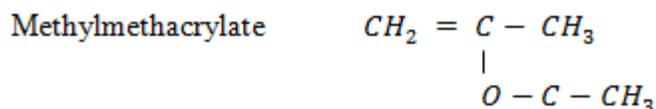
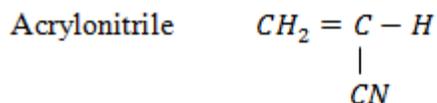
This reaction occur if the carbon is stabilized by a suitable electron withdrawing group



Vinylacetate

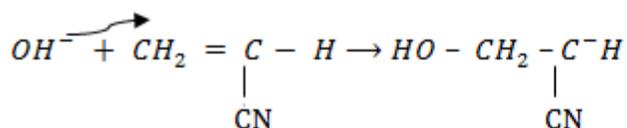


Styrene

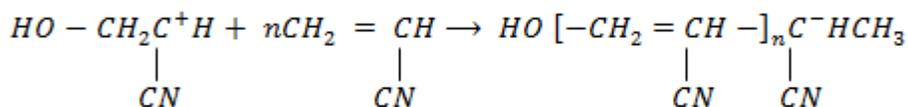


Mechanism

1. Chain initiation step

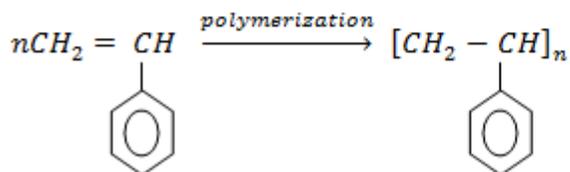
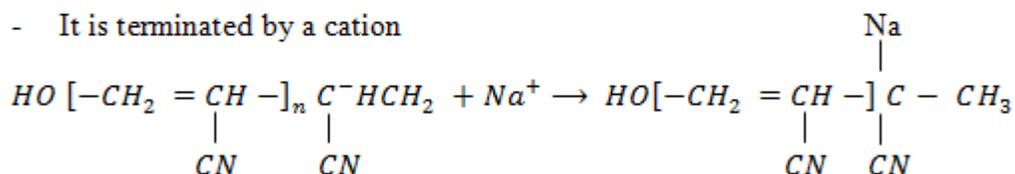


2. Chain propagation step

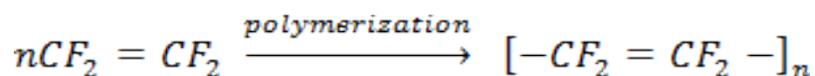
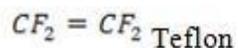
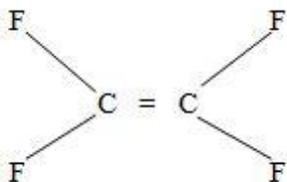


3. Chain termination step

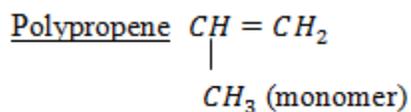
- It is terminated by a cation



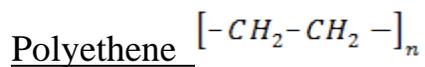
Polytetrahaloroethene



Uses of polymers :



Used in making pipes, bags, container and unbreakable bottles



Used in making pipes, containers, bottles, electrical insulation

Styrene

Monomer $CH = CH_2$



Polymer $[-CH - CH_2 -]_n$



USES:

- Household goods
- Electrical insulation
- Optical lenses

Polychloroethane

Monomer $CH = CH_2$
|
Cl

Typical chain section

| $[-CH - CH_2 -]_n$

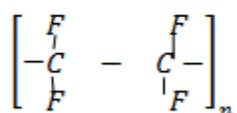
Cl

USES;

- Cable insulation
- Pipes
- Hoses
- Fabrics
- Flooring

Polytetrafluoroethane

Monomer $CF_2 = CF_2$

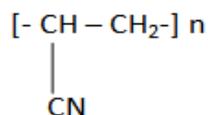
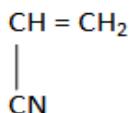


USES:

- -Surface coating of fans (non stick)
- -Pipes
- -Apparatus for chemical plants

6. Polypropanonitrile

Monomer

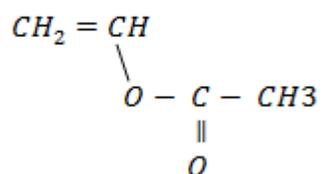


USES:

-Tertiles

7.Polyethanylethanoate (vinyl acetate)

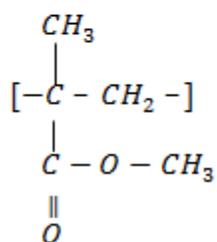
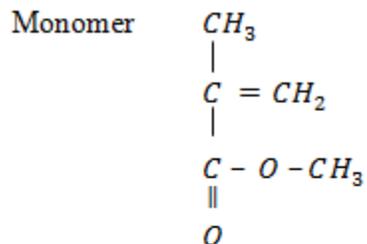
Monomer



USES:

- -Paints
- -Adhesives
- -Water repellent coating

8.Perspex (polymethyl-2- methyl(propanoate)



USES:

- -Optical lenses
- -Glasses
- -Used as glue and paint

CONDENSATION POLYMERIZATION

It takes place through condensation reaction between two bifunctional or trifunctional monomers with simultaneous loss of small molecules such as H₂O, HCl, NH₃ etc.

Example:

- i. Polyesters

ii. Polyamides or polypeptides

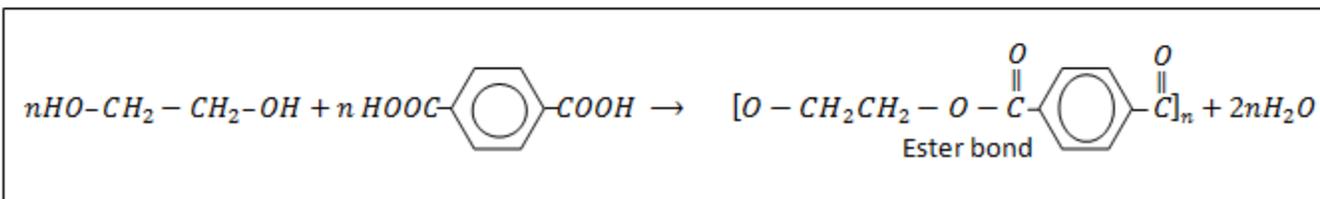
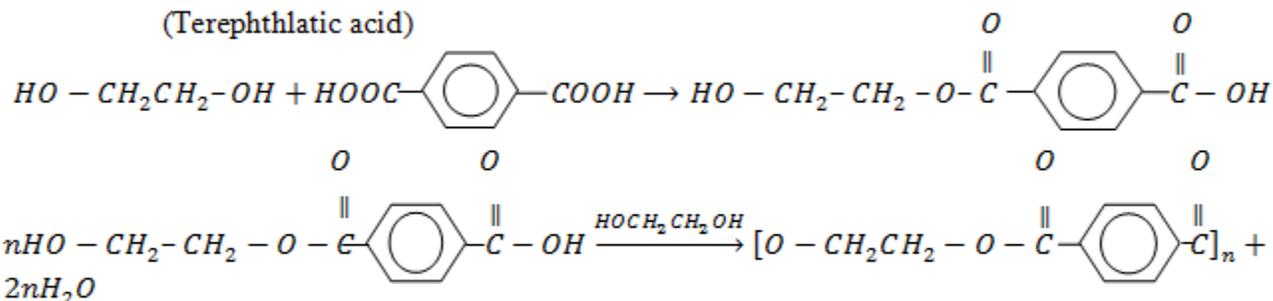
iii. Terylene

It is made up of two monomers

Polyester e.g Terylene.

1. $HO-CH_2-CH_2-OH$ Ethane-1,2-diol

2. $HOOC-\text{C}_6\text{H}_4-COOH$ Benzene-1,4-dicarboxylic acid
(Terephthalic acid)

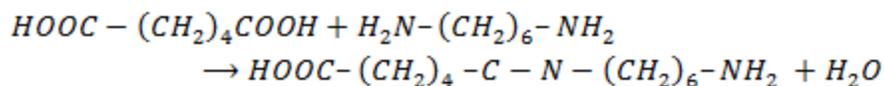


Polyamides e.g Nylon 6, 6 (polyamide)

It is made up of two monomers

i. $HOOC - (CH_2)_4COOH$ Hexane -1,6-dicarboxylic acid

ii. $H_2N - (CH_2)_6 - NH_2$ Hexane -1,6- diamine

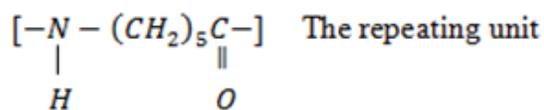


Nylon 6,6

Nylon 6

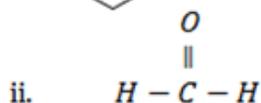
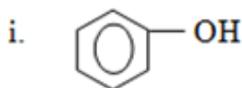
The monomer here is $H_2N - (CH_2)_5COOH$

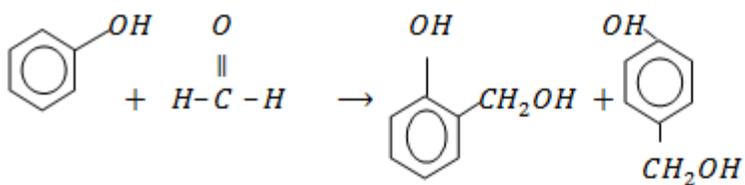
The polymer will be



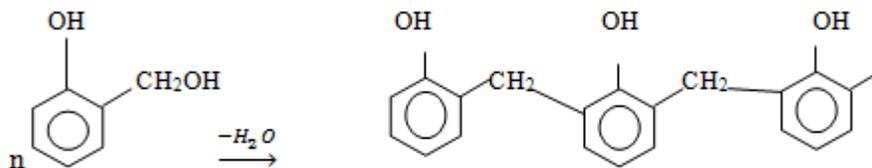
Bakelite

It is made up of two monomers

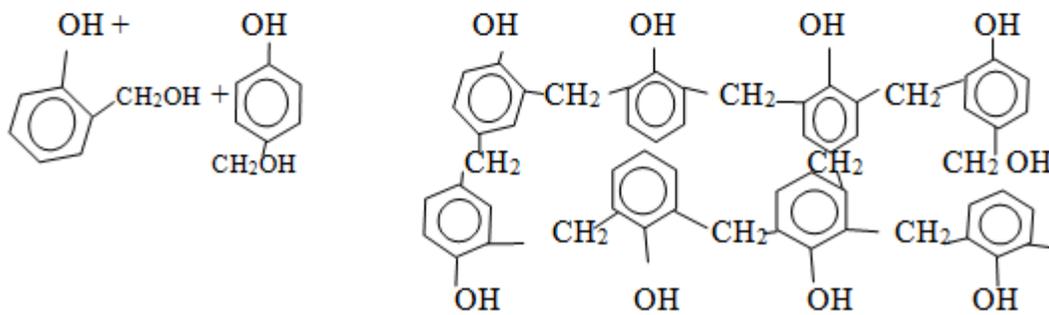




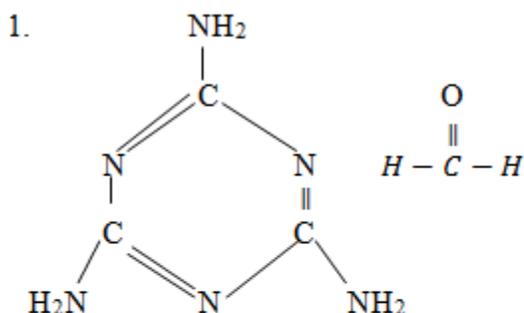
Polymerization



There will be formation of cross linked polymer



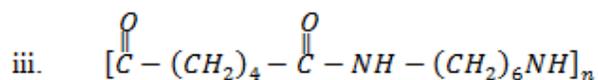
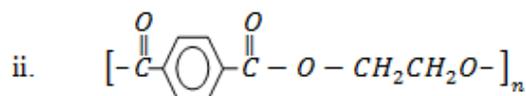
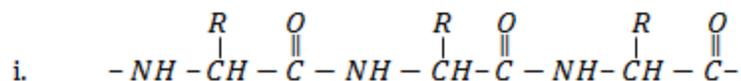
Home work



Melamine (thermosetting)

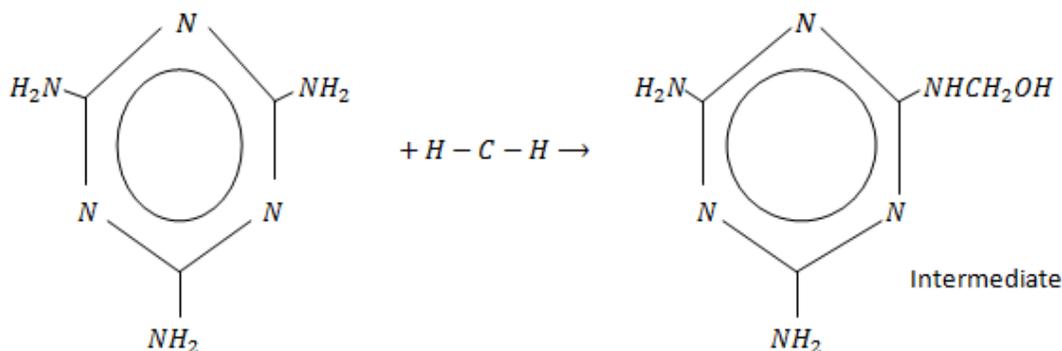
- Water will be lost

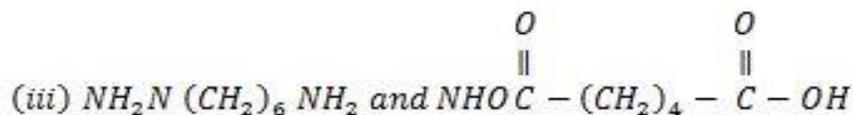
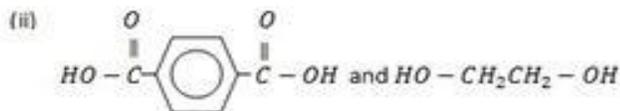
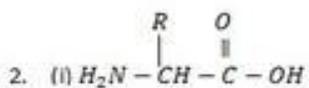
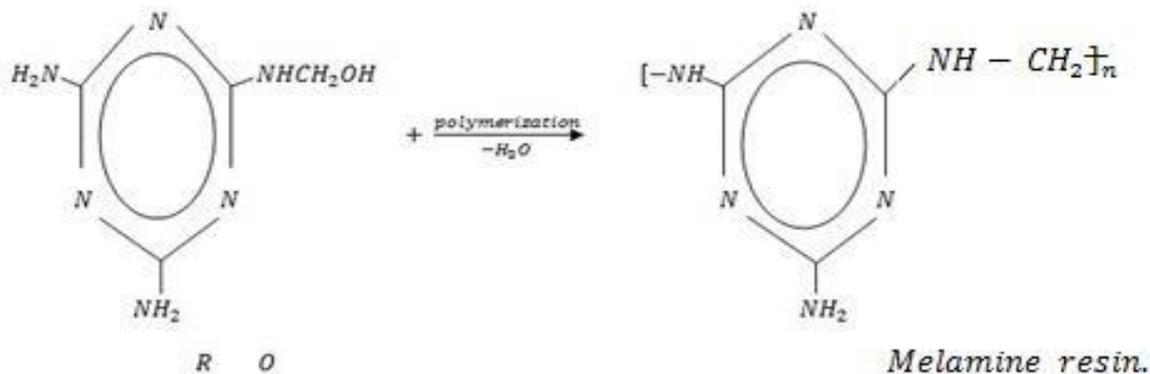
2. Write the complete structure of monomers which are used to prepare each of the following condensation polymers:



ANSWERS:

1. Melamine and formaldehyde (methanal) copolymerize to give another polymer called melamine resin



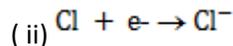
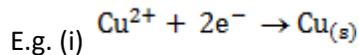


PHYSICAL CHEMISTRY 1.3- ELECTROCHEMISTRY

Is a branch of science which deals with the study of chemical/physical processes in which electricity is either produced or consumed.

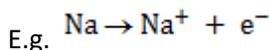
REDUCTION-OXIDATION (REDOX) REACTIONS

Reduction is the addition of electrons to an atom or ion.



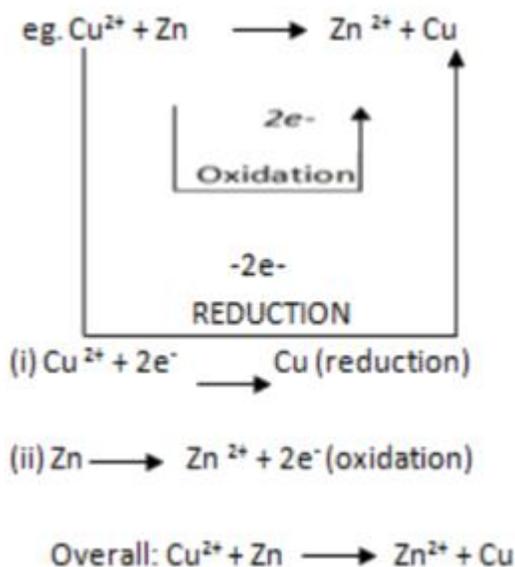
There is an overall decrease in oxidation state.

Oxidation is the reaction in which electrons are being lost therefore removal of electrons from the atom or ion.



Redox reaction is the reaction in which both oxidation and reduction processes takes place at the same time. In a redox reaction, electrons are transferred between ions or atoms thus electrons are lost and gained in the same reaction.

NOTE: - In a balanced redox reaction, the number of electrons lost should be equal to the number of electrons gained.

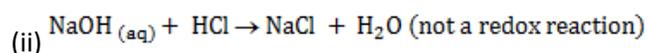
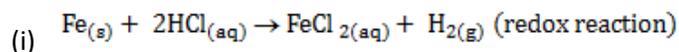


From the above reaction (overall reaction)

The substance in a redox reaction which loose electrons is called reducing agent or reductant i.e. Zn the substance in a redox reaction which gains electrons is called oxidizing agent (oxidant) i.e. Cu^{2+}

NOTE: An oxidizing agent which cause other species to undergo oxidation but itself being reduced.

Not all reactions are redox reaction :-

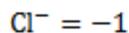
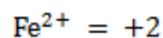


Reason

To identify a redox reaction one should look for the change in oxidation number of an element in the course of the reaction. If there is increase in oxidation number, oxidation has taken place and if there is a decrease in oxidation state, reduction has taken place.

Guidelines or rules for determination of oxidation number of an element in a compound.

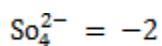
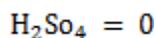
1. In a free element, each atom has an oxidation number of zero.
2. For ions consisting of single atom, the oxidation number is equal to the charge of that ion.



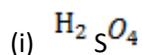
3. The oxidation of hydrogen is $+1$ except in ionic hydrides where the oxidation is -1 . E.g. NaH, KH.

The oxidation state of oxygen is -2 in most compounds except in peroxide where the oxidation state becomes -1 and +2 in oxygen fluoride (OF_2) due to electronegativity of fluorine.

4. The algebraic sum of oxidation number in a neutral compound must be zero and a polyatomic atom must be equal to the ion charge.



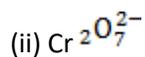
E.g.: calculate the oxidation number of the underlined elements in the following.



$$(2 \times 1) + \text{S} + (-2 \times 4) = 0$$

$$2 + \text{S} - 8 = 0$$

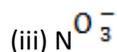
$$\text{S} = +6$$



$$2 \text{Cr} + (-2 \times 7) = -2$$

$$2 \text{Cr} = 12$$

$$\text{Cr} = +6$$



$$\text{N} + (-2 \times 3) = -1$$

$$\text{N} - 6 = -1$$

$$\text{N} = +5$$



$$1 + \text{Mn} + (-2 \times 4) = 0$$

$$1 + \text{Mn} - 8 = 0$$

$$\text{Mn} - 7 = 0$$

$$\text{Mn} = +7$$

(v) P^4

$$4\text{P} = 0$$

$$\text{P} = 0$$

(vi) $\text{N}^{\text{H}_4^+}$

$$\text{N} + (1 \times 4) = 0$$

$$\text{N} = -4$$

(vii) $\text{S}_2\text{O}_3^{2-}$

$$2\text{S} + (-2 \times 3) = -2$$

$$2\text{S} - 6 = -2$$

$$2\text{S} = 4$$

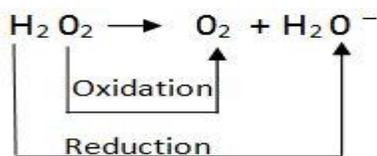
$$\text{S} = +2$$

Disproportionation reaction

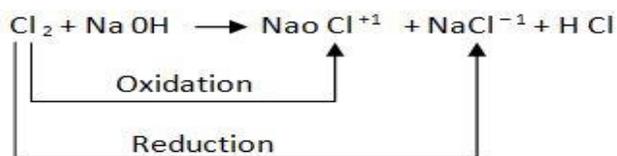
Is the reaction in which an atom undergoes both oxidation and reduction reaction simultaneously in the same reaction.

OXIDATION - REDUCTION PROCESS

(i)



(ii)



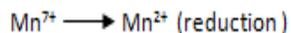
Rules for balancing redox reaction

eg.



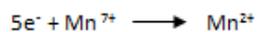
1. By using oxidation number identify which element is oxidized or reduced.

eg.



2. Write the half reaction for each process.

eg.



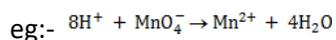
3. Balance the atoms that are reduced or oxidized.

4. Balancing number of oxygen atoms

a) In acidic solution

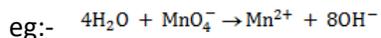
i. Add water molecules to the side that is deficient of oxygen atoms.

ii. Add appropriate number of hydrogen ions to the other side to complete oxygen balance.



b) In basic solution.

- i. For every oxygen atom required add OH⁻ to the side deficient of oxygen atoms.
- ii. Add water molecule to the other side to complete the oxygen balance



5. Balancing the number of hydrogen atom

(a) In acidic solution.

Add hydrogen ions to the side in deficient of hydrogen atoms.

(b) In basic solution.

(i) To every hydrogen atom required add water molecule to the side deficient of hydrogen atom.

(ii) To the other side add hydroxyl ion to complete hydrogen balance.

6. Balance the charge by adding number of electrons to the side which is more positive.

7. Multiply oxidation/reduction by the smallest number to ensure that the numbers of electrons lost/gained are equal.

8. Add the two balanced half reactions by omitting species which appear on both side to obtain the final equation.

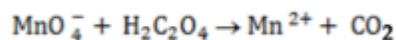
9. Check the final result to ensure that species and charge are balanced.

eg. Overall reaction



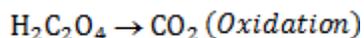
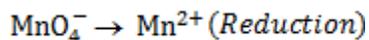
Example 2

(a) Balance the following redox reaction equation under acidic medium.

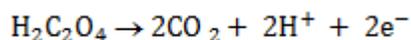
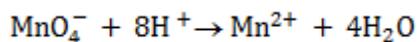


SOLUTION

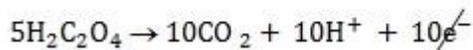
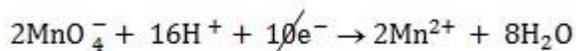
1. Half reaction equation



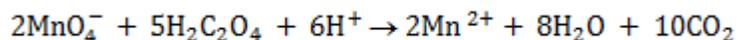
2. Balance under acidic medium



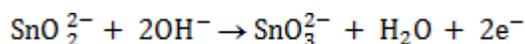
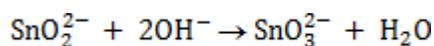
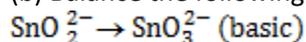
3. Balanced charged.



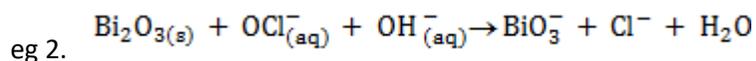
4. Overall reaction equation



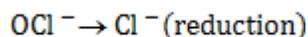
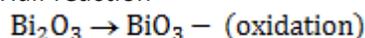
(b) Balance the following redox reaction equation under basic medium



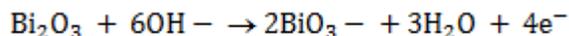
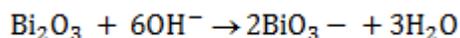
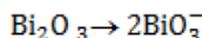
Therefore overall reaction :-



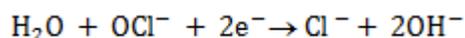
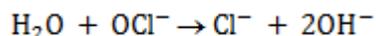
1. Half reaction



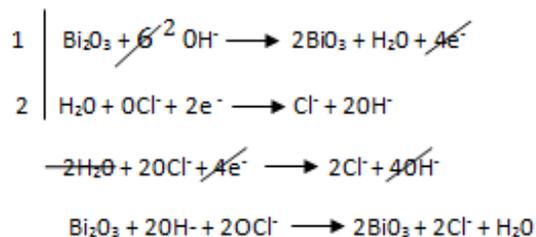
2. Half reaction under basic medium



3. Half reaction under basic medium



4. Balanced of charged

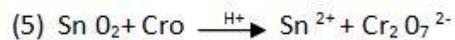
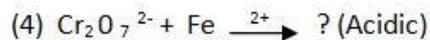
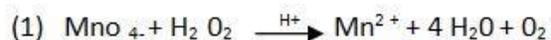


Overall reaction equation



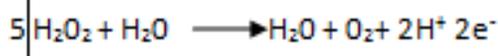
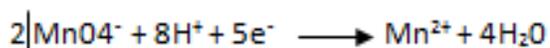
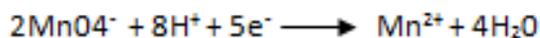
Example 3

Balance the following redox reactions according to the media given.



ANSWERS

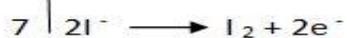
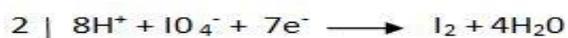
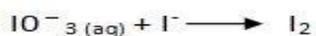
Solution



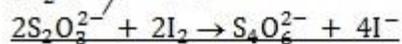
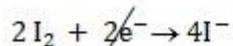
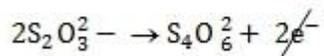
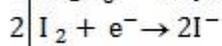
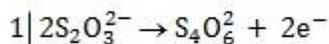
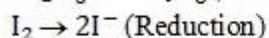
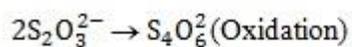
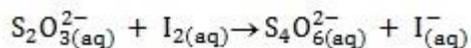
Overall Reaction Equation



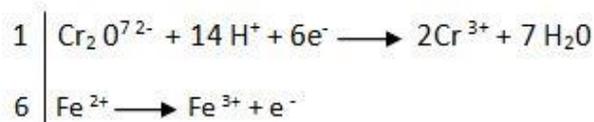
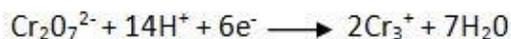
Solution



3. Solution



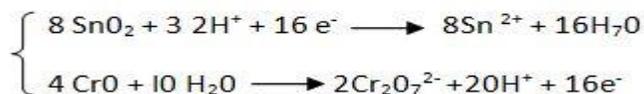
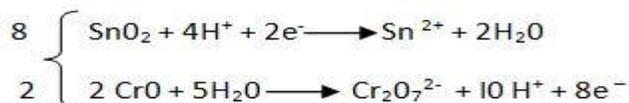
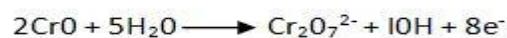
Solution



The overall reaction



Solution



The overall redox reaction

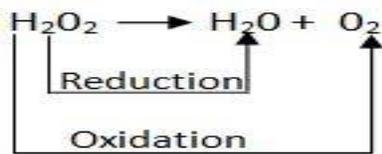


\therefore SnO_2 is an oxidant

CrO is a reductant

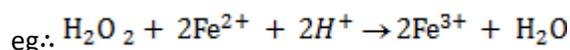
ACTION OF HYDROGEN PEROXIDE

Hydrogen peroxide (H_2O_2) has both oxidizing and reducing power. However its reaction depends on the state of the second reagent whether it has to be reduced or oxidized,



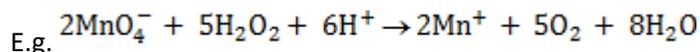
(i) H_2O_2 as an oxidizing agent

Like any oxidizing agent H_2O_2 is capable of accepting electrons when treated with any electron donating species and itself being reduced to water.



(ii) H_2O_2 as reducing agent

H_2O_2 is capable of supplying electrons when treated with electron accepting species and itself being oxidized to oxygen gas.



APPLICATION OF REDOX REACTIONS

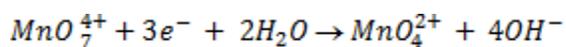
(i) PERMANGANOMETRY TITRATION

It is applied on permanganometry titration. These are titration in which potassium permanganate is the titrants and indicators are used. This is because permanganate itself acts as an indicator. It changes its colour due to the formation of manganese (Mn^{2+}) from manganese (Mn^{7+}) [in acidic media]

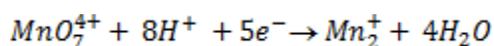
NOTE

Oxidizing power of permanganate depends on the media used.

a) In neutral media or weakly alkali medium.

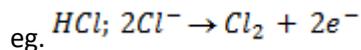


b) In acidic medium



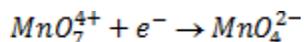
NOTE

Dilute. Sulphuric acid (H_2SO_4) is only used HCl cannot be used because MnO_4^- will oxidize it to chlorine gas thus is interfering the power of permanganate



NOTE :- Concentration. H_2SO_4 and HNO_3 are also not used because they are also oxidizing agents.

c) In strong alkali medium.



$$1. \quad \text{Equivalent weight} = \frac{\text{Relative Molecular Mass}}{n}$$

n = number of electrons transferred per mole.

$$\text{Equivalent weight} = \frac{\text{Relative Molecular Mass}}{\text{basicity}}$$

Basicity is the number of H^+ per 1 molecule of acid when dissolved in H_2O .

$$\text{Equivalent weight} = \frac{\text{atomic mass}}{\text{valency}}$$

$$\text{Normal (N)} = \frac{\text{concentration in g/dm}^3}{\text{Equivalent weight}}$$

$$\text{Morality} = \frac{\text{concentration in g/dm}^3}{\text{Relative molecular mass}}$$

$$\text{Normality} = \frac{\text{Concentration in g/dm}^3}{\text{Relative molecular mass / n}}$$

$$= \frac{\text{concentration in g/dm}^3 \times n}{\text{Relative Molecular Mass}}$$

$\text{Normality} = \text{morality (M)} \times n$



$$\text{Molarity (M)} = \frac{\text{normality}}{n}$$

Examples

1. A standardization of $KMnO_4$ in acidic solution gave the following data:

0.16g of potassium salt i.e. $K_2C_2O_4 \cdot 2H_2O$ needed $24.5cm^3$ of $KMnO_4$ solution. What is the molarity of the solution ($KMnO_4$)

Solution:

(i) To find molarity of $K_2C_2O_4 \cdot 2H_2O$

$$\text{Molarity} = \frac{\text{conc. In g/dm}^3}{R.M.M}$$

$$\text{Conc.} = \frac{n}{V}$$

$$= \frac{m}{MV}$$

$$= \frac{0.16}{202 \times 0.0245}$$

Concentration = $0.032gL^{-1}$

$$202g = 1 \text{ mol}$$

$$0.16g = x$$

$$X = \frac{0.16}{202}$$

$$X = 7.92 \times 10^{-4} \text{ moles}$$

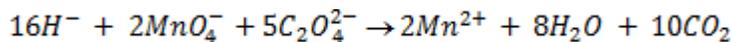
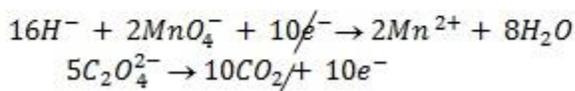
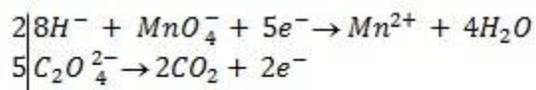
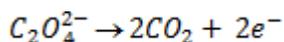
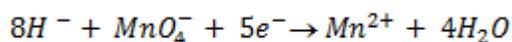
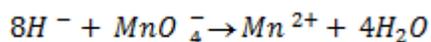
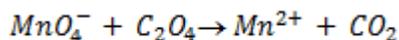
$$\text{Conc.} = \frac{n}{V}$$

$$= \frac{7.92 \times 10^{-4}}{0.024}$$

Concentration = 0.032 g dm^{-3}

Molarity = 2.038×10^{-4}

(ii) To find molarity of KMnO_4 from reaction equation :-



2:5

$$\text{Moles of salt} = \frac{\text{mass of salt}}{\text{Molecular Mass}}$$

$$= \frac{0.16}{202}$$

= 7.92×10^{-4} moles

From the reaction equation :-

2 moles of KMnO_4 = 5 moles of $\text{K}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

$$X = 7.92 \times 10^{-4}$$

$$X = \frac{7.92 \times 10^{-4} \times 2}{5}$$

$$X = 3.168 \times 10^{-4} \text{ moles}$$

$$3.168 \times 10^{-4} \rightarrow 24.5 \text{ cm}^3$$

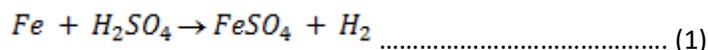
$$X \leftarrow 1000 \text{ cm}^3$$

$$X = 0.013 \text{ M}$$

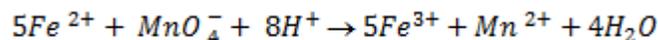
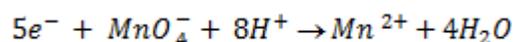
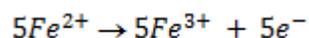
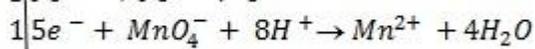
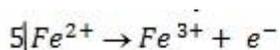
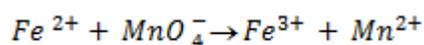
2. Calculate the percentage of iron from the following data in a sample of iron wire:

1.4g of the wire was dissolved in excess dilute sulphuric acid and the solution was made up to 250cm³. 25cm³ of this solution required 25.3cm³ of 0.0196M of KMnO₄ for oxidation. [If it was concentration. H₂SO₄, it could have oxidized Fe to Fe³⁺ since it is a STRONG oxidizing agent]

Solution:



Reaction of FeSO₄ and KMnO₄



5: 1

$$M_{Fe^{2+}} = ?$$

$$V_{Fe^{2+}} = 25 \text{ cm}^3$$

$$M_{MnO_4^-} = 0.0196$$

$$V_{MnO_4^-} = 25.37 \text{ cm}^3$$

$$n_{MnO_4^-} = 1$$

$$n_{Fe^{2+}} = 5$$

$$\frac{M_{Fe^{2+}} V_{Fe^{2+}}}{M_{MnO_4^-} V_{MnO_4^-}} = \frac{n_{Fe^{2+}}}{n_{MnO_4^-}}$$

$$M_{Fe^{2+}} = \frac{M_{MnO_4^-} V_{MnO_4^-} n_{Fe^{2+}}}{n_{MnO_4^-} V_{Fe^{2+}}}$$

$$= \frac{0.0196 \times 25.37 \times 5}{1 \times 25}$$

$$M_{Fe^{2+}} = 0.0995 \text{ M}$$

$$0.0995 \text{ moles} \rightarrow 1000 \text{ cm}^3$$

$$X \leftarrow 250 \text{ cm}^3$$

$$X = \frac{0.0995 \times 250}{1000}$$

$$X = 0.0249 \text{ mole}_s$$

1 mole of Fe \rightarrow 1 mole of FeSO₄

? x mole \rightarrow 0.0249 moles

X = 0.0249 moles of Fe

$$n = \frac{m}{M}$$

$$= \frac{1.4}{56}$$

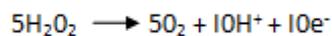
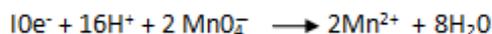
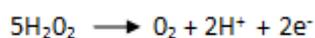
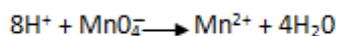
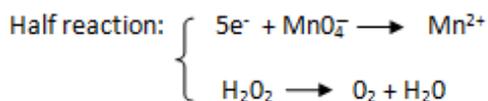
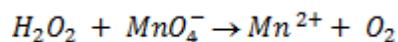
$$n = 0.025 \text{ moles}$$

$$\% = \frac{0.025}{0.0249}$$

$$\% = 99.6\%$$

3. 100cm³ of H₂O₂ solution was diluted to 1 dm³ of solution. 25cm³ of this solution, when acidified with dilute H₂SO₄ reacted with 47.8cm³ of 0.02M KMnO₄ solution. Calculate the concentration of the original H₂O₂ solution.

Solution:



Ratio is 5: 2

$$M_{KMnO_4} = 0.02$$

$$V_{KMnO_4} = 47.8cm$$

$$M_{H_2O_2} = ?$$

$$V_{H_2O_2} = 25cm^3$$

$$n_{H_2O_2} = 5$$

$$n_{KMnO_4^-} = 2$$

$$\frac{M_{H_2O_2} V_{H_2O_2}}{M_{KMnO_4^-} V_{KMnO_4^-}} = \frac{n_{H_2O_2}}{n_{KMnO_4^-}}$$

$$M_{H_2O_2} = \frac{M_{KMnO_4^-} V_{KMnO_4^-} n_{H_2O_2}}{n_{KMnO_4^-} V_{H_2O_2}}$$

$$= \frac{0.02 \times 47.8 \times 5}{2 \times 25}$$

$$M_{H_2O_2} = 0.0956M$$

$$0.0956 \text{ moles} \rightarrow 1000\text{cm}^3$$

$$X \rightarrow 100\text{cm}^3$$

$$X = 9.5 \times 10^{-3} \text{ moles}$$

$$M_C V_C = M_D V_D$$

$$M_D = 0.0956$$

$$V_D = 1000\text{cm}^3$$

$$M_C = ?$$

$$V_C = 100$$

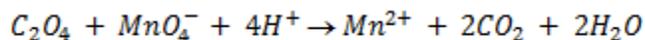
$$M_C = \frac{0.0956 \times 1000}{100}$$

$$\underline{M_C = 0.956M}$$

4. 25cm³ of sodium oxalate (Na₂C₂O₄) solution acidified with dilute sulphuric acid and heated to 80°C is titrated with standard KMnO₄ solution of concentration 3g l⁻¹. 26.4cm³ of KMnO₄ solution was required for complete reaction.

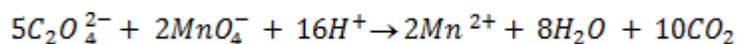
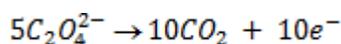
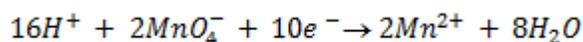
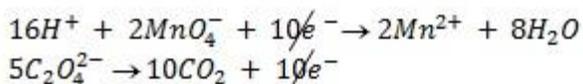
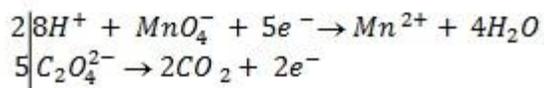
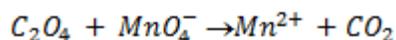
a. Calculate the concentration of oxalate ions in Na₂C₂O₄ in g l⁻¹

b. Hot acidified Na₂C₂O₄ reacts with MnO₂ according to the equation.



What volume of sodium oxalate (Na₂C₂O₄) will be required to react with 0.1g of MnO₂.

Answer



$$5 : 2$$

$$\text{Molarity} = \frac{\text{conc.}}{\text{Molar mass}}$$

$$= \frac{3}{39 + 55 + 64}$$

$$M_{KMnO_4} = 0.0189M$$

$$V_{KMnO_4} = 26.4cm^3$$

$$M_{Na_2C_2O_4} = ?$$

$$V_{Na_2C_2O_4} = 25cm^3$$

$$N_{Na_2C_2O_4} = 5$$

$$n_{KMnO_4} = 2$$

$$\frac{M_{C_2O_4} V_{C_2O_4}}{M_{KMnO_4} V_{KMnO_4}} = \frac{n_{C_2O_4}}{n_{KMnO_4}}$$

$$M_{C_2O_4} = \frac{M_{KMnO_4} V_{KMnO_4} n_{C_2O_4}}{n_{KMnO_4} V_{C_2O_4}}$$

$$= \frac{0.0189 \times 26.4 \times 5}{25 \times 2}$$

$$M_{C_2O_4} = 0.049M$$

$$\text{Conc.} = M_{C_2O_4} \times \text{M.M}$$

$$= 0.049 \times [(23 \times 2) + (12 \times 2) + 64]$$

$$\text{Conc.} = 6.566 \text{ g l}^{-1}$$

b) 1 mole of C_2O_4 = 1 mole of MnO_2

$$x = 1.149 \text{ moles of } MnO_2$$

$$x = 1.149 \times 10^{-3} \text{ moles of } C_2O_4$$

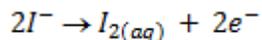
$$0.049 \text{ moles} \rightarrow 1000 \text{ cm}^3$$

$$1.149 \times 10^{-3} \rightarrow x$$

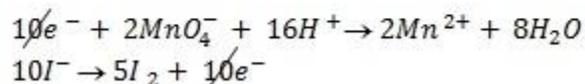
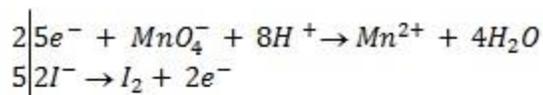
$$X = 23.45 \text{ cm}^3$$

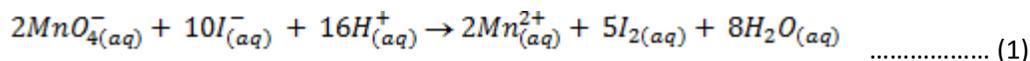
(ii) Iodometry titration

These are titrations in which iodine is produced by using of starch as an indicator. All iodometry titrations use KI as source of Iodine.



a) If the oxidant is acidified $KMnO_4$

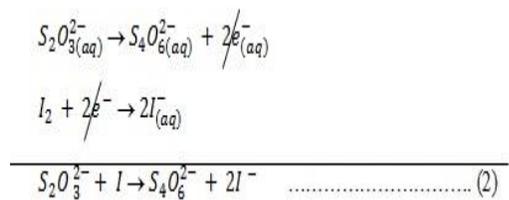




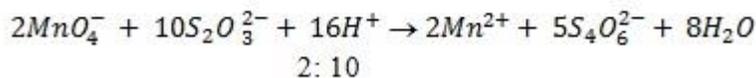
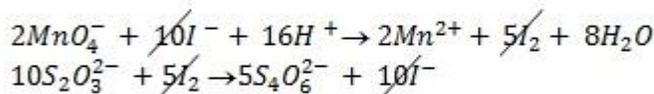
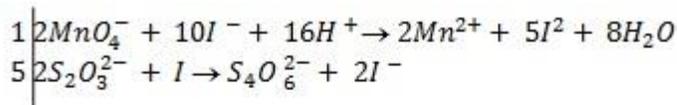
The iodine produced is titrated with $Na_2S_2O_3$ to pale yellow, then add starch and continue titrating until the blue-black colour is discharged.

Starch is not added at the beginning because the concentration of iodine is large. Iodine react with starch to form the blue black complex hence more volume of $Na_2S_2O_3$ is required to discharge the blue black complex.

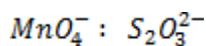
Reaction with $Na_2S_2O_3$



When equation (1) and (2) are combined

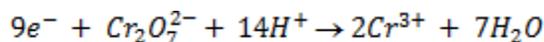
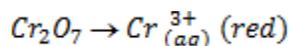


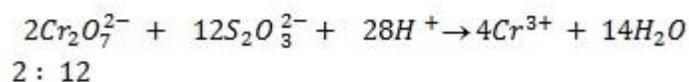
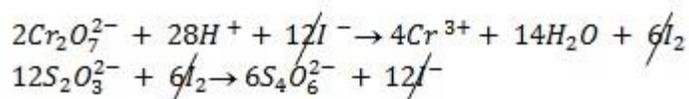
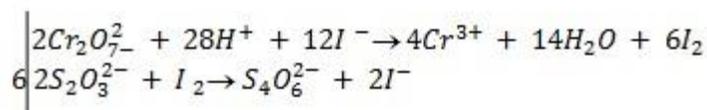
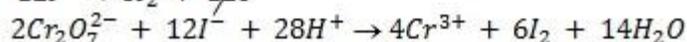
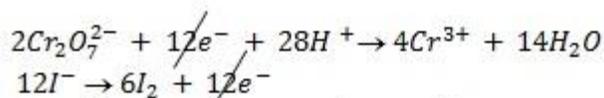
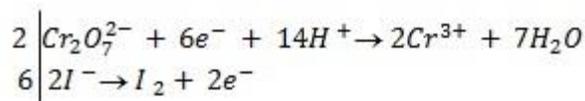
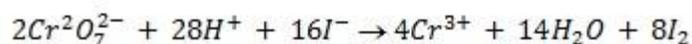
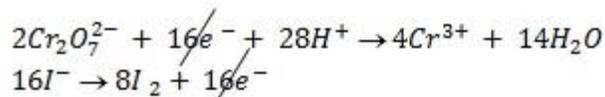
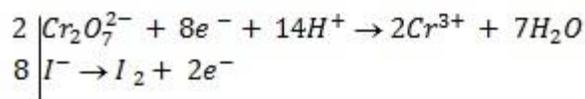
1: 5



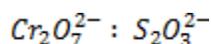
1: 5

b) If the oxidant is acidified $K_2Cr_2O_7$



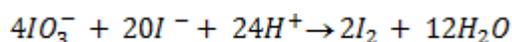
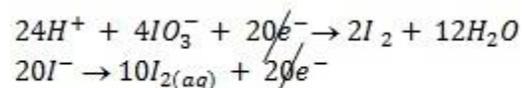
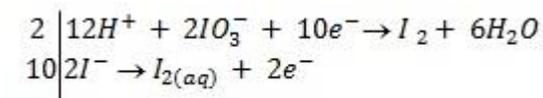
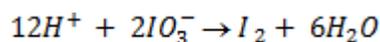


Mole ratio will be

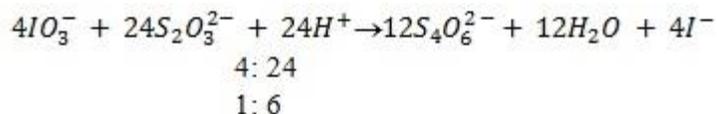
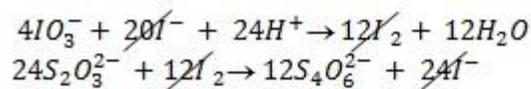
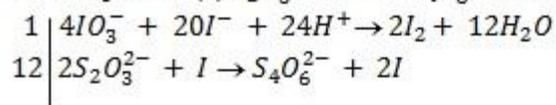


1: 6

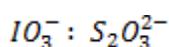
c) If the oxidant is acidified KIO_3



From equation (2) $S_2O_3^{2-} + I \rightarrow S_4O_6^{2-} + 2I^-$



The mole ratio is

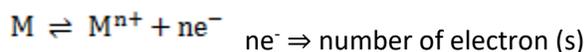


1: 6

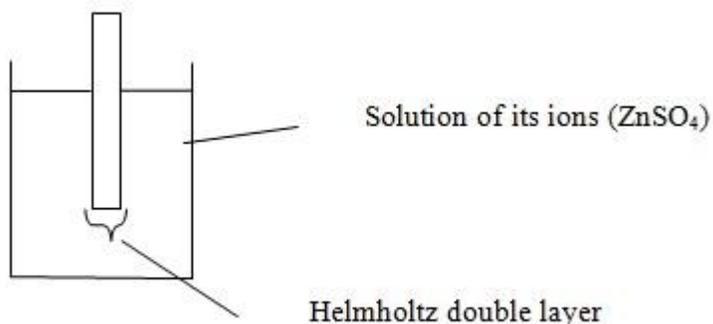
ELECTRODE POTENTIAL AND ELECTROCHEMICAL SERIES

ELECTRODE POTENTIAL

Metals have a small tendency to dissolve in solution of their ions producing cations leaving their valency electrons on the metal rod. The metal acquires a negative potential which prevents further release of cations and equilibrium is established



As a result the region of solution very close to the rod suffers an increase in charge while the rod carries a layer of negative charge (electrons). Then an electric double layer is set up and this layer is known as "Helmholtz double layer"



Whenever there is a separation of negative and positive charges we should be able to measure the voltage i.e. voltage between the electrode and surrounding solution and this is called Electrode potential.

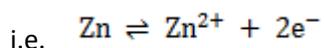
Definition:

Electrode potential – is the potential difference formed between an electrode and its hydrated ions.

Magnitude of electrode potential

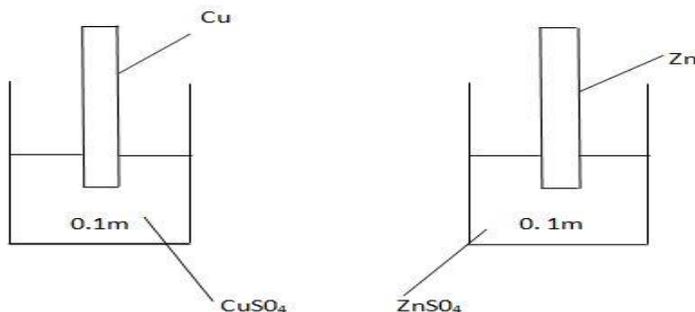
This depends on the position of equilibrium of reversible reaction. The further to the right the greater is the electron density on the surface of metal and larger is the Potential Difference (P.D) between metal and solution. The opposite is true.

For a given metal the position of equilibrium forward or backward depends on the concentration of solution into which the electrode is dipped



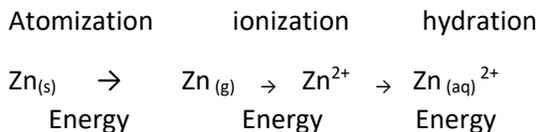
If the concentration of the solution is high the equilibrium will lie towards the left i.e. tendency of zinc rod to dissolve decrease and vice versa.

For different metals placed in solution contain same concentration of their ions at the same temperature i.e. the positions of equilibrium is governed by the overall energy change forming hydrate ions from the metal.



Electrode potential involves the following stages

- (i) Atomization of electrode
- (ii) Ionization of gaseous atoms
- (iii) hydration of ions



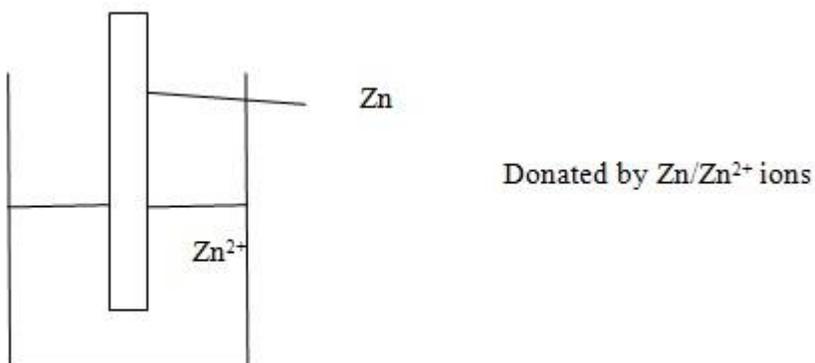
If the total energy is low, electrode dissolve more easily and its equilibrium will move forward hence large potential (electrode potential) value

Metals with large electrode potential release electrons easily and are good reducing agents

TYPES OF ELECTRODES FOUND IN ALL GALVANIC CELLS

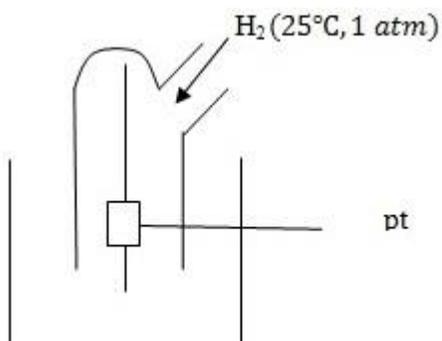
I. Metal – metal ion electrodes

This consists of metal dipped into its soluble salts.



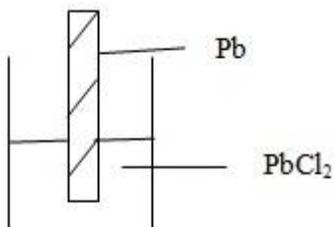
II. Gaseous electrode

This consists of platinum to which a gas at 1 atm, and 25°C is bubbled and dipped in ions of gas at a given concentration.



III. Metal – insoluble salt electrode

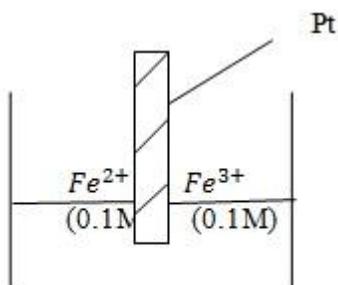
This consists of metal dipped into its insoluble salts at 25°C



Denoted by Pb/PbCl_2

IV. Redox electrodes

It consists of platinum dipped in cations having different oxidation states at a given concentration at 25°C .

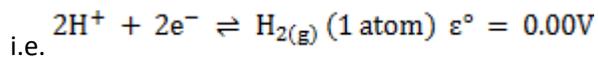


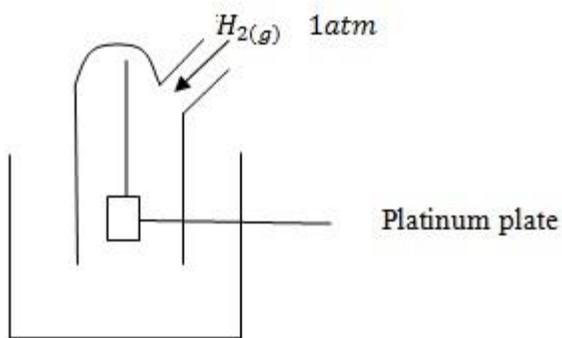
Denoted by $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e^{-}$

Measurements of electrode potential

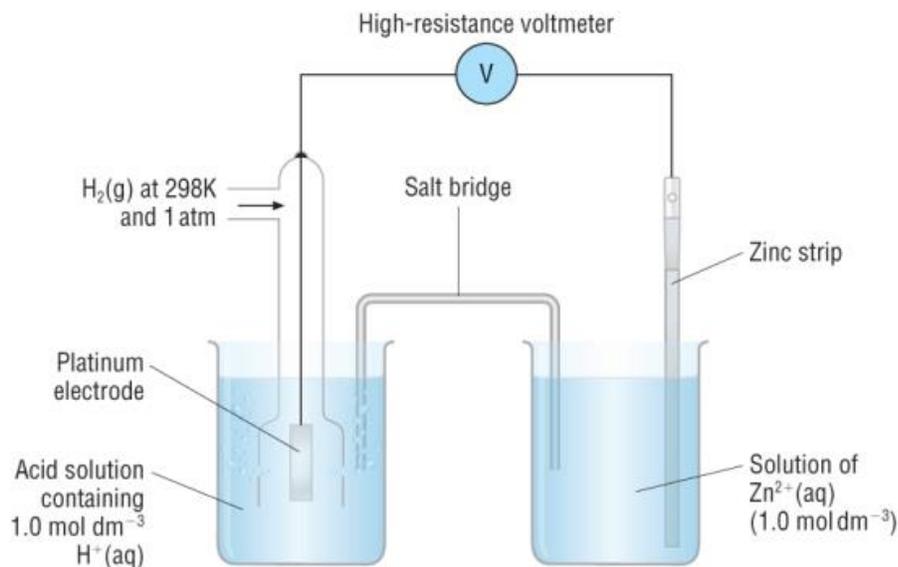
We can always measure the electrode potential for an electrode in combination with standard electrode which is standard hydrogen electrode (SHE)

It was conventionally agreed that electrode potential for hydrogen is zero.





When electrode potential of any element is measured against hydrogen electrode at 25°C 1 atm and 1M concentration is called standard electrode potential.



Salt Bridge

Is an inverted U-tube that contains an electrolyte (e.g. KCl) which connects the solution of two half cells to balance the charge and to complete the circuit.

NOTE

The standard redox potential is actually reduction potential. All elements below hydrogen have negative reduction potential and positive oxidation potential hence strong reducing agents.

All elements above hydrogen have positive reduction potential and negative oxidation potential hence strong oxidizing agents.

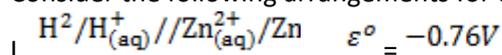
When writing the cell description the hydrogen electrode is placed on the left conventional to determine the polarity of the right hand electrode.

Functions of salt bridge

- I. To complete the circuit
- II. To balance the charge

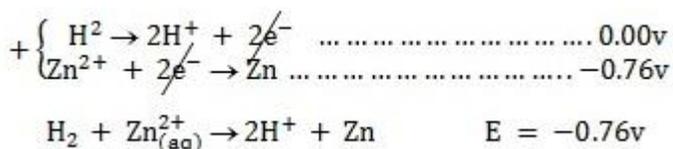
Example

Consider the following arrangements for determine electrode potential fo

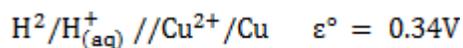


The zinc electrode is negative.

Cell reaction:

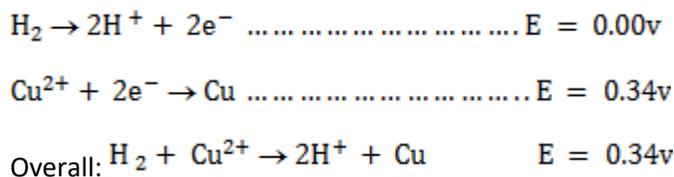


II. Copper



The copper electrode is positive. (It can easily be reduced)

Cell reaction:



Application of standard electrode potential

- I. Construction of electrochemical cells.
- II. Prediction of occurrence of chemical reaction
- III. Determination of P^{H} of a solution without P^{H} meter
- IV. Replacement of elements in the electrochemical series.

Electrolytic cell = produce electrical power through chemical reaction in electrochemical cells.

I. CONSTRUCTION OF ELECTROCHEMICAL CELLS

Electrochemical cells are devices that use chemical reactions to produce electrical power. These are sometimes known as Galvanic or Voltaic cells.

e.g. dry cells, car batteries.

It contains two half cells connected together by external circuits.

Half cell is an arrangement which consists of an electrode dipped into a solution containing its ions. When the two half cells are connected, the resulting component is called electrochemical power. A good example is Daniel cell. It is constructed from Zinc and copper electrode.

PROCEDURE FOR CONSTRUCTION OF ELECTROCHEMICAL CELL

1. Identify between the electrodes, which electrode is supplying or gaining electrons by studying their electrode potential.

II. An electrode with negative standard electrode potential is more reactive (supplies electrodes) than the positive one.

III. If both are negative the one which has more negative electrode potential is more reactive.

E.g. Sn = -0.16

Mg = -0.25 (more reactive)

If both electrodes are positive, the one which has less positive value is more reactive.

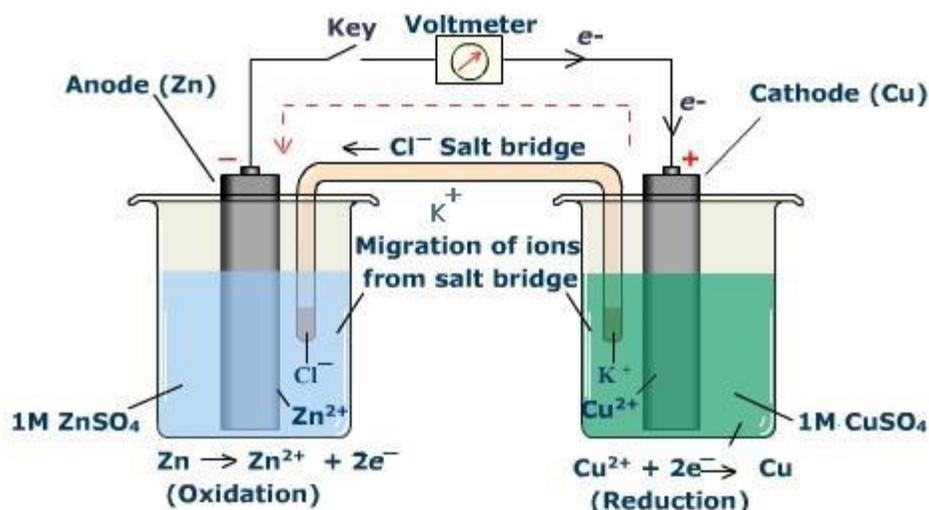
E.g. 0.07v (more reactive)

0.2v

The electrode which supplies electrons should be placed on the left and electrode which gains electrons should be on the right hand side.

E.g. construct a Daniel cell and shows the direction of flow of electrons and current given that $\text{Cu}^{2+}/\text{Cu} \quad \epsilon^\circ = -0.34\text{v}$

$\text{Zn}^{2+}/\text{Zn} \quad \epsilon^\circ = -0.76\text{v}$

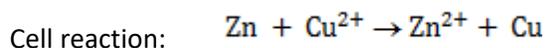
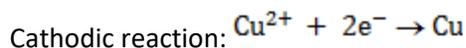
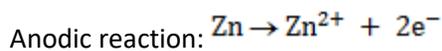


The electrode which supplies electrons oxidation takes place and the electrode is oxidized. This electrode is called ANODE. The electrode which receives electrons reduction takes place and the electrode is REDUCED. It is called CATHODE.

Zn – anode

Cu – cathode

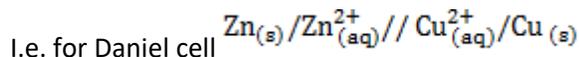
Overall reaction is obtained by adding the two half reactions and is called cell reaction.



Electrochemical cell can also be represented in an abbreviation way known as cell notation.

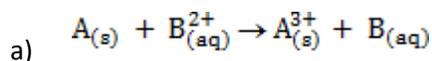


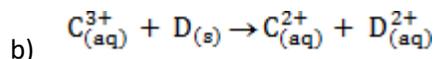
Anode cathode



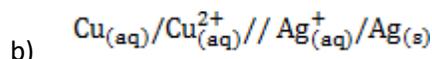
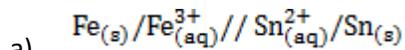
Questions

1. Given the overall reactions, write their corresponding cell notations

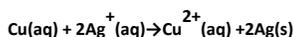
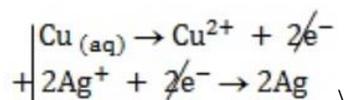
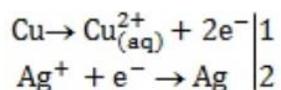
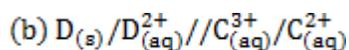
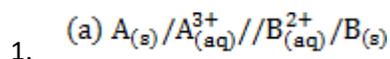




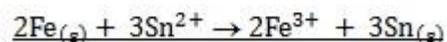
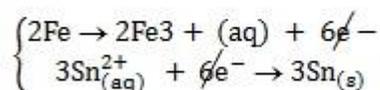
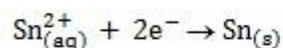
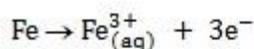
2. From the cell notation give the cell reactions



Answers



2.



ELECTROMOTIVE (EMF) FORCE OF A CELL

The difference between electrode potential of the two electrodes constituting an electrochemical cell is known as electromotive (emf) or cell potential.

This acts as a driving force for a cell reaction and it is expressed in volts.

The emf of a cell is calculated by subtracting the standard electrode potential (E^{θ}) of the left electrode from that of the right electrode.

$$E_{cell}^{\theta} = E_{right}^{\theta} - E_{left}^{\theta}$$

For Daniel cell $Zn_{(s)}/Zn^{2+}_{(aq)} // Cu^{2+}_{(aq)}/Cu_{(s)}$

$$Zn_{(s)}/Zn^{2+}_{(aq)} = -0.76 \text{ v}$$

$$Cu^{2+}_{(aq)}/Cu_{(s)} = 0.34 \text{ v}$$

$$Cu^{2+}_{(aq)}/Cu_{(s)} = 0.34$$

$$E_{\text{cell}}^{\theta} = E_{\text{copper}}^{\theta} - E_{\text{zinc}}^{\theta}$$

$$= 0.34 - (-0.76)$$

$$E_{\text{cell}}^{\theta} = 1.1 \text{ v}$$

$$E_{\text{cell}}^{\theta} = E_{\text{oxidized}}^{\theta} + E_{\text{reduced}}^{\theta}$$

Alternatively

Since standard electrode potentials are in reduced form, for oxidation half reaction the sign of electrode potential should be reversed.

$$E_{\text{cell}}^{\theta} = E_{\text{oxidized}}^{\theta} + E_{\text{reduced}}^{\theta}$$

$$= 0.76 + 0.34$$

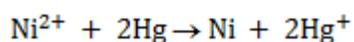
$$E_{\text{cell}}^{\theta} = 1.1 \text{ v}$$

1. Prediction of the occurrence of chemical reaction.

If the emf of the cell calculated is negative the reaction is non spontaneous i.e. the reaction does not occur in the way it is written unless external forces apply but the reaction is spontaneous in the opposite direction.

If the emf of the cell is positive the reaction is spontaneous

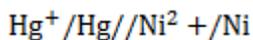
Example: given the following reaction



Predict the direction of the reaction given that reduction potential of nickel (Ni^{2+}/Ni) $E^\circ = -0.25\text{v}$ of mercury Hg^+/Hg $E^\circ = 0.14\text{v}$

Solution

Cell notation



$$E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

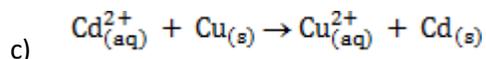
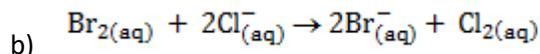
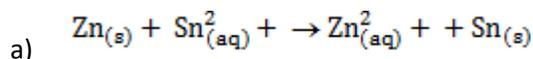
$$= -0.25 - 0.14$$

$$= \underline{-0.39\text{v}}$$

The reaction is non spontaneous since emf is negative hence backward reaction is favored.

Example

For each of the following reactions at standard condition, decide if it occurs spontaneously in the direction written.



Given for $\text{Cd}^{2+}/\text{Cd} = -0.4$

$$\text{Cu}/\text{Cu}^{2+} = 0.34\text{v}$$

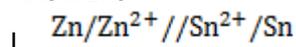
$$\text{Br}_2/\text{Br}^- = 1.09\text{v}$$

$$\text{Cl}^-/\text{Cl} = 1.36\text{v}$$

$$\text{Sn}/\text{Sn}^{2+} = -0.14\text{v}$$

$$\text{Zn}/\text{Zn}^{2+} = -0.76\text{v}$$

ANSWERS



$$E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

$$= -0.14 - (-0.76)$$

$$= 0.62\text{V}$$

II. Cell notation: $\text{Cl}^-/\text{Cl} // \text{Br}_2/\text{Br}^-$

$$E_{\text{cell}}^{\theta} = E_{\text{right}}^{\theta} - E_{\text{left}}^{\theta}$$

$$= 1.09 - (1.36)$$

$$= -0.27\text{V}$$

III. Cell notation: $\text{Cu}/\text{Cu}^{2+} // \text{Cd}^{2+}/\text{Cd}$

$$E_{\text{cell}}^{\theta} = E_{\text{right}}^{\theta} - E_{\text{left}}^{\theta}$$

$$= -0.4 - 0.34$$

$$= -0.74\text{V}$$

Therefore reaction (1) is spontaneous while reaction (2) and (3) are non-spontaneous

Example

Briefly explain what happen when

I. Fe is dipped in CuSO_4 solution

II. Cu is dipped in FeSO_4 solution

$$\text{Fe}^{2+}/\text{Fe} = -0.44\text{v}$$

$$\text{Cu}^{2+}/\text{Cu} = 0.34\text{v}$$

Example

Given the following E^{θ} values

$$\text{Ag}^+/\text{Ag} = 0.080\text{v}$$

$$\text{Fe}^{2+}/\text{Fe} = -0.44\text{v}$$

$$\text{Zn}^{2+}/\text{Zn} = -0.76\text{v}$$

$$\text{Cu}^{2+}/\text{Cu} = 0.34\text{v}$$

$$\text{Pb}^{2+}/\text{Pb} = -0.13\text{v}$$

$$\text{Mg}^{2+}/\text{Mg} = -2.37\text{v}$$

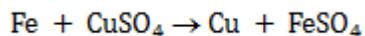
a) State which species are the strongest oxidant and which oxidant and weakest reductant.

b) State which species is the strongest oxidant and weakest reductant.

c) The lead rods are placed in a solution of each CuSO_4 , FeSO_4 , AgNO_3 and ZnSO_4 . In which solution do you expect coating of another metal on lead rod. Explain.

ANSWERS

2. (i) since Fe has a negative reduction potential then it has a positive oxidation potential and hence will displace copper metal from CuSO_4 solution



(ii) Since Cu has positive reduction potential, then it has a negative oxidation potential and hence it will NOT displace Fe from FeSO_4 solution therefore no reaction will be possible.

3. (a) strongest oxidant

Weakest reductant

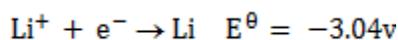
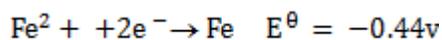
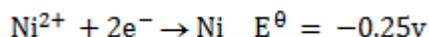
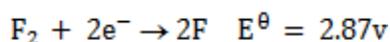
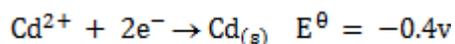
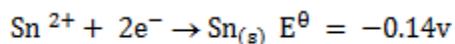
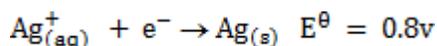
Maximum and minimum emf of a cell

It is possible to decide which cell has to be constructed either of great or smallest emf for a given electrodes. A cell with greatest emf is obtained by

choosing two electrodes of greatest cell reactivity difference. A cell with minimum emf, choose two electrodes with closest reactivity.

Example

Study the following electrodes.



4. Explain how you can construct a cell that will yield

- i. Maximum emf
- ii. Minimum emf

ANSWER

For maximum emf, we choose two electrodes of greatest cell reactivity difference.

$$E_{\text{cell}}^{\circ} = 2.87 - (-3.04)$$

$$E_{\text{cell}}^{\circ} = 5.91\text{v}$$

For minimum emf, we choose two electrodes with closest reactivity



$$E_{\text{cell}}^{\circ} = -0.4 - (-0.44)$$

$$E_{\text{cell}}^{\circ} = 0.04\text{v}$$

EFFECTS OF CONCENTRATION AND TEMPERATURE ON CELL POTENTIALS

We have been considering electrode potential under standard conditions of molar solution, pressure of 1 atm and 298K. When the conditions are altered the values of electrode potential changes thus we have to define the potential of the cell under non-standard conditions.

The Nernst equation shows the relationship between emf of the cell at standard conditions and emf under non-standard conditions.

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{RT}{nF} \frac{\ln [\text{products}]}{[\text{reactants}]}$$

Where; E_{cell} – emf of a cell at any conditions

E_{cell}^{θ} – emf of a cell under standard conditions

R – Universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)

n – Number of moles electrons being transferred

F – Faraday's constant (96500c)

At standard temperature (298K)

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{8.314 \times 298 \ln [\text{products}]}{96500n [\text{reactants}]}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0256 \ln [\text{products}]}{n [\text{reactants}]}$$

OR

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591 \log [\text{products}]}{n [\text{reactants}]}$$

The above equation can be applied to half reactions and overall reactions

NOTE

Always write a balanced cell reaction to obtain 'n' and position of ions, either reactants or products together with their stoichiometry

Example

Calculate the emf of the given cell at standard temperature.



Given

$$\text{Al}^{3+} / \text{Al} \quad E^{\theta} = -2.56\text{v}$$

$$\text{Pb}^{2+} / \text{Pb} \quad E^{\theta} = -0.13\text{v}$$

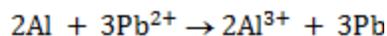
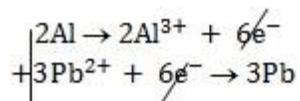
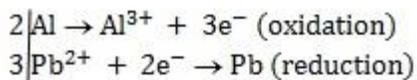
Alternative Solution 1

$$E_{\text{cell}}^{\theta} = E_{\text{right}}^{\theta} - E_{\text{left}}^{\theta}$$

$$= -0.13 - (-2.56)$$

$$E_{\text{cell}}^{\theta} = 2.43\text{v}$$

Alternative Solution 2



$$n = 6$$

Now;

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{n} \log \frac{[\text{products}]}{[\text{reactants}]}$$

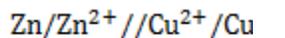
$$E_{\text{cell}} = 2.43 - \frac{0.0591}{6} \log \frac{[0.052]}{[0.123]}$$

$$E_{\text{cell}} = 2.428\text{v}$$

Example 2

Calculate the emf of Daniel cell at 35°C using 2M ZnSO₄ solutions and 0.5M CuSO₄ solution
 $\text{Zn}^{2+}/\text{Zn} = -0.76\text{v}$ $\text{Cu}^{2+}/\text{Cu} = 0.34\text{v}$

Alternative Solution 1



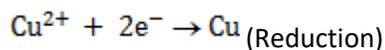
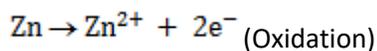
$$E_{\text{cell}}^{\circ} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ}$$

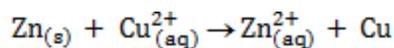
$$= 0.34 - (-0.76)$$

$$E_{\text{cell}}^{\circ} = 1.1\text{v}$$

Alternative Solution 2

Half reactions





Here $n = 2$

Now using

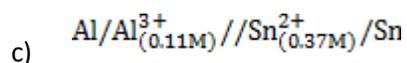
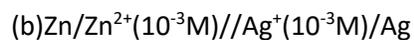
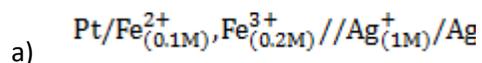
$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{RT}{nF} \ln \frac{[\text{products}]}{[\text{reactants}]}$$

$$E_{\text{cell}} = 1.1 - \frac{8.314 \times 308}{2 \times 96500} \ln \frac{[2]}{[0.5]}$$

$$E_{\text{cell}} = 1.08\text{v}$$

Example 3

Calculate the emf for the following voltaic cells



Given

$$\text{Fe}^{3+}/\text{Fe}^{2+} = 0.77\text{v}$$

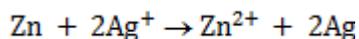
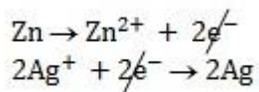
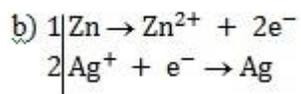
$$\text{Ag}^{+}/\text{Ag} = 0.8\text{v}$$

$$\text{Zn}^{2+}/\text{Zn} = -0.76\text{v}$$

$$\text{Al}^{3+}/\text{Al} = -2.56\text{v}$$

$$\text{Sn}^{2+}/\text{Sn} = -0.14\text{v}$$

Alternative Solution 1



$$n = 2$$

$$\text{Now; } E_{\text{cell}}^{\theta} = E_{\text{right}}^{\theta} - E_{\text{left}}^{\theta}$$

$$= 0.8 - (-0.76)$$

$$E_{\text{cell}}^{\theta} = 1.56\text{v}$$

Alternative Solution 2

$$\text{From } E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{n} \log \frac{([\text{products}])}{([\text{reactants}])}$$

$$E_{\text{cell}} = 1.56 - \frac{0.0591}{2} \log \frac{[0.001]}{[0.0012]}$$

$$E_{\text{cell}} = 1.47\text{v}$$

d) Solution

Alternative Solution 1

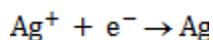
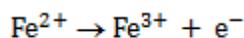
$$E_{\text{cell}}^{\circ} = E_{\text{right}}^{\theta} - E_{\text{left}}^{\theta}$$

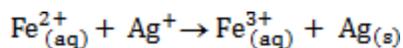
$$= 0.8 - (0.77)$$

$$E_{\text{cell}}^{\circ} = 0.03\text{v}$$

Alternative Solution 2

Half reactions





$$n = 1$$

$$\text{From } E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{products}]}{[\text{reactants}]}$$

$$E_{\text{cell}} = 0.03 - \frac{0.0591}{1} \log \left[\frac{0.2}{0.1 \times 1} \right]$$

$$E_{\text{cell}} = 0.0122\text{v}$$

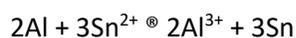
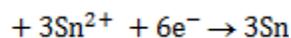
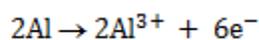
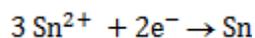
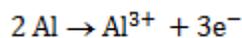
c) Solution

$$E_{\text{cell}}^{\theta} = E_{\text{right}}^{\theta} - E_{\text{left}}^{\theta}$$

$$= -0.14 - (-2.56)$$

$$E_{\text{cell}}^{\theta} = 2.42\text{v}$$

Half reactions



$$n = 6$$

$$\text{Now; } E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{products}]^2}{[\text{reactants}]^3}$$

$$E_{\text{cell}} = 2.42 - \frac{0.0591}{6} \log \frac{[0.112]}{[0.373]}$$

$$E_{\text{cell}} = 2.418\text{v}$$

EQUILIBRIUM CONSTANT OF GALVANIC CELL

Consider to what happens to a Daniel's cell if we use it to do some electrical work i.e. it can be connected to a small electric motor. After sometimes the motor will stop. The cell will run down. When this happens $E_{\text{cell}} = 0$ and there is no overall transfer of electricity from one half cells to the other. When there is no overall change taking place in a chemical reaction the equilibrium has been established. At equilibrium, electron density of both electrodes is equal and there is no transfer of electricity between the two half cells.

Applying the Nernst equation to a Daniel's cell

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{n} \log \frac{[\text{products}]}{[\text{reactants}]}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Since the reaction is at equilibrium, the ratio $\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = K_{\text{C}}$

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{2} \log K_{\text{C}}$$

$$E_{\text{cell}} = 0$$

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{2} \log K_{\text{C}}$$

$$1.1 = E_{\text{cell}}^{\theta} - \frac{0.0591}{2} \log K_{\text{C}}$$

$$K_{\text{C}} = 1.67 \times 10^{37}$$

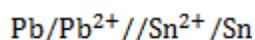
The large value tells us that, the equilibrium lies almost entirely in favour of copper metal and zinc ions.

Generally, the cell at equilibrium at standard temperature is given by the following expression;

$$E_{\text{cell}}^{\theta} = \frac{0.0591}{2} \log K_{\text{C}}$$

Example

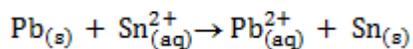
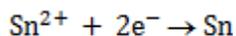
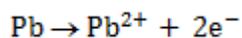
Calculate K_{C} for the following voltaic cell



$$\text{Given } \text{Pb}^{2+} / \text{Pb} = -0.46\text{v}$$

$$\text{Sn}^{2+}/\text{Sn} = -0.12\text{v}$$

Cell reaction



From

$$E_{\text{cell}}^{\theta} = E_{\text{right}}^{\theta} - E_{\text{left}}^{\theta}$$

$$= -0.12 - (-0.46)$$

$$= 0.34\text{v}$$

$$\text{Now, } E_{\text{cell}}^{\theta} = \frac{0.0591}{n} \log K_{\text{C}}$$

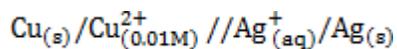
$$0.34 = \frac{0.0591}{2} \log K_{\text{C}}$$

$$\log K_{\text{C}} = 13.53637$$

$$K_{\text{C}} = 3.20 \times 10^{13}$$

Example

What concentration of $\text{Ag}_{(aq)}^{+}$ will emf of the cell be zero at 25°C if concentration of Cu^{2+} is 0.01M .

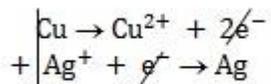
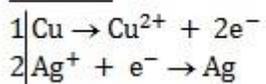


$$\text{Ag}^{+}/\text{Ag} = 0.8\text{v}$$

$$\text{Cu}^{2+}/\text{Cu} = 0.33\text{v}$$

Solution

Solution



$$n = 2$$

From

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{RT}{nF} \ln \frac{[\text{products}]}{[\text{reactants}]}$$

When $E_{\text{cell}} = 0$

$$E_{\text{cell}}^{\theta} = \frac{RT}{nF} \ln \frac{[\text{products}]}{[\text{reactants}]}$$

Now,

$$E_{\text{cell}}^{\theta} = E_{\text{right}}^{\theta} - E_{\text{left}}^{\theta}$$

$$= 0.8 - (0.338)$$

$$E_{\text{cell}}^{\theta} = 0.462\text{v}$$

$$0.462 = \frac{8.314 \times 298}{2 \times 96500} \ln \frac{[\text{P}]}{[\text{R}]^2}$$

$$35.989 = \ln \left(\frac{0.01}{[\text{R}]^2} \right)$$

$$\frac{0.01}{[\text{R}]^2} = 4.265 \times 10^{15}$$

$$[\text{R}]^2 = 2.344 \times 10^{-18}$$

$$[\text{Ag}^+] = 1.5 \times 10^{-9}\text{M}$$

3. Given $\text{Cu}^{2+}/\text{Cu} = 0.34\text{v}$ and $\text{Cu}^{2+}/\text{Cu}^+ = 0.153\text{v}$. Calculate the equilibrium constant for the reaction $\text{Cu} + \text{Cu}^{2+} \rightleftharpoons 2\text{Cu}^+$. State the significance of equilibrium constant.

Solution

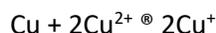
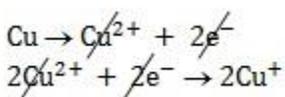
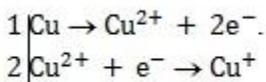
$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{n} \log \frac{[\text{products}]}{[\text{reactants}]}$$

$$E_{\text{cell}} = 0$$

$$E_{\text{cell}}^{\theta} = \frac{0.0591}{n} \log K_{\text{C}}$$

$$K_{\text{C}} = \frac{[\text{products}]}{[\text{reactants}]}$$

$\text{Cu}/\text{Cu}^{2+} // \text{Cu}^{2+}/\text{Cu}^+$



$$n = 2$$

$$\text{Using } E_{\text{cell}}^{\theta} = E_{\text{right}}^{\theta} - E_{\text{left}}^{\theta}$$

$$= 0.53 - 0.34$$

$$E_{\text{cell}}^{\theta} = -0.187\text{v}$$

$$-0.1787 = \frac{0.0591}{2} \log K_{\text{C}}$$

$$\log K_{\text{C}} = -6.3282$$

$$K_{\text{C}} = 4.69 \times 10^{-7}$$

Question

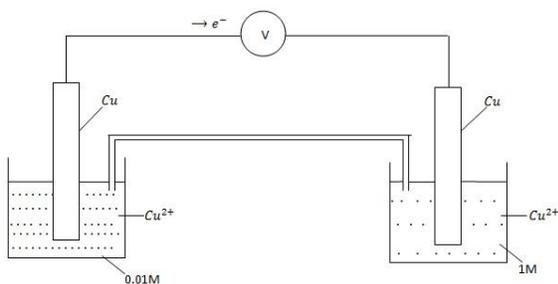
(a) Given the $\text{Ag}^+/\text{Ag} = 0.8\text{v}$, $\text{Cu}^{2+}/\text{Cu} = 0.34\text{v}$ which is thermodynamically feasible, the reduction of Cu^{2+} by Ag or reduction of Ag^+ by Copper.

(b) Calculate the standard emf of the cell and the equilibrium constant.

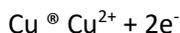
CONCENTRATION CELL

A half concentration cell which consists of two half cells with identified electrode that differs in ion concentration because the electrodes are identified. E° for oxidation is numerically equal and opposite in sign to E° for reduction. As a result $E_{\text{cell}} = 0$

The reaction in the cell takes place in order to reduce the difference in concentration until (when the two concentrations are equal. The higher concentration is reduced and the lower concentration is increased.)



Oxidation



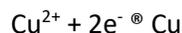
Electrochemical cell: Anode (-)

Cathode (+)

Electrolytic cell: Anode (+)

Cathode (-)

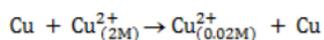
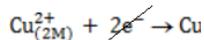
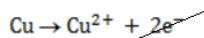
reduction



Question

Calculate the emf of the following concentration cell $\text{Cu}/\text{Cu}^{2+}_{(0.02\text{M})} // \text{Cu}^{2+}_{(2\text{M})}/\text{Cu}$

Solution



Using Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{n} \log \frac{[\text{products}]}{[\text{reactants}]}$$

$$E_{\text{cell}} = 0$$

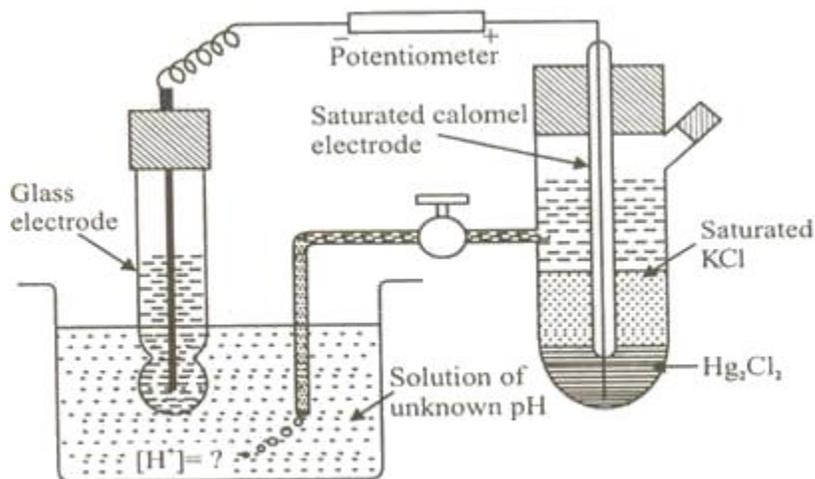
$$E_{\text{cell}} = \frac{-0.0591}{2} \log \frac{[0.02]}{[2]}$$

$$E_{\text{cell}} = 0.0591\text{v}$$

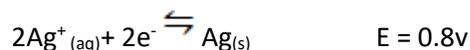
3. MEASUREMENT OF pH OF A SOLUTION USING STANDARD ELECTRODE POTENTIAL

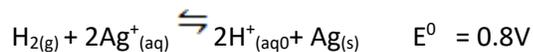
pH is the degree of alkalinity, or acidity of a substance. It is obtained by using the hydrogen ion concentration $\text{pH} = -\log[\text{H}^+]$

The pH of a solution is determined by using any electrode provided its standard electrode potential is known and the concentration of ions in that electrode should be 1M. This will be one of the half cells another half cell is made up hydrogen electrode dipped into the solution whose pH is to be determined



Reaction:





Applying Nernst equation at standard temperature

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{n} \log \frac{(\text{H}^+)^2}{(\text{Ag}^+)^2}$$

$$= 0.8 - \frac{0.0591}{2} \log \frac{(\text{H}^+)^2}{1^2}$$

$$= 0.8 + \frac{0.0591}{2} 2(-\log[\text{H}^+])$$

$$E_{\text{cell}} = 0.8 + 0.0591 \text{pH}$$

$$\text{pH} = \frac{E_{\text{cell}} - E_{\text{cell}}^{\theta}}{0.0591} = \frac{E_{\text{cell}} - E_{\text{Ag}}^{\theta}}{0.0591}$$

Question: Calculate the pH of the following cell and hydrogen ion concentration.



$$\text{Zn}^{2+}/\text{Zn} = -0.76\text{v}$$

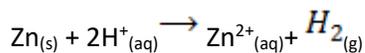
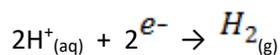
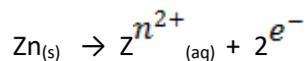
$$E_{\text{cell}} = 0.115\text{v}$$

Solution

$$E_{\text{cell}}^{\theta} = 0 - (-0.760)$$

$$E_{\text{cell}}^{\theta} = 0.76\text{v}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{n} \log \frac{[\text{P}]}{[\text{R}]}$$



$$E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{1} \log \frac{(1)^2}{(\text{H}^+)^2}$$

$$E_{cell} = E_{cell}^{\theta} + \frac{0.0591}{2} \times 2 \log(H^+)$$

$$0.115 = 0.76 + 0.0591 \log(H^+)$$

$$-0.0591 \log(H^+) = 0.645$$

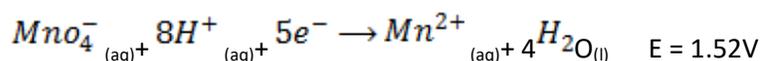
$$\log(H^+) = 10.913$$

$$pH = 10.91$$

pH DEPENDENCE OF REDOX POTENTIALS

Whenever a redox half equation involves H^+ or OH^- ion, its redox potential depends on the pH of the solution.

Example



The Nernst equation at standard temperature is

$$E_{cell} = E_{cell}^{\theta} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

$$E_{cell} = E_{cell}^{\theta} - \frac{0.0591}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

Under standard conditions, all effective concentrations are 1M

$$E_{cell} = 1.52 - \frac{0.0591}{5} \log \frac{1}{1}$$

$$E_{cell} = 1.52 - 0$$

$$E_{cell} = 1.52V$$

Suppose the pH is changed from 0 to 5 i.e. the concentration changes from 1M to $1 \times 10^{-5}M$

$$E_{cell} = 1.52 - \frac{0.0591}{5} \log(1 \times 10^{-5})^8$$

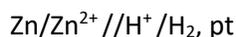
$$E_{cell} = 1.52 + \frac{0.0591 \times 8}{5} \log(1 \times 10^{-5})$$

$$E_{cell} = 1.04 \text{ v}$$

Due to change of P^H from 0 to 5, the electrode potential decreases from 1.52 to 1.047v.
That means, permanganate (vii) becomes a less powerful oxidizing agent when PH increases

Question1.

Calculate P^{OH} of the following cell;-



$$\text{Zn}^{2+} / \text{Zn} = -0.76\text{v}$$

$$E_{cell} = 0.115\text{v}$$

Question2.

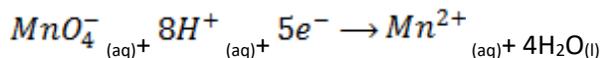
If E for Zn /Zn²⁺//Cu²⁺/Cu is 1.1v

i. Calculate the E_{cell} when concentration of Zn²⁺ is 2M and Cu²⁺ is 0.5M

ii. What is E_{cell} when concentration of Zn is 0.4M, $[\text{Cu}^{2+}] = 0.1\text{M}$

Question3.

Write down the expression for the cell emf for the following reaction;



Briefly explain why the oxidizing power of permanganate (Vii) ion is quite sensitive to the concentration of H⁺ in the solution.

ELECTROCHEMICAL SERIES

Is the series of standard electrode potential with respect to their elements from more negative standard electrode potential to the more positive standard electrode potential.

Is the arrangement of electrodes of elements in order of reducing power

Uses

It is a good guide for predicting reaction that takes place in solution especially displacement reaction.

Displacement reaction

Is a types of reaction in which an atom or element displace another element or atom in a compound

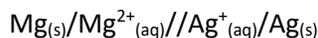
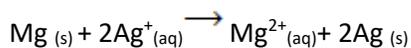
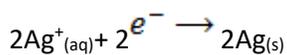
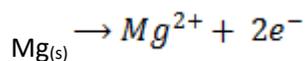
Example

What will happen when magnesium ribbon is added to a solution of AgNO_3 ?

$$E_{Mg}^{\theta} = -2.37\text{v}$$

$$E_{Ag}^{\theta} = 0.8\text{v}$$

The more negative the electrode potential the greater is the reducing power of that element i.e. the more likely it is to give out the electrons and acts as a reducing agent therefore Mg will reduce Ag^+ ions to Ag (s) .



$$E_{cell}^{\theta} = E_R^{\theta} - E_L^{\theta}$$

$$= 0.8 - (-2.37)$$

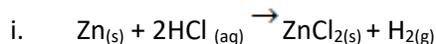
$$E_{cell}^{\theta} = 3.17\text{v}$$

Thus, the element higher in electrochemical series will displace the one lower in the series.

2. Displacement of hydrogen from mineral acids

Metals which are higher in the electrochemical series than hydrogen reacts with acids and replaces hydrogen but metals below hydrogen have no action with mineral acids.

Complete the following reaction:-



3. The knowledge of electrochemical series helps as on choosing method for extraction of metals.

Example

Higher most metal can't be extracted from the oxides by chemical reduction process. This is because they are strong reducing agent hence they can be reduced easily from their oxide by electrolysis.

Questions

For electrolysis, fused or molten metal should be used and not aqueous solution. Why?

Answer:-

In aqueous solution, there are H^+ ions. Hence metals prefer to react with element in lower electrochemical series than the metal itself, hence for electrolysis we use fused or molten metal and not aqueous solution.

CORROSION AND ITS PREVENTION

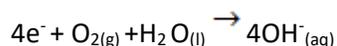
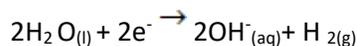
Corrosion is the deterioration of the metals due to the chemical reactions taking place on the surface. Usually, the process is due to the loss of metal to a solution in some forms by a redox reaction (unwanted redox reactions)

For corrosion to occur on the surface of a metal there must be anodic area where a metal can be oxidized to metal ions as electrons are produced.

Anode area:-

$M_{(s)} \rightarrow M^{n+} + ne^-$ And cathodes area where electrons are consumed by any of all of several half reactions.

Cathodic reaction:-



Anodic reactions occur at cracks or around the area with some impurities.

RUSTING OF IRON

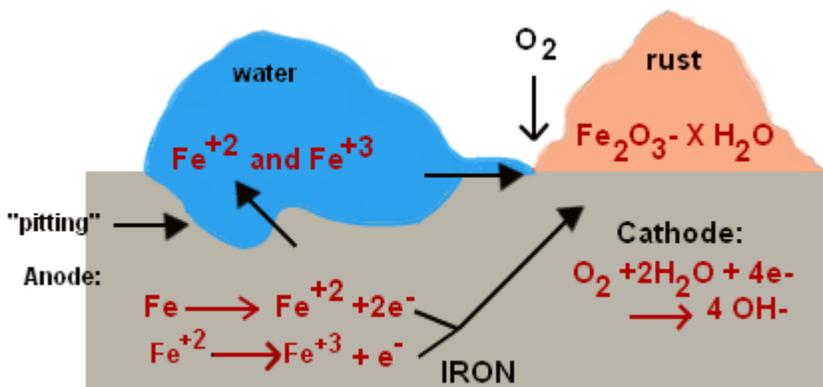
The most common corrosion process is rusting of iron

Rust is hydrated iron (III) Oxide ($Fe_2O_3 \cdot xH_2O$) which appears as a reddish brown substance on the surface of the iron bar.

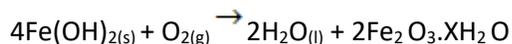
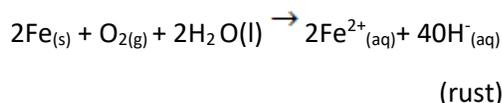
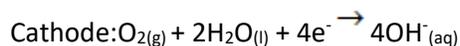
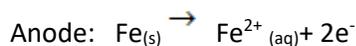
Both water and air (oxygen) are required for rusting to occur.

The presence of dissolved salts and acid in water increases its conductivity and speed up the process of rusting.

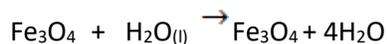
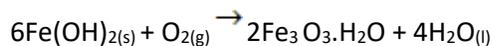
If the iron object has free access to oxygen and H₂O as in flowing water, a reddish brown iron (III) oxide will be formed which is a rust.



For iron:



If oxygen is not freely available: The further oxidation of iron (II) hydroxide is limited to formation of magnetic iron oxide.



Black magnetite

Prevention of rusting

Corrosion can't be made non-spontaneous but it can be prevented by making the rate of the reaction negligible. This can be done by covering the metal surface with protective coating or by providing alternative redox pathways (oxidation-reduction pathways).

Protective coatings are usually of 3 types:

i. Painting: - is the simplest and most common method where a metal surface is properly cleaned and then applied with several layers of rust – proofing paint.

ii. Corrosion inhibitors: - these interfere with flow of charges needed for corrosion to take place i.e. phosphate (II) coating on a surface of iron of steel. Using phosphoric acid serves that purpose.

iii. Galvanization: (sacrificial protection) a metal can also be protected by coating with a thin film of second metal where the second metal is oxidised instead of the 1st metal.

Often iron is coated with another metal like zinc, tin or chromium for protection on the surface.

Note

zinc is preferred to tin because zinc protects iron against rusting when its coating has broken down. This is because it has a more negative reduction potential than iron: it acts as a cathode hence it is not changed. This is called cathodic protection.

Tin protects iron only as long as coating is intact. Once the coating is broken down, tin actually promotes corrosion of iron as iron has more negative reduction potential than tin. Thus iron acts as anode and dissolves while tin acts as cathode and does not change.

Factors which affect corrosion:

i. Position of metal in the electrochemical series (E.C.S). the reactivity of metal depends upon its position in the electrochemical series. More the reactivity, the more likely it is to be corroded.

ii. Presence of impurities in the metal. The impurities help to set up the voltaic cells which increase the speed of corrosion.

iii. Presence of electrolytes: Presences of electrolytes in water also increase the rate of corrosion. E.g. Corrosion of iron in sea water takes place to a large extent than in distilled water.

iv. Presence of CO₂ in water: water containing CO₂ acts as an electrolyte and increases the flow of electrons from one place to another. (CO₂ + H₂O) form carbonic acid which dissolves into ions and hence acts as an electrolyte).

Examples

1. Why do you think zinc on iron is sometimes called sacrificial anode?
2. Explain why blocks of Mg can be attached to hulls of ship or iron pipes with the aim of preventing rusting.
3. Tin cans are made of iron coated with thin film of tin. After a crack occurs in the film, a can corrodes much more rapidly than zinc coated with iron. Explain this behavior.
4. Why is it that with enough time, corrosion will always defeat the protection applied to iron?

ANSWERS

Zinc or iron is sometimes called sacrificial anode because after it wears off, the metal can get exposed and hence starts to undergo rust.

Conductivity in solutions

Electrolytes

These are substances which allow electricity to pass through them in their molten state or in form of their aqueous solution, and undergo chemical decomposition e.g., acids, bases and salts.

Classification of electrolytes

All electrolytes do not ionize by the same extent in the solution. According to this we have strong and weak electrolytes

Strong electrolytes are those that ionize completely into ions in the solution

e.g. Salts, mineral acids, some bases.

Weak electrolytes are these that ionize partially into ions in the solution

e.g. in organic acids. HCN, Na₄OH.

Electrolytic conduction

When a voltage is applied to the electrodes dipped into an electrolytic solution, ions of the electrolyte move towards their respective electrodes and therefore electric current flows through the electrolytic cell. The process of the electrolyte to conduct electric current is termed as conductance or conductivity.

Like metallic conductors, electrolytic solution also obey ohm's law which states that "the strength of the current flowing through a conductor is directly proportional to the potential difference applied across the conductor and inversely proportional to the resistance of the conductor

i.e. $V = RI$.

Resistance of any conductor is directly proportional to the length L and inversely proportional to the area of cross – section.

$$R \propto \frac{L}{A}$$

$$R = \rho x \frac{L}{A}$$

ρ =Resistivity

Resistivity is the resistance of a conductor having unit length and unit area of cross-section. SI unit Ohm-meter (Ωm).

Conductance is the measure of the ease with which the current flows through a conductor a (λ or Λ)

Conductance is the reciprocal of electric resistance. ($\lambda = \frac{1}{R} (\Omega^{-1})$)

From the above expression high resistance means low conductance and vice versa.

Conductivity is the reciprocal of resistivity and is also called specific resistance \bar{k} (kappa)

$$\bar{k} = \frac{1}{\rho} (\Omega^{-1}m^{-1} \text{ or } \Omega^{-1}cm^{-1}) Sm^{-1}$$

For an electrolytic cell, l is the distance apart between the two electrodes and A is the total area of cross-section of the two electrodes. Therefore, for a given cell, l and A are constant. If the dimensions of

the cell are not altered, the ratio $\frac{l}{A}$ is referred as cell constant (K)

$$\frac{l}{A} = K$$

$$R = \rho \frac{l}{A} \Rightarrow \frac{1}{R} = \frac{A}{\rho l}$$

$$\frac{1}{R} = \lambda, \frac{1}{\rho} = \bar{K} \quad \frac{A}{l} = K$$

$$\lambda = \frac{\bar{K}}{K}$$

Molar conductance (λ_m)

Is the conductivity of volume of a solution which contains 1 mole of the solute.

Or

It is the conducting power of the ions produced by dissolving 1 mole of an electrolyte in a solution.

Molar conductance is given by $\lambda_m = \bar{k} v$ where v = volume containing 1 mole of a solute and is called dilution.

Concentration of an electrolyte depends on the volume i.e.

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

$$\therefore \lambda_m = \frac{\bar{K}}{C}$$

Where C is the concentration in mol/dm³ and \bar{k} is S m⁻¹

$$\lambda_m = \text{D...m}^2\text{mol}^{-1} \text{ or } \text{m}^2\text{dm}^{-3}\text{mol}^{-1}$$

Example

1. What is the dilution of 0.2M, NaOH solution?

Solution:

Given $l = 0.2 \text{ mol/dm}^3$

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

$$V = 5 \text{ dm}^3 \text{ mol}^{-1}$$

2. 0.0055M silver nitrate has a molar conductivity of $2.98 \times 10^{-3} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$. Calculate conductivity of that solution.

Solution

$$\lambda_m = \frac{\bar{K}}{C}$$

$$\begin{aligned} \bar{K} &= \lambda_m \times c \\ &= 2.98 \times 10^{-3} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1} \times 0.0055 \text{ mol dm}^{-3} \\ &= 2.98 \times 10^{-3} \text{ m}^2 \Omega^{-1} \times 5.5 \text{ cm}^{-3} \\ \bar{K} &= 0.01529 \text{ } \Omega^{-1} \text{ m}^{-1} \end{aligned}$$

3. Calculate the molar conductivity of 0.3M, KOH solution which has a conductivity of $391 \text{ } \Omega^{-1} \text{ m}^{-1}$.

$$\begin{aligned} \lambda_m &= \frac{\bar{K}}{C} \\ &= \frac{391 \text{ } \Omega^{-1} \text{ m}^{-1}}{0.3 \text{ Mol dm}^{-3}} \\ &= \frac{391 \text{ } \Omega^{-1} \text{ m}^{-1}}{300 \text{ mol m}^{-3}} \\ &= \frac{391}{300} \text{ m}^3 \Omega^{-1} \text{ mol}^{-1} \\ \lambda_\infty &= 1.303 \text{ } \frac{\text{m}^3 \Omega^{-1} \text{ mol}^{-1}}{\text{mol}^{-1}} \end{aligned}$$

5. The cell constant of the conductivity cell was stated as 0.215 cm^{-1} .

The conductance of the 0.01 mol dm^{-3} solution of KNO_3 was found to be $6.6 \times 10^{-4} \text{ } \Omega^{-1}$...

- What is the conductivity of the solution?
- What results does this give for the molar conductivity of KNO_3 ?

Solution:

$$i) R = \rho \frac{l}{A}$$

$$\lambda = \frac{A}{\rho l} = \frac{\bar{K}A}{l} = \bar{K}$$

$$K = 0.215 \text{ cm}^{-1}$$

$$\lambda = 6.6 \times 10^{-4} \text{ s}$$

$$\bar{K} = \lambda K$$

$$= 6.6 \times 10^{-4} \text{ s} \times 0.215 \text{ cm}^{-1}$$

$$= 1.419 \times 10^{-4} \text{ s cm}^{-1}$$

$$ii) \lambda_m = \frac{\bar{K}}{C}$$

$$= \frac{1.419 \times 10^{-4} \text{ s cm}^{-1}}{0.01 \text{ mol dm}^{-3}}$$

$$\lambda_m = 14.195 \frac{\text{cm}^2 \text{ mol}^{-1}}{\text{mol dm}^{-3}}$$

Questions

- How many grams of acetic acid must be dissolved in 1 dm^3 of water in order to prepare a solution with a conductivity and molar conductivity of 575 cm^{-1} and $9255 \text{ cm}^2 \text{ mol}^{-1}$ respectively?
- 0.05 M NaOH solution offered a resistance of $31.6 \frac{\Omega}{\text{cm}}$ in a conductivity cell at 298 K . If the cell constant of a cell is 0.367 cm^{-1} . Calculate the molar conductivity of NaOH solution.
- The conductivity cell filled with 0.01 M KCl has a resistance of $747.5 \frac{\Omega}{\text{cm}}$ at 25°C , when the same cell was filled with aqueous solution of 0.05 M CaCl_2 , the resistance was $876 \frac{\Omega}{\text{cm}}$. Calculate.

i. Conductivity of the solution

ii. Molar conductivity of the solution if given \bar{K} of 0.01 M KCl is $0.4114 \frac{\Omega \cdot \text{cm}^2}{\text{mol}}$

VARIATION OF MOLAR CONDUCTIVITY WITH CONCENTRATION

The intensity of electricity that can pass through the solution depends on

- The number of concentration of free ions present in the solution.
- Speed with which ions move to their respective electrodes.

An increase in concentration gives an increase in total number of solute particles in a given volume of solution and this might well be expected to give an increased conductivity.

Conduction in strong electrolytes.

The molar conductivity is high since strong electrolytes ionize completely into free ions and the molar conductivity increases slightly in dilution. WHY?

In strong electrolytes, there are vast numbers of ions which are close to each other. These ions tend to interfere with each other as they move towards their respective electrodes. The positive ions are held back by the negative ions and vice versa which in turn interrupts their movement to the electrodes (reduce the speed with which they move)

Dilution ions get separated from each other and at an average distance they can move freely or easily.

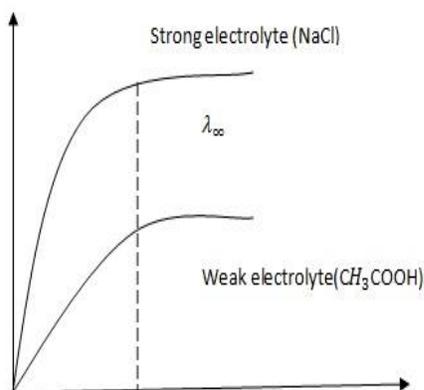
NOTE:-

As the dilution increases, there comes a time for amount of interference become small so that further dilution to has no effect.

At this point the molar conductivity remains constant and it is known as molar conductivity at zero concentration λ_0 .

Conduction in weak electrolyte

The molar conductivity is less because there is less number of particles as the minority of particles are dissociated into ions. On dilution the molar conductivity increases as the molecules dissociate more into ions which increases the number of free ions. Therefore for weak electrolytes the molar conductivity depends on the degree of dissociation of molecules into ions.



Question 1

At infinity dilution, will the molar conductivity of strong and weak electrolyte of same concentration be the same?

Answer

NO, the molar conductivity will be different because it also depends on the size of the ions which would either increase or decrease the speed of ions.

Question 2

Why at infinity dilution, the molar conductivity of weak electrolyte remains constant?

Answer

Because at infinity dilution the molecule must have to dissociate into free ions.

MOLAR CONDUCTIVITY AND DEGREE OF DISSOCIATION

The molar conductivity of weak electrolyte is proportional to the degree of dissociation.

i.e. $\lambda_m \propto \alpha$

$$\lambda_m = K \alpha^2 \dots\dots\dots (i)$$

At infinity dilution, the weak electrolyte is completely ionized.

$$\alpha = 1 \text{ or } 100\%$$

$$\lambda_\infty = K \text{ (Constant)} \dots\dots\dots (ii)$$

Taking ratio of equation (i) and (ii)

$$\frac{\lambda_m}{\lambda_\infty} = \frac{K \alpha^2}{K}$$

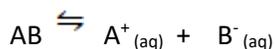
$$\alpha = \frac{\lambda_m}{\lambda_\infty}$$

Ostwald's dilution law

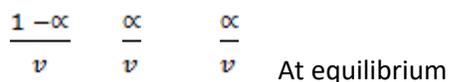
It states that

“For a weak electrolyte the degree of dissociation is proportional to the square root of reciprocal of concentration”

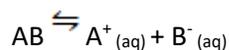
Consider a weak binary electrolyte AB (i.e. ethanoic acid) in solution with concentration C (mol/dm^3).



1mole 0 0 start



$$\text{But } V = \frac{1}{c}$$



$$K = \frac{[A^+][B^-]}{[AB]}$$

But $AB = \text{CH}_3\text{COOH}$

$$K_a = \frac{(C\alpha)^2}{(1-\alpha)C}$$

For a weak electrolyte, degree of dissociation is very small thus the expression

$$1 - \alpha \approx 1$$

$$\therefore K_a = \frac{C^2\alpha^2}{C}$$

$$K_a = C\alpha^2$$

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

Example

- At 25°C the solution of 0.1M of ethanoic acid has a conductivity of $5.0791 \times 10^{-2} \Omega^{-1} \text{m}^{-1} \text{mol}^{-1}$. calculate the pH of the solution and dissociation constant K_a (Answer $K_a = 1.69 \times 10^{-2} \text{M}$)
- A $0.001 \text{ mol dm}^{-3}$ solution of ethanoic acid was found to have molar conductivity of $14.35 \text{ S m}^2 \text{ mol}^{-1}$. Use this value together with molar conductivity at infinity dilution of ethanoic acid $\lambda_\infty (\text{C}_2\text{H}_3\text{COOH})$ is $390.7 \text{ S m}^2 \text{ mol}^{-1}$ to calculate :-
 - Calculate degree of dissociation of acid
 - Equilibrium constant K_a

3. The resistivity of $\frac{1}{50}$ M KCl solution is 361Ω and conductivity cell containing such a solution was found to

have a resistance of 550Ω

a. Calculate the cell constant

b. The same cell filled with 0.1M $ZnSO_4$ solution had resistance of 72Ω . What is the conductivity of this solution?

KOHLRAUSCH'S LAW OF INDEPENDENT IONIC MOBILITY

Kohlrausch notes that the difference between molar conductivity at infinity dilution λ^∞ values for the two salts which were strong electrolytes and of the same cation and anion was always constant. Using the λ^∞ values in D.. $cm^2 mol^{-1}$

Same cation	↓	→	Same cation
$KCl(130)$			$KNO_3(126.3) \rightarrow 3.7$
$NaCl(108.9)$			$NaNO_3(105.2) \rightarrow 3.7$
	↓		↓
	21.1		21.1

This observation shows that each type of ion (cation or anion) contribute a definite amount of molar conductivity of an electrolyte of infinity dilution independently from other ions present in the solution i.e. a fraction of current that an ion carry is always constant and it doesn't depend on the compound in which it is contained.

Hence Kohlrausch's law

States that; "The molar conductivity of an electrolyte at infinity dilution is equal to the sum of the molar conductivities of the cation and anion".

OR State that the molar conductivity at infinity dilution of the solution equal to the sum of molar conductivity at infinity dilution of its components ions.

$$\text{i.e. } \lambda_\infty = \lambda_\infty^+ + \lambda_\infty^-$$

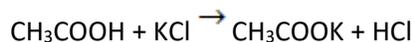
$$\text{E.g. } \lambda_\infty (NaCl) = \lambda_\infty (Na^+) + \lambda_\infty (Cl^-)$$

$$\lambda_\infty (Al_2(SO_4)_3) = 2\lambda_\infty (Al^{3+}) + 3\lambda_\infty (SO_4^{2-})$$

Application of Kohlrausch's law

In direct determination of molar conductivity at infinity dilution for weak electrolytes. Thus by using strong electrolytes we can easily. Calculate the molar conductivities at infinity. Dilution for weak electrolytes.

E.g.: The λ_{∞} ($\text{C}^{\text{H}_3}\text{COOH}$) can be determined from λ_{∞} of potassium ethanoate ($\text{C}^{\text{H}_3}\text{COOK}$) hydrochloric acid (HCl) and potassium chloride (KCl)



$$\begin{aligned}\lambda_{\infty}(\text{CH}_3\text{COOH}) &= \lambda_{\infty}(\text{CH}_3\text{COOK}) + \lambda_{\infty}(\text{HCl}) - \lambda_{\infty}(\text{KCl}) \\ &= \lambda_{\infty}(\text{CH}_3\text{COO}^-) + \lambda_{\infty}(\text{K}^+) + \lambda_{\infty}(\text{H}^+) + \lambda_{\infty}(\text{Cl}^-) - \lambda_{\infty}(\text{K}^+) - \lambda_{\infty}(\text{Cl}^-) \\ \lambda_{\infty}(\text{CH}_3\text{COOH}) &= \lambda_{\infty}(\text{CH}_3\text{COOH}^-) + \lambda_{\infty}(\text{H}^+)\end{aligned}$$

REVIEW QUESTIONS

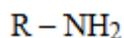
1. Calculate $\lambda_{\infty}(\text{NH}_4\text{OH})$ given that λ_{∞} of three strong electrolyte NaCl, NaOH and NH_4Cl in $\text{D}\dots\text{cm}^2 \text{mol}^{-1}$ are 126.4, 248.4, 149.8 respectively.
2. The molar conductivity of 0.093 CH_3COOH solution at 298k is $536 \times 10^{-4} \text{Sm}^2\text{mol}^{-1}$. The molar conductivity at infinity dilution of H^+ and CH_3COO^- are 3.5×10^{-2} and $0.41 \times 10^{-2} \text{Sm}^2 \text{mol}^{-1}$. What is the dissociation constant of CH_3COOH
3. A 0.05M HF solution has a conductivity of $91.81 \text{mol}^{-1} \text{m}^{-1}$ at 298k. At the same temperature λ_{∞} (NaF), $\lambda_{\infty}(\text{NaOH})$ and $\lambda_{\infty}(\text{H}_2\text{O})$ are 493360 and $162 \text{Sm}^2\text{mol}^{-1}$ respectively. Calculate dissociation constant.
4. The $\lambda_{\infty}(\text{NaI})$, $\lambda_{\infty}(\text{CH}_3\text{COONa})$ and $\lambda_{\infty}(\text{CH}_3\text{COO}_2\text{Mg})$ are 12.69, 9.10 and $18.78 \text{Sm}^2 \text{mol}^{-1}$ respectively at 25°C . What is the molar conductivity of MgI_2 at infinity dilution.

ORGANIC CHEMISTRY 1.2- AMINES

i) STRUCTURES OF AMINES

Amines are derivatives of ammonia in which one or more hydrogen have been replaced by alkyl group or aryl group.

General formula:



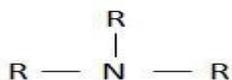
1^o amine

If two hydrogens have been replaced we have;



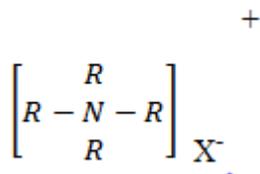
2° amine

If 3 hydrogens have been replaced we have;



3° amine

NOTE:



Quaternary salt of amine

ii) (NOMENCLATURE) IUPAC SYSTEM

$\text{CH}_3 \text{NH}_2$ IUPA name: methanamine (methylamine)

$\text{CH}_3 \text{CH}_2 \text{NH}_2$ Ethanamine

Common name: ethylamine

$\text{CH}_3 - \text{NH}$ N- methylamine \rightarrow 1^o Amine .

$$\begin{array}{c} \text{H} \\ | \\ \text{CH}_3 \text{N}-\text{CH}_2 \text{CH}_3 \end{array}$$
 N - methylethylamine \rightarrow 2^o - Amine .

$\text{CH}_3\text{N}-\text{CH}_2 \text{CH}_3$

$$\begin{array}{c} | \\ \text{CH}_3 \end{array}$$

N,N - Dimethyl ethylamine- 3^o-Amine

$\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH} - \text{CH}_3$,

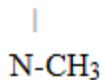
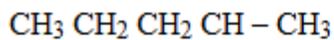
$$\begin{array}{c} | \\ \text{NH}_2 \end{array}$$

Pent-an - 2 - amine

$\text{CH}_3 \text{CH} - \text{CH}_2 \text{CH} - \text{CH}_3$

$$\begin{array}{c} | \quad | \\ \text{CH}_3 \quad \text{NH}_2 \end{array}$$

4 - Methyl - pentan - 2 - amine



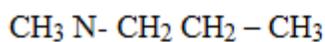
N, N - dimethyl pentan - 2 - amine



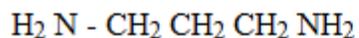
OR



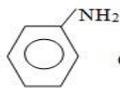
2 - (N, N - dimethyl) pentanamine



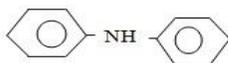
N - Ethyl - N - methylpropananmine



Propane - 3 - diamine



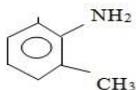
Common name: Aniline or phenylamine
IUPAC name: Benzenamine



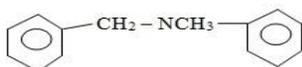
N, N - diphenylamine



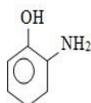
N - Methylbenzenamine



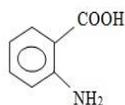
2 - Methylbenzenamine



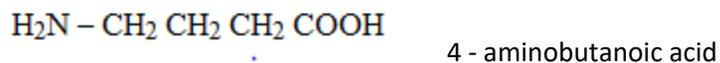
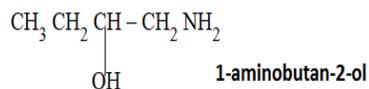
N - benzyl - N - methylbenzenamine



2 - aminophenol

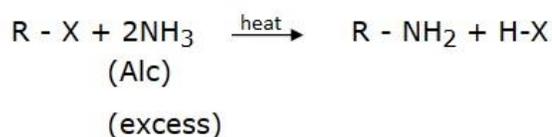


2 - aminobenzoic acid



iii) PREPARATION OF AMINES

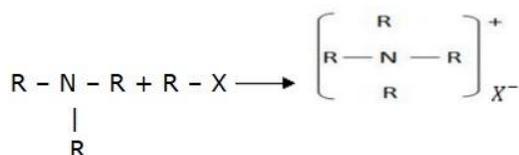
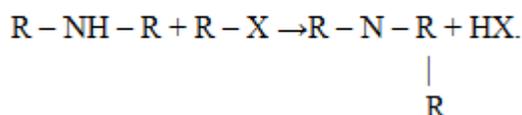
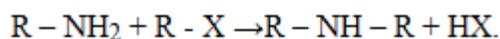
1. ALKYLATION OF AMMONIA WITH HALOALKANES



1^o amine can be obtained by reaction of alkyl halide with excess ammonia.

Why excess ammonia?

So as to prevent the formation of 2^o amine or 3^o amine. Therefore, this is not a suitable for preparation of amine because the substitution of hydrogen does not stop at the first stage.



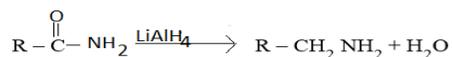
2. REDUCTION OF NITROALKANES (R-NO₂)

1^o amines can be obtained by reduction of nitroalkane. The reducing agent is LiAlH₄ or Sn/HCl or Fe/HCl

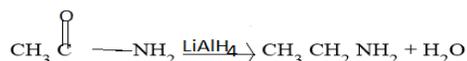
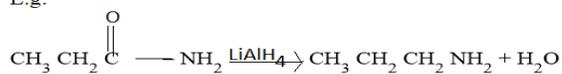


3. REACTION OF AMIDES WITH LiAlH₄

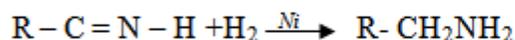
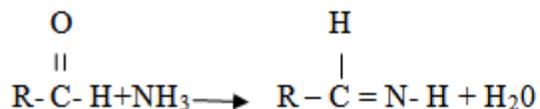
1^o amides can be reduced to 1^o amines



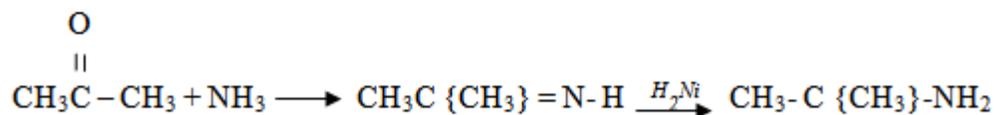
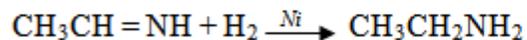
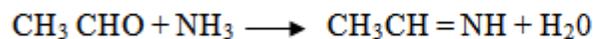
E.g:



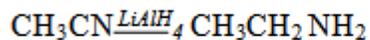
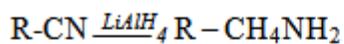
4. AMMONIATION OF CARBONYL COMPOUND FOLLOWED BY REDUCTION WITH HYDROGEN IN THE PRESENCE OF NICKEL



E.g.

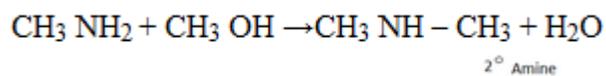
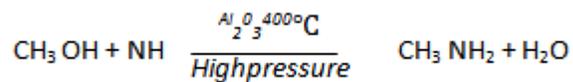


5. REDUCTION OF NITRILES

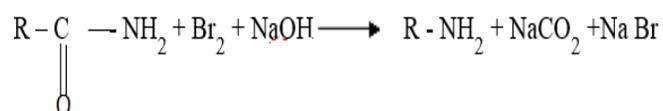


6. REACTION OF ALCOHOLS WITH AMMONIA

Catalytic ammoniation of alcohol gives a mixture of amines.



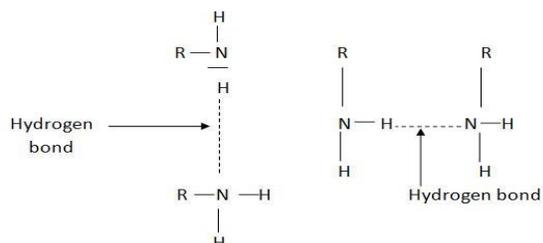
7. HOFFMAN'S DEGRADATION OF AMIDES



It is important reaction in the conversion of amide to amine with one carbon less.

Boiling point and melting point

Amines have high boiling and melting points due to their ability to form hydrogen bonding as compared to hydrocarbons.



(i) Its boiling point is lower than alcohol (R - OH)

Reason: In oxygen, there are 2 lone pairs which increase its chance of hydrogen bonding.

It also has lower boiling point than carboxylic acid.

1^0 amines have high boiling point than 2^0 amines. For 3^0 amines, there is no possibility of H-bonding since Nitrogen is not attached to hydrogen.

(ii) Solubility:

Lower aliphatic amines are soluble in water.

Reason:- They can form hydrogen bond with water.

As the molecular mass increases, solubility decreases.

Reason: -The long chain of hydrocarbon (R) is insoluble since it is water phobic. As the alkyl group becomes bigger, solubility decreases.

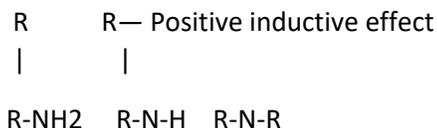
Amines containing 6 or more carbon do not dissolve in water.

E.g: aniline is insoluble due to this reason.

b)CHEMICAL PROPERTIES OF AMINES

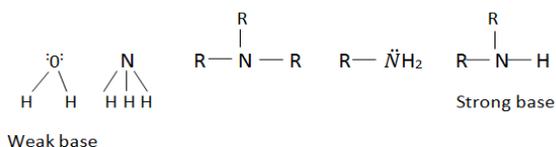
1. Basic character

Amines are the most important organic bases. Aliphatic amines are slightly stronger Lewis bases than ammonia. Lone pair on the nitrogen is readily available to accept proton in amines than it is in ammonia.



2° amine the strongest base among the three

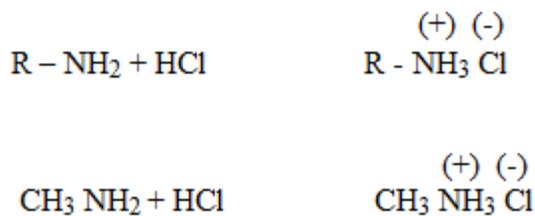
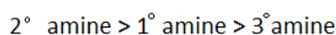
The stability of hydrated ion decrease from 1° amine 3° amine



Reason:- 3° amines form a very unstable ammonia salt. Although it can easily donate a lone pair of electrons as compared to 1° and 2° amines, it forms a very unstable hydrated ion.

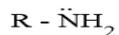
Note:

The inductive effect on alkyl group tends to make 3° amines more basic while hydration effect tends to make 1° amine more basic. As a result of the combined effect of these two the observed order of the base strength will be;



Methylammonium chloride

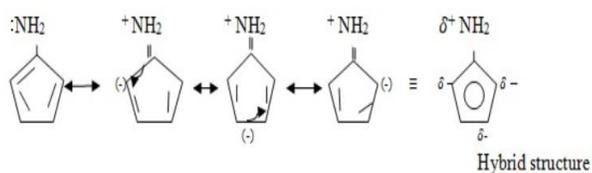
Q. Between the following amines, which is stronger base



Answer: $R - \ddot{N}H_2$ is stronger base

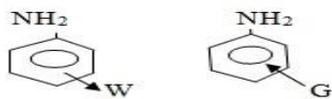
Reason:- In Aniline there is negative mesomeric effect since lone pair is withdrawn from the amine group.

Mesomerism of aniline



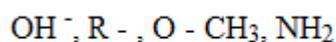
For aromatic compounds, the lone pair is less readily available for protonation (addition of proton)

EFFECT OF SUBSTITUENT GROUP ON THE BASICITY OF ANILINE

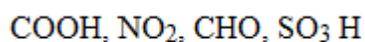


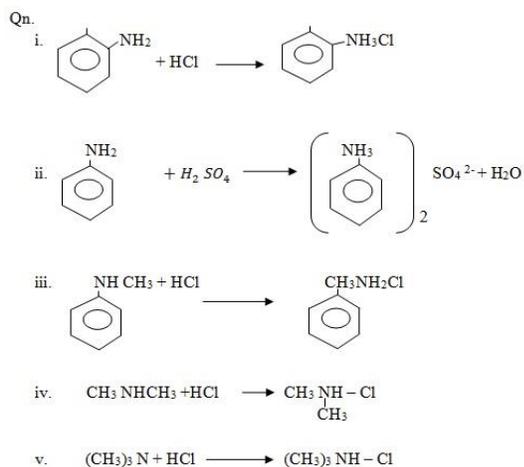
· All activators make aniline more basic while deactivators make aniline less basic.

Electrons supplying groups

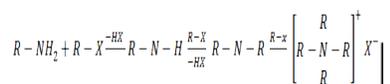


Electrons withdrawing groups





2. Alkylation (reaction with haloalkanes)



Example:



1⁰ Amine

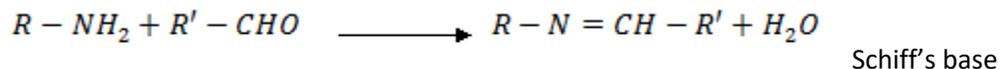
2⁰ amine



Quaternary salt

3. Reaction with ketones and aldehydes

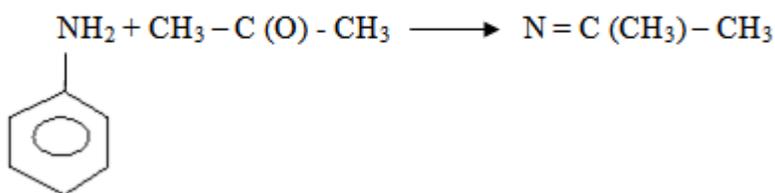
Both aliphatic and aromatic 1^o amines react with aldehydes and ketones to form a base known as Schiff's bases.



E.g:



-Lewis acid is a substance that accepts a lone pair of electrons



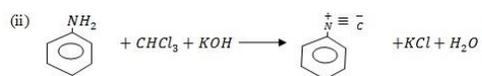
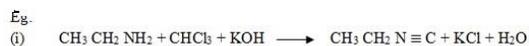
4. Reaction of 1^o amines with chloroform (carbylamines reaction)

- Both aliphatic and aromatic amines on heating with chloroform and alcoholic KOH give isocyanides (carbylamines)
- The isocyanide form has an offensive smell. It is used as an identification test for 1^o amine

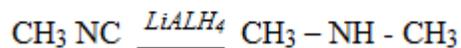
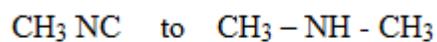


Carbylamines (offensive smell)

This reaction is a **Test for 1^o amine**



(i) Convert;



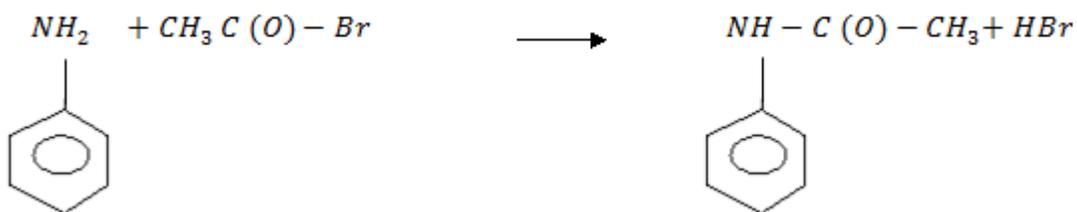
5 . Acylation



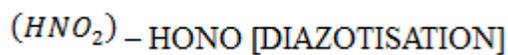
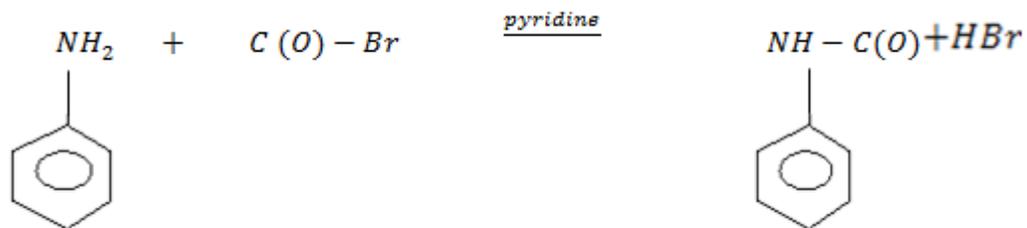
E.g.



N - methylethanamide



N - phenylethanamide



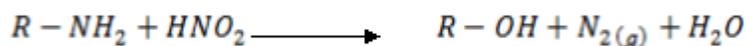
6. Reaction with Nitrous acid



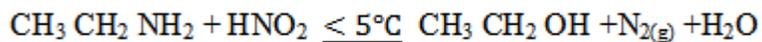
Note: It is used as a distinguishing test between different classes of amines.

1° Amine

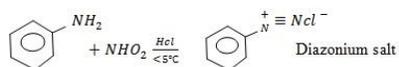
Aliphatic 1° amine reacts with HONO to form alcohol and nitrogen gas (you will see bubbles)



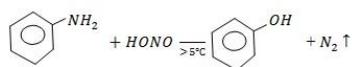
E.g:



- For aromatic amine react with HNO_2 in cold (below 5°C) to form diazonium salt.



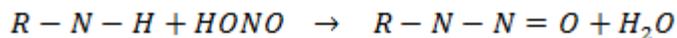
- But above 5°



2° Amine

- 2° amines react with nitrous acid to give N - nitrosoamine which separate out as a yellow oily liquid.

|



R

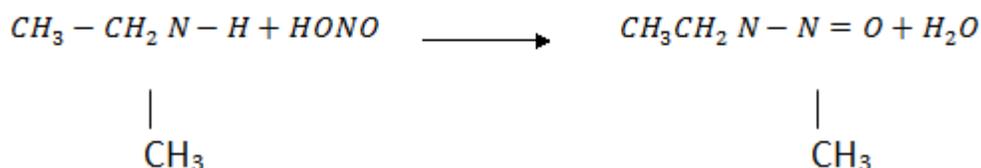
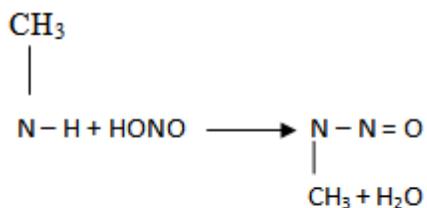
R

N- nitrosoamine

(Yellow oil liquid)

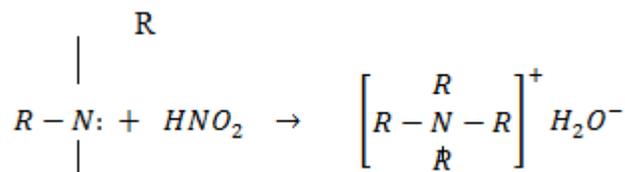
It is a distinguishing test since we see yellow oil liquid

Eg:

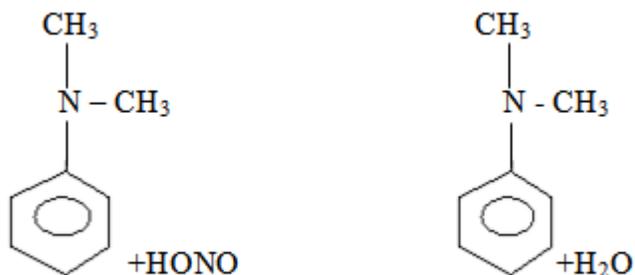


3° Amine

3° Amine reacts with nitrous acid to form a soluble trialkylammonium salt which is colourless. It is not a distinguishing test since there is no observable change.



Aromatic 3° amines react with HONO to give green colour p - nitrosoamine



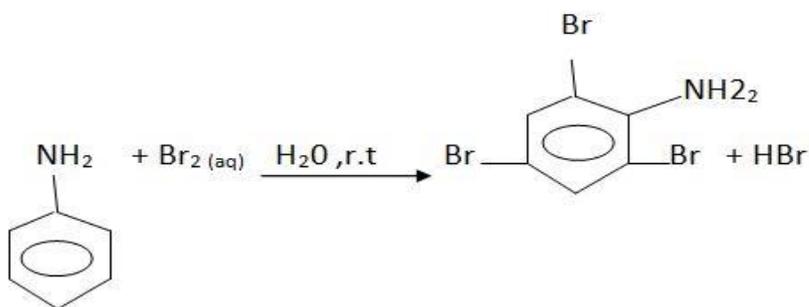
This is a distinguishing Test since there is a green colored

Reaction of amines with metal ions Ag^+ & Cu^{2+}

Reaction of aromatic amine due to benzene ring

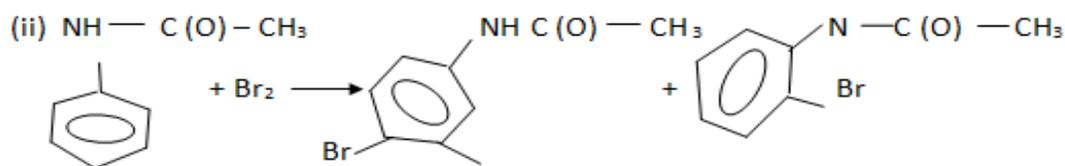
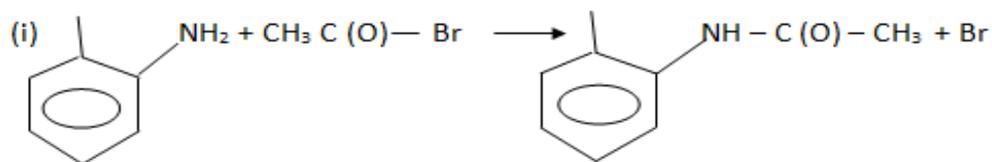
1. reaction with bromine water

- Aniline undergoes halogenations even in the absence of catalyst. With bromine it gives 2, 4, 6 - tribromoaniline (white solid)

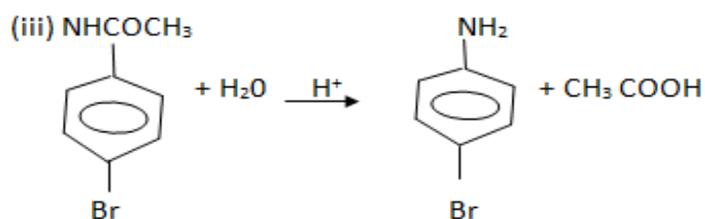


Here benzene ring is highly activated due to the presence of amine

To obtain mono substituted derivative, aniline should be first acylated then halogenation. After halogenations, the acyl group is removed by hydrolysis to obtain mono substituted aniline.

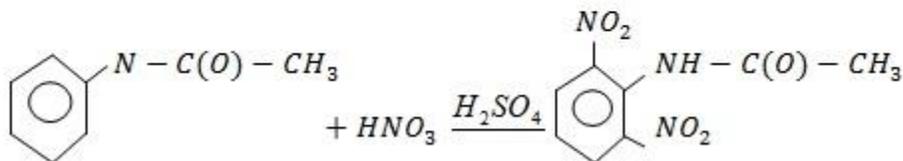
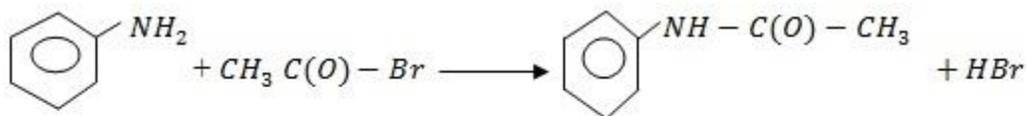


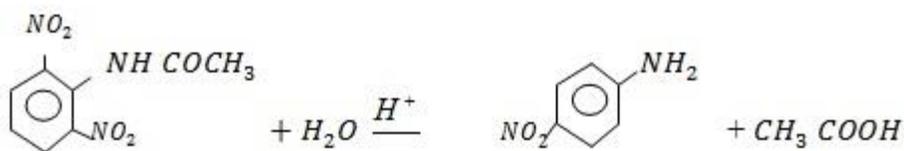
Major product (It experiences minor product steric hindrance)



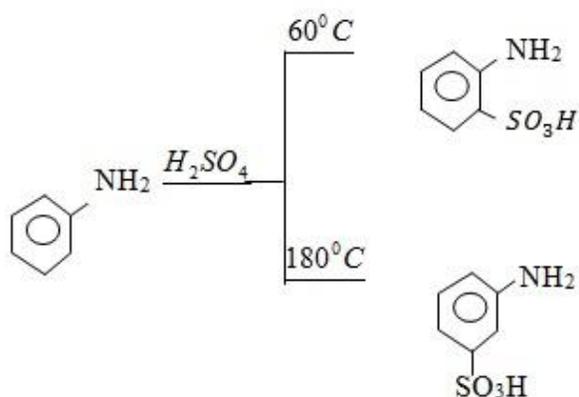
2. Nitration

Direct Nitration is not possible because aniline gets oxidized. Amine group should be protected by acylation, then nitration and finally hydrolysis.





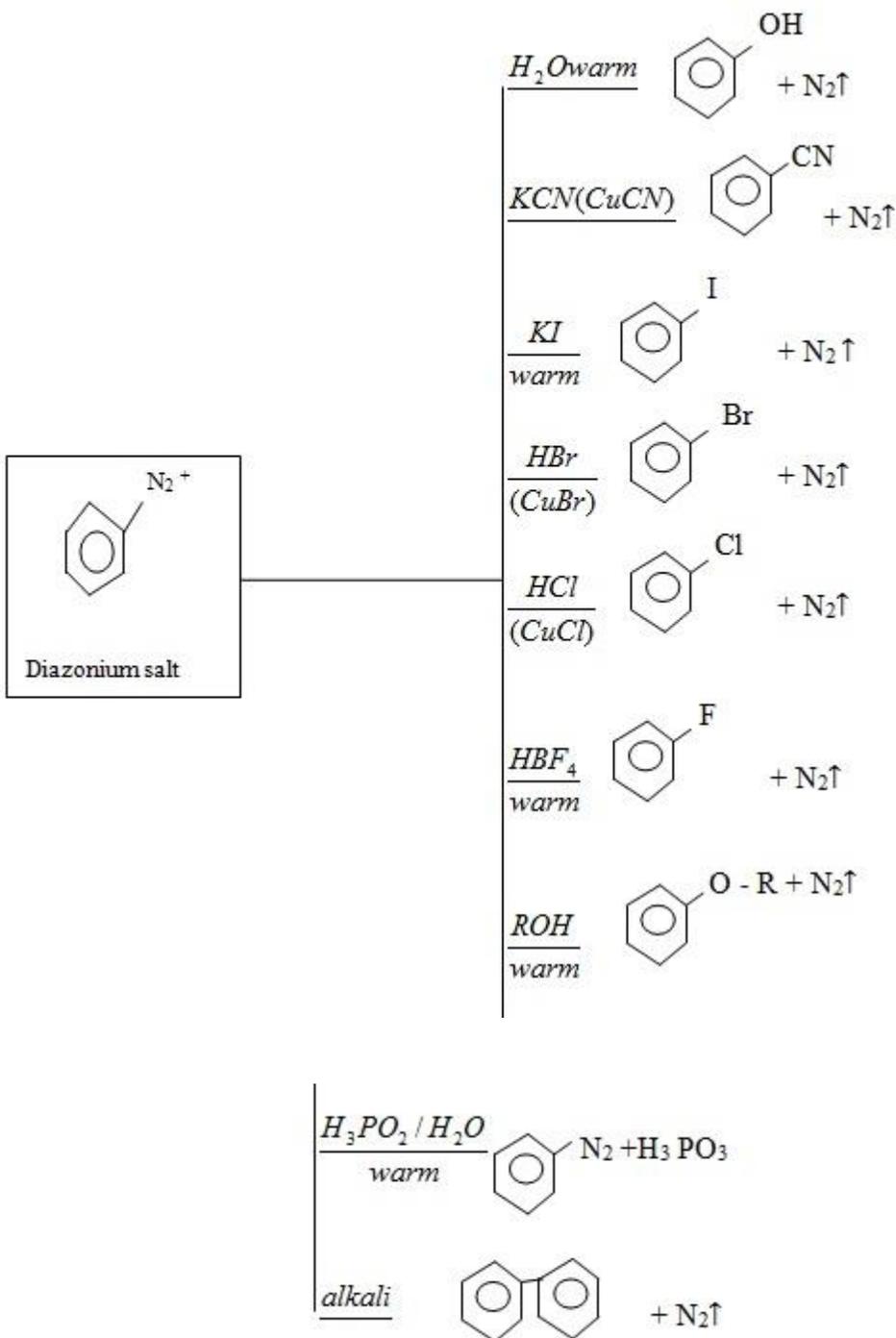
3. Sulphonation



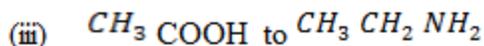
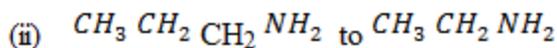
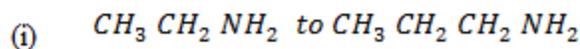
We have different products due to H - bonding. At 180°C, H - bonding will not be effective hence SO₃H will be at para position.

4. Diazonium salt

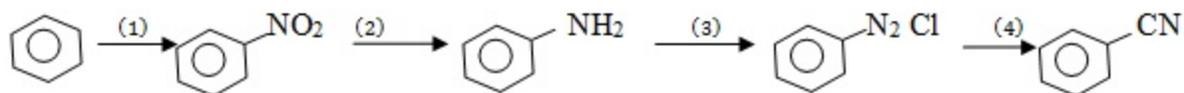
- It is used to form many other products.
- Reaction is nucleophilic substitution *reaction*.



H/W

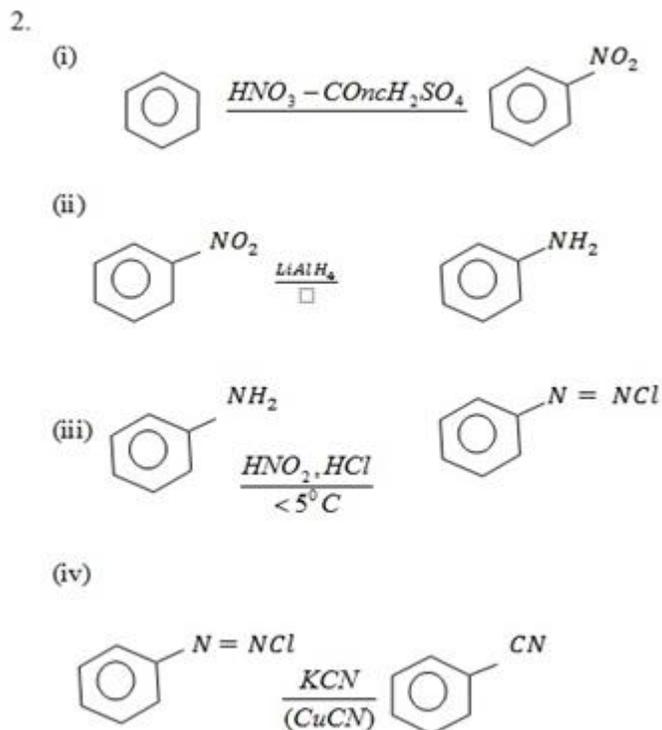


2. Identify the reagents 1, 2, 3 & 4



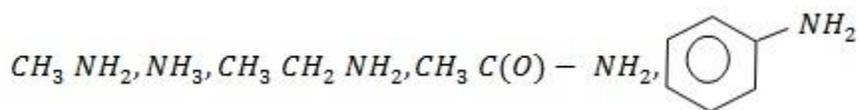
3. Why is phenylamine more soluble in HCl than in H_2O ?
4. Define the term “base.” Write down structural formula of the following compounds and arrange them in order of increasing basic strength; Methylamine, ammonia, ethylamine, ethanamide, phenylamine. Give reasons.
5. Give structural formula of the organic products that are obtained when;
- Ethylamine
 - Phenylamine
 - Phenylmethanamine
 - N - methylphenylamine are treated with;
 - Chloromethane
 - A mixture of $NaNO_2$ and HCl
 - Benzoylchloride

ANSWERS



Phenylamine is more soluble in HCl since they will form a stable hydrated ion but it is less soluble in water due to the large hydrophobic part i.e. the benzene ring.

4. A base is a substance which releases OH^- as the only negative ion.



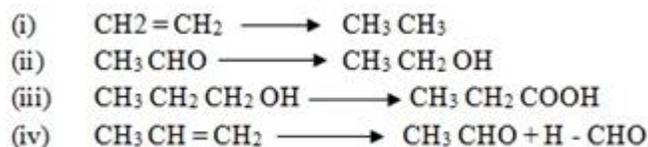
QUESTIONS

1. An aromatic compound contains 80% carbon, 9.6% hydrogen and nitrogen. Its relative molecular mass is 135g/mol. It is slightly basic and form salts but given no other reaction nitric (III) acid. Identify the structure of this compound.
2. An organic base A contains 61% carbon, 15.3% hydrogen, 23.7% nitrogen. When treated with nitric (III) acid A yield an alcohol B and nitrogen gas is evolved. The alcohol B contains 60%

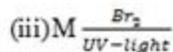
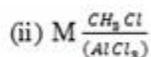
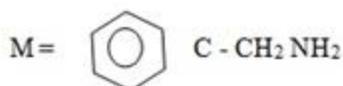
carbon, 13.33% hydrogen and on careful oxidation yields compound C, which has a vapour density of 29. Compound C forms an oxime with hydroxylamine ($\text{H}_2\text{N} - \text{OH}$) but does not react with Fehling's solution. Suggest structures for the compounds A, B and C and indicate the cause of the above reactions.

3. How does the introduction of nitro group – 2 - and – 4 - positions of phenylamine affect its basicity? Give reasons

(a) Give the conditions under which the following reactions proceed



(b) Write the structural formula for each of the organic compound formed when compound M reacts with each of the following;



ANSWERS:

1.

	C	H	
--	---	---	--

Percentage	80	9.6	
R.M.M	12	1	
\div by R.M.M	6.666	9.6	
\div by smallest number	8.97 ≈ 9	12.924 ≈ 13	

\therefore Structure of the compound is $C_9 H_{13} N$

$$n (C_9 H_{13} N) = 135$$

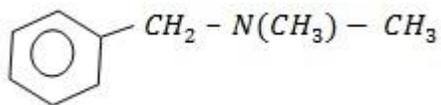
$$n (108 + 13 + 14) = 135$$

$$135n = 135$$

$$n = 1$$

Molecular formula: $C_9 H_{13} N$

Probable structural formula:

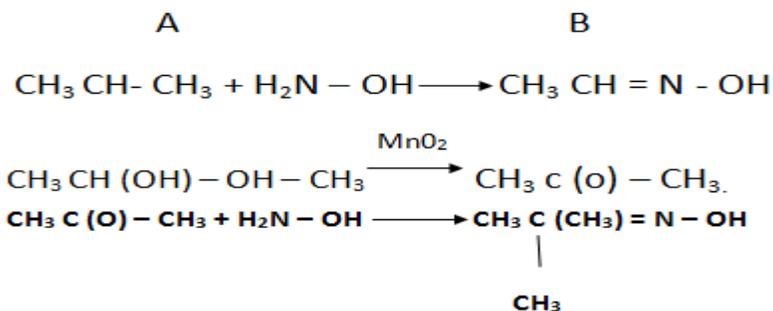
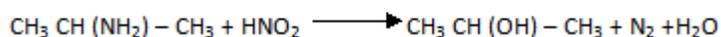
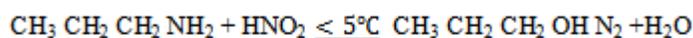


2.

	C	H	N
Percentage	61	15.3	23.7
R.M.M :	12	1	14
Percentage divide by R.M.M	5.083	15.3	1.69
divide by the smallest no	3	9.05	1

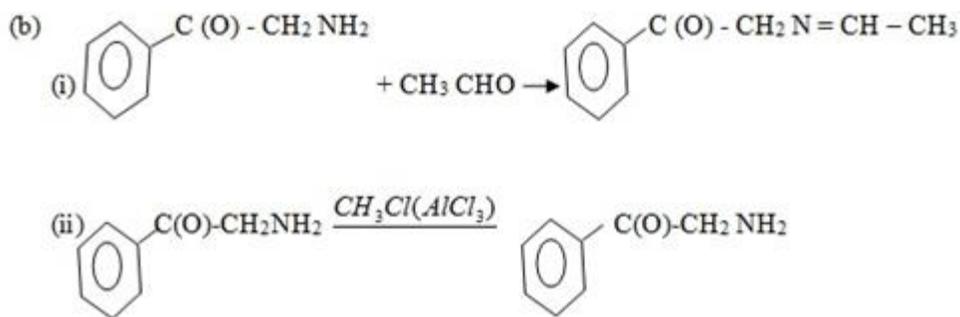
Empirical formula C₃ H₉ N

The organic base will be $CH_3 CH_2 CH_2 NH_2$



3. The nitro group attached to position - 4 - will make phenylamine to be more basic than the nitro group attached to position - 2

Reason:- This is because in - 2 - nitrophenylamine there might be hydrogen bonding between the hydrogen and oxygen hence basicity will decrease.

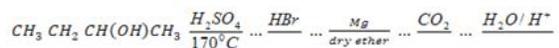


QUESTIONS

Give the equations for preparation of propanoic acid stating with;

- Haloalkane
- Ethene

Give equations (including reagents and conditions) for the following conversions;



- Arrange the following compounds in order of their increasing acidity. Explain the differences in their acidity.
 - ethanol
 - Ethanoic acid
 - Pentanoic acid
 - Ethanedioic acid
 - 1, 2 - benzenedicarboxylic acid
 - Trichloroethanoic acid

g) Butenedioic acid

4. Convert the ethanoic acid into;

a) Ethylethanoate

b) Ethanoylchloride

c) Ethanol

d) Trichloromethanoic acid

e) Ethanamide

For each conversion give a chemical equation

5. A compound A of molecular formula $C_4H_8O_2$ gives propane when fused with alkali. When A reacts with $Na_2CO_3(aq)$, CO_2 is evolved. When A reacts with molecular formula $C_8H_{14}O_4$ which on strong heating yield 2, 4 – dimethylpentanone. Establish the structural formula of A & B and give reason.

6. (a) An unknown compound W undergoes ozonolysis and hydrolysis. This produces an acid and a compound of formula C_4H_8O and Y which gives a positive Iodoform test. When X is reacted with $LiAlH_4$ the product Z, is mixed with an equal amount of ethanol, a little conc. H_2SO_4 is added and the mixture is heated to $140^\circ C$ major products are formula of R.M.M 74, 88 and 107 called P, Q and R.

(b) Why has an acid been produced on ozonolysis?

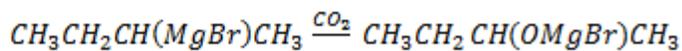
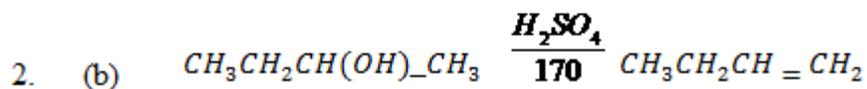
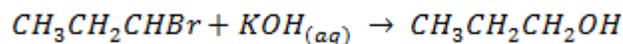
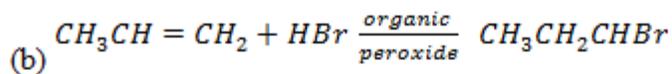
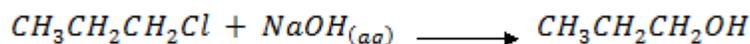
7. Describe, giving necessary experimental conditions, the reactions which occur between sulphuric (VI) acid and;

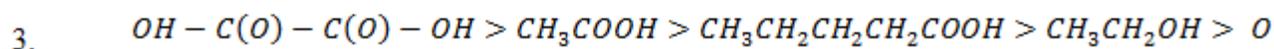
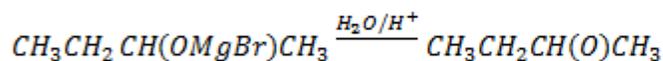
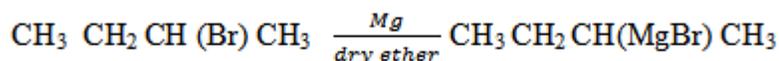
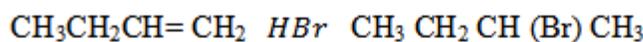
(a) Ethene

- (b) Ethanol
(c) Benzene
(d) Methanoic acid

ANSWERS

1. (a) Let the haloalkane be $CH_3CH_2CH_2Cl$

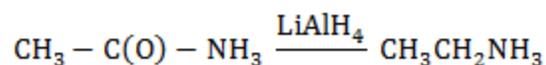
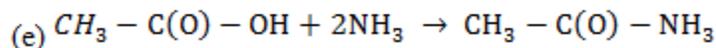
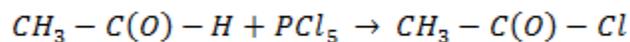
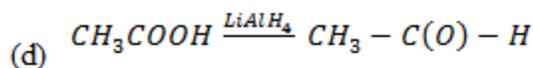
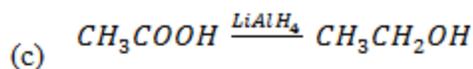
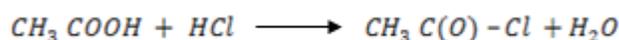




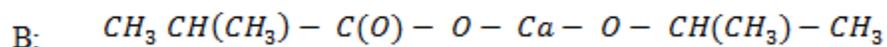
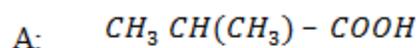
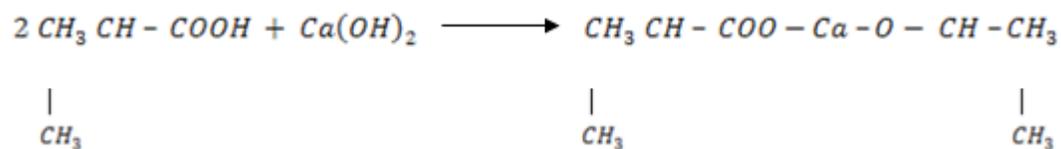
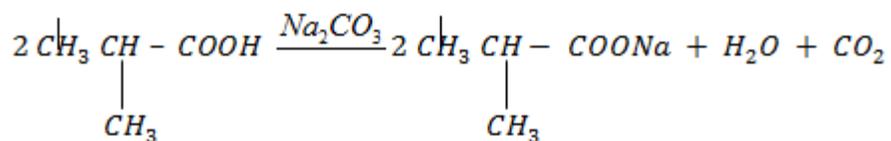
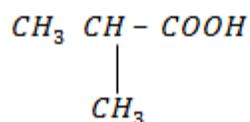
4. (a)



(b)

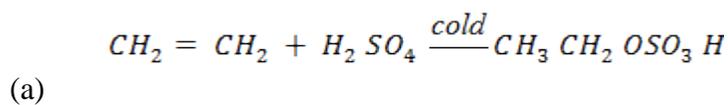


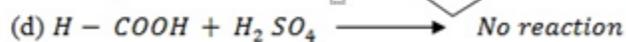
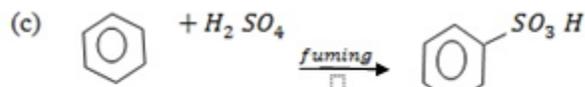
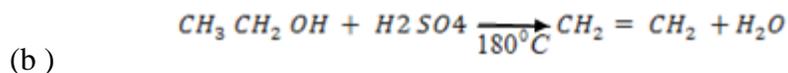
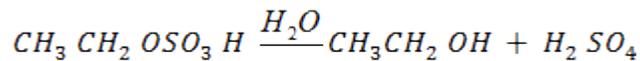
5 A:



When you oxidize 2, 4 - dimethylpentanone you will get carboxylic acid A.

7.





Reason:- They are both acids.

EXERCISE

1. Suggest the reagents that bring about the following conversions:-

- i. Pent – 2 - yne to pentan – 3 – one
- ii. Benzoylchloride to Benzaldehyde
- iii. Ethanenitrile to ethanol
- iv. 1 - hexyne to hexan – 2 – one
- v. 4 - fluorotoluene to 4 – florobenzaldehyde

2. How will you convert ethanal into the following compounds:-

- i. Butane 1, 2 - diol
- ii. But – 2 – enal
- iii. Butan - 1 - ol
- iv. Butanoic acid
- v. Butan – 2 – one
- vi. But – 2 - enoic acid

3. How will you bring about the following in not more than 2 steps:-

- i. Propanone to propene
- ii. Propanal to Butanone
- iii. Benzaldehyde to benzophenone
- iv. Ethanol to 3 - hydroxybutanal

ANSWERS

1.

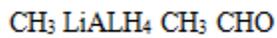
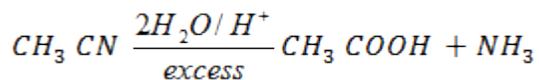
- i. Pent - 2 - yne to pentan - 3 - one



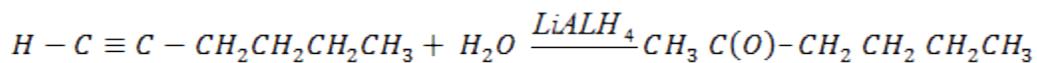
- ii. Benzoylchloride to Benzaldehyde



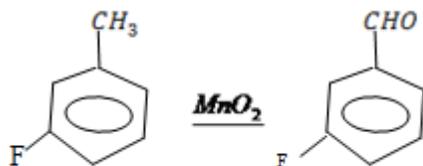
- iii. Ethanenitrile to Ethanal



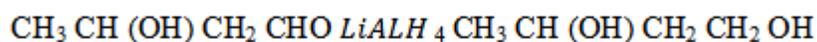
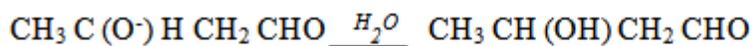
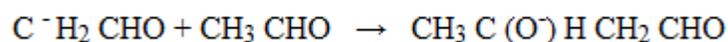
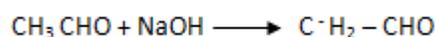
- iv. 1 - hexyne to hexan - 2 - one



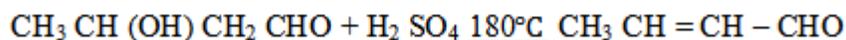
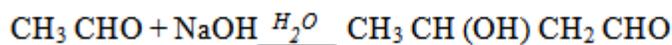
- 4 - Florotoluene to 4 - florobenzaldehyde



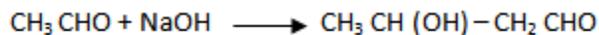
1. (i) By aldo - keto condensation

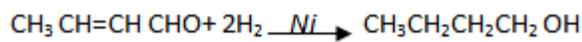


(ii) To convert ethanal to but - 2 - enal

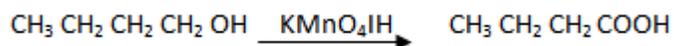
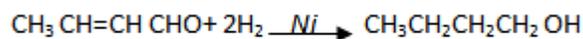
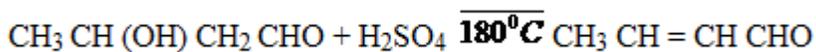
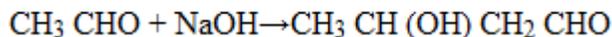


(iii) Ethanal to butan - 1 - ol

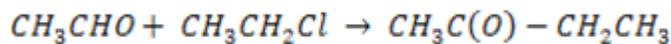




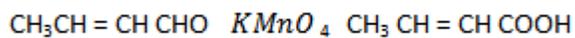
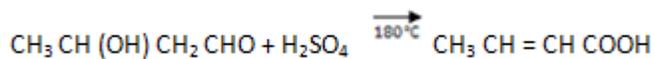
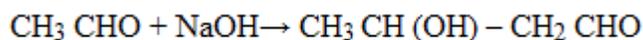
(iv) Ethanal to butanoic acid



(v) Ethanal to butan - 2 - ol

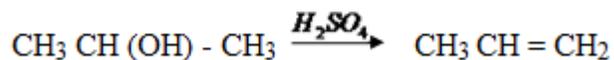


(vi) Ethanal to but - 2- enoic acid

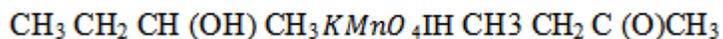
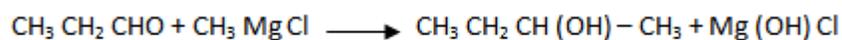


But – 2 – enic acid

2. (i) Propanone to propene



(ii) Propanal to butanone



(iv) Ethanol to 3 - hydroxybutanal

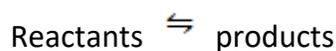
Solution



PHYSICAL CHEMISTRY 1.4-CHEMICAL EQUILIBRIUM

Chemical reactions which takes place in both directions are called reversible reactions .These reactions do not proceed to completion rather to dynamic equilibrium between products and reactants.

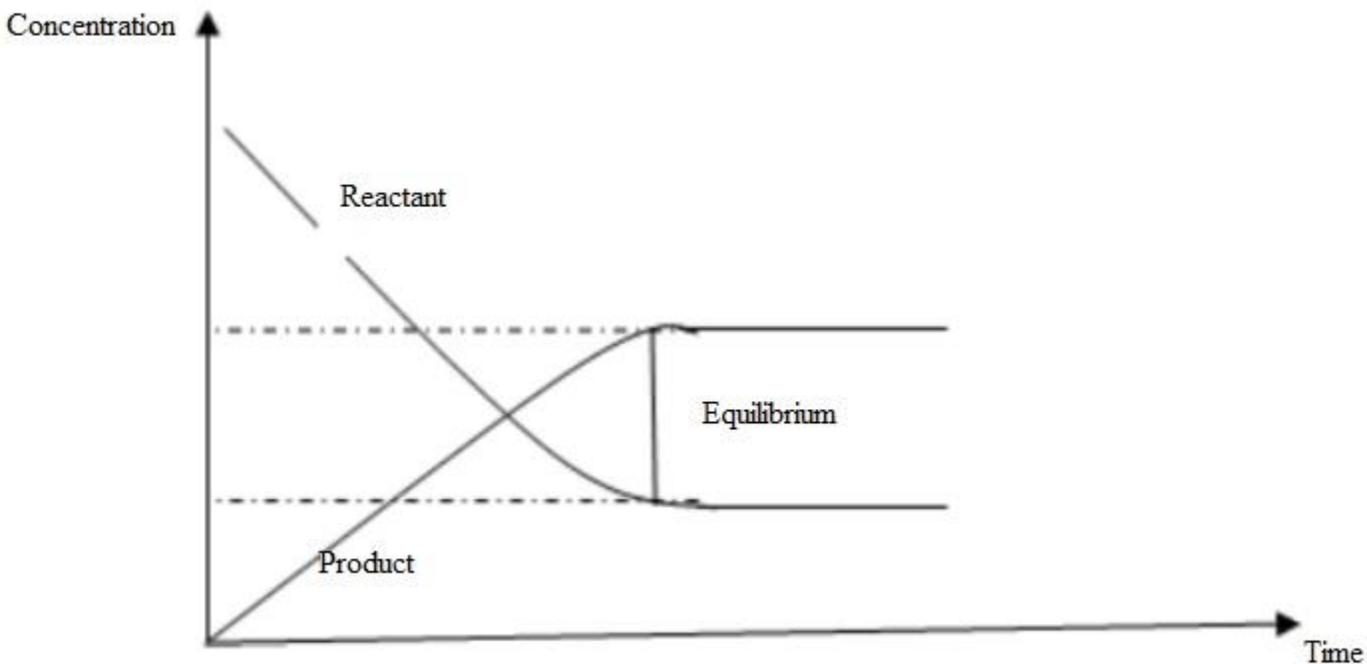
As a result of this, the concentration of reactants and products becomes constant (but not equal)



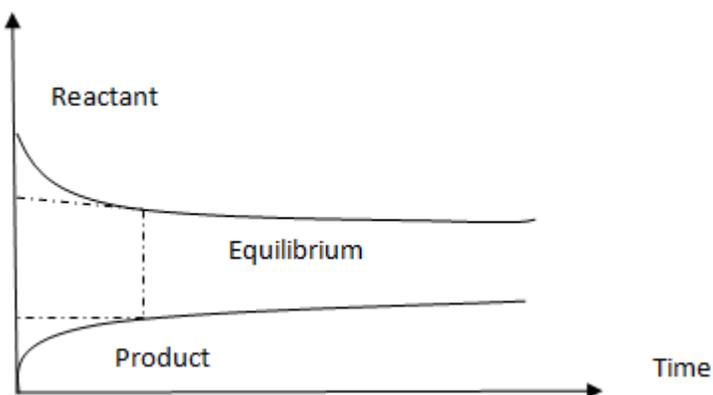
At equilibrium, the rate of forward reaction is equal to the rate of backward reaction.

Note: The concentration of all species in the equilibrium remains constant since both opposing reactions proceed at the same rate.

The concentration of reactants decreases with time while those of products increases with time until equilibrium is reached where the concentrations are constant (not equal).

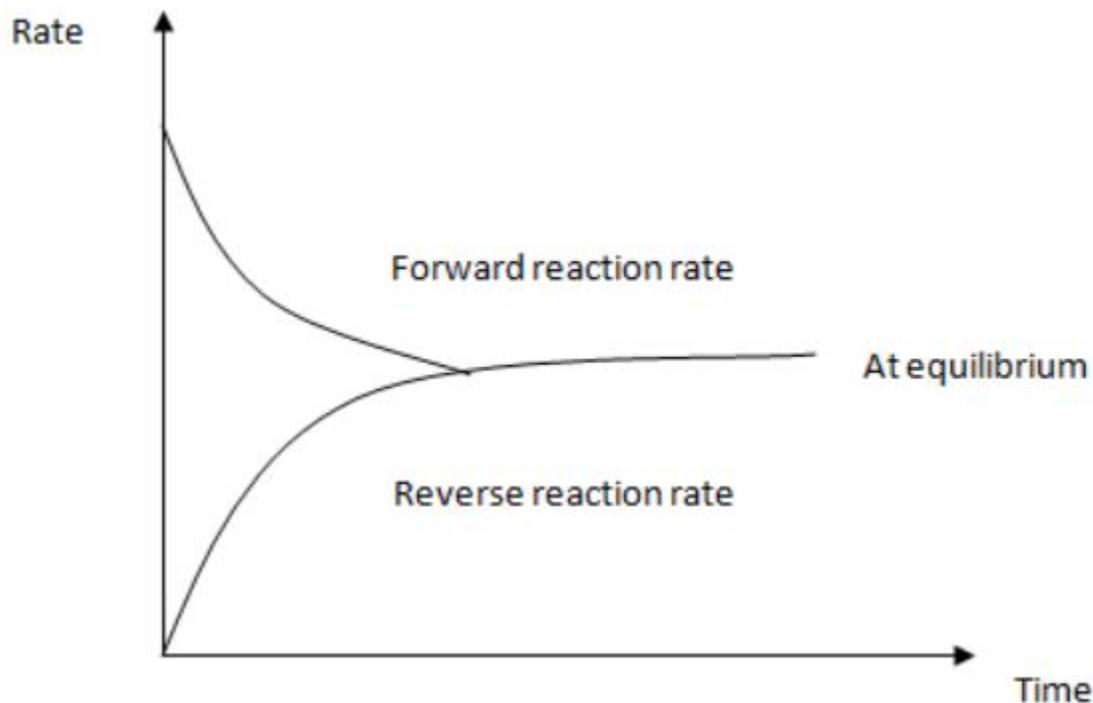


The equilibrium has been attained with high concentration of products than reactants therefore equilibrium lies on product side.



The equilibrium has been attained with high concentration of reactants than products therefore equilibrium lies on reactants side.

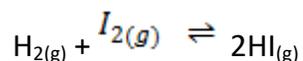
The rate of reaction depends on the concentration of reactants. As the concentration of reactants decreases, the rate of forward reaction decreases too. The rate of backward reaction increases since the concentration of products increases until equilibrium is attained.

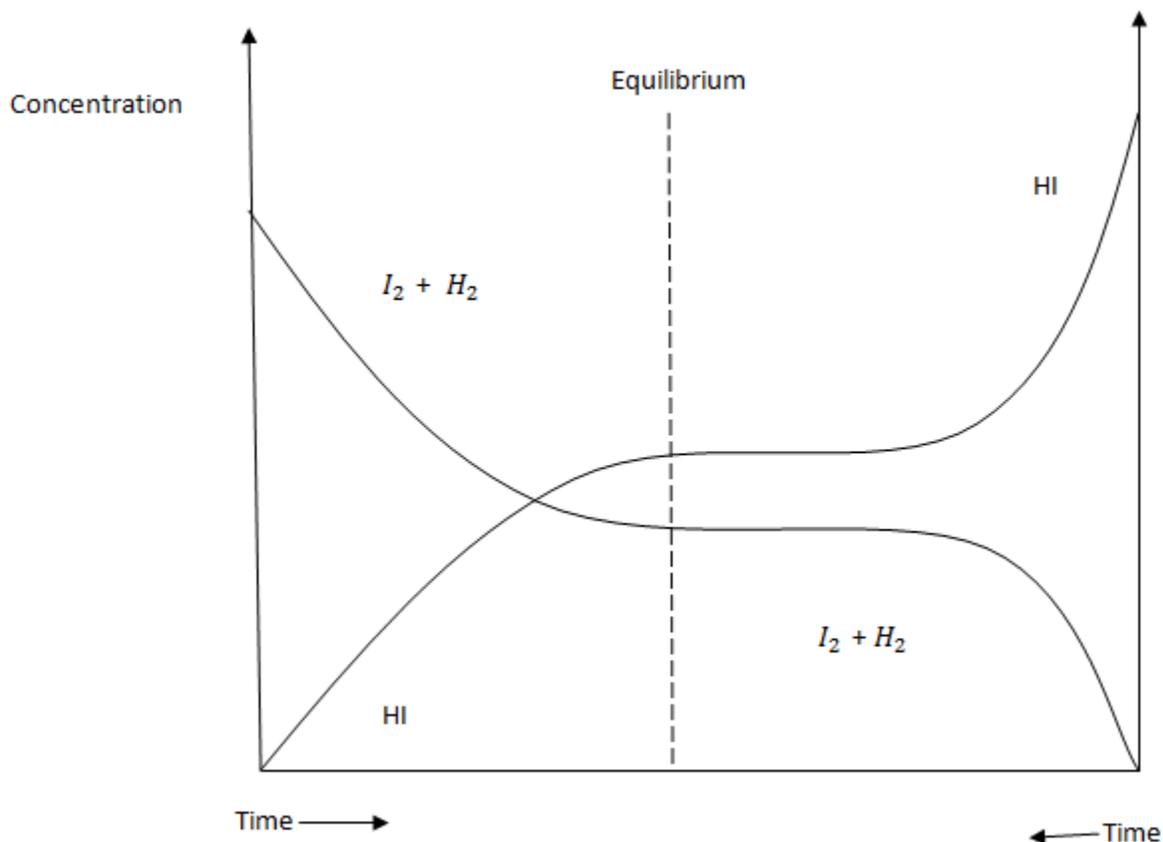


Characteristics of chemical equilibrium

1. The equilibrium can be established or attained in a closed system (no part of the reactants or products is allowed to escape out.)
2. The equilibrium can be initiated from either side. The state of equilibrium of a reversible reaction can be approached whether we start from reactants or products.

Consider the reactions:-





3. Constancy of concentration

When a chemical equilibrium is attained, concentration of various species in the reaction mixture becomes constant.

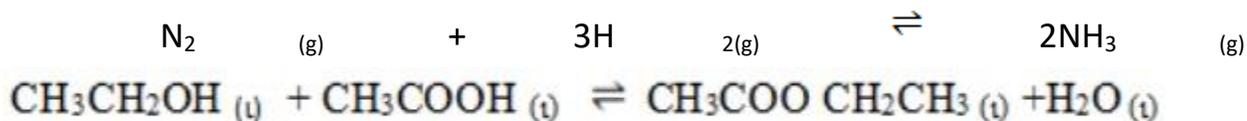
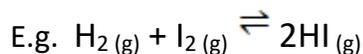
4. A catalyst cannot change the equilibrium point. When a catalyst is added to a system in equilibrium, it speeds up the rate of both forward and

backward reactions to equal extent. Therefore a catalyst cannot change equilibrium point except that it is reached earlier.

Types of chemical equilibrium

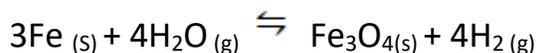
1. **Homogeneous equilibrium:**

This is equilibrium where reactant and products are in the same physical states i.e. all solids, all liquids or all gases.



2. Heterogeneous equilibrium;

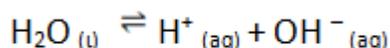
This is equilibrium when the reactants and product are in the different physical states



3. Ionic equilibrium:

This is an equilibrium which involves ions.

E.g.

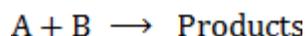


LAW OF MASS ACTION

The law relates the rates of reactions and the concentration of the reacting substances. The law states that, "the rate of a chemical reaction is directly proportional to the product of the molar concentration of the reactants at constant temperature, at any given time".

The molar concentration means number of moles per litre and is also called **active mass**

Consider the following simple reactions:



The rate of the reaction, $R \propto [A] [B]$

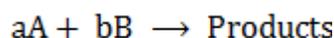
$$R = k [A] [B] \text{Rate equation}$$

Or $R = k [A] [B]$

Where [A] and [B] are the molar concentrations of the reactant A and B respectively and that K is a constant of proportionality known as rate constant or velocity constant.

If the concentration of each of the reactants involved in the reaction is unity i.e. the concentration of $[A] = [B] = 1$, thus the rate constant of a reaction at a given temperature may be defined as a rate of the reaction when the concentration of each of the reactants is unity.

Generally for a reaction



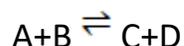
Where a and b are stoichiometric coefficients or mole ratio of the reactants, A and B

$$r = k [A]^a [B]^b \text{ or } R = k [A]^a [B]^b$$

LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

The law of mass action is applied to reversible reaction to derive a mathematical expression for equilibrium constant known as the law of chemical equilibrium.

Consider a simple chemical reaction (reversible)



The forward reaction is $A+B \rightarrow C+D$

$$\text{Rate of forward (Rf)} \propto [A] [B]$$

$$R_f = K_f [A] [B]$$

K_f = Rate constant for forward reaction

Similarly for the backward reaction



$$\text{Rate of backward (Rb)} \propto [C] [D]$$

$$R_b = K_b [C] [D]$$

K_b = Rate constant for backward reaction

At equilibrium both rates are equal

$$R_{\text{forward}} = R_{\text{backward}}$$

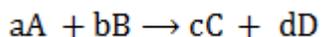
$$K_f [A] [B] = K_b [C] [D]$$

$$\frac{K_f}{K_b} = \frac{[C] [D]}{[A] [B]}$$

$$K_e = \frac{[C] [D]}{[A] [B]}$$

Generally:-

For the reaction



The equilibrium constant for this expression is given by

$$K_e = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

K_e is changed to K_c for equilibrium concentration (equilibrium constant) .

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Where K_c is equilibrium concentration (equilibrium constant)

[C], [D] etc are molar concentration of species in mol per litre a, b etc are mole ratios or stoichiometric coefficients.

But for gaseous equilibrium we know that $PV = nRT$

$$PV = nRT$$

$$\frac{n}{v} = \frac{P}{RT}$$

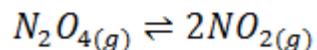
Concentration of a gas is directly proportional to partial pressure therefore the equilibrium constant can be represented in terms of both concentration and partial pressure.

For the above equilibrium;

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

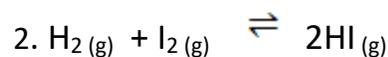
Example1.

1. $N_2O_4(g)$ dissociates to give $NO_2(g)$



$$K_c = \frac{[NO_2]^2}{[N_2][O_4]}$$

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2})(P_{O_4})}$$



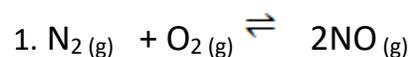
$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_p = \frac{(P_{HI})^2}{(P_H)(P_I)}$$

The law of chemical equilibrium states that, "For any system in equilibrium at a given temperature, the ratio of product of concentration of products to the product of the concentration of reactants raised to the power of their mole ratios is constant".

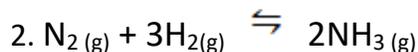
UNITS OF EQUILIBRIUM CONSTANT

The units of equilibrium constants, K_c and K_p depends on the number of moles of reactants and products involved in the reaction



$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})}$$

$$K_p = \frac{(atm)^2}{(atm)(atm)} = \text{Unit less}$$



$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3}$$

$$K_p = \frac{(\text{atm})^2}{(\text{atm})^1 (\text{atm})^3}$$

$$K_p = \text{atm}^{-2}$$

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

$$= \frac{[\text{mol/l}]^2}{[\text{mol/l}]^1 [\text{mol/l}]^3}$$

$$K_c = \text{mol}^{-2}$$

A large value of K_p or K_c means the equilibrium lies on the sides of the product and a small value of K_c and K_p means equilibrium lies on the sides of the reactants thus the equilibrium constant shows to what extent the reactant are converted to the product.

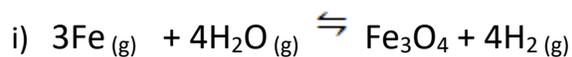
- If K_c is greater than 10^3 , products pre- dominate over reactants equilibrium therefore the reaction proceeds nearly to completion.
- If K_c is less than 10^{-3} , reactants dominate over products, the reaction proceeds to very small extent.
- If K_c is in the range of 10^{-3} and 10^3 , appreciable concentrations of both reactants and products are present.

SOLIDS AND PURE LIQUIDS IN EQUILIBRIUM EXPRESSION

The concentration of a solid or pure liquid (but not a solution) is proportional to its density. Therefore, their densities are not affected by any gas pressure hence remain constant; hence their concentration never appear in the equilibrium expression.

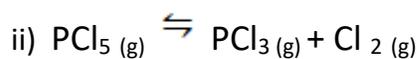
Example

1. What is the equilibrium expression for the following reactions?



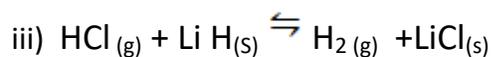
Solution

$$K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4} \quad \text{OR} \quad K_p = \frac{(P_{\text{H}_2})^4}{(P_{\text{H}_2\text{O}})^4}$$



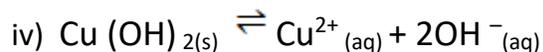
$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

$$K_p = \frac{(P_{\text{PCl}_3})(P_{\text{Cl}_2})}{(P_{\text{PCl}_5})}$$

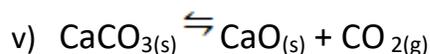


$$K_c = \frac{[\text{H}_2]}{[\text{HCl}]}$$

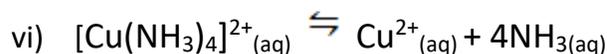
$$K_p = \frac{(P_{\text{H}_2})}{[P_{\text{HCl}}]}$$



$$K_c = [\text{Cu}^{2+}] [\text{OH}^{-}]^2$$

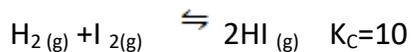
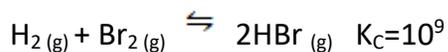
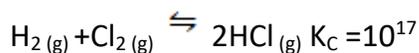


$$K_c = [\text{CO}_2]$$



$$K_c = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4]^{2+}}$$

2. The equilibrium constant for the synthesis of HCl, HBr and HI are given below;



3. a) What do the value of K_c tell you about the extent of each reaction?

b) Which of these reactions would you regard as complete conversion? Why?

Answers

a) For all the 3 reactions, the equilibrium lies on the product side (i.e. RHS) and the extent of formation of HCl is greater than HBr which in turn is greater than HI.

b) For the 1st and 2nd reaction, it can be regarded as complete conversion because products pre-dominates over reactants at equilibrium.

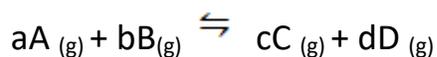
Characteristics of equilibrium constant

1. Equilibrium constant is applicable only when the concentrations of reactants and products have attained their equilibrium.
2. The value of equilibrium concentration is independent of the original concentration of reactants.
3. The equilibrium constant has a definite value for every reaction at a particular temperature.
4. For a reversible reaction the equilibrium constant for the forward reaction is the inverse of the equilibrium constant for the backward reaction.
5. The value of equilibrium constant tells the extent to which reaction proceeds in the forward or reverse direction.
6. Equilibrium constant is independent of the presence of catalyst. This is because the catalyst affects the rate of forward and backward reaction equally.

Relationship between K_c and K_p for a gaseous equilibrium

For any given reaction, K_c or K_p is a function of the reaction itself and temperature.

Consider the following gaseous equilibrium



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \text{ ----- (1)}$$

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} \text{ ----- (2)}$$

From $PV = nRT$

$$[X] = \frac{n}{V} = \frac{P}{RT}$$

i.e. $[A] = \frac{P_A}{RT}$, $[B] = \frac{P_B}{RT}$

Substitute these concentration in terms of partial pressures in equation (1)

$$K_c = \frac{\left(\frac{P_C}{RT}\right)^c \left(\frac{P_D}{RT}\right)^d}{\left(\frac{P_A}{RT}\right)^a \left(\frac{P_B}{RT}\right)^b}$$

$$= \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \cdot \left(\frac{\left(\frac{1}{RT}\right)^c \left(\frac{1}{RT}\right)^d}{\left(\frac{1}{RT}\right)^a \left(\frac{1}{RT}\right)^b} \right)$$

$$= K_p \left(\frac{\left(\frac{1}{RT}\right)^{(c+d)}}{\left(\frac{1}{RT}\right)^{(a+b)}} \right)$$

$$= K_p \left(\frac{1}{RT}\right)^{(c+d)-(a+b)}$$

But; $(c+d)$ = total number of moles in the products.

$(a+b)$ = total number of moles in the reactants.

$(c+d) - (a+b)$ = The difference between moles of products and reactants

So, $(c+d)-(a+b) = \Delta n$

$$K_c = K_p \left(\frac{1}{RT} \right)^{\Delta n}$$

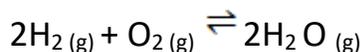
OR

$$K_p = K_c (RT)^{\Delta n}$$

Thus, the numerical value of K_p and K_c are equal when there is the same number of moles on products and reactants side numerically.

Example:

1. What is the relationship between K_p and K_c in the following reactions?

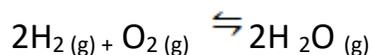


$$\text{From; } K_p = K_c (RT)^{\Delta n}$$

$$= K_c (RT)^{(2 - (1+2))}$$

$$K_p = K_c (RT)^{-1}$$

ii) Derive the relationship between K_p and k_c for the particular reaction.



$$K_c = \frac{[\text{H}_2\text{O}]^2}{[\text{O}_2][\text{H}_2]^2} \dots\dots\dots (1)$$

$$K_p = \frac{(P_{\text{H}_2\text{O}})^2}{(P_{\text{O}_2})(P_{\text{H}_2})^2} \dots\dots\dots (2)$$

From $PV = nRT$

$$P = \left(\frac{n}{v}\right) RT$$

$$P = [X] RT$$

$$\therefore P_{H_2} = [H_2] RT, \quad P_{O_2} = [O_2] RT \dots \dots \dots \text{etc}$$

Substitute the partial pressure in equation (2)

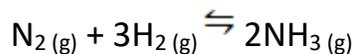
$$K_p = \frac{([H_2O] RT)^2}{([O_2] RT)([H_2] RT)^2}$$

$$K_p = \frac{[H_2O]}{[O_2][H_2]} \cdot \frac{(RT)^2}{(RT)(RT)^2}$$

$$K_p = K_c (RT)^{(2-(1+2))}$$

$$K_p = K_c (RT)^{-1}$$

2. a) Derive the relationship between K_p and K_c for ammoniac synthesis.



$$K_c = \frac{[NH_3]^2}{[H_2]^3 [N_2]} \dots \dots \dots (1)$$

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})^3 (P_{H_2})} \dots \dots \dots (2)$$

From $PV = nRT$

$$P = \left(\frac{n}{v}\right) RT$$

$$P = [X] RT$$

$$\therefore P_{NH_3} = [NH_3] RT, P_{H_2} = [H_2] RT, P_{N_2} = [N_2] RT$$

Substitute the partial pressure in equation (2)

$$K_p = \frac{([NH_3]RT)^2}{([H_2]RT)^3 ([N_2]RT)}$$

$$K_p = \frac{[NH_3]^2}{[H_2]^3 [N_2]} \cdot \frac{[RT]^2}{(RT)^3 [RT]}$$

$$K_p = K_c \times (RT)^{(2-(3+1))}$$

$$\underline{K_p = K_c (RT)^{-2}}$$

b) If $K_c = 0.105 \text{ mol}^{-2} \text{ dm}^6$ at 472°C . Calculate K_p

$$[R=8.31 \text{ dm}^3 \text{ KPa mol}^{-1} \text{ K}^{-1}]$$

Solution:

$$K_p = K_c \times (RT)^{-2}$$

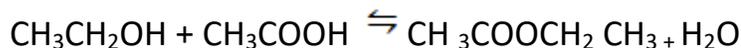
$$= 0.105 \times (8.31 \times 745)^{-2}$$

$$= 0.105 \times (6190.95)^{-2}$$

$$= \underline{2.7395 \times 10^{-9} (\text{KPa})^{-2}}$$

DETERMINATION OF EQUILIBRIUM CONSTANT

Consider the reaction:-



At start	a	b	0	0
Equilibrium	(a-x)	(b-x)	($\frac{x}{v}$)	($\frac{x}{v}$)

$$\therefore [\text{CH}_3\text{CH}_2\text{OH}] = \frac{a-x}{v}; [\text{CH}_3\text{COOH}] = \frac{b-x}{v} \dots\dots\dots\text{etc}$$

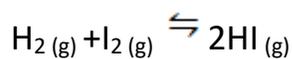
$$\therefore K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{OH}][\text{CH}_3\text{COOH}]}$$

$$= \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}$$

$$K_c = \frac{x^2}{(a-x)(b-x)}$$

Example:

1. An equilibrium system for the reaction between H₂ and I₂, to form HI at 670K in 5l flask contains 0.4 moles of H₂, 0.4 moles of I₂ and 2.4 moles of HI. Calculate the equilibrium constant K_c.



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$[\text{HI}] = \frac{2.4}{5} = 0.48 \text{ molL}^{-1}$$

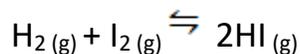
$$[\text{H}_2] = \frac{0.4}{5} = 0.08 \text{ molL}^{-1}$$

$$[\text{I}_2] = \frac{0.4}{5} = 0.08 \text{ molL}^{-1}$$

$$\therefore K_c = \frac{(0.48)^2}{(0.08)(0.08)}$$

$$K_c = 36$$

2. A mixture of $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ H}_2$ and $2.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ I}_2$ are placed into a container at 450°C . After equilibrium was reached the HI concentration was found to be $1.87 \times 10^{-3} \text{ mol dm}^{-3}$. Calculate the equilibrium constant.



At $t=0$ a b 0

Equilibrium: a-x b-x 2x

$$\therefore 2x = 1.87 \times 10^{-3}$$

$$x = 9.35 \times 10^{-4} \text{ mol dm}^{-3}$$

$$a = 1.0 \times 10^{-3}$$

$$a-x = 1.0 \times 10^{-3} - 9.35 \times 10^{-4}$$

$$= 6.5 \times 10^{-5} \text{ mol dm}^{-3}$$

$$b = 2.0 \times 10^{-3}$$

$$b - x = 2.0 \times 10^{-3} - 9.35 \times 10^{-4}$$

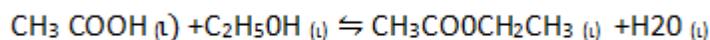
$$= 1.065 \times 10^{-3} \text{ mol dm}^{-3}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.605 \times 10^{-3})}$$

$$K_c = 50.51$$

3. a) It was found that if 1 mole of acetic acid and half a mole of ethanol react to equilibrium at certain temperature, 0.422 moles of ethyl acetate are produced. Show that the equilibrium constant for this reaction is about 4.



Start: -	1mol	0.5mol	0	0
Equilibrium:	1-0.422	0.5-0.422	0.422	x
	0.578	0.078	0.422	0.422
Equilibrium	$\frac{0.578}{V}$	$\frac{0.078}{V}$	$\frac{0.422}{V}$	$\frac{0.422}{V}$

Concentration

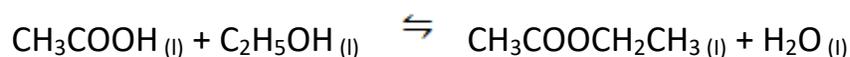
$$K_c = \frac{[\text{H}_2\text{O}] [\text{CH}_3\text{COOCH}_2\text{CH}_3]}{[\text{C}_2\text{H}_5\text{OH}] [\text{CH}_3\text{COOH}]}$$

$$= \frac{\left(\frac{0.422}{V}\right)\left(\frac{0.422}{V}\right)}{\left(\frac{0.578}{V}\right)\left(\frac{0.078}{V}\right)}$$

$$K_c = 3.95$$

$$K_c \approx 4 \text{ shown}$$

b) From the same reaction above, 3 moles of acetic acid and 5 moles of ethanol reacted. Find the amounts which will be present equilibrium.



$$t=0 \qquad \qquad \qquad 3 \qquad \qquad \qquad 5 \qquad \qquad \qquad 0 \qquad \qquad \qquad 0$$

$$t = t \qquad \qquad \qquad (3-x) \qquad \qquad \qquad (5-x) \qquad \qquad \qquad x \qquad \qquad \qquad x$$

Equilibrium

$$\text{Concentration} \qquad \qquad \frac{3-x}{V} \qquad \qquad \frac{5-x}{V} \qquad \qquad \frac{x}{V} \qquad \qquad \frac{x}{V}$$

$$K_c = \frac{[\text{H}_2\text{O}][\text{CH}_3\text{COOCH}_2\text{CH}_3]}{[\text{C}_2\text{H}_5\text{OH}][\text{CH}_3\text{COOH}]}$$

$$4 = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{3-x}{V}\right)\left(\frac{5-x}{V}\right)}$$

$$4 = \frac{x^2}{(3-x)(5-x)}$$

$$4 = \frac{x^2}{15-8x+x^2}$$

$$4x^2 = 60 - 32x + 4x^2$$

$$3x^2 - 32x + 60 = 0$$

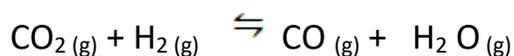
$$X = 8.24 \text{ or } x = 2.43$$

Logically; $x = 2.43$

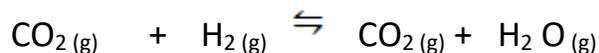
At equilibrium $\text{CH}_3\text{COOH} \rightarrow 3 - 2.43 = \underline{0.57 \text{ moles}}$

$\text{C}_2\text{H}_5\text{OH} \rightarrow 5 - 2.43 = \underline{2.57 \text{ moles}}$

4 .For the reaction;



The value of K_c at 552°C is 0.137. If 5moles of CO_2 , 5moles of H_2 , 1 mole of CO and 1 mole of H_2O are initially present, what is the actual concentration of CO_2 , H_2 , CO and H_2O at equilibrium?



At start; 5 1 1 1

At equilibrium 5-x 1-x 1x 1x

$$K_c = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]}$$

$$0.137 = \frac{[x][x]}{[5-x][5-x]}$$

$$0.137 = \frac{x^2}{25-10x+x^2}$$

$$3.425 - 1.37x + 0.137x^2 = x^2$$

$$3.425 - 1.37x + 0.137x^2 - x^2 = 0$$

$$3.425 - 1.37x - 0.863x^2 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

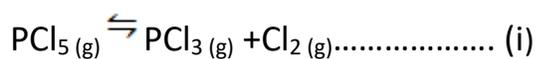
$$x = \frac{1.37 \pm \sqrt{(-1.37^2) - (4 \times 0.863 \times 3.24225)}}{2(0.863)}$$

$$x = \frac{1.37 \pm 3.7}{2 \times 0.863} = \underline{x = 1.349}$$

COMBINING EQUILIBRIUM REACTIONS

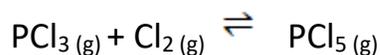
1. Reversing an equilibrium reaction

Consider the reaction



$$K_{c(i)} = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \dots \dots \dots \text{(i)}$$

Reversing the reaction;



$$K_{c(ii)} = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} \dots \dots \dots \text{(2)}$$

When reaction equation is reversed, the equilibrium constant is reciprocated i.e. from equation (1) and (2)

$$K_{c(ii)} = \frac{1}{K_{c(i)}}$$

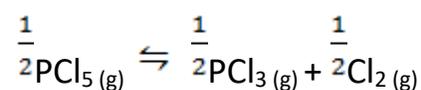
2. Multiplying an equilibrium reaction by a number

When the stoichiometric coefficient of a balanced equation is multiplied by the same factor, the equilibrium constant for the new equation is old equilibrium constant raised to the power of the multiplied factor.



$$K_{c(i)} = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

If the equation (i) is multiplied by $\frac{1}{2}$



$$K_{c(ii)} = \left(\frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \right)^{\frac{1}{2}}$$

$$K_{c(ii)} = (K_{c(i)})^{\frac{1}{2}} \quad \text{OR} \quad K_{c(ii)} = \sqrt{K_{c(i)}}$$

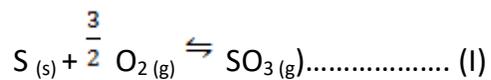
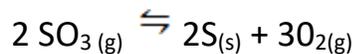
Note; if an equilibrium reaction is multiplied by $\frac{1}{n}$ then;

$$K_{c(ii)} = (K_{c(i)})^{\frac{1}{n}}$$

$$K_{c(ii)} = \sqrt[n]{K_{c(i)}}$$

Example: The K_c for the reaction below is 1.1×10^{65}





Equation (2) has been reversed and multiplied by 2

When reversed

$$K_{c(i)} = \frac{[\text{SO}_3]}{[\text{O}_2]^{\frac{3}{2}}} = 1.1 \times 10^{65}$$

$$K_{c(ii)} = \frac{1}{K_{c(i)}}$$

$$K_{c(ii)} = \frac{1}{1.1 \times 10^{65}}$$

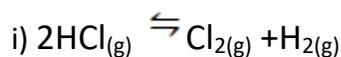
$$K_{c(ii)} = 9.09 \times 10^{-66}$$

When multiplied

$$K_{c(ii)} = (K_{c(i)})^2$$

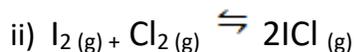
3. Adding the equilibrium.

The equilibrium constant for the reaction



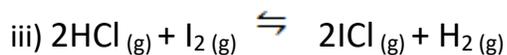
$$K_{c(i)} = 4.17 \times 10^{-34} \quad (\text{At } 25^\circ \text{C})$$

The equilibrium constant for reaction



$$K_{\text{c(ii)}} = 2.1 \times 10^5 \text{ (At } 25^\circ\text{C)}$$

Calculate the equilibrium constant for the reaction



$$K_{\text{c(iii)}} = ?$$

$$K_{\text{c(i)}} = \frac{[\text{Cl}_2][\text{H}_2]}{[\text{HCl}]^2}$$

$$K_{\text{c(ii)}} = \frac{[\text{ICl}]^2}{[\text{I}_2][\text{Cl}_2]}$$

$$K_{\text{c(iii)}} = \frac{[\text{ICl}]^2[\text{H}_2]}{[\text{HCl}]^2[\text{I}_2]}$$

When equation (i) + equation (ii) = equation (iii), Hence

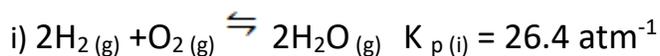
$$K_{\text{c(iii)}} = K_{\text{c(ii)}} \times K_{\text{c(i)}}$$

$$= (2.1 \times 10^5) \times (4.17 \times 10^{-34})$$

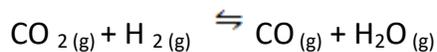
$$K_{\text{c(iii)}} = \underline{8.757 \times 10^{-29} \text{ (mol dm}^{-3}\text{)}^{1/2}}$$

Question 1:

The following are reactions which occurs at 3500K



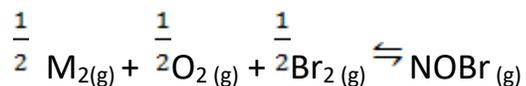
Calculate equilibrium constant for reaction



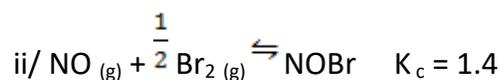
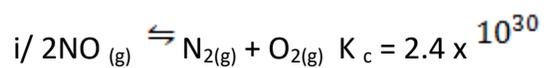
$$K_p(\text{iii}) = ?$$

Question 2

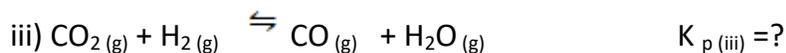
.Determine the Equilibrium constant for reaction;



Given that:-



Answers

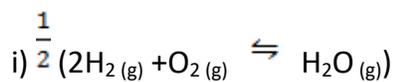


$$K_p(\text{i}) = \frac{(P_{\text{H}_2\text{O}})}{(P_{\text{H}_2})^2(P_{\text{O}_2})}$$

$$K_p(\text{ii}) = \frac{(P_{\text{CO}_2})^2}{(P_{\text{CO}})^2(P_{\text{O}_2})}$$

$$K_p(\text{iii}) = \frac{(P_{\text{CO}})(P_{\text{H}_2})}{(P_{\text{CO}_2})(P_{\text{H}_2})}$$

Reverse (ii), multiply (i) and (ii) by $\frac{1}{2}$

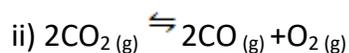


$$K_{p(i)} = \sqrt{26.4}$$



$$K_{p(i)} = 5.138 \text{ atm}^{-1}$$

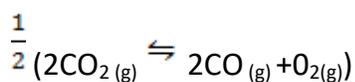
Reverse (ii)



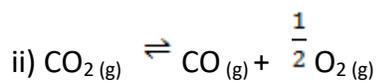
$$K_{p(ii)} = \frac{1}{0.376}$$

$$= \underline{2.6595 \text{ atm}^{-1}}$$

Now multiply by (ii) by $\frac{1}{2}$



$$K_{p(ii)} = \sqrt{2.6595}$$



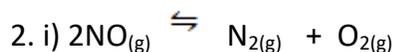
$$= 1.63079$$

Add equation (i) + (ii), then

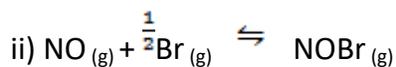
$$K_{p(iii)} = K_{p(i)} \times K_{p(ii)}$$

$$= 5.138 \times 1.63079$$

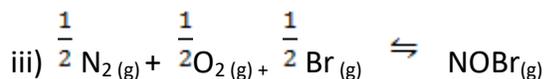
$$= \underline{8.379 \text{ atm}^{-1}}$$



$$K_{c(i)} = 2.4 \times 10^{30}$$



$$K_{c(ii)} = 14$$



$$K_{c(iii)} = ?$$

Reverse (i)



Now multiply (i) by $\frac{1}{2}$



Equation (i) + (ii) = (iii)

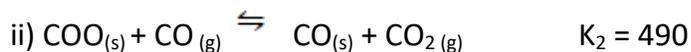
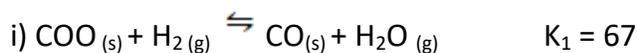
Therefore:

$$K_{c(iii)} = K_{c(i)} \times K_{c(ii)}$$

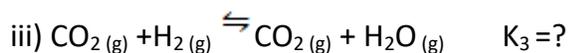
$$= 6.455 \times 10^{-16} \times 1.4$$

$$= \underline{9.0369 \times 10^{-16}(\text{mol dm}^{-3})^{1/2}}$$

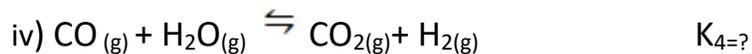
3. The equilibrium constants for the reactions which have been determined at 878K are as follows:-



Using these information, calculate K's (at the same temperature) for;



And commercially important water gas reaction



Reverse (ii)



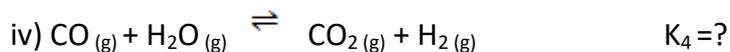
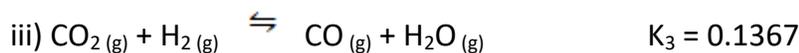
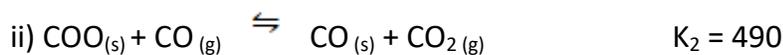
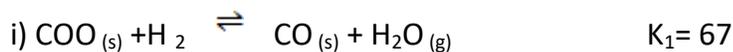
Equation (i) + (ii) = (iii)

$$\therefore K_3 = K_1 \times K_2$$

$$= 67 \times 2.0408 \times 10^{-3}$$

$$\underline{K_3 = 0.1367}$$

To find K_4



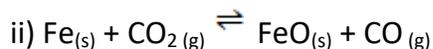
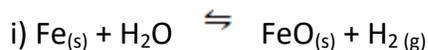
When equation (iii) is reversed, it is equal to equation (iv)

$$\therefore K_4 = \frac{1}{K_3}$$

$$= \frac{1}{0.1367}$$

$$\underline{= 7.315}$$

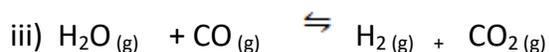
4. The heterogeneous equilibrium



Have been studied at 800 °c and 1000 °c. Also the rate $\left(\frac{P_{\text{CO}}}{P_{\text{CO}_2}} \right)$ is constant = 1.81 at 800 °c and 2.48 at 1000 °c.

i) Why are the ratios constant?

ii) Calculate equilibrium constant at two temperatures of the reaction



Answer:

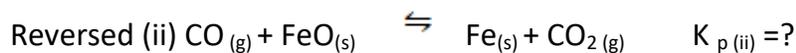
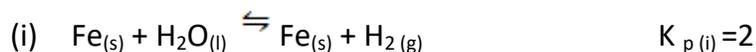
i) The ratios are constant because for any system in equilibrium at a given temperature, the ratio of products of concentration of products to the product of concentration of reactants raised to the point of their mole ratios is constant.

ii) At 800 °C

$$K_{p1} = 2$$

$$K_{p2} = 1.81$$

$$K_{p3} = ?$$



Equation (i) + (ii) = (iii)

$$K_{p1} \times K_{p2} = K_{p3}$$

$$K_{p3} = K_{p1} \times K_{p2}$$

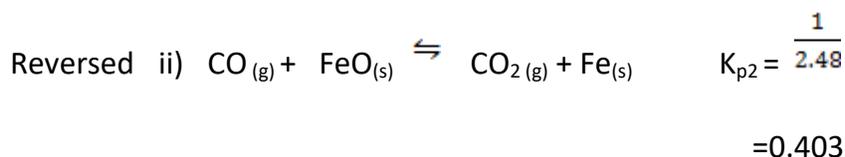
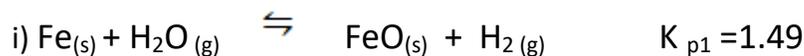
$$= 2 \times 0.55$$

$$\underline{K_{p3} = 1.1}$$

At 1000 °C

$$K_{p1} = 1.49$$

$$K_{p2} = 2.48$$



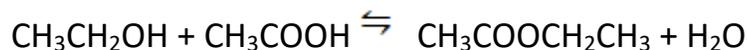
Equation (i) + (ii) = (iii)

$$\therefore K_{p3} = K_{p1} \times K_{p2}$$

$$= 1.49 \times 0.403$$

$$\underline{K_{p3} = 0.6}$$

1: When 1 mole of ethanoic acid is maintained at 25 °C with 1 mole of ethanol, 1/3 of ethanoic acid remain when equilibrium is attained. How much would have remained if 3/4 of 1 mole of ethanol had been used instead of 1 mole at the same temperature.



At start: 1mol 1mol 0 0

At time: 1-x 1-x x x

At equilibrium: $1 - \frac{2}{3}$ $1 - x = \frac{1}{3}$ $\frac{2}{3}$ $\frac{2}{3}$

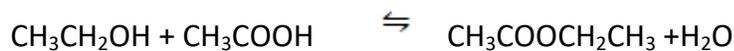
$$x = \frac{1}{3} \quad x = \frac{2}{3}$$

$$K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{OH}][\text{CH}_3\text{COOH}]}$$

$$= \frac{\begin{bmatrix} 2 \\ 3 \end{bmatrix} \begin{bmatrix} 2 \\ 3 \end{bmatrix}}{\begin{bmatrix} 1 \\ 3 \end{bmatrix} \begin{bmatrix} 1 \\ 3 \end{bmatrix}}$$

$$= \frac{\begin{bmatrix} 4 \\ 9 \end{bmatrix}}{\begin{bmatrix} 1 \\ 9 \end{bmatrix}}$$

$$\underline{K_c = 4}$$



At start;	1mol	1mol	0	0
At time	1-x	1-x	x	x
At equilibrium	$(1 \times \frac{3}{4}) - x$	1-x	x	x

$$K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{OH}][\text{CH}_3\text{COOH}]}$$

$$4 = \frac{[x][x]}{\left[\frac{3}{4} - x\right][1-x]} = \frac{[x^2]}{\left[\frac{3}{4} - \frac{7}{4}x + x^2\right]}$$

$$4 \left[\frac{3}{4} - \frac{7}{4}x + x^2 \right] = x^2$$

$$3 - 7x + 4x^2 = x^2$$

$$3 - 7x + 4x^2 - x^2 = 0$$

$$3x^2 + 3 - 7x = 0$$

$$3x^2 - 7x + 3 = 0$$

a b c

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(-7) \pm \sqrt{(-7)^2 - 4(3 \cdot 3)}}{2(3)}$$

$$= \frac{7 \pm \sqrt{49 - 36}}{6}$$

$$= \frac{7 + 3.6}{6}$$

$$x = \frac{7 + 3.6}{6} \quad \text{or} \quad x = \frac{7 - 3.6}{6}$$

$$= 1.76 \quad = 0.566$$

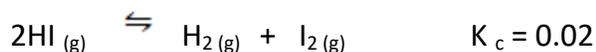
X cannot be 1.76

$$\therefore \underline{X = 0.566}$$

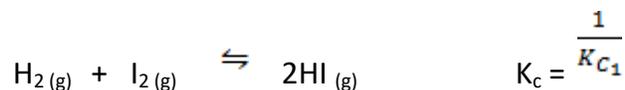
$$\frac{3}{4} - 0.566 = 0.184 \text{ moles or } \frac{23}{125} \text{ moles}$$

\therefore 0.184 moles of ethanol would have remained

2. The equilibrium constant (K_c) for the reaction; $2\text{HI}_{(g)} \rightleftharpoons \text{H}_{2(g)} + \text{I}_{2(g)}$ is 0.02 at 400°C . If 2 moles of H_2 and 1 mole of I_2 were mixed together in a 1.0dm^3 at 400°C , how many moles of HI , I_2 and H_2 would be present at equilibrium.



Reverse the equation above



At start 2 1 0

At time 2-x 1-x 2x $= \frac{1}{0.02} = 50$

At equilibrium $\frac{2-x}{1}$ $\frac{1-x}{1}$ $\frac{2x}{1}$

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$50 = \frac{[2x]^2}{[2-x][1-x]}$$

$$50 = \frac{4x^2}{2-3x+x^2}$$

$$50(2-3x+x^2) = 4x^2$$

$$100 - 150x + 50x^2 = 4x^2$$

$$100 - 150x + 50x^2 - 4x^2 = 0$$

$$100 - 150x + 46x^2 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{+150 \pm \sqrt{(150)^2 - 4(46 \times 100)}}{2 \times 46}$$

$$= \frac{150 \pm \sqrt{22500 - 18400}}{92}$$

$$x = \frac{150+164}{92} \quad \text{or} \quad x = \frac{150-164}{92}$$

$$x = 2.33$$

$$x = 0.934$$

x cannot be 2.33

$$\underline{x = 0.934}$$

At equilibrium:

Number of moles of H₂ = 2 - 0.934

$$= \underline{1.066 \text{ moles}}$$

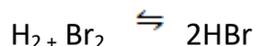
Number of moles of I₂ = 1 - 0.934

$$= \underline{0.066 \text{ moles}}$$

Number of moles of HI = 2 x 0.934

$$= \underline{1.868 \text{ moles}}$$

3. The equilibrium constant for the reaction; H_{2(g)} + Br_{2(g)} ⇌ 2HBr_(g) at 1024K is 1.6 x 10⁵. Find the equilibrium pressure of all gases if 10 atm of HBr is introduced into a second container at 1024K.



PREDICTION OF DIRECTION AND EXTENT OF CHEMICAL EQUILIBRIUM

At each point in the progress of a reaction, it is possible to formulate the ratio of concentration having the same form as the equilibrium

constant expression. This generalized ratio is called reaction quotient (Q).

For the reaction; $aA + bB \rightleftharpoons cC + dD$ then:-

$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$Q_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

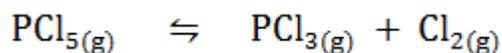
Q_c differs from K_c in that the concentration in the expression is not necessarily the equilibrium concentration.

When the values of K_c and Q_c are compared, one can predict the direction of the chemical reaction.

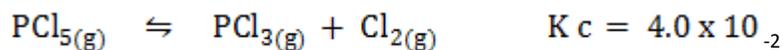
- If $Q_c < K_c$ the system is not at equilibrium, the reactants must further be converted to products to achieve equilibrium therefore net reaction proceeds from left to right.
- If $Q_c = K_c$ the system is at equilibrium
- If $Q_c > K_c$ the system is not an equilibrium, the products must be converted to reactants to achieve equilibrium therefore a net reaction proceeds from right to left.

Example:

1. Consider the reaction



At 250°C, $K_c = 4.0 \times 10^{-2}$. If the concentration of Cl_2 and PCl_3 are both 0.30 M while that of PCl_5 is 3.0M, is the system at equilibrium? If not, in which direction does the reaction proceed?



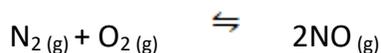
$$Q_c = \frac{[PCl_3] [Cl_2]}{[PCl_5]}$$

$$= \frac{[0.3] [0.3]}{[3]}$$

$$Q_c = 0.03 \quad Q_c \neq K_c, \quad Q_c < K_c$$

The system is not at equilibrium and the reaction proceeds from left to right

2. At 200k, the K_p for the formation of NO is 4×10^{-4}



If at 200k the partial pressure of N_2 is 0.5 atm and that of O_2 is 0.25 atm, that of NO is 4.5×10^{-3} atm, decide whether the system is at equilibrium, if not in which direction does the reaction proceed.

$$K_p = 4.0 \times 10^{-4}$$

$$Q_p = \frac{(P_{\text{NO}})^2}{(P_{\text{O}_2})(P_{\text{N}_2})}$$

$$= \frac{(4.5 \times 10^{-3})^2}{(0.25)(0.5)}$$

$$Q_p = 1.4112 \times 10^{-4} \quad K_p \neq Q_p, \quad K_p > Q_p$$

The system is not at equilibrium, therefore the reaction proceeds from left to right

EQUILIBRIUM CONSTANT WITH DEGREE OF DISSOCIATION (α)

-It gives to what extent the reactants are converted to products by dissociation.

-This has to be treated similar to moles.

Example1. 0.01 moles of PCl_5 was placed in 1L vessel at 210K. It was found to be 52.6% dissociated into PCl_3 and Cl_2 . Calculate the K_c at that temperature.



At start: 0.01 0 0

At equilibrium: 0.01-(5.26 x 10⁻³) 5.26 x 10⁻³ 5.26x10⁻³

$$= \frac{52.6}{100} \times 0.01$$

$$= \underline{5.26 \times 10^{-3}}$$

PCl₅ = 4.74 x 10⁻³ moles

PCl₃ = 5.26 x 10⁻³ moles

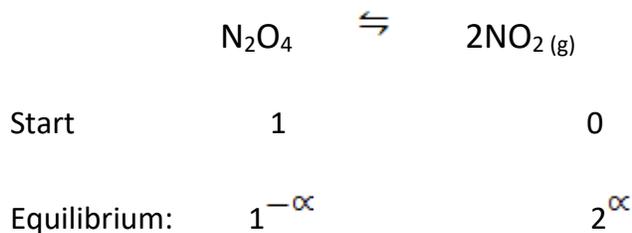
Cl₂ = 5.26 x 10⁻³ moles

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

$$= \frac{[5.26 \times 10^{-3}][5.26 \times 10^{-3}]}{[4.74 \times 10^{-3}]}$$

K_c = 5.837 x 10⁻³ moles

2. At 1 atm and 85°C, N₂O₄ is 50% dissociated, Calculate the equilibrium constant in terms of pressure and calculate the degree of dissociation of the gas at 10⁰ c and 55⁰c.



But α = 50% = 0.5

$$1 - 0.5$$

$$2(0.5)$$

$$0.5$$

$$1$$

$$n_T = 0.5 + 1$$

$$= 1.5 \text{ moles}$$

$$P_{N_2O_4} = \frac{0.5}{1.5} \times 1$$

$$P_{NO_2} = \frac{1}{1.5} \times 1$$

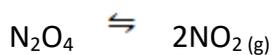
$$= 0.33 \text{ moles}$$

$$= 0.66 \text{ moles}$$

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})}$$

$$= \frac{(0.66)^2}{(0.33)}$$

$$\underline{K_p = 1.32}$$



Start: 1 0

Equilibrium: $1 - \alpha$ 2α

$$n_T = (1 - \alpha) + 2\alpha$$

$$= 1 + \alpha$$

$$P_T = 10 \text{ atm}$$

$$P_{N_2O_4} = \frac{1 - \alpha}{1 + \alpha} \times 10$$

$$P_{NO_2} = \frac{2\alpha}{1 + \alpha} \times 10$$

$$K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})}$$

$$= \frac{\left(\left(\frac{2\alpha}{1+\alpha}\right) \times 10\right)^2}{\left(\left(\frac{1-\alpha}{1+\alpha}\right) \times 10\right)}$$

$$= \frac{40\alpha^2}{(1+\alpha)} \times 100 \times \frac{1+\alpha}{1-\alpha} \times \frac{1}{10}$$

$$= \frac{40\alpha^2}{(1+\alpha)(1-\alpha)}$$

$$1.32 = \frac{40\alpha^2}{1-\alpha^2}$$

$$1.32 - 1.32\alpha^2 = 40\alpha^2$$

$$1.32 = 40\alpha^2 + 1.32\alpha^2$$

$$1.32 = 41.32\alpha^2$$

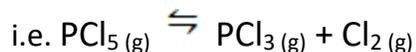
$$\alpha^2 = 0.0319$$

$$\alpha = 0.1787$$

∴ Degree of dissociation = 17.87%

DEGREE OF DISSOCIATION BY DENSITY MEASUREMENT

This method is used for the determination of degree of dissociation of gases in which 1 molecule produces 2 or more molecules.



Thus at constant temperature and pressure, the volume increases. The density at constant pressure decreases.

The degree of dissociation can be calculated from the difference in density between the undissociated gas and that of partially dissociated gas at equilibrium.

If we start with 1 mole of the gas (PCl_5) and the degree of dissociation (α), Then



Moles at equilibrium: $1 - \alpha$ α α

Total moles: $1 - \alpha + \alpha + \alpha$

$$= 1 + \alpha$$

Note:

The density of an ideal gas at constant temperature and pressure is inversely proportional to the number of moles for a given weight.

Hence the ratio of density

$$\frac{\rho_1}{\rho_2} = \frac{n_2}{n_1}$$

$$\frac{\rho_1}{\rho_2} = \frac{1 + \alpha}{1}$$

$$\alpha = \frac{\rho_1 - \rho_2}{\rho_2}$$

When ρ_2 = Density of gas mixture of equilibrium

ρ_1 = Density of gas before dissociation

α = Degree of dissociation

Examples1. When PCl_5 is heated, it gasifies and dissociates into PCl_3 and Cl_2 . The density of the gas mixture at 200°C is 70.2 Find the degree of dissociation of PCl_5 at 200°C

Solution

Observed density, $\rho_2 = 70.2$

$$\rho_1 = ?$$

$$\begin{aligned} \text{V.D} &= \frac{\text{Molar mass}}{2} \\ &= \frac{31 + (35.5 \times 5)}{2} \\ &= 104.25 \end{aligned}$$

$$\alpha = \frac{\rho_1 - \rho_2}{\rho_2}$$

$$= \frac{104.25 - 70.2}{70.2}$$

$$\alpha = 0.485$$

$$= \underline{48.5\%}$$

2. At 90°C , the V.D of N_2O_4 is 24.8. Calculate the % dissociation into NO_2 molecules at this temperature.



Density at equilibrium, $\rho_2 = 24.8$

$$\rho_1 = V.D = \frac{\text{Molar mass}}{2} = \frac{(14 \times 2) + (16 \times 4)}{2} = 46$$

$$\alpha = ?$$

$$\alpha = \frac{\rho_1 - \rho_2}{\rho_2}$$

$$= \frac{46 - 24.8}{24.8}$$

$$\alpha = 0.8548$$

$$= \underline{85.48\%}$$

DETERMINATION OF DEGREE OF DISSOCIATION BY MOLECULAR MASS

Molecular masses are proportional at constant temperature and pressure to the density of their gases; therefore we can substitute the molecular masses for the density in the degree of dissociation.

$$\alpha = \frac{\rho_1 - \rho_2}{\rho_2}$$

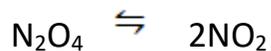
$$\alpha = \frac{M_1 - M_2}{M_2}$$

Where:-

M_1 = Molecular mass of undissociated gas

M_2 = Average Molecular mass of gases at equilibrium

Example1: 1.588g of N_2O_4 gives a total pressure of 1atm when partially dissociated at equilibrium in a 500cm^3 glass vessel at 25°C . What is the degree of dissociation at this temperature?



$$M_1 = (14 \times 2) + (16 \times 4)$$

$$= 92\text{gmol}^{-1}$$

$$M_2 = ?$$

From $PV = nRT$, where $n = \frac{m}{M}$

$$M_2 = \frac{RTm}{PV}$$

$$= \frac{0.0821 \times 298 \times 1.588}{1 \times 0.5}$$

$$= \underline{77.7\text{gmol}^{-1}}$$

$$\alpha = \frac{M_1 - M_2}{M_2}$$

$$= \frac{92 - 77.7}{77.7}$$

$$= 0.184$$

$$\alpha = \underline{18.4\%}$$

FACTORS AFFECTING EQUILIBRIUM REACTION

These factors are as follows:-

i) Temperature

ii) Concentration

iii) Pressure

- The first three affects both rates and position of chemical equilibrium (i, ii and iii)
- The other three affects the rate of chemical equilibrium

1) Temperature

a) Increasing the temperature, increases the rate of reaction because usually at high temperature the collision factor increases also the number of molecules having necessary activation energy is large.

b) Effect on the position of equilibrium is explained by using Le-Chateliers principle which states that “when a system at equilibrium is subjected to a change, processes occur which tend to counteract the change” (If a system in equilibrium is disturbed (change in temperature and pressure) the system adjusts itself so as to oppose the disturbance).

Consider the reaction



Reactants \rightleftharpoons Products

If temperature is increased in the system, the equilibrium moves in a direction where there is a absorption of heat and if the temperature is decreased in the system, the equilibrium moves in a direction where there is release of heat.

Effect of temperature, on the position of equilibrium can be explored by **Vant Hoff's law of mobile chemical equilibrium** which states that

“For any system in equilibrium high temperature favours endothermic reactions and low temperature favours exothermic reactions.

The way in which equilibrium constant changes with temperature is found both theoretically and experimentally governed by the following relationship;

$$\int \frac{d(\ln K)}{dT} = \int \frac{\Delta H_m}{RT^2}$$

ΔH_m = change in molar heat

K = Equilibrium constant

On intergrating the equation above;

$$\ln K = \frac{-\Delta H_m}{RT} + c$$

Where c = constant

If K_1 and K_2 are equilibrium constants corresponding to T_1 and T_2 , the constant term can be eliminated from the equation above so as to give Vant Hoff's equation i.e.

$$\ln K_1 = \frac{-\Delta H_m}{RT_1} + C \dots\dots\dots (1)$$

$$\ln K_2 = \frac{-\Delta H_m}{RT_2} + C \dots\dots\dots (2)$$

Subtracting equation (1) from (2) i.e.

$$\ln K_2 - \ln K_1 = \left(\frac{-\Delta H_m}{RT_2} + C \right) - \left(\frac{-\Delta H_m}{RT_1} + C \right)$$

$$= \ln \left(\frac{K_2}{K_1} \right) = \frac{\Delta H_m}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \dots\dots\dots 1$$

But 1 ln = 2.303log

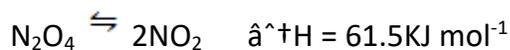
$$\log \left(\frac{K_2}{K_1} \right) = \frac{\Delta H_m}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \dots\dots\dots 2$$

$$\text{But } \frac{1}{T_1} - \frac{1}{T_2} = \frac{T_2 - T_1}{T_1 T_2}$$

$$\therefore \log \left(\frac{K_2}{K_1} \right) = \frac{\Delta H_m}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \dots\dots\dots 3$$

Where 1 = 2 = 3

Example1: For the reaction;



$$K_p = 0.113 \text{ at } 298\text{K}$$

- i) What is the value of K_p at 0°C ?
- ii) At what temperature will $K_p = 1$?

Answers:

i) From
$$\log \left(\frac{k_2}{k_1} \right) = \frac{\Delta H_m}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$K_{p2} = 0.113$$

$$K_{P1} = ?$$

$$T_1 = 273\text{K}$$

$$T_2 = 298\text{K}$$

$$\hat{\Delta}H_m = 61.5\text{KJmol}^{-1}$$

$$R = 8.314$$

$$\log\left(\frac{0.113}{K_{P1}}\right) = \frac{61500}{(2.303 \times 8.314)} \left(\frac{298-273}{298 \times 273}\right)$$

$$\log\left(\frac{0.113}{K_{P1}}\right) = 3211.9676 (3.0729896 \times 10^{-4})$$

$$\log\left(\frac{0.113}{K_{P1}}\right) = 0.987$$

To remove 'log' make $10^{0.987}$

$$\frac{0.113}{K_{P1}} = 10^{0.987}$$

$$\frac{0.113}{K_{P1}} = 9.7051$$

$$K_{P1} = 0.0116$$

ii) From $\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H_m}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$

$$K_{P2} = 0.113 \quad T_1 = ?$$

$$K_{P1} = 1 \quad T_2 = 298\text{K}$$

$$\hat{\Delta}H_m = 61.5 \text{ kJ mol}^{-1}$$

$$R = 8.314$$

$$\log\left(\frac{0.113}{1}\right) = \frac{61500}{2.303 \times 8.314} \left(\frac{298 - T_1}{298T_1}\right)$$

$$-0.9469 = 3211.9676 \left(\frac{298 - T_1}{298T_1}\right)$$

$$-2.948 \times 10^{-4} = \frac{298 - T_1}{298T_1}$$

$$-0.0878T_1 = 298 - T_1$$

$$-0.0878T_1 + T_1 = 298$$

$$0.912T_1 = 298$$

$$T_1 = 326.7 \text{ k}$$

VARIATION OF EQUILIBRIUM CONSTANT WITH TEMPERATURE

According to Vant Hoff's law of chemical equilibrium

i) Exothermic reaction

-Increasing to temperature decreases the K_c value as the equilibrium shifts to the left hand side to decrease the concentration of products and increase the concentration of reactants.

-Decreasing the temperature increase the K_c value

ii) Endothermic reaction

-Increasing the temperature increases the K_c value

-Decrease the temperature decreases the K_c value

2) Concentration

a) Effects on rate of reaction

-Increase in concentration of reactants in the same amount of space/volume increases the number of molecules thus increases the chances of collision between the molecules and hence this increases the rate of reaction.

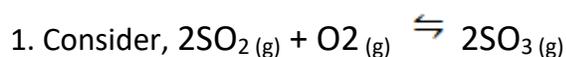
-Decreases in concentration result to decrease in rate of reaction as it decreases the number of molecules per unit volume, hence less collision.

b) Effect on the position of equilibrium

-This depends on either the concentration of products or reactants have been increased or decreased

-It also depends on Le-Chateliers principle

Example



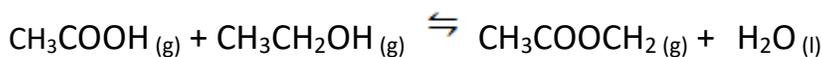
State what happens when:

- i) $[\text{SO}_2]$ is increased at the same temperature
- ii) $[\text{O}_2]$ is increased at same temperature
- iii) $[\text{SO}_3]$ is increased at same temperature

According to Le-Chateliers principle the system will adjust itself so as to cancel out the effect by shifting the equilibrium to the right side i.e.

increase the number of products hence decreasing the amount of SO_2

2. Using;



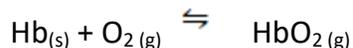
What happens when;

- i) H₂O is added
- ii) CH₃CH₂OH is added
- iii) NaOH is added
- iv) Anhydrous copper (II) sulphate is added
- v) CH₃COOCH₂ is added

Answers:

- i) H₂O will react with CH₃COOH and concentration of CH₃COOH will decrease hence forward reaction, equilibrium will lie on the products side.
- ii) Forward reaction since it will get on converted to products
- iv) Reverse reaction since H₂O will react with CuSO₄ to form CuSO₄.5H₂O

3. The following reaction occurs in human body

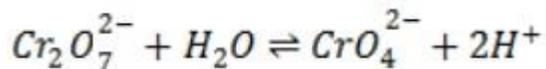


- i) What happens in the tissues?
- ii) What happens in the lung?

Answers:

- i) In the tissue the amount of O₂ is less and hence according to Le-Chateliers principle the system will adjust itself so as to increase the amount of O₂ by favouring the decomposition of HbO₂ (backward reaction). Hence the equilibrium shifts to left hand side.
- ii) In the lung, the amount of O₂ is a lot more and hence according to Le-Chateliers principle the system will adjust itself so as to decrease the amount of O₂ by favouring the forward reaction hence, the equilibrium shifts to the right hand side.

4. Consider the following equilibrium



Orange yellow

What would you expect to see it:

- i) Dilute NaOH is added to the equilibrium mixture
- ii) Dilute HCl is added to the equilibrium mixture

Answers:

i) When Dilute NaOH is added to the mixture, it will react with H^+ to form H_2O and Na^+ . This will decrease the concentration of H^+ ions

hence equilibrium will shift to left hand side. The colour will change yellow to orange.

ii) Dilute HCl dissociated to form H^+ and Cl^- therefore when added to the mixture, the concentration of H^+ ions increases. According to

Le Chateliers principle the equilibrium will adjust itself in such a way that the concentration of H^+ ions decreases hence backward

reaction is favoured

3) Pressure

a) Effect on the rate of reaction

Increase in pressure, increases the rate of reaction. This is because increases in pressure decreases the concentration per unit volume

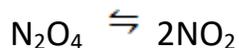
hence increases effective collision thus increase the rate of reaction, vice versa is also true.

b) Effect on position of equilibrium

Effect if number of moles of reactants and products are differ

Homogeneous gaseous equilibrium

Consider the reaction



What will be the effect of equilibrium, when;

i) Pressure is increased?

ii) Pressure decreased?

Answers:

i) When the pressure is increased according to Le Chateliers principles the equilibrium will adjust itself in such a way that the backward reaction is favoured

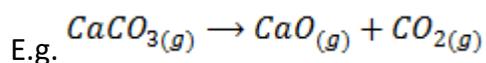
ii) According to Le Chateliers principle when pressure is decreased the equilibrium will adjust itself in such a way that the forward reaction is favoured

N.B:

Pressure has no effect on position of equilibrium if the number of moles in reactants side is equal to number of moles in products side.

Heterogeneous equilibrium

Position of equilibrium is affected by changing the partial pressure of the gases only



If partial pressure of CO_2 is decreased, the equilibrium shifts to the right hand side to increase the partial pressure of CO_2 . Vice versa is true.

4) Catalyst

a) **Low temperature**

The temperature should be kept as low as possible but at very low temperature, the rate of reaction becomes slow. It has been found that the yield of NH_3 is maximum at about 500°C which is the optimum temperature of the reaction.

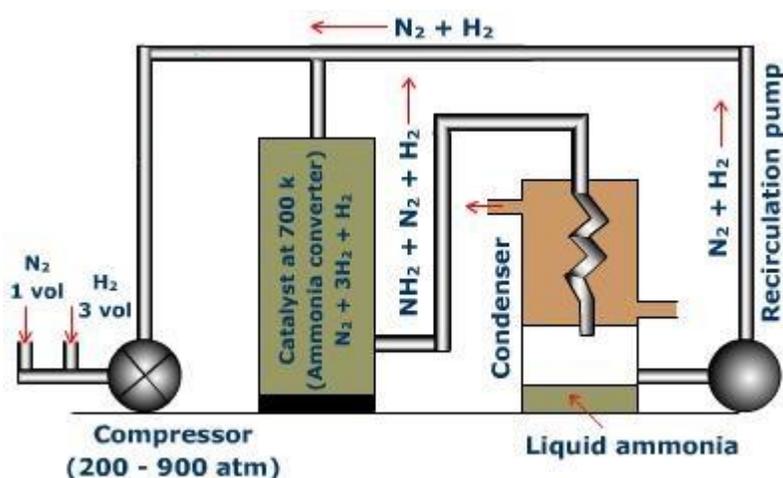
b) **High pressure**

High pressure favours reaction which is accompanied by a decrease in volume. In actual practice, a pressure of 200-900atm is employed in this process.

c) **Catalyst**

To increase the speed of the reaction, a catalyst should be finely divided iron containing molybdenum or alumina is used as a catalyst. Molybdenum or alumina (Al_2O_3) acts as a promoter and increases the efficiency of the catalyst. A mixture of iron oxide and potassium aluminate has been found to work more effectively. A catalyst iron oxide containing Al_2O_5 and K_2O is also used in the process.

A diagram to show the manufacture of ammonia by Born Harber process



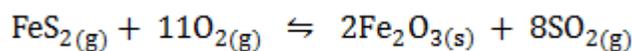
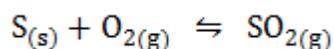
MANUFACTURE OF SULPHURIC ACID BY CONTACT PROCESS

In contact process sulphur dioxide is oxidized by air in the presence of catalyst Vanadium pentaoxide. Sulphur trioxide produced is absorbed in concentration H_2SO_4 to produce oleum ($H_2S_2O_7$). Oleum is then reacted with calculated amount of H_2O to form H_2SO_4 of the desired concentration.

The chemistry involved in the contact process is described as follows:

i) **Production of SO_2**

Sulphur dioxide (SO_2) is obtained by burning sulphur or iron pyrites



ii) **Catalytic oxidation of SO_2 to SO_3**

SO_2 is oxidized by air in the presence of a catalyst to give SO_3



The reaction is exothermic and proceeds with a decrease in volume. Therefore according to Le Chateliers principle, the favourable conditions for the maximum yield of SO_3 are:-

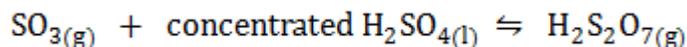
- Air or oxygen required for oxidation of SO_2 must be in excess
- The temperature must be low, a temperature between $350 - 450^\circ C$ gives maximum yield of the products.
- The pressure must be high, 2atm.
- Platinised asbestos was used as a catalyst previously, but now days it is replaced by much cheaper Vanadium pentaoxide (V_2O_5).

A V_2O_5 remains unaffected the impurities while platinised arbestos is poised by the impurities in the gases.

e) The gases used (SO_2 and O_2) must be free of impurities, viz, dust particles, arsenious oxide e.t.c, to prevent catalyst poisoning

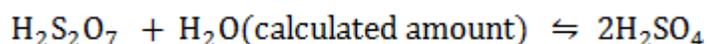
iii) Conversion of SO_3 to Oleum

SO_3 is dissolved in concentrated H_2SO_4 to produce oleum or fuming H_2SO_4 .



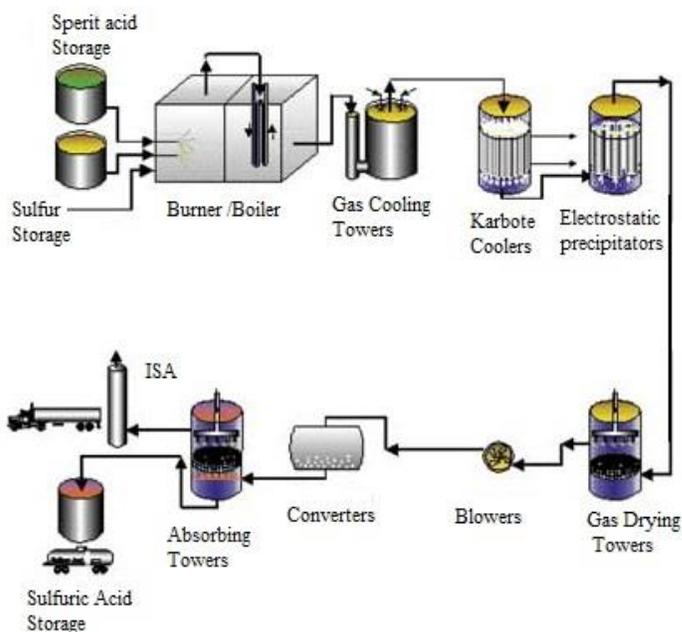
iv) Conversion of oleum to sulphuric acid

Oleum is diluted with a calculated amount of H_2O to get H_2SO_4 of desired concentration.



The great advantage of the contact process is that it produces a pure acid of any desired concentration and especially the fuming acid which is of great value in chemical industry.

THE CONTACT PROCESS



INORGANIC CHEMISTRY 1.2-TRANSITION ELEMENT

Is an element which has half filled 'd' orbital. Transition Element are element which have at least one unpaired electron in the outer most sub energy level 'd'. The transition element is an elements which have incompletely field d – orbital. The transition element is known as transition because have intermediate properties which differ from. 'S' block element and 'P' block element. Transition elements are d – block element, but not all d-block elements are transition elements. Most of transition element are metal element which called transition metal.

There are three series of transition metal:-

- (i) Transition Metal of the first series.
- (ii) Transition metal of the second series or LANTHANIDE METALS.
- (iii) Transition Metal of third series or are sometime known as ACTINAMIDE METAL. (The strongest metal)

II. TRANSITION METALS OF THE FIRST SERIES

Are these which have half filled 3d – orbital are those which have at least ONE UNPAIRED ELECTRON IN SUB ENERGY LEVEL 3D.

Transition metals of the first series are given below

ATOMIC NUMBER	ELEMENT	SYMBOL	ELECTRONIC	STRUCTURE
21	SCANDIUM	Sc	[Ar]4S ² 3d ¹	
22	TITANIUM	Ti	[Ar]4S ² 3d ²	
23	VANADIUM	V	[Ar] 4S ² 3d ³	
24	CHROMIUM	Cr	[Ar] 4S ¹ 3d ⁵	
25	MANGANESE	Mn	[Ar] 4S ² 3d ⁵	
26	IRON	Fe	[Ar] 4S ² 3d ⁶	
27	COBALT	CO	[Ar] 4S ² 3d ⁷	
28	NICKEL	Ni	[Ar] 4S ² 3d ⁸	
29	COPPER	Cu	[Ar] 4S ¹ 3d ¹⁰	
30	ZINC	Zn	[Ar] 4S ² 3d ¹⁰	
To remember use				

Science	Teacher	Are very	Craver mostly	From
Congo	Nigeria	and	Coastal	Zanzibar

GENERAL PROPERTIES OF TRANSITION METALS

Transition metals have the following general properties.

- (i) Form colour (colour formation)
- (ii) Are paramagnetic substance
- (iii) Have variable oxidation states
- (iv) Form complex compound
- (v) Have catalytic action.

A. COLOUR FORMATION BY TRANSITION METALS

Transition metal appear coloured at room temperature of form colour when occur in ionic or combined state. But non – transition metal does not form colour at room temperature. The non – transition metal appear coloured when heated during flame test. The energy of flame excite electron which jump from low energy level. This cause atom to be unstable. In order to maintain the stability the effective nuclear force returns back the electron to the ground state. When the electron drop back emit the radiant energy which have a wavelength detected by a human eye. This radiant have definite colour.

But Magnesium does not produce colour during flame test instead remain colourless because energy of the flame is not enough to excite electron of Magnesium.

Transition metals colour formation can be explained by two theories.

- (i) 4s – 3d electron transition theory
- (ii) d- Electron transition theory (crystal field theory)

(i) 4s - 3d ELECTRON TRANSITION THEORY

According to this theory colour formation is a result of movement of electron between sub energy level 4s and 3d. The energy difference between sub energy level 3d and 4s (ΔE) is so small that normal radiant energy absorbed cause electron to move from 4s level to 3d level. Radiant energy absorbed from the sun makes 4s electrons to jump to 3d orbitals and the atoms becomes UNSTABLE. To maintain stability of the atoms excited electrons fall back to 4s orbital. During this process when electrons (excited) fall to their ground state heat energy is emitted and came out in form of radiation those wave have wavelength which are within the range that can be detected by human eyes with specified definite colour.

(ii) d – d ELECTRON TRANSITION THEORY OR CRYSTAL FIELD THEORY

Colour formation by transition metal can be explained by crystal field theory. This theory suggested that for transition metals to express colour there are two conditions which are necessary and must be fulfilled.

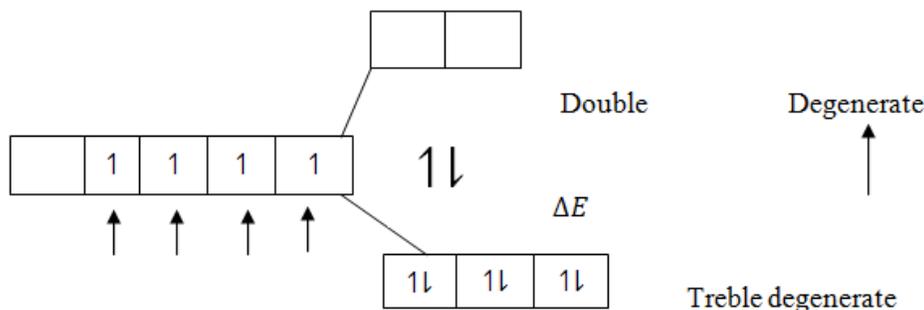
a. There must be at least one unpaired electrons in 3d – orbital

b. Presence of ligands.

PROCESS OF COLOUR FORMATION

In isolated Transition atoms all five 3d – orbitals are degenerate and have equal energy. In presence of ligands the d- orbitals split into two degenerates i.e.

“Double degenerate and Treble degenerate” and which have different energy. Ligands exert electric field (Repulsion force) to unpaired 3d electrons. Repulsion cause orbital to split down into two degenerates. Double and Treble degenerates.

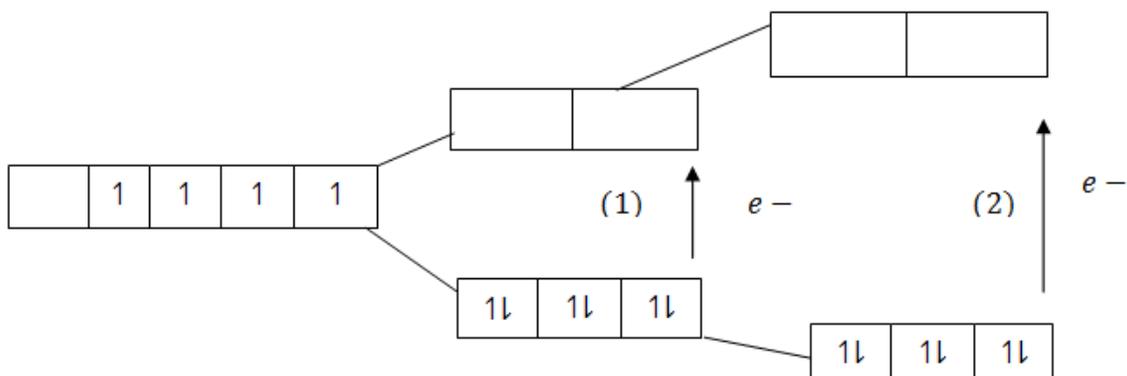


The energy of separation (ΔE) between the two degenerates is small. Such that the normal Radiant energy absorbed from the sun is enough to make electrons jump from treble degenerates orbital to double degenerates orbital and atoms excited, electrons fall back to their ground states, the process which is accompanied by emission of heat energy absorbed from the sun. The energy emitted by the falling electrons comes out in the form of radiation whose wave have specific definite colour.

NOTE:

Intensive of the colour whether to be faint or deep it depends on electric field and splitting power of the ligand. If the ligands exert weak electric field (Weak Repulsive forces) the d – orbital will split and separates to a small extent, The energy of separation ΔE becomes very small. If the energy of separation ΔE between the two degenerates is small. Low energy will be required to excite electrons and make them jump to double degenerate orbital. Similarly, low amount of heat energy will be emitted in the form of radiations when the excited electrons fall to their ground state. Intensity of the waves in the radiations will be low and hence the resulting colour appears to be light or faint. Ligands which exert weak electric field and cause small separation of the d orbital resulting to formation of light or faint colour are said to be “Ligands of high spin” .Ligands of high spin include Oxygen containing Halogens E.g. OH^- , Cl^- , Br^- etc. On the other hand if ligands exert strong electric field (strong repulsive force) the d – orbitals split down and will separate to a large extent. The energy of separation (ΔE) becomes large. In this case large heat energy will be required to excite electrons. Equally well large energy is emitted in the form of radiation, when the electrons fall back to their ground state. Intensity of the waves in the coming radiation will be high and hence the resulting colour appear deep. Ligands which exert strong electric field and cause large

separation of the d- orbitals resulting to the formation of deep colours are said to be “ligands of low spin”
Ligands of low spin include Nitrogen containing compound e.g NH_3 , CN^- , CN etc.



1. Ligands of high spin

- Extent weak electric field
- d- orbitals split to small extent
- ΔE energy of separation is small
- The colour is faint or light.

2. Ligands of low spin

- Extent strong electric field
- D – orbitals separates to a large extent
- ΔE is large (energy of separation)
- The colour is deep.

NOTE:

It has been noted that colour formation by transition metals can be explained by two Theories.

(a) 4s – 3d electron transition theory

(b) Crystal field theory.

Now which one is the TRUE THEORY between 4s – 3d electron transition theory and crystal field theory.

The theory of crystal field is the True Theory and accounts better for colour formation by Transition metals

The following fact justify the statement

(i) Transition metals express their colours whenever they are in ionic form. In ionic form 4s - orbital is always empty. Since during ionization of the transition metallic atoms 4s electrons are given before 3d – electrons. This means that movement of electrons between 4s and 3d orbitals is not possible.

(ii) 4s – 3d electron transition theory cannot account for change in colour intensity. But crystal field theory accounts for change in intensity depending on the type of ligands weather are of high or low spin.

(iii) 4s – 3d electron transition theory cannot explain why Sc^{3+} , Zn^{2+} and Cu^+ are colourless in aqueous solution but crystal field theory can account for this observation.

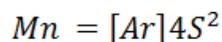
(iv) Observation has shown that Sc^+ and Sc^{2+} are coloured in aqueous solution because the two ions have one unpaired electron in sub energy level 3d. $Sc = (Ar) 4S^2 3d^1$ has no electron in 3d orbitals. All the five orbitals in Sc^{3+} are empty. I.e. $Sc^{3+} = [Ar] 4S^0 - 3d^0$.

When ligands come with their lone pairs there will be no repulsion since d – orbital have no electrons. So no splitting of the d – orbital and no d – electron transition in Sc^{3+} Cu^+ and Zn^{2+} are colourless because all the five 3d orbitals on these ions are full occupied by two electrons ie [sub energy level 3d in Cu^+ and Zn^{2+} have Ten electrons]. No unpaired electron in 3d – orbital of Zn^{2+} and Cu^+ .

NOTE:

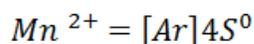
Despite the fact crystal field theory explains better colour formation by transition metals than 4s -3d electron transition theory yet it has some weakness. Crystal field theory fails to account for colour formation in Manganese (ii) ion (Mn^{2+}). Manganese (iii) ion has unpaired electrons in its 3d – orbitals but in aqueous solution it is colourless

3d



1	1	1	1	1
---	---	---	---	---

3d



1	1	1	1	1
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Manganese in the permanganate ion $[MnO_4^-]$ has no unpaired electrons in the 3d - orbitals. Manganese in the permanganate ion has an oxidation state of +7. Oxidation state of +7 is attained after losing all the 4s and 3d electrons. However permanganate, ions in aqueous solution are coloured, make the aqueous solution PURPLE.

[B] COMPLEX COMPOUND

Is a compound which contain central atom and several ligand. The complex compound consists of central atom attached to the several atoms or group of atoms .

Central Atom

Is a metallic ion which accepts or accommodate pair of electrons during formation of complex compound. Most of central atoms are transition element.

The characteristics features which result into a transition metal or another metal to form a complex compound include the following:-

- They have vacant orbit or empty orbital which accommodate pair of electrons.
- They have high nuclear charge which exerts nuclear attractive force.
- They have small atomic size which exerts a strong nuclear attractive force.

These central atom or metallic ions have constant total number of ligand accommodate during complex compound formation. This is according to the number of vacant orbitals and atomic size of metallic

ions. If the central atoms accommodate ligand above those required result the compound to be unstable. The following include the central atom together with their total number of ligand.

Ag^+	-	2
Hg^{+2}	-	4
Al^{+3}	-	4
Zn^{+3}	-	4
Pb^{+2}	-	4
Cu^{+2}	-	4
Cr^{+3}	-	6
Mn^{+2}	-	5/6
$\text{Fe}^{+2/+3}$	-	4/6
Ni^{+2}	-	4/6
CO^{+2}	-	4/5
Pb^{+2}	-	4/6

LIGAND

Is a non metallic ion or molecules which donate pair of electrons to the central metal atom/ion during complex compound / ion formation. The non metallic ions or molecules have pair of electrons in the valency orbital. These pair of electrons called lone pair.

There are two kind of ligand :

(i) Neutral ligand is a ligand which is electrically neutral. These are not charged ligand Such ligands are generally the molecular species having one or more lone-pair of electrons.

Eg. Amine NH_3

Aqua H_2O

Carbonyl CO

Ethane – 1, 2 – diamine [en] $\text{NH}_2 - \text{CH}_2 - \text{NH}_2$

(ii) Anionic ligands: Are ligand which are electrically charged.

These are ligands which carry negative charge on them. These charged ligand include the following:-

Fluoro F^-

Chloro Cl^-

Iodo I^-

Cyano CN^-

Hydroxo OH^-

Nitro NO_2^-

Nitrate NO_3^-

Carbonate CO_3^{2-}

Sulphate SO_4^{2-}

Oxalato $\text{C}_2\text{O}_4^{2-}$

Anionic ligands generally form anionic complex ions. For example $[\text{AgCl}_2]^-$, $[\text{PbCl}_4]^{2-}$, $[\text{AlF}_6]^{3-}$, $[\text{Ag}(\text{CN})_2]^-$

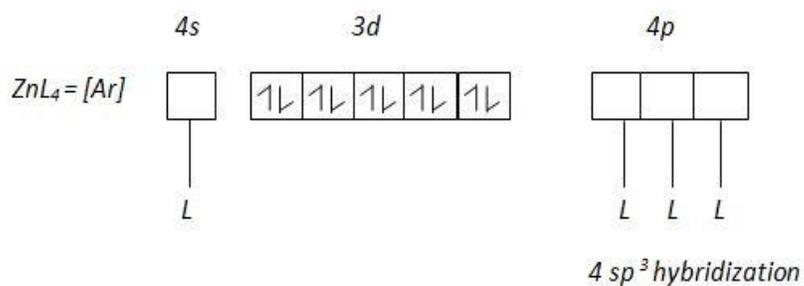
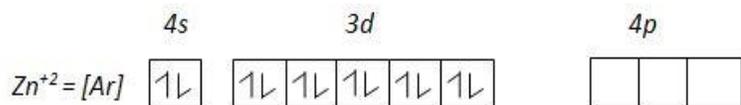
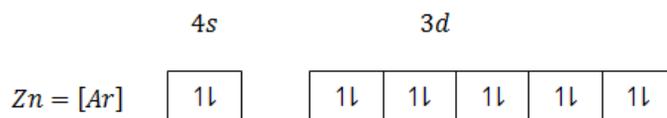
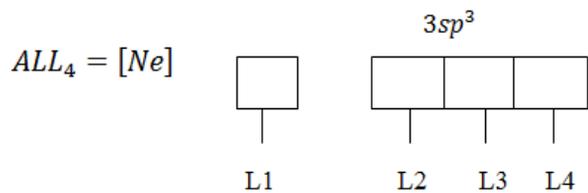
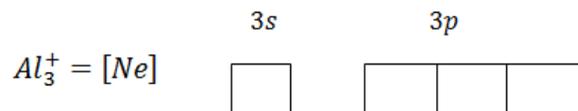
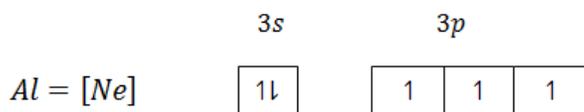
Ligands can also be classified based on the mode of attachment.

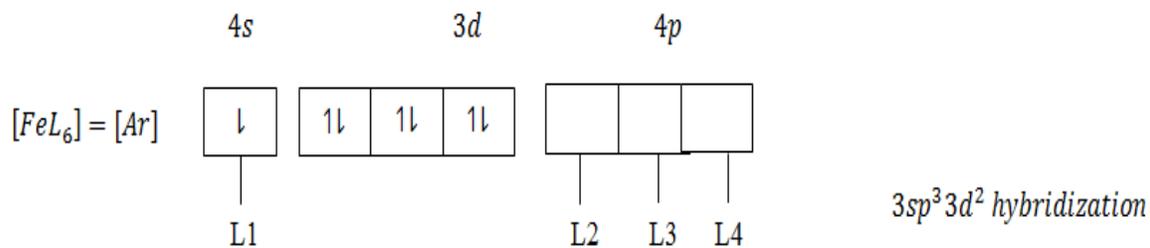
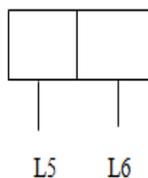
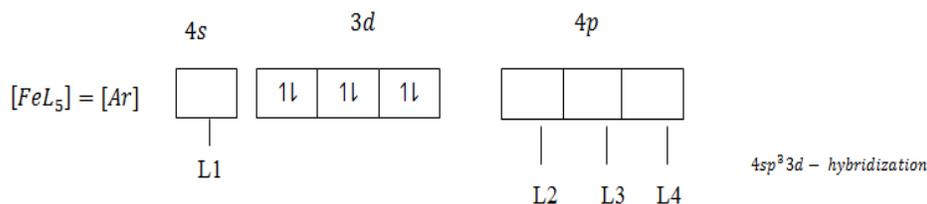
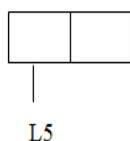
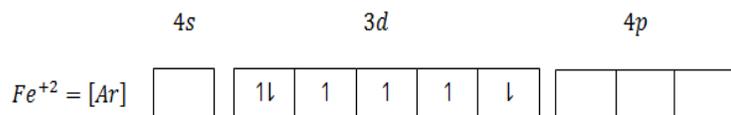
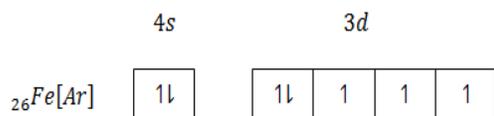
- (i) Monodentate (Unidentate) ligands: There are ligands which can attach to the central metal atom/ion only through one point.
- (ii) Bidentate ligands: These are ligands which get attached to the metal ion through two points.
- (iii) Tridentate ligands: These ligands get attached to the metal ion through 3 points.
- (iv) Tetradentate ligands:
- (v) Pentadentate ligands

Neutral	Anionic	Anionic
H ₂ O - Aqua	F ⁻ (Fluorido)	OH ⁻ (hydroxo)
NH ₃ - ammine	Cl ⁻ (chlorido)	HS ⁻
CO - carbonyl	Br ⁻ (Bromido)	O ²⁻ Oxo
NO - Nitrosyl	I ⁻ (Iodido)	S ²⁻
C ₅ H ₅ N	H ⁻	O ₂ ²⁻ Peroxo
NH ₂ - NH ₃	CN ⁻ Cyano	NO ₃ ²⁻ (Nitrate)
	CH ₃ COO ⁻ acetate	-ONO ⁻
	SCN ⁻ thiocyanato	C ₂ O ₄ ²⁻ (oxalate)
	NCS ⁻ isothianato	CO ₃ ²⁻ (carbonate)
		NO ⁻ (Nitro)

FORMATION OF COMPLEX COMPOUND

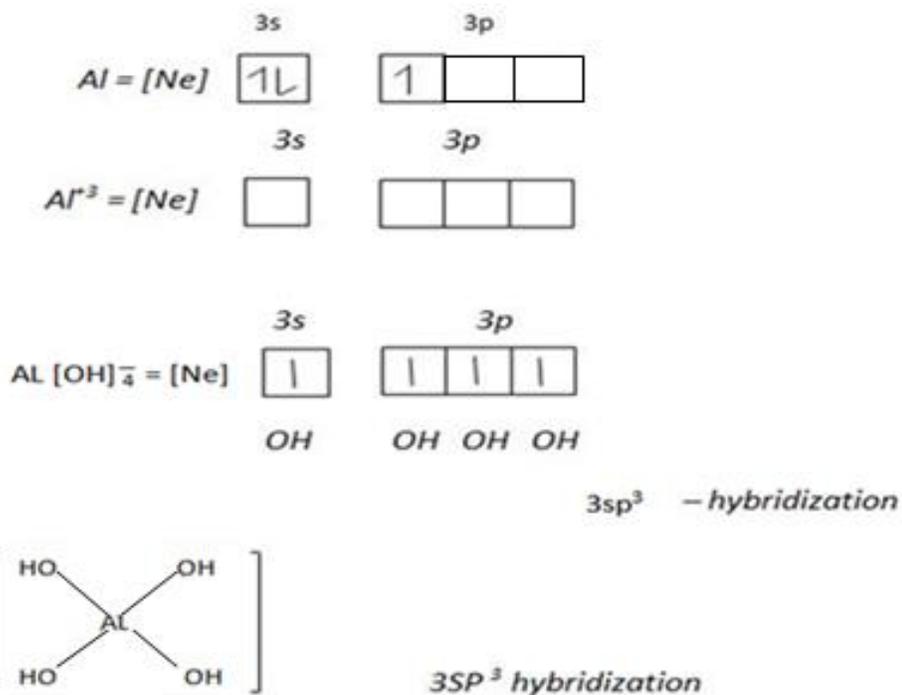
The central atom provides vacant orbitals and ligands provide a pair of electrons. In order for a central atom to form a complex compound, it first should lose electrons equivalent to its valency, which become metallic ions and then attract ligands. For transition elements which form complex compounds, use the following vacant orbitals. For a central atom which accommodates four ligands, use ns and np vacant orbitals which result in sp^3 hybridization.





The central atom form complex compound if the ligand occurs in excess or high concentration Al^{+3} in a dilute or low amount of NaOH form simple compound $\text{Al}^{+3} + \text{NaOH} \rightarrow \text{Al}[\text{OH}]_3 + \text{Na}^+$

But when the ligand occur in excess or high concentration cause Al^{3+} to form complex compound.



TYPES OF COMPLEXES

1. Cationic complexes are complex compound which are electrically positively charged. The total charge of central atom or metallic ions and all ligand result into the compound to be positively charged. Example of cationic complexes $[Cr Cl (H_2O)_3 (NH_3)_2]^+$
2. Anionic complexes are complexes compound which are negatively charged. The total charge of metallic ions and all ligand result into the compound to be negatively charged. The total charge of metallic ions and all charge ligand result into the compound to have negative charge (Fe $(CN)_6]^{-6}$).
3. Neutral complexes are complex compound which are electrically neutral and has no net charge. The total number charge of metallic ions and all ligand form the neutral compound. $[Al(NH_3) (OH)_3]$.

RULES FOR NAMING INORGANIC COMPLEXES

The system adopted is that developed by the international union of pure and applied chemistry (IUPAC).

i) Cations are always named before anions

The oxidation states of the central metal atom or ion is shown in Roman numerals in brackets immediately after it's name.

Eg. $[Fe(H_2O)_6]Cl_3$ Hexaaquairon (III)Chloride.

ii) Within complex ,ligands are named first followed by the central metal ion . Ligands are named in alphabetical order.

Eg. $[Co(NH_3)_4Cl_2]$ Tetraamminedichlocobalt (III) ion

iii) The number of particularly are ligands present must be specified by using the following prefixes.

di - 2 ligands

tri - 3 ligands

tetra - 4 ligands etc.

iv) Names of negative ligands end up with suffix O. eg. CN^- cyano , Cl^- chloro etc.

Neutral ligands usually retain their normal names except for the special cases :
 H_2O (aqua), NH_3 (ammine) etc

v) Anionic complexes end up in the suffix - ate often appended to the to the Latin or English name of the metal

Eg, $[Co(CN)_6]^{3-}$ Hexacyanocobaltate (III) ion

$[Fe(CN)_6]^{3-}$ Hexacyanoferrate (III) ion

vi) Cationic complexes use up their English name unchanged for the central metal ion.

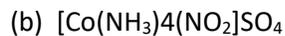
Eg, $[Cr(NH_3)_4Cl_2]^+$ Tetraamminedichlorochromium (III) ion.

Questions

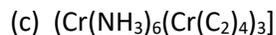
Name the following complexes



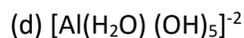
Potassium hexacyanoFerric (ii)



Tetra aminebromonitrocobalt (iii) sulphate



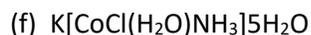
Hexaminechromium (iii) trioxalatochromium (iii)



Aquopentahydroxoaluminium (iii)

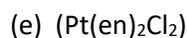


Dichlorodimethyldiamine platinum

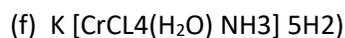


$$(1) + Cr + (-4) + (0) + 5(0) = 0$$

$$Cr = +3$$



Dichromethyldiamine platinum



$$(1) + Cr + (-4) + (0) + (0) (5(0) =)Cr = +3.$$

Pentahydrate potassium amine aquatetrachlorochromate (iii)

Question

(a) Complex compound $[\text{Co}(\text{NH}_3)_5(\text{Br})\text{SO}_4]$

(i) Name the complex compound above

(ii) What the coordinate number of central atom

(iii) If all ligand replaced by chloride ligand what is the charge of complex compound.

(iv) Write isomers of compound

(b) Using hybridization principles prove the following.

$\text{Fe}(\text{CN})_6^{4-}$ $d^2 sp^3$ hybridized

CoF_6^{3-} $d^2 sp^3$ hybridized

$\text{Ni}(\text{CN})_5^{3-}$ dsp^3 hybridized

Solution

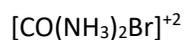
(a) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$

(i) Diaminebromocobalt (iii) Sulphate

(ii) Co – ordinate number = 6

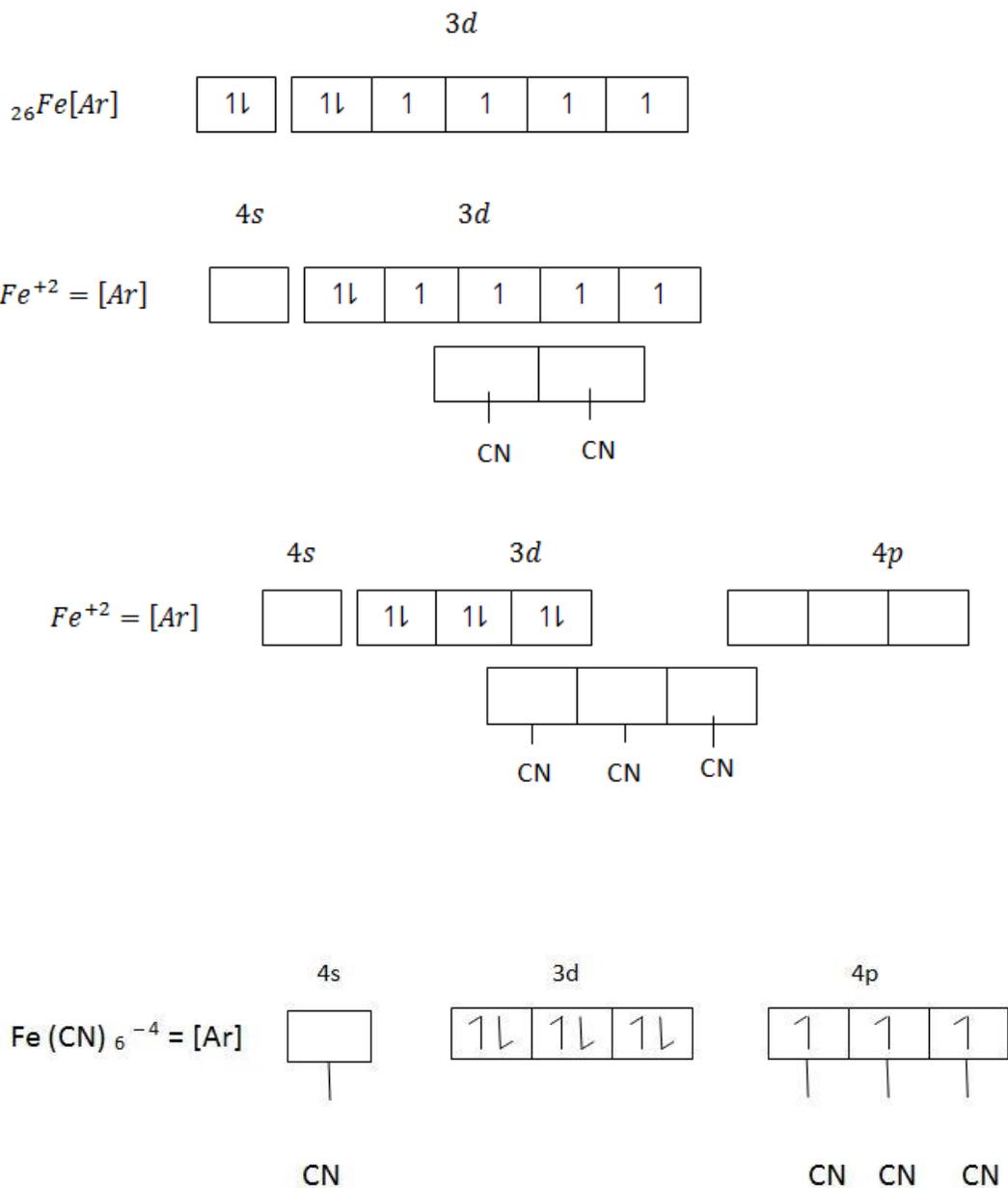
(v) $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}[\text{SO}_4]^{2-}$ the complex compound so neutral

(vi) Isomers of complex compound



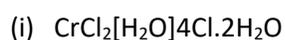
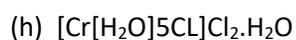
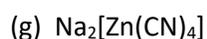
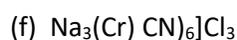
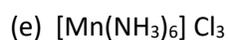
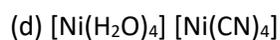
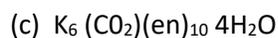
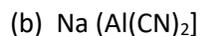
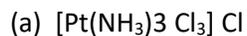
Isomers of ligand obtain through changing the number of each ligand

(b) $[\text{Fe}(\text{CN})_6]^{-4}$ $d^2 sp^3$ hybridization



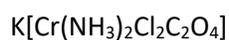
Question:

Provide the IUPAC name of the following compound



Question

Consider the complex compound



- What is the name of central atom
- List neutral ligand in the compound
- Name the charged ligand in the compound
- What is the name of complex compound

(e) What is the co – ordinate number of central atom

Solution

(a) Cr = Chromium

(b) NH₃ = Amine

(c) Cl⁻¹ = Chloro and C₂O₄⁻²

(d) Potassiumdiamminedichrolooxalatochromium (III)

(e) Co – ordinate number = 6

Question

Write the formula of the following complex compounds

(i) Dichlorotetra ammine cobalt (iii) chloride Tetraammine aquacopper

(ii) sulphate

(iii) Chloropentaaquacobalt (III) sulphate

(iv) Diaquatetraammine manganese (II) bromide

(v) Calcium di – iodo oxoltoferrate (III)

(vi)Trichlorotriammine chromium (III)

(vii) Trichlorotroammine planum (IV) chloride

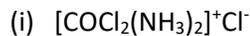
(viii)Potassium disulphat atotetra aquachromate (III)

(ix)Tetrammine copper (II) sulphate monohydrate

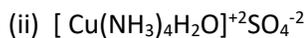
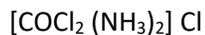
(x) Potassium hepta axodichromate (vi)

(xi) Trichlorotriammine platinum (IV) chloride.

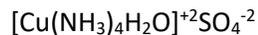
Solution



$$P = [3] + [2] + [0] = 1$$



$$[2] + [0] + [0] = 2$$



Reaction of the following salt with dilute NaOH

Salt solution	Small quantity	Excess
AgNO ₃	Ag (OH) ppt	Ag (OH)
Zn (NO ₃) ₂	Zn (OH) ₂ ppt	Soluble – Na ₂ (ZnO) ₂
Ca (NO ₃) ₂	Ca (OH) ₂ ppt	(COH) ₂ ppt
Pb (NO ₃) ₂	Pb (OH) ₂	Soluble – Na ₂ [pbo] ₂
Fe (NO ₃) ₂	Fe (OH) ₂	Fe (OH) ₂
KOH	-	-
Mg (NO ₃) ₂	Mg (OH) ₂	Mg (OH) ₂
Al (NO ₃) ₃	Al (OH) ₃	Soluble – Na[ACO ₂]

NOTE: Precipitates of Zn, Pb and Al are able to dissolve in excess alkali because they form soluble complexes.

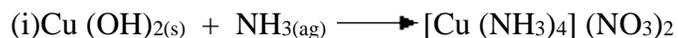
Reaction of the following salt with dil NH₃ solution.

Salt solution	Small quantity	Excess
Ag NO ₃	Ag (OH) ppt + NH ₄ OH	[Ag (NH ₃) ₂] NO ₃ CO
Zn (NO ₃) ₂	Zn (OH) ₂ ppt + NH ₄ OH	Zn (OH) ₂ ppt
Ca (NO ₃) ₂	Ca (OH) ppt + NH ₄ OH	Ca (OH) ₂ ppt
Pb (NO ₃) ₂	Pb (OH) ₂ ppt + NH ₄ OH	Pb (OH) ₂ – Insoluble ppt
Fe (NO ₃) ₂	Fe (OH) ₂ ppt + NH ₄ OH	Fe (OH) ₂
Cu (NO ₃) ₂	Cu (OH) ₂ ppt + NH ₄ OH	[Cu (NH ₃) ₄] (NO ₃) ₂
Mg (NO ₃) ₂	Mg (OH) ₂ ppt + NH ₄ OH	Mg (OH) ₂ ppt
Al (NO ₃) ₂		

NOTE: All complex compounds are SOLUBLE

Bp is insoluble in excess NH₃ (It form ppt)

Complete the following equations.



GEOMETRIC SHAPE OF COMPLEX COMPOUND

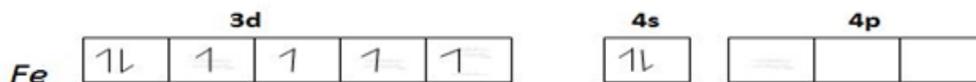
The number of ligands direct coordinated to the metal ion is the coordination number, of that atom in the complex.

(a) Coordination Number 6:

Complexes belonging to this coordination number have octahedral structure'

Eg, [Fe (CN)₆]⁴⁻ hexacyanoferrate (II) ion

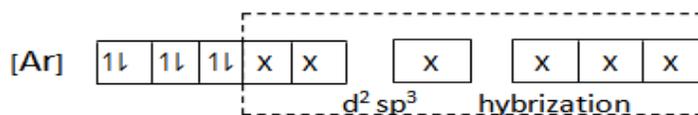
This is an inner orbital complex because the cyano - ligands are so strong that they push unpaired electrons inwards and force them to pair up.



Fe²⁺ ion uncomplexed.



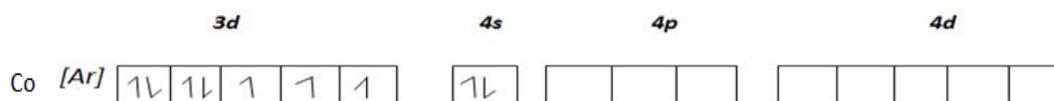
Fe²⁺ ion in the complex [Fe (CN)₆]⁴⁻



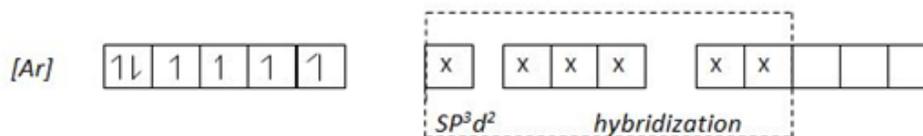
(b) [CoF₆]³⁻ hexafluorocobaltate (iii) ion.

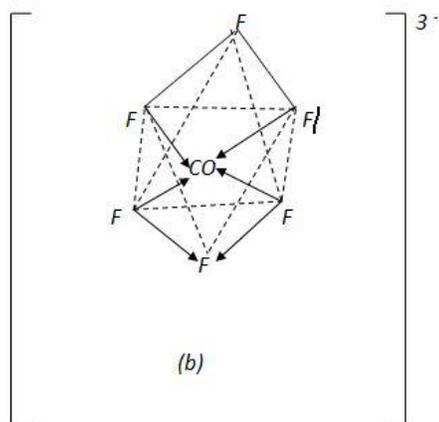
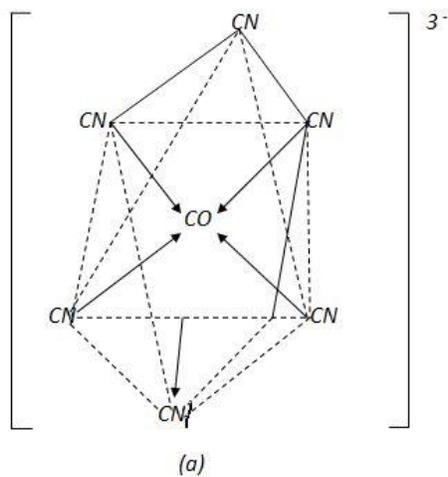
This is an outer orbital complex because the fluoro - ligands are weak. They cannot force electrons to pair inwards.

The six fluoro - ligands manage to occupy the orbitals in the 4th quantum shell.



Co³⁺ complexed





(a) Octahedral

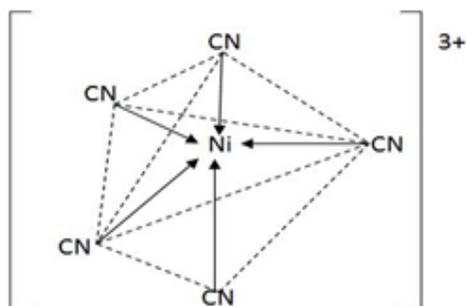
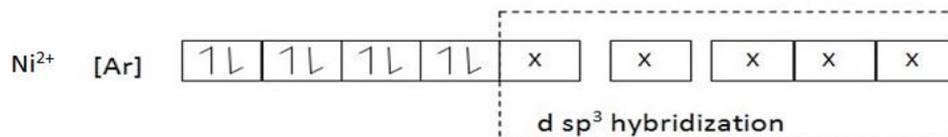
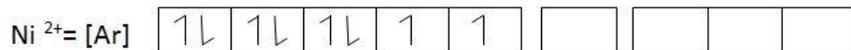
structure of $[\text{Fe}(\text{CN})_6]^{4-}$

(b) Octahedral structure of $[\text{CoF}_6]^{3-}$

(b) **Coordination number 5**

Complexes with coordination number have trigonal bipyramidal structure .

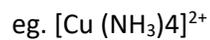
eg. $[\text{Ni}(\text{CN})_5]^{3-}$

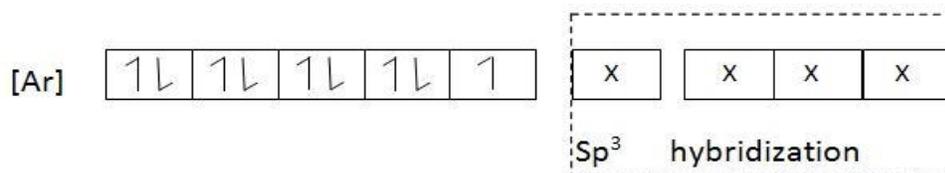
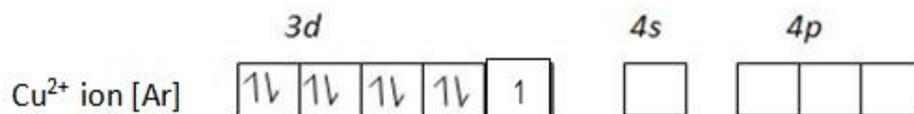
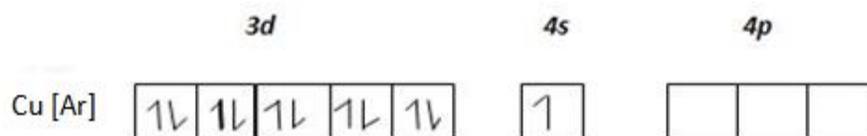


Trigonal by pyramidal structure of $[Ni (CN)_5]^{3-}$

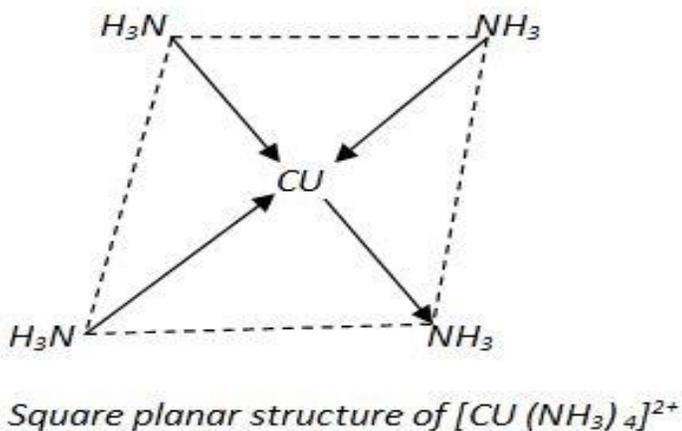
(C) Coordination number 4.

The most common complexes with this coordination number have square planar structure





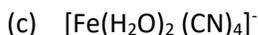
The shape of square planar complexes is flat



Question

Write the geometrical shape of the following complex.

- (a) $[\text{Zn}(\text{OH})_4]^{2-}$



(C) CATALYTIC ACTION

With exception to zinc, transition metals have catalytic action. They are used as catalysts in most chemical reactions catalytic power of catalyst is explained by their ability exist into stable oxidation states. In their catalytic ion, transition metals act as electron carries electrons in electron donors and pass them to electron acceptors.

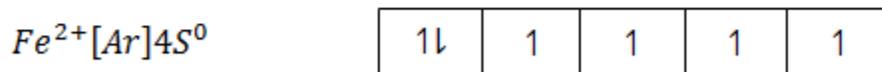
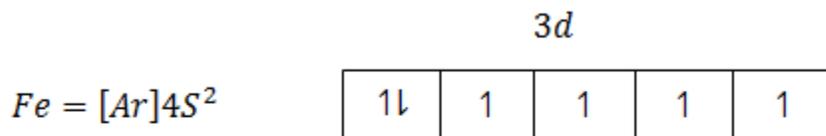
Example iron and Nickel are catalyst during hydrogenation of alkene. Example V_2O_5 , are used as catalyst during contact process. Example Manganese (iv)oxide used as catalyst during preparation of oxygen,iron used as a catalyst during Harber process.

(D) PARAMAGNETIC PROPERTY

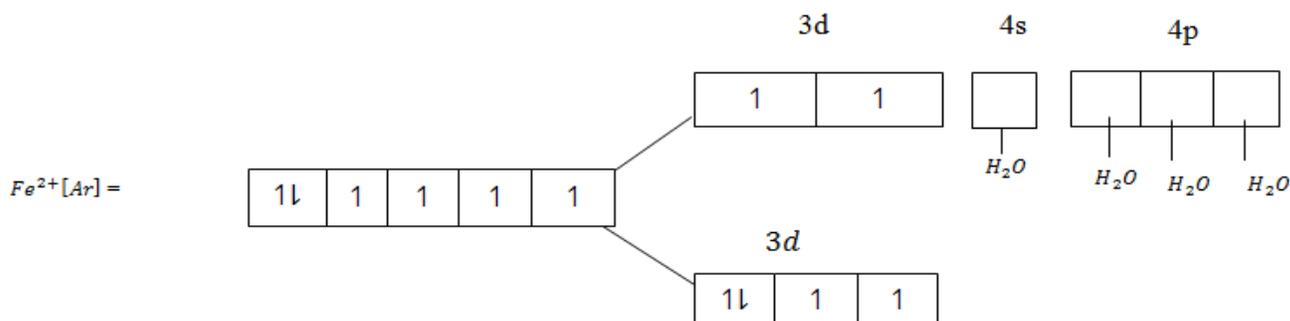
Is a substance which can be induced with magnetism and can be attracted by magnetic bar. For a substance to be a paramagnetic it must possesses unpaired electrons in its electronic structure. Transitional metals with exception to zinc are paramagnetic. This is because they have unpaired electrons in 3d – orbital. Unpaired electrons form weak magnetic field and magnetic forces arise due to weak electric current so formed in the orbitals as a result of spinning of electrons in the orbitals. When a magnetic bar is brought near to a paramagnetic object there is a tendency of domains or unpaired electrons to shift from a side of weak magnetic field [from the object] to the side of strong magnetic field which is strong and the whole object appear to be attracted towards the [Magnetic field] magnet. When electrons in the orbitals are paired there is interference and cancellation of magnetic fields occur as the magnetic field of two paired electrons move towards exactly opposite to each other (Vector) . All the magnetic fields cancel each other. Such substances cannot be induced with magnetic and cannot be attracted by a magnetic bar. Substances which cannot be induced with magnetic and cannot be attracted by a magnetic bar substances which cannot be attracted by an external magnetic field are said to be DIAMAGNETIC SUBSTANCES.

Transition metals are paramagnetic in pure metal or electrons are present in the delectronic structure of the transition metallic ion, for example Ferrous suphate $[\text{FeSO}_4]$ is paramagnetic just because Fe^{2+} has

unpaired electrons in 3d orbitals.



This is because ligands of high spin when approaches the d – orbitals and cause small separation of the d – orbitals. The energy of separation (ΔE) between double degenerate and treble is small, electrons will spread in accordance to Hund’s Rule in which each electron occupy its orbital singly before pairing. In that case the central transition metallic ion remains with unpaired electrons in the electronic structure. Hence the complex combined will be paramagnetic. Consider Fe^{2+} ion when complexes with ligands of high spin like water [H_2O]



This complex $[Fe(H_2O_4)4]^{2+}$ is a $4sp^3$ – hybrid complex and is paramagnetic. Since Fe^{2+} ion in the complex contains unpaired electrons in the d – electrons. If on the other hand Fe^{2+} complexes with ligands of low spin the paramagnetic property will be destroyed. The complex will be diamagnetic. Why? This is because ligands of low spin split the d – orbitals and cause large separation. The energy of separation [ΔE] between the two degenerates becomes large. If the energy of separation is large electrons fill in the orbital in accordance to AUFBAU’S PRINCIPLE in which electron pair themselves in

Treble degenerate orbitals, which have low energy according to AUFBAU'S PRINCIPLE. Consider Fe^{2+} complexes with ammonia which is ligand of low spin. This complex is $3d^24sp^3$ hybrid complex and is diamagnetic since there are no unpaired electrons in electronic structure of Fe^{2+} . All electrons Fe^{2+} are paired in Treble degenerate orbitals.

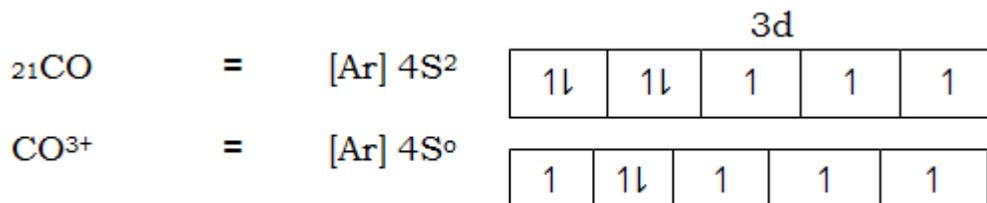
QUESTIONS

NECTA 2001 P₂ Question 6c

Use the configuration of 3d – orbital electron on cobalt (iii) ion to explain why $[\text{CoF}_6]^{3-}$ is paramagnetic while $[\text{CoCN}_6]^{3-}$ is not paramagnetic? [10%]

Solution

Consider electronic structure of CO and CO^{3+} ions given below



Then

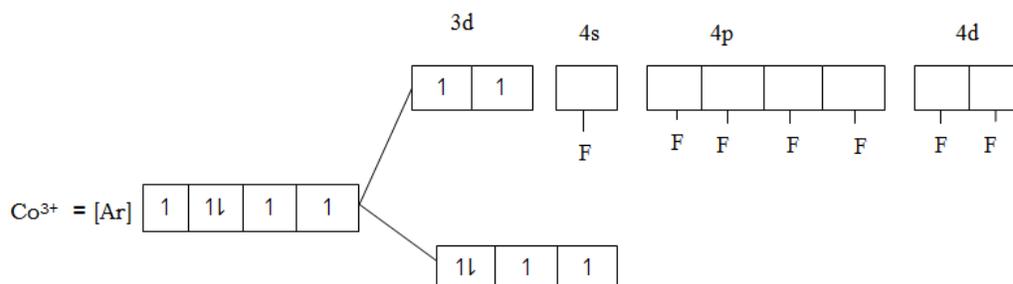
Complex $[\text{CoF}_6]^{3-}$ is paramagnetic because fluoride ion is a ligand of high spin hence cause small magnetic field 3d – orbit of cobalt (iii) ion hence the energy separation is small and filling of electrons in according to Hund's Rule, thus cobalt (iii) ion contains unpaired electrons in the 3d – orbitals. Hence a paramagnetic substance.

Consider

This is $4sp^3$ hybrid complex. And it is paramagnetic due to the in 3d – orbital

But

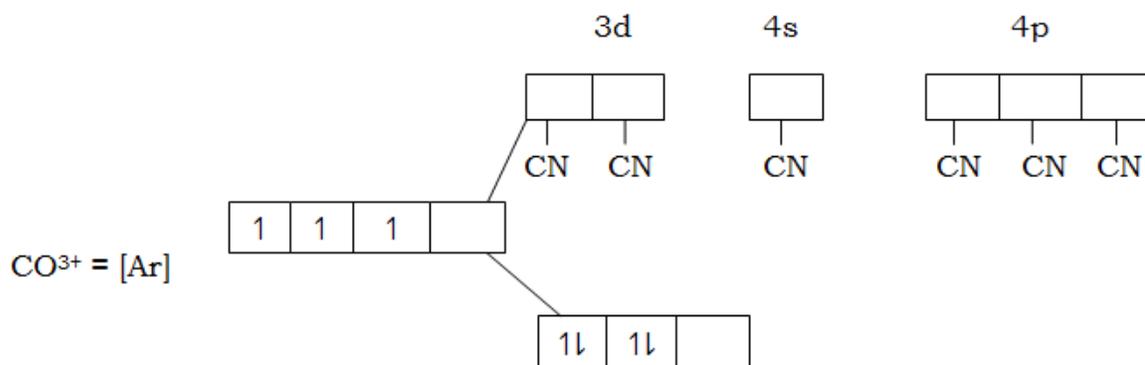
The complex $[\text{CoCN}_6]^{3-}$ is not paramagnetic due to absences of unpaired electrons in 3d – orbital in cobalt (iii) ion in the complex caused by complexing with ligands of low spin the cyano. This ligands exert strong magnetic field to the unpaired 3d – orbital hence large separation which cause excitation of be



This is $4sp^3$ hybrid complex. And it is paramagnetic due to the in 3d – orbital

But

The complex $[\text{Co}(\text{CN})_6]^{3-}$ is not paramagnetic due to absence of unpaired electrons in 3d – orbital in cobalt (iii) ion in the complex caused by complexing with ligands of low spin the cyano. This ligands exert strong magnetic field to the unpaired 3d – orbital hence large separation which cause excitation of be difficult hence filling of electrons is according to AUFBAU'S PRINCIPLE.

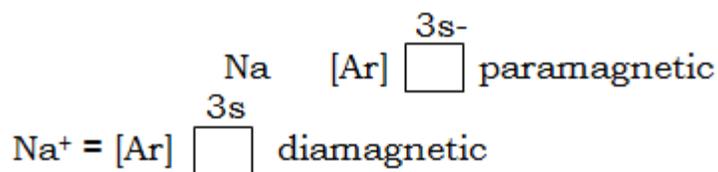


Paramagnetic property of transition metals can be destroyed in two ways

- a. Temperature/ oxidation process
 - b. Complex compound formation
- a. TEMPERATURE/ OXIDATION

Raise in temperature destroy magnetic property of the elements. Raise in temperature causes excitations of electrons and ionization of the atoms by losing electron.

Ionization to an extend of losing all unpaired electrons destroys magnetic property of the substance.



b. COMPLEX COMPOUND FORMATION

Formation of complex compounds by coordination with ligand may also destroy magnetic property of transition metals. However this will depend on oxidation state of the metals and nature of the ligands involved in complex compound formation whether are ligand of high or low spin.

When the complex compound formed by ligand of high spin such as $\text{C}_2\text{O}_4^{2-}$, OH^- , F^- , Br^- , I^- , Cl^- energy separation between treble and degenerate. Electron filled according to the Hund's rule this result electron to be unpaired in the double and treble degenerate the complex remain paramagnetic example CoF_6^{3-} is paramagnetic substance. The F^- filled in 4s, 4p and 4d vacant orbital the 3d remain with unpaired electron which result paramagnetic

Question

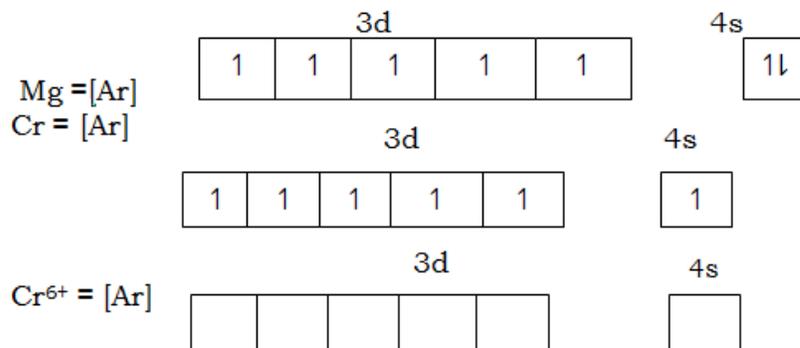
a. Predict the coordination number of Ni^{2+} and state whether the complex will be paramagnetic or diamagnetic if Ni^{2+} complex with

- i) Bromine ions, Br^- [Ligands of high]
- ii) Ammonia molecules NH_3 [ligands of low spin]

b. Fe^{3+} complexing with NH_3 of low spin

c) VARIABILITY IN OXIDATION STATES

With exception to zinc, transition metals form more than one stable oxidation state. They have variable oxidation state. Variability in oxidation state in transition metals is explained by the ability to ionize by losing electron from both sub energy levels 4s and 3d. The energy present between 4s and 3d is very small. The gap existing between 4s and 3d is small. The difference between the two degenerated is so small that just normal radiant energy from the sun is enough to excite electrons and so small that electrons from sub energy level 4s and 3d can be removed by almost the same amount of ionization energy. So that during ionization, transition metals give off 4s – electrons first followed by 3d. Transition metals depends on the number of electrons present in 4s – orbital. Chromium has lowest oxidation state of $+2$, loses two electrons in 4s – orbital and copper the lowest oxidation state is $+1$. The maximum or the highest oxidation state is (achieved) attained after losing all the 3d electrons.

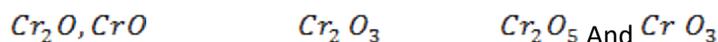


The extent of losing all the 3d – electrons is possible only for the first five elements from Sc to Mn. Elements beyond manganese can ionize to an extent of losing all the electrons because of large nuclear charge in these elements which cause strong effective charge pull, over the 3d electrons. The only oxidation state for elements found beyond manganese is +3 and for copper stable oxidation state is +2 which is attained after loss of the single 4s - electron and another from sub energy level 3d. The nuclear charge is high in zinc and hence the nuclear pull in 3d electron for zinc is maximum. Hence it is difficult to remove electrons from sub energy 3d in zinc. Zn has only one stable oxidation state of +2 which is formed after losing the two electrons. Only one stable oxidation state for zinc is one of the factors which excludes zinc from transition metals.

NOTE:

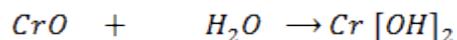
For these elements with atomic number 21 to 25 which can ionize to an extent of losing all the d – electrons, the tendency is that increase in oxidation states accompany with increase in acidic character. Lower oxidation states have basic character and higher oxidation states are acidic in nature. This is caused by increase in ionization energy needed to form the ions. The increase in acidic character with increasing oxidation states can be justified by considering the various oxides of chromium.

The various oxides of chromium include.



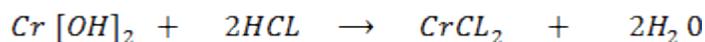
Base oxides	amphoteric oxides	Acidic oxides
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The first two oxides, chromium (iii) oxide [Cr₂O] and chromium (ii) oxide [CrO] are basic solutions which have no chemical reaction with other basic solution even alkaline solutions.



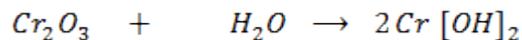
Then $Cr [OH]_2 + NaOH \rightarrow$ *No reaction*

$Cr [OH]_2$ react with acidic solution



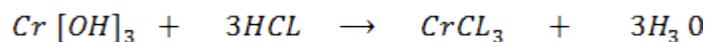
Chromium (ii) chloride

Chromium (iv) oxide [Cr₂O₃] is amphoteric. It dissolve in water and form hydroxides which dissolve in both alkaline solutions and acidic solutions.



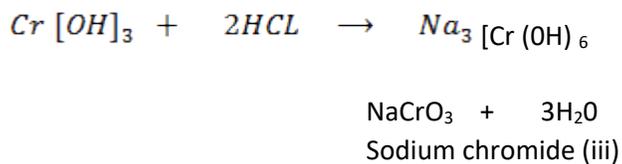
As base

Chromium (iv) hydroxide react acid solution



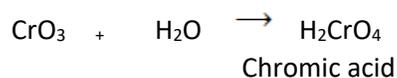
As acid

Chromium (iv) hydroxide dissolves in alkaline solution and form complex salt

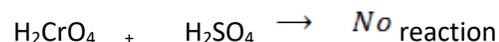


The last two oxides, chromium (v) oxide Cr₂O₅ and chromium (vi) oxide (CrO₃) are ACIDIC

OXIDES. They dissolve in water and form strong acidic solutions



Chromic acid is so strong acid that has no chemical reaction with other acidic solution



Chromic acid reacts with basis solutions and form normal salts



Reaction of the various oxides of chromium real justify with increase in Acidic character.

NOTE

Change in base acidic character in transition metals during ionization explain why Redox reactions take place either in acidic medium or basic medium, lower oxidation states which are basic in nature, become more stable if the medium in which they are formed is acidic. On the other hand, high oxidation states which are acidic tend to be more stable if they are formed in basic medium. Therefore in redox reactions, when the elements change its oxidation states from high to lower oxidation state the process will take place in acidic medium from low oxidation state to high oxidation state, the process will occur in basic medium.

SUMMARY

i. Low oxidation state $\xrightarrow{OH^-}$ High oxidation state

Basic in nature $Mn^{2+} \xrightarrow{OH^-} MnO_4^-$

ii. High oxidation state $\xrightarrow{H^+}$ lower oxidation state

[Acid] $MnO_4^{-1} \xrightarrow{H^+} Mn^{2+}$ [base]
Purple Colourless

Or

$Cr^{3+} \xrightarrow{OH^-} Cr_2O_7^{2-}$

And

$Cr_2O_7^{2-} \xrightarrow{H^+} Cr^{3+}$

SOIL CHEMISTRY

Soil - may be defined as the unconsolidated mineral on the top layer of the earth's crust that serves as a natural medium for the growth of land plants.

SOIL COLLOIDS:

Definition: Soil Colloids - are very small organic and inorganic particles present in the soil which are responsible for potential fertility of the soil determine the physical and chemical properties of the soil.

1. How soil colloids are formed

- As soil is formed during weathering processes, some minerals and organic matter are broken down to extremely small particles.
- Chemicals changes further reduce these particles until they cannot be seen with the naked eyes.
- The very smallest particles are what we call soil colloids.

2.

Types of soil colloids

Soil collards may be

a) Inorganic colloids

- Clay minerals (layer silicate clay).
- Iron and Aluminium oxide clays.
- Allophane and amorphous clays.

b) Organic colloids

- Includes highly decomposed organize matter called humus.
- Organic colloids are more reactive chemically and generally have greater influence on soil properties.

Therefore the four major colloids present in the soil are,

i) Layer silicate clay

- These are most important silicate known as phyllosilicates (life-like).
- They comprised of two kinds of horizontal sheets, one dominated by silicon and other by aluminium magnesium.

ii) Iron and Aluminium

These are remnant material which remain after extensive weathering due to its low solubility these are sesquioxides

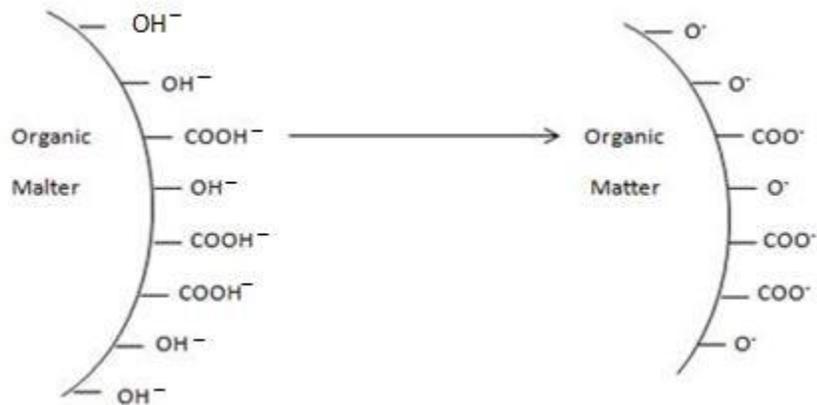
Sesquioxides are either Al oxide or iron (iii) oxide contaminated with $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$

iii) Allophane and other amorphous minerals

- Mainly these silicates are mixture of silica and alumina.
- They are amorphous in nature.

iv) Humus

- Humus is amorphous, dark-brown to black nearly insoluble in water but more soluble in dil. Alkali e.g NaOH, KOH solution.
- It consists of various chain loops of linked carbon atoms.
- Humus is a temporary intermediate product left after considerable decomposition of plant and animal remains.
- Humus contains partially dissociated enolic, carboxyl and phenolic groups.



PROPERTIES OF SOIL COLLOIDS

-Includes

- i. Surface area
- ii. Electric charge (surface charge)
- iii. Ion exchange (adsorption of cation)

i) **Surface area.**

Because of their small size, all soil colloids expose a large external surface area per unit mass.

The external surface area of 1g of colloidal clay is at least 1000 times of 1 g of colloidal clay is at least 1000 times that of 1g of coarse sand.

ii) **Electric charge**

- Soil colloids surface, both external and internal characteristically carry +ve and or -ve charge.
- Most soil colloids the +ve charge predominate.
- Both organic and inorganic soil colloids when suspended in water carry a negative charge.

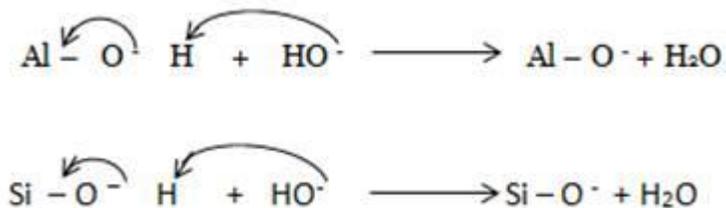
Where the negative charge on colloidal particles comes from?

- Negative charge on clays comes from
 - i) Ionizable hydrogen ions.
 - ii) Isomorphous substitution.

i) Ionizable hydrogen ions are hydrogen ions from hydroxyl group on clay surfaces

- The O-H bond from Al –OH or Si – O –H portion of clay heterolytically breaks and ionizes to give H⁺ leaving unneutralized negative charge on oxygen.

- Presence of strong alkaline solution activates the cleavage of O-H bond yielding H⁺ which will combine with OH⁻ from strong alkaline solution in the neutralization reaction.



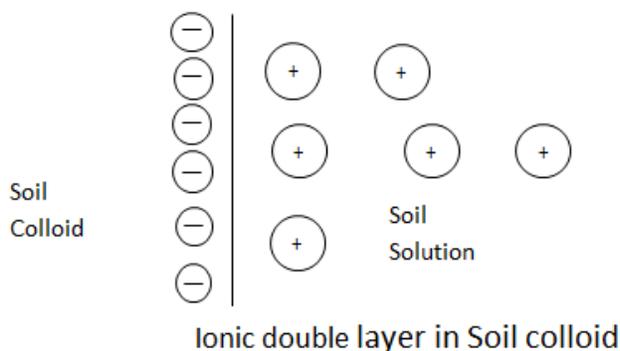
Hence soil colloids becomes more negative in more alkaline solutions. The same applies to organic colloids which also contain OH in enolic, phenolic or enol.

ii) Isomorphous substitution.

This is due to the substitution of one ion for another of similar size often with lower charge

iii) Ion exchange (Adsorption of cations)

As soil colloids possess negative charge, they attract the ions of an opposite charge i.e. positively charged ions to the colloidal surfaces. The attraction of cations such as H^+ , Ca^{2+} , and Mg^{2+} to colloid surface leads to the formation of an ionic double layer. The outer layer is made up of a swarm of rather loosely held cations attracted to the negatively charged colloidal surface.



ION EXCHANGE IN A SOIL

Colloids are primarily responsible for chemical reactivity in soil

Each colloid has net negative charge thus making possible for the colloid to attract and hold positively charged particles (cations) like Na^+ , H^+ , Ca^{2+} and Mg^{2+}

- Thus there are cations attached to colloids and in the soil.
- When one of the cations in the soil solution replaces one of the cations on the soil colloids cation exchange is said to take place.
- This exchange only takes place when the cations in the soil solution are not in equilibrium to the cations on the soil colloid.

Definition

Ion exchange :

Is reversible reaction which involves an interchange of ions between ion in soil solution and another ion or surface of soil colloid.

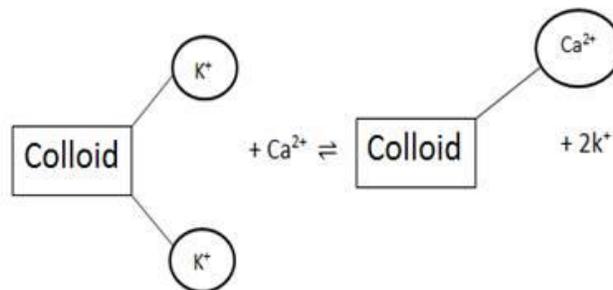
It can be anion exchange or cation exchange.

Cation exchange:

Is the interchange between a cation in a solution and another cation on surface of any negatively charged material such as clay or organic matter.

In the soil: Cation exchange is the interchange between cation in a soil solution and another cation on the surface of soil colloid.

e.g



Anion exchange

Soil colloids being negatively charged cannot attract and hold negatively charged particles (like charged repels) like SO_4 and NO_3

Why? Nitrate is more leached from the soil than ammonium.

- This is because nitrate (NO_3) has negative charge like soil colloids. So NO_3 is not held by the soil solution to be leached under rainfall conditions.
- NH_4 being positively charged is attracted and held by soil colloids and hence it become difficult for NH_4 to be leached.

Mechanism of ion exchange in the soil.

- Ion exchange in the soil is well explained by electron –kinetic theory of ion exchange.

According to the theory:

The negative and positive charge associated with soil colloids (clay minerals and organic matter) are balanced by electrostatic attraction of cations and anions respectively.

The balancing ions are turned as EXCHANGEABLE CATIONS OR ANIONS.

- Exchangeable cations and anions form outer sphere complexes with charged surfaces in which water of hydration exist between the charged ion and the oppositely charged colloids.
- Thus the adsorbed cations and anions are said to being state of oscillation forming a diffuse double layer.
- Due to these oscillations, some of the ions move away from the surface of the colloid micelles.
- In presence of the solution of an electrolyte an ion of the soil solution slips in between the inner charged layer and the outer oscillating ion.
- The ion in the soil solution is now adsorbed on the colloid micelles and the surface in remains in solution as an exchange ion and hence the ion exchange occurs.

Factors affecting composition of exchangeable ions in the ion exchange

Explain the factors affecting composition of exchangeable ions in the soil.

- i. Strength of adsorption
- ii. Relative concentration of the ion in the soil solution.

CATION EXCHANGE CAPACITY (CEC)

- Is the maximum quantity of total cations of any class, that a soil is capable of holding at a given P^H value, available for exchange with soil solution.

- It is a measure of the quantity of the negatively charged sites on soil surfaces that can retain positively charged ions by electrostatic force.

Significance of CEC

CEC is useful in the following ways:

It is a measure of soil fertility

-The more cation exchange capacity a soil has the more likely the soil will have fertility.

It is a measure of nutrient retention capacity

-Soil with large value of CEC has large nutrient retention capacity.

It is a measure of the capacity of soil to protect ground water from cation contamination.

-Soil with large CEC has good ability to protect ground water from cation contamination as it exerts more resistance for its cations to be leached away.

Expression of CEC value

It is expressed in terms of number of equivalents (or more specifically as number of millequivalents) of cations per 100 grams of dry soil written as:

e.g 100g (meq /100g)

$$\text{No of equivalents} = \frac{\text{mass of cation}}{\text{equivalent wt}} \text{----- (i)}$$

Equivalent ω_t means the mass of cation that will replace (exchange) 1g (1mole) of H^+ .

E.g

23g of Na^+ (i.e 1mole of Na^+) exchange 1g of 1^+ and hence Na^+ has equivalent wt of 23g.

40g of Ca^{2+} (1 mole of Ca^{2+}) exchange 2g (2moles of H^+ which means $20g \left(\frac{40g}{2}\right)$ of Ca^{2+} exchange $1g \left(\frac{2g}{2}\right)$ of H^+

Hence Ca^{2+} have equivalent wt of 20.

$$\therefore \text{equivalent } \omega_t = \frac{\text{Atomic wt}}{\text{Amount of ionic charge}} \text{----- (iii)}$$

$$\text{but } \frac{\text{mass of a cation}}{\text{atomic wt}} = \text{no of moles of the cation}$$

$$\therefore \text{number of equivalents} = \frac{\text{Number of mole of cation}}{\text{Amount of ionic charge}}$$

Where no of mill moles = No of moles x 1000

$$\text{No of mill moles} = \frac{\text{Mass of cation}}{\text{Atomic wt}} \times 1000$$

$$= \frac{\text{Mass of cation in milligrams}}{\text{Atomic wt}}$$

Factors affecting value of cation exchange capacity.

Cation exchange capacity is affected by the following factors:

- Amount of clay (soil texture)
- Type of clay
- Soil organic matter
- P^H of the soil.

i) Amount of clay in soil

A high silicate- clay soil hold more exchangeable cations than a low silicate clay soil and hence have greater CEC value.

Silicate clay (Si – (OH) easily lose H⁺ off Hydroxy group in basic medium resulting into net negative charge i.e the greater the –ve charge the greater the CEC

(ii) Clay types

Different clay types have different CEC value due to difference in surface area.

(iii) Soil Organic Matter

Organic matter in the Soil, also are negative charged. Therefore

- High – Organic Soil have greater CEC value than a low organic Soil.
- On another hand if an organic matter continue to decay, the CEC tends to decrease with the decomposition.
- They can retain more cations.

Therefore organic matter particles have greater CEC than clay particles.

(iv) P^H of the soil.

P^H affects CEC of colloids that are charged based on hydroxyl group instead isomorphous substitution.

Under acidic (low P^H) condition.

H⁺ are in excess resulting to less ionization of the colloids, less negative charge and hence low CEC value.

Under basic (High P^H) condition.

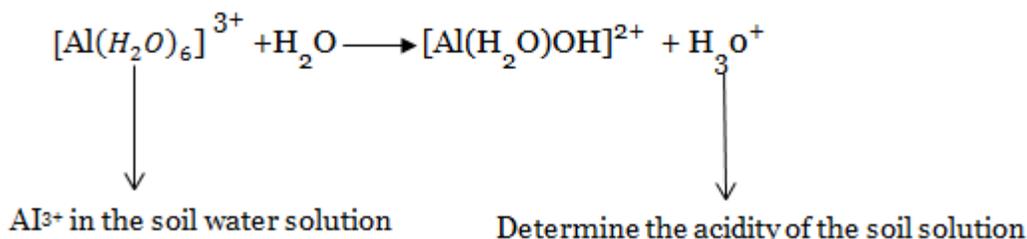
OH⁻ are in excess resulting to more ionization of the colloids, more negative charge on the colloids surface and hence high CEC value.

PERCENTAGE BASE SATURATION

Acid cations and Base cations

Acid cations are exchangeable cations (mainly H⁺ and Al³⁺) which tend to acidify the soil

- They are also known as exchangeable acids
- In very acidic soil, H⁺ and Al³⁺ dominates other adsorbed cations.
- The acidity of Al³⁺ is explained by its cationic hydrolysis according to the following equation:



Base cations (or exchangeable bases) are exchangeable cations which are capable of neutralizing soil acidity. Common exchangeable bases are Ca²⁺, Mg²⁺, K⁺ and Na⁺

Base saturation

Base saturation is the fraction of exchangeable cations that are base cations.

-It is expressed as percentage and hence the name percentage base saturation.

$$\text{Percentage base saturation} = \frac{\text{Number of adsorbed exchangeable base}}{\text{CEC of the soil}} \times 100\%$$

Relationship between percentage base saturation and percentage acid saturation

Percentage base saturation + percentage acid saturation

$$\begin{aligned} \frac{\text{Number of base cations}}{\text{CEC of the Soil}} \times 100\% + \frac{\text{Number of acid cations}}{\text{CEC of the soil}} \times 100\% \\ = \left(\frac{\text{Number of base cations} + \text{Number of acid cations}}{\text{CEC of the soil}} \right) \times 100\% \end{aligned}$$

but number of base cations + Number of acid cations = Total number Of exchangeable cations = CEC of the soil

$$= \frac{\text{CEC of the soil}}{\text{CEC of the soil}} \times 100\% = 100\%$$

Therefore

Percentage base saturation + percentage acid = 100% Saturation.

Q. 1. (a) Define the following terms as applied to soil:

- (i) Cation Exchange Capacity
- (ii) Percentage Base saturation
- (iii) Salinity

(b) A soil sample has a CEC of 25meq per 100g of 200mg of soil sample were shaken with 40c^m³ of 0.1M HCl. After filtering and washing the soil the filtrate and washing were titrated against NaOH solution, 24.0cm³ of 0.1 M NaOH were required for complete neutralization. Calculate the percentage base saturation of the soil sample.

(c) A soil sample (20g) was analyzed and found to contain 0.0015g of calcium, what is the concentration of Ca in the soil sample in meq/100g of soil.

NOTE: $1\text{eq} = \frac{\text{r. a. m}}{\text{valency}}$

$$1\text{eq of Ca}^{2+} = \frac{40}{2} = 20\text{g} = 0.02\text{meq}$$

$$1\text{eq of Na}^+ 23\text{g} = 0.023\text{meq}$$

ANSWERS:

(b) Solution:

$$\text{Molarity} = \frac{\text{Conc}}{\text{M.M}}$$

$$0.1 = \frac{\text{Conc}}{1}$$

$$\text{Conc} = 0.1$$

$$\text{Conc} = \frac{n}{v}$$

$$0.1 = \frac{n}{40 \times 10^{-3}}$$

$$n_{H^+} = 0.004 \text{ moles}$$

Remaining HCl will react with NaOH hence HCl was in excess

$$\text{Molarity} = \frac{\text{Conc}}{\text{M.M}}$$

$$0.1 = \frac{\text{Conc}}{40}$$

$$\text{Conc} = 4 \text{ gdm}^{-3}$$

$$\text{Conc} = \frac{n}{v}$$

$$4 = \frac{n}{24 \times 10^{-3}}$$

$$n = 0.0024 \text{ moles}$$

$$\text{Used} = 0.004 - 0.0024$$

= 0.0016 moles of H^+ (No of moles which attached themselves to the soil colloid)

Now we know 1eq = 1 mole of H⁺

0.0016 eq was in 200g of soil

? 100g

0.0016 e.g. = 200

? = 100g

$8 \times 10^{-4} \times 1000 = 0.8\text{meq}/100\text{g}$

$$\text{P.B.S} = \frac{\sum EB}{CEC} \times 100\%$$

$$= \frac{0.8 \text{ meq}/100\text{g}}{25 \text{ meq}/100\text{g}} \times 100\%$$

P. B.S. = 3.2%

Example 4

A Soil test shows the following:

Nutrient meq / 100 soil

Ca²⁺ 9.9

Mg ²⁺	2.1
K ⁺	2.0
Al ³⁺	7.6
NH ₄ ⁺	0.6
Na ⁺	0.1

- Calculate the CEC of the Soil.
- Calculate the percent base saturation of the Soil
- Calculate the percent aluminium saturation of the soil

SOLUTION:

a) CEC of the Soil

= number of exchangeable base cations + number of exchangeable acid cations.

$$= (9.9 + 2.1 + 2.0 + 7.6 + 0.6 + 1.0) \text{ meq} = 22.3 \text{ meq}$$

Hence CEC of the soil is 22.3 meq

b) From a given cations, are acid cations

$$= (22.3 - (0.6 + 7.6)) = 14.1$$

(Recall: CEC = Number of exchangeable base cation + Number of exchangeable acid cations, and therefore number of exchangeable base cation = CEC – Number of exchangeable acid cations)

Using; Percent base saturation

$$= \frac{\text{number of exchangeable base cations}}{\text{CEC of the soil}} \times 100\%$$

$$= \frac{14.1}{22.3} \times 100\% = 63.23\%$$

Hence percent base saturation is 63.23

Percent aluminium saturation

$$= \frac{\text{number of Al}^{3+}\text{ions}}{\text{CEC of the soil}} \times 100\%$$

$$= \frac{14.1}{22.3} \times 100\% = 34.1\%$$

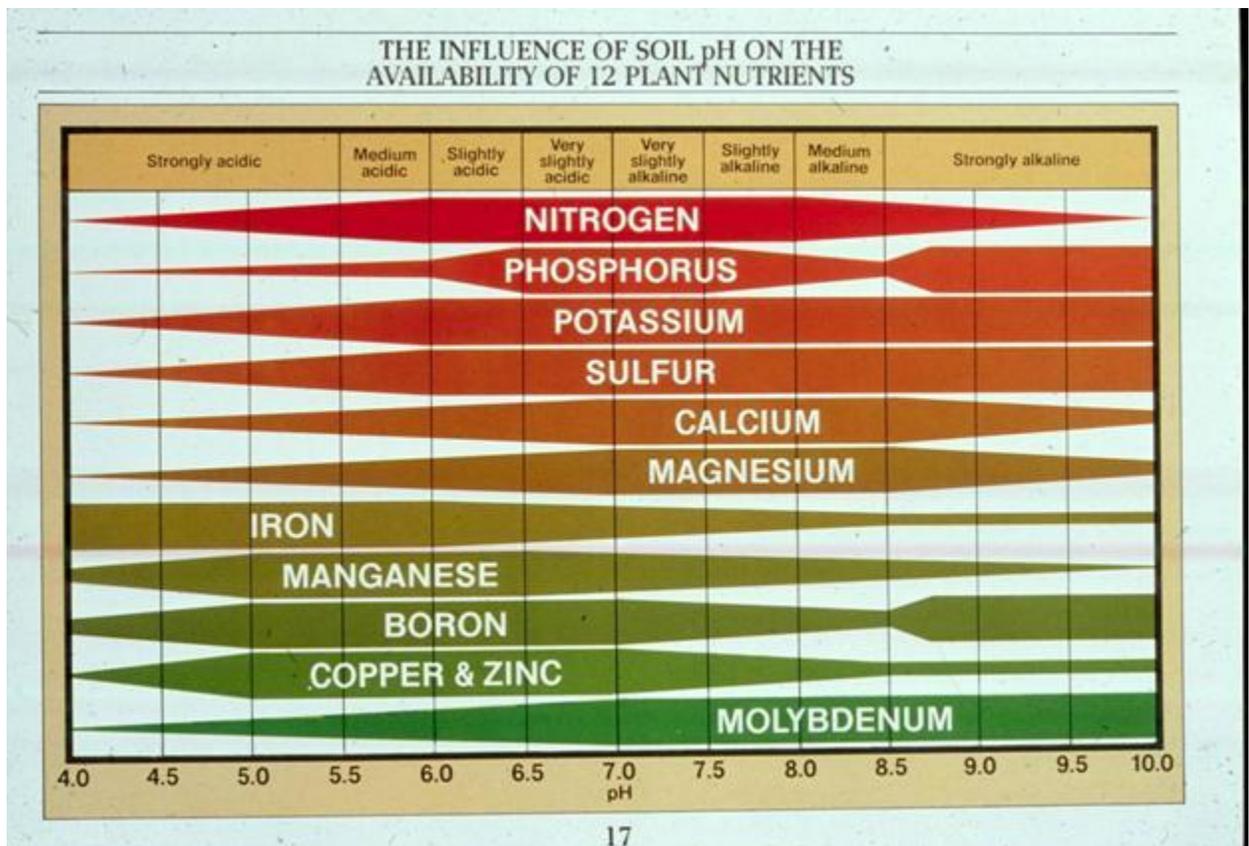
Hence aluminium base saturation is 34.1%

SOIL REACTION - It is the acidity or alkalinity of the soil. The soil reaction can be acidic, neutral or alkaline due to the soil solution. It is measured in P^H using electrometric methods (P^H – meter). All soil P^H range from 4 to 8. Soils with P^H < 4 generally contain sulphuric acids while those with P^H > 8 contain high percentage of Na⁺ and thus are alkaline.

Importance of soil P^H

- Most crop plant prefers P^H to be between 6 and 7.5 i.e slightly acidic up to slightly alkaline.
- The availability of nutrients to plant depends on soil P^H. All plant nutrients are reasonably available between P^H 6 and 7.5 which is the optimum P^H. The availability of N, P, K, S, Ca, Mg decreases with the increase in soil acidity. Thus acidic soils are often deficient of these nutrients.
E.g. Nutrient phosphorus is found as phosphate (v) in the soil. At P^H < 5, the soluble iron, aluminium and manganese react with phosphates (v) to form insoluble complexes and then fix them (makes them unavailable for plants).

Fe, Mn and Cu precipitate at high P^H . Thus deficiency of these nutrients often limits plants growth in alkaline soils. Manganese and Iron become plant toxic at low P^H .



The problem with heavy metals toxic to humans arises near industrial area due to acid rain.

E.g. Cadmium and lead, below P^H 4 get dissolved and may enter plant and make crops unfit for human consumption

Conclusion:

Determination of P^H of agricultural soil is very important for the selection of suitable crops. Below the P^H 4.8 a soil may need liming in order to avoid aluminum toxicity.

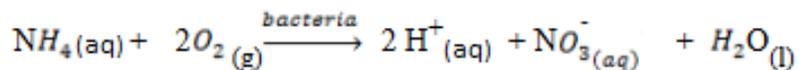
CAUSES OF SOIL ACIDITY

. Soil acidity is caused when heavy rains leach bases like Ca^{2+} , Mg^{2+} , K^+ and Na^+ from the soil to the ground water table leave surplus H^+ in the soil.

. Also industrial regions may bring sulphuric (vi) acid and nitric (v) acid to the soil which increases its acidity.

. Acidic mineral fertilizers like ammonium sulphate (vi) and ammonium chloride make the soil more acidic due to hydrolysis.

. Also the nitrification of ammonium ions by bacteria produces $H^+_{(aq)}$



NOTE: Organic acids are produced during the decomposition of organic matter. Due to this, most soils in humid tropics are Acidic.

Liming & liming materials

Discuss:

- Meaning and significance of liming as treatment to soil P^H .
- The efficiency of liming materials i.e. neutralizing values of carbonates, oxides, hydroxides and silicates.
- Beneficial effects of liming
- Detrimental effects of over-liming

Liming:

It refers to the process of adding basic compounds of calcium and magnesium to acid soil ($P^H < 5$) in order to raise the P^H of the soil to the required level.

The compound of calcium and magnesium (oxides, hydroxides, carbonates and silicates) are called agricultural limes. Such compounds are contained in limestone, dolomite, building (slaked) lime, oyster shells and blast furnace slag which can be used for liming soil if finely grind.

Significance of Liming:

- To raise the soil P^H

- Q. 1. Explain similarities and differences between industrial fertilizers and manure
- Q. 2. To mention the advantages of straight and mixed fertilizers of N, P and K
- Q. 3. Mention examples of straight and mixed fertilizers and classify them
- Q. 4. Compare the relative advantages and disadvantages of manures as compare industrial fertilizers.

How to maintain and improve soil fertility:

A fertile soil provides all essential plant nutrients in amounts which are suitable for the growth of most plants.

How can a soil be made more fertile

1. Good cropping system

2. Adding manure to the soil
3. Adding industrial fertilizers to the soil

1.GOOD CROPPING SYSTEM:

Crop rotation should be practiced. Every season, another crop should be planted on a given field. Legumes should be rotated with cereals, shallow rooted plants with deep rooted ones .

2.ADDING MANURE:

Manures are organic materials that can be added to the soil to increase soil fertility.

E.g. Kraal manure – from cattle kraal

Farmyard manure – wastes from animals

Compost manure-mixture of soil and decomposing organic matter

Bio gas manure – from effluent of bio gas plants

3.ADDING INDUSTRIAL FERTILIZERS:

- Fertilizers are most inorganic compounds which contain one or more plant nutrients in a concentrated form.

E.g. Nitrogen fertilizers, phosphorus fertilizers, potassium fertilizers.

Similarities between manure and industrial fertilizers.

- They both increase humus to the soil and promote good soil structure
- Both manure and industrial fertilizers contain minerals Nitrogen, phosphorus and potassium which are essential for plant growth.

Differences between manure and industrial fertilizers

Manure	Industrial fertilizers
1. It is organic material	1. It is inorganic compound

2. It is composition varies depending on the type of manure	2. It is composition is fixed
3. It is less toxic	3. It is toxic if used in large amounts
4. It has low contents of nutrients	4. It has high content of nutrients

PHYSICAL CHEMISTRY 1.5-SOLUBILITY

What is solubility ?

Is amount of substances dissolves in water completely so as give free ions.

Since the amount can be in gram (g) or in moles (mol) then the S.I unit for solubility is g/L or g/dm³

Also solubility can be expressed in mol / dm³ or mol/L . When solubility of substances is expressed in mol / dm³ and that is called molar solubility.

What is molar solubility ?

It is amount of solute in moles dissolve in a given dm³ of of solvent to give free ions.

When solubility is expressed in it's S.I unit , that is the same as concentration in g /L or g /dm³ and when it is expressed as molar solubility , that is the same as molarity.

example. a) Define the following :

i) Solubility

ii) Molarity solubility

b) Calculate the following solubility in g /L 0.0004 M NaOH :-

i) Solubility is defined as the amount of a substance dissolve in water completely to give free ions.

ii) Molar solubility is the amount of solute dissolves in moles in a given dm³ of to give free ions.

Solution :-

$$\begin{aligned} \text{i) NaOH Solubility} &= \text{solubility in mol / dm}^3 \times \text{Mr} \\ &= 0.0004 \times 40 \\ &= 0.016 \text{ g/L} \end{aligned}$$

The solubility of NaOH is 0.016 g /L

Solution:

ii) $2.7 \times 10^{-3} \text{ mol /dm}^3 \text{ Ca(OH)}_2$

$$\begin{aligned} \text{Solubility} &= \text{molar} \times \text{Mr} . \\ &= 2.7 \times 10^{-3} \times 74 \\ &= 0.1998 \text{ g/ L} \end{aligned}$$

The Solubility of Ca(OH)₂ is 0.998 g/ L .

iii) 3.24 g of sodium chloride .

Solution:

Solubility = Molar Solubility x Mr

$$= 3.24 \text{ g/L} \times 58.5$$

$$58.5$$

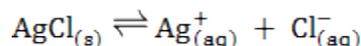
$$= 3.24 \text{ g/L}$$

These solubility of sodium chloride = 3.24 g/L

SOLUBILITY PRODUCT OF SPARINGLY SOLUBLE SALTS

Many salts which are referred to as insoluble do infact dissolve to a small/limited extent. They are called sparingly or slightly soluble salts.

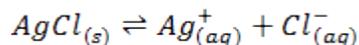
In a saturated solution, equilibrium exists between the ions and undissolved salt.



NOTE;

There is a limited number of ions that can exist together in water and this cannot be increased by adding more salts.

In a saturated solution of AgCl in contact with the ions, the equilibrium law can be applied



$$K_c = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

The concentration of solid is taken as constant at constant temperature

$$K_c = \frac{[\text{Ag}^+][\text{Cl}^-]}{K}$$

$$K_c \times K = [\text{Ag}^+][\text{Cl}^-]$$

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

K_{sp} = Solubility product constant.

By definition, K_{sp} is the product of maximum concentration of ions of sparingly soluble salt that can exist together in a solution at a given temperature.

OR

It is the product of concentration of all the ions in a saturated solution of sparingly soluble salts.

OR

Solubility product is the product of ions concentration in mol/dm³ of a certain solution raised to their stoichiometric coefficient

Solubility product is denoted by K_{sp}

The unit for K_{sp} depends on the stoichiometric coefficients of the respective ions of such particular substance

How to write K_{sp} expressions

In writing K_{sp} expressions one should look on

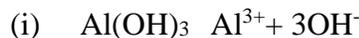
Ionization equation should be written correctly and balanced.
Stoichiometric coefficients become powers of the respective ion.

Generally, for sparingly soluble salts



$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

E.g. Write K_{sp} expression for the following equilibrium



Solutions:

(i) $K_{sp} = [Al^{3+}] [OH^-]^3$

(ii) $K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$



$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$$

Significance of K_{sp}

(i) K_{sp} value is used in the prediction of occurrence of precipitates if ions in the solution are mixed.

If concentrations of ions are enough to reach K_{sp} value, salt precipitation occurs

Determination of Solubility product from solubility measurements

The K_{sp} value of the salt can be determined from its solubility in moles per litre (mol/L)

When concentrations are given in any other units such as g/L, they must be converted to mol/L

Example 1

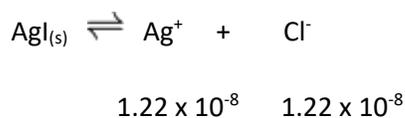
The solubility of AgI is 1.22×10^{-8} mol/L. Calculate the K_{sp} for AgI

Solution



Each 1 mole of AgI that dissolves gives 1 mole of Ag⁺ and 1 mole of I⁻ in solution, concentration of each ion solution is 1.22×10^{-8} mol/L.

Hence



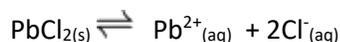
$$K_{sp} = [\text{Ag}^+] [\text{Cl}^-]$$

$$= (1.22 \times 10^{-8})^2$$

$$K_{sp} = 1.4884 \times 10^{-16} \text{ mol}^2\text{L}^{-2}$$

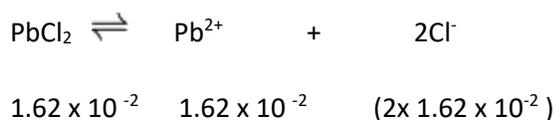
Example 2

PbCl₂ dissolves to a slightly extent in water according to the equation



Calculate the K_{sp} for PbCl₂ if (Pb²⁺) has been found to be 1.62×10^{-2} mol l⁻¹.

Solution



$$K_{sp} = [\text{Pb}^{2+}] [\text{Cl}^-]^2$$

$$= 1.62 \times 10^{-2} \text{ molL}^{-1} \times 1.0497 \times 10^{-3} \text{ mol}^2\text{L}^{-2}$$

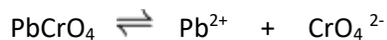
$$K_{sp} = 1.7005 \times 10^{-5} \text{ mol}^3\text{L}^{-3}$$

Example 3

The solubility of Pb(CrO₄) is 4.3×10^{-5} g l⁻¹. Calculate the K_{sp} of Pb(CrO₄)

(Pb = 207, Cr = 52, O = 16)

Solution



$$4.3 \times 10^{-5} \text{gl}^{-1} \quad 4.3 \times 10^{-5} \text{gl}^{-1} \quad 4.3 \times 10^{-5} \text{gl}^{-1}$$

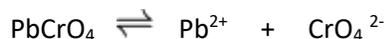
To calculate the molar mass of (PbCrO₄)

$$\text{Pb}(207) + \text{Cr}(52) + \text{O}(16)4 = 323 \text{gmol}^{-1}$$

$$323 \text{g} \rightarrow 1 \text{mole}$$

$$4.3 \times 10^{-5} \rightarrow x$$

$$x = 1.33 \times 10^{-7} \text{mol}$$



$$1.33 \times 10^{-7} \quad 1.33 \times 10^{-7} \quad 1.33 \times 10^{-7}$$

$$K_{sp} = [\text{Pb}^{2+}] [\text{CrO}_4^{2-}]$$

$$= (1.33 \times 10^{-7})^2$$

$$K_{sp} = 1.76 \times 10^{-14} \text{M}^2$$

Example 4

100 ml sample is removed from water solution saturated with MgF₂ at 18°C. The water is completely evaporated from the sample and 7.6mg of MgF₂ is obtained. What is the K_{sp} value for MgF₂ at 18°C

Solution

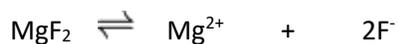
$$V = 100 \text{ ml}$$

$$m = 0.076 \text{g.}$$

$$62 \text{g} \rightarrow 1 \text{ mole}$$

$$0.076 \text{g} \rightarrow x$$

$$x = 1.22 \times 10^{-3} \text{ molel}^{-1}$$



$$1.22 \times 10^{-3} \quad 1.22 \times 10^{-3} \quad (2 \times 1.22 \times 10^{-3})$$

$$K_{sp} = [Mg^{2+}] [F^-]^2$$

$$= (1.22 \times 10^{-3}) (2.44 \times 10^{-3})$$

$$K_{sp} = 7.33 \times 10^{-9} \text{ mol l}^{-1}$$

DETERMINATION OF MOLAR SOLUBILITY FROM K_{sp} VALUE

If the K_{sp} value is known, the molar solubility can be obtained since K_{sp} shows the maximum concentration of ions which exists together in a solution.

Example 1

Calculate the molar solubility of Ag₂CrO₄ in water at 25°C if its K_{sp} is 2.4 × 10⁻¹² M³.



Let the solubility be S



$$S \qquad 2S \qquad S$$

$$\text{From } K_{sp} = [Ag^+]^2 [CrO_4^{2+}]$$

$$2.4 \times 10^{-12} = (2S)^2$$

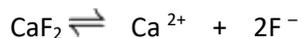
$$2.4 \times 10^{-12} = 4S^3 \implies S = \sqrt[3]{\frac{2.4 \times 10^{-12}}{4}}$$

$$S = 8.434 \times 10^{-5} \text{ mol l}^{-1}$$

Example 2

Calculate the solubility of CaF₂ in water at 25°C if its solubility product is 1.7 × 10⁻¹⁰ M³

Solution



$$S \qquad S \qquad 2S$$

$$K_{sp} = [Ca^{2+}] [F^-]^2$$

$$=S(2S)^2$$

$$1.7 \times 10^{-10} = 4S^3$$

$$S^3 = \frac{1.7 \times 10^{-10}}{4} = 4.25 \times 10^{-11}$$

$$S = 3.489 \times 10^{-4} \text{ mol L}^{-1}$$

SOLUBILITY AND COMMON ION EFFECT

The solubility of sparingly soluble salts is lowered by the presence of second solute that furnishes (produce) common ions. Since the concentration of the common ion is higher than the equilibrium concentration, some ions will combine to restore the equilibrium (Le Chatelier's principle)

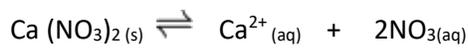
Example 1

In solubility equilibrium of CaF_2 , adding either Calcium ions or F^- ions will shift the equilibrium to the left reducing the solubility of CaF_2 .

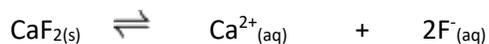
- Find the molar solubility of CaF_2 ($K_{sp} = 3.9 \times 10^{-11} \text{ M}^3$) in a solution containing 0.01M $\text{Ca}(\text{NO}_3)_2$

Solution

Since $\text{Ca}(\text{NO}_3)_2$ is strong electrolyte, it will dissociates completely according to the equation.

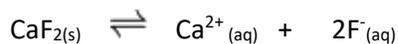


$$0.01 \qquad \qquad 0.01 \qquad 2(0.01)$$



$$S \qquad \qquad S \qquad 2S$$

Letting solubility of CaF_2 be S



$$S \qquad \qquad S \qquad 2S$$

$$0.01$$

From Ca (NO₃)₂

In absence of Ca(NO₃)₂

$$K_{sp} = [Ca^{2+}] [F^-]^2$$

$$3.9 \times 10^{-11} = S (2S)^2$$

$$3.9 \times 10^{-11} = 4S^3$$

$$S^3 = 9.75 \times 10^{-12}$$

$$S = 2.136 \times 10^{-4} \text{ molL}^{-1}$$

Assume the concentration of Ca²⁺ from Ca (NO₃)₂ does not affect the solubility of CaF₂ then concentration of Ca²⁺ will be

$$[Ca^{2+}] = S + 0.01$$

$$= (2.136 \times 10^{-4}) + 0.01$$

$$0.0102 \text{ M} \approx 0.01$$

Since the K_{sp} value is very small, the expression 0.01 + S is approximated to 0.01

$$K_{sp} = [Ca^{2+}] [F^-]^2$$

$$3.9 \times 10^{-11} = 0.01 (2S)^2$$

$$3.9 \times 10^{-11} = 0.04S^2$$

$$S^2 = 9.75 \times 10^{-10}$$

$$S = 3.122 \times 10^{-5} \text{ mol/l}$$

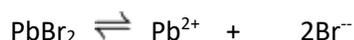
Conclusion

Hence, because of common ions effect, the solubility of CaF₂ has reduced from 2.13 x 10⁻⁴ M to 3.122 x 10⁻⁵ M

Example 2

Calculate the mass of PbBr₂ which dissolves in 1 litre of 0.1M hydrobromic acid (HBr) at 25°C (K_{sp} for PbBr₂ at 25°C is 3.9 x 10⁻⁸ M³) (Pb = 207, Br = 80)

Solution



S S 2S

0.1 After adding HBr

At equilibrium



S S 2S + 0.1

2S + 0.1 = 0.1 since K_{sp} is very small

$$K_{sp} = [\text{Pb}^{2+}][\text{Br}^-]^2$$

$$3.9 \times 10^{-8} = S(0.1)^2$$

$$S = 3.9 \times 10^{-6} \text{ mol l}^{-1}$$

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

$$C = \frac{m}{M}$$

$$3.9 \times 10^{-6} = \frac{m}{207 + (2 \times 80)}$$

$m = 1.43 \times 10^{-3} \text{ g l}^{-1}$ of PbBr_2

Example 3

The solubility product of BaSO_4 in water is $10^{-10} \text{ mol}^2 \text{ l}^{-2}$ at 25°C

(a) Calculate the solubility in water in mol dm^{-3}

(b) 0.1 M of Na_2SO_4 solution is added to a saturated solution of BaSO_4 . What is the solubility of BaSO_4 now?

Example 4

Calculate the molar solubility of $\text{Mg}(\text{OH})_2$ in

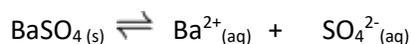
(a) Pure water

(b) 0.05M MgBr_2

(c) 0.17 M KOH

(K_{sp} for Mg(OH)₂ is 7.943 x 10⁻¹² M³)

(a) Solution



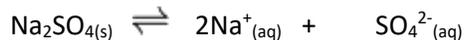
S S S

$$10^{-10} \text{mol}^2 \text{l}^{-2} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}]$$

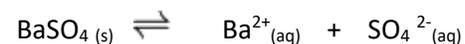
$$10^{-10} \text{mol}^2 \text{l}^{-2} = S^2$$

$$S = 1 \times 10^{-5} \text{ mol/dm}^3$$

(b) Solution



0.1 2 x 0.1=0.2 0.1



S S S + 0.1 after adding Na₂SO₄

S + 0.1 ≈ 0.1 K_{sp} is very small

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

$$1 \times 10^{-4} \text{ mol}^2 \text{l}^{-2} = S(0.1)$$

$$S = 1 \times 10^{-19} \text{ mol l}^{-1}$$

$$S = 1 \times 10^{-9} \text{ mol l}^{-1}$$

The value of S has reduced after adding NaSO₄

4. (a) Solution



S S 2S

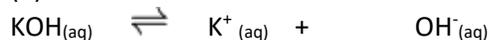
$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^{-}]^2$$

$$7.943 \times 10^{-12} = 4S^3$$

$$S^3 = 1.985 \times 10^{-12}$$

$$S = 1.25 \times 10^{-4} \text{ mol l}^{-1}$$

(b) Solution



$$0.17 \qquad 0.17 \qquad 0.17$$



$$S \qquad S \qquad 2S$$

$$2S + 0.17$$

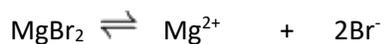
$$2S + 0.17 = 0.17 \text{ Ksp is very small}$$

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

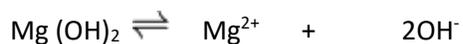
$$7.943 \times 10^{-12} \text{ M}^3 = S(0.17)^2$$

$$S = 2.748 \times 10^{-10} \text{ mol l}^{-1}$$

(c) Solution



$$0.05 \qquad 0.05 \qquad 2 \times 0.05 \approx 0.1$$



$$S \qquad S + 0.05 \qquad 2S$$

$$S + 0.05 \approx 0.05 \text{ Ksp is very small}$$

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$7.943 \times 10^{-12} \text{ M}^3 = (0.05)(2S)^2$$

$$S^2 = 3.9715 \times 10^{-11}$$

$$S = 6.3 \times 10^{-6} \text{ mol l}^{-1}$$

PRECIPITATION OF SPARINGLY SOLUBLE SALTS

If the equilibrium of sparingly soluble salts are approached by starting with ions in solutions and producing pure undissolved solute, then the process involved is precipitation reaction.

By definition, precipitation is the reaction where solid particles are formed by mixing ions in solution.

A substance will start precipitating as the reaction quotient (Q) becomes greater than the solubility product. Therefore, knowing the solubility product of a salt, it is possible to predict whether on mixing the solutions of ions precipitations will occur or not and what concentration of ions are required to begin the precipitation of the salt.

As for K_{sp} , Q_{sp} are also given by

$$Q_{sp} = [A^{y+}]^x [B^{x-}]^y$$

Where $[A^{y+}]$ and $[B^{x-}]$ are the actual ions concentrations and not necessary those at equilibrium

If $Q_{sp} = K_{sp}$ the system is at equilibrium.

If $Q_{sp} < K_{sp}$ The solution is unsaturated and precipitation does not occur.

If $Q_{sp} > K_{sp}$ the solution is super saturated and precipitations occurs. REASON : So as to maintain K_{sp} value.

Example 1

The concentration of Ni^{2+} ions in a solution is $1.5 \times 10^{-6} M$. If enough Na_2CO_3 is added to make the solution $6.04 \times 10^{-4} M$ in the CO_3^{2-} ions will the precipitates of Nickel carbonate occur or not?

K_{sp} for Ni^{2+} $6.6 \times 10^{-9} M^2$

Solution



$$Q_{sp} = [Ni^{2+}][CO_3^{2-}]$$

$$= (2 \times 1.5 \times 10^{-6})^2 (6.04 \times 10^{-4})$$

$$Q_{sp} = 5.4 \times 10^{-4} M^2$$

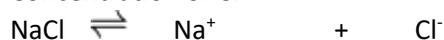
$Q_{sp} > K_{sp}$ (Precipitation will occur)

Example 2

Predict whether there will be any precipitates on mixing 50cm³ of 0.001m NaCl with 50cm³ of 0.01m of AgNO₃ solution. (K_{sp} for AgCl $1.5 \times 10^{-10} M^2$)

Solution

Concentration of Cl⁻



$$0.01 \quad 0.001 \quad 0.001$$

$$0.001 \rightarrow 1000cm^3$$

$$x \rightarrow 50\text{cm}^3$$

$x = 5 \times 10^{-5}$ moles (These are in 100cm³ since we added 50cm³ of AgNO₃)

Now 50×10^{-5} moles $\rightarrow 100 \text{ cm}^3$

$$x \rightarrow 1000\text{cm}^3$$

$$x = 5 \times 10^{-4} \text{ mol l}^{-1}$$

Now for Ag⁺



0.01m 0.01m 0.01m

0.01 moles $\rightarrow 1000\text{cm}^3$

$$x \rightarrow 50\text{cm}^3$$

$x = 5 \times 10^{-4}$ moles

5×10^{-4} moles $\rightarrow 100\text{cm}^3$

$$x \rightarrow 1000\text{cm}^3$$

$x = 3 \times 10^{-3} \text{ mol l}^{-1}$



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

$$Q_{sp} = (5 \times 10^{-3})(5 \times 10^{-4})$$

$$Q_{sp} = 2.5 \times 10^{-6} \text{ M}^2$$

$$Q_{sp} > K_{sp}$$

Precipitation will occur.

Example 3

If a solution contains 0.001M CrO₄²⁻, what concentration of Ag⁺ must be exceeded by adding AgNO₃ to the solution to start precipitation Ag₂CrO₄? Neglect any increase in volume due to additional of AgNO₃ (K_{sp} of Ag₂CrO₄ = 9.0 x 10⁻¹²M²)

Solution



$$K_{sp} = [\text{Ag}^+][\text{CrO}_4^{2-}]$$

$$9 \times 10^{-12} = [\text{Ag}^+]^2 \cdot 0.001$$

$$[\text{Ag}^+]^2 = 9 \times 10^{-9}$$

$$[\text{Ag}^+] = 9.48 \times 10^{-5} \text{ M}$$

Example 4

The K_{sp} value of AgCl at 18°C is $1 \times 10^{-10} \text{ mol}^2\text{l}^{-2}$, What mass of AgCl will precipitate if 0.585g of NaCl is dissolved in 1l of saturated solution of AgCl.

(Ag = 108, Na = 23, Cl = 35.5)

Solution



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

$$1 \times 10^{-10} = S^2$$

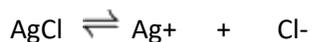
$$S = 1 \times 10^{-5} \text{ M}$$

$$n = \frac{m}{Mr}$$

$$= \frac{0.585}{23 + 35.5}$$

$$n = 0.01 \text{ moles}$$

$$n = 0.01 \text{ moles}$$



$$S \quad S \quad 0.01 + S$$

$$0.01 \quad S \approx 0.01$$

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

$$1 \times 10^{-10} = S(0.01)$$

$$S = 1 \times 10^{-8} \text{ mol l}^{-1} \text{ (Solubility has decreased)}$$

To find the amount which has precipitated,

$$S = 10^{-5} - 10^{-8}$$

$$S = 9.99 \times 10^{-6} \text{M}$$

$$9.99 \times 10^{-6} \text{ mole} \rightarrow 1 \text{ l}$$

$$143.5 \text{g} \rightarrow 1 \text{ mole}$$

$$9.99 \times 10^{-6}$$

$$m = 1.43 \times 10^{-3} \text{g of AgCl}$$

Question 1

Should precipitation of PbCl_2 be formed when 155cm^3 of 0.016M KCl is added to 245cm^3 of 0.175M $\text{Pb}(\text{NO}_3)_2$? K_{sp} is 3.9×10^{-5}

Question 2

If concentration of Zn^{2+} in 10cm^3 of pure water is $1.6 \times 10^{-4} \text{M}$. Will precipitation of $\text{Zn}(\text{OH})_2$ occur when 4mg of NaOH is added. (K_{sp} for $\text{Zn}(\text{OH})_2$ is 1.2×10^{-17})

Question 3

A cloth washed in water with manganese concentration exceeding 1.8×10^{-6} may be stained as $\text{Mn}(\text{OH})_2$ (K_{sp} 4.5×10^{-14}). At what pH will Mn^{2+} ions concentration be equal to $1.8 \times 10^{-6} \text{M}$

Solution 1



$$K_{sp} = [\text{Mn}^{2+}][\text{OH}^-]^2$$

$$4.5 \times 10^{-14} = 1.8 \times 10^{-6} [\text{OH}^-]^2$$

$$[\text{OH}^-]^2 = 2.5 \times 10^{-8}$$

$$[\text{OH}^-] = 1.58 \times 10^{-4} \text{M}$$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$= -\log(1.58 \times 10^{-4})$$

$$\text{p}(\text{OH}) = 3.801$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14 - 3.801$$

$$\text{pH} = 10.199$$

Solution 2

We find concentration of OH⁻ in NaOH

$$n = \frac{m}{Mr}$$

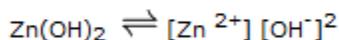
$$= \frac{4 \times 10^{-3}}{40}$$

$$n = 1 \times 10^{-4} \text{ moles}$$

$$1 \times 10^{-4} \text{ moles} \rightarrow 10 \text{cm}^3$$

$$x \quad \quad \quad \rightarrow 1000 \text{cm}^3$$

$$x = 0.01 \text{ M}$$



$$Q_{sp} = [\text{Zn}^{2+}] [\text{OH}^-]^2$$

$$= (1.6 \times 10^{-4})(0.01)^2$$

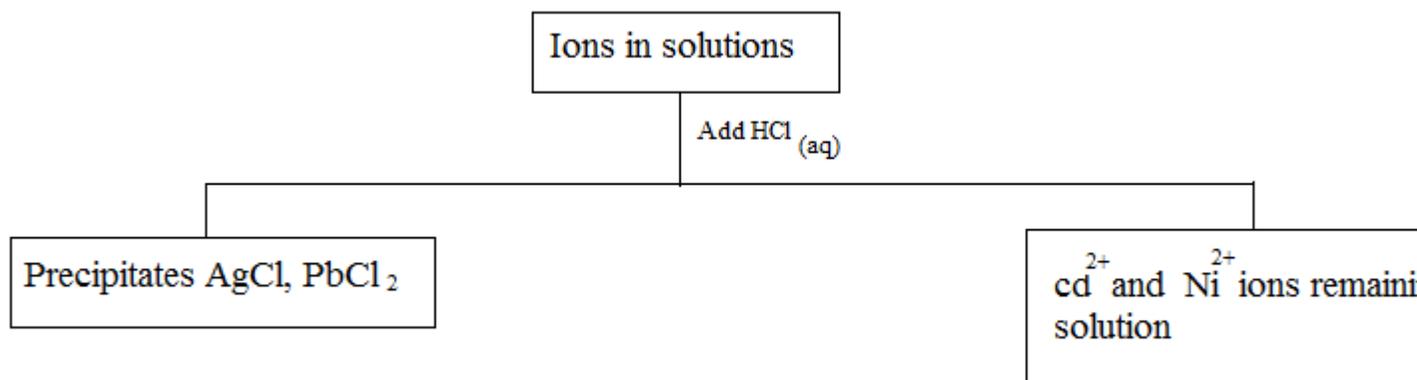
$$Q_{sp} = 1.6 \times 10^{-8} \text{ M}^3$$

$Q_{sp} > K_{sp}$ Hence precipitation will occur

PRECIPITATION REACTION IN QUALITATIVE ANALYSIS (ION SEPARATION)

Qualitative analysis refers to a set of laboratory procedures that can be used to separate and test for presence of ions in solutions. This can be done by precipitations with different reagents or by selective precipitation.

Consider an aqueous solution which contains the following metal ions Ag⁺, Pb²⁺, Cd²⁺ and Ni²⁺ which have to be separated. All the ions form very insoluble sulphides (Ag₂S, PbS, CdS, NiS). Therefore sulphide is a precipitating reagent of all the above metal ions. However, only two of them form insoluble chlorides (AgCl and PbCl) i.e aqueous HCl can be used to precipitate them while the other two ions remain in solution.



The separation of PbCl_2 from AgCl is not difficult since PbCl_2 dissolves in hot water while AgCl remains insoluble

The separation of Cd^{2+} and Ni^{2+} can be done by selective precipitation with sulphide ions by considering the K_{sp} values of the two compounds.

Example $K_{sp}(\text{CdS}) = 3.6 \times 10^{-29}$ and $K_{sp}(\text{NiS}) = 3.0 \times 10^{-21}$

The Compound that precipitate first is the one whose K_{sp} is exceeded first (one with smaller K_{sp}).

Suppose the solution contains 0.02M in both Cd^{2+} and Ni^{2+} , the sulphide ions concentration necessary to satisfy the solubility product expression for each metal sulphide is given by

$$\begin{aligned} \text{For Cds needed } [\text{S}^{2-}] &= \frac{K_{sp}}{[\text{Cd}^{2+}]} \\ &= \frac{3.6 \times 10^{-29}}{0.02} \\ [\text{S}^{2-}] &= 1.8 \times 10^{-27} \text{ M} \end{aligned}$$

Concentration of S^{2-} can exist in which the solution without precipitation (above which precipitation occurs)

$$\begin{aligned} \text{For Nis, needed } [\text{S}^{2-}] &= \frac{K_{sp}}{[\text{Ni}^{2+}]} \\ &= \frac{3.0 \times 10^{-21}}{0.02} \\ [\text{S}^{2-}] &= 1.5 \times 10^{-19} \text{ M} \end{aligned}$$

The much smaller S^{2-} concentration is needed to precipitate (CdS than to begin forming NiS thus CdS precipitate first before NiS.

Just before NiS begins to precipitate, how many Cd²⁺ remains in the solution?

Concentration of S²⁻ needs to be slightly in excess of 1.5 x 10⁻¹⁹ M for NiS to begin precipitation. The [Cd²⁺] that can exist in solution when the concentration of S²⁻ ions is 1.5 x 10⁻¹⁹ is given by

$$[Cd^{2+}] = \frac{K_{sp}}{[S^{2-}]}$$

$$= \frac{3.6 \times 10^{-29}}{1.5 \times 10^{-19}}$$

$$[Cd^{2+}] = 2.4 \times 10^{-10} \text{ M}$$

To find % of Cd²⁺ which has precipitated.

$$\frac{0.02 - 2.4 \times 10^{-10}}{0.02}$$

$$= 99.99\%$$

This means that we can separate Cd²⁺ and Ni²⁺ ions in aqueous solution by careful controlling concentration of S²⁻ ions.

Question 1

1. The K_{sp} of AgX are (AgCl) = 1.7 x 10⁻¹⁰

$$(AgBr) = 5.0 \times 10^{-13}$$

$$(AgI) = 8.5 \times 10^{-17}$$

A solution contains 0.01M of each of Cl⁻, Br⁻, and I⁻. AgNO₃ is gradually added to the solution. Assume the addition of AgNO₃ does not change the volume.

- Calculate the concentration of Ag⁺ required starting precipitation of all three ions.
- Which will precipitate first
- What will be the concentrations of this ion when the second ion start precipitating
- What will be the concentration of both ions when the third ion starts precipitation

Solution

$$\begin{aligned} \text{(a) For AgCl, needed } [Ag^+] &= \frac{K_{sp}}{[Cl^-]} \\ &= \frac{1.7 \times 10^{-10}}{0.01} \\ [Ag^+] &= 1.7 \times 10^{-8} \text{ M} \end{aligned}$$

$$\begin{aligned} \text{For AgBr, needed } [Ag^+] &= \frac{K_{sp}}{[Br^-]} \\ &= \frac{5 \times 10^{-13}}{0.01} \\ [Ag^+] &= 5 \times 10^{-11} \text{ M} \end{aligned}$$

$$\begin{aligned} \text{For AgI, needed } [Ag^+] &= \frac{K_{sp}}{[I^-]} \\ &= \frac{8.5 \times 10^{-17}}{0.01} \\ [Ag^+] &= 8.5 \times 10^{-15} \text{ M} \end{aligned}$$

(b) AgI will precipitate first because the Ag concentration is very small

(c) When second ion starts to precipitate ie AgBr start to precipitate, concentration of Ag will be

$$\begin{aligned} [Ag^+] &= \frac{K_{sp}}{5 \times 10^{-11}} \\ &= \frac{8.5 \times 10^{-17}}{5 \times 10^{-11}} \\ [Ag^+] &= 1.7 \times 10^{-6} \text{ M} \end{aligned}$$

(b) For $[I^-]$ when AgBr starts to precipitate

$$\begin{aligned} [I^-] &= \frac{K_{sp}}{1.7 \times 10^{-8}} \\ &= \frac{8.5 \times 10^{-17}}{1.7 \times 10^{-8}} \\ [I^-] &= 5 \times 10^{-9} \text{ M} \end{aligned}$$

For $[Br^-]$ when AgBr starts to precipitate

$$\begin{aligned}
 [\text{Br}^-] &= \frac{K_{sp}}{1.7 \times 10^{-8}} \\
 &= \frac{5 \times 10^{-13}}{1.7 \times 10^{-8}} \\
 [\text{Br}^-] &= 2.94 \times 10^{-5} \text{ M}
 \end{aligned}$$

Question 2

A solution contains 0.01M of Ag^+ and 0.02M of Ba^{2+} . A 0.01M solution of Na_2CrO_4 is added gradually to it with a constant stirring.

(a) At what concentration of Na_2CrO_4 will precipitation of Ag^+ ions and Ba^{2+} starts?

(b) What will precipitate first?

(c) What will be the concentration of the first precipitated species when the precipitation of the second species starts?

($K_{sp}(\text{Ag}_2\text{CrO}_4) = 2 \times 10^{-12} \text{ M}^3$, $K_{sp}(\text{BaCrO}_4) = 8.0 \times 10^{-11} \text{ M}^2$)

Question 3

To precipitate calcium and magnesium ions, ammonium oxalate $(\text{NH}_4)_2\text{C}_2\text{O}_4$ is added to a solution i.e 0.02M in both metal ions. If the concentration of the oxalate ions is adjusted properly, the metal oxalate can be precipitated separately.

(a) What concentration of oxalate ions ($\text{C}_2\text{O}_4^{2-}$) will precipitate the maximum amount of Ca^{2+} ions without precipitating Mg^{2+} ions.

(b) What concentration of Ca^{2+} ions remain when Mg^{2+} ions just begin precipitation.

(c) The K_{sp} of two slightly soluble salts, AB_3 and PQ_2 are each equal to 4.0×10^{-18} . Which salt is more soluble?

(d) What is the minimum volume of water required to dissolve 3g of CaSO_4 at 298K

($K_{sp}(\text{CaSO}_4) = 9.1 \times 10^{-6} \text{ M}^2$)

ANSWERS

Question 2 solution

Given $[\text{Ag}^+] = 0.01 \text{ M}$ $[\text{Ba}^{2+}] = 0.02 \text{ M}$

For Ag_2CrO_4 to begin precipitating

$$[\text{CrO}_4^{2-}] = \frac{K_{sp}}{[\text{Ag}^+]}$$

$$= \frac{2 \times 10^{-12}}{0.01}$$

$$[\text{CrO}_4^{2-}] = 2 \times 10^{-10} \text{M}$$

For BaCrO₄, $[\text{CrO}_4^{2-}] = \frac{K_{sp}}{[\text{Ba}^{2+}]}$

$$= \frac{8 \times 10^{-11}}{0.02}$$

$$[\text{CrO}_4^{2-}] = 4 \times 10^{-9} \text{M}$$

ii. Ag₂CrO₄ will start to precipitate since of the lower concentration of CrO₄²⁻ needed.

iii. When BaCrO₄ start to precipitate

$$[\text{Ag}^+] = \frac{K_{sp}}{4 \times 10^{-9}}$$

$$[\text{Ag}^+] = \frac{2 \times 10^{-12}}{4 \times 10^{-9}}$$

$[\text{Ag}^+] = 5 \times 10^{-4}$ (This is much smaller than the original concentration which was 0.01M)

$$[\text{Ag}^+] = 5 \times 10^{-4} \text{M}$$

Question 3 solution



S S S

$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

$$9.1 \times 10^{-6} = S^2$$

$$S = 3.02 \times 10^{-3} \text{ mol l}^{-1}$$

Molecular mass of CaSO₄

$$\text{CaSO}_4 = 40 + 32 + 64$$

$$= 136 \text{ g mol}^{-1}$$

$$136 \text{ g} \rightarrow 1 \text{ mol}$$

$$3g \rightarrow x$$

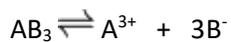
$$x = 0.022 \text{ moles}$$

$$3.02 \times 10^{-3} \text{ moles} \rightarrow 1 \text{ dm}^3$$

$$0.022 \text{ moles} \rightarrow x$$

$$x = 7.3 \text{ dm}^3$$

Question 4 solution



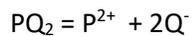
$$K_{sp} = [A^{3+}][B^-]^3$$

$$4 \times 10^{-18} = S(3S)^3$$

$$4 \times 10^{-18} = 27S^4$$

$$S^4 = 1.48 \times 10^{-19}$$

$$S = 1.96 \times 10^{-5} \text{ M for } AB_3$$



$$K_{sp} = [P^{2+}][Q^-]^2$$

$$4 \times 10^{-18} = S(2S)^2$$

$$S^3 = 1 \times 10^{-18}$$

$$S = 1 \times 10^{-6} \text{ M for } PQ_2$$

Therefore AB_3 will be more soluble.

ENVIRONMENTAL CHEMISTRY

ENVIRONMENT CONSERVATION

Is the protection of natural resources for the future use.

SIGNIFICANCES OF ENVIRONMENTAL CONSERVATION

- To avoid soil erosion.
- To ensure sufficient of water.
- To Adequate supply of resources.
- Reduce Ozone layer depletion.

PROTECTION AND UTILIZATION OF NATURAL RESOURCES

a) Protection of mineral (s) are against over exploitation.

Over exploitation: is the overuse of natural resources.

This cause scarcity of natural resources and environmental destruction.

Protection: - use of scrap metal is instead of extracting minerals from the ground, Recycling.

- Establishing other economic activities instead of mining industries.
- Reducing population pressure through establishment of family planning birth control. This reduces dependency in mining industries for exploiting use.

Note :- *Utilization:* Is the use of natural resources.

ENVIRONMENTAL DESTRUCTION

Environmental destruction means destroying the environment which make it not friendly to human survival.

Environmental destruction are die the following reasons.

- i) Agricultural chemicals .

ii) Damping of solid and liquid waste on the land and into large water masses , engravers, wells and oceans.

iii) Opening up gaseous effluent from industries into the air.

AGRICULTURE CHEMICALS

- Use of the pesticides and fertilizer.
- This causes a loss in biodiversity and soil destruction .
- Pesticides causes water pollution , facilitate growth of sea weeds causing oxygen deficiency for marine organism.
- Pollination decline, pesticides kills organisms which are agent of pollination.

EFFECT IN ORGANIC FERTILIZERS

- Soil Acidification.
- Energy consumption.
- Climate Change.

Suggestions

- Use of organic biodegradable.
- Manure.
- Avoid monoculture practices.

ii) DAMPING OF SOLID AND LIQUID INDUSTRIAL WASTE OF THE LAND AND INTO LARGE WATER

- Damping of solid and liquid industrial wastes on land and into large water cause deterioration of water quality and land in general.

Petroleum product, heavy metals from the industries may leads to environmental destruction.

- Destruction of environment from petroleum product is mainly due to accidental spills from the ships , tanker trucks , pipe lines and leaky of underground storage tanks.
- Heavy metals such as mercury often deposited with sediment in the bottoms of stream . They may become incorporated into plants.

iii) OPENING UP GASEOUS EFFICIENT FROM INDUSTRIES INTO THE AIR

- Working on the thermal plants and different plants that are used to manufacture different types of fertilizers or pesticides, ,also production of building materials can encourage of the production toxic materials which goes into air in form of smoke.

- Poisonous gases eg. Sulphur dioxide may be emitted also inform of smoke. These cause destruction of air, causing harmfully diseases to human beings.

ENVIRONMENTAL MANAGEMENT INTERVENTIONS

Environment management and interventions should be done through the following: -

- i) Management waste.
- ii) Chemical treatment of urban sewage.
- iii) Chemical treatment of urban supplies of edible / portable water.

POLLUTION

Environmental pollution is the contamination of air, water, and land form man made wastes. Pollution leads to depletion of ozone layer global warming and climate change.

1. WATER POLLUTION (AQUATIC POLLUTION)

Water pollution is the contamination of water by foreign matter that deteriorates the quality of water. It occurs in lakes, oceans and rivers.

- It involves the release of toxic substances, pathogens, substances that require much oxygen to decompose ,easy – soluble substances and radioactive substances.

i) Sources of water pollution

The major forms and the sources of water pollution are: -

a) Oil (Petroleum Product) discharged

- These including manufacture of plastics, lubricants solvents and synthetic fabrics fractional distillation of clued oil to produce vehicle fuel , paraffin wax , refinery gases for domestic cooking and bitumen for road surfacing and products is mainly due to accidental spills from the ships , tanker truckers , pipeline and leakage , from underground storage tanks.

b) *Synthetic chemical pesticides*

- Pesticides such as herbicides, Fungicides used in agriculture and public health programmes to control pests are important source of water pollution.
- They get into water sources through run – off and atmospheric transport and deposition.
- Pesticides accumulates in plants and animals, when they die, they spread to water sources, thus increasing water toxicity.

c) *Heavy metals*

Heavy metals such as mercury are dangerous pollutants. They are often deposited with sediment in the bottom of the streams. When deposited on surface they become incorporated in plants food crops and animals. If they dissolve and water is withdrawn for agriculture or human being use, poisoning can result.

i) *Management of water*

Water management refers to practices of planning developing, distribution and optimum, utilizing of water resources under defined water polices and regulations.

These are: -

- a) Management of water treatment of drinking water, industrial water ,sewage or waste water .
- b) Management of water resources.
- c) Management of irrigation.

Treatment of water maybe divided into two;-

- i) Purification of domestic use.
- ii) Treatment for specialized industrial application.

2. *AIR POLLUTION*

Air pollution includes all contaminants found in the atmosphere. These are dangerous substances can be either in the form of gases or particles.

Sources of air pollution are natural and human – based.

CAUSES OF AIR POLLUTION

The biggest causes are the operation of fossil fuel , burning power plants, and automobiles that combust fuel.

TYPES OF AIR POLLUTION

i) **Smog** – This is the first type of air pollution.

When smoke present in the atmosphere combine fog present in the air. A mixture formed is Smog or photochemical smog.

ii) **Green House effect** – It is formed due to the contamination of several important gases with the air. These gases are called green house gases.

eg. Methane, sulphur, nitrogen, Carbon monoxide, hydrogen and ozone. These are very harmful for the human skin and causes cancer.

Effects of air pollution

Air pollution affects human health, vegetation and livestock.

i) Effects on human health

Severe air pollution cause many fatal diseases and disorders some of the effects caused by inhaling polluted air are: -

a) Sulphur dioxide enters soft tissues causing drying of the mouth, scratchy throat and smarting eyes.

b) Hydrocarbons and many other air pollutants cause skin cancers.

c) Oxides carbon , sulphur , nitrogen diffuse into the blood and combine with haemoglobin causing reduction in it is oxygen carrying capacity.

ii) Effects on vegetation

Air pollution has serious harmful effects on vegetation.

Effects of air pollution on vegetation are :-

a) Sulphur dioxide causes chlorosis i.e. loss of effects on tress , plants and vegetation.

b) Oxides of nitrogen and fluorides reduces crop yields.

c) Photochemical Smog bleaches and blazes foliage of economically important of plants and crops.

iii) *Effects on Livestock*

General effects of air pollution on livestock are the same as in the case of human being.

Various fluorine compounds which fall on foliage plants are eaten by livestock causing abnormal calcification of bones and teeth, called fluoride toxicity. Fluorosis can causes loss of weight and frequent diarrhea in animals.

3. *LAND POLLUTION*

This is contamination of land surface through dumping , urban wastes , industrial wastes , mineral exploitation and misusing the soil by harmful ,agriculture process.

Causes Of land pollution

- Increase in urbanization is major cause of land pollution.
- Construction uses up forest. This leads to the exploitation and destruction of forests.
- Disposal of non – biodegradable wastes included containers, bottles and cans made of plastics, used cars and electronics goods used to the pollution of land.

EFFECTS OF LANDS POLLUTION

- Makes places look dirty due of tonnes and tonnes domestic wastes dumped without proper disposal of them.
- Land pollution affects respiratory system of human being.
- Land pollution has serious effects on wildlife. Flora which provides food and shelter to wild life destroyed.

Prevention of Land pollution

- People should be educated and made aware about the harmful effects of littering.
- Items used for the domestic purpose should be reused or recycled.
- Inorganic matter such as paper , glass , plastics and metals should be reclaimed and then recycled.

Questions:

1. Industries are among the leading sources of air pollutant.

- (a) Name four substances from industries which contribute to air pollution.
 - (b) Explain two other sources of air pollutants.
 - (c) Give 3 effects of air pollution.
 - (d) Explain how industrial worker can be protected against harmful chemical fumes.
2. (a) How is ozone formed?
- (b) What are the causes of depletion of ozone layer?
- (c) Explain harmful effects of depletion of ozone layer.
3. What is green house effect and what are its effects.
4. Write short notes on:-
- (i) Acid rain.
 - (ii) Smog.
 - (iii) Environmental effect caused by mining.
5. What do you understand by the term Eutrophication and its causes? – How does it threaten the development of marine life?

ANSWER:

Q1. (a) Substances;-

- . Carbon dioxide.
- . Carbon monoxide.
- . Methane.
- . Sulphur dioxide.

(b) Other sources:-

- . Burning fuels from car.

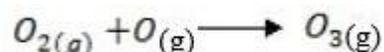
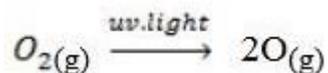
(c) Depletion of ozone layer:-

- . Spread of air borne diseases E.g. Tuberculosis.
- . Acid rain.
- . Global warming.

(d) Industrial worker can be protected against harmful chemical fumes by:-

- . using protective masks to protect them from harmful fumes.
- . Good ventilation systems in industries i.e. air circulation.
- . Close chambers for chemical processes.

2. (a) Ozone layer formation;-

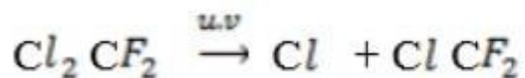


(b) Causes of depletion of ozone layer

- (a) *Natural destruction.*
- (b) *Artificial destruction.*

(a) Artificial destruction

- . Through gases e.g: CFC'S



This is a chain reaction which later leads to the destruction of ozone layer

(b) Natural destruction

. Using Nitrous oxide



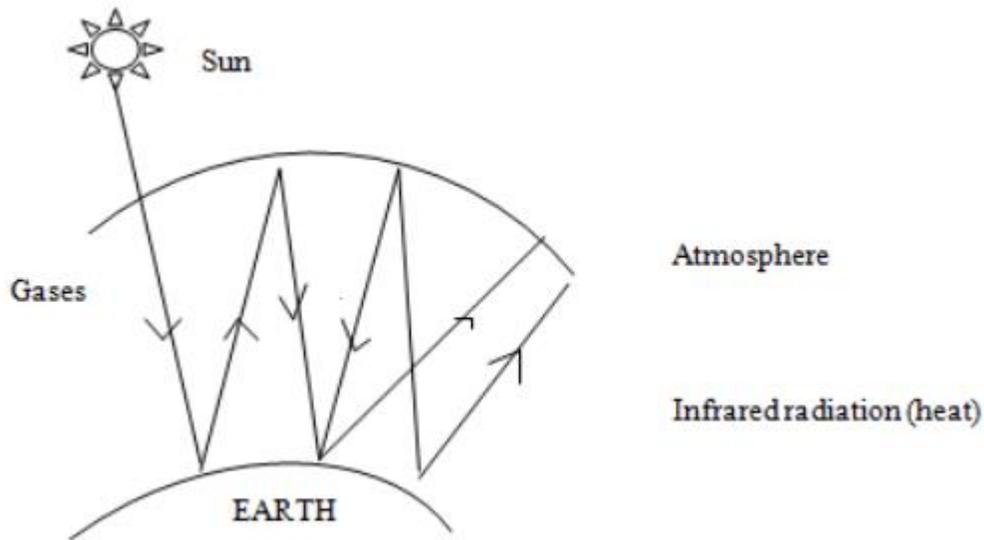
(c) Harmful effects of ozone layer depletion

- . It may result to skin cancer due to UV-rays.
- . Damage immune system leading to increase in viral infection.
- . Damage or death of marine plants and animals which are important to human survival.

3. - Green house effect

Is the process of trapping of heat in the atmosphere. This result in the overall increase in the average temperature of the Earth. The gases are the one's which

trap the heat in the atmosphere.



- Effects of green house:-

- . Leads to global warming. Ice caps will melt and this leads to increase in sea level which in turn lead to flooding (islands may disappear)
- . Change in weather patterns (unpredictable weather)

4. (i) *Effects of Acid Rain*:-

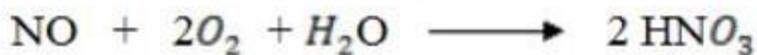
On Humans

- . Irritation of the respiratory system.
- . People with bronchitis become highly affected.

On the Soil

- . Soil not having proper liming becomes highly acidic.
- . Acid rain may cause corrosion on buildings.
- . It can cause the death of micro organism in water bodies or on the land.

Reactions for the formation of acidic rain



4. (ii) *Smog*: Contains soot, sulphur dioxide and other gases. It is usually found in cities.

5. Eutrophication:-

Is the process of adding of healthy adequate nutrition to water bodies or Addition of artificial or natural substances such as nitrates or phosphate through water runoffs sewages etc. This increases number of marine plants such as phytoplanktons.

Causes of Eutrophication

- It is due to adding of nutrients such as Nitrates phosphates.
- Runoffs from sewage.
- Overflow of sanitary sewers.
- Runoffs from industries.
- Untreated sewage.
- Overusing of pesticides and fertilizers.
- Cultivation near water bodies.

Effects of Eutrophication

. Decrease of biodiversity

Death of marine organisms. This is because of depletion of oxygen. When the phytoplanktons die, they decompose and marine organisms use up oxygen to decompose them. Hence the concentration of oxygen in water decreases which causes death of the marine organisms.

. Toxicity effect.

. Decrease in water transparency.

Questions:

1. Explain the meaning and significance of soil colloids.

2. Discuss the properties of soil colloids:

. Surface area.

. Electric charge.

. Ion exchange.

3. Explain the mechanism of ion exchange soil.

4. Describe cation exchange capacity of soil.

5. Calculation of percentage base saturation of a soil sample.

1. 6. (a) Why are the configurations of copper and chromium peculiar?

(b) Would you classify scandium and zinc as transition metal? Give the reasons for your answer.

(c) When is copper considered as transition metal?

(d) When does it not show transition behavior?

7. (i) Why are the elements with atomic numbers 21 to 30 classified together as a series in the periodic table?

(ii) List the main characteristics of these elements and their compounds

8. Explain the following observations:-

(i) Water molecules readily coordinate with cations of the above series but Hydronium ion (H_3O^+).

(ii) Addition of excess silver nitrate to an aqueous solution containing 0.01mole of $CoCl_3 \cdot 6NH_3$ leads to immediate precipitation of 0.03moles of silver chloride. However, similar addition to an aqueous

solution containing 0.01mole of $\text{CoCl}_3 \cdot 5\text{NH}_3$ leads to immediate precipitation of only 0.02 moles of silver chloride.

GENERAL QUESTIONS

1. Explain very briefly using equations where possible the extraction of copper from its commercial ore under the heading of reduction and

purification.

2. (a) Write down:

(i) Four reasons which justify the placement of hydrogen in group I of the periodic table

(ii) Four reasons which put hydrogen in group (vii) of periodic table

(b) (i) In which group do you think hydrogen should strictly belong

(ii) Give reasons for your answer for (i) above

(c) Describe the action of water on hydrides of period III

(d) Compare the thermal stability of carbonates of group I and II by using a specific example show their differences.

3. Comment with help of chemical equations where necessary in the following:

(i) Iron(II) chloride cannot be prepared by heating iron filings in a steam of chlorine gas.

(ii) Hydrochloric acid cannot be used as acidic medium during redox titration of KMnO_4 against FeSO_4 .

(iii) Solid $\text{Al}(\text{OH})_3$ is soluble in aqueous solution of NaOH .

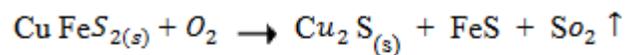
ANSWER:

1. Extraction of copper

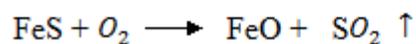
Steps:

Roasting:

Cu Fe^{S₂} is heated in plenty supply of air



Also



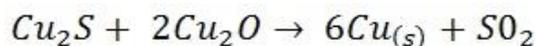
Now silica is added to Fe to remove FeO



Slag (removed)

Self – Reduction reaction:

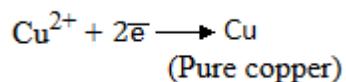
In self-reduction reaction, C^u₂S reacts with C^u₂O to form molten copper which later solidifies



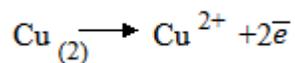
Purification:

Purification is done electrolytically.

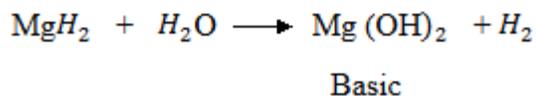
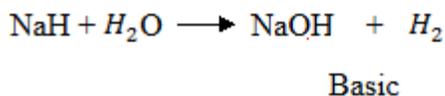
At cathode



At anode

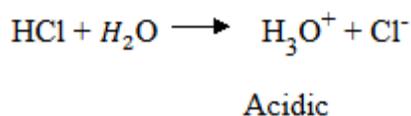
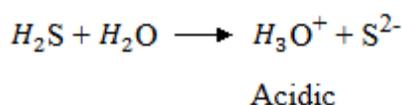


(c) Solution.



The hydrides of Na and Mg form basic solution.

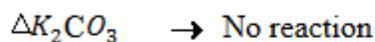
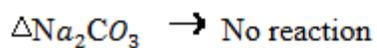
The hydride of sulphur – chlorine form acidic solutions due to presence of hydroxonium ion.



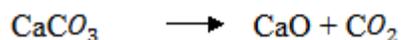
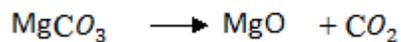
The hydrides of phosphorus i.e. phosphine is amphoteric

(d) Group I:

Carbonates of group I are thermally stable due to the large size of the atoms hence it will be capable of accommodating the carbonate ion.



Group II elements are easily decomposed



3. (i) Chlorine is a strong oxidizing agent hence it will oxidize iron straight to Iron III chloride



(ii) Cl^- may react with Fe^{3+} (titration product) which will form FeCl_3 which is red in colour.

This will make change in colour of MnO_4^- be difficult to account for (or difficult to notice)



1.

4. (a) Define the following

(i) Atomic radius

(ii) Ionization energy

(b) Contrast the action of heat on the following pairs of compounds

(i) NaN_3 and $\text{Ca}(\text{N}_3)_2$

(ii) $\text{N}_2\text{C}_3\text{O}_3$ and PbC_3O_3

(c) Describe how you can distinguish chemically the following pairs of compounds

(i) $\text{Mg}(\text{OH})_2$ and MgCO_3

(ii) NaCl and AlCl_3

(iii) CuSO_4 and $\text{Cu}(\text{N}_3)_2$

2. 5. (a) Explain the following by chemical equation. where necessary:

Solid carbonate of iron (iii) and Al have never been isolated

(i) Lime water is used to test the presence of CO_2 gas

(ii) When sodium hydrogen carbonate is added to copper (ii) sulphate effervescence is observed.

(iii) Lead hydroxide ppt dissolves in excess sodium hydroxide solution.

(b) By using equation. Where necessary describe:

(i) Two methods of preparing copper (ii) chloride in the lab.

(ii) Describe how ZnO reacts with both acid & bases.

(c) List 2 important uses of CaO in daily life

6. (a) Define

(i) Heat of reaction

(ii) Bond energy

(b) The enthalpy of formation of CCl_4 is $-135.5 \text{ KJmol}^{-1}$ and enthalpies of atomization of graphite and chloride are 715 and 121.2KJ respectively. Calculate the C-Cl bond energy

(c) (i) When 1g of C, H_2 and CH_4 are completely burnt in excess oxygen 32, 143 and 56 KJ of heat is liberated. Calculate the standard enthalpy of formation of CH_4

(ii) The heat of formation of Fe_2O_3 is $-824.0 \text{ KJmol}^{-1}$. What will ΔH of the reaction



ANSWERS:

4. (a) (i) Atomic radius is half the internuclear distance between two similar atoms covalently bonded by a single bond

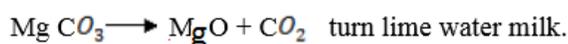
(ii) Ionization energy is the energy required to remove the most loosely held electron from the shell of an atom.

(b) (i) NaN^{O_3} is more stable than $\text{Ca}(\text{N}^{\text{O}_3})_2$ because sodium is highly electropositive hence bond energy between sodium and nitration is high hence it comes very stable.

(ii) $\text{N}^{\text{a}_2}\text{C}^{\text{O}_3}$ is more stable than PbC^{O_3} since sodium is highly electropositive hence there is high bond energy between sodium and

carbonate thus it becomes stable.

(c) (i) MgC^{O_3} will release C^{O_2} upon heating which will turn lime water milky.



(ii) AlCl_3 is a Lewis acid, hence it can react with a base to give a salt and HCl. But NaCl cannot react with a base

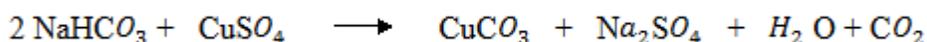


(iii) $\text{Cu}(\text{N}^{\text{O}_3})_2$ will form a brown ring due to formation of N^{O_2} but CuS^{O_4} does not.

5. (a) (i) FeC^{O_3} and AlC^{O_3} have never been isolated due to the small size of Fe and Al hence they have high polarization power. Hence they will decompose as soon as they are formed.

(ii) Lime water is used to test the presence of C^{O_2} since calcium carbonate is insoluble hence the it becomes milky.

(iii) The reaction between sodium bicarbonate and copper (ii) sulphate, effervescence is observed due to formation of carbon dioxide



(iv) Lead hydroxide ppt dissolves in sodium hydroxide due to the formation of a soluble complex compound



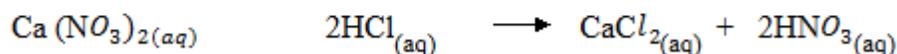
(b) (i) 1st method is by reacting copper carbonate with HCl



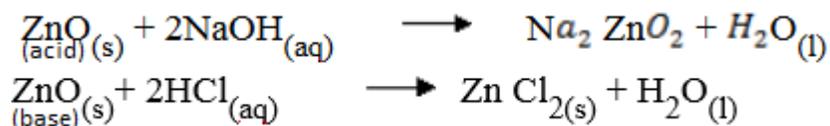
2nd method is by reacting Cu(OH)_2 with HCl



(ii) $\text{Ca(NO}_3)_2$ can be converted to CaCl_2 by reacting with HCl



(iii) ZnO is amphoteric hence it reacts with both acids and bases



(c) Uses of CaO

⇒ Manufacture of cement

⇒ Used as a drying agent for ammonium

⇒ Lining of furnaces

⇒ Formation of slag in Blast furnace

⇒ Making Ca^{C_2} which interns is used in making methane

6. (a) (i) Heat of reaction is the enthalpy change when number of moles of reactants as represented by a balanced chemical equation change into products.

Bond energy is the amount of energy required to break 1mole of a bond

$$\Delta H_r = -\Delta H_f + \Delta H_{\text{atm}} + 4\Delta H_{\text{atm}}$$

$$4(\text{C} - \text{Cl}) = (-135.5) + 715 + 4(121.1)$$

$$\text{C} - \text{C} \text{ I} = 333.725 \text{ KJ mol}^{-1}$$

(c) (i) Solution:

$$n = \frac{1}{2}$$

$$n = 0.083 \text{ moles}$$

$$0.083 \text{ moles} \longrightarrow 32 \text{ KJ}$$

$$1 \text{ mole} \longrightarrow x$$

$$x = 384 \text{ KJ mol}^{-1} \text{ of C}$$

$$nH_2 = \frac{1}{2}$$

$$= 0.5 \text{ moles}$$

$$0.5 \text{ moles} \longrightarrow 143 \text{ KJ}$$

$$1 \text{ mole} \longrightarrow x$$

$$x = 286 \text{ KJ mol}^{-1} \text{ of H}$$

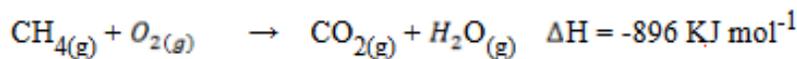
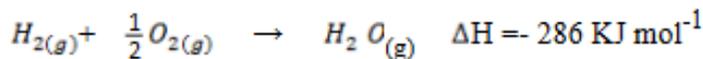
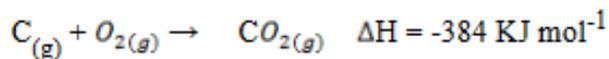
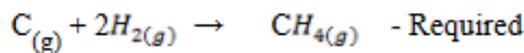
$$nCH_4 = \frac{1}{12+4}$$

$$= 0.0625 \text{ moles}$$

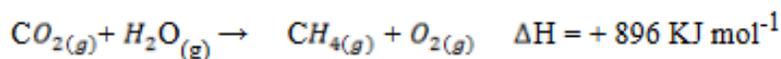
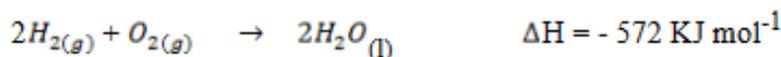
$$0.0625 \text{ moles} \longrightarrow 56 \text{ KJ}$$

$$1 \text{ mole} \longrightarrow x$$

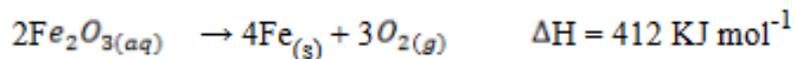
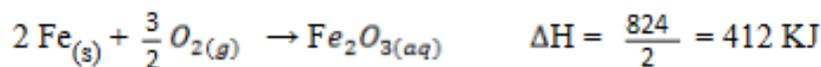
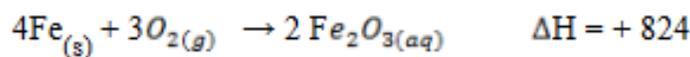
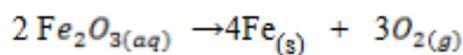
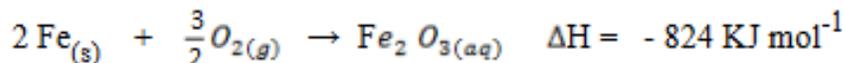
$$x = 896 \text{ KJ mol}^{-1}$$



Applying Hess's law



(ii) Solution:



7. Define the following terms

(a) (i) Hydrogen spectrum

Series of arrangement of various wavelength of radiation formed when hydrogen atoms are exposed

under high voltage electric discharge in

a discharge tube.

(ii) Convergence Limit

Is the point at which the distance from the nucleus is so large such that electron moving beyond this point cannot go back to its ground state:

(iii) Degenerate orbitals:

- . These are orbitals with equivalent energies
- . They share the same azimuthal quantum number.

(b) (i) Solution:

$$E_n = - \frac{2.176 \times 10^{-18} \text{ J}}{n^2}$$

$$\begin{aligned} \Delta_E &= E_2 - E_1 \\ &= -2.176 \times 10^{-18} \left(\frac{1}{9} - \frac{1}{1} \right) \end{aligned}$$

$$\Delta_E = 1.934 \times 10^{-18} \text{ J}$$

(ii) For shortest wavelength, $E_n, n = \infty$

$$\begin{aligned} \Delta_E &= E_\infty - E_1 \\ &= -2.176 \times 10^{-18} \left(\frac{1}{\infty} - \frac{1}{1} \right) \end{aligned}$$

$$\Delta_E = 2.176 \times 10^{-18}$$

$$2.176 \times 10^{-18} = \frac{hc}{\lambda}$$

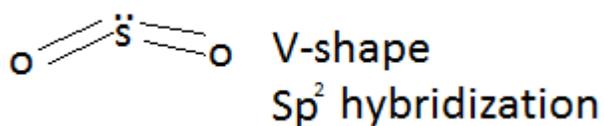
$$\lambda = \frac{hc}{2.176 \times 10^{-18}}$$

$$\frac{6.63 \times 10^{-34} \times 3 \times 10^8}{2.176 \times 10^{-18}}$$

$$\lambda = 9.13 \times 10^{-8} \text{ m}$$

(c) Solution

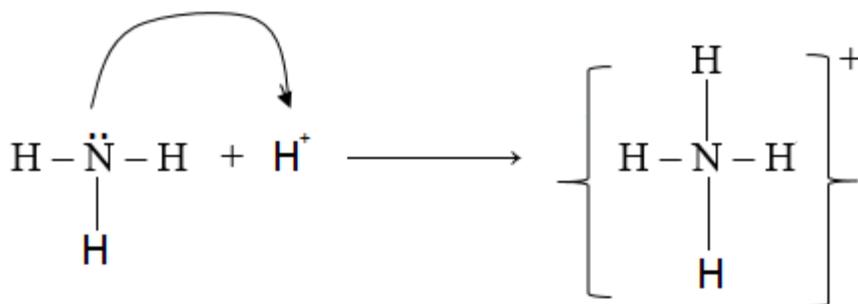
$$n = 2 \quad l = 1 \quad m_l = -1 \quad m_s = -\frac{1}{2}$$



VSEPR – Valency shell electron pair repulsion. We use lines to indicate the bonds

8. (a) Dative bond

It a type covalent bond in which one atom contributes both electrons



Van – Der Waals force is the dipole-dipole interaction between two non polar atoms.

London forces are temporary dipole dipole interactions.

Experiment:

A: Is a solution made by dissolving 4.28g/ 500 cm³ of KI^{O₃} of distilled water

B: Is 10[%] KI solution

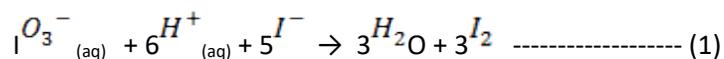
C: Is dilute H₂S^{O₄}

D: Is 0.12M solution Na₂ S₂ O₃ . SH₂ O

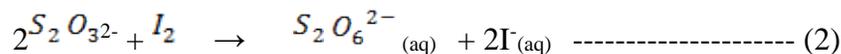
S: Is starch indicator solution

THEORY:

In acidic media Iodate ions (I^{O₃}) reacts with excess Iodine ions (I⁻) to liberate Iodine according to the following reaction



The iodine I liberate with a standard solution of thiosulphate ions according to the following reaction equation.



Procedure:

1. Pipette 25 cm³ of solution A into titration flask
2. Using measuring cylinder add 5 cm³ of solution B into titrating flask containing solution A
3. To the resultant solution in (2) above add 5 cm⁵ of solution C using measuring cylinder
4. Titrate the resulting solution in (3) above with a standard solution D till the colour becomes pale yellow. Then add few drops of solution S and continue to titrate till the blue colour just disappears.
5. Repeat the titration 3 times

Results:

The volume of pipette used was 10cm³

The volume of burette used was 50cm³

Burette reading

Titration No.	Pilot	1	2	3
Final reading (cm ³)	10.50	10.40	10.50	10.40
Initial reading (cm ³)	0.00	0.00	0.00	0.00
Titre value (cm ³)	10.30	10.40	10.40	10.40

10cm³ of solution A requires **10.40** cm³ of solution D for complete reaction

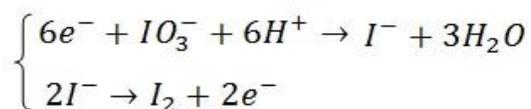
ANSWER THE FOLLOWING

- (a) Write down half reaction equation to show oxidation and reduction taking place in the reaction (1) and (2)
- (b) Calculate the number of moles of D used during titration
- (c) Calculate the number of moles of A used during titration
- (d) Calculate molarity of solution A'
- (e) Calculate the R.A.M of metal M in the formula MI^{O_3}

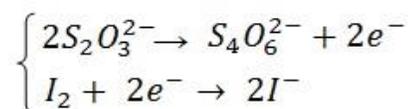
$$I = 127, O = 16$$

ANSWERS:

- (a) Half reactions in (1) and (2)



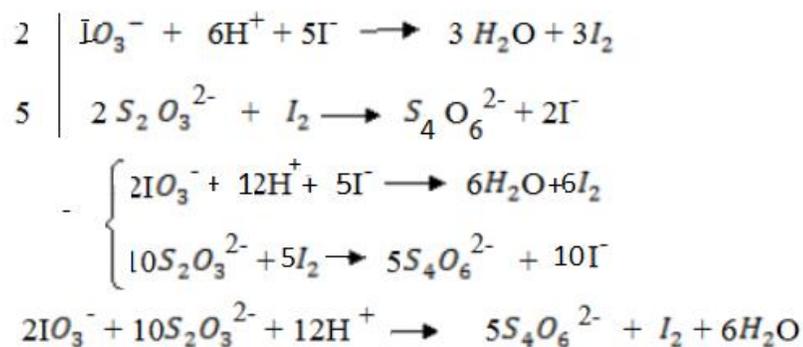
And also



- (b) Solution:

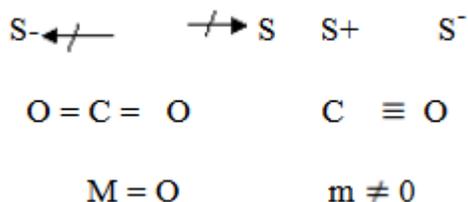
$$\begin{array}{l} 0.12 \text{ moles} \quad \longrightarrow \quad 1000 \text{ cm}^3 \\ x \quad \longrightarrow \quad 10.43 \text{ cm}^3 \end{array}$$

$$x = 1.25 \times 10^{-3} \text{ moles of D was used}$$



Conditions of hydrogen bonding

- (i) The highly electronegative atom should be small in size
- (ii) The more electronegative atom must have a lone pair
- (iii) Hydrogen should be bonded to one of the most electronegative atom N, O, F



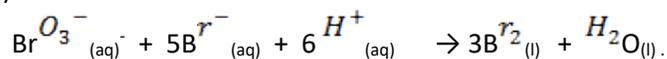
CO₂ is non polar since its dipole moment cancel each other since it is symmetrical. But CO is polar since it has a dipole moment caused by electronegativity difference between carbon and oxygen.

Na and K

- Na has higher Boiling Point since it has stronger metallic bond than K
- Ca has a small size with high charge (+2) hence high polarizing power to C^{l-}. Thus CaC₂ is more covalent. N^{a+} has high size with low charge (+1) this results to low p.p to CC⁻ hence NaCl is ionic.

1. 9. (a) Give the meaning of second order reaction and derive the units of its rate constant

(b) The reaction between BrO₃⁻ and Br⁻ in acidic medium is given by the equation.



The following table gives the results of four different experiments

Experiment. No	1	2	3	4
BrO_3^-	0.2	0.4	0.4	0.2
Br^-	0.2	0.2	0.4	0.2
H^+	0.2	0.2	0.2	0.4
Initial rates	1.56×10^{-2}	2.56×10^{-2}	5.12×10^{-2}	5.12×10^{-2}

Calculate:

- (i) Order of reaction with respect to each reactant
- (ii) The value of rate constant

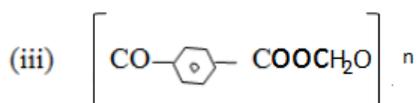
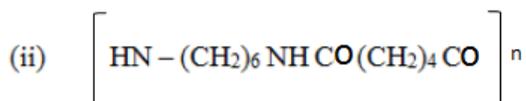
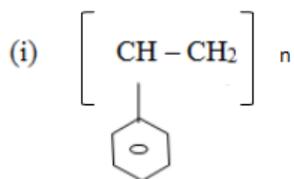
2. 10. (a) Briefly explain the meaning of:

(i) Metallurgy

(ii) An ore

(b) Describe the essential steps used during extraction of tin(Sn) show clearly the reaction equations

3. (c) Indicate the structure of monomers and polymerization method which is likely to be used in making of each of the following commercial polymer



- (d) Describe the preparation of benzanamine benzene
- (e) Write the chemical equation to show how propanamine reacts with
- (i) Mixture of trichloromethane and potassium hydroxide
 - (ii) Ethanoic acid
 - (iii) Chloromethane

ANSWERS:

9.(a) Second order reaction is the reaction in which the rate of reaction is proportional to the Second power of concentration of a single reactant

or first powers of concentration of two reactants.

$$R = K[A]^2$$

$$K = \frac{R}{[A]^2}$$

$$= \frac{\text{mole}^{-1}\text{s}^{-1}}{\text{mol}^2\text{l}^{-2}}$$

$$K = \frac{\text{l}^+}{\text{mol}^+}$$

(b) Solution:

(i) $R = K [\text{Br O}_3^-]^x [\text{Br}^-]^y [\text{H}]^2$

$$\frac{1.28 \times 10^{-4}}{2.56 \times 10^{-4}}$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^x$$

$$K = 1$$

$$\frac{2.56 \times 10^{-2}}{5.12 \times 10^{-2}} =$$

$$\left(\frac{1}{2}\right) = \left(\frac{1}{2}\right)_y$$

$$y = 1$$

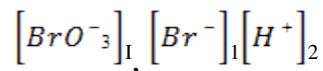
$$\frac{2.56 \times 10^{-2}}{5.12 \times 10^{-2}} = \frac{K(0.4)^{x^y}(0.2)^2}{K(0.2)^{x^y}(0.4)^2}$$

$$\frac{1}{2} = \frac{L^1}{L} \times \frac{1^2}{2}$$

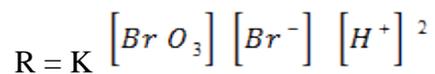
$$\frac{1}{4} = \left(\frac{1}{2}\right)^2$$

$$\left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^2$$

$$Z = 1, Y = 1, Z = 2$$



(ii) Solution:



$$1.28 \times 10^{-L} = K (0.2) (0.2) (0.2)^2$$

$$\underline{K = 8 \text{ l}^3 \text{ mol}^{-3} \text{ S}^{-1}}$$

10. (a) Ore

(b) Solution:

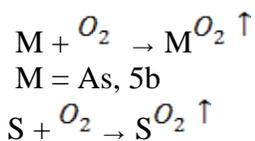
The ore in which tin is extracted is called cassiterite (SnO_2)

Concentration of ore:

Cassiterite is pulverized in ball mills. Magnetic impurities such as Fe and Mn are separated out by magnetic separation while other

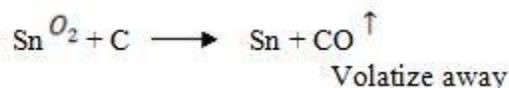
impurities are removed by Wilfley's table or hydraulic classifier method. This is done in a reverberatory furnace excess supply of air where

volatile impurities are given out. Impurities of sulphur and arsenic are volatilized away.

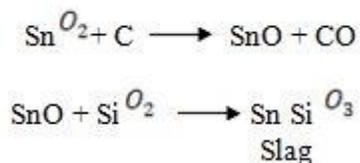


Smelting:

In this process, there is reduction of tin oxide to tin using coal. Temperature should be around 1200°C to 1300°C



But some of the tin oxide will give SnO which will react with silica to form slag



Purification:

This is done in a chamber with no entrance of oxygen

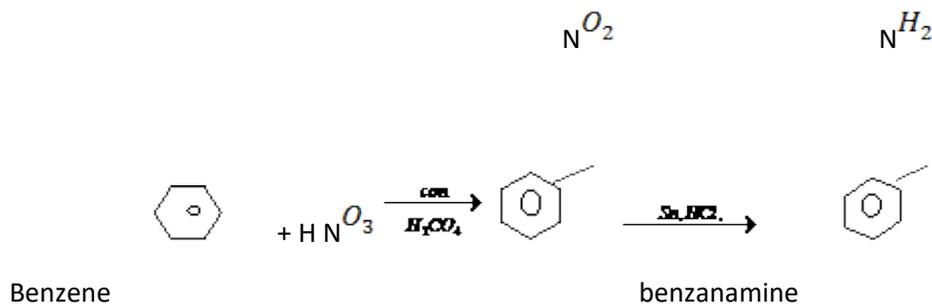
3(a) (i) $\text{CH}=\text{CH}_2$ styrene \Rightarrow Addition polymerization



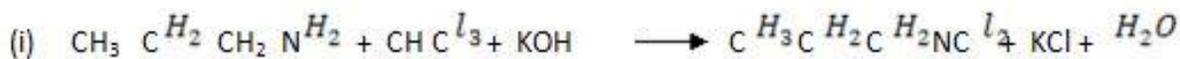
(ii) $\text{H}_2\text{N}-(\text{CH}_2)_6\text{N}$ and $\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \Rightarrow$ Condensation Polymerization

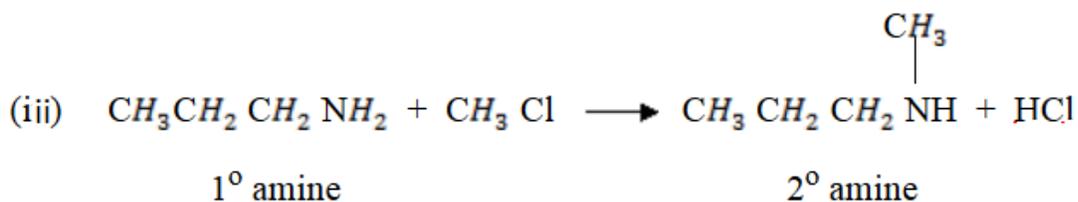
(iii) $\text{HO}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ and $\text{HO}-\text{CH}_2\text{CH}_2\text{OH} \Rightarrow$ (condensation Polymerization)

(b) Solution:



(c) Solution





1. 11. (a) (i) State the partition law

(ii) Write down the conditions for the law above to hold

(iii) The partition coefficient for iodine between water and CS_2 at 20°C is 2.43×10^{-3} . A 100 cm^3 sample of solution of iodine in H_2O of conc $1.00 \times 10^{-3} \text{ M}$ is shaken with 10.00 cm^3 of CS_2 . What fraction of iodine is extracted by CS_2 .

(b) Define precisely the following terms:

(i) Standard molar enthalpy of formation

(ii) Heat of solution of a substance

(iii) Ionization energy

(c) (i) State Hess's law of constant heat summation

(ii) Calculate the standard heat of formation of carbon-monoxide if standard heat of combustion of carbon and carbon monoxide are 393 KJ mol^{-1} and -285 KJ mol^{-1} respectively.

(iii) Determine the enthalpy change for the isomerization reaction:



The heat of formation of $\text{C}_2\text{H}_5\text{OH}$ is $= 276 \text{ KJ mol}^{-1}$

The heat of combustion of $\text{C}^{\text{H}_3} - \text{O} - \text{C}^{\text{H}_3}$ is $= 1456 \text{ kJmol}^{-1}$

The heat of formation of H_2O is $=284 \text{ KJ mol}^{-1}$

The heat of combustion of carbon is $=394 \text{ KJ mol}^{-1}$

2. 12. (a) Explain the meaning of the following and give one example:

- (i) Nucleophilic addition reaction
- (ii) Nucleophilic substitution reaction
- (iii) Elimination reaction

(b) How can you distinguish the following compounds

(i) $CH_3 CH(OH) CH_3$ and $CH_3 CH_2 CH_2 OH$

(ii) $CH_3 \overset{Cl}{\underset{|}{CH}} CH_3$ and $CH_3 CH_2 CH_2 Cl$

(iii) $CH_3 CH - CHO$ and $CH_3 CH_2 - \overset{O}{\parallel} C - CH_2 CH_3$

(c) Illustrate the preparation of the following compounds

- (i) Propanoic acid from ethane
- (ii) Propan - 2 - ol from propan -1-ol
- (iii) Propyne from ethyne

13.(a) Explain the following with vivid example and relevant chemical equations.

- (i) Li and Mg are more related chemically than Li and Na although both Li and Na are group I
- (ii) F is the most oxidizing element of all in the periodic table
- (iii) Electron affinity of F is unusually low

(b) Distinguish between the following:

- (i) Coordination number and oxidation number

(ii) Paramagnetism and ferromagnetism

(iii) Strong ligand and weak ligand

ANSWERS:

1. 11. (a) (i) Partition law:

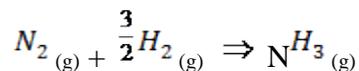
“When a solute is dissolved in a mixture of two immiscible solvents, it distributes itself in a constant ratio of concentration”.

(ii) Conditions

1. The two solvents must be completely immiscible.
2. Temperature should be constant.
3. There should be no change in molecular state of the solute i.e. should not dissociate or associate in any of the solvents.

(b) (i) Standard molar enthalpy of formation:

Is the heat change when 1 mole of a substance is formed from its elements in their standard states.



Heat of solution of a substance:

Is the enthalpy change when 1 mole of a substance is added to so much water that further addition of water produces no farther change.

Ionization energy:

Is the energy required to remove the most loosely held electron from the shell of an atom or ion.

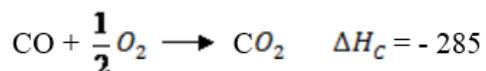
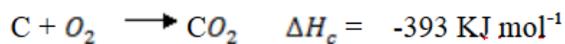
(c) (i) Hess's law:

The enthalpy change for a particular reaction is same whether the reaction takes place in one step or in a series of steps.

(ii) Solution:



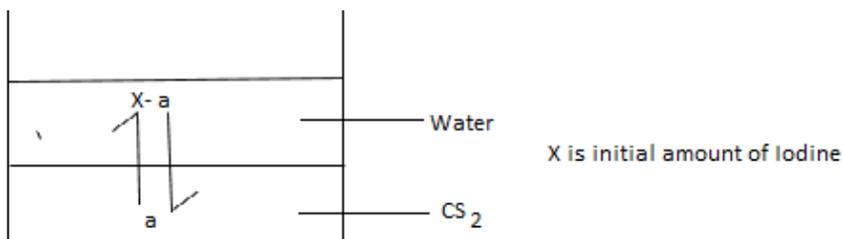
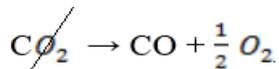
Given:



Applying Hess's law

$$\Delta_{Hc} = -393 \text{ KJ mol}^{-1}$$

$$\Delta_{Hc} = +285 \text{ KJ mol}^{-1}$$



$$\text{Initial amount of iodine} = 1 \times 10^{-3} \text{ mol} / \times 0.1 \text{ dm}^{-3}$$

$$X = 1 \times 10^{-4} \text{ Moles}$$

$$K.D = \frac{\text{Conc of } I_2 \text{ in water}}{\text{Conc of } I_2 \text{ in } CS_2}$$

$$2.43 \times 10^{-3} = \frac{1 \times 10^{-4} a / 100}{a / 10}$$

$$2.43 \times 10^3 = \frac{10^{-4} - a}{10a}$$

$$0.0243a = 10^{-4} - a$$

$$1.0243a = 10^{-4}$$

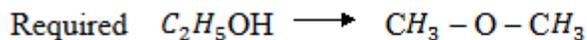
$$a = 9.76 \times 10^{-5} \text{ moles}$$

Fraction of Iodine extracted by CS_2 will be

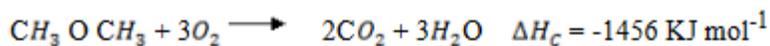
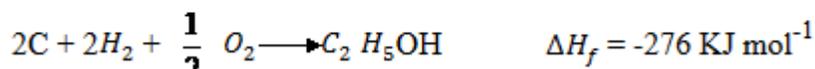
$$= \frac{9.76 \times 10^{-5}}{1 \times 10^{-4}}$$

$$= 0.976$$

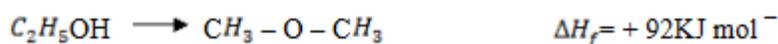
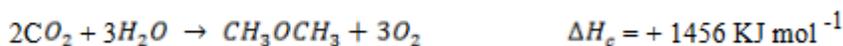
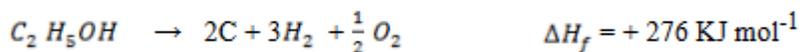
(iii) Solution:



Given



Applying Hess's law:

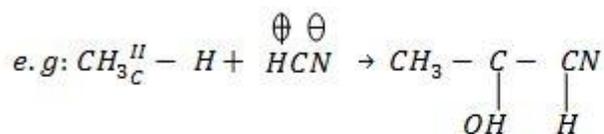


12.(a) (i) Nucleophilic addition reaction is the reaction in which nucleophile is added

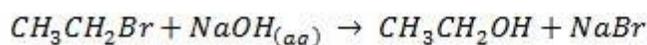
First followed by electrophile.

Elimination reaction is the reaction whereby an atom or group of atoms are removed from a compound



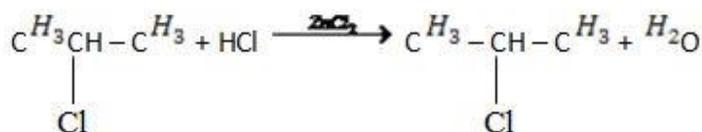
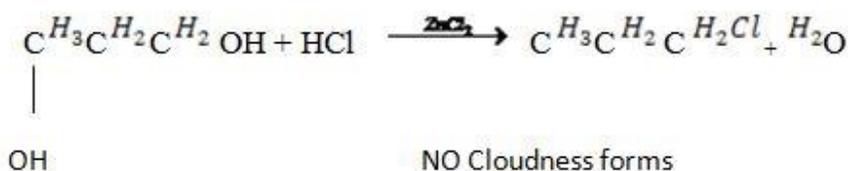


Nucleophilic substitution reaction is the reaction in which Nucleophile is substituted by a group of a

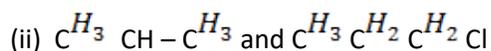


By Lucas Test

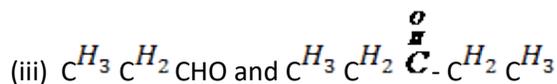
Propanol will not form cloudiness when it undergoes Lucas test but propan -2-ol will form cloudiness after 5 minutes upon Lucas test.



Cloudness after 5 minutes.



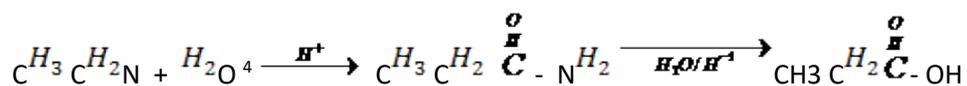
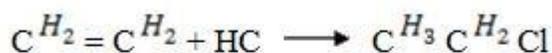
Using KOH followed by $AgNO_3$ in the presence of HNO_3 , yellow ppt will be observed for $C^H_3C^H_2C^H_2Cl$ while there is



$C^H_3C^H_2CHO$ will react with Tollen's reagent $[Ag(NH_3)_2]OH$ to form a white ppt of silver at the bottom of the test-tube while

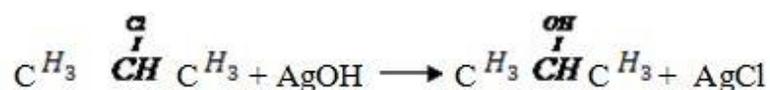
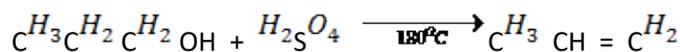
$\text{C}^{\text{H}_3}\text{C}^{\text{H}_2}\text{C}^{\text{O}}\text{CH}_2\text{C}^{\text{H}_3}\text{C}^{\text{H}_2}\text{C}^{\text{O}}\text{C}^{\text{H}_2}\text{C}^{\text{H}_3}$ will not react.

(c) (i) Propanoic acid from ethane

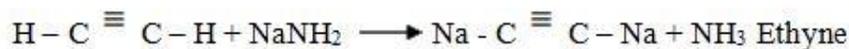


Propanoic acid

(ii) Propan-2-ol from propan-1-ol



(iii) Propyne from Ethyne



$$\lambda_m = \frac{\bar{\kappa}}{c}$$

$$\lambda_{\infty} = 133 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\bar{\kappa} = 6.4 \times 10^{-3} \text{ g cm}^{-1}$$

$$C = 5 \times 10^{-2} \text{ M}$$

$$\lambda_m = \frac{\bar{\kappa}}{C}$$

$$1 \text{ dm}^3 = 10^3 \text{ cm}^3$$

$$x = 1 \text{ cm}^3$$

$$= 10^{-3}$$

$$\frac{6.4 \times 10^{-3} \text{ g cm}^{-1}}{5 \times 10^{-2} \text{ mol cm}^{-3}} \propto \frac{\lambda_m}{\infty}$$

$$\frac{6.4 \times 10^{-3} \text{ g cm}^{-1}}{5 \times 10^{-2} \times 10^{-3} \text{ mol cm}^{-3}} = \frac{128}{133}$$

$$\lambda_m = 128 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = 0.96$$

13. Salt hydrolysis is the reaction between salt and water to form an acidic or alkaline solution:

Order of reaction:

- It cannot be determined

Molecularity:

- Can be determined from the equation

From equation (determined experimentally).

- It can be a whole number or fraction .
- It is the sum of concentrations terms on Which the rate of reaction actually depends (It is sum of exponents of the concentrations in the rate law).
- It cannot be obtained from the stoichiometry Of an unbalanced equation.
- It can only be a whole number
- It is the number of ions atoms or molecules that must collide so as to results in a chemical reaction.
- It can be obtained from the Stoichiometry of the equation.

$$t_{\frac{1}{2}} = 30 \times 60 = 1800\text{s at } 27^{\circ}\text{C}$$

$$t_{\frac{1}{2}} = 10 \times 60 = 600\text{s at } 47^{\circ}\text{C}$$

$$\text{Log} \left(\frac{t_2}{t_1} \right) = \frac{E_a}{2.303R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

$$\ln \log \left(\frac{600}{1800} \right) = \frac{E_a}{2.30 \times 8.314} \left(\frac{300 - 320}{300 \times 320} \right)$$

$$\log \left(\frac{6}{18} \right) = -1.088 \times 10^{-5} E_a$$

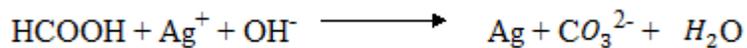
$$t_{\frac{1}{2}} = \frac{\ln 2}{K} \quad E_a = 4.3833$$

$$K = \frac{\ln 2}{t_{\frac{1}{2}}}$$

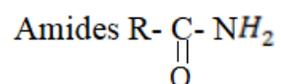
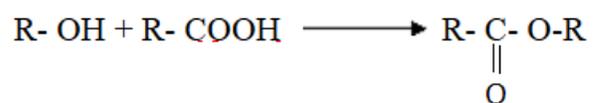
$$K = \frac{\ln 2}{1800}$$

$$K = 3.85 \times 10^{-4}$$

Tollen's reagent (silver mirror test)

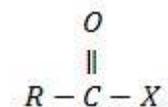


Esters

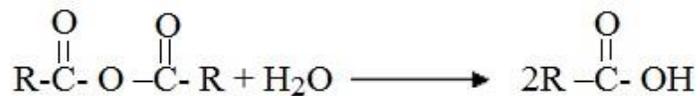


Amides $\text{R}-\text{NH}_2$

Acyl halides (Acid halide)



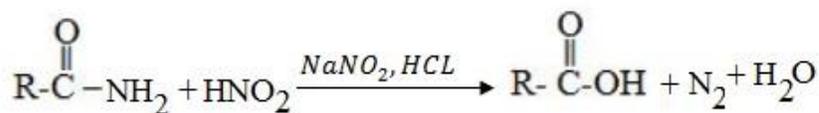
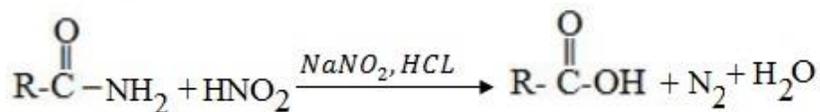
Derivatives of carboxylic acids upon hydrolysis go back to carboxylic acids



Transesterification is the reaction between ester and alcohol to form another ester



Amide



Conditions for a chemical reaction to take place

- i. The collision of the molecules must be energetic enough to break the bonds between the molecule
- ii. The colliding molecule must have right orientation (geometry)

$$\text{Log } K_1 = \text{log } A - \frac{E_a}{2.303RT_1}$$

$$\text{Log } K_2 = \text{log } A - \frac{E_a}{2.303RT_2}$$

$$\text{Log } K_1 - \text{log } K_2 = \frac{E_a}{2.303RT_2} - \frac{E_a}{2.303RT_1}$$

$$\text{Log} \left(\frac{k_1}{k_2} \right) = \frac{E_a}{2.303R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

$$\ln \left(\frac{(A)_0}{(A)_t} \right) = Kt \quad t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

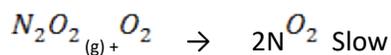
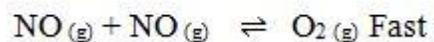
$$\frac{1}{(A)_t} - \frac{1}{(A)_0} = Kt \quad t_{\frac{1}{2}} = \frac{1}{k(A)_0}$$

Homolytic bond cleavage.

Is the type of bond cleavage in which the covalent bond breaks symmetrically so that one electron moves to each end.

Heterolytic bond cleavage.

Here the covalent bond breaks unsymmetrically and all bonding electrons are taken by the more electronegative atom



$R = K_o [N_2O_2] [O_2]$ this slow step will determine rate law

$$R_f = K_f [NO] [NO]$$

$$R_f = [NO]^2$$

$$R_b = K_b [N_2O_2]$$

At equilibrium $R_f = R_b$

$$K_f [NO]^2 = K_b [N_2O_2]$$

$$\frac{K_f}{K_b} [NO]^2 = [N_2O_2]$$

$$R = K_o \frac{K_f}{K_b} [\text{NO}]^2 [\text{O}_2]$$

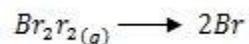
$$R = K [\text{NO}]^2 [\text{O}_2]$$



The slow step will determine the rate law

$$R = K_o [\text{Br}] [\text{H}_2]$$

Consider the equilibrium reaction



$$R_f = K_f [\text{Br}_2]$$

$$R_b = K_b [\text{Br}]^2$$

At equilibrium:

$$R_f = R_b$$

$$K_f [\text{Br}_2] = K_b [\text{Br}]^2$$

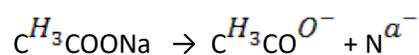
$$\frac{K_f}{K_b} [\text{Br}_2] = [\text{Br}]^2$$

$$[\text{Br}] = \sqrt{\frac{K_f}{K_b}} [\text{Br}]^{1/2}$$

$$R = K_0 \frac{K_f^{1/2}}{K_b^{1/2}} \text{Br}^{1/2} H_2$$

$$R = K [\text{Br}]^{1/2} [H_2]$$

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



Start	0.1	0	0
	0.1 - x	x	x

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$\alpha = \frac{0.1 - x}{0.1} \times 100$$

$$[\text{H COONa}] = \frac{n}{V}$$

Let added volume be x

$$[\text{H COONa}] = \frac{n}{x}$$

$$0.1 = \frac{n}{x}$$

$$n = 0.1x$$

$$[\text{HCOONa}] = \frac{0.1x}{0.05 + x}$$

$$[\text{HCOOH}] = \frac{0.1x}{0.05 + x}$$

14. Explain the meaning and significance of colloids

15. Discuss the properties of soil colloids

- Surface area
- Electric charge
- Ion exchange (diagram)

16. Explain the mechanism of ion exchange in soil

17. Calculation of percentage base saturation of a soil sample. With worked examples (how to calculate)

18. Aluminum has high polarizing power hence the compound formed between Al and carbon will be unstable therefore it will decompose immediately after formation.

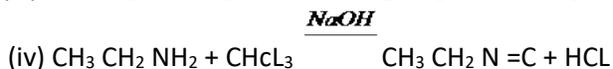
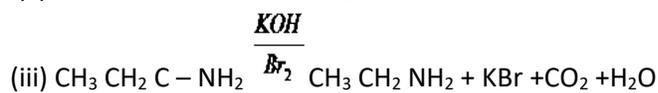


The chloride outside is not part of the complex meaning that it is ionization. Therefore Ag will react. In $[\text{Pt}(\text{NH}_3)_2 \text{Cl}_4]$ the chloride is part of the complex hence there is no ionizable chloride ion and there no reaction

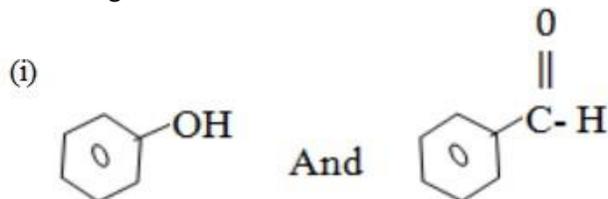




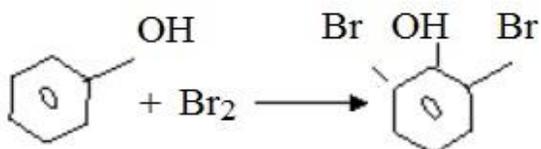
Soluble complex



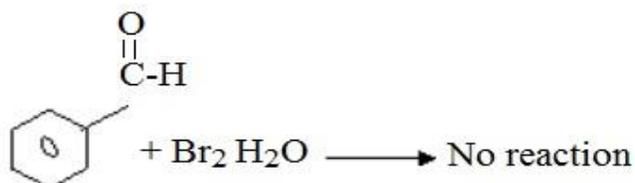
20. Distinguish between



When $\text{Br}_2/\text{H}_2\text{O}$ is added to phenol, white ppt is formed



When $\text{Br}_2/\text{H}_2\text{O}$ is added, no reaction



(ii) $\text{CH}_3\text{C}-\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C}-\text{H}$

By Iodoform test or by silver mirror test



(iii) $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$



Yellow



22. With the aid of chemical equations explain the following

(i) Mercury(ii) iodide solution but not in potassium iodide solution but in water

(ii) The pink solution of cobalt (ii) chloride turns blue when conc. HCL is added
gelatinous ppt of

(iii) Copper (ii) hydroxide turns deep blue in excess ammonia

(iv) ZnO and PbO dissolves in hot conc sodium hydroxide solution

23. using relevant balanced chemical equation describe the process of extracting copper from copper pyrite under the following heading.

(i) Concentration

(ii) Roasting

(iii) Removal of ion impurities

(iv) Self- reduction reaction

24. Cobalt copper, Iron and manganese are d-block elements

- a. What is meant by the term d- block element
- b. Write E.C of Cu, Fe²⁺, Mn²⁺
- (i) Explain in terms of E.C why Fe²⁺ ions are readily oxidized to Fe³⁺ ions but manganese (ii) ions are not readily oxidized to Mn³⁺

25. 2.5×10^{-3} moles of a compound with a formula was dissolved in 0.1M a silver nitrate solution. 50 cm³ were required for complete precipitation of the chloride ions present.

- (i) Deduce the ionic formula of the compound
- (ii) Draw the structure of the complex ion present and name it

26. Write the formula of the following complexes

- (i) Tetra ammine copper(ii) Sulphate mono hydrate
- (ii) Potassium

27. Write down a balanced chemical equation for the following

- (i) Adding of excess ammonia solution to aluminium ion
- (ii) Ion(iii) oxide is heated with aluminium powder
-