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Chemistry 11th and 12th Book

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BASIC PRINCIPLES OF CHEMISTRY

Branches of chemistry

- Organic chemistry : This branch deals with study of compounds of carbon and its compounds with any number of other elements, including hydrogen (most compounds contain at least one carbon–hydrogen bond), nitrogen, oxygen, halogens, phosphorus, silicon, and sulfur. Except carbonates, bicarbonates, cyanides, isocyanides, carbides and oxides
- Inorganic chemistry: This branch deals with study of known elements and their compounds except organic compounds. It is concerned with materials obtained from minerals, air, sea and soil.
- Physical chemistry: This branch deals with study of physical properties and constitution of matter, the laws of chemical combination and theories governing reactions. The effect of temperature, pressure, light, concentration on reaction.
- Analytical chemistry: This branch deals with various methods of analysis of chemical substances both qualitative and quantitative.
- Industrial chemistry : Chemistry involved in industrial process is studied in this branch.
- Biochemistry : It comprise the studies of substances for the prevention and cure of various diseases in living beings
- Nuclear chemistry : This branch deals with study of nuclear reaction, the production of radioactive isotopes and their application in various field.

Measurement in chemistry

A physical quantity is expressed in terms of pure number and unit
Physical quantity = (a pure number) × unit
For example when we say 5 kg. It means 5 times of 1kg
‘A unit is defined as the standard of reference chosen in order to measure a definite physical quantity”.
Standard weight and measure are given by International system of Unit (SI)

Basic physical quantity	Symbol of quantity	Name of SI unit	Symbol of SI unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Thermodynamic temperature	T	kelvin	K
Amount of substance	n	mole	mol
Luminous Intensity	I_v	candela	Cd

Some time Sub-multiple and Multiples are used to reduce and enlarge the size of different units

Sub – multiples			Multiples		
Prefix	Symbol	Sub-multiple	Prefix	Symbol	Multiple
deci	d	10^{-1}	deca	da	10
centi	c	10^{-2}	hecto	h	10^{2}
milli	m	10^{-3}	kilo	k	10^{3}
micro	μ	10^{-6}	mega	M	10^{6}
namo	n	10^{-9}	giga	G	10^{9}
pico	p	10^{-12}	tera	T	10^{12}
femto	f	10^{-15}	peta	P	10^{15}
atto	a	10^{-18}	exa	E	10^{18}

Following convention is followed in writing a unit or its symbol

1. The symbols of the units are never expressed in plural form. For example, we write 15 cm and not 15 cms.
2. If a unit is named after the name of a person, it is not written with capital letter. For example, we write newton and not Newton
3. The symbol of the unit named after the name of a person is expressed in capital letter. For example, the symbol for unit newton is N and not n. Symbols of the other units are not written in capital letters. For example, symbol for unit meter is m and not M
4. Not more than one solidus is used. For example 1 poise is expressed as

1g/s cm or 1 g s^{-1} cm^{-1} and not 1g/s/cm.

Some derived units

a) Area = length × breadth
= m × m = m^2
b) Volume = length × breadth × height
= m × m× m =m^3
c) Density = mass/ volume
= kg/ m^3 = kg m^3
d) Speed = distance / time
= m/s = m s^{-1}
e) Acceleration = change in velocity / time
= m s^{-1} /s = m s^{-2}
f) Force = mass × acceleration
= kg m s^{-2}
g) Pressure = force per unit area
= kg m s^{-2} / m^2
= kg m^{-1} s^{-2} or N m^{-2} (pascal – Pa)
h) Energy = force × distance travelled
= kg m s^{-2} × m
= kg m^2 s^{-2} (joule – J)

Some conversions

a) Temperature
Degree Centigrade = Kelvin – 273.15

$^{o}C = K - 273.15$

$$^{o}F = \frac{9}{5} \times (\ ^{o}C) + 32$$

b) Volume
1 litre (lit or L) = 1000 cm^3
1 L = $(10\ cm)^3$
1 L = $(10 \times 10^{-2}\ m)^3$
1 L = $10^3 \times 10^{-6}\ m^3$
1 L = $10^{-3}\ m^3$
OR 1m^3 = 1000 L
Also

1 L = 1000 mL = 10^{-1} m^3 = 1 dm^3

c) Energy

1 cal = 4.184 J

1eV = 1.6 $\times 10^{-19}$ J

d) Pressure

1 atm = 760 torr = 760 mmHg = 76 cmHg = 1.013×10^5 Pa

Significant figures

To indicate the precision of measurement, scientists use the term significant figure.

The following rules are observed in counting the number of significant figures in a given measured quantity.

1)All non-zero digits are significant : for example

24.3 has three significant figure

243.2 has four significant figure

2) A zero becomes significant figure if it appears between two non-zero digits: for example

3.04 has three significant figure

3.506 has four significant number

3) Leading zeros or the zero placed to the left of the numbers are never significant : For example

0.542 has three significant number

0.054 has two significant number

0.006 has one significant number

4) Trailing zero or the zeros placed to the right of the decimal are significant: For example

431.0 has four significant figures

432.00 has five significant number

5) If a number ends in zero but these zeros are not to the right of decimal point, these zeros may or may not be significant

For example , 11400 g may have three, four or five significant figures. Such a number is first written in exponential form. The above mass may be written in the following exponential forms

1.14×10^4 g which has three significant figures

1.140×10^4 g has four significant figures

1.1400×10^4 g has five significant figures

6) The non-significant figures in the measurements are round off

a) If the figure following the last number to be retained is less than 5, all the unwanted figures are discarded and the last number is left unchanged e.g.

5,6724 is 5.67 to three significant figure

b) If the figure following the last number to be retained is greater than 5, the last figure to be retained is increased by 1 unit and the unwanted figures are discarded e.g 8.6526 is 8.653 to four significant figures

c) If the figure following the last number to be retained is 5, the last figure is increased by 1 only in case it happened to be odd. In case of even number the last figure remains unchanged. For example 2.3524 is 2.4 to two significant figures (3 is odd hence increased by 1)

7.4511 is 7.4 to two significant figure (4 is even hence no increase)

7) Exact number have an infinite number of significant figures because infinite number of zero can be placed after decimal point Example 20 = 20.00000 …..

Calculations Involving Significant Figures

Rule 1 : The resultant of an addition or subtraction in the numbers having different precisions should be reported to the same number of decimal places as are present in the number having the least number of decimal places. The rule is illustrated by the following examples

a) 33.3 (only one decimal place)
03.11
+00.313

Sum 36.723 (Answer should be reported to one decimal place)

Correct answer 36.7

b) 3.1421
0.241
0.09 (two decimal places)

Sum 3.4721 (answer should be reported to 2 decimal place

Correct answer = 3.47

c) 62.831
- 24.5495

Difference = 38.2815 (Answer should be reported to 3 decimal place after round off)

Correct answer = 38.282 (as 1 is odd number hence increased by one)

Rule 2: The answer to a multiplication or division is rounded off to the same number of significant figures as is possessed by the least precise term used in the calculation. Example

a) 142.06

× 0.23 (two significant figures)

32.6738 (answer should have two significant figures, after rounding off)

Correct answer = 33

b) 51.028

× 1.31 (three significant figures)

66.84668

Correct answer = 66.8

$$c)\frac{0.90}{4.26} = 0.2112676$$

Correct answer = 0.21

$$d)\frac{3.24 \times 0.0866}{5.046} = 0.055653$$

Correct answer = 0.0556

$$e)\frac{4.28 \times 0.146 \times 3}{0.0418} = 44.84784$$

Correct answer = 44.8

Elements and compounds

Elements are pure substances that cannot decomposed into simpler substances by chemical change. The smallest particles of an element possess the same properties as the bigger particles. An element can also be defined as a pure substance which consists of only one type of atoms (smallest particle)

Elements are classified in Metals, non-mental and metalloids

Compounds are also pure substances that are composed of two or more different elements in a fixed proportion by mass. The property of compound is altogether different than the constituent elements. For example water is made up of hydrogen which can burn and oxygen which helps to burn but Water extinguishes fire. Components of the compound cannot be separated by physical process but only by chemical process. If we just boil water Hydrogen and oxygen cannot be separated for that we have to go for electrolysis process

Compound are classified into two types:

i) Organic compounds : The compounds obtained from living sources are termed organic compounds. The term organic is now applied to hydrocarbons (compounds of carbon and hydrogen) and their derivatives

ii) Inorganic compounds: The compounds obtained from non-living sources such as rock and minerals are termed inorganic compounds. The compounds of all elements except hydrocarbons and their derivates are included in this category.

Some specific properties of substances:

i) Deliquescence: The property of certain compounds of taking up the moisture present in atmosphere and becomes wet when exposed is known as deliquescence. For example Sodium hydroxide, potassium hydroxide, calcium chloride, magnesium chloride anhydrous ferric chloride

ii) Hygroscopicity : Certain compounds combine with the moisture and are converted into hydroxides or hydrates. Such substances are called hygroscopic. Anhydrous copper sulphate, quick lime (CaO), anhydrous sodium carbonate etc are of hygroscopic nature

iii) Efflorescence: The property of some crystalline substances of losing their water of crystallization on exposure and becoming powdery on the surface is called efflorescence. Such salts are known as efflorescent. The examples are Ferrous sulphate ($FeSO_4 . 7H_2O$), sodium carbonate (

Na_2CO_3. $10H_2O$), Sodium sulphate (Na_2SO_4 .$10H_2O$) potash alum [K_2SO_4 . $Al_2(SO_4)_3$. $24H_2O$] etc

iv) Malleability : this property show by metals. When solid is beaten and does not break but converted into a thin sheet, it is said to posses the property of malleability. Example Gold , silver, copper

v) Ductility : The property of metal to be drawn into wires is termed ductility. Example Gold , silver, copper. Platinum is most ductile.

vi) Elasticity : When the stress (force per unit area normal to cross-section) is small, the solid completely regain its original shape, size or volume after deforming force is removed. The solid is then said to be elastic. Steel, glass, ivory etc are elastic bodies

vii) Plasticity : When stress is increased on a metal, a limit is reached beyond which, if the stress is removed, the solid does not come back to its original shape or size. It acquires a permanent deformation. Such material can be given any shape without any difficulty

viii) Brittleness: The solid materials which break into small pieces on hammering are called brittle. The solids of non-metals are generally brittle in nature

ix) Hardness: A material is said to be harder than the other if it can scratch it. The hardness is measured on Mho's scale. For this purpose, ten minerals have been selected which have been assigned hardness from 1 to 10
On Mho's scale, hardness of diamond is maximum and that of talc is minimum.

Law of Chemical Combination

(i) Law of conservation of mass : The law was first stated by Lavoisier in 1774 .According to this law, in all chemical changes, the total mass of the system remains constant or in chemical change, mass is neither created nor destroyed.
Total mass of reactant = Total pass of products + masses of the un-reacted reactants

(ii) Law of definite or constant proportions: This law was presented by Proust in 1799 . According to this law “ A chemical compound always contains the same element combined together in fixed proportion by mass. i.e. a chemical compound has fixed composition and it does not depends on the method of its preparation or the source from which it has been obtained.

For example carbon dioxide can be obtained by any of the following methods

a) by heating calcium carbonates
b) By burning carbon in oxygen
c) by reacting calcium carbonate with hydrochloric acid

Whatever sample of carbon dioxide is taken it is observed that carbon and oxygen are always combined in the ratio of 12:32 or 3:8

The converse of this law that when same elements combines in the same proportion, the same compound will be formed, is always not true.

For example. Carbon, hydrogen and oxygen when combined in the ratio of 12:3:8 may form either ethyl alcohol (C_2H_5OH) or dimethyl ether (CH_3OCH_3) under different experimental condition

(iii) Law of multiple proportions : this law was put forward by Dalton in 1808 . According to this law, if two elements combine to form more than one compound, then the different masses of one element which combines with a fixed mass of the other element, bear a simple ratio to one another.

Nitrogen forms five stable oxides

N_2O	Nitrogen 28 parts	Oxygen 16 parts
N_2O_2	Nitrogen 28 parts	Oxygen 32 parts
N_2O_3	Nitrogen 28 parts	Oxygen 48 parts
N_2O_4	Nitrogen 28 parts	Oxygen 64 parts
N_2O_5	Nitrogen 28 parts	Oxygen 80 parts

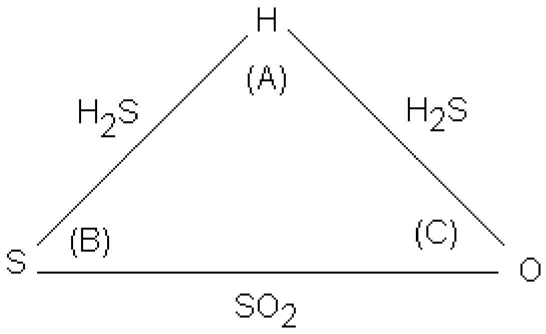
Thus for same mass of nitrogen combines with different masses of oxygen and the ratio of oxygen with same mass of Nitrogen is in ratio
16:32:48:64:80 or 1:2:3:4:5

(iv) Law of reciprocal proportion : This law was given by Richter in 1794. The law states that when definite mass of an element A combines with two other elements B and C to form two compounds and if B and C also combine to form a compound, their combining masses are in same proportion or bear a simple ration to the masses of B and C which combine with a constant mass of A.

(v) For example , hydrogen combines with sodium and chorine to form compounds NaH and HCl respectivey

In NaH	Sodium 23 parts	Hydrogen one part
In HCl	Chlorine 35.5 parts	Hydrogen one part

Thus according to law when Sodium combines with Chlorine to from NaCl is 23 parts of sodium and 35.5 parts of chlorine
However in following example it do not hold good



In H_2S	Hydrogen two parts	Sulphur 32 parts
In H_2O	Hydrogen two parts	Oxygen 16 parts

Thus expected that 32 part of Sulphur should combine with 16 parts of oxygen but actually both combine to form SO_2 in the ratio of 32:32 or 1:1

The law of reciprocal proportions is a special caase of a more general law, the law of equivalent masses, which can be stated as " In all chemical reactions, substances always react in the ratio of their equivalent masses"

DALTON’S ATOMIC THEORY

Main postulates of this atomic theory are

- Matter is discrete (i.e. discontinuous) and is made up of atoms. An atom is the smallest (chemically) indivisible part of an element, which can take part in a chemical change
- Atoms of the same element are identical in all aspect, size, shape, structure etc and especially weight.
- Atoms of different elements have different properties and weights
- Atoms cannot be created or destroyed. So a chemical reaction is nothing but a rearrangement of atoms and the same number of atoms must be present before and after reaction
- A compound is formed by the union of atoms of one element with atoms of another in a fixed ratio of small whole numbers (1:, 1:2, 1:3 etc)

All the postulates of Dalton’s atomic theory have been proved to be incorrect.

Atom is divisible in the sense that it has structure. Sub-atomic particles are known.

The existence of isotopes for more elements shows that atoms of the same element need not have same mass. The atomic weight of an element is , in fact, a mean of the atomic masses of the different isotopes of the element.

Part of atomic mass can be destroyed and an equivalent amount of energy is released during nuclear fission.

Atoms combine in fixed integral ratios; however there are instances where atoms combine in non-integral ratios. E.g. iron(II) with a composition $Fe_{(1-x)}S$ ($x = 0$ to 0.2).

In zinc oxide, zinc and oxygen have not combined in exactly an integral ratio. The atomic ratio of Zn : = (1+x) : 1, where x is a very small fraction. Compounds of this kind are called non-stoichiometric compounds or Berthollide compounds as against compounds whose formulae are accordance with atomic theory and law of definite proportion.

Atomic Weight or Atomic mass

The atomic mass of an element can be defined as the number which indicates how many times the mass of one atom of the element is heavier in comparison to the mass of one atom of hydrogen. If Hydrogen atom selected as standard

Thus Atomic weight of element

$$= \frac{Weight\ of\ 1\ atom\ of\ the\ element}{Weight\ of\ 1\ atom\ of\ hydrogen}$$

When we sate atomic mass of chlorine is 35.5, we mean that an atom of chlorine is 35.5 times heavier than an atom of hydrogen.

It was later felt that the standard for reference for atomic weight may be oxygen, the advantage being that the atomic weights of most other elements become close to whole number

Thus Atomic weight of element

$$= \frac{Weight\ of\ 1\ atom\ of\ the\ element}{\frac{1}{16} \times Weight\ of\ 1\ atom\ of\ oxygen}$$

The modern reference standard for atomic weight is carbon isotope of mass number 12

Thus Atomic weight of element

$$= \frac{Weight\ of\ 1\ atom\ of\ the\ element}{\frac{1}{12} \times Weight\ of\ 1\ atom\ of\ carbon - 12}$$

On this basis, atomic weight of oxygen 16 was changed to 15.9994

Nowadays atomic weight is called relative atomic mass and denoted by amu or u (atomic mass unit). The standard for atomic mass is C^{12}

Atomic mass unit : The quantity of one twelfth mass of an atom of carbon-12 (C^{12}) is known as the atomic mass unit (amu). The actual mass of one atom of carbon -12 is 1.9924×10^{-23}g or 1.9924×10^{-26}kg

Atomic mass of Hydrogen is 1.008 amu. In terms of gram it will be

$=1.008\times1.9924\times10^{-23}g = 1.6736\times10^{-24}$ g

Atomic mass of oxygen is 16.00 amu. In terms of gram it will be

$=16\times1.9924\times10^{-23}g = 2.656\times10^{-23}$ g

It is clear from above that

- Atomic weight or mass is not a weight but a number
- Atomic weight is not absolute but relative to the weight of the standard reference element C^{12}
- Gram atomic weight is atomic weight expressed in gram, but it has a special significance with reference to a mole

Most of the elements occur in nature as a mixture of isotopes. Thus average atomic masses of various elements are determined by multiplying the atomic mass of each isotope by its fractional abundance and adding the values thus obtained. The fractional abundance is determined by dividing percentage abundance by hundred

If a, b are the atomic masses of isotopes in the ratio m:n then average isotopic mass

$$=\frac{m\times a+n\times b}{m+n}$$

If x and y are percentage abundance of the two isotopes (y = 100 – x) then

$$=\frac{x}{100}\times a+\frac{y}{100}\times b$$

Illustration

Q) Given that the abundance of isotopes ^{54}Fe, ^{56}Fe, ^{57}Fe are 5%, 90% and 5% respectively. The atomic mass of Fe is

Solution

From the formula

$$= \frac{x}{100} \times a + \frac{y}{100} \times b + \frac{z}{100} \times c$$

X = 5, y = 90, z = 5 and a = 54, b = 56, c = 57

On substitution of above data in Formula we get

$$= \frac{5}{100} \times 54 + \frac{90}{100} \times 56 + \frac{5}{100} \times 57 = 55.95\ amu$$

Q) Carbon occurs in nature as a mixture of carbon-12 and carbon-13. The average atomic mass of carbon is 12.011amu. the percentage abundance of Carbon-13 is

Solution

Let x be the percentage abundance of carbon-12 then (100-x) will be the percentage abundance of carbon-13. From formula

$$12.011 = \frac{x}{100} \times 12 + \frac{(100-x)}{100} \times 13$$

On simplification we get x = 98.9 or abundance of C-12 is 98.9% and C-13 is 1.1%

Avogadro’s number

It is the number of atoms in exactly 12 grams of carbon -12. This experimentally determined value is approximately 6.0221 x 10^{23} particles.

Gram-atomic mass or gram atom

Gram-atomic mass can be defined as the absolute mass in gram of 6.02×10^{23} atoms of any element.

Mass of Oxygen = 16 u = $16 \times1.66\times10^{-24}$ g

Thus Absolute mass of 6.02×10^{23} atoms of oxygen = $16 \times1.66\times10^{-24} \times6.02\times10^{23}$ g = 16g

Thus mass of 1 atom of Oxygen is 16 amu or u and Gram-atomic mass of Oxygen is 16g

The Molecule

Avogadro suggested that the fundamental; chemical unit is not an atom but a molecule, which may be a cluster of atoms held together in some manner causing them to exist as unit. The term molecule means the smallest particle of an element or a compound that can exist free and retain all its properties.

Consider a molecule of carbon dioxide. It has been established that in contains one atom of carbon and two atoms of oxygen. This molecule can be split into atoms of carbon and oxygen. So the smallest particle of carbon dioxide that can exist free and retain all its properties is the molecule of carbon dioxide. A compound molecule should contain at least two different atoms.

The term molecule is also applied to describe the smallest particle of an element which can exist free. Thus a hydrogen molecule is proved to contain two atoms; when it is split into atoms there will be observed a change in property.

Molecules of elementary gases like hydrogen, oxygen, nitrogen, chlorine etc contain two atoms in molecules=; they are diatomic. Molecules of noble gas like helium, neon argon, krypton and xenon are monoatomic. Molecule of Sulphur contains eight atoms while molecule of phosphorus contains four atoms.

The number of atoms of an element in a molecule of the element is called its atomicity

Molecular weight

It is the number of times a molecule is heavier than one twelve of an atom of caron-12

Molecular weight

$$= \frac{wight\ of\ 1\ molecule}{\frac{1}{12} \times weight\ of\ 1\ carbon - 12\ atom}$$

- Molecular weight is not a weight but a number
- Molecular weight is relative and not absolute.
- Molecular weight expressed in grams is called gram-molecular weight
- Molecular weight is calculated by adding all the atomic weight of all the atoms in a molecule
  The molecular weight of carbon dioxide CO_2 is calculated as
  Atomic mass of carbon 12 u and atomic mass of oxygen is 6 u
  Thus molecular mass of $CO_2 = 1\times12 + 2\times16 = 44$ u
- Molecular weight is now called relative molecular mass

Gram-molecular Mass or Gram molecule

A quantity of substance whose mass in gram is numerically equal to its molecular mass is called gram-molecular mass. In other words, molecular mass of a substance expressed in gram is called gram-molecular mass or gram molecule.

For example the molecular mass of chlorine is 71u and therefore its gram-molecular mass or gram molecule is 71g which is the mass of 6.02×10^{23} molecules of chlorine

Gram molecular mass of oxygen is 32 and Nitric acid $HNO_3 = 1 + 14 + 3\times16 = 63$ g

Gram-molecular mass should not be confused with mass of one molecule of the substance in gram. The mass of one molecule of a substance is known as its actual mass. For example, the actual mass of one molecule of oxygen is equal to

$32\times1.66\times10^{-24}$g i.e 5.32×10^{23}

Avogadro's Hypothesis

It state that equal volumes of gases at the same temperature and pressure contain equal number of molecules. It means that 1ml of hydrogen, oxygen, carbon dioxide or mixture of gases taken at the same temperature and pressure contains the same number of molecules

Application of Avogadro's hypothesis

a) To prove that simple elementary gas molecules are diatomic
Consider the experimental result
1 volume of hydrogen + 1 volume of chlorine → 2 volume of hydrogen chloride as the same temperature
1 volume of contains 'n' molecules.
Then n molecules of hydrogen + n molecules of chlorine → 2n molecules of hydrogen chloride
A molecules of hydrogen chloride should contain at least 1 atom of hydrogen and 1 atom of chlorine. Two molecules of hydrogen chloride should contain at least 2 atoms of hydrogen and 2 atoms of chlorine and these should have come from 1 molecule of hydrogen and 1 molecule of chlorine respectively. Thus Avogadro's hypothesis enable us to establish that hydrogen and chlorine molecules must contain at least 2 atoms.

b) To establish the relationship between molecular weight and vapour density of a gas
The absolute density of gas is the weight o 1 L of gas at STP (Standard temperature 0°C and pressure 1 atm)
The relative density or vapour density of gas (V.D.)
= Density of the gas / Density of hydrogen

$$V.D. = \frac{Weight\ of\ 1\ L\ of\ gas\ at\ STP}{Weight\ of\ 1\ L\ of\ Hydrogen\ gas\ at\ STP}$$

$$V.D. = \frac{Weight\ of\ a\ certan\ volume\ of\ the\ gas}{Weight\ of\ the\ same\ volume\ of\ hydrogen\ at\ the\ same\ temperature\ and\ pressure}$$

So Vapour density of gas is defined as the ratio of the weight of a certain volume of the gas to the weight of the same volume of hydrogen at the same temperature and pressure.

Let V litres of the gas contains 'n' molecules

$$V.D. = \frac{Weight\ of\ 'n'molecules\ of\ the\ gas}{weight\ of\ 'n'molecules\ of\ hydrogen}$$

$$V.D. = \frac{1}{2} \times \frac{Weight\ of\ 1\ molecule\ of\ gas}{Weight\ of\ 1\ atom\ of\ hydrogen}$$

$$V.D. = \frac{1}{2} \times Molecular\ weight\ of\ the\ gas$$

Molecular weight of gas = 2×Vapour density of the gas

c) Gram-Molecular volume or Molar Volume
Molecular weight of gas = 2×Vapour density of the gas

$$\text{Molecular weight of gas} = 2 \times \frac{\text{Weight of 1L of gas at STP}}{\text{Weight of 1L of hydrogen at STP}}$$

$$\text{Gram} - \text{Molecular weight of gas} = 2 \times \frac{\text{Weight of 1L of gas at STP}}{0.089\text{g}}$$

Gram-Molecular weight of gas = 22.4 × Weight of 1L of the gas at STP
Gram-Molecular weight of gas = Weight of 22.4L of gas at STP
This establish that gram –molecular weight of any gas (or vapour) occupies the same volume of 22.4L at STP. The volume occupied by a gram-molecular weight of any gas is called a molar volume and its value is 22.4L at STP

MOLE

The term 'mole' was introduced by Ostwald in 1896. This is the Latin word 'moles' means heap or pile.

A mole(mol) is defined as the number of atoms in 12.0 g of carbon-12 which is equal to 6.02×10^{23} . This number is also known as Avogadro's number

Thus mole is a unit which counts, similar to dozen or gross.

Thus heap of 6.02×10^{23} particles, atoms , ions, molecules or object is called one mole

Now if mole is heap then it must have weight and occupy volume

Mass of One mole of substance is equal to gram-molecular mass for example

One mole of water (H_2O)contains 6.02×10^{23} particles (molecules of water) and weight of this molecules = 18 g (2+16)

One mole of Chlorine (Cl_2) contains 6.02×10^{23} particles (molecules of chlorine) and weight of this molecules = 71 g (2×35.5)

So one mole of substance will have mass equal to formula mass of that substance.

$C + O_2 \rightarrow CO_2$

In above reaction one mole of carbon (C) reacted with one mole of Oxygen gas (O_2) to produce one mole of carbon dioxide (CO_2) or

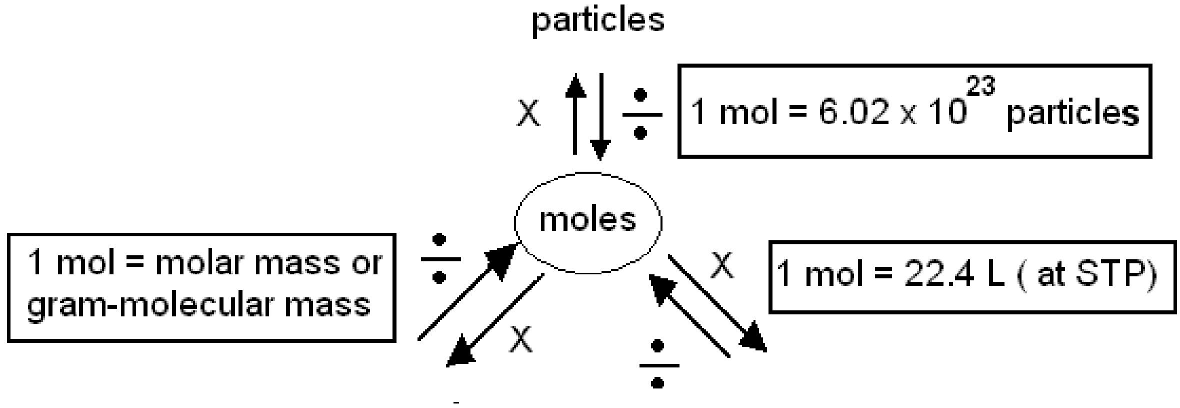
CO_2 is made up of one mole of carbon and one mole of Oxygen gas

It is established by Avogadro's hypothesis that one gram-moleular mass which is mass of one mole of gaseous substance occupy volume of 22.4 L at NTP.

1 mole = 22.4 L at STP

1mole = 6.02×10^{23} number of particles, atom, molecules, ions

1mole = gram-molecular weight



Illustrations

Q) What is the mass of one molecule of water

Solution

Molecular weight of water =18 g

One mole contains 6.02×10^{23} number of molecules of water

Thus Wt of one molecule of water = $18/6.02\times10^{23} = 3\times10^{-23}$ g

Q) At STP, 5.6 L of gas weight 60g. The vapour density of gas will be

Solution

Molecular mass = 2 × Vapour density --- eq(1)

Calculate molecular mass

5.6 L = 60 g

22.4 L = ?

Thus 22.4 L have mass = molecular mass = $\frac{60\times22.4}{5.6} = 240\ g/mol$

Now from equation(1)

240 = 2× Vapour density

∴ Vapour density = 120

Q) x gram of $CaCo_3$ was completely burnt in air. The mass of the solid residue formed is 28. What is the value of 'x' in gram. [Molecular weight of Ca=40, O =16, C =12]

$CaCO_3\,(s) \rightarrow CaO(s) + CO_2\,(g)\uparrow$

Solution

From given data molecular weight of $CaCO_3$ = 40 +12 +48 = 100

CaO = 40 +16 = 56g

From given chemical equation 100 g of $CaCO_3$ produces 56 g of CaO

Or 56g = 100 g ∴ 28 = x? On simplification we get 50g

Q) If an organic compound contain 4% sulphur. Then, what will the minimum molecular mass of the organic compound.

Solution

Here we will assume organic compound contain one atom of sulphur, so that we can estimate minimum molecular weight

Now molecular weight of sulphur = 32 g/mol

From given

5 g of S= 100 g of compound

32 = ? of compound

On simplification we get 740 g/mole

Or 740 amu is the weight of one molecule of Compound

Q) How many atoms are present in one mole of water

Solution

Molecular formula of water is H_2O

One molecule of water contains 3 atom

Thus One mole of water contain 3 mole of atom

Now 1 mole of atom = 6.02×10^{23} atoms

∴ 3 mole atom = $3\times6.02\times10^{23}$ atoms= 1.806×10^{24} atoms

Q) Which of the following have maximum number of molecules present

a) 15 L of H_2 gas at STP b) 5 L of N_2 gas at STP

c) 0.5g of H_2 gas d) 10g of O_2 gas

Solution

22.4 L of gas at STP = 1 mol

Thus 15L of H_2 gas at STP = 15/22.4 = 0.669 mol

5 L of N_2 gas at STP = 5/22.4 = 0.223 mol

Molecular weight of H_2 gas = 2 g or

2g of H_2 gas = 1 mol

∴ 0.5g = 0.25 mol

Molecular weight of O_2 gas = 32 g or

32 g = 1 mole

∴ 10 g of O_2 = 10/32 = 0.312 mol

Thus

15 L of H_2 gas at STP = 0.669 mol

5 L of N_2 gas at STP = 0.223 mol

0.5g of H_2 gas = 0.25 mol

10 g of O_2 = 0.312 mol

From above 15 L of H_2 gas at STP contain more number of moles thus more number of molecules

Percentage Composition of a Compound

Percentage composition of a compound is the relative mass of the each of the constituent element in 100 parts of it. It is readily calculated from the formula of the compound. Molecular mass of a compound is obtained from its formula by adding up the masses of all the atoms of the constituent elements present in the molecule.

For example : formula of methyl alcohol is CH_3OH

Molecular weight of CH_3OH =12+ 3(1) +16+1 = 32g

Amount of carbon = 12 g there for % of carbon

32 g of CH_3OH = 12 g

100 g = ?

On simplification we get % of Carbon (C) = 37.5%

Similarly hydrogen = 12.5%

And Oxygen = 50%

Empirical formula and molecular formula

Empirical formula represents the simplest relative whole number ratio of atoms of each element present in the molecule of the substance. For example CH is the empirical formula of benzene in which ratio of the atoms of carbon and hydrogen is 1:1. It also indicate ratio of carbon and hydrogen is 12:1 by mass.

Molecular formula of a compound is one which expresses as the actual number of atoms of each element present in one molecule. C_6H_6 is the molecular formula of benzene indicating that six carbon atoms and six hydrogen atoms are present in a molecule of benzene. Thus

Molecular formula = n× Empirical formula

Determination of Empirical and molecular formula.

The following steps are followed to determine the empirical formula of the compound

i) The percentage composition of the compound is determined by quantitative analysis

ii) The percentage of each element is divided by its atomic mass. It gives atomic ratio of the elements present in the compound

iii) The atomic ratio of each element is the divided by the minimum value of atomic ratio as to get the simplest ratio of the atoms of element present in the compound.

Iv) If the simplest ratio is fractional, then values of simplest ratio of each element is multiplied by a smallest integer to get a simplest whole number for each of the element

v)To get the empirical formula, symbols of various elements present are written side by side with their respective whole ratio as a subscript to lower right hand corner of the symbol

Illustration

Q) Caffeine has the following percent composition: carbon 49.48%, hydrogen 5.19%, oxygen 16.48% and nitrogen 28.85%. Its molecular weight is 194.19 g/mol. What is its molecular formula?

Solution

1) Calculate the empirical formula:

carbon: 49.98 g ÷ 12.011 g/mol = 4.16
hydrogen: 5.19 g ÷ 1.008 g/mol = 5.15
nitrogen: 28.85 g ÷ 14.007 g/mol = 2.06
oxygen: 16.48 g ÷ 15.999 g/mol = 1.03

carbon: 4.16 ÷ 1.03 = 4.04 = 4
hydrogen: 5.15 ÷ 1.03 = 5

nitrogen: 2.06 ÷ 1.03 = 2
oxygen: 1.03 ÷ 1.03 = 1

2) Empirical formula is $C_4H_5N_2O$. The "empirical formula weight" is about 97.1, which gives a scaling factor of two.

3) The molecular formula is $C_8H_{10}N_4O_2$.

Method 2:

Number of carbon atoms in molecule

$$=\frac{\%}{100}\times\frac{Molecular\ mass}{Atomic\ mass}$$

$$=\frac{49.48}{100}\times\frac{194.19}{12}=8.00$$

Number of oxygen atoms in molecule

$$=\frac{\%}{100}\times\frac{Molecular\ mass}{Atomic\ mass}$$

$$=\frac{16.48}{100}\times\frac{194.19}{16}=2.00$$

Number of nitrogen atoms in molecule

$$=\frac{\%}{100}\times\frac{Molecular\ mass}{Atomic\ mass}$$

$$=\frac{28.85}{100}\times\frac{194.19}{14}=4.00$$

Number of hydrogen atoms in molecule

$$= \frac{\%}{100} \times \frac{Molecular\ mass}{Atomic\ mass}$$

$$= \frac{5.15}{100} \times \frac{194.19}{1} = 10.00$$

Thus formula is $C_8H_{10}N_4O_2$

Chemical Equation and Stoichiometry

Stoichiometry is the calculation of the quantities of reactant and products involved in a chemical reaction.

Consider a reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

The calculation based on mole-mole relationship

In such calculations, number of moles of reactants are given and those of products required. Conversely if the number of moles of products are given, the number of moles of reactants are required. Above reaction can be interpreted as

1 mole of N_2 + 3 mole of H_2 → 2 mol of NH_3

Calculation based on mass- mass relationship

It making necessary calculations, following steps are followed

a) Write down the balanced chemical equation
b) Write down the theoretical amount of reactants and products involved in the reaction
c) Calculate the unknown amount of substance using unitary method

28 g of N_2 + 6g of H_2 → 34 g of NH_3

Calculation based on volume-volume relationship

In such calculation after balancing reaction quantity of gases are expressed in volume based on STP conditions

1 Volume N_2 + 3 Volume of H_2 → 2 Volume of NH_3

Or 22.4L of N_2 + 67.2L of H_2 → 44.8L of NH_3

Limiting reagent:

Limiting reactant or reagent is the reactant that is entirely consumed when a reaction goes to completion. Other reactants which are not completely consumed in the reaction are called excess reactant

Calculation involving percent yield

The amount of the product actually obtained is called the actual yield. Theoretical yield is expected quantity of product to achieve.

$$Percent\ yield = \frac{Actual\ yield}{Theoretical\ yield} \times 100$$

CONCENTRATION OF SOLUTION

1. Molarity

$$M = \frac{Number\ of\ moles\ of\ solute}{Volume\ of\ solution\ (\ in\ litre)}$$

$$M = \frac{W \times 1000}{M_0 \times V}$$

W : Wight of solute in grams
M_0 : Molecular mass of solute
V: Volume of solution in ml

2. Normality

$$N = \frac{Number\ of\ gram\ equivalents\ of\ \ solute}{Volume\ of\ solution\ (\ in\ litre)}$$

$$N = \frac{W \times 1000}{Eq \times V}$$

W : Wight of solute in grams
Eq : Equivalent weight of solute
V: Volume of solution in ml

Equivalent weight of solute

$$Eq = \frac{molecular\ mass\ of\ solute}{n}$$

n factor : is acidity, basicity, Charge on ion, change in oxidation state

Acidity : Number replaceable -OH group in basic compound

Example: NaOH : number of -OH groups 1, Thus Acidity = 1

$Ca(OH)_2$: Number of –OH groups 2, Acidity = 2

$Al(OH)_3$: Number of –OH groups 3, Acidity = 3

Basicity of acid is defined as the no of ionizable hydrogen (H^+) ions present in one molecule of an acid.

Example: HCl, HNO_3, CH_3COOH : H^+ ions are 1, thus Basicity is 1,

H_2SO_3 : H^+ ions are 2, thus Basicity is 2,

Oxalic acid : H^+ ions are 2, thus Basicity is 2

Charge: Na^+ thus take charge as 1

Ca^{++} thus take charge as 2

SO_4^{-2} thus take charge as 2

Change is oxidation state:

Example $KMnO_4$

Basic medium : Change in oxidation state of Mn= +1

Acidic medium : Change in oxidation state of Mn= +5

Neutral medium : Change in oxidation state of Mn= +3

From equation

$$N = \frac{W \times 1000}{Eq \times V}$$

$$NV = \frac{W \times 1000}{Eq}$$

Here NV is called milliequlivalence

The law of equivalence

The law of equivalence provide, us the molar ratio of reactants and products without knowing the complete balanced reaction, which is as good as having a balanced chemical reaction. The molar ratio of reactants and products can be known by knowing the n-factor of relevant species. According to the law of equivalence, whenever two substances react, the equivalents of one will be equal to the equivalents of other and the equivalents of any product will also be equal to that of the reactant.

In general, whenever two substance react with their n-factor in the ratio of a:b, then their molar ratio in a balanced chemical reaction would be b:a

Also for dilution of solution and titration

$N_1V_1 = N_2V_2$

Illustration

Q) 28 g of metal requires 24.5 g of sulphuric acid to het dissolved. Calculate the equivalent weight of metal and the volume of hydrogen liberated at STP

Solution

Molecular weight of Sulphuric acid = 98 and basicity = 2 (because of two H^+)

Thus Equivalent weight = 98/2 = 49

Let E be the equivalent weight of metal

According to law of chemical equivalence,

Number of gram equivalent of metal = Number of gram equivalents of sulphuric acid

$$\frac{28}{E} = \frac{24.5}{49}$$

E = 56

Now one equivalent of a metal liberate one equivalent volume of hydrogen

Hydrogen is a diatomic gas with valency 1

Equivalent volume of hydrogen = 11.2L at STP

It means 56 g of metal liberate 11.2 L hydrogen

∴ Volume of hydrogen liberated by 28g metal

$$= \frac{11.2 \times 28}{56} = 5.6L$$

Q) 6.78 g of copper is displaced from copper sulphate solution by 7 g zinc. Find the equivalent weight of copper, if equivalent weight of zinc is 32.5

Solution

According to law of chemical equivalence

Let E be the equivalent weight of copper

Number of gram equivalents of copper = number of gram equivalents of zinc

$$\frac{6.78}{E} = \frac{7}{31.5}$$

E = 31.5

Q) 100 mL of 0.1N NaOH solution is required for neutralisation of 0.49 g of dibasic acid. What is the molecular weight of acid.

Solution:

From the formula of miliequivalence

$$NV = \frac{W \times 1000}{Eq}$$

we will calculate miliequivalence of acid = NV = 0.1×100 = 10

Milliequivalence of base $=\frac{W\times1000}{Eq}$

$$\frac{0.49 \times 1000}{Eq}$$

Milliequivalence of base = milliequivalence of acid

$$\therefore$$

$$10 = \frac{0.49 \times 1000}{Eq}$$

Eq= 49

Molecular weight = Equivalent weight × basicity

Given acid is dibasic thus Molecular weight = 49×2 = 98

Q) Calculate the volume of each of the two hydrochloric acids of strength 12N and 4N respectively that are mixed to make one litre solution of strength 5N

Solution

Let Volume of 12N solution be = x

Then volume of 4N solution will be = 1000 −x

Now $N_1V_1 + N_2V_2 = NV$

$12x + 4(1000 - x) = 5(1000)$

On simplification we get x = 125 mL

That is if 125 mL of 12 N solution is mixed with 875mL of 4 N solution we will get 1000mL of 5N solution.

THE SOLID STATE

SECTION I
STRUCTURE AND CLOSE PACKING

A solid is a state of matter which possesses
i) definite shape and volume.
ii) incompressibility, rigidity and mechanical strength.
iii) the particles in solids are very closely packed in some geometric pattern with small voids and interparticle forces are very strong.
iv) particle motion is restricted to vibratory motion only.

CLASSIFICATION OF SOLIDS

The solids are of two types:

(i) Amorphous solids

Solids in which constituents do not possess the orderly arrangement over the long range are called ***amorphous*** solids. Region in an amorphous solid having an orderly arrangement are known as ***crystallite***. They may have only short range order and do not posses sharp melting points. They undergo irregular cleavage (cut). Structures of amorphous solids are similar to that of liquid. Amorphous solids soften over range of temperature and can be molded and blown in to various shapes. On heating they become crystalline at some temperature. Therefore some time they are called as ***pseudo solids*** or ***super cooled liquids*** Glass become milky some times on heating is due to this property. Due to lack of long range arrangement of particles or irregular arrangement of particles, amorphous solids are isotropic in nature. It is physical properties like resistivity. Refractive index is independent of direction

Examples: Glass rubber and plastics are typical examples of amorphous solids. Structure of quartz is crystal while quartz glass is amorphous. Amorphous silicon is one of the best photovoltaic materials available for conversion of sunlight to electricity

(ii) CRYSTALLINE SOLIDS

Solids in which various constituents unit like atoms, ions or molecules are arranged in an orderly manner which repeats itself over long distance are called ***crystalline*** solids. They exhibit very sharp melting points and undergo clean cleavage (cut). Crystalline solids are ***anisotropic*** in nature, that is, some physical property like electrical resistance, refractive index shows different values when measured along different direction in the same crystal. Reason for such behavior is particles are arranged differently along different direction.
Examples: all metallic elements, non-metallic elements like sulphur, phosphorous and ionic compound like sodium chloride, zinc sulphide and naphthalene

CLASSIFICATION OF CRYSTALLINE SOLIDS

Crystalline solids can be classified on the basis of nature of intermolecular forces operating between them in to following four categories

i) Molecular ii) Ionic iii) metallic iv) covalent

(i) Molecular solids:

Further divided in into three categories

a) Non-polar molecular solids :

i	Constituent particles	Non-polar molecules
Ii	Bonding force	Dispersion forces or London forces
iii	Binding energy in (kJ/mol)	0.05-40
iv	Melting point	Very low about 84
v	Physical nature	Soft
vi	Electrical conductivity	Insulator
	Examples	H_2, N_2, O_2,He, NA Ar, Kr

b) Polar molecular solids:

i	Constituent particles	Polar molecules
Ii	Bonding force	Dipole -dipole interaction
iii	Binding energy in (kJ/mol)	5-25
iv	Melting point	low about 158
v	Physical nature	Soft
vi	Electrical conductivity	Insulator
	Examples	HCl, HBr, SO_2, SO_3 etc

c) H-bonded molecular solids :

i	Constituent particles	Polar molecules containing O, N F and H
Ii	Bonding force	Hydrogen bonding and Dipole -dipole interaction
iii	Binding energy in (kJ/mol)	10-40
iv	Melting point	low about 273
v	Physical nature	Hard
vi	Electrical conductivity	Insulator
	Examples	H_2O (ice)

(ii) Ionic solids:

i	Constituent particles	Ions
Ii	Bonding force	Electrostatic force of attraction
iii	Binding energy in (kJ/mol)	400-4000
iv	Melting point	High 1500
v	Physical nature	Hard but brittle
vi	Electrical conductivity	Insulator in solid state but conductor in molten and in aqueous state
	Examples	NaCl, KCl, $CuSO_4$ CaF_2 CsCl etc

iii) Metallic solids:

i	Constituent particles	Positively charged ions (kernels) in a sea of mobile electrons
Ii	Bonding force	Metallic bonding
iii	Binding energy in (kJ/mol)	70-1000
iv	Melting point	800-1000
v	Physical nature	Hard but malleable and ductile except Na, K, Li etc
vi	Electrical conductivity	conductor
	Examples	Fr, Cu, Zn, Ni, Co, Al, Au, Pt etc

iv) Covalent or Network solids:

i	Constituent particles	Atoms
Ii	Bonding force	Covalent bonds
iii	Binding energy in (kJ/mol)	150-500
iv	Melting point	High 4000
v	Physical nature	Hard
vi	Electrical conductivity	Insulator except graphite
	Examples	SIO_2, diamond, graphite, SiC (carborundum)

CRYSTAL LATTICE AND UNIT CELL

Crystal lattice:

The regular arrangement of an infinite set of points which describes the three dimensional arrangement of constituent particles (atom, ions, molecules) in space is called a ***crystal lattice or space lattice*** The space lattice may be one, two or three dimensional depending upon the number of parameters required to define it.

There are only 14 possible three dimensional lattices. They are called ***Bravais Lattice***

Following are the characteristics of a crystal lattice

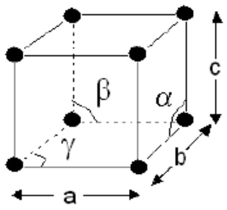
(i) Each point in a lattice is called lattice point or lattice site

(ii) Each point in a crystal lattice represents one constituent particle which may be atom, ion or molecule

(ii) Lattice points are joined by straight line to bring out the geometry of the lattice

The smallest repeating units of space lattice which when repeated over and over again in three dimensions, result into whole of the space lattice of crystal is called ***unit cell***. The crystal may, therefore be considered to consists of infinite number of unit cells.

A unit cell is characterized by :



(i) its dimensions along the three edges a, b, c. These edges may or may not be perpendicular to each other

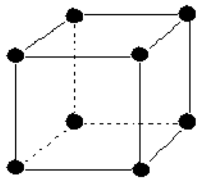
(ii) angle between edges α (between b and c) ; β (between a and c) and γ (between a and b).

Thus unit cell is characterized by six parameters

Types of unit cells:

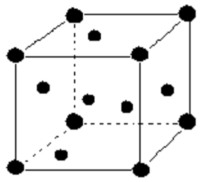
(i) Simple or primitive

The unit cells in which, particles (i.e. atoms ions, or molecules) are present only at the corners of the unit cell are called simple or primitive cells



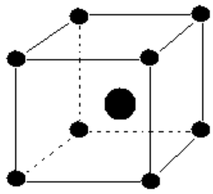
(ii) Face-centered

In this type of unit cells, points are represented at the corners as well as centers of each six faces



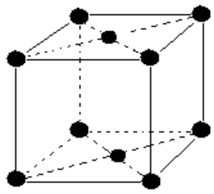
(ii) Body-centered

These are the unit cells in which points are present at the corners and an additional point is present at the centre of the unit cell



(iv) End centered

The unit cell in which points are present at the corners and at the centre of the two ends faces



Number of atoms in unit cell

It should be noted that

(i) An atom present at the corner is equally shared by eight unit cells. Therefore contribution of an present at the corner to each unit cell is 1/8

(ii) An atom present at the face centre is equally shared between two unit cells. Therefore, contribution of an atom present at the face centre towards each unit cell is ½

(iii) An atom present within the body of the unit cell (body centre) is shared by no other unit cell. Hence, contribution of an atom present within body of unit cell is 1.

(iv) An atom present at the edge centre of unit cell is equally shared by four unit cells. Therefore, contribution of an atom present at the edge centre towards each unit cell is ¼

The point representing the atoms, molecules or ions in a unit cells are known as ***lattice point*** and is denoted by Z. also called as ***Rank of a crystal***

The number of lattice point (or number of atoms) per unit cell in the above four types of unit cells may be calculated as follows -

a	Simple or Primitive	$8 \times \frac{1}{8}(fromcorners) = 1$
b	Face-centered	$8 \times \frac{1}{8}(fromcorners) + 6 \times \frac{1}{2}(from\ face\ centre) = 4$
c	Body-centered	$8 \times \frac{1}{8}(fromcorners) = 1 + 1(from\ body\ centre) = 2$
d	End-centered	$8 \times \frac{1}{8}(fromcorners) + 2 \times \frac{1}{2}(from\ end\ faces) = 2$

Unit cells of 14 types of Bravais Lattices

	System	Axial Ratio	Axial angles	Unit cells	Examples
1	Cubic regular	a = b = c	$\alpha = \beta = \gamma$ all 90^{o}	1) simple 2) face centered 3) body centered	NaCl, KCl, ZnS, Cu_2O, Pb,Ag, Au, Hg, diamond, Alums
2	Tetragonal	a = b ≠ c	$\alpha = \beta = \gamma$ all 90^{o}	4) simple 5) Body centered	SnO_2, ZnO_2, TiO_2, $NiSO_4$, $ZrSiO_4$ $PbWO_4$, White Sn
3	Hexagonal	a = b≠ c	$\alpha = \beta = 90$ $\gamma = 120$	6)simple	ZnO, PBI_2, CdS, HgS, Graphite, Ice, Beryl, Mg, Zn, Cd
4	Trigonal or Rhombohedral	a = b = c	$\alpha = \beta = \gamma$ $\neq 90$	7) simple	$NaNO_3$, $CaSO_4$ Calcite, , Quarts, As, Sb, Bi
5	Orthorhombic (Rhombic)	a ≠ b≠ c	$\alpha = \beta = \gamma$ all 90^{o}	8) Simple 9)face centered 10) Body centered 11) end centered	KNO_3, K_2SO_4, Calcite, $BaSO_4$ Rhombic sulphure, $MgSO_4.7H_2O$
6	Monoclinic	a ≠ b≠ c	$\alpha = \gamma = 90$ $\beta \neq 90$	12)Simple 13)End centered	$Na_2SO_4.10H_2O$, $Na_2B_4O_7.10H_2O$ $CaSO_4.2H_2O$. Monoclinic sulphur
7	Triclinic	a ≠ b≠ c	$\alpha \neq \beta \neq \gamma$ $\neq 90$	14) Simple	$CuSO_4.5H_2O$, $K_2Cr_2O_7$, H_3BO_3

Solved example :

Q) A compound formed by the element X and Y crystallizes in cubic structure in which X atoms are at the corners of the cube with Y atoms are at the centre of the face. What is the formula of the compound.

Solution :

The number of X–atoms per unit cell $8 \times \frac{1}{8}(from corners) = 1$

Number of Y atoms per unit cell = $6 \times \frac{1}{2}(from face\ centre) = 3$

Thus chemical formula = XY_3

CLOSE PACKING OF CRYSTALLINE SOLIDS

Close packing refers to tight arrangement of spheres in a given space in such a way that they occupy the maximum available space and hence the crystal has maximum density.
The number of nearest neighbors of a particle is called ***coordination number***

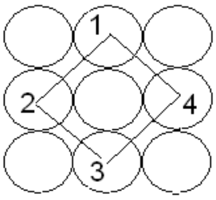
a) Close packing in one dimension:

There is only one way of arranging spheres in a one dimensional close packed structure, that is to arrange in row and touching each other. Coordination number is 2

b) Two dimensional close packing

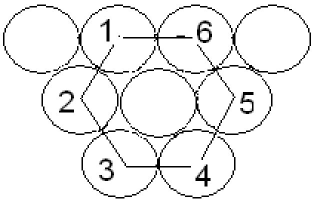
(1) Square close packing

Here spheres are arranged in such a way that every sphere is in contact with four other spheres coordination number 4 since second row exactly below first such arrangement is called AAA type arrangement



(2) Hexagonal close packing :

In this kind of packing, spheres are arranged in such a way that every sphere is in contact with six other spheres. Coordination number 6



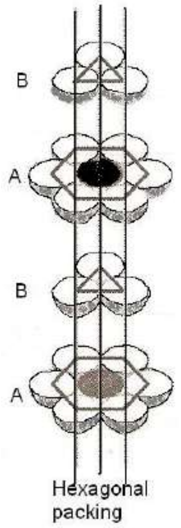
The second row may be placed above the first in a staggered manner such that its spheres fit in the depressions of the first row. If the arrangement of first row is called A type, the one in second row is different type and may be called B type. When third row is placed are line with first row then this row is also A. And arrangement is known as ABAB type

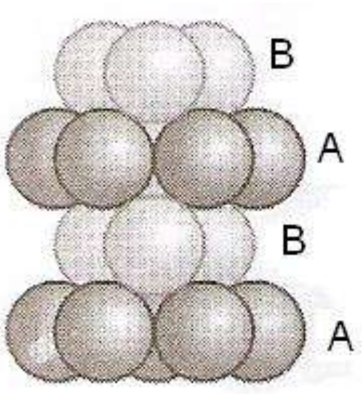
C) Three dimensional close packing

Two types of three dimensional close packing are obtained from hexagonal close packing layers a) Hexagonal close packing (hcp) b) Cubic close packing (ccp)
While other two types of three dimensional close packing are obtained from square close packed layers. c) Body Centered cubic arrangement (bcc) and d) simple cubic arrangement

a) Hexagonal Close –packing (hcp)

In this arrangement, atoms are located at the corners and centre of two hexagonal placed parallel to each other , three more atoms are placed in a parallel to midway between these two planes:





<u>Characteristic features of hcp</u>

(i) This type of packing is ABAB… type of arrangement of the layers which indicates that every alternate layers are alike

(ii) It has a 6-fold axis of symmetry

(iii) Each atom is surrounded by 12 another atoms, 6 in own layer and 3 above and 3 blow layers. Coordination number 12

(iv) In hcp arrangement, the atom occupy 74% of the available space and thus 26% of space is empty

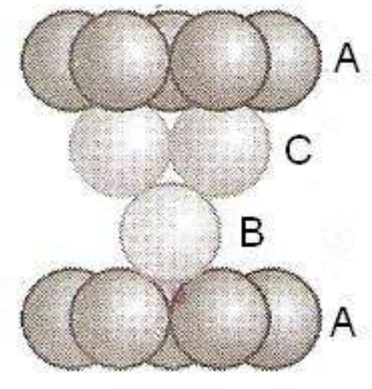
(v) It has only one set of parallel close –packed layers. Hence, the chances for slipping of one layer over the other is less..

Example : BE, Cd, Li, Ca, Cr, Mo, V, Mg, Zn, Ce, Zr, OS, Ru, He

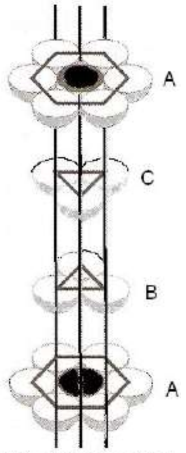
b) Cubic closed packing (ccp) or face centered cubic (fcc)

In this type of close packing, atoms are arranged at the corners and at the centers of all six faces of a cube.

If we start with hexagonal layers of spheres as shown in figure and second layer of spheres is arranged placing the spheres over the holes in first layer, one half of the holes can be filled by these spheres. Suppose that spheres in third layers are so arranged that they cover holes in second layer. , the third layer neither resembles first layer or second layer. The fourth layer resembles first , fifth resembles second and sixth resembles third layer, then this type of arrangement is known as cubic closed-packed (ccp) arrangement or face centered cubic (fcc) arrangement. The percentage of free space is 26% and coordination number is 12.



Cubic



Cubic close packing

Characteristic features of ccp:

(i) This type of packing has ABCABC…. type of arrangement of the layer i.e. the first three layers are quite different from each other but this set of layer is repeated over and again the addition of more layers

(ii) It has cubic symmetry, the whole structure has four 3-fold axis of symmetry

(iii) As in hcp, each atom in ccp arrangement has 12 nearest has 12 nearest neighbors i.e. the coordinate number of each atom is 12

(iv) The ccp arrangement of atoms occupies 74% of the available space and thus 26% of the space remains empty.

(v) It has four sets of parallel close packed layers. Hence, the chances for slipping of one layer over the other are more in the ccp arrangement than in the hcp arrangement. Hence, metals having ccp structure

(vi) Example : Cu, Ag, Au, Pt, Al, Cr, Co, Cu, Ag, Fe, PB, Mn, Ni, Ca, Sr, Pt all noble gases except He are found to posses cubic close packed structure. Nearly 60% of the metals have been found to possess either hcp or ccp structure.

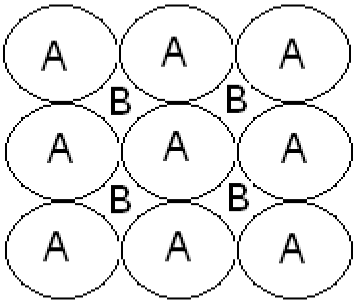
c) Body – Centered cubic structure (bcc)

Characteristic feature of body centered cubic arrangement:

i) In a body centered cubic arrangement, the atoms occupy corners of a cube with an atom at its centre.

(ii) Each atom is in contact with eight other atoms (four atoms in the layer just above and four atoms in the layer just below) and hence the coordination number in this type of arrangement is only eight

(iii) This arrangement of atoms occupies only 68% of the total volume, so this arrangement is found in Na, K, Cs, Rb, W, V, Mo, and Ba. Only 20% of the metallic elements found to posses bcc arrangement.



d) Simple cubic arrangement

The particles in the adjacent rows may show a horizontal as well as a vertical alignment forming cubic. A central sphere is surrounded by four other spheres in two dimension and in three dimension surrounded by 6 spheres

VOIDES OR HOLES

A crystal is formed as result of close packing of its constituting particles which are supposed to have spherical shape. Since they are touching each other only at one point, there must remain some empty spaces are called ***voids or holes or interstitial site***

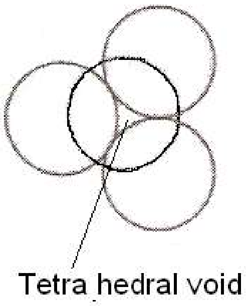
a) Tetrahedral voids

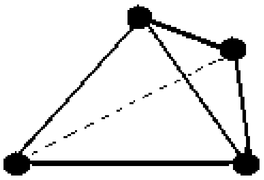
The voids, which are surrounded by four spheres which lie at the vertices of a regular tetrahedron are called ***tetrahedral void***. There are 8 tetrahedral voids around each sphere. If N are the number of close packed sphere than tetrahedra voids are 2N. coordination number of tetrahedral void is 4

If r =radius of the spherical tetrahedral site

R= radius of closely packed sphere

Size of the tetrahedral void = 0.225R





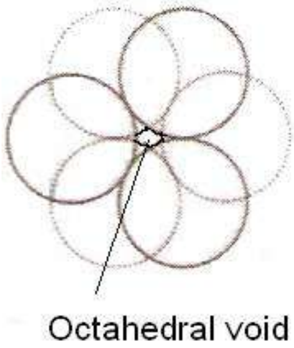
b) Octahedral voids

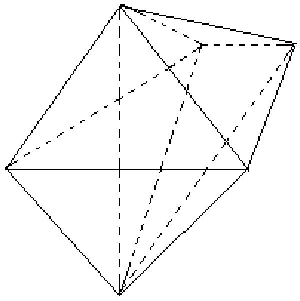
The void, which are surrounded by six sphere which lie at the vertices of a regular octahedron, is known as ***octahedral void***. There are six octahedron void around each sphere . There is one void per atom in a crystal. If N are the number of close packed sphere than octahedral voids are N . coordination number of octahedral void = 6

If r =radius of the spherical octahedral site

R= radius of closely packed sphere

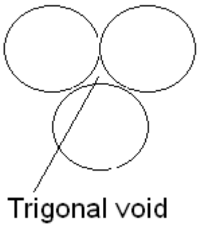
Size of the tetrahedral void = 0.414R





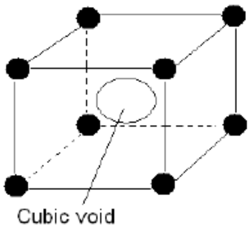
c) Trigonal void

The void, enclosed by three sphere in contact is called a ***Trigonal void***. This void and the spheres surrounding it are in same plane. There are 24 void around each sphere. There are 8 Trigonal voids per atom in a crystal.
If r =radius of the spherical Trigonal site
R= radius of closely packed sphere
Size of the tetrahedral void = 0.155R



d) Cubic void

This type of void is formed between 8 closely packed spheres which occupy all eight corners of cube. This site is surrounded by eight spheres which touches each other. Size of the cubical void is given as
If r =radius of the spherical cubical site
R= radius of closely packed sphere
R=0.732R



Decreasing order of the size of the various voids :
Cubic > Octahedral > Tetrahedral >Trigonal

Number of tetrahedral void = 2 (Number of atoms or octahedral voids)

PACKING EFFICIENCY OF ccp AND hcp STRUCTURE

Packing efficiency is the percentage of total space filled by the particles.

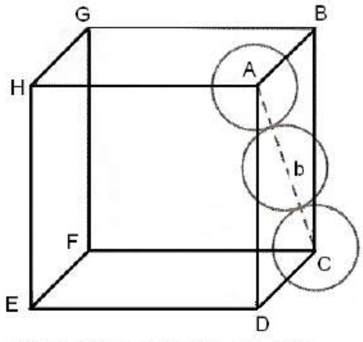
a) Packing efficiency of ccp and hcp structure

In figure, let cell edge length be 'a' and face diagonal AC = b

In ΔABC

$AC^2 = BC^2+AB^2$

$b^2 = a^2 + a^2$ Thus $b = \sqrt{2}\, a$ –(i)



other sides spheres are not shown for clarity

If radius of sphere is r, we find b = 4r

From eq(i) $\sqrt{2}\, a = 4r$ Thus $r = \frac{a}{2\sqrt{2}}$

There are four spheres per unit cell in ccp structure.

Volume of four spheres = $4 \times \frac{4}{3}\pi r^3$

Volume of the cube = $a^3 = \left(2\sqrt{2}r\right)^3 = 16\sqrt{2}r^3$

Percentage of packing efficiency =

$$\frac{Volume\ occupied\ by\ four\ spheres\ in\ unit\ cell}{Total\ colume\ of\ the\ unit\ cell} \times 100\%$$

$$= \frac{4 \times \frac{4}{3}\pi r^3 \times 100}{16\sqrt{2}r^3} \times 100\%$$

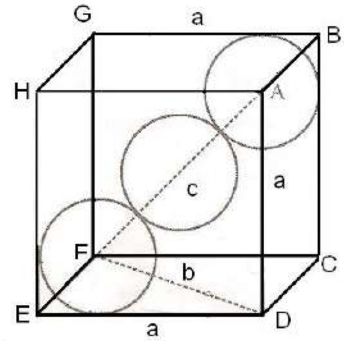
$$= \frac{\pi}{3\sqrt{2}} \times 100\%$$

Thus efficiency = 72%

OR Packing factor = $\frac{\pi\sqrt{2}}{6} = 0.72$

b) Packing efficiency of Body Centered Cubic Structure

In figure, let cell edge length be ‘a’ and face diagonal FD = b , diagonal FD = c



From ΔEFD $b^2 = a^2 + a^2$ Thus $b = \sqrt{2}\,a$ –(i)

From ΔAFD $c^2 = a^2 + b^2$

From eq(i)

$c^2 = a^2+2a^2 = 3a^2$

$c = \sqrt{3}\,a$ –(ii)

The length of the body digonal c is equal to 4r . Here r is the radius of the sphere (atom)

From eq(ii) we get $\sqrt{3}\,a = 4r$

$$r = \frac{\sqrt{3}}{4}a$$

There are two spheres per unit cell in bcc

Volume of two sphere = $2 \times \frac{4}{3}\pi r^3$

Volume of cube = $a^3 = \left(\frac{4}{\sqrt{3}}r\right)^3$

Percentage of packing efficiency =

$$\frac{Volume\ occupied\ by\ two\ spheres\ in\ unit\ cell}{Total\ colume\ of\ the\ unit\ cell} \times 100\%$$

$$= \frac{2 \times \frac{4}{3}\pi r^3 \times 100}{\left(\frac{4}{\sqrt{3}}r\right)^3} \times 100\%$$

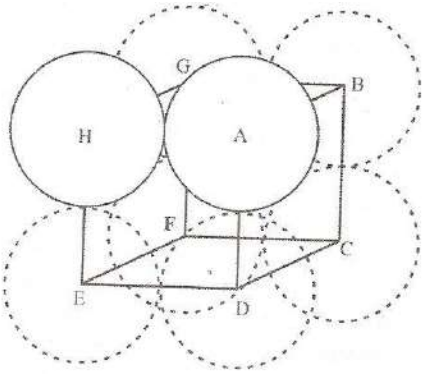
$= \frac{\sqrt{3}\pi}{8} \times 100\%$ = 68%

Thus efficiency = 68%

OR Packing factor = $\frac{\pi\sqrt{3}}{6} = 0.68$

c) Packing efficiency in simple cubic lattice

In simple cubic lattice, 8 lattice points are on the corners of the cube. Since a simple cubic has only one atom. Let edge length be a then a = 2r, here r is the radius of sphere



Percentage of packing efficiency =

$$\frac{Volume\ occupied\ by\ one\ spheres\ in\ unit\ cell}{Total\ colume\ of\ the\ unit\ cell}\times 100\%$$

$$=\frac{\frac{4}{3}\pi r^3\times 100}{(2r)^3}\times 100\%$$

$=\frac{\pi}{6}\times 100\%$ = 52.4%

Density of cubic crystal

Density of unit cell (ρ)

$$\rho=\frac{mass\ of\ unit\ cell}{volume\ of\ unit\ cell}$$

Mass of unit cell = number atoms in a unit cell X mass of one atom

$mass\ of\ unit\ cell = Z\times\frac{M}{N_0}$ here N_0= Avogadro’s number and M = Molar mass

If length of edge = a then volume = a^3

$$\rho=\frac{M\times Z}{N_0 a^3}$$

SUMMARY OF STRUCTURE OF METALS

Sr.No	Property	Hexagonal close packed (hcp)	Cubic close packed (ccp or fcc)	Body centered cubic (bcc)
1	Arrangement of packing	Closed pack	Closed pack	**Not** closed pack
2	Type of packing	AB AB AB A…	ABC ABC AB…	AB AB AB A…
3	Packing efficiency	74%	74%	68%
4	Coordination number	12	12	8
5	Malleability and ductility	Less malleable, hard and brittle	malleable and ductile	-------
6	Examples	BE, Mg, Ca, Cr, MO, V, Zn	Cu, Ag, Au, Pt	Alkali metals, Fe

Radius ratio

In ionic compounds, the geometrical shape of ionic crystals as well as the coordinate number depends on the relative size of the ions. Positive ions are small in size thus occupy positions in voids. And negative ions are larger in size occupy positions in corners.
The ratio of the radii of the cation to the anion in crystal lattice is called ***radius ratio***

$$Radius\ ratio = \frac{r_+}{r_-} = \frac{Radius\ of\ the\ cation}{Radius\ of\ the\ anion}$$

Relation ship between Radius ratio, Coordinate Number and Geometrical Shape

Radius ratio	Coordination number	Structural arrangement	Structure type	Example
0.155 – 0.225	3	Planer triangular	--	B_2O_3
0.225-0.414	4	Tetrahedral	ZnS	CuCl, CuBr, CuI, BaS, HgS
0.414 – 0.732	6	Octahedral	Sodium chloride	NaBR, KBr, MgO, MnO,CaO,CaS
0.732 -1	8	Body- centred cubic	Cesium chloride	CsI, CsBR, NH_4Br

Solved examples

Example 1: Potassium metal crystallises in face-centred cubic arrangement with rdge length 574pm. What is the shortest separation of any two potassium nuclei

Solution: For fcc arrangement ditance of neighbour = 2r =2 × $\frac{a}{2\sqrt{2}}$ = $\frac{a}{\sqrt{2}}$ = 0.707a

=0.707X574 = 46pm

Example 2: The cubic unit cell of aluminium (molar mass 27.0 g/mole) has an edge length of 405 pm and density 2.70 g/cm^3. What tpe of unit cell is?

Solution : from formula for density $\rho = \frac{M\times Z}{N_0 a^3}$

$$Z = \frac{\rho N_0 a^3}{M}$$

$$Z = \frac{2.7\times6.023\times10^{23}\times\left(405\times10^{-10}\right)^3}{27.0} = 4$$

i.e number of atoms per unit cell is 4. Hence, unt cell is face centred type

Example 3: Crystalline CsCl has density 3.988 g/cc. Caluclate the volume occupied by single CsCl ion pair in the crystal (CsCl = 168.4)

Solution: CsCl has simple cubic arrangement hence Z=1

Thus volume of unit cell = volume of single CsCl ion pair

From formula for density $\rho = \frac{M\times Z}{N_0 a^3}$

$a^3 = \frac{M\times Z}{N_0\rho} = \frac{168.4\times 1}{6.023\times 10^{23}\times 3.998}$ =7.014X10^{-23} cc

Example 4: A metal is found to have a specific gravity of 10.2 at 25^{O}C. It crystallises in a body-centred cubic lattice with a unit cell edge length of 3.0 Å. Calculate the atomic weight

Solution : From formula for density $\rho = \frac{M\times Z}{N_0 a^3}$,for body centred Z=1

$$M = \frac{\rho N_0 a^3}{Z} = \frac{10.2\times 6.023\times 10^{23}\times \left(3\times 10^{-8}\right)^3}{2} = 82.9u$$

Example 5: If the anions (B0 form hexagonal close packing and cation (A) occupy only 2/3 octahedral sites in it, then what would be the general formula of the compound

Solution: Number of anions (B) per unit cell = 6 (**for hcp arragement**)
Total number of octahedral sires = 6
Nuber of cations per unit cell = 6 X(2/3) = 4
A:B = 4 :6 or A:B = 2:3
Hence formula of compound is A_2B_3

Example 6: A metallic element has cubic lattice. Each edge of unit cell is 3 Å . the denity of the metal is 8.5 g/cc. How many unit cells will be present in 50g of metal?
Solution : Volume of unit cell = a^3 = (3X10^{-8})^3 cm^3
Mass of unit cell =density X volume = 8.5 X(3X10^{-8})^3
Number of unit cell = Mass of sample / mass of unit cell
Number of unit cell = $\frac{50}{8.5\times 27\times 10^{-24}}$ = 2.178 X 10^{23}

Example 7 : Tungsten is arranged in face-centred cube having unit cell volume of 31.699 Å^3 Calculate the radius and atomic volume of tungsten.
Solution : Volme (a^3) = 31.699 Å^3
Edege length a = 3.165 Å.
For fcc arrangement

$$Radius\ \ r = \frac{\sqrt{2}a}{4} = \frac{1.414\times 3.165}{4} = 1.1188\ \text{Å}$$

Example 8: A substance has a face centred cubic crystal with density of 1.984g/cm^3 and edgelength 630 pm. Caluclate the molar mass of the substance.

Solution :

From the formula of density $\rho = \frac{M\times Z}{N_0 a^3}$ for fcc Z = 4

$$M = \frac{\rho N_0 a^3}{Z} = \frac{1.984\times 6.023\times 10^{23}\times \left(630\times 10^{-10}\right)^3}{4} = 74.70$$

Example 9 : Analysis shows that nickel oxide has formula $Ni_{0.98}\ O_{1.0}$. What fraction of the nickel exists as Ni^{+2} and Ni^{+3} ions?

Solution: If there are 100 oxygen then Ni = 98.
Let Ni^{+2} ions = x
then Ni^{+3} ions = 98-x
Since lectric neutrality is maintained
Charge on Ni ions = Change on oxygen
2(x) + 3(98-x) = 2(100)
-x + 294 = 200
X = 94
Thus Ni^{+2} =94% and Ni^{+3} =6%

Example 10: A mineral having the formula AB_2 crystallises in the cubic closed lattice, with the A atoms occupying the lattice points. What are the co-ordinatation number of the A and B

Solution : In ccp of AB_2 , A- atom occupy the lattice points, aand number of B are twice the A thus must be occupying terahedral void. Thus A must have Coordination number 8 and B coordination number 4.

Example11 : An element (atomic mass = 60) having face-centred cubic unit cell has a density of 6.23 g/cm³. What is the edge length of the unit cell

Solution

From the formula for density $\rho = \frac{ZM}{a^3 N_A}$

$a = \left(\frac{ZM}{\rho N_A}\right)^{\frac{1}{3}}$ For fcc Z = 4,

$$a = \left(\frac{4 \times 60}{6.23 \times 6.023 \times 10^{23}}\right)^{\frac{1}{3}}$$

[First adject power of 10 such that we can find cube root we will make power from 23 to 24]

$$a = \left(\frac{4\times60}{0.623\times6.023\times10^{24}}\right)^{\frac{1}{3}} = \left(\frac{240}{0.623\times6.023\times10^{24}}\right)^{\frac{1}{3}}$$

[Take log of all the terms]
log(240) = 2.3802
log (0.623) = $\bar{1}.7945$
log(6.023) = 0.7771
[Apply log rules]
Denominatur terms are in multiplication thus log should be added
log (0.623) = $\bar{1}.7945$
+
log(6.023) = 0.7771

= 0.5716 ---(1)

Subtract (1) from log(240)

log(240) = 2.3802

$$\begin{array}{r} - \quad \underline{= 0.5716} \end{array}$$

1.8086 -- (2)

[Totake cube root divide (2) by three]

1.8086 / 3 =0.6029 –(3)

Now take antilong of (3) = 4.007

And cube root of $10^{24} = 10^{8}$

thus answer is 4 X10^{8} cm or 400 pm

Important formulae

1) Density of the unit cell $\rho = \frac{ZM}{a^3 N_A}$

Z : rank of unit cell (number of atoms per unit cell)

M : Molecular mass

A : length of edge

N_A : Avogadro’s number

2) Relation ship between nearest neighbour distance(d) edge length of unit cell(a) and radius of atom(r)

Simple	Face-centered	Body-centered
$d = a$	$d = \frac{\sqrt{2}}{2}a = 0.707a$	$d = \frac{\sqrt{3}}{2}a = 0.866a$
$r = a/2$	$r = \frac{\sqrt{2}}{4}a = 0.3535a$	$r = \frac{\sqrt{3}}{4}a = 0.433a$

STRUCTURE OF SIMPLE IONIC COMPOUNDS

Ionic compounds consisting of cations and anions are of the type AB, AB_2 and A_2B

A) Ionic compounds of AB type

AB type compounds may have one of the following types of structure.

(1) Rock Salt (NaCl) type structure

(2) Cesium Chloride (CsCl) type structure

(3) Zinc blend (ZnS) type structure

(1) Rock Salt (NaCl) type structure

(i) NaCl has fcc (also called ccp) arrangement of Cl^- ions in which Cl^- is present at the corners and face centres of the cube

(ii) Na^+ ions occupy all the tetrahedral site. i.e body centre and edge centres.

(iii) Each Na^+ ion is surrounded octahedrally by six Cl^- ions and each Cl^- ion is surrounded octahedrally by six Na^+ ions. Hence, coordination number of both Na^+ ion and Cl^- ion is six

(iv) On applying pressure NaCl tructure (6:6 coordination) changes to CsCl structure (8:8 coordination)
(v) edge length = 2(nearest neighbour distance)
Other examples : Halides of Li, Na, K, AgCl, AgBr, CaO etc

2) Caesium Chloride (CsCl) type structure
(i) In this type of ionic crystal, the size of Cs^+ ion is quite big as compared to Cl^- ion. Therefore, it acquires the body centred cubic lattice structure
(ii) It has bcc arrangement
(iii) The Cl^- ions arrangeed in a simple cubic arrangement i.e. are present at the cornors of the cubic unit cell
(iv) Cs^+ ion is surrounded by 8 chloride ions and each Cl^- ion is surrounded by $8Cs^+$ ions. THErefore, the structure has 8:8 coordination
(v) Cs^+ ion occupy cubic interstitial site i.e. body centre
(vi) At high temperature CsCl (8:8 coordination) changes to NaCl structure (6:6 coordination)
Other examples : CsBr, CsI, CsCn, TlCl, TlBr, TlI, TlCN, CaS

3) Zinc Blend (zinc sulphide) type structure
(i) The sulphide ions (S^{2-}) form fcc by occupying corners and face centres of cubic unit cell.
(ii) Zinc ions(Zn^{2+}) occupy half of the total availble tetrahedral voids in alternate manner
(iii) Each sulphide ion is urrounded tetrahedrally by 4 Zn^{2+} ions and each Zn^{+2} ion is surrounded tetrahedrally by $4S^{2-}$ ions. therefore, ZnS has 4:4 coordination
Other examples having structure : ZnCl, CuCl, CuBr, CUI, CgS, AgI, BES etc.
Note : Znic sulphide ZnS exists in to form: Znic blend and Wurtzite which differs only interms of arrangement of S^{2-} ions. In case of znic blends, S^{2-} ions have cubic close packing (ccp) arrangement thus , 4 formula units per unit cell. Whereas in Wurtzite, S^{2-} ions have hexagonal close packing (hcp)

B) Ionic compounds of AB_2 type

Fluorite (CaF_2) type structure (i) It has ccp arrangement of Ca^{2+} in which Ca^{2+} ions are present at the corners and face centres of unit cell (ii) Fluoride ions(F^-) occupy all available tetrahedral voids
(iii) Each calicum atom is surrounded by eight fluoride ions i.e coordination number of calcium ion is eight. Each fluoride ion is in contact with four calcium ion it is coordination number is 4. Thus CaF_2 has 8:4 coordination
Other examples : SrF_2, BaF_2 CdF_2, HgF_2, PbF_2, CuF_2, $SrCl_2$ etc

C) Ionic compounds of A_2 B type

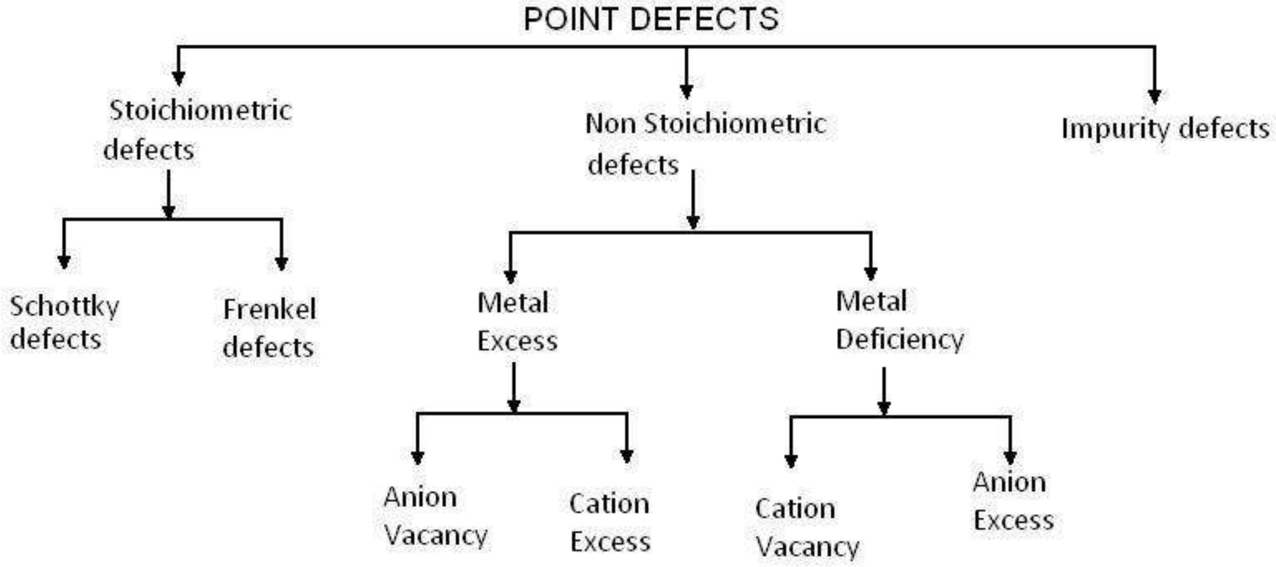
Antifluorite (Na_2O) type structure
(i) In the crystal structure of Na_2O, the O^{2-} ions constitute a cubic close packed lattice (fcc structure) and the Na^+ ions occupy all availabe tetrahedral voids

(ii) Each oxide ion, O^{2-} ion, is in contact with 8 Na^+ ions and each Na^+ ion is surrounded by 4 oxide ions . Therefore Na_2O has 4:8 coordination
Other example : Li_2O, K_2O, K_2O and Na_2S etc

SECTION II

DEFECTS AND PROPERTIES OF SOLIDS

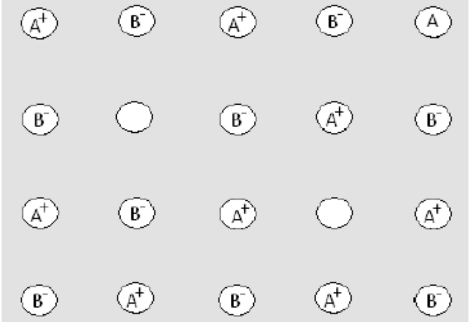
Any deviation from regular arrangement in cystallline solids are called as ***crystal defect***
Brodly defects are of two types i) Line defect ii) Point defect
The ***line line defects*** are the irregularites or deviations from ideal arrangement in entire rows of lattice points.
Point defects are the irregularties or deviations from ideal arrangement around point or an an atom in crystalline substance.
Vaerious types of defects in inoic compounds are as follows



(A) Defects in stoichiometric compounds

(i) Schottky defect

This type of defect is characterised by missing equal number of cations and anions from their lattice sites so that the electrical neutrality of the system is maintained



This type of defect is shown by the compound with

(a) High coordination number
(b) Small difference in size of the positive and negative ions i.e $\frac{r^+}{r^-} \approx 1$
Or cations and anions do not differ in size appreciably

Consequences of Schottky defect

(a) Since crystal lattice have lesser number of ions, density of the crystal deecreases

(b) The persence of a number of ionic vacancies lowers lattice energy or the stability of the crystal

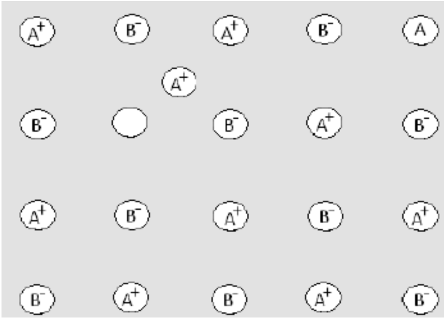
(c) The crystal shows electrical conductivity to small extent by ionic mechanism

Exampals: NaCl, CsCl, KBr, KCl

In NaCl there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In $1cm^3$ there are about 10^{22}. Thus, there is one defect per 10^{16} ions.

(ii) Frenkel defect

In this defect, an ion shifts from its orginal lattice site to interstitial site, so that electric neutrality as ell as stoichiometry of the compound is meaintained. Since carions are smaller in size, so it is generly cations that dshifts from lattice to interstetial site.



This type of defect is shown by

(a) Compounds having low coordination number because in such compounds the attaractive forces, being less, are very easy to overcome and hence the cation can easily move into the interstitial site

(b) Compound having large difference in size of cations and anions. i.e $\frac{r^+}{r^-}$ is low

(c) Compounds having highly polarising cations and an easily polarizable anions.

Consequences of Frankel defect

(a) Since nothing is lost from crystal as a whole, therefore density of the crystal is not effected

(b) The crystal shows electrical conductivity to a small extent by ionic mechanism

(c) The closeness of like charges tends to increase the dielecrtic constant of the crystal

Note : The number of these two defects in a crystal generally increases with the rise of temperature, hence they are sometimes called as ***thermodynamic defects***

AgBr shows both Frenkel and Skhottky defect.

(B) Defects in non-stoichiometric compounds

Non-stoichiometric defects are the defects by virtue of which stoichiometry of the compound gets distrubed. Ratio of positive and negative ions becomes different from the ratio indicated by their ideal chemical formulae.

For example in FeO ratio of positive and negative ions ia 0.94:1. The balnce of positive or negative charge is maintained either by having extra electrons or extra positive charge which makes the structure irregular. These defects arises due to the presence of either the metal or non-metal in excess.

a) Metal excess defect

In this type of defect cations are in excess. This situation may ariese either due to 1) Anion vacancies 2) Extra Cation in interstitial site

1) Anion inexcess

i) Inthis case, anions are missing from their lattice site leving a hole behid and causing excess in the cation (metal) concentration
ii) The hole formed are occupied by by electrons, thus system is electiclly neutral
iii) The nonmetal atom may leave the surface in the form of gas.
iv) The electrons trapped in anion vacancies are called ***F-centres*** because they impart colour to the crystal

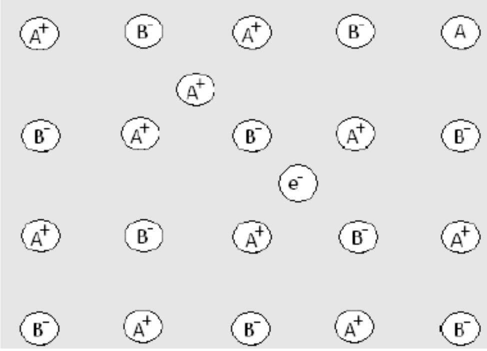
When alkalihalide like NaCl is heated in an atmosphere of vapours of the sodium metal, Sodium atoms deposit on surface of crystal , the chloride ions (anion) diffused to the crystal surface to combine with newly generated sodium cation ,leaving behind anionic vacancy behind. The electron lost by the sodium atom diffuses through the crystal to occupy the anion vacancies. Thses centres are kown as F-centres

$Na + Cl^- \rightarrow NaCl + e^-$ (electron lost by metal atom)

Note this defect is shown by the compounds which have Schottky defects.

2) Extra Cation in interstitial site

i) In this type of metal excess, , extra positive ions are present in ineterstitial site
ii) Electrical neutrality is maintained by presence of an electron, in another interstial position.



The common example is ZnO

When ZnO is heated, it loses oxyen atom and turn yellow. The excess Zn^{+2} are trapped in interstitial site and the electrons in the nearest neighbouring interstitials. Yellow coloue of ZnO, when it is hot is due to these trapped electrons.

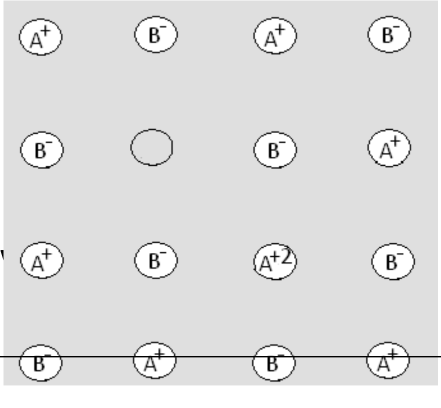
Note this trpe of defetc is is found in crystal having Frenkel defect.

Consequences of metal excess defects
(i) Comounds have increased conductivity due to the presence of free electrons
(ii) Compounds are usually coloured .Excess Na makes NaCl yellow in colour. Excess Li makes LiCl pink, Excess K makes KCl violet (lilac)

2) Metal deficiency defect

Metal deficiency defect may also arise due to 1) Cation vacancies 2) Extra anion occupying the interstitial sites

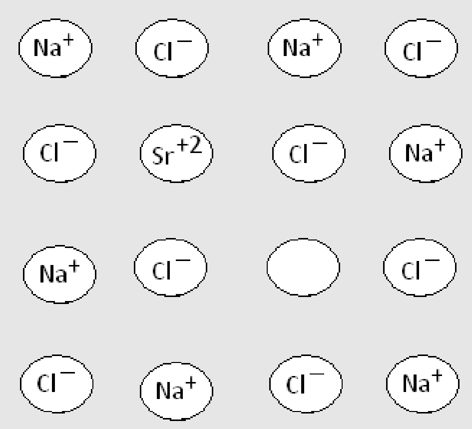
1) Cation vacancies: This type of defect occurs when a positive ion is missing from its lattice site and the charge is balance by the oxidation of some of cations to higher valency state. Thus lattice remains deficient of metal atoms



Example : FeO which is mostly found with a composition of $F_{0.93}O$ to $F_{0.96}O$. In crystal of FEO soume Fe^{+2} ions are missing and the loss of positve chage is made up by the presence of required number of Fe^{+3} ions

<u>2) Extra anions occupying the interstitial sites </u>: This type of defect involves the the presence of an extra anion in an interstitial site, the electrical neutrality is mentened by an extra charge on cation. No example of crystal possessing this defect is known at present because anions are usually larger in size, so it is improper to expect them to fint into intersitial sites

(C) Impurity defect : When some foreign atom is present in crystal, the defect is called impurity defect. If the foreign atom is present at lattice site, the solid is called ***substitutional solid solution***, where as if impurity is present at vacant inerstitial site, the solid is called ***interstitial solid solution***



Example: If moltan NaCl containing a littele amout of $SrCl_2$ is crystallize,
some of the sites of Na^+ is occupied by Sr^{+2} ions.
Each Sr^{+2} replaces two Na^+ ions. It occupy the site of one ion and other site remains vacant. the cationic vacancies are produced equal in number to that of Sr^{+2}

PROPERTIES OF SOLIDS (CRYSTALS)

The propertie sare soild sdepends on their composition, lattice structure and the nature of bond. Some properties of solid are as follows
1) Electrical properties
2) Magnetic properties
3) Dielectric properties

<u>1) Electrical properties</u>

Solids may be classified into three categores depending upon their values of electric condutivity.
Condutors : electrical condutivity = 10^4 to 10^7 ohm^{-1} cm^{-1}
Insulators : electrical condutivity = 10^{-20} to 10^{-10} ohm^{-1} cm^{-1}

Semiconductors: electrical condutivity = 10^{-6} to 10^{4} ohm^{-1} cm^{-1}

Causes of conductance in solid

(i) In most of the solids, conduction is through electron movement under an electric field
(ii) In ionic solids condution is by movement of ions
(iii) The magnitude of electrical condutivity strongly depend upon the number of electrons availabee to take part in conduction process.
(iv) In metals, conductivity strongly depends upon the number of electrons available per Atom
(v)The atomic orbitals form molecular orbitals which forms band conduction band and valance band
(vi) In a case of metals conduction band and valance bands are to close or overlap and electrons flow evry easily under electric file shoing conductivity
(vii) gap between conduction band and valance band is kown as forbidden gap
(viiii) In case of insulators, the gap between valance band and conduction band is too large , so electrons cannot jump from valence band to conduction band and very small conductivity is observed.
(ix) In case of semiconductors, the gap between valance band and conduction band is small and therefore some of the electons may jump from valance band and some condutivity is observered
(x) electrical conductivity of semiconductors increases, with increase in temperature. This is due to the fact that with increase in temperature, large number of valence electrons from valance band can jump to conduction band. Pure substances like silicon and germanimum that exhibit this type conducting behavior are called ***intrinsic semiconductor***.

Conduction in semiconductors

Conductivity of semiconductors can be increaed by by the introduction of impurity in semiconductors is called ***doping***

n-type semiconductors:

When a silicon crystal is doped with a group 15 elemnts such as P, As, Sb, Bi, structure of crystal lattice is left unchanged but an dopent atom with five valance electrons occupy the site normmaly occupied by silicon atom
The foreign atom (dopent) uses four of its electrons for covalent bonding but fifth electron becomes delocalised and if thus free to contribute to electriccal conduction.
Silicon doped with group 15 element is called n-type semiconductor. ‘n’ stands for negative since electrons are responcible for condution.

p-type semiconductors

When a silicon crystal is doped with a group 13 elemnts such as B, Al, Ga, In, structure of crystal lattice is left unchanged but an dopent atom with three valance electrons occupy the site normmaly occupied by silicon atom
The foreign atom (dopent) uses three of its electrons for covalent bonding but fourth electron is missing is caled an electron vacancy or hole.Such holes can move through the crystal like positive charge giving rise to electrical conductivity. Direction of motion of

holes is opposite to that of electron. Silicon doped with group 13 element is called p-type semiconductor. 'p' stands for positive since electrons are responcible for condution.

13-15 compounds: When the solid state materials are produced by combination of elements of groups 13 and 15, the compounds thus obtained are called 12-16 compound. Example InSb, AlP, GaAs
12-16 Compound. When the soild state compunds are obtained by combination of elements of group 12 and 16, the compounds are called 12-16 compounds.
Example ZnS, CdS, CdSe and HgTe
Transition metal oxides. Some transition metal oxide like TiO, Cro, ReO_3 behaves like metals. ReO_3 behaves like copper in appearance as well as conductance. VO, VO_2 VO_3 and TiO_3 also show electrical conductance depending on temperature.

2) Magnetic properties

Magnetic property of an atom is due to i) electrons orbital motion around nucleus ii) its spin around its own axis
(i)Electron is being charge particles and undergoes above mentioned motion can be considered as a small loop of current which posses a magnetic moment.
(ii)Each electron has a permanent spin and orbital magnetic moment associated with it
(iii) Magnitude of magnetic moment is small is measured in the unit called Bohr magneton μ_B. Its value is $9.27X10^{-24}$ Am^2
On the basis of their magnetic properties substances are divided in five categories
(i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic (v) ferromagnetic

(i)Paramagnetic material:
Paramagnetism is due to presence of unpaired electrons Paramagnetic materials are attracted by magnetic field They are magnetized in a magnetic field in same direction. They looses their magnetism in absence of magnetic field .
Examples: O2, Cu+2, Fe+3 Cr+3

(ii) Diamagnetic material:
Diamagnetism is shown by those substances in which all the electrons are paired and there is no unpaired electrons. Pairing cancels their magnetic moments and they lose their magnetic character
Diamagnetic materials are repelled by magnetic field
They are weakly magnetized in a magnetic field in opposite direction
Examples : H_2O, NaCl and C_6H_6

(iii) Ferromagnetic material :
a) Ferromagnetic substances shows permanent magnetism even when magnetic field is removed.

b)The metal ions of ferromagnetic substances are grouped together into small region called as ***domain***. Each domain acts like as tiny magnet.
c) In an unmagnetised piece of a ferromagnetic substances the domain are randomly arranged and their magnetic moment gets cancelled.
d) When substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field and a strong magnetic field is produced. This ordering of domain persists even when the magnetic field is removed and ferromagnetic substance becomes permanent magnet
e) On heating ferromagnetic substance becomes paramagnetic
Examples CrO_2, Co, Ni, Fe

(iv) Antiferromagntic substance.
When magnetic moments of domain are aligned in such a way that net magnetic moment is zero, then magnetism is called antiferromagnetism.
Example MnO

(v) Ferrimagnetism:
When magnetic moments are aligned in parallel and anti-parallel directions in unequal numbers resulting in net moment then the magnetism is called ferrimagnetism
Examples Fe_3O_4, $MgFe_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$ etc

ELECTROCHEMISTRY

SECTION I

Electrolytes

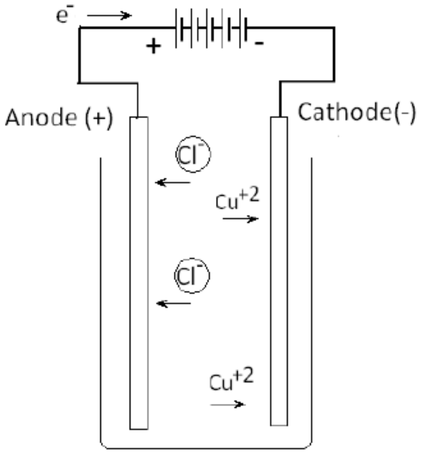
Solids and liquid substances, which are able to conduct the electric current, can be divided in two categories i.e. metallic conductors and electrolytic conductors

In metallic conductors or electronic conductors, the electric current is carried by the free electrons. When an electric potential is applied to metallic conductors, the electrons start to move in one direction while positive ions remains stationary. Thus the flow of electrons is no accompanied by appreciable movement of the matter

Electrolytic conductors or electrolytes are distinguished from metallic conductors by the fact that the current is carried by ions and not by electrons. The application of an electric potential causes these charged particles of matter to move, the positive ions move towards the cathode and the negative ions move towards anode. Thus, passage of an electric current is accompanied by the transfer of matter. This transfer is manifested by change in concentration and also by visible separation of material at the points where the electric charge enters and leaves the electrolyte. Electrolytes generally employed are salts in molten form or are dissolved in water

Sr	Electronic conduction	Electrolytic conduction
1	Pure metal and their solution as alloys are called as metallic conductors	Ionic compound conduct electricity in molten state or in solution due to movement of ions
2	Free mobile electrons of metallic atom or alloys are responsible for conduction	Ions with positive charge move towards cathode while negative charge move towards anode
3	Positive holes in the metal moves in opposite to the direction of electrons in case of semiconductors	Electrolysis occur when current pass through ionic solution
4	There is no chemical change in the material when electricity is passed.	Chemical change occurs
5	There is only flow of energy but no transfer of matter	There is actual transfer of matter since ions move to electrodes
6	Conductivity of metals decreases with increase in temperature due to enhanced vibration of metal ions disrupting movement of electrons	With increase in temperature conductivity increases due to increased mobility of ions

Electrolysis



Take two rods of suitable metals called as electrodes, which are immersed in electrolytic solution (Water soluble salt of metals) g.g. $CuCl_2$. The rods are now connected to a source of e.m.f (battery) The electrode through which electron enters in the cell is called the negative electrode or cathode while that at which electrons leave is known as the positive electrode or anode. The cations carry positive charge while anion carry negative charge.

As soon as the electrodes are connected to battery, the cations Cu^{+2} starts moving towards cathode, take up electrons from rod and get reduced to deposit as metal (Cu) while anions (Cl^-) move towards anode and get oxidized to release Cl_2 gas.

Thus at anode , oxidation takes place while at cathode reduction takes place

The reaction at the two electrodes are

At cathode $Cu^{+2} + 2e^- \rightarrow Cu$

At anode $2Cl^- \rightarrow Cl_2 + 2e^-$

Electrolysisis the process of chemical decomposition of the electrolyte by the passage of electric current. It is carries out in a cell called electrolytic cell.

Electrolytic cell convert electrical energy in to chemical energy.

Faraday's laws of electrolysis

Faraday established the relationship between the quantity of electricity passes through electrolyte and the amount of material liberated or deposited at the electrode.

First law of electrolysis

The amount of any substance deposited or dissolved at a particular electrode is proportional to the quantity of electricity utilized. $m \propto Q$

$M = Z it$ as $Q = It$

Here m is the mass of substance deposited Q is the amount of charge utilized in Coulombs, I is the current in Ampere and t is time in seconds and Z is electrochemical equivalent

Remember that Q is the amount of charge utilized not charge passing

Electrochemical equivalent is the mass of substance deposited in gram either by passing one coulomb of charge or by passing one ampere of current for one second.

One faraday is the quantity of charge carried by one mole of electrons

$\therefore 1\ F = 1.6\times10^{-19}\times6.023\times10^{23} = 96500$ coulombs

Or One Farady is the quantity of charge which must be passed in order to deposited or dissolved one gram equivalent of any substance

Let E be the equivalent mass of substance deposited at any electrode. Since 96500 coulombs of charge is required to deposit E grams of substance, therefore one coulomb charge would deposit (E/96500) grams, which is the electrochemical equivalent (Z) of the substance. Z =(E/96500)

Second law of electrolysis

The amounts of different substances deposited or dissolved by the same quantity of electricity are proportional to their respective chemical equivalent weights.

From first law

$$m = \frac{EIt}{96500}$$

Rearranging the terms we get

$$\frac{m}{Z} = \frac{It}{96500} = \frac{Q}{96500} = Number\ of\ equivalents$$

$$\frac{m}{Z} = constant$$

Or

$$\frac{m}{E} = constant$$

As charge utilized is same

Note equivalent mass E = M/p Here M is atomic mass and p is valency

This means that if the quantity of charge passed through electrolytic cells connected in series is same, the equivalents of substances deposited at various electrodes would be same.

For example, consider the given reactions at two different cathodes in two different electrolytic ells connected in series.

$Ag^+ + e^- \rightarrow Ag$

$Cu^{2+} + 2e^-$ - >Cu

Let us assume x mole of electrons is passed through both the cells

Mole of Ag deposited = x

Equivalent of Ag deposited = x × 1 = x

Mole of cu deposited = x/2

Equivalent of Cu deposited = (x/2) × 2 = x

Thus, it is evident that the equivalents of both metals (Ag &Cu) deposited are same (i.e x). The Farady's laws are universally accepted laws, applicable at all temperatures, for non-aqueous, aqueous solutions and fused electrolytes and whether the electrode reaction leads to metal depositions or not.

Solved Numerical

If 50 milli ampere of current is passed through copper coulometer for 60 min, calculate the amount of copper deposited.

Solution : Electrical charge input = I × t coulombs

= $50 \times 10^{-3} \times 60 \times 60$ sec

= 180 coulombs.

The chemical reaction is, $Cu^{2+} + 2e^- \rightarrow Cu(s)$

1 mole of copper requires 2F current

$$\therefore amount\ copper\ deposited = \frac{63.5 \times 180}{2 \times 96500}$$

Amount of copper deposited = 0.0592 gm.

Q) An electric current is passed through three cells in series containing respectively solutions of copper sulphate, silver nitrate and potassium iodide. What weights of silver and iodine will be liberated while 1.25 g of copper is being deposited ?

Solution

$$\frac{weight\ of\ copper}{weight\ of\ Iodine} = \frac{Eqivalent\ wt\ of\ copper}{Equivalent\ wt\ of\ Iodine}$$

$$\frac{1.25}{x} = \frac{31.7}{127}$$

Weight of Iodine x = 0.5 g

Also

$$\frac{weight\ of\ copper}{weight\ of\ silver} = \frac{Eqivalent\ wt\ of\ copper}{Equivalent\ wt\ of\ Silver}$$

$$\frac{1.25}{y} = \frac{31.7}{108}$$

Weight of silver y = 4.26 g

Electrolytic conductance

Molten electrolytes and the aqueous solutions of electrolytes contains free ions and conducts electricity due to the movement of ions

We know that Ohm's law is applicable to metallic conductors but it is also valid for electrolytic conductors. According to the Ohm's law, the resistance of a conductor is directly proportional to the length and is inversely proportional to cross-sectional area

Now consider a electrolyte cell in which electrodes are separated by distance 'l 'and surface area is 'a.' Then resistance of the electrolyte enclosed by the electrodes is

$$R = \rho \frac{l}{a}$$

Now if l = 1 unit and a = 1 unit the R =ρ

ρ is the resistivity of the solution held between the electrodes unit is ohm×m in SI unit

Conductivity of solutions

$$Conductance\ (G)\ = \frac{1}{Resistance(R)}$$

$$G = \frac{1}{R}$$

SI unit is ohm^{-1} or mho. Is now a days called Siemens (S). Therefore 1 ohm^{-1} = 1S

$$G = \frac{1}{\rho}\frac{a}{l} = k\frac{a}{l}$$

Where k is called conductivity of the solution or specific conductance. This gives

$$k = G \times \frac{l}{a}$$

l/a is called cell constant

$$k = Conductance \times cell\ constant$$

If l = 1 and a=1 then

K =G

Thus, the conductivity may be defined as the conductance of any solution held between two electrodes of one unit area and seperataed by a distance of one unit.

The unit of conductivity depends upon the unit in which the quantities G, l and a are measured.

In SI system k = Sm^{-1} (Siemens/metre) In CGS system S cm^{-1}

Equivalent conductivity

The equivalent conductivity (Λ_{eq}) of an electrolyte in solution may be defined as

"The conducting power of all ions furnished by one equivalent of an electrolyte in any solution is termed as its equivalent conductivity"

Equivalent conductivity is expressed as

$$Equivalaent\ conductivity\ (\Lambda_{eq}) = \frac{conductivity\ (k)}{Concentration\ in\ equivalents\ per\ unit\ volume\ (C_{eq})}$$

$$\Lambda_{eq} = \frac{k}{C_{eq}}$$

Units of Λ_{eq} depends on the units of k and C_{eq}

If the conductivity is measured in Scm^{-1} and concentration in **Normality** the expression of Λ_{eq} becomes

$$\Lambda_{eq} = \frac{k}{C_{eq}} \frac{(Scm^{-1})}{(equivalant\ wt \times L^{-1})}$$

But 1 litre = 1dm = 10^3 cm thus

$$\Lambda_{eq} = \frac{k}{C_{eq}} \frac{(Scm^{-1} \times 10^3 \times cm^3)}{(equivalant\ wt)}$$

$$\Lambda_{eq} = \frac{1000k}{C_{eq}} (Scm^2 equiv^{-1})$$

$$\Lambda_{eq} = \frac{1000k}{Normality} (Scm^2 equiv^{-1})$$

Molar conductivity

The conducting power of a solution can also be described in terms of molar conductivity(Λ_m) may be defined as

"The conducting power of all the ions furnished by one mole of an electrolyte in the solution is termed as its molar conductivity"

Thus

$$Molar\ conductivity\ (\Lambda_{\mathrm{m}}) = \frac{conductivity\ (k)}{Concentration\ in\ equivalents\ per\ unit\ volume\ (C_m)}$$

$$\Lambda_{\mathrm{m}} = \frac{k}{C_m}$$

Units of Λ_m depnds on the the units of conductivity and concentration
When the conductivity is measured in Scm^{-1} and concentration is measured in mole/litre then the expression of Λ_m becomes

$$\Lambda_{\mathrm{m}} = \frac{k}{C_m}\frac{(Scm^{-1})}{(mol \times L^{-1})}$$

But 1 litre = 1dm = 10^3 cm thus

$$\Lambda_{\mathrm{m}} = \frac{k}{C_m}\frac{(Scm^{-1} \times 10^3 \times cm^3)}{(mol)}$$

$$\Lambda_{\mathrm{m}} = \frac{1000k}{C_m}(Scm^2mol^{-1})$$

$$\Lambda_{\mathrm{m}} = \frac{1000k}{Molarity\ of\ the\ solution}(Scm^2mol^{-1})$$

Molar conductivity increases with decrease in concentration. This is because the total volume, *V*, of solution containing one mole of electrolyte also increases. It has been found that decrease in k on dilution of a solution is more than compensated by increase in its volume. .

Solved Numerical

Q) The resistance of a 0.01 N solution of an electrolyte was found to 210 ohm at 25°C using a conductance cell with a cell constant 0.88 cm^{-1}. Calculate the specific conductance and equivalent conductance of the solution.

Solution

R = 210 ohm, l/a = 0.88 cm^{-1}

Specific conductance

$$k = \frac{l}{a} \times \frac{1}{R}$$

$$k = \frac{0.88}{210} = 4.19 \times 10^{-3} mho\ cm^{-1}$$

$$\Lambda_{\mathrm{eq}} = \frac{1000k}{Normality}(Scm^2equiv^{-1})$$

$$\Lambda_{\mathrm{eq}} = \frac{1000 \times 4.19 \times 10^{-3}}{0.01}(Scm^2equiv^{-1})$$

Λeq =419 S cm2 equiv-1

Relationship between molar and equivalent conductivities

According to the definition

$$\Lambda_{\mathrm{m}} = \frac{k}{C_m}$$

And

$$\Lambda_{\mathrm{eq}} = \frac{k}{C_{eq}}$$

For a solution containing a certain mass of the solute per unit volume of the solution (let us say ‘w’ gram per litre) we can write

$$C_m = \frac{w}{molar\ mass\ of\ the\ electrolyte}$$

And

$$C_{eq} = \frac{w}{equivalent\ mass\ of\ the\ electrolyte}$$

From these relations, we can write

$$\frac{C_m}{C_{eq}} = \frac{Equivalent\ mass\ of\ the\ electrolyte}{Molar\ mass\ of\ the\ electrolyte}$$

We know that molar mass of an electrolyte = z× Equivalent mass of the electrolyte
Where z is the charge on per metal ions of electrolyte.

$$\frac{C_m}{C_{eq}} = \frac{1}{z}$$

Kohlrausch’s law

This law states that, ‘‘at infinite dilution wherein the ionisation of all electrolytes is complete, each ion migrates independently and contributes a definite value to the total equivalent conductance of the electrolyte’’. Consider an electrolyte AB in aqueous solution. It dissociates as

$A_mB_n \rightarrow mA^{+n} + nB^{+m}$

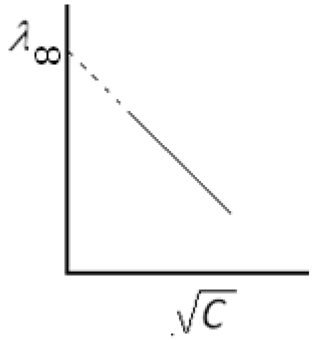
Then at infinite dilution, according to Kohlrausch’s law, the total equivalent conductance of the electrolyte.

$$\lambda_\infty = \frac{1}{n^+}\lambda_A^+ + \frac{1}{m^+}\lambda_B^-$$

where $\lambda_A{}^+$ and $\lambda_B{}^-$ are the cationic and anionic equivalent conductances at infinite dilutions and n^+ and m^- correspond the valency of cations and anions furnished from each molecule of the electrolyte.

For infinite dilution

λ_∞ , NaCl = $\lambda_\infty{}^+ Na^+ + \lambda_\infty{}^- Cl^-$



λ_∞ , $BaCl_2$ =(1/2) λ_∞^+ Ba^{2+} + λ_∞^- Cl^-
λ_∞ , $AlCl_3$ =(1/3) λ_∞^+ Al^{3+} + λ_∞^- Cl^-
λ_∞ , $Al_2(SO_4)_3$ =(1/3) λ_∞^+ Al^{3+} +(1/2) λ_∞^- Cl^-

The molar conductivity of strong electrolyte at infinite dilution can be determined by extrapolation of graph of equivalent conductivity vs concentration

For weak electrolytes,

λ_∞ , CH_3COOH = λ_∞^+ H^+ + λ_∞^- CH_3COO^-
λ_∞ , NH_3OH = λ_∞^+ NH_3^+ + λ_∞^- OH^-

The molar conductivity of a weak electrolyte at infinite dilution (λ_∞) can not be determined by extrapolation method. But λ_∞ can be determined by Kohlrausch's equation. $\lambda_\infty$of CH_3COOH which is a weak electrolyte is deduced from λ_∞ values of NaCl, HCl, and CH_3COONa in such a manner that λ_∞ of CH_3COOH is obtained. Sodium acetate (CH_3COONa) is a strong electrolyte and it ionises to acetate (CH_3COO^-) and sodium (Na^+) ions at all concentrations in water. Applying Kohlraush's law,

$$\lambda_\infty CH_3COONa + \lambda_\infty HCl - \lambda_\infty NaCl =$$
$$\lambda_\infty CH_3COO^- + \lambda_\infty Na^+ + \lambda_\infty H^+ + \lambda_\infty Cl^- - \lambda_\infty Na^+ - \lambda_\infty Cl^-$$

$\lambda_\infty\ CH_3COO^- + \lambda_\infty\ H^+ = \lambda_\infty\ CH_3COOH$

This method produces agreeable values of λ_∞ for weak electrolytes

Similarly λ_∞ NH_4OH can be deduced as,

λ_∞ NH4OH = $\lambda_\infty\ NH_4^+ + \lambda_\infty\ OH^-$
$= \lambda_\infty\ NH_4^+ + \lambda_\infty\ Cl^- + \lambda_\infty\ Na^+ + \lambda_\infty\ OH^- - \lambda_\infty\ Na^+ - \lambda_\infty\ Cl^-$
$= \lambda_\infty\ NH_4Cl + \lambda_\infty\ NaOH - \lambda_\infty\ NaCl$

In case of weak electrolytes, degree of dissociation (α) increases when concentration decreases. Hence, (1 – α) value tends to zero at infinite dilution, such that λ_{eq} increases and tends to λ_∞ value.

λ_∞ of weak electrolytes are experimentally obtained by extrapolating the upper arm of the curve to the Y axis and the intercept value corresponds to λ_∞. In the intermediate concentration range, λ_{eq} is lower than λ_∞ since the weak electrolyte exists in partially ionised state. The degree of dissociation α equals to the ratio of λ_{eq} to λ_∞ value. (i.e., $\alpha = \lambda_{eq} / \lambda_\infty$).

Solved numerical

Q) 0.04 N solution of a weak acid has a specific conductance 4.23×10^{-4} S.cm^{-1}. The degree of dissociation of acid at this dilution is 0.0612. Calculate the equivalent conductance of weak acid at infinite dilution

Solution

Specific conductance k = 4.23×10^{-4} mho.cm^{-1}

$$\Lambda_{eq} = \frac{1000k}{Normality} (Scm^2 equiv^{-1})$$

$$\Lambda_{\text{eq}} = \frac{1000 \times 4.23 \times 10^{-4}}{0.04} = 10.575(Scm^2 equiv^{-1})$$

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

$$0.0612 = \frac{10.575}{\Lambda_\infty}$$

$\Lambda_\infty = 172.79\ S.cm^2.equiv^{-1}$

Q) Equivalent conductivity of acetic acid at infinite dilution is 390.7 and for 0.1 M acetic acid the equivalent conductance is 5.2 mho.cm^2. equiv^{-1}. Calculate degree of dissociation, H^+ ion concentration and dissociation constant of the acid.

Solution

$$\alpha = \frac{\Lambda_{eq}}{\Lambda_\infty} = \frac{5.2}{390.7} = 0.01333$$

$\alpha = 1.33\%$

$$\begin{array}{ccc} CH_3COOH \leftrightharpoons & CH_3COO^- + & H^+ \\ C(1-\alpha) & C\alpha & C\alpha \end{array}$$

$\therefore [H^+] = C\alpha = 0.1 \times 0.01333 = 0.00133\ M$

Q) Ionic conductances at infinite dilution of Al^{3+} and SO_4^{2-} are 189 ohm^{-1} cm^2 equiv^{-1} and 160 ohm^{-1} cm^2 equiv^{-1}. Calculate equivalent and molar conductance of the electrolyte at infinite dilution of electrolytes $Al_2(SO_4)_3$

Solution

$$\lambda_\infty = \frac{1}{n^+}\lambda_A^+ + \frac{1}{m^+}\lambda_B^-$$

$$\lambda_\infty = \frac{1}{3} \times 189 + \frac{1}{2} \times 160 = 143\ Scm^2 equiv^{-1}$$

SECTION II

Electrochemical cell

When a strip of Zinc is dipped in $CuSO_4$, we start to see that Zn strip starts to dissolved in $CuSO_4$ and Cu starts to deposit on the surface.

This happens because Zn is oxidized to Zn^{2+} which passes into the solution and two electrons remains on the Zn rod taken up by Cu^{+2} ions from solution to is reduced to Cu.

In this reaction, Zn acts as reducing agent, which is able to reduce Cu^{2+} to Cu by transfer of 2 electrons and Cu^{2+} ions acts as an oxidizing agent, which oxidizes Zn to Zn^{2+} ions and itself gets reduced to Cu. In this case there is a direct transfer of electrons from Zn rod to Cu^{2+} ions and some heat is also evolved

The above experiment is slightly modified in a manner that for the same redox reaction transfer of electrons takes place indirectly and the heat of the reaction is converted into electrical energy.

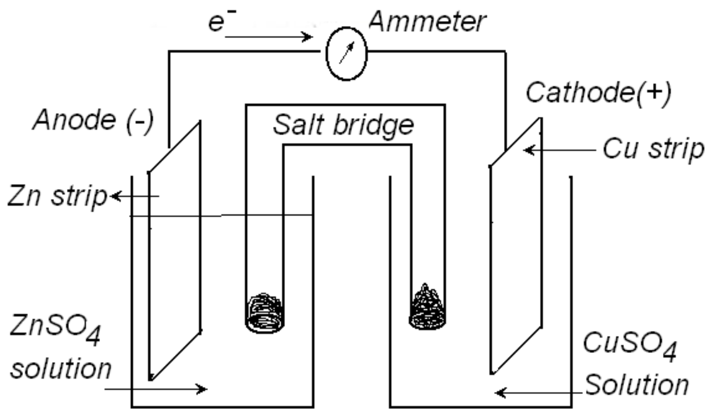
This necessities that separation of Zn rod from $CuSO_4$ solution. Such cells in which the oxidised and reduced species are separated and connected through electric wires are called electro-chemical cells.

Electrochemical cells are the cells in which chemical energy is transformed into electrical energy. This means that chemical reactions produce electric current.

An electrochemical cell consists of two half-cells or electrodes. The electrodes are metallic conductors dipped in an electrolyte, which is an ionic conductor dissolved in water. A metallic rod and its electrolyte comprises an electrode or half cell compartment. The two electrodes may share the same or different electrolyte. The various electrodes used are

(i) Metal –metal ion electrode
(ii) Gas-gas ion electrode
(iii) (ii) Redox electrode
(iv) Metal-insoluble metal salt-anion electrodes

The simplest electrochemical cell to study is Daniel cell ,



it is prepared by dipping Zn rod in $ZnSO_4$ solution in one beaker and Cu strip is dipped in another beaker containing $CuSO_4$

Since Zinc is more reactive than copper, so it has higher tendency to get oxidized than Cu. At this stage no reaction takes place in any beaker. Now when both the electrodes are connected with each other though a ammeter by conducting wire, Zn start to dissolve in $ZnSO_4$ i.e. Zn atom changes to Zn^{2+} by losing 2 electrons, there by increases Zn^{2+} concentration in solution. Electron remains on Zn rod there by there is a charge separation of 4 units between Zn rod and $ZnSO_4$ solution.

The zinc rod which has the electron left becomes negatively charged while Cu rod which lost electrons to Cu^{2+} becomes positively charged.
Thus electric current flows through the connected wire, which is indicated by the deflection in ammeter showing that a chemical reaction is occurring in the cell.
During the process weight of zinc rod get reduced while weight of copper rod increases.
Thus the Concentration of $CuSO_4$ decreases while concentration of Zn^{2+} increases.
Since Oxidation reaction takes placed at Zn strip is called Anode which is the negatively charged electrode
While reduction reaction takes place at Cu is called cathode, is positively charged electrode.
The flow of electron takes place from Anode to cathode through external circuit or connecting wire while indirectly from cathode to anode inside the cell
As we have seen that Zn^{2+} ions concentration goes on increasing in solution at a particular concentration of Zn^{2+} further oxidation of Zn will be prevented by the Zn^{2+} ions present in the solution thus it will stop the working of cell.
We could maintain the neutrality of solutions we could get continuous flow of current.
This can be achieved by using salt bridge. The salt bridge contains a highly soluble electrolytes (like KCl, NH_4NO_3, NH_4Cl, KNO_3) in which ionic mobility of cation and anion are of comparable order
Since zinc ions are produced as electrons leaves the zinc electrode, this tends to produce a net positive charge into the solution to neutralize the chare the salt bridge then throws anions having equivalent charge into the solution to maintain electrical neutrality.
Thus salt bridge maintains the neutrality in both the half
Salt bridge do not participate chemically in the cell reaction but it is essential to cell to operate continuously

Cell notation of an electrochemical cell

(i) Anode is written on the left side and cathode is written on the right side
(ii) Phase boundaries are indicated by vertical bar or slash
(iii) Concentration of the electrolytes in the anode and cathode must be written in parenthesis
(iv) In case of gas, the partial pressure is to be mentioned in atm or mm Hg
(v) A comma is used to separate two chemical species present in the same solution
(vi) A double vertical line i.e || denotes that a salt bridge is present
(vii) EMF of the cell is written on the extreme right of the representation

For examples

(i) $Zn(s)|ZnSO_4\ (C_1M)\ ||\ CuSO_4\ (C_2M)|Cu(s)\ ;\ E_{cell}$
(ii) $Pt|H_2(P_1\ atm)|HCl(cM)|AgCl(s)|Ag\ ;\ E_{cell}$
(iii) $Pt|Fe^{2+}\ (C_1M),Fe^{3+}(C_2M)||Ag^+(cM)|Ag\ ;\ E_{cell}$

In cell representation as in (ii) the salkt bridge is not indicated which implies that the electrolyte is common to both anode and cathode compartments

Single electrode potential

An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution.

Thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called the **Single electrode potential.**

Thus in Daniel cell in which the electrodes are not connected externally, the anode Zn/Zn^{2+} develops a negative charge and the cathode Cu/Cu^{2+}, a positive charge.

The amount of the charge produced on an individual electrode determines its single electrode potential. The single electrode potential of a half-cell depends on : (a) concentration of ions in solution ; (b) tendency to form ions ; and (c) temperature.

Standard emf of a cell

The emf generated by an electrochemical cell is given by the symbol E.

It can be measured with the help of a potentiometer. The value of emf varies with the concentration of the anode and cathode solutions and the temperature of the cell. When the emf of a cell is determined under standard conditions, it is called the standard emf.

The standard conditions are :

(a) 1 M solutions of anode and cathode

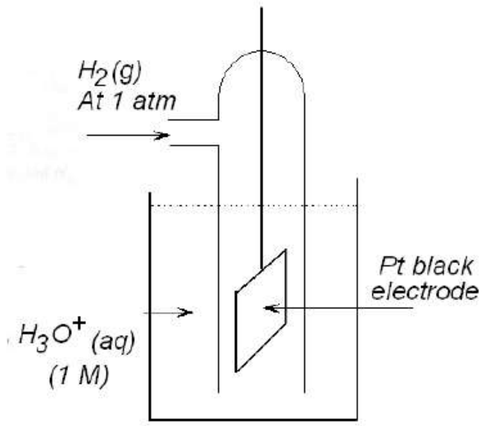
(b) temperature of 25^o C.

Thus standard emf may be defined as the emf of a cell with 1 M solutions of reactants and products in solution measured at 25^o C. Standard emf of a cell is represented by the symbol E^O. For gases 1 atm. pressure is a standard condition instead of concentration.

For Zn-Cu voltaic cell, the standard emf, E_o is 1.10V.

$$Zn(s)|ZnSO_4\ (1M)\ ||\ CuSO_4\ (1M)|Cu(s)\ ;\ E^0_{\ cell} = 1.10\ V$$

Standard Hydrogen Electrode (SHE)



The standard hydrogen half-cell or Standard Hydrogen Electrode (SHE), is selected for coupling with the unknown half-cell. It consists of a platinum electrode immersed in a 1 M solution of H^+ ions maintained at 25^oC.

Hydrogen gas at one atmosphere enters the glass hood and bubbles over the platinum electrode. The hydrogen gas at the platinum electrode passes into solution, forming H^+ ions and electrons.

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts.

$H_2 \text{-->} 2H^+ + 2e^-$ 0.0 V (Anode)

$2H^+ + 2e^- \text{-->} H_2$ 0.0 V (Cathode)

So, SHE can be used as a standard for other electrodes.

The half-cell whose potential is desired, is combined with the hydrogen electrode and the emf of the complete cell determined with a voltmeter. The emf of the cell is the emf of the half-cell.

For example, it is desired to determine the emf of the zinc electrode, Zn | Zn^{2+}. It is connected with the SHE. The complete electrochemical cell may be represented as :

Zn | Zn^{2+} || H+ | H2 (1 atm), Pt

Since SHE is used as cathode we get oxidation potential of Zn which found to be

Electrode potential

Depending on the nature of the metal electrode to lose or gain electrons, the electrode potential may be of two types:

(i) Oxidation potential:

When electrode is negatively charged with respect to solution, i.e., it acts as anode. Oxidation occurs.

$M \rightarrow M^{n+} + ne^-$

(ii) Reduction potential:

When electrode is positively charged with respect to solution, i.e., it acts as cathode. Reduction occurs.

$M^{n+} + ne^- \rightarrow M$

It is not possible to measure the absolute value of the single electrode potential directly. Only the difference in potential between two electrodes can be measured experimentally. It is, therefore, necessary to couple the electrode with another electrode whose potential is known. This electrode is termed as **reference electrode**. The emf of the resulting cell is measured experimentally. The emf of the cell is equal to the sum of potentials on the two electrodes.

Emf of the cell= Oxidation potential of anode - Oxidation potential of cathode

OR

Emf of the cell= Reduction potential of Cathode - Reduction potential of Anode

OR

Emf of the cell= Oxidation potential of anode + Reduction potential of cathode

Knowing the value of reference electrode in case of SHE it is zero, the value of other electrode can be determined.

Note that Oxidation potential = - reduction potential

SOLVED NUMERICAL

Q) Calculate the standard e.m.f. of the cell : Cd| Cd^{2+} || Cu^{2+}|Cu and determine the cell reaction. The standard reduction potentials of Cu^{2+}| Cu and Cd^{2+}| Cd are 0.34V and –0.40 volts respectively. Predict the feasibility of the cell reaction.

Solution:

Cell reaction is

$Cd^{2+} + Cu \rightarrow Cu^{2+} + Cd$
Here $Cd|Cd^{2+}$ is anode = -0.40V while $Cu^{2+}|Cu$ is cathode = 0.34V
Since reduction potential are given
Emf of the cell= Reduction potential of Cathode - Reduction potential of Anode
Emf of the cell = 0.34 – (- 0.40) = 0.74 V
Since cell potential is positive, reaction is feasible

Q) Determine the standard emf of the cell and predict its feasibility.
$Ag| Ag^+ || H^+| H2(g)1atm, Pt.$
Solution:
The standard reduction potential of Ag^+, Ag is 0.80 volts which is positive thus Ag acts as cathode
The right hand side electrode is SHE.
E cell = [Std. reduction potential of SHE] – [Std. reduction potential of Ag+, Ag]
= 0 – (+ 0.8 V) = – 0.8 Volts.
Since E^o cell is negative, the cell reaction is not feasible.

Relation between EMF and free energy

When a cell produces a current, the current can be used to do work – to run a motor, for instance. Thermodynamic principles can be employed to derive a relation between electrical energy and the maximum amount of work, Wmax, obtainable from the cell. The maximum amount of work obtainable from the cell is the product of charge flowing per mole and maximum potential difference, E, through which the charge is transferred.
Wmax = – *n* FE ... (1)
where *n* is the number of moles of electrons transferred and is equal to the valence of the ion participating in the cell reaction. F stands for Faraday and is equal to 96,500 coulombs and E is the emf of the cell.
According to thermodynamics, the maximum work that can be derived from a chemical reaction is equal to the free energy (ΔG) for the reaction,
Wmax = ΔG ... (2)
Therefore, from (1) and (2), we can write
ΔG = – *n* FE ... (3)
Thus only when E has a positive value, ΔG value will be negative and the cell reaction will be spontaneous and the e.m.f. of the cell can be measured.
Here E refers to the Ecell.
Thus, the electrical energy supplied by the cell is (*n*FE) equal to the free energy decrease (–ΔG) of the cell reaction occurring in the cell.

Q) Determine the standard emf of the cell and standard free energy change of the cell reaction. $Zn| Zn^{2+} || Ni^{2+}| Ni$. The standard reduction potentials of $Zn^{2+}| Zn$ and $Ni^{2+}| Ni$ half cells are – 0.76 V and – 0.25 V respectively.
Solution:
Cell reaction

$Zn^{2+} + Ni \rightarrow Ni^{2+} + Zn$

Here $Zn | Zn^{2+}$ = -0.76 V is anode $Ni^{2+} | Ni$ = -0.25V is cathode

Emf of the cell = Reduction potential of Cathode - Reduction potential of Anode

Emf of the cell = -0.2-0.76 = 0.51V

$\Delta G = -nFE$

N = 2

$\Delta G = -2 \times 96500 \times +0.51 = -97460$ Joules = – 97.46 kJ

ΔG is negative thus reaction is spontaneous

Cell potential and Nernst equation

Nernst equation is used top relate either half-cell potential or EMF of a cell with concentration of the involved species..

Consider a redox reaction of cell

$aA + bB \leftrightharpoons cC + dD$

Where A, B, C, D are the species whose concentration vary. i.e they are either gases or solution pauses. For species A, the free energy permole of A can be given thermodynamically as

$G_A = G_A^O + Rt \ln [A]$

For a moles of A

$aG_A = aG_A^O + a\,RT\ln[A] = aG_A^O + RT\ln[A]^a$

Similarly for other species

$bG_B = bG_B^O + RT\ln[B]^b$

$cG_C = cG_B^O + RT\ln[C]^c$

$dG_D = dG_D^O + RT\ln[D]^d$

Now, the free energy changes for the overall cell reaction can be deducted as

$\Delta G = (cG_C + dG_D) - (aG_A + bG_B)$

$= (cG_B^O + RT\ln[C]^c + dG_D^O + RT\ln[D]^d) - (aG_A^O + RT\ln[A]^a + bG_B^O + RT\ln[B]^b)$

$= cG_B^O + dG_D^O) - (aG_A^O + bG_B^O) + (RT\ln[C]^c + RT\ln[D]^d - RT\ln[A]^a - RT\ln[B]^b)$

$$\Delta G = \Delta G^O + RTln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Where ΔG^O is the free energy change when all the reactants and products are present at one molar concentration

From the relation between free energy and cell potential

$$-nFE_{cell} = -nFE_{cell}^O + RTln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Dividing both sides by –nF gives

$$E_{cell} = E_{cell}^O - \frac{RT}{nF}ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Putting T = 398K, R = 8.314 J/mol , F = 96500C we get

$$E_{cell} = E_{cell}^O - \frac{0.059}{n}log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

SOLVED NUMERICAL

Q) What is the potential of a half-cell consisting of zinc electrode in 0.01 M $ZnSO_4$ solution 25^oC. E^o = 0.763 V.

Solution:

$Zn \rightarrow Zn^{2+} + 2e^-$

The Nernst equation for the oxidation half-cell reaction is

$$E_{cell} = E_{cell}^{O} - \frac{0.059}{2}\log[Zn^{2+}]$$

The number of electrons transferred n = 2 and E^o = 0.763 V.

Substituting these values in the Nernst equation we have

$$E_{cell} = 0.763 - \frac{0.059}{2}\log[0.01]$$

$$E_{cell} = 0.763 + 0.059 = 0.822V$$

Q) Calculate the emf of the cell.

$Zn \mid Zn^{2+}$ (0.001 M) || Ag+ (0.1 M) | Ag

The standard potential of Ag/Ag^+ half-cell is + 0.80 V and Zn/Zn^{2+} is –0.76 V.

Solution:

Cell reaction is

$Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$

$Zn|Zn^{2+}$ is anode and its reduction potential is = -0.76 V

$Ag|Ag^+$ is cathode anad its reduction potential is = +0.80 V

Emf of the cell = Reduction potential of Cathode - Reduction potential of Anode

Emf of the cell = +0.8 – (-0.76) = 1.56

Applying Nernst equation to the net cell reaction gives

$$E_{cell} = E_{cell}^{O} - \frac{0.059}{2} log\frac{c_2}{{c_1}^2}$$

C_2 is concentration of anode solution and C_1 is concentration of cathode solution

$$E_{cell} = 1.56 - \frac{0.059}{2} log\frac{0.001}{(0.1)^2}$$

$$E_{cell} = 1.56 - \frac{0.059}{2} log 10^{-1}$$

$$E_{cell} = 1.56 + 0.02955 = 1.58955 \text{ V}$$

Relation between standard free energy and equilibrium constant

Let us assume that the redox changes occurring in Danial cell attains equilibrium. At equilibrium, the reduction potential values of the two electrodes become equal and EMF of the cell becomes zero

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

The equilibrium constant for this reaction is given as

$$K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Applying Nernst equation to the complete cell reaction

$$E_{cell} = E_{cell}^{O} - \frac{RT}{nF} ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell}^{O} = -\frac{RT}{nF} ln \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad [as\ E_{cell} = 0]$$

$nFE_{cell}^{O} = RT\ lnK_{eq}$ ---- eq(1)

$$logK_{eq} = \frac{nE_{cell}^{O}}{0.059} \quad ---eq(2)$$

Since $nFE_{cell}^{O} = -\Delta G^{O}$

From equation (1)

$\therefore -\Delta G^{O} = RT\ lnK_{eq}$

$\Delta G^{O} = -2.03RTlogK_{eq}$ ------eq(3)

Q) Calculate the equilibrium constant for the reaction between silver nitrate and metallic zinc. $E_{cell}^{O} = 1.56$

Solution :

Cell reaction

$$2Ag^{+} + Zn \rightleftharpoons Zn^{2+} + 2Ag$$

$$logK_{eq} = \frac{nE_{cell}^{O}}{0.059}$$

$$logK_{eq} = \frac{2 \times 1.56}{0.059} = 52.79$$

$K_{eq} = 6.19 \times 10^{52}$

Q) Calculate the E.M.F. of the zinc - silver cell at 25°C when $[Zn^{2+}] = 0.10$ M and $[Ag^{+}] = 10$ M. (E^{o}_{cell} at 25°C = 1.56 volt]

Solution : The cell reaction in the zinc - silver cell would be

$$2Ag^{+} + Zn \leftrightharpoons 2Ag + Zn^{2+}$$

The Nernst equation for the above all reaction may be written as :

$$E_{cell} = E_{cell}^{O} - \frac{0.059}{2} log \frac{[Zn^{2+}]}{[Ag^{+}]^{2}}$$

$$E_{cell} = 1.56 - \frac{0.059}{2} ln \frac{[0.10]}{[10]^{2}}$$

$E_{cell} = 1.648$ V

Concentration cells

The cells whose E_{cell}^{O} is zero are called concentration cells. This means that the two compartments (cathode and anode) of the electrochemical cell involve same chemical species but the concentrations of the chemical species in the two compartments are different. The concentration cells are basically two types

(a) Electrolyte concentration cells and
(b) Electrode concentration cells

Electrolyte concentration cells

In such cells, two electrodes of the same metal are dipped in solutions of metal ions of different concentrations. Let an electrochemical cell represented as

$Ag|AgCl\ (C_1\ M)\ ||\ AgCl(C_2)|Ag$

For the given cell

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

At anode $Ag \rightarrow Ag^+ + e^-$

Applying Nernst equation to the net cell reaction gives

$$E_{cell} = E_{cell}^{O} - \frac{0.059}{2} log \frac{c_2}{c_1}$$

Since both anode and cathode are of same elements $E^{O}_{Cell} = 0$

$$E_{cell} = -\frac{0.059}{2} log \frac{c_2}{c_1}$$

The net cell reaction is spontaneous only when EMF of the cell is positive, which is possible only when concentration of cathode compartment is (C_2) is grater then the concentration of anode compartment (C_1). Higher concentration compartment will act as cathode .

Electrode concentration cells

In such cells, two similar electrodes at different concentrations/ pressures are dipped in the same solution with similar concentration.

Let us have an electrochemical of the electrode concentration cell is that of an amalgam with two different concentrations of the same metal dipped in same electrolyte solution

The cell is represented as

$Hg\text{-}Pb(c_1M)\ |\ PbSO_4(cM)|Hg\text{-}Pb(c_2M)$

The reaction for the given cell are

At cathode: $Pb^{2+}(c) + 2e^- \rightarrow Pb(c_2)$

At anode : $Pb(c_1) \rightarrow Pb^{2+}(c) + 2e^-$

Net cell reaction: $Pb(c_1) \rightarrow Pb(c_2)$

Since, the concentration of Pb^{2+} for the two half cells is same as the electrolyte solution for the two compartments is same, so the net reaction is independent of the electrolyte concentration.

Applying Nernst equation to the net cell reaction gives

$$E_{cell} = E^{O}_{cell} - \frac{0.059}{2} log \frac{c_2}{c_1}$$

Since $E^{O}_{Cell} = 0$

$$E_{cell} = -\frac{0.059}{2} log \frac{c_2}{c_1}$$

The net cell reaction would be spontaneous, when The emf of the cell is positive, which is possible only when $C_1 > C_2$

I.e electrode with more concentration will act as anode

Solved numerical

Given overall formation of the $[Fe(CN)_6]^{4-}$ ion as 10^{35} and the standard potential for half reactions

$Fe^{+3} + e^- \leftrightharpoons Fe^{2+}$; $E^O = 0.77$ V

$[Fe(CN)_6]^{3-} + e^- \leftrightharpoons [Fe(CN)_6]^{3-}$ $E^O = 0.36$ V

Calculate the overall formation constant of the $[Fe(CN)_6]^{3-}$ ion

Solution

Let K_f be the formation constant of $[Fe(CN)_6]^{3-}$ ion

A) $Fe(CN)_6]^{4-}$ is formed by following reaction

$Fe^{2+} + 6CN^- \leftrightharpoons Fe(CN)_6]^{4-}$; $K_f = 10^{35}$ ---------eq(1)

From the relation $\Delta G^O = 2.303RT \log K_f$ for above equation

$\Delta G_1^O = -2.303RT \log K_f$ (T = 398K, R = 8.314 J/mol

$\Delta G_1^O = 2.303 \times 8.314 \times 398 \log 10^{35} = -199704.69$ J

B) $Fe^{+3} + e^- \leftrightharpoons Fe^{2+}$ $E^O = 0.77V$ -------eq(2)

From equation $\Delta G^O =- nFE$ for equation n=1

$\Delta G_2^O = -1 \times 96500 \times 0.77 = -74305$ J

C) $[Fe(CN)_6]^{3-} + e^- \leftrightharpoons [Fe(CN)_6]^{3-}$ $E^O = 0.36$ V

$[Fe(CN)_6]^{3-} \leftrightharpoons [Fe(CN)_6]^{3-} + e^-$ $E^O = -0.36$ --------eq(3)

From equation $\Delta G^O =- nFE$ for equation n=1

$\Delta G_3^O = -1 \times 96500 \times (-0.36) = 34740$ J

Adding equation (1), (2) and (3)

$Fe^{2+} + 6CN^- \leftrightharpoons Fe(CN)_6]^{4-}$ $\Delta G_1^O = -199704.69$ J

$Fe^{+3} + e^- \leftrightharpoons Fe^{2+}$ $\Delta G_2^O = -74305$ J

$[Fe(CN)_6]^{3-} \leftrightharpoons [Fe(CN)_6]^{3-} + e^-$ $\Delta G_3^O = 34740$ J

$Fe^{3+} + 6CN^- \leftrightharpoons [Fe(CN)_6]^{3-}$ $\Delta G_4^O = \Delta G_3^O + \Delta G_2^O + \Delta G_1^O = -239269.69$ J

Now

$\Delta G_4^O = -2.03RT \log K_f$

$K'_f = 8.59 \times 10^{41}$

Q) By how much is the oxidizing power of the $MnO_4^-|Mn^{2+}$ couple decreases if the H^+ concentration is decreased from 1M to 10^{-4}M at 25^OC? Assume that the concentration of other species do not change

Solution

In acidic medium, MnO_4^- acts as oxidizing agent and reduce to Mn^{2+} as per the reaction

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$$E_{MnO_4^-|Mn^{2+}} = E^O_{MnO_4^-|Mn^{2+}} - \frac{0.059}{5} log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$E_{MnO_4^-|Mn^{2+}} = E^O_{MnO_4^-|Mn^{2+}} - \frac{0.059}{5} log \frac{[Mn^{2+}]}{[MnO_4^-][1]^8}$$

And

$$E_{MnO_4^-|Mn^{2+}} = E^O_{MnO_4^-|Mn^{2+}} - \frac{0.059}{5} log \frac{[Mn^{2+}]}{[MnO_4^-][10^{-4}]^8}$$

$$\therefore \Delta E_{MnO_4^-|Mn^{2+}} = \frac{0.059}{5} log \left[\frac{[MnO_4^-][1]^8}{[Mn^{2+}]} \times \frac{[Mn^{2+}]}{[MnO_4^-][10^{-4}]^8}\right]$$

$$\therefore \Delta E_{MnO_4^-|Mn^{2+}} = 0.3776V$$

Thus, the oxidizing power of $MnO_4^-|Mn^{2+}$ couple **decreases** by 0.3776V

Q) The potential of the following cell is 1.02 V at 298K temperature Calculate the pH of the HCl solution (E^o_{Ag} = 0.8 V)

Pt|H_2(1 bar)|HCl(x M)||Ag^+(0.01M)|Ag

Solution

Reductio npotential is given

E^O_{Cell} = Reduction potential of cathode – Reduction potential of anode

E^O_{Cell} = 0.8 – 0 = 0.8 V

Cell reaction

$(1/2)H_2 + Ag^+ \leftrightharpoons H^+ + Ag$ here $n = 1$

$$E_{cell} = E^o_{cell} - \frac{0.059}{n} log \frac{[H^+]}{[Ag^+]}$$

$$1.02 = 0.80 - \frac{0.059}{1} log \frac{[H^+]}{[0.01]}$$

$$3.729 = - log[H^+] + (-2)$$

$$- log[H^+] = 5.729$$

$$pH = 5.729$$

Q) EMF of the following cell is 067V at 298K

Pt|H_2(1atm)|H^+(pH=X)||KCl(1N) | Hg_2Cl_2|Hg

Calculate pH of the anode compartment. Given $E^O_{Cl|Hg2cl2Hg}$ = 0.28V

Solution

Anode reaction $H_2 \rightarrow 2H^+ + 2e^-$

Cathode reaction $Hg_2 Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$

Cell reaction

$H_2 + Hg_2Cl_2 \rightarrow 2H^+ + 2Hg + 2Cl^-$

$$E_{cell} = E^O_{Cl^-|Hg_2Cl_2|Hg} - E^O_{H^+|H_2} - \frac{0.059}{2} log \frac{[H^+]^2[Cl^-]^2}{H_2}$$

(Hg and Hg_2Cl_2 are pure solids hence don't appear)

[Cl] = 1 as KCl is 1N and [H_2] = 1 atm

$$0.67 = 0.28 - 0 - \frac{0.059}{2} log \frac{[H^+]^2[1]^2}{1}$$

0.67 = 0.28 - 0.059 log[H^+]

-log[H^+] = 6..61

pH = 6.61

Q) The emf of the cell, Hg|Mercurous nitrata (0.01M)|| Mercurous nitrate (0.1M) |Hg was found to be 0.0295V at 250^O. Calculate the molecular formula of merrcurous nitrate.

Solution

Let the formula of mercurous nitratae be $Hg_n(BO_3)_n$

For the given cell, the reactions occurring at two electrodes are

At anode : $nHg \rightarrow (Hg_n^{n+})_A + ne^-$

At cathode : $(Hg_n^{n+})_C + ne^- \rightarrow nHg$

Net cell reaction : $(Hg_n^{n+})_C \rightarrow (Hg_n^{n+})_A$

So, this is an electrolyte concentration cell for which E^O_{cell} = 0. The E_{cell} will be given as

$$E_{cell} = -\frac{0.059}{n} log \frac{[(Hg_n^{n+})_A]}{[(Hg_n^{n+})_C]}$$

$$0.0295 = -\frac{0.059}{n} log \frac{0.1}{0.01}$$

$$0.0295 = \frac{0.059}{n} log \frac{0.01}{0.00.1}$$

n = 2

Thus , the formula of mercurous nitrate is $Hg_2(NO_3)_2$

Q) Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K, if the emf of the cell,

Ag|Ag^+(std. Ag_2CrO_4 solution)||Ag^+(0.1M) |Ag is 0.164V at 298K

Solution

For the given cell, the reaction occurs at anode and cathode are

Anode: $Ag \rightarrow Ag^+_A + e^-$

Cathode : $Ag^+_C + e^- \rightarrow Ag$

Net cell reaction $Ag^+_C \rightarrow Ag^+_A$

Thus it is an electrolyte concentration cell with $E^O_{cell} = 0$

$$\therefore E_{cell} = -\frac{0.059}{1} log \frac{[Ag^+_A]}{[Ag^+_C]}$$

$$E_{cell} = \frac{0.059}{1}\ log \frac{[Ag^+_C]}{[Ag^+_A]}$$

The anode compartment have saturated solution of Sg_2CrO_4, supplying Ag^+ ion concentration.

Let the solubility of Sg_2CRO_4 be 'x' moles/lit

$$Ag_2CrO_{4(S)} \rightleftharpoons \underset{2x}{2Ag^+} + \underset{x}{CrO_4^{2-}}$$

$$K_{SP} = [Ag^+_A]^2[CrO_4^{2-}] = (2x)^2x = 4x^3$$

$$x = \sqrt[3]{\frac{K_{SP}}{4}}$$

$$[Ag^+_A] = 2x$$

$$[Ag^+_A] = 2 \times \sqrt[3]{\frac{K_{SP}}{4}}$$

$$\therefore E_{cell} = \frac{0.059}{1}\ log \frac{0.1}{2 \times \sqrt[3]{\frac{K_{SP}}{4}}}$$

$$0.164 = \frac{0.059}{1}\ log \frac{0.1}{2 \times \sqrt[3]{\frac{K_{SP}}{4}}}$$

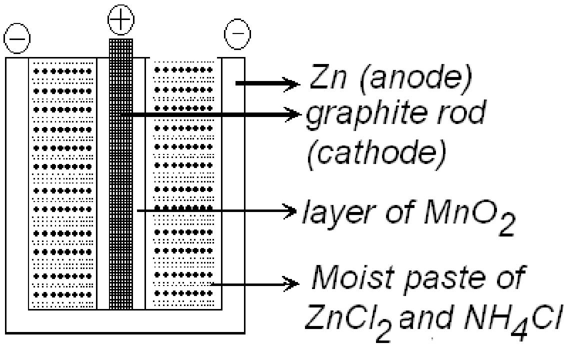
$$K_{SP} = 2.24 \times 10^{-12} M^3$$

Type of batteries

A battery is an electrochemical cell, or a series of combined electrochemical cells, that can be used as source of direct electric current at a constant voltage. The operation of a battery is similar in principle to that of the electrochemical cells except that they are completely self contained and require no slat bridge. There are generally two types of batteries. Primary batteries and secondary batteries

A primary battery act as a source of electricity without being previously charged by an electric current from external source. In such battery, electrical energy is obtained at the expense of chemical reactivity as long as the active materials are present. A battery, which can be recharged after it has been used once is called secondary battery. Certain chemical changes occur when the cell is charged with electricity and these changes are reversed during discharge process

Dry Cell Batter



The most familiar example of this type is the dry cell (known as Leclanche cell after its discoverer) which is used commonly in our transistors and clocks.

The cell consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon (Fig). The space between the electrodes is filled by a moist paste of ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$). The electrode reactions are complex, but they can be written approximately as follows.

$$\text{At Anode : } Zn(s) \rightarrow Zn^{2+} + 2e^-$$

$$\text{At Cathode: } 2MnO_2(S) + 2NH_4^+ + 2e^- \rightarrow Mn_2O_3 + 2NH_3 + H_2O$$

$$\text{Net cell reaction : } Zn(s) + 2MnO_2(S) + 2NH_4^+ \rightarrow Mn_2O_3 + Zn^{2+} + 2NH_3 + H_2O$$

In the reaction at cathode, manganese is reduced from the + 4 oxidation state to the +3 state. Ammonia produced in the reaction forms a complex with Zn^{2+} to give $[Zn(NH3)4]^{2+}$. The cell has a potential of nearly 1.5 V.

Mercury cell

Mercury cell, suitable for low current devices like hearing aids, watches, etc. consists of zinc – mercury amalgam as anode and a paste of HgO and carbon as the cathode.

The electrolyte is a paste of KOH and ZnO. The electrode reactions for the cell are given below:

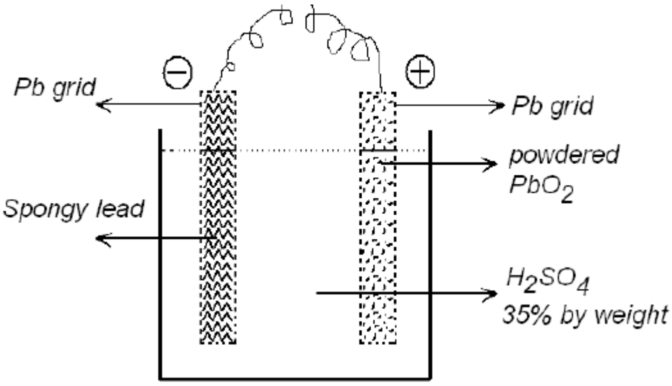
$$\text{Anode: } Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H2O + 2e^-$$

$$\text{Cathode: } HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$$

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

The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

Secondary cell



Lead storage battery

A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles.

The most important secondary cell is the lead storage battery commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

The cell reactions when the battery is in use are given below:

Anode: Pb(s) + SO42–(aq) → PbSO4(s) + 2e–

Cathode: PbO2(s) + SO4 2–(aq) + 4H+(aq) + 2e– → PbSO4 (s) + 2H2O (l)

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

$$Pb(s)+PbO_2(s)+2H_2SO_4(aq)\rightarrow 2PbSO_4(s) + 2H2O(l)$$

On charging the battery the reaction is reversed and $PbSO_4$(s) on anode and cathode is converted into Pb and PbO_2, respectively

Under normal operating conditions, each cell produce potential of 2V. Thus a total of 12V from six cells.

The cell reaction are easily reversed, if $PBSO_4$ is freshly precipitated, but on long standing, $PbSO_4$ changes its crystalline structure and ages to less reactive form, which cannot be reconverted back into Pb and PBO_2

Four aspects are noteworthy

(i)There is no slat bridge and both the electrodes are immersed in the same solution.

(ii) Battery is rechargeable i.e normal electrochemical reactions are reversed by applying an external voltage at the cathode and the anode.

(iiI)As the battery is used, the electrolyte solution becomes more dilute as $H_{21}O$ is produced and H_2SO_4 is used up. Thus, the density of electrolyte solution decreases and the degree to which the battery has been discharged can be checked by measuring the density of the electrolyte

(iv) The temperature coefficient for lead storage battery is 1.5×10^{-4} V/^{O}C.

Thus even for 40^{O}C change in temperature, the decrease in voltage amount to only 6×10^{-3} V, which is about 0.05% of the operating voltage

Nickel-Cadmium battery

Nickel-cadmium cell has longer life than the lead storage cell but more expensive to manufacture.

The reaction at two electrodes are
At anode : Cd(s) + 2OH$^-$ → Cd(OH)$_2$(s) + 2e$^-$
At cathode : NiO$_2$(s) + 2H$_2$O +2e$^{-+\rightarrow \text{Ni(OH)}}{}_2$(s) + 2OH$^-$
Net cell reaction while discharging is
Cd (s)+2Ni(OH)3 (s) → CdO (s) +2Ni(OH)2 (s) +H2O(l)

Solved numerical

Q) A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 34.6% by weight (density 1.261 g mL$^-$ at 25^{O}C)to one of 27% by weight. The original volume of the electrolyte is one litre. Calculate the total charge released at anode of the battery. Note that the water is produced by the cell reaction as H_2SO_4 is used up. Overall reaction is
Pb(s) + PbO$_2$(s) + 2H$_2$SO$_4$(l) → 2PbSO$_4$(s)+ 2H$_2$O(l)
Solution
Before the discharge of lead storage battery
Mass of solution = 1000×1.261 = 1261 g
Mass of H_2SO_4 = (1261 × 34.6) /100 = 436.3 g
Mass of water = 1261 – 436.3 = 824.7 g
After the discharge of lead storage battery
Let the mass of H_2O produced as a result of net reaction during discharge is ‘x’ g
Since it is a mole to mole relation between H_2SO_4 and water
Moles of H_2O produced = moles of H_2SO_4 consumed = x/18
Mass of H_2SO_4 consumed = (x/18) × 98
Now mass of the solution after discharge =

$$1261-\frac{98x}{18}+x$$

% by mass of H_2SO_4 after discharge =

$$\frac{Mass\ of\ H_2SO_4 left}{Mass\ of\ solution\ after\ discharge}\times 100 = 27$$

$$27 = \frac{436.3-\frac{98x}{18}}{1261-\frac{98x}{18}+x}\times 100$$

X= 22.59g
From the reaction, it is evident that the moles of electron exchanged at anode or cathode is two and this is also the moles of H_2O produced or moles of H_2SO_4 consumed
∴ moles of electrons released at anode =

$$\frac{22.59}{18}$$

∴ total charge released at anode =

$$\frac{22.59}{18}\times 96500 = 1.21\times 10^5 Coulomb$$

Fuel cell

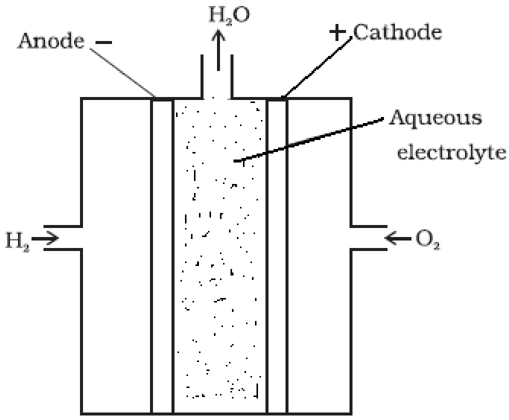
A hydrogen – oxygen fuel cell consists of an electrolyte solution, such as KOH solution and two inert carbon electrodes. Hydrogen and oxygen gases are bubbled through the anode and cathode compartments, where the following reaction takes place

At anode : $2H_2(g) ++ 4OH^- \rightarrow 4H_2O(l) + 4e^-$

At cathode : $O_2(g) + 2H_2O(l) + 4e- \rightarrow 4OH^-$

Net cell reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

The standard emf of the cell is 1.23V, which indicates that the cell reaction is spontaneous under standard conditions, The porous carbon electrodes serves as electrical conductions and provide the necessary surface for the initial decomposition of the molecules into atomic species prior to electron transfer. A hydrogen –oxygen fuel cell assembly is shown in figure

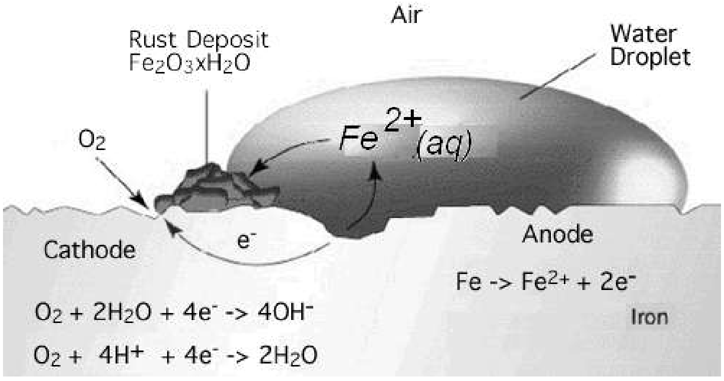


Unlike batteries, fuel cells do not store chemical energy. Reactants must be constantly resupplied and products must be constantly removed from fuel cell. The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70 % compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells.

These have been used in automobiles on an experimental basis. Fuel cells are pollution free and in view of their future importance, a variety of fuel cells have been fabricated and tried.

In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon.

At a particular spot (Fig) of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction



Anode: $2\ Fe\ (s) \rightarrow 2\ Fe^{2+} + 4\ e^{-}$ $E_{Fe2+/Fe} = -0.44$ V

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction

Cathode: $O_2(g) + 4\ H^+(aq) + 4\ e^{-} \rightarrow 2\ H_2O\ (l\ )$ E =1.23 V

The overall reaction being:

$2Fe(s)+O_2(g) + 4H^+(aq) \rightarrow 2Fe_2 +(aq)+\ 2H_2O\ (l\ )$ E = 1.67 V

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($Fe_2O_3.\ x\ H_2O$) and with further production of hydrogen ions.

Prevention of corrosion is of prime importance. One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol).

Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.

CHEMICAL KINETICS

Rate of chemical reactions

The rate of a reaction tells us how fast the reaction occurs. Let us consider a simple reaction.

$A + B \rightarrow C + D$

As the reaction proceeds, the concentration of the reactant A and B decreases with time and the concentration of the products C + D increase with time simultaneously. The rate of the reaction is defined as the change in the concentration of any reactant or product in the reaction per unit time. For the above reaction,

Rate of the reaction
= Rate of disappearance of A
= Rate of disappearance of B
= Rate of appearance of C
= Rate of appearance of D

During the reaction, changes in the concentration is infinitesimally small even for small changes in time when considered in seconds.

Therefore differential form of rate expression is adopted. The negative sign shows the concentration decrease trend and the positive sign shows the concentration increase trend.

$$\therefore Rate = \frac{concentration\ change}{time\ taken}$$

$$Rate = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

For a general balanced reaction,

$aA + bB \rightarrow cC + dD$

$$Rate = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Example Consider the reaction, $2NO + 2H_2 \rightarrow N_2 + 2H_2O$

$$Rate = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{1}{2}\frac{d[H_2]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt}$$

Units of Rate

Reaction rate has units of concentration divided by time. Since concentration is expressed in mol lit^{-1} or mol dm^{-3} the unit of the reaction rate is mol lit^{-1} s^{-1} or mol dm^{-3} s^{-1}.

Factors influencing reaction rates

There are number of factors which influence the rate of the reaction. These are :
(i) Nature of the reactants and products
(ii) Concentration of the reacting species
(iii) Temperature of the system
(iv) Presence of catalyst
(v) Surface area of reactants
(vi) Exposure to radiation

(i) Effect of nature of the reactant and product

Each reactant reacts with its own rate. Changing the chemical nature of any reacting species will change the rate of the reaction. For example, in halogenation reaction, the reactions involving iodine is found to be slower than those involving chlorine.

In case of products, some of them are capable of reacting back to form reactants or some other kind of products. In such cases, the overall rate will be altered depending on the reactivity of the products.

(ii) Effect of reacting species

As the initial concentration of the reactants increase in the reaction mixture, the number of reacting molecules will increase. Since the chemical reaction occurs when the reacting species come close together and collide, the collisions are more frequent when the concentrations are higher. This effect increases the reaction rate.

(iii) Effect of temperature

Increase in temperature of the system increases the rate of the reaction. This is because, as the temperature increases the kinetic energy of the molecules increases, which increases the number of collisions between the molecules. Therefore the overall rate of the reaction increases. This condition is valid only for endothermic reaction. For exothermic reaction the overall rate decreases with increasing temperature.

(iv) Effect of presence of catalyst

A catalyst is a substance that alters the rate of a chemical reaction, while concentration of catalyst remaining the same before and after the reaction. The addition of catalyst generally increases the rate of the reaction at a given temperature. Also, catalyst is specific for a given reaction.

(v) Effect of surface area of reactants

In case of reactions involving solid reactants and in case of heterogeneous reactions, surface area of the reactant has an important role. As the particle size decreases surface area increases for the same mass.

More number of molecules at the surface will be exposed to the reaction conditions such that the rate of the reaction increases. Thus the reactants in the powdered form (or) in smaller particles react rapidly than when present in larger particles.

(vi) Effect of radiation

Rates of certain reactions are increased by absorption of photons of energy. Such reactions are known as photochemical reactions. For example, H_2 and Cl_2 react only in the presence of light. With increase in the intensity of the light (or) radiation, the product yield increases. For photosynthesis light radiation is essential and the process does not proceed in the absence of light.

Solved numerical

Q) In the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, NO_2 is being formed at the rate of 0.0072 $molL^{-1}$. What is the rate of reaction at this time?

Solution

Rate of reaction can be given in terms of any reactant or product

$$Rate = \frac{1}{4}\frac{d[NO_2]}{dt}$$

$$Rate = \frac{1}{4} \times 0.0072 = 0.0018\, moleL^{-1}s^{-1}$$

Q) The concentration of a reactant changes from 0.06 mol L^{-1} to 0.05 mol L^{-1} in 25 minutes. Calculate the average rate of reaction

Solution

$$rate_{av} = \frac{change\ in\ concnetration}{time}$$

$$rate_{av} = \frac{0.06 - 0.05}{25} = 4 \times 10^{-4} molL^{-1}min^{-1}$$

Q) For reaction ; $4NH_3 + 5O_2 \rightarrow NO + 6H_2O$ if the rate of disappearance of NH_3 is 3.6×10^{-3} mol $L^{-1}sec^{-1}$. Then what is the rate of formation of H_2O

Solution

(1/4) [rate of disappearance of NH_3] = (1/6) [Rate of formation of H_2O]

$$\frac{d[H_2O]}{dt} = \frac{6}{4} \times 3.6 \times 10^{-3} molL^{-1}sec^{-1}$$

Rate law

The rate of a chemical reaction is proportional to the product of effective concentration (active mass) of the reacting species, each raised to a power that is equal to the corresponding stoichiometric number of the substance appearing in the chemical reaction

Consider a general reaction

$aA + bB \rightarrow cC + dD$.

The rate law is given by the expression,

Rate $\propto [A]^a [B]^b$

Rate = $k[A]^a [B]^b$ ---------eq(1)

where k is proportionality constant also known as the rate constant or velocity constant of the reactions.

If the rate of a reaction is determined experimentally, it is found that equation (1) is not applicable always. However, the experimental results can benefitted to satisfy a relation of the type equation(1) where the exponents may or may not be equal to the respective stoichiometric coefficients. In general, we may write the rate as

Rate = $k[A]^p [B]^q$ ---------eq(2)

Here p and q may or may not be equal to a and b , they may be negative or fraction or hole numbers

Equation (2) , which relates the rate of reaction, with the concentrations of reacting species is known as **differential rate law**

Rate constant

In the above general equation k represents the rate constant. Rate constant or velocity constant (or) specific reaction rate is defined as the rate of the reaction when the concentration of each of the reactants is unity in the reaction.

When concentration of A and B is unity then, the rate constant is equal to the rate of the reaction. When the temperature of the reaction mixture changes, the value of rate constant changes.

Characteristics of rate constant

1. Rate of reaction is proportional to rate constant. Greater the value of rate constant, faster is the reaction
2. Value of rate constant is definite for a reaction at a particular temperature. With the change of temperature, rate constant also changes
3. The value of rate constant is independent of concentration of reactant
4. Units of rate constant depend upon the order of reaction
5. Presence of catalyst changes the rate of reaction and thus rate constant as well, by lowering the activation energy

Order of the reaction

Order of a reaction is defined as the sum of the exponential powers to which each concentration is raised in the rate expression. For example, if the overall rate is given by the expression Rate = $k[A]^p [B]^q$

Then, the overall order of the reaction is (p+q). The order with respect to A is p. The order with respect to B is q. If p+ q=1 the order of the reaction is 1, and the reaction is called first order. If p+q=2 the order of the reaction is 2 and the reaction is called second order and so on.

A zero order reaction is one where the reaction rate does not depend upon the concentration of the reactant. In this type of reaction, the rate constant is equal to the rate of the reaction.

Unit of rate constant

In general, rate expression for the reaction, Rate = $k[A]^p [B]^q$

$$k = \frac{Rate}{[A]^p[B]^q}$$

$$k = \frac{\frac{mol\ lit^{-1}}{time}}{\left[\frac{mol}{lit}\right]^p \left[\frac{mol}{lit}\right]^q} = \frac{(mol\ lit^{-1})^{p+q-1}}{time} = \frac{(mol\ lit^{-1})^{1-n}}{time}$$

Here n is order of reaction

Thus $k = (\text{concentration})^{1-n}\ \text{time}^{-1}$

Order	Units
Zero	mol L^{-1} sec^{-1}
First	Sec^{-1}
Third	mol^{-2} L^2 sec^{-1}

In case of gaseous reaction, concentration is expressed in terms of pressure with the unit of atmosphere

Following are the important differences between rate and rate constant of a reaction

Sr.No.	Rate of reaction	Rate constant of reaction
1	It represents the speed at which the reactants are converted into products at any instant	It is the constant of proportionality in the rate law expression.
2	At any instant of time, the rate depends upon the concentration of reactants at that instant	It refers to the rate of a reaction at the specific point when concentration of every reacting species is unity
3	It decreases as the reaction proceeds	It is constant and does not depend on the progress of the reaction.
4	Rate of rate determining step determines overall rate value.	It is an experimental value. It does not depend on the rate determining step.

Zero order reaction

In zero order reaction, the rate does not depend on concentration of reactants. Thus, rate of reaction remains constant throughout the course of time

For example $H_2+Cl_2 \rightarrow 2HCl$ (in presence of infra red radiation)

Rate = $k[H_2]^0+[Cl_2]^0 = k$

i.e k = dx/dt unit of k = mol L^{-1} $time^{-1}$

Integrated rate expression

For a general reaction A → product

Integrated rate equation for zero order reaction is given by

$$\text{Rate } = \frac{d[A]}{dt} = [A]^0$$

$$d[A] = -kdt$$

Integrating both the sides

$$[A] = -kt + C$$

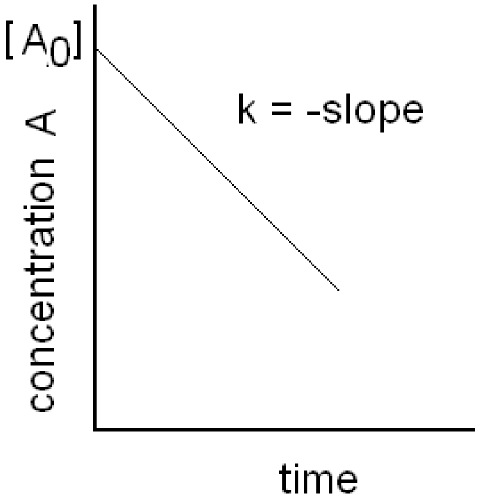
At t= 0 $[A] = [A_0]$ thus $C = [A_0]$

Where $[A_0]$ is initial concentration, on substituting value of C

$$[A] = -kt + [A_0]$$

$$k = \frac{1}{t}\{[A_0] - [A]\}$$

Where k is rate constant
t is reaction time
[A_0] is initial reactant concentration
[A] is final reactant concentration



Example of zero order reaction: The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure

$$2NH_3(g) \xrightarrow[\text{pt catalyst}]{1130K} N_2(g) + 3H_2(g)$$

In this reaction, platinum metal acts as a catalyst. At high pressure the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration. The thermal decomposition of HI on gold is another example of zero order reaction

Half-life period

Half –life period $t_{1/2}$ is the time in which half of the reaction has been completed i.e. half of the reactant concentration undergoes the reaction
It means final concentration of reactant [A] = [A_0]/2
And becomes $t_{1/2}$ then

$$k = \frac{1}{t_{1/2}}\left\{[A_0] - \frac{[A_0]}{2}\right\} = \frac{1}{t_{1/2}}\frac{[A_0]}{2}$$

$$t_{1/2} = \frac{1}{k}\frac{[A_0]}{2}$$

Thus half life period of zero order reaction is directly proportional to initial concentration of reactant $t_{1/2} \propto [A_0]$

First order reaction

In first order reaction the rate of reaction depends upon one concentration term only
For reaction A → product
Rate = k [A] or rate = k[B]
i.e only one concentration term affect the rate of reaction
Unit of rate constant = time^{-1}

Integrated rate expression

For general reaction A → Product

$$\text{Rate} = -\frac{\mathrm{d[A]}}{\mathrm{dt}} = \mathrm{k[A]}^1$$

$$\frac{d[A]}{[A]} = -kdt$$

Integrating, we get

ln[A] = -kt +C

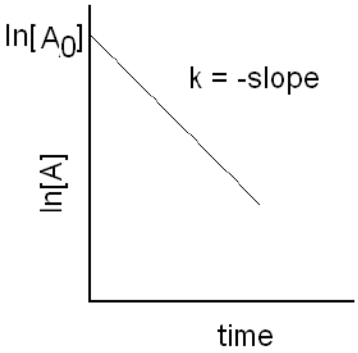
When t = 0 [A] = [A_0] , where [A_0] is initial concentration

ln[A_0] = C

Substituting value of C in equation

ln[A] = -kt + ln[A_0] ---------eq(1)

graph of equation (1) is straight line and negative of slope is rate constant k



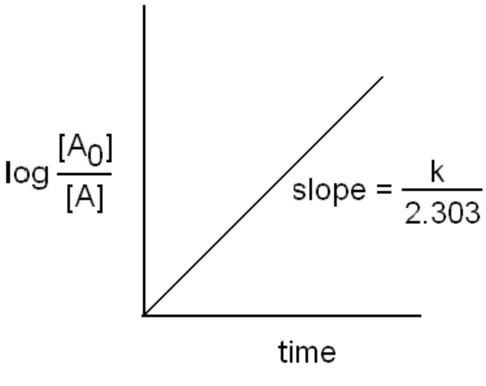
Rearranging equation (1)

$$ln\frac{[A]}{[A_0]} = -kt \quad or \quad [A] = [A_0]e^{-kt}$$

$$ln\frac{[A_0]}{[A]} = kt \quad -----eq(2)$$

$$log\frac{[A_0]}{[A]} = \frac{kt}{2.303}$$

Graph of the above equation is straight line passing through origin



$$k = \frac{2.303}{t}log\frac{[A_0]}{[A]} \quad ----eq(3)$$

At time t_1 Concentration be [A_1] from equation(1)

ln[A_1] = = - kt_1 + ln[A] -------eq(4)

At time t_2 concentration be [A_2] from equation(1) ln$[A_2]$ = = - kt_2 + ln[A] -------eq(5)

Subtracting equation(5) from equation(4)

ln$[A_1]$ - ln$[A_2]$ = k (t_2 - t_1)

$$ln\frac{[A_1]}{[A_2]} = k(t_2 - t_1)$$

$$k = \frac{1}{(t_2 - t_1)} ln\frac{[A_1]}{[A_2]}$$

Here t_2- t_1 = t is time period

Half-life period

For half life period t = $t_{1/2}$ and [A] = $[A_0]$ /2

$$k = \frac{2.303}{t_{1/2}} log\frac{[A_0]}{\left[\frac{A_0}{2}\right]}$$

$$t_{1/2} = \frac{2.303}{k} log2$$

$$t_{1/2} = \frac{0.693}{k}$$

Thus, half life period of the first order reaction is independent of any concentration

Amount of substance left after ‘n’ half life can be calculated as

$$amount\ left\ after'n'half\ life = \frac{[A_0]}{2^n}$$

Hydrogenation of ethane is an example of first order reaction

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

Rate = k$[C_2H_4]$

All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

Decomposition of N_2O_5 and N_2O are some more examples of first order reactions

Note half life of nth order reaction $t_{1/2} \propto [A_0]^{1-n}$

$$t_{1/2} = \frac{(2^{n-1} - 1)}{(n-1)[A]_0^{n-1}k_n}$$

For reaction of type **n**A → Product

-Zero order

$$k = \frac{1}{\boldsymbol{n}t}\{[A_0] - [A]\}\ \ and\ t_{1/2} = \frac{1}{\boldsymbol{n}k}\frac{[A_0]}{2}$$

-First order reaction

$$k = \frac{2.303}{\boldsymbol{n}t} log\frac{[A_0]}{[A]}\ \ and\ \ t_{1/2} = \frac{0.693}{\boldsymbol{n}k}$$

Solved numerical

Q) A first order reaction takes 34.64 minutes for 50% completion. How much time will it take for 75% completion

Solution:

Half life = 34.64 minutes

Left over after first half life is 50% thus at the end of the second half life 50% of 50% = 25%is left over = 75% completion

Thus time for second half life = 34.64 minutes

Total time = 34.64 + 34.64 = 69.28 minutes

Q) The decomposition of N_2O_5 according to the equation $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$, is a first order reaction. After 30 minutes from the start of the reaction in a closed vessel the total pressure developed is found to be 305.5 mm of Hg and on complete decomposition the total pressure is 587.5mm Hg. Calculate the rate constant of reaction

Solution

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

$$N_2O_5(g) \rightarrow 2NO_2(g) + (1/2)\ O_2(g)$$

Initial concentration	p_0	0	0
After 30 minutes	$p_0 - p$	2p	p/2
After complete Decomposition	0	$2p_0$	$p_0/2$

Total pressure after 30 minutes = $(p_0 - p) + 2p + (p/2) = 305.5$

$P_0 + (3p/2) = 305.5$ -------eq(1)

Total pressure after complete decomposition

$2p_0 + (p_0/2) = 587.5$

$(5p_0/2) = 587.5$ ------eq(2)

From equation (1) and (2) $p_0 = 235$ and $p = 47$

Given reaction is of first order thus and 2A → product thus

$$\mathrm{k} = \frac{2.303}{\mathrm{nt}}\log\frac{[\mathrm{A_0}]}{[\mathrm{A}]}$$

$$\mathrm{k} = \frac{2.303}{2 \times 30}\log\frac{\mathrm{p_0}}{\mathrm{p_0} - \mathrm{p}} = \frac{2.303}{60}log1.25$$

$$k = 3.72\times10^{-3}\ \text{min}^{-1}$$

Pseudo-Unimolecular reaction

The reactions which are not truly of the first order but become reactions of the first order under certain conditions are called pseudo-unimolecular or pseudo-first order reaction

For example, acidic hydrolysis of an ester

$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

In this reactions concentration of water (one of the reactants) is in excess and its concentration remains constant throughout the reaction

Thus rate = k' $[CH_3COO\ C_2H_5]\ [H_2O]$

The term $[H_2O]$ can be taken as constant. The equation, thus, becomes

Rate = $k[CH_3COO\ C_2H_5]$

Where $k = k'[H_2O]$

Hydrolysis of cane sugar is another example

$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

Molecularity of the reaction

Molecularity is defined as the number of atoms or molecules taking part in an elementary step leading to a chemical reaction. The overall chemical reaction may consist of many elementary steps. Each elementary reaction has its own molecularity which is equal to number of atoms or molecules participating in it. If the reaction takes place in more than one step there is no molecularity for the overall reaction. However molecularity and order are identical for elementary reaction (one step). There are many differences between the concepts of order and molecularity.

Sr.No	**Order of a reaction**	**Molecularity of a reaction**
1	It is the sum of powers raised on concentration terms in the rate expression	It is the number of molecules of reactants taking part in elementary step of a reaction
2	Order of a reaction is an experimental value, derived from rate expression	It is a theoretical concept.
3	Order of a reaction can be zero, fractional or integer.	Molecularity can neither be zero Nor be fractional.
4	Order of a reaction may have negative value.	Molecularity can never be negative
5	It is assigned for overall reaction	It is assigned for each elementary step of mechanism
6	It depends upon pressure, temperature and concentration (for pseudo order)	It is independent of pressure and temperature.

TEMPERATURE DEPENDANCE OF RATE CONSTANT

It is a common observation that rates of reactions increase with increase in temperature of the reaction mixture. Keeping the concentration of the reactants constant, the rate is found to be two times its initial value, when measured at a temperature 10 K greater than the initial temperature. However, the exact value of the rate constant determined at various temperature is predicted by using Arrhenius equation. This expression is obeyed by most of the reactions. Arrhenius equation is given as

$$k = A\, e^{-Ea/RT}$$

taking log on both sides

$$lnk = lnA - \frac{E_a}{RT}$$

$$logk = logA - \frac{E_a}{2.303RT}$$

where k = rate constant, E_a = activation energy, A = frequency factor, or Arrhenius constant , R = gas constant, T = temperature in Kelvin.

If k_1 and k_2 are the rate constants measured at two different T_1 and T^2 temperatures respectively, then E_a can be determined as follows :
Arrhenius equation for two different temperatures T_1 and T_2 are :

$$logk_1 = logA - \frac{E_a}{2.303RT_1}$$

And

$$logk_2 = logA - \frac{E_a}{2.303RT_2}$$

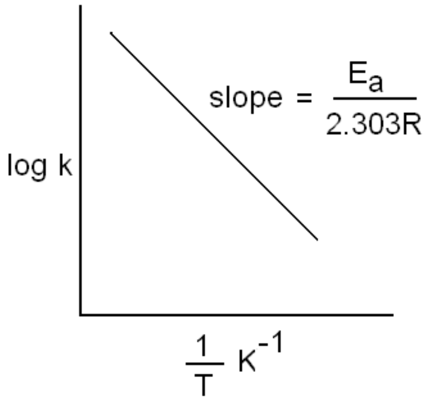
where k_1 and k_2 are the rate constants at temperature T_1 and T_2 respectively.

$$logk_2 - logk_1 = -\frac{E_a}{2.303RT_2} + \frac{E_a}{2.303RT_1}$$

$$log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

If R = 1.987 cals.mol^{-1}, then unit of E_a is 10^{-3} k.cal.
Also, a plot of log k against 1/T values gives a straight line with slope value equals to –Ea/2.303 R and intercept value equals to log A. When E_a is a positive value, and if $T_2 > T_1$ then $k_2 > k_1$.
That is, rate constant value at higher temperature is greater than rate constant value at lower temperature.
Under such conditions, plot of log k against 1/T gives a negative slope straight line. From the slope of the straight line, E_a can be calculated.
Note

$\frac{k_2}{k_1}$ is known as temperature coefficient



Main characteristics of Arrhenius equation

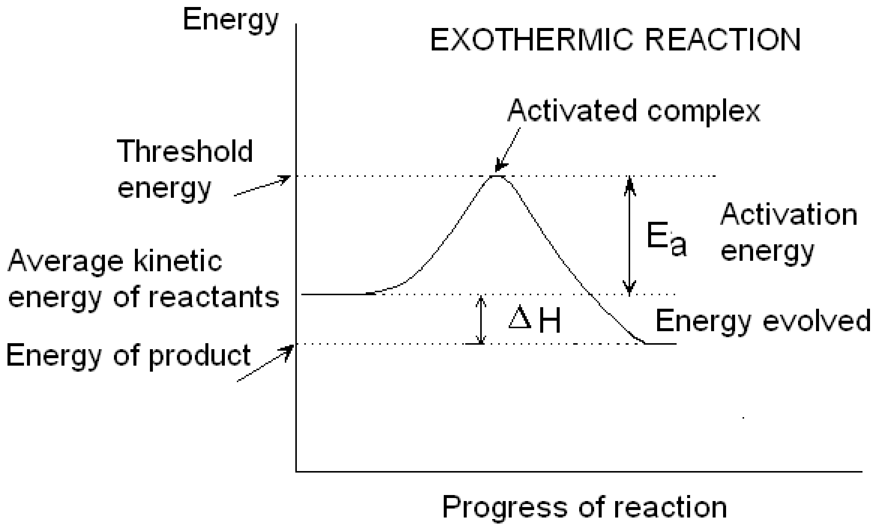
1) Larger the activation energy of reaction, smaller is the value of rate constant
2) Larger the activation of a reaction, greater is the influence of change in temperature
3) For lower temperature range, increase in temperature causes more change in the value of k than the same increase in temperature for high temperature range

Activation energy

The minimum amount of energy absorbed by the reactant molecules so that their energy becomes equal to the energy is called activation energy

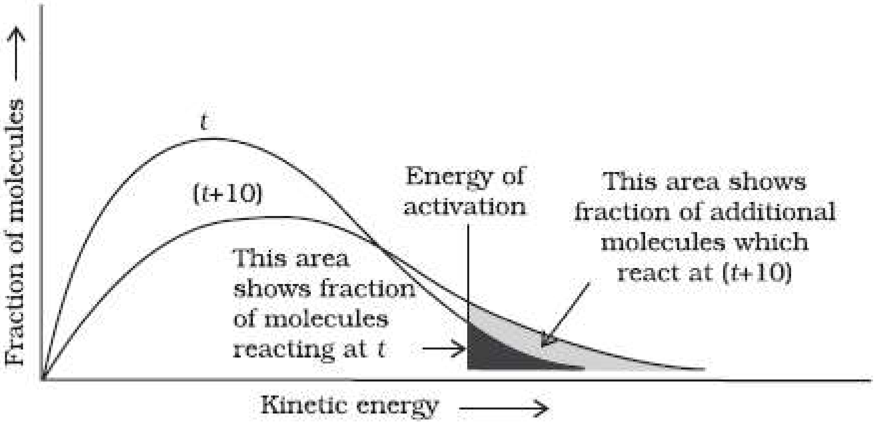
Or we can say that it is the difference between threshold energy and the average kinetic energy possessed by the reactant molecules

Activation energy = threshold energy – Average kinetic energy of reactant

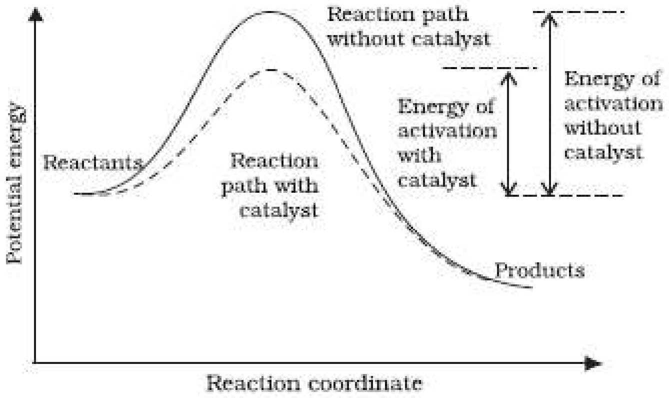


It has been found that for a chemical reaction with rise in temperature by 10^O, the rate constant is nearly doubled. It can be explained on the basis of activation energy

All the molecules in the reactant species do not have same kinetic energy. According to Boltzman and Maxwell , the distribution of kinetic energy may be described by plotting the reaction of molecules (N_E/N_T) with a given kinetic energy (E) Vs kinetic energy. Here N_E is the number of molecules with kinetic energy E and E_T is total number of molecules. The peak of the curve corresponds to the most probable kinetic energy. i.e kinetic energy of maximum fraction of molecules. There are decreasing number of molecules with energies higher than or lower than this value. Curve 1 represents the distribution at temperature t while curve 2 represent the distribution at temperature t+10. Clearly from the graph, for temperature t+10 curve broadens out. i.e spreads to the right side such that there is a greater proportional molecules with much higher energies capable to undergo reaction. The area under the curve must be constant since total probability must be one at all times It is clear from the graph at temperature (t+10) , the area showing fraction of molecules having energy equal to or greater than activation energy gets doubles leading to doubling the rate of reaction



Effect of catalyst



A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change.

For example, MnO_2 catalyses the following reaction so as to increase its rate considerably.

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

The action of the catalyst can be explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex.

This has a transitory existence and decomposes to yield products and the catalyst.

It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier

Characteristic of catalyst

1.A small amount of the catalyst can catalyse a large amount of reactants.

2. A catalyst does not alter Gibbs energy, ΔG of a reaction.

3. It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.

4.It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster.
5.it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

Solved numerical

Q) Temperature coefficient for the saponification of an ester by NaOH is 1.75 calculate the activation energy
Solution
Temperature coefficient i.e. $k_2/k_1 = 1.75$
In general practice $T_1 = 25\ ^{O}C$ i.e 298K and $T_2 = 35^{O}C = 308K$

$$log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log 1.75 = \frac{E_a}{2.303 \times 1987}\left[\frac{308 - 298}{298 \times 308}\right]$$

$E_a = 10.207$ kcal mol^{-1}

Q) For a first order reaction at $300^{O}C$, activation energy is 35kcal mol^{-1} and the frequency constant 1.45×10^{11} sec^{-1}. Calculate the rate constant
Solution

$$logk = logA - \frac{E_a}{2.303RT}$$

R = 1.987 = 2 cal/K/mole, $E_a = 35\times10^{3}$cal, T = 573K

$$logk = log1.45 \times 10^{11} - \frac{35 \times 10^3}{2.303 \times 2 \times 573}$$

logk = 11.161 – 13.26 = -2.099
Taking antilog, $k = 7.96\times10^{-3}$ sec^{-1}

Q) From the following data for the reaction between A and B, calculate the order of the reaction with respect to A and with respect to B

[A]/moll^{-1}	[B]/mol L^{-1}	Initial rate/mol L^{-1}s^{-1}
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}
1.0×10^{-3}	63.0×10^{-5}	1.6×10^{-2}

Solution
Let the order with respect to A be p and with respect to B be q. The rate law would be represented as
Rate = $k[A]^p\ [B]^q$
Therefore from first data of table $5.0\times10^{-4} = k\ [2.5\times10^{-4}]^p\ [3.0\times10^{-5}]^q$ ------eq(1)

Second date gives $4.0\times10^{-3} = k\ [5.0\times10^{-4}]^p\ [6.0\times10^{-5}]^q$ ---eq(2)

Third data for table $1.6\times10^{-2} = k\,[1.0\times10^{-3}]^p\,[6.0\times10^{-5}]^q$ ---eq(3)

Dividing equation (2) by (1)

$$\frac{4.0\times10^{-3}}{5.0\times10^{-4}} = \frac{k[5.0\times10^{-4}]^p[6.0\times10^{-5}]^q}{k[2.5\times10^{-4}]^p[3.0\times10^{-5}]^q}$$

$$8 = (2)^{p+q}$$

$$2^3 = (2)^{p+q}$$

$$\therefore p+q = 3$$

Similarly dividing equation(2) by (3)

$$\frac{4.0\times10^{-3}}{1.6\times10^{-2}} = \frac{k[5.0\times10^{-4}]^p[6.0\times10^{-5}]^q}{k[1.0\times10^{-3}]^p[6.0\times10^{-5}]^q}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^p$$

Or $4 = 2^p$ Thus p = 2

So order with respect to A is two and with respect to B is one

Q) The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K. If the pre-exponential factor (A) for the reaction is 3.56×10^9 sec^{-1}, calculate its rate constant at 318K and also the energy of activation

Solution

For a first-order reaction, the rate constant expression is

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A_t]}$$

At 298k

$$t_{298} = \frac{2.303}{k_{298}}\log\frac{[A_0]}{0.9[A_0]}$$

At 308k

$$t_{308} = \frac{2.303}{k_{308}}\log\frac{[A_0]}{0.75[A_0]}$$

Time taken at 298K (for completion of 10% of reaction) and at 308K(for completion of 25% of reaction) are same

$$\frac{2.303}{k_{298}}\log\frac{[A_0]}{0.9[A_0]} = \frac{2.303}{k_{308}}\log\frac{[A_0]}{0.75[A_0]}$$

$$\frac{k_{308}}{k_{298}} = \frac{0.1249}{0.0457} = 2.73$$

Activation energy of the reaction can be calculated using

$$\log\frac{k_{308}}{k_{298}} = \frac{E_a}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$\log 2.73 = \frac{E_a}{2.303\times8.314}\left[\frac{308-298}{298\times308}\right]$$

Ea = 76651 J mol^{-1} = 76.65 kJ mol^{-1}

Rate constant at 318K can be calculated using

$$logk = logA - \frac{E_a}{2.303RT}$$

$$logk_{318} = log3.56 \times 10^9 - \frac{76.65}{2.303 \times 8.314 \times 10^{-3} \times 318}$$

$K_{318} = 9.13 \times 10^{-4}\ {}_s{}^{-1}$

Q) A catalyst lowers the activation energy for a certain reaction from 75 to 20kJmol^{-1}. What will be the effect on the rate of the reaction at 20^{O}C, other things being equal?

Solution According to Arrhenius equation

$K = A\ e^{-Ea/Rt}$

In absence of catalyst $k_1 = Ae^{-75/RT}$ ---------eq(1)

In presence of catalyst, $k_2 = A\ e^{-20/RT}$ ---------eq(2)

Here we have assumed that the value of A is unchanged by the presence of catalyst

Dividing (2) by (1) we get

$$\frac{k_2}{k_1} = e^{\frac{55}{RT}}$$

$$ln\frac{k_2}{k_1} = \frac{55}{RT}$$

$$log\frac{k_2}{k_1} = \frac{55 \times 10^3}{2.303 \times 8.314 \times 293} = 9.8037$$

Taking antilog

$$\frac{k_2}{k_1} = 6.363 \times 10^9$$

Thus, in the presence of catalyst, rate of the reaction increases 6.39×10^9 times with respect to uncatalysed reaction

Collision theory of chemical reaction

According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other.

The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).

Another factor which affects the rate of chemical reactions is activation energy For a bimolecular elementary reaction

A + B → Products

rate of reaction can be expressed as

Rate = $Z_{AB}\ e^{-Ea/RT}$ --------eq(1)

where Z_{AB} represents the collision frequency of reactants, A and B

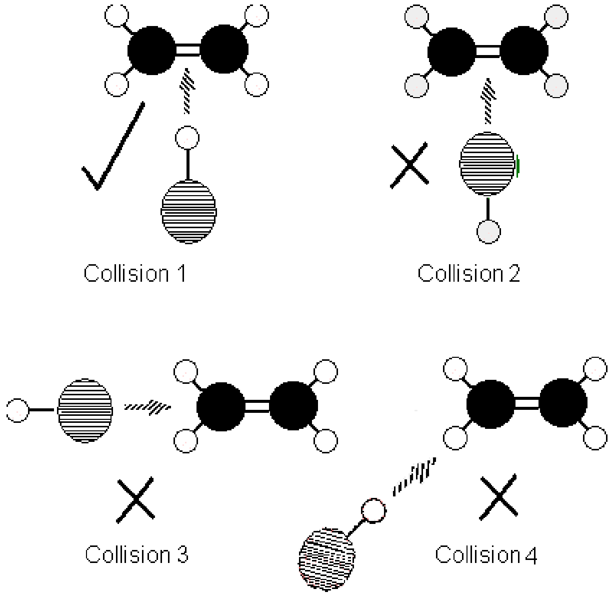
and $e^{-Ea/RT}$ represents the fraction of molecules with energies equal to or greater than *E*a.

Comparing this equation with Arrhenius equation, we can say that *A* is related to collision frequency. Equation (1) predicts the value of rate constants fairly accurately for the reactions that involve atomic species or simple molecules but for complex molecules significant deviations are observed. The reason could be that all collisions do not lead to the formation of products. The collisions in which molecules collide with sufficient kinetic energy (called threshold energy*) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collisions.

Consider a simple reaction involving a collision between two molecules - ethene, $CH_2=CH_2$, and hydrogen chloride, HCl, for example. These react to give chloroethane.

$$CH_2=CH_2 + HCl \longrightarrow CH_3CH_2Cl$$

As a result of the collision between the two molecules, the double bond between the two carbons is converted into a single bond. A hydrogen atom gets attached to one of the carbons and a chlorine atom to the other. The reaction can only happen if the hydrogen end of the H-Cl bond approaches the carbon-carbon double bond. Any other collision between the two molecules doesn't work. The two simply bounce off each other. In any collision involving unsymmetrical species, you would expect that the way they hit each other will be important in deciding whether or not a reaction happens.



Collision 1 Collision 2

Collision 3 Collision 4

The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.

To account for effective collisions, another factor *P*, called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.

Rate = $PZ_{AB}\, e^{-Ea/RT}$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction. Collision theory also has certain drawbacks as it considers atoms/molecules to be hard spheres and ignores their structural aspect.

Rate of Reversible reaction

Most chemical reactions are not simple unimolecular or bimolecular reactions, but combination. The simplest of these is the reversible, or opposed, reaction. In reversible reactions, there is a pair of forward and reverse reactions.

For example,

$$aA + bB \leftrightarrow cC + dD$$

The rate equation for this reaction, assuming each step is elementary is

$$\text{Rate} = k_f\,[A]^a\,[B]^b - k_r\,[C]^c\,[D]^d$$

where k_f is the rate coefficient for the forward reaction that consumes A and B; k_r is the rate coefficient for the reverse reaction, which consumes X and Y and produces A and B. When the reaction is at equilibrium, the rate = 0. Therefore,

$$k_f [A]^a [B]^b = k_r [C]^c [D]^d$$

this equation can be used to give the equilibrium coefficient (K_{eq}) for the entire reaction:

$$k_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{k_f}{k_r}$$

Now it should make sense why increasing the reactant concentration will make more products. The forward rate increases, which uses up reactants and decreases the forward rate. At the same time, products are made, which increases the reverse reaction until both reaction rates are equal again.

Consecutive (Chain) Reactions

Another example of a complex reaction is one that occurs in several, consecutive steps. Take, for example, this reaction: $A \rightarrow B \rightarrow C$

where rate from A to B is k_1 and the rate from B to C is k_2. The rate laws for each of the steps is: Consumption of A

$$\frac{d[A]}{dt} = -k_1[A]$$

(production of B minus consumption of B)

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

(production of C)

$$\frac{d[C]}{dt} = -k_1[B]$$

The integrated rate law for A is:

$$[A_t] = [A_0]e^{-k_1 t}$$

Substituting this equation into the equation for rate B gives:

$$\frac{d[B]}{dt} = k_1[A_0]e^{-k_1 t} - k_2[B]$$

The concentration of B can be solved for using differential equations to give the equation:

$$[B_t] = [A_0]\left(\frac{k_1}{k_2} - k_2\right)e^{-k_1 t} - e^{-k_2 t}$$

Finally, since $[C] = [A]_0 - [B] - [A]$, we can substitute in and use differential equations to get the integrated rate law for C:

$$[C_t] = [A_0]\left\{1 + \left(\frac{k_1 e^{k_2 t} - k_2 e^{k_1 t}}{k_2 - k_1}\right)\right\}$$

Competing (Parallel) Reactions

Another common complex reaction is a competing, or parallel reaction. In a competing reaction, a substance reacts simultaneously to give two different products. For example, A → B And A→ C

where k_1 is the rate constant for the formation of B and k_2 is the ate constant for formation of C.

The rate laws for this reaction are:

(rate of consumption of A by both reactions)

$$\frac{dA}{dt} = -(k_1 + k_2)[A]$$

(rate of production of B)

$$\frac{dB}{dt} = k_1[A]$$

(rate of production of C)

$$\frac{dC}{dt} = k_2[A]$$

Using substitution and differential equations as above, the integrated rate laws are:

$$[A_t] = [A_0]e^{-(k_1+k_2)}$$

$$[B_t] = \left(\frac{k_1}{k_1 + k_2}\right)[A_0]\left(1 - e^{-(k_1+k_2)}\right)$$

$$[C_t] = \left(\frac{k_2}{k_1 + k_2}\right)[A_0]\left(1 - e^{-(k_1+k_2)}\right)$$

1. **p-Block elements:** Elements belonging to groups 13 to 18 of the periodic table are called p-block elements.

2. **General electronic configuration of p-block elements:** The p-block elements are characterized by the ns^2np^{1-6} valence shell electronic configuration.

3. **Representative elements:** Elements belonging to the s and p-blocks in the periodic table are called the representative elements or main group elements.

4. **Inert pair effect:** The tendency of ns^2 electron pair to participate in bond formation decreases with the increase in atomic size. Within a group the higher oxidation state becomes less stable with respect to the lower oxidation state as the atomic number increases. This trend is called 'inert pair effect'. In other words, the energy required to unpair the electrons is more than energy released in the formation of two additional bonds.

5. **Nitrogen family:** The elements of group 15 – nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi) belong to configuration is ns^2np^3.

6. **Oxygen family:** Group 16 of periodic table consists of five elements – oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). Their general electronic configuration is ns^2np^4.

7. **The halogen family:** Group 17 elements, fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At), belong to halogen family. Their general electronic configuration is ns^2np^5.

8. **Group 18 elements:** Helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn) are Group 18 elements. They are also called noble gases. Their general electronic configuration is ns^2np^6 except helium which has electronic configuration $1s^2$. They are called noble gases because they show very low chemical reactivity.

GROUP 15 ELEMENTS

9. **Atomic and ionic radii**: Covalent and ionic radii increase down the group. There is appreciable increase in covalent radii from N to P. There is small increase from As to Bi due to presence of completely filled d or f orbitals in heavy elements.

10**. Ionisation energy**: It goes on decreasing down the group due to increase in atomic size. Group 15 elements have higher ionisation energy than group 14 elements due to smaller size of group 15 elements. Group 15 elements have higher ionization energy than group 16 elements because they have stable electronic configuration i.e., half filled p-orbitals.

11. **Allotropy**: All elements of Group 15 except nitrogen show allotropy. Catenation: Nitrogen shows catenation to some extent due to triple bond but phosphorus shows catenation to maximum extent. The tendency to show catenation decreases down the group. 13. Oxidation states: The common oxidation states are +3, +5, –3. The tendency shows –3 oxidation state decreases down the group due to decrease in electronegativity which is due to increase in atomic size. The stability of +5 oxidation state decreases whereas stability of +3 oxidation state increases due to inert pair effect. Nitrogen shows oxidation states from –3 to +5. Nitrogen and phosphorus with oxidation states from +1 to +4 undergo oxidation as well as reduction in acidic medium. This process is called disproportionate.
$3\ HNO_2 \rightarrow HNO_3 + H_2O + 2\ NO$

12. **Reactivity towards hydrogen**: All group 15 elements from trihydrides, MH_3. Hybridisation - sp^3
The stability of hydrides decrease down the group due to decrease in bond dissociation energy down the group.
$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
Boiling point: $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$
Boiling point increases with increase in size due to increase in van der Waals forces. Boiling point of NH3 is more because of hydrogen bonding.
Bond angle: NH_3 (107.8°) > PH_3 (99.5°) > AsH_3 (91.8°) ≈ SbH_3 (91.3°) > BiH_3 (90°)
Electronegativity of N is highest. Therefore, the lone pairs will be towards nitrogen and hence more repulsion between bond pairs.
Therefore bond angle is the highest. After nitrogen, the electronegativity decreases down the group.
Basicity decreases as NH3 > PH3 > AsH3 > SbH3 < BiH3.
This is because the lone pair of electrons are concentrated more on nitrogen and hence the basicity will be maximum in the case of NH_3. It will decrease down the group as the electronegativity decreases down the group.
The reducing power of hydrides increases down the group due to decrease in bond dissociation energy down the group.

13. **Reactivity towards oxygen**: All group 15 elements from trioxides (M_2O_3) and pentoxides (M_2O_5).
Acidic character of oxides decreases and basicity increases down the group. This is because the size of nitrogen is very small. It has a strong positive field in a very small area. Therefore, it attracts the electrons of water's O-H bond to itself and release H+ ions easily. As we move down the group, the atomic size increases. Hence, the acidic character of oxides decreases and basicity increases as we move down the group.

14. **Reactivity towards halogen**: Group 15 elements form trihalides and pentahalides.
Trihalides – covalent compounds and become ionic down the group. sp^3 hybridisation , pyramidal shape
Pentahalides - sp^3d hybridisation, TBP shape
They are lewis acids because of the presence of vacant d – orbitals.
$PCl_5 + Cl^- \rightarrow [PCl6]^-$
PCl_5 is ionic in solid state and exist as $[PCl_4]^+ [PCl_6]^-$
In PCl_5, there are three equatorial bonds and two axial bonds.
The axial bonds are longer than equatorial bonds because of greater repulsion from equatorial bonds.
Nitrogen does not form pentahalides due to absence of d- orbitals.

15**. Reactivity towards metals**: All elements react with metals to form binary compounds in –3 oxidation state.

16. **Anomalous behaviour of nitrogen**: The behaviour of nitrogen differs from rest of the elements.
Reason:
i. It has a small size.
ii. It does not have d – orbitals
iii. It has high electronegativity
iv. It has high ionization enthalpy

17. **Dinitrogen**:
Preparation:

$$NH_4Cl(aq) + NaNO_2(aq) \xrightarrow{heat} N_2(g) + 2H_2O(l) + NaCl(aq)$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{heat} N_2 + 4H_2O + Cr_2O_3$$

$$Ba(N_3)_2 \xrightarrow{heat} Ba + 3N_2$$

Properties:

It is a colouless, odourless, tasteless and non – toxic gas. It is chemically un-reactive at ordinary temperature due to triple bond in . N ≡ N which has high bond dissociation energy.

18**. Ammonia**: Ammonia molecule is trigonal pyramidal with nitrogen atom at the apex. It has 3 bond pairs and 1 lone pair. N is sp^3 hybridised.
Preparation:
Haber's process:

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2\ NH_3\ (g) \qquad \Delta_f H^\circ = -\ 46.1\ kJ\ mol^{-1}$$

Pr essure = 200×10^5 Pa
Temperature = 773 K
Catalyst is FeO with small amounts of K_2O and Al_2O_3

19. **Nitric Acid:**
a. Ostwald Process:

$$4NH_3 + 5O_2 \xrightarrow[500\ K,9bar]{Pt/Rhgauge} 4NO + 6H_2O \ ......(i)$$

$$2NO + O_2 \rightleftharpoons 2NO_2 ......(ii)$$

$$3NO_2\ (g) + H_2O(l) \rightarrow 2HNO_3\ (aq) + NO(g)\ ......(iii)$$

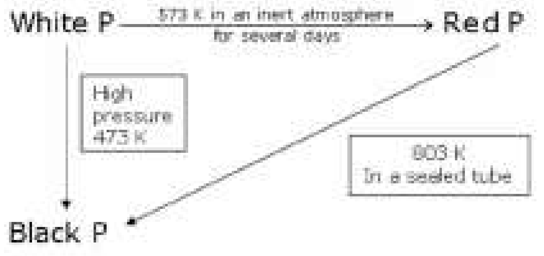
NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4.
Nitric acid is strong oxidizing agent in the concentrated as well as in the dilute state.

20. **Phosphorus:**
a. It shows the property of catenation to maximum extent due to most stable P – P bond.
b. It has many allotropes, the important ones are :
i. White phosphorus
ii. Red phosphorus

iii. Black phosphorus

White phosphorus	Red phosphorus	Black phosphorus
Discrete tetrahedral P_4 molecules	Polymeric structure consisting of chains of P_4 units linked together	Exists in two forms - α black P and β black P
Very reactive	Less reactive than white P	Very less reactive
Glows in dark	Does not glow in dark	-
Translucent waxy solid	Has an iron grey luster	Has an opaque monoclinic or rhombohedral crystals
Soluble in CS_2 but insoluble in water	Insoluble in water as well as CS_2	-
It has low ignition temperature, therefore, kept under water	-	-

Preparation:



21. **Phosphine:**

i. $\underset{\text{(calcium phosphide)}}{Ca_3P_2} + \underset{\text{(water)}}{6H_2O} \rightarrow \underset{\text{(calcium hydroxide)}}{3Ca(OH)_2} + \underset{\text{phosphine}}{2PH_3}$

$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + \underset{\text{(phosphine)}}{2PH_3}$

Phosphine is highly poisonous, colourless gas and has a smell of rotten fish.

ii. $P_4 + 3NaOH + 3H_2O \rightarrow \underset{\left(\begin{array}{l}\text{sodium}\\ \text{hypophosphite}\end{array}\right)}{3NaH_2PO_2} + \underset{\text{(phosphine)}}{PH_3}$

22. **Chlorides of Phosphorous:**

PCl_3	PCl_5
Colourless oily liquid	Yellowish white powder
$P_4 + 6Cl_2 \rightarrow 4PCl_3$ $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$	$P_4 + 10Cl_2 \rightarrow 4PCl_5$ $P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$
Is hydrolysed in the presence of moisture $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$	$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$ $POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$
$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$	$3CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$
$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$	$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$
Pyramidal shape, sp^3 hybridisation	TBP geometry, sp^3d hybridisation
-	$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$ $Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$

GROUP 16 ELEMENTS

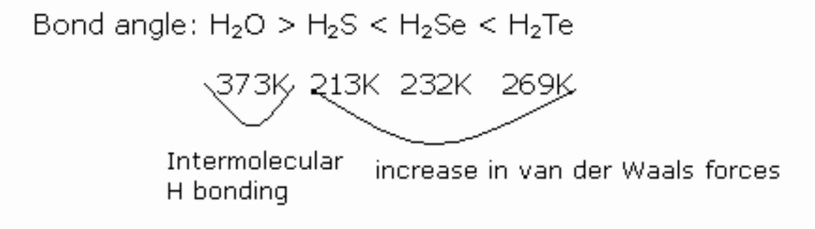
23. **Oxidation states:** They show -2, +2, +4, +6 oxidation states. Oxygen does not show +6 oxidation state due to absence of d – orbitals. Po does not show +6 oxidation state due to inert pair effect.
The stability of -2 oxidation state decreases down the group due to increase in atomic size and decrease in electronegativity.
Oxygen shows -2 oxidation state in general except in OF_2 and O_2F_2
The stability of +6 oxidation state decreases and +4 oxidation state increases due to inert pair effect.

24. **Ionisation enthalpy:** Ionisation enthalpy of elements of group 16 is lower than group 15 due to half filled p-orbitals in group 15 which are more stable. However, ionization enthalpy decreases down the group.

25. **Electron gain enthalpy:** Oxygen has less negative electron gain enthalpy than S because of small size of O. From S to Po electron gain enthalpy becomes less negative to Po because of increase in atomic size.

26. **Melting and boiling point:** It increases with increase in atomic number. Oxygen has much lower melting and boiling points than sulphur because oxygen is diatomic (O_2) and sulphur is octatomic (S_8).

27. **Reactivity with hydrogen:**
All group 16 elements form hydrides.
Bent shape



Acidic nature: $H_2O < H_2S < H_2Se < H_2Te$
This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.
Thermal stability: $H_2O < H_2S < H_2Se < H_2Te < H_2Po$
This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.
Reducing character: $H_2O < H_2S < H_2Se < H_2Te < H_2Po$
This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.

28. **Reactivity with oxygen:** EO_2 and EO_3 Reducing character of dioxides decreases down the group because oxygen has a strong positive field which attracts the hydroxyl group and removal of H^+ becomes easy.
Acidity also decreases down the group.
SO_2 is a gas whereas SeO_2 is solid. This is because SeO_2 has a chain polymeric structure whereas SO_2 forms discrete units.

29. **Reactivity with halogens:** EX_2 EX_4 and EX_6 The stability of halides decreases in the order $F^- > Cl^- > Br^- > I^-$. This is because E-X bond length increases with increase in size.
Among hexa halides, fluorides are the most stable because of steric reasons.

Dihalides are sp^3 hybridised, are tetrahedral in shape.

Hexafluorides are only stable halides which are gaseous and have sp^3d^2 hybridisation and octahedral structure.

H_2O is a liquid while H_2S is a gas. This is because strong hydrogen bonding is present in water. This is due to small size and high electronegativity of O.

30. **Oxygen:** Preparation:

$$2KClO_3 \xrightarrow[MnO_2]{heat} 2KCl + 3O_2$$

$$2H_2O_2(aq) \xrightarrow{\text{finely divided metals}} 2H_2O(l) + O_2(g)$$

$$2Ag_2O(s) \xrightarrow{heat} 4Ag(s) + O_2(g)$$

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

$$2Pb_3O_4(s) \xrightarrow{\Delta} 6PbO(s) + O_2(g)$$

(Red lead)

$$2PbO_2(s) \xrightarrow{\Delta} 2PbO(s) + O_2(g)$$

31. **Oxides:** The compounds of oxygen and other elements are called oxides.

Types of oxides:

a. Acidic oxides: Non- metallic oxides are usually acidic in nature.

$$SO_2 + H_2O \longrightarrow H_2SO_3 \text{ (sulphurous acid)}$$

b. Basic oxides: Metallic oxides are mostly basic in nature. Basic oxides dissolve in water forming bases e.g.,

$$Na_2O + H_2O \longrightarrow 2NaOH$$

$$K_2O + H_2O \longrightarrow 2KOH$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

c. Amphoteric oxides: They show characteristics of both acidic as well as basic

$$Al_2O_3 + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2O$$

oxides. $Al_2O_3 + 6NaOH(aq) + 3H_2O(l) \longrightarrow 2Na_3[Al(OH)_6](aq)$

d. Neutral oxides: These oxides are neither acidic nor basic.

Example: CO, NO and N_2O

32. **Ozone:** Preparation:
i. It is prepared by passing silent electric discharge through pure and dry oxygen 10 – 15 % oxygen is converted to ozone.

$$3O_2(g) \longrightarrow 2O_3(g); \Delta H = +142\ \text{kJ mol}^{-1}$$

Structure of Ozone: Ozone has angular structure. Both O = O bonds are of equal bond length due to resonance.

33. **Sulphur:**
Sulphur exhibits allotropy:

a. Yellow Rhombic (α - sulphur):
b. Monoclinic (β- sulphur):

$$\alpha - \text{Sulphur} \xrightleftharpoons{369\ \text{K}} \beta - \text{Sulphur}$$

At 369 K both forms are stable. It is called transition temperature.
Both of them have S_8 molecules. The ring is puckered and has a crown shape.
Another allotrope of sulphur – cyclo S_6 ring adopts a chair form.
S_2 is formed at high temperature (~ 1000 K). It is paramagnetic because of 2 unpaired electrons present in anti bonding π* orbitals like O_2

34. **Sulphuric acid:** Preparation: By contact process

$$\frac{1}{8}S_8 + O_2 \longrightarrow SO_2$$

$$2SO_2(g) + O_2(g) \xrightarrow[\substack{2\text{bar} \\ 720\text{K}}]{V_2O_5} 2SO_3(g) \qquad \Delta H^\ominus = -196.6\text{kJ mol}^{-1}$$

Exothermic reaction and therefore low temperature and high pressure are favorable

$$SO_3(g) + H_2SO_4 \longrightarrow H_2S_2O_7\ \text{(Oleum)}$$

$$H_2S_2O_7 + H_2O \longrightarrow \underset{(96-98\%)}{2\ H_2SO_4}$$

It is dibasic acid or diprotic acid. It is a strong dehydrating agent.
It is a moderately strong oxidizing agent.

GROUP 17 ELEMENTS

35. **Atomic and ionic radii:** Halogens have the smallest atomic radii in their respective periods because of maximum effective nuclear charge.

36. **Ionisation enthalpy:** They have very high ionization enthalpy because of small size as compared to other groups.

37. **Electron gain enthalpy:** Halogens have maximum negative electron gain enthalpy because these elements have only one electron less than stable noble gas configuration.
Electron gain enthalpy becomes less negative down the group because atomic size increases down the group.

38. **Eelctronegativity:** These elements are highly electronegative and electronegativity decreases down the group. They have high effective nuclear charge.

39. **Bond dissociation enthalpy:**

Bond dissociation enthalpy follows the order $Cl_2 > Br_2 > F_2 > I_2$
This is because as the size increases bond length increases.

Bond dissociation enthalpy of Cl_2 is more than F_2 because there are large electronic repulsions of lone pairs present in F_2.

40. **Colour:** All halogens are coloured because of absorption of radiations in visible region which results in the excitation of outer electrons to higher energy levels.

41. **Oxidising power:** All halogens are strong oxidizing agents because they have a strong tendency to accept electrons.
Order of oxidizing power is $F_2 > Cl_2 > Br_2 > I_2$

42. **Reactivity with H_2:**
Acidic strength: $HF < HCl < HBr < HI$
Stability: $HF > HCl > HBr > HI$
This is because of decrease in bond dissociation enthalpy.
Boiling point: $HCl < HBr < HI < HF$
HF has strong intermolecular H bonding
As the size increases, van der Waals forces increases and hence boiling point increases.

% Ionic character: HF > HCl > HBr > HI
Dipole moment: HF > HCl > HBr > HI
Electronegativity decreases down the group.
Reducing power: HF < HCl < HBr < HI

43. **Reactivity with metals:** Halogens react with metals to form halides.
Ionic character: MF > MCl > MBr > MI
Halides in higher oxidation state will be more covalent than the one in the lower oxidation state.

44. **Interhalogen compounds: Reactivity of halogens towards other halogens:**
Binary compounds of two different halogen atoms of general formula
XX'_n are called interhalogen compounds where n = 1, 3, 5, or 7
These are covalent compounds.
Interhalogen compounds are more reactive than halogens because X-X' is a more polar bond than X-X bond.
All are diamagnetic.
Their melting point is little higher than halogens.
XX' (ClF, BrF, BrCl, ICl, IBr, IF) (Linear shape)
XX'_3 (ClF_3, BrF_3, IF_3, ICl_3) (Bent T- shape)
XX'_5 – ClF_5, BrF_5, IF_5, (square pyramidal shape)
XX'_7 – IF_7 (Pentagonal bipyramidal shape)

45. **Oxoacids of halogens:**
Fluorine forms only one oxoacid HOF (Fluoric (I) acid or hypofluorous acid) due to high electronegativity.
Acid strength: $HOCl < HClO_2 < HClO_3 < HClO_4$
Reason: $HClO_4 \rightarrow H^+ + ClO_4^-$ most stable
Acid strength: HOF > HOCl > HOBr > HOI
This is because Fluorine is most electronegative.

<u>GROUP 18 ELEMENTS</u>:

46. **Ionisation enthalpy:** They have very high ionization enthalpy because of completely filled orbitals.
Ionisation enthalpy decreases down the group because of increase in size.

47. **Atomic radii:** Increases down the group because number of shells increases down the group.

48. **Electron gain enthalpy:** They have large electron gain enthalpy because of stable electronic configuration.

49. **Melting and boiling point:** Low melting and boiling point because only weak dispersion forces are present.

50. XeF_2 is linear, XeF_4 is square planar and XeF_6 is distorted octahedral. KrF_2 is known but no true compound of He Ne and Ar are known.

51. **Compounds of Xe and F:**

$$Xe + F_2 \xrightarrow{673\ K,\ 1bar} XeF_2$$

$$Xe + 2F_2 \xrightarrow[7bar]{873\ K} XeF_4$$

$$Xe + 3F_2 \xrightarrow[60-70\ bar]{573\ K} XeF_6$$

$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

XeF_2, XeF_4 and XeF_6 are powerful fluorinating agents.

52. **Compounds of Xe and O**

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

Conceptual questions and answers

Q1) Why penthalides more covalent than trihalides
Ans) Higher the positive oxidation state of central atom, more will be its polarizing power. Which it turns increases the covalent character of bond formed between the central atom and the other atom

Q2) Why is BiH_3 the strong reducing agent amongst all the hydrides of group 15 elements
Ans) Because BiH_3 is the least stable amongst the hydrides of group 15. Bi –H bond is the weakest amongst the hydrides of elements of group 15.

Q3) Why does the reactivity of nitrogen differs from Phosphorous?

Ans) Nitrogen forms pπ – pπ multiple bonds with itself where as phosphorous does not form pπ – pπ multiple bonds. Thus nitrogen exists as s diatomic molecule with a triple bond (N≡N) between the two atoms, consequently, its bond enthalpy is very high. Therefore nitrogen is inert and unreactive in its elemental state. In contrast, phosphorous forms single bonds and exists as P_4 molecule. Since P-P single bond is much weaker than N≡N triple bond, therefore, phosphorous is much more reactive than nitrogen.

Q4) Why does NH_3 forms hydrogen bond but PH_3 does not?
Ans) The electro negativity of Nitrogen is much higher than that of phosphorous, as a result, N-H bond is quite polar and hence NH_3 undergoes intermolecular H-bonding where as P-H bond is less polar and hence PH_3 does not undergo H – bonding.

Q5) PH_3 has lower boiling point than NH_3 why?
Ans) N3 undergoes extensive intermolecular H-bonding and hence it exists as an associated molecule. On the other hand, PH_3 does not undergo H-bonding and thus exists as discrete molecules. Therefore PH3 has lower boiling point than NH_3

Q6) Why does NH_3 act as a Lewis base?
Nitrogen atom in NH_3 has lone pair of electrons which is available for donation. Therefore, it acts as Lewis base.

Q7) Give reason for anomalous property of Nitrogen
Ans) Nitrogen differs from the rest of the members of group 15 due to its smaller size, high electro negativity, higher ionization enthalpy and non-availability of d-orbitals

Q8) Write the reaction for thermal decomposition of Sodium azide
Ans) $2NaN_3 \rightarrow 2Na+3N_2$

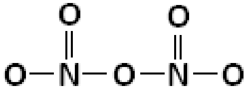
Q9) Nitrogen exists as diatomic molecule and phosphorous as P_4 why?
Ans) Nitrogen because of its small size and higher electro negativity forms pπ – pπ multiple bonds with itself. Therefore it exists as a diatomic molecule having a triple bond between two Nitrogen atoms. Phosphorous, on the other hand, due to its large size and lower electro negativity does not form pπ – pπ multiple bonds with itself. Instead it prefers to form P-P single bonds and hence exists as P_4 molecules

Q10) Nitrogen exists in gaseous state whereas Phosphorous in solid state why?
Ans) Refer Q9

Q11) Explain why NH_3 is basic while BiH_3 is only feebly basic?
Ans) N in NH_3 and Bi in BiH_3 have a lone pair of electrons on the central atoms and hence should behave as Lewis base. Since atomic size of 'N' is much smaller than that of Bi therefore, electron density on the N-atom is much higher than that of Bi atom. Consequently, the tendency of N in NH_3 to donate its pair of electrons is much higher than BiH_3

Q12) Why does $R_3P=O$ exist but $R_3N=0$ does not (R = alkyl group)
Ans) Nitrogen due to the absence of d-orbital's cannot form pπ – dπ multiple bonds and hence cannot expand its covalency beyond 4. Therefore N cannot form $R_3N=0$ in which the covalency of N is 5. In contrast, P due to the presence of d-orbitals forms pπ – dπ multiple bonds and hence can expand its covalency beyond 4. Therefore P forms R_3P+o in which the covalency of P is 5

Q13) What is the covalency of Nitrogen in N_2O_5
The covalency of nitrogen in N_2 O_5 is four



$$O-\overset{\overset{O}{\|}}{N}-O-\overset{\overset{O}{\|}}{N}-O$$

Q14) Name the various oxides of Nitrogen. Mention their oxidation states. Give their preparation

1) N_2O , Dintrogen oxide or Nitogen (I)oxide, oxidation State +1
$NH_4 \xrightarrow{heat} N_2O + H_2O$

2) NO Nitrogen oxide , oxidation state +2
$NaNO_2 + 2FeSO_4 + 3H_2SO_4 \xrightarrow{heat} NO + Fe_2(SO_4)_3 + 2NaHSO_4$

3) N_2O_3 Dintrogen trioxide or Nitrogen (III) oxide, oxidation state +3
$2NO + N_2O_4 \xrightarrow{250K} 2N_2O_3$

4) NO_2 , Nitrogen dioxide or Nitrogen (IV) oxide, oxidation state +4
$Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO$

5) N_2O_4 Dinitrogen tetraoxide or Nitrogen (IV) oxide, oxidation state +5
$2NO_2 \xrightleftharpoons[Heat]{Cool} N_2O_4$

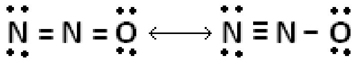
6) N_2O_5 (Dintrogen pentoxide) or Nitrogen (V) oxide, oxidation state +6
$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$

Q15) Why does NO_2 dimerise?
Ans) NO_2 contains odd number of valence electrons. It behaves as a typical odd molecule. On dimerisation it is converted to stable N_2O_4 molecule with even number of electrons

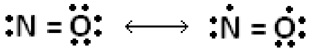
Q16) Why does nitrogen show catenation property less than Phosphorus?
Ans) The property of catenation depends upon the strength of the element – element bond. Since the single N-N bond is weaker than single P-P bond strength, therefore nitrogen shows less catenation properties than phosphorus

Q17) Give resonating structures of following oxides
Ans)

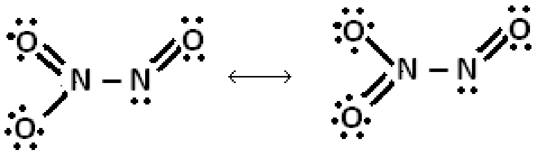
1) N_2O



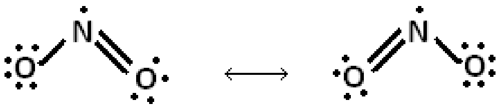
2) NO



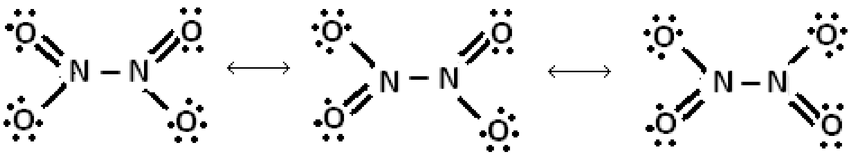
3) N_2O_3



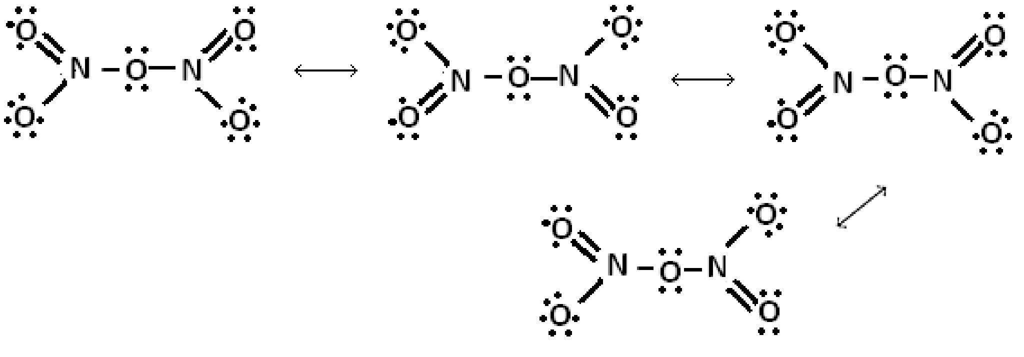
4) NO_2



5) N_2O_4



6) N_2O_5



Q18) Metals like Cr, Al do not dissolve in concentrated HNO_3 why?
Ans) It is because of the formation of passive film of oxide on the surface

Q19) Bond angle in PH_4^+ is higher than in PH_3 why?
Ans) Both are sp^3 hybridised. In PH_4^+, all the four orbitals are bonded where as in PH_3, there is a lone pair of electrons on P. Which is responsible for lone pair-bond pair repulsion PH_3 reducing the bond angle to less than $109^O28'$

Q20) What happens when white phosphorous is heated with conc. NaOH solution in an inert atmosphere of CO_2?
Ans) White phosphorous reacts with NaOH solution in an inert atmosphere to form Phosphine
$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$

Q21) Why does the PCl_3 fume in moisture?
Ans) PCl_3 hydrolyses in the presence of moisture giving fumes of HCl
$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

Q22) Are all the five bonds in PCl_5 molecule equivalent? Justify your answer
Ans) PCl_5 has a trigonal bipramidal structure and the three equal P-Cl bonds are equivalent, while two axial bonds are different and longer than equatorial bond

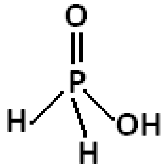
Q23) What happens when PCl_5 is heated?
Ans) When heated PCl_5 sublimates but decomposes on strong heating

$$PCl_5 \xrightarrow{Heat} PCl_3 + Cl_2$$

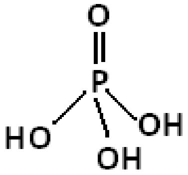
Q24) Write a balanced chemical equation for the hydrolysis reaction of PCl_5 in heavy water

$$PCl_5 + D_2O \xrightarrow{Heat} POCl_3 + 2DCl$$

Q25) how do you account for the reducing behavior of H_3PO_2,
Ans) In H_3PO_2, Two H atoms are bounded directly to P atom which imports reducing character to the acid.

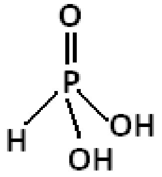


Q26) What is the basicity of H_3PO_4?
Ans) Since it contains three ionizable H-atoms which are present as OH group, it behaves as a tribasic acid i.e the basicity is three



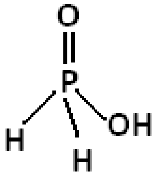
Q27) H_3PO_3 is a dibasic acid why?

Ans) Since it contains two ionizable H atoms which are present as OH groups, it behaves as a dibasic acid. i.e. the basicity is two



Q28) What happens when H_3PO_2 is a monobasic acid why?

Ans) Since it contains only one ionizable H-atom which is present as OH group it behaves as a monobasic acid i.e basicity is one



Q29) What happens when H_3PO_3 is heated?

Ans) Phosphorous acid on heating disproportionate to give phosphoric acid and phosphine

$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

Q30) Give an example for reducing property of H_3PO_2 ?

Ans) H_3PO_2 reduces $AgNO_3$ to Ag

$4AgNO_3 + 2H_2O + H_3PO_2 \rightarrow 4Ag + 4\ HNO_3 + H_3PO_4$

Q31) NO (nitric oxide) is paramagnetic in the gaseous state but diamagnetic in the liquid and solid state why?

Ans) NO has an odd number of electrons and hence is paramagnetic in gaseous state, but in the liquid and solid state it exists as dimer and hence diamagnetic in these states

Q32) NCl_3 gets readily hydrolyzed while NF_3 does not. Why?

Ans) In NCl_3, Cl has vacant d-orbital to accept the lone pair of electrons donated by O-atom of H_2O molecules but in NF_3 , F does not have d-orbital

Q33) PCl_5 is in ionic in nature in the solid state. Give reason

Ans) In the solid state it exists as $[PCl_4]^+ [PCl_6]^-$. Therefore PCl_5 is ionic nature in the solid state

Q34) Can PCl_5 act as an oxidizing as well as reducing agent? Justify

Ans) The oxidation state of P in PCL_5 is +5. Since P has five electrons in its valence shell, therefore, it cannot increase its oxidation state beyond +5 by donating electrons, therefore PCl_5 cannot act as a reducing agent. However, it can decrease its oxidation state from +5 to lower oxidation state, therefore PCl_5 can act as an oxidizing agent

$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$

$Sn + 2PCl_5 \rightarrow SnCl_4 + 2 PCl_3$

Q35) H_2S is less acidic than H_2Te. Why?

Ans) H-S bond dissociation energy is higher than that of H-Te bond dissociation energy and hence H-S bond breaks less easily than H-Te bond. Hence H_2S is a weaker acid than H_2 Te

Q36) Why is H_2O is liquid and H_2S a gas?

Ans) Because of small size and high electronegativity of oxygen, molecules of water are highly associated through hydrogen bonding resulting in its liquid state. In contrast, H_2S does not undergo H-bonding and exists as discrete molecules. Therefore, H_2S is gas at room temperature

Q37) Give reason for anomalous behavior of Oxygen

Ans) Oxygen differs from the rest of members of the group due to its smaller size, high electronegativity and non-availability of d-orbitals

Q38) Which of the following do not reacts with oxygen directly. Zn, Ti, Rt, Fe

Ans) Platinum does not reacts with oxygen directly. It is because the sum of first four ionization enthalpy is very large

Q39) Why is dioxygen is a gas while sulphur is solid

Ans) Due to small size and high electronegativity, oxygen form pπ-pπ multiple bonds, as a result oxygen exists as diatomic molecules (O_2) and has less intermolecular force of attraction. Therefore, O_2 is a gas at room temperature. Sulphur, on the other hand, because of its bigger size and lower electronegativity, does not form pπ-pπ multiple bonds. Instead, it prefers to form S-S single bond as a result, sulphur exists as octa-atomic (S_8) and has high intermolecular force of attraction. Therefore, sulphur is a solid at room temperature

Q40) What are acidic oxide? Give examples

Ans) An oxide which give a acid with water is known as acidic oxides. E.g CO_2, SO_2, N_2O_5

Q41) What are basic oxides? Give examples

Ans) An oxide which give a base with water is known as basic oxide. E.g. N_2O, CaO, BaO

Q)42) What are amphoteric oxides? Give example
Ans) Those oxides which shows characteristics of both acidic as well as basic oxides are known as amphoteric oxides . they react with acids as well as bases e.g. Al_2O_3, ZnO, PbO, SnO

Q43) What are neutral Oxides? Give examples
Ans) Oxides which neither react with acid nor with bases are called as neutral oxides. E.g. No, CO, N_2P

Q44) High concentration of ozone is dangerously explosive. Explain
Ans) The decomposition of ozone into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS) . these two effects reinforce each other resulting in large negative Gibbs energy change (ΔG is negative) for its conversion into oxygen. Therefore, higher concentrations of ozone is dangerously explosive

Q45) Why does the ozone acts as a power oxidizing agent?
Ans) Due to the ease with which it liberates atom of nascent oxygen it acts as powerful oxidizing agent

Q46) How is O_3 estimated quantitatively
Ans) When O_3 is treated with excess of KI solution buffered with Borate buffer (pH = 9.2). I_2 is liberated quantitatively which can be titrated against a standard solution of sodium thiosulphate
$2I^-_{(aq)} + O_3 + H_2O \rightarrow 2OH^- + I_{2\,(S)} + O_{2\,(g)}$

Q47) Which aerosols deplete ozone?
Ans) Freons deplete the ozone layer supplying Cl free radical which converts O_3 to O_2

Q48) Explain how nitrogen oxides deplete ozone layer
An) Nitrogen oxides emitted from the exhaust system of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone in the upper atmosphere
$NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$

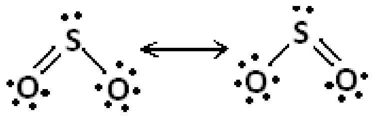
Q48) What is meant by transition temperature of sulphur
Ans) The temperature at which both α –sulphur and β-sulphur are stable is known as transition temperature. The transition temperature of sulphur is 369K .

Below 369K α –sulphur is stable where as above 369K β-sulphur is stable

Q49) Which form of sulphur shows paramagnetic behavior
Ans) In vapour state sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding π^* orbitals like O_2 and hence, exhibits paramagetism

Q50) What happens when SO_2 (sulphur dioxide) is passed through an aqueous solution of Fe(III) salt
Ans) SO_2 acts as a reducing agent and hence reduces an aqueous solution of Fe(III) salt to Fe(II) salt
$2Fe^{+3} + \ + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$

Q51) Comment on the two S-O bonds formed in SO_2 molecule , are the two bonds in this molecule equal
Ans) Both S-O bonds are covalent and have equal strength due to resonating structures



Q52) Why is $Ka_2 << Ka_1$ for H_2SO_4 in water
Ans) H_2SO_4 (aq) + H_2O(l) → H_3O^+(aq) + HSO_4^- (aq) , Ka_1
$HSO_4^-{}_{(aq)}$ + H_2O(l) → H_3O^+(aq) + SO_4^{-2} (aq) , Ka_2
Ka_2 is less than Ka_1 because the negatively changed HSO_4^- ion has much less tendency to donate a proton to H_2O as compared to neutral H_2SO_4 to donate a proton to water

Q53) Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table why
Ans) Halogens have the smallest size in the respective periods and therefore high effective nuclear change. As a consequence they readily accept one electron to acquire noble gas electronic configuration.

Q54) The electron gain enthalpy of fluorine is less than that of chlorine why?
Ans) It is due to small size of fluorine atom. AS a result, there is strong interelectronic repulsion in the relatively small 2p orbitals of fluorine and thus the incoming electron does not experience much attraction

Q55) Although electrogain enthalpy in a stronger oxidizing agent than chlorine why?
Ans) It is due to

(i) Low enthalpy of dissociation of F-F bond
(ii) High hydration and enthalpy of F^- ion

Q)56) Give two examples to show the anomalous behavior of fluorine?
Ans) (i) Fluorine shows only an oxidation state of -1 while other halogens. Show positive oxidation states of +1, +3, +5 and +7 besides oxidation state of -1
(ii) The band dissociation enthalpy of F-F bond is lower than that of Cl-Cl bond

Q57) Explain why fluorine forms only one oxoacid, HOF?
Ans) Fluorine is the most electronegative element and can exhibit only -1 oxidation state. Secondly Fluorine does not have d-orbitals in its valence shell and therefore cannot expand it octet. Hence Fluorine form only one oxoacid

Q58) What are interhalogen compounds? Give examples
Ans) When two different halogens react with each other to form a number of compound called interhalogen compounds. There general formula is XX'_n where X is a less electronegative halogen while X' is a more electronegative halogen (smaller size halogen) and n is its number e.g IF_7, BrF_5, IF_5

Q59) Explain why inspite of nearly same electronegativity oxygen forms hydrogen bonding while chlorine does not
Ans) Oxygen has smaller size than chlorine. As a result electron density per unit volume on oxygen atoms is much higher than that of on chlorine atom. Therefore, oxygen forms H-Bonds while chlorine does not

Q60) Why Halogens are coloured
Ans) All the halogens are coloured. This is due to absorption of radiation in visible region which result in the excitation of outer electrons to higher energy level. While the remaining light is transmitted. The colour of the halogens is actually the colour of this transmitted light. By absorbing different quanta of radiation they display different colours

Q61) Give the bleaching action of Cl_2
Ans) In presence of moisture or in aqueous solution, Cl_2 liberates nascent oxygen which is responsible for bleaching action of Cl_2
$Cl_2 + H_2O \rightarrow 2HCl + O$ (nascent oxygen)
The bleaching action of Cl_2 is due to oxidation

Q62) Why is ICl more reactive than I_2?
Ans) In general, interhalogen compounds are more reactive than halogen due to weaker X-X' bonding than X-X bond thus ICl is more reactive than I_2

Q63) Why are the elements of Group 18 known as noble gases?
Ans) The elements present in Group 18 have their valance shell orbitals completely filled and therefore, react with a few elements only under certain condition. Therefore, they are known as noble gases

Q64) Noble gases have very low boiling points. Why?
Ans) Noble gases being mono-atomic have no inter-atomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling point.

Q65) Noble gases are least reactive. Why?
Ans) It is due to following reasons

i) The noble gases except helium ($1s^2$) have completely filled ns^2np^6 electronic configuration in their valence shell
ii) They have higher ionization enthalpy and more positive electron gain enthalpy

Q66) What inspired N. Bartlett for carrying out reaction between Xe and PtF_6?
Ans) N.Bartlett observed that PtF_6 reacts with O_2 to yield an ionic solid $O_2^+PtF_6^+$. Since the first ionization enthalpy of molecular oxygen (1175 $KJmol^{-1}$) is almost identical with that of xenon is (1170 $KJmol^{-1}$). Bartlett thought that PtF_6 should also Oxidises Xe to Xe^+. This inspired Bartlett to carry out the reaction between Xe and PtF_6. He prepared $X^+[PtF_6]^-$ mixing PtF_6 and Xe
$Xe + PtF_6 \rightarrow Xe^+ [PtF_6]^-$

Q67) Does the hydrolysis of XeF_6 leads to a redox reaction
Ans) No, the products of hydrolysis are $XeOF_4$ and $XeO_2 F_2$ where oxidation states of all elements remain the same as it was in the reacting state

Q68) Why is helium used in diving apparatus?
Ans) Because of its low solubility compared to N_2 in blood a mixture of oxygen and helium is used in diving apparatus

Q69) Why has been difficult to study the chemistry of radon?
Ans) Radon is radioactive with very short half life which makes the study of chemistry of radon difficult

Q70) With what neutral molecule is ClO^- iso-electronic . is that molecule is a Lewis base
Ans) ClF , Yes it is Lewis base due to presence of lone pair of electrons

Q71) Bismuth is a strong oxidizing agent in the pentavalent state. Why?
Ans) Due to inter pair effect, +5 oxidation state of Bi is less stable than +3 oxidation state. Therefore, Bismuth in the pentavalent state can easily accept two electrons and this gets reduced to trivalent bismuth
$Bi^{+5} + 2e^- \rightarrow Bi^{+3}$

Q72) Nitric oxide becomes brown when released in air. Why?
Ans) Nitric oxide readily combines with O_2 of the air to form a nitrogen dioxide (NO_2) which has brown colour
$2NO + O_2 \rightarrow 2NO_2$

Q73) H_2S is less acidic than H_2Te. Why?
Ans) H-S bond dissociation enthalpy is higher than that of H-Te bond dissociation enthalpy and hence H-Te bond breaks easily than H-S bond. Therefore H_2S is a weaker acid than H_2Te

Q74) H_2S acts only as a reducing agent but SO_2 acts as a reducing agent as well as an oxidizing agent. Why?
Ans) The minimum oxidation state of S is -2 while its maximum oxidation state is +6. In SO_2, the oxidation state of S is +4 therefore, it can not only increase its oxidation state by losing electrons but can also decrease its oxidation state by gaining electrons. As a result, SO_2 acts both as a reducing agent as well as oxidizing agent. On other hand, in H_2S, S has an oxidation state of -2. As a result it can only increase its oxidation state by losing electrons and hence it acts only as a reducing agent

Q75) Why the compounds of Fluorine with oxygen are called fluorides of oxygen (Oxygen fluorides) and not the oxides of fluorine (Fluorine oxide)
Ans) This is because fluorine is more electronegative than oxygen

Q76) Both NO and ClO_2 are odd electron species whereas. NO dimerises but ClO_2 does not. Why?
Ans) In NO, the odd electron on N is attracted by only one O-atom but in ClO_2, the odd electron on Cl is attracted by two O-atoms. As a result the odd electron on N in NO is localized while the odd electron on Cl in ClO_2 is delocalized. Consequently NO has a tendency to dimerize but ClO_2 does not.

Q77) Bleaching by Chlorine is permanent while that by SO_2 is temporary Why?
Ans) Cl_2 bleaches coloured material by Oxidation and hence bleaching is permanent. On the other hand, SO_2 bleaches coloured material by reduction and hence is temporary since when the bleached colour material exposed to air, it gets oxidized and the colour is restored.

Q78) Hydrogen iodide is stronger acid than Hydrogen fluoride in aqueous solution. Why?
Ans) Because of larger size of Iodine as compared to fluorine, the bond dissociation enthalpy of H-I bond is much lower than that of H-F bond. As a result, in aqueous solution, H-I bond breaks more easily to form H^+ ion than H-F bond. Thus HI is strong acid than HF in aqueous solution

Q79) Helium and Neon do not forms compounds with fluorine why?
Ans) He and Ne do not contain d-orbitals in their respective valence shells and hence their electrons cannot be promoted to higher energy levels. Therefore, He and Ne do not forms compounds with fluorine

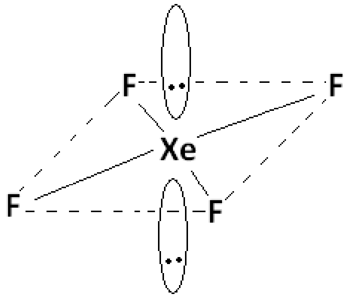
Q80) Neon is generally used for warning signals. Why?
Ans) Neon lights are visible from long distance even in fog and Mist and hence Neon is generally used for warning signals

Q81) Xenon does not form fluorides such as XeF_3 and XeF_5
Ans: As all the filled orbitals of Xe have paired electrons. The promotion of one, two or three electrons from the 5P – filled orbitals to 5d- vacant orbitals will give rise two , four and six half filled orbitals. So Xe can combine with even but not odd number of F atoms. Hence it cannot form XeF_3 and XeF_5

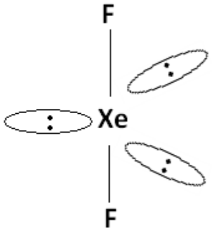
Q82) Out of noble gases, only Xenon is known to form chemical; compounds why?
Ans) Except radon, which is radioactive, Xe has least ionization enthalpy among noble gases and hence it readily forms chemical compounds particularly O_2 and F_2

Q83) Knowing the electron gain enthalpy values of $O_2 \rightarrow O^-$ and $O \rightarrow O^{2-}$ as 141 KJ mol^- and 700 KJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^-
Ans) It is because lattice energy of Oxides which overcome second electron gain enthalpy that is oxides are formed with O^{2-}

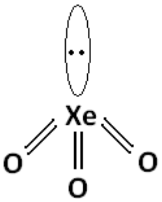
Q84) Give the formula and describe the structure of a noble gas species which is isostructural with (i) ICl_4^- (ii) IBr_2^- 3) BrO_3^-
Ans (i) ICl_4^- is isostructural with XeF_4. XeF_4 has four bonding pair and two loan pairs of electrons. Therefore according to VSER theory XeF_4 has square planar structure.



(II) IBr_2^- : is isostructural with XeF_2. XeF_2 has two bonding pairs and three lone pairs of electrons. Therefore according to VSEPER theory, XeF_2 has linear shape.



(III) BeO_3^- is isostructural with XeO_3 , XeO_3 has three bonding pairs and one lone pairs of electrons. Therefore according to VSEPR theory, XeO_3 has pyramidal structure



Q85) Deduce the molecular shape of BrF_3 on the basis of VSEPR theory
Ans) The central atom Br has seven electrons in the valence shell. Three of these will form electron pair with three fluorine atoms leaving behind four electrons. Thus there are three bond pairs and two loan pairs.
According to VSEPR theory, these will occupy the corners of trigonal bipyramid. The two loan pairs will occupy the equatorial position to minimize. Lonepair – lone pair repulsion. Which are greater than the bond pair –bond pair repulsion. In addition the axial Fluorine atom will be bent towards the equatorial fluorine in order to minimize the lone pair –loan pair repulsions. The shape will be that of slightly bent 'T'

Q86) Which one of PCl_4^+ and PCl_4^+ is not likely to exist and why?
Ans) PCl_4^- does not exists because octet of "P' is not complete and it is unstable

Q87) Despite lower value of its electron gain enthalpy with negative sign, fluorine (F_2) is a stronger oxidizing agent than Cl_2
Ans) It is due to higher reduction potential of F_2 which is due to low bond dissociation energy of F-F bond due to repulsion among small size atoms, high electron gain enthalpy and highest hydration enthalpy

Q88) Which is stronger reducing agent, SbH_3 or BiH_3 and why?
Ans) BiH_3 is stronger reducing agent because it has low bond dissociation energy than SbH, due to longer bond length
Q89) Fluorine does not exhibit any positive oxidation state. Why?
Ans) Because it is most electronegative element and best oxidizing agent.

Q90) Explain why phosphorus forms PF_5 while nitrogen does not form NF_5
Ans) Phosphorous form PF_5 because it has d-orbitals where as nitrogen does not form NF_5 due to non-availability of d-orbitals

Q91) Why are covalent fluorides more inert than other covalent halides
Ans) Covalent fluorides are inert due to strong covalent bonds as compared to other covalent halides in which halogens are bigger in size, therefore, bond formed is weaker

d and f –block elements in Nutshell

1. The elements lying in the middle of periodic table belong to group 3 to 12 are known as d-block element. d block elements are also called as transition elements

2.General electronic configuration of d-block elements: The d-block elements are characterized by the $(n-1)d^{1-10}\ ns^{1-2}$ valence shell electronic configuration.

3. Some exceptional electronic configurations of transition elements

i) Cr = $3d^5$, $4s^1$, Cu = $3d^{10}4s^1$

ii) Nb = $4d^45s^1$, Mo = $4d^5$, $5s^1$ Ru = $4d^7\ 5s^1$, Rh = $4d^85s^1$, Pd = $4d^{10}5s^0$

iii) Pt = $5d^9\ 6s^1$, Au = $5d^{10}\ 6s^1$

These irregularities due to

(i) Nuclear electron attraction

(ii) Shielding of one electron by several other electrons

(iii) Inter electron repulsion

(iv) Exchange energy force

4. d- block elements have wide range of oxidation states

They exhibit a wide range of oxidation states or positively charged forms.

The positive oxidation states allow transition elements to form many different ionic and partially ionic compounds. Oxidation states of first period of d block elements are stated below

Scandium	+3
Titanium	+2, +3, +4
Vanadium	+2, +3, +4, +5
Chromium	+2, +3, +6
Manganese	+2, (+3), +4, (+6), +7
Iron	+2, +3, (+4), (+6)
Cobalt	+2, +3, (+4)
Nickel	(+1), +2, (+3), (+4)
Copper	+1, +2, (+3)
Zinc	+2

5. Atomic and ionic radii:

In a series, the atomic radii first decreases with increase in atomic number upto the middle of the series then become constant and at the end of the series show slight increase

This is because nuclear charge goes on increasing when going from left to right causes contraction but due to shielding effect increases in middle of element counterbalance contraction due to increased nuclear charge

6. Metallic character:

All transition element are having hcp, ccp or bcc lattice. This is because of presence of one or two electrons in ns subshell and also unpaired d-electrons. Greater the number of unpaired d-electron stronger is the metallic character and metals are hard and have higher melting points

On the other hand Zn , Cd and Hg are soft and low melting point because of absence of unpaired d-electrons

Also because of strong metallic bond transition elements have higher density

7. Low ionization energies

First ionization enethalpies of d-block elements are higher than those of s-block elements and are less than p-block lements.There is slightly and irregular variation in ionization energies of transition metals due to irregular variation of atomic size

8. Higher enthalpy of atomization

Because of large number of unpaired electrons in their atoms, they have strong inter-atomic interactions and hence stronger bonds between atoms resulting in higher enthalpies of atomization

9. Electrode potential and reducing character:

Lower the electrode potential (i.e more negative the standard reduction potential) of the electrode, more stable is the oxidation state of the transition metal ion in aqueous solution

ELEMENT	E^O (M^{2+}/M) in Volts	M^{3+}/M^{2+}
V	-1.18	-0.26
Cr	-0.90	-0.41
Mn	-1.18	+1.57
Fe	-0.44	+0.77
Co	-0.28	+1.97
Ni	-0.25	---
Cu	+0.34	---
Zn	-0.76	----

10. Catalytic properties:

Many transition elements (like Co, Ni, Pt, Fe, Mo etc) and their compounds are used as catalysts because

(i) they have variable oxidation states, they easily absorb and reemit wide range of energies to provide the necessary activation energy

(ii) Because of variable oxidation states, they easily comnine with one of the reactants to form, an intermediate which reacts with second reactant to form the final products.

(iii) Because of presence of free valencies on the surface, they can adsorb the reacting molecules, thereby increasing the concentration of the reactants on the surface and hence the rate of reaction.

11. Coloured ions

Most of the transition metal compounds are coloured both in the solid state and in aqueous solution. This is because of the presence of incompletely filled d-orbitals. When a transition metal compound is formed the degenerate s-orbitals of the metal split into two sets, one having three orbitals d_{xy}, d_{yz} and d_{xz} called t_{2g} orbitals with lower energy and the other having two orbitals $dx^2 - y^2$ and dz^2 called e_g orbitals with slightly higher energy in an octahedral field. This is called crystal field splitting When white light falls on these compounds, some wavelength is absorbed for promotion of electrons from one set of lower energy orbitals to another set of slightly higher energy within the same d-subshell. This is called d-d transition. The remainder light is reflected which has a particular colour. The colours of some 3d metal ions

Ti^{3+} ($3d^1$)	Purple	V^{4+} ($3d^1$)	Blue	V^{3+} ($3d^2$)	Green
Cr^{3+} ($3d^4$)	Violet green	Mn^{3+} ($3d^4$)	Violet	Cr^{2+} ($3d^4$)	Blue
Mn^{2+} ($3d^5$)	Pink	Fe^{3+} ($3d^5$)	Yellow	Fe^{2+} ($3d^6$)	Green
Co^{2+} ($3d^6$)	Green	Ni^{2+} ($3d^8$)	Green	Cu^{2+} ($3d^9$)	Blue

Colours of $Cr_2O_7^{2-}$, CrO_4^{2-}, MnO_4^-, Cu_2O are due to charge transfer transition

12. Magnetic properties

Due to presence of unpaired electrons in (n-1) d orbitals, the most of the transition metal ions and their compounds are paramagnetic. The magnetic moment is expressed in Bohr magnetons (B.M.)

A paramagnetic substance is characterized by its effective magnetic moment (μ_{eff}) which is given by the expression

$$\mu_{eff} = \sqrt{n(n+2)} \text{ B.M.}$$

Where n is the number of unpaired electrons and B.M stands for Bohr magneton.

Note mercurous ion is diamagnetic in nature which explains that it exists as dimer, Hg_2^{2+} and not monomer Hg^+

13. Complex formation

Transition metal ions form a large number of complex in which the central metal ion is linked to a number of ligands. This is because

- (i) They have higher nuclear charge and small size . i.e. charge/size ration (charge density) is large
- (ii) They have empty d-orbitals to accept the lone pairs of electrons donated by ligands

Thus in complexes metal ions behave as Lewis acids and ligands behave as Lewis bases.

14. Interstitial compounds

Transition metals form a number of interstitial compounds in which small non-metal atoms such as H, C, B, N and He occupy the empty spaces (interstitial sites) in their lattices and also form bonds with them. These new compounds known as hydrides, carbides, borides, nitrides and halides respectively have higher melting points than respective pure metals, are chemically inert, hard and rigid.

15. Ally formation:

Due to similarity in atomic size, atoms of one transition metal can easily take up positions in the crystal lattice of the other in molten state and are miscible with each other forming solid solutions

16. Preparation of potassium dichloride from iron chromite ore

$K_2Cr_2O_7$ is prepared from Chromite ore ($FeCr_2O_4$).

The finely powdered ore is fused with Na_2CO_3 in free access of air.

$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

The yellow solution of Na_2CrO_4 is filtered and acidified with H_2SO_4 to give a solution from which orange sodium dichromate $Na_2Cr_2O_7 \cdot H_2O$ can be crystallized

$2Na_2Cr_2O_7 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

$K_2Cr_2O_7$ is prepared by treating the solution of $Na_2Cr_2O_7$ with potassium chloride

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

$K_2Cr_2O_7$ being less soluble than $Na_2Cr_2O_7$ Crystallizes out on cooling as Orange crystal

Effect of pH

On increasing pH, the orange colour solution of dichromate, a yellow coloured solution of chromate is formed

$$\underset{\text{(Orange)}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{(Yellow)}}{2CrO_4^{2-}} + H_2O$$

17. Preparation of potassium permanganate.

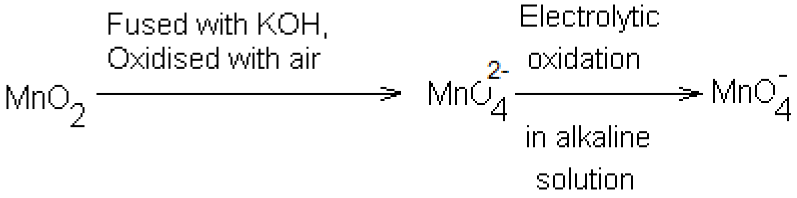
$KMnO_4$ is prepared from the mineral, pyrolusite, MnO_2

(a) The finely powdered pyrolusite mineral is fused with KOH and an oxidizing agent like KNO_3. This produces the dark green K_2MnO_4 which disproportionate in a neutral acidic solution to give permanganate

$2MnO_2 + 4KOH + O_2 \rightarrow K_2MnO_4 + 2H_2O$

$MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO^2 + 2H_2O$

(b) Commercially $KMnO_4$ is prepared by alkaline oxidative fusion of MnO_2 followed by electrolytic oxidation of MnO_4^{2-}



18. Lanthanoid contraction:

The regular decrease in the size of lanthanoid ions from La^{3+} to Lu^{3+} is known as lanthanoid contraction. It is due to greater effect of increased nuclear charge than that of the screening effect.

19. Consequences of Lanthanoid contraction

(a) It results in slight variation in their chemical properties which helps in their separation by ion exchange method

(b) Each element beyond lanthanum has same atomic radius as that of element lying above it in the same group

(c) The covalent character of hydroxides of lanthanoids increases as the size decreases from La^{3+} to Lu^{3+}. Hence the basic strength decreases.

(d) Tendency to form stable complexes from La^{3+} to Lu^{3+} increases as the size decreases in that order

(e) There is a slight increase in electronegativity of the trivalent ions from La to Lu

(f) Since the radius of Yb^{3+} ion is comparable to the heavier lanthanoid, therefore, they occur together in natural minerals

20. Colour of lanthanoid

Most of the trivalent lanthanoid ions are coloured both in the solid state and in aqueous solution. This is due to the partly filled f-orbitals which permit f-f transition.

21. Magnetic properties of lanthanoid

All lanthanoid ions except Lu^{3+}, Yb^{3+} and Ce^{4+} are pramegentic because they contain unpaired electrons in the 4f orbitals. They do not follow simple formula as for transition elements.

Magnetic moments of lanthanoids are calculated by taking into consideration spin as well as orbital contributions and more complex formula

$$\mu_{eff} = \sqrt{4S(S+1) + L(L+1)}$$

Which involves the orbital quantum number L and spin quantum number S

22. Actinoid contraction:

There is a regular decrease in ionic radii with increase in atomic number. It is caused due to imperfect shielding of one 5f electron by another in the same shell. This results in increase in the effective nuclear charge which causes contraction in size of the electron cloud.

23. Colour of Actinoid:

Ions of actinoids are generally coloured which is due to f-f transitions. It depends upon the number of electrons in 5f orbitals.

24. Magnetic properties of Actinoid

Like Lanthanoids, actinoids elements are strongly paramagnetic. The magnetic moment is less than the theoretically predicted values. This is due to the fact that 5f electrons of Actinoids are less effectively shielded which results in quenching of orbital contribution

25. Complex formation of Actinoid

Actinoids have greater tendency to form complexes because of higher nuclear charge and smaller size of their atoms. They form complexes even with π-bonding ligands such as alkyl phosphines, thioethers etc.

26. Comparison of Lanthanoides and Actinoides

(i) Electron configuration: In Lanthanoids , 4f orbitals are progressively filled whereas in , 5f orbitals are progressively filled. The general electronic configuration of Lanthanoids is $[xe]4f^{1-14}\ 5d^{0-1}6s^2$ where as the general electronic configuration of actinoids is $[Rn]5f^{1-14}\ 6d^{0-1}7s^2$

(ii) Oxidation States: Lanthanoids shows limited oxidation states (+2, +3, +4) out of which +3 is most common. This is because of large energy gap between 4f, 5d, and 6s subshells. On the other hand, Actinoids show a large number of oxidation states (+3,+4,+5,+6,+7) out of which +3 is most common. This is due to large small energy gap between 5f, 6d and 7s subshells

(iii) Atomic and ionic size: Both show decrease in size of their atoms or M^{3+} ions across the series. In Lanthanoids, the decrease is called lanthanoid contraction, where as in actinoids it is called Actinoid contraction. However, the contraction is greater from element to element in Actinoids due to poor shielding by 5f electrons

(iv) Chemical reactivity: Actinoids are more reactive than Lanthanoids due to bigger atomic size and lower ionization energy. The action of boiling water on actinoids give mixture of oxide and hydrid and combination with most non metals takes place at moderate temperature. HCl attacks all metals but most slightly affected by HNO_3. The first few members of Lanthanoids are quite reactive, almost like calcium. However with increasing atomic number, their behavior becomes similar to that of Aluminium. They combines with H_2 on gentle heating. When heated with carbon they form carbides. They react with acids to liberate hydrogen gas.

Conceptual questions on d – and f-block elements

Q1) What is meant by transition elements

Ans) A transition element is defined as the one which has incompletely filled d orbitals in its ground sate or in any one of its oxidation states

Q2) What is general electron configuration of transition elements

Ans) $(n-1)d^{1-10}\ ns^{1-2}$

Q3) Zn, Cd and Hg are not regarded as transition elements why?

Ans) Zinc, Cadmium and Mercury have completely filled d orbitals in their ground state as well as in their oxidized state, hence they are not regarded as transition elements

Q4) On what ground you can say that Scandium (Z = 21) is a transition element but Zinc (Z= 30 is not?

Ans) On the basis of incompletely filled 3d orbitals in case of Scandium atom in its ground state ($3s^1$) , iti is regared as transition element. On the other hand, zinc atom has completely filled d-orbitals($3d^{10}$) in its ground state as well as in its oxidized state, hence it is not regarded as a transition element

Q5) Silver atom has completely filled d orbitals $4d^{10}$ in its ground state. How can you say that it is a transition element?

Ans) Silver (Z = 54) can exhibit +2 oxidation state where it will have incompletely filled d orbital s(d4d), hence a transition element.

Q6) Why do the transition elements exhibit higher enthalpy of atomization

Ans) Because of large number of unpaired electrons in their atoms, they have strong inter-atomic interactions and hence stronger bonds between atoms resulting in higher enthalpies of atomization

Q7) In the series Sc(Z=21) to Zn (Z=30) , the enthalpy of atomization of zinc is the lowest i.e 126KJ mol^{-1}. Why?

Ans) In the formation of metallic bonds, no electrons from d-orbitals are involved in case of Zinc, while in all other metals of 3d series, electrons from the d-orbitals are always involved in the formation of metallic bonds

Q8) Why are Mn^{+2} compounds more stable than F^{2+} towards oxidation to their +3 state?

Ans) Electron configuration of Mn^{2+} is 3d^5 which is half filled and hence stable. Therefore, third ionization enthalpy is very high. In case of Fe^{2+}, electronic configuration is 3d^6. Hence it can lost one electron easily to give stable configuration 3d^5

Q9) Name a transition element which does not exibit variable oxidation states

Ans) Scandium (Z=21) does not exhibit variable oxidation states

Q10) Which of the 3d series of the transition metals exhibits the large number of oxidation states and why?

Ans) Manganese (Z=25), as its atom has maximum number of unpaired electrons

Q11) Why is Cr^{2+} reducing and Mn^{+3} oxidizing whom both have d^4 configuration?

Ans) Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half filled t_{2g} level. On the other hand, the change from Mn^{3+} to Mn^{2+} results in the half filled (d^5) configuration which has extra stability

Q12) What may be stable oxidation states of the transition element with following 'd' electron configuration in the ground state of their atoms : 3d^3, 3d^5, 3d^8, 3d^4?

Ans) (1) 3d^3 (Vanadium) : = +2, +3, +4 and +5

(2) 3d^5 (chromium) = +3, +4, and +6

(3) 3d^5 (Manganese) : +2, +4, +6 and +7

(4) 3d^8 (Nickel) : +2, +3, +4

(5) 3d^4 – There is no d^4 configuration in the ground state

Q13) To what extent do the electronic configuration decides the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples

Ans) In a transition series, the oxidation states which lead to exactly half-filled or completely filled d-orbitals are most stable. For example, in the first transition series, electronic configuration of Mn(Z=25) is $[Ar]3d^5 4s^2$. It shows oxidation sates +2 to +7 but +2 is more stable than Mn^{3+} because Mn^{2+} has half filled d orbitals. Similarly Fr^{3+} is more stable than Fe^{2+} due to half filled d-orbital's

Q14) Name oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group member

(i) $Cr_2O_7^{2-}$ and Cr_4^{2-} , oxidation states of Cr is +6 which is equal to its group numbers

(ii) Mn_4^-, Oxidation state of Mn is +7 which is equal to its group number

Q15) What is lantanoid contraction? What are the consequences of Lanthanoid contraction

Ans) The decrease in atomic and ionic size with increase in atomic number in lanthanoids is called lanthanoid contraction

Consequences

(i)The ionic radii of the second (4d) and the third (5d) series of transition elements are similar

(ii) Lanthanoids have similar chemical and physical properties

Q16) In what way is the electronic configuration of the transition elements differ from that of the non transition elements

Ans) In transition elements penultimate d-orbitals [(n-1) orbitals] are progressively filled and their electronic configuration si $(n-1)d^{1-10}$ ns^{1-2} where as in non transition elements outermost s or p orbitals are progressively filled and their electronic configuration is ns^{1-2} or ns^2 np^{1-6}

Q17) Transition metals and many of their compounds show paramagnetic behavior. Why?

Ans) This is due to the presence of unpaired electrons in the (n-1)d orbitals

Q18) The transition elements generally form coloured compounds

Ans) It is due to presence of unpaired electrons, they undergo d-d transitions by absorbing light from visible region and radiate complementary colour

Q19) transition metals and their many compounds act as good catalyst

Ans) It is because of their ability to adopt multiple oxidation states and to form complexes. They have large surface area and can form intermediate with reactants which readily change into products.

Q20) What are interstitial compounds? Why are such compounds well known for trasition metals?

Ans) Interstitial compounds are those which are formed when small atoms like K,C, or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic non covalent

The transition metals have voids between atoms in their crystal lattice. Therefore they are known to form interstitial compounds

Q21) How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples

Ans) In transition elements the oxidation states vary from +1 to any highest oxidation state by one. For example, for manganese it may vary as +2,+3,+4,+5,+6,+7. In the non transition elements the variation is selective, always differing by 2; +2, +4, or +3, +5 etc

Q22) Predict which of the following will be coloured in aqueous solution of

MnO_4^-, Ti^{+3}, V^{3+}, Cu^+, Sc^{3+}, Mn^{2+}, Fe^{2+} and Co^{2+} . Give reason for each

Ans) Ti^{+3}, V^{3+}, Mn^{2+}, Fe^{2+} and Co^{2+} are coloured due to presence of unpaired electrons, they undergo d-d transition by absorbing light from visible region and radiate complementary colour.

MnO_4^- is coloured ion due to charge transfer from oxygen to manganese, it absorbs light from visible region and radiate complementary colour

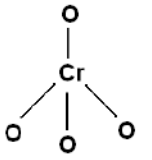
Cu^+, Sc^{3+} are colourless due to absence of unpaired electrons

Q23) Why d^1 configuration is very unstable ions?

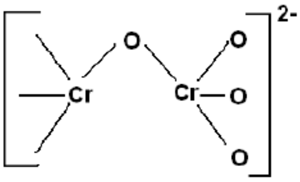
Ans) The ions with d^{1+} configuration have the tendency to lose the only electron present in d-subshell to acquire stable d^0 configuration. Hnece they are unstable and undergo oxidation.

Q24) Draw the structure of (i)Chromate ion (ii) Dichromate ion (iii) Manganate ion (4) Permanganate ion

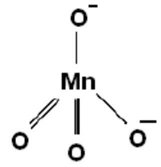
Ans)



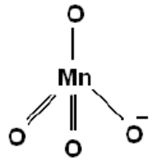
Chromate ion



Dichromate ion



Manganate ion



Permanganate ion

Q25) For M^{2+}/M and M^{3+}/M^{2+} systems the E^{Θ} values for some metals are follows

$Cr^{2+}/Cr = -0.9V$, $Cr^{3+}/Cr^{2+} = -0.4V$

$Mn^{2+}/Mn = -1.2V$, $Mn^{3+}/Mn^{2+} = +1.5V$

$Fe^{2+}/Fe = -0.4V$, $Fe^{3+}/Fe^{2+} = 0.8V$

Using this data to comment upon (i) the stability of Fe^{3+} in acidic solution as compared to that of Cr^{3+} or Mn^{3+} and (2) thee ease with which ion can be oxidized as compared to similar process of either chromium or manganese metal

(i) Cr^{3+}/Cr^{2+} has a negative reduction potential. Hence Cr^{3+} cannot be reduced to Cr^{2+} I.e Cr^{3+} is most stable,
Mn^{3+}/Mn^{2+} has large positive E^{Θ} value. Hence Mn^{3+} can be easily reduced to Mn^{2+} i.e Mn^{3+} is least stable
E^{Θ} value for Fe^{3+}/Fe^{2+} is positive but small. Hence, Fe^{3+} is more stable than Mn^{3+} nut less stable than Cr^{3+}

(ii) Oxidation potential for the given pairs will be +0.9V, +1.2V and +0.4V. thus the order of their getting oxidized will be in the order Mn>Cr>Fe

Q26) What is meant by disproportionation? Give two examples of disproportionate reaction in aqueous solution

Ans) When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation

$$\underset{+6}{3MnO_4^{2-}} + 4H^+ \rightarrow \underset{+7}{2MnO_4^-} + \underset{+4}{MnO_2} + 2H_2O$$

$$\underset{+1}{2Cu^+} \rightarrow \underset{+2}{Cu^{2+}} + \underset{0}{Cu}$$

Q27) Which metal in the first series of transition metals exhibits +1 oxidation state most frequenctly and why?

Ans) Copper exhibits +1 oxidation state frequently due to stable electronic configuration ($3d^{10}$)

Q28) Why the lowest oxide of transition metals is basic, the highest is amphoteric/acidic.

Ans) The lower oxide of transition metals is basic because the metals atom has low oxidation state, where as highest is acidic due to higher oxidation state. In lower oxidation state, ionic bonds are formed where as in highest oxidation state covalent bonds are formed. MnO is basic while Mn_2O_7 is acidic

Q29) Why transition metals exhibits highest oxidation state in oxides and fluorides

Ans) It is because oxygen and fluorine are highly electronegative and strong oxidizing agents.

Q30) Comment on the statement that the elements of the first transition series posses many properties different from those of heavier transition elements

Ans) Melting and boiling point of heavier transition elements are greater than those of the lower transition series due to strong intermetallic bonding

The ionization enthalpy of 5d transition series is higher than 4s and 3d transition series

The elements of first transition series do not form complexes with higher coordination number of 7 and 8

Atomic radii of the heavier transition elements (4d and 5d) are larger than of the corresponding elements of the first transition series

The elements of the first series can form high spin or low spin complexes depending upon strength of ligand’s but elements of other series forms low spin complex irrespective of strength of ligand’s

Q31) Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

Ans) The 5f electrons are more effectively shielded from nuclear charge. In other words the 5f electrons themselves provide poor shielding. From element to element

Q32) Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?
Ans) It is due to increase in effective nuclear charge after losing 2 electrons from s-orbitals, ionic size decreases, stability increases

Q33) Transition elements form large number of complex compounds why?

Ans) This is due to the comparatively small size of the metal ions, high ionic charge and the availability of d orbitals for bond formation

Q34) Transition elements show variable oxidation states. Why?

Ans) In the transition elements, the energies of (n-1)d orbitals and ns orbitals are very close. Hence, electrons from both can participate in bonding

Q35) Why Zr(Zirconium) and Hf(Hafnium) have similar chemical properties?

Ans) Due to lantanoid contraction, Hf has size similar to that of Zr (i.e. almost identical radii). Hence their properties are similar

Q36) Why Nb and Ta have similar properties?

Ans) Due to lanthanoid contaction Nb has same size tothat of Ta. Hnece they have similar properties

Q37) What is the separation of Lanthanide elements difficult

Ans) Due to Lanthanoide contraction, the change in the atomic or ionic radii of these elements is very small. Hence their chemical properties are similar

Q38) Why Zn, Cd and HG are soft and have low melting and boiling points

Ans) In Zn, Cd and Hg all the electrons in d-shell are paired. Hence the metallic bond present in them are weak. Therefore they are soft.

Q39) Why Transition Metals Are Good Catalysts

The most important reason transition metals are good catalysts is that they can lend electrons or withdraw electrons from the reagent, depending on the nature of the reaction. The ability of transition metals to be in a variety of oxidation states, the ability to interchange between the oxidation states and the ability to form complexes with the reagents and be a good source for electrons make transition metals good catalysts.

A salt is formed by the neutralization of an acid by a base. There are different types of salts. They are:-

a) Simple salt

b) Molecular (or) addition compounds

a) Simple salt

A simple salt is formed by the neutralization of an acid by a base.

$KOH + HCl \rightarrow KCl + H_2O$

Normally, a simple salt ionizes in water and produces ions in solution. The solution of the simple salt exhibits the properties of its component ions.

b) Molecular (or) addition compounds

i) Double salts

These are molecular compounds which are formed by the evaporation of solution containing two (or) more salts in stoichiometric proportions. Hence the molecular compounds which dissociate in solution into its constituent ions are known as double salt. Double salts retain their properties only in solid state. They are also called as lattice compounds.

Example

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ - Potash alum

$FeSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O$ - Mohr's salt

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \rightarrow 2K^+ + 2Al^{3+} + 4SO_4^{2-} + 24H_2O$

The double salts give the test of all their constituent ions in solution.

ii) Coordination (or complex) compounds

Coordination compound is 'a compound formed from a Lewis acid and a Lewis base'. The molecular compounds, do not dissociate into its constituent ions in solution are called coordination compounds.

Example

$Fe(CN)_2 + 4KCN \rightarrow Fe(CN)_2 \cdot 4KCN$ (or) $K_4[Fe(CN)_6]$

Ferrous cyanide

$Fe(CN)_2 \cdot 4KCN \rightarrow 4K^+ + [Fe(CN)6]^{4-}$

Complex anion

In $K_4[Fe(CN)_6]$ the individual components lose their identity.

The metal of the complex ion is not free in solution unlike metal in double salt in solution.

Nature of coordination (or) complex compounds

i) An anionic complex compound contains a complex anion and simple cation.

$$K_4[Fe(CN)_6] \rightarrow \underbrace{4K^+}_{\text{simple cation}} + \underbrace{[Fe(CN)6]^{4-}}_{\text{complex anion}}$$

ii) A cationic complex contains complex cation and simple anion

$$[Co(NH_3)_6]Cl_3 \rightarrow \underbrace{[Co(NH_3)_6]^{3+}}_{\text{Complex cation}} + \underbrace{3Cl^-}_{\text{simple anion}}$$

iii) In the case of a complex compound, $[Cr(NH_3)_6][Co(CN)_6]$, it gives both complex cation and complex anion

$$[Cr(NH_3)_6][Co(CN)_6] \rightarrow \underbrace{[Cr(NH_3)_6]^{3+}}_{\text{complex cation}} + \underbrace{[Co(CN)_6]^{3-}}_{\text{complex anion}}$$

TERMINOLOGY USED IN COORDINATION CHEMISTRY

(a) Lewis Acid

All electron acceptors are Lewis acids.

(b) Lewis Base

All electron donors are Lewis base.

(c) Central metal ion

In the complex ion an acceptor accepts a pair of electrons from the donor atoms. The acceptor is usually a metal / metal ion to which one (or) more of neutral molecules (or) anions are attached. The acceptor metal cation is referred to as central metal cation. Hence, central metal cation in a complex serves as a lewis acid.

(d) Ligand (Latin word meaning to bind)

A ligand is an ion (or) a molecule capable of functioning as an electron donor. Therefore the neutral molecules or ions which are directly attached to the central metal ion are called as ligand (or) coordination groups. These coordination groups or ligands can donate a pair of electrons to the central metal ion (or) atom. Hence, in a complex compound ligands act as Lewis bases.

Examples:

$[Ni(NH_3)_6]^{2+}$: Ligand = NH_3 molecule and Central metal ion = Ni^{2+}

$[Co(NH_3)_5Cl]^{2+}$: Ligands = NH_3 molecule and Cl^- ion

Types of ligands

Ligands can be classified on the basis of charge, number of donor site and bonding

(a) On the basis of charge

(i) Negative ligands : ligands which carry negative charge e.g. CN^-, Cl^-, Br^-, NH_2^-, $NO_2^–$ etc

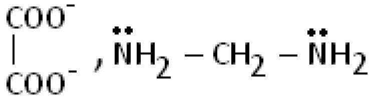
(ii) Positive ligands : ligand which carry positive charge e.g. NO_2^+, NO^+, NH_3^+ etc

(iii) Neutral ligands: ligands which do not carry any charge e.g. H_2O, NH_3, PH_3, CO etc

(b) On the basis of number of donor sites

(i) **Monodentate or unidentate ligands**: Ligands which coordinate to central atom or ion through one donor atom and form only one coordinate bond are called monodentate/ unidentate ligands
E.g. H_2O, NH_3, OH^-, CN^-, O^{2-} etc

(ii) **Bidentate ligands** : ligands which coordinate to central metal atom or ion through two donor atoms and form coordinate bonds are called bidentate ligands eg,

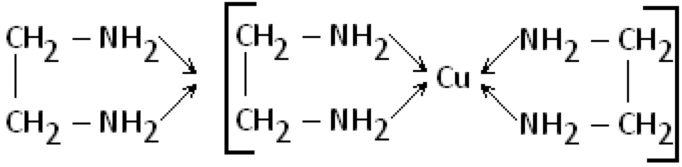


$$\begin{matrix}COO^- \\ | \\ COO^-\end{matrix},\ \ddot{N}H_2 - CH_2 - \ddot{N}H_2$$

(iii) **Plolydentate ligands**: Ligands which coordinate to central metal atom or ion through more than two donor atoms are called polydentate ligands and the resulting comples is called polydentate ligands e.g. EDTA is hexadentatae ligand

(c) On the basis of bonding

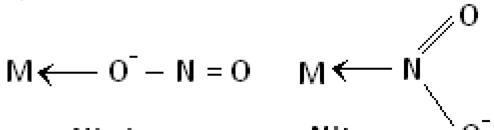
(i) Chelating ligands: A bidentate or polydentate ligand which forms two or more coordinate bond with central metal atom or ion in such a way that a five or six membered ring is formed is called chelating ligand and the resulting complex is called metal chelate. This property is called chelation e.g.



Chelating ligand Chelate

(ii) **Ambidentate ligands**: Monodentate ligand containing more than one coordinating atoms are called ambidentate ligands

e.g NO_2^- can coordinate with metal atom or ion through either N or O atom



Nitrito Nitro

(e) Coordination number

The total number of coordinate bonds through which the central metal ion is attached with ligand is known as coordination number

Example For example in

$K_4[Fe(CN)_6]$ the coordination number of Fe(II) is 6 and in $[Cu(NH_3)_4]SO_4$ the coordination number of Cu(II) is 4.

(f) Coordination sphere

The central metal ion and the ligands that are directly attached to it, are enclosed in a square bracket, called coordination sphere or first sphere of attraction

(g) Oxidation number or Oxidation state of central metal atom/ ion

It is the number that represent an electric charge with an atom or ion actually has or appears to have when combined with other atom

e.g. $[Cu(NH_3)_4]^{2+}$ NH_4 is neutral, monodentate ligand. Let oxidation state of the metal ion be x then

$x + 4(0) = +2 \Longrightarrow x = 2$. Oxidation number of Cu is +2

Rules for writing formula of coordination compounds

(i) Formula of the cation whether simple or complex must be written first followed by anion

(ii) The coordination sphere the sequence of symbols is :
First metal name followed by anionic ligand then neutral ligand finally cationic ligand. Ligands of same type are arranged alphabetically

(iii) Polyatomic ligands are enclosed in parentheses
e.g In $Na[PrBrCl(NO^{+2})_2NH_3(NO)]$ sequence in coordination sphere is metal atom, alphabetical sequence of anionic ligand Br^-, Cl^-, NO_2^-, followed by neutral ligand NH_3 and then cationic ligand NO^+

IUPAC nomenclature of coordination compounds

The rules are outlined below

1. In naming the entire complex, the name of the cation is given first and the anion second (just as for sodium chloride), no matter whether the cation or the anion is the complex species.

2. In the complex ion, the name of the ligand or ligands precedes that of the central metal atom (This procedure is reversed for writing formulae).

3. Ligand names generally end with ‘O’ if the ligand is negative (‘chloro’ for Cl^-, ‘cyano’ for CN-, ‘hydrido’ for H-) and unmodified if the ligand is neutral (‘methylamine’ for $MeNH_2$). Special ligand names are ‘aqua’ for water, ‘ammine’ for ammonia, ‘carbonyl’ for CO, nitrosyl’ for NO.

4. A Greek prefix (mono, di, tri, tetra, penta, hexa, etc.) indicates the number of each ligand (mono is usually omitted for a single ligand of a given type). If the name of the ligand itself contains the terms mono, di, tri, liketriphenylphosphine, ligand name is enclosed in parentheses and its number is given with the alternate prefixes bis, tris, tetrakis instead.

For example, $[Ni(PPh_3)_2Cl_2]$ is named dichlorobis(triphenylphosphine) nickel(II).

5. A Roman numeral or a zero in parentheses is used to indicate the oxidation state of the central metal atom.

6. If the complex ion is negative, the name of the metal ends in ‘ate’ for example, ferrate, cuprate, nickelate, cobaltate etc.

7. If more than one ligand is present in the species, then the ligands are named in alphabetical order regardless of the number of each.

For example, NH_3 (ammine) would be considered as ‘a’ ligand and come before Cl-(chloro).

Some additional notes

i) Some metals in anions have special names

B Borate ,Au Aurate, Ag Argentate, Fe Ferrate, Pb Plumbate, Sn Stannate, Cu Cuprate, Ni Nickelate

ii) Use of brackets or enclosing marks. Square brackets are used to enclose a complex ion or neutral coordination species.

Examples

$[Co(en)_3]Cl_3$ tris(ethylenediamine)cobalt(III) chloride

$[Co(NH_3)_3(NO_2)_3]$ triamminetrinitrocobalt (III)
$K_2[CoCl_4]$ potassiumtetrachlorocobaltate(II)
note that it is not necessary to enclose the halogens in brackets.

Name of Negative ligands

Ligand	Name	Ligand	Name
H^-	Hydrido	HS^-	Mercapto
O^{2-}	Oxo	NH_2^-	Amido
O_2^{2-}	Peroxo	NH^{2-}	Imido
O_2H^-	Perhydroxo	NO_3^-	Nitrato
OH^-	Hydroxo	ONO^-	Nitrito
F^-	Fluoro	NO_2^-	Nitro
Cl^-	Chloro	N^{-3}	Nitride
Br^-	Bromo	P^{3-}	Phosphido
I^-	Iodo	N_3^-	Azido
CO_3^-	Carbonato	CNO^-	Cyanato
$C_2O_4^-$	Oxalate	NCO^-	Cyanato
$CH_3CO_2^-$	Acetate	SCN^-	Thiocyanato
SO_4^{2-}	Sulphato	HCO_3^-	Hydrogencarbonato
SO_3^{2-}	Sulphito	$S_4O_6^{2-}$	Tetrathionato
S^{2-}	Sulphido	HSO_3^-	Hydrogensulphito
$NH_2CH_2CO_2^-$	glycinato	$C_5H_5^-$	Cyclopentadienyl
$(^-OCCH_2)_2NCH_2CH_2CH_2N$ $(CH_2CO_2^-)_2$	Ethylenediammine tetraacetato (EDTA)	$S_2O_3^{2-}$	Thiosulpahato

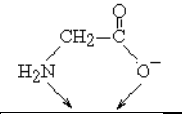
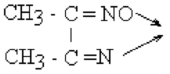
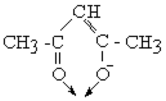
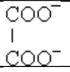
Name of neutral ligands

Ligand	Name	Ligand	Name
C_5H_5N (py)	pyridine	$NH_2(CH_2)_2NH_2$ (en)	ethlenediammine
NH_3	Ammine	CH_3NH_2	Methylamine
H_2O	Aqua/aquo	CO	Carbonyl
C_6H_6	Benzene	NO	Nitrosyl
N_2	Dinitrogen	CS	Thiocarbonyl
O_2	Dioxygen	NS	Thionitrosyl
Ph_3P	Triphenylphosphine	CH_3COCH_3	Acetone

Name of Positive ligands

Ligand	Name
NO^+	Nitosonium
NO_2^+	Nitronium
$NH_2NH_3^+$	hydrazinium

Bidentate ligands

Name of the species	Formula	Charge	Abbr.	Donor site	IUPAC name of ligand
Glycinate ion		-1	gly	2, One N and one O atom	Glycinato
Dimethyl glyoxime ion		-1	dmg	2,one N and one O	Dimethyl glyoximato
Acetyl acetonate		-1	Acac	Two O atom	Acetylacetonato
Oxalate ion	 $COO^- \mid COO^-$	-2	Ox	Two O atoms	Oxalato
Ethylene diamine(en)	$\ddot{N}H_2CH_2CH_2\ddot{N}H_2$	Zero	En	Two N atoms	Ethylenediamine

Multidentate ligands

Name of the species	Charge	Abbri	Donor site	IUPAC name of ligand
Diethylene triamine	Zero	Dien	3, three N atoms (tridentate)	Diethylene triamine
Triethyylene tetramine	Zero	Trien	4, Four N atoms (Tetradentate)	Triethylene amine
Ethylenediamine triacetate ion	-3	$EDTA^{3-}$	5, Three O atoms and two N atoms (pentadenate)	Ethylenediamine triacetate
Ethylenediamine tetra-acetate ion	-4	$EDTA^{4-}$	6, two N and four O atoms (Hexadentate	Ethylenediamine tetraacetato

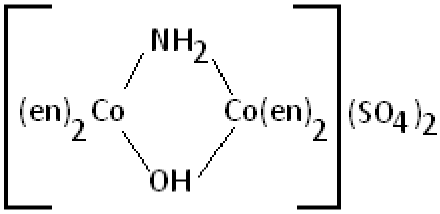
Few examples to elaborate above rules

$[PtCl_2(C_2H_5N)(NH_3)]$	Amminedichloro (pyridine)platinum(II)
$[Fe(CO)_5]$	Pentacarbonyliron(0)
$[PtCl_2(NH_3)_4][PtCl_4]$	Tetraamminedichloroplatinum (IV) tetrachloroplatiate(II)
$[Cr(NH_3)_4][CuCl_4]$	Tetraammine chromium(0) tetrachlorocuperate(IV)
$Na[PtBrCl(NO_2)(NH_3)]$	Sodium amminebromochloronitro
$[Pt(py)_4][PtCl_4]$	Tetrapyridineplatinum(II) Tertrachloroplatinate(II)
$[CoCl(ONO)(en)_2]^+$	Chlorobis(ethylenediamine)nitritocobalt (III) ion
$[\{(C_6H_5)_3P\}Rh]Cl$	Tris(triphenylphosphine)rodium(I)chloride
$[Fe(H_2O)_4(C_2O_4)]_2SO_4$	Tetraaquooxalatoiron(III)sulphate

$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$K_3[Fe(CN)_5NO]$	Potassium pentacyanonitrosylferrate(II)
$Na[Ag(CN)_2]$	Sodim dicyanoargentate (I)
$[Fe(CO)_5]$	Pentacarbonyliron(0)
$Fe_4[Fe(CN)_6]_3$	Ferric hexacyanoferrate(II)
$[Fe(C_5H_5)_2]$	Bis(cyclopentadienyl)iron(II)
$Na_2[Ni(NC)_4]$	Sodium tetraisocyanonickelate(II)
$K_2[HgCl_4]$	Potassium tetrachloromercurate(II)
$[Cr(Ox)_3]^{3-}$	Tris (oxalato) chromate (III) ion
$[CoCl(NO_2)(NH_3)_4]Cl$	Choronitrito tetraamine cobat(III) chloride
$[Co(en)_3]Cl_3$	Tris(ethylene diammine) cobalt(III) chloride
$Na_3[AlF_6]$	Sodium hexafluoro aluminate(III)
$K[Cr(NH_3)_2(CO_3)_2]$	Potassium dicarbonate diammine chromate(III)
$Na_3[Cr(en)_2(C_2O_4)_3]$	Sodium tri oxalate bis (ethylene diammine) chromate(III)
$[Co(NH_3)_5(NCS)]Cl_2$	Pentaammineisocyannatocobalt(III)Chloride
$[Cr(H_2O)_4Cl_2]_2SO_4$	Tetraaquodichlorochromium(III) sulphate
$[Ni(DMG)_2]$	Bis(dimethylglyoximato)nickel(II)
K_2HgI_4	Potassium tetraiodomercurate(IV)

8) naming of the bridging ligands of the bridged polynuclear complexes

Complexes having two or more atoms are called polynuclear complexes. In these complexes, the bridge group is indicated by separating it from the rest of the complex by hyphen and adding the prefix μ-before the name of each different bridging group. Two or more bridging groups of the same type are indicated by di-μ, tri-μ etc. When a bridging ligand is attached to more than two metal atoms or ion, this is indicated by subscript to μ



Is named as Bis(ethylenediammine)cobalt(III)-μ-amido-μ-hydroxo-bis(ethylenediamine)cobalt(III)sulphate

Or μ-amido-teyrakis (ethylenediammine)-μ-hydroxo-dicobat(III)sulphate

Werner's coordination theory

Postulates of Werner's theory

1) Every metal atom has two types of valencies

i) Primary valency or ionisable valency

ii) Secondary valency or non ionisable valency

2) The primary valency corresponds to the oxidation state of the metal ion. The primary valency of the metal ion is always satisfied by negative ions.

3) Secondary valency corresponds to the coordination number of the metal ion or atom. The secondary valencies may be satisfied by either negative ions or neutral molecules.

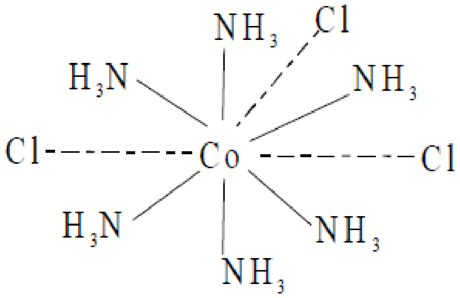
4) The molecules or ion that satisfy secondary valencies are called ligands.

5) The ligands which satisfy secondary valencies must project in definite directions in space. So the secondary valencies are directional in nature where as the primary valencies are non-directional in nature.

6) The ligands have unshared pair of electrons. These unshared pair of electrons are donated to central metal ion or atom in a compound. Such compounds are called coordination compounds.

Werner's representation

Werner represented the first member of the series $[Co(NH_3)_6]Cl_3$ as follows.
In this representation, the primary valency (dotted lines) are satisfied by the three chloride ions. The six secondary valencies (solid lines) are satisfied by the six ammonia molecules.



Defects of Werner's theory

Werner's theory describes the structures of many coordination compounds successfully. However, it does not explain the magnetic and spectral properties.

Valence bond theory (VB Theory)

Valence bond theory, primarily the work of Linus Pauling regarded bonding as characterized by the overlap of atomic or hybrid orbitals of individual atoms.
The postulates of valence bond theory:
1) The central metal atom/ion makes available a number of vacant orbitals equal to its coordination number.
These vacant orbitals form covalent bonds with the ligand orbitals.
3) A covalent bond is formed by the overlap of a vacant metal orbital and filled ligand orbitals. This complete overlap leads to the formation of a metal ligand, σ (sigma) bond.

4) A strong covalent bond is formed only when the orbitals overlap to the maximum extent. This maximum overlapping is possible only when the metal vacant orbitals undergo a process called ‘hybridisation’. A hybridised orbital has a better directional characteristics than an unhybridised one.
The following table gives the coordination number, orbital hybridisation and spatial geometry of the more important geometrics

Coordination number	Types of hybridization	Geometry
2	sp	linear
4	sp^3	tetrahedral
4	dsp^2	square planar
6	d^2sp^3	octahedral
6	sp^3d^2	octahedral

Magnetic moment

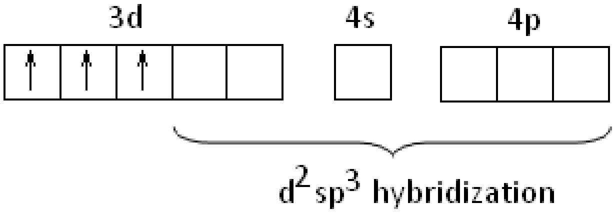
A species having at least one unpaired electron, is said to be paramagnetic.
It is attracted by an external field. The paramagnetic moment is given by the following spin-only formula.
$\mu_S = \sqrt{n(n+2)}$ BM
μ_s = spin-only magnetic moment
n = number of unpaired electrons
BM = Bohr magneton, the unit which expresses the magnetic moment.
When the species does not contain any unpaired electron, it is diamagnetic.

Applications of valence bond theory

(i) If the ligand is very weak like F^-, H_2, Cl^- etc. It does not force the pairing of 3d electrons and hence outer orbital octahedral complexes are formed by sp^3d^2 hybridization.

(ii)But if the ligand is strong like CN^-, $(COO)_2^{2-}$, ethylenediammine (en) etc, it forces the paring of 3d electrons and hence inner orbital octahedral complexes are formed by d^2sp^3 hybridization

(1) Atom or ion of d-block element contain 1,2 or 3 electrons in d-orbit (d^1,d^2,d^3 system)



Ti^{3+}, V^{3+}, Cr^{3+}
Since two 3d orbitals are available for d^2sp^3 hybridization. Hence, these systems may accept six lone pairs from six ligands and they form octahedral complexes
$[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$

Since due to complexation the unpaired electrons in (n-1) d-orbitals are not disturbed, the magnetic moment of free metal ions remains intact in octahedral complexes

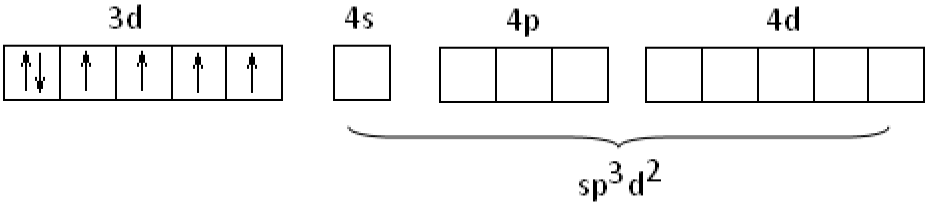
More possibility

In addition to d^2sp^3 hybridisation metal ions may undergo sp^3 or dsp^2 hybridization forming tetrahedral or square planar complexes respectively

Since in sp^3 or dsp^2, the d-electrons are not disturbed, the magnetic moment of free metal ion remains intact n tetrahedral or square planar complex

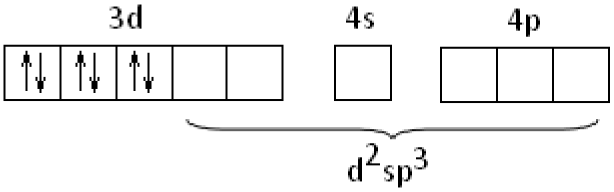
(2) Atom or ion of d-block element contain 4,5 or 6 electrons in d-orbit (d^4,d^5,d^6 system)

Mn(III), Fe(III), Co(III), Fe(II)



In above type ions, in ground state two 3-d orbitals are not vacant to participate thus 3d electrons are not disturbed and hence magnetic moment of free metal ions remains intact in outer orbital octahedral complex. Energy gap between 4s and 4d is large, the sp^3d^2 hybridisation is not perfect hybridization and hence outer orbital complexes are comparatively less stable. Moreover, 4d orbitals are more extended in space than 3dorbitals and hence sp^3d^2 hybrid orbitals are also more extended in space than d^2sp^3 hybrids. So bond length in outer orbital octahedral complexes is comparatively longer and so they are less stable. Such complex is possible if ligand is weak

Another possibility



For strong ligand like CN^- maximizes pairing of 3d electrons, two 3d orbitals may be maid vacant for d^2sp^3 hybridisation forming octahedral complex.

As two d-orbitals of inner shell are involved in hybridisation, complex are said to be inner orbital octahedral complex.

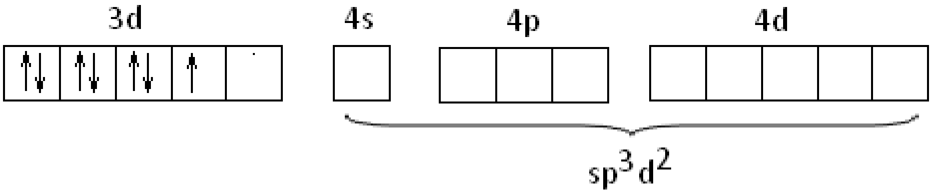
The energy of the orbitals involved in hybridisation is in continuation. The d^2sp^3 hybridisation is perfect and at the same time due to less extension of 3d orbitals in space, bond length is also short. So, inner orbital octahedral complexs are more stable than outer orbital octahedral complex

As the paring of 3d electrons is forced in d^2sp^3 hybridisation in these systems, hence the magnetic moment of the free metal ion undergoes change on complexation

One more possibility

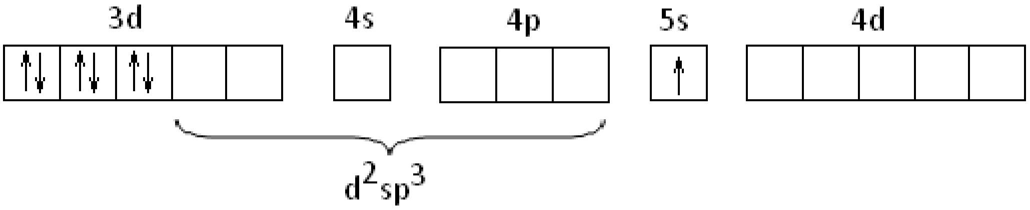
In addition to inner orbital octahedral and outer octahedral complexes ions may also form tetrahedral and square planner complex by sp^3 and dsp^2 hybridization

(3) Atom or ion of d-block element contain 7,8 or 9 electrons in d-orbit
(d^7,d^8,d^9 system)
Co(II), Ni(II, Cu(II)



Two vacant 3d orbitals cannot be made available for d^2sp^3 hybridization even after maximum pairing. So, there is no chance of the formation of inner orbital octahedral complex

Co^{2+} under the influence of HN_3 as ligand



In $d^{7,}$, with promotion of one electron to 5s or 4d, it becomes loosely bonded to the nucleus and hence, it may easily be removed and so, Co(II) will easily be oxidized to Co(III)

In d^8 , after maximum pairing of 3d electrons, one 3d orbital may be vacated for dsp^2 hybridization and hence d^7 , d^8 systems favour the formation of square planar complexs with changed magnetic nature

In d^9, one d-orbital is not made available for dsp^2 hybridization. So there is no question of the formation of square planar complex by d^9

More possibility (weak ligand)

However they may undergo sp^3d^2 hybridization forming outer orbital octahedral complex with same magnetic properties as in free metal.

One more possibility

Also sp^3 hybridizations can easily occur favouring the formation of tetrahedral complexes with unchanged magnetic character

(4) In d^{10} Zn(II) , Cu(I)
In d^{10}, 3d orbitals are completely filled up, so, it may form tetrahedral complex by sp^3 hybridization or outer orbital octahedral complexes by sp^3d^2 hybridization
Magnetic properties of the free metal ion remains unchaged in tetrahedral or outer orbital octahedral complexes

Defects of Valence bond theory

While the VB theory, to a larger extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following shortcomings:
(i) It involves a number of assumptions.
(ii) It does not give quantitative interpretation of magnetic data.
(iii) It does not explain the colour exhibited by coordination compounds.
(iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
(v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
(vi) It does not distinguish between weak and strong ligands.

Crystal field theory (CFT)

Main postulates of crystal field theory are

(i) In a coordination compound there are electrostatic interaction between metal atom/ion and ligands. Ligand assumed to be a point charge
(ii) In an isolated metal atom or ion all five d-orbitals have equal energy i.e. they are degenerate
(iii) When metal atom/ion gets surrounded by ligands, there occur interaction between d-electron cloud of metal atom/ion and ligands
(iv) If the field due to ligan around metal atom is spherically symmetrical, d-orbitals of metal remains degenerated
(v) If filed due to ligand surrounding metal is unsymmetrical (as in octahedral and tetra hedral complexes) the degeracy of d-orbitals is splitted into two sets of orbitals
(vi) Orbitals lying in the direction of ligands (point charges) are raised to higher energy state than those orbitals lying between theligands (point charges)
(vii) The energy difference between two sets of orbitals is denoted by Δ_o for octahedral and Δ_t for tetrahedral
(viii) The magnitude of Δ_o and Δ_t depends upon the field strength of ligand around the metal
(ix) Ligands which cause larger splitting (large Δ) are called strong field ligands while those which causes small splitting (small Δ) are called weak filed ligands

Spectrochemical series

Arrangement of ligands in order of their ability to cause splitting (Δ) is called spectrochemical series

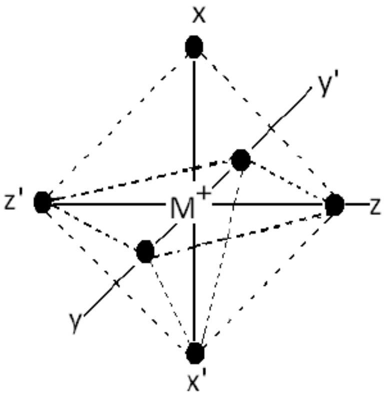
$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < NH_3 <$ en $< NO_2^- < CN^- < CO$

The spectrochemical series is an experimentally determined series. It is difficult to explain the order as it incorporates both the effect of σ and π bonding.
A pattern of increasing σ donation is as follows

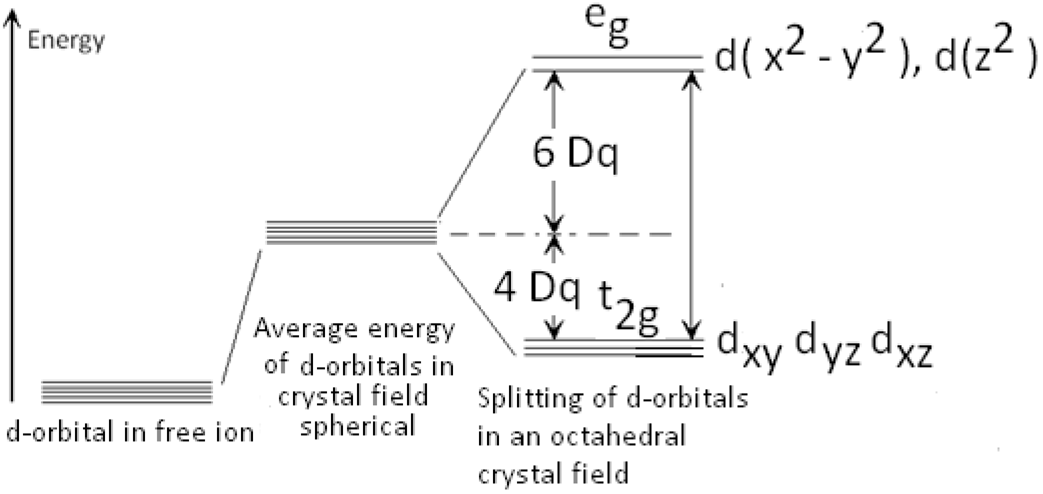
Halides donors < O donors < N donors < C donors

Crystal field splitting in octahedral complexes

The octahedral arrangement of six ligands surrounding the central metal ion can be shown as follows



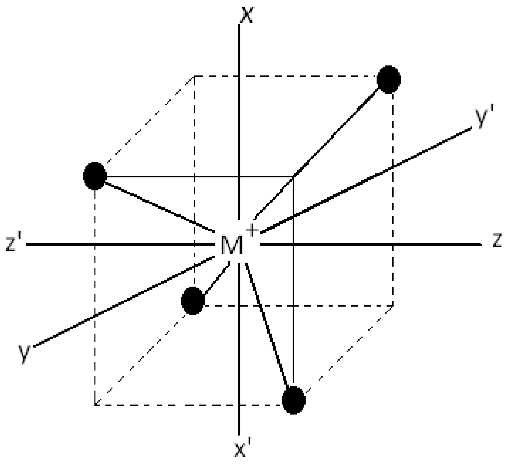
It is obvious from the figure, that ligands approaching the x, y, and z axis. The two d orbitals namely d(x^2 –y^2) and d(z^2) will suffer more electrostatic repulsion and hence their energy will be grater than other three orbitals d(xy), d(yx) and d(xz) which will have their lobes lying between the axis
Thus degenerate set of d-orbitals split into two sets:
e_g orbitals of higher energy including d(x^2 –y^2) and d(z^2)
and t_{2g} orbitals of lower energy including d(xy), d(yx) and d(xz)
The crystal field splitting is measured in terms of energy difference between t_{2g} and e_g orbital and is denoted by a symbol Δ_o . It is generally measured in terms of D_q. It is called as crystal field splitting energy or crystal field stabilization energy
E_g orbitals are 6Dq above the average energy level and t_{2g} orbitals are 4Dq below the average energy level



Significance of Δ_0

A strong field ligand approaches the central metal atom/ion strongly and thus the magnitude of Δ_0 is high. Hence in the case of strong field ligand, the magnitude of Δ_0 is grater than, the pairing energy (the energy required to pair up two negatively charged electrons having opposite spin in an orbital). However, under the influence of weak field ligand, Δ_0 is smaller than pairing energy (P)
Now, let us consider the d^4 configuration of the central atom/ion. The first three electrons will go into t_{2g} orbitals using Hund’d rule of maximum multiplicity. The fourth electron will go in the e_g orbital when the ligands are weak as, Δ_0 < P giving the configuration $t_{2g}^3e_g^1$. But if the ligands are strong, then the fourth electron will pair up when any of the singly occupied t_{2g} orbitals (as Δ_0 >P) to give the configuration $t_{2g}^4e_g^0$

Crystal field splitting in tetrahedral complexes



The tetrahedral arrangement of four ligands surrounding the metal ions can be shown as shown in figure.

It is obvious from the figure that none of the d-ornital point exactly towards the ligands. However, three d-orbitals d(xy), d(yz) and d(zx) are pointing close towards ligands

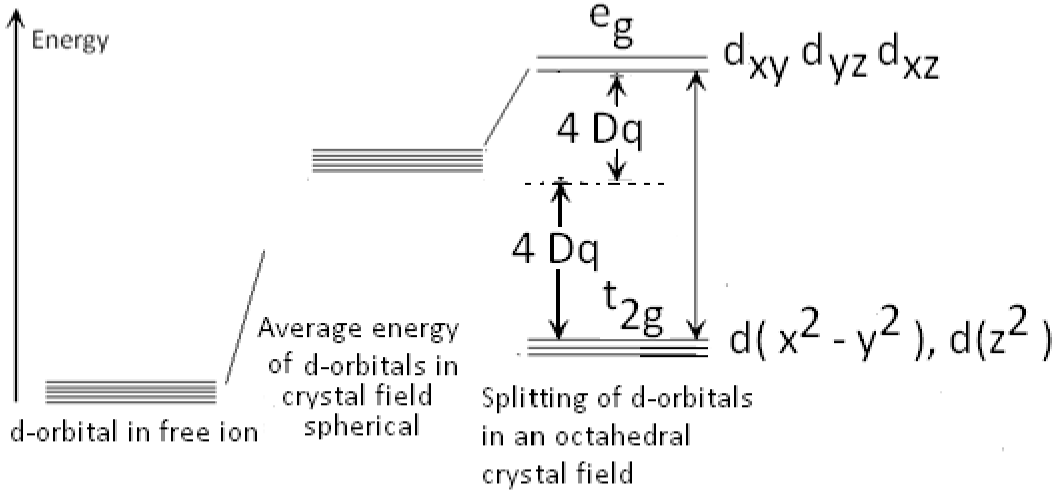
As a result of this, the energy of these three orbitals increases much more than the other two d-orbitals d(x^2 –y^2) and d(z^2). The d-orbitals thus split in two sets of orbitals: t_{2g} orbitals of higher energy including d(xy), d(yz), d(xz) and e_g orbitals of lower energy including d(x^2 –y^2) and d(z^2)

Energy difference between two sets of orbitals is represented by Δ_f. However splitting is much smaller than that in octahedral complexes

$$\Delta_t \approx -\frac{4}{9}\Delta_o$$

Negative sign denotes that order of splitting in tetrahedral complexes is reverse of that in octahedral complexes.

Because of the small value of Δ_t, electrons generally do not pair and results in formation of high-spin complex.



Limitation of Crystal field theory

The crystal field model is successful in explaining the formation, structures, colour and magnetic properties of coordination compounds to a large extent.

However, from the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. The anionic ligands actually are found at the low end of the spectrochemical series.

Further, it does not take into account the covalent character of bonding between the ligand and the central atom.

These are some of the weaknesses of CFT, which are explained by ligand field theory (LFT) and molecular orbital theory

Factors affecting the stability of complexes

1) A coordinate compound is formed in solution by the stepwise addition of ligands to metal ion. The overall stability constant is given by
   M + nL ⇋ MLn

$$\beta_f = \frac{[MLn]}{[M][L]^n}$$

Higher the value of β_f more stable is the complex or more the quantity of ML_n be exists in solution.

Free metal ions rarely exist in the solution so that M will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them.

For simplicity, we generally ignore these solvent molecules and write stability constants as follows in the formation of MLn are

$M + L \leftrightharpoons ML \quad K_1 = [ML]/[M][L]$

$ML + L \leftrightharpoons ML_2 \quad K_2 = [ML_2] / [ML][L]$

$ML_2 + L \leftrightharpoons ML_3 \quad K_3 = [ML_3] / [ML_2][L]$

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$ML_{n-1} + L \leftrightharpoons [ML_n] / [ML_{n-1}][L]$

where *K*1, *K*2, etc., are referred to as **stepwise stability constants.**

Alternatively, we can write the **overall stability constant** thus:

M + nL ⇋ ML4

$\beta = [ML_n]/[M][L]^n$

The stepwise and overall stability constant are therefore related as follows:

$\beta 4 = K_1 \times K_2 \times .... \times K_n$

2) Higher is the charge density on the central metal ion, grater is the stability of the complexes. For example $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(CN)]^{4-}$
3) More is the basic character of ligand, more stable is the complex
4) Chelating ligands form more stable complexes than the monodentated ligands

ISOMERISM

Compounds having the same chemical formula but different physical and chemical properties due to the different structural arrangements are called isomers.
This phenomenon is known as isomerism.
Coordination compounds exhibit two major types of isomerism, namely
(A) structural isomerism and (B) stereoisomerism (space isomerism).
Each of these is further classified as shown below.

A) Structural isomerism

a) Coordination isomerism b) Ionisation isomerism
c) Hydrate or Solvate isomerism d) Linkage isomerism
e) Ligand Isomerism

B) Stereoisomerism

a) Geometrical isomerism b) Optical isomerism

A) Structural isomerism

a) Coordination isomerism

In a bimetallic complex, both complex cation and complex anion may be present. In such a case the distribution of ligands between the two coordination spheres can vary, giving rise to isomers called the coordination isomers. This phenomenon is called coordination isomerism. This isomerism is illustrated by the following pairs of complexes where the complex cation and anion contain different metal centres.

1. $[Co(NH_3)_6]$ [Cr(CN)6] and $[Cr(NH_3)_6]$ $[Co(CN)_6]$
Hexammine hexacyano Hexamine hexacyano
cobalt(III) chromate(III) chromium (III) cobaltate (III)

2. [PtII(NH3)4] [CuCl4] and [Cu(NH3)4] [PtCl4]
Tetraammine Tetrachloro Tetraammine Tetrachloro
platinum (II) cuparate (II) copper (II) platinate (II)

b) Ionisation isomerism

Coordination compounds having the same molecular formula but forming different ions in solution are called ionisation isomers. This property is known as ionisation isomerism.
An example of this type of isomerism is furnished by the red-violet,
$[Co(NH_3)_5Br]SO_4$ $[Co(NH_3)_5SO_4]Br$
pentaamminebromocobalt(III) sulphate pentaamminesulphatocobalt (III) bromide

The red-violet isomer yields sulphate ion and the red isomer furnishes bromide ion in solution.

$[Co(NH_3)_4Cl_2]NO_2$ and $[Co(NH_3)_4NO_2Cl]Cl$
Tetraamminedichlorocobalt(III) nitrite Tetraamminechloronitrocobalt(III) chloride

$[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5 SO_4]NO_3$

pentaamminenitratocobalt(III) sulphate pentaamminesulphatocobalt(III) nitrate

c) Hydrate isomerism or Solvate isomerism

The best known examples of this type of isomerism occurs for chromium chloride "$CrCl_3.6H_2O$" which may contain 4, 5, (or) 6 coordinated water molecules.

1. $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ - Bright green
Tetraaquadichlorochromium(III) chloride dihydrate
2. $[Cr(H_2O)_5Cl]Cl_2.H_2O$ - grey-green
Pentaaquachlorochromium(III) chloride monohydrate
3. $[Cr(H_2O)_6]Cl_3$ - Violet
Hexaaquachromium(III) chloride

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl^- ions, would find 1,2, and 3 Cl^- ions in solution respectively.

d) Linkage isomerism

Linkage isomerism occurs with ambidentate ligands. These ligands are capable of coordinating in more than one way. The best known cases involve the monodentate ligands SCN^-/NCS^- and NO_2 -/ONO

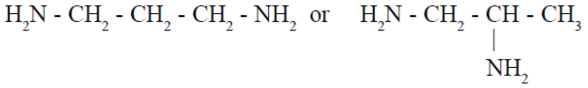
Forexample

$[Co(NH_3)_5ONO]Cl_2$ the nitrito isomer - red colour
pentaamminenitritocobalt(III) chloride - O attached

$[Co(NH_3)_5 NO_2]Cl_2$ the nitro isomer - yellow colour
pentaamminenitrocobalt(III) chloride - N attached

e) Ligand isomerism

Ligand isomerism arises from the presence of ligands which can adopt different isomeric forms. An example is provided by diaminopropane, which may have the amine groups in the terminal (1,3-) positions or in the 1,2-positions.



$H_2N - CH_2 - CH_2 - CH_2 - NH_2$ or $H_2N - CH_2 - \underset{\displaystyle NH_2}{\underset{|}{CH}} - CH_3$

B)Stereoisomerism (space isomerism)

Consider two compounds containing the same ligands attached to the same central metal ion, but the arrangement of ligands in space about the central metal ion are different, then these two compounds are said to be stereoisomers and this phenomenon is known as stereoisomerism. There are two different types of stereoisomerism.

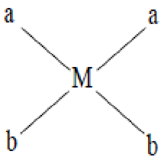
a) Geometrical isomerism or b) Optical isomerism.

a) **Geometrical (or) cis-trans isomerism**
Geometrical isomerism is due to ligands occupying different position around the central ion. The ligands occupy position either adjacent to one another or opposite

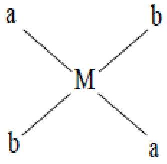
to one another. These are referred to as cis-form respectively. This type of isomerism is, therefore, also referred to as cis-trans isomerism. Geometric isomers are possible for both square planar and octahedral complexes, but not tetrahedral

Geometrial isomerism in 4-coordinate complex

.(1) [Ma_2b_2] type complexes Square planar



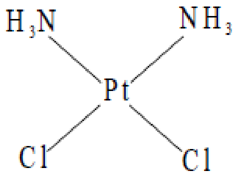
cis-isomer



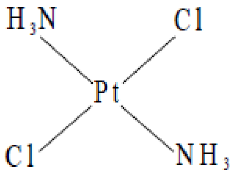
trans-isomer

In a cis-isomer two identical (or) similar groups are adjacent to each other whereas in a trans-isomer they are diametrically opposite to each other.

Square planar complexes of the type $[Ma_2b_2]^{n+}$ where a and b are monodentate ligands, exist as cis and trans-isomers as shown



cis-isomer



trans-isomer

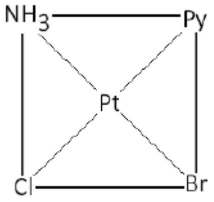
Example of this type of complexes are [Pt $(NH_3)_2$ Cl_2] and [Pd$(NH_3)_2$ $(NO_2)_2$].

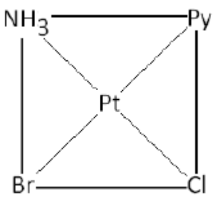
The cis trans isomers of these compounds are represented as Cis-diamine dichloroplatinum(II) and trans- diammine dichloroplatinum(II)

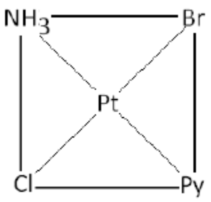
(2) [Mabcd] type complexs

Square planar complex of this type exist in three isomeric forms for example

[Pt(NH_3)(Py)(Cl)(Br)] exist in the following structures



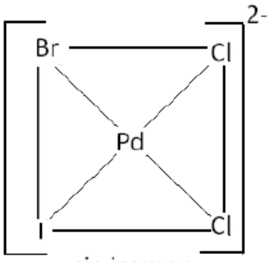




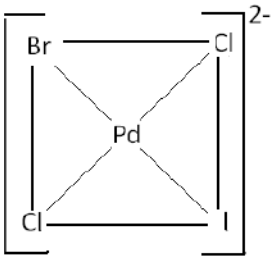
(3) [Ma_2bc] type complexes

Square planar complexes of this type also shows cis-trans isomerism.

For example $[Pd(Cl)_2Br\ I]^{2-}$ exists in the following cis-trans



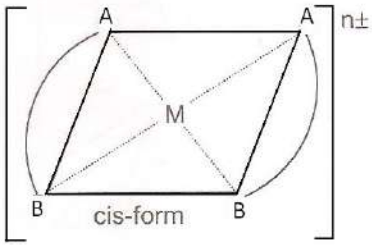
cis-isomer

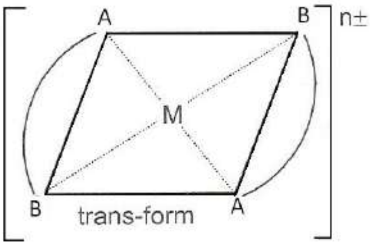


trans-isomer

(4)$[M(AB)_2]^{n\pm}$ type complex

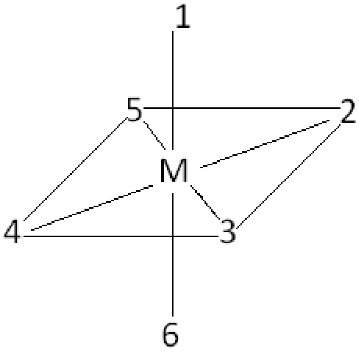
Here m is the central metal ion and (AB) represents an unsymmetrical bidentate ligand(A) and (B) arethe two ends (i.e. coordinating atoms) of the bidentates ligands such type of complexes also show trans and cis isomerism





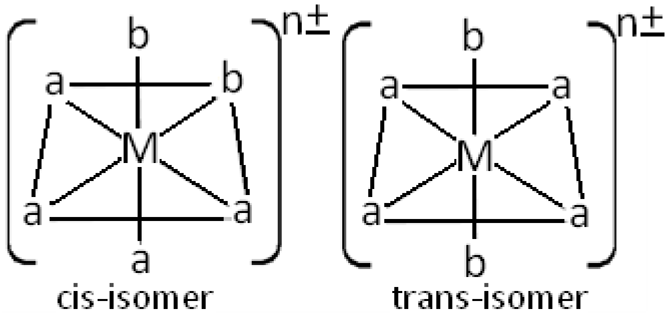
For example [Pt(gly)$_2$]; here gly represents the glycinato ligands, $NH_2CH_2COO^-$ which has N (A)and O (B)atoms as its donar

Geometrial isomerism in 6-coordinate complex, octahedral complex

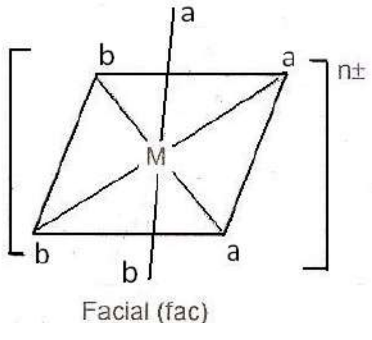


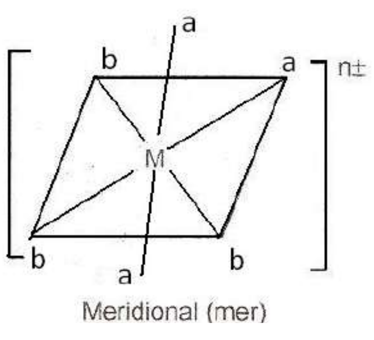
A complex compound having the central metal ion with coordination number equal to 6 has octahedral shape. The system used for numbering different positions of ligands in an generally it is assumed that the 1,2 positions are cis-positions. Normally it is taken that 1,6 positions are trans-positions

(1)An octahedral complex of the type [Ma$_4$b$_2$] where a and b are monodentate ligands, exists as two geometrical Isomers:



(2) [Ma$_3$b$_3$] type complexes





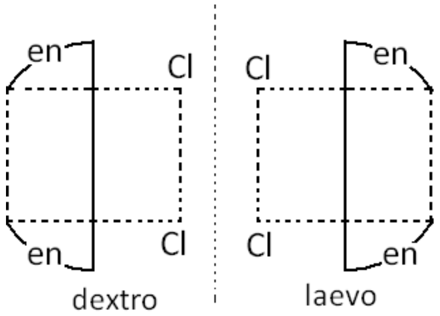
When each trio of donor atoms(viz ligands (a, a and a) occupy adjacent position at the corners of an octahedral face, we have facial isomers

When the positions are around the meridian of octahedron, . 0we get Meridional (mer) isomer

b) Optical Isomerism

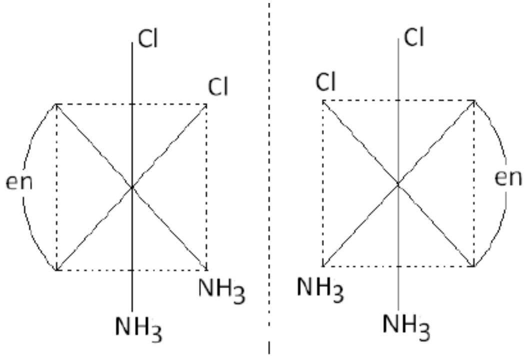
This is a phenomenon in which certain organic or inorganic compounds have the property of rotating plane polarized light. The compounds which exhibit this property are called optical isomers. The optical isomers of a compound have identical physical and chemical properties. The only distinguishing property is that the isomers rotate the plane of polarized light either to the left or right. If the rotation is on the leftside, then that isomer is levo and if on right side, then isomer is dextro. The equal proportion of levo and dextro mixture is called racemic mixture

It is generally found octahedral chelate ions. The two isomers of this type of complex are mirror image of each other and cannot super impose on each other, hence they possess chirality character.

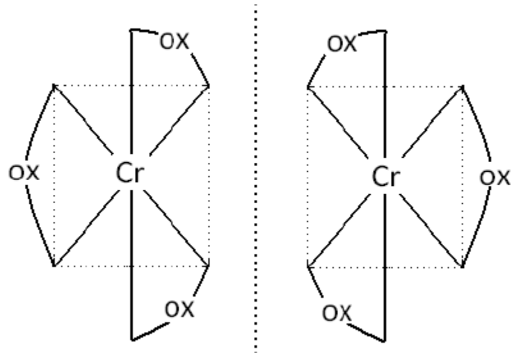


coordination compound of type $[PtCl_2(en)_2]^{2+}$ two geometrical isomers are possible. They are cis and trans. Among these two isomers, cis isomer shows optical activity because the whole molecule is asymmetric.

The optical isomers of $[CoCl_2(en)(NH_3)_2]^+$ are as follows



Optical isomeric structure of $[Cr(ox)_3]^{3-}$ or $[Cr(C_2O_4)_3]^{3-}$ as follows



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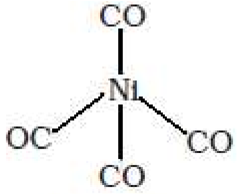
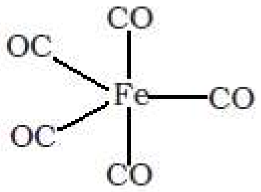
Bonding in Metal Carbonyls

The homoleptic carbonyls (compounds containing carbonyl ligands only) are formed by most of the transition metals. These carbonyls have simple, well defined structures. Tetracarbonylnickel(0) is tetrahedral,



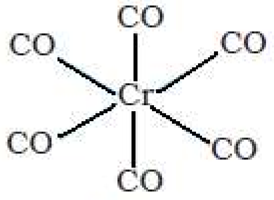
$Ni(CO)_4$
Tetrahedral

Pentacarbonyliron(0) is trigonalbipyramidal



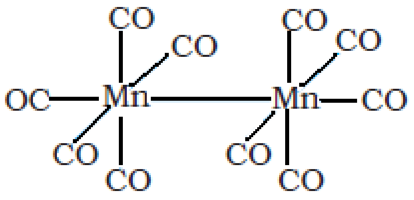
$Fe(CO)_5$
Trigonal bipyramidal

Hexacarbonyl chromium(0) is octahedral.



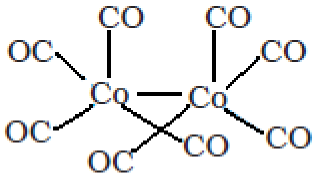
$Cr(CO)_6$ Octahedral

Decacarbonyldimanganese(0) is made up of two square pyramidal $Mn(CO)_5$ units joined by a Mn – Mn bond.



$[Mn_2(CO)_{10}]$

Octacarbonyldicobalt(0) has a Co – Co bond bridged by two CO groups



$[Co_2(CO)_8]$

Colour of coordination complexes

(i)Colour of a complex is not because of the light absorbed but is due to the light reflected (complementary colour) e.g. If radiation corresponding to red light are absorbed from visible region, the compound appears to have blue colour
(ii0 In coordination complexes energy difference (Δ) between two d-sets of d-orbitals is small. Radiations of appropriate frequency absorbed from visible region can cause excitation of d-electron from lower energy orbital to higher energy orbital. Remaining light is transmitted and compound appears coloured
(iii)IF there are no d-electrons present or completely filled d-orbitals are present then there is no d-d transition possible and complex appears colourless

Importance and applications of Coordination Compounds

Coordination compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine.
These are described below:

- Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α–nitroso–β–naphthol, cupron, etc.
- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.
- Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc
- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.
For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.
- Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin B_{12}, cyanocobalamine, the anti–pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).
- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.

- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ than from a solution of simple metal ions.
- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.
- There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by the chelating ligands D–penicillamine and desferrioxime B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: *cis*–platin and related compounds.

BASICS OF REACTION MECHANISM

Electronic effect in a covalent bond

(A)Inductive effect (I-effect)

When an electron withdrawing or electron releasing group is attached to the carbon chain, the displacement of σ – electrons along the saturated carbon chain takes place due to the difference in electro negativities. This induces a permanent polarity in the compound. This is called as inductive effect or simply I –effect. This effect weakens with the increasing distance from electronegative atom and becomes negligible after three carbon atoms.

(i)- I effect

When an electron withdrawing group is attached to the carbon chain, it pulls the electron towards itself and renders the carbon chain with partial positive charge. Thus electron withdrawing group is said to exert a -I effect

$\overset{\delta+}{C} \rightarrow \overset{\delta-}{X}$

Some important electron withdrawing groups in order of –I effect in the order of decreasing inductive effect are as follows

$-NR_3^+$, $-SR_2^+$, $-NH_3^+$, $-NO_2$, $-SO_2R$, -CN, $-CO_2H$, -F, -Cl, -Br, -I, -OAr, -COOR, -OR, -COR, -SH, $-C\equiv CR$, -Ar, $-CH=CR_2$

Amongst sp, sp^2, sp^3 hybridized carbon, the order of -I effect is $sp>sp^2>sp^3$

Because of –I effect (electron withdrawing group) electron density decreases hence

-basic nature of compound decreases

Acidic nature of compound increases

Phenol is more acidic than water because of electron withdrawing nature of benzene ring.

Acidic strength of various haloacetic acid is in the order

$F-CH_2COOH > Cl-CH_2COOH > Br-CH_2COOH > I-CH_2COOH$

ii)+I effect

When an electron releasing group is attached to the chain, it develops negative charge on the chain and said to exert +I effect

$\overset{\delta-}{C} \leftarrow \overset{\delta+}{Y}$

Some important electron releasing group in order of their +I effect are as follows

$-O^- > -COO^- > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3 > -CH_3 > D > H$

Because of +I effect (electron releasing group) electron density on the carbon chain increases, hence

-basic nature of compound is increases

-acidic nature of compound is decreases

Eg. methanol is more basic than water because of +I effect of C_2H_5 group

Solved problem

Q) Of the ethanol and trifluoro ethanol which is more acidic?

Solution

Trifluoro ethanol is more acidic because strong –I effect of trifluoromethyl group stabilizes the anion of trifluoroethanol.

$$F_3C-CH_2-OH \rightleftharpoons F_3C \leftarrow CH_2 \leftarrow O^- + H^+$$

While +I effect of ethyl group destabilizes the anion of ethanol

$$H_3C-CH_2-OH \rightleftharpoons H_3C \rightarrow CH_2 \rightarrow O^- + H^+$$

Q) Write the order of basicity of NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ in aqueous medium

Solution

$(CH_3)_2NH$ (dimethyl amine) is more basic than CH_3NH_2 (methyl amine), which is more basic than NH_3 because of +I effect of CH_3 group. which increases the availability of loan pairs on the nitrogen atom

However $(CH_3)_3N$ is less basic than dimethyl amine and methyl amine due to steric hinderance of three bulky methyl groups and less solvation effect

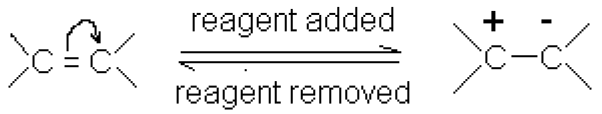
Thus order of basicity

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

Electromeric effect

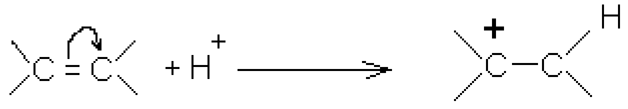
It is a temporary effect involving complete transfer of π- electrons of a multiple bond towards one of the bonded atom in the presence of an attacking reagent

If attacking reagent is removed, charge disappear and compound regains its original form. Therefore this effect is temporary and reversible

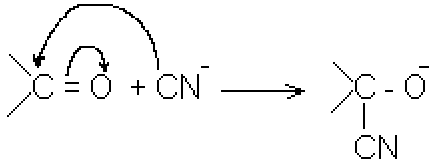


a)+E effect

If π-electrons transfer towards the atom to which attacking species attacks, the effect is known as +E effect



b) If π-electrons transfer towards the atom of the double bond other than the one to which attacking species finally attach, the effect is known as –E effect.



Resonance effect or mesomeric effect (M-effect or R effect)

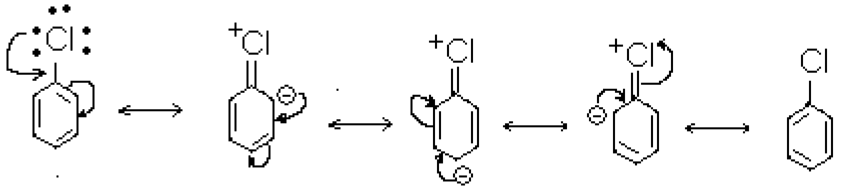
Mesomeric effect takes place in conjugated system i.e. having alternate σ and π –bonds or in system having lone pair in conjugation with π bond. It is defined as permanent polarization effect in which electron pair get displaced from one part of the conjugated system to another part, thus producing polarity in the molecule.

a)+M effect or +R effect

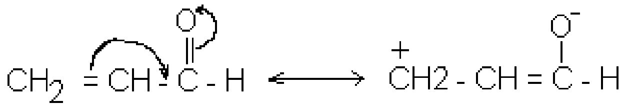
a group is said to have +M effect if flow of electrons is away from it e.g. –OH, -OR, -SH, -NH_2, -NHR, -NR_2 , -Cl, -Br, -I etc

$$CH_2 = CH - NH_2 \longleftrightarrow {}^-CH_2 - CH = \overset{+}{N}H_2$$

This effect extends the degree of delocalization and thus imparts stability to the molecule +M effect of halogen atom explains the low reactivity of vinyl chloride and aryl chloride.



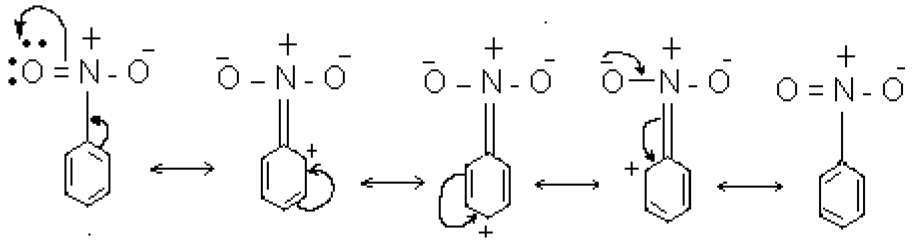
b) –M effect or –R effect



$$CH_2 = CH - \overset{O}{\overset{\|}{C}} - H \longleftrightarrow \overset{+}{C}H2 - CH = \overset{O^-}{\overset{|}{C}} - H$$

A group is said to have –M effect if electrons are displaced towards that group. Electron withdrawing group exert ---M effect

e.g >C=0, -CHO, -COOR, -CN, -NO_2 etc



Conditions for writing resonance structures

The following are essential conditions for writing resonating structures

1.The contributing structure should have same atomic positions

2.The contributing structures should have same number of unpaired electrons

3.The contributing structures should have nearly same energy

4.The structures should be so written that negative charge is present on an electronegative atom and positive charge is present on an electropositive atom

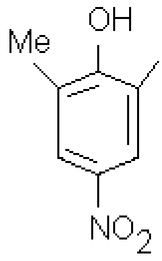
5.In contributing structures, the like charges should not reside on adjacent atoms

Resonance energy = Actual bond energy – energy of the most stable resonating structures

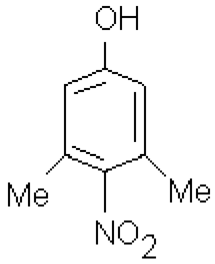
For example, the resonance energy of carbon dioxide is 138 kJ/mol. This means that the actual molecule of CO_2 is about 138kJ/mol more stable than the most stable structure among the contributing structures.

Solved problem

Q) Which phenol is more acidic



(I)



(II)

Solution

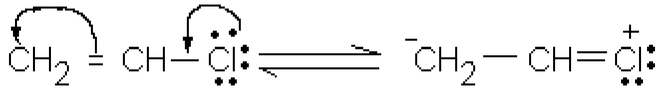
2,6-dimethyl-4-nitophenol(I) is more stable than 3,5-dimethyl -4-nitrophenol(II)

The pheoxide of (I) is stabilized by -I and -R effect of NO_2 group and destabilized by +I effect of the two Me groups at the ortho positions. The major contribution comes from –R effect of NO_2 group. The phenoxide ion of (II) is stabilized by –I effect of NO_2 and destabilized by two Me groups at meta positions. The NO_2 group in (II) is not coplanar with benzene ring due to the bulky methyl group attached to the adjacent C-atoms. Thus, the –R effect of NO_2 group is ruled out

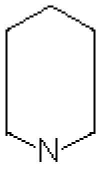
Q) $CH_2=CH-Cl$ does not give $CH_2=CH – OH$ easily on treatment with OH^- explain

Solution

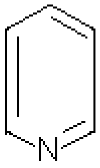
As C – Cl bond acquires double bond character due to resonance, substiturion of Cl^- by OH^- is difficult



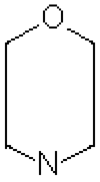
Q)State the order of basicity of the following compounds



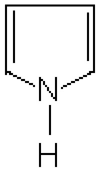
(I)



(II)



(III)



(IV)

In iv, lone pair of electrons are involved in aromaticity so least easily available for donation.

In II, lone pair of electrons is involved in resonance.

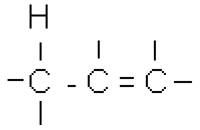
In I and III availability of loan pair is maximum but presence of higly electronegative oxygen in atom (iii) makes it comparatively less readily available for donation. Thus order of basicity is

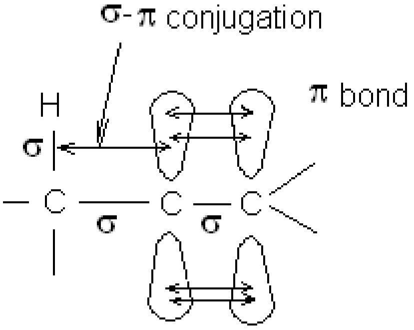
I > III > II> IV

Hyperconjugation effect

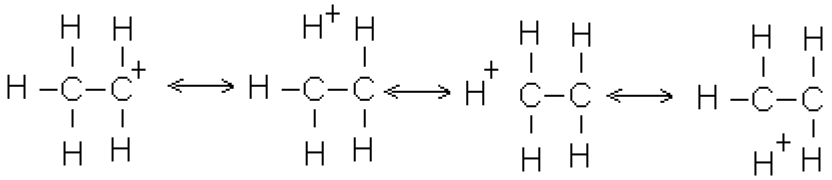
This involves the conjugation between σ – electrons of a single carbon-hydrogen bond and the π-electron of the adjacent multiple bond.

p-orbital of the double bond overlaps with σ orbital of α C-H bond of alkyl group, thus there occurs delocalization of 4 electrons over 4 atom. 1 hydrogen and 3-carbon atoms

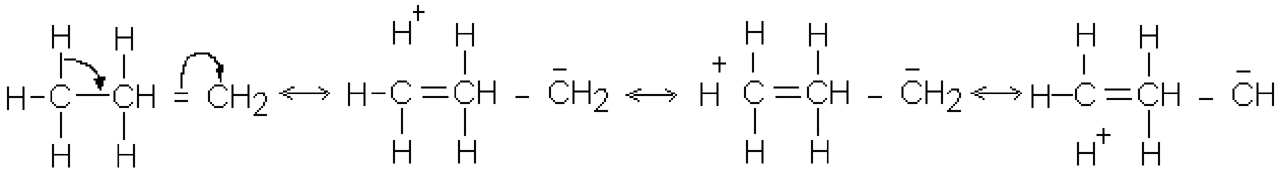




It is also called as no bond resonance because in the different cannonical form, no bond exists between carbon and H-atom of the alkyl group. For example, resonance structure of ethyl cation can be shown as follows



Hyperconjugation is also possible in alkenes and alkyl arenes. For example, for propene can be shown as follows



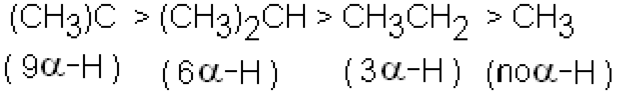
Significance of hyperconjugation

(a)Stability of alkenes

Greater the number of α – H atom in an alkene. Greater will be its stability. i.e more the number of alkyl groups attached to the doubly bonded carbon atom are more stable

(b)Stability of carbocation and alkyl free radicals

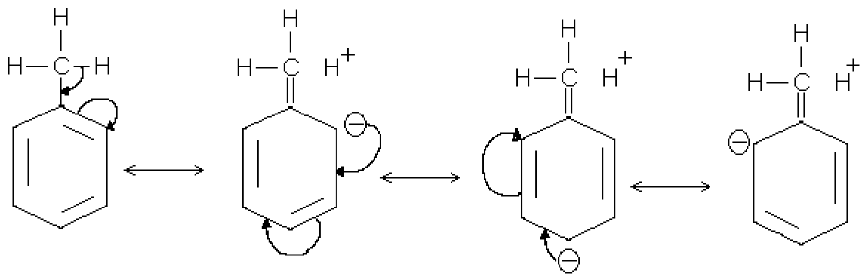
On the basis of number of hydrogen atoms order of stability of carbocations is given by



$$\underset{(9\alpha\text{-H})}{(CH_3)\overset{+}{C}} > \underset{(6\alpha\text{-H})}{(CH_3)_2\overset{+}{C}H} > \underset{(3\alpha\text{-H})}{CH_3\overset{+}{C}H_2} > \underset{(\text{no}\alpha\text{-H})}{\overset{+}{C}H_3}$$

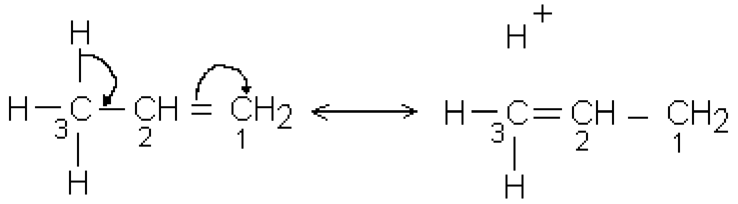
(c) Directive influence of alkyl groups

The o,p- directive influence of an alkyl group can be explained on the basis of hyperconjugation



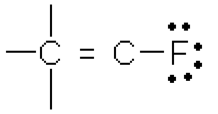
Since electron density at o and p-position with respect to CH_3 group is more and thus electrophilic substitution takes place preferentially at o, p-position with respect to Ch or any alkyl group

(d)Shortening of carbon-carbon single bond adjacent to multiple bond

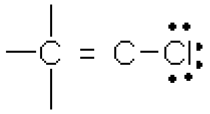


Because of hyperconjugation C_3C_2 single bond acquires some double bond character and $C_3 - C_2$ bond length (1.49Å) becomes slightly shorter than a normal single C-C bond length (1.54Å)

Solved problems



(I)



(II)

In which case lone pair – π conjugation will be more preferred?

Solution

Lone pair - π conjugation in structure (I) is preferred because the overlapping of 3p orbital of chlorine with 2p orbital of carbon atom does not take place effectively due to the difference in energy states of the orbitals involved

Q) Arrange $(CH_3)_3C$ - , $(CH_3)_2CH$- , CH_3CH_2 – when attached to benzene or an unsaturated group in increasing order of inductive effect is

Solution

When above groups are attached to benzene or an unsaturated group, there occurs hyperconjugation and hyperconjugative effect and thus inductive effect given by alkyl group follows the order

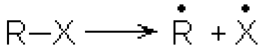
$$\underset{2\alpha\text{-H}}{CH_3CH_2-} < \underset{1\alpha\text{-H}}{(CH_3)_2CH-} < \underset{0\alpha\text{-H}}{(CH3)3C-}$$

Cleavage of covalent bonds

A covalent bond can be cleaved in two different ways

a) Homolytic cleavage

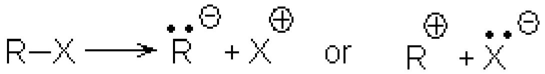
In homolytic cleavage each atom separate with one electron leading to the formation of highly reactive intermediate called free radicals. Such type of cleavage occurs generally in a gas phase or in solution in non-polar solvents and is catalyzed by ultraviolet light or high temperature or by radical initiators like peroxides. Free radicals are paramagnetic in nature and are extremely reactive.



$$R{-}X \longrightarrow \dot{R} + \dot{X}$$

b) Heterolytic cleavage or fission

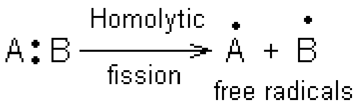
In heterolytic cleavage both the electrons of a covalent bond (shared pair of electrons) are taken away by one of the more electronegative atom. That’s why it is also known as unsymmetrical fission. Such cleavage occurs in polar solvents because of the ease of separation of charge and stabilization of the resultant ion-pair through solvation. In such heterolytic fission, the charged species formed are either carbon bearing positive charge called carbocation or carbon bearing negative charge called carbanion



$$R{-}X \longrightarrow \ddot{R}^{\ominus} + X^{\oplus} \quad \text{or} \quad R^{\oplus} + \ddot{X}^{\ominus}$$

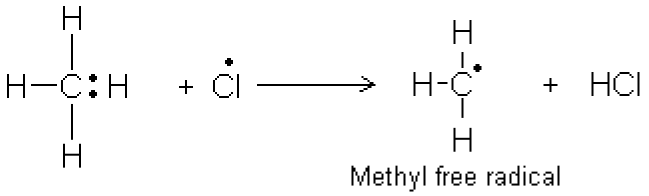
C) Free radical

A free radical may be defined as an atom or group of atoms having an unpaired electron. These are produced during the homolytic fission of a covalent bond

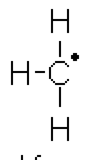


$$A{:}B \xrightarrow[\text{fission}]{\text{Homolytic}} \underbrace{\dot{A} + \dot{B}}_{\text{free radicals}}$$

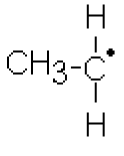
These free radicals are very reactive. This is because of the fact that they have a strong tendency to pair up their unpaired electron with another electron from wherever available. These are short lived and occur only as reaction intermediate during reaction. The alkyl free radical may be obtained when free radical chlorine attack methane.



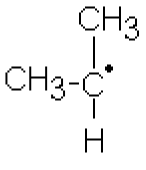
The free radicals may be classified as primary, secondary or tertiary depending upon whether one , two or three carbon atoms are attached to the carbon atom carrying the odd electron



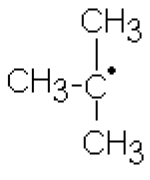
Methyl free radical



primary (1°)



secondary (2°)



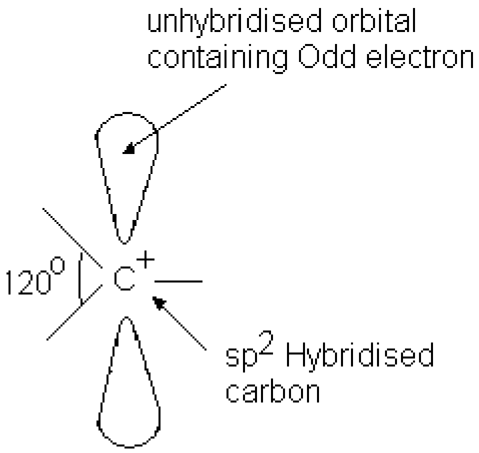
tertiary (3°)

Stability of free radicals: the order of stability of alkyl free radicals is

$$CH_3 < 1^{o} < 2^{o} < 3^{o}$$

This order of stability can easily be explained on the basis of hyperconjugation. Larger the number of alkyl groups attached to the carbon atom carrying the odd electron, greater this the delocalization of electrons and hence more stability of free radical.

Structure of alkyl free radical



The carbon atom in alkyl free radicals involves sp^2 hybridisation. Therefore, it has planar structure. The three hybrid orbitals are used in the formation of three σ bonds with three H atoms or alkyl group. The unpaired electron is present in unhybridised p-orbital

Attacking reagents

There are basically two types of reagents used in organic chemistry, the electrophiles and nucleophiles. In organic chemistry, the interaction of electrophile i.e. electron pair acceptors and nucleophiles i.e. electron pair donors are generally observed. Electrophiles in other words are called lewis acids and nucleophiles are called lewis bases

Electrophiles

Electrophiles are electron loving chemical species.(Electro-electron, phile loving).Therefore electrophiles are electron deficient species in search of electrons. These can be either positively charged or neutral. Or have an empty orbital or a heterolytically breakable bond (to a leaving group)

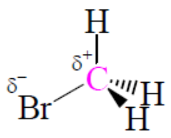
Positive Electrophiles

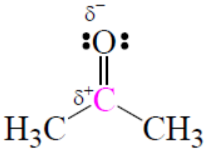
H^+, H_3O^+, NO_2^+, NO^+, R^+, Cl^+, Br^+, RCO^+ etc

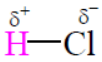
Neutral Electrophiles

BF_3, $AlCl_3$, $FeCl_3$, $ZnCl_2$, SO_3, $SnCl_4$, $R^{\cdot}$ (free radicals), $:CR_2$ (carbenes), :NR(nitrenes), $BeCl_2$

Polar







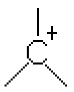
Polarizable

Br- Br, Cl – Cl, I – I

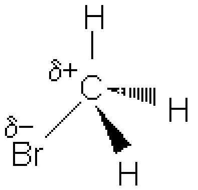
Since electrophiles are electron deficient species they are also termed as Lewis acids

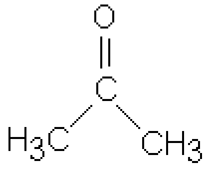
Electrophiles strength

Given the same electrophilic atom, a greater degree of positive charge gives a stronger Electrophile

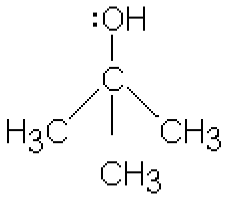


is better electrophile than





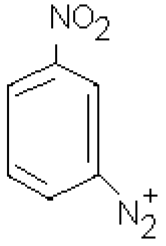
is a better electrophile than



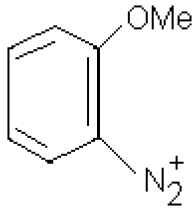
The strength of electrophiles without empty orbitals (to which a bond must be broken before another can form) is also influenced by the nature of the group to which the bond will be broken (leaving group)

Solved problem

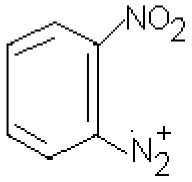
Q) Arrange the following electrophiles in the decreasing order of electrophilicity



(I)



(II)



(III)

Solution

(III) is the strongest electrophile because of –R effect of nitrogroup is also operative along with its –I effect but (I) has greater +R effect (lesser _I effect) and NO_2 from metaposition will only show –I effect. Thus, the decreasing order of electrophilicity is (III) > (c I) > (II)

Nucleophiles

Nucleophiles are electron rich species in the search of nucleus or positive centre or have π bonds Therefore they can be positively charged or neutral

Negative nucleophiles

OH^-, H^-, CN^-, CL^-, Br^-, I^-, $RCOO^-$, $RC\equiv C^-$, NH_2^-, SR^-, S^{2-}

Neutral nucleophiles

$H_2\ddot{O}:$, $R\ddot{O}H$, $\ddot{N}H_3$, $R\ddot{N}H_2$, $R\ddot{\underset{..}{S}}H$, $R\ddot{\underset{..}{O}}R$, $H_2\ddot{S}:$

Pi bonds

C_2H_4, C_2H_2 ,C_6H_6

Since nucleophiles are electron rich chemical species, these are also regarded as Lewis bases

Relative nucleophilic strength : depends on Charge , Solvent, aprotic solvent

Strength depending on Charge

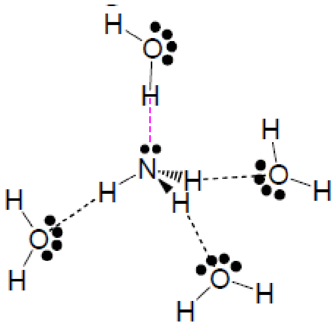
Given two nucleophiles with the same nucleophilic atom, a negative charge makes the atom more reactive In more general terms, the stronger base is the stronger nucleophile (given the same nucleophilic atom)

OH^- is better nucleophile than H_2O

Br^- is better nucleophile than HBr

Strength depending on Solvent

Hydrogen-bonding solvents (protic solvents) reduce nucleophilicity by interacting with the free electrons in the nucleophile

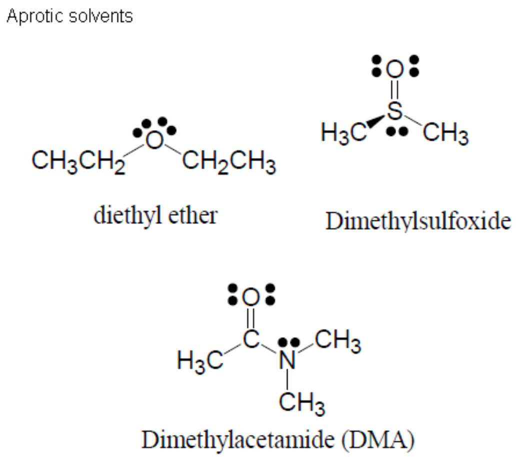


This effect is particularly strong for small atoms with concentrated charges, thus larger atoms are more nucleophilic in protic solvents (~opposite basicity)

$HS^- > HO^-$

$I^- > Br^- > Cl^- > F^-$

Strength depending on aprotic solvent



diethyl ether

Dimethylsulfoxide

Dimethylacetamide (DMA)

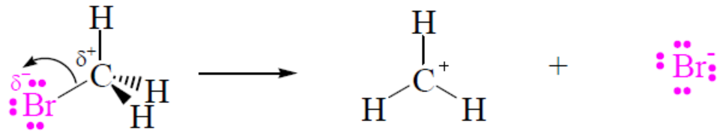
In solvents that can accept, but not donate hydrogen bonds, nucleophiles are not solvated (but the cations providing countercharges are) Thus the nucleophilicity and basicity are more closely correlated:

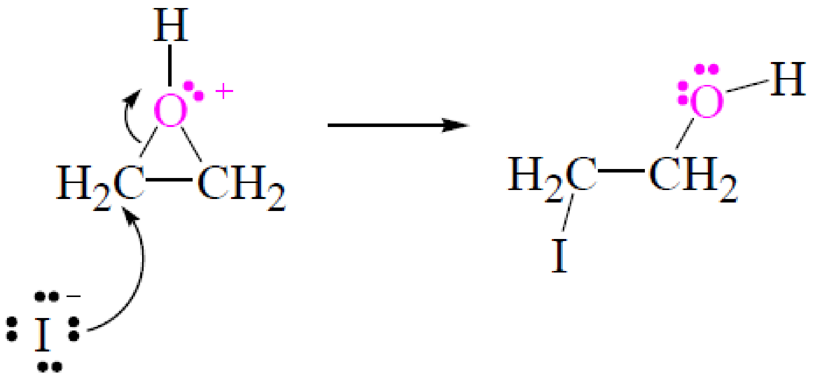
$F^- > Cl^- > Br^- > I^-$

Basicity is a thermodynamic property and nucleophilicity is a kinetic property thus Strong nucleophiles tend to be strong bases, but these properties are not measured the same way

Leaving Groups

Leaving groups are the fragments that retain the electrons in a heterolytic bond cleavage:





Leaving Group Stability

- Weaker bases are more stable with the extra pair of electrons and therefore make better leaving groups

$H_2O > OH^-$

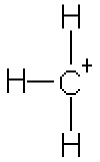
$I^- > Br^- > Cl^- > F^-$

Various intermediates

Whenever reaction takes place in organic chemistry, the reactants are not directly transformed into the products. The reaction proceeds via some intermediates, which are formed during the course of reaction and not very stable species. Intermediates are formed , by the attack of a reagent or by covalent fission in a reacting molecule. Some important reaction intermediates are discussed below

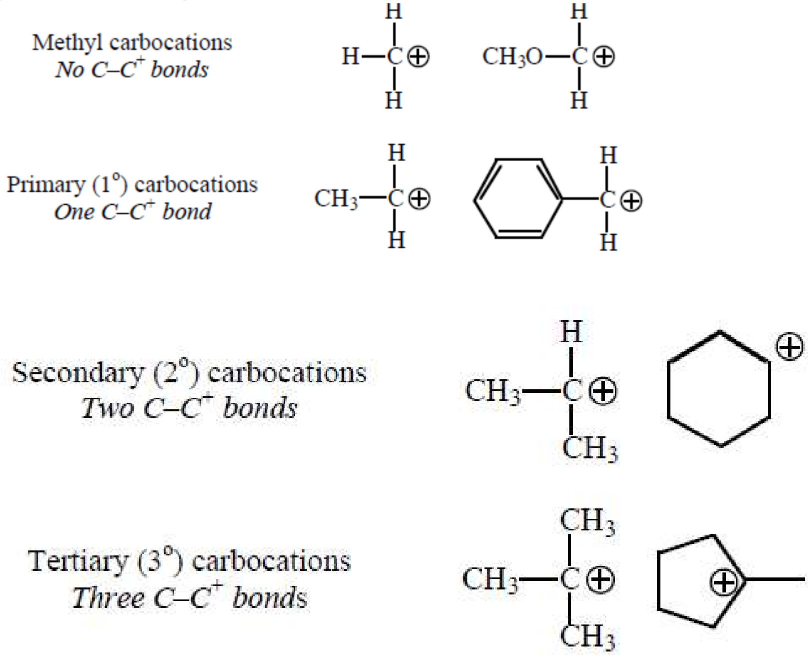
1.Carbocations (carbonium ions)

A carbocation is molecule in which a carbon atom bears three bonds and a positive charge. Carbocations are generally unstable because they do not have eight electrons to satisfy the octet rule.

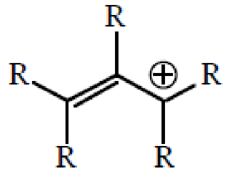


Carbocation Classification

In order to understand carbocations, we need to learn some basic carbocation nomenclature. A primary carbocation is one in which there is one carbon group attached to the carbon bearing the positive charge. A secondary carbocation is one in which there are two carbons attached to the carbon bearing the positive charge. Likewise, a tertiary carbocation is one in which there are three carbons attached to the carbon bearing the positive charge



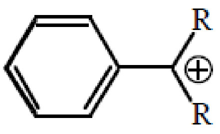
If the carbon bearing the positive charge is immediately adjacent to a carbon-carbon double bond, the carbocation is termed an allylic carbocation. The simplest case (all R = H) is called the allyl carbocation.



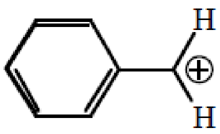
Generic allylic carbocation

The allyl carbocation

If the carbon bearing the positive charge is immediately adjacent to a benzene ring, the carbocation is termed a benzylic carbocation. The simplest case is called the benzyl carbocation.

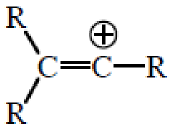


Generic benzylic carbocation

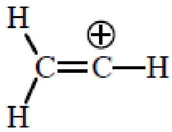


The benzyl carbocation

If the carbon bearing the positive charge is part of an alkene, the carbocation is termed a vinylic carbocation. The simplest case is called the vinyl carbocation. Note that the carbon bearing the positive charge has two attachments and thus adopts sp hybridization and linear geometry

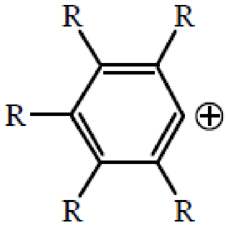


Generic vinylic carbocation

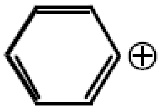


The vinyl carbocation

If the carbon bearing the positive charge is part of a benzene ring, the carbocation is termed an aryl carbocation. The simplest case is called the phenyl carbocation.



Generic aryl carbocation



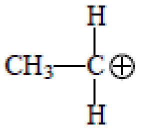
The phenyl carbocation

Carbocation Stability

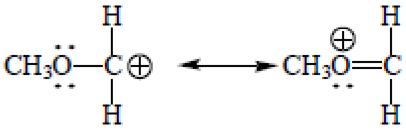
The stability of carbocations is dependent on a few factors

Resonance

Resonance is a stabilizing feature to a carbocation because it delocalizes the positive charge and creates additional bonding between adjacent atoms. Decreasing the electron deficiency increases the stability



No resonance



Resonance

The structure on the left does not have any resonance contributors in which electrons are donated to the carbon with the open octet. Compare this with the carbocation that has resonance and a delocalized positive charge. Charge delocalization imparts stability, so the structure with resonance is lower in energy.

In the example shown above, an oxygen atom lone pair is involved in resonance that stabilizes a carbocation.

In general, any adjacent lone pair or π bond can also be involved in resonance delocalization of a carbocation positive charge.

Allylic and benzylic carbocations enjoy resonance stabilization by delocalization of the positive charge to the adjacent π bond(s).

Vinylic and aryl carbocations do not enjoy resonance stabilization because their π electron clouds are perpendicular to the vacant p orbital of the carbocation. (Recall that resonance requires the interacting orbitals to be parallel so they can overlap. Without overlap there can be no resonance.)

Note the influence of inductive effect versus resonance on the energies of these molecules. The oxygen atom that is bonded to the carbocation on the right is more electronegative than the corresponding hydrogen atom in the left-hand structure. We would think that the inductive effect would pull electron density away from the carbocation, making it higher in energy. In actuality, resonance usually (but not always) outweighs other factors. In this case, carbocation stabilization by resonance electron donation is a more significant factor than carbocation destabilization by inductive electron withdrawal.

Inductive effect

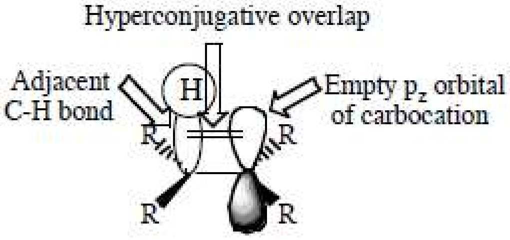
Methyl and primary carbocations without resonance are very unstable, and should never be involved in a reaction mechanism unless no other pathway is possible. More stable carbocations (secondary or tertiary with resonance, or any carbocation with resonance) is sufficiently stable to be formed in a mechanism under reasonable reaction conditions.

The second factor that should be considered when thinking about carbocation stability is the number of carbons attached to the carbon carrying the positive charge.

CH_3^+ (methyl; less stable) < RCH_2^+(1^o) < R_2CH^+(2^o) < R_3C^+ (3^o; more stable)

Hyperconjugation

We look at the number of bonding electrons that are attached to the carbocation because those bonding electrons will help in alleviating the positive charge. Bonding electrons from adjacent σ bonds may overlap with the unoccupied p orbital of the carbocation.



This phenomenon is termed hyperconjugation. Since the overlap supplies electron density to the electron-deficient carbocation carbon, we predict that increasing the number of hyperconjugative interactions increases carbocation stability.

Extending this idea, we predict that increasing the number of bonds adjacent to the carbocation by increasing the number of alkyl groups attached to the carbocation carbon results in an increase in carbocation stability. For example, a tertiary carbocation should be more stable than a secondary carbocation. This prediction is accurate.

Our simple prediction suggests that any adjacent bonding electron pair will participate in carbocation hyperconjugation. However, only C–H and C–C bonds provide a significant level of increased stability.

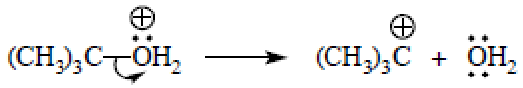
When considering the importance of hyperconjugation versus resonance as the more important stabilizing feature, resonance usually wins out. For example, a primary carbocation with resonance is more stable than a secondary carbocation without resonance. A secondary carbocation with resonance is usually more stable than a tertiary carbocation without resonance.

In vinylic carbocations, the positive charge is assigned to a carbon with sp hybridization. How does this influence the carbocation's stability? An sp orbital has more s character than an sp^2 orbital. Electrons in an s orbital are closer to the nucleus and therefore more tightly held than electrons in a p orbital. This can be taken to mean that the electronegativity of carbon increases with increasing s character.
Thus:
sp carbon (most s character; most electronegative) > sp^2
> sp^3 (least s character; least electronegative).

Electronegativity is a measure of electron attraction. So the stability of a cation is influenced by the electronegativity of the atom bearing the positive charge. The more electronegative the atom the less stable the cation. A vinylic carbocation carries the positive charge on an sp carbon, which is more electronegative than an sp^2 carbon of an alkyl carbocation. Therefore a primary vinylic carbocation is less stable than a primary alkyl carbocation.
Similar reasoning explains why an aryl carbocation is less stable than a typical secondary alkyl carbocation such as cyclohexyl carbocation. Because of their reduced stability, vinyl and aryl carbocations are not often encountered.

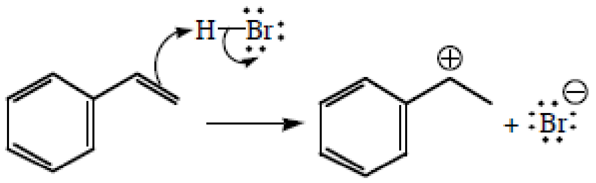
Carbocation Formation

Ionization of a Carbon - Leaving Group Bond. When a bond between a carbon atom and a leaving group ionizes, the leaving group accepts the pair of electrons that used to be shared in the covalent bond. This may leave the carbon atom with an open octet, resulting in a carbocation. The ionization is indicated with a curved arrow starting at the bond and pointing to the leaving group atom that accepts the electron pair. Better leaving groups or formation of a more stable carbocation result in lower activation energy and faster ionization. Carbon - leaving group bonding ionization is illustrated using an oxonium ion



$$(CH_3)_3C-\overset{\oplus}{\ddot{O}}H_2 \longrightarrow (CH_3)_3\overset{\oplus}{C} + \ddot{O}H_2$$

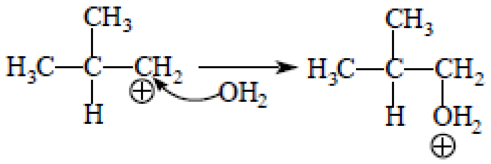
Electrophilic Addition to a π Bond. When an electrophile attacks a π bond, the π electron pair may form a new σ bond to the electron-deficient atom of the electrophile. (Not all additions to π bonds involve electrophiles or carbocations.) The other π bond carbon no longer shares the π electron pair, resulting in a carbocation. This addition is indicated with a curved arrow starting at the π bond and ending at the electron deficient atom of the electrophile. More powerful electrophiles or the formation of more stable carbocations result in lower activation energy and faster addition. Electrophilic addition to a π bond is illustrated by the reaction of HBr (an electrophile) with styrene ($PhCH=CH_2$). Note that the more stable carbocation (secondary with resonance) is formed. This is a key mechanistic feature of Markovnikov's Rule.



Three Facts of a Carbocation

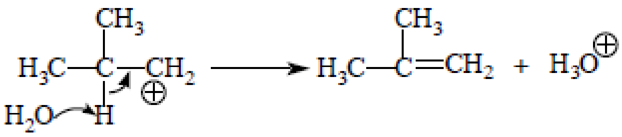
Now we consider how carbocations behave in reaction mechanisms. Generally speaking, carbocations are unstable due to their open octets and positive charges. Thus, their reactions will be strongly influenced by filling the octet of the carbon bearing the positive charge, or at least making this positive charge more stable. There are three common mechanism pathways (or ways) by which carbocations may achieve this stability. These ways are (a) capture a nucleophile, (b) lose a proton to form a π bond, and (c) rearrange. Note in each case that the carbon bearing the open octet gains a pair of electrons thus completing its octet.

Capture a nucleophile. The carbocation is electrophilic because it has a positive charge and (in most cases) a carbon atom with an open octet. The positive charge is neutralized when an electron pair is accepted and a new covalent bond is formed. By definition, a species that donates a pair of electrons to form a new covalent bond is a nucleophile. Because carbocations are very reactive, even weak nucleophiles such as water can be captured with ease.

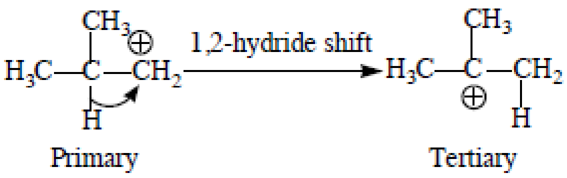


When carbocation deprotonation can lead to more than one product, the more stable product is major.

Rearrangement. The bonding electrons of a carbocation may shift between adjacent atoms to form a more stable carbocation. For example, rearrangement will occur if a secondary carbocation can be formed from a primary carbocation because a secondary carbocation is more stable than the primary carbocation. There can be two types of rearrangements. Shift of an alkyl group is called a 1,2-alkyl shift.



Shift of a hydrogen atom is called a 1,2-hydride shift. Hydride ion = H:$^-$



Of these two examples, hydride shift leads to a tertiary carbocation whereas alkyl shift leads to a secondary carbocation. Because a tertiary carbocation is more stable than a secondary carbocation, the hydride shift is favored in preference to the alkyl shift.

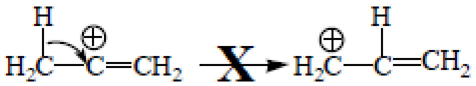
Any C–H or C–C bond adjacent to a carbocation may shift (including C–C bonds that are part of a ring), but only C–C and C–H bonds can migrate during carbocation rearrangement.

The most common carbocation rearrangements involve a carbocation rearranging into a more stable carbocation, such as 2° → 3°

with resonance. (So use these rearrangements with impunity.) Rearrangements that transform a carbocation into another of apparently equal stability are less common, but they do occur. (So before invoking this kind or rearrangement ask yourself if a better rearrangement, or some other mechanism step, is possible.) Rearrangement to a less stable carbocation is very unusual, but also does occur.

(This is the pathway of last very last resort. All other reasonable options must be ruled out first.)

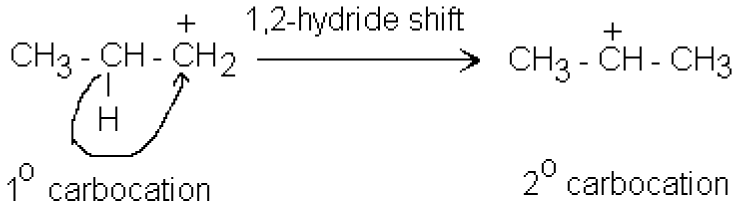
Vinylic carbocations generally do not rearrange, even if they can become more stable. For example, the rearrangement shown below does not occur, even though a secondary carbocation would rearrange to become a more stable allylic carbocation (primary with resonance).

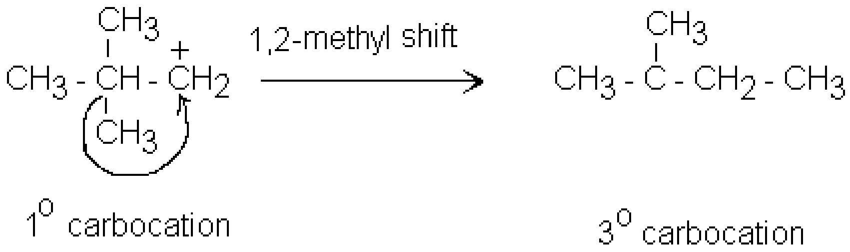


This resistance to rearrangement is probably due to orbital alignment restrictions during the rearrangement transition state.

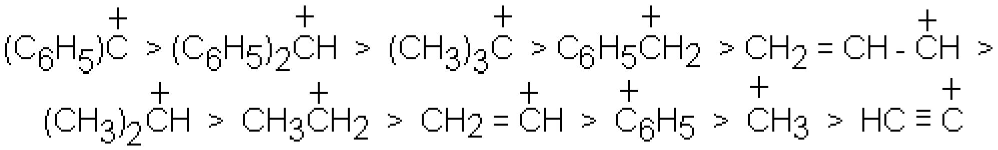
Rearrangement of carbocations

Carbocations have the property of rearrangement i.e. less stable primary carbocation gets converted to more stable secondary or tertiary carbocation either 1,2 – hydride shift or 1,2-methyl shift





Over all order of stability of carbocations is given by



$$(C_6H_5)_3\overset{+}{C} > (C_6H_5)_2\overset{+}{C}H > (CH_3)_3\overset{+}{C} > C_6H_5\overset{+}{C}H_2 > CH_2=CH-\overset{+}{C}H >$$
$$(CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > CH_2=\overset{+}{C}H > \overset{+}{C}_6H_5 > \overset{+}{C}H_3 > HC\equiv\overset{+}{C}$$

Solved problem

Q) Arrange following carbcations in increasing order of stability

$C_6H_5C^+H_2$, $C_6H_5CH_2C^+ H_2$, $C_6H_5C^+HCH_3$, $C_6H_5C^+(CH_3)_2$

Solution

-C_6H_5 group provide carbocation stabilization through resonace where as alkyl group –CH_3 stabilizes the carbocation by +I effect. Thus order of stability is

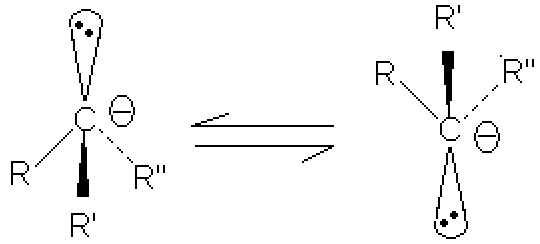
$C_6H_5C^+(CH_3)_2 > C_6H_5C^+ HCH_3 > C_6H_5C^+H_2 > C_6H_5CH_2C^+ H_2$

2.Carbanion

These are the chemical species having a trivalent carbon-atom carrying a negative charge and eight electrons in its valance shell

Structure

Carbanion assumes pyramidal configuration, as carbon atom here is sp^3 hybridised. The unshared electron pair would be accommodated in an sp^3 hybridized orbital. The carbanions readily undergo pyramidal inversion also called umbrella effect



Classification of carbanion

Carbanion are calssified as primary(1°), secondary (2°), tertiary (3°) depending upon the nature of carbon atom bearing negative charge

Stability

Inductive effect

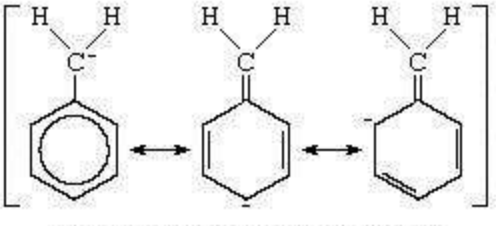
The relative stability of various alkyl carbanion can be explained on the basis of inductive effect. Greater the number of alkyl groups, greater the intensity of negative charge and hence lesser the stability, that why tertiary carbanion are least stable

Hybridization

Since the electronegativity of the carbon increases with increasing *s*-character of the bonding (that is, in the order *sp*^{3}, *sp*^{2}, and *sp*) the carbanion stability follows the same trend.

Resonance

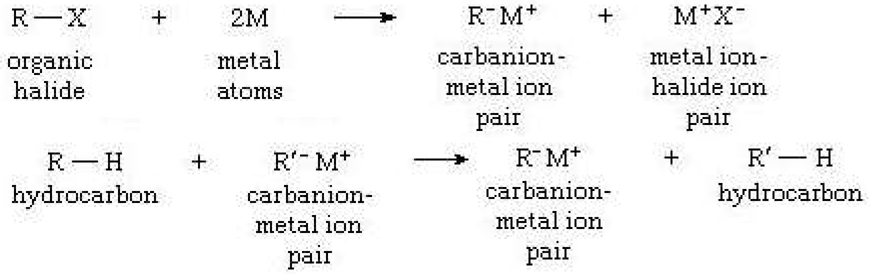
Stability of carbanions is also influenced by resonance in those cabanions in which negative charge is in conjugation with the double bond, e.g. stability of benzyl and triphenyl methyl carbanion is explained with the help of resonance



resonance forms of benzylic anion

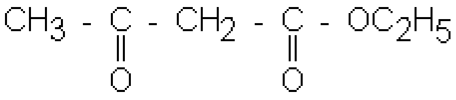
As the number of phenyl groups attached to the carbon atom bearing the negative charge increases, the stability increases due to increase in resonating structure
An electron withdrawing group on the benzene ring increases the stability of aryl carbanion due to inductive effect whereas an electron donating group on the benzene ring decreases the stability. Overall stability order of carbanion is given as
$HC\equiv C^- > (C_6H_5)_3C^- > (C_6H_5)_2CH^- > (C_6H_5)CH_2^- > CH_2 = CHCH_2^- >$ methyl > 1°, 2°, 3°

Preparation.
Any preparation of organic-alkali-metal compounds is a source of carbanions. The reaction of organic compounds containing atoms of chlorine, bromine, or iodine with alkali metals is one of the most often used methods. This reaction can be expressed:



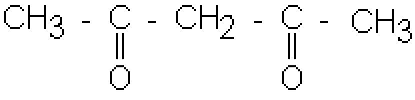
Solved Problem

Q) When (I) and (II) are treated with base, separately carbanion results. Which carbanion will be more stable



$CH_3-C(=O)-CH_2-C(=O)-OC_2H_5$

(I)



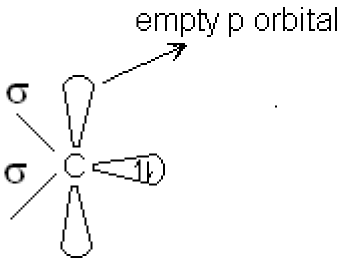
$CH_3-C(=O)-CH_2-C(=O)-CH_3$

(II)

Solution
Carbanion from (II) will be form because of more stability due to greater resonance as –COR group is more electron withdrawing than CO_2R

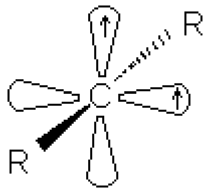
Carbene

A Carbenes can be defined as neutral, divalent carbon intermediates in which a carbon is covalently bonded to two atoms and have two non-bonded orbitals containing two electrons between them.
Carbenes are short-lived highly reactive chemical species. Since carbenes have only six electrons in the valence shell of central carbon –a atom. These are electron deficient and acts as Lewis acids or electrophiles
Types of carbenes
(i)Single carbenes
In the singlet state, a carbon atom is presumed to approximate sp^2 hybridization. Two of the three sp^2 hybrid orbitals are utilized in forming two covalent bonds whereas the third hybrid orbital contains the unshared pair of electrons. The remaining p-orbital remains vacant. Thus singlet carbine resembles a carbonium ion very closely.



sp^2 hybridised carbon

(iii) Triplet carbenes
The central carbon atom is sp shbridised and is in a linear or near-linear species. These two hybride orbitals are involved in the bond formation with two groups and the remaining two electrons are placed , one each, in the equivalent, mutually perpendicular p_y and p_z orbitals. These electrons have parallel spins and a carbenes with this structure is said to be in triplet state.

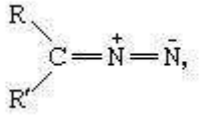


sp hybridised carbon

Triplet carbene is more stable than singlet carbene and expected to be the ground state, because of inter electronic repulsions in singlet carbene. Energy is required to overcome these repulsions which makes the singlet carbene comparatively less stable

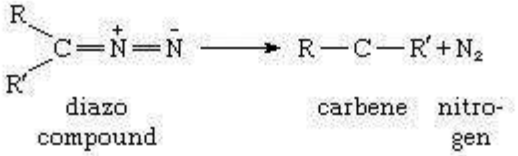
Formation

Because carbenes are molecules with high energy content, they must be made from high-energy precursors, or extra energy must be provided from external sources. Chemical transformations induced by light, so-called photochemical reactions, often are used to prepare carbenes, because the energy of the absorbed light is taken into the high-energy structures. Organic compounds containing a diazo group (two nitrogen atoms joined to one another and to a carbon atom by a double bond) are the most frequently used precursors of carbenes. The molecular structure of diazo compounds is represented by the generalized formula

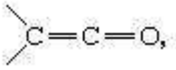


$RR'C=\overset{+}{N}=\overset{-}{N}$,

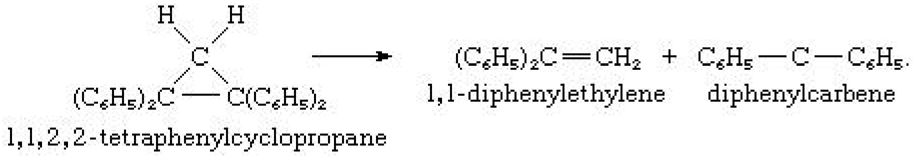
in which R and R′ represent two organic groups, which may be the same or different. On eitherphotolysis or pyrolysis (treatment with light or heat, respectively), diazo compounds cleave to yield the corresponding carbene and a free molecule of nitrogen gas. Diazirins, which are ring, or cyclic, compounds, with a structure similar to that of the diazo compounds, undergo the same cleavage reaction and are frequently used as precursors of carbenes. The production of a carbene from a diazo compound occurs as shown below:



The photolytic decomposition of certain ketenes, substances the molecules of which contain two carbon atoms and an oxygen atom joined by double bonds,

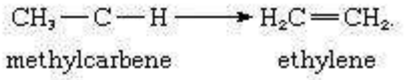


Under certain circumstances, cyclopropanes, the molecules of which contain three-membered carbon rings, can serve as carbene precursors in photochemical reactions. For example, 1,1,2,2,-tetraphenylcyclopropane is converted to diphenylcarbene by the reaction

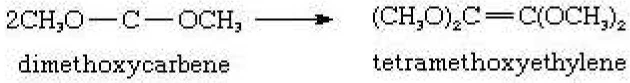


Reactions.

The various chemical reactions that carbenes undergo can be classified as either intramolecular or intermolecular reactions. Intramolecular reactions, or rearrangements, involve only the carbene itself and include no other outside substances; if structurally possible, they lead to stable molecules in which the carbon atom is in its normal, or tetravalent, state. An example of an intramolecular reaction is the rearrangement of methylcarbene to ethylene, in which a hydrogen atom undergoes a shift from one carbon atom to the next:



Intermolecular reactions are those involving two or more separate molecules. Three important classes of intermolecular reaction of carbenes are known: dimerization, addition, and insertion reactions. Dimerization of carbenes—combination of two molecules of the carbene—gives olefins, the molecular formulas of which are exactly twice that of the carbene. An example is the formation of tetramethoxyethylene from dimethoxycarbene



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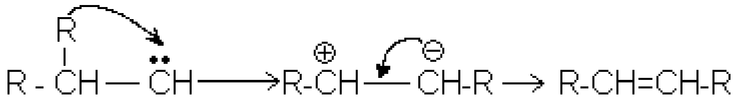
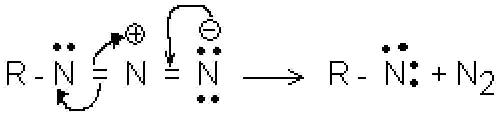
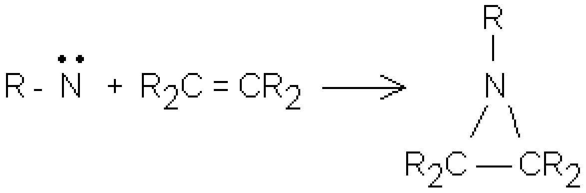
Alkylated and phenylated carbenes can also undergo ready rearrangement, to directly give final product (Alkene)



Nitrenes

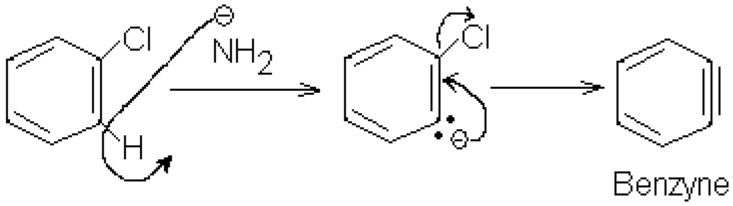
These are the monovalent nitrogen species in which nitrogen is bonded to only one monovalent atom or group and has two unshared pair of electrons. These nitren contains a nitrogen atom having a six electrons and so it is electron-deficient. These are generally produced by thermolysis of azids





Benzyne

These intermediates are generated by the elimination of α – proton and leaving group (generally halogen) form the adjacent carbons from a benzene ring system. For example



Benzyne

Benzynes are very reactive. Neither benzyne nor any other aryne (sunstituted benzyne) has yet been isolated under ordinary conditions. The triplebond in benzynes is not identical with the formal triple bond of alkynes because here the two π-bonds are formed by the overlapping of p_z-p_z and sp^2-sp^2 orbitals where as in alkynes, they are formed by the overlap of p_z-p_z and p_y-p_y orbitals.

HYDROCARBON

Organic compounds composed of only carbon and hydrogen are called hydrocarbon.

CLASSIFICATION OF HYDROCARBONS

On the basis of structure, hydrocarbons are broadly divided into main types

1. Acyclic or open chain hydrocarbon
2. Cyclic or closed chain hydrocarbon

Acylic hydrocarbon

These hydrocarbon contains open chain of carbon atom in their molecule. These are also called as aliphatic hydrocarbon

These are further classified as

i) Alkanes: C – C bond (saturated compounds)
ii) Alkene : C = C bond (Unsaturated compounds)
iii) Alkyne: C≡ C bond (Unsaturated compounds)

Cyclic hydrocarbon

These contains closed chain or rings of carbon atom in their molecule

These are further divided in two groups

(i) Alicyclic hydrocarbon: The hydrocarbon which contains ring of carbon atom in a molecule and resemble aliphatic hydrocarbon in their properties
(ii) Aromatic hydrocarbon: These hydrocarbon contains at least one special type of hexagonal ring of carbon atom with three double bonds in alternate position.

The major source of aliphatic hydrocarbon are petroleum and natural gas, where as aromatic hydrocarbons are main obtained from coal

PETROLEUM

(Petra = rock , oleum = oil)

- It is dark viscous fluid with unpleasant smell found at various depth under the earth crust.

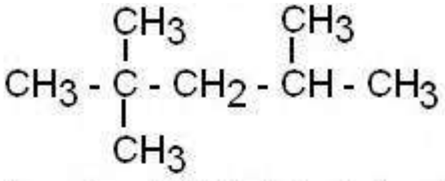
- Crude petroleum is a mixture of hydrocarbons containing 80-85% of carbon 10-14% hydrogen and small amount of oxygen, nitrogen and sulphur.

Petroleum products

1. Gaseous ($C_1 – C_4$)
   Boiling range : 113 – 303 K
   Uses: As a full, for production of carbon black
2. Petroleum ether ($C_5 – C_7$)
   Boiling range : 303 – 363K
   Use : As of solvent for rubber, oil, fasts and varnishes, for dry cleaning
3. Gasoline or Petrol ($C_8 – C_{11}$)
   Boiling range : 343 -373K
   Uses: As a motor fuel, for dry cleaning
4. Kerosene oil or Paraffin oil ($C_{12} – C_{15}$)
   Boiling range : 448 – 548K
   Uses: AS an illuminate fuel, just engine fuel and for making oil gas
5. Gas oil, fuel and diesel gas ($C_{15} – C_{18}$)
   Boiling range : 573 – 673
   Use: Furnace fuel, fuel for diesel engine
6. Lubrication or Mineral oil ($C_{16} – C_{20}$)
   Boiling range : 623 K and above
   Uses: As a lubricant
7. Grease, Vaseline, petroleum jelly ($C_8 – C_{22}$)
   Use: pharmaceutical preparations
8. Paraffin wax ($C_{20} – C_{30}$)
   Uses: In the manufacture of candles, waxed papers and for water proofing.

OCTANE NUMBER

- Quality of petrol or gasoline is graded terms of octane number
- Octane number is defined as the percentage by volume of iso-octane present in the mixture of iso-octane and n-heptane which has same knocking properties.
- Metallic sound which arises due to violent jerk in piston is known as knocking
  $CH_3 – CH_2 – CH_2 – CH_2 – CH_2 – CH2 – CH_3$
  (n – heptanes , octane number = 0)



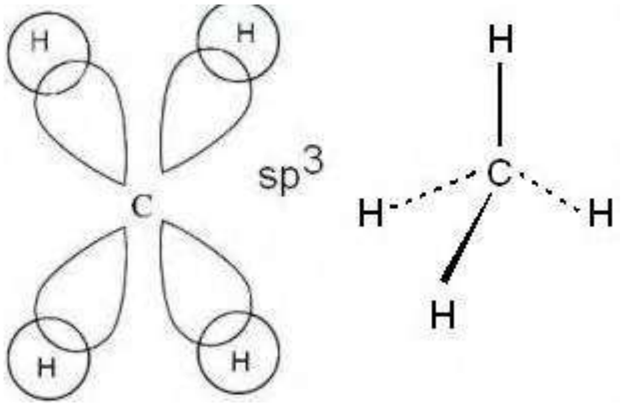
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3$$

iso-octane [2,2,4 - trimethylpentane]
octane number = 100

- Higher the octane number of fuel, better is the fuel. Octane number of gasoline is 80
- Straight chain hydrocarbon have low octane number.
- Presence of multiple bond increases octane number.
- Aromatic hydrocarbon have higher octane number.
- Octane number decreases with increase in chain length but increases with branching of chain
- Octane number follows the following order
  Aromatic hydrocarbons > cycloalkanes > branched chain alkane
  > straight chain alkanes

ALKANES

- Alkanes are saturated open chain hydrocarbon containing carbon-carbon single bond
- General formula of alkanes is C_nH_{2n+2}



- Methane has a tetrahedral structure which is multiplanar, in which carbon lies at the centre and four hydrogen atoms lie at the four corners of a regular tetrahedron. All H-C-H bond angles are of 109.5^O
- In alkanes, tetrahedral are joined together in which C – C and C – H bond lengths are 154 pm and 112pm

ISOMERISM OF ALKANES

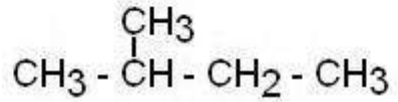
- Difference in properties due to difference in their structures are known as structural isomers
- Structural isomers which differ in chain of carbon atoms are known as chain isomers

  Eg. C_5H_{12}

  I) $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

  Pentane (n-pentane)

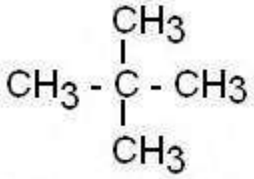
  II)



$$CH_3 - \overset{CH_3}{\overset{|}{C}H} - CH_2 - CH_3$$

2 - methylbutane (isopentane)
b.p 301K

  III)



$$CH_3 - \underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}} - CH_3$$

2,2- dimethylpropane
(neopentane)

PREPARATION OF ALKANES

1. Hydrogenation of unsaturated hydrocarbons

$$CH_2 = CH_2 + H_2 \xrightarrow{Pb,Pd,Ni} CH_3 - CH_3$$

Ethane ethane

$$CH_3 - \ CH = CH_2 + H_2 \xrightarrow{Pt,Pb \ or \ Ni} CH_3 - CH_2 - CH_3$$

Propene Propane

- Metals like platinum, palladium adsorbs dihydrogen gas on their surface and activate the hydrogen bond
- Platinum and Palladium catalyse the reaction at room temperature
- Nickel requires high temperature and pressure

2. Reduction of alkyl halide

$$R - X + H_2 \rightarrow R - H + HX$$

Order of reactivity of different alkyl halides is

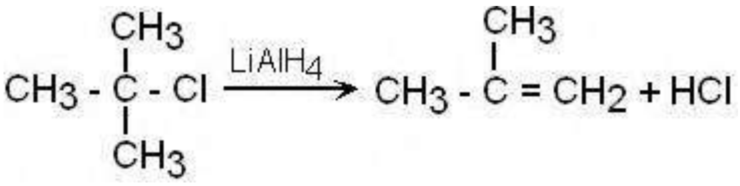
R – I > R – Br > R – Cl > R – I

$$CH_3 - I + H_2 \xrightarrow[\text{Zn - Cu / }C_2H_5OH]{\text{Zn + HCl}} CH_4 + HI$$

- The purpose of using of red phosphorus is to remove iodine
- 1^O and 2^O alkyl halides are readily reduced by $LiAlH_4$ but 3^O halides give **alkene**

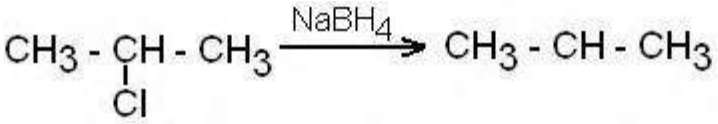
$$CH_3 - CH_2 - Cl \xrightarrow{LiAlH_4} CH_3 - CH_3$$

BUT



$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - Cl \xrightarrow{LiAlH_4} CH_3 - \overset{CH_3}{C} = CH_2 + HCl$$

- $NaBH_4$ reduces 2^O and 3^O halides but 1^O



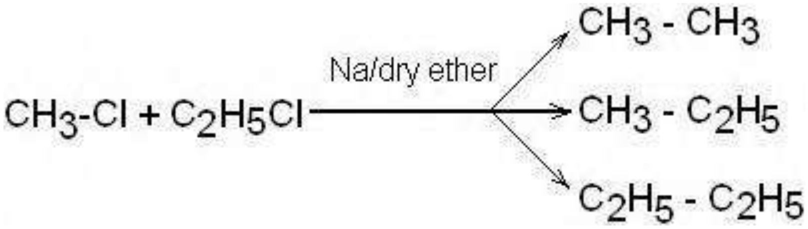
$$CH_3 - \underset{Cl}{CH} - CH_3 \xrightarrow{NaBH_4} CH_3 - CH - CH_3$$

3. Wurts reaction

$$R - X + 2Na + X - R \xrightarrow{\text{dry ether}} R - R + 2NaX$$

- If two different alkyl halides are used mixture of three different alkanes are obtained.

Eg



The separation of the mixture into individual members is not easy

- Wurtz reaction is used for the preparation of higher alkanes containing even number of carbon atoms

Mechanism

$$R - X \longrightarrow \dot{R} + \dot{X} \xrightarrow{+Na} \dot{R} + NaX$$

$$\dot{R} + \dot{R} \longrightarrow R - R$$

Wurtz reaction is supposed to follow free radical mechanism

- Ionic mechanism is suggested for Wurtz reaction

$$R-X + 2Na \longrightarrow [R^- - Na^+] + NaX$$

$$R-X + [R^- - Na^+] \longrightarrow R-R + NaX$$

Reactivity order of alkyl halides towards Wurtz reaction is
$1^O > 2^O > 3^O$ and RI > RBr > RCl

4. Decarboxylation of carboxylic acid.

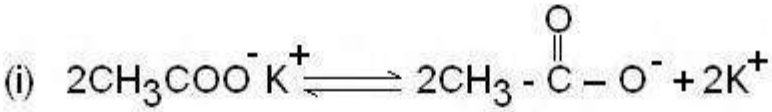
$$R-COONa + NaOH \xrightarrow{CaO} R-H + Na_2CO_3$$
$$CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$$

Alkane obtained in this method have one carbon less than the parent compounds

5. Kolbe's electrolytic method

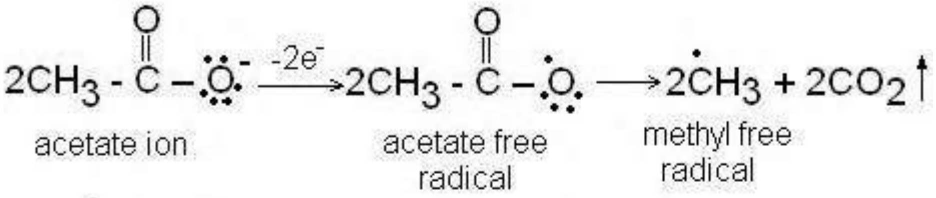
$$RCOOK + RCCOK \xrightarrow{electrolysis} R-R + 2CO_2 + H_2 + 2KOH$$

Mechanism



$$\text{(i)}\quad 2CH_3COO^-K^+ \rightleftharpoons 2CH_3-\overset{O}{\overset{\|}{C}}-O^- + 2K^+$$

(ii) At anode:



$$2CH_3-\overset{O}{\overset{\|}{C}}-\ddot{\underset{..}{O}}:^- \xrightarrow{-2e^-} 2CH_3-\overset{O}{\overset{\|}{C}}-\underset{..}{\dot{O}}: \longrightarrow 2\dot{C}H_3 + 2CO_2\uparrow$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3$$

(iii) At cathode

$$H_2O + e^- \longrightarrow OH^- + \dot{H}$$
$$2\dot{H} \longrightarrow H_2\uparrow$$

If number of carbon atoms in potassium carboxylate = n
Number of carbon atoms in alkane formed = 2(n-1)
Therefore, methane cannot be prepared by this method

6. Hydrolysis of aluminium and beryllium carbide

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

Aluminium carbide

$$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$$

Beryllium carbide

PHYSICAL PROPERTIES OF ALKANES

(1) Physical state

Due to weak intermolecular forces, alkanes from C_1 to C_4 are colourless gas, next thirteen C_5 to C_{17} are colourless, odourless liquid. Higher members form C_{18} onwards are waxy solids

(2) Solubility

Alkanes are non-polar, hence insoluble in polar solvents like water but readily soluble in non-polar solvents like benzene, ether etc.

The solubility decreases with increase in molecular mass

(3) Density
The relative densities of alkanes increases with increase in molecular mass, but very slowly till it becomes constant at about 0.8. thus all alkanes are lighter than water

(4) Boiling point
Boiling point of alkane increases with increasing molecular mass
The greater the branching of the chain, lower is the boiling point. This is because surface area of branched chain alkanes is less than that of straight chain alkanes. As a result they experience lower magnitude of van der Waals forces

(5) Melting point
Melting point of alkanes also increases with the increase in molecular weight
Alkanes with odd number of carbon atoms have lower melting point than the next lower or next higher alkanes having even number of carbon atoms.

(6) Viscosity
Viscosity of alkanaes (in liquid states) increases with chain length
For isomeric alkanes, viscocity increases with branching

CHEMICAL PROPERTIES OF ALKANES

1) Halogenation

$$CH_4 + Cl_2 \overset{hv}{\rightarrow} CH_3Cl + HCl$$
$$CH_3Cl + Cl_2 \overset{hv}{\rightarrow} CH_2Cl_2 + HCl$$
$$CH_2Cl_2 + Cl_2 \overset{hv}{\rightarrow} CHCl_3 + HCl$$
$$CHCl_3 + Cl_2 \overset{hv}{\rightarrow} CCl_4 + HCl$$

Reactivity of halogens is in order

$F_2 > Cl_2 > Br_2 > I_2$

For a given halogen, abstraction of 1^O, 2^O, 3^O hydrogen follows the order

$3^O > 2^O > 1^O$

Reactivity of different hydrogen towards halogenations is

Bemzyl > Allyl > $3^O > 2^O > 1^O$

Mechanism

Free radical substitution

(1) Chain initiation step

$$Cl - Cl \xrightarrow{hv} 2\dot{Cl}$$

(2) Chain propagation step

$$CH_4 + \dot{Cl} \longrightarrow \dot{C}H_3 + H - Cl$$

$$\dot{C}H_3 + Cl - Cl \longrightarrow CH_3Cl + \dot{Cl}$$

And so on……

(3) Chain terminating step

$$\dot{Cl} + \dot{Cl} \longrightarrow Cl_2$$

$$\dot{C}H_3 + Cl \longrightarrow CH_3Cl$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3$$

Iodination is very slow and reversible reaction. It can be carried out in the presence of oxidizing agents like HNO_3 or HIO_3

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

$$5HI + HIO_3 \rightarrow 3I_2 + 3H_2O$$

2) Nitration

$$R - H + HONO_2 \xrightarrow{high\ temp} R - NO_2 + H_2O$$

Nitration follows free radical mechanism

$$HONO_2 \xrightarrow{150 - 400^0C} H\dot{O} + \dot{N}O_2$$

$$C_3H_7\text{-}H + H\dot{O} \longrightarrow C\dot{H}_7 + H_2O$$

$$C_3\dot{H}_7 + \dot{N}O_2 \longrightarrow CH_7\text{-}NO_2$$

3) Oxidation

(a) Combustion or complete oxidation

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)H_2O$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

(b) Incomplete combustion

$$2CH_4 + 3O_2 \xrightarrow{burn} 2CO + 4H_2O$$

$$CH_4 + O_2 \xrightarrow{burn} C + 4H_2O$$

(c) Catalytic oxidation

$$2CH_4 + O_2 \xrightarrow{Cu, 523K, 100atm} 2CH_3OH$$

$$CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$$

Methanal

$$2CH_3 - CH_3 + 3O_2 \xrightarrow{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$$

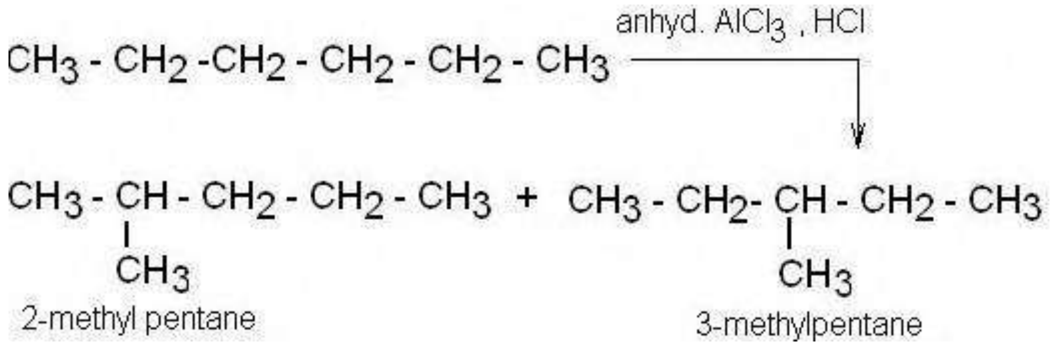
Ethanoic acid

$$(CH_3)_3CH \xrightarrow{KMnO_4} (CH_3)_3COH$$

2-methyl propane 2-methylpropan-2-ol

4) Isomerisation

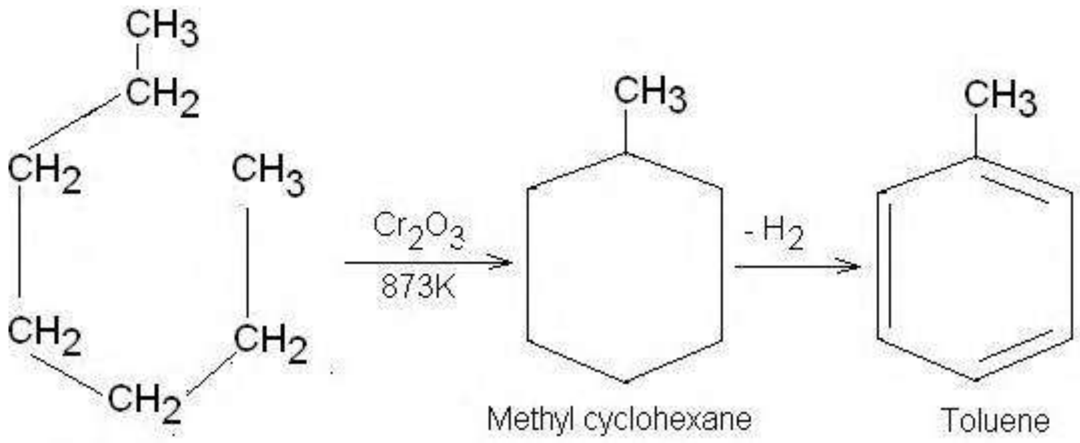
The process of conversion of one isomer into another isomer is called isomerisation.



Isomerisation involves 1, 2 shift of hydride or methyl group

5) Aromatization

The conversion of aliphatic compounds into aromatic compounds is known as aromatization

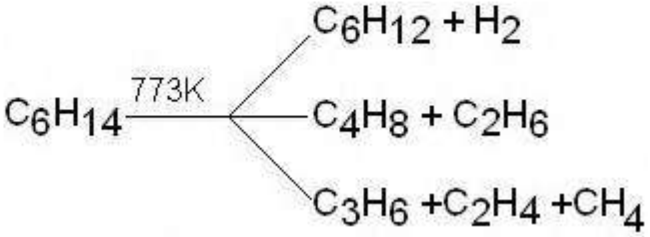


6) Reaction with steam

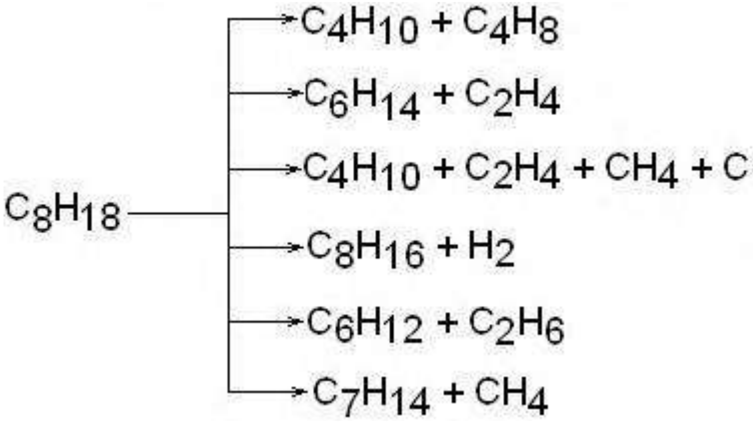
$$CH_4 + H_2O \xrightarrow{Ni, Al_2O_3, 1073K} CO + 3H_2$$

7) Pyrolysis

The decomposition of a compound by heat is called pyrolysis.



Mechanism of cracking follows free radical mechanism



Use of alkanes

- Methane is used in the preparation of carbon black which is used for making printing ink, black paint
- Methane in the form of natural gas used for running the cars, buses etc
- Ethane is used for making hexachloroethane which is artificial camphor.

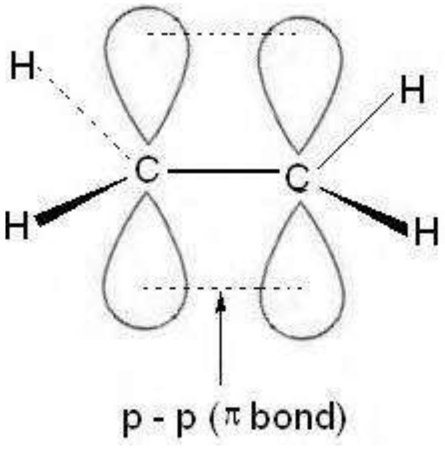
ALKENES

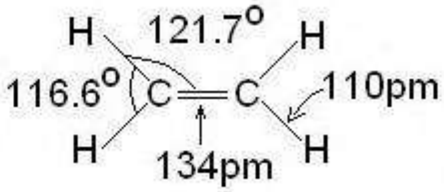
Alkenes are unsaturated hydrocarbons having double bond (C = C)

Their general formula is C_nH_{2n}

They are also known as olefins since the lower members form oily product on treatment with chlorine or bromine.

STRUCTURE OF ALKENES





Carbon-Carbon double bond in alkenes consists of one strong sigma (σ) bond due to head on overlapping of sp^2 hybridised orbitals and one weak pi (π) bond obtained by sideways overlapping of the two 2p orbitals of the two carbon atoms

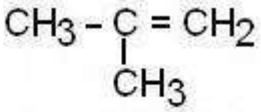
The double bond is shorter in bond length (134pm) than the C-c single bond (154pm)

The bond enthalpy of double bond is 681kJ/mol which is greater than single bond (348kJ/mol)

ISOMERISM IN ALKENES

(a) Position isomerism: This is due to the position of double bond in the same molecular formula
$CH_3 – CH_2 – CH = CH_2$) But – 1- ene)
$CH_3 – CH = CH – CH_3$ (But – 2 – ene)

(b) Chain isomerism: This is due to the difference in the nature of carbon skeleton
$CH_3 – CH_2 – CH = CH_2$ (But – 1 – ene)

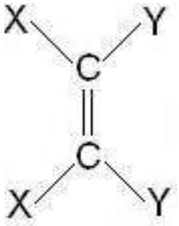


$CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2$

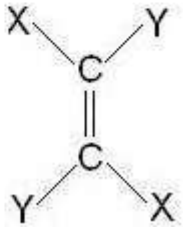
2 - methylpropane

(c) Geometrical isomerism : Isomers, which possess the same molecular and structural but differ in the arrangement of atom or groups in space due to restricted rotation around the double bonded atom are known as geometrical isomer and the phenomenon is known as geometrical isomerism

(1) If two identical atoms or groups lie on the same side of the double bond is called cis-isomer



(2) If two identical atoms or groups lie on the opposite side of the double bond is called trans-isomer.



Physical properties of cis-trans isomers

(i) Melting point of trans-isomer is more than that of cis-isomer

(ii) Boiling point : p.pt. of cis-isomer is more than that of trans isomer

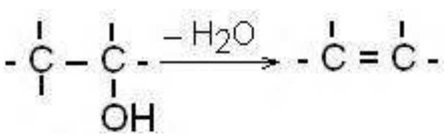
(iii) Solubility: The solubility viscosity and refractive index of cis-isomer is more than the trans isomer in a given solvent

(iv) Dipole moment: Cis-isomer has higher dipole moment than trans –isomer

(v) Stability: Trans-isomer is more stable but less reactive than cis-isomer

PREPARATION METHODS OF ALKENES

1. By dehydration of alcohol



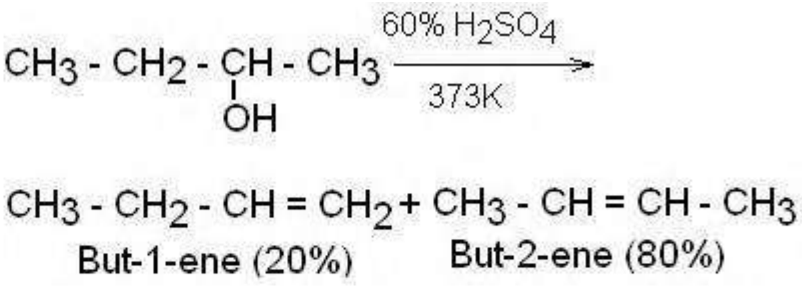
$-\underset{|}{\overset{|}{C}}-\underset{\underset{OH}{|}}{\overset{|}{C}}- \xrightarrow{-H_2O} -\overset{|}{C}=\overset{|}{C}-$

Ease of dehydration follows the order

Tertiary (3^{O}) > Secondary(2^{O}) > Primary(1^{O})

In the dehydration of secondary and tertiary alcohol, when there is a possibility of formation of two isomers, the hydrogen atom is preferentially eliminated from the number of hydrogen atom

This is Saytzeff's rule

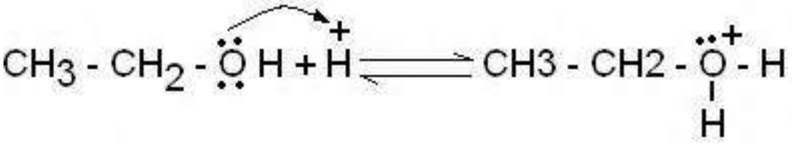


$$CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow[373K]{60\%\ H_2SO_4} CH_3-CH_2-CH=CH_2 + CH_3-CH=CH-CH_3$$

But-1-ene (20%) But-2-ene (80%)

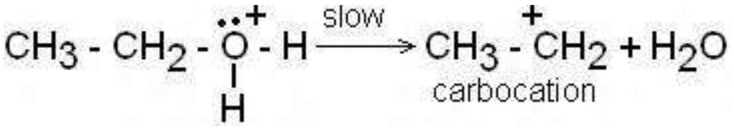
Mechanism

Step I



$$CH_3-CH_2-\ddot{\underset{..}{O}}H + \overset{+}{H} \rightleftharpoons CH3-CH2-\overset{..+}{\underset{\underset{\displaystyle H}{|}}{O}}-H$$

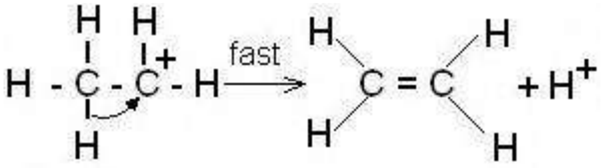
Step II



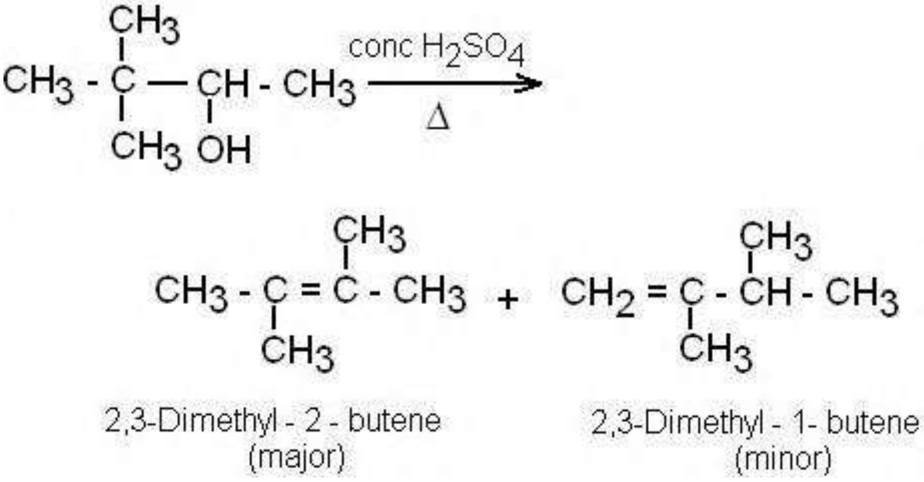
$$CH_3-CH_2-\overset{..+}{\underset{\underset{\displaystyle H}{|}}{O}}-H \xrightarrow{slow} CH_3-\overset{+}{C}H_2 + H_2O$$

carbocation

Step III



Retropinacol rearrangement (Wagner – rearrangement)

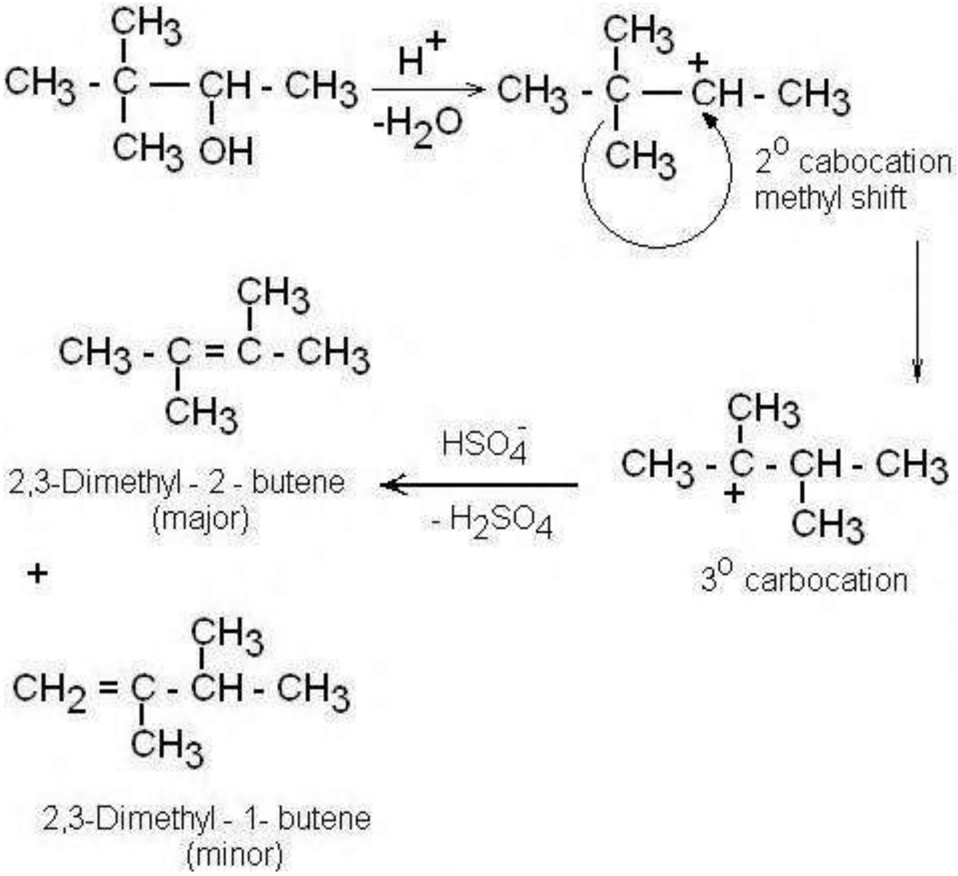


$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3 \xrightarrow[\Delta]{conc\ H_2SO_4}$$

$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_3 + CH_2=\underset{\underset{\displaystyle CH_3}{|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3$$

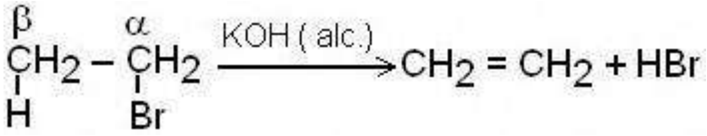
2,3-Dimethyl - 2 - butene (major) 2,3-Dimethyl - 1- butene (minor)

The above reaction can be explained as follows



2. Dehydrohalogenation of alkyl halides

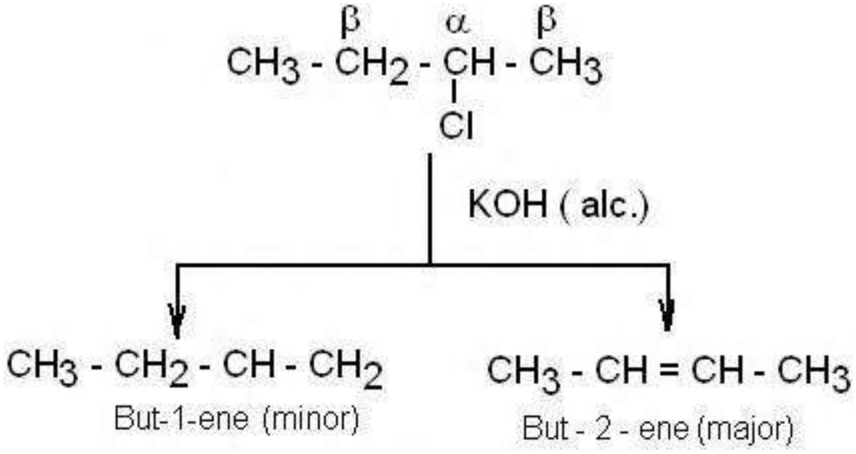
   It involves removal of halogen atom along with β-hydrogen atom on heating with alcoholic solution of potassium hydroxide



$$\overset{\beta}{CH_2}(H) - \overset{\alpha}{CH_2}(Br) \xrightarrow{KOH\ (alc.)} CH_2 = CH_2 + HBr$$

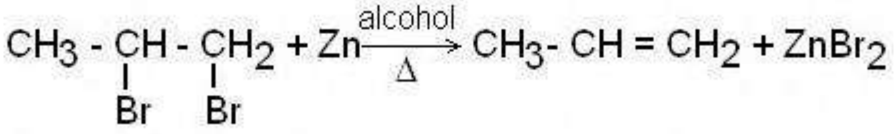
   Reactivity order of different alkyl halides

   $3^o > 2^o > 1^o$ and RI > RBr > RCl



   It follows Saytzeff's rule

3. Dehalogenation of vicinal dihalides

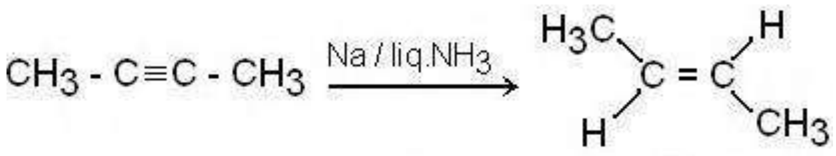


$$CH_3-\underset{Br}{CH}-\underset{Br}{CH_2}+Zn\xrightarrow[\Delta]{alcohol}CH_3-CH=CH_2+ZnBr_2$$

NaI in acetone can also be used in place of Zinc

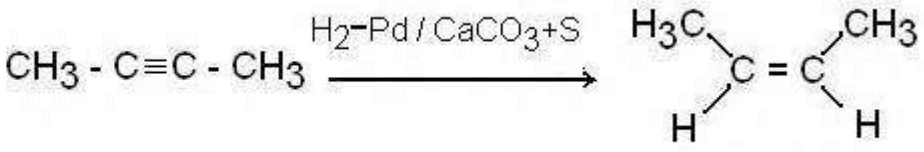
$$Br-CH_2-CH_2-\ Br+NaI\xrightarrow{acetone}CH_2=CH_2+NaBr+IBr$$

4. Partial reduction of alkynes
   (i) Birch reduction



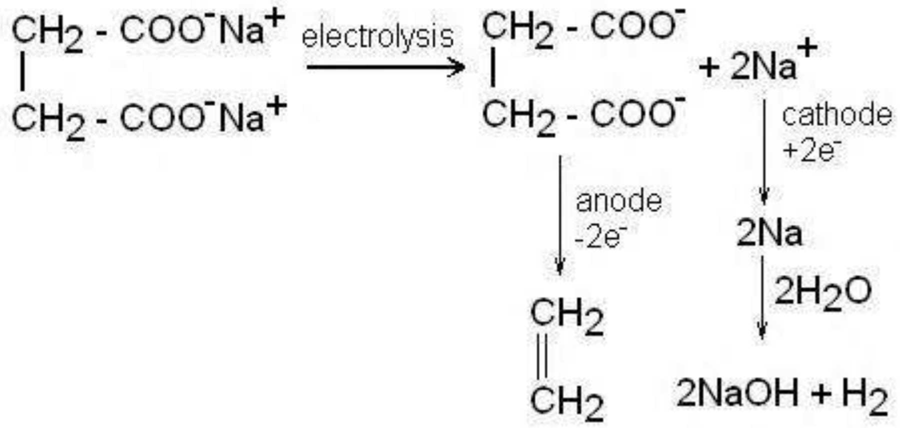
trans-but-2-ene

   (ii) Lindlar’s catalyst

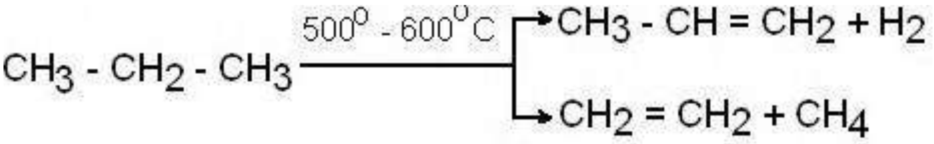


cis -but-2-ene

5. Kolbe’s electrolytic method



6. Pyrolysis or cracking



7. Dehydrogenation of alkanes

$$CH_3-CH_2-CH_3\xrightarrow[450^{0}C]{Cr_2O_3,\ Al_2O_3}CH_2=CH-CH_3+H_2$$

PHYSICAL PROPERTIES OF ALKENES

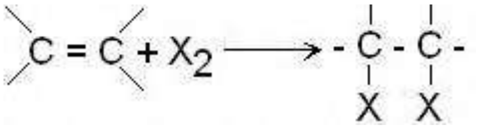
1. Physical state
   $C_2 – C_4$ are colourless gases, next fourteen members ($C_5 – C_{18}$) are liquids and next higher members are solid at room temperature
2. Meting point
   Melting point increases with increase in molecular mass.
3. Boiling point
   Boiling point also increases with increase in molecular mass
   Like alkanes, branching in alkenes lower the boiling point
4. Solubility
   Alkenes are insoluble in water but soluble in non-polar solvents like CCl_4, benzene, ether, etc.
5. Density
   Alkenes are lighter than water
6. Dipole moment
   Alkenes are generally non-polar but certain unsymmetrical alkenes are slightly polar.

CHEMICAL PROPERTIES OF ALKENES

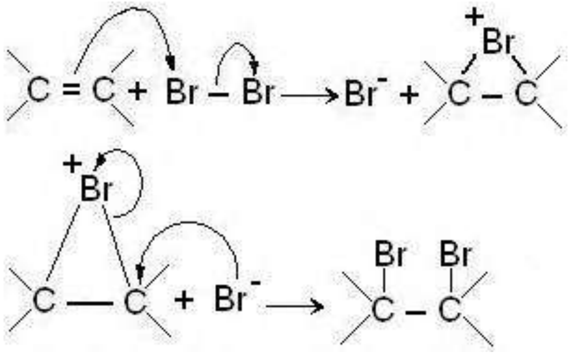
1. Addition of dihydrogen (H_2) [Hydrogenation]

$$CH_2 = CH_2 + H_2 \overset{Ni}{\rightarrow} CH_3 - CH_3$$

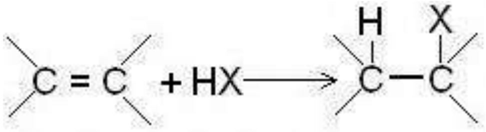
   The order of reactivity of various alkenes towards catalytic hydrogenation is
   $CH_2 = CH_2 > RCH = CH_2 > RCH = CHR > R_2C = CHR > R_2C = CR_2$
2. Addition of halogens



   The order of reactivity of halogens is
   Fluorine > Chlorine > Bromine > Iodine
   Mechanism



3. Addition of halogen acids



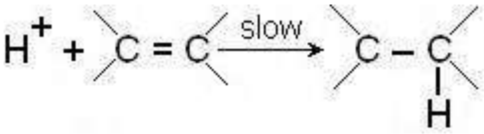
Mechanism

Step I

$$HX \rightleftharpoons H^{+} + :X^{-}$$

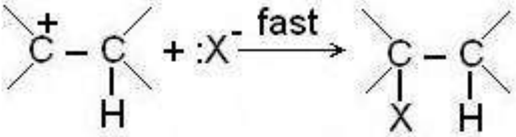
Step II

Electrophile (H^+) attacks the double bond to form carbocation



Step III

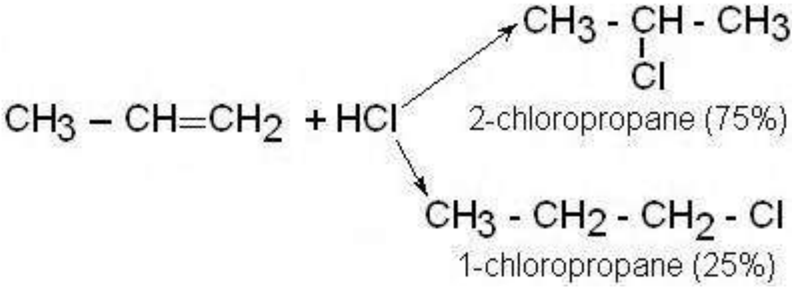
Nucleophile attacks the carbocation to from the alkyl halide



In case of unsymmetrical alkene having group on either side of double bond, two theoretically possible product is obtained

$CH_2 = CH_2 + HBr \rightarrow CH_3 - CH_2Br$

In case of unsymmetrical alkenes having groups on either side of double bond, two theoretically possible products are obtained.



This can be explained by Markownikoff's rule

Markownikoff's rule

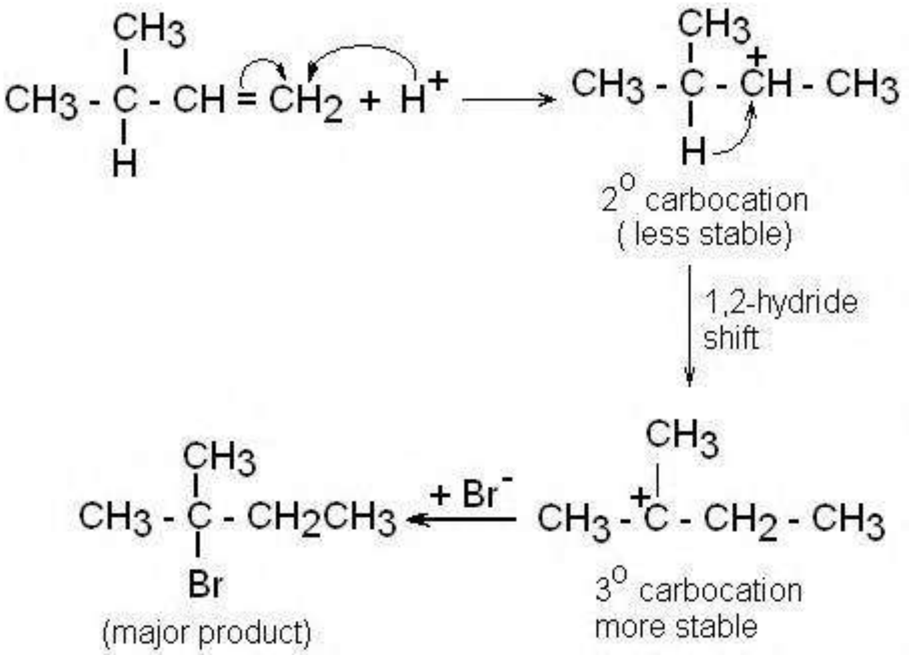
The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms

Mechanism

Step I

$$HBr \rightarrow H^{+} + :Br^{-}$$

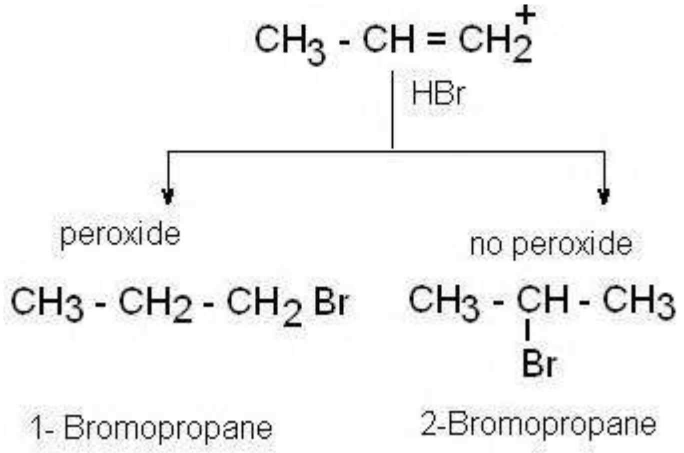
Step II



Since tertiary carbocation is more stable than secondary carbocation, therefore, the former predominates because it is formed at faster rate.

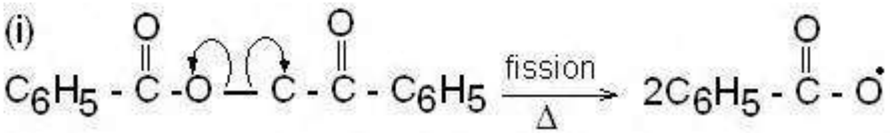
Peroxide effect or Kharasch effect

Addition of Hbr to an unsymmetrical alkene in the presence of peroxides gives the product contrary to Markownikoff's rule. It is also known as anti-markonikoff addition.

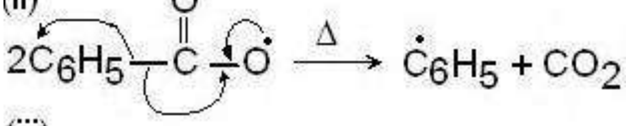


Free radical mechanism

Step I : Peroxide (like benzoyl peroxide undergoes hemolytic fission to give free radicals



(ii)

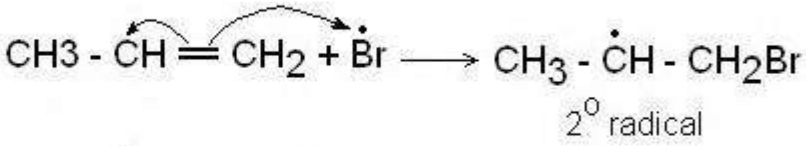


$$2C_6H_5-\overset{O}{\overset{\|}{C}}-\dot{O} \xrightarrow{\Delta} \dot{C}_6H_5 + CO_2$$

(iii)

$$\dot{C}_6H_5 + H - Br \longrightarrow C_6H_6 + \dot{Br}$$

Step II : Propagation



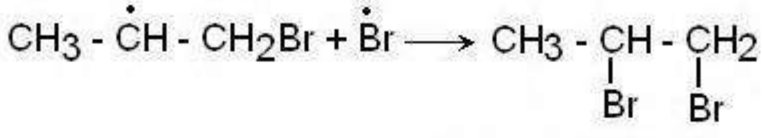
$$CH3 - CH = CH_2 + \dot{Br} \longrightarrow CH_3 - \dot{C}H - CH_2Br$$

2° radical

$$CH_3 - \dot{C}H - CH_2Br + H - Br —— CH_3CH_2\text{-}CH_2Br + \dot{Br}$$

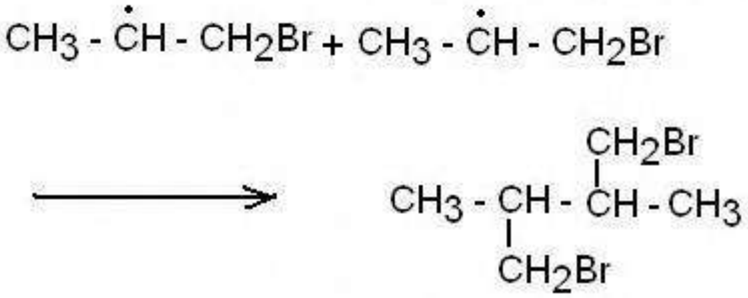
Step III : Termination

$$\dot{Br} + \dot{Br} \longrightarrow Br_2$$



$$CH_3 - \dot{C}H - CH_2Br + \dot{Br} \longrightarrow CH_3 - \underset{Br}{\underset{|}{CH}} - \underset{Br}{\underset{|}{CH_2}}$$

1, 2 - Dibromopropane



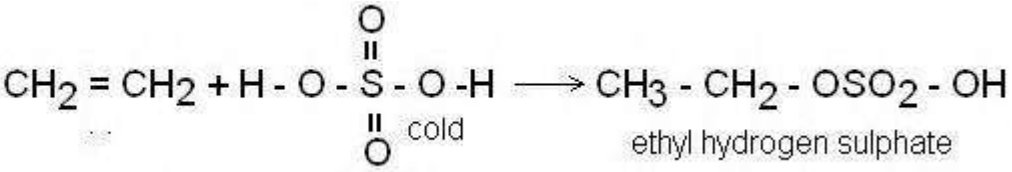
$$CH_3 - \dot{C}H - CH_2Br + CH_3 - \dot{C}H - CH_2Br \longrightarrow CH_3 - \underset{CH_2Br}{\underset{|}{CH}} - \overset{CH_2Br}{\overset{|}{CH}} - CH_3$$

Peroxide effect is observed only in case of HBr and not in HCl and HI

This may be due to the fact that the H-Cl bond being stronger than H-Br bond, is not cleaved by the free radical.

Whereas the H-I bond is weaker and iodine free radicals combine to form iodine molecules instead of adding to the double bond

4. Addition of sulphuric acid



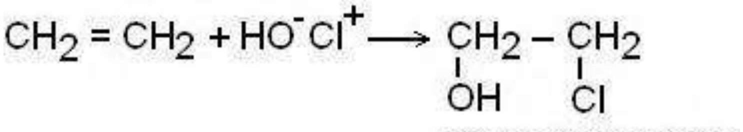
$$CH_2 = CH_2 + H - O - \underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}} - O - H \xrightarrow[\text{cold}]{} CH_3 - CH_2 - OSO_2 - OH$$

ethyl hydrogen sulphate

Since alkenes are soluble in cold concentrated acid, this method can be used for separating them from insoluble compounds like akanes and alylhalides.

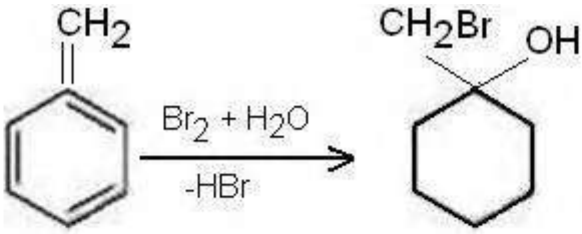
5. Addition of hypohalous acid

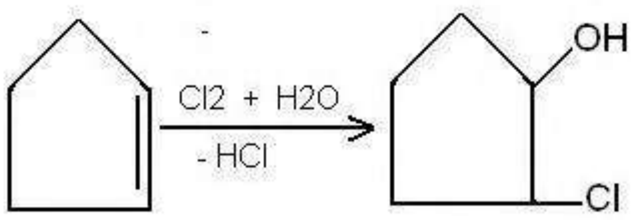
   Hypohalous acid (HOX) [Chlorine or bromine + H_2O] readily added on alkenes to form corresponding halohydrins



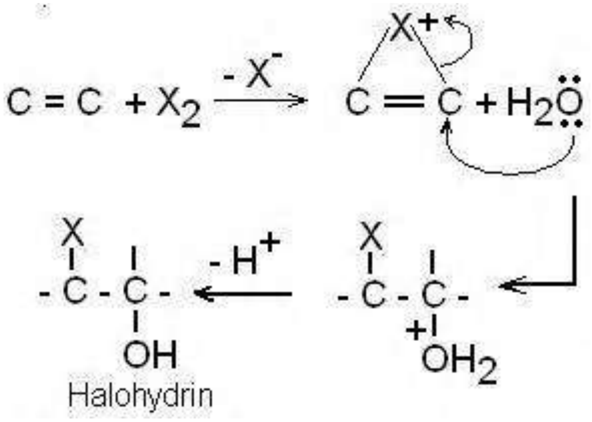
$$CH_2=CH_2 + HO^-Cl^+ \longrightarrow \underset{OH}{CH_2}-\underset{Cl}{CH_2}$$

ethylene chlorohydrin





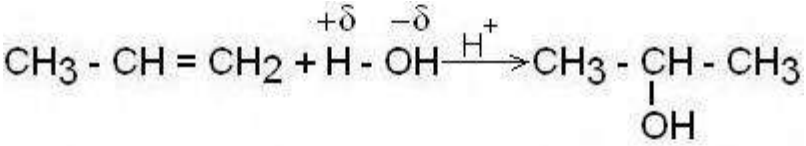
Mechanism



The order of reactivity HOX is

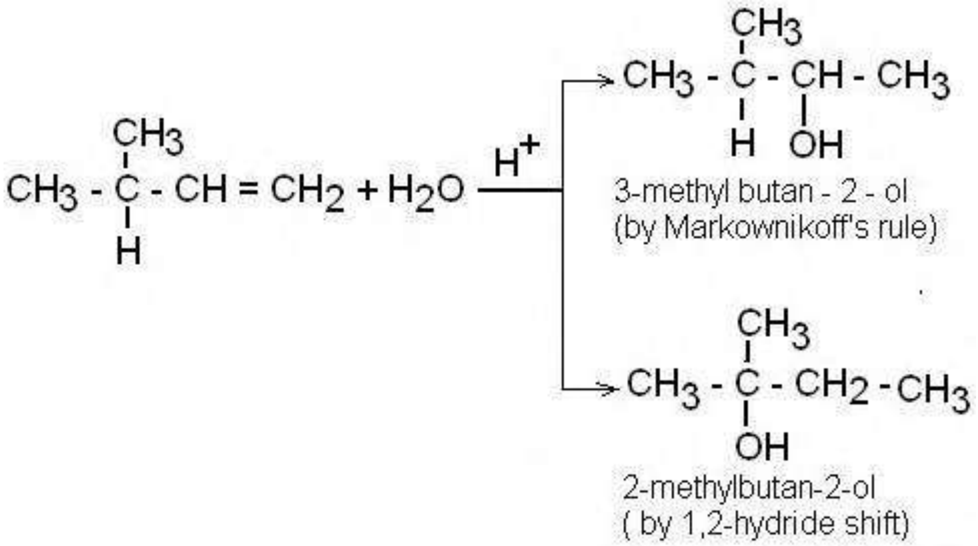
HOCl > HOBr > HOI

6. Addition of water



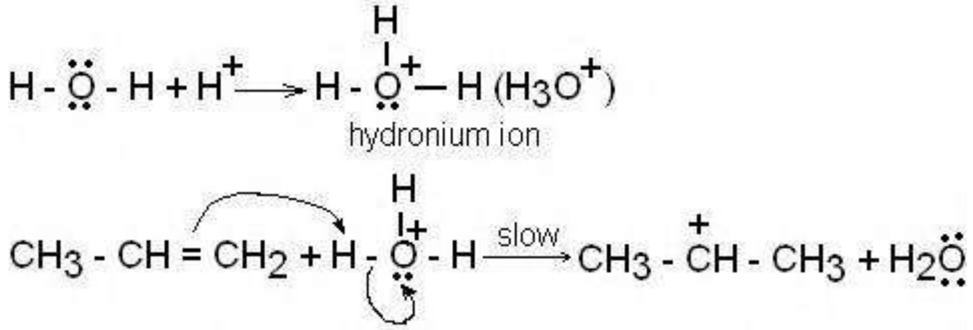
$$CH_3-CH=CH_2+\overset{+\delta}{H}-\overset{-\delta}{OH}\xrightarrow{H^+}CH_3-\underset{OH}{CH}-CH_3$$

This reaction involves formation of carbocation intermediate that may result into some unexpected product due to carbocation rearrangement

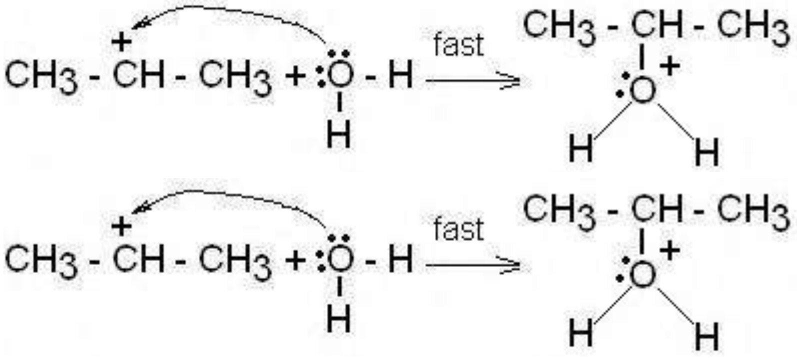


Mechanism

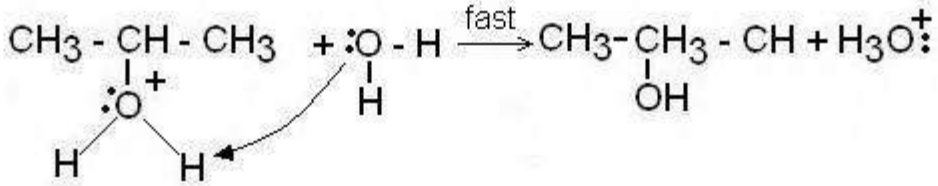
Step I : Electrophilic attack by hydronium ion (H_3O^+) on alkene gives an intermediate carbocation.



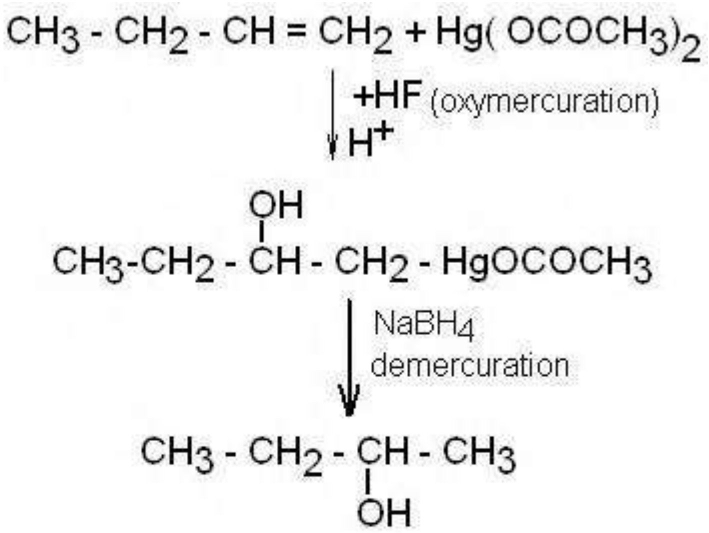
Step II : Nucleophilic attack by water on carbocation to yield protonated alcohol



Step III: Deprotonation to form alcohol

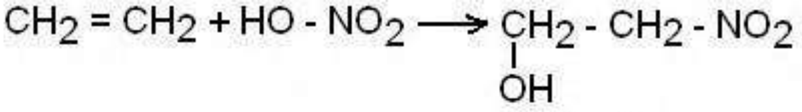


7. Oxymercuration – demercuration



$$CH_3-CH_2-CH=CH_2+Hg(OCOCH_3)_2 \xrightarrow[H^+]{+HF\ \text{(oxymercuration)}} CH_3-CH_2-\overset{OH}{\overset{|}{C}}H-CH_2-HgOCOCH_3 \xrightarrow[\text{demercuration}]{NaBH_4} CH_3-CH_2-\underset{OH}{\underset{|}{C}}H-CH_3$$

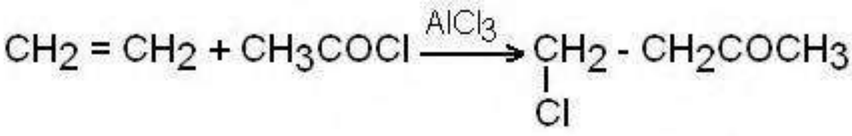
8. Addition of HNO_3



$$CH_2=CH_2+HO-NO_2 \longrightarrow \underset{OH}{\underset{|}{C}}H_2-CH_2-NO_2$$

2-nitroethane

9. Addition of acetyl chloride

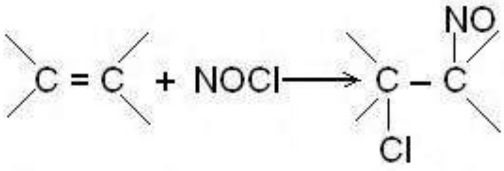


$$CH_2=CH_2+CH_3COCl \xrightarrow{AlCl_3} \underset{Cl}{\underset{|}{C}}H_2-CH_2COCH_3$$

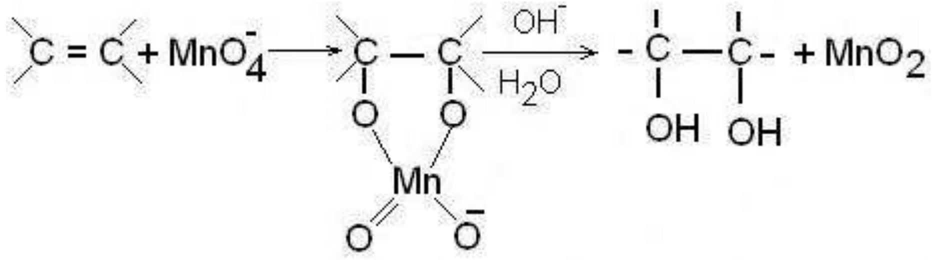
4-chlorobutan-2-ene

10. Addition of nitrosyl chloride (Tildens Reagent)

NOCl → $Cl^- - N^+ = O$



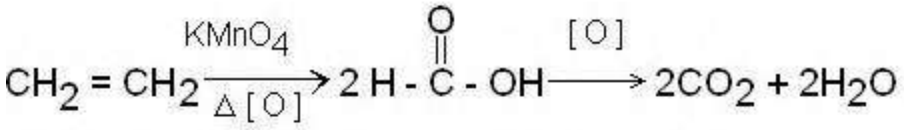
11. Oxidation
    (i) Complete combustion
        $CH_2 = CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O + 1411$ kJ/mol
    (ii) Oxidation with potassium permanganate
        (a) Oxidation with cold dilute neutral or alkaline $KMnO_4$ cold alkaline $KMnO_4$ is known as Baeyer's reagent



This reaction is used for testing presence of unsaturation

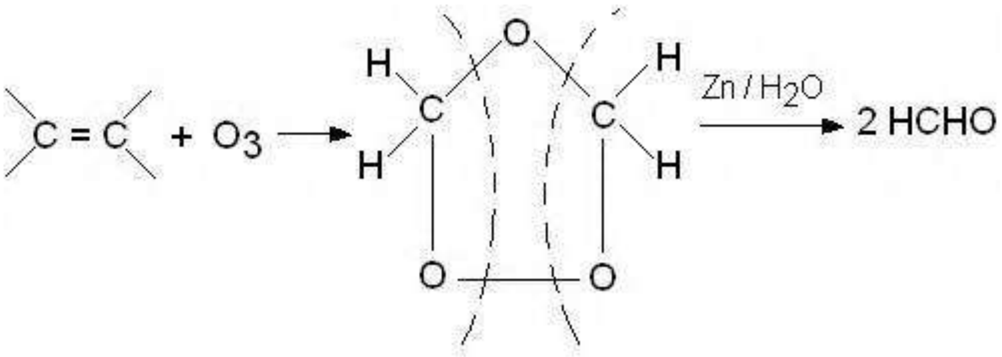
As soon as $KMnO_4$ reacts with alkene its pink colour gets discharged and brown precipitate of MnO_2 is obtained

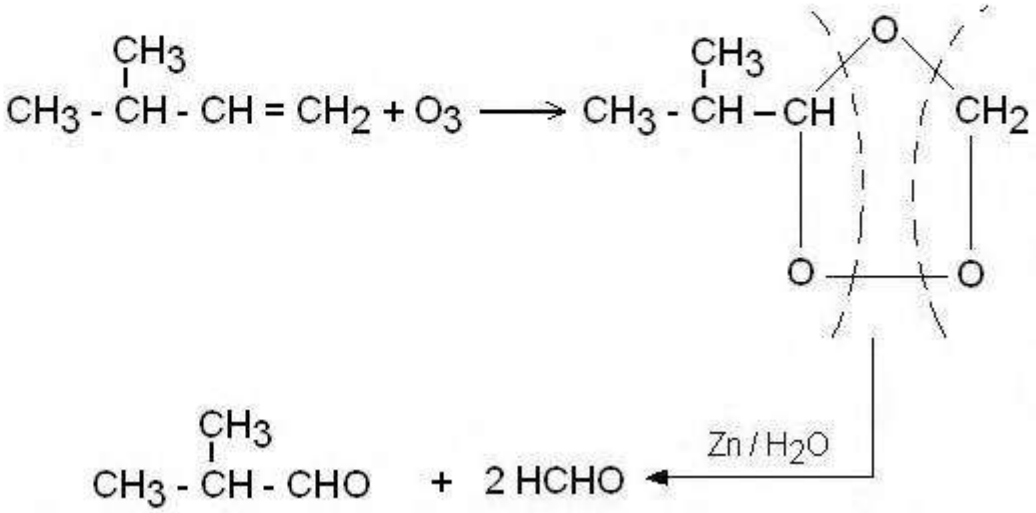
(b) Oxidation with hot $KMnO_4$



$$CH_2 = CH_2 \xrightarrow[\Delta\,[O]]{KMnO_4} 2\,H-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{[O]} 2CO_2 + 2H_2O$$

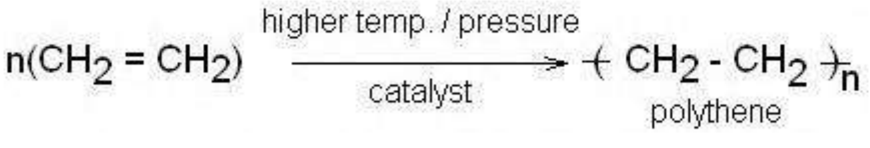
12. Ozonolysis



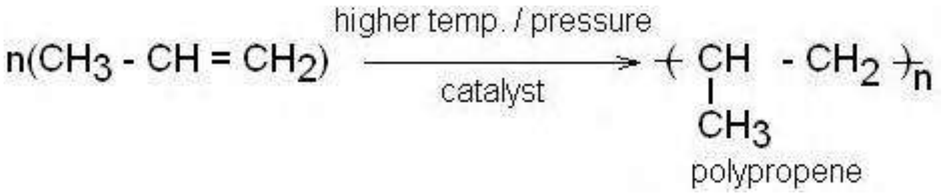


13. Polymerisation

Two or more molecules of an alkene link together to form a new bigger molecule of higher molecular mass. This process is called polymerization



$$n(CH_2 = CH_2) \xrightarrow[\text{catalyst}]{\text{higher temp. / pressure}} \underset{\text{polythene}}{\left(CH_2 - CH_2 \right)_n}$$



$$n(CH_3 - CH = CH_2) \xrightarrow[\text{catalyst}]{\text{higher temp. / pressure}} -\!\!\left(\underset{\substack{|\\ CH_3}}{CH} - CH_2\right)\!\!-_n$$

Polymers are used for manufacture of plastic bags, toys, pipe, etc

Uses of alkenes

Ethene is used:

(i) For the manufacture of polythene – a plastic material
(ii) For artificial ripening of fruits
(iii) As a general anaesthetic.
(iv) As a starting material for a large number of compounds such as glycol, ethyl alcohol etc
(v) For making poisonous mustard gas (war gas)
(vi) For making ethylene – oxygen flame for cutting and welding metals

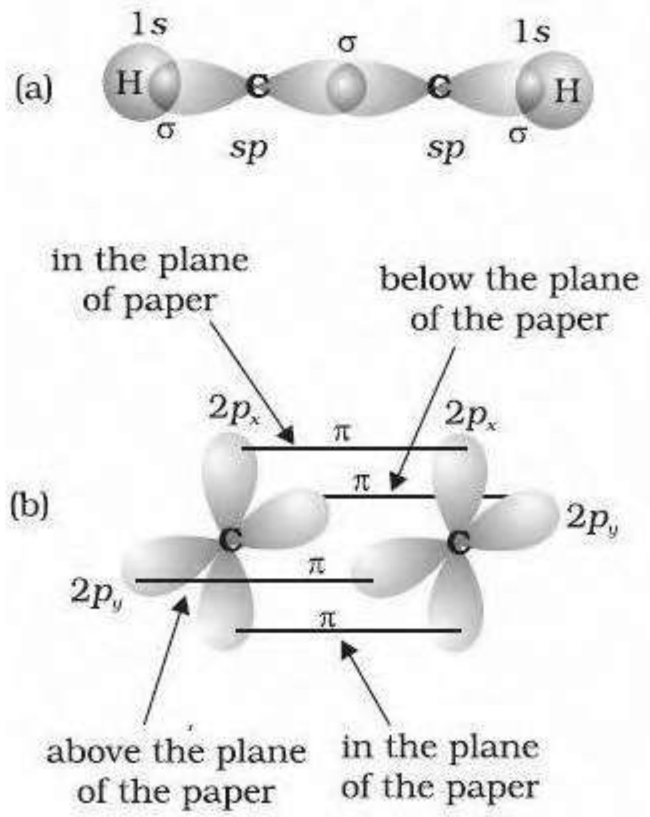
ALKYNES

Alkynes are unsaturated hydrocarbon with at least one triple bond between two carbon atoms (C = C)

Their general formula is $C_n H_{2n-2}$

They are also called as a acetylenes

STRUCTURE OF ALKYNES



Each carbon atom of ethyne has two sp hybridised orbitals.

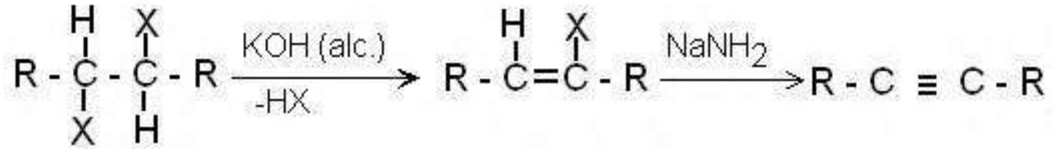
Carbon – carbon sigma (σ) is obtained by the head – on overlapping of the two sp hybridized orbitals of the two carbon atoms

The remaining sp hybridized orbital of each carbon atom undergoes overlapping along the internuclear axis with 1s orbital of each of the two hydrogen atom forming two sigma bond (C-H bond) H-C-C bond angle is of 180^o

Each carbon has two unhybridised p orbitals which are perpendicular to each other as well as to the plane of the C-C sigma bond. The 2p orbitals of one carbon atom are parallel to the 2p orbitals of the other carbon atom, which undergo lateral or sideways overlapping to form two pi(π) bonds between two carbon atoms.

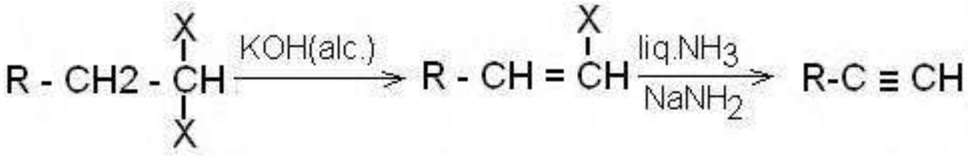
METHOD OF PREPARATION OF ALKYNES

1. Dehydrohalogenation of vicinal dihalides



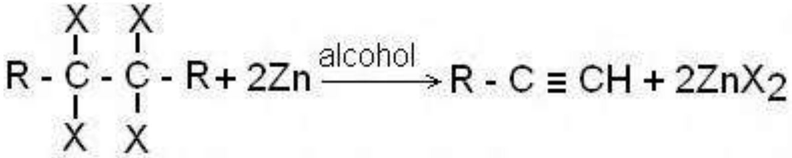
$$R-\overset{H}{\underset{X}{C}}-\overset{X}{\underset{H}{C}}-R \xrightarrow[-HX]{KOH\ (alc.)} R-\overset{H}{C}=\overset{X}{C}-R \xrightarrow{NaNH_2} R-C\equiv C-R$$

2. Dehydrohalogenation of germinal dihalides



$$R-CH2-\overset{X}{\underset{X}{CH}} \xrightarrow{KOH(alc.)} R-CH=\overset{X}{CH} \xrightarrow[NaNH_2]{liq.NH_3} R-C\equiv CH$$

3. Dehalogenation of tetrahalides

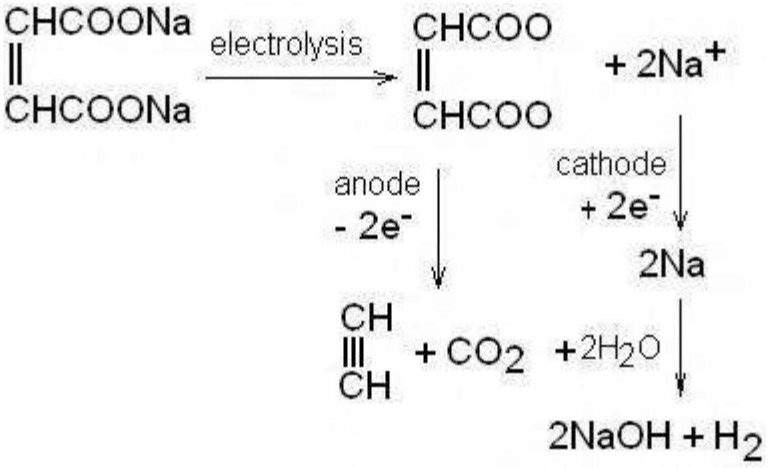


$$R-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}-R+2Zn \xrightarrow{alcohol} R-C\equiv CH+2ZnX_2$$

4. Reaction of iodoform with silver

$$CHI_3 + 6Ag + I_3CH \xrightarrow{alcohol} CH \equiv CH + 6AgI$$

5. Kolbe's electrolysis



6. From calcium carbide

$$CaCO_3 \overset{\Delta}{\rightarrow} CaO + CO_2$$

$$CaO + 3C \rightarrow CaC_2 + CO$$

Calcium carbide

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

PHYSICAL PROPERTIES OF ALKYNES

1. Physical state
    - Alkynes are colour less and odourless with the exception of acetylene which has a characteristic odour.
    - (C_2 to C_4) members are colourless gas, next eight are liquids and higher ones are solids
2. Melting and boiling point
   Melting and boiling point of simple alkynes are slightly higher than corresponding alkenes and alkenes. This can be attributed to their symmetrical linear shape, so that molecules can pack closely in the crystal lattice
3. Solubility
   Alkynes are insoluble in water but readily soluble in non-polar solvents like benzene, ether etc
4. Density : Alkyene are lighter than water.

5. Polarity
   Alkynes are slightly more polar than alkenes because sp hybridized carbon is more electronegative in comparison of sp^2 hybridized carbon atom of alkenes

CHEMICAL PROPERTIES OF ALKYNES

1. Reactivity of alkynes
   Alkynes are less reactive than alkene towards electrophilic addition reactions. This is due to following reasons
   (i) Sp – hybridized carbon atom of triple bond is more electronegative hence π – electrons of alkynes are more tightly held and thus less readily available for reaction with electrophile
   (ii) Π – electron cloud of alkynes is more delocalized in cylindrical form and thus less readily available for addition reactions
2. Acidic character of alkynes
    - Acetylene is weaker acid than water or alcohol but stronger than ammonia
    - Acidic character of alkynes can be explained on the basis of percentage of s-character of the hybrid orbital.

Hydrocarbon	Hybrid orbital	%of s-character
Alkanes	sp^3	25%
Alkenes	sp^2	33.33%
Alkynes	Sp	50%

- More s-character, more is electronegativity. Therefore C-H bond in acetylene are strongly held by carbon nuclei which facilitates the removal of hydrogen.
- Order of acidic character can be given as
  $H_2O > ROH > CH\equiv CH > NH_3 > CH_2 = CH_2 > CH_3 - CH_3$

(i) Formation of sodium acetylides.

$$R - C \equiv CH \xrightarrow[\text{or Na/NH3 liquid}]{NaHN_2} R - C \equiv C^- Na^+$$

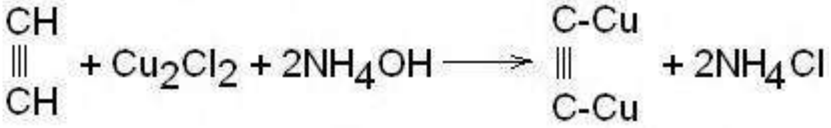
$$R - C \equiv C^- Na^+ + H_2O \longrightarrow R - C \equiv CH + NaOH$$

Sodium alkynides are stable when dry but readily hydrolysed by water, regenerating the alkyne.

(ii) Formation of heavy metal alkynide

$$R - C \equiv CH + AgNO_3 + NH_4OH \rightarrow R - C \equiv C - Ag + NH_4NO_3 + H_2O$$

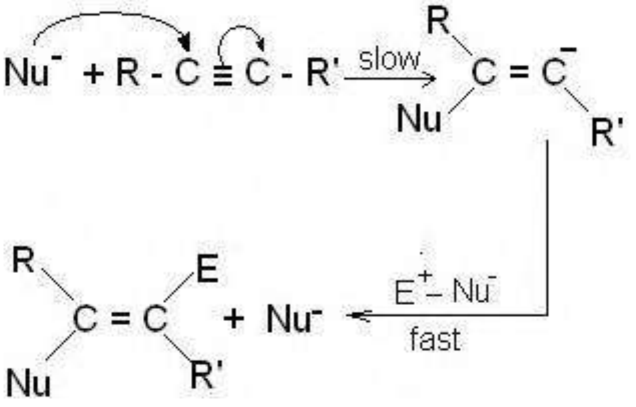
silver alkynide(white ppt)



$$CH \equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow Cu\text{-}C \equiv C\text{-}Cu + 2NH_4Cl$$

3. Addition reaction

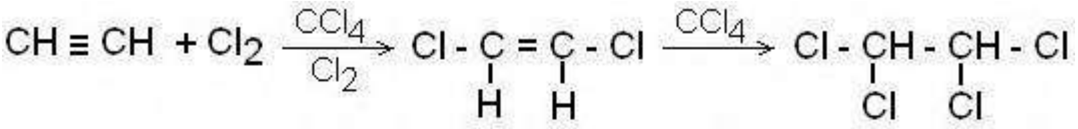
Alkynes are susceptible for nucleophilic addition reaction.



(i) Addition of hydrogen

$$CH \equiv CH \xrightarrow[\text{catalyst}]{H_2} CH_2 = CH_2 \xrightarrow[\text{catalyst}]{H_2} CH_3 - CH_3$$

(ii) Addition of halogens

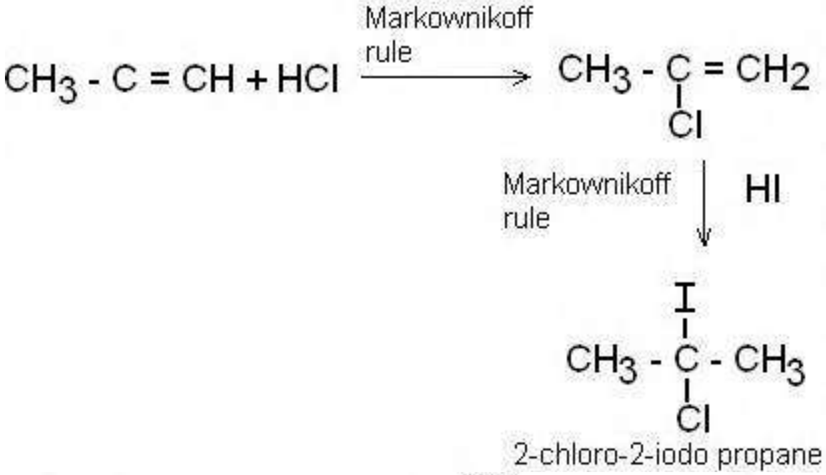


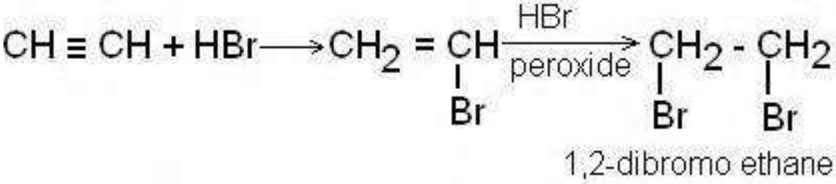
$$CH \equiv CH + Cl_2 \xrightarrow[Cl_2]{CCl_4} Cl - CH = CH - Cl \xrightarrow{CCl_4} Cl - CH(Cl) - CH(Cl) - Cl$$

Order of reactivity of halogens is

$Cl_2 > Br_2 > I_2$

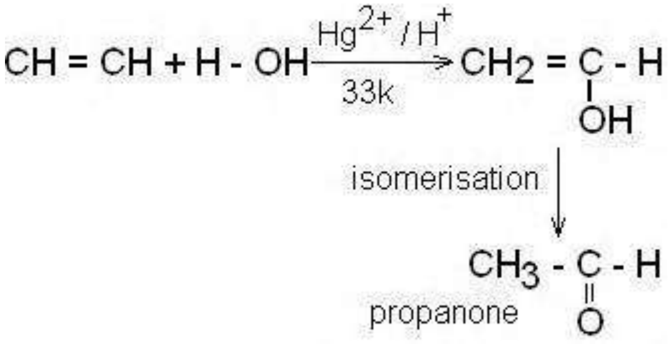
(iii) Addition of hydrogen halides



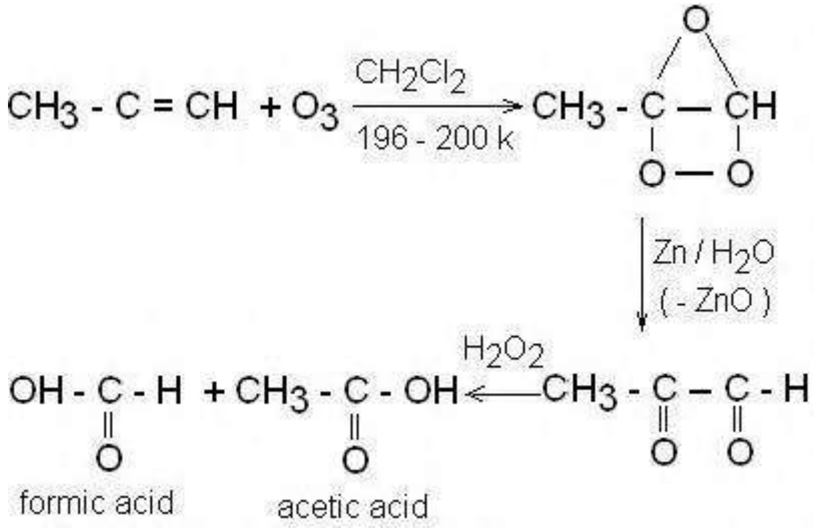


Order of reactivity of halogen acids is
HI > HBr > HCl > HF

(iv) Addition of water



(v) Addition of ozone



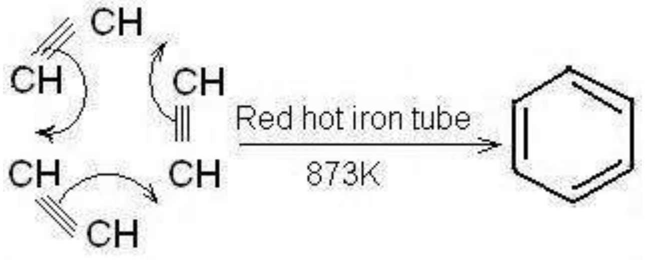
(vi) Polymerisation

(a) Linear polymerization

$$CH \equiv CH + CH \equiv CH \xrightarrow{Cu_2Cl_2, NH_4Cl} CH_2 = CH - C \equiv CH \xrightarrow{CH \equiv CH}$$

$CH_2 = CH - C \equiv C - CH = CH_2$ (divinyl acetylene)

(b) Cyclic polymerization



Uses of alkynes

(i) Acetylene is used as illuminant

(ii) It is used for the production of oxy-acetylene flame. The temperature of the flame is above 3000°C. It is employed for cutting and welding of metals

(iii) It is used as general anesthetic under the name Naracylene.

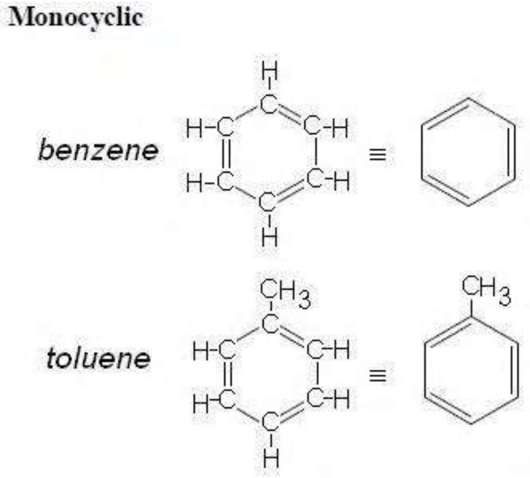
AROMATIC HYDROCARBONS OR ARENES

The term aromatic has been derived from the greek word aroma meaning pleasant odour, but in present form the aromatic compounds are cyclic closed chain) compounds having double bond in alternate positions

Aromatic compound containing benzne ring are known as benzoid and those not containing a benzene ring are known as non-benzoid.

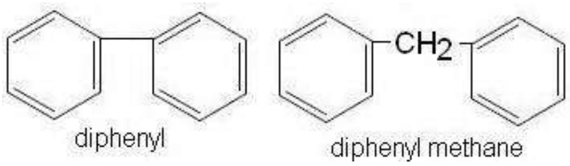
CLASSIFICATION OF ARENES

(i) Monocyclic aromatic hydrocarbons: These consist of only benzene ring, with general formula C_nH_{2n-6} and includes benzene and its homologues

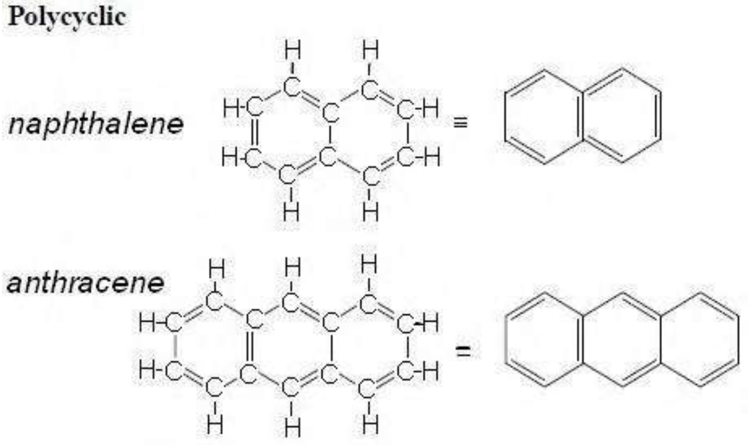


(ii) Polycyclic aromatic hydrocarbons: These consists of more than one benzene ring

(a) Isolated

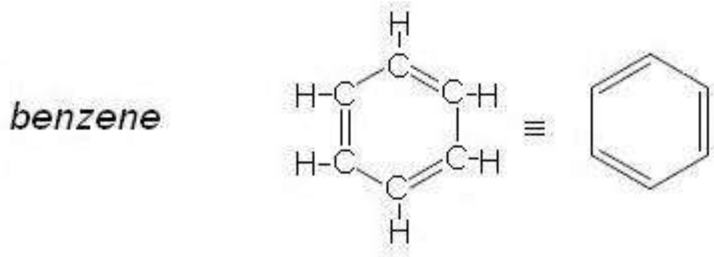


(b) Fused or condensed

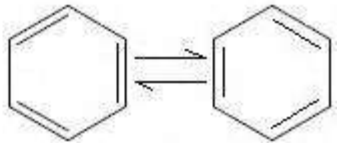


STRUCTURE OF BENZENE

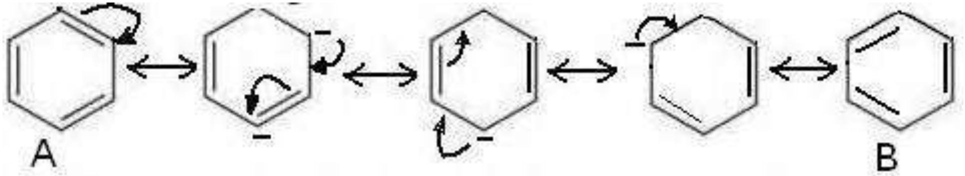
- Benzene was isolated by Michael Faraday in 1825
- The molecular formula of Benzene is C_6H_6 which indicates a high degree of unsaturation
- August Kekule in 1865 proposed a structure of Benzene having cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon atom



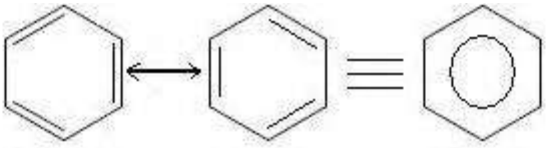
- Kekule suggested the oscillating nature of double bond in benzene as shown



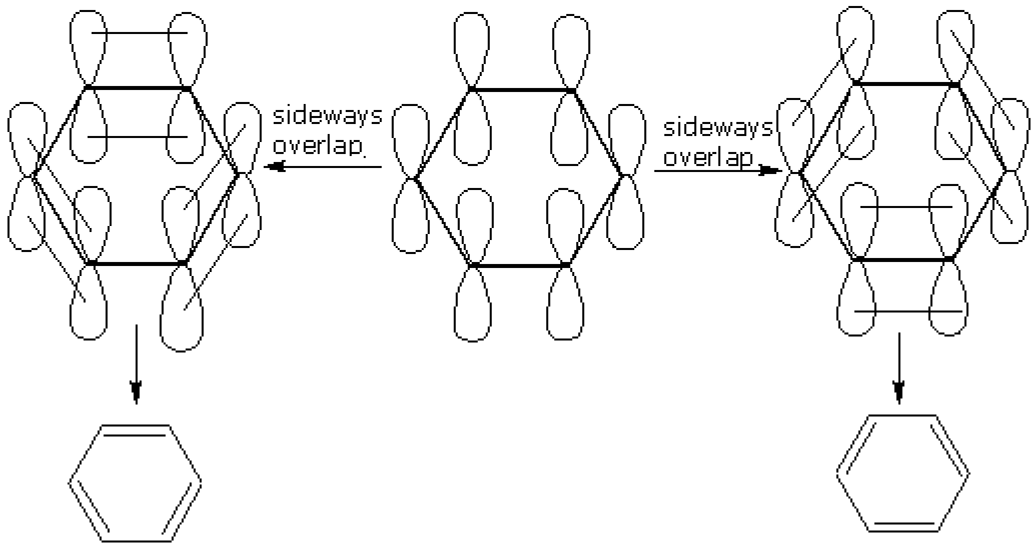
- Benzene is a hybrid of various resonating structure



- A and B are main contributing structures. The hybrid structure is represented by a circle which represents six electrons are delocalized between the six carbon atom of the benzene ring



- Benzene is sp^2 hybridised. Two sp^2 hybrid orbitals of each carbon atom overlap with sp^2 hybrid orbitals of adjacent carbon atoms to form C-C sigma bonds which are in hexagonal plane. The remaining sp^2 hybrid orbitals of each carbon atom to form six C-H bond. Each carbon atom is now left with one unhybridised p orbital perpendicular to the plane of ring



- All the six C-C bond lengths are of the same order (139pm) which is intermediate between C-C single bond (154pm) and C-C double bond (133pm).
- Thus the absence of pure double bond in benznene accounts for benzene to show addition reactions under normal conditions

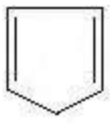
AROMATICITY – HUCKEL RULE

Huckel rule states that " An aromatic compound having a reasonably planar cyclic structure with $(4n+2)\pi$ electron clouds and possessing unusual stability due to delocalization of π – electrons

(a) Benzene
In benzene three double bond i.e. 6π electrons
Now $4n + 2 = 6$ Therefore $n = 1$
Benzene shows aromatic character

(b) Naphthalene
There are five double bonds in naphthalene i.e. 10π electrons
$4n + 2 = 10$ Therefore $n = 1$
Nephthalene shows aromatic character

(c) Cyclopentadine
The molecule has two double bonds i.e. 4π electrons

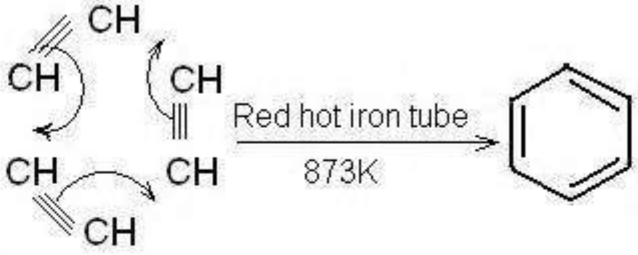


$4n + 2 = 4$ Therefore $n = 0.5$

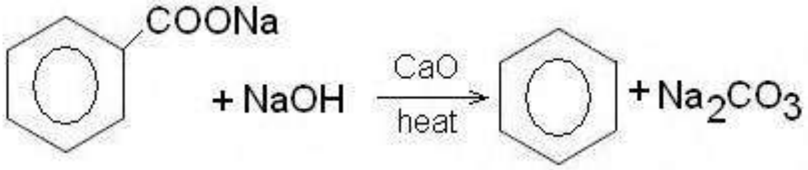
Cyclopentadine is non-aromatic
Note: Cyclopentadine ion is aromatic because it has 6π electrons used in delocalization

METHOD OF PREPARATION OF BENZENE

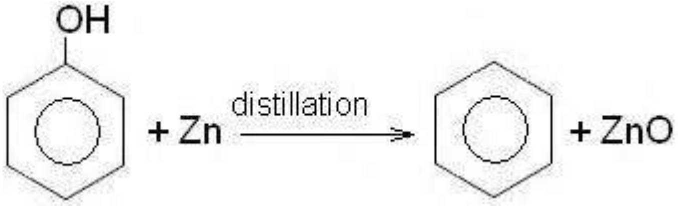
1. Cyclic polymerization of ethyne



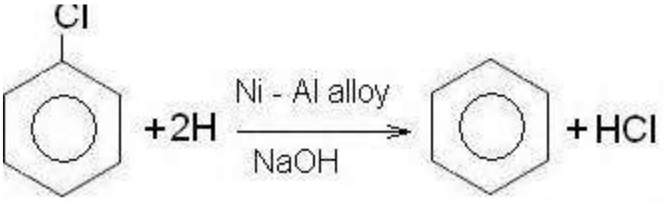
2. Decarboxylation of aromatic acids



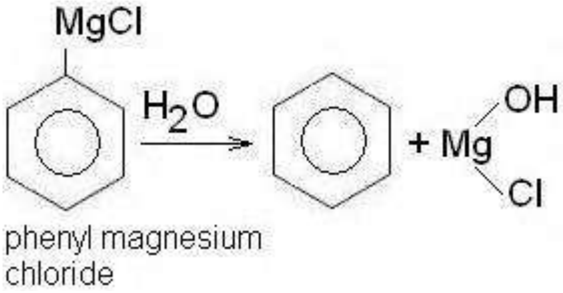
3. Deoxygenation of phenols



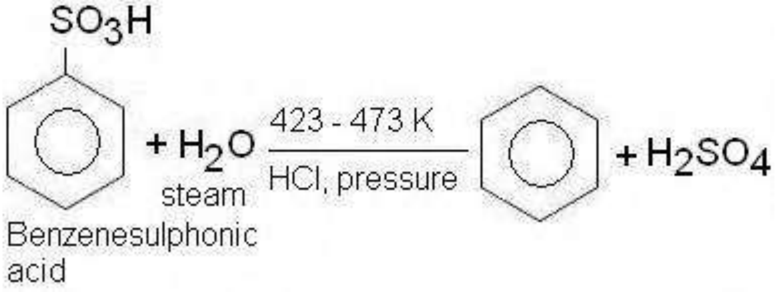
4. Reduction of chlorobenzene



5. Hydrolysis of Grignard reagent



6. Hydrolysis of benzene sulphonic acid

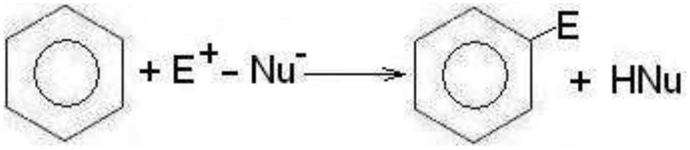


PHYSICAL PROPERTIES OF AROMATIC HYDROCARBONS

1. Lower members of aromatic hydrocarbons are colourless liquid while higher ones are solid with characteristic smell
2. These are non-polar compounds insoluble in water but soluble in organic solvent
3. Benzene itself is a good solvent. Fats, resins, rubber etc dissolves in it
4. They are lighter than water
5. They are inflammable and burn with sooty flame because of high carbon contents
6. Their boiling point increases with increase in molecular mass.

CHEMICAL PROPERTIES OF AROMATIC HYDROCARBONS

I) Electrophilic substitution reactions

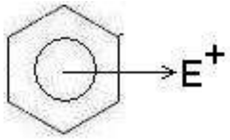


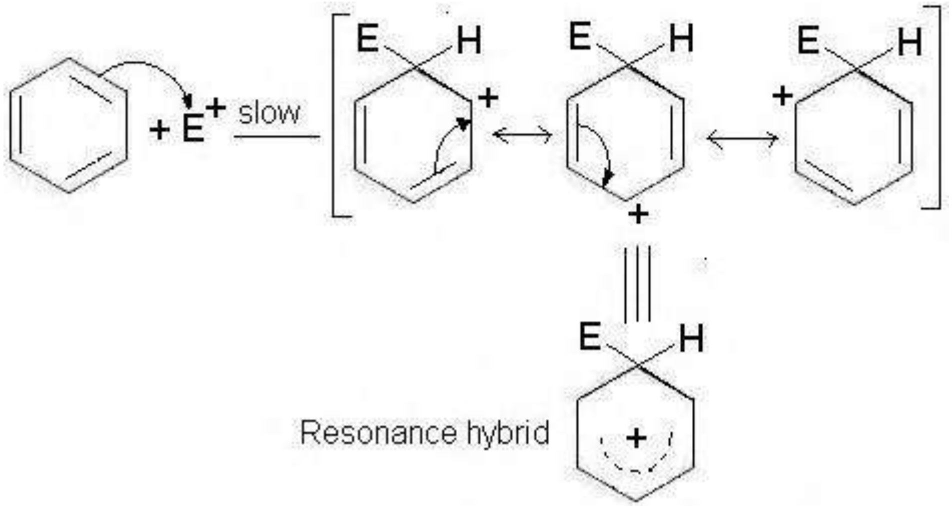
General mechanism

Step I : Attacking electrophile is generated from the reagent

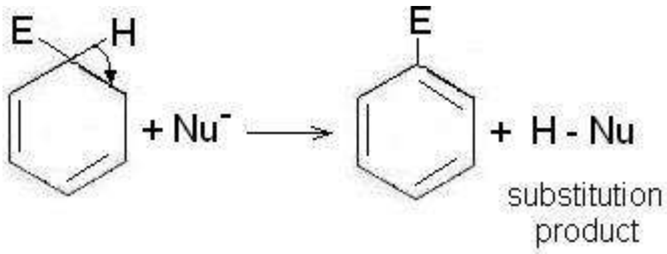
$$\underset{\text{reagent}}{E - Nu} \longrightarrow \underset{\text{electrophile}}{E^+} + \underset{\text{nucleophile}}{Nu^-}$$

Step II : As soon as the electrophile is generated, it is attracted by π electron cloud of benzene to form a π- complex. π- complex is then rearranged to form carbocation which is resonance stabilized

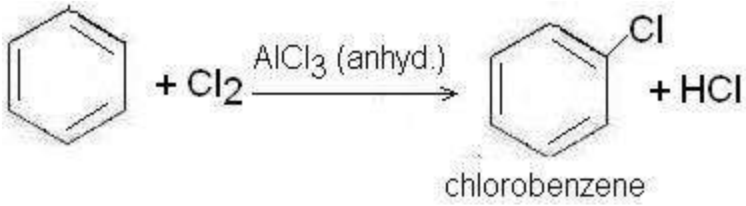




Step III: The carbocation intermediate loses a proton to the nucleophile (Nu^-) present in reaction mixture to form substitution product.



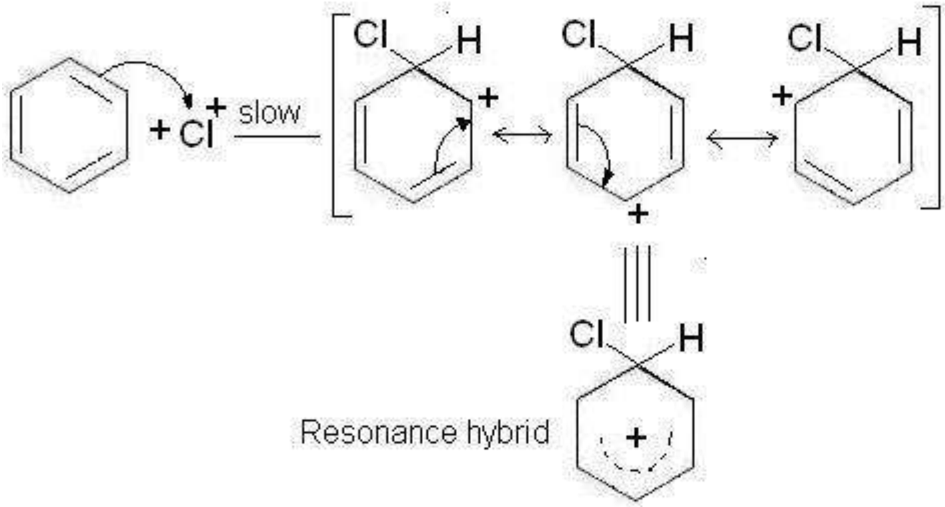
1. Halogenation



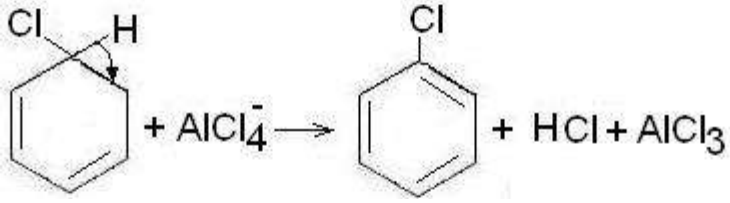
Mechanism

Step I : Cl – Cl + $AlCl_3 \rightarrow AlCl_4^- + Cl^+$

Step II:

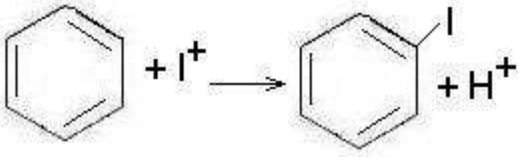


Step III:

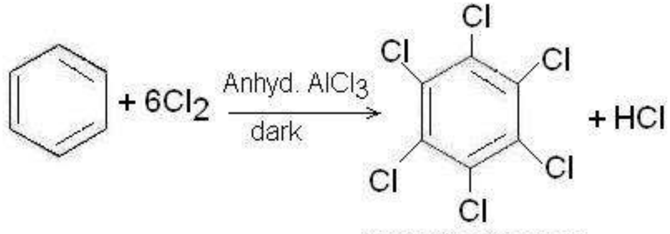


- Fluorine is extremely reactive and gives very poor yield under similar conditions
- Iodination is carried out in presence of oxidizing agents such as hydrogen peroxide or cupric chloride which oxidize molecular iodine into an electrophile

  $I_2 + 2Cu^{2+} \rightarrow 2I^+ + 2Cu^+$

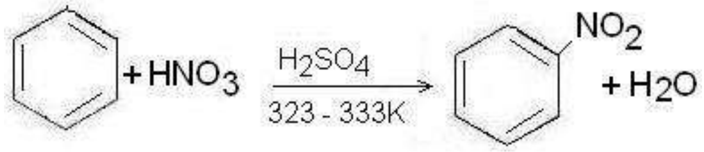


With excess of halogens in presence of anhydrous $AlCl_3$ (catalyst) and dark, all the hydrogen atoms of benzene ring may be successively replaced.



hexachlorobenzene

2. Nitration

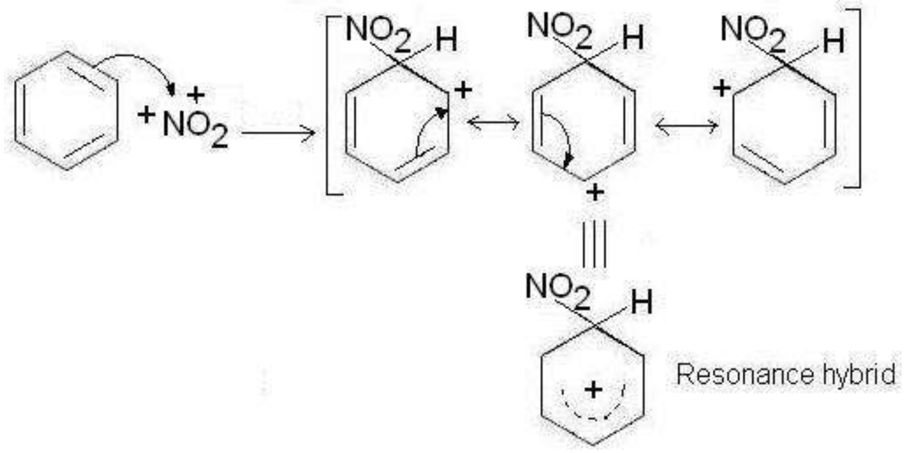


Mechanism

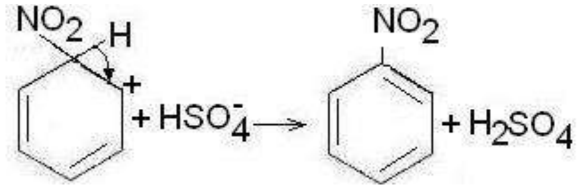
Step I

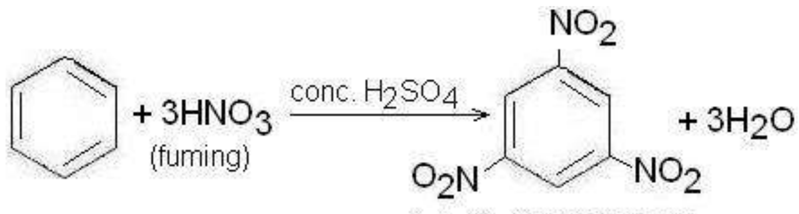
$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

Step II



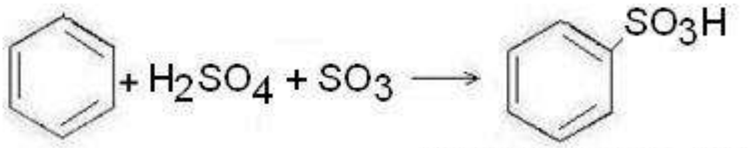
Step III





1, 3, 5 - Trinitrobenzene

3. Sulphonation



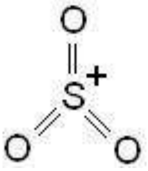
Benzene sulphonic acid

Mechanism

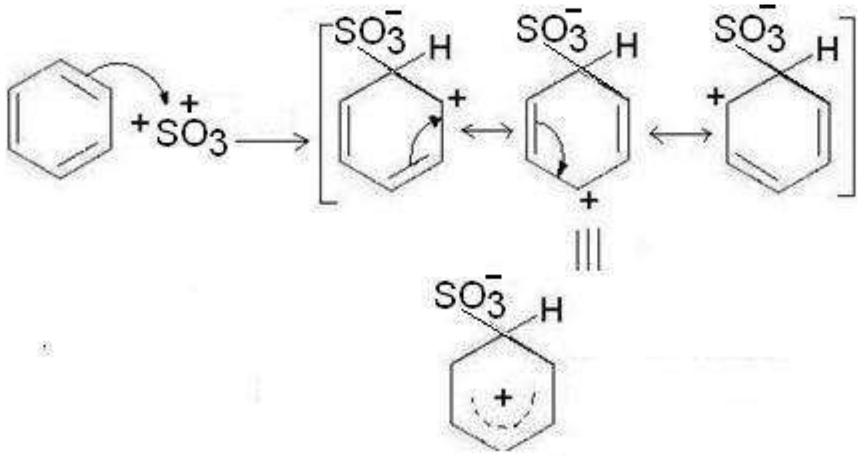
Step I

$2H_2SO_4 \rightarrow SO_3 + HSO_4^- + H_3O^+$

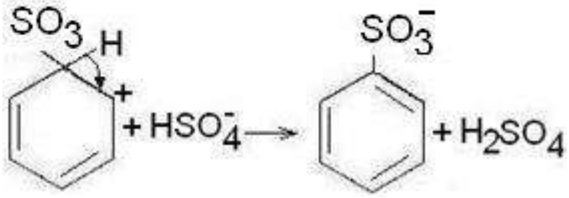
In sulphonation SO_3 acts as attacking electrophile since sulphur atom in SO_3 is electron deficient

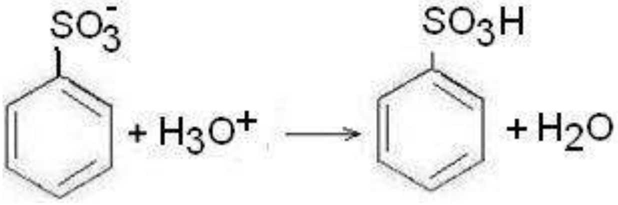


Step II

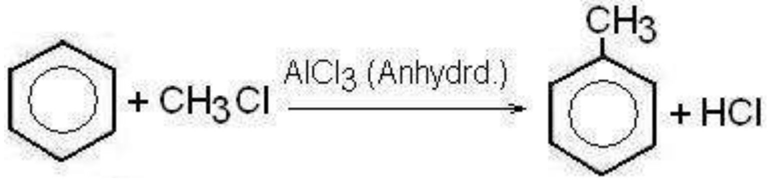


Step III





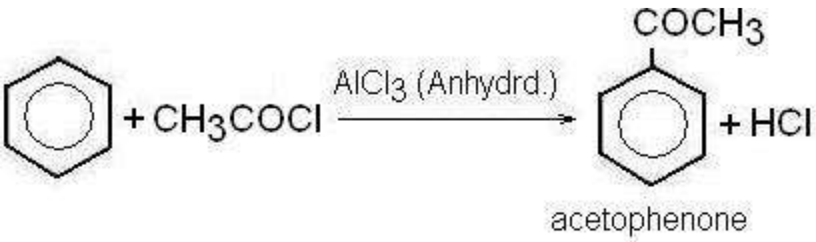
4. Friedel Crafts alkylation

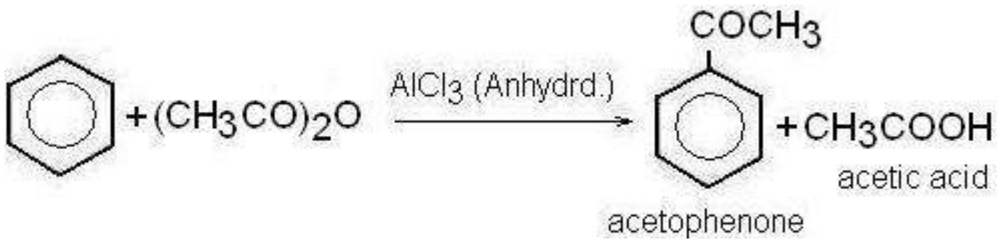


Mechanism

Step I

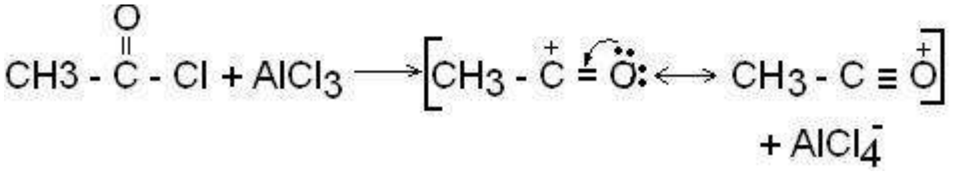
$CH_3 – Cl + AlCl_3 \rightarrow CH_3^+ + AlCl_4^-$





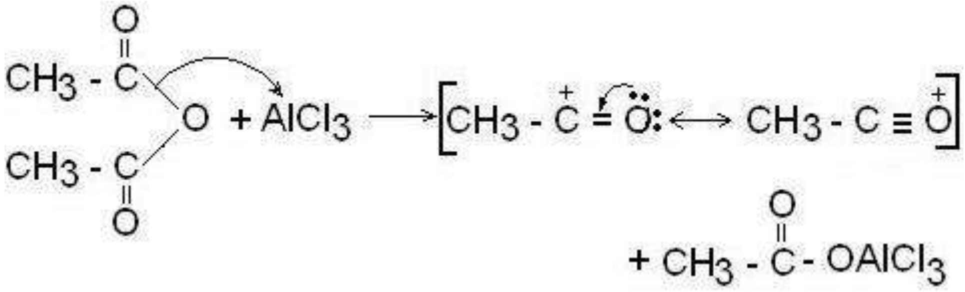
Mechanism

Step I

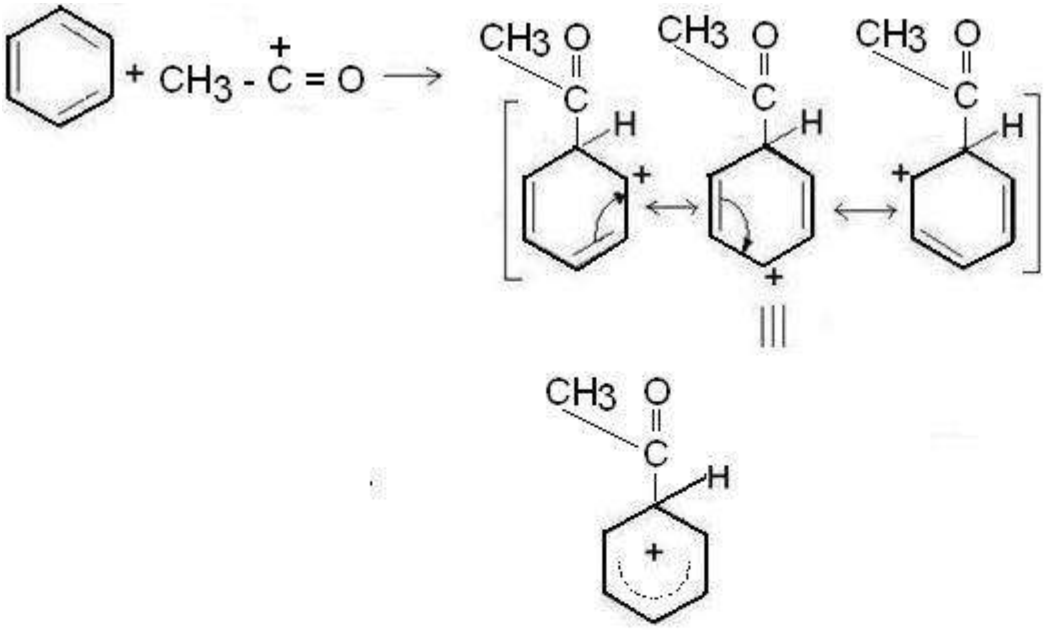


$$CH3 - \overset{O}{\overset{\|}{C}} - Cl + AlCl_3 \longrightarrow \left[CH_3 - \overset{+}{C} = \ddot{O}: \longleftrightarrow CH_3 - C \equiv \overset{+}{O}\right] + AlCl_4^-$$

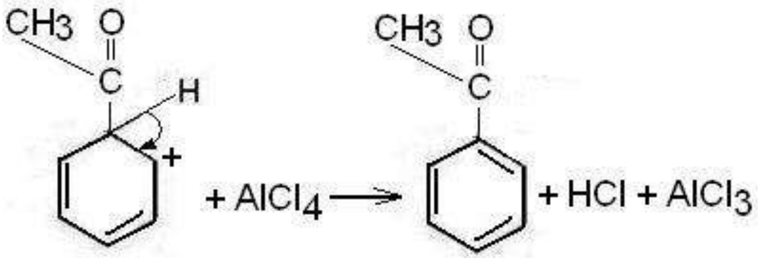
OR



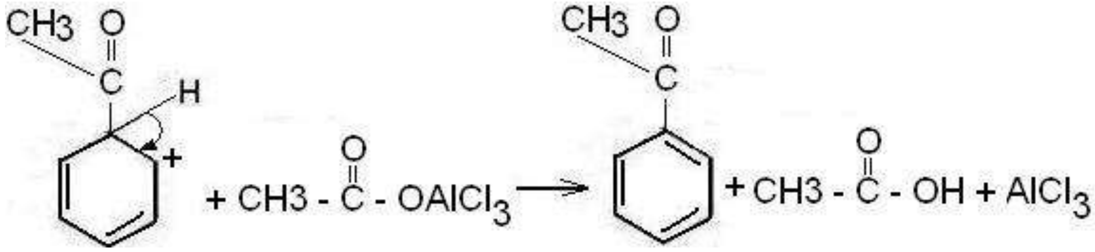
Step II



Step III

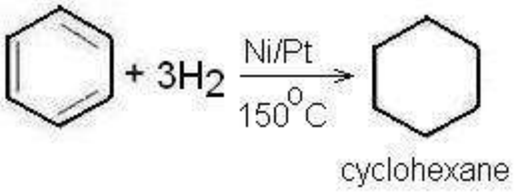


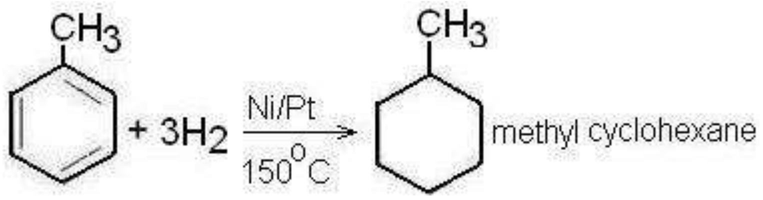
OR



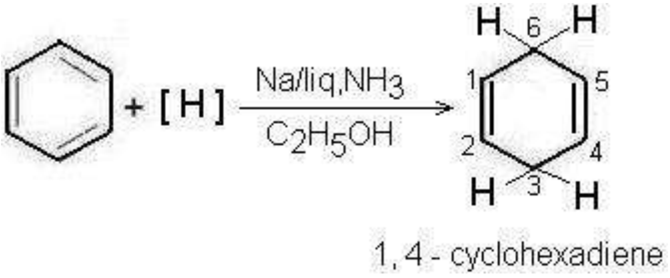
II) Addition reactions

1. Catalytic hydrogenation

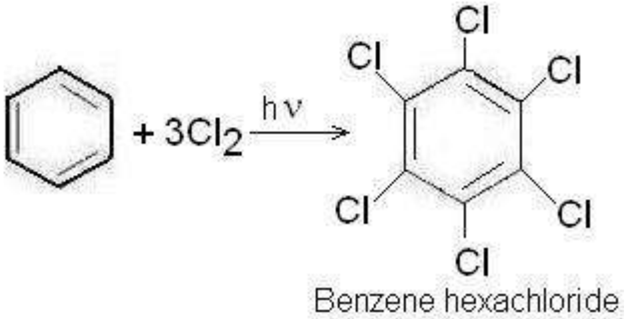




Birch reduction takes place in presence of Na metal and liquid NH_3



2. Addition of halogen



Benzenehexachloride is used as powerful insecticide under the name of gammexane or 666 or lindane

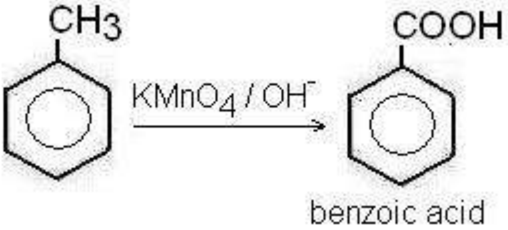
III) Oxidation

1. Complete combustion

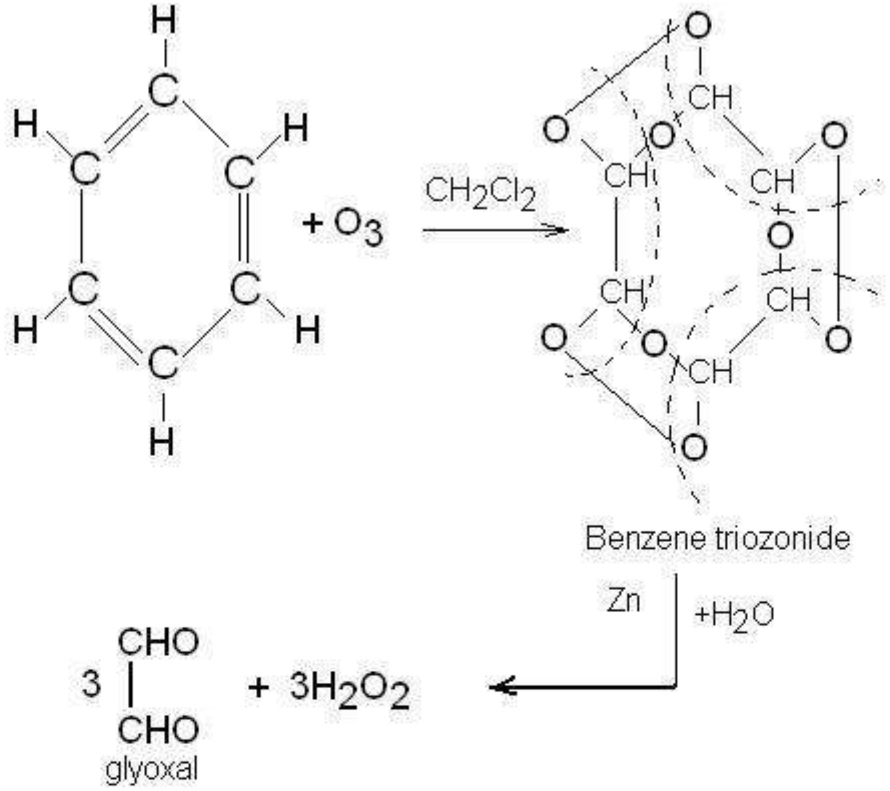
$$C_xH_y + \left(x + \frac{y}{2}\right) O_2 \rightarrow xCO_2 + \frac{y}{2} H_2O$$

$$C_6H_6 + \frac{15}{2} O_2 \rightarrow 6CO_2 + 3H_2O$$

2. Oxidation with potassium permanganate

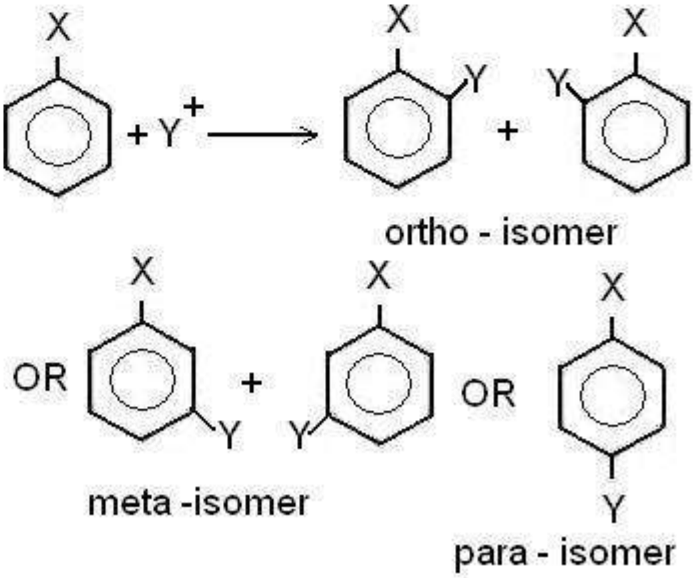


(IV) Ozonolysis



DIRECTIVE INFLUENCE OF A FUNCTIONAL GROUP IN MONOSUBSTITUTED BENZENE

1. Directive or orientation effect



(i) o, p – directing groups

The substituent’s or groups which direct the incoming group to ortho and para positions are acalled o,p – directing groups

Example: -R (alkyl), -C_6H_5, -OH, - SH, -NH_2, -NHR, -NR_2 , -NHCOR, -OR(alkoxy), -Cl, -Br, I.

- In general electron-donating group are o,p directing. Halogens (-Cl, -Br, -I) and nitroso (-N=O) are exception to it which are electron withdrawing but o,p – directing.
- Out of ortho- and para-, gerally para- substitution predominates because ortho – substitution is accompanied with steric hindrance.

(ii) m- directing groups

The substituents or groups which direct the incoming group at the meta position are called m-directing groups.

Example: -SO_3H, -COOH, -COOR, -COR, -CHO, -CCl_3, -CF_3 , -CN, -COCl, -NO_2, -N^+H_3, -N^+H_2R, -N^+HR_2, -N^+R_3, -SO_2Cl, -N^+H_3Cl

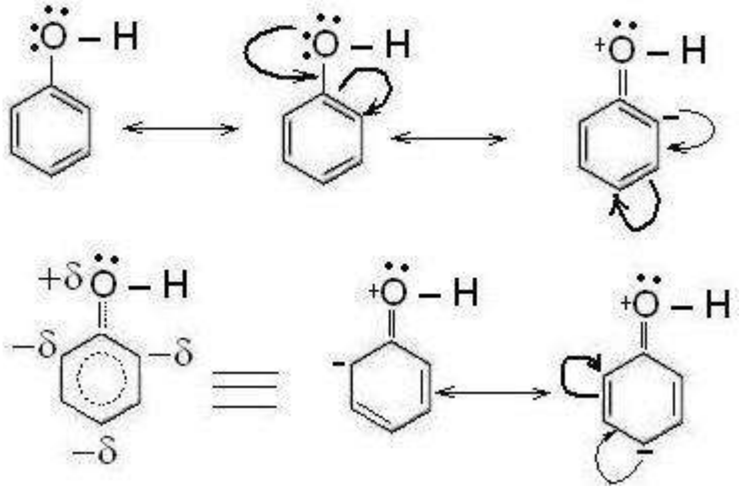
- In general all electron withdrawing are m-directing

2. Activity effect (Effect of substituent on reactivity)

(i) Activating groups

- Electron releasing group i.e. o,p-directing groups activate the benzene ring by increasing its nucleophilicity for further substitution.

Example



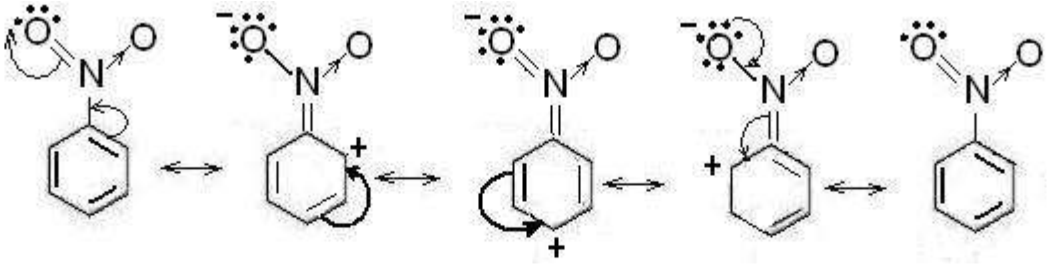
It is clear from the above resonating structures that the electron density is more on o- and p- positions

- Halogens (-Cl, -Br, -I) and nnitroso group (- N = O) which are o, p – directing but deactivates the benzene ring being electron withdrawing
- Order of electron donating capability

$-O^- > -NR_2 > -OH > -NH_2 > -OCH_3 > -NHCOCH_3 > -CH_3$

(ii) Deactivating group

Electron withdrawing groups i.e. m-directing group deactivate the ring by decreasing nucleophilicity for further substitution.

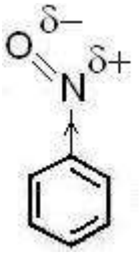


In this case, the overall electron density on benzene ring decreases making further substitution difficult.

Electron withdrawing ability order:

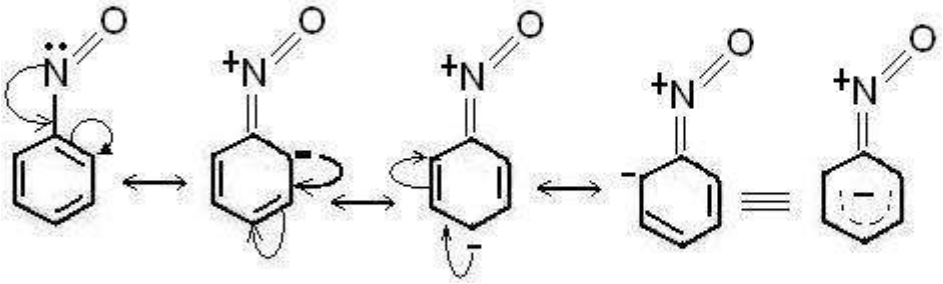
$-N^+(CH_3)_3 > -NO_2 > -CN > -SO_3H > -CHO > -COCH_3 > -COOH$

Halogens also come under the category of deactivating group, with the exception that they are o, p- directing. Because of –I effect, halogens are electron withdrawing but o, p- directing due to +R effect.



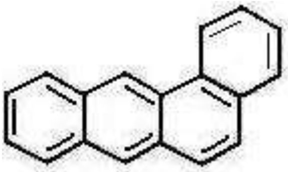
Nitroso group (-N = O) is also deactivating but o,p –directing. Oxygen is more electronegative than nitrogen and hence NO group as a whole withdraws electrons from benzene ring and produce deactivating effect on the ring.

But lone pair of electrons on the N atom can be donated towards the benzene ring, thus increasing electron density more at o,p –positions rather than at m-position which makes it o,p – directing.

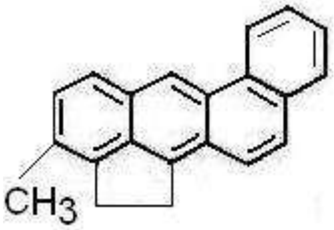


CARCINOGENITY AND TOXICITY OF PLYNUCLEAR HYDROCARBONS

- Polynuclear hydrocarbons are toxic and said to possess cancer producing (carcinogenic) property. In fact, polynuclear hydrocarbons are the products of incomplete combination of organic matter such as coal, petroleum, tobacco etc.
- They enter into the human body and undergo various biochemical reactions and finally damage DNA to cause cancer.

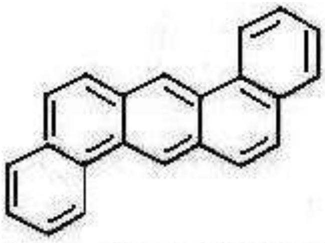


1,2-benzanthracene



3-methyl cholanthrene

1,2-benzopyrene



1, 2, 5, 6 -dibenzanthracene

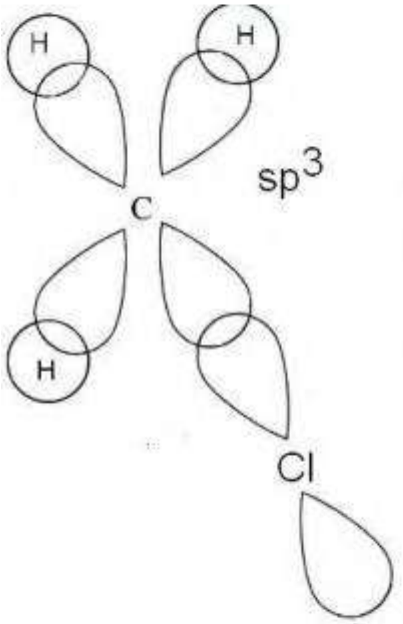
SECTION I
HALOAKANES

Compounds derived from alkanes by the replacement of one or more Hydrogen atoms by corresponding number of halogen atoms (fluorine, chlorine, bromine or iodine) are termed as haloalkanes.

Alkyl halides are represented by general formula $C_nH_{2n+1}X$, here X is halogen atom

ORBITAL STRUCTURE

In alkyl halides, carbon-halogen σ bond is formed by overlap of sp^3 hybrid orbital of carbon and half filled valence p-orbital of halogen atom:



Haloalkanes may be classified on the basis of number of halogen atoms

(1)Monohalogen derivatives

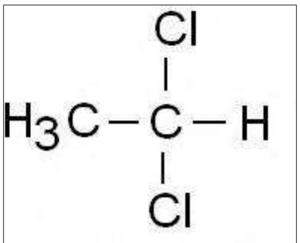
One halogen atom is attached to carbon atom. Its general formula is $C_nH_{2n+1}X$
Example CH_3Cl (methyl chloride).

(2)Dihalogen derivatives

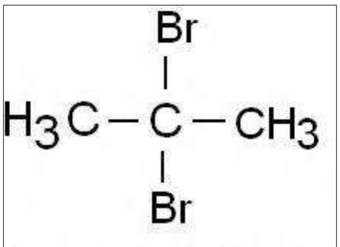
These are derived by replacement of two hydrogen atoms by two halogen atoms
Dihalides derivatives are of three types

(a) Gem-dihalides

Halogen atoms are attached to same carbon atom. These are called alkylidene halides.



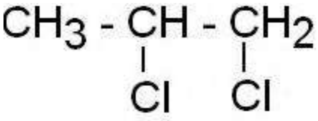
Ethylidene chloride
(1,1-Dichloroethane)



Isopropylidene bromide
(2,2-Dibromoprpane)

(b) Vic-dihalides

Halogen atoms are attached to adjacent (vicinal) carbon atoms. These are termed as alkylene halides.



$CH_3-CH(Cl)-CH_2Cl$

Propylene chloride
(1,2 - Dichloropropane)

(c) α – ω halides (terminal halides)

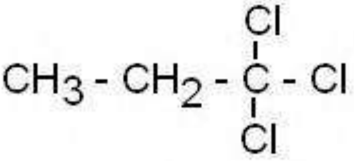
Halogen atoms are attached to terminal carbon atoms. These are also called polymethyl halides

$Br-CH_2-CH_2-CH_2-Br$

Trimethyl di bromide (1,3 – dibromopropane)

(3)Trihalogen derivatives

Trihalogen derivatives are derived by replacing three hydrogen atoms by three halogen atoms. General formula is $C_nH_{2n-1}X$

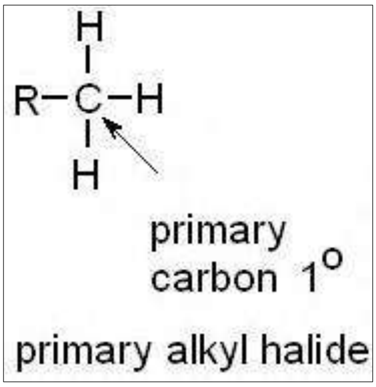


$CH_3-CH_2-CCl_3$

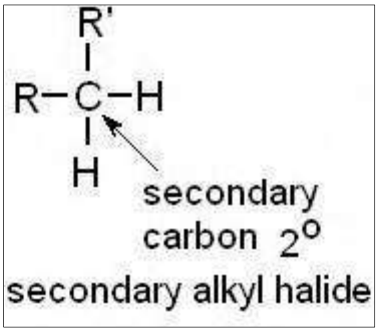
1,1,1-trichloropropane

CLASSIFICATION OF MONOHALOGEN COMPOUND

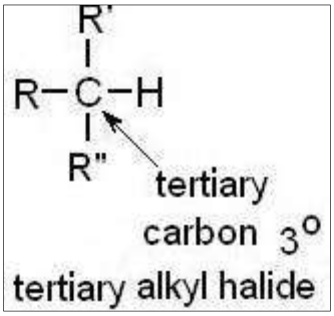
(1) Alkyl halides are classified as primary 1^{O}, secondary 2^{O}, tertiary 3^{O} depending upon nature of carbon to which halogen is attached



primary alkyl halide



secondary alkyl halide



tertiary alkyl halide

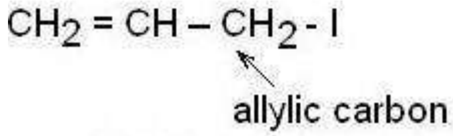
(2) Compounds containing sp^3 , C – X bond

(a) Alkyl halides

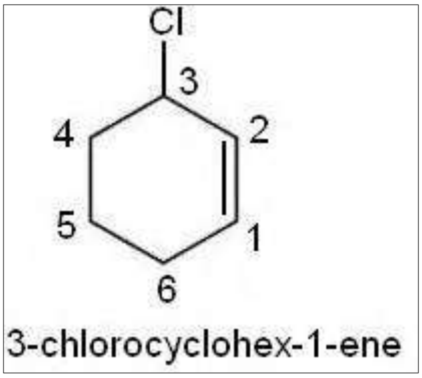
$CH_3 – CH_2 – CH_2 – Cl$ (1- chloropropane)

(b) Allylic carbon

Halogen atom attached to allylic carbon. i.e. carbon atom next to C = C.
Example



3-iodoprop-1-ene



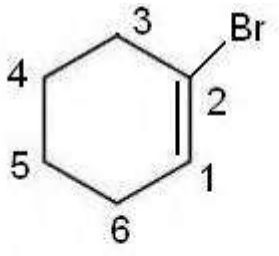
3-chlorocyclohex-1-ene

(3) Compound containing sp^2 ,C – X bond

Vinylic halides

In these halides, halogen atom is attached to vinylic carbon i.e. one of the carbon atoms of C = C

$CH_2 = CH – Cl$ (Chloroethene or vinyl chloride)



1-bromocyclohex-1-ene

(4) Compounds containing sp ,C – X bond Haloalkynes

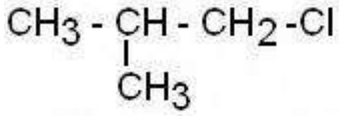
In these halides, the halogen atom is attached to one of the carbon atoms of

$C \equiv C - Br$ (Bromoethyne)

ISOMERISM OF MONOHALOGEN COMPOUNDS

(1) Chain isomerism: This is due to different arrangement of carbon in alkyl group

$CH_3 - CH_2 - CH_2 - CH_2 - Cl$ (1 –chlorobutane)

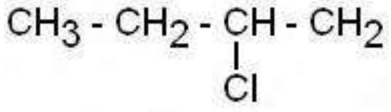


$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - Cl$$

1-chloro-2-methylpropane

(2) Position isomerism: This is due to different position of halogen atom in the molecules

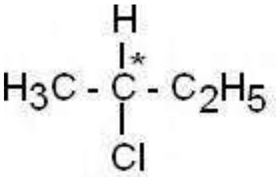
$CH_3 - CH_2 - CH_2 - CH_2 - Cl$



$$CH_3 - CH_2 - \underset{\underset{Cl}{|}}{CH} - CH_2$$

2- chlorobutane

(3) Optical isomerism: This is due to presence of an asymmetric carbon atom (asymmetric carbon atom : all four substituent atoms or molecules attached to carbon are different)



$$H_3C - \overset{\overset{H}{|^*}}{\underset{\underset{Cl}{|}}{C}} - C_2H_5$$

* asymmetric carbon atom

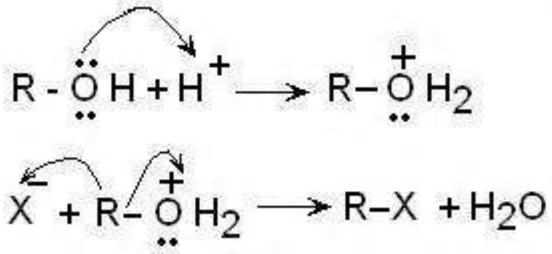
(4) Conformations: Haloalkanes can also form conformers due to free rotation of C-C bond.

GENERAL METHODS OF PREPARATION

(1)From alcohol

(a) Action of hydrogen halides

1^O alcohols follows S_N2 whereas 2^O and 3^O alcohol follows S_N1 mechanism.
In these S_N mechanisms, the nucleophile (X^-) attacks the protonated alcohol molecule with elimination of water.



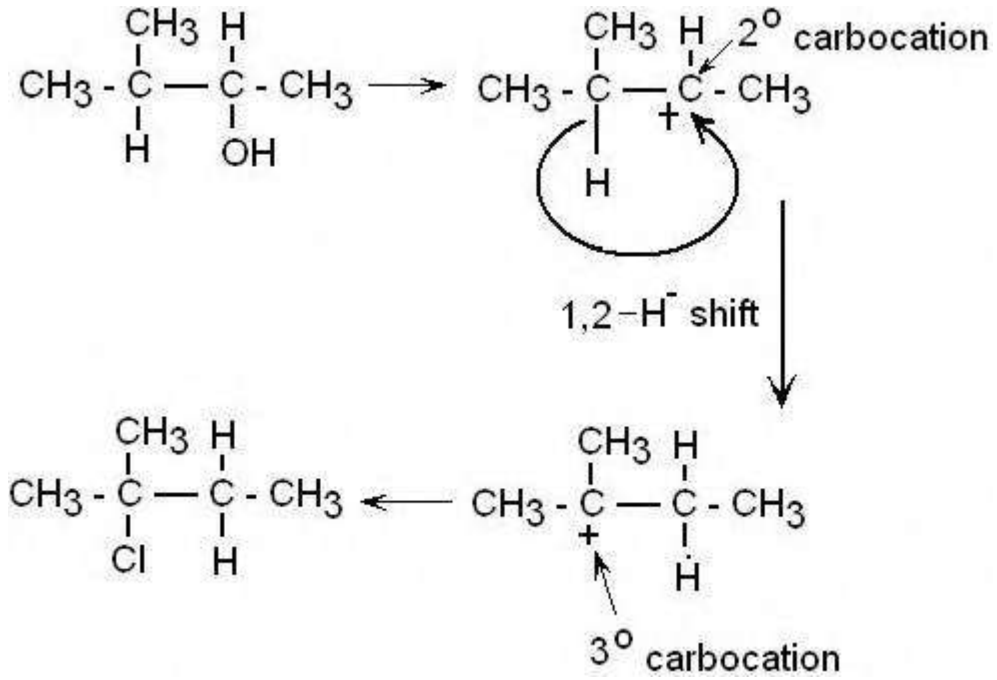
Since nucleophilicity (i.e. tendency to donate electron pair to the carbon) of halide ion decreases in the order $I^- > Br^- > Cl^-$, the order of reactivity of halogen acid decreases in the same order HI > HBr > HCl
Order of reactivity of different alcohol is
Allyl > 3^o alcohol > 2^o alcohol > 1^o alcohol

$$R - OH \xrightarrow{HCl(conc)Anhyd.ZnCl_2} R - Cl + H_2O$$

HCl do not require anhyd. $ZnCl_2$ for 3^o alcohol because 3^o are very reactive.
The mixture (1:1) of con. HCl and anhyd $ZnCl_2$ is called LUCAS reagent. It is used to distinguish 3^o, 2^o, 1^o alcohols because their reactivity towards this reagent is 3^o alcohol > 2^o alcohol > 1^o alcohol

$$R - OH \xrightarrow{HBr/H_2SO_4 reflux} R - Br + H_2O$$
$$R - OH \xrightarrow{\frac{KBr}{conc}.H_2SO_4 reflux} R - Br + H_2O$$

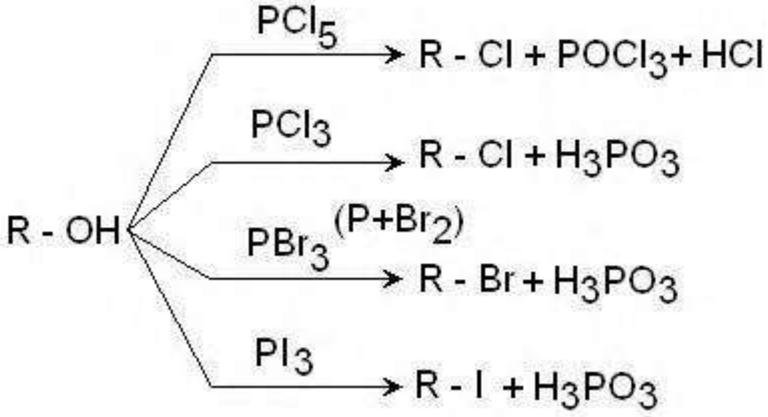
The mixture of KBr and H_2SO_4 is not used in case of secondary and tertiary alcohol as they can cause dehydration.
Rearranged product may also be obtained due to hydride or methyl shift in carbocation intermediate



$$R-OH \xrightarrow{HI\ reflux(57\%)} R-I+H_2O$$

$$R-OH \xrightarrow{HK+H_3PO_4 reflux} R-I+H_2O$$

(b) Action of phosphorous halide



4th method gives good yield of 1° haloalkanes but poor yields 2° and 3° haloalkanes because secondary and tertiary alcohol on heating forms alkene.

PBr_3 and PI_3 are obtained in situ by action of red phosphorus and bromine or iodine respectively

(c) Action of thionyl chloride

Darzen's method

$$R-OH+SOCl_2 \xrightarrow{pyridine} R-Cl+SO_2(g)+HCl(g)$$

This method is preferred because other two byproducts are escapable gases.

$SOBr_2$ is less stable and SOI_2 does not exist. Thus R-Br and RI can't be prepared by Darzen's method.

(d) Hunsdiecker reaction

$$RCOOAg + Br_2 \xrightarrow{CCl_4(Reflux)} R - Br + CO_2(g) + AgBr$$

$$CH_3CH_2COOAg + Br_2 \xrightarrow{CCl_4(Reflux)} CH_3CH_2 - Br + CO_2(g) + AgBr$$

The reaction gives product with one carbon atom less than fatty acid and yield of halide is $1^o > 2^o > 3^0$

(2)Halide exchange method

(a) Finkelstein reaction

$$R - X + NaI \xrightarrow{acetone} R - I + NaX; X = Cl, Br$$

NaCl or NaBr is precipitated in dry acetone. It facilitates forward reaction

(b) Swarts reaction

$$CH_3 - Br + AgF \rightarrow CH_3 - F + AgBr$$

Other than AgF, Hg_2F_2, CoF_2 or SbF_3 can also be used.

(3)Halogenation of alkanes

$$\mathrm{R - H + X_2 \xrightarrow{h\nu} R - H + HX}$$

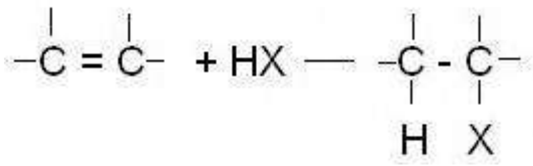
$$CH_3CH_2CH_2CH_3 \xrightarrow{h\nu} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

Iodination being reversible process requires the presence of oxidizing agent such as HIO_3, conc. HNO_3

a) Abstraction of hydrogen for a particular halogen follows order
   Allylic > $3^o > 2^o > 1^o > CH_4$
b) Abstraction of halogen go the above reaction follows order
   $F_2 > Cl_2 > Br_2 > I_2$
c) Direct halogenation proceed through free radical mechanism

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl \xrightarrow{h\nu} CH_2Cl_2 \xrightarrow{h\nu} CHCl_3 \xrightarrow{h\nu} CCl_4$$

(4)Addition of hydrogen halide to alkene



Reaction follows electrophilic addition mechanism

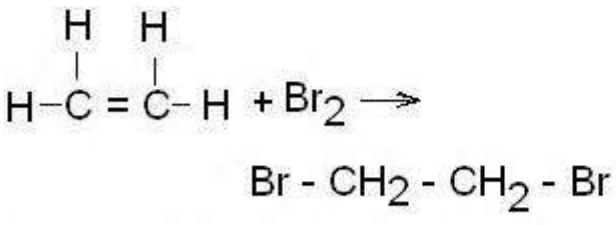
CH_3-CH = CH_2 + HBr → $CH_3CHBrCH_3$ [absence of peroxide, Markonikoff's addition]

CH_3-CH = CH_2 + HBr → CH_3CH_2 CH_2Br [presence of peroxide, Antimarkonikoff]

HCl and HI do not show peroxide effect.

Product may be obtained due to 1,2-hydide or 1,2-methyl shift.

Addition of bromine in CCl_4 to an alkene results in discharge of reddish brown colour of bromine constitutes an important method for detection of double bond in a molecule.



$$H_2C=CH_2 + Br_2 \rightarrow Br-CH_2-CH_2-Br$$

PHYSICAL PROPERTIES OF ALKYL HALIDES

(1)Physical state and smell:

Haloalkanes, the lower members are colourless gas at room temperature. The other alkyl halides up to C_{18} are colourless sweet smelling liquids while higher members are colourless solids.

(2)Boiling point:

(i) The boiling point increases from R – F to R – I

$R\text{-}F < R\text{-}Cl < R\text{-}Br < R\text{-}I$

Iodine has a larger surface area and outer electrons are loosely bounded. This makes iodine a highly polarizable atom. A polarizable atom increases London forces of attraction which causes an increase in boiling point.

(ii) Boiling point increases with increase in size of alkyl group

$CH_3X < C_2H_6 < C_3H_7X$ ....etc

For isomeric alkyl halides, boiling point decreases with branching.

(3)Solubility

Halo-alkanes are polar in nature. Yet they are insoluble in water but soluble in organic solvents. It is not soluble in water because they are not able to form hydrogen bond with water molecule.

(4)Bond strength

In haloalkanes, bond strength of carbon-halogen bond decreases with increase in the bond length as one move from fluorine to iodine

$C-F > C-Cl > C-Br > C-I$

(5)Density

The densities of haloalkanes increases with atomic mass of halogen and decreases with increase in size of alkyl group.

(i) For same alkyl group, density follows the order

R-I > R – Br > R-Cl > R-F

(ii) Same halogen density follows

$CH_3X > C_2H_5X > C_3H_7Cl$

(iii) Fluoro and chloroalkanes are lighter than water whereas bromides and iodides are heavier than water.

(6) Dipole moment

(i) Haloalkanes are polar compounds and their polarity depends on electro negativity of halogen. Dipole moment of halomethanes are

CH_3Cl >	CH_3F >	CH_3Br >	CH_3I
1.86 D	1.84D	1.83D	1.63D

(ii) Dipole moment of fluoromethane is less than chloromethane is due to very small size of fluorine.

CHEMICAL PROPERTIES, REACTIVITY OF HALOALKANES

1) Nucleophilic substitution reaction

(a) S_N1 mechanism (Unimolecular nucleophilic substitution)

(i) In this type, the rate of reaction depends only on the concentration of the substrate i.e. haloalkane and the reaction is of the first order change i.e. Rate ∝ [substrate] or Rate = [R-X]

(ii) This type of reaction proceeds in TWO steps as

STEP I: The haloalkanes undergoes heterolytic fission forming an intermediate, carbocation. This step is slow and hence is the rate determining step of the reaction.

$$R - X \xrightarrow{slow\ step} R^+ + X^-$$

STEP II: The carbocation ion being a reactive species, immediately reacts with the nucleophile [$:Nu^-$] to give the substitution product

$$R^+ + :Nu^- \rightarrow R\text{-}Nu$$

(iii) If the haloalkane is optically active then the product is racemic mixture.

(iv) The order of reactivity depends upon the stability of carbocation in the first step:

$R_3C – X$ >	$R_2CH – X$ >	$R – CH_2\text{-}X$ >	$CH_3 – X$
Tertiary	Secondary	Primary	Methyl

(v) S_N1 order

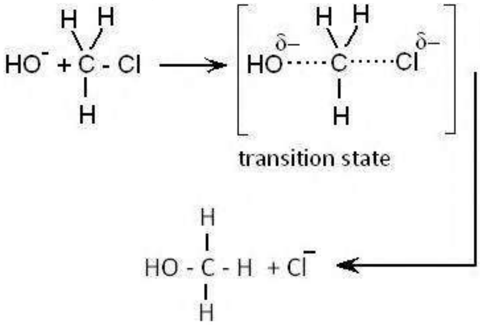
Benzyl > allyl > 3° > 2° > 1° > methyl halide

(b) S_N2 mechanism (Bimolecular nucleophilic substitution)

(i) In this type, the rate of reaction depends on the concentration of both substrate and nucleophile and the reaction second order change.
Rate ∝ [Substrate] [nucleophile]
Rate = k [R – X] [:Nu$^-$]

(ii) Hydrolysis of methyl chloride is an example of S_N2 reaction and high concentration of nucleophile (OH^-) favours S_N2 reaction. The chlorine atom present in methyl chloride is most electronegative than carbon atom. Therefore C-Cl bond is partially polarised $H_3C^{\delta+}- Cl^{\delta-}$.

(iii) When the methyl chloride is attacked by OH^- strong nucleophile form the opposite side of chlorine atom, a transition state results in which both OH and Cl are partially attached to carbon atom



(iv) In transition state chlorine starts taking hold of electron pair through which it is bonded to carbon and OH^- ion offers a pair of electrons for the formation of bond with carbon. Finally chlorine leaves the molecule as a chloride ion (Cl^-). S_N2 reaction of optically active halides are concentrated reactions and configuration of carbon is changed. This process is called inversion of configuration also known as Walden inversion

(v) S_N2 reaction is favoured by small groups on the carbon, atom attached to halogens, so
$CH_3 – X > RCH_2 –X > R_2\text{-}CH\text{-}X > R_3C – X$

(vi) S_N2 order
Methyl > 1° > 2° > 3° > allyl > benzyl

NUCLEOPHILIC SUBSTITUTION REACTION OF ALKYL HALIDES SUMMARY

$$R - X + KOH(aq) \rightarrow R - OH + KX$$

$$R - X + AgOH(\, or\ Ag_2O) \rightarrow R - OH + AgX$$

$$R - X + Ag_2O(dry) \rightarrow R - O - R + 2AgX$$

$$R - X + KSH \rightarrow R - SH + KX$$

$$R - X + \quad R'ONa \quad \rightarrow R - S - R' + NaX$$

Sodium alkoxide

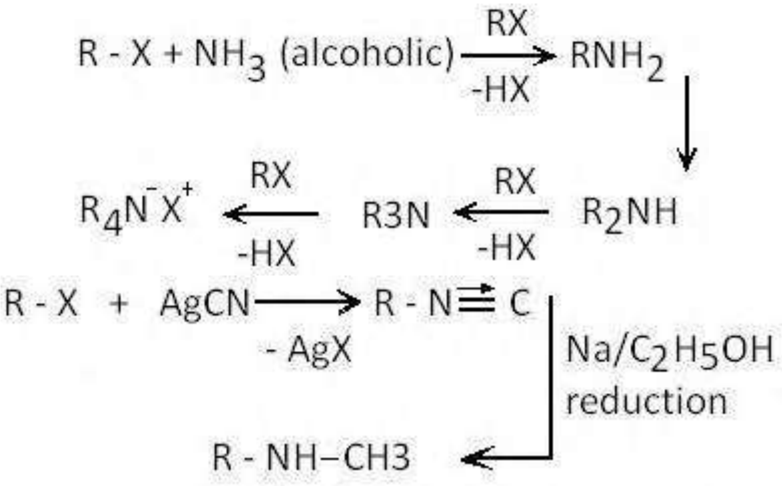
$$R - X + R'C \equiv C^{-}Na^{+} \rightarrow R - OH + KX$$

Sodium alkynide

$$R - X + R'COOAg \rightarrow R - COOR' + AgX$$

$$R - X + KNO_2 \rightarrow R - O - N = O + KX$$

$$R - X + AgNO_2 \rightarrow R - NO_2 + KX$$



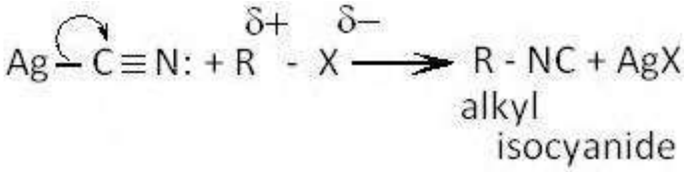
Some important points

(i) Groups which possess two nucleophilic centre are called ambident nucleophiles. Example cyanides and nitrites.

(ii) KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in position to donate electron pairs, the attack takes place mainly through carbon atom and not nitrogen atom since C- C bond is more stable than C- N bond. Therefore when haloalkanes reacts with KC≡N alkyl cyanides is obtained.

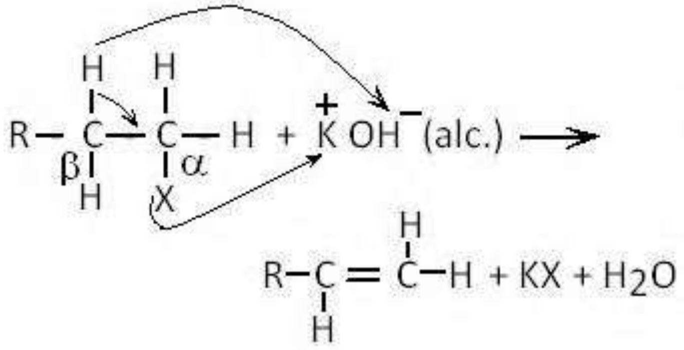
$K^{+} C^{-} \equiv N + R^{\delta+} - X^{\delta-} \rightarrow R - C \equiv N + K\text{-}X$

(iii) AgCN is mainly covalent and nitrogen is free to donate electron pair forming isocyanide as main product.



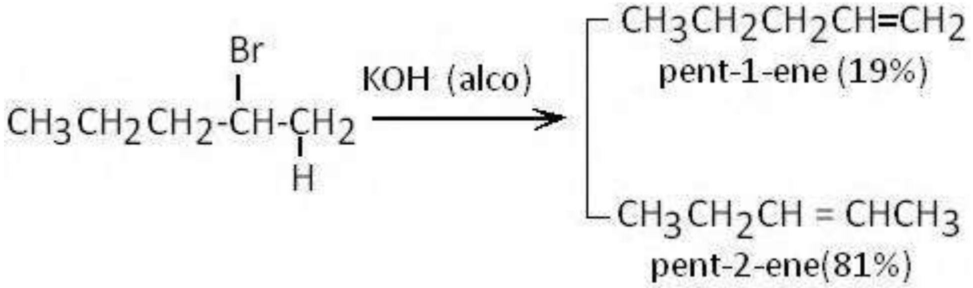
2) Elimination reaction-dehydro-halogenation

(a) Alkyl halides undergoes β – elimination reaction in presence of potassium hydroxide in ethanol to yield alkene



(b) Reactivity of haloalkanes towards elimination reaction is
Tertiary > Secondary > primary
This is due to +I effect of the alkyl group which increases polarity of C-X bond

(c) In dehdrohalogenation of secondary and tertiary haloalkanes there is a possibility of formation of two isomers, then it is governed by Saytzeff's rule which can be summarized as
"In dehydrohalogenation reactions, the preferred product is that alkene which has greater number of alkyl group attached to doubly bonded carbon atoms."



3) Reaction with metals

(a) With magnesium (Grignard reagent)

$$R - X \quad + \quad \underset{\text{Dry powder}}{Mg} \quad \xrightarrow{dry\ ether} \quad \underset{\text{Grignard reagent}}{R - Mg - I}$$

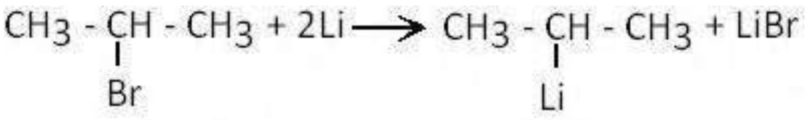
$$CH_3 - X \quad + \quad Mg \quad \xrightarrow{dry\ ether} \quad CH_3 - Mg - I$$

Carbon –magnesium is highly polar covalent where as magnesium halogen bond is ionic

(b) Reaction with sodium (Wurtz reaction)

$$R - X + 2Na + X - R \xrightarrow{dry\ ether} R - R + 2NaX$$

(c) Reaction with lithium

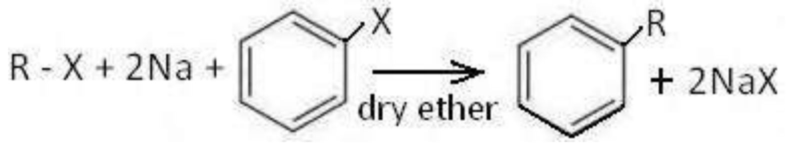


$$CH_3 - \underset{Br}{CH} - CH_3 + 2Li \longrightarrow CH_3 - \underset{Li}{CH} - CH_3 + LiBr$$

(d) Reaction with zinc (Frankland reagent)

$$2C_2H_5Br + 2Zn \xrightarrow{ether\ ,\Delta} (C_2H_5)_2Zn + ZnBr_2$$

(e) Wurtz – Fiting reaction



(f) Corey-house reaction

$$RX \xrightarrow{Li/Et_3O} RLi \xrightarrow{CuI} R_2CuLi$$

$$R' - X + R_2CuLi \rightarrow R' - R + RCu + LiX$$

SECTION II
HALOARENES

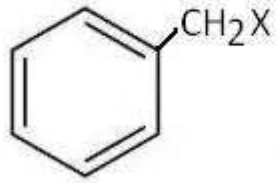
Compound in which the halogen atom is linked directly to the carbon atom of benzene are called arylhalides or haloarenes.

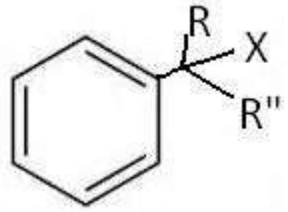
CLASSIFICATION OF HALOARENES

(1)Compounds containing sp^3 C – X bond

Benzylic halides

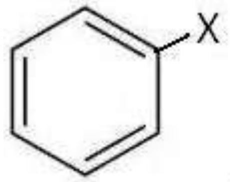
In these halides, the halogen atom is attached to a benzylic carbon i.e. the carbon atom of the side chain carrying the aryl group.

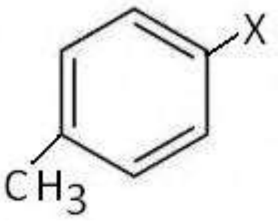




(2)Compound containing sp^2 C – X bond

Aryl halides: These are the compounds in which the halogen atom is bonded to sp^2 – hybridized carbon atom of an aromatic ring.

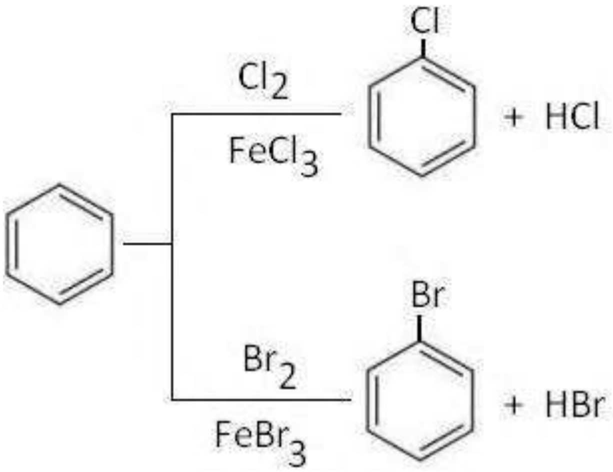


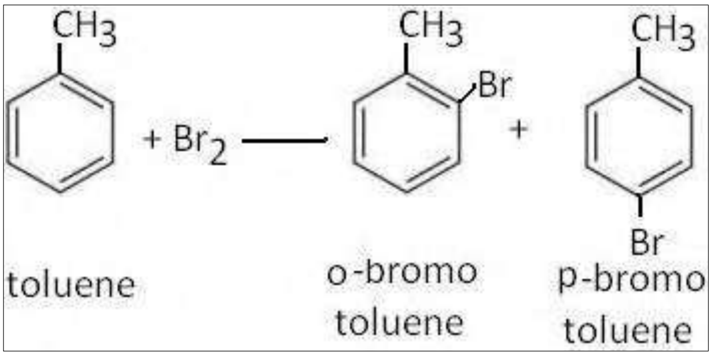


(3)On the basis of number of halogen atoms

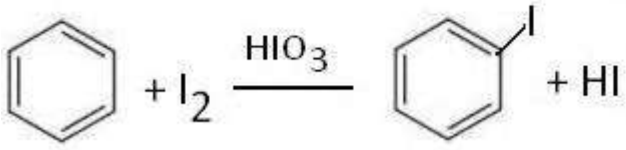
GENERAL METHODS OF PREPARATION OF HALOARENES

1) Direct halogenations of aromatic hydrocarbon





Direct iodination is not possible since, the reaction is reversible with iodine. Thus the reaction is carried in the presence of oxidizing agent. Such as HIO_3, HNO_3.



$5HI + HIO_3 \rightarrow 3I_2 + 3H_2O$

MECHANISM OF HALOGENATION

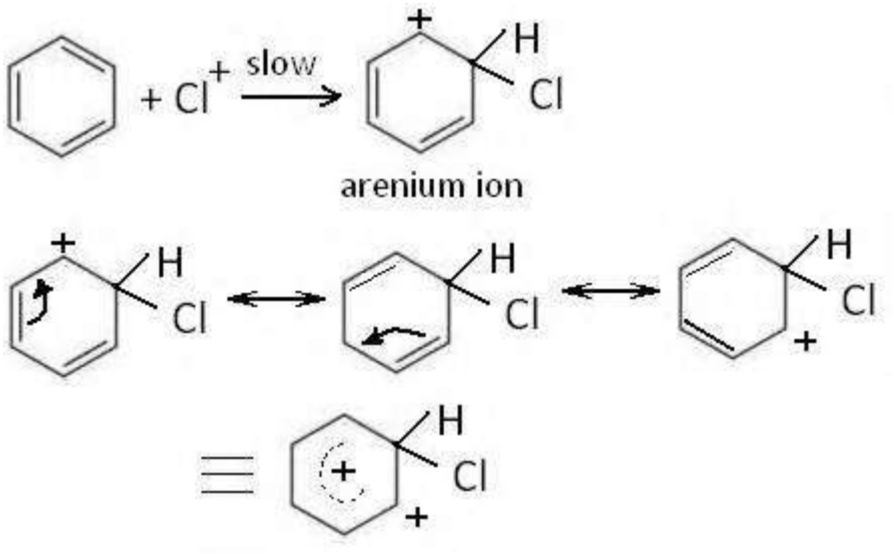
STEP I

Generation of electrophile i.e. halonium in by action of Lewis acid on the halogen

$$Cl - Cl + FeCl_3 \rightarrow \underset{\substack{\uparrow \\ \text{electrophile}}}{Cl^+} + FeCl_4^-$$

STEP II

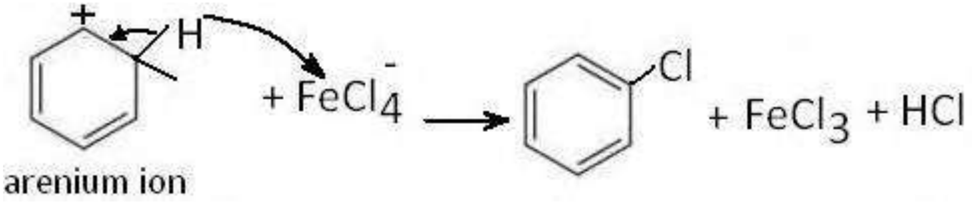
The electrophile attacks the benzene ring to form an intermediate known as σ – complex or a carbocation (arenium ion) which is stabilized by resonance.



The formation of intermediate arenium ion is slow and hence is the rate determining step of the reaction.

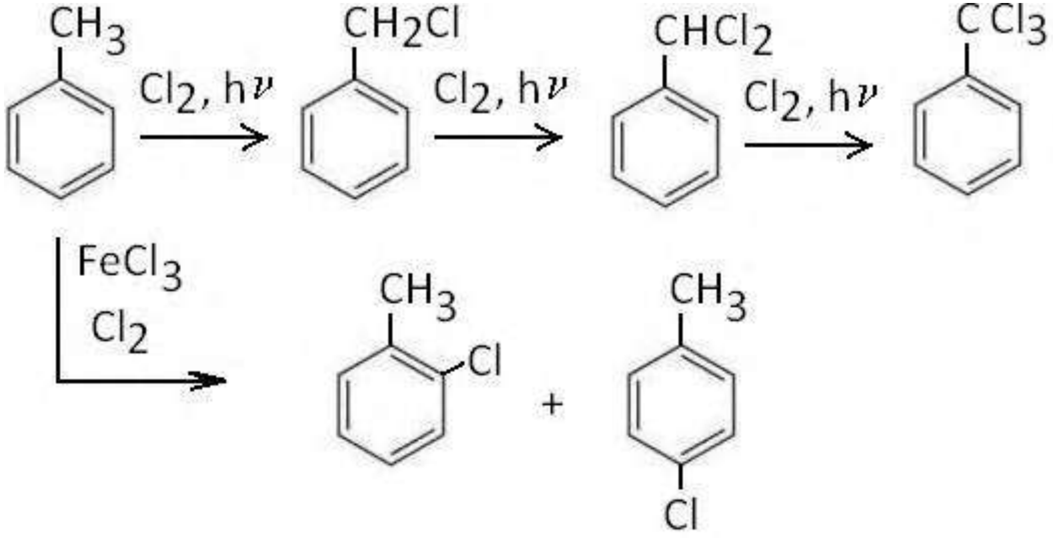
STEP III

The carbocation, loses a proton (H^+ to the base $FeCl_4^-$ to give chloro-benzene)



2) Side chain halogenations

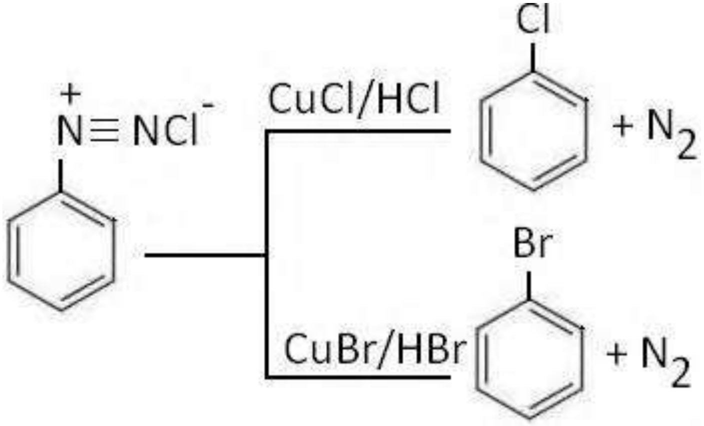
Halogenation in the presence of heat or sunlight and in absence of halogen carrier takes place at the side chain



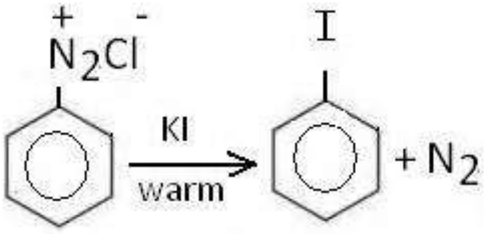
Side chain halogenations takes place by free radical mechanism.

3) From diazonium salt

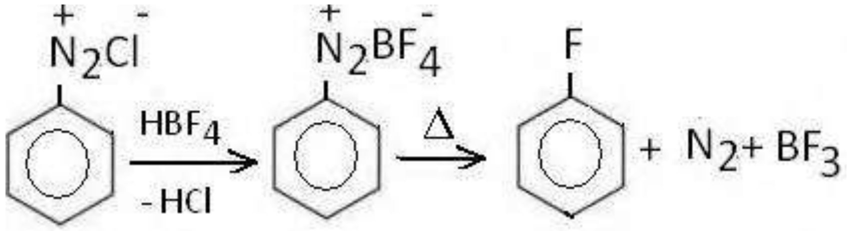
i) Sandmeyer’s reaction



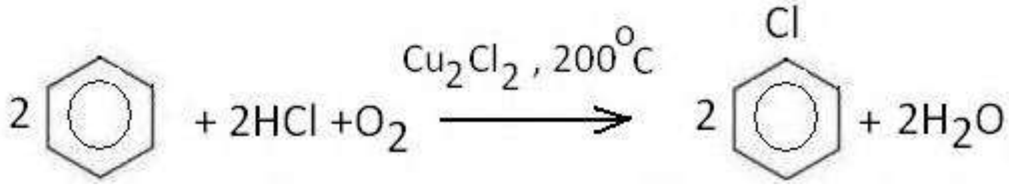
Replacement of the diazonium group by iodine is done simply by shaking the diazonium salt with potassium iodide.



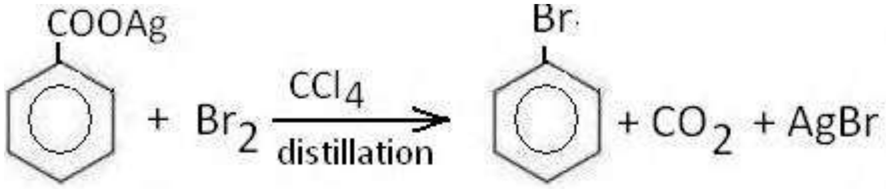
ii) Balz-Schiemann reaction



4) Rasching process



5) Hunsdiecker reaction



PHYSICAL PROPERTIES OF HALOARENES

1) Physical state and smell

Haloarenes are generally colourless liquids with pleasant odour or are crystalline solids with characteristic smell

2) Boiling point

i) The boiling point of monohalogen derivatives of benzene are in order

Iodo > Bromo > Chloro > Fluoro

ii) Boiling and melting points increases as the size of the aryl group increases

iii) Melting point of the para isomers are always higher than that of ortho or meta isomers. This is due to the reason that para isomer is more symmetrical and hence its molecules pack closely in the crystal lattice. As a result intermolecular and therefore, greater energy lattice and it melts at higher temperature.

3) Solubility

Aryl halides are insoluble in water but readily miscible with organic solvents.

4) Density

Aryl halides are heavier than water. Their density follows the order

Aryl iodide > aryl bromide > aryl chloride

5) Dipole moment

The dipole moment of haloarenes lies as follows

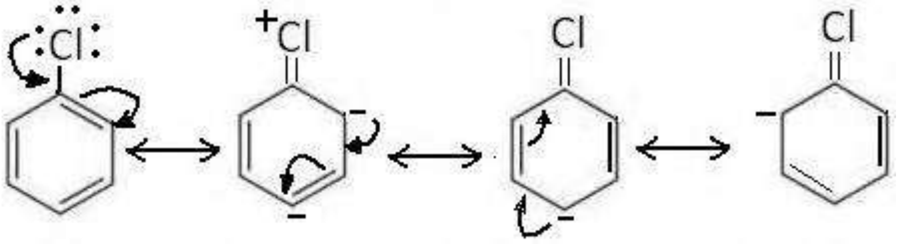
Flurobenzene < Chlorobenzene < Bromobenzene ≈ Iodobenzene

CHEMCIAL PROPERTIES OF HALOARENES

1) Nucleophilic substitution

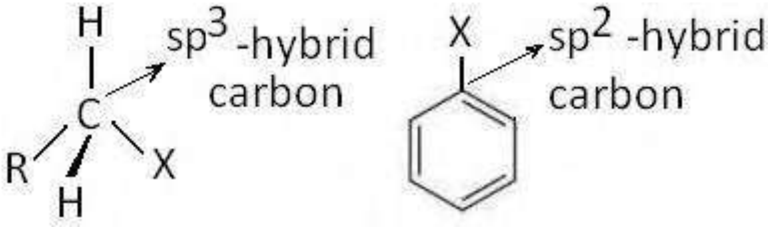
Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to following reasons

(i) Resonance effect : In haloarenes, the electron pairs of halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible



C-Cl bond aquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

(ii) Difference in hybridistaion of carbon atom in C-X bond
In haloalkane, the carbon atom attached to halogen is sp^3 hybridized, where in case of haloarenes, the carbon atom attached to halogen is sp^2 hybridized

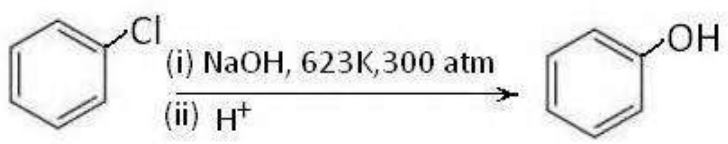


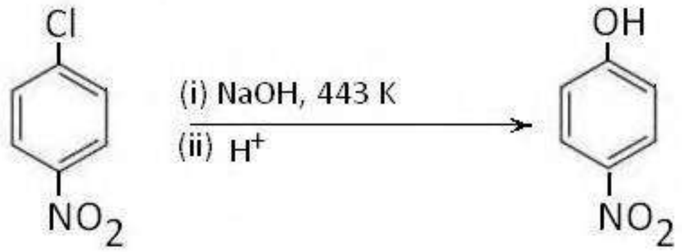
The sp^2 hybridised carbon with a greater s-character is more electro-negative and can hold the electron pair of C-X bond more tightly than sp^3-hybridised carbon in haloalkanes with less s-character. Thus C-Cl bond length in haloalane is 177pm. While in haloarenes is 169pm. Since it is difficult to break a shorter bond than a longer bond, Therefore haloarenes are less reactive than haloalkanes towards nucleohilic substitution reaction

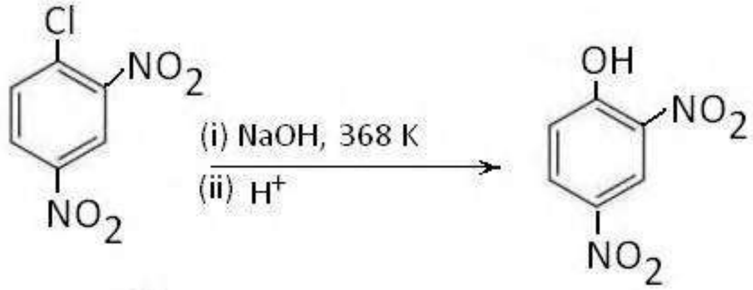
(iii) Instability of phenyl cation
In case of haloarenes, the phenyl cation formed as a result of self ionization, will not be stabilized by resonance and therefore S_N1 mechanism is ruled out

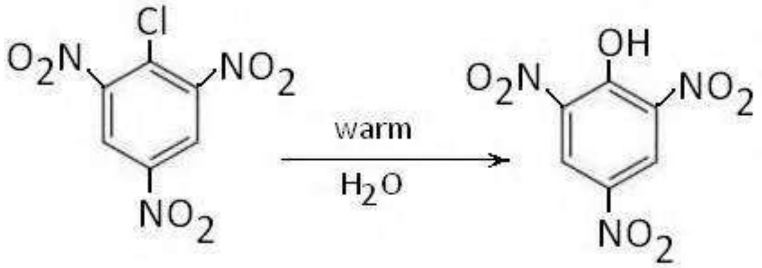
(iv) Because of the possible repulsion it is less likely for the electron rich nucleophile to approach electron rich arenes

2) Replacement by hydroxyl group



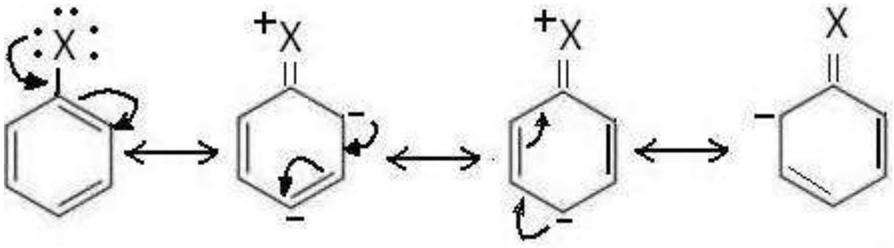






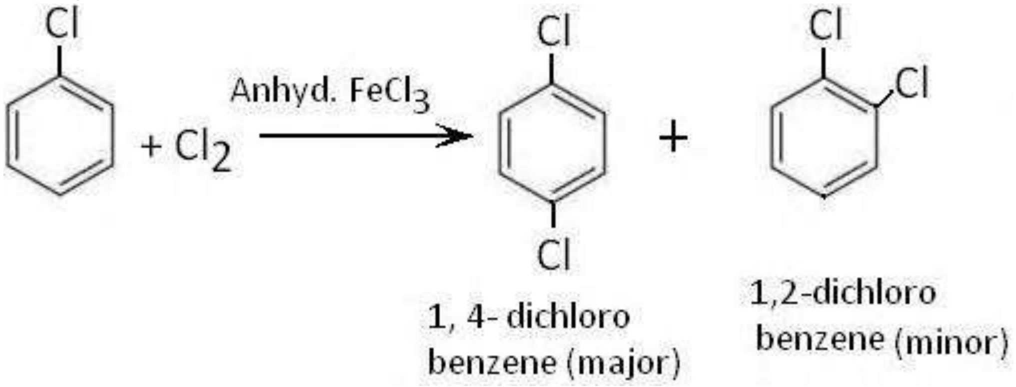
The presence of electron withdrawing group (-NO_2) at ortho and para positions increases the reactivity of haloarenes

3) Electrophilic substitution

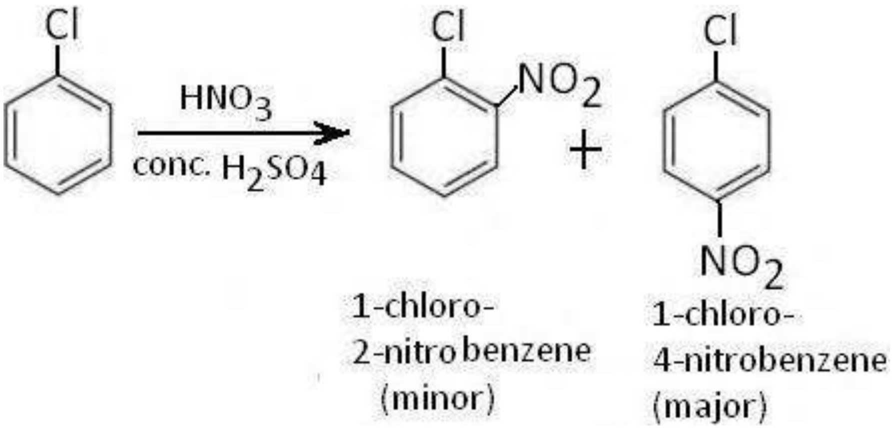


- Due to resonance, the electron density increases more at ortho and para-positions than at meta- positions and hence the electrophile is more likely to attack on these position resulting in formation of o- and p- substituted product
- Halogen atom because of its –I effect has some tendency to with-draw electron from benzene ring. As a result, the ring gets somewhat deactivated and hence the electrophilic substitution reactions in haloarenes occur slowly

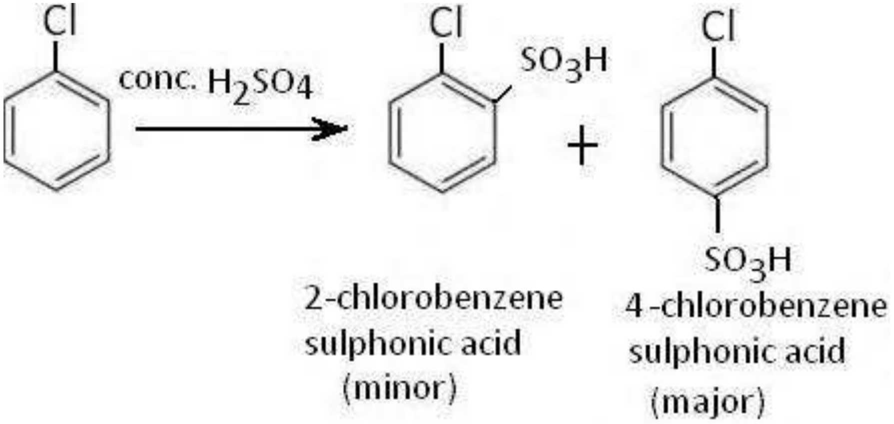
(i) Halogenation



(ii) Nitration

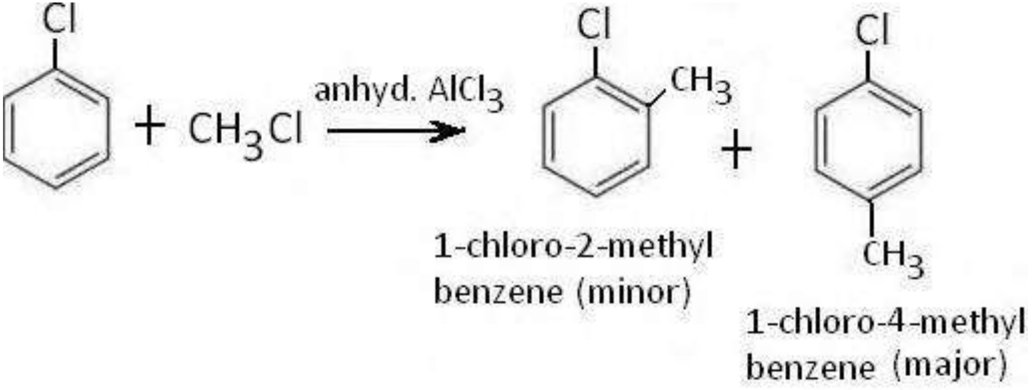


(iii) Sulphonation

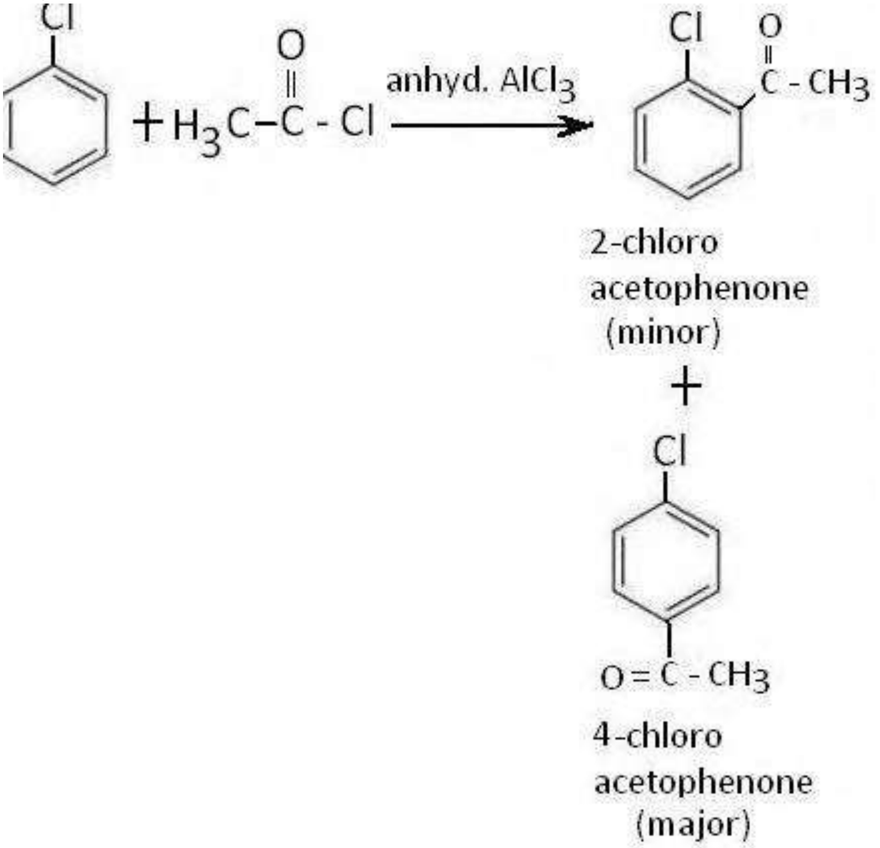


(iv) Friedel-Craft reaction

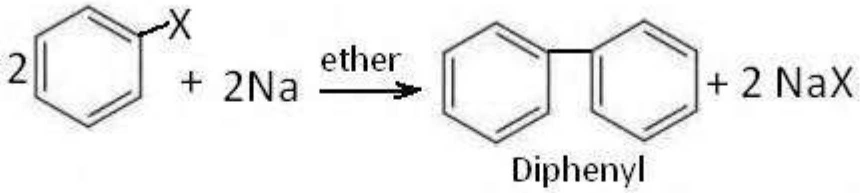
(a) Alkylation



(b) Acylation



4) Fitting reaction



POLYHALOGEN COMPOUNDS

1. Dichloromethane (CH_2Cl_2)
   (A) Uses: It is used as
      (i) A solvent in drug industry
      (ii) Paint remover and propellant in aerosols
      (iii) A cleaning agent for metals
   (B) Environmental impact
      (i) Its direct contact to our skin develops redness and burning sensation
      (ii) It is harmful to our central nervous system
      (iii) Its high level in air causes nausea, numbness in figure and toes
2. Trichloromethane $CHCl_3$ (Chloroform)
   - Chlorofrom is a sweet smelling liquid boiling point 334K, non-inflammable but its vapour causes unconsciousness.

- When exposed to sunlight and air it slowly decomposes into phosgene ($CoCl_2$), a poisonous gas. It is therefore stored in closed dark coloured bottle completely filled so that air is kept out
  $2CHCl_3 + O_2 \rightarrow 2COCl_2 + 2HCl$

(A) Uses : It is used

(i) As a solvent for fats, oils, varnishes, waxes, resins and rubber etc.
(ii) For the preparation of chloretone (a drug) and chloropicrin (insecticide)
(iii) As an anesthetic after being mixed with ether
(iv) In the manufacture of Freon (refrigerant)

(B) Environmental impact

(i) On inhalation, it depresses the central nervous system an causes headache and dizziness.
(ii) Chronic exposure damages liver and kidneys.
(iii) On exposure to sunlight and air it slowly decomposes into phosgene.
(iv) Ethanol (1%) is added to retard the oxidation of phosgene into harmless ethyl carbonate.

(C) Tests of chloroform: It gives isocyanide test (Pungent smell). Pure $CHCl_3$ does not give white precipitate with $AgNO_3$, but with Tollen's reagent, it gives grey precipitate of silver. On heating with Fehling's solution, it gives brown precipitate

3. Tri-iodomethane CHI_3 (Iodoform)

- It is a yellow crystalline solid pungent characteristic odour. Melting point is 392K and is steam volatile. It is used as a antiseptic for dressing wound

(A) Uses : It is used as

(i) As an antiseptic for dressing of wound.
(ii) In the manufacture of certain pharmaceuticals.

(B) Environmental impact

(i) When it comes in contact with skin, iodine is liberated which is responsible for antiseptic properties.
(ii) It has an objectionable smell.

4. Tetra chloromethane CCl_4(carbon tetra chloride)

- It is a liquid, boiling point 350K, non-flammable, hence used as a solvent for fats, oils, waxes and resins etc. It is used as a fire extinguishers under the same name pyrene.

(A) Uses : It is used

(i) As a fire extinguishers
(ii) As a solvent and also dry-cleaning
(iii) In medicine as helmenthicide for elimination of hook worm

(B) Environmental impact

(i) Its vapours when breathed causes nausea, dizziness, vomiting and may cause damage nerve cells permanently
(ii) On exposure it causes cancer, irregular heart beat and a person may go to coma.

(iii) Its vapour depletes ozone layer. Ozone hole permits the ultraviolet radiation to reach on earth and may cause skin cancer, eye disease and disorder, it may adversely affect our immune system

5. Freons (CFC's)

* Freons are small organic molecules containing C, Cl and F. The most common freons are CF_2Cl (Freon -12) and CF_3Cl (Freon -11)

(A) Uses

(i) In air conditioning and domestic refrigerators for cooling purpose

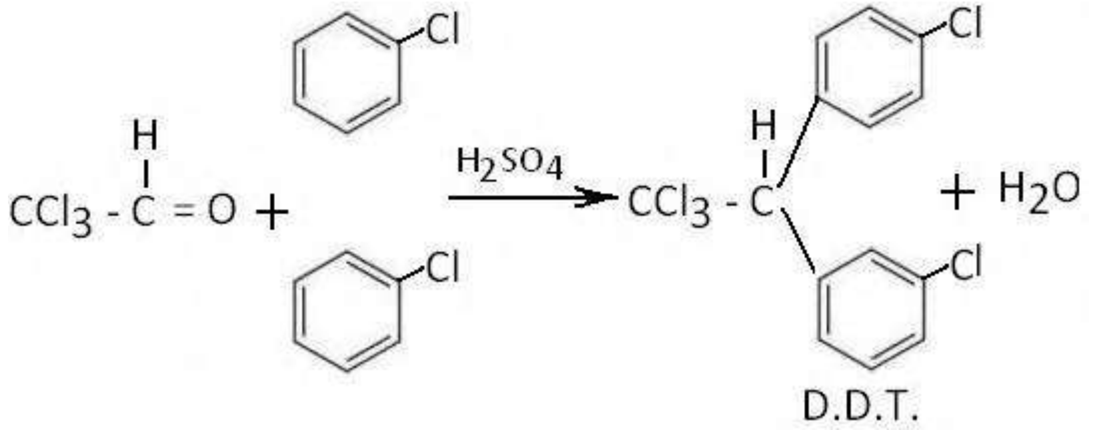
(ii) As propellents in aerosol and foams to spray out deodorants, cleaners and Insecticides. Halothane ($CF_3CHBrCl$) is used as inhalation anaesthetic.

(B) Environmental impact

Most Freon eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere. In stratosphere, Freon is able to initiate radical chain reaction that can upset the natural ozone layer surrounding earth.

6. p,p' – Dichlorodiphenyl trichloro ethane (DDT)

- It is prepared by heating chlorobenzene with chloral in presence of conc H_2SO_4



(A) Uses :

(i) As an effective insecticide for mosquitoes, flies and crop pests.

(ii) As an antimalarial.

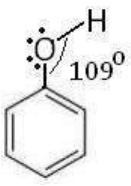
(B) Environmental impact

It is non-biodegradable and its residue accumulates in environment, a cause of danger. It is not metabolized by the system and get deposited on the tissue, thus raises alarming danger. It is highly toxic to fish.

PHENOL

- Phenol are the aromatic compounds having hydroxyl group (-OH) directly attached to benzene ring.

ELECTRONIC STRUCTURE OF PHENOL

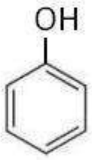


- In phenols the –OH group is attached to sp^2 hybrid carbon of an aromatic ring and the oxygen atom of the hydroxyl group has two lone pairs of electrons and the bond angle in phenol is 109°. The C-O bond length in phenol (136pm) is slightly less than in methanol(412pm) due to resonance in aromatic ring of phenol
- Phenol has dipole moment 1.54D where as methanol has dipole moment 1.71D. This smaller dipole moment of phenol is due to the electron attracting effect of phenyl group in contrast to the electron releasing effect of methyl (or alkyl) group in alcohol

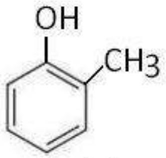
CLASSIFICATION OF PHENOL

- Phenols are classified as mono, di and trihydric phenols according to the number of hydroxyl groups attached to the aromatic ring.

1. Monohydric phenols

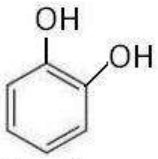


Phenol

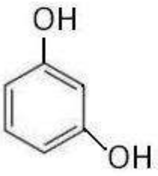


2-methyl phenol
o-cresol

2. Dihydric phenols

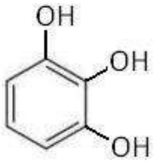


Phenol
1,2-Dihydroxy
benzene
(catechol)

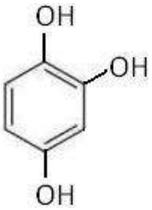


1,3-Dihydroxy
benzene
(resorcinol)

3. Trihydric phenols



1,2,3 -Trihydroxy benzene (pyrogallol)

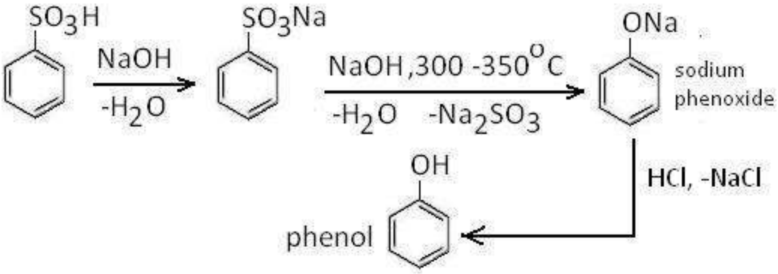


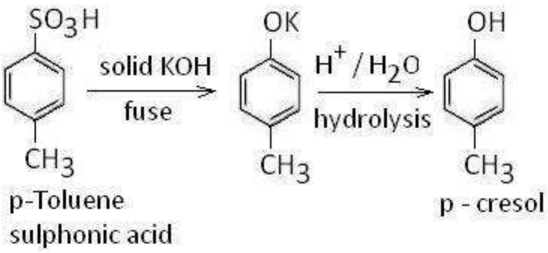
1,2,4 - Trihydroxy benzene (Hydroxiquinol)

GENERAL METHODS OF PREPARATION OF PHENOLS

1. Alkali fusion of sulphonates

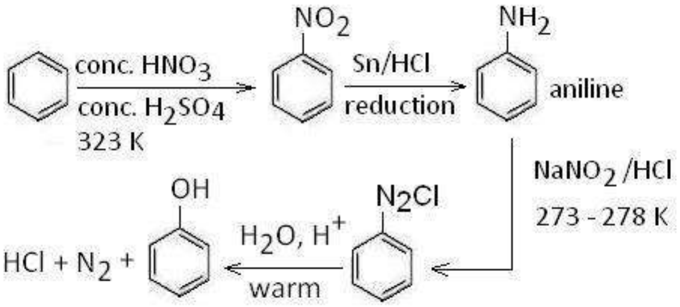
   Sodium salt of aryl sulphonic acids on fusion with sodium hydroxide at 300-350°C yield phenol





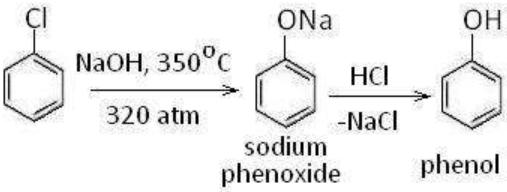
   The above reaction is laboratory method for preparation of phenol

2. Hydrolysis of diazonium salt

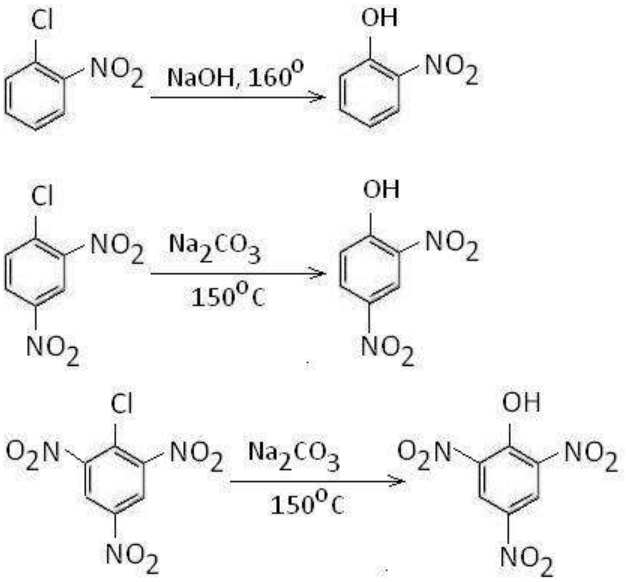


3. Hydrolysis of aryl halides (Dow's process)

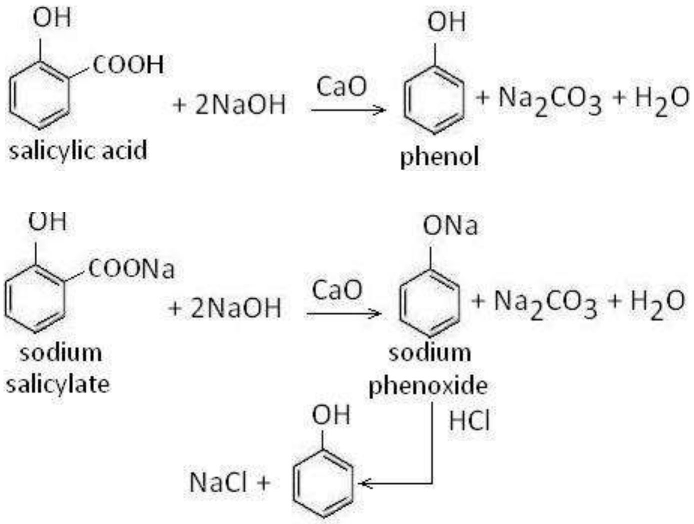
- Aryl halides on hydrolysis yield phenol but the process is not so simple because halogen atom attached to benzene ring does not undergo S_N2 reaction since C-X bond is resonance stabilized. Hence reaction takes place at high pressure and elevated pressure.



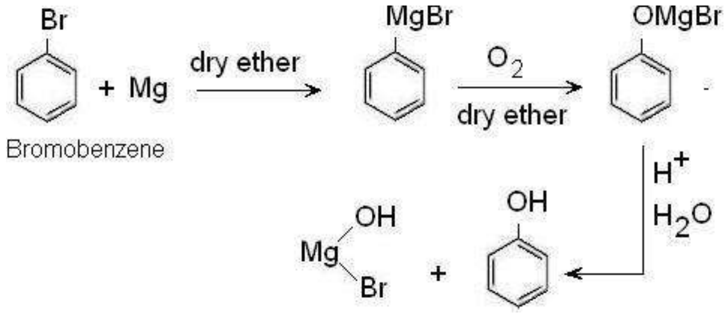
- However if some electron withdrawing group is attached to benzene ring, then reaction conditions get relaxed



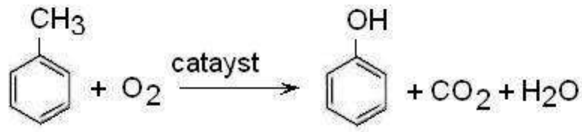
4. Decarboxylation of salicylic acid



5. Oxidation of Grignard reagent



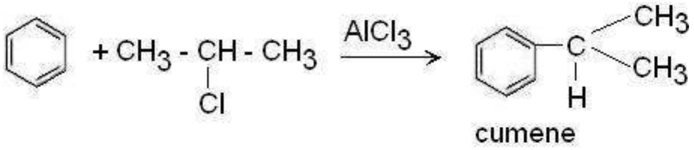
6. Oxidation of aromatic hydrocarbons

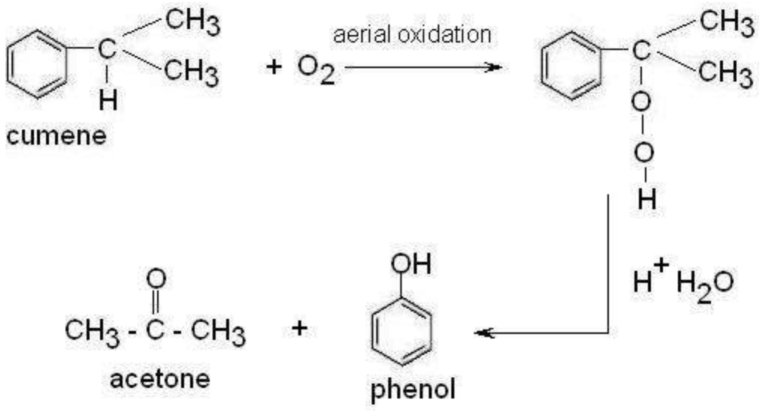


Catalyst used in this reaction is cupric salt.

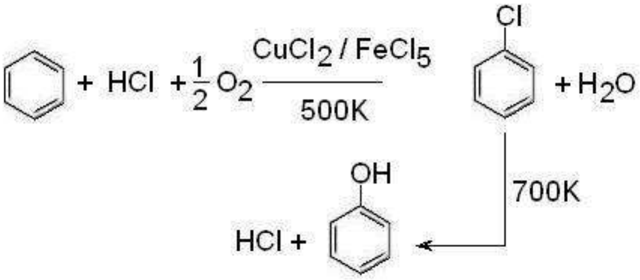
7. Oxidation of iso-propyl benzene (Cumene)

Cumene is prepared by Friedel Crafts alkylation of benzene with 2-Chloropropane.





8. Rasching's process



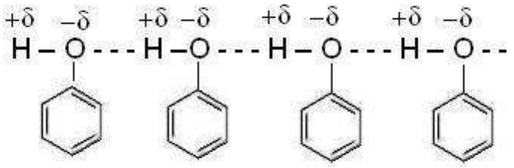
PHYSICAL PROPERTIES OF PHENOL

1. Physical state

- Phenols are colourless liquids or low melting point solids, but they reddish brown due to auto oxidation on exposure to air and light.
- Phenols are poisonous in nature but act as disinfectant and antiseptic.

2. Solubility

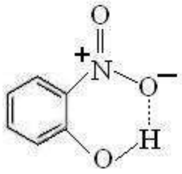
Phenols form H-Bonds with water molecule and hence soluble in water, but their solubility is lower than that of alcohols because of large hydrocarbon part



Intermolecular H-bonding among water and phenol molecules

3. Boiling point

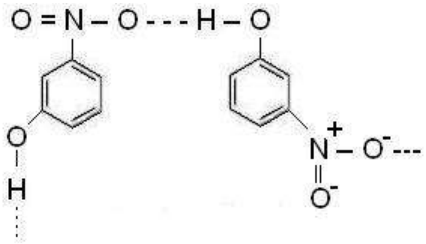
- Phenols have much higher boiling point than there corresponding hydrocarbons due to intermolecular hydrogen bonding
- Amongst the isomeric nitrophenols, O-nitrophenol has much lower melting point and solubility than meta and para isomers of nitrophenol because of intramolecular H-bonding. Thus it does not undergo association with other molecules. In fact ortho-nitrophenol is steam volatile



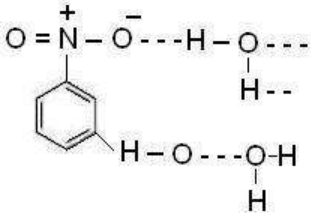
Intramolecular
H - bonding

- On the other hand meta and para nitrophenol exhibit intermolecular H-bonding with their own molecules as well as with water molecules and hence show comparatively higher melting and solubility.

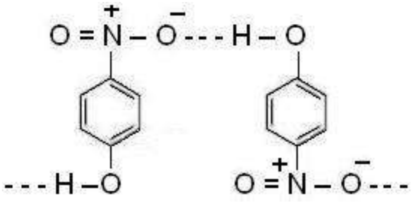
i) Intermolecular H-bonding (m –nitrophenol)



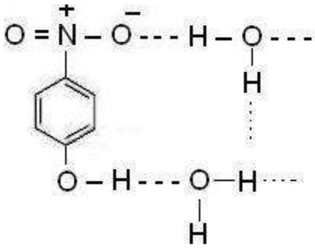
ii) H- bonding with water molecules (m-nitrophenol)



iii) Intermolecular H- bonding (p –nitrophenol)



iv) H – bonding with water molecules (p – nitrophenol)

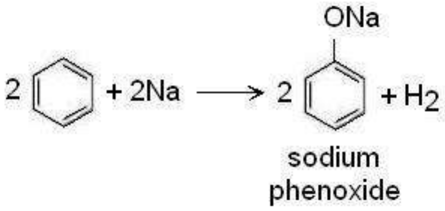


CHEMCIAL PROPERTIES OF PHENOL

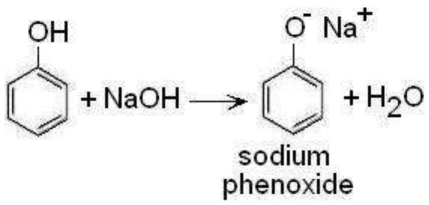
(A) Reactions involving cleavage of O-H bond

1. Acidic character of phenol

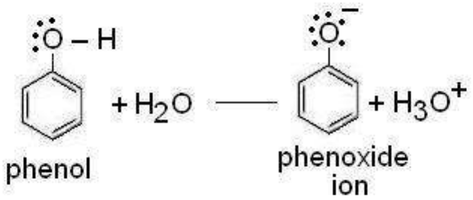
(i) Reaction with active metals



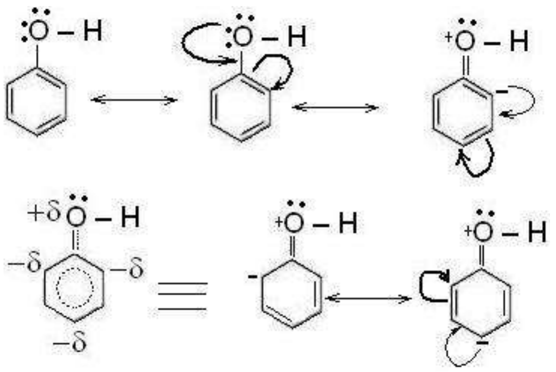
(ii) Reaction with alkalies



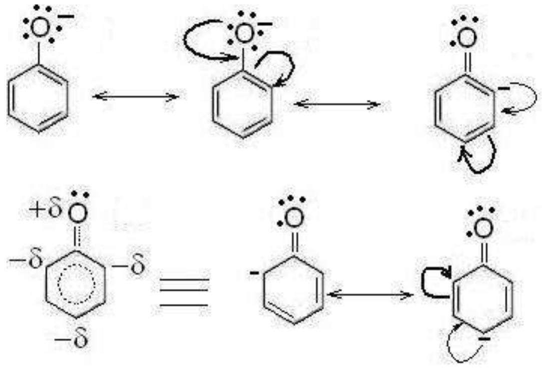
- They do not react with carbonates and bicarbonates. Phenols are weaker acid as compared to carboxylic acid because of polar O-H group in them. The acidic nature of phenol is due to formation of stable phenoxide ion in solution to give H^+ ions



- Phenol behaves as stronger acid than alcohol
  - i. The greater acidity of phenol is due to stability of phenoxide ion is resonance stabilised .
  - ii. Resonance structure of phenol



  - iii. As a result of resonance it weakens the polar O-H bond and thus facilitates the release of proton (H^+) to give phenoxide ion which is also stable due to resonance
  - iv. Resonating structure of phenoxide ion

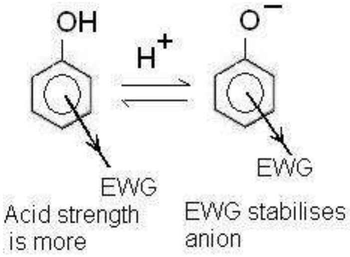


  - v. Both phenol and phenoxide ion are stable due to resonance. But phenoxide ion is more stabilized than phenol because the resonating structure of phenoxide ion carry only negative structure of phenol involves separation of positive and negative charge. This charge delocalization is a stabilizing factor in phenoxide ion and increases acidity of phenol.

vi. Effect of substituent on the acidity of phenols

a. Electron withdrawing group (EWG)

1. Electron withdrawing groups NO_2 , -X, -CHO, -COOH, -CN etc stabilizes the phenoxide ion more by dispersing the negative charge relative to phenol (i.e. proton release become easy) and thus increases the acidic strength of phenols

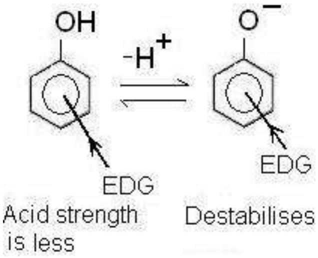


2. Particular effect is more when the substituent is present on O – and p- positions than in m-position. Thus acidic strength of nitrophenol decreases in the order
p-nitrophenol > o-nitrophenol > m-nitrophenol > phenol

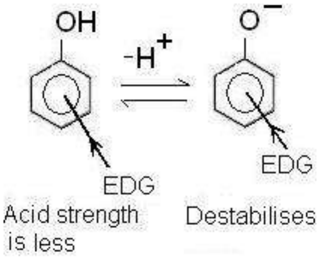
3. Further greater the number of electron withdrawing groups at o- and p – position, more acidic the phenol.

b. Electron donating group (EDG)

(i) Electron donating group –R, $-NH_2$, -OR etc destabilize the phenoxide ion by donating electrons and intensify the negative charge relative to phenol (i.e. proton release become difficult)and thus decreases the acidic strength of phenol.



(ii) The effect is more when the substituent is present on o- and p- position than on m-position with respect to –OH group. Thus cresol are less acidic than phenol.

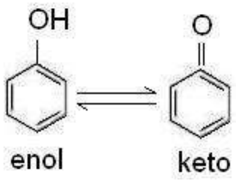


m – methoxy and m-amnion phenols are stronger acid than phenols because of –I effect (of $–OCH_3$ and $–NH_2$ groups) and absence of +R effect.

m –methoxy phenol > m-amino phenol > phenol > O-methoxy phenol > p-methoxy phenol

vii) Reaction of –OH group

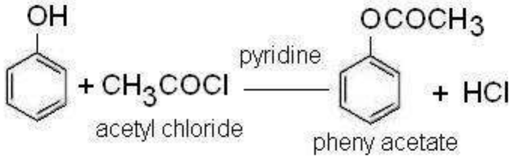
i. Reaction with $FeCl_3$ is the test of phenol

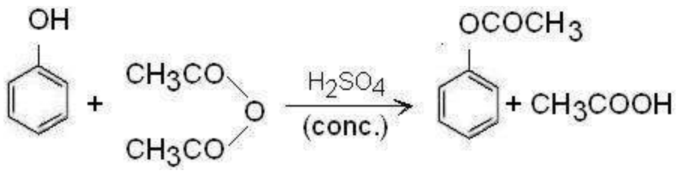


$3C_6H_5OH + FeCl_3$ ✳ $(C_6H_5O)_3Fe + 3HCl$

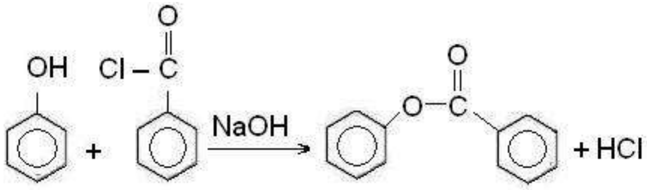
$(C_6H_5O)_3Fe$: Ferric phenoxide (violet complex)

ii. Ester formation



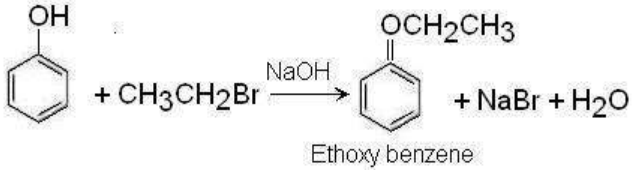


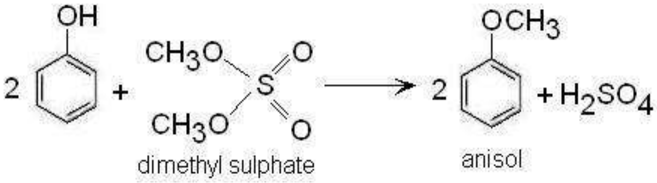
Reaction with benzoyl chloride is known as benzoylation



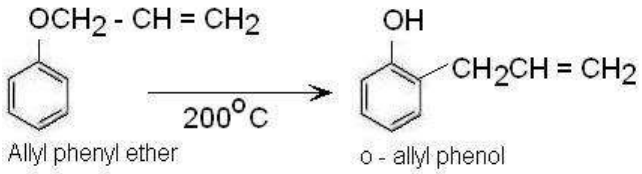
Benzoylation of alcohols o phenols in presence of NaOH is called Schotten-Baumann reaction.

iii. Ether formation



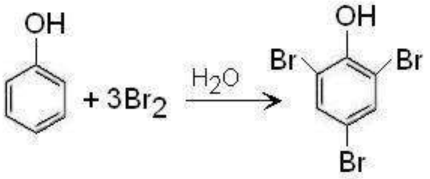


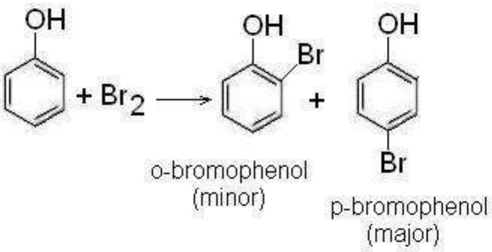
- Claisen rearrangement



(B) Electrophilic aromatic substitution reaction

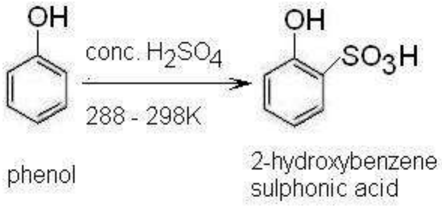
1. Halogenation

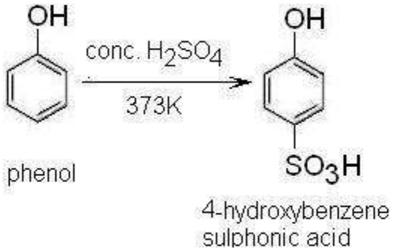




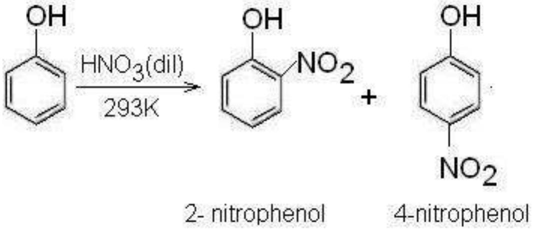
Due to steric hinderance at ortho position, para-product predominates

2. Sulphonation

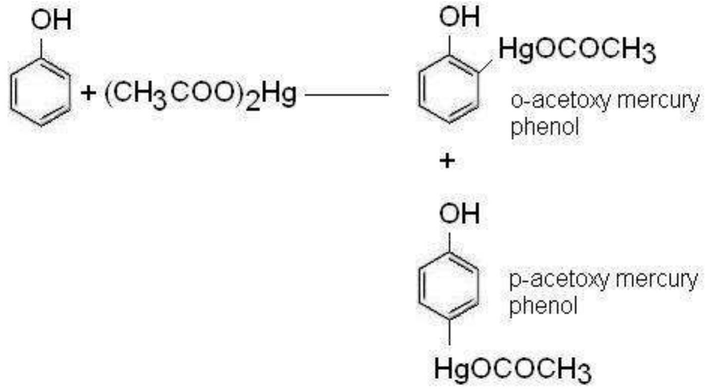




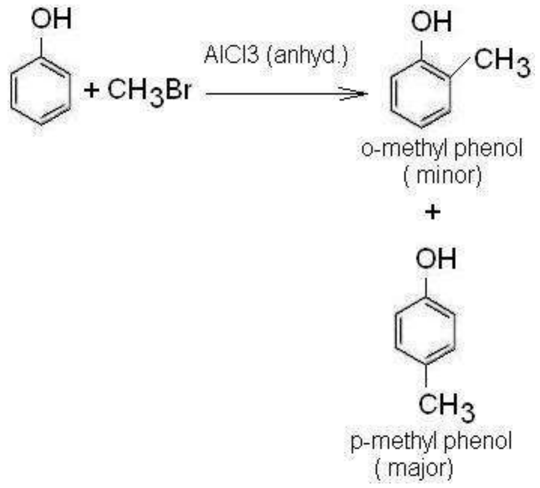
3. Nitration

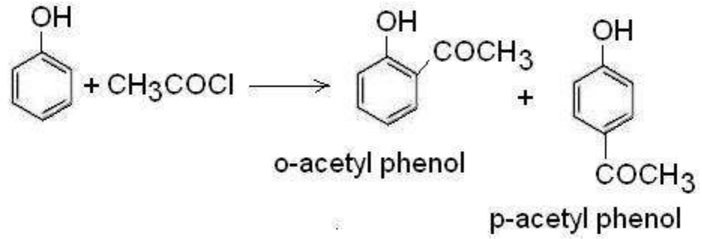


4. Mercuration

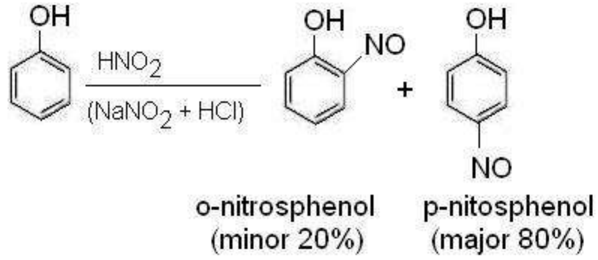


5. Friedel crafts alkylation and acylation

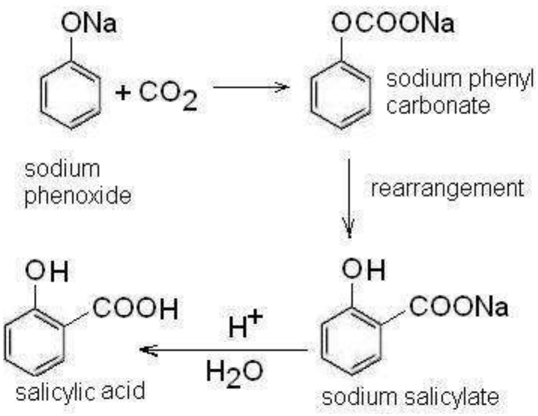




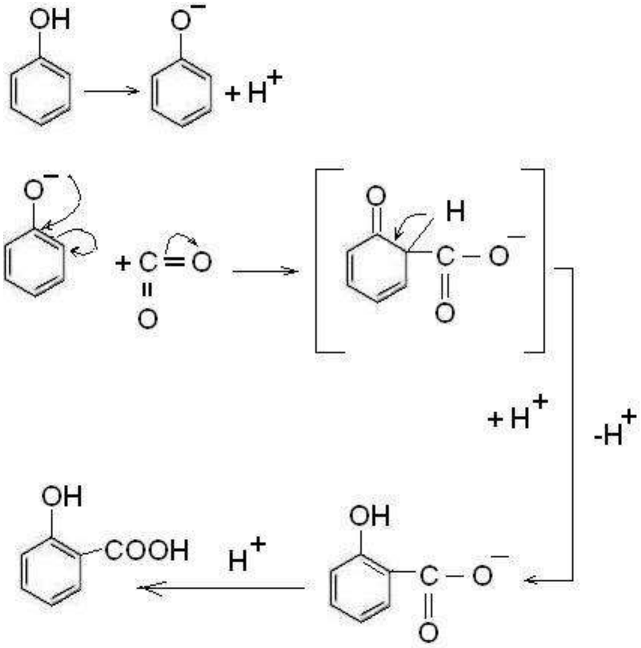
6. Nitrosation



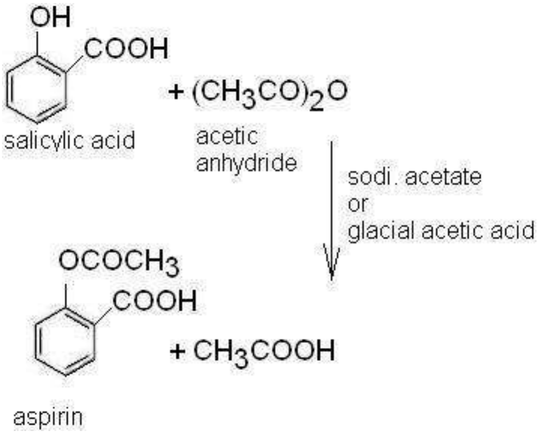
7. Kolbe’s reaction



Mechanism

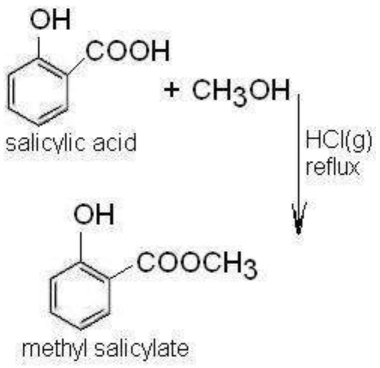


(a) Acetyl salicylic acid (Asprine)



It is a white solid (m.pt. 408K) and is used for relieving pain (analgesic) and to bring down the body temperature (antipyretic during fever)

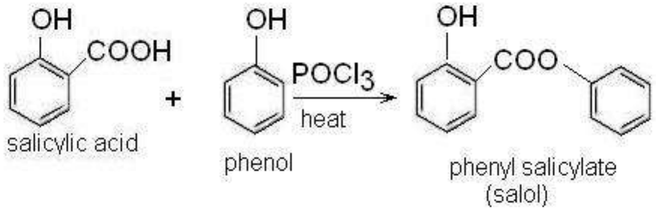
(b) Methyl salicylate



It is an oily liquid (b.pt. 495K) with pleasant odour (oil of wintergreen) used in perfumery and flavouring agent.

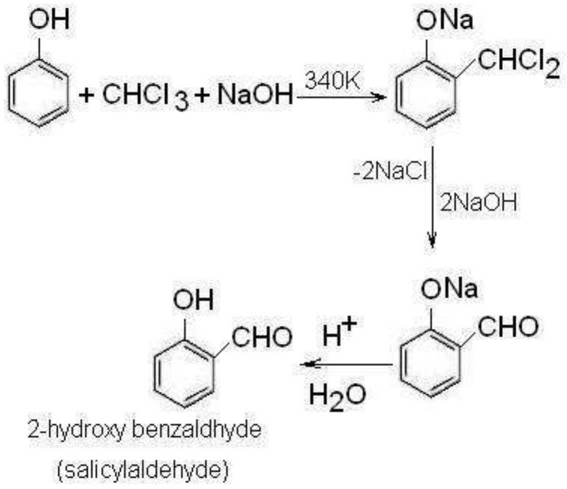
It is also used in medicine in the treatment of rheumatic pain and as a remedy for aches, sprains and bruises.

(c) phenyl salicylate (salol)



It is white solid (m.pt 316K) and is used as an intestinal antispeptic.

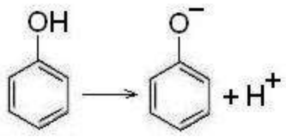
8. Reimer-Tiemann reaction



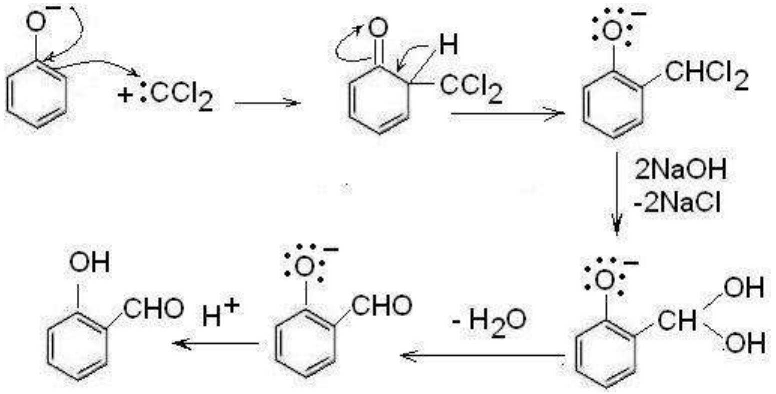
Mechanism

The electrophile, dichloromethylene CCl_2 is generated from chloroform by action of base

$OH^- + CHCl_3 \leftrightharpoons HOH + CCl_3 \rightarrow Cl^- + CCl_2$

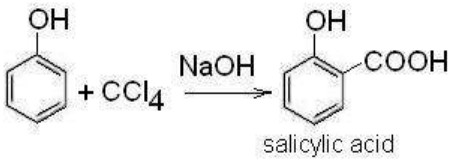


Attack of electrophile (:CCl_2) on phenoxide ion



Salicyaldehyde

If the reaction is carried out with carbon tetrachloride (CCl_4) instead of chloroform, o-hydroxy benzoic acid (salicylic acid) is formed.



TESTS TO DISTINGUISH BETWEEN ALCOHOLS AND PHENOLS

1. Litmus test

   Phenol turns blue litmus red being acidic in nature but alcohol do not.
2. Ferric chloride test

   Phenol react with neutral ferric chloride solution to form violet or green coloured solution where as alcohol do not undergo such reactions.

3. Bromine water test

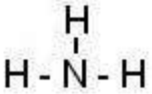
   Aqueous solution of phenol forms white precipitate of 2,4,6-tribromo phenol, when treated with bromine water. However alcohol so not give such precipitation.

AMINES

Amine may be regarded as derivative of ammonia formed by replacement of one or more hydrogen atoms by corresponding number of alkyl or aryl group

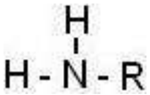
CLASSIFICATION

1. Ammonia



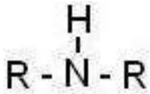
$H-\overset{\overset{H}{|}}{N}-H$

2. Primary amine



$H-\overset{\overset{H}{|}}{N}-R$

3. Secondary
   When two hydrogen atoms are replaced by two alkyl or aryl groups.



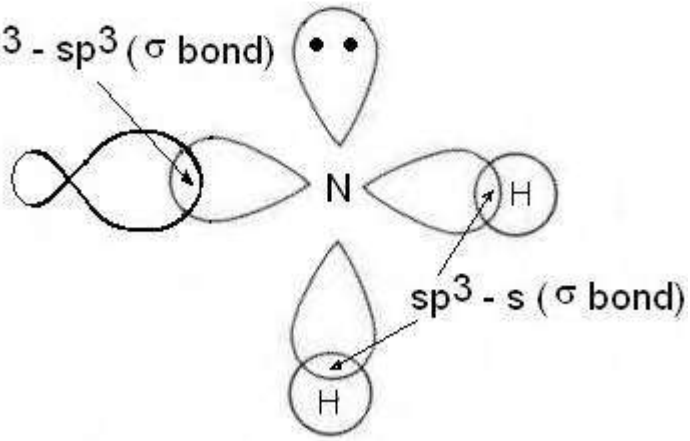
$R-\overset{\overset{H}{|}}{N}-R$

4. Tertiary amine

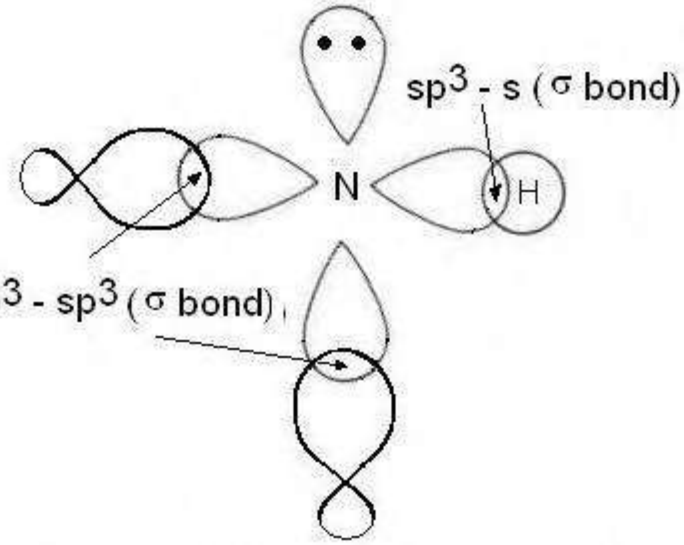
$R-\overset{\overset{R}{|}}{N}-R$

STRUCTURE OF AMINO GROUP

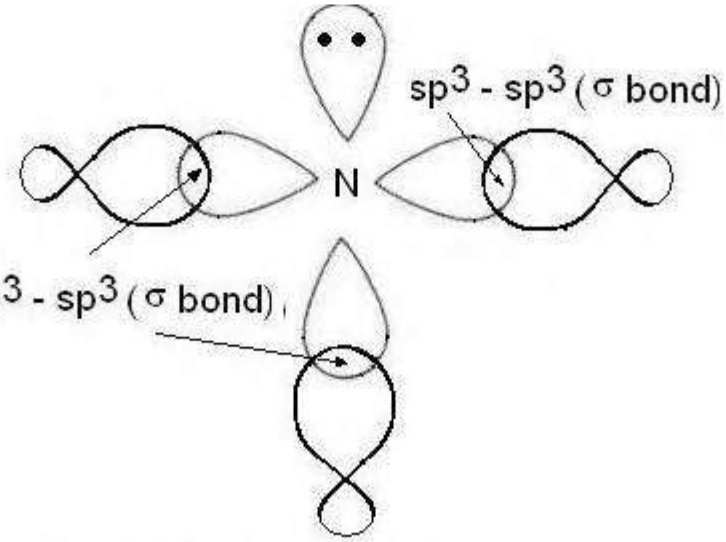
- Nitrogen atom of amino group is sp^3 hybridised. Three of these orbitals get involved in sigma bond formation with other atoms where as the fourth orbital contains lone pair of electrons
- Due to presence of unshared pair of electron, the angle is less than 109.5^o
- The angle around N atom in amines is not fixed and depends upon the number and size of alkyl group bonded to N atom. Therefore, in 1^o and 2^o amines, the bond angle between any two H atoms (in 1^o) or alkyl group (in 2^o) decreases from the tetrahedral angle of $109^o28'$ to 107^o
- In case of 3^o amines, the three bulky alkyl group around N atom due to steric hinderance, the bond angle increases from 107^o to 108^o in trimethylamine



Orbital structure of primary amine



Orbital structure of secondary amine



Orbital structure of tertiary amine

ISOMERISM

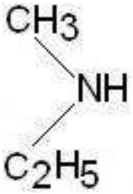
1. Functional Isomerism: This is due to presence of different functional groups

- Molecular formula C_3H_9N represent three functional isomers

Primary

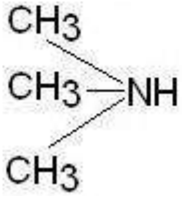
$CH_3 – CH_2 – CH_2 – NH_2$ (n- propyl amine 1°)

Secondary



(Ethylmethylamine 2°)

Tertiary

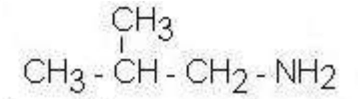


(Triethylamine 3°)

2. Chain isomerism : This is due to difference in the carbon skeleton of the alkyl group attached to amino group

- $C_4H_{11}N$

$CH_3 – CH_2 – CH_2 – CH_2 – NH_2$ [Butan - 1- amine (n butylamine)]



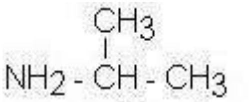
$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-NH_2$

2-methylpropane-1-amine
(isobutylamine)

3. Position isomerism : This is due to difference in chain of amino group

- C_3H_9N

$CH_3 – CH_2 – CH_2 – NH_2$ [propan -1 - amine]

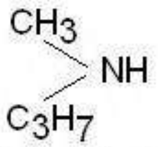


$NH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3$

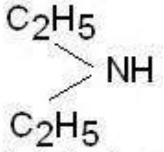
propan -2 - amine

4. Metamerism : This is due to different alkyl groups attached to same functional group.

- $C_4H_{11}N$



methylpropylamine

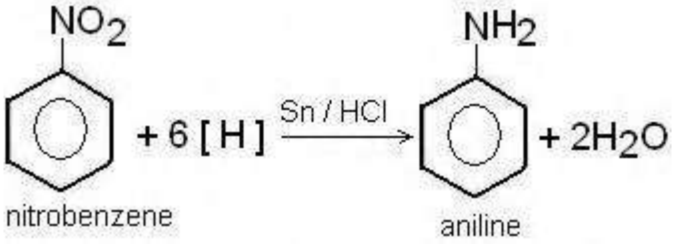


diethylamine

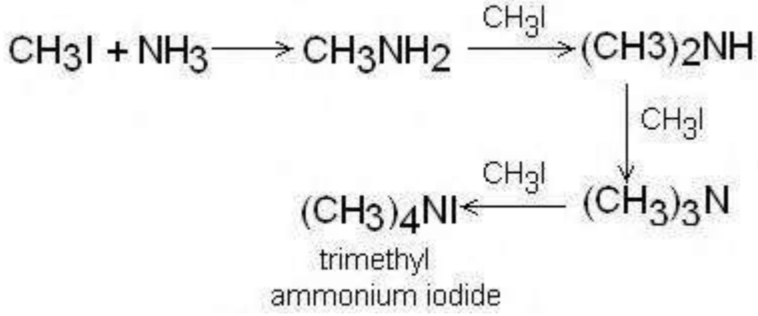
GENERAL METHODS OF PREPARARTION OF AMINES

1. Reduction of nitro compounds

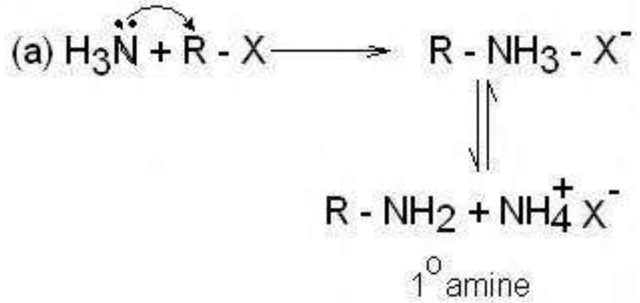
$$R - NO_2 + 6\,[H] \xrightarrow[\text{or Ni or LiAlH}_4\text{/ ether}]{\text{Sn/HCl or Zn/HCl}} R - NH_2 + 2H_2O$$

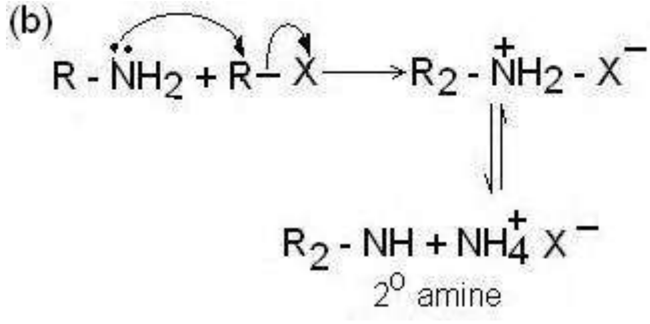


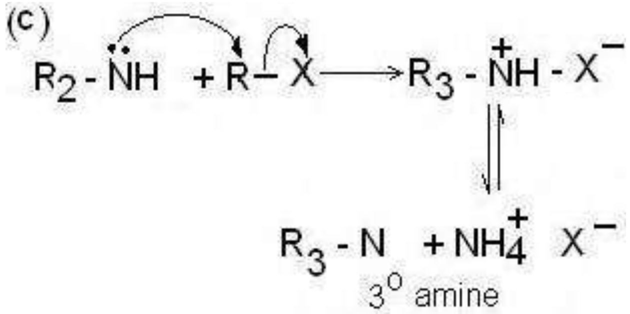
2. Hofmann's ammonolysis method

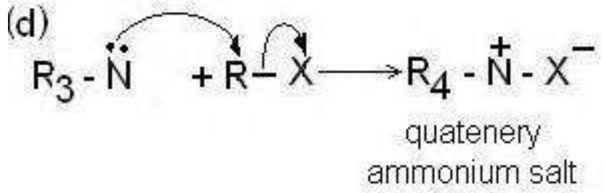


Mechanism







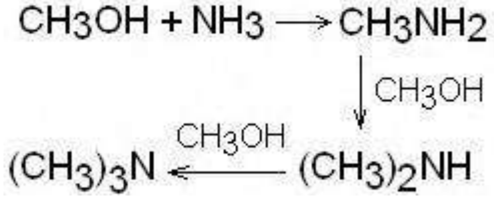


Order of reactivity for this reaction
R – I > R – Br > R – Cl and $1^o > 2^o > 3^o$ > alkyl halide

This reaction is not suitable for aryl amines

- If excess of ammonia is used in the above reaction, primary amine is obtained as main product.
- If excess of alkyl halide is used, tertiary amine is obtained as main product.

3. Ammonolysis of alcohol

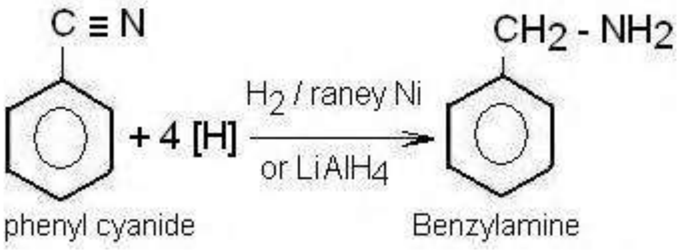


4. Reduction of primary acid amides

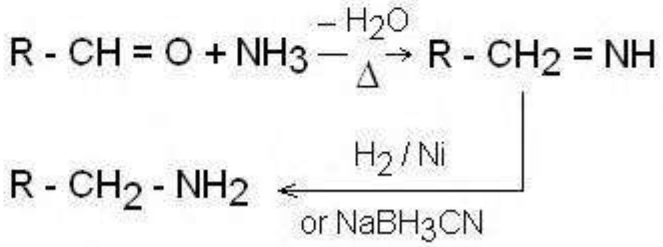
$$CH_3CONH_3 + 4[H] \xrightarrow[LiAlH_4\ (ether)]{Na\ /\ C_2H_5OH} CH_3 - CH_2 - NH_2 + H_2O$$

5. Reduction of alkyl cyanides or nitriles (Mendius reaction)

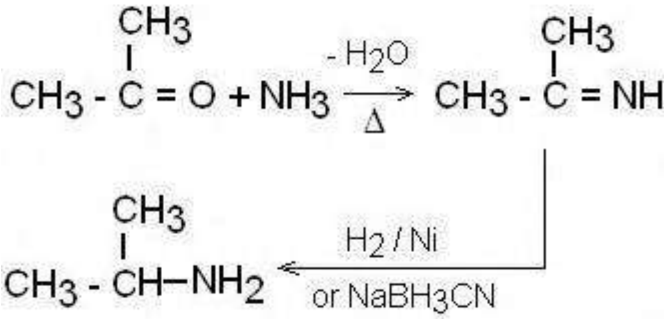
$$\underset{\text{alkyl nitrile}}{R - C \equiv N} + 4\ [H] \xrightarrow[or\ LiAlH_4]{H_2\ /\ raney\ Ni} R - CH_2 - NH_2$$



6. Reductive amination of aldehydes and ketones

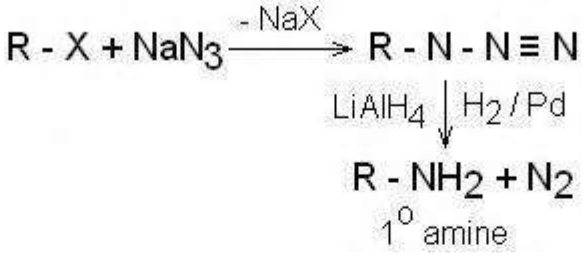


$$R-CH=O+NH_3\xrightarrow[\Delta]{-H_2O}R-CH_2=NH\xrightarrow[\text{or }NaBH_3CN]{H_2/Ni}R-CH_2-NH_2$$



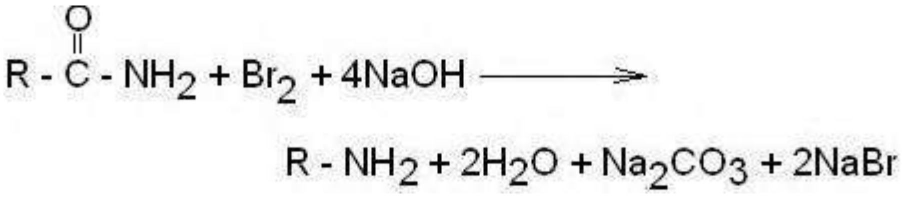
$$CH_3-\overset{\overset{CH_3}{|}}{C}=O+NH_3\xrightarrow[\Delta]{-H_2O}CH_3-\overset{\overset{CH_3}{|}}{C}=NH\xrightarrow[\text{or }NaBH_3CN]{H_2/Ni}CH_3-\overset{\overset{CH_3}{|}}{C}H-NH_2$$

7. Reduction of azides



$$R-X+NaN_3\xrightarrow{-NaX}R-N-N\equiv N\xrightarrow{LiAlH_4\ |\ H_2/Pd}\underset{1^o\text{ amine}}{R-NH_2}+N_2$$

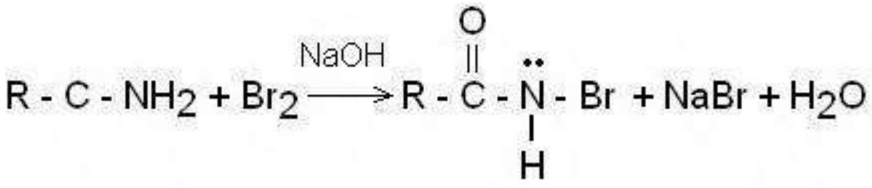
8. Hoffmann bromamide degradation reaction



$$R-\overset{\overset{O}{||}}{C}-NH_2+Br_2+4NaOH\longrightarrow R-NH_2+2H_2O+Na_2CO_3+2NaBr$$

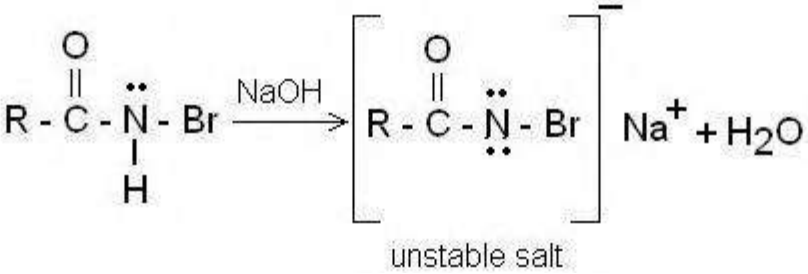
Mechanism

Step I

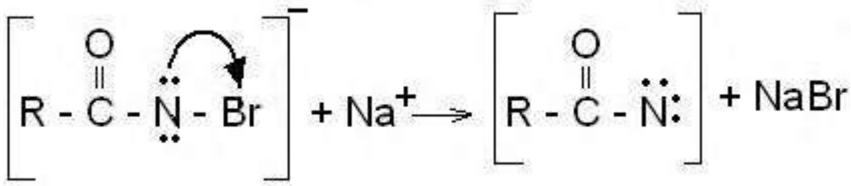


$$R-C-NH_2+Br_2\xrightarrow{NaOH}R-\overset{\overset{O}{||}}{C}-\underset{\underset{H}{|}}{\overset{\bullet\bullet}{N}}-Br+NaBr+H_2O$$

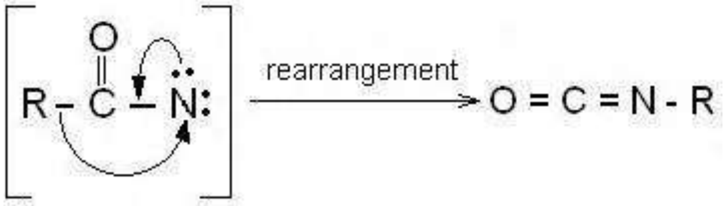
Step II



Step III



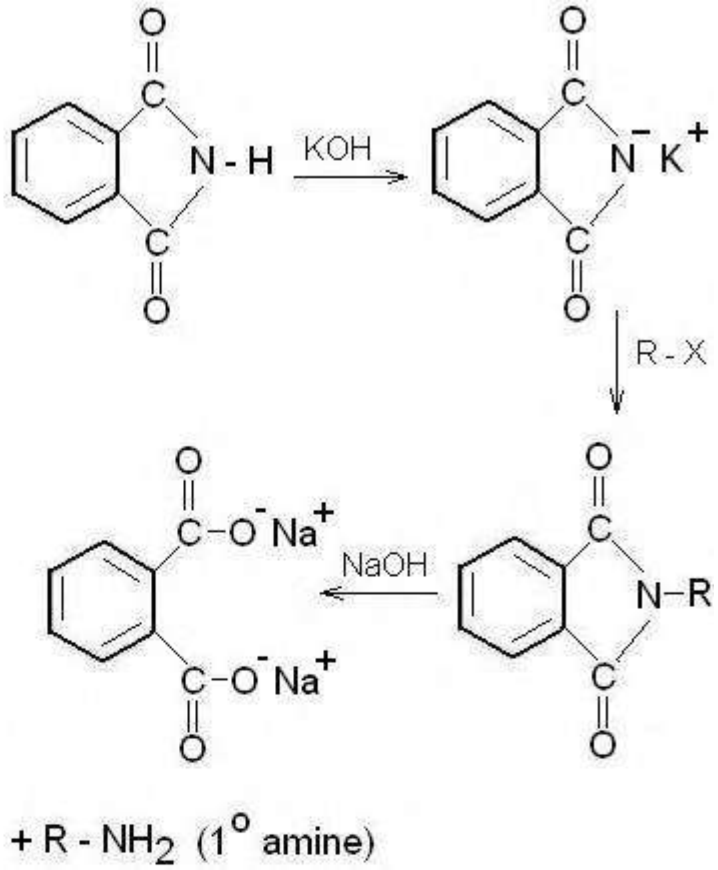
Step IV



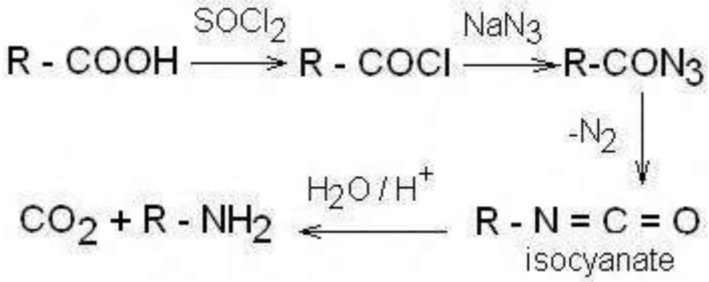
Step V

$$O=C=N-R \xrightarrow{2NaOH} R-NH_3 + Na_2CO_3$$

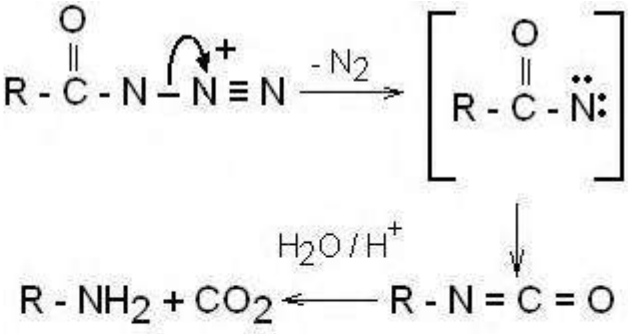
9. Gabriel phthalimide synthesis



10. Curtius degradation or Curtius rearrangement



Mechanism



11. Using Grignard reagent

$$R - Mg - X + ClNH_2 \rightarrow R - NH_2 + MgClX$$

PHYSICAL PROPERTIES OF AMINE

1. Physical state and smell

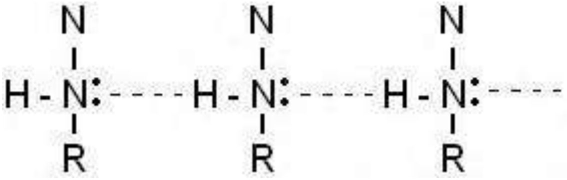
- Lower members are gases, higher amines (C_4 to C_{11}) are volatile liquids while still higher members are solids.
- Lower members have fishy ammonical odour.
- Pure amines are almost colourless but develop colour on keeping in air for long time because amines are readily oxidized in air to form coloured oxidation product.

2. Solubility

- Lower members are soluble in water, but solubility decreases with increase in molecular weight. Aromatic amines are insoluble in water. Both aliphatic and aromatic amines are fairly soluble in organic solvents.

3. Boiling point

- Amines have higher boiling points than hydrocarbons of comparable molecular masses because of intermolecular hydrogen bonding



- But amines have lower boiling points than those of alcohols or carboxylic acid since intermolecular H-bonding in amines is not as strong as in case of alcohols or acid
- Among the isomeric amines, the boiling point are in order
  Primary > Secondary > Tertiary

BASIC CHARACTER OF AMINES

$$RNH_2 + H_2O \rightleftharpoons R\overset{+}{N}H_3 + \overset{-}{OH}$$

$$K_b = \frac{[R^+NH_3][OH^-]}{[RNH_2]}$$

Greater the value of K_b , stronger is the base

$$pK_b = -logK_b = log\frac{1}{K_b}$$

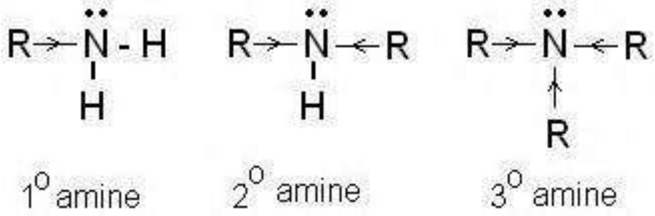
Smaller the value of pK_b, stronger is the base

FACTORS INFLUENCING BASIC STRENGTH OF AMINE

1. Ability of nitrogen atom to donate lone pair of electrons
2. Stability of cation formed after accepting a proton

Basic strength of ammonia and aliphatic amines

- Aliphatic amines are stronger than ammonia
- Since alkyl group exert electron donating inductive effect (+I effect) on nitrogen, electron density on nitrogen atom increases and thus aliphatic amines can donate pair of electrons more easily. Whereas ammonia has no such electron density groups.



- Cation formed after accepting a proton from acid is stabilized by +I effect in aliphatic amines, whereas there is no stabilization in case of ammonia
- Basic strength of amines follows (in gas phase)
  3^O amine > 2^O amine > 1^O amine > NH_3
- Actual order of basic strength in aqueous solution in case of lower members is found to be as
  2^O amine > 1^O amine > 3^O amine > NH_3
  i.e. $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
  However, if the alkyl group is bigger than CH_3 group i.e. ethyl, propyl etc, there will be some steric hindrance to H-bonding. As a result the overall decreasing strength of ethylamine is 2^O amine > 3^O amine > 1^O amine > NH_3
  $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
- Basic strength of different alkyl amines depends on following factors
  (I) +I effect

  \+ I effect of alkyl groups tend to increase the electron density on nitrogen atom and hence the basic strength. Greater the number of alkyl groups attached to nitrogen more is the basic strength

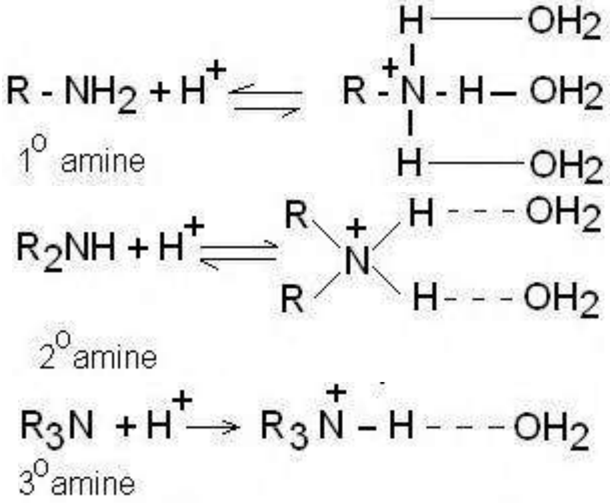
  It follows the following order 3^O amine > 2^O amine > 1^O amine > NH_3

  (II) Steric effect

- Presence of alkyl group hinders the attack of acid on amine, thus reduces the basic strength
- Greater the number of bulky alkyl groups attached to nitrogen, less will be the basic strength
- It follows the following order 1^O amine > 2^O amine > 3^O amine

(III) Solvation effect

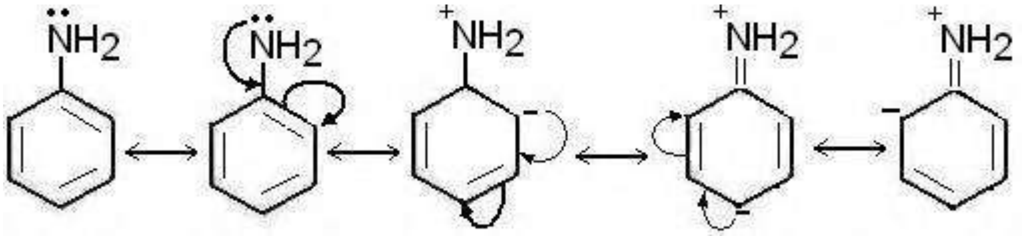
- Amines get protonated by accepting a H^+ ion from aqueous solution and thus ammonium cation. These ammonium cations are stabilized by intermolecular H – bonding
- Greater the number of H-atoms on N-atom, greater will be the extent of hydrogen bond and thus higher will be stability of ammonium cation.



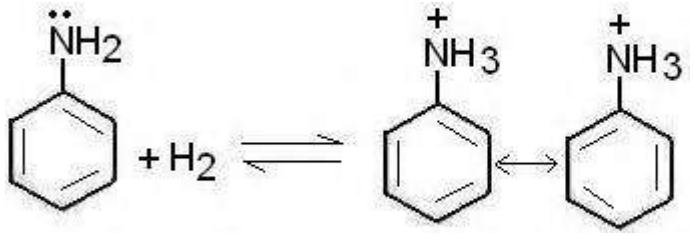
Hence the order of basic strength of different alkyl amines in their aqueous solution is given by the combined effect of the above factors.

Basic strength of aromatic amines

- Aromatic amines are far less basic than ammonia
- Aromatic amines are resonance stabilized as a result of which lone pair of electrons on nitrogen atom gets delocalized over benzene and hence less easily available for protonation.



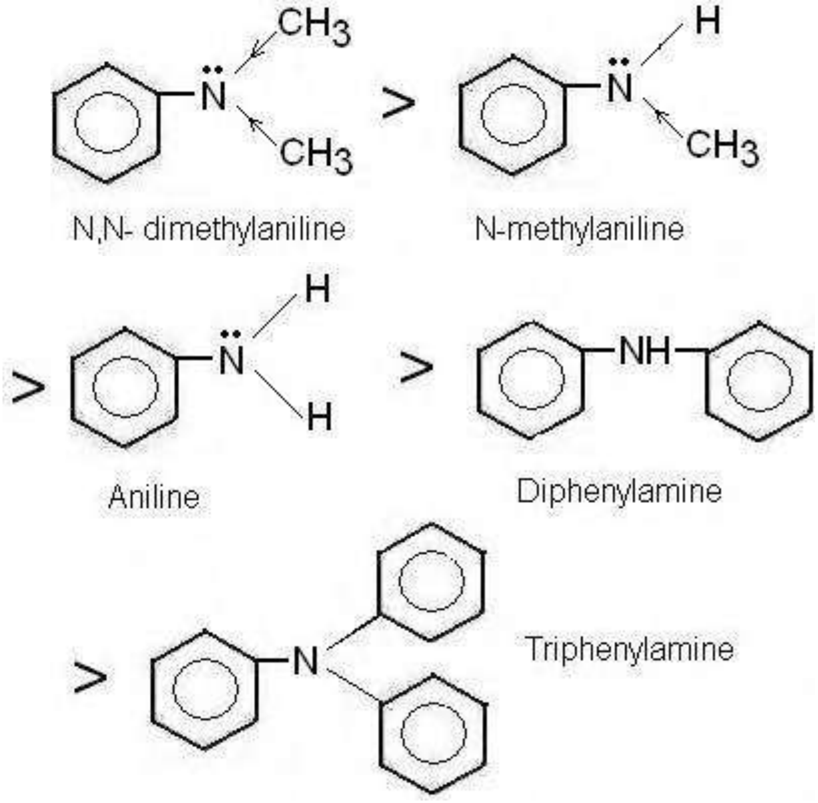
- Cation formed form aromatic amines after protonation is less stable than original amine since it is resonance hybrid of only two structures



- As a result, aromatic amines have less tendency towards protonation.

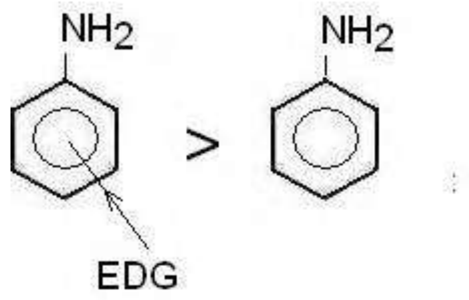
Aniline and N-substituted anilines

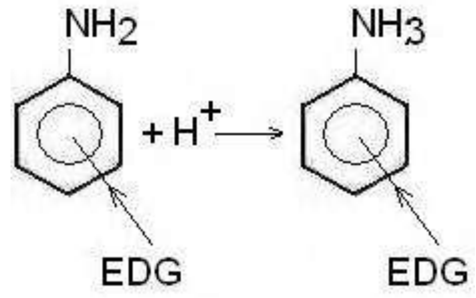
- Substitution of hydrogen atom of aniline with some electron donating group (like alkyl) increases the basic strength
- Whereas if substitution is made by an electron – withdrawing group (like phenyl group), the basic strength of amine decreases



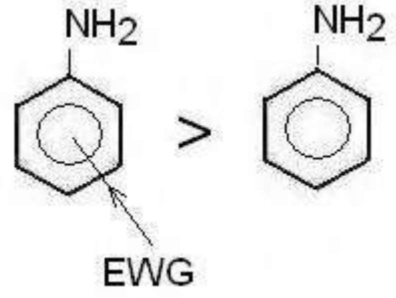
Effect of substitution on basic strength of aromatic amines

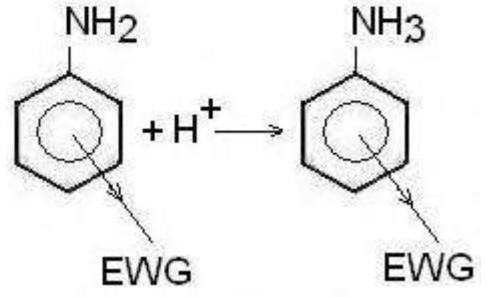
- Electron donating group (like $-CH_3$, $-OCH_3$, $-NH_2$, etc) increases the electron density of amino group so that electron releasing tendency of amine and thus its basic strength increases.
- In addition to it an electron donation group stabilizes the cation formed after protonation by dispersing its positive charge.



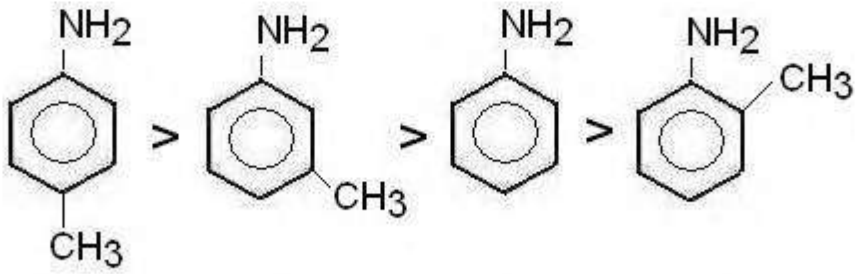


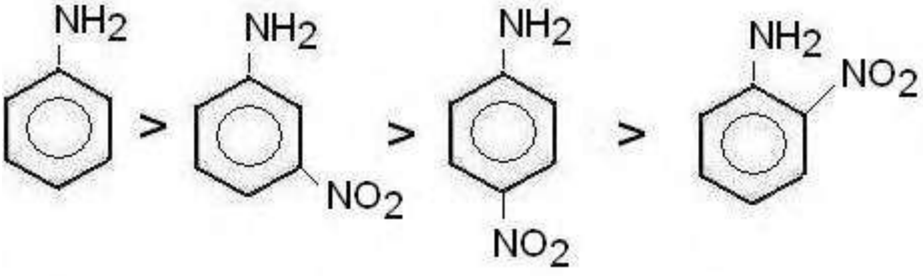
- Electron withdrawing group (like –NO_2, -CN, - X etc) decreases the electron, density of amino group. So that electron releasing tendency of amine and thus its basic strength decreases.
- In addition to its an electron withdrawing group destabilizes the cation formed after protonation by intensifying its positive charge.



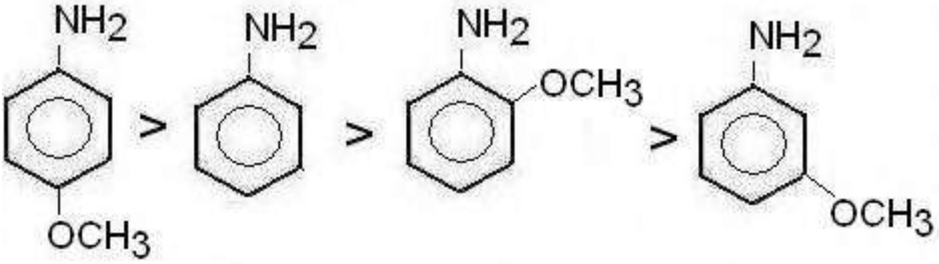


- Effect of any substituent (whether electron donating or electron withdrawing) is more pronounced at para-position than meta-position
- Ortho substituted anilines are weaker bases than anilines.

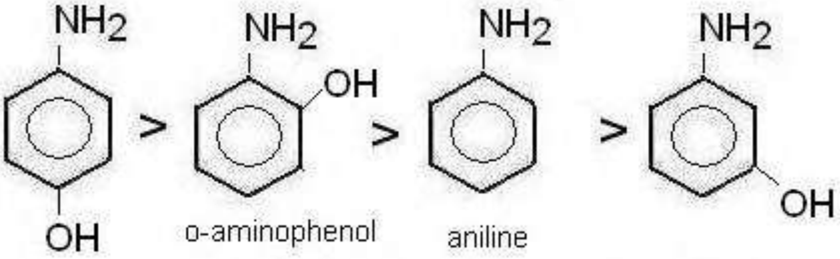




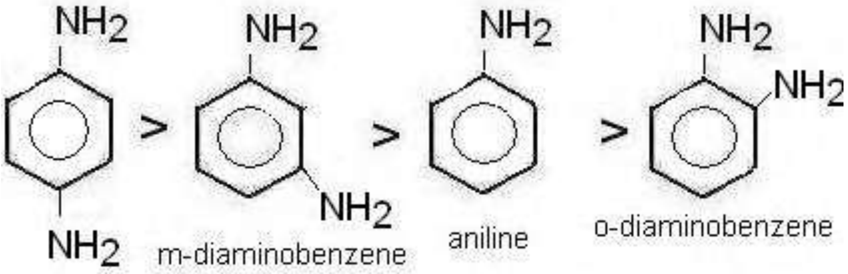
- OCH_3 ⟶ **strong +R effect, weak -I effect**



- OH ⟶ **strong +R effect, weak -I effect**



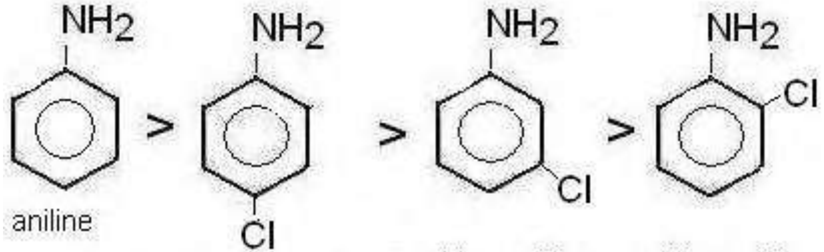
$-NH_2 \longrightarrow$ strong +R effect, strong + I effect



m-diaminobenzene aniline o-diaminobenzene

p-diaminobenzene

$-Cl \longrightarrow$ strong +R effect, strong –I effect



aniline p-chloroaniline m-chloroaniline o-chloroaniline

CHEMICAL PROPERTIES OF AMINES

1. Reaction with acids (salt formation)

$$R-NH_2 + HCl \longrightarrow RNH_2\cdot HCl \text{ or } R\overset{+}{N}H_3\ \overset{-}{Cl}$$

Alkyl ammonium chloride

$$2R_2NH + H_2SO_4 \longrightarrow [R_2\overset{+}{N}H_2]_2\ SO_4^{-}$$

dialkylammonium sulphate

$$R_3N + HNO_3 \longrightarrow [\ R_3\overset{+}{N}\ H\ ]\ NO_3^{-}$$

trialkylammonium nitrate

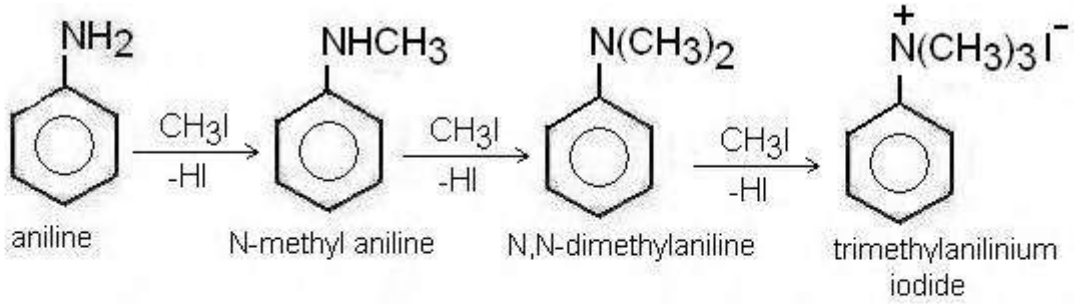
2. Reaction with water

$$R-NH_2 + HOH \rightleftharpoons R\overset{+}{N}H_3OH^{-} \rightleftharpoons [\ RNH3\ ]^{+} + [OH]^{-}$$

alkylammonium hydroxide

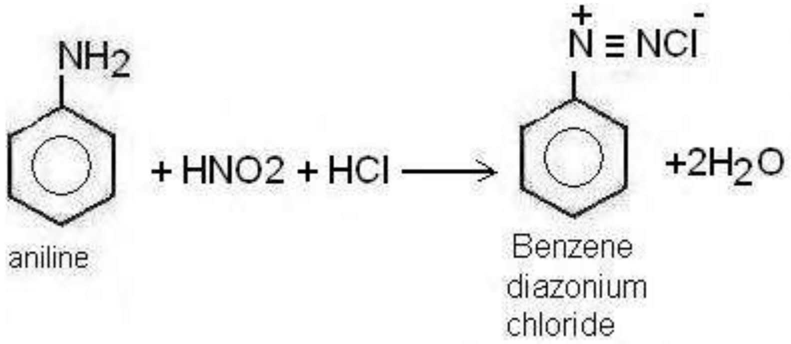
3. Reaction with alkyl halides (Alkylation)

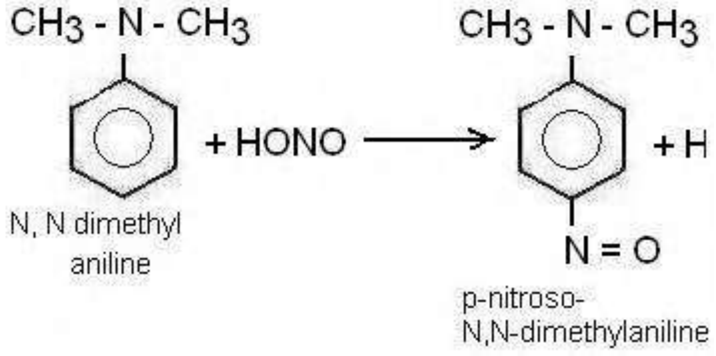
$$\underset{\text{pri. amine}}{RNH_2} \xrightarrow[-HX]{R' - X} \underset{1^0\text{amine}}{R - NH - R'} \xrightarrow[-HX]{R' - X} \underset{3^0\text{amine}}{R - NR'_2} \xrightarrow[-HX]{R' - X} \underset{\text{quaternery salt}}{(R - NR_3) X^-}$$



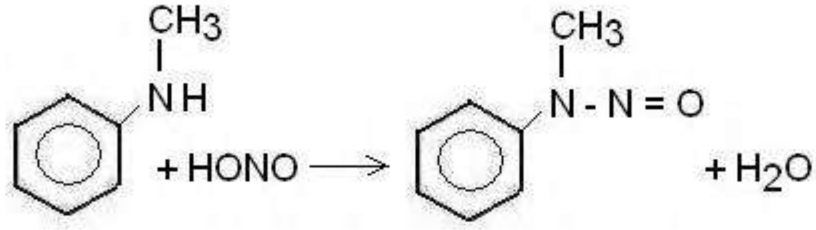
4. Reaction with nitrous acid

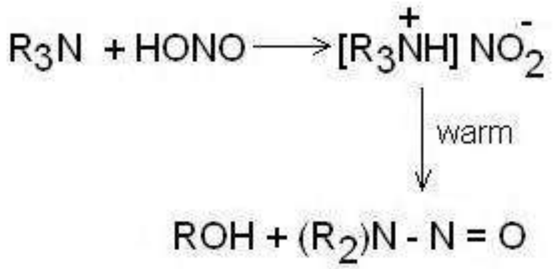
$$R - NH_2 + HONO \xrightarrow{0^0 - 5^0\ C} R - OH + N_2 + H_2O$$





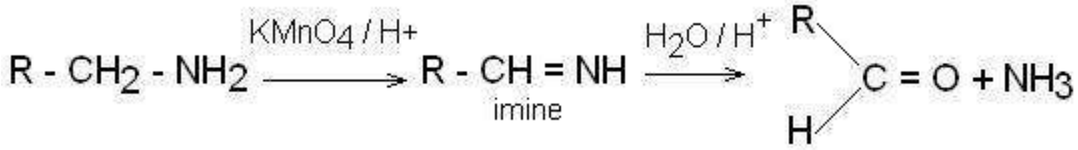
$$R_2 - NH + HONO \longrightarrow R_2N - N = O + H_2O$$

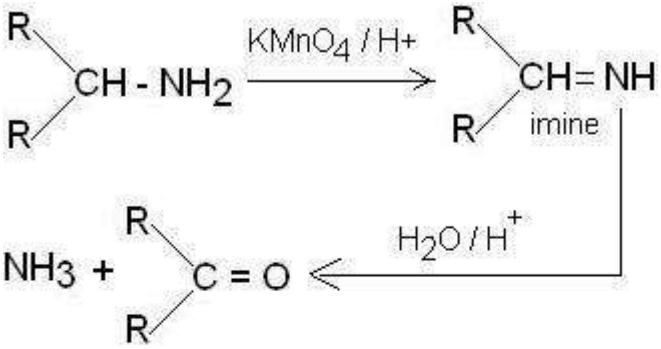


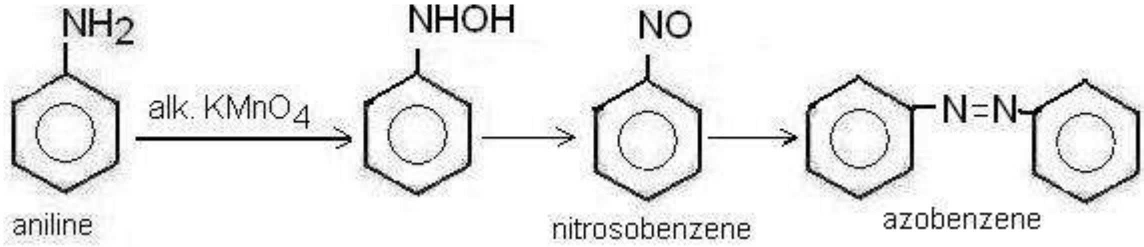


$$R_3N + HONO \longrightarrow [R_3\overset{+}{N}H]\,NO_2^- \xrightarrow{\text{warm}} ROH + (R_2)N-N=O$$

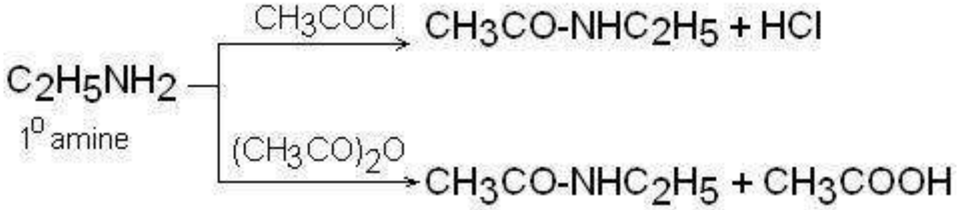
5. Oxidation







6. Acylation

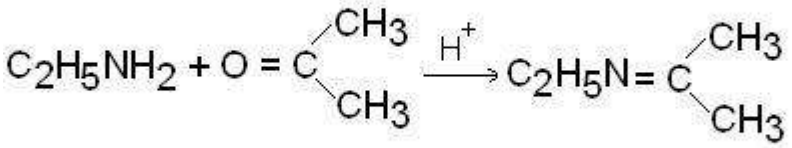


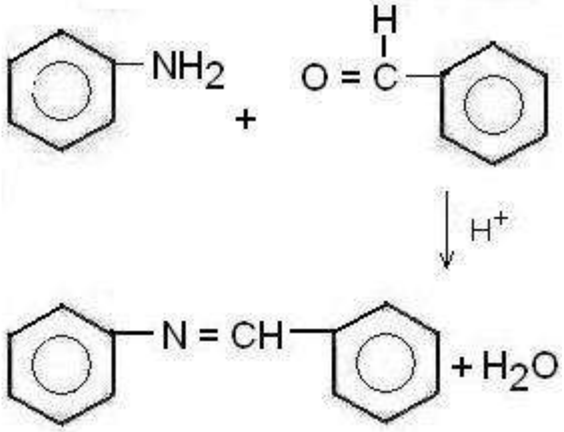
$$\underset{1^0\text{ amine}}{C_2H_5NH_2} \xrightarrow{CH_3COCl} CH_3CO\text{-}NHC_2H_5 + HCl$$

$$C_2H_5NH_2 \xrightarrow{(CH_3CO)_2O} CH_3CO\text{-}NHC_2H_5 + CH_3COOH$$

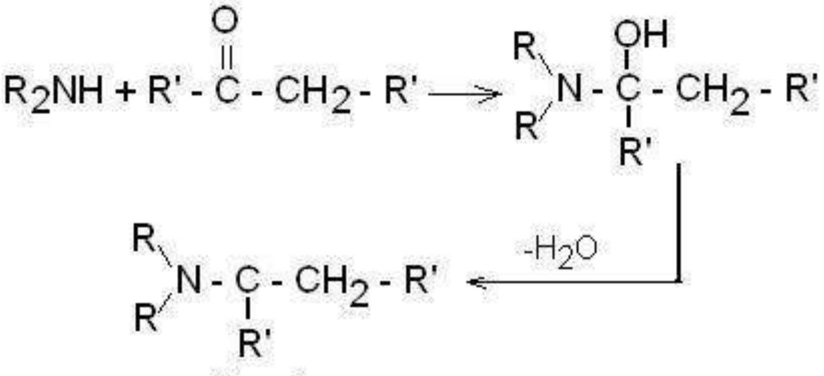
7. Reaction with aldehydes and ketones.

$$C_2H_5NH_2 + CHO - CH_3 \xrightarrow{H^+} C_2H_5N = CH - CH_3$$





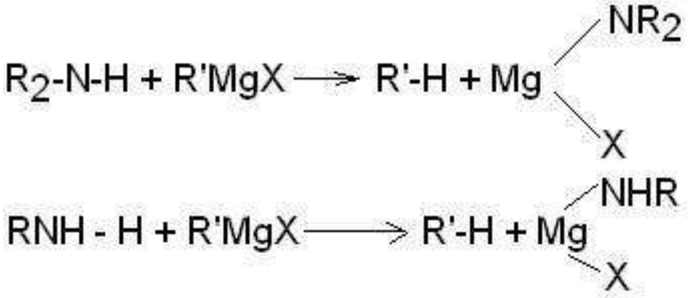
Benzylidene aniline



Enamine

Tertiary amines do not react with aldehydes and ketones

8. Reaction with Grignard reagent



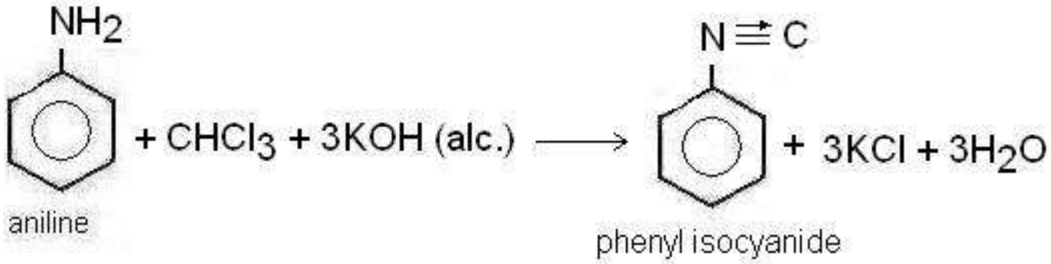
$$R_2\text{-N-H} + R'MgX \longrightarrow R'\text{-H} + Mg\begin{matrix}\diagup NR_2 \\ \diagdown X\end{matrix}$$

$$RNH\text{ - }H + R'MgX \longrightarrow R'\text{-H} + Mg\begin{matrix}\diagup NHR \\ \diagdown X\end{matrix}$$

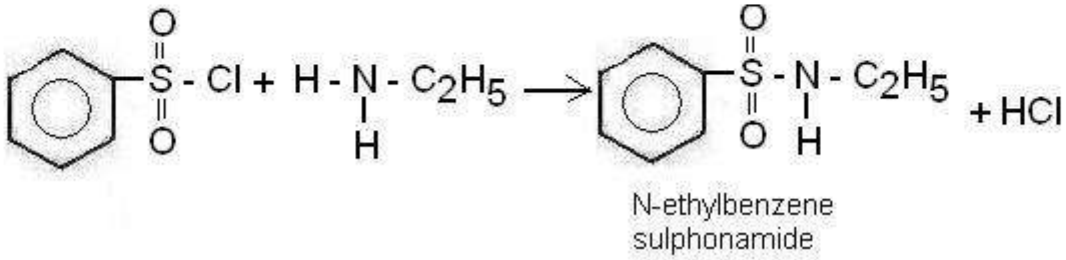
Tertiary amines do not give such reaction due to lack of hydrogen atom attached to Nitrogen

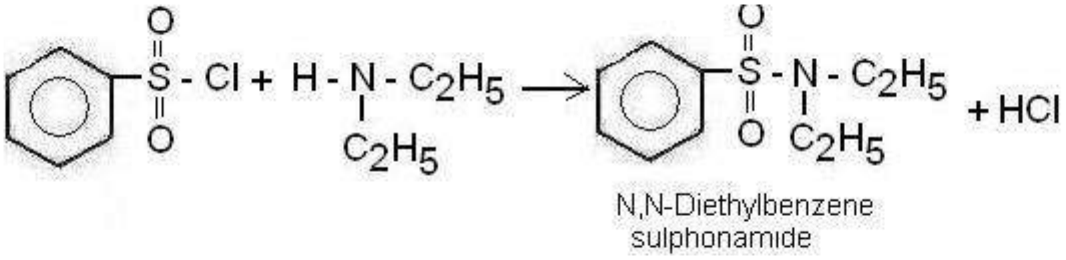
9. Carbylamine reaction (Isocyanide test)

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH(alc) \longrightarrow 3H2O + \underset{\text{ethyl isocyanide}}{C2H5N \overset{\rightarrow}{=} C} + 3KCl$$



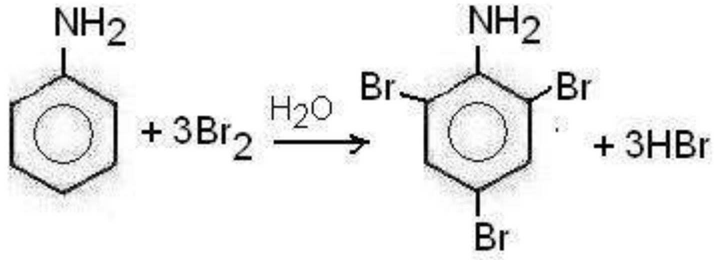
10. Reaction with arylsulphonyl chloride



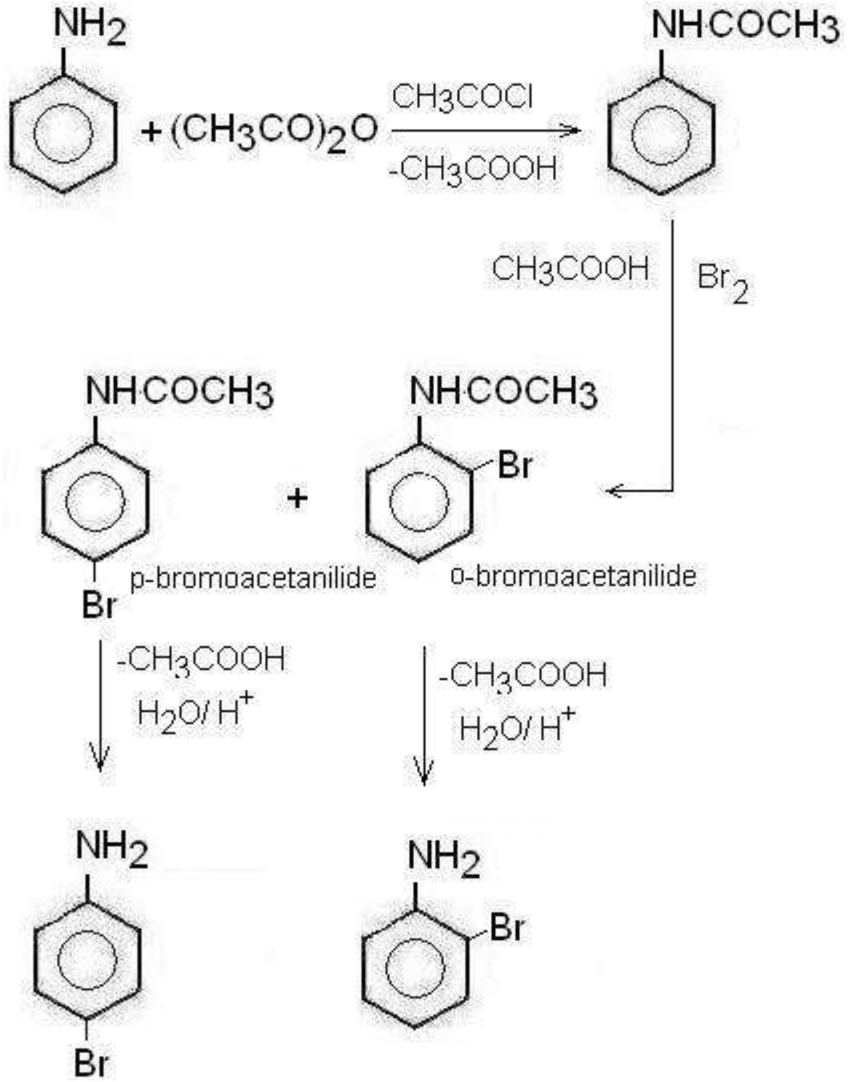


11. Electrophilic substitution

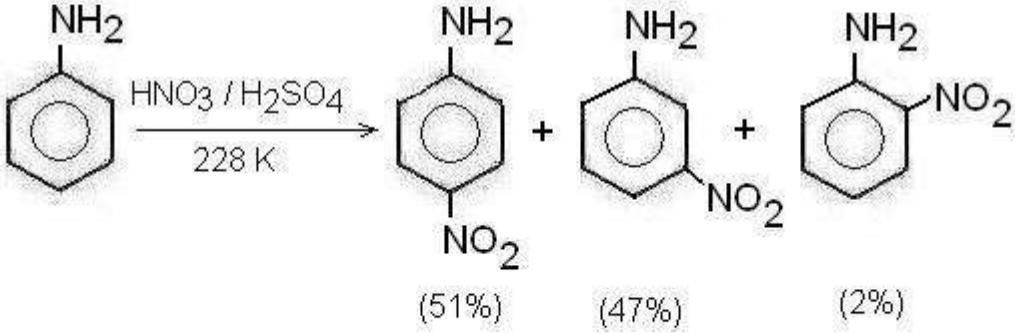
(1) Bromination

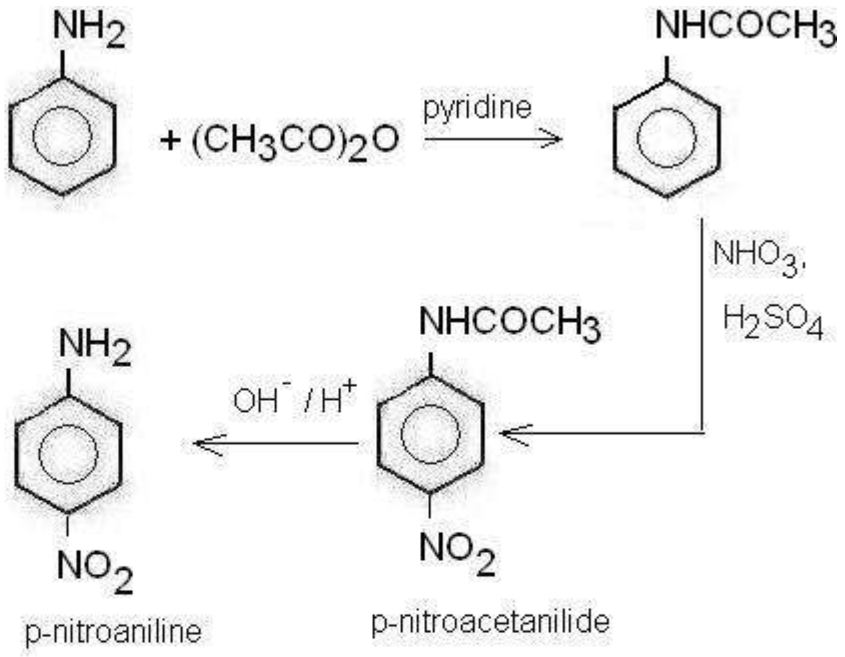


- If a monohalogenated derivatives is required, then activation of benzene ring has to lowered down which can be done by acylating the amino group. Thus Bromination takes place only at one position, either ortho or para.

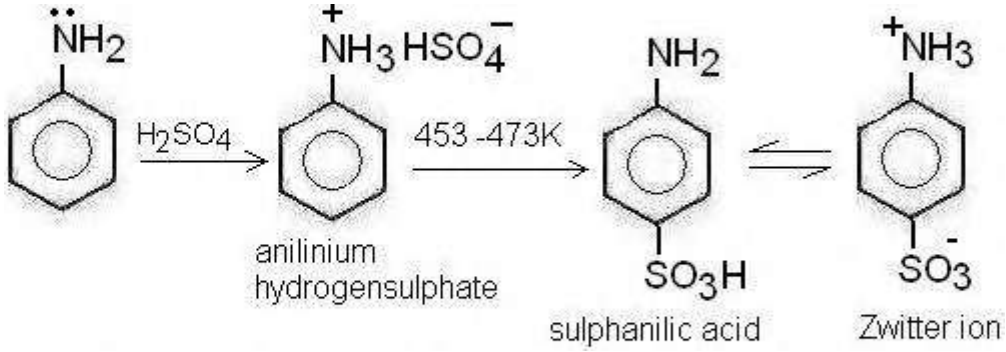


(ii) Nitration





(iii) Sulphonation



DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY AMINES

1. Action of $CHCl_3$ and alcoholic KOH (Carbylamine test)
   Primary amines : Bad smelling carbylamines (Isocyanide) is formed
   Secondary amines: No reaction
   Tertiary amines : No action.
2. Action of CS_2 and $HgCl_2$
   Primary amines : Alkyl isothiocyanate is formed which has pungent smell like mustard oil.
   Secondary amines: No action
   Tertiary amines : No action
3. Action of nitrous acid
   Primary amines : Alcohol is formed with evolution of nitrogen gas.

Secondary amines: Forms nitrosoamine which gives green colour with phenol and conc.H_2SO_4 (Liebermann’s test)
Tertiary amines : Forms nitrite in cold which on heating gives nitrosoamine which responds to Liebermann’s test.

4. Action of acetyl chloride
   Primary amines : Acetyl derivative is formed
   Secondary amines: Acetyl derivatives is formed
   Tertiary amines : No action
5. Action of Benzene sulphonyl chloride (Hinsberg’s reagent) in excess of potassium hydroxide solution
   Primary amines : Monoalkyl sulphonamide is formed which is soluble in KOH
   Secondary amines: Dialkyl sulphonamide which is insoluble in KOH
   Tertiary amines : No action
6. Action of methyl iodide
   Primary amines : 3 molecules (moles) of CH_3I to form quaternary salt with one mole of secondary amine.
   Secondary amines: 2 molecules (moles) of CH_3I to form quaternary salt with one mole of secondary amine.
   Tertiary amines : 1 mole of CH_3I to form quaternary salt with one mole of tertiay amine

USES

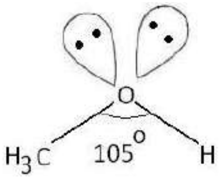
1. Lower aliphatic amines are used:
   (i) As solvent in laboratory and industry
   (ii) As stabilizers for rubber latex
   (iii) In petroleum refining and manufacture of detergents
   (iv) As reagents in organic synthesis
2. Aromatic amines (Such as aniline) are used:
   (i) For the preparation of benzenediazonium salt which is starting material for preparation of many organic compounds
   (ii) For preparing many useful derivatives such as acetanilide, sulphanilic acid, sulpha drugs etc
   (iii) For the preparation of phenyl isocyanide needed for the manufacture of polyurethane plastics.

ALCOHOLS

Alcohols are the hydroxyl derivatives of aliphatic hydrocarbon in which the –OH group is attached to alkyl group.

ORBITAL STRUCTURE

- In alcohols, both carbon and oxygen atoms are sp^3 hybridised. Two of the four sp^3 hybridised orbitals of oxygen get involved in formation of σ-bond with hydrogen and carbon respectively where as rest of two sp^3 hybridised orbitals contain lone pair of electrons. C - O – H bond angle is found to be as 105° (rather than normal tetrahedral angle 109.5°) Deviation from normal angle can be explained on the basis of greater repulsion by lone pairs than bond pairs.



CLASSIFICATION OF ALCOHOLS

Alcohols can be classified as

- On the basis of number of hydroxyl groups

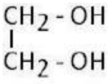
(1) Monohydric alcohol

Compounds in which hydrogen atom is replaced by one hydroxyl group.

CH_3OH : methyl alcohol

$(CH_3)_3C\text{-}OH$: Tert butyl alcohol

(2) Dihydric alcohol

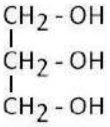


$CH_2\text{-}OH$ | $CH_2\text{-}OH$

glycol

Compounds in which two hydrogen atoms are replaced by two hydroxyl groups.

(3) Trihydric alcohol



$CH_2\text{-}OH$ | $CH_2\text{-}OH$ | $CH_2\text{-}OH$

glycerol

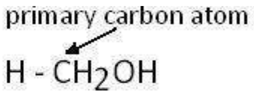
Compounds in which three hydrogen atoms are replaced by three hydroxyl groups.

CLASSIFICATION OF MONOHYDRIC ALCOHOLS

1) Compound containing sp^3 C – OH bond.

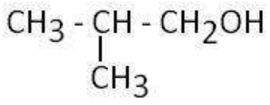
In these alcohols, the –OH group is attached to sp^3 –hybridised carbon atom of an alkyl group.

(1) Primary alcohol(1°): In these alcohols, the hydroxyl group is attached with primary (1°) carbon atom. The general formula is $R\text{-}CH_2\text{-}OH$. R may be H or alkyl group



$H-CH_2OH$

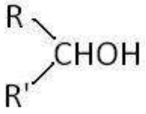
methyl alcohol (1°)



$CH_3-CH(CH_3)-CH_2OH$

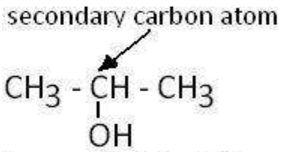
isobutyl alcohol

(2) Secondary alcohol (2°): In these alcohols, the hydroxyl group is attached with secondary (2°) carbon atom. The general formula is



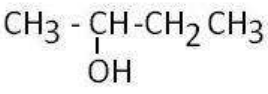
$R(R')CHOH$

R and R' may be same or different



$CH_3-CH(OH)-CH_3$

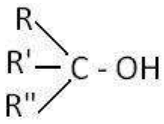
isopropyl alcohol 2°



$CH_3-CH(OH)-CH_2CH_3$

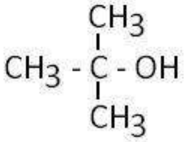
sec. butyl alcohol

(3) Tertiary alcohol(3°): In these alcohols, the hydroxyl group is attached with, tertiary (3°) carbon atom. General formula is



$R(R')(R'')C-OH$

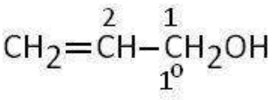
R, R', R" may be same or different



$CH_3-C(CH_3)_2-OH$

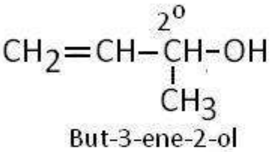
tert butyl alcohol

(4) Allylic alcohol : In these alcohol, the –OH group is attached to an sp³ hybridized carbon next to the carbon-carbon double bond. i.e. to an allylic carbon



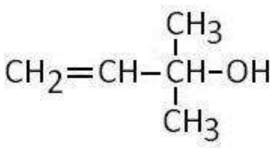
$CH_2{=}CH-CH_2OH$

prop-2-en-1-ol
primary 1°



$CH_2{=}CH-CH(CH_3)-OH$

But-3-ene-2-ol
secondary (2°)



$CH_2{=}CH-C(CH_3)_2-OH$

2-methyl but -3-en-2-ol
tertiary (3°)

(5) Benzylic alcohols:

In these alcohols, the –OH group is attached to an sp³- hybridized carbon atom next to an aromatic ring.

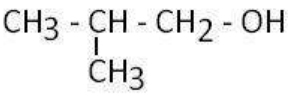
(2) Compound containing sp² C-OH bond

In these alcohols, the –OH group is attached to a carbon atom of double bond i.e. vinylic carbon

$CH_2 = CH_2 - OH$ (vinyl alcohol, unstable)

ISOMERISM IN ALCOCHOLS

(1) Chain isomerism : Alcohols containing four or more carbon atoms exhibit chain isomerism in which the isomers differ in the chain of carbon atoms attached to the hydroxyl group
$CH_3 = CH_2 - CH_2 - CH_2 - OH$ (Butan – 1 –ol)



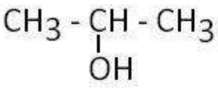
$CH_3 - \underset{\overset{|}{CH_3}}{CH} - CH_2 - OH$

2-methylpropan-1-ol

(2) Position isomerism : Alcohols containing three or more carbon atoms show position isomerism in which the isomers differ in the position of hydroxyl group when carbon chain is the same

$CH_3 - CH_2 - CH_2 - OH$

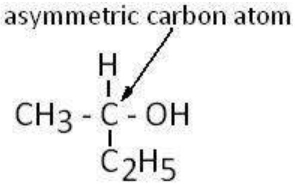
propan-1-ol



$CH_3 - \underset{\overset{|}{OH}}{CH} - CH_3$

propan-2-ol

(3) Functional group isomerism: Saturated monohydric alcohols containing two or more carbon atom show functional isomerism with ethers e.g.
$CH_3 - CH_2 - OH$ (ethanol) and $CH_3 - O - CH_3$ (methoxymethane)
Besides the structural isomerism, alcohols having asymmetric carbon atom exhibit optical isomerism e.g.



asymmetric carbon atom

$CH_3 - \overset{\overset{H}{|}}{\underset{\underset{C_2H_5}{|}}{C}} - OH$

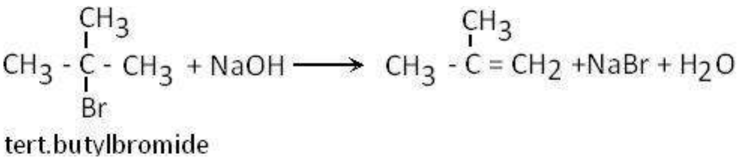
GENERAL METHOD OF PREPARATION OF ALCOHOL

1. Hydrolysis of alkyl halide

$$R - X + KOH(aq) \rightarrow R - OH + KX$$

$$R - X + Ag_2O(moist)(aq) \rightarrow R - OH + AgX$$

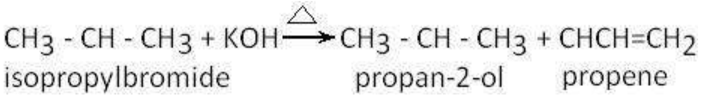
- This method is not satisfactory for preparing alcohol because haloalkanes are themselves obtained from alcohols and in higher halides, the alkenes are formed as side products.
- However, satisfactory results are obtained by using moist silver oxides (AgOH)
- Primary alkyl halides gives good yield of alcohols, while tertiary butyl halides mainly give alkenes due to dehydrohalogenation



$$CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_3 + NaOH \longrightarrow CH_3-\overset{CH_3}{C}=CH_2 + NaBr + H_2O$$

tert.butylbromide

- Secondary(2°) alkyl halides gives a mixture of alcohol and alkene



$$CH_3-CH-CH_3 + KOH \xrightarrow{\triangle} CH_3-CH-CH_3 + CHCH=CH_2$$

isopropylbromide propan-2-ol propene

- Hydrolysis of 1° halides proceeds by S_N2 mechanism while those of 3° halides by S_N1 mechanism. The hydrolysis 2° alkyl halides may proceed by S_N1 or S_N2 mechanism

2. Hydration of alkene

(1) Direct hydration

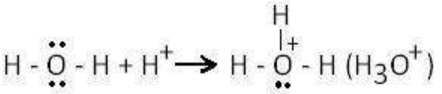
$CH_2 = CH_2 + H_2SO_4 \rightarrow CH_3 - CH_2 - H_2SO_4 + H_2O \rightarrow CH_3CH_2OH$

Mechanism:

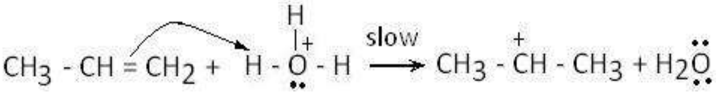
The mechanism of acid catalysed addition of water (hydration) to alkenes involves following steps:

Step I : Electrophilic attack by hydronium ion (H_3O^+) on alkene gives an intermediate carbocation

$H_2SO_4 \rightarrow H^+ + HSO_4^-$

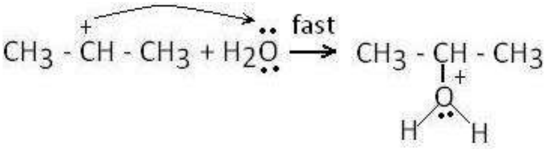


$$H-\ddot{\underset{\cdot\cdot}{O}}-H + H^+ \longrightarrow H-\overset{H}{\underset{\cdot\cdot}{\overset{|+}{O}}}-H\ (H_3O^+)$$



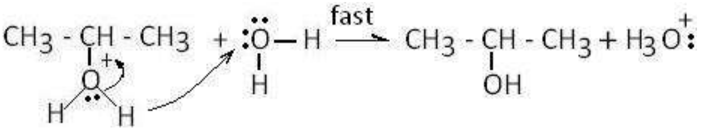
$$CH_3-CH=CH_2 + H-\overset{H}{\underset{\cdot\cdot}{\overset{|+}{O}}}-H \xrightarrow{slow} CH_3-\overset{+}{C}H-CH_3 + H_2\ddot{\underset{\cdot\cdot}{O}}$$

Step II: Nucleophilic attack by water on carbocation to yield protonated alcohol



$$CH_3-\overset{+}{C}H-CH_3 + H_2\ddot{\underset{\cdot\cdot}{O}} \xrightarrow{fast} CH_3-\underset{H-\overset{+}{\ddot{O}}-H}{CH}-CH_3$$

Step III: Deprotonation (loss of proton) to form an alcohol

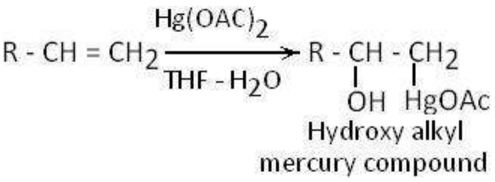


$$CH_3-\underset{H-\overset{+}{\ddot{O}}-H}{CH}-CH_3 + :\ddot{\underset{H}{O}}-H \xrightarrow{fast} CH_3-\underset{OH}{CH}-CH_3 + H_3\overset{+}{O}:$$

Addition of H_2SO_4 follows Markownikoff's rule

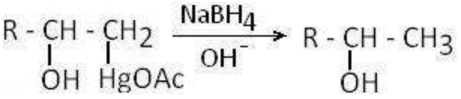
(2) Indirect hydration

(a) Oxymercuration-demercuration



$$R-CH=CH_2 \xrightarrow[THF-H_2O]{Hg(OAC)_2} R-\underset{OH}{CH}-\underset{HgOAc}{CH_2}$$

Hydroxy alkyl mercury compound



$$R-\underset{OH}{CH}-\underset{HgOAc}{CH_2} \xrightarrow[OH^-]{NaBH_4} R-\underset{OH}{CH}-CH_3$$

(b) Hydroboration – oxidation

$$R - CH = CH_2 + B_2H_6 \xrightarrow{ether} RCH_2 - CH_2 - BH_2$$

$$RCH_2 - CH_2 - BH_2 + R - CH = CH_2 \rightarrow (RCH_2CH_2)_2BH$$

$$(RCH_2CH_2)_2BH + + R - CH = CH_2 \rightarrow (RCH_2CH_2)_3B$$

$$(RCH_2CH_2)_3B \xrightarrow{H_2O_2/OH^-} 3R - CH_2 - CH_2 - OH + H_3PO_3$$

Reaction ultimately results in anti Markownikoff's addition of water.

3. Hydrolysis of esters

$$RCOOR' + H_2O \xrightarrow{H^+ \ OR \ OH^-} RCOOH + R' - OH$$

Ester acid alcohol

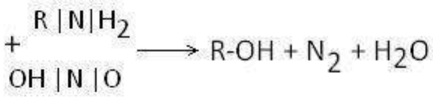
4. Hydrolysis of ethers

$$ROR' + H - O - H \xrightarrow{H_2SO_4} R - OH + R' - OH$$

5. Action of nitrous acid (HONO) on primary amines

$RNH_2 + HONO \rightarrow R\text{-}OH + N_2 + H_2O$

Or



$$\begin{array}{l} R|N|H_2 \\ + \\ OH|N|O \end{array} \longrightarrow R\text{-}OH + N_2 + H_2O$$

- Methylamine does not yield methyl alcohol only, but in excess of nitrous acid the other products may be formed as, methyl nitrite or dimethyl ether

$CH_3NH_2 + 2HNO_2 \rightarrow CH_3 - O - N = O + 2H_2O + N_2$

Methyl nitrite

$2CH_3NH_2 + 2HNO_2 \rightarrow CH_3 - O - CH_3 + 2H_2O + N_2$

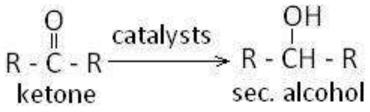
6. Reduction of aldehydes and ketones

Catalysts : H_2/Ni or Na/C_2H_5OH or $LiAlH_4$ or $NaBH_4$

$$H - CHO \xrightarrow{catalysts} CH_3 - OH$$

$$R - CHO \xrightarrow{catalysts} R - CH_3 - OH$$

Aldehyde primary alcohol

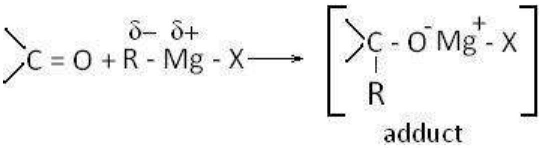


$$\underset{\text{ketone}}{R - \overset{\overset{O}{\|}}{C} - R} \xrightarrow{\text{catalysts}} \underset{\text{sec. alcohol}}{R - \overset{\overset{OH}{|}}{CH} - R}$$

7. Action of Grignard reagents

It occurs in two steps

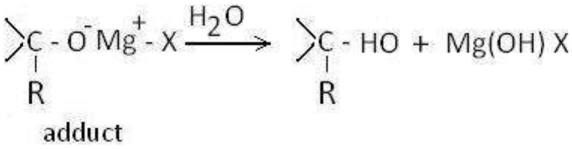
Step I : Nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct



$$>C=O + \overset{\delta-}{R}-\overset{\delta+}{Mg}-X \longrightarrow \left[>\underset{R}{C}-\bar{O}\overset{+}{Mg}-X \right]$$

adduct

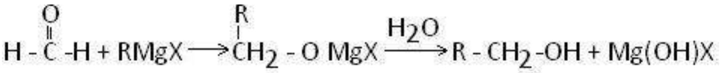
Step II : hydrolysis of adduct to yield alcohol



$$>\underset{R}{C}-\bar{O}\overset{+}{Mg}-X \xrightarrow{H_2O} >\underset{R}{C}-HO + Mg(OH)X$$

adduct

(i) Primary alcohol is produced with formaldehyde

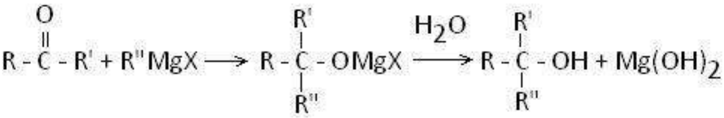


$$H-\overset{O}{\overset{\|}{C}}-H + RMgX \longrightarrow \overset{R}{C}H_2-O\,MgX \xrightarrow{H_2O} R-CH_2-OH + Mg(OH)X$$

(ii) Secondary alcohol is obtained with other aldehydes

$$R-\overset{O}{\overset{\|}{C}}-H + R'MgX \longrightarrow R-\overset{R'}{C}H-OMgX \xrightarrow{H_2O} R-\overset{R'}{C}H-OH + Mg(OH)X$$

(iii) Tertiary alcohol is produced with ketones



$$R-\overset{O}{\overset{\|}{C}}-R' + R''MgX \longrightarrow R-\underset{R''}{\overset{R'}{C}}-OMgX \xrightarrow{H_2O} R-\underset{R''}{\overset{R'}{C}}-OH + Mg(OH)_2$$

8. Reduction of carbonyl group including carboxylic acid and esters

$$R-COOH \xrightarrow{LiAlH_4} R-CH_2OH$$

$$R-COCl \xrightarrow{LiAlH_4} R-CH_2OH + HCl$$

Acid chloride

$$R(CO)_2O \xrightarrow{LiAlH_4} 2R-CH_2OH$$

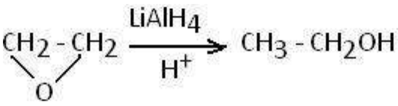
Acid anhydride

$$R-C-OR' \xrightarrow{LiAlH_4} RCH_2OH + R'-OH$$

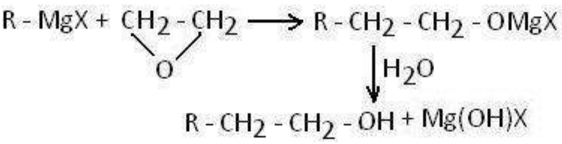
Reduction of carboxyl compounds and esters to alcohol by using alcoholic sodium is called Bouveault – Blance reduction.

9. From epoxides

(i) Reduction



(ii) Action of Grignard reagent



10. Oxo process

This reaction is also known as carbonylation or hydroformylation reaction

$$2CH_2 - CH = CH_2 + 2CO + 2H_2 \rightarrow CH_3CH_2CH_2 - CHO$$

$$CH_3CH_2CH_2 - CHO \xrightarrow{Cu-Zn(H_2)} CH_3CH_2CH_2CH_2OH$$

11. Fermentation of carbohydrates

(i) Molasses is the mother liquor after crystallization of sugar from sugar solution

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{invertase} C_6H_{12}O_6 + C_6H_{12}O_6$$

Glucose fructose

$$C_6H_{12}O_6 \xrightarrow{zymase} 2C_2H_5OH + 2CO_2$$

Ethyl alcohol

(ii) From starch

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{diatase} nC_{12}H_{22}O_{11} \xrightarrow{H_2O(maltase)} 2n\ C_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow{zymase} 2C_2H_5OH + 2CO_2$$

12. Reduction of water gas

It is an industrial method for preparation of methanol

$$CO + H_2 \xrightarrow{ZnO + Cr_2O_3} CH_3OH$$

PHYSICAL PROPERTIES OF ALCOHOLS

(i) Physical state

The lower members upto C_{11} are colourless liquids. Higher members are wax like solids The lower members have a characteristic smell and a burning taste while solid members are almost colourless and tasteless

(ii) Density

Alcohol are lighter than water

(iii) Boiling point

- Boiling points of alcohols increases gradually with increase of carbon chain
- Among isomeric alcohol, the boiling points are in the following order
  Primary > Secondary > tertiary
- The boiling point decreases with branching
- The boiling points of alcohols are much higher as compared to the corresponding alkanes, ether and haloalkanes

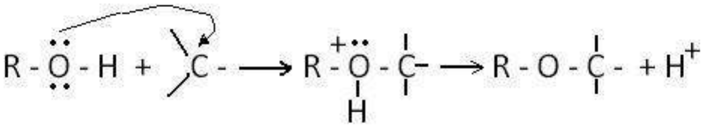
The high boiling points of alcohol are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ether and hydrocarbons

(iv) Solubility

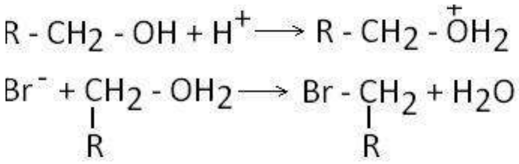
- Lower alcohols are soluble in water due to hydrogen bonding but solubility decreases with increase of molecular mass since hydrocarbon part increases which interrupts the hydrogen bond formation
- Solubility increases with branching since surface area of hydrocarbon part decreases with increase of branching
- Alcohols can form hydrogen bonds with water and break H-bond between water molecule

CHEMICAL PROPERTIES OF ALCOHOLS

- Alcohols are versatile compounds. They react both as nucleophile and electrophile
- Alcohol as nucleophile



- Alcohol as electrophile



$$R-CH_2-OH + H^+ \longrightarrow R-CH_2-\overset{+}{O}H_2$$

$$Br^- + \underset{\substack{|\\ R}}{CH_2}-OH_2 \longrightarrow Br-\underset{\substack{|\\ R}}{CH_2} + H_2O$$

- Chemical reactions of alcohols can be classified into following categories

(A) Reactions due to O-H bond, breaking

(B) Reactions due to C-OH bond breaking

(C) Reaction of alcohol molecule as a whole

(A) Reactions due to O-H bond, breaking

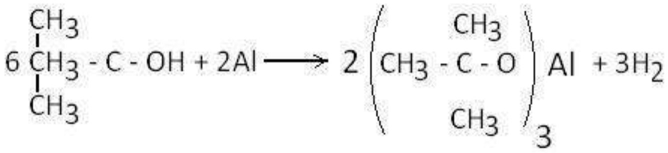
Order of ease of cleavage of O-H bond and thus order of reactivity is

CH_3OH > primary > secondary> tertiary

1. Reaction with metals (acidic nature):

$2R - O - H + 2Na \rightarrow$ 2R-O-Na + H_2

Sodium alkoxide



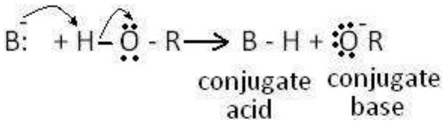
$$6\,CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH + 2Al \longrightarrow 2\left(CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O\right)_3 Al + 3H_2$$

Alcohols are stronger acid than acetylenes and acidic nature is in the order

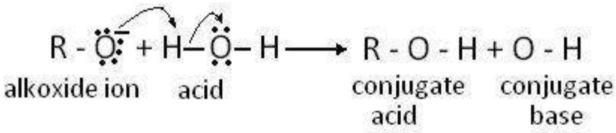
H-OH > ROH> CH≡CH > NH_3RH

Acidic character of alcohol and water

- Alcohols act as Bronsted acids which lose a proton to strong base
- Electron releasing inductive effect (+I) of the alkyl group makes the alcohol weaker acids than water.



- On treating alkoxide ion with water, the starting alcohol is obtained.



Comparison of acidic character of primary, secondary and tertiary alcohols

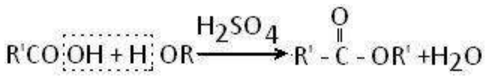
The acidic character of alcohols is due to the polar nature of O – H bond. An electron releasing group increases electron density on oxygen tending to decrease the polarity of O – H bond. This decreases the acidic strength and so the acid strength of alcohol decreases in the following order

$RCH_2OH > R_2CHOH > R_3COH$

Order of +I effect in various isomeric alcohols is

CH_3OH < Primary < secondary < tertiary

2. Esterification



$$R'CO\,OH + H\,OR \xrightarrow{H_2SO_4} R'-\overset{\overset{O}{\|}}{C}-OR' + H_2O$$

- If the above reaction is carried out with dry HCl gas as catalyst, the reaction is known as Fischer-Speier esterification.
- Order of reactivity of different alcohols towards esterification is
  $CH_3OH > RCH_2OH > R_2CHOH > R_3COH$
  AS the size of hydrocarbon part (R) around –OH increases, rate of reaction decreases due to steric hinderance

3. Reaction with inorganic acid

C_2H_5OH + $HOSO_2OH$ → $C_2H_5OS_2OH$ + H_2O

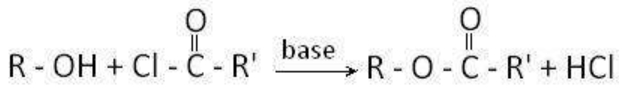
Sulphuric acid ethyl hydrogen sulphate

$C_2H_5OH + HO\text{-}NO_2$ → $C_2H_5\text{-}O\text{-}NO_2 + H_2O$

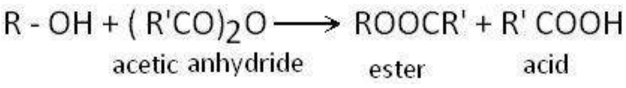
Nitric acid ethyl nitrate

4. Acylation or reaction with acid chloride and acid anhydrides

- When alcohols reacts with acid chloride or acid anhydrides, the hydrogen of the hydroxyl group is replaced by an acyl group (RCO-) resulting in the formation of esters. The process is known as acylation
- When the hydrogen of –OH group is replaced by CH_3CO- (acetyl) group, the process is termed acetylation.



$$R-OH + Cl-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{base} R-O-\overset{\overset{O}{\|}}{C}-R' + HCl$$



$$R-OH + (R'CO)_2O \longrightarrow ROOCR' + R'COOH$$

- The acetylation of alcohol is usually carried out in the presence of base such as pyrimidine

(B) Reaction due to C – OH bond breaking

Order of ease of cleavage of C – OH bond and thus reactivity of different alcohols is

Tertiary > Secondary > Primary > CH_3OH

(1) Reaction with halogen acids

- Order of reactivity of HX is

  HI > HBr > HCl

- For a given hydrogen halide order of reactivity of different alcohol is

  Allyl > benzyl > 3° > 2° > 1°

  $R - \underline{OH + H} - X \rightarrow R\text{-}X + H_2O$

- Alcohols require some catalyst like $ZnCl_2$ or acidic conditions to undergo nucleophilic substitution, since – OH is a poor leaving group

$$CH_3CH_2 - OH + HBr \xrightarrow{conc\ H_2SO_4\ reflux} CH_3CH_2 - Br + H_2O$$

Mechanism above reaction is hydride shift.

- It has been discussed in detail in alkyl halides

(2) Reaction with phosphorus halides and thionyl chloride

$R - OH + PCl_5 \rightarrow R\text{-}Cl + POCl_3 + HCl$

$3R - OH + PCl_3 \rightarrow 3R\text{-}Cl + H_3PO_3$

$3R - OH + PBr_3 \rightarrow 3R\text{-}Br + H_3PO_3$

$R - OH + SOCl_2 \rightarrow R\text{-}Cl + SO_2 + HCl$

(3) Reaction of Nitric acid

$R\text{-}OH + HONO_2 \rightarrow R\text{-}O - NO_2 + H_2O$

Alkyl nitrate

(4) Reaction with ammonia

$$R - OH + NH_3 \xrightarrow{Al_2O_3} R - NH_2 + H_2O$$

$$R - OH + R - NH_2 \xrightarrow{Al_2O_3} R_2 - NH + H_2O$$

2° amine

$$R - OH + R_2 - NH_3 \xrightarrow{Al_2O_3} R_3 - N + H_2O$$

3° amine

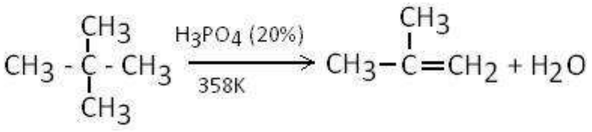
$$R - OH + R_3 - NH \xrightarrow{Al_2O_3} (R_4N^+)OH^-$$

$(R_4N^+)\ OH^-$: Quaternary alkyl ammonium hydroxide

(C) Reaction involving alcohol molecule as a whole

1. Dehydration

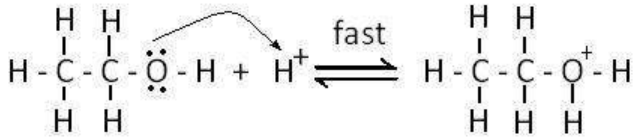
$$CH_3CH_2OH \xrightarrow{conc.H_2SO_4, 443K} CH_2 = CH_2 + H_2O$$



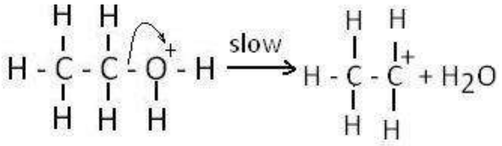
$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - CH_3 \xrightarrow[358K]{H_3PO_4\ (20\%)} CH_3 - \overset{CH_3}{C} = CH_2 + H_2O$$

Mechanism of dehydration

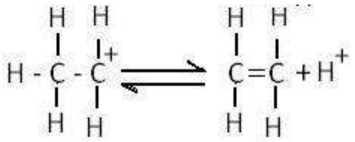
Step I: Formation of protonated alcohol



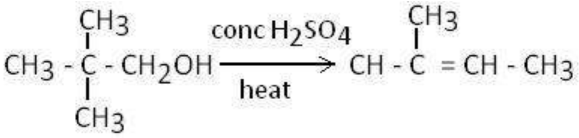
Step II : Formation of carbocation. It is the slowest step and hence the rate determining step of the reaction



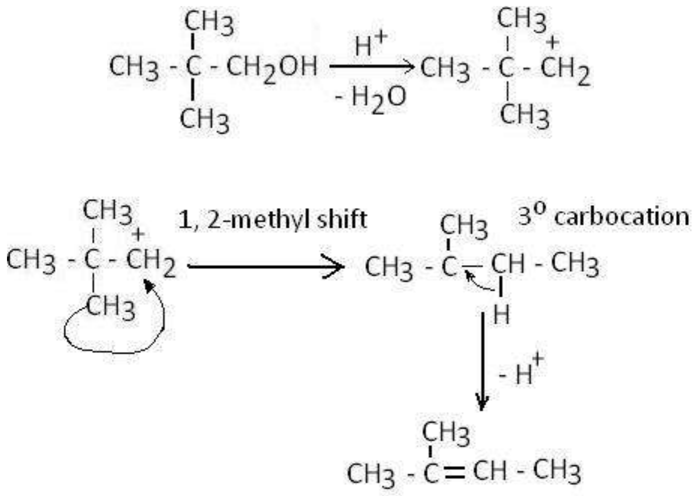
Step III : Formation of ethene by elimination of proton



- Formation of 2-methyl but-2-ene



Mechanism



In case of secondary and tertiary alcohols, Saytzeff's rule is followed and the ease of dehydration of alcohol is in the order

Tertiary > Secondary > Primary

2. Dehydration

(a) A primary alcohol loses hydrogen and forms aldehyde

$$RCH_2OH \xrightarrow{Cu\ /573K} RCHO + H_2$$

(b) A secondary alcohol loses hydrogen and form a ketone

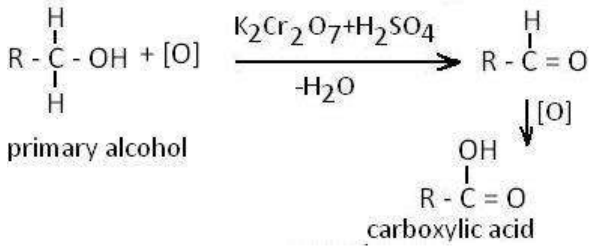
$$(R)_2CHOH \xrightarrow{Cu,573K} (R)_2C = O + H_2$$

(c) A tertiary alcohol undergoes dehydration of alkene

$$(CH_3)_3COH \xrightarrow{Cu,573K} (CH_3)_2C = CH_2 + H_2$$

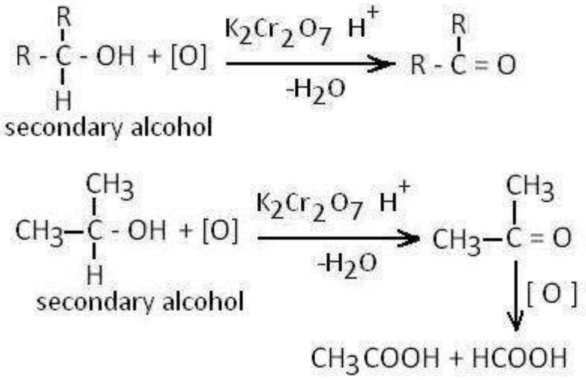
3. Oxidation

(i) Primary alcohols on oxidation gives aldehydes which further get oxidized to carboxylic acid



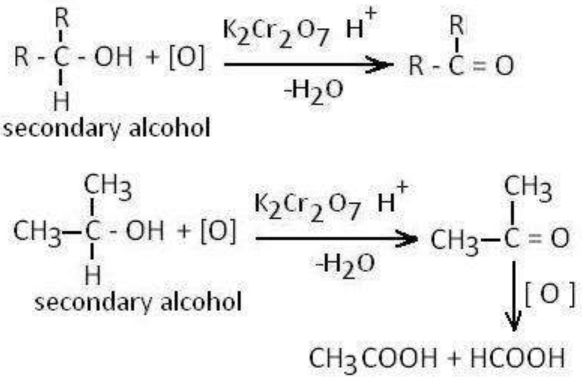
Oxidation can be stopped at aldehyde stage by using collin's reagent ($CrO_3 \cdot 2C_5H_5N$, chloroform trioxide-pyridine complex) or pyridinium chlorochromate, PCC ($CrO_3 \cdot 2C_5H_5N \cdot HCl$)

(ii) Secondary alcohols on oxidation give mixture of carboxylic acids



This oxidation can be stopped at ketone stage by using chromium anhydride (CrO_3)

(iii) A tertiary alcohol having no oxidisable hydrogen linked to carbon atom bearing hydroxyl group, is stable to oxidation in neutral or alkaline $KMnO_4$ solution



4. Reaction with bleaching powder

$$CH_3CH_2OH + CaOCl_2 \xrightarrow{oxidation} CH_3CHO + CaCl_2 + H_2O$$

$$2CH_3CHO + 6CaOCl_2 \xrightarrow{chlorination} 2CCl_3CHO + 3Ca(OH)_2 + 3CaCl_2$$

$$2CCl_3CHO + 3Ca(OH)_2 \xrightarrow{hydrolysis} 2CHCl_3 + (HCOO)_2Ca$$

5. Haloform reaction

$$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{heat} CHI_3 + 5NaI + HCOONa + 5H_2O$$

Sodium formate

This reaction like the preparation of chloroform also occurs in three steps

$$C_2H_5OH \xrightarrow{(NaOH+I_2)Oxidation} CH_3CHO \xrightarrow{iodination(I_2)} CI_3CHO \xrightarrow{hydrolysis(NaOH)} CHI_3$$

In place of iodine, bromide or chlorine can be taken when the corresponding compounds bromoform or chloroform are to be formed. This reaction in general is known as haloform reaction

SOME COMMERCIALLY IMPORTANT ALCOHOLS

1. Methanol

- Methanol is produced by catalytic hydrogenation of carbon monoxide at high temperature and pressure and in presence of ZnO-Cr_2O_3 catalyst

$$CO + 2H_2 \xrightarrow{ZnO-Cr_2O_3(200-300atm.573-673K)} CH_3OH$$

- Methanol is a colourless liquid and boiling point is 337K
- It is poisonous in nature.
- Ingestion of small quantities of methanol can cause blindness.
- It is used as solvent in paints, varnishes and chiefly for making formaldehyde

2. Ethanol

Ethanol is produced by fermentation of molasses into glucose and fermentation gives ethanol and carbon dioxide

$$C_{12}H_{22}O_{12} + H_2O \xrightarrow{invertase} C_6H_{12}O_6 + C_6H_{12}O_6$$

Glucose fructose

$$C_6H_{12}O_6 \xrightarrow{zymase} 2C_2H_5OH + CO_2$$

- In wine making, grapes are the source of sugar. As grapes ripen the quantity of sugar increases and yeast grows on outer skin. When grapes are crushed, sugar and the enzyme comes in contact and fermentation starts. Fermentation takes place in anaerobic conditions. i.e in absence of air
- The action of zymase is inhibited once the percentage of alcohol formed exceeds 14%
- Ethanol is a colourless liquid with boiling point 351K. It is used as a solvent in paint industry
- The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

ETHERS

- Ethers have a general formula R - O - R′ , where R and R′ may be same or different
- Ethers are isomeric with mono-hydric alcohol

  Eg. C_2H_6O

  CH_3CH_2OH (ethyl alcohol); $CH_3 – O –CH_3$ (dimethyl ether)
- Ethers can be classified as follows:

  (i) Aliphatic ethers

  If both R and R′ groups are alkyl groups, then ether is aliphatic ether

  $CH_3 – O – CH_2CH_3$ (ethyl methyl ether)

  $CH_3CH_2 – O – CH_2CH_3$ (diethyl ether)

  (ii) Aromatic ether

  If both R and R′ or any of them is aryl group then ether is aromatic ether

  $CH_3 – O – C_6H_5$ (methyl phenyl ether)

  $C_6H_5 – O – C_6H_5$ (Diphenyl ether)

  (iii) Simple or symmetrical ether

  If two group R and R′ present in ether are same, then it is known as simple or symmetric ether

  $CH_3 – O – CH_3$ (Dimethyl ether)

  $C_2H_5 – O – C_2H_5$ (Diethyl ether)

  $C_6H_5 – O – C_6H_5$ (Diphenyl ether)

  (iv) Mixed or unsymmetrical ether

  If R and R′ present in ether are different, then ether is known as mixed or unsymmetrical ether

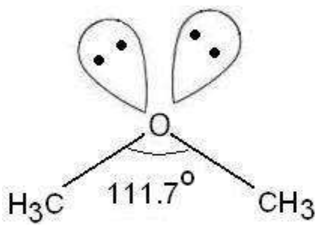
  $CH_3 – O – C_2H_5$ (ethyl methyl ether)

  $CH_3 – O\text{-}C_6H_5$ (methyl phenyl ether)

  $C_6H_5 – O – CH_2C_6H_5$ (Benzyl phenyl ether)

STRUCTURE

Ether may be considered as dialkyl derivative of water



- Oxygen atom in ether is sp^3 hybridised and forms two sigma bonds with sp^3 hybridised alkyl group
- Oxygen atom has two lone pairs of electron in remaining two sp^3 hybridised orbital C – O – C bond angle in ether is slightly greater, than tetrahedral bond angle due to repulsion between two bulky alkyl group. In dimethyl ether C – O – C bond angle is 111.7°

- As the size of R (alkyl group) in ethers increases, van der Waals repulsion increases and hence bond angle also increases

GENERAL METHOD OF PREPARATION OF ETHERS

1. Acidic dehydration of alcohols

$$ROH + HOR \xrightarrow{H_2SO_4(con.)413K} ROR + H_2O$$

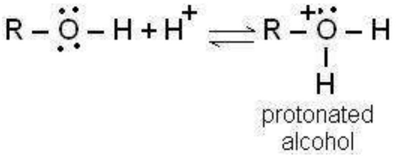
This method is used to prepare simple or symmetrical ether

$$C_2H_5 - OH + HO - C_2H_5 \xrightarrow{H_2SO_4(con.)413K} C_2H_5 - O - C_2H_5 + H_2O$$

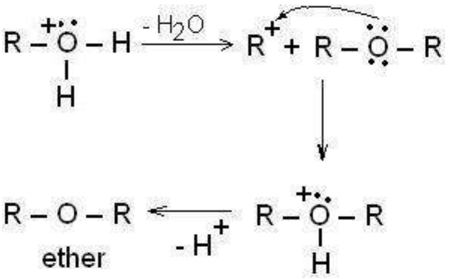
In this reaction, reaction conditions have to be carefully controlled, to get the maximum yield of ether. At a slightly higher temperature (150°C) alkene is obtained instead of ether.

$$C_2H_5 - OH \xrightarrow{H_2SO_4(con.)413K} CH_2 = CH_2 + H_2O$$

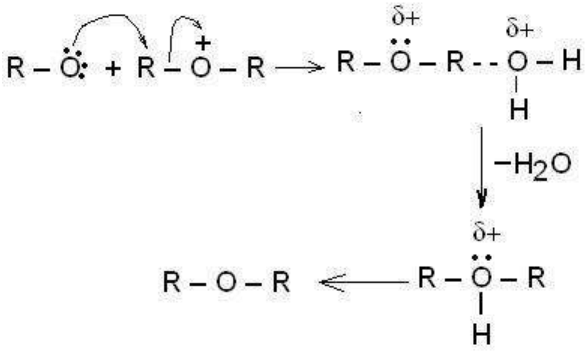
Mechanism



S_N1 mechanism



S_N2 mechanism



- Primary alcohols reacts by generally S_N2 mechanism where as secondary and tertiary alcohols undergo the reaction by S_N1 mechanism
- Order of ease of dehydration of alcohol to form ethers
  1^O alcohol > 2^O alcohol >3^O alcohol
- Catalytic dehydration

$$2R - OH \xrightarrow{Al_2O_3\,(523K)} R - O - R + H_2O$$

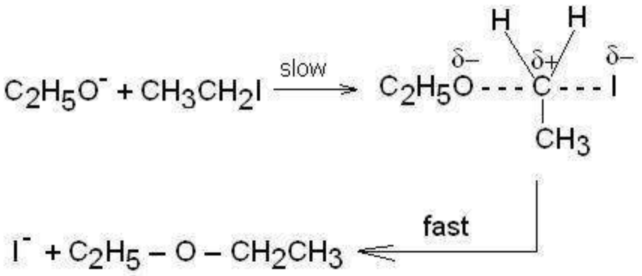
2. Williamson synthesis

   $R' - ONa \; + \; X - R \; \rightarrow \; R' - O - R \; + \; NaX$

- Both symmetric and unsymmetrical ethers can be prepared by this method

  Mechanism

  $C_2H_5ONa \rightleftharpoons C_2H_5O^- + Na^+$



Order of reactivity of alkyl halides towards this reaction is

Primary > secondary > tertiary

For better yield, the alkyl halide should be primary and alkoxide should be secondary or tertiary

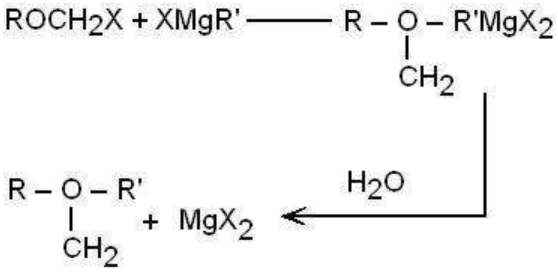
3. Action of silver oxide on alkyl halide

$$2RX + Ag_2O \xrightarrow{heat} R - O - R + 2AgX$$

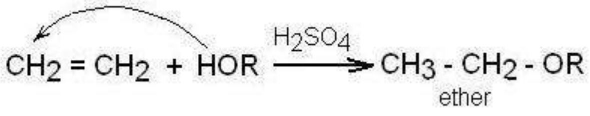
4. Action of diazomethane on alcohols

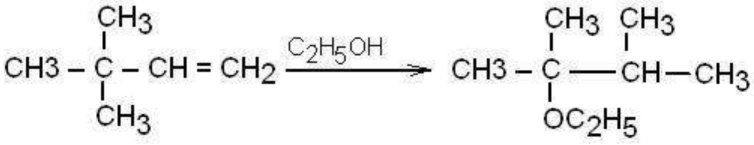
$$R - OH + \underset{\text{Diazomethane}}{CH_2N_2} \xrightarrow{HBF_4} R - O - CH_3 + N_2$$

5. Reaction of lower halogenated ether with Grignard reagent



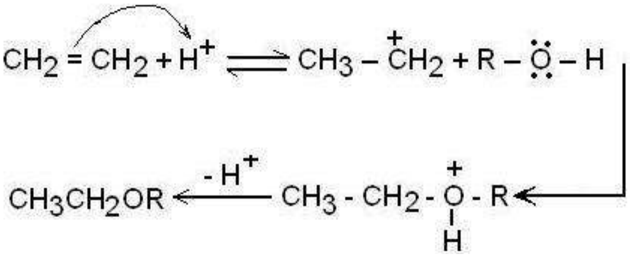
6. Addition of alcohols to alkene





Mechanism

$H_2SO_4 \rightarrow H^+ + H_2SO_4^-$



PHYSICAL PROPERTIES OF ETHERS

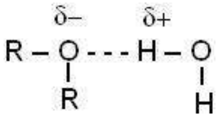
- All ethers are colourless liquids except dimethyl ether and ethyl ether are gases at room temperature

1. Boiling point

- Ether have lower boiling points than isomeric alcohols
- Lower ethers have slightly higher boiling point than n-alkanes of comparable molecular masses due to weak van der Waals force of attraction

2. Solubility

- Ethers are soluble in water to a certain extent due to hydrogen bonding



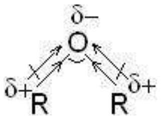
- Ethers are fairly soluble in organic solvent

3. Density

Ether have low density. All ethers are lighter than water and are highly volatile and flammable

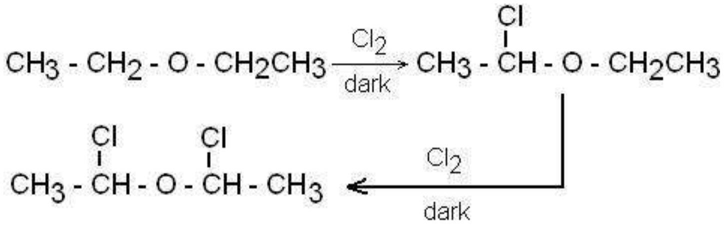
4. Polarity

Ethers are polar in nature and its dipole moment ranges from 1.15D to 1.30D



CHEMICAL PROPERTIES OF ETHERS

1. Halogenation



α , α' - dichlorodiethyl ether

2. Hydrolysis

$$R-O-R+H_2O \xrightarrow{dil.H_2SO_4,\Delta,under\ high\ pressure} 2R-OH$$

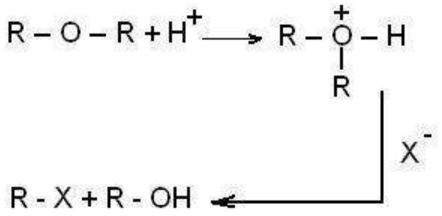
3. Reaction with halogen acid

$$R-O-R+HX \rightarrow RX+R-OH$$

Reactivity of halogen acid

HI > HBr > HCl

Mechanism

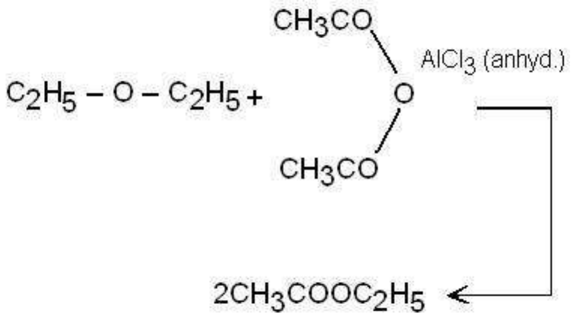


During the cleavage of unsymmetrical ethers, smaller alkyl group produces alkyl halides

4. Reaction with acid chlorides and anhydrides

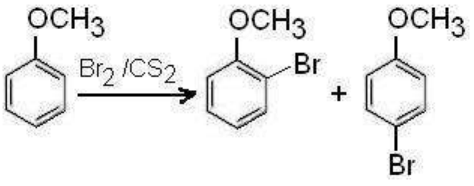
$$C_2H_5-O-C_2H_5+CH_3COCl \xrightarrow{ZnCl_2(anhyd.)\Delta} C_2H_5Cl + CH_3COOC_2H_5$$

Acetyl chloride ethyl acetate

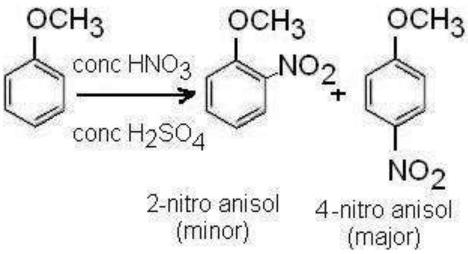


5. Electrophilic substitution reaction

(i) Halogenations

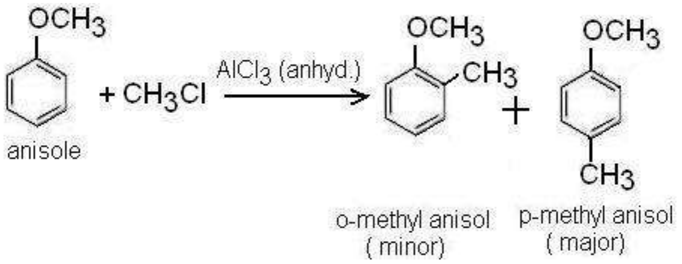


(ii) Nitration

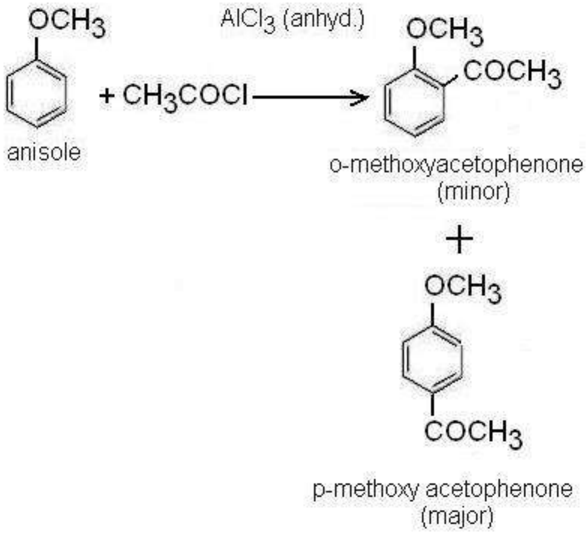


(iii) Friedel crafts reaction

- Alkylation



- Acetylation



USES OF ETHER

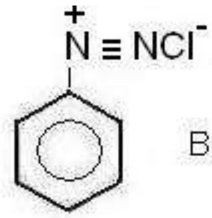
- It act as a solvent for oil, fat, waxes, plastics.
- It is used in perfumery.
- It is used as an inhalation.
- It is used as an inhalation anesthetic agent in surgery.
- It is used as refrigerant for cooling.

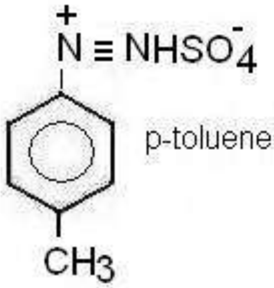
DIAZONIUM SALTS

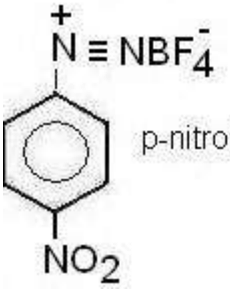
The diazonium salts have general formula $R^+N_2X^-$ where R stands for aryl and X^- ion may Cl^-, Br^-, HSO_4^-, BF_4^- etc

NOMENCLATURE

Arenediazonium salts are named by adding the suffix diazonium to the name of parent aromatic hydrocarbon Example:

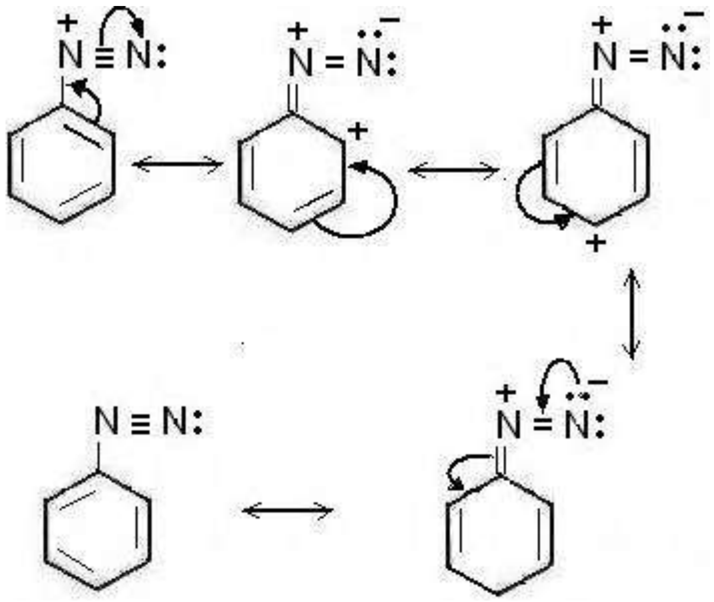

Benzenediazonium chloride


p-toluenediazonium hydrogen sulphate

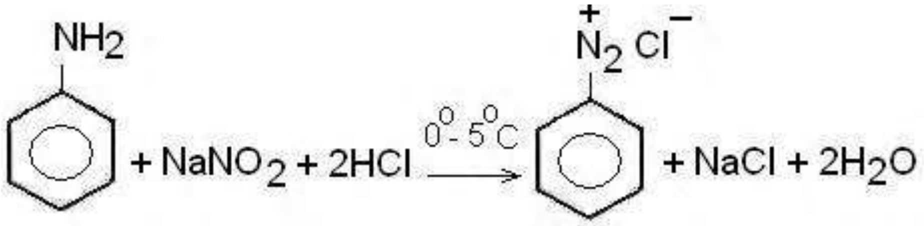

p-nitrobenzene diazonium fluoborate

STABILITY OF DIAZONIUM SALT

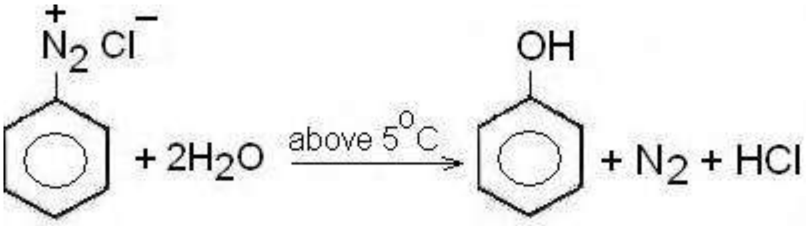
Aryldiazonium salts are stable because of dispersal of positive charge over benzene ring due to resonating structures.



PREPARATION OF ARENEDIAZONIUM CHLORIDE



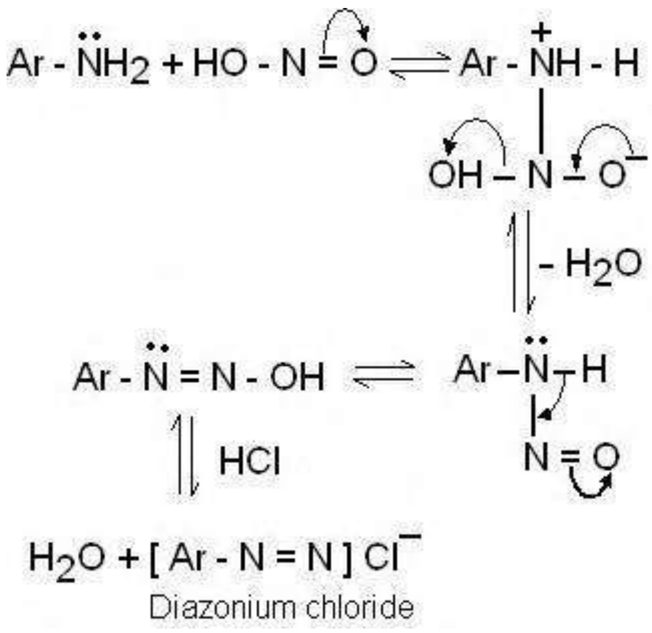
- This process of converting an aromatic primary amile into diazonium salt is called diazotization
- Diazotisation should be carried out at low temperature since at higher temperature benzenediazonium salt reacts with water to form phenol.



- Aromatic amines substituted with electron withdrawing groups require more concentrated acids than unsubstituted amines because of their weak basic character

  Mechanism

  $NaNO_2 + HCl \rightarrow HNO_2 + NaCl$



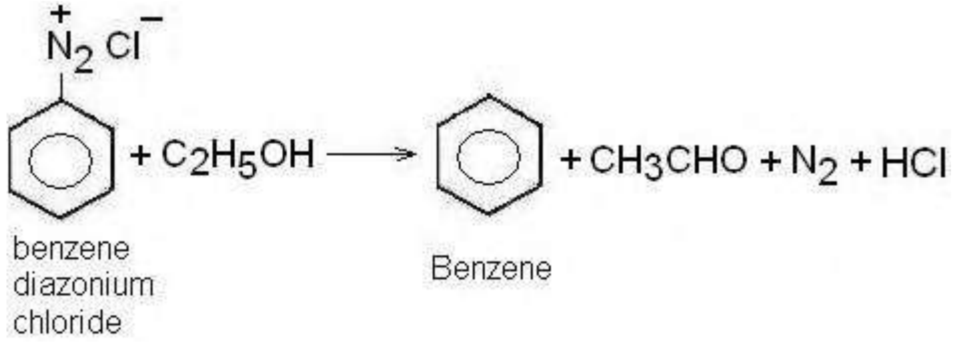
PHYSICAL PROPERTIES

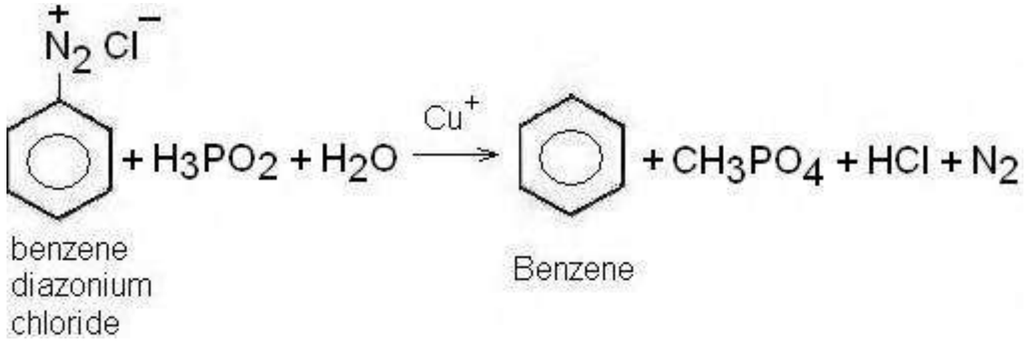
- Aryl diazonium salts are colourless crystalline solids which turn brown when come in contact with air
- They are highly soluble in water but sparingly soluble in ethanol and insoluble in ether
- They are unstable and decomposes easily when dry

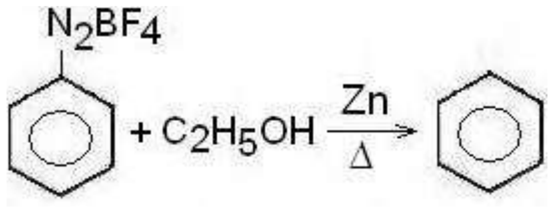
CHEMICAL PROPERTIES

A) Replacement reactions: The reactions in which the diazonium group (-N_2X) as a whole is replaced by monovalent atom or group

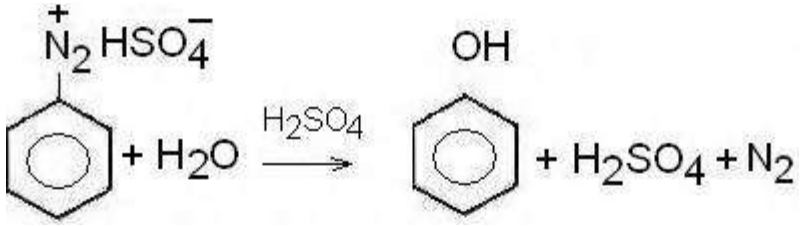
1. Replacement by hydrogen







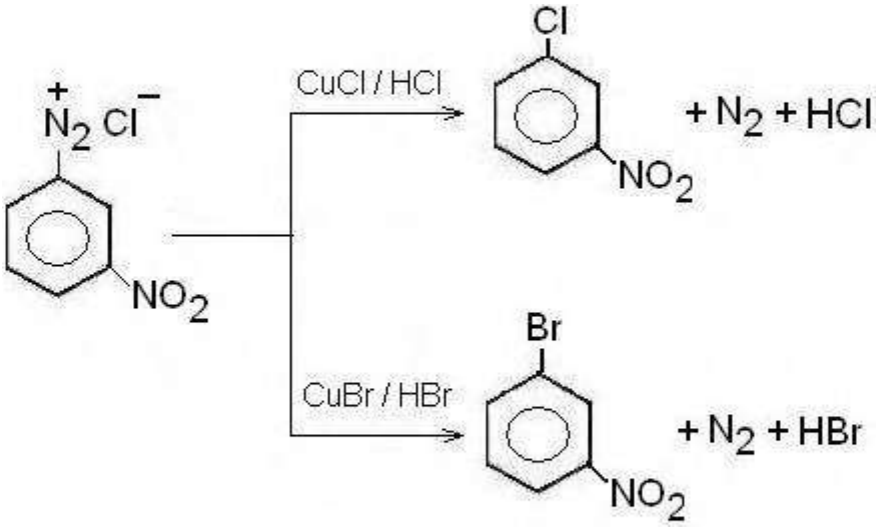
2. Replacement by hydroxyl group



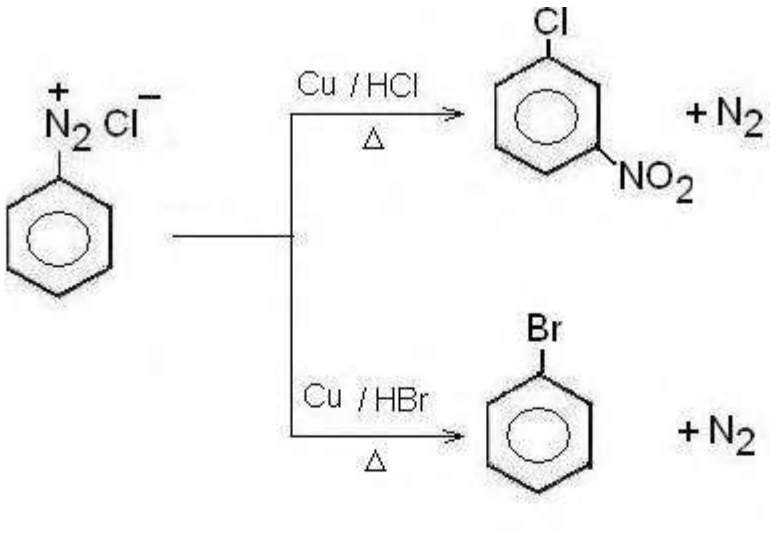
Highly acidic conditions avoid chances of coupling reaction between phenol and diazonium salt

3. Replacement by halogen

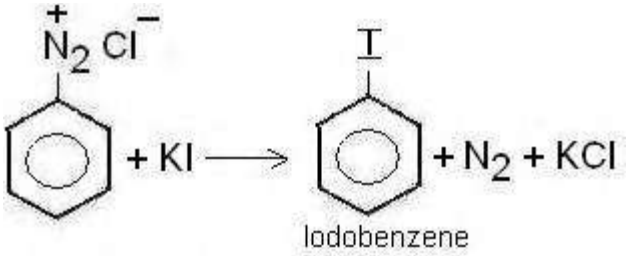
(i) Sandmeyer reaction



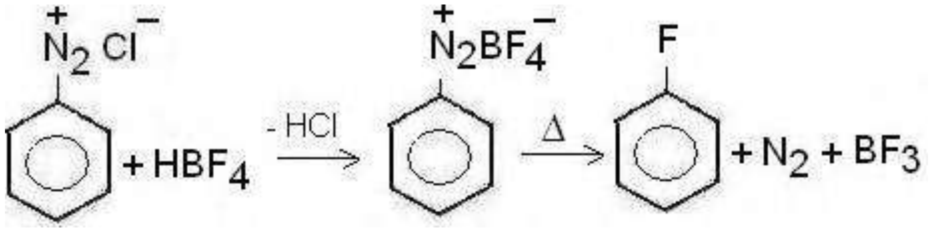
(ii) Gattermann reaction



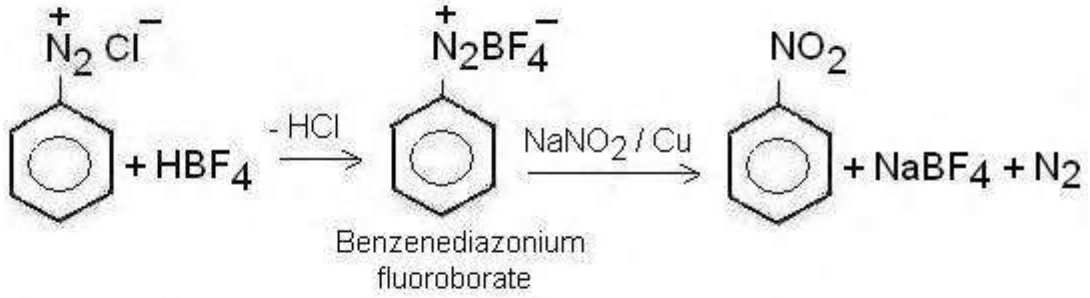
(iii) Replacement by iodine



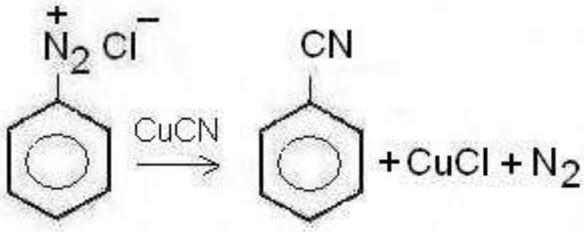
(iv) Replacement by fluorine (Balz –Schiemann reaction)



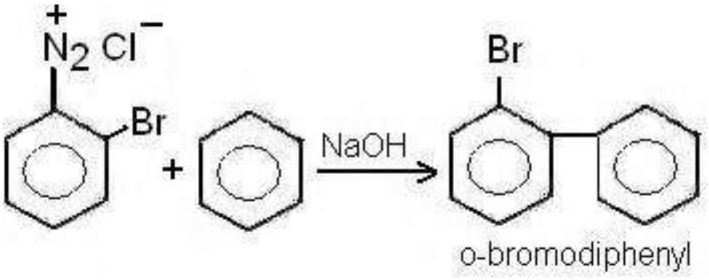
4. Replacement by (-NO$_2$) group



5. Replacement by cyano (-CN) group

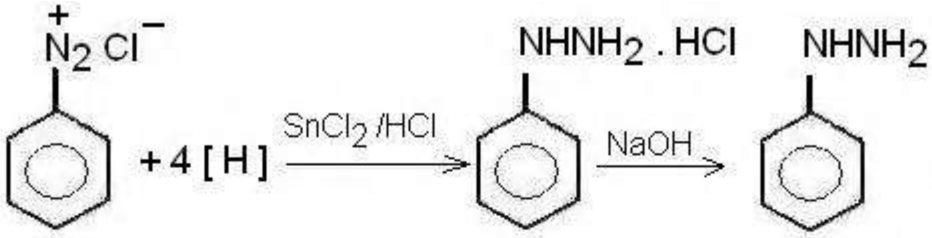


6. Replacement by aryl group (Gomberg Bachmann reaction)

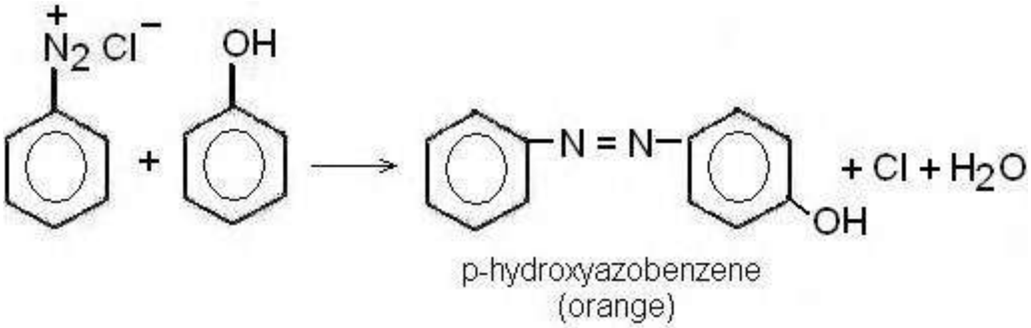


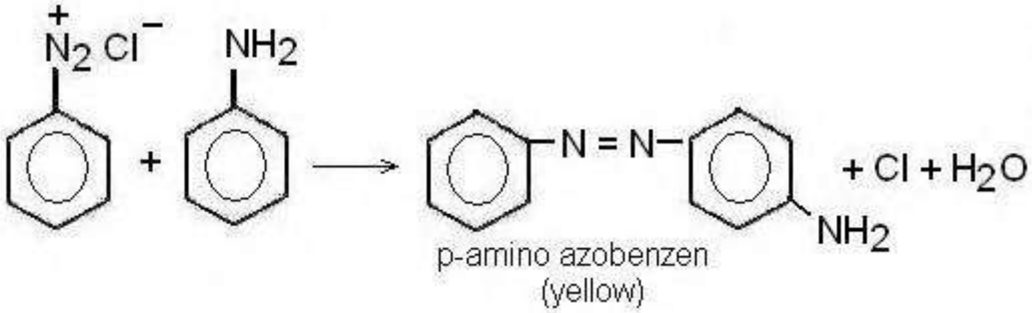
B) Coupling reactions: The reactions in which both the nitrogen atoms are retained and only halogen is replaced

1. Reduction

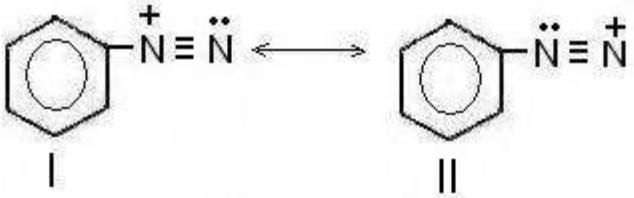


2. Coupling reaction

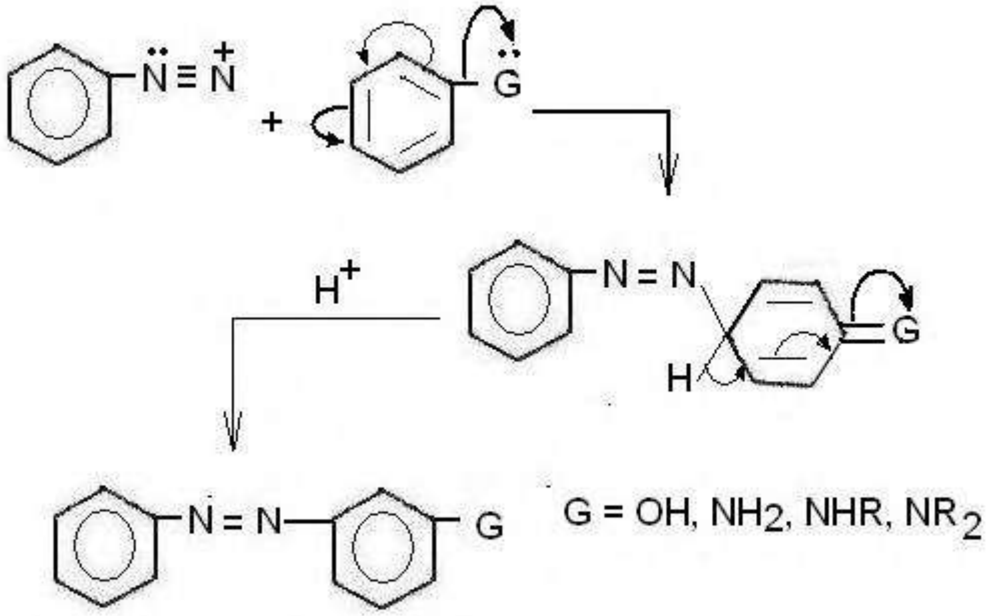




Mechanism



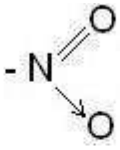
Diazonium ion



$G = OH, NH_2, NHR, NR_2$

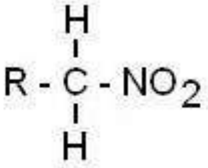
NITRO COMPOUNDS

- When nitro group is attached to an alkyl group the compounds are known as nitro-alkanes and nitro group attached to aryl group are known as nitroarenes

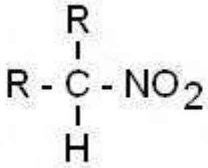


Nitro group

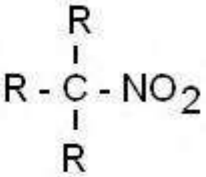
- Nitro compounds are classified as primary, secondary and tertiary depending upon whether the nitro group is attached to a primary, secondary or tertiary carbon respectively



primary nitroalkane

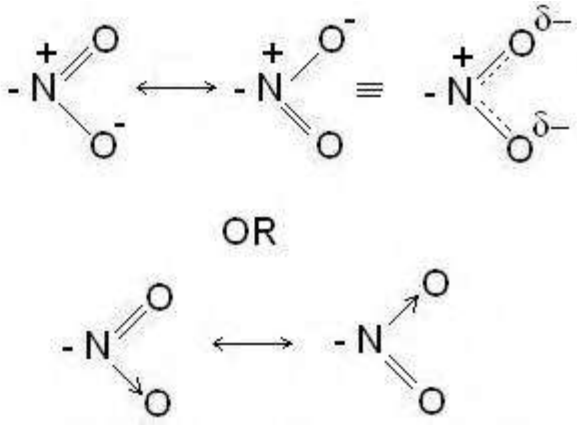


secondary nitroalkane



tertiary nitroalkane

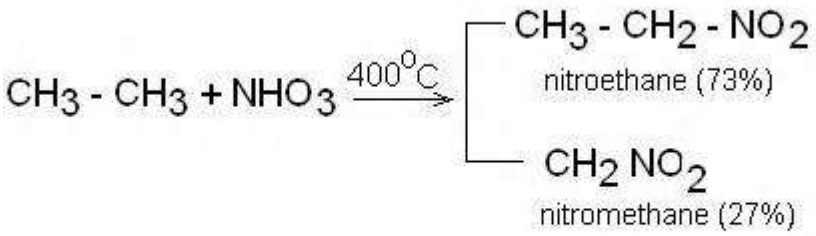
STRUCTURE OF –NO_2 GROUP



PREPARATION OF NITRO COMPOUNDS

1. Nitration

$$CH_4 + NHO_3 \xrightarrow{400^0C} \underset{\text{nitromethane}}{CH_3NO_2} + H_2O$$



$$CH_3 - CH_3 + NHO_3 \xrightarrow{400^0C} \underset{\text{nitroethane (73\%)}}{CH_3 - CH_2 - NO_2} + \underset{\text{nitromethane (27\%)}}{CH_2\,NO_2}$$

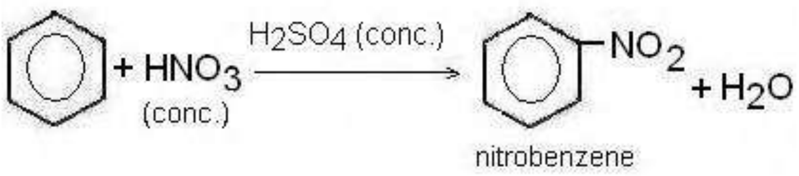
Mechanism

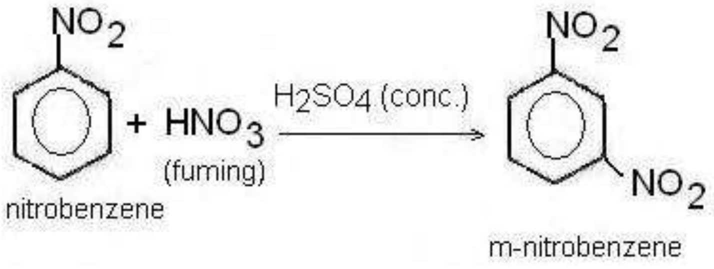
$$HO\!:\!NO_2 \longrightarrow H\dot{O} + \dot{N}O_2$$

$$R - H + \dot{N}O_2 \longrightarrow R\text{-}NO_2 + \dot{H}$$

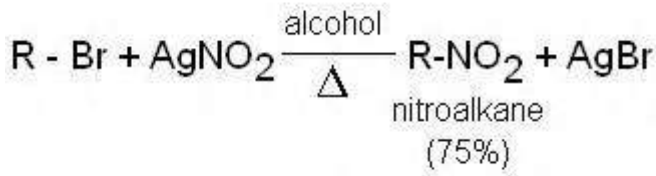
$$\dot{O}H + \dot{H} \longrightarrow H_2O$$

Ease of substitution follows the order tertiary > secondary > primary





2. From alkyl halides

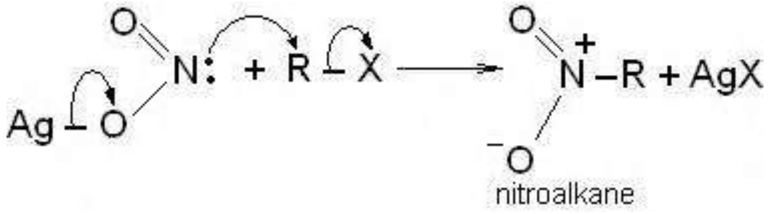


$$R - Br + AgNO_2 \xrightarrow[\Delta]{\text{alcohol}} \underset{\substack{\text{nitroalkane} \\ (75\%)}}{R\text{-}NO_2} + AgBr$$

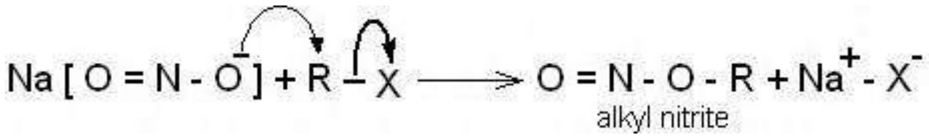
- If we use sodium nitrate ($NaNO_2$) in place of $AgNO_2$ in the above reaction, then alkyl nitrite is obtained as major yield

  Reason

  Nitrite ion is an ambidient nucleophile. Silver nitrite being covalent compound attacks electrophilic carbon of alkyl halide through a lone pair. Since nitrogen is less electronegative than oxygen, its lone pair is easily available for bonding.



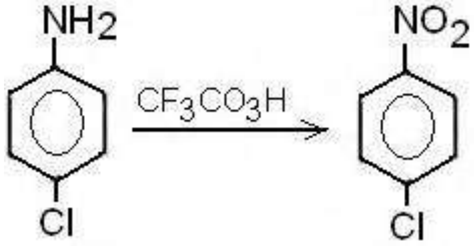
But sodium nitrite is an ionic compound with negative charge on oxygen



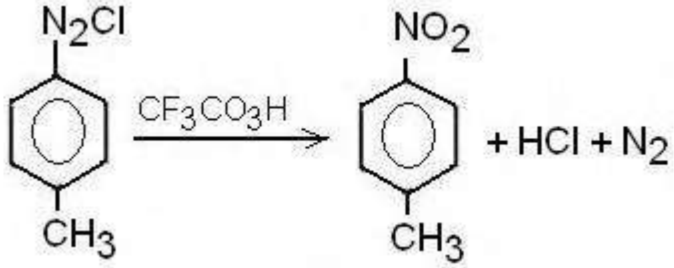
$$Na[O = N - \bar{O}] + R - X \longrightarrow \underset{\text{alkyl nitrite}}{O = N - O - R} + Na^+ - X^-$$

- Order of reactivity of alkyl halides towards **nitroalkane** formation is
  Primary > secondary > tertiary
- Order of reactivity of alkyl halides towards **nitrite** formation is
  Tertiary > secondary > primary

3. Oxidation of aromatic amine



4. From diazonium salts

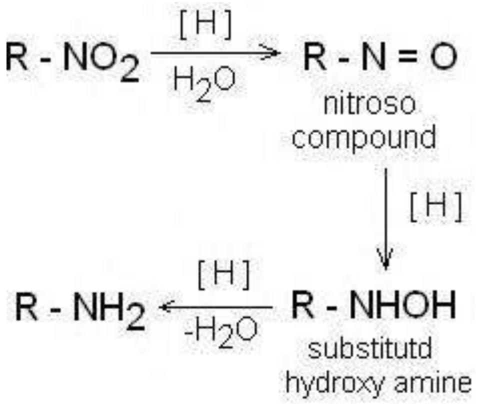


PHYSICAL PROPERTIES

- Nitroalkanes are colourless, pleasant smelling liquids, whereas nitroarenes are pale yellow crystalline solids except nitrobenzene. Which is pale yellow liquid with an odour of bitter almond
- Both nitroalkanes and nitroarenes are insoluble in water but fairly soluble in organic solvents
- Being highly polar in nature, nitroalkanes and nitroarenes possess strong dipole-dipole interactions
  Hence they have much higher boiling points than hydrocarbons of comparable molecular masses

CHEMICAL PROPERTIES

1. Reduction



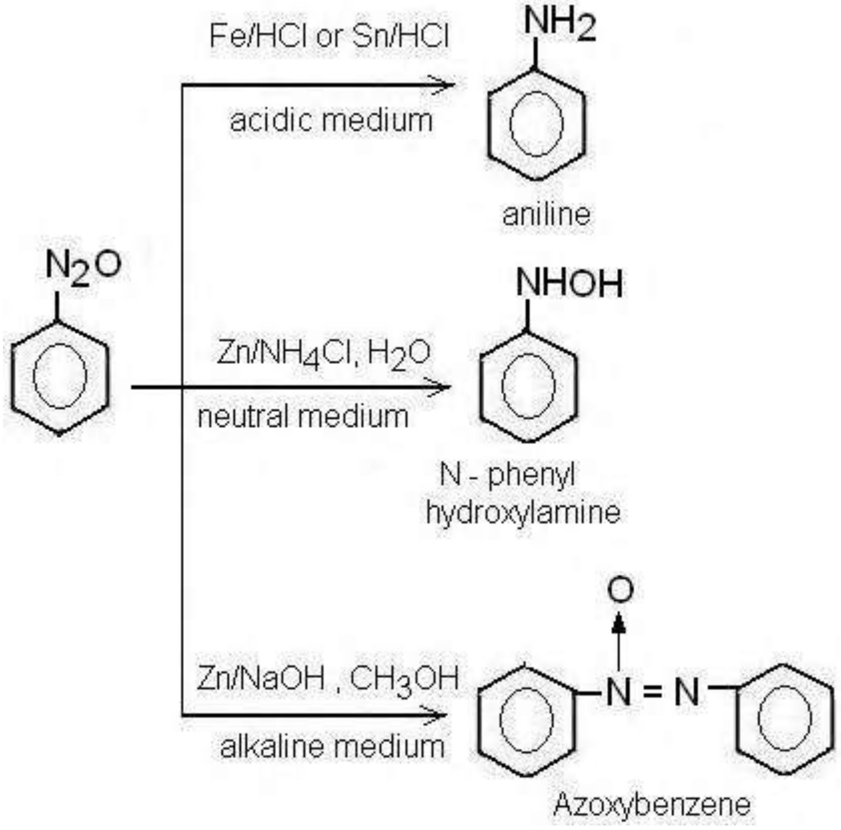
$$CH_3CH_2NO_2 \xrightarrow[\text{acidic medium}]{Sn / HCl} CH_3\text{-}CH_2\text{-}NH_2$$

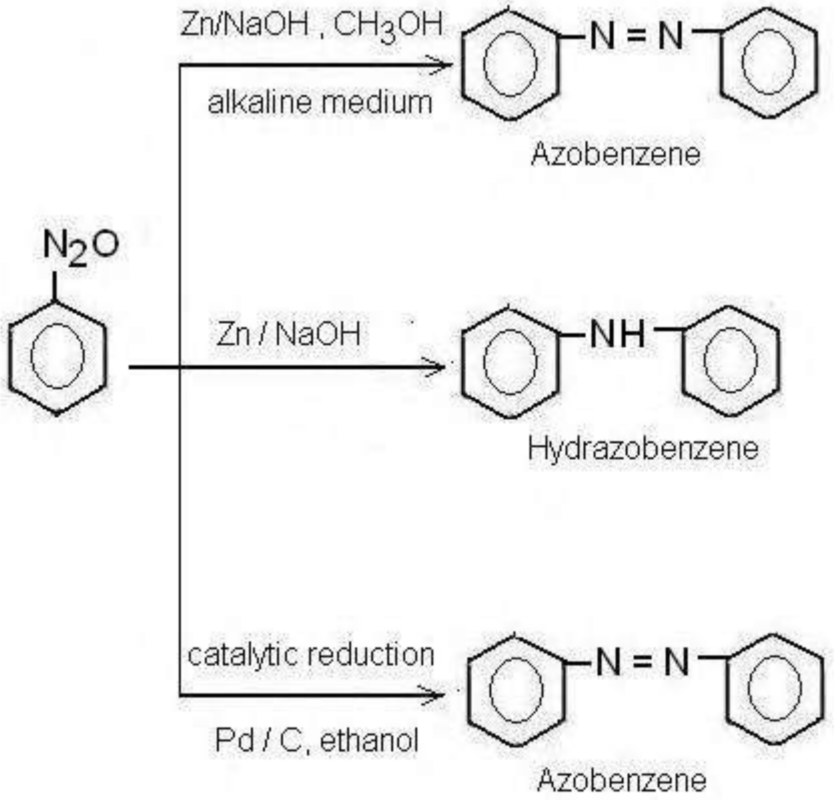
$$CH_3CH_2NO_2 \xrightarrow[\text{neutral medium}]{Zn / NH_4Cl,\ H_2O} CH_3\text{-}CH_2\text{–}\ NHOH + ZnO$$

N-ethyl hydroxylamine

$$CH_3CH_2NO_2 \xrightarrow[\text{catalytic reduction}]{Pd/\ C,\ \text{ethanol}} CH_3\text{-}CH_2\text{-}NH_2$$

$$CH_3CH_2NO_2 \xrightarrow{LiAlH4,\ \text{ether}} CH_3\text{-}CH_2\text{-}NH_2$$



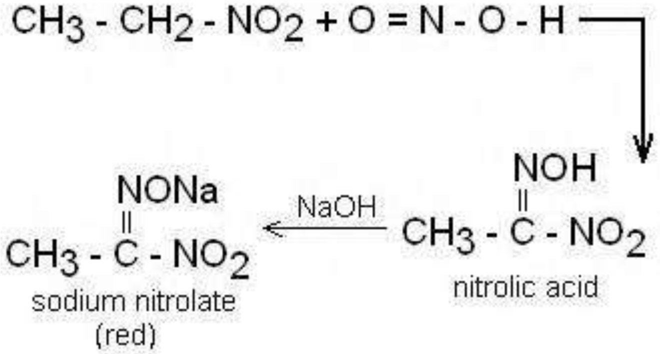


2. Hydrolysis

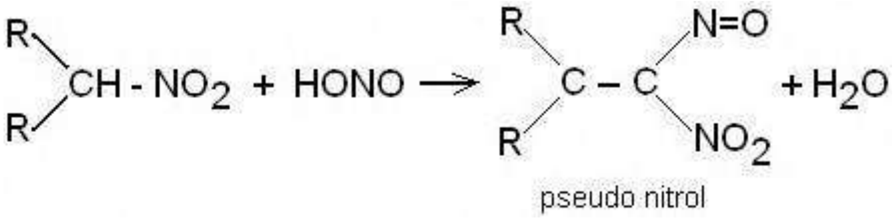
$$R-CH_2-NO_2 + H_2O \xrightarrow[\Delta]{HCl\ or\ H_2SO_4} \underset{\text{carboxylic acid}}{RCOOH} + \underset{\text{hydroxylamine}}{NH_2OH}$$

$$2R_2CHNO_2 \xrightarrow[\Delta]{HCl\ or\ H_2SO_4} \underset{\text{ketone}}{2R_2CO} + \underset{\text{nitrous oxide}}{N_2O} + H_2O$$

3. Reaction with nitrous acid



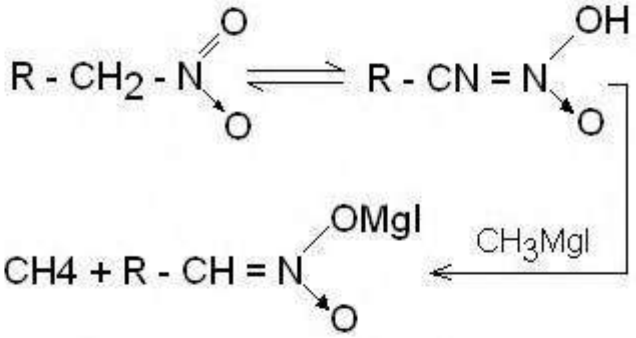
$$CH_3-CH_2-NO_2 + O=N-O-H \longrightarrow \underset{\text{nitrolic acid}}{CH_3-\overset{\overset{\displaystyle NOH}{\|}}{C}-NO_2} \xrightarrow{NaOH} \underset{\text{sodium nitrolate (red)}}{CH_3-\overset{\overset{\displaystyle NONa}{\|}}{C}-NO_2}$$



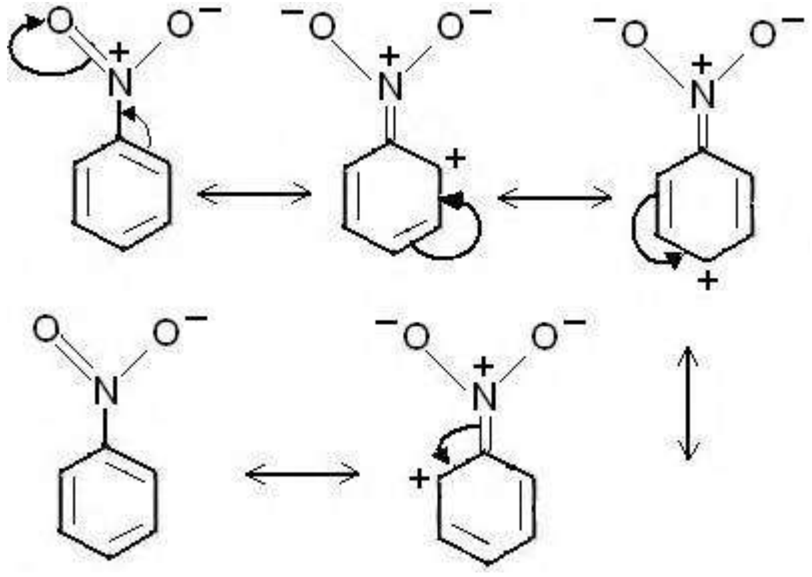
Tertiary nitroalkanes do not react with HNO_2, as they lack α-hydrogen atom

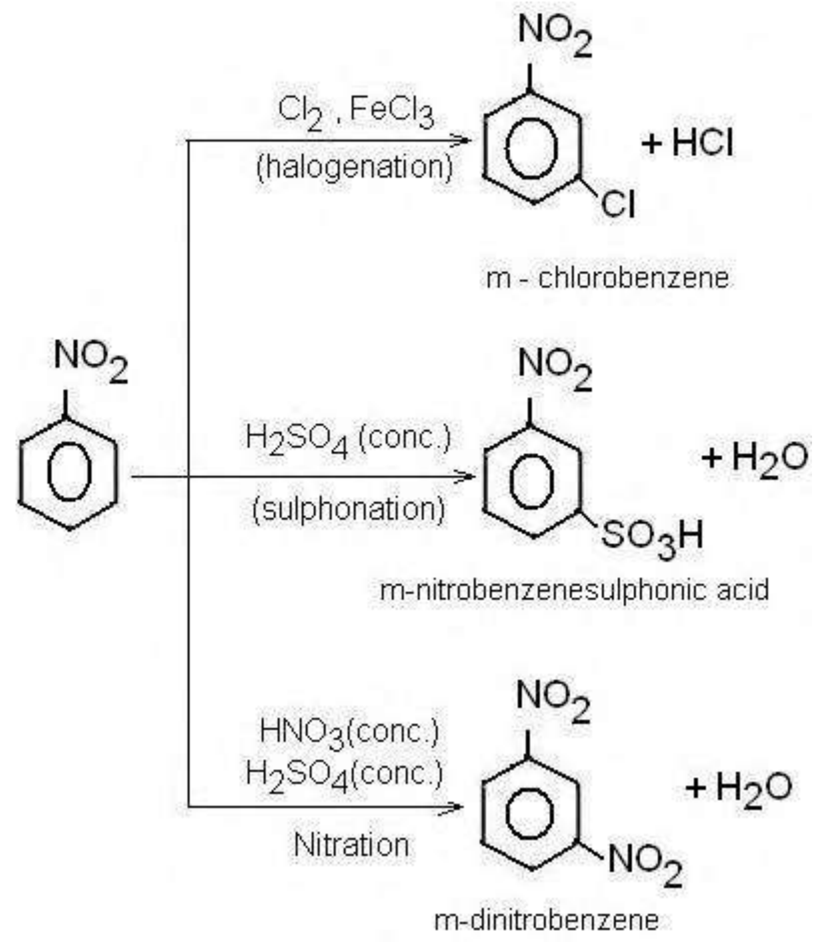
This is also known as Victor Meyer's test for distinction of 1^o, 2^o and 3^o nitroalkanes

4. Reaction with Grignard reagent.

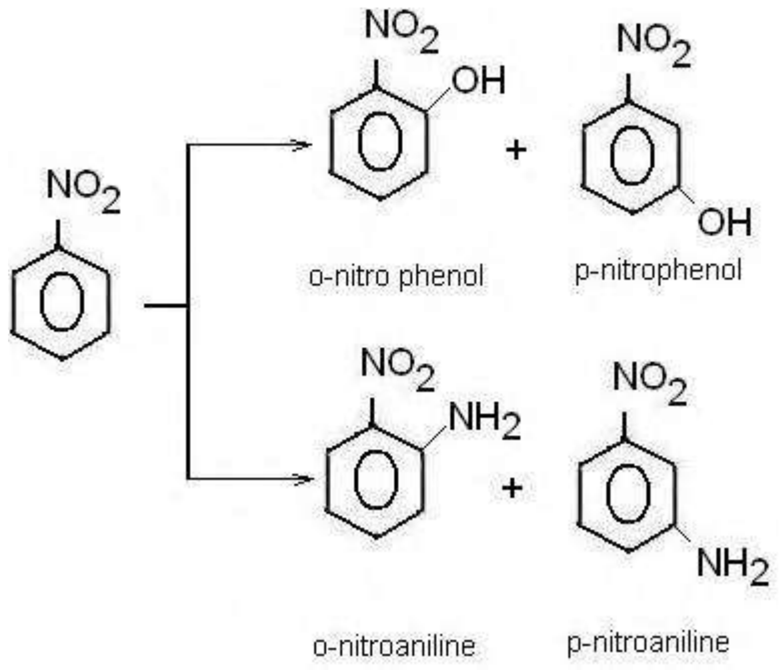


5. Electrophilic substitution reaction





6. Nucleophilic substitution reaction



7. Action of heat

$$RCH_2 - CH_2 - NO_2 \xrightarrow[\Delta]{300^{o}C} \underset{\text{alkene}}{RCH = CH_2} + NO_2$$

On strong heating they decompose with violence

$$2CH_2 - NO_2 \xrightarrow{\Delta} N_2 + 2CO_2 + 3H_2$$

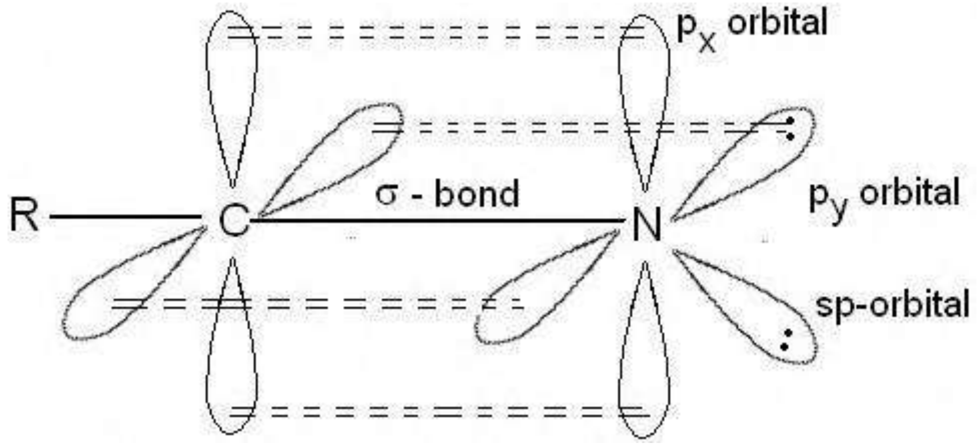
CYANIDES AND ISOCYANIDES

- Cyanides and isocyanides are isomeric to each other and are considered as derivative of two tautomeric forms of hydrogen cyanides

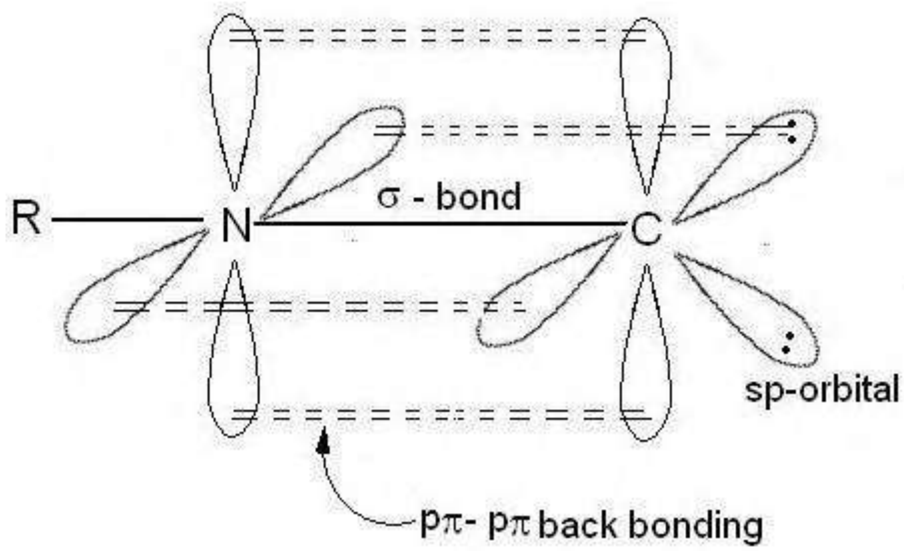
$$\underset{\text{cyanide form}}{H - C \equiv N} \rightleftharpoons \underset{\text{isocyanide form}}{H - N \overset{\rightarrow}{\equiv} C}$$

- -CN can attach either through carbon or nitrogen atom. Such a group which has more than one attacking sites is known as ambidient group

STRUCTURE OF -CN or –NC group



ORBITAL STRUCTURE OF ALKYL CYANIDES



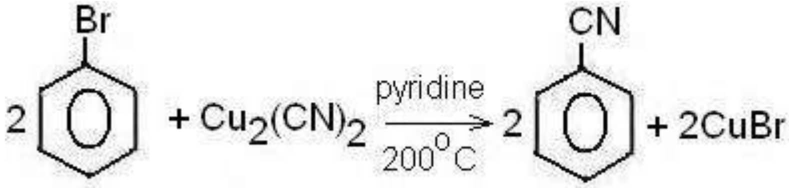
GENERAL METHOD OF PREPARATION OF CYANIDES

1. From alkyl halide

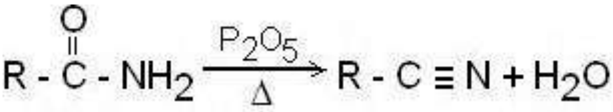
   R – X + NaCN (alc.) → R – CN + NaX

   Aryl cyanides cannot be prepared by this method, since Ar-X bond is not easy to be cleaved by CN^-

   For preparing aryl cyanides, aryl halides are heated with anhydrous cuprous cyanide at 200°C in the presence of pyridine.

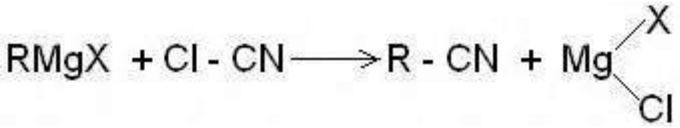


2. From acid amides



$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\Delta]{P_2O_5} R-C\equiv N + H_2O$$

3. From Grignard reagent

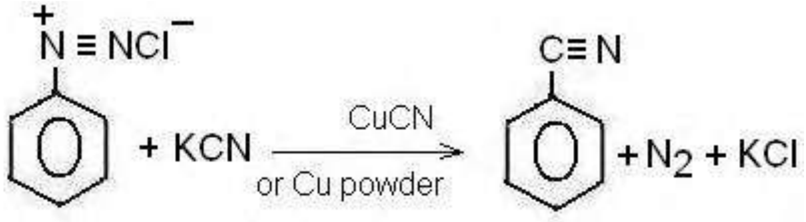


$$RMgX + Cl-CN \longrightarrow R-CN + Mg\begin{matrix}X\\Cl\end{matrix}$$

4. From carboxylic acid

$$RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow[250^{o}C]{Al_2O_3} RCONH_2 \xrightarrow[-H_2O]{Al_2O_3\ 500^{o}c} R-CN$$

5. From arene diazonium salts



6. From sodium salt of carboxylic acid

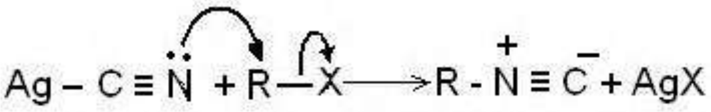
$$RCOONa + Br-CN \xrightarrow{\Delta} R-CN + CO_2 + NaBr$$

GENERAL METHOD OF PREPARATION OF ISOCYANIDES

1. From alkyl halides

$$R-X + AgCN\ (alco.) \longrightarrow R-N \equiv C + AgX$$

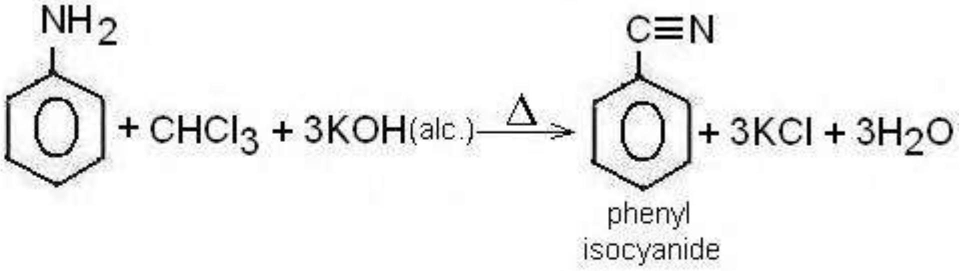
- AgCN is covalent in nature. Only nitrogen atom has lone pair of electrons available for nucleophilic attack, thus attack takes place mainly through nitrogen atom leading to formation of isocyanide along with small amount of cyanide



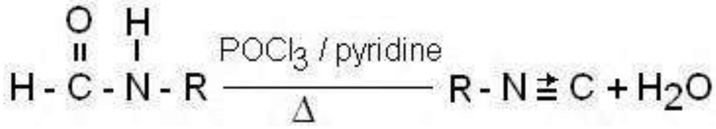
$$Ag-C\equiv \ddot{N} + R-X \longrightarrow R-\overset{+}{N}\equiv \overset{-}{C} + AgX$$

2. Carbylamine reaction

$$R-NH_2 + CHCl_3 + 3KOH\ (alc.) \xrightarrow{\Delta} R-N \equiv C + 3KCl + 3H_2O$$



3. From N-alkyl formamides



$$H-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R \xrightarrow[\Delta]{POCl_3\ /\ \text{pyridine}} R-N\equiv C + H_2O$$

PHYSICAL PROPERTIES OF CYANIDES AND ISOCYANIDES

1. Physical state and smell:
   Lower members of alkyl cyanides and isocyanides are colourless liquids whereas higher members are crystalline solids
   Alkyl cyanides are pleasant smelling, while alkyl isocyanides have extremely unpleasant smell
2. Solubility
   Lower member of alkyl cyanide are sparingly soluble in water due to intermolecular hydrogen bonding, but the solubility decreases with increase of molecular weight
   However isocyanides (both alkyl and aryl) and aryl cyanides are insoluble in water. All members of cyanides and isocyanides are fairly soluble in organic solvents
3. Boiling points
   Both –CN and –NC group are polar in nature hence they possess strong intermolecular dipole-dipole interaction
   As a result of which they have higher boiling point than that of alkyl halides or hydrocarbons of comparable molecular mass
   However boiling points of alkyl ioscyanides are lower than that of alkyl cyanides since –NC group is less polar than –CN group

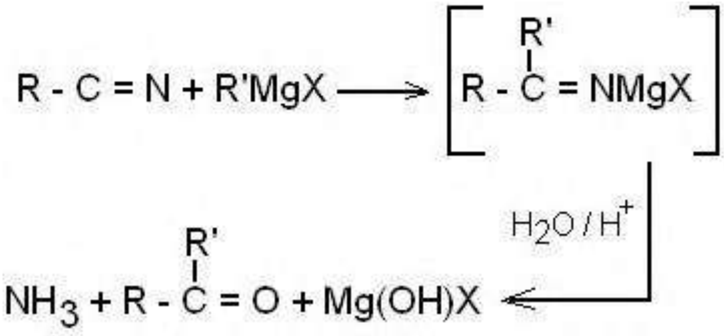
CHEMICAL PROPERTIES OF CYANIDES AND ISOCYANIDES

(A) Chemical reactions shown by cyanides only

(1) Basic nature of cyanides

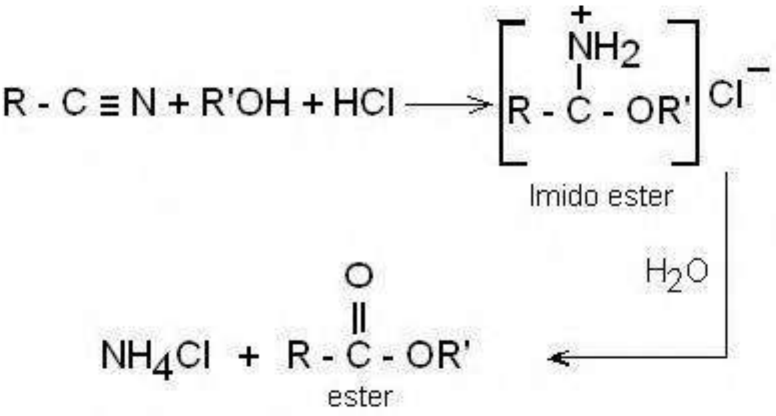
Inspite of the presence of unshared pair of electrons on nitrogen atom, the nitriles or cyanides are not enough basic to form salt with aqueous acids
Because in nitriles, nitrogen atom is sp-hybridised and hence highly electronegative. Electron pair present in sp-orbitals are less easily available for donation and hence nitriles behave as weak base, weaker than amines and ammonia.

(2) Reaction with Grignard reagent



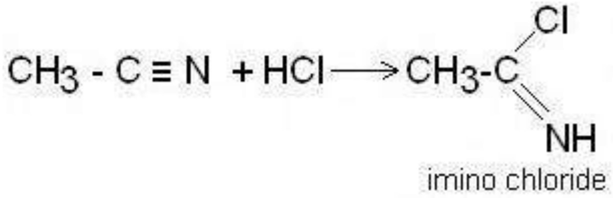
$$R-C=N+R'MgX\longrightarrow\left[R-\overset{R'}{\overset{|}{C}}=NMgX\right]\xrightarrow{H_2O/H^+}NH_3+R-\overset{R'}{\overset{|}{C}}=O+Mg(OH)X$$

(3) Reaction with alcohol

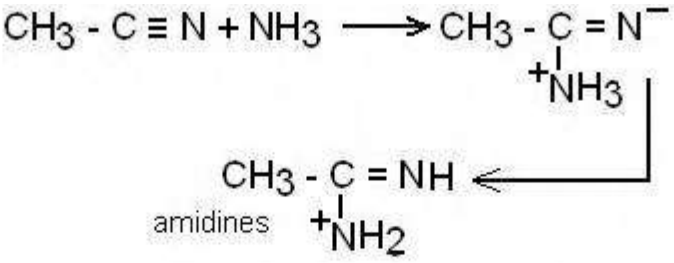


$$R-C\equiv N+R'OH+HCl\longrightarrow\left[R-\overset{\overset{+}{N}H_2}{\overset{|}{C}}-OR'\right]Cl^-\xrightarrow{H_2O}NH_4Cl+R-\overset{O}{\overset{\|}{C}}-OR'$$

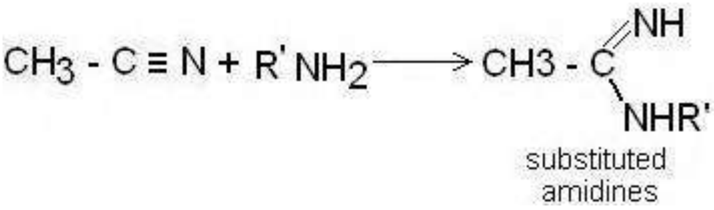
(4) Addition reactions



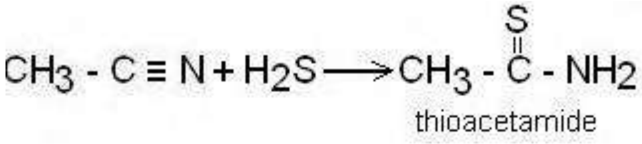
$$CH_3-C\equiv N+HCl\longrightarrow CH_3-C\begin{matrix}\diagup Cl\\ \diagdown\!\!\diagdown NH\end{matrix}$$



$$CH_3-C\equiv N+NH_3\longrightarrow CH_3-\underset{^+NH_3}{\underset{|}{C}}=N^-\longrightarrow CH_3-\underset{^+NH_2}{\underset{|}{C}}=NH$$



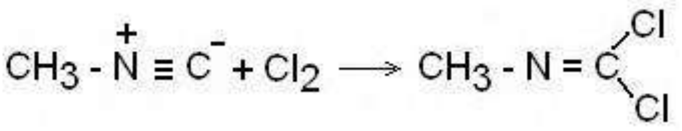
$$CH_3-C\equiv N+R'NH_2\longrightarrow CH3-C\begin{matrix}\diagup\!\!\diagup NH\\ \diagdown NHR'\end{matrix}$$



$$CH_3-C\equiv N+H_2S\longrightarrow CH_3-\overset{S}{\overset{\|}{C}}-NH_2$$

(B) Chemical reaction shown by isocyanides only

(1)



$$CH_3-\overset{+}{N}\equiv \overset{-}{C} + Cl_2 \longrightarrow CH_3-N=CCl_2$$

$$CH_3-\overset{+}{N}\equiv \overset{-}{C} + S \longrightarrow CH_3-N=C=S$$

methyl isothiocyanate

$$CH_3-\overset{+}{N}\equiv \overset{-}{C} + 2HgO \longrightarrow CH_3-N=C=O + Hg_2O$$

methyl isocyanate

(2) Action oh heat

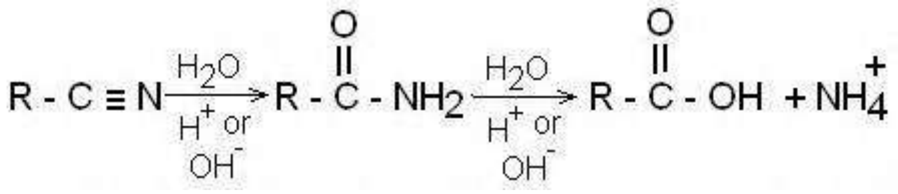
$$R-N \rightleftarrows C \xrightarrow{\Delta} R-C\equiv N$$

isocyanide cyanide

(C) Reaction shown by both cyanides and isocyanides

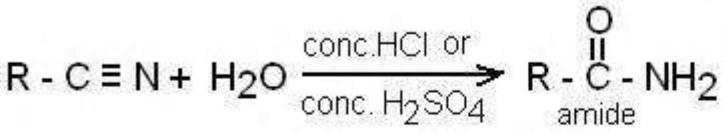
(1) Hydrolysis

(a) Hydrolysis of cyanides: complete hydrolysis



$$R-C\equiv N \xrightarrow[H^+ \text{ or } OH^-]{H_2O} R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[H^+ \text{ or } OH^-]{H_2O} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + \overset{+}{NH_4}$$

Partial hydrolysis



$$R-C\equiv N + H_2O \xrightarrow[\text{conc. } H_2SO_4]{\text{conc.HCl or}} R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

amide

(b) Hydrolysis by isocyanide.

$$R-N \rightleftarrows C + 2H_2O \xrightarrow{H^+} R\text{-}NH_2 + HCOOH$$

1^o amine formic acid

(2) Reduction

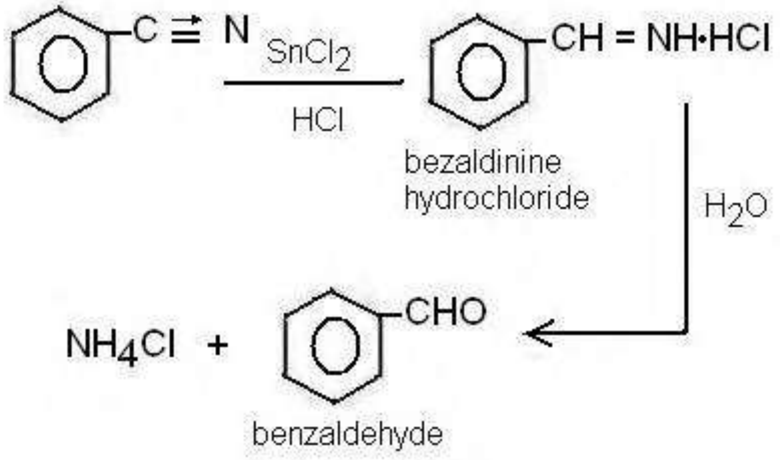
(a) Complete reduction

$$R - C \equiv N + 2H_2 \xrightarrow{\text{Ni or Pt}} \underset{1^{\circ}\text{ amine}}{R - CH_2 - NH_2}$$

$$R - N \equiv C + 2H2 \xrightarrow{\text{Ni or Pt}} \underset{2^{\circ}\text{ amine}}{R\text{-}NH - CH_3}$$

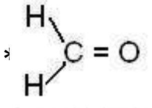
(b) Partial reduction

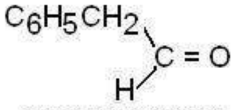
$$R - C = N \xrightarrow{SnCl_2 / HCl} \underset{\text{imine hydrochloride}}{[\,R - CH = NH \cdot HCl\,]} \xrightarrow{H_2O} \underset{\text{aldehyde}}{RCHO} + NH_4Cl$$

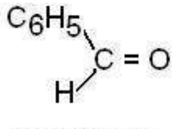


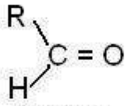
ALDEHYDES AND KETONES

- In aldehydes, the carbonyl group is linked to either two hydrogen atom or one hydrogen atom and one carbon containing group such as alkyl, aryl or aralkyl group Examples

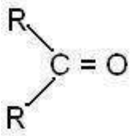

formaldehyde

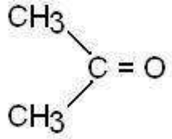

phenyl acetaldehyde

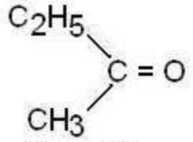

benzaldehyde


aldehyde

- In ketones, the carbonyl group is linked to two carbon containing groups which may be same or different alkyl, aryl group. If two R and R' groups are same, the ketone is called simple or symmetrical ketone and if R and R' are different, then ketone is known as mixed or an unsymmetrical ketone.

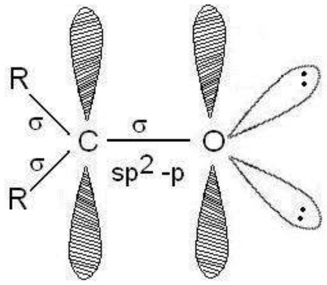

ketone

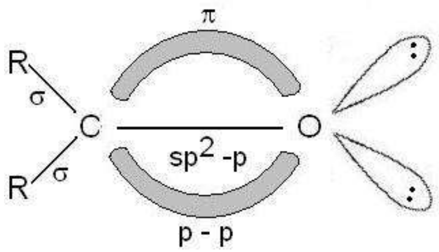

dimethyl ketone (simple ketone)

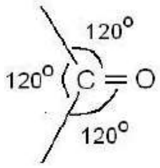

ethyl methyl ketone (mixed ketone)

STRUCTURE

- Carbonyl carbon of both aldehyde and ketones is sp^2 – hybridised, One of the three sp^2 hybridised orbital get involved in σ- bond formation with half –filled p-orbital of oxygen atom whereas rest of the two are consumed in σ-bond formation with hydrogen and carbon depending on the structure of aldehyde or ketone.
- Unhybridised p-orbital of carbonyl carbon form π-bond with another half-filled p-orbital of oxygen atom by sideways overlapping.





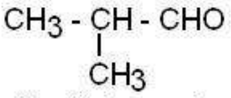


ISOMERISM IN ALDEHYDES AND KETONES

(a) Chain isomerism: Aldehydes (with 4 or more carbon atoms) and ketone (with 5 or more carbon atoms) show chain isomerism. Example

i) C_4H_8O

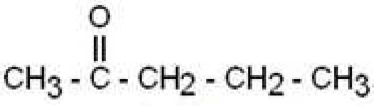
$CH_3-CH_2-CH_2-CHO$ (butanal)



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHO$

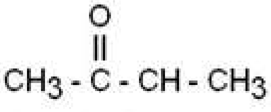
2-methylpropanal

ii) $C_5H_{10}O$



$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$

pentan-2-one

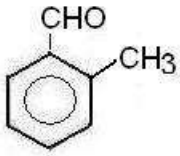


$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH-CH_3$

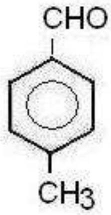
3-methylbutan-2-one

(b) Position isomerism: aliphatic aldehydes do not show position isomerism, because –CHO group is always present at the end of carbon chain.
Aromatic aldehyde show position isomerism. Example

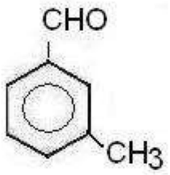
(c) Metamerism: Higher ketones show metamerism due to presence of different alkyl groups attached to the same functional group
$C_5H_{10}O$



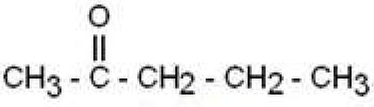
2-methylbenzaldehyde or
o - tolualdehyde



4-methylbenzaldehyde
or p-tolualdehyde

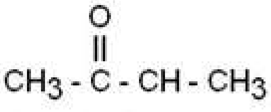


3-methylbenzaldehyde
or m-tolualdehyde



$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$

pentan-2-one

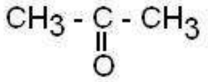


$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH-CH_3$

3-methylbutan-2-one

(d) Functional isomerism : Aldehydes and ketones show functional isomerism in them. In addition, they are also related to alcohols, ethers and other cyclic compounds. Example
C_3H_6O

CH_3CH_2CHO propanal



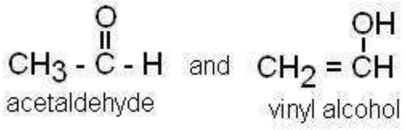
$CH_3-\underset{\underset{O}{\|}}{C}-CH_3$ propanone

$CH_2=CH-CH_2-OH$ Prop-2-en-1-ol

$CH_2=CH-OCH_3$ methoxy ethene

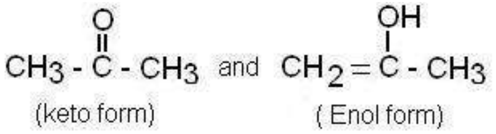
(e) Tautomerism : Aldehydes and ketones also show tautomerism

(I) C_2H_4O



$\underset{\text{acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H}$ and $\underset{\text{vinyl alcohol}}{CH_2=\overset{\overset{OH}{|}}{CH}}$

(II) C_3H_6O



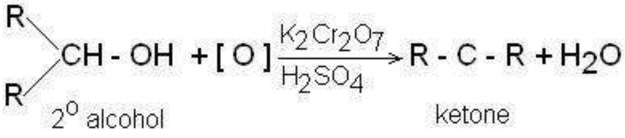
$\underset{\text{(keto form)}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$ and $\underset{\text{(Enol form)}}{CH_2=\overset{\overset{OH}{|}}{C}-CH_3}$

GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

1. From alcohol

(i) Oxidation of alcohol

$$R-CH_2-OH+[O]\xrightarrow[H_2SO_4]{K_2Cr_2O_7}R\text{-}CHO+H_2O$$



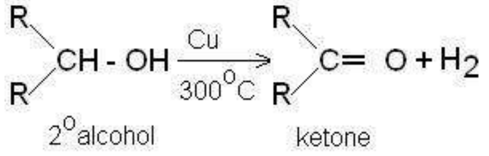
$$\underset{2^o\text{ alcohol}}{\genfrac{}{}{0pt}{}{R}{R}\!\!>CH-OH}+[O]\xrightarrow[H_2SO_4]{K_2Cr_2O_7}\underset{\text{ketone}}{R-C-R}+H_2O$$

- Since the oxidizing agent used in the above reactions is a strong oxidizing agent, it oxidizes aldehydes and ketone further to carboxylic acids
- To prevent further oxidation, a mild oxidizing agent such as pyridinium chlorochromate (pcc), $CrO_3.C_5H_5N\cdot HCl$ or $CrO_3NH^+CrO_3Cl^-$ are used Collin's reagent [$(C_5H_5N)_2\cdot CrO_3$] can also used.

$$\underset{1^o\text{ alcohol}}{R-CH_2OH}\xrightarrow[\text{collin's reagent}]{\text{pcc,}}\underset{\text{aldehyde}}{RCHO}$$

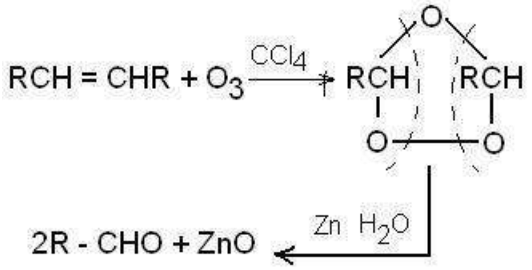
(ii) Catalytic dehydrogenation of alcohols

$$\underset{1^o\text{ alcohol}}{RCH_2OH}\xrightarrow[300^oC]{Cu}\underset{\text{Aldehyde}}{RCHO}+H_2$$

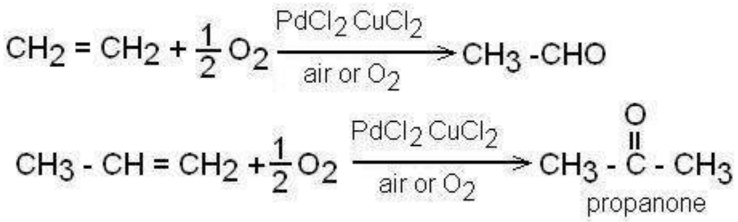


$$R_2CH-OH \xrightarrow[300^oC]{Cu} R_2C=O + H_2$$

2. From alkenes
   (i) Reductive ozonolysis of alkenes.



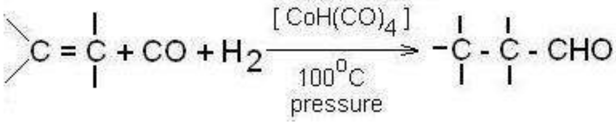
   (ii) Wacker process.



$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow[\text{air or } O_2]{PdCl_2\ CuCl_2} CH_3-CHO$$

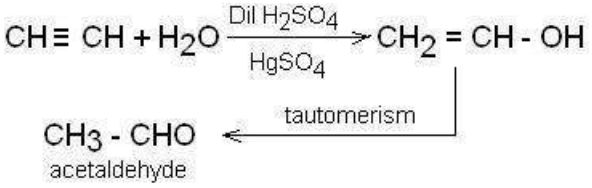
$$CH_3-CH=CH_2 + \frac{1}{2}O_2 \xrightarrow[\text{air or } O_2]{PdCl_2\ CuCl_2} CH_3-\overset{O}{\overset{||}{C}}-CH_3$$

   (iii) OXO process [Carbonylation / Hydroformylation]

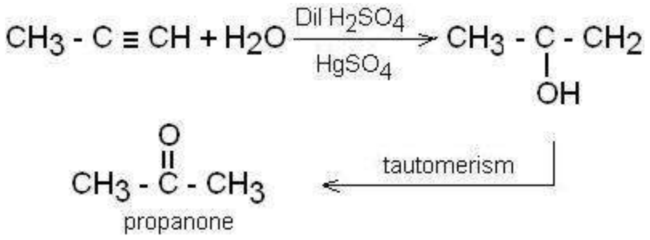


$$>C=C< + CO + H_2 \xrightarrow[\substack{100^oC \\ \text{pressure}}]{[CoH(CO)_4]} -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-CHO$$

3. From alkynes

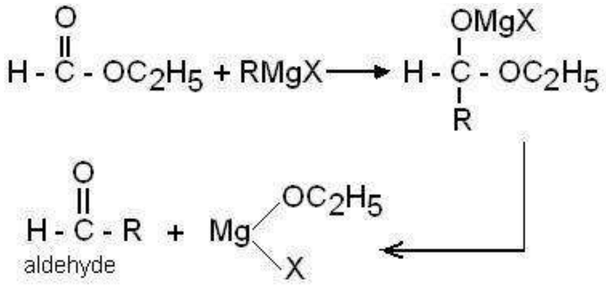


$$CH\equiv CH + H_2O \xrightarrow[HgSO_4]{\text{Dil } H_2SO_4} CH_2=CH-OH \xrightarrow{\text{tautomerism}} CH_3-CHO$$

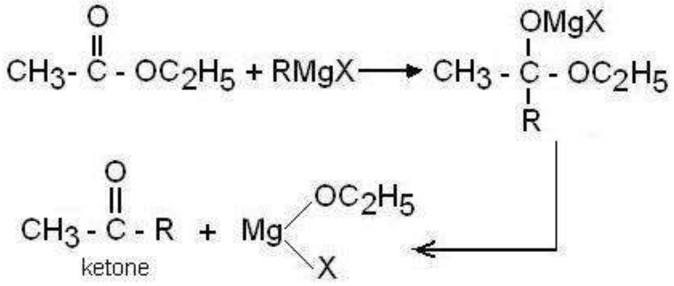


$$CH_3-C\equiv CH + H_2O \xrightarrow[HgSO_4]{\text{Dil } H_2SO_4} CH_3-\underset{OH}{\underset{|}{C}}=CH_2 \xrightarrow{\text{tautomerism}} CH_3-\overset{O}{\overset{||}{C}}-CH_3$$

4. From Grignard reagent
   (1) By addition to ester

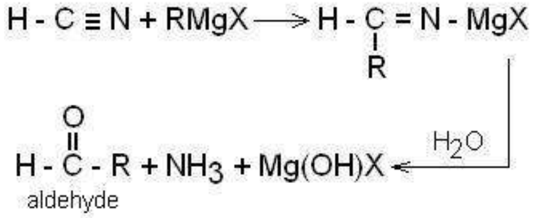


$$H-\overset{O}{\overset{\|}{C}}-OC_2H_5 + RMgX \longrightarrow H-\underset{R}{\overset{OMgX}{C}}-OC_2H_5 \longrightarrow \underset{\text{aldehyde}}{H-\overset{O}{\overset{\|}{C}}-R} + Mg\begin{matrix}OC_2H_5\\X\end{matrix}$$

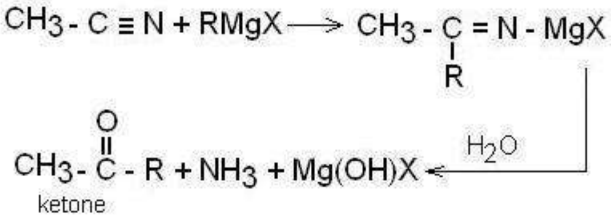


$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + RMgX \longrightarrow CH_3-\underset{R}{\overset{OMgX}{C}}-OC_2H_5 \longrightarrow \underset{\text{ketone}}{CH_3-\overset{O}{\overset{\|}{C}}-R} + Mg\begin{matrix}OC_2H_5\\X\end{matrix}$$

(iii) By addition to nitriles



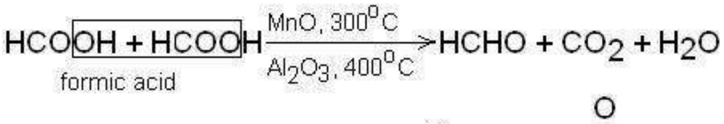
$$H-C\equiv N + RMgX \longrightarrow H-\underset{R}{C}=N-MgX \xrightarrow{H_2O} \underset{\text{aldehyde}}{H-\overset{O}{\overset{\|}{C}}-R} + NH_3 + Mg(OH)X$$



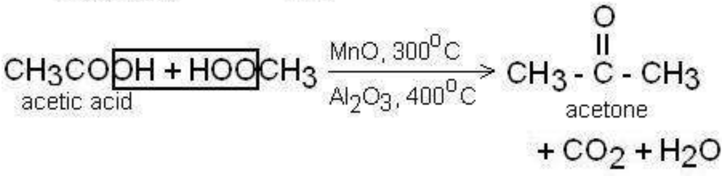
$$CH_3-C\equiv N + RMgX \longrightarrow CH_3-\underset{R}{C}=N-MgX \xrightarrow{H_2O} \underset{\text{ketone}}{CH_3-\overset{O}{\overset{\|}{C}}-R} + NH_3 + Mg(OH)X$$

5. From carboxylic acids

(i) Catalytic decomposition of carboxylic acid.

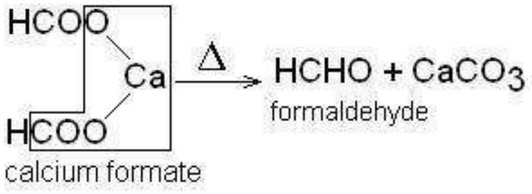


$$\underset{\text{formic acid}}{HCO\boxed{OH + HCOO}H} \xrightarrow[Al_2O_3,\ 400^0C]{MnO,\ 300^0C} HCHO + CO_2 + H_2O$$

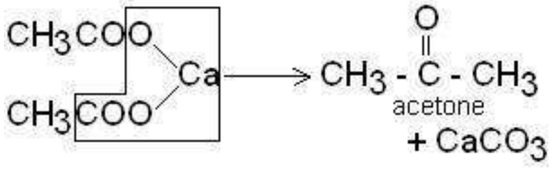


$$\underset{\text{acetic acid}}{CH_3CO\boxed{OH + HOO}CH_3} \xrightarrow[Al_2O_3,\ 400^0C]{MnO,\ 300^0C} \underset{\text{acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + CO_2 + H_2O$$

(ii) From calcium salt of carboxylic acids



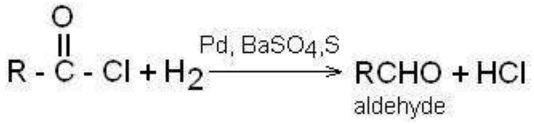
$$(HCOO)_2Ca \xrightarrow{\Delta} HCHO + CaCO_3$$



$$(CH_3COO)_2Ca \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CaCO_3$$

6. From derivatives of carboxylic acids

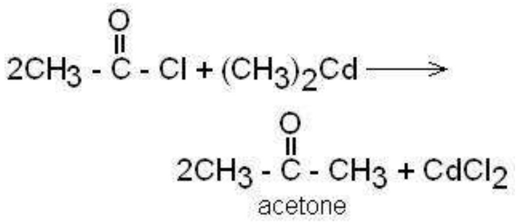
(i) Reduction of acid chlorides (Rosenmund's reaction)



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + H_2 \xrightarrow{Pd,\ BaSO_4, S} RCHO + HCl$$

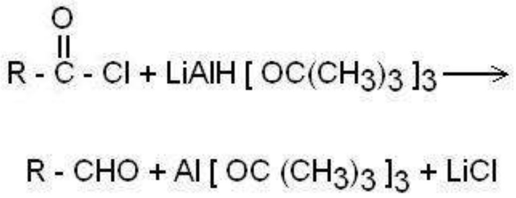
- Above reaction is known as Rosenmund's reduction and is applicable for preparation of aldehydes
- $BaSO_4$, sulphur act as poison for Pd catalyst and prevents reduction of RCHO into RCH_2OH

(ii) Reduction of acid chloride with dialkyl cadmium.



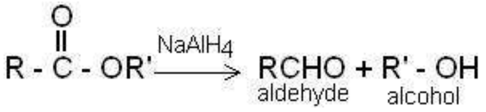
$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + (CH_3)_2Cd \longrightarrow 2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CdCl_2$$

Reduction of acid chloride into ester can also be carried out by lithium tri--butoxy aluminium hydride, $LiAlH[OC(CH_3)_3]$



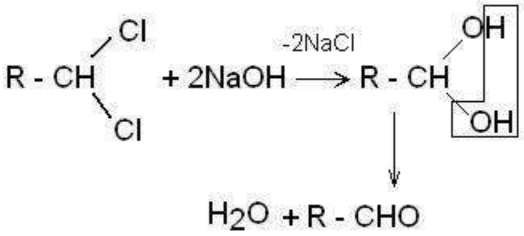
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + LiAlH[OC(CH_3)_3]_3 \longrightarrow R-CHO + Al[OC(CH_3)_3]_3 + LiCl$$

(iii) Reduction of esters

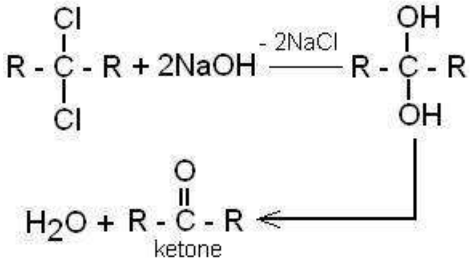


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' \xrightarrow{NaAlH_4} RCHO + R'-OH$$

7. From gem-dihalides by hydrolysis

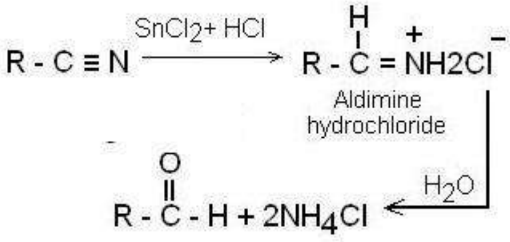


$$R-CHCl_2 + 2NaOH \xrightarrow{-2NaCl} R-CH(OH)_2 \longrightarrow H_2O + R-CHO$$



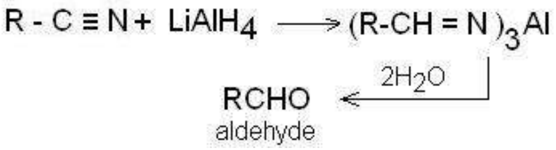
$$R-CCl_2-R + 2NaOH \xrightarrow{-2NaCl} R-C(OH)_2-R \longrightarrow H_2O + \underset{\text{ketone}}{R-\overset{O}{\overset{\|}{C}}-R}$$

8. From nitriles by reduction
   (i) Stephen's reduction.

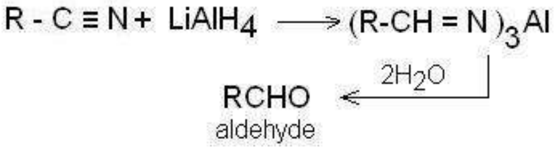


$$R-C\equiv N \xrightarrow{SnCl_2+HCl} \underset{\substack{\text{Aldimine}\\ \text{hydrochloride}}}{R-\overset{H}{\overset{|}{C}}=\overset{+}{N}H2\overset{-}{Cl}} \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-H + 2NH_4Cl$$

   (ii) Reduction with $LiAlH_4$

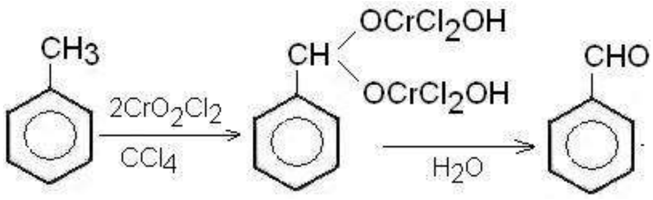


$$R-C\equiv N + LiAlH_4 \longrightarrow (R-CH=N)_3Al \xrightarrow{2H_2O} \underset{\text{aldehyde}}{RCHO}$$



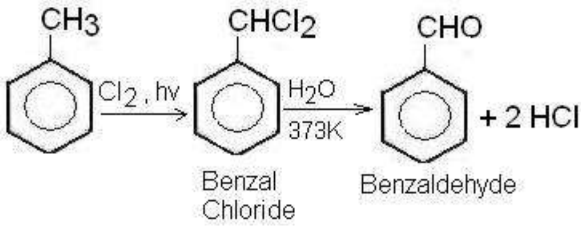
$$R-C\equiv N + LiAlH_4 \longrightarrow (R-CH=N)_3Al \xrightarrow{2H_2O} \underset{\text{aldehyde}}{RCHO}$$

9. Preparation of aromatic carbonyl compounds.
   (i)

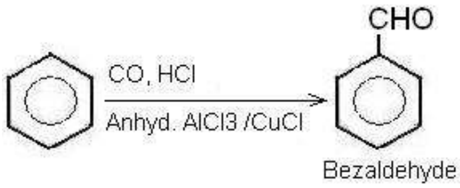


This is known as Etard reaction

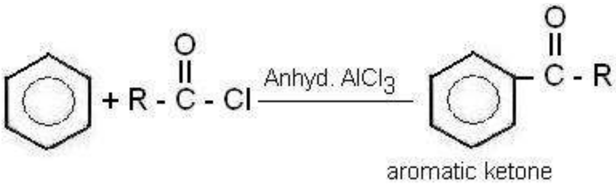
(ii) By side chain chlorination followed by hydrolysis

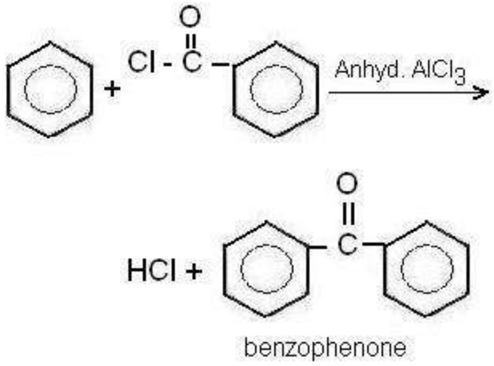


(iii) Gatterman – Koch reaction

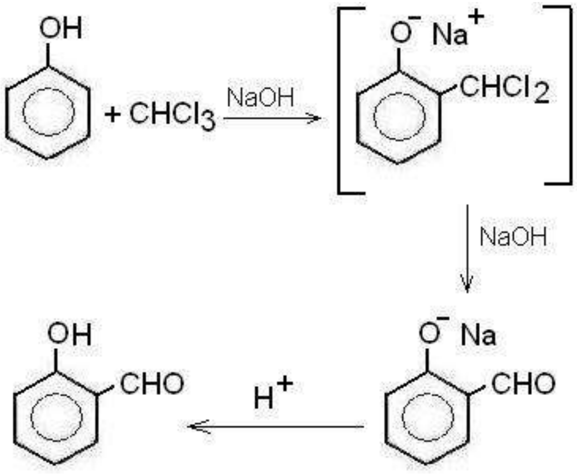


(iv) Friedel Craft Acylation





(v) Reimer – Tiemann reaction



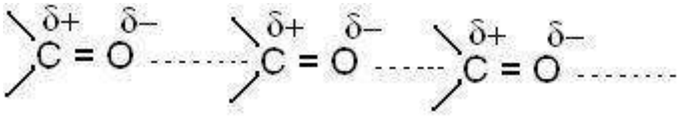
PHYSICAL PROPERTIES OF ALDEHYDES AND KETONE

1. Physical state

- Lower members of aldehydes and ketones (upto C_{10}) are colourless volatile liquids except formaldehyde which is gas at ordinary temperature
- Higher members of aldehyde and ketones are solids with fruity odour
- Lower aldehydes have unplesent odour but ketones posses pleasant smell

2. Boiling point

- Boiling point of aldehyde and ketones is slightly lower than corresponding alcohol due to lack of hydrogen bonding. However their boiling point is slightly higher than that of corresponding non-polar hydrocarbon or weakly polar ether. This may attributed to reason that aldehydes and ketones are polar compounds and thus possess intermolecular dipole-dipole interaction



- Among isomeric aldehydes and ketones, boiling point of ketones is slightly higher than that of aldehydes due to the presence of two electron donating alkyl groups making them more polar.

3. Solubility

- Lower members of aldehydes and ketones (upto C_4) are soluble in water due to H-bonding between polar carbonyl group and water.
- However, solubility decreases with increase in molecular weight
- Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to large benzene ring. However all carbonyl compounds are fairly soluble in organic solvents.

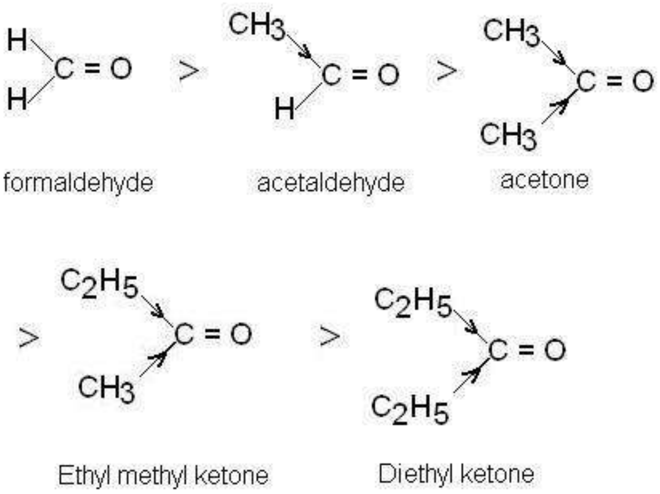
RELATIVE REACTIVITY OF ALDEHYDES AND KETONES

Aldehydes are more reactive than ketones on account of the following facts:

(a) Aliphatic aldehydes and ketones

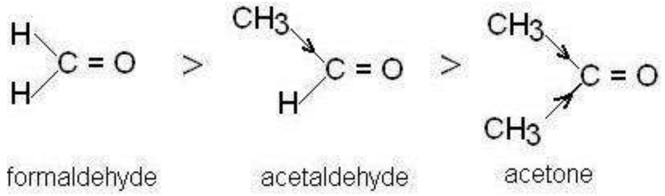
(i) Inductive effect:

The reactivity of the carbonyl group towards the addition reaction depends upon the magnitude of the positive charge on the carbonyl carbon atom. Hence, any substituent that increases the positive charge on the carbonyl carbon must increase its reactivity towards addition reactions. The introduction of negative group (-I effect) increases the reactivity, while introduction of alkyl group (+I effect) decreases the reactivity, therefore, greater the number of alkyl groups attached to the carbonyl group and hence, lower is its reactivity towards nucleophilic addition reactions. Thus, the following decreasing order of reactivity is observed



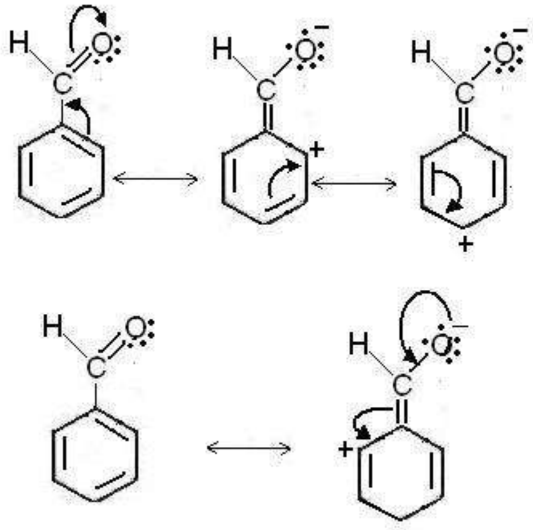
(ii) Steric effect

- In formaldehyde there is no alkyl group while in all other aldehyde there is one alkyl group so here the nucleophile attack is relatively more easy but in ketones there are two alkyl groups attached to carbonyl group and these causes hinderance, to the attacking group. This factor is called steric hinderance (crowding). In other words the hindrance increases, the reactivity decreases accordingly. Thus order of reactivity is

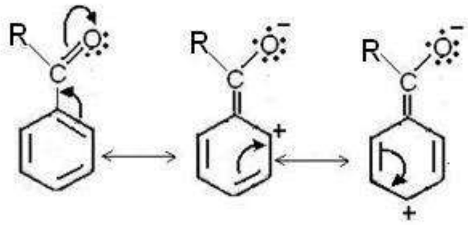


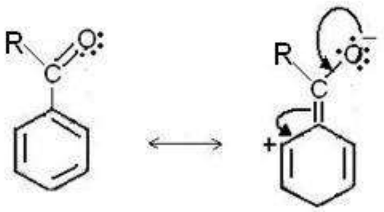
(b) Aromatic aldehydes and ketones

- In general, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones. It is due electron releasing resonance effect of bezene ring



- Due to electron withdrawing resonance effect (-R effect) of benzene ring, the magnitude of positive charge on carbonyl group decreases and consequently it becomes less susceptible to nucleophilic attack.



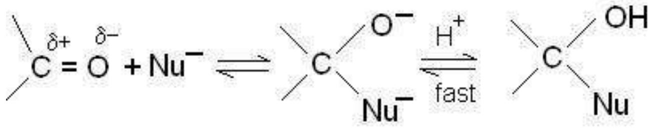


The order of reactivity of aromatic aldehydes and ketones is

$C_6H_5CH_2CHO$ (phenyl acetaldehyde) > C_6H_5CHO (benzaldehyde) > $C_6H_5COCH_3$ (acetophenone) > $C_6H_5COC_6H_5$ (benzophenone)

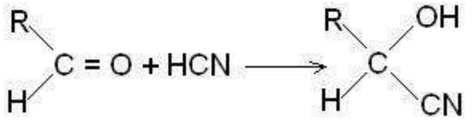
CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

Nucleophilic addition reaction

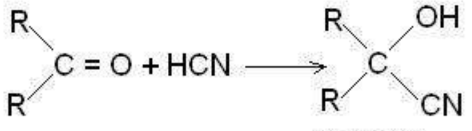


In this reaction carbon atom of carbonyl group changes from sp^2 to sp^3 hybridised

(i) Addition of hydrogen cyanide (HCN)



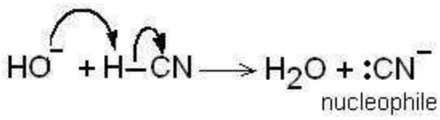
cyanohydrien



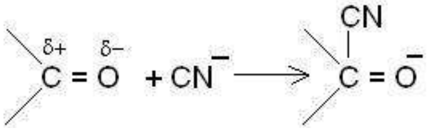
cyanohyrin

Mechanism

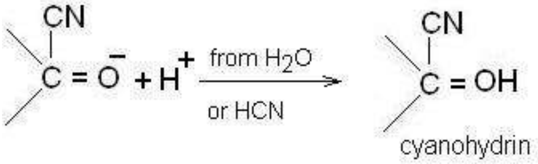
Step I : The hydrogen cyanide interacts with the base to form nucleophile



Step II : The nucleophile attacks the carbonyl carbon to form an anion

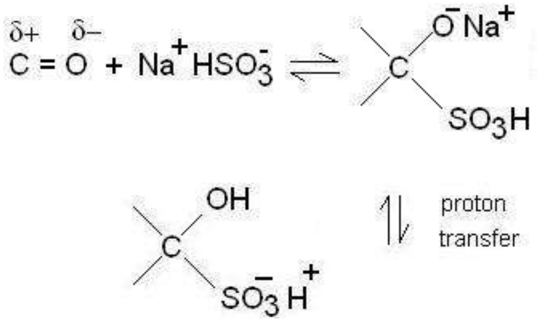


StepIII: The proton from the solvent (usually water) combines with the anion to form cyanohydrin.

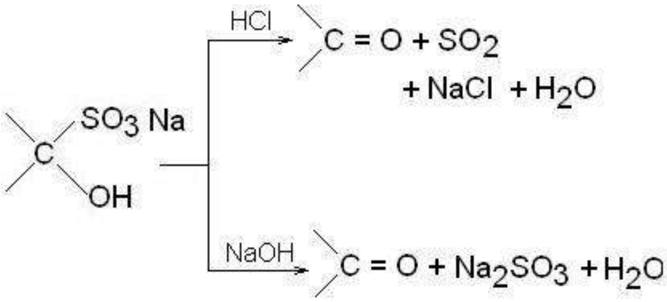


Cyanohydrins are formed by all aldehydes but in ketones, only acetone, butanone, 3-pethenone and pinacolone form cyanohydrins.

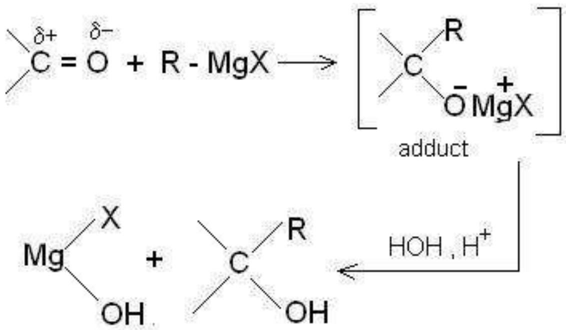
(ii) Addition of sodium bisulphate ($NaHSO_4$)



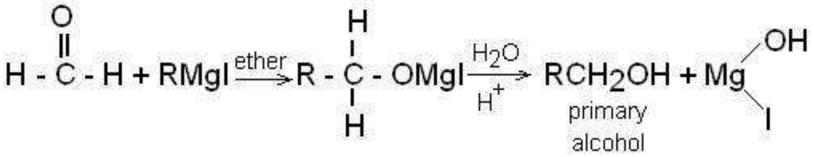
- All ketones do not undergo this reaction only methyl ketone form addition product with sodium bisulphate
- On reacting the crystalline solid bisulphate derivative with dilute HCl or alkali, these adducts decompose to regenerate the original aldehyde or ketones. Hence, this reaction is used in the separation and purification of aldehydes and ketones from non-carbonyl compounds.



(iii) Addition of Grignard reagent

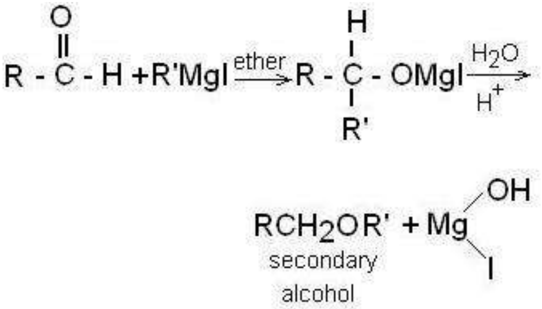


Formaldehyde form a primary alcohol



$$H-\overset{O}{\overset{\|}{C}}-H + RMgI \xrightarrow{ether} R-\underset{H}{\overset{H}{C}}-OMgI \xrightarrow[H^+]{H_2O} \underset{\text{primary alcohol}}{RCH_2OH} + Mg\begin{matrix}OH\\ I\end{matrix}$$

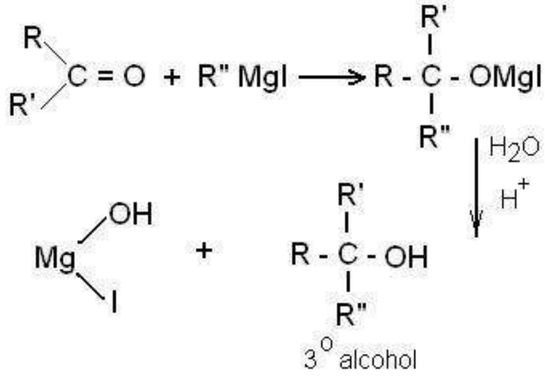
- Higher aldehydes give secondary alcohol



$$R-\overset{O}{\overset{\|}{C}}-H + R'MgI \xrightarrow{ether} R-\underset{R'}{\overset{H}{C}}-OMgI \xrightarrow[H^+]{H_2O}$$

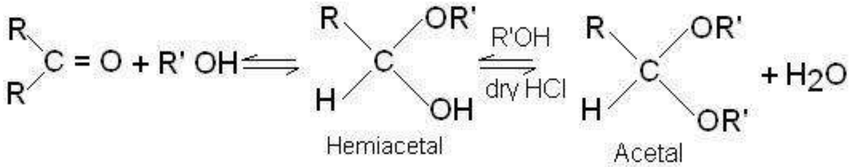
$$\underset{\text{secondary alcohol}}{RCH_2OR'} + Mg\begin{matrix}OH\\ I\end{matrix}$$

- Ketone give tertiary alcohols



$$\begin{matrix}R\\ R'\end{matrix}C=O + R''MgI \longrightarrow R-\underset{R''}{\overset{R'}{C}}-OMgI \xrightarrow[H^+]{H_2O} Mg\begin{matrix}OH\\ I\end{matrix} + \underset{3^{0}\text{ alcohol}}{R-\underset{R''}{\overset{R'}{C}}-OH}$$

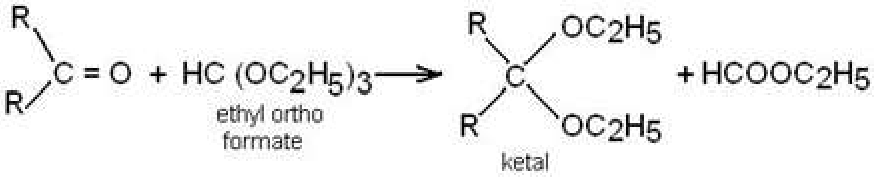
(iv) Addition of alcohols



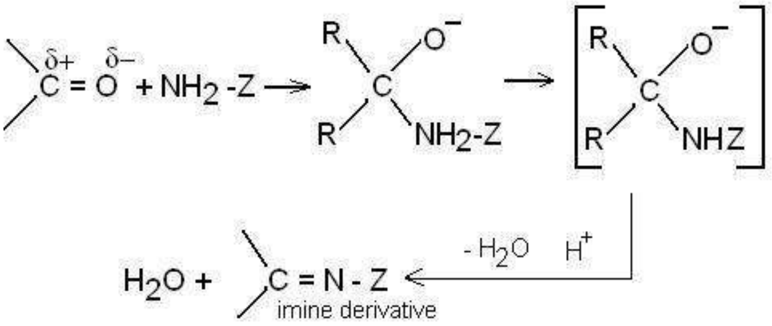
$$\begin{matrix}R\\ R\end{matrix}C=O + R'OH \rightleftharpoons \underset{\text{Hemiacetal}}{\begin{matrix}R & & OR'\\ & C & \\ H & & OH\end{matrix}} \underset{\text{dry HCl}}{\overset{R'OH}{\rightleftharpoons}} \underset{\text{Acetal}}{\begin{matrix}R & & OR'\\ & C & \\ H & & OR'\end{matrix}} + H_2O$$

Dry HCl protonates the oxygen atom of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon and hence facilitating the nucleophilic attack by the alcohol molecule. Dry HCl gas also absorbs the water produced in these reactions and thereby shifting equilibrium in forward direction.

Ketals can be prepared by treating the ketone with ethyl ortho formate



(v) Addition of ammonia derivative

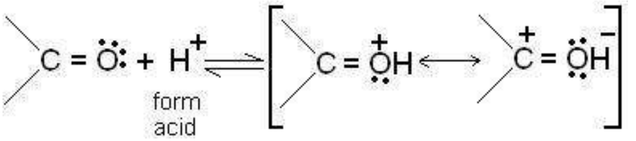


Z = OH, NH_2 , NHC_6H_5 , $NHCOCH_2$ etc.

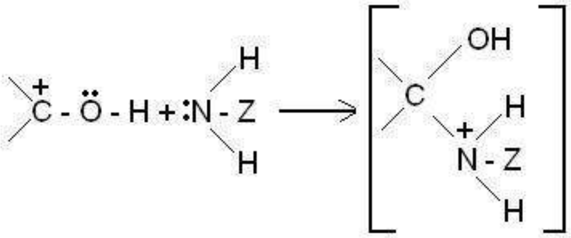
The reaction of ammonia derivatives to aldehydes and ketones is called by acids

Mechanism

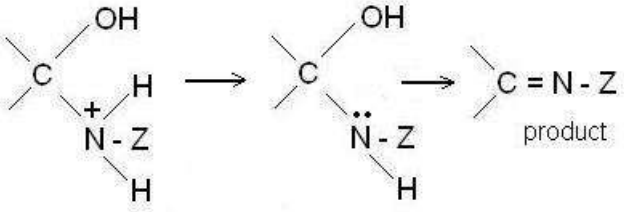
Step I: In acidic medium, the carbonyl oxygen gets protonated.



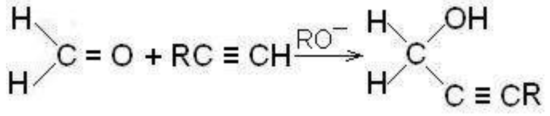
Step II : In ammonia derivatives, the nitrogen atom has a lone pair of electrons, which attack the positively charged carbonyl carbon and results in positive charge on nitrogen atom



Step III : The unstable intermediate loses a proton, H^+ and water molecule to form stable product (imines)



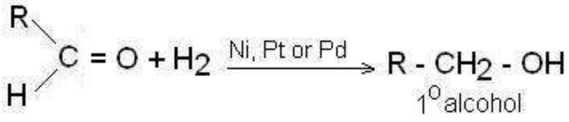
(vi) Addition of alkynes

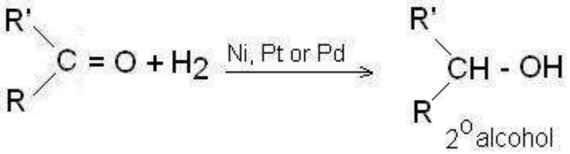


This reaction is also known as ethinylation

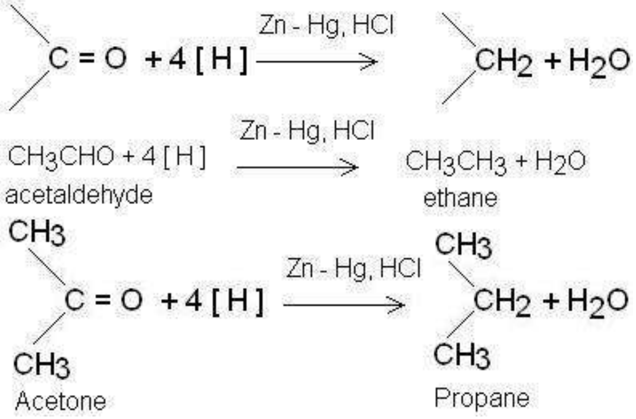
2. Reduction reactions

I. Catalytic reduction to alcohol

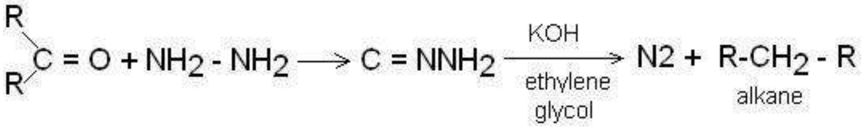


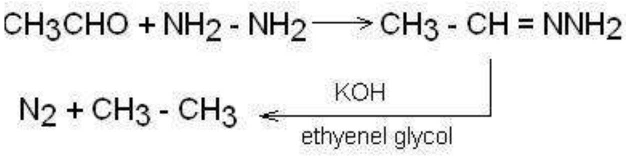


II. Clemmensen reduction



III. Wolf-Kishner reduction





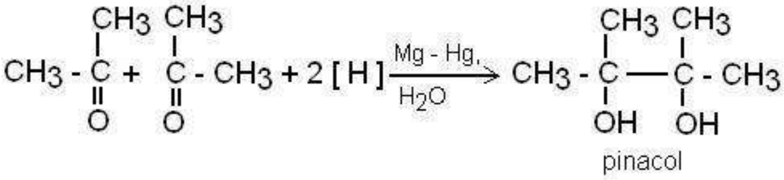
$$CH_3COCH_3 \xrightarrow[\text{ethylene glycol}]{NH_2\text{-}NH_2 + KOH} CH_3 - CH_2 - CH_3 + H_2O$$

IV. Reduction with HI + P (red)

$$CH_3 - CHO + 4HI \xrightarrow[150^0C]{\text{red P}} CH_3\text{-}CH_3 + H_2O + 2I_2$$

$$CH_3COCH_3 + 4HI \xrightarrow[150^0C]{\text{red P}} CH_3 - CH_2 - CH_3 + H_2O + 2I_2$$

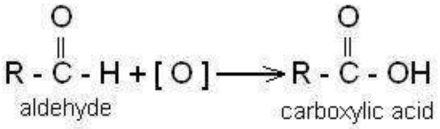
V. Reduction to pinacols



$$CH_3 - \underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}} + \underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3 + 2[H] \xrightarrow[H_2O]{Mg - Hg,} CH_3 - \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} — \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$

3. Oxidation reactions

i. Oxidation with mild oxidizing agents



$$\underset{\text{aldehyde}}{R - \overset{\overset{O}{\|}}{C} - H} + [O] \longrightarrow \underset{\text{carboxylic acid}}{R - \overset{\overset{O}{\|}}{C} - OH}$$

Ketones are not oxidized by mild oxidizing agents

(a) Aldehydes reduces Tollen's reagent to metallic silver which appears as a silver mirror on wall of test tube. Thus the reaction is also known as silver mirror test.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow$$

$$RCOO^- + \underset{\text{silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

(b) Reduction of Fehling's solution

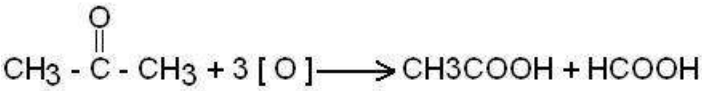
Fehling's solution is an alkaline solution of $CuSO_4$ mixed with Rochelle slat i.e. sodium potassium tartarate. Aldehydes reduces cupric ion (Cu^{2+}) of Fehling's solution to cuprous ions (Cu^+) to form red precipitate of cuprous oxide

$$RCHO + 2Cu_2^+ + 5\,OH^- \longrightarrow RCOO^- + Cu_2O + 3H_2O$$

Fehling's solution is reduced by aliphatic aldehydes only. Aromatic aldehydes and ketones so not give this reaction.

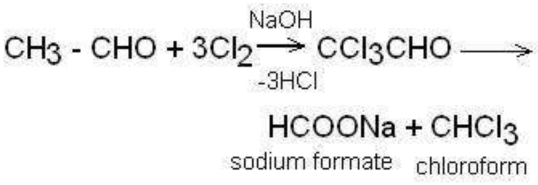
ii. Oxidation with strong oxidizing agent

$$\underset{\text{aldehyde}}{RCHO} + [O] \xrightarrow{NHO_3\ (\text{conc.})} \underset{\text{carboxylic acid}}{RCOOH}$$

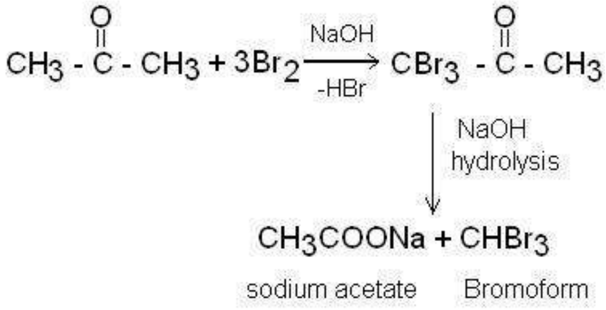


$$CH_3 - \overset{\overset{O}{\|}}{C} - CH_3 + 3[O] \longrightarrow CH3COOH + HCOOH$$

iii. Haloform reaction



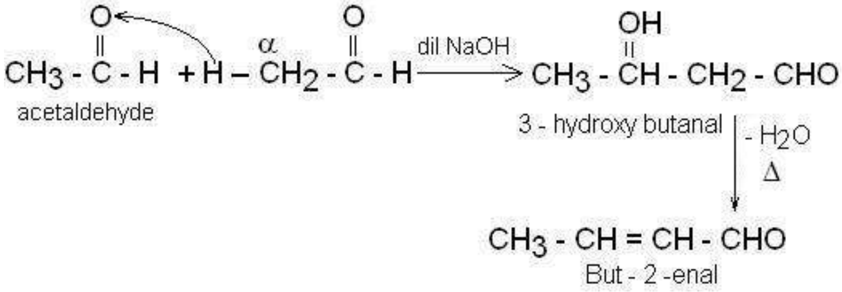
$$CH_3-CHO + 3Cl_2 \xrightarrow[-3HCl]{NaOH} CCl_3CHO \longrightarrow \underset{\text{sodium formate}}{HCOONa} + \underset{\text{chloroform}}{CHCl_3}$$



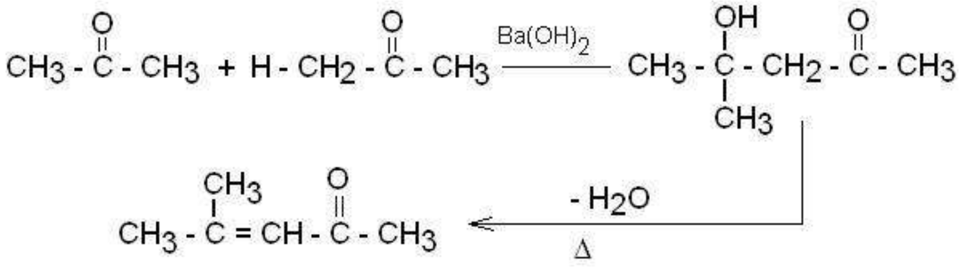
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 3Br_2 \xrightarrow[-HBr]{NaOH} CBr_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{NaOH hydrolysis}} \underset{\text{sodium acetate}}{CH_3COONa} + \underset{\text{Bromoform}}{CHBr_3}$$

4. Condensation reactions

(1) Aldol condensation

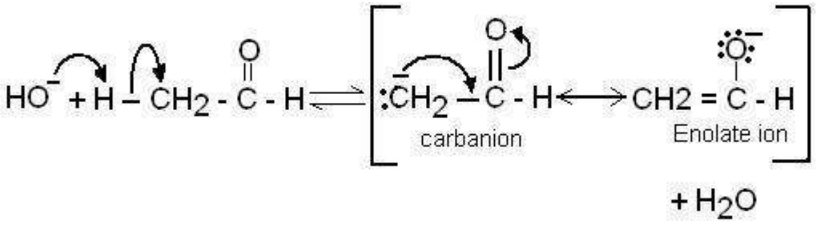


$$\underset{\text{acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + H-\overset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{dil NaOH}} \underset{\text{3 - hydroxy butanal}}{CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-CHO} \xrightarrow[\Delta]{-H_2O} \underset{\text{But - 2 -enal}}{CH_3-CH=CH-CHO}$$

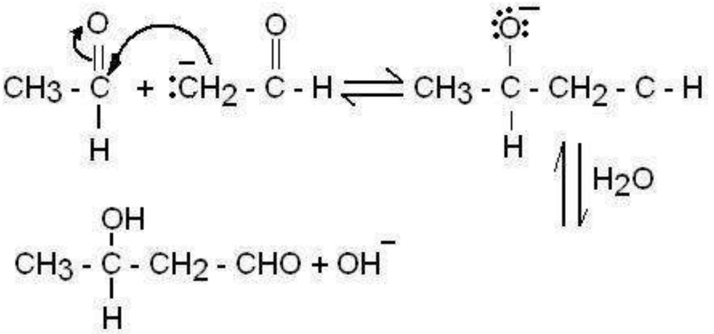


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{Ba(OH)_2} CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\Delta]{-H_2O} CH_3-\overset{CH_3}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3$$

Mechanism



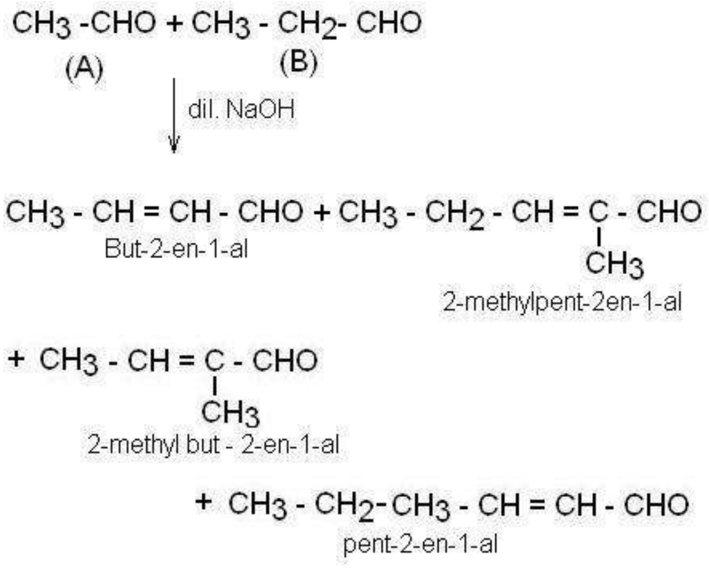
$$HO^- + H-CH_2-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons \left[\underset{\text{carbanion}}{:\bar{C}H_2-\overset{O}{\overset{\|}{C}}-H} \longleftrightarrow \underset{\text{Enolate ion}}{CH2=\overset{:\ddot{O}:^-}{\overset{|}{C}}-H}\right] + H_2O$$



$$CH_3-\underset{H}{\underset{|}{\overset{O}{\overset{\|}{C}}}} + :\bar{C}H_2-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons CH_3-\underset{H}{\underset{|}{\overset{:\ddot{O}:^-}{\overset{|}{C}}}}-CH_2-C-H \xrightleftharpoons{H_2O} CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-CHO + OH^-$$

Aldehyde or ketones which do not contain α-hydrogen atom like formaldehyde (HCHO), benzaldehyde (C_6H_5CHO) and benzophenone ($C_6H_5COC_6H_5$) do not undergo aldol condensation.

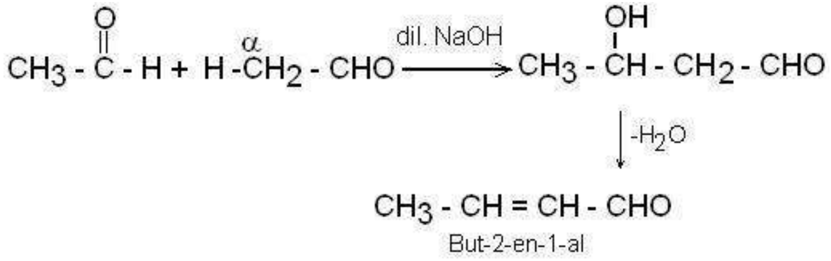
(2) Cross aldol condensation



$$\underset{(A)}{CH_3-CHO} + \underset{(B)}{CH_3-CH_2-CHO} \xrightarrow{\text{dil. NaOH}} \underset{\text{But-2-en-1-al}}{CH_3-CH=CH-CHO} + \underset{\text{2-methylpent-2en-1-al}}{CH_3-CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CHO}$$

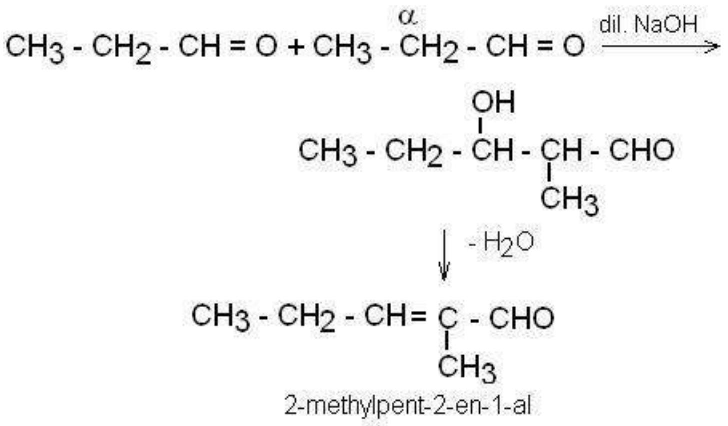
$$+ \underset{\text{2-methyl but - 2-en-1-al}}{CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CHO} + \underset{\text{pent-2-en-1-al}}{CH_3-CH_2-CH_3-CH=CH-CHO}$$

 # A- A Condensation



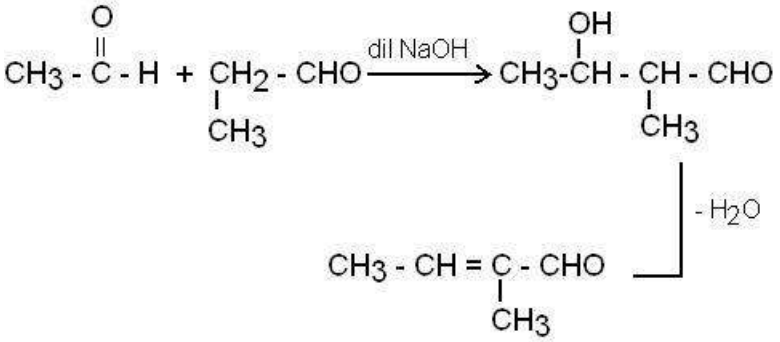
$$CH_3-\overset{O}{\overset{||}{C}}-H + H-\overset{\alpha}{C}H_2-CHO \xrightarrow{\text{dil. NaOH}} CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CHO \xrightarrow{-H_2O} \underset{\text{But-2-en-1-al}}{CH_3-CH=CH-CHO}$$

B-B Condensation



$$CH_3-CH_2-CH=O + CH_3-\overset{\alpha}{C}H_2-CH=O \xrightarrow{\text{dil. NaOH}} CH_3-CH_2-\overset{OH}{\overset{|}{C}H}-\underset{CH_3}{\underset{|}{C}H}-CHO \xrightarrow{-H_2O} \underset{\text{2-methylpent-2-en-1-al}}{CH_3-CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CHO}$$

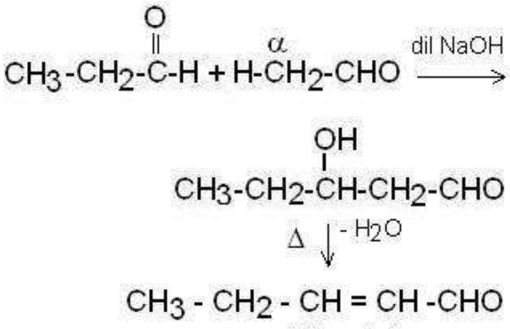
A-B Condensation



$$CH_3-\overset{O}{\overset{\|}{C}}-H + \underset{CH_3}{\underset{|}{CH_2}}-CHO \xrightarrow{\text{dil NaOH}} CH_3-\overset{OH}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CHO \xrightarrow{-H_2O} CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CHO$$

2-methyl but - 2-en-1-al

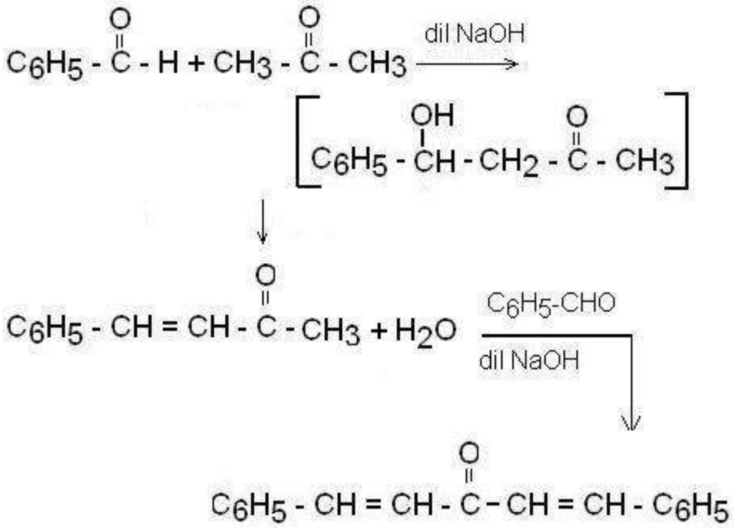
B-A Condensation



$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + H-\overset{\alpha}{CH_2}-CHO \xrightarrow{\text{dil NaOH}} CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2-CHO \xrightarrow[\Delta]{-H_2O} CH_3-CH_2-CH=CH-CHO$$

pent-2-en-1-al

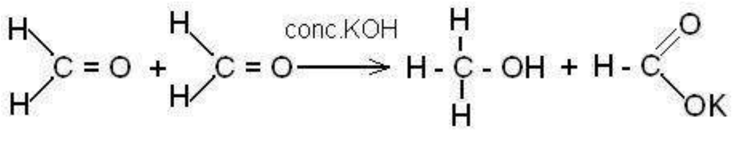
(3) Claisen – Schmidt condensation



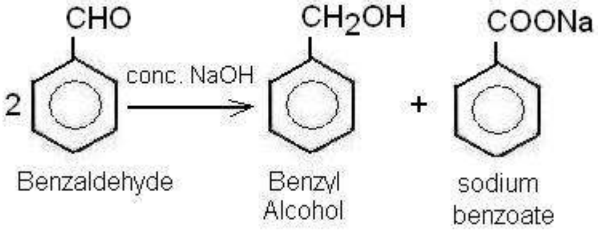
$$C_6H_5-\overset{O}{\overset{\|}{C}}-H + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{dil NaOH}} \left[C_6H_5-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3\right] \rightarrow C_6H_5-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O \xrightarrow[\text{dil NaOH}]{C_6H_5\text{-}CHO} C_6H_5-CH=CH-\overset{O}{\overset{\|}{C}}-CH=CH-C_6H_5$$

Dibenzal acetone

5. Cannizzaro reaction

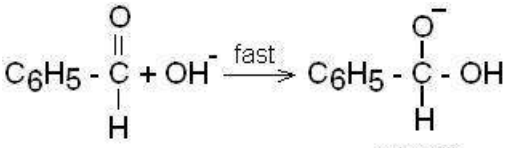


$$H_2C=O + H_2C=O \xrightarrow{\text{conc.KOH}} H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OH + H-C(=O)OK$$



Mechanism

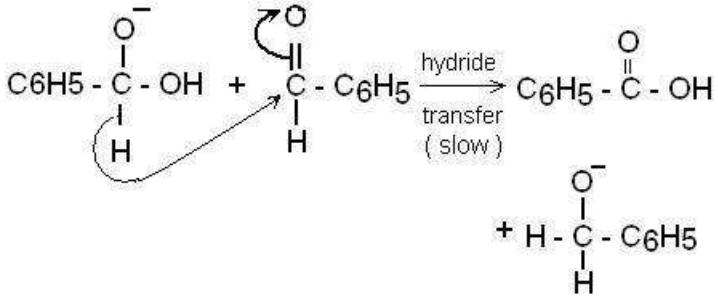
Step I : The OH^- ion attacks the carbonyl carbon to form hydroxyl alkoxide



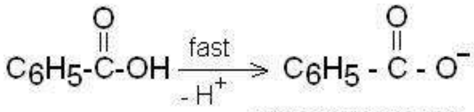
$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{C}} + OH^- \xrightarrow{fast} C_6H_5-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH$$

anion (I)

Step II : Anion (I) acts as hybride ion donor to the second molecule of aldehyde. In the final step of the reaction, the acid and the alkoxide ion transfer H^+ to acquire stability.

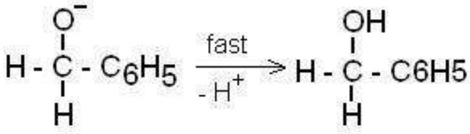


$$C6H5-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH + \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C_6H_5 \xrightarrow[\text{(slow)}]{\text{hydride transfer}} C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C6H5$$



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[-H^+]{fast} C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O^-$$

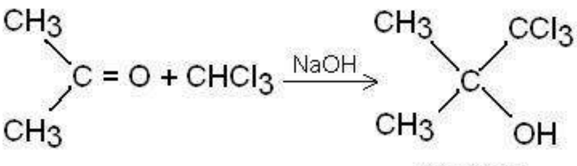
salt of benzoic acid



$$H-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C_6H_5 \xrightarrow[-H^+]{fast} H-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C6H5$$

benzyl alcohol

6. Reaction with chloroform



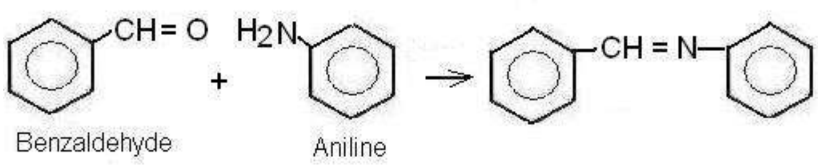
chloretone

Chloretone is used as hypnotic.

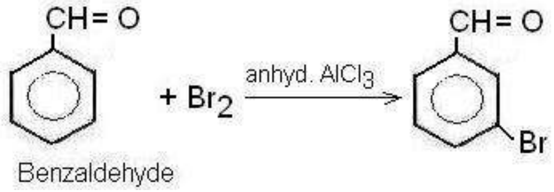
7. Reaction with primary amine

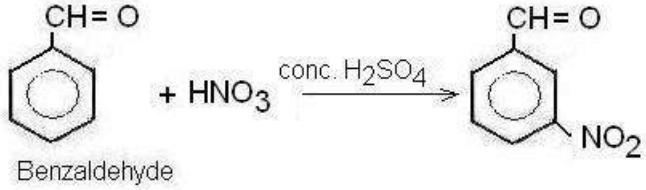
$$RCH\boxed{O + H_2}NR' \xrightarrow[\Delta]{H^+} R\,CH = NR' + H_2O$$

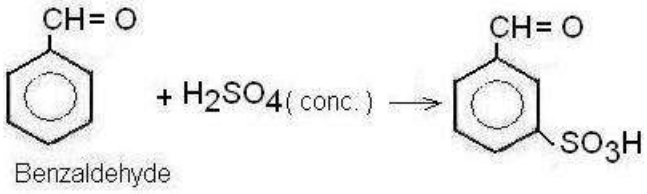
schiff's base



8. Electrophilic substitution reaction of aromatic carbonyl compounds







USES OF ALDEHYDES AND KETONES

(a) Uses of formaldehyde
   i. The 40% solution of formaldehyde in water (formaline) is used as disinfectant, germicide and antiseptic. It is used for the preservation of biological specimens
   ii. It is used for silvering of mirrors
   iii. It is used for making synthetic plastics, like Bakelite, urea- formaldehyde resin etc

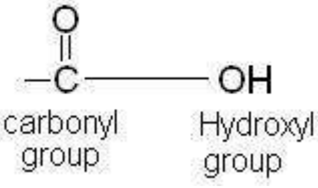
(b) Uses of acetaldehyde
   i. It is used in preparation of acetic acid, dyes, drugs, etc
   ii. As an antiseptic inhalant in nose troubles

(c) Uses of benzaldehyde
   i. As flavouring agent in perfume industry
   ii. In manufacture of dyes.

(d) Uses of acetone
   i. As a solvent for cellulose acetate, resin etc.
   ii. As a nailpolish remover
   iii. In the preparation of an artificial scent and synthetic rubber

CARBOXYLIC ACIDS

Organic compounds containing carboxylic group –COOH are called carboxylic acids.

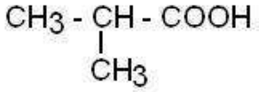


ISOMERISM IN CARBOXYLIC ACIDS

(i) Chain isomerism: This is due to the difference in the structure of carbon chain

$CH_3 - CH_2 - CH_2 - COOH$

Butanoic acid



$CH_3 - CH(CH_3) - COOH$

2 - methyl propanoic acid

(ii) Functional isomerism : Monocarboxylic acids show functional isomerism with esters of the acids, hydroxyl carbonyl compounds and hydroxyl oxiranes.

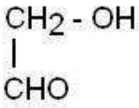
Example : $C_2H_4O_2$

CH_3COOH

acetic acid

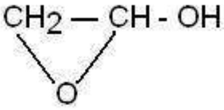
$HCOOCH_3$

methyl formate



$CH_2(OH) - CHO$

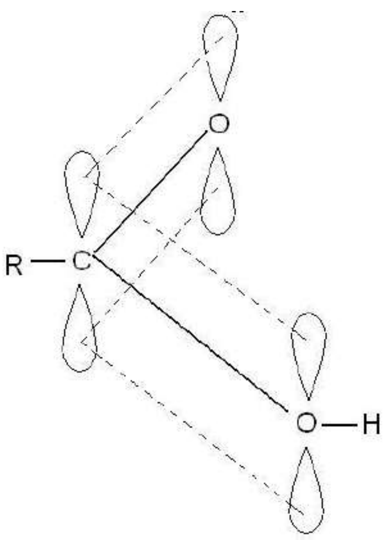
glycol aldehyde



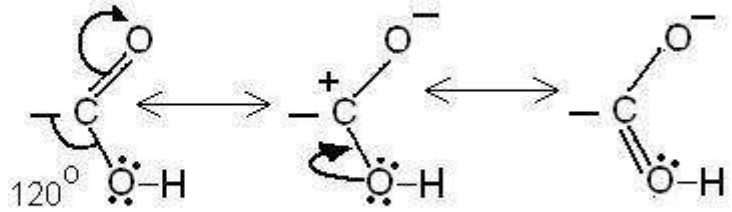
hydroxy ethylene oxide

STRUCTURE OF CARBOXYLIC ACID

- Carbon atom of carboxyl group is sp^2 – hybridized and forms one σ- bond with hydrogen or carbon atom depending upon the structure of carboxylic acid. Half filled p-orbital of each oxygen atom and unhybridised p-orbital of carbon atom lies in the same plane and overlaps to form a π- bonds, one carbon and two oxygen atoms

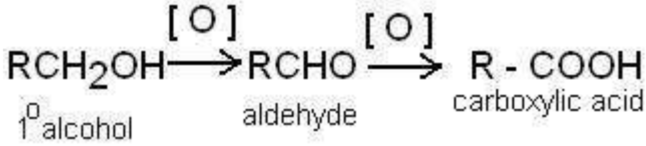


- In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. The carboxylic carbon is less electrophilic than carboxyl carbon because of the possible resonance structure shown below.

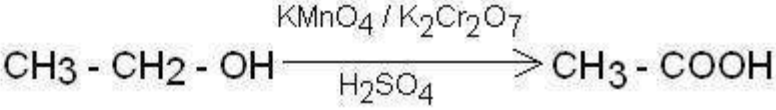


GENERAL METHOD OF PREPARATION OF CARBOXYLIC ACIDS

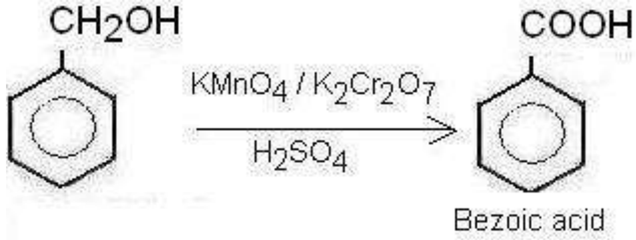
1. Oxidation of alcohols



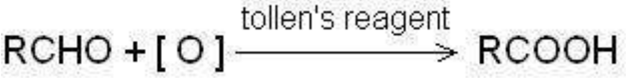
$$\underset{1^{o}\,\text{alcohol}}{RCH_2OH} \xrightarrow{[O]} \underset{\text{aldehyde}}{RCHO} \xrightarrow{[O]} \underset{\text{carboxylic acid}}{R-COOH}$$



$$CH_3-CH_2-OH \xrightarrow[H_2SO_4]{KMnO_4\,/\,K_2Cr_2O_7} CH_3-COOH$$

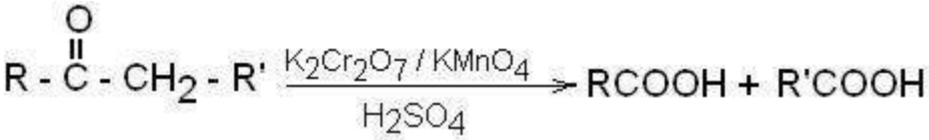


2. Oxidation of carbonyl compounds



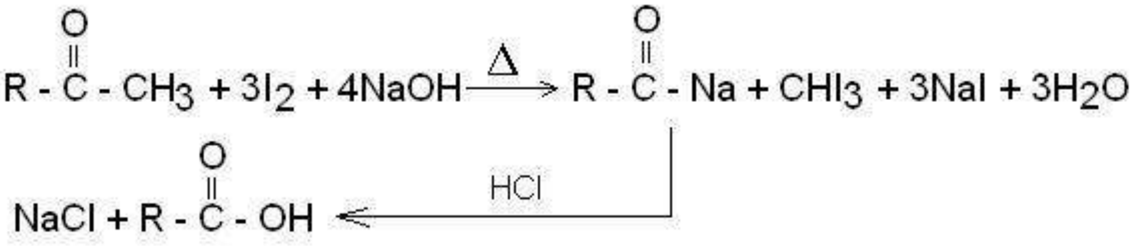
$$RCHO + [O] \xrightarrow{\text{tollen's reagent}} RCOOH$$

Ketones can only be oxidized with strong oxidizing agents to mixture of carboxylic acid with lesser number of carbon atoms



$$R-\overset{O}{\overset{\|}{C}}-CH_2-R' \xrightarrow[H_2SO_4]{K_2Cr_2O_7\,/\,KMnO_4} RCOOH + R'COOH$$

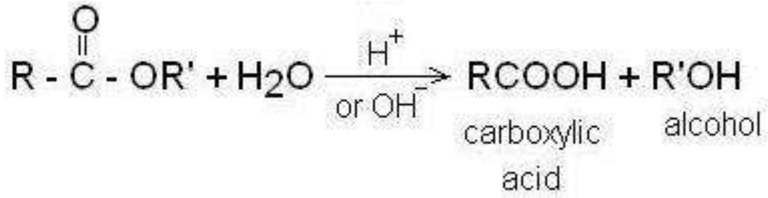
3. Haloform reaction



$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3I_2 + 4NaOH \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-Na + CHI_3 + 3NaI + 3H_2O$$

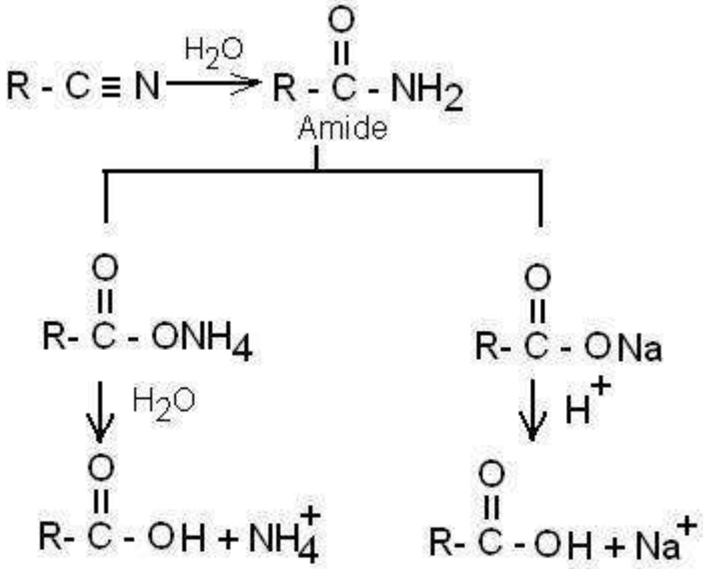
$$\xrightarrow{HCl} NaCl + R-\overset{O}{\overset{\|}{C}}-OH$$

4. Hydrolysis of ester



$$R-\overset{O}{\overset{\|}{C}}-OR' + H_2O \xrightarrow[\text{or } OH^-]{H^+} RCOOH + R'OH$$

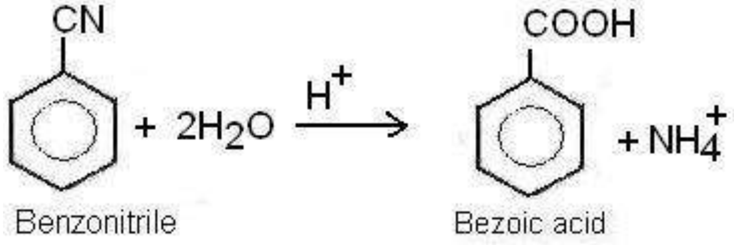
5. Hydrolysis of nitriles



$$R-C\equiv N \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-NH_2$$

$$R-\overset{O}{\overset{\|}{C}}-ONH_4 \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-OH + NH_4^+$$

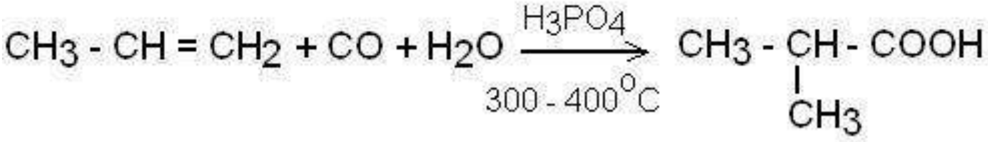
$$R-\overset{O}{\overset{\|}{C}}-ONa \xrightarrow{H^+} R-\overset{O}{\overset{\|}{C}}-OH + Na^+$$



6. Koch reaction

$$CH_2 = CH_2 + CO + H_2O \xrightarrow[300-400^oC]{H_3PO_4} CH_3-CH_2-COOH$$

ethene propanoic acid



$$CH_3-CH=CH_2 + CO + H_2O \xrightarrow[300-400^oC]{H_3PO_4} CH_3-\underset{CH_3}{\underset{|}{CH}}-COOH$$

propene Iso-butyric acid

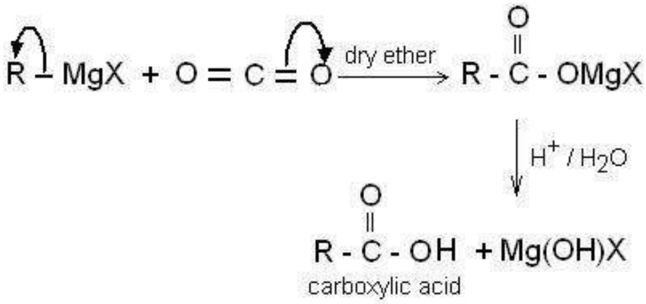
7. Carbonation of sodium alkoxide

$$\underset{\text{sodium alkoxide}}{R - \overset{-}{O} - \overset{+}{Na}} + CO \xrightarrow{\Delta} \underset{\text{sodium carboxylate}}{RCO\overset{-}{O}\,\overset{+}{Na}} \longrightarrow \underset{\text{carboxylic acid}}{RCOOH} + NaCl$$

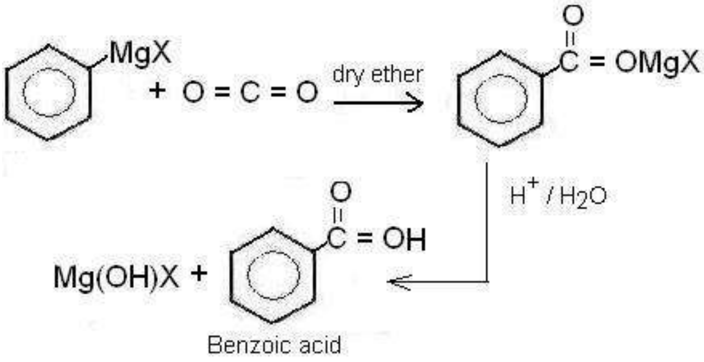
Formic acid can be produced by carbonation of NaOH

$$NaOH + CO \xrightarrow[\text{8-10 atm}]{100^{0}C} HCO\overset{-}{O}\,\overset{+}{Na} \xrightarrow{HCl / H_2O} H\text{-}COOH$$

8. Carbonation of Grignard reagent



$$R - MgX + O = C = O \xrightarrow{\text{dry ether}} R - \overset{\overset{O}{\|}}{C} - OMgX \xrightarrow{H^+ / H_2O} \underset{\text{carboxylic acid}}{R - \overset{\overset{O}{\|}}{C} - OH} + Mg(OH)X$$



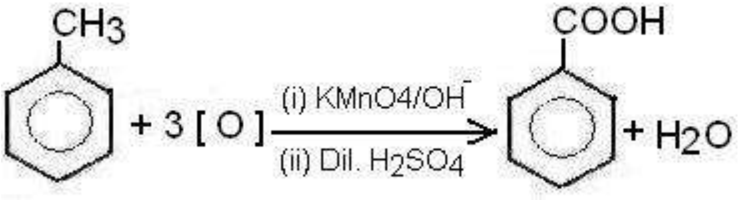
9. Oxidative cleavage of alkenes and alkynes

$$RCH = CHR + 4[O] \xrightarrow{\text{alkaline hot } KMnO_4} 2RCOOH$$

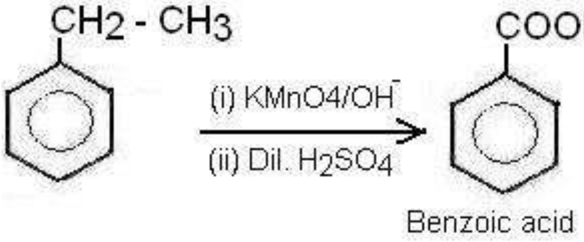
$$R-C \equiv C-R + 4[O] \xrightarrow{\text{alkaline hot } KMnO_4} 2RCOOH$$

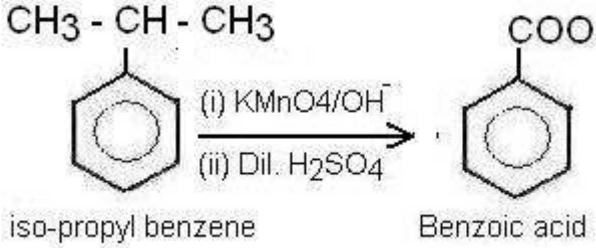
$$CH_3-C \equiv C-CH_2-CH_3 + 4[O] \xrightarrow{\text{alkaline hot } KMnO_4} \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{propanoic acid}}{CH_3-CH_2-COOH}$$

10. Oxidation of alkyl benzene

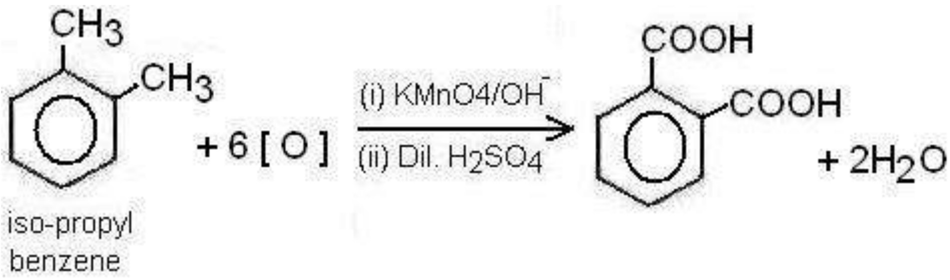


- During oxidation side chain is oxidised to –COOH group irrespective of the length of the chain
- Only primary and secondary alkyl side chain are oxidized to carbonyl group

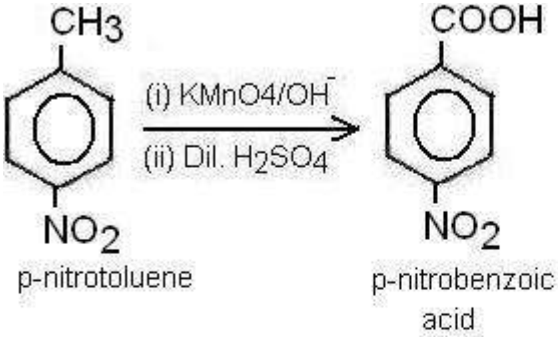




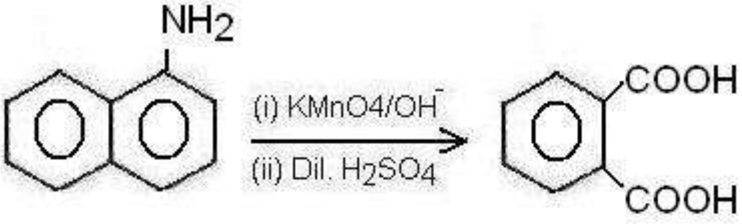
Greater the number of benzylic hydrogen atoms, greater is the ease of oxidation.
Thus order of ease of oxidation is $1^O > 2^O > 3^O$
If two alkyl groups are attached to benzene ring then each side chain is oxidized to carboxylic group



If an electron withdrawing group is present it stabilizes the benzene ring and oxidation produces substituted benzoic acid.

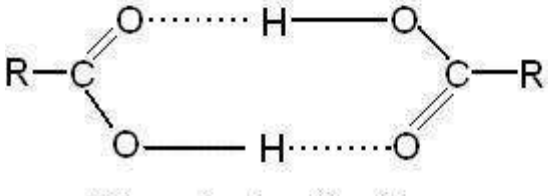


Whereas electron releasing group like –OH, -NH_2 destabilize the benzene ring and make it susceptible to oxidation.



PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

- First three members are colourless, pungent smelling liquids. Next members butyric acid has odour of rancid butter, whereas next five members (C_5 to C_9) have goat like odour. But higher member (above C_{10}) are colourless and odourless waxy solids due to low volatility acids are colourless, odourless solids.
- Lower aliphatic carboxylic acids ($C_1 – C_4$) are soluble in water due to H-bonding. Solubility decreases with increased molecular weight and $C_6H_{13}COOH$ is fairly soluble in water. Aromatic acids are nearly insoluble in water due to large hydrocarbon part.
- Carboxylic acid are polar in nature and exist as dimer in vapour state or in aprotic solvents due to formation of H-bonding.



Dimer of carboxylic acid

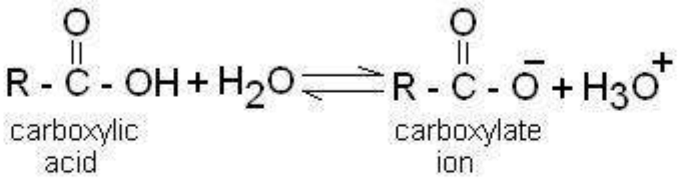
- Carboxylic acids have higher boiling point than hydrocarbons, aldehydes and ketones and alcohols comparable molecular hydrogen bonding.
- Carboxylic acids having even number of carbon atoms have higher melting points as compare to homologous member just above or below in the series containing odd number of carbon atoms. This is because of carbon atoms. This is because zig-zag carbon chain of

even number of carbon atoms fit closely in crystal lattice, so that intermolecular forces of attraction increase and also melting point.

- Aromatic acids have higher melting and boiling point than aliphatic acids of comparable molecular weight due to close packing in crystal lattice.

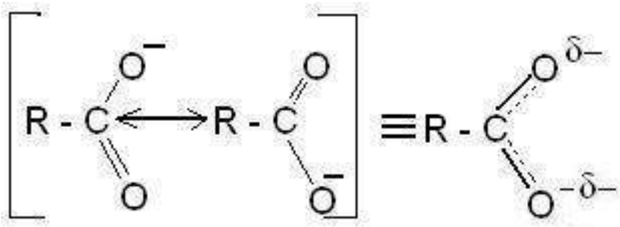
ACIDIC STRENGTH OF CARBOXYLIC ACIDS

Carboxylic acids ionize in aqueous solution and exists in equilibrium with carboxylate ion.



$$\underset{\text{carboxylic acid}}{R-\overset{\overset{O}{\|}}{C}-OH} + H_2O \rightleftharpoons \underset{\text{carboxylate ion}}{R-\overset{\overset{O}{\|}}{C}-\bar{O}} + H_3O^+$$

Carboxylate ion is stabilized by resonance



Strength of carboxylic acids is expressed in terms of dissociation constant K_a

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH][H_2O]}$$

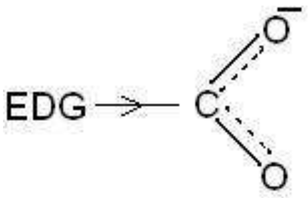
Greater the value of K_a, greater is the tendency to ionize and hence stronger the acid

$pK_a = -\log K_a$

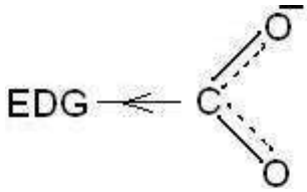
Greater the value of K_a, smaller the value of pK_a and hence stronger is the carboxylic acid.

EFFECT OF SUBSTITUENT ON ACIDIC STRNGTH OF CARBOXYLIC ACIDS

Electron donating group (+ I effect) destabilizes the carboxylate ion by intensifying the negative charge and thus decreases the acidic strength



Electron withdrawing group (- I effect), stabilizes the carboxylate ion by dispersing negative charge on carboxylate ion and hence increases the acid strength



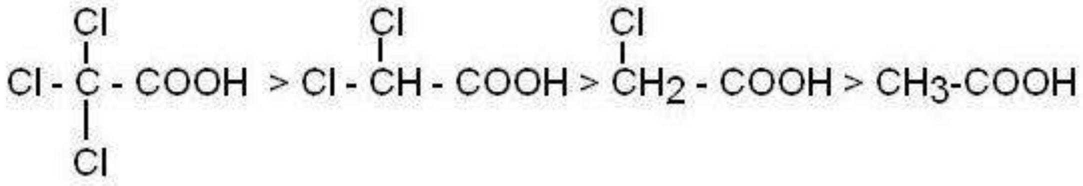
- Halogens are electron withdrawing nature and hence increase the acidic strength. -I effect of halogens decreases in the order.

  F > Cl > Br > I

  Hence acidic strength of α – haloacids decreases in the order

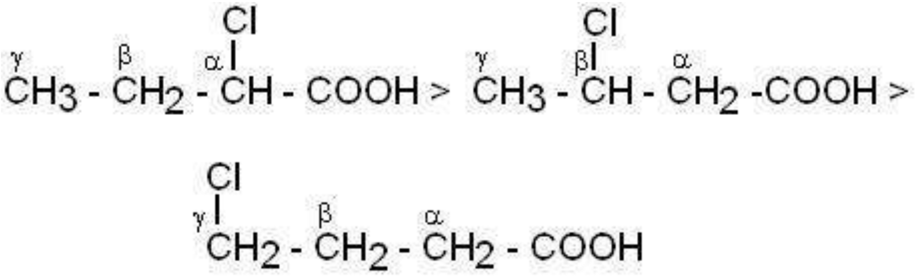
  $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

- Greater the number of electron withdrawing groups or halogens greater is the acidic strength thus



$$\mathrm{Cl-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-COOH > Cl-\overset{\overset{Cl}{|}}{C}H-COOH > \overset{\overset{Cl}{|}}{C}H_2-COOH > CH_3-COOH}$$

Effect of halogen group decrease as its distance from –COOH group increases. Thus α – haloacid are more stronger than β – haloacids and γ- haloacids.



$$\mathrm{\overset{\gamma}{C}H_3-\overset{\beta}{C}H_2-\overset{\overset{Cl}{|}}{\overset{\alpha}{C}}H-COOH > \overset{\gamma}{C}H_3-\overset{\overset{Cl}{|}}{\overset{\beta}{C}}H-\overset{\alpha}{C}H_2-COOH > \overset{\overset{Cl}{|}}{\overset{\gamma}{C}}H_2-\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2-COOH}$$

$CH \equiv C – CH_2COOH$ is stronger acid than $CH_2 = CH – CH_2COOH$ because in C≡C bond carbon is sp hybridized which is more electronegative than sp^2 hybridised carbon of –C=C-. Hence -C≡C – exerts better electron withdrawing effect (-I) effect than C = C .

RELATIVE ACIDIC STREHGTH OF UNSUBSTITUTED ALIPHATIC AND AROMATIC ACIDS

Acidic strength of un-substituted aliphatic acid follows the order

$HCOOH > CH_3COOH > CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C\text{-}COOH$

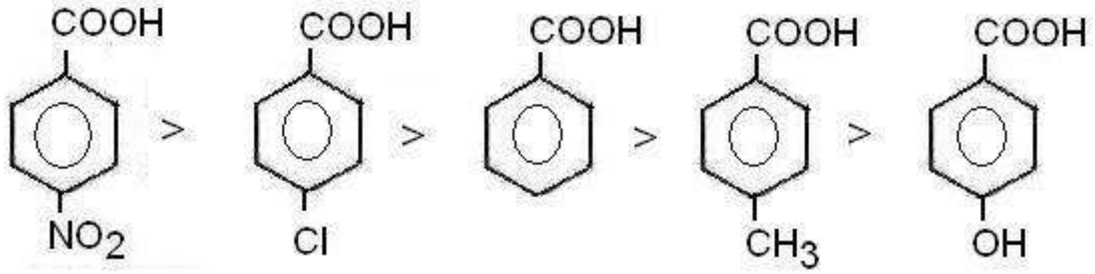
Phenyl group directly attached to carboxyl group exerts –I effect which is weaker than +I effect of CH_3 of an alkyl group and hence acidic strength follows the order:

$HCOOH$	>	C_6H_5COOH	>	CH_3COOH
Formic acid		Benzoic acid		Acetic acid

But phenyl group attached to carboxyl group through some saturated carbon atom exerts weak electron withdrawing inductive effect (- I effect), so the acidic strength follows the order : Benzoic acid > phenyl acid > acetic acid.

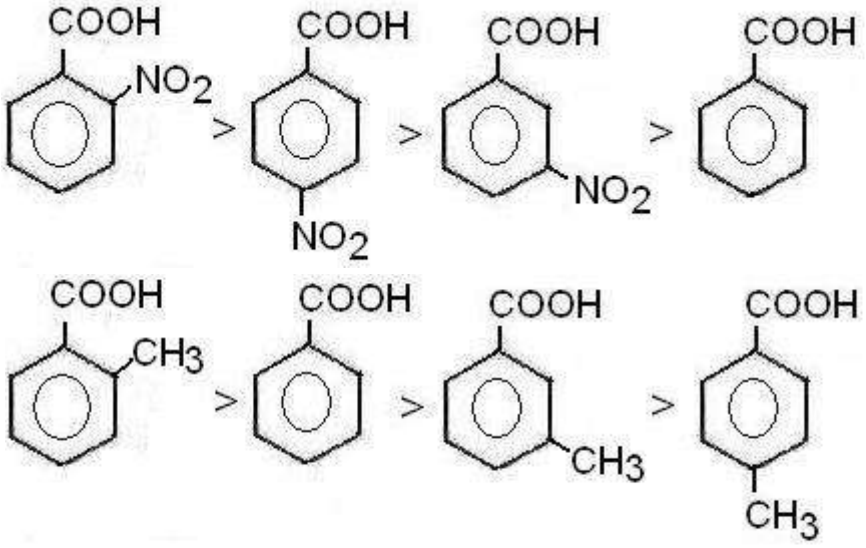
RELATIVE ACIDIC STRENGTH OF SUBSTITUTED AROMATIC ACIDS

Electron donating substituent (+I effect) decrease the acidic strength where as electron withdrawing group (- I effect) increase the acidic strength of substituted benzoic acid thus,



Ortho substituted acids are stronger than benzoic acid irrespective of the nature of the substituent.

Effect of any substituent is more pronounced at para-position than meta-position.

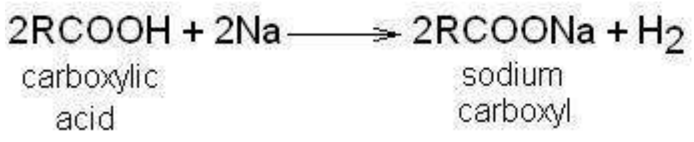


CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS

(A) Reactions due to H-atom of carboxyl group

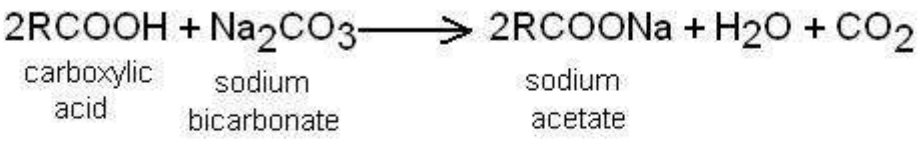
$RCOOH + H_2O \rightarrow RCOO^- + H_3O^+$

(1) Reaction with metals



$$\underset{\text{carboxylic acid}}{2RCOOH} + 2Na \longrightarrow \underset{\text{sodium carboxyl}}{2RCOONa} + H_2$$

(2) Reaction with metal carbonates and bicarbonates



$$\underset{\text{carboxylic acid}}{2RCOOH} + \underset{\text{sodium bicarbonate}}{Na_2CO_3} \longrightarrow \underset{\text{sodium acetate}}{2RCOONa} + H_2O + CO_2$$

$$\underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{sodium bicarbonate}}{NaHCO_3} \longrightarrow \underset{\text{sodium acetate}}{CH_3COONa} + H_2O + CO_2$$

(3) Reaction with ammonia

$RCOOH + NH_3 \rightarrow RCOONH_4$

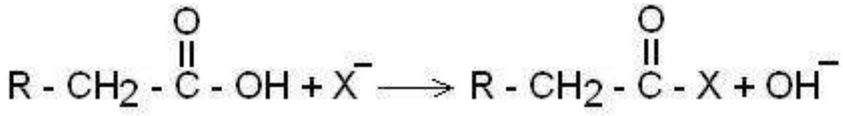
(4) Reaction with alkali

$RCOOH + NaOH \rightarrow RCOONa + H_2O$

(5) Reaction with diazomethane (ester formation)

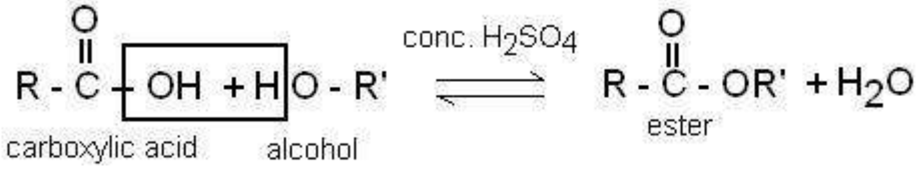
$RCOOH + CH_2N_2 \rightarrow RCOOCH_3 + N_2$

(B) Reactions due to –OH group of carboxylic acids

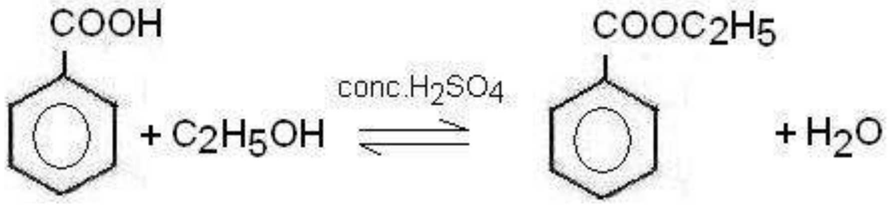


$$R-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH + X^- \longrightarrow R-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-X + OH^-$$

1. Formation of ester (esterification)



$$\underset{\text{carboxylic acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{OH\ +H}}\underset{\text{alcohol}}{O-R'} \xrightleftharpoons{\text{conc. } H_2SO_4} \underset{\text{ester}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OR'} + H_2O$$

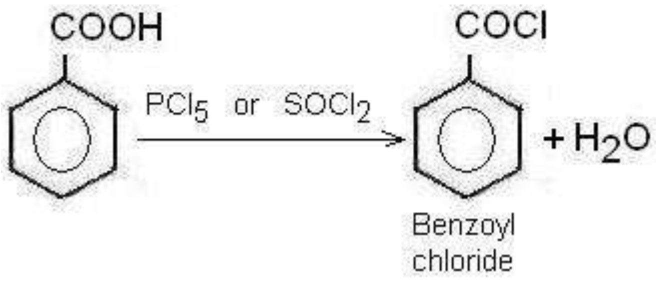


2. Formation of acid chloride

$$3\,RCOOH + PCl_3 \longrightarrow 3ROCl + H_3PO_3$$

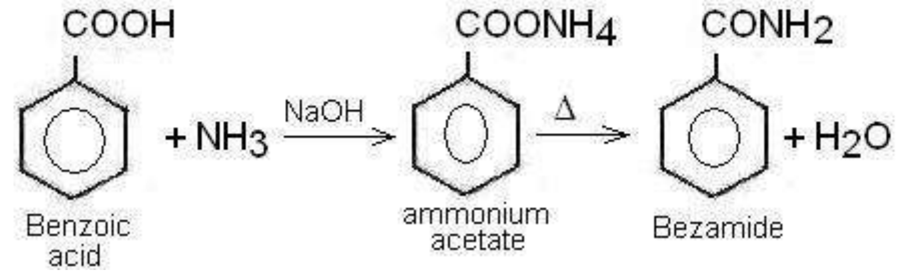
$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl3 + HCl$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

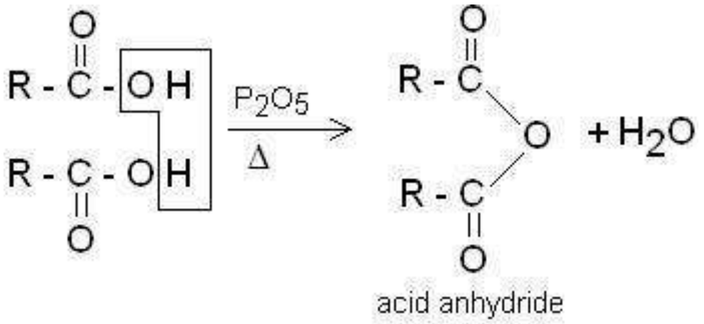


3. Formation of amides

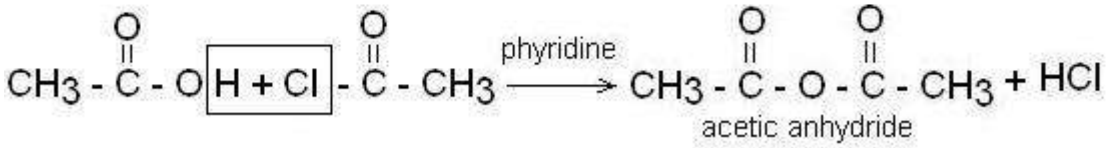
$$RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow{\Delta} \underset{\text{Amide}}{RCONH_2} + H_2O$$



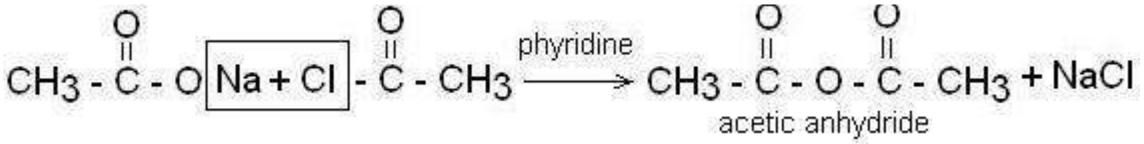
4. Formation of acid anhydride (Dehydration)



Acid chloride on reaction with carboxylic acid in presence of pyridine or with sodium salt of carboxylic acid also produce acid anhydride.

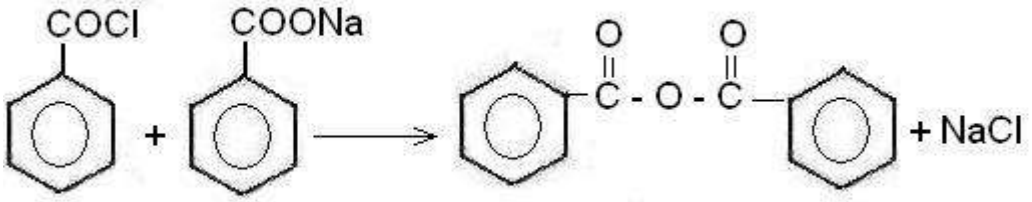


$$CH_3-\overset{O}{\overset{\|}{C}}-O\boxed{H+Cl}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{phyridine}} \underset{\text{acetic anhydride}}{CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3} + HCl$$



$$CH_3-\overset{O}{\overset{\|}{C}}-O\boxed{Na+Cl}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{phyridine}} \underset{\text{acetic anhydride}}{CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3} + NaCl$$

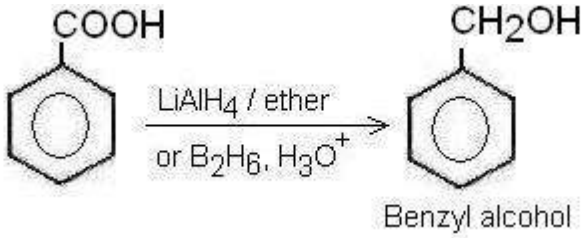
Aromatic carboxylic acid produces anhydride by reaction of acid chloride



(C) Reactions due to carboxylic group as a whole

1. Reduction
   (i) Reduction to alcohols

$$RCOOH \xrightarrow[\text{or } B_2H_6,\ H_3O^+]{LiAlH_4\ /\ \text{ether}} \underset{\text{alcohol}}{RCH_2OH}$$



(ii) Reduction to alkanes

$$RCOOH + 6HI \xrightarrow{\text{red P}} RCH_3 + 2H_2O + 3I_2$$

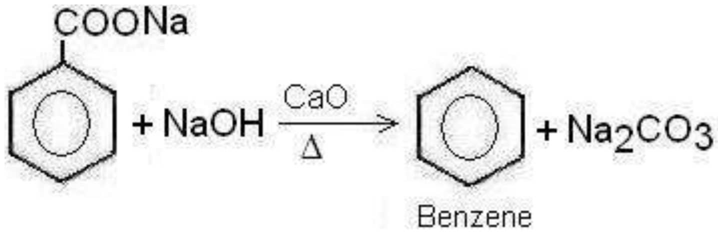
2. Schmidt's reaction (Formation of primary amines)

$$\underset{\text{carboxylic acid}}{RCOOH} + \underset{\text{hydrazoic acid}}{HN_3} \xrightarrow{H_2SO_4\,(\text{conc.})} \underset{1^0\text{ amine}}{R - NH_2} + N_2 + CO_2$$

3. Decarboxylation

(i) Decarboxylation with sodalime

$$\underset{\text{sodium carboxylate}}{RCOONa} + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{alkane}}{R\text{-}N} + Na_2CO_3$$



NaOH and CaO should be in the ratio of 3:1

Presence of an electron withdrawing group favours decarboxylation.

(ii) Kolbe's reaction (Electrolytic decarboxylation)

$$2R-COONa \xrightarrow{\text{electrolysis}} 2RCOO^- + 2Na^+$$

At anode:

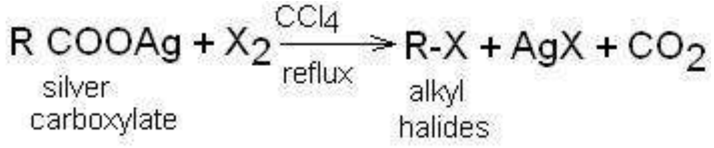
$$2RCOO^- \longrightarrow R-R + 2CO_2 + 2e^-$$

At cathode:

$$2\,Na+ + 2e^- \longrightarrow 2Na$$

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

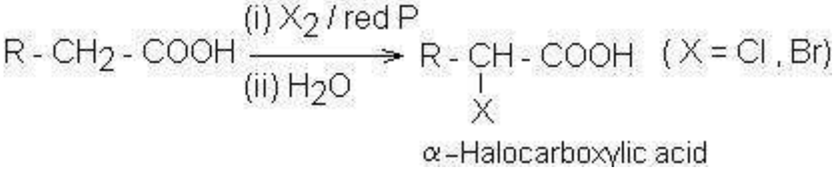
(iii) Hunsdiecker reaction (Formation of alkyl halides)



$$\underset{\text{silver carboxylate}}{R\,COOAg} + X_2 \xrightarrow[\text{reflux}]{CCl_4} \underset{\text{alkyl halides}}{R-X} + AgX + CO_2$$

(D) Reactions due to alkyl group of carboxylic acids

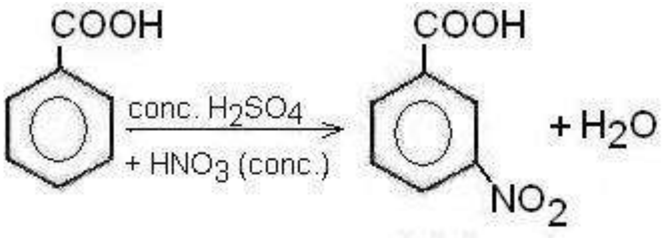
1. Hell –Volhard-Zelinsky reaction



$$R-CH_2-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{ / red P}} \underset{\alpha\text{–Halocarboxylic acid}}{R-\underset{X}{\underset{|}{C}}H-COOH} \quad (X = Cl\,,Br)$$

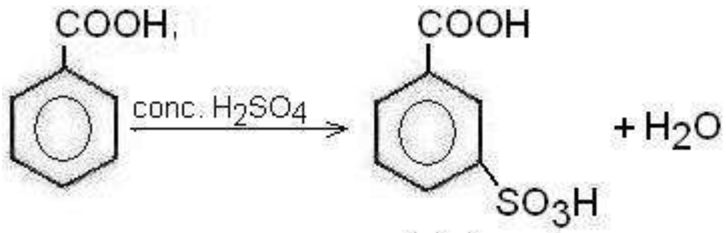
2. Electrophilic aromatic substitution reaction

(i)Nitration



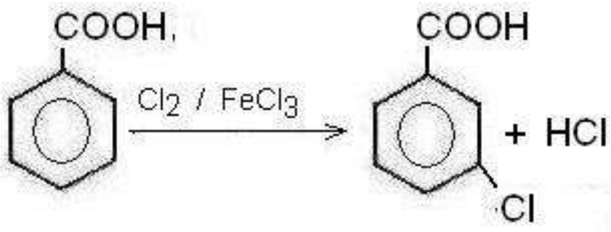
m-Nitrobenzoic acid

(ii)Sulphonation



m-sulphobenzoic acid

(iii)Chlorination



GENERAL TESTS FOR CARBOXYLIC GROUP

(i) The aqueous solution of the acid turns blue litmus red

(ii) The aqueous solution of the acid gives brisk effervescence of carbon dioxide with sodium bicarbonate or sodium carbonate (sodium bicarbonate test)

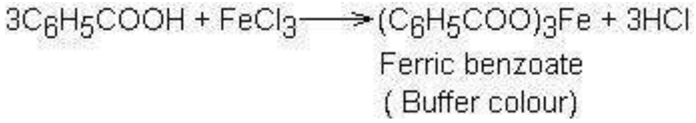
(iii) On heating with alcohol and concentrated sulphuric acid, a fruity smell of ester is formed.

(iv) Acetic acid gives blood-red or wine-red colour on treatment with ferric chloride; formation of ferric acetate; formation of ferric acetate takes place in this reaction.

$$3CH_3COOH + FeCl_3 \rightarrow (CH_3COO)_3Fe + 3HCl$$

(v) Neutral solution of formic acid gives red precipitate with Fehling's solution, black precipitate with Tollen's reagent.

(vi) Benzoic acid gives buff colour on treatment with neutral ferric chloride.



$$3C_6H_5COOH + FeCl_3 \longrightarrow \underset{\text{(Buffer colour)}}{\underset{\text{Ferric benzoate}}{(C_6H_5COO)_3Fe}} + 3HCl$$

USE OF CARBOXYLIC ACIDS

(i) Acetic acid is used as vinegar and in the manufacture of pickles

(ii) Acetic acid is used in the manufacture of plastics, rayon and silk industries

(iii) Acetic acid is used in the manufacture in antiknocking agent.

(iv) Salts of benzoic acid is used as urinary antiseptics.

(v) Benzoic acid is used in the treatment of skin diseases like eczema

(vi) Formic acid is used in the preservation of fruits

(vii) Formic acid is used as reducing agent.

GROUP -1 (ALKALI METALS)

1. Electronic configuration : ns^1
2. Physical state : Silvery white, soft and light
3. Atomic and ionic radii, volume : Atomic and ionic radii increases from Li to Fr due to presence of extra shell of electrons. Volume increases from Li to Cs
4. Density : Densities are quite low and increases from Li to Cs. K is lighter than Na due to unusual increase in atomic size. Li, Na and K are lighter than water
5. Melting point and boiling points: Decrease in melting and boiling point from to Li to Cs due to weak intermetallic bonding
6. Metallic character : Increases from Li to Cs
7. Conductivity: Good conductor.
8. Oxidation state : +1 oxidation state
9. Ionization enthalpy: Ionization enthalpy decreases from Li to Cs due to decrease in atomic size
10. Hydration of ions: Smaller the size of cation, greater degree of hydration $Li^+ > Na^+$, $K^+ > Rb^+ > Cs^+$
11. Hydration energy : Hydration energy of alkalimetals decreases from Li^+ to Cs^+
12. Flame colouration:

Li	Crimson
Na	Yellow
K	Pale violet
Rb	Red violet
Sc	Blue

When an alkali metal is heated in a flame the electrons absorbs energy from flame and are excited to next higher level. When these excited electrons returns back to their original position they emit energy in the form of visible radiations which impart a characteristics colour to the flame

13. Reducing property: Strong reducing agent. Li is strongest reducing agent in solution
14. Complex formation: Alkali metals have little tendency to form complexes. Since Lithium has a small size, it forms certain complexes. Alkali metals form stable complexes with polydentate ligand such as crown ether.

15. Action of air: Stability of peroxides and superoxide increases from Li to Cs. It can be explained by stabilization of larger anion by larger cation through lattice energy. Peroxides and superoxides are important oxidizing agent
16. Nature of hydroxide and halide: Thermal stability of Group-I hydrides decreases down the group, hence reactivity increases from LiH to CsH. Melting and boiling point of halides follows order: Fluorides > Chlorides > Bromides > iodides.
    The ease of formation of alkali metal halides increases from Li to Cs
17. Nature of oxide and hydroxide: Alkali metal oxides are basic in nature and their basic character increases gradually on moving down the group. The basic character of alkali metal hydroxide
    LiOH < NaOH < KOH < RbOH < CsOH
18. Nature of carbonates and bicarbonates: Alkali metal carbonates and bicarbonate stability increases down the group. Since electropositive character increases from Li to Cs
    All carbonates and bicarbonate are water soluble and their solubility increases from Li to Cs

CHEMICAL PROPERTIES

Alkalimetals are highly reactive due to low ionization energy. Reactivity decreases down the group

i) Reaction with oxygen and air

The alkali metals tarnish in air due to formation of carbonates , oxides and hydroxides at their surface and hence kept in kerosene oil or paraffin wax. When burnt in oxygen lithium form Li_2O

Sodium form peroxide Na_2O_2 and other alkali metals form super oxide MO_2 (M = K, Rb, Cs)

Lithium when burnt in air it form nitride by reacting with nitrogen along with Lithium oxide

$6Li (s) + N_2(g) \rightarrow 2Li_3N (s)$

Other alkali metals do not react with Nitrogen

Lithium oxide is very stable due to small size of lithium and O^{2-} ions and have higher charge density

Sodium peroxide and KO are stable because of ions are of comparable size.

Increasing stablility of peroxide and super oxide is due to stabilization of larger anions by larger cation through lattice energy

Superoxide ion (O^{2-} has a three-electron bond which makes it paramagnetic and coloured where as peroxides are diamagnetic and colour less.

Both peroxide add oxide acts as a oxidizing agents.

Alkali metal oxides are basic in nature and basic character increases down the group

ii) Reaction with water:

Alkali metals reacts vigorously and readily with water to form hydroxides with liberation of hydrogen

The reactivity increases down the group due to increased electro positivity.

K, Rb, Cs lower alkali metals in group reacts so vigorously that evolved hydrogen catches fire spontaneously. Because of their high reactivity they are kept in kerosene.

Alkali metals reacts with compound containing acidic hydrogen atoms such as alcohol and acetaldehyde

$2M + 2\,C_2H_5OH \rightarrow H_2 + 2C_2H_5OM$ (metal ethoxide)

$2M + HC \equiv CH \rightarrow H_2 + M - C \equiv C - M$ (alkali metal acetylide)

Alkali metal hydroxides are strong basic. Basic character increases from LiOH to CsOH

$LiOH < NaOH < KOH < RbOH < CsOH$.

As metal ion size increases down the group distance between metal ion and OH group increases. Thus more basic hydroxides down the group also thermal stability of hydroxide increases down the group.

iii) Reaction with hydrogen:

Hydrogen reacts with alkali metals to form hydride M^+H^-. Reactivity increases down the group as electro positive character increases down the group. And thermal stability decreases and heat of formation decreases down the group.

Hydrides liberate hydrogen at anode on electrolysis. Therefore they are used as reducing agent.

$LiH(s) + H_2O \rightarrow LiOH(aq) + H_2(g)$

$NaH + CH_3OH \rightarrow CH_3ONa + H_{2(g)}$

iv) Reaction with halogens

The alkali metals combine readily with halogens(X_2) forming halides

$2M + X_2 \rightarrow 2M^+X^-$. The ease of formation of halides increases down the group

$Li < Na < K < Rb < Cs$

Reactivity of halogen towards particular alkali metal follows the order

$F_2 > Cl_2 > Br_2 > I_2$

Except halides of Li all are ionic and are soluble in water.

K, Rb, C forms simple and mixed polyhalides because of large size e.g CsI_3, KI_3, CsI_2Cl, $RbIBr_2$, $RbClI_4$. Polyhalides of Cs are thermally more stable.

Melting point nad boiling point of particular alkali metal follow the order Fluorides > Chlorides > Bromides > Iodides.

Lithium halides LiBr and LiI are covalent compound.

LiF is soluble in non-polar solvents like kerosene.

v) Solubility in liquid ammonia

Alkali metals dissolves and form solution in liquid ammonia. When alkali metals are dissolved in liquid ammonia, there is a considerable expansion in total volume hence such solutions are called expanded metals.

$M \rightarrow M^+ + \text{electron}$

$M^+ + xNH_3 \rightarrow [M(NH_3)_x]^+$ (Ammoniated metal ion)

Electron + yNH_3 -- > $[e(NH_3)_y]^-$ (Ammoniated electron)

Colour of such solution is blue . Solution is paramagnetic and has electrical conductivity due to presence of unpaired electron in the cavities of ammonical solution and ammoniated cations and electrons respectively.

The free ammoniated electrons make the solution a very powerful reducing agent. Thus ammonical solution of an alkali metal is preferred as reducing agent than its aqueous solution because in aqueous solution evolution of hydrogen from water takes place (thus H_2O acts as a oxidizing agent). While its solution in ammonia is quite stable

vi) Reaction with oxoacids

Alkali metal hydroxide being basic in nature react with oxoacid (such as H_2CO_3), H_3PO_4 HNO_3 , H_2SO_4 etc.) to form different slats such as metal carbonates, bicarbonates, sulphates, nitrates, etc.

Alkali metal carbonates and bicarbonates are highly stable towards heat and their stability increases down the group, since electropositive character increases from Li to Sc. However Li_2CO_3 is less stable and readily decomposes to form oxide.

$Li_2CO_3 \rightarrow Li_2O + CO_2$

Alkali metal bicarbonates on heating decompose to give respective carbonates

$2MHCO_3 \rightarrow M_2CO_3 + CO_2 + H_2O$

All carbonates and bicarbonates are water soluble. Their solubility increases down the group since their lattice energy decreases more rapidly than their hydration energy in the group.

Alkali metal nitrates (MNO_3) decompose on strong heating to corresponding nitrite and O_2 except $LiNO_3$ which decomposes to its oxides

$2NaNO_3 \rightarrow 2NaNO_2 + O_2$

But $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

ANOMALOUS BEHAVIOUR OF LITHIUM

Lithium, the first member of alkali metals differs in many properties from the other alkali-metals due to the following reasons:

i) Li has smallest atomic and ionic size in the group
ii) Li^+ has highest polarizing power in its group which makes its compounds covalent
iii) Li has highest ionization energy, high heat of hydration, highest electro-negativity or minimum electropositive character in its group.
iv) Li does not have d-orbitals also.

Difference between lithium and other alkali metals

i) Lithium is harder and higher than other alkali metals due to strong metallic bonding.
ii) Its m.pt. And b.pt are higher than the rest of alkali metals
iii) Li on burning in air or oxygen forms monoxide while other alkali metals form higher oxides like peroxides and superoxides
iv) Li forms nitride with nitrogen whereas other alkali metals do not $6Li + N_2 \rightarrow 2Li_3N$
v) Some lithium salts like LiF, Li_2CO_3 and Li_3PO_4 are sparingly soluble in water where as corresponding slats of other alkali metals are freely soluble
vi) Li form imide (LiNH) with ammonia while other alkali metals form amides (MNH_2)
vii) $LiHCO_3$ does not exist as solid but it occurs in solution. Other alkali metals bicarbonates are known in solid state.
viii) Unlike other alkali metals Li does not form alum

Similarities between and magnesium or diagonal relationship between lithium and magnesium

Lithium and magnesium resemble in number of properties due to similarity in their atomic and ionic size. The properties of resemblance are as follows

i) Both Li and Mg form monoxides Li_2O and MgO on heating with air or oxygen.

ii) Both Li and Mg form ionic nitrides when heated in nitrogen
$6Li + N_2 \rightarrow 2Li_{3N}$
$3Mg + N_2 \rightarrow Mg_3N_2$

iii) Hydroxides, carbonates and nitrates of both Li and Mg decomposes on heating to yield respective oxide
$2LiOH \rightarrow Li_2O + H_2O$
$Mg(OH)_2 \rightarrow MgO + H_2O$
$Li_2CO_3 \rightarrow Li_2O + CO_2$
$MgCO_3 \rightarrow MgO + CO_2$
$4LiNO_3 \rightarrow 2Li_2 + 4NO_2 + O_2$
$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$

iv) Fluorides, carbonates, oxalates and phosphates of both metals are sparingly soluble in water.

v) Both LiCl and $MgCl_2$ are deliquescent salts.

SOME IMPORTANT COMPOUNDS OF ALKALI METALS

SODIUM CHLORIDE, NaCl (Common salt)

NaCl obtained from sea water may have impetrates like $CaSO_4$, Na_2SO_4, $CaCl_2$, $MgCl_2$ etc. $MgCl_2$ and $CaCl_2$ are deliquescent in nature (absorbs moisture from air) hence impure common salt gets wet in rainy reason. Pure NaCl can be prepared by passing HCl gas into saturated solution of commercial salt. Pure salt gets precipitated due to common ion effect.
NaCl is used as table salt
NaCl is used in preparation of number of compounds such as Na_2CO_3, NaOH, Na_2O_2 etc

SODIUM HYDROXIDE, NaOH (CAUSTIC SODA)
Sodium hydroxide is known as caustic soda, since it breaks down the protein of skin to a pasty mass.

PREPARATION

1. **Causticization process (Gossage process)**

This process involves heating of sodium carbonate with milk of lime
$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons CaCO_3 \downarrow + 2NaOH$

2. **Electrolysis of NaCl**

Electrolysis of saturated aqueous solution of NaCl gives NaOH , Cl_2 and H_2

$$NaCl(aq) \xrightarrow{electrolysis} Na^+ + Cl^-$$

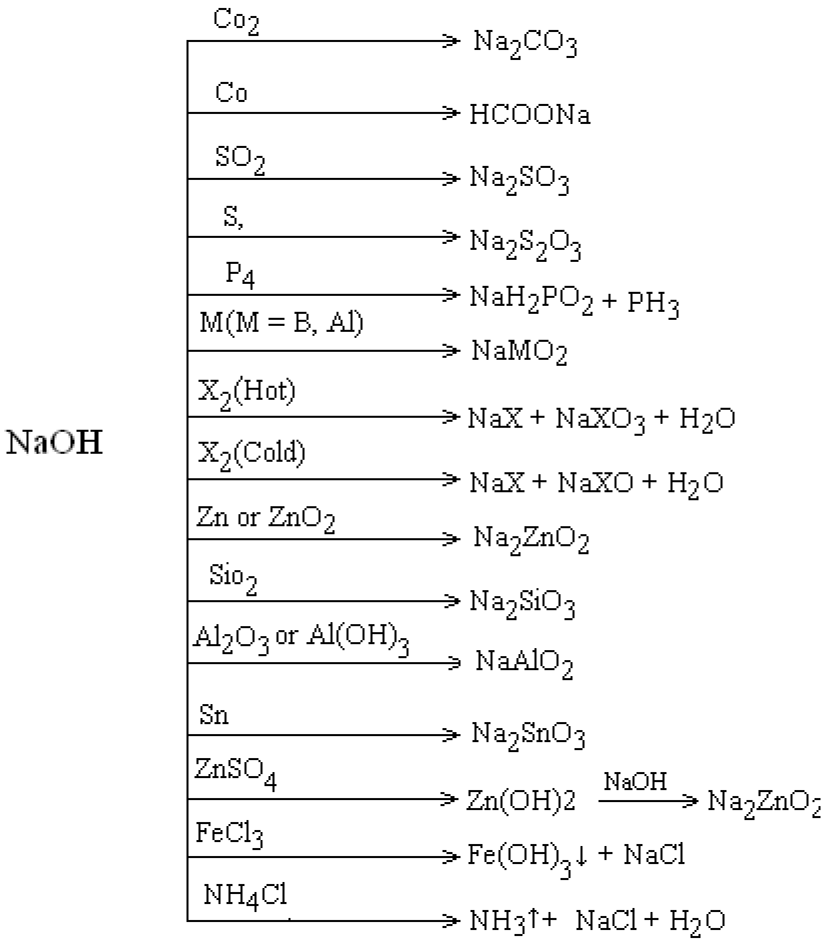
At anode: $2Cl^- \rightarrow Cl_2 + 2e^-$
At cathode : $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$
$Na^+ + OH^- \rightarrow NaOH$
Cl_2 gas, one of the byproduct reacts with NaOH to form other byproduct
$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$

3. **Porous diaphragm process (Nelson cell process)**
In this process a perforated cathode made up of steel lined up with asbestos is used. In this process Cl_2 formed at anode is taken out so that extent of impurities in NaOH is quite low

4**. Castner-kellner cell (Mercury cathode process)**
This process involves the electrolysis of conc. Brine solution in such a way so that reaction between NaOH and Cl_2 does not takes place. In this process three compartments are made in electrolytic cell and mercury used as cathode moves freely from one compartment to another. Graphite rods are used as anode.

Properties
NaOH is deliquescent, white crystalline solid which absorbs moisture and carbon dioxide from atmosphere to form aq.NaOH layer around pellet first and finally white powder of Na_2CO_3.
$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$
NaOH dissolves readily in water to yield higher alkaline solution which is corrosive, soapy in touch and bitter in test.
Uses :
NaOH is widely used in soap industry, paper industry, textile industry (for mercerization of cotton)
It is used in the manufacture of dyes and drugs
NaOH is used for absorbing acids and gases, in petroleum refining and as a regent in laboratories.

Chemical reactions of NaOH



SODIUM CARBONATE, Na_2CO_3 (WASHING SODA)

Sodium carbonate exists in various forms such as:

Na_2CO_3 - soda ash or light ash

$Na_2CO_3 . H_2O$ - Monohydrate, widely used in glass manufacturing

$Na_2CO_3 . 7H_2O$ - Hepta hydrate

$Na_2CO_3 . 10H_2O$ - Washing soda or sal soda (used in soap and detergents)

PREPARATION

Sodium carbonate is manufactured by Solvay process which is efficient and economic. In this process compounds used as raw material are brine (NaCl), NH_3 and $CaCO_3$

Solvay process involves following reaction

$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$ (ammonium bicarbonate)

$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$

$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$ (at 150^{O}C)

CO_2 is obtained by decomposition of $CaCO_3$

$CaCO_3 \rightarrow CaO + CO_2$ (at 1100^{O}C)

CaO forms slaked lime with water which decomposes NH_4Cl to ammonia thus NH_3 is recycled.

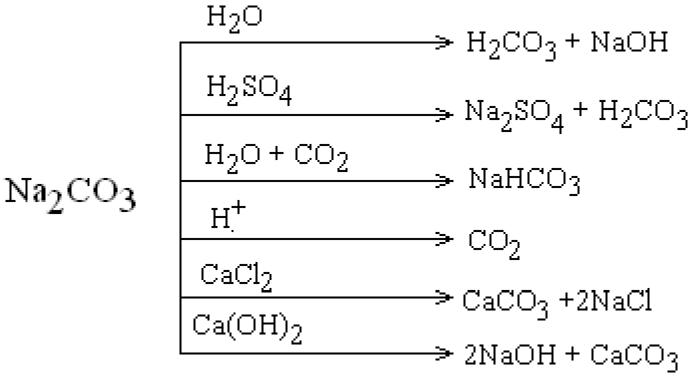
$CaO + H_2O \rightarrow Ca(OH)_2$

$Ca(OH)_2 + 2NH_4Cl \rightarrow 2NH_3 + 2H_2O + CaCl_2$

PROPERTIES

Sodium carbonate is a white crystalline solid which readily dissolves in water. Its solubility decreases with increase in temperature.

Chemical reactions of Na_2CO_3



Uses

Sodium carbonate is used in laundries as washing soda
It is also used to remove hardness of water
Na_2CO_3 is used to manufacture glass, caustic soda etc
It is used in petroleum refining and in textile industry

SODIUM BICARBONATE, $NaHCO_3$ (BAKING SODA)

Preparation:

Sodium bicarbonate or sodium hydrogen carbonate is obtained as intermediate compound in Solvay process

It can also be prepared by passing CO_2 through solution of sodium carbonate

$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$

Properties

$NaHCO_3$ on heating decomposes to produce bubbles of CO_2 which make the cakes and pastries fluffy

$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$

It is amphiprotic i.e. it can acts as H^+ donor as well as H^+ acceptor

$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

USES

$NaHCO_3$ is used in the preparation of baking powder

[Baking powder = $NaHCO_3$ (30%) + $Ca(H_2PO_4)_2$ (10%) + Starch (40%) + $NaAl(SO_4)_2$]

It is used in fire extinguisher : $NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$

Such kind of fire extinguisher are known as soda-fire extinguisher

It is used as antacid and mild antiseptic

MICROCOSMIC SALT, $Na(NH)_4HPO_4 . 4H_2O$

Microcosmic salt exists in colourless crystalline solid form. It is prepared by dissolving NH_4Cl nad Na_2HPO_4 in 1:1 ,molar ratio in hot water.

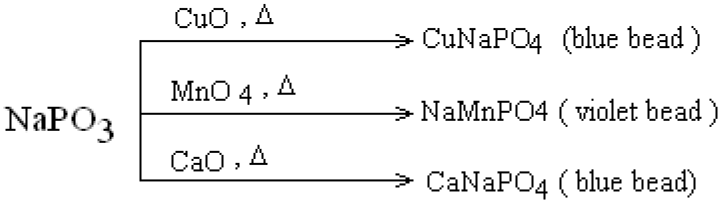
$NH_4Cl + N_2HPO_4 \rightarrow Na(NH_4)HPO_4 + NaCl$

USES

It is used for performing ‘bead test’ (like borax) for detecting colour ions in qualitative analysis.

On heating microcosmic salt form $NaPO_3$ which form coloured beads of orthophosphates with oxides of transition metal and cloudy bead with SiO_2

$Na(NH_4) \rightarrow NaPO_3 + H_2O + NH_3$



BIOLOGICAL SIGNIFICANCE OF SODIUM AND POTASSIUM

Na^+ and K^+ are essential for proper functioning of human body
Different ratio of Na^+ to K^+ inside and outside cells produce an electrical potential across the cell membrane which is essential for functioning of nerve and muscle cells.
These ions activate many enzymes
These ions primarily help in transmission of nerve signals in regulating the flow of water across cell membrane, transport of sugars and amino acids into cells, etc.

GROUP –II (ALKALINE EART METAL)

1. Electronic configuration : ns^2
2. Physical state: Grayish white luster when freshly cut, malleable and ductile.
3. Atomic and ionic radii, volume : Small compared to Group_I (due to extra nuclear charge). Atomic and ionic radii increases from Be to Ra. Volume increases from Be to Ra
4. Density: Greater than alkali metals. Do not show regular trend due to difference in crystal structure. Decreases from Be to Ca and increases upto Ra
5. Melting point and boiling points: Decreases from Be to Ba
6. Metallic character : Less compared to group-I. Increases from Be to Ra
7. Conductivity: Good conductor
8. Oxidation state : +2 oxidation state
9. Ionization enthalpy: Greater than alkali metals. Decreases down the group
10. Hydration of ions: Smaller the size of cation, greater hydration
$$Be^{+2} > Mg^{+2} > Ca^{+2}, Sr^{+2} > Ba^{+2} > Ra^{+2}$$
11. Hydration energy : Hydration energy decreases from Be^{2+} to Ra^{2+}, Number of molecules of water of crystallization decreases as ion becomes larger
12. Flame colouration:

Ca	Brisk red
Sr	Crimson red
Ba	Grassy green
Ra	Crimson

Beryllium and Magnesium do not impart any colour to the flame as their atoms are smaller and consequently require higher energies for excitation of the electrons to higher levels.

13. Strong reducing agent but weaker as compared to Group-I
14. Complex formation: Be^{+2} being smallest in size shows a great tendency to form complexes such as $[BeF_3]^-$, $[BeF_4]^{-2}$ Tendency of other ions to form complexes decrease with the increase of size of M^{2+} ion
15. Action of air: the reactivity of oxygen increases as we go down the group since their electropositive character increases. The tendency to form peroxides increases down the group.
16. Nature of hydroxide and halide: Group-II hydrides are all reducing agent CaH_2, SrH_2 and BaH_2 are ionic and BeH_2 are ionic and BeH_2 and MgH_2 are covalent. Halides of Group-II are ionic and ionic character increases down the group. Solubility of halides in water decreases from Be to Ba
17. Nature of oxide and hydroxide: Alkaline earth metals are basic in nature. Their basic strength is $BaO > SrO > CaO > BeO$.
    Basic character of Group II hydroxide is $Ba(OH)_2 > Sr(OH)_2 > Ca(OH)_2 > Mg(OH)_2 > Be(OH)_2$
18. Nature of carbonates and bicarbonates: Solubility of carbonates decreases down the group from Be to Ba. Thermal stability of carbonates of alkaline earth metal increases as we go down group from Be to Ba

CHEMICAL PROPERTIES

Due low ionization energy and high negative value of standard electrode potential alkaline earth metals are highly reactive.

Since ionization energy decreases and electrode potential become more negative therefore reactivity of alkaline earth metal increases from Be to Ba.

Alkaline earth metals have higher ionization energy than corresponding alkali metals

i) Reaction with oxygen and air

Since electropositive nature of increases down the group reactivity with oxygen increases.

Beryllium metal is relatively unreactive but readily react with oxygen in powder form

$2Be + O_2$ (air) → $2BeO$

Ba and Sr form peroxide on heating with excess of oxygen. The tendency to form peroxide increases as we move down the group, since larger cation stabilizes large anion

$$2BaO + O_2 \xrightarrow{773K} 2BaO_2$$

CaO_2 can also be prepared as the hydrate by treating $Ca(OH)_2$ with H_2O_2 and then dehydrating the product.

$Ca(OH)_2 + H_2O_2$ → $CaO_2 . 2H_2O$

Crude MgO_2 has been made using H_2O_2 but peroxide of Beryllium is not known

Peroxides are white ionic solids containing $[O\text{-}O]^{2-}$ ion and can be regarded as salt of the weak acid hydrogen peroxide

Nature of alkaline earth metal oxides and peroxide

Oxides of Alkaline earth metals are basic in nature. Their basic character increases decreases the group

BaO > SrO > CaO > MgO > BeO

Size of Be^+ is small thus BeO is covalent in nature and occurs in polymeric form. Hence BeO has higher melting point and is harder than other oxides

On heating peroxides liberate oxygen and form monoxide MO. Their thermal stability increases with increasing cation size on moving down the group.

Formation of nitrides

All alkali metals burn in dinitrogen to form ionic nitrides of the formula, M_3N_2

(This is in contrast with alkali metal where only Li form Li_3N_2)

Their ionic character increases with the increase in the size of metal ion down the group.

Be_3N_2 being covalent is volatile while other nitrides are crystalline solids. All these nitrides on heating liberate NH_3 and on reacting with water.

$$Be_3N_2 \overset{\Delta}{\rightarrow} 3Be + N_2$$

$$Ca_3N_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2NH_3$$

ii) **Reaction with water (formation of hydroxides)**

Alkali earth metals are less reactive with water as compared to alkali metals. Their reactivity with water increases down the group. Be. Does not react with water at all, magnesium reacts only with hot water while other metals Ca, Sr and Ba react with cold water.

Order of the reactivity with water Ba > Sr > Ca > Mg

$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$ or $Mg + H_2 \rightarrow Mg(OH)_2 + H_2$

Mg form a protective layer of oxide, it does not readily react, and reacts only on removal of oxide layer

Nature of Hydroxides: $Be(OH)_2$ is amphoteric, but the hydroxides of Mg, Ca Se and Ba are basic. Basic strength increases down the group. Solution of $Ca(OH)_2$ is called lime water and $Ba(OH)_2$ is called barty water. Aqueous suspension of $Mg(OH)_2$ is called milk of magnesia and is used as antacid

iii) **Reaction with hydrogen (Formation of hydrides)**

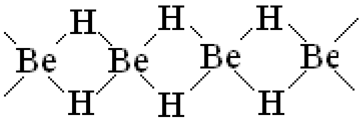
All alkaline earth metals except Be combine with hydrogen to form hydride MH_2 on heating.

CaH_2 is called hydrolith and is used for production of H_2 by action of water on it.

Nature of hydrides

Alkaline earth metal hydrides are reducing agent and are hydrolysed by water and dilute acids with evolution of hydrogen $CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$

CaH_2, SrH_2 and BaH_2 are ionic and contain the hydride ion H^-. beryllium and magnesium hydride are covalent compounds having polymeric structure in which hydrogen atom between beryllium atoms are held together by three centre-two electron bond



The structure involves three-centre bonds formation in which a ‘banana-shaped’ molecular orbital (or three-centre bond) covers three atoms Be … H … Be, and contains two electrons (this is called a three-centre two electron bond). This is an example of a cluster compound which is ‘electron deficient’

iv) **Reaction with carbon**

Alkali earth metal except Be or their oxides on heating with carbon form carbides of general formula MC_2

$$Ca + 2C \xrightarrow{1100^{O}C} CaC_2$$

$$CaO + 3C \xrightarrow{2000^{O}C} CaC_2 + CO$$

All the carbide are ionic in nature and have NaCl type structure. On treatment with water they liberate acetylene CH≡CH. Thus they are called as acetylides
On heating MgC_2 it changes to Mg_2C_3 and reacts with water to liberate propyne
On heating BeO with C at 1900-2000^{O}C a brick red coloured carbide of formula Be_2 C is formed, this has anti-fluotite structure

On heating CaC_2 in an electric furnace with atomospheric dinitrogen at 100^{O}C, calcium cyanide CaNCN is formed, which is widely used as fertilizer
$CaC_2 + N_2 \rightarrow CaNCN + C$
BaC_2 also reacts with N_2 but forms cyanide $Ba(CN)_2$ and not cyanamide

v) Action of halogen

All Group 2 elements forms halides of MX_2 type either by the action of halogen acid (HX) on metals, metal oxides, hydroxide or carbonates or directly heating metal with halogen

$$M + 2HX \rightarrow MX_2 + H_2$$
$$MO + 2HX \rightarrow MX_2 + H_2O$$
$$M(OH)_2 + 2HX \rightarrow MX_2 + 2H_2O$$
$$MCO_3 + 2HX \rightarrow MX_2 + CO_2 + H_2O$$
$$M + X_2 \xrightarrow{\Delta} MX_2$$

Nature of Halides

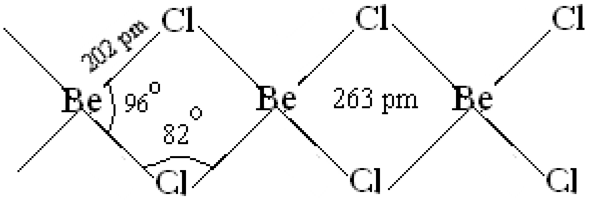
Beryllium halides are covalent and are soluble in organic solvents, due to small size and high charge density
The halides of all other alkaline earth metals are ionic. Their ionic character, however, increases as the size of the metal ion increases
They are hygroscopic, and fume in air due to hydrolysis. On hydrolysis, they produce acidic solution
Some of the halides are hydrated, but all chlorides are found in hydrated form e.g. $BeCl_2.4H_2O$, $MgCl_2.6H_2O$ etc.

Solubility of Halides

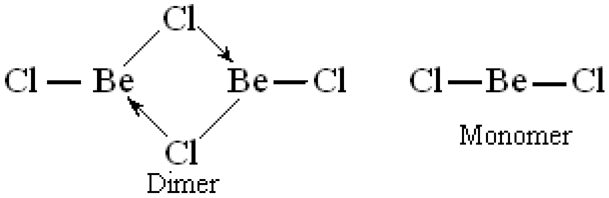
The halides of Beryllium (except BeF_2) being covalent in nature are insoluble in water (soluble in organic solvents) where as halides of other alkaline earth metals except fluorides are ionic solids and thus water soluble. The solubility in water decreases from Be to Ba due to the decrease in the hydration energy. The fluorides of alkaline earth metals (MF_2) except BeF_2 are insoluble in water owing to large values of lattice energy BeF_2 is readily soluble in water because of smaller size of Be^{2+}, large hydration energy is released which overcomes the lattice energy.

Structure of $BeCl_2$

In solid phase $BeCl_2$ has polymeric structure with halogen bridges in which a halogen atom bonded to one beryllium atom uses a lone pair of electrons to form a coordinate bond to another beryllium atom as shown below



In vapour phase it tends to form a chloro bridge dimer which dissociates into the liner triatomic monomer at high temperature (nearly 1200K)



vi) Reaction with acids

All alkali metals react with acids liberating H_2

$M + 2HCl \rightarrow MCl_2 + H_2$ (M = BE, Mg, Ca, Sr, Ba)

Since basic character of these metal increases down the group, their reactivity towards acid increases from Be to Ba. Be reacts slowly with acids, Mg reacts faster rate while Ca, Sr and Ba reacts explosively with acids

$Be + 2NaOH + 2H_2O \rightarrow H_2 + Na_2[Be(OH)_4]$ (sodium beryllate)

Mg, Ca, Sr and Ba do not reacts with NaOH. Illustrate basic character of group 2 elements increases on descending the group.

Be is redered passive with HNO_3 . As HNO_3 is strong oxidizing agent forms a layer of oxide on metal which protects the inner core of metal

vii) Solubility in liquid ammonia

All metals of group 2 dissolves in liquid ammonia to form bright blue coloured solution

$M \rightarrow M^{2+} + 2e^-$

$2NH_3 + 2e^- \rightarrow 2NH_2^- + H_2$

$M^{2+} + 2NH_2^- \rightarrow M(NH_2)_2$

Evaporation of ammonia from solution gives hexaammoniates of metal which slowly decomposes to give amides

$M(NH_3)_6 \rightarrow M(NH_2)_2 + 4NH_3\uparrow + H_2\uparrow$

Concentrated solution of meatl in ammonia are bronze coloured due to formation of metal clusters.

viii) Alkaline earth metal nitrates are prepared in solution and can be crystallized as hydrated salts by the action of HNO_3 on oxides, hydroxides and carbonates

Beryllium nitrate is unusual because it forms basic nitrate [$Be_4O(NO_3)_6$] in addition of the normal salt.

ix) Sulphates

The sulphates of alkaline earth metals (MSO_4 are prepared by the action of sulphuric acid on metals, metal oxides, hydroxides and carbonates.

Nature of sulphates

Sulphates of Be, Mg, and Ca are crystallize in the hydrated form where as sulphates of Sr and Ba crystallize without water of crystallization.

The solubility of sulphates decreases down the group mainly due to decrease in hydration energy from Be^{2+} to Ba^{2+} . thus high solubility of $BeSO_4$ and $MgSO_4$ can be attributed to high hydration energies of smaller Be^{2+} and Mg^{2+} ions.

Because of large size of sulphate ion lattice energy remains constant down the group

The sulphate decomposes on heating, giving the oxides:

$MgSO_4 \rightarrow MgO + SO_3$

More basic the metal, more stable is the sulphate. Basic nature of metals increases down the group thus thermal stability of sulphates increases on descending the group.

x) Carbonates and Bicarbonates

Carbonates of alkaline earth metals can be produced by passing CO_2 through their hydroxides

$M(OH)_2\ (aq) + CO_2(g) \rightarrow MCO_3(s) + H_2O(l)$

Alkaline earth metal carbonates are ionic but beryllium carbonates is unusual because of hydrated ion $[Be(H_2O)_4]^{2+}$ rather than Be^{2+}. The solubility of carbonates decreases down the group from Be to Ba. $MgCO_3$ is sparingly soluble in water but $BaCO_3$ is almost insoluble because hydration energy of metal cations decreases from Be^{2+} to Ba^{2+}. However all carbonates are more soluble in presence of CO_2 due to formation of corresponding bicarbonates

$CaCO_3(s) + CO_2(s) + H_2O\ (g) \rightarrow Ca(HCO_3)_2\ (g)$

Thermal stability increases as we go down the group because size of the positive ion increases and polarizing ability decreases, causing more stability. If positive ion is small such as Be which distort electron cloud of carbonate ion makes $BeCO_3$ easily thermal decomposable.

Bicarbonates of alkaline earth metal do not exists in solid state. They exists in solution only. On heating, bicarbonates decomposes to carbonates with evolution of CO_2

$$M(HCO_3)_2 \overset{\Delta}{\rightarrow} MCO_3 + CO_2 + H_2O$$

ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium when compared to rest of the members anomalous behavior, mainly because of the following reasons

Small size of atom or its ion

Highly ionization energy, electronegativity and charge density, absence of d-orbital

Important difference between Beryllium and rest of the members

Beryllium is harder than other members

Beryllium does not reacts with water, even at elevated temperatures

It has higher boiling and melting points as compared to other members

It do not combine directly to form hydride, whereas other metals do so

Beryllium forms covalent compounds while other members form ionic compounds

With water, beryllium carbide gives methane while carbides of other members give acetylene

BeO is amphoteric in nature while oxides of other alkaline earth metals are basic

DIAGONAL SIMILARITIES OF BERYLLIUM AND ALUMINIUM

Due to diagonal relationship existing between beryllium and aluminium, they both show some similarities

Both Be and Al form covalent compounds

On treatment with concentrated HNO_3, both beryllium and aluminium are rendered passive.

Both form complexes

BeO and Al_2O_3 are amphoteric. They dissolve in acid as well as in base

$BeO + 2HCl \rightarrow BeCl_2 + H_2O$

$Be + 2NaOH \rightarrow Na_2BeO_2 + H_2O$

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$
$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2$ (sodium metaaluminate) + H_2O
The carbides of both B and Al liberate methane when reacts with water
$Be_2C + 2H_2O \rightarrow 2BeO + CH_4$
$Al_4C_4 + 6H_2O \rightarrow 2Al_2O_3 + 3CH_4$
Both the metals are weakly electropositive in nature
Beryllium and aluminium form fluoro complex anions $[BeF_4]^{2-}$ and $[AlF_6]^{3-}$ in aquepos solution. Stable fluoro complexes in solution are not formed by other metals of the group.
Beryllium dissolves in alkalies to give beryllate ion $[Be(OH)_4]^{2-}$ while aluminium dissolves to give $[Al(OH)_6]^{3-}$
$BeCl_2$ like Al_2Cl_6 has a bridged polymeric structure
Similar solubility are observed in halides of both beryllium and aluminium.

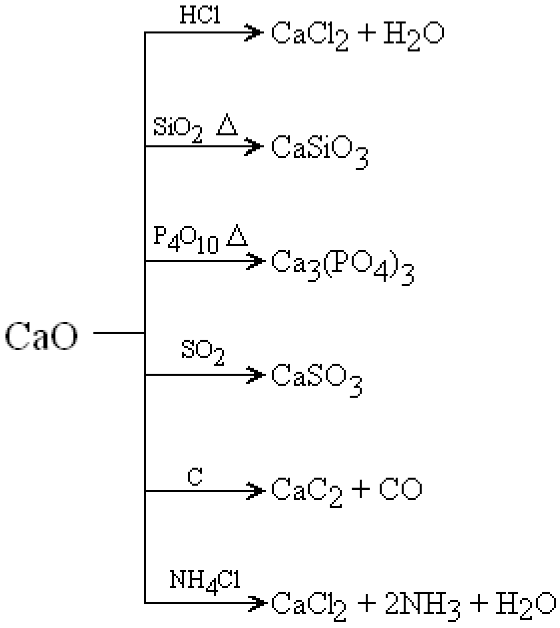
SOME IMPORTANT COMPOUNDS OF ALKALINE EARTH METALS

CALCIUM OXIDE (CaO)
Quick lime (CaO) is prepared by strong heating of lime stone ($CaCO_3$) in lime kiln. Smaller piece of limestone are introduced from the top and heating is done from lower end. Lime stone decomposes at about 1000°C to give calcium oxide
$CaCO_3 (s) \rightarrow CaO (s) + CO_2(g)$ at 1000°C ; $\Delta H = 180$ kJ/mol
The temperature of kiln is not allowed to rise above 1000°C otherwise silica SiO_2 present as impurity in lime stone would react with CaO to form slag $CaSiO_3$

Properties
Calcium oxide is a white amorphous solid. On heating, quick lime CaO glows at high temperature. This glow of white dazzling light is called lime light. Quick lime melts at 2870K or 2597°C
On exposure to the atmosphere, it absorbs moisture and carbon dioxide to finally give calcium carbonate
When water is poured over quicklime, a lot of heat is produced giving out steam with a hissing sound. This is called slaking of lime and is due to the following reaction.
$CaO + H_2O \rightarrow Ca(OH)_2$; $\Delta H = -65$ kJ/mole
Quick lime when slaked with caustic soda gives a solid called sodalime
Uses
For white washing of buildings
For the manufacture of bleaching powder, glass, calcium carbide, soda ash, etc
For tanning of leather.
As a fertilizer for acidic soil
In building and construction industry as an important raw material.

Chemical reactions of calcium oxide

CaO is basic oxide and hence reacts with acids and acidic oxides to form salts



CALCIUM CARBONATE, ($CaCO_3$)

Calcium carbonate occurs abundantly as dolomite, $MgCO_3$. $CaCO_3$, a mixture of calcium and magnesium carbonates. It is the chief constituent of shells of sea animal and also of bones along with tricalcium phosphate.

Preparation

Laboratory preparation

Calcium carbonate is prepared in the laboratory by passing carbon dioxide gas into lime water

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

Calcium carbonate is also obtained by adding the solution of a soluble carbonate to soluble calcium salt

$CaCl_2 (aq) + Na_2CO_3 (aq) \rightarrow CaCO_3 + 2NaCl(aq)$

The resulting precipitate is filtered, washed and dries. The product obtained is known as precipitated chalk.

Excess of carbon dioxide should be avoided since this leads to the formation of calcium hydrogen carbonate

$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$

Properties

Calcium carbonate is a white fluffy powder. It is almost insoluble in water

Action of heat

When heated to 1200K, it decomposes to give lime and carbon dioxide

With acid

Calcium carbonate reacts with dilute acids to liberated carbon dioxide

Uses

In the manufacture of quick lime

As a building material in form of marble

As a raw material for manufacture of sodium carbonate in Solvay process

In the extraction of metals such as iron (as flux)

As a constituent of tooth paste, an antacid, chewing gum and filler in cosmetics.

PLASTER OF PARIS, ($CaSO_4 . ½ H_2O$)

Calcium sulphate with half molecule of water per molecule of the salt (hemi-hydrate) is called plaster of paris

Preparation

It is preparation

It is prepared by heating gypsum ($CaSO_4 . 2H_2O$) at $120^{O}C$ in in rotary kilns, where it gets partially dehydrated.

$$2(CaSO_4 \cdot H_2O) \xrightarrow{120^{O}C} 2(CaSO_4) \cdot H_2O + 3H_2O$$

The temperature should be kept below $140^{O}C$otherwise further dehydration will take place resulting in anhydrous $CaSO_4$ which is known as dead burnt plaster because it loses the property of setting with water

Properties

It is a white powder. When mixed with water (1/3 rd of its mass), it evolves heat and quickly sets to a hard porous mass within 5 to 15 minutes. . During setting, a slight expansion (about 1%) in volume occurs so that it fills the mould completely and takes a sharp impression. The process of setting occurs as follows.

$$CaSO_4 \cdot \frac{1}{2}H_2O \xrightarrow{H_2O} CaSO_4 \cdot H_2O \xrightarrow{hardening} CaSO_4 \cdot 2H_2O$$

The first step is called the setting stage and the second, the hardening stage. The setting of plaster is catalyzed by sodium chloride, while it is reduced by borax, or alum

Use

For making casts in density, for surgical instruments, and toys, etc

In surgery for setting broken or fractured bones

In making statues, models and other decorative items

In construction industry

Cement

Cement is grayish, finally powder mixture of calcium silicates and aluminates along with small quantities of gypsum which sets into hard mass when mixed with water

This hardened stone-like mass resembles a natural rock mined on Isle of Portland, a famous building stone of England. Since then the name Portland cement is given to the product.

Composition of cement: The average composition of Portland cement is

Compound	Pecentage
CaO	50 – 60%
SiO_2	20 – 25 %
Al_2O_3	5 – 10%
MgO	1 - 3 %
Fe_2O_3	1 – 2%
SO_3	1 – 2%
Na_2O	1%
K_2O	1%

Raw materials

Raw material for the manufacture of cement are limestone provides lime , clay (provides both silica and alumina) and gypsum ($CaSO_4 . 2H_2O$). Small amount of magnesia (MgO) and iron oxide (Fe_2O_3) are also used for imparting colour to cement.

Setting of cement

Cement absorbs water on mixing to form a gelatinous mass. This sets to hard mass and is very resistant to pressure. This process is called the setting of cement. This process involves a complicated set of reaction of hydration and hydrolysis, leading to the formation of Si-O-Si and Si-O-Al chains

CALCIUM SULPHATE, ($CaSO_4.2H_2O$) – GYPSUM

It is found in nature as anhydride ($CaSO_4$) and gypsum ($CaSO_4.2H_2O$)

Preparation

It can be prepared by reacting any calcium salt with either sulphuric acid or a soluble sulphate

$CaCl_2 + H_2SO_4 \rightarrow CaSO_4 + 2HCl$

$CaCl_2 + Na_2SO_4 \rightarrow CaSO_4 + 2NaCl$

Properties

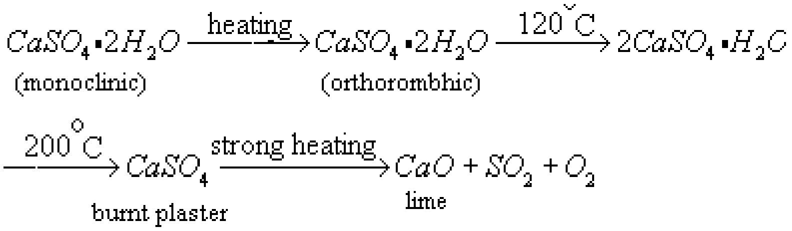
It is white crystalline solid. It is sparingly soluble in water

It dissolves in dilute acids

When strongly heated with carbon, it forms calcium sulphide

$CaSO_4 + 4C \rightarrow CaS + 4CO$

Gypsum when heated at different temperature gives burnt plaster and finally lime (CaO)



$$\underset{\text{(monoclinic)}}{CaSO_4\cdot 2H_2O} \xrightarrow{\text{heating}} \underset{\text{(orthorombhic)}}{CaSO_4\cdot 2H_2O} \xrightarrow{120^{\circ}C} 2CaSO_4\cdot H_2C$$

$$\xrightarrow{200^{\circ}C} \underset{\text{burnt plaster}}{CaSO_4} \xrightarrow{\text{strong heating}} \underset{\text{lime}}{CaO} + SO_2 + O_2$$

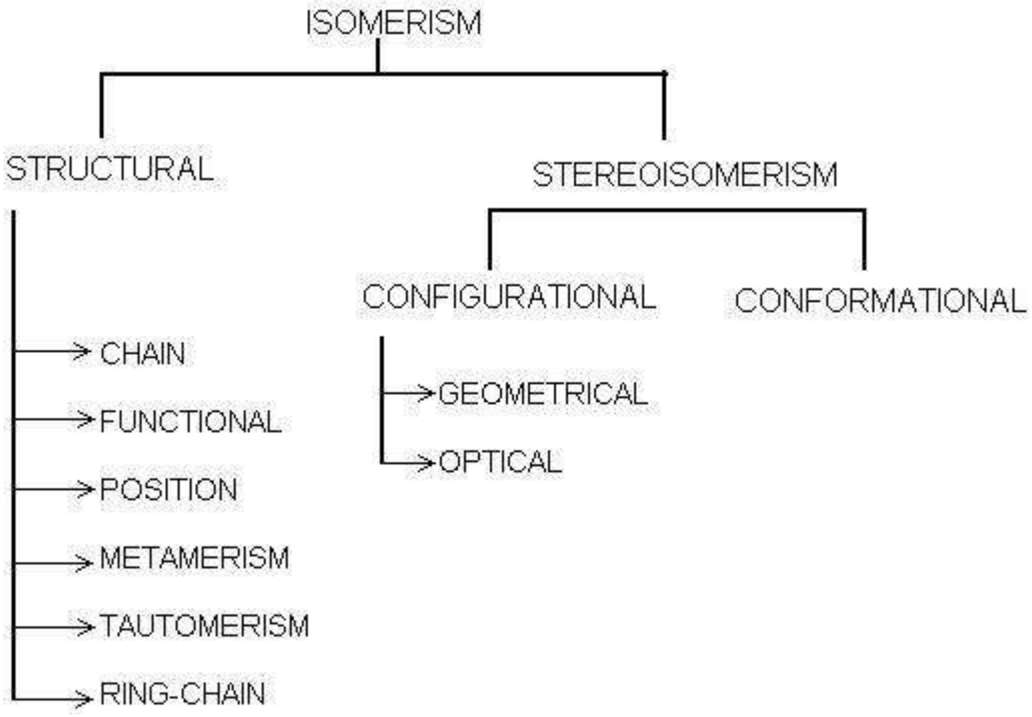
ALKALINE EARTH MATELS IN BIOLOGICAL ACTION

Biological role of Mg^{+} and Ca^{2+}

Mg^{2+} ions are concentrated in animal cells and Ca^{2+} are concentrated in the body fluids outside the cell. Mg^{2+} ion form a complex with ATP. They are also essential for the transition of impulse along nerve fibres. Mg^{2+} is an important constituent of chlorophyll, in the green parts of plants. Ca^{2+} is present in bones and teeth as apatite $Ca_3(PO_4)_2$ and the enamel on teeth as fluoroapatite $[3(Ca_3(PO_4)_2 . CaF_2]$, Ca^{2+} ions are important in blood clotting and are required to trigger the contraction of muscles and to maintain the regular beating of the heart.

ISOMERISM

- The phenomenon of existence of two or more compounds with same molecular formula but different properties (physical, chemical or both) is known as isomerism and the compound exhibiting this phenomenon are called isomers
- The term was used by Berzelius
- Isomerism are of two types



STRUCTURAL ISOMERISM:

- It is due to the difference in arrangement of atoms or groups within the molecule, without any reference to space.
- Structural isomers are compound having same molecular formula but different structural formula.
- These are of following types

(a) CHAIN ISOMERISM

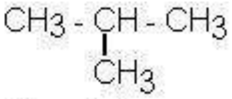
When the isomers have similar molecular formula but differ in nature of carbon chain are called chain isomers and phenomenon is known as chain isomerism.

Example:

C_4H_{10} (Butane) exists in two forms

$CH_3 - CH_2 - CH_2 - CH_3$

butane (n-butane)



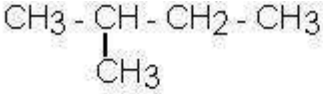
$CH_3 - \underset{\overset{|}{CH_3}}{CH} - CH_3$

2-methylpropane
(isobutane)

Pentane (C_5H_{12}) exists in three form

$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

pentane (n-pentane)



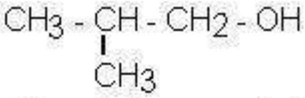
$CH_3 - \underset{\overset{|}{CH_3}}{CH} - CH_2 - CH_3$

2-methylbutane
(isobutane)

$C_4H_{10}O$

$CH_3 - CH_2 - CH_2 - CH_2 - OH$

Butan-1-ol



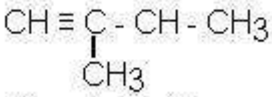
$CH_3 - \underset{\overset{|}{CH_3}}{CH} - CH_2 - OH$

2-methylpropan-1-ol

C_5H_8

$CH \equiv C - CH2 - CH2 - CH3$

pent-1-yne



$CH \equiv \underset{\overset{|}{CH_3}}{C} - CH - CH_3$

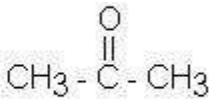
3-methylbut-1-yne

(b) FUNCTIONAL ISOMERISM

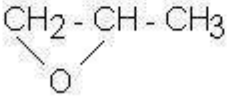
Compounds having same molecular formula but different functional group are known as functional isomers and the phenomenon is functional isomerism.

Examples

- Alcohol and ether ($C_nH_{2n+2}O$)
  C_3H_8O
  $CH_3 – CH_2 – CH_2\text{-}OH$: n-propyl alcohol
  $C_2H_5 – O – CH_3$: ethyl methyl ether
- Aldehydes, ketones, ethers etc. ($C_nH_{2n}O$)
  C_3H_6O
  $CH_3 – CH_2 – CHO$: propanal



$CH_3 - \overset{\overset{O}{\|}}{C} - CH_3$ propanone



: 1,2-epoxy propane

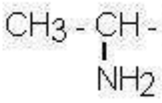
$CH_2 = CH - CH_2OH$: prop-2-en-1-ol
(allyl alcohol)

- Amines (Primary, secondary, tertiary)

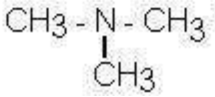
  C_3H_9N

  $CH_3 - CH_2 - CH_2 - NH_2$: propan -1- amine

  $CH_3\text{-}CH_2\text{-}NH\text{-}CH_3$: N-methylethene



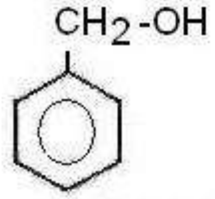
  $CH_3 - \underset{NH_2}{\underset{|}{CH}} - CH_3$: propane - 2 - amine



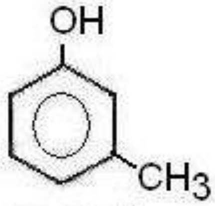
  $CH_3 - \underset{CH_3}{\underset{|}{N}} - CH_3$: N,N - Dimethy methanamine

- Alcohol, phenol and ethers

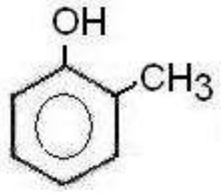
  C_7H_8O



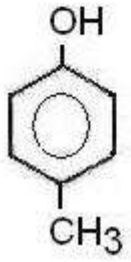
Benzyl alcohol



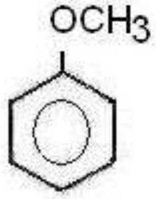
m- cresol



o - cresol



p- cresol



anisole

(c) POSITION ISOMERISM

It is due to the difference in the positions occupied by the particular atom or group (substituent) in the same carbon chain or due to different positions of double or triple bonds in alkenes and alkynes.

Example:

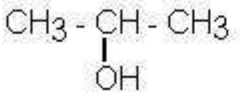
- C_4H_6

  $CH_3 - CH_2 - C \equiv CH$: But – 1 – yne

  $CH_3 - C \equiv C - CH_3$: But – 2 – yne

- C_3H_8O

  $CH_3 - CH_2 - CH_2 - OH$: propan – 1 – ol

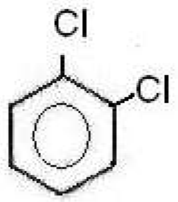


  $CH_3 - \underset{OH}{\underset{|}{CH}} - CH_3$ propan-2-ol

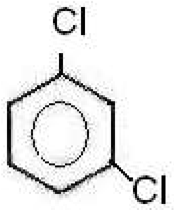
- C_4H_8

  $CH_3 – CH_2 – CH = CH_2$: But-1-ene

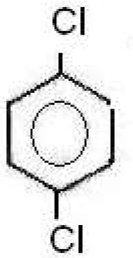
  $CH_3 – CH = CH – CH_3$: But – 2 – ene
- $C_6H_4Cl_2$



o-dichlorobenzene



m-dichlorobenzene



p-dichlorobenzene

Aldehydes, carboxylic acid and their derivatives do not exhibit position isomerism

(d) Metamerism

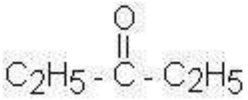
Metamers are the isomers which have same molecular formula but differ in nature of alkyl group, groups attached to the either side of the same functional group. This isomerism is shown by ethers, ketones, esters, secondary amines.

Examples

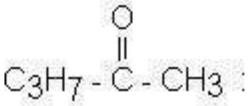
- $C_4H_{10}O$

  $C_2H_5 – O – C_2H_5$: Diethyl ether

  $C_3H_7 – O – CH_3$: Methyl propyl ether
- $C_5H_{10}O$



$C_2H_5 - \overset{\overset{O}{||}}{C} - C_2H_5$: Diethyl ketone



$C_3H_7 - \overset{\overset{O}{||}}{C} - CH_3$: Methyl propyl ketone

- $C_4H_{10}S$

  $C_2H_5 - S - C_2H_5$: Diethyl thio ether

  $C_3H_7 - S - CH_3$: Methyl propyl ketone
- $C_4H_{11}N$

  $C_2H_5 – NH – C_2H_5$: Diethyl amine

  $C_3H_7 – NH – CH_3$: Methyl propyl amine

(e) TAUTOMERISM

(Greek word : tauto = same ; meros = parts)

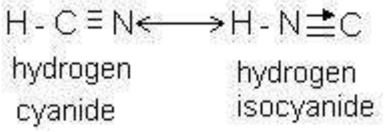
It was used by Laar in 1885

Tautomerism may be defined as the phenomenon in which a single compounds exists in two readily inter convertible structures that differ markedly in the relative position of at least one atomic nucleus generally hydrogen. The two different structures are known as tautomers of each other.

There are two types of tautomerism

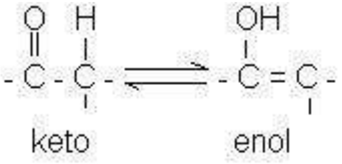
(i) Dyad system

If two hydrogen atom oscillates between two polyvalent atoms, linked together, then system is called dyad system.



(ii) Triad system

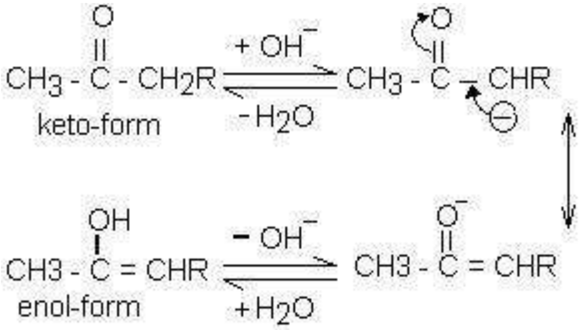
- If the hydrogen atom travels from first to third in a chain, the system is triad
- The most important type of triad system is keto-enol tautomerism keto-enol system



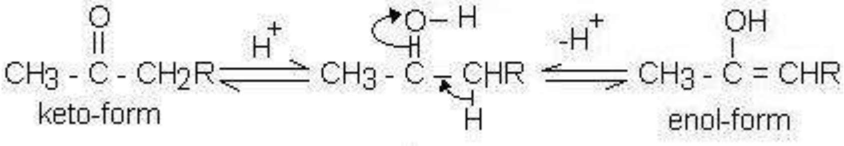
The keto form is more stable

Mechanism of tautomerism

(i) Base catalysed tautomerism

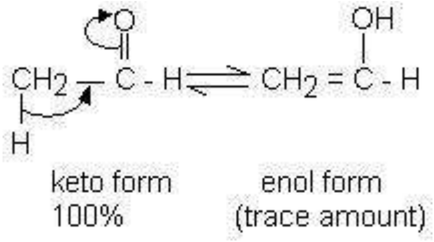


(ii) Acid catalysed tautomerism

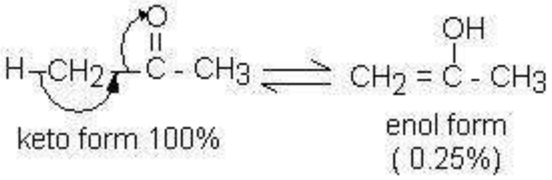


Examples of keto-enol system

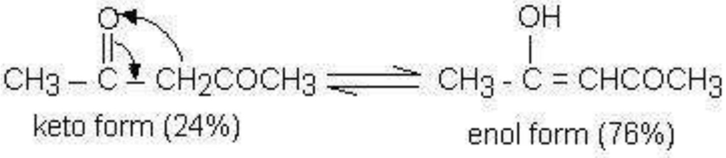
- Acetaldehyde



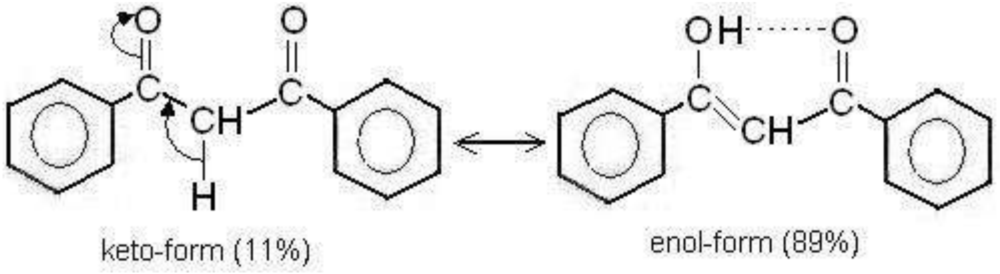
- Acetone



- Acetyl acetone



- Benzoyl acetophenone



Enolisation

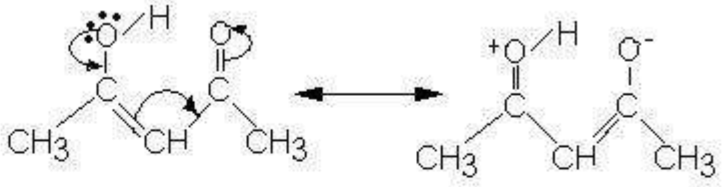
- The conversion of keto form into enol form is known as enolisation.
- The percentage of enol from has been found to increase in the order: Simple aldehydes and ketone < β keto ester < β diketones having phenyl group < phenols
- Enolisation is in order
  $CH_3COCH_3 < CH_3COCOOC_2H_5 < C_6H_5COCH_2COOC_2H_5 < CH_3COCH_2CHO < CH_3COCH_2CHO < CH_3COCH_2COCH_3 < C_6H_5COCH_2COCH_3 <$ phenoxide ion $< C_6H_5COCH_2COC_6H_5$

Composition of tautomeric mixture

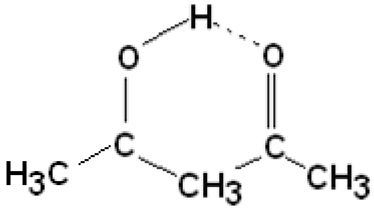
The relative amount of keto and enol form of tautomeric mixture depends upon their relative stabilities. In simple monocarbonyl compounds like acetaldehyde, acetone etc, the amount of enolic form is negligibly small because of comparatively lower stability.

However if enolic form is stabilized by intermolecular bonding, the amount of enolic form becomes higher. In 1,3-dicarbonyl compounds also called β-dicarbonyl compounds can be attributed to the following reasons.

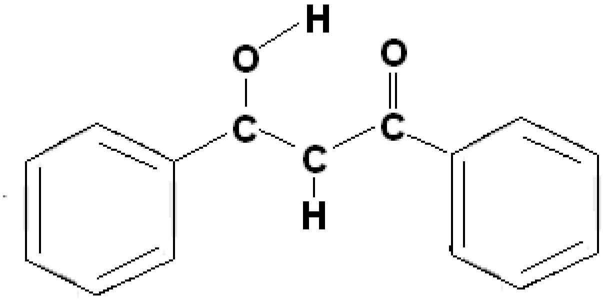
i) Stability gained through reasonance stabilization of conjugated double bond eg. Acetylacetone



ii) H –Bonding in enol form results in the formation of cyclic structure. Eg. Acetyl

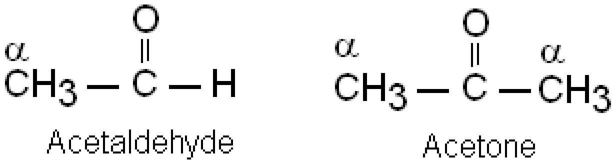


iii) Stabilisation of enolic form increases if double bond of enol form is in conjugation with electron cloud of benzene ring. Eg. Benzoylacetophenone.



Essential conditions for tautomerism.

In order to exhibit keto-anol tautomerism, an aldehyde or ketone or ester must possess at least, one α- hydrogen atom. Which can show 1,3 – migration. Example



Difference between tautomerism and resonance

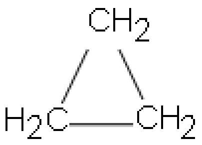
i) Tautomers are definite compounds and can be separated and characterized by suitable methods, but resonating structure cannot be separated as they are imaginary structures of same compounds
ii) Two tautomers have different functional groups, but the various resonating structures have the same functional group.
iii) Tautomerism has no effect on bond length, while resonance is accompanied by an increase in bond length of double bond and decrease of a single bond length.
iv) Tautomerism has no contribution in stabilizing the molecule but resonance give rise to extra stability to molecule.
v) Tautomerism may occur in planar or non-planar molecules while resonance occurs only in planar molecules.

(f) RING-CHAIN ISOMERISM

In this type of isomerism compounds are having same molecular formula but differ in modes of linking of carbon atoms, i.e. it may either be open chain or closed chain structures.

Eg. 1 C_3H_6

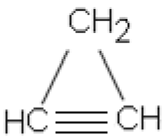
$CH_3 – CH = CH_2$: Propene



: Cyclopropane

Eg2 C_3H_4

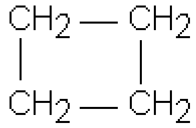
$CH_3 – C \equiv CH$: Propyne

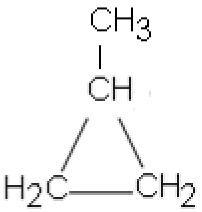


: Cyclopropene

Eg 3 C_4H_8

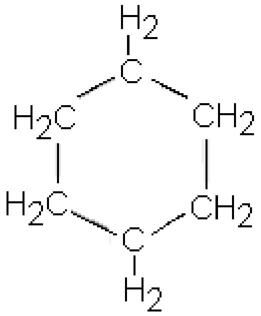
$CH_3 – CH_2 – CH = CH_2$: But -1 – ene

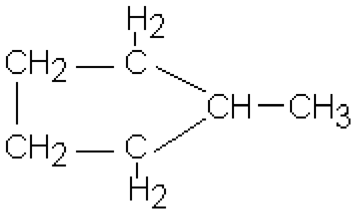

: Cyclobutane


: Methylcyclopropane

Eg 4

C_6H_{12}




: Methylcyclopentane

$CH_3 - CH_2 - CH_2 - CH_2 - CH = CH_2$: hex-1-ene

DOUBLE BOND EQUIVALENT (D.B.E)

Number of structural isomers can be predicted using double bond equivalents.

Double bond equivalent gives the number of double bonds (π – bonds) or rings in compounds

$$D.B.E = \sum \frac{n(V-2)}{2} + 1$$

N = number of different kinds of atoms present in molecules

V= valency of each atom.

Eg 1 C_4H_6

$$D.B.E = \frac{4(4-2)+6(1-2)}{2} + 1$$

$$D.B.E = 2$$

Thus the compound may contain

- i) Two double bond or a triple bond
- ii) One ring and one double bond
- iii) Two rings

For the compounds of general formula $C_aH_bN_cO_d$

$$D.B.E = a + 1 - \frac{(b-c)}{2}$$

Univalent atoms such as halogen atom may be replaced by one hydrogen atom and bivalent atom such as oxygen may be ignored example

Eg, Benzene (C_6H_6)

$$D.B.E = 6 + 1 - \frac{6}{2} = 4$$

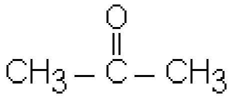
4 D.B.E. in benzene corresponds to 3 double bond and one ring

C_3H_6O

$$D.B.E = 3 + 1 - \frac{6}{2} = 1$$

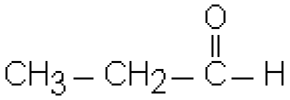
i.e. Molecule may contain double bond (C=C) or (C = O) or a ring

It’s possible isomers are



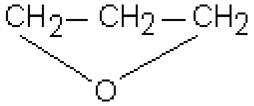
$CH_3 - \overset{\overset{O}{\|}}{C} - CH_3$

Acetone

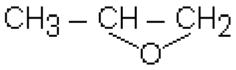


$CH_3 - CH_2 - \overset{\overset{O}{\|}}{C} - H$

Propanal

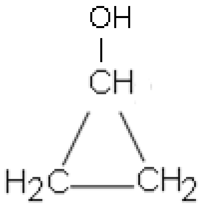


1, 3 - epoxypropane



1, 2 - epoxypropane

$CH_2 = CH - CH_2 - OH$ (prop-2-en-1-ol) $CH_2 = CH - O - CH_3$ (Methoxy ethane)



: Cyclopropanol

STEREOISOMERISM

Compounds have same molecular and structural formulae but different spatial arrangement of atoms or groups

There are two types of stereoisomerism:

a) Conformational isomerism.
b) Configurational isomerism.

a) CONFORMATIONAL ISOMERISM

The different arrangements of atoms in space that result from the free rotation of groups about C – C bond axis are called conformation or conformational isomers or rotational isomers and the phenomenon as conformational isomerism

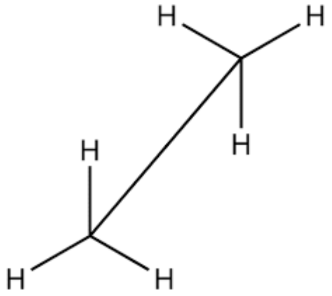
This type of isomerism is found in alkanes, cycloalkanes and their derivatives.

Representation of conformers

(i) Sawhorse formula

In this representation, molecule is viewed slightly from above and from right side of one carbon atom

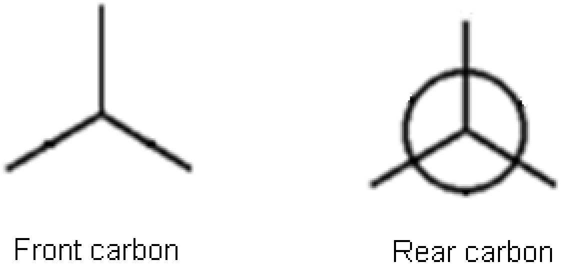
Carbon – carbon bond is drawn diagonally and slightly elongated and remaining six bonds attached to each carbon atom are represented as straight line



(ii) Newman projection formula

In this representation, the molecule is viewed along the carbon – carbon single bond

The front carbon atom is represented by a point and groups attached to it are represented by equally spaced radii. Whereas rear carbon atom is represented by circle and groups attached to it are represented by three equally spaced radial extensions



Conformations of ethane ($CH_3 – CH_3$)

Two extreme conformation are important, staggered and eclipsed. There can be number of arrangements between staggered and eclipsed forms and these arrangements are called skew forms.

(i) Eclipsed conformation

In this conformation rotation about C – C single bond is such that hydrogen atoms of front carbon atom completely cover or eclipse the hydrogen atom of rear carbon atom.

In this conformation, hydrogen atoms of two carbon atoms are at minimum distance which makes conformation unstable

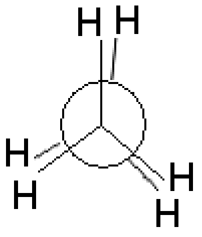
(ii) Staggered conformation

In this confirmation rotation about C – C bond is by an angle of 60^{O} so that hydrogen atoms of two carbon atoms are at maximum distance from each other making it stable.

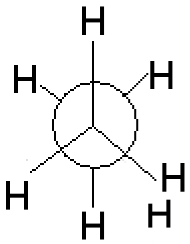
In staggered conformation, all the six hydrogen atoms are visible

(iii) Skew conformation

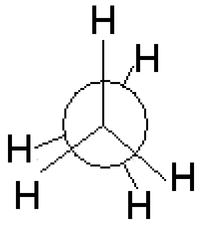
In this conformations, hydrogen atoms are closer than in staggered but way than in eclipsed conformation



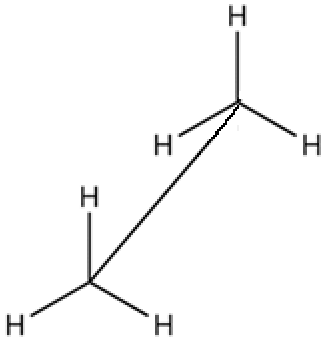
Eclipsed



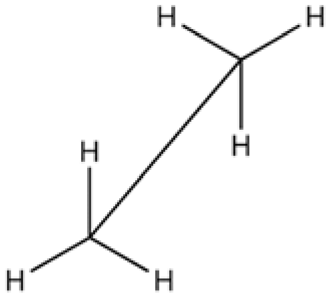
Staggered



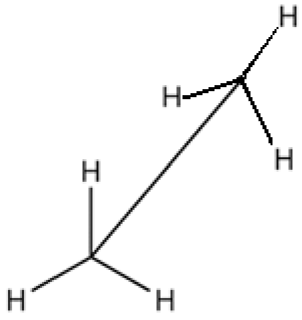
skew



Eclipsed



Staggered



Skew

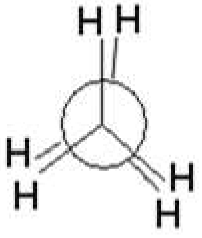
The relative stabilities of the various conformation of ethane are in the following order

Staggered > Skew > eclipsed

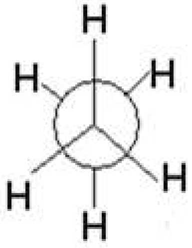
Ethane is mostly in staggered form.

Conformations of propane

Since it has two C – C single bonds, rotation about any of C-C bond give rise to two extreme conformation like that of ethane



Eclipsed



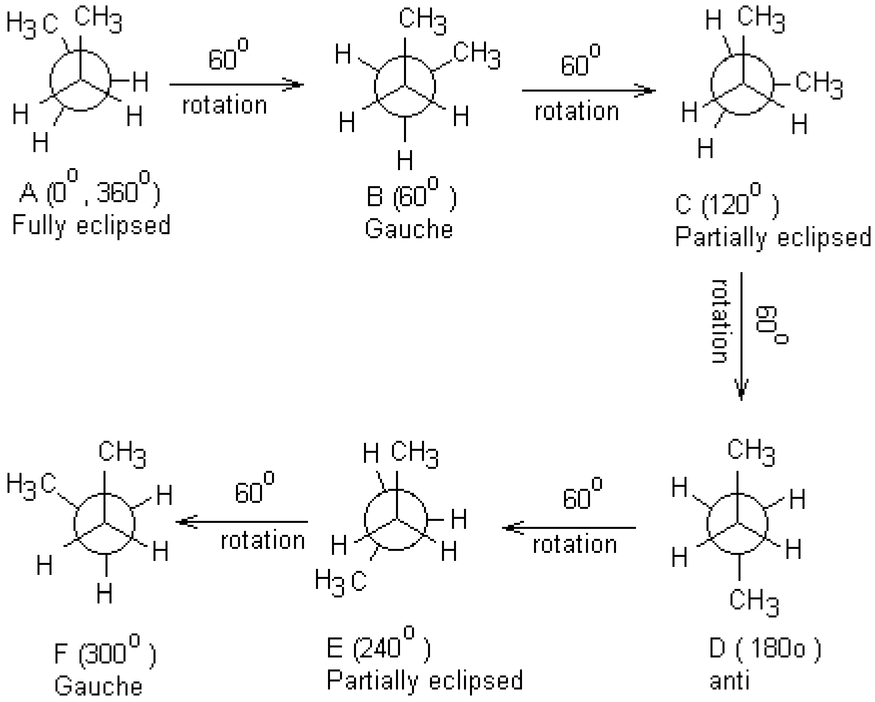
Staggered

Propane molecules exist mostly in the more stable staggered conformation.

Conformation of Butane

n-Butane may be considered as derivative of ethane whose one hydrogen of each carbon atom is replaced by a methyl group

1) Eclipsed conformations of n-butane
   There are three eclipsed conformations of n-butane. In the fully eclipsed form, a methyl group is eclipsed by another methyl group, while in partially group is eclipsed by hydrogen.
   Fully eclipsed feel more repulsive force than partially eclipsed. Thus fully eclipsed is less stable than partially eclipsed
2) Staggered conformations of n-Butane
   Three staggered conformations are possible; anti and two gauche.
   In anti –conformation, the methyl groups are 180^{O} apart and hence confirmations is most stable. In gauche conformations, the two methyl group are only 60^{O} apart and hence less stable than anti-form



The order of stability of n-Butane conformations is

Anti > gauche = gauche > partially eclipsed = partially eclipsed > fully eclipsed

Factors affecting stability of conformations

(i) Torsional strain

Torsional strain arise due to repulsive interaction between bonds on adjacent atoms

As the repulsive interaction between electronic cloud increases, torsional strain increases and thus stability decreases.

(ii) Steric strain

Steric strain arises due to crowding around central atom more the bulky groups present around the central more will be steric strain and thus less will be stability.

For example, gauche conformation of n-Butane is less stable than anti-conformation

(iii) Dipole – dipole interactions

Molecule in which polar bonds are attached in central atom, stability of greatly affected by dipole-dipole interactions.

Stronger the dipole – dipole interaction lesser will be the stability

(iv) Angle strain

Any deviation from the band angle suggested by the state of hybridization bring angle strain in the molecule. It mainly influences stability of cycloalkane.

Baeyer's strain theory

In year 1885, Baeyer proposed a theory of angle stain for cycloalkanes and the main postulates of this theory are

(i) Baeyer assumed the planer structure for all cycloalkanes. Thus the deviation from the tetrahedral bond angle varies with the size of the ring.

(ii) Deviation from regular tetrahedral angle introduces strain in the ring which brings unstability. Larger the deviation, greater will be the strain and thus lesser will be its stability.

Amount of deviation (d) = ($109^{O}28^{'}$ – Bond angle of the ring)

In cyclopropane = 109^{O} 28' – 60^{O} = 49.5^{O}

In cyclobutane = 109^{O} 28' – 90^{o} = 19^{o} $28^{'}$

In cyclopentane = 109^{O} 28' – 180^{O} = $1^{O}28^{'}$

Thus relative order of their stability is

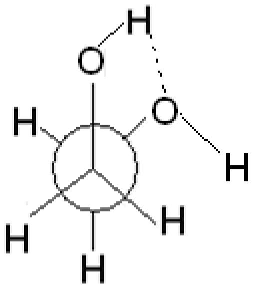
Cyclopentane > cyclobutane > cyclopropane

In cyclohexane = 109^{O} 28' – 120^{O} = 10.5^{O}

Cyclohexane is free from angle strain and hence is quite stable and unreactive.

Therefore, cyclohexane adopts a non-planar structure.

(v) Intramolecular hydrogen bonding also influences the relative stability of conformations of a molecule

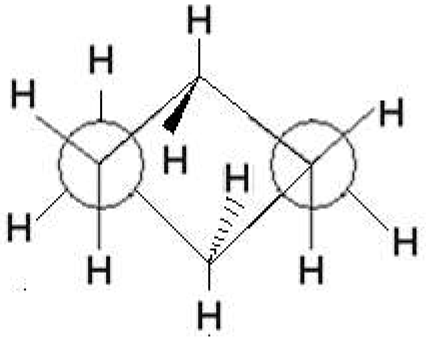


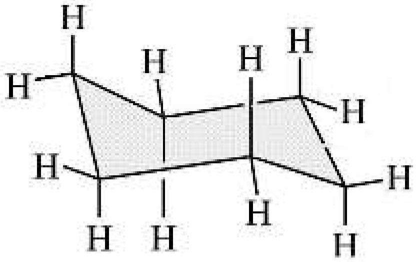
For example in ethylene glycol gauche conformations are more stable than anti form due to intramolecular hydrogen bonding.

Conformations of cyclohexane

1. Chair conformations

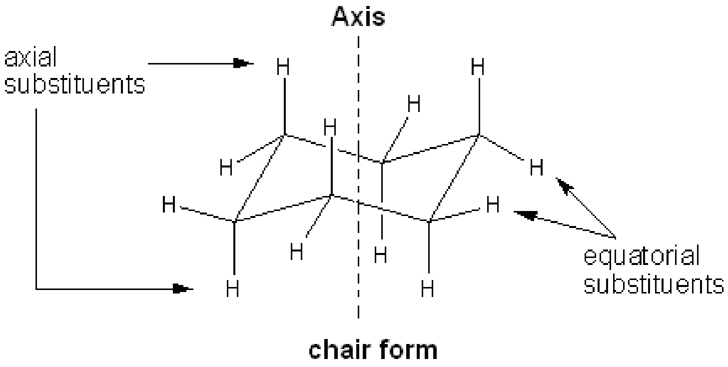
   It is most stable conformation of cyclohexane as it is free angle and torsional strain as all groups are staggered and bond angles are tetrahedral.

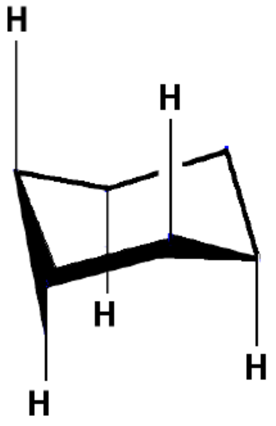


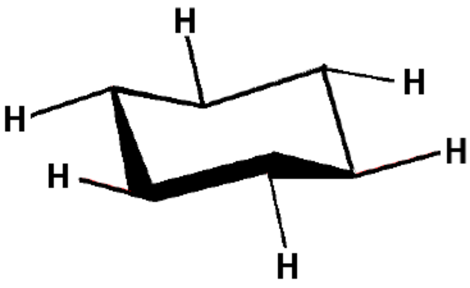


   Axial and equatorial bond in cyclohexane

   Hydrogen atoms are perpendicular to the ring are called axial hydrogen atoms and hydrogen atom lying in the plane of ring are called equatorial hydrogen atom.



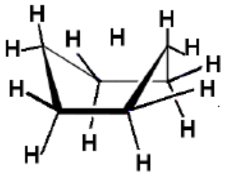


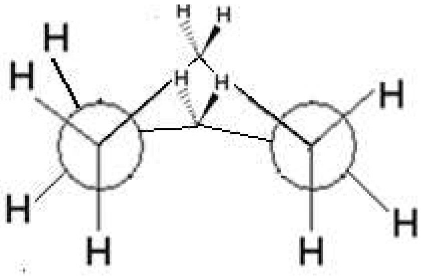


2. Boat conformation

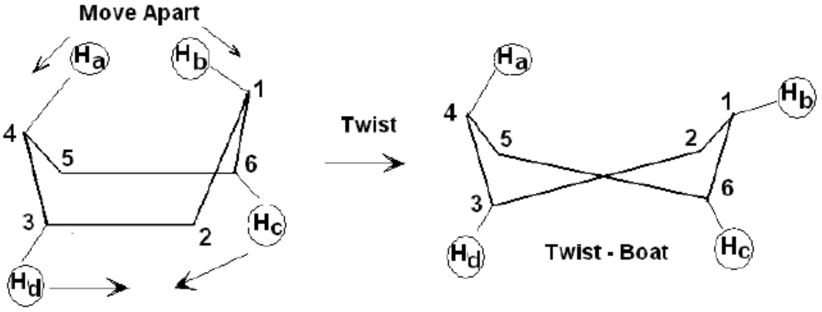
   If left end of the chair conformation is flipped, keeping rest of the molecule fixed, we get boat conformation of cyclohexane

   It is highly unstable conformation

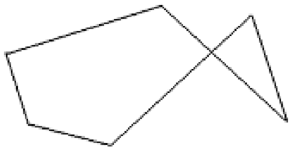




3. Twist boat confirmation
   If in the boat conformation of cyclohexane bond along $C_2 – C_3$ and $C_5 – C_6$ is twisted in such a way that flagpole hydrogens move away.
   Torsional strain in this conformation is less, making it more stable than boat conformation



4. Half chair conformation
   It transition state conformation chair and twist boat conformation



Order of relative stabilities of various conformations of cyclohexane is :
chair > twist boat > boat > half chair

CONFIGURATIONAL ISOMERISM

These are the stereoisomers which differ in spatial arrangement of atoms and thus show different properties.

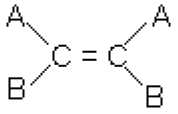
The isomers cannot be obtained by free rotation around C-C single bond

1. Geometrical isomerism
   Geometrical isomers are the stereoisomers which have different arrangement of groups or atoms around rigid framework of double bonds

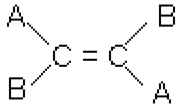
Geometrical isomerism is generally seen in alkenes (>C=C<) and oximes (>C=NOH)

Geometrical isomerism in alkene

Isomer in which similar groups or atoms lie on the same side of double bond are called cis-isomer where as isomers in which similar groups lie on the opposite side of double bond are called trans-isomer.



cis



trans

Necessary conditions for geometrical isomerism

i) The molecule must have a C - C double bond.

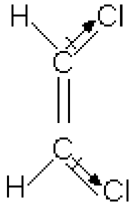
ii) Two atoms or groups attached to doubly bonded carbon atom must be different.

Distinction between *cis* and *trans* isomer

1. Dipole moment **:**

Cis –isomer

In cis isomer, dipole moment of polar groups have additive effect thus have higher dipole moment than corresponding trans isomer



$\mu = 1.89$ D

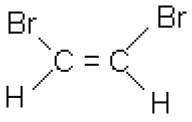
Trans-isomer

In trans isomer, dipole moment of polar groups have opposing effect, thus tends to cancel each other

2. Melting point

Cis isomer

Cis-isomer has lower melting point because the structure is not symmetrical

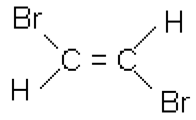


cis

m.pt = 220 K

Trans isomer

Due to symmetry, trans isomer fits better in crystal lattice, thus has higher lattice energy and hence higher melting point.



trans

m.pt = 260 K

3. Solubility

   Cis isomer

   Cis isomer have higher solubility because these are weakly held in lattice

   Trans isomer

   Trans – isomers have lower solubility because these are tightly held in the lattice

4. Density

   Cis isomers

   Cis – isomers have lower density

   Trans isomers

   Trans isomer due to higher lattice energy has higher density

5. Boiling point

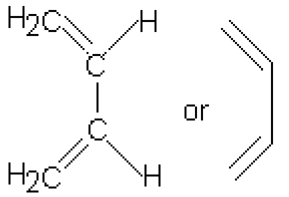
   Cis isomer

   Cis-isomer have higher boiling point due to dipole-dipole interaction

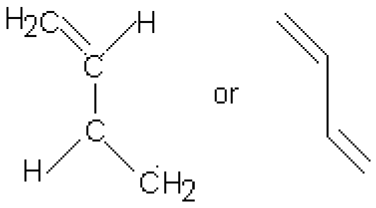
   Trans isomer

   Trans isomers have comparatively low boiling point

Cis – trans isomer around single bond



S -cis



S-trans

S : single bond

Geometrical isomerism in oximes and azo compounds

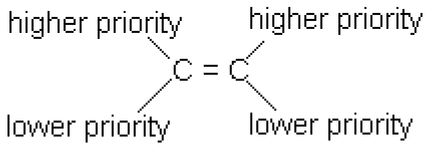
In syn-isomers H atom of doubly bonded carbon and –OH group of doubly bonded nitrogen lie on the same side of double bond

In anti-isomers H atom of doubly bonded carbon and –OH group of doubly bonded nitrogen lie on opposite side of double bond

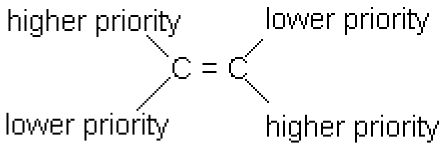
E – Z NOTATION OF GEOMETRICAL ISOMERISM

This new system of nomenclature of geometrical isomerism was developed by Ingold and Prelog

In this system we assign a priority to the groups attached to double bonded carbon atom. If groups of similar priority lie on the similar side of double bond, the isomer is designated as Z (Zusammen, means together). If groups of similar priority lie on the opposite side of double bond, the isomer is designated as E (Entgegen, means opposite)



Z - isomer



E - isomer

Sequence rules: The following rules are followed for deciding the precedence order of the atoms or groups:

(i) Higher atomic number atoms get higher priority.

(ii) Among the isotopes of same element, isotope of higher mass is given higher priority.

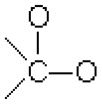
(iii) In the groups, the order of precedence is also decided on the basis of atomic number of first atom of the group.
For example
The order of precedence

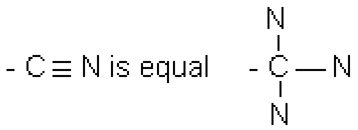
$$\begin{array}{ccccccccc} -Cl & > & -SO_3H & > & -OH & > & -NHCH_3 & > & -COOH \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ \text{at. no17} & & \text{at. no16} & & \text{at. no 8} & & \text{at. no7} & & \text{at. no 6} \end{array}$$

When the order of precedence of the groups cannot be settled on the first atom, the second atom or the subsequent atoms in the groups are considered.
For example
The order of precedence

$$\begin{array}{ccccc} -COOH & > & -CH_2CH_3 & > & -CH_3 \\ \downarrow & & \downarrow & & \downarrow \\ \text{at.No 8} & & \text{at.no 6} & & \text{at.no 1} \end{array}$$

(iv) A double or triple bonded atom is considered equivalent to two or three such atoms

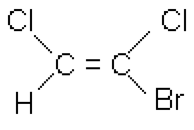
For example, the group >C=O is equal to  and the group



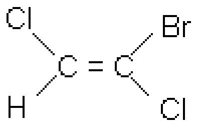
$-C\equiv N$ is equal $-\overset{N}{\underset{N}{C}}-N$

(v) If one of the position is occupied by lone pair, it is given higher priority over the bonded group.

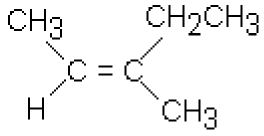
Examples of E-Z isomerism



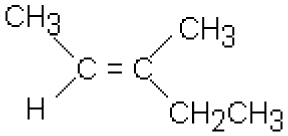
E - isomer



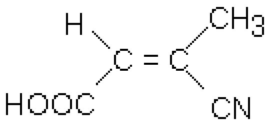
Z-isomer



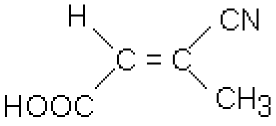
Z-isomer



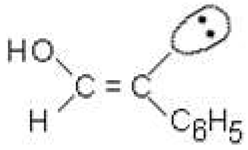
E - isomer



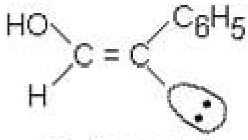
Z-isomer



E - isomer



Z-isomer



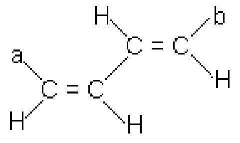
E - isomer

Number of geometrical isomers

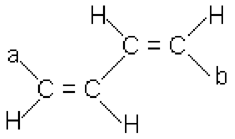
If a compound has more than one double bond, the number of geometrical isomers is 2^n, where n is number of double bond

This formula applies only to the molecules in which ends are different. For example,

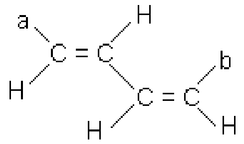
CHa = CH – CH = CHb occurs in four geometrical isomers



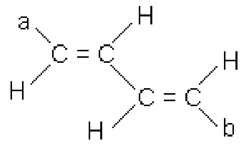
cis-trans



cis - cis



trans - cis



trans - trans

When the ends of polyene are same

i) When n is even number of geometrical isomers = $2^{(n-1)} + 2^{\left(\frac{n}{2}-1\right)}$

ii) When n is geometrical isomers = $2^{(n-1)} + 2^{\left(\frac{n-1}{2}\right)}$

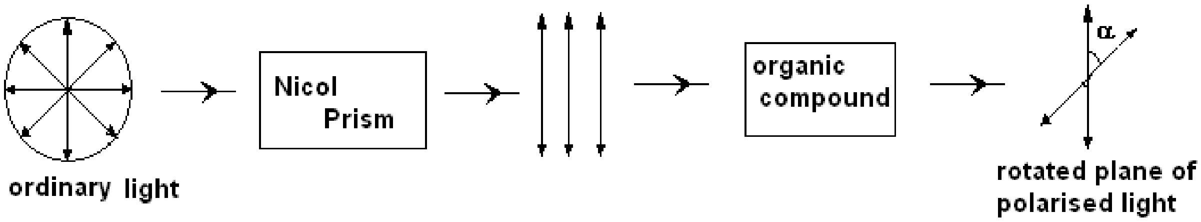
OPTICAL ISOMERISM

Compounds having similar physical and chemical properties but differing only in the behavior towards polarized light are called optical isomers and this phenomenon is known as optical isomerism

Plane polarized light and optical activity

The beam of light which vibrate only in one plane is called plane polarized light. It can be obtained by passing ordinary light through a nicol prism which cuts vibrations in all planes except in one.

Sometimes on passing a plane polarized light through solution of certain substances, a change in plane polarized light. Such substances which rotate the plane of plane polarized light are called optically active substances



On the basis of study of optical activity, the various organic compounds were divided into three types.

i) The optical isomer which rotates the plane polarized light to the right (clockwise) is known as dextro-rotatory isomer or d-form or indicated by +ve sign

ii) The optical isomer which rotates the plane polarized light to the left (anticlockwise) is known as laevo-rotatory isomer or l- form or indicated by –ve sign

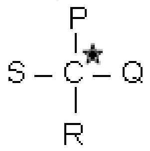
iii) The optical powers of the above two isomers are equal in magnitude but opposite in sign. An equimolar mixture of the two forms, therefore, will be optically inactive. This mixture is termed as racemic mixture or fl- form or (±) mixture

Enantiomers

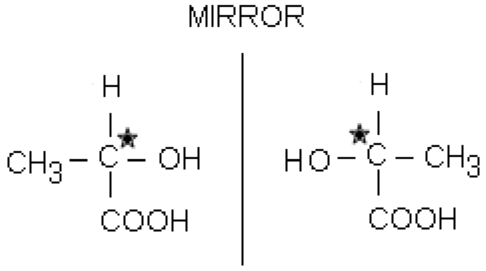
An optically active substances may exist in two or more isomeric forms which have same chemical and physical properties but differ in terms of direction of rotation of plane polarized light. Such optical isomers which rotate the plane of polarized light with equal angle but in opposite directions are known as enantiomers and phenomenon is known as enantiomerism.

In order to exhibit optical activity an object must be chiral. A carbon atom whose tetra valency is satisfied by four altogether different substituents is called chiral carbon atom or asymmetric carbon atom. A molecule possessing chiral carbon atom and non-superimposable to its own mirror image is said to be chiral and the property is called chirality.

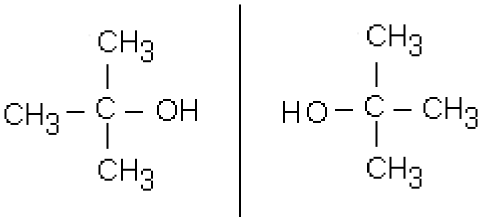
Molecule which is superimposable on its own mirror image is said to achiral



C★ - Chiral carbon atom



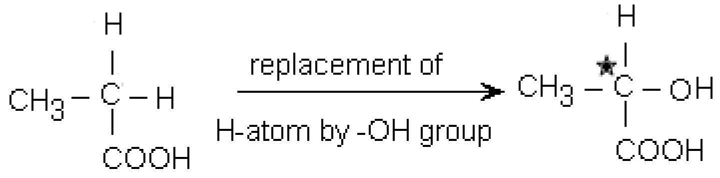
Lactic acid (chiral molecule)



Achiral molecule

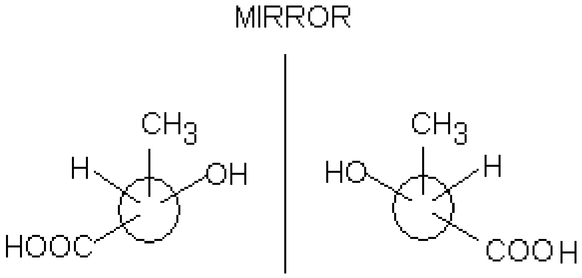
Prochiral carbon

A carbon atom is said to be prochiral if replacement of one of its group or atom by other substituent makes it chiral centre. For example propanoic acid is prochiral molecule.

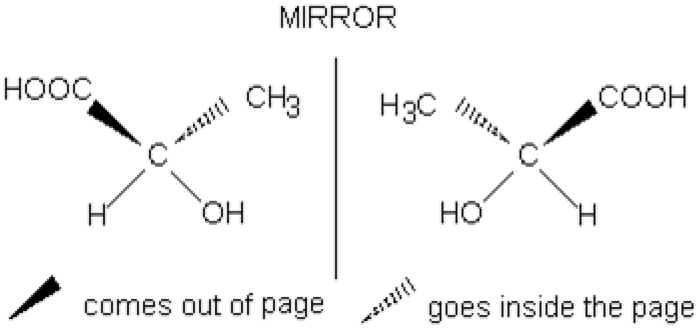


Representation of enantiomers

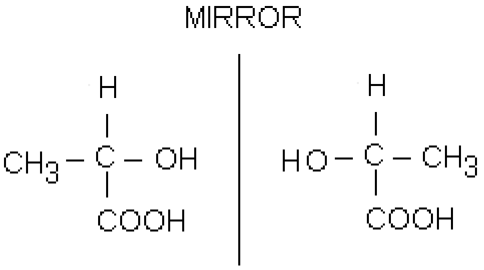
i) Newman projection formulae



ii) Wedge and dash formulae



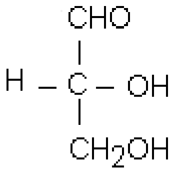
iii) Fischer projection



Specification of configuration

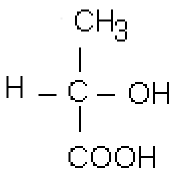
i) Relative configuration (D, L – Nomenclature)

Earlier than 1951, the absolute configuration of a compound was not known. Therefore glyceraldehydes was chosen as standard compound and all compounds were studied which respect is

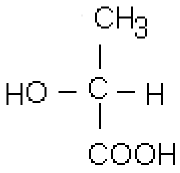


Now the configuration with –OH group at right side was given D-configuration where as the configuration with –OH group at left side was given L-configuration.

Example

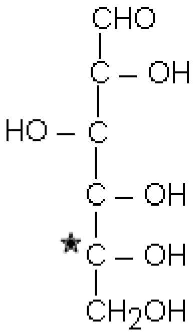


D - Latic acid

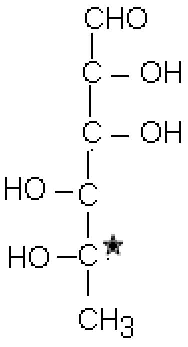


L - Latic acid

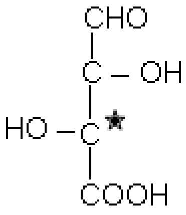
In polyhydroxy compounds (sugars) having more than one chiral centre, the configuration of stereocentre farthest from carbonyl group is compared with glyceraldehydes. Example



D- glucose

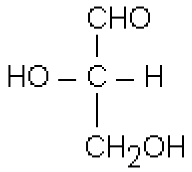


L -Rhamnose



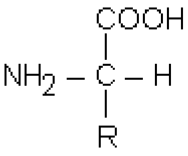
L -tartaric acid

In case of α- amino acids, the configuration is assigned by comparing $-NH_2$ group of α- amino acid with –OH group of glyceraldehydes.



$$HO-\overset{CHO}{\underset{CH_2OH}{C}}-H$$

L (-) - Glyceraldehyde



$$NH_2-\overset{COOH}{\underset{R}{C}}-H$$

L (-) -α- amino acid

The sign (+) or (-) added after D- and L- letters indicates the direction of optical rotation

(iii) Absoulte configuration (R, S – nomenclature)

Limitations of D and L notations were overcome by R and S notations developed by R.S. Cahn and C.K. Ingold and V. Prelog

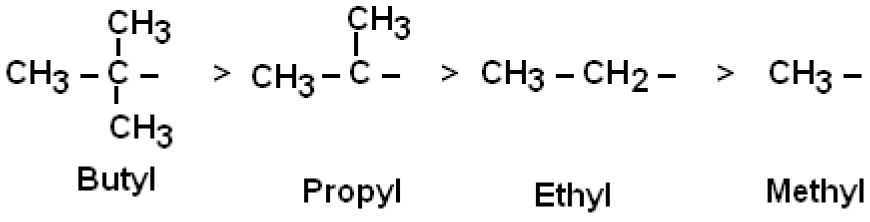
The centre is then viewed with the substituent with lowest priority pointing away from the viewer.

If the path for remaining three substituents going from highest priority to lowest priority is clockwise, the configuration is R (R stands for Rectus i.e. right) and if the path is anticlockwise the configuration is assigned as S (S stands for sinister i.e. left)

Sequence rules for assigning the priority order :

Rule 1: The atom with highest atomic number has highest priority. For example I > Br > Cl > F > C > H

Rule 2 : If the atom attached to the asymmetric carbon atom are the same. We determine the priority by considering the next atom from the asymmetric carbon atom. For example



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}- \;>\; CH_3-\overset{CH_3}{C}- \;>\; CH_3-CH_2- \;>\; CH_3-$$

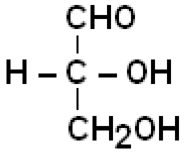
Ethyl has a higher priority than methyl because the ethyl group has (C, H, H) attached to first carbon, where as the methyl carbon has only hydrogen (H, H, H)

Rule3: If the atoms attached to two group are of the same atomic number then the priority is given to the group which have more substituent $CHCl_2$ > CH_2Cl

Rule 4 : If the groups attached to the asymmetric carbon atom has double bond or triple bond then the priority is given to the group which has the maximum bonds.

$-\overset{O}{\overset{\|}{C}}-H \quad > \quad -CH_2-OH$

Example Glyceraldehyde



Priority order : $OH > CHO > CH_2OH > H$

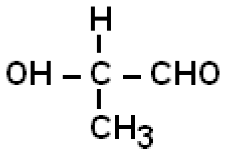
The priority sequence for most common groups

-I , -Br , -Cl, -SH. _F, -OCOR , -OR , -OH, $-NO_2$, -COCl, -COOR, -COH, $-CONH_2$, -COR, -CHO, -CN, CH_2OH, $-C_6H_5$, $-CR_3$, $-CHR_2$, $-CH_2R$

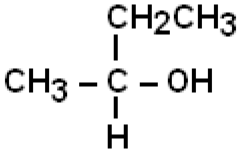
Golden rule

There is an easy way of assigning R and S configuration to optical isomers represented by Fischer projection formula. First assign priorities to the group, atom attached to chiral centre.

If the lowest priority group occupies vertical position in the original Fisher projection then the configuration obtained above gives the actual configuration in the molecule

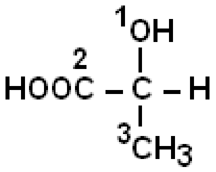


R - configuration

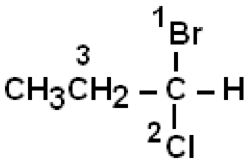


S - configuration

If the lowest priority group occupies horizontal position in the Fischer projection formula, then change the configuration obtained above from (R) to (S) or (S) to (R)

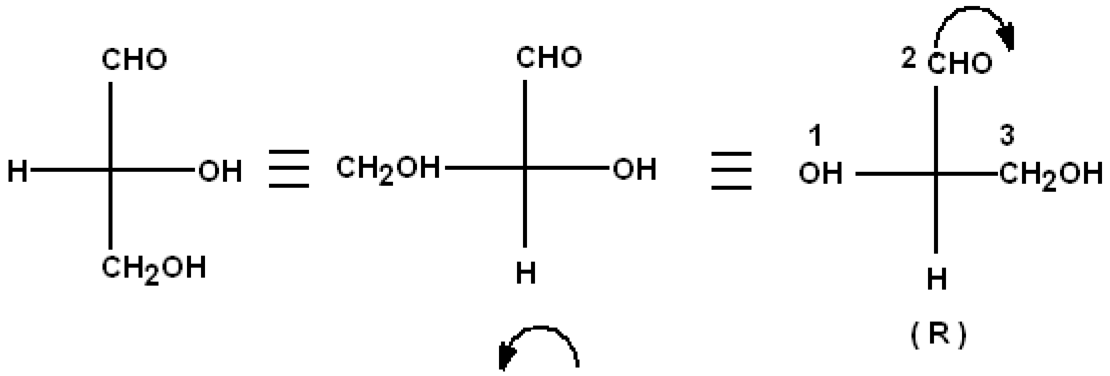


change S → R
(R) -configuration

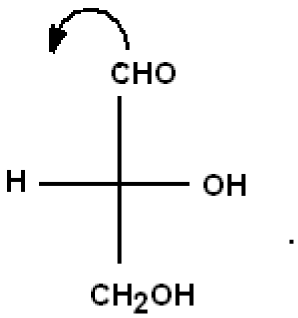


change R → S
(S) - configuration

Examples

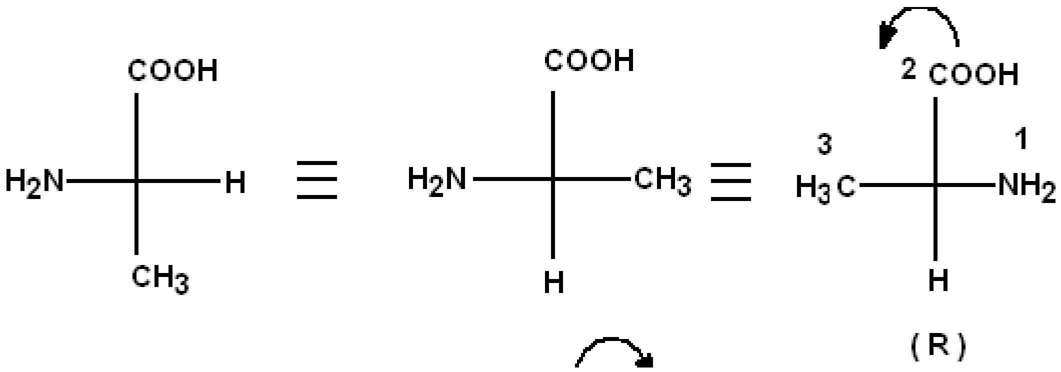


OR

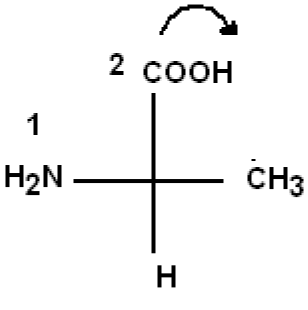


Change (S) → (R)

Example II



OR

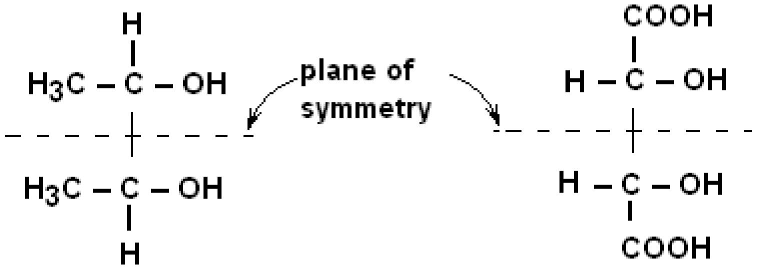


S- configuration

Change (S) → (R)

MESO COMPOUNDS:

A compound with two or more asymmetric carbon atoms but also having a plane of symmetry (a mirror plane) is called meso compounds. The figure shows two meso compounds. These molecules have plane of symmetry dividing them midway between the two asymmetric carbon in each. Notice that one half of the molecule is the mirror image of the other. Both molecules are optically inactive; even though each has two asymmetric centres. Neither will rotate the plane polarized light.



- A solution is a homogenous mixture of two (or more) chemically non reacting substances which can be varied within certain limits.
- When the solution is composed of only two chemical substances it is termed a binary solution. Solution is composed of solvent and solute. Solvent is that component in large amount and in same physical state as that of the resulting solution. Component present in smaller amount is called solute.
- The constituent of solution cannot be separated by filtration settling or centrifugal action. All solutions are characterized by

(i) Homogeneity
(ii) Absence of settling
(iii) The molecular or ionic state of sub-division of the components.

TYPE OF SOLUTIONS

Sr.No	SOLUTE	SOLVENT	EXAMPLES
1	Gas	Gas	Air
2	Liquid	Gas	Humidity in air
3	Solid	Gas	Camphor in N_2 gas
4	Gas	Liquid	Aerated drink
5	Liquid	Liquid	Alcohol in water
6	Solid	Liquid	Salt in water
7	Gas	Solid	Dissolved gases in mixture
8	Liquid	Solid	Amalgams
9	Solid	Solid	Alloys

CONCENTRATION OF SOLUTION

1. Molarity

$$M = \frac{Number\ of\ moles\ of\ solute}{Volume\ of\ solution\ (\ in\ litre)}$$
$$M = \frac{W \times 1000}{M_0 \times V}$$

W : Wight of solute in grams
M_0 : Molecular mass of solute
V: Volume of solution in ml

2. Normality

$$M = \frac{Number\ of\ gram\ equivalents\ of\ \ solute}{Volume\ of\ solution\ (\ in\ litre)}$$
$$M = \frac{W \times 1000}{Eq \times V}$$

W : Wight of solute in grams
Eq : Equivalent weight of solute
V: Volume of solution in ml

Equivalent weight of solute

$$Eq\ = \frac{molecular\ mass\ of\ solute}{Acidity, Basicity, charge\ on\ compound, change\ in\ oxidationstate}$$

Acidity : Number replaceable -OH group in basic compound
Example: NaOH : number of -OH groups 1, Thus Acidity = 1
$Ca(OH)_2$: Number of –OH groups 2, Acidity = 2
$Al(OH)_3$: Number of –OH groups 3, Acidity = 3

Basicity of acid is defined as the no of ionizable hydrogen (H^+) ions present in one molecule of an acid.
Example: HCl, HNO_3, CH_3COOH : H^+ ions are 1, thus Basicity is 1,
H_2SO_3 : H^+ ions are 2, thus Basicity is 2,
Oxalic acid : H^+ ions are 2, thus Basicity is 2

Charge: Na^+ thus take charge as 1
Ca^{++} thus take charge as 2
SO_4^{-2} thus take charge as 2

Change is oxidation state:
Example $KMnO_4$
Basic medium : Change in oxidation state of Mn= +1
Acidic medium : Change in oxidation state of Mn= +5
Neutral medium : Change in oxidation state of Mn= +3

3. Molality

$$m = \frac{moles\ of\ solute}{Weight\ of\ solvent\ in\ Kg}$$
$$m = \frac{W \times 1000}{M_0 \times W_S}$$

W : Wight of solute in grams
M_0 : Molecular mass of solute
M_S: Weight of solvent in grams

4. Formality

In case of ionic compounds like NaCl, formality is used in place of molarity

$$F = \frac{weight\ of\ solute}{Formula\ weight\ \times Volume\ if\ solution\ in\ ml}$$

Formula weight : Example NaCl = 23 +35.5 = 58.5

5. Mass percentage

$$m\% = \frac{weight\ of\ solute \times 1000}{weight\ of\ solution}$$

6. Volume percentage

$$V\% = \frac{volume\ of\ solute \times 1000}{volumeof\ solution}$$

7. Strength

Strength of a solution may be defined as weight of solute in gram present per litre of the solution. It is expressed as gram/litre

8. Mole fraction

$$X_{solute} = \frac{n}{n+N};\ X_{solvent} = \frac{N}{n+N}$$

N = Number of moles of solvent; n = number of moles of solute
Sum of mole fraction of binary solution (one solute and one solvent) is 1

9. Parts per million (ppm)

$$ppm = \frac{mass\ of\ component}{total\ mass\ of\ solution} \times 10^6$$
$$This\ concentration\ term\ is\ used\ for\ very\ dilute\ concentration.$$

- When one substance (the solute) dissolves in another (the solvent), particles of the solute disperse throughout the solvent molecules the ease with which a solute particles replaces a solvent molecules depends on relative strength of three types of interactions

(i) Solvent – Solvent interaction
(ii) Solute – Solute interaction
(iii) Solute – solvent interaction

It involves three stapes

Step I : Involves the separation of solvent molecules (ΔH_1)

Step II: Separation of solute molecules (ΔH_2)

Step III: Solute and solvent molecules mix (ΔH_3)

The heat of solution

$\Delta H_{solution} = \Delta H_1 + \Delta H_2 + \Delta H_3$

- If the solute – Solvant attraction is stronger than Solvent – Solvent and Solute –Solute interaction, the solution process will be favorable i.e. its exothermic ($\Delta H_{solution} < 0$)
- If the solute –solvent interaction is weaker than solvent –solvent and solute –solute interaction then the process is endothermic and solute still dissolves in solvent because along with energy factor, entropy factor plays a major role
- Dissolution of a substance in a solvent in a solvent is associated with a free energy change , ΔG. If ΔG is negative, the process is spontaneous and substance dissolve on its own. If ΔG is positive the process is non-spontaneous and substance does not dissolve
  $\Delta G = \Delta H_{solution} - T\Delta S_{solution}$
- "Like dissolve like ". Polar compound dissolve in polar solvent whereas non-polar compounds dissolve in non-polar solvent

SOLUTIONS OF GASES IN LIQUIDS

- The solubility of a gas in liquid is expressed in terms of absorption coefficient. It is defined as the volume of the gas in ml that can be dissolved by 1ml of liquid solvent at the temperature of the experiment at one atmospheric pressure.
- The following factors affect the solubility of gases in liquids
  (i) Nature of the gas and solvent.
  Chemical similarity between the gas and solvent leads to higher solubility of gas in solvent.
  Eg. H_2 , N_2, O_2 etc are less soluble in water than CO_2, NH_3, HCl etc. because later gases react with the solvent.
  (ii) Effect of temperature
  The solubility of most of the gases in liquids decreases with increase of temperature as the dissolution is an exothermic process
  Change in entropy i.e. ΔS is negative for dissolution of gas in a liquid, it means ΔH has to be negative (exothermic), so that the process becomes spontaneous.
  $\Delta G = -ve$
  (iii) Effect of pressure
  Effect of pressure on solubility of a gas in a liquid is given by Henry's Law which states that the solubility of gas in a liquid at a particular temperature is directly proportional to the pressure of gas in equilibrium with the liquid at that temperature
  Mole fraction ∝ partial pressure of gas (P)
  $X = K_H P$; K_H – Henry constant

  Henry's law holds good if the following conditions are fulfilled

a) The pressure is not too high
b) The temperature is not very low
c) The gas does not chemically combine with the solvent.

Applications of Henry's law

a) Carbonated beverages: Effect of pressure on solubility of gas, is used in producing carbonated beverages like soft drinks, beer etc. these are bottled under carbon dioxide pressure greater than 1atm
b) Deep sea diving
The solubility of gases increases with increasing pressure. The deep sea divers who breath compressed air must be concerned about the solubility of gases in their blood. The scuba divers must ascend gases from being released rapidly from blood and other body fluids. The bubbles of nitrogen and other gases affect nerve impulses and give rise to the decompression sickness or the bends which is painful and can be fatal. Deep sea divers substitute helium from nitrogen in the air that they breathe because helium has a much lower solubility in biological fluids than nitrogen. Generally the scuba divers use the air tank filled with 11.7% helium, 56.2% nitrogen and 32.1% oxygen
c) High altitude sickness
At high altitudes, partial pressure of oxygen is low, therefore concentration of dissolved oxygen in the blood and tissues of the people diving there is also low. At low concentration of oxygen in blood, the people suffer from anoxia i.e. people suffer from weakness and inability to think properly.

SOLUTIONS OF LIQUIDS IN LIQUIDS

When two liquids are mixed, the mixture may be of following types

(i) The two liquids do not mix but form separate layer. These are termed as immiscible. Ex: water and benzene
(ii) The two liquids may be partially miscible Eg. Water and ether
(iii) The two liquids dissolve in each other in all proportions. These are said to be miscible

SOLUTIONS OF SOLID IN A LIQUID

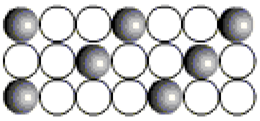
- Solubility of a solid in a liquid can be defined as the amount of solid (solute) in grams dissolved in 100 gm of the liquid (solvent) to form a saturated solutions at a given temperature.
- Factors affecting the solubility of a solid in a liquid
  (i) Nature of solute and solvent : Ionic solids dissolve in polar solvants like warter and non-ionic or covalent compounds dissolve readily in non-polar solvent " Like dissolves like" rule
  (ii) Temperature: The solubility increases continuously with increase of temperature if the dissolution process is endothermic Eg. $NaNO_3$, KNO_3, NaCl
  If the dissolution process is exothermic then solubility decreases with increase of temperature Eg Li_2CO_3, $Na_2CO_3 . H_2O$

SOLID SOLUTIONS

Solid solutions are homogeneous mixture of two or more solid components

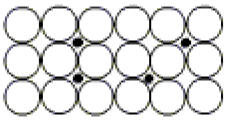
Solid solutions are of two types

(i) Substitution solid solutions : Solid elements, which are quite similar in atomic size, can mutually substitute one another in crystal lattices. This gives solid solutions and smooth alloys Eg. Silver and copper alloy



substitutional solid solution

(ii) Interstitial solid solutions: In this type of solid solutions smaller atoms are accommodated in the voids or interstices of the solid have bigger atoms. Transition elements have a very strong tendency to combine with atoms of relatively small size to form interstitial compounds eg. Carbides and hydrides. Tungsten carbides and hydrides. Tungsten carbide (WC) is a very hard substance used for cutting and grinding.



Interstitial solid solution

VAPOUR PRESSURE

- The pressure exerted by vapours over the liquid surface at equilibrium is called vapour pressure of the liquid
- Factors affecting vapour pressure of liquid are
  1. Nature of liquid: Weaker the intermolecular forces, greater is the amount of vapour because molecules can leave the liquid easily and can come to the vapour phase easily. Eg. Ether have lighter vapour pressure as compared to alcohol
  2. Temperature: For a particular liquid, higher the temperature, more will be the vapour pressure. The reason for this is the increase in the kinetic energy of molecules to leave the surface of the liquid easily to come to the vapour state
     Effect of temperature on vapour pressure of a liquid is given by Clausius – Clapeyon equation

$$ln\frac{P_2}{P_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

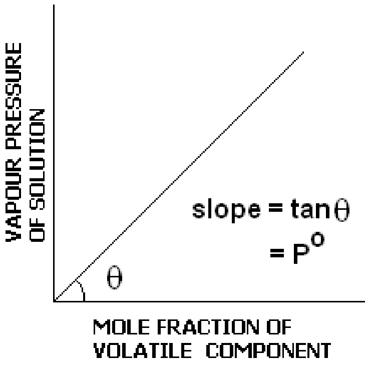
ΔH : Enthalpy of vapourisation

VAPOUR PRESSURE OF SOLUTION

- If solute is non volatile solid or liquid, the vapour pressure of solution is equal to partial vapour pressure of solvent in the solution.
- If solute is volatile solid or liquid the vapour pressure will be equal to the sum of partial vapour pressure of solute and that of solvent.

RAOULT'S LAW

- For any solution, the partial vapour pressure of each volatile components in the solution is directly proportional to its mole fraction



RAOULT'S LAW FOR VOLATILE SOLUTES

- For volatile solute it states that " Partial vapour pressure of any components of solution at given temperature is equal to its mole fraction and its vapour pressure in pure state.
- For binary solutions of A and B
  $P_A = P_A^O X_A$ and $P_B = P_B^O X_B$
  $P_{TOTAL} = P_A + P_B$
  $= P_A^O X_A + P_B^O X_B$
  $= P_A^O (1 - X_B) + P_B^O X_B$
  $= P_A^O + (P_B^O - P_A^O) X_B$

RAOULTS LAW FOR NON-VOLATILE SOLUTE

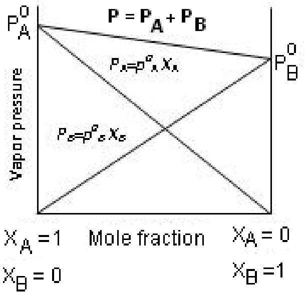
For non-volatile solute, vapour pressure of solution is equal to mole fraction of solvent

$P_{SOLVENT} = P_O X_{SOLVANT}$

- Raoult's law is special case of Henry's law
  If we compare the solute with the gas dissolved in liquid then in the above expression it can be seen that K_H is just replaced by P^O

IDEAL AND NON-IDEAL SOLUTIONS

1. IDEAL SOLUTIONS



IDEAL SOLUTION

A solution is said to be ideal which obey's Raoult's law in the entire concentration range and at all temperature

An Ideal Solution should have following characteristics

a. It should obey Raoult's law
b. $\Delta H_{MIXING} = 0$, i.e. no heat should be absorbed or evolved during mixing
c. $\Delta V_{MIXING} = 0$, i.e. no expansion or contraction on mixing

Examples: Ethyl bromide and ethyl chloride, n-hexane and n-heptane, Benzene and toluene

2. NON-IDEAL SOLUTION

The solutions which do not obey Raoult's law are called non-ideal solution

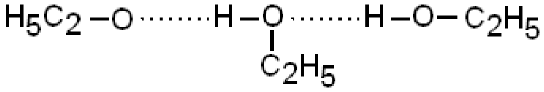
i. Non – ideal solution showing positive deviation

$P_A > P_A^O X_A$; $P_B > P_B^O X_B$

ΔH_{MIXING} = Positive; ΔV_{MIXING} = Positive

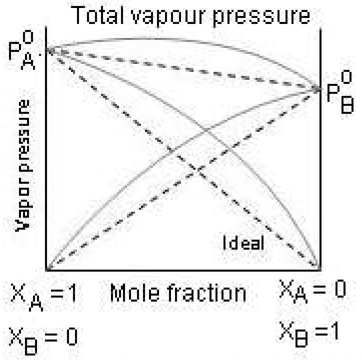
Such solution shows positive deviation from Raoult's law. The observed vapour pressure of each component and total vapour pressure of the solution is greater than the expected from Raoult's law, thus boiling point of such solution is found to be less than the calculated value, this is because the new interactions are weaker than those in the pure components i.e. A-B interactions are weaker than A-A interactions and B-B interactions

Cyclohexane and ethanol. In ethanol, the molecules are held together by hydrogen bonding when cyclohexane is added to ethanol, the molecules of cyclohexane tend to occupy the space between ethanol molecules due to which some hydrogen bonds are broken down. So that intermolecular interactions between cyclohexane and ethanol are reduced and hence, shows higher vapour pressure



$$H_5C_2-O\cdots\cdots H-\underset{\displaystyle C_2H_5}{\underset{|}{O}}\cdots\cdots H-O-C_2H_5$$

Some examples of non-ideal solutions showing positive deviations are acetone + ethyl alcohol, water + ethyl alcohol, CCl_4 + $CHCl_3$, acetone + carbon disulphide, acetone + benzene



Positive deviation

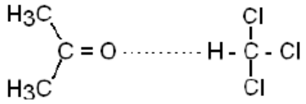
ii. Non – ideal solutions showing negative deviation

$P_A < P_A^O X_A$; $P_B < P_B^O X_B$

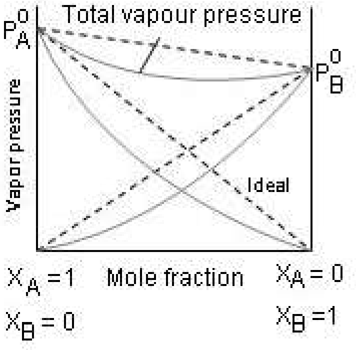
ΔH_{MIXING} = Negative; ΔV_{MIXING} = Negative

Solutions of above type shows negative deviations from Raoult's law. The observed vapour pressure of each component and total vapour pressure of the solution is lower than expected from Raoult's law, thus boiling point of such solution is found to be higher than the calculated values this is because the new interactions are stronger than those in pure components i.e. A – B interactions and B – B interactions

When acetone and chloroform are mixed together a hydrogen bond is formed between them which increases intermolecular interactions between them and hence decreases the vapour pressure



Some example of non-ideal solutions showing negative deviation are
Acetone + aniline , HCl + water, HNO_3 + water; water + H_2SO_4 , acetone + chloroform , Nitric acid + Chloroform; Benzene + chloroform, Pyridine + glacial acetic acid



Negative deviation

AZOTROPIC MIXTURE

A mixture of two real miscible liquids having a definite composition which boils at constant temperature without undergoing any change in compostion is called as azeotropic mixture or constant boiling mixture or azeotrope

Azeotropic mixture cannot be separated into heir constituent by fractional distillation

MINIMUM BOILING AZEOTROPES

These are the mixture of two liquids whose boiling point is less than either of the two pure component. They are formed by non-ideal solutions showing positive deviations

Eg ethanol – 95.5% (B.P. 351.3K) + water -4.5% (B.P. 373K) mixture boling at 351.15 K

Ethanol – 6.8% (B.P. 351.3 K) + chloroform - 93.2% (B.P. 334.2K) mixture boiling at 332.3K

MAXIMUM BOILING AZEOTROPES

These are the mixtures of two liquids whose boiling points is less than either of the two pure components. They are formed by no-ideal solutions showing negative deviations

Eg NH_3 – 68% (B.P. 359K) + Water -32% (B.P. 373K) mixture boiling at 393.5K

H_2O – 43% (B.P. 373K) + HI -57% (B.P. 293K) mmixture boiling at 400K

COLLIGATIVE PROPERTIES

The properties of dilute solutions which depends only on number of particles of solute present in the solution and not on their nature are called colligative properties

Colligative properties are

1. Realtive lowering of vapour pressure
2. Osmotic pressure

3. Elevation in boiling point
4. Depression in freezing point

RELATIVE LOWERING OF VAPOUR PRESSURE

- Vapour pressure of a solvent in the solution is less than that of pure solvent
- According to Raoult's law, the vapour pressure of the solvent (P_1) in an ideal solution is given by $P_1 = x_1P_1^O$; X_1 = mole fraction of solvent
  Reduction in vapour pressure of solvent (ΔP_1)
  $\Delta P_1 = P_1^O - P_1$
  $= P_1^O - P_1^OX_1$
  $= P_1^O (1- X_1)$
  Mole fraction of solute $X_2 = (1-X_1)$
  $\Delta P_1 = X_2P_1^O$
- In a solution containing several non-volatile solutes, the lowering of the vapour pressure depends on the sum of mole fraction of different solutes
  $\Delta P_1 = X_2P_1^O$

$$\frac{\Delta P_1}{P_1^O} = \frac{P_1^O - P_1}{P_1^O} = X_2$$

$$\frac{P_1^O - P_1}{P_1^O} = \frac{n}{n+N}$$

N: number of moles of solvent ; n = number of moles of solute

For dilute solution n << N

$$\frac{P_1^O - P_1}{P_1^O} = \frac{n}{N}$$

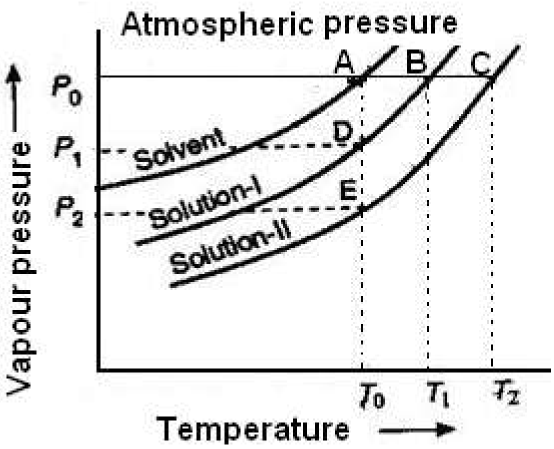
$$\frac{P_1^O - P_1}{P_1^O} = \frac{w_2 \times M_1}{w_1 \times M_2}$$

w_1 = mass of solvent ; M_1 : Molar mass of solvent

w_2 = mass of solute ; M_2 mass of solute

ELEVATION IN BOILING POINT (EBULLIOSCOPY)

- The boiling point of a liquid is the temperature at which its vapour pressure is equal to the atmospheric pressure.
- The vapour pressure of a liquid is lowered when a non-volatile solute is added to it. Hence, at the higher temperature of solution, than solvent , vapour pressure of solution equal the atmospheric pressure .
- Elevation in boiling point ΔT = Boiling point of solution – Boiling point of pure solvent
- The curves of the solutions always lie below the curve of the pure solvent. The line P_oC represents the atmospheric pressure. T_o, T_1 and T_2 represents the boiling points of pure solvent, solution I and solution II at temperature T_o are P_1 and P_2 respectively.



Assuming that the solutions are very dilute, these curves may be approximately taken as straight lines near the boiling point. Thus ΔACE and ΔABD are similar

$$\frac{AC}{AB}=\frac{AE}{AD}$$

$$\frac{T_2-T_0}{T_1-T_0}=\frac{P_0-P_2}{P_0-P_1}$$

$$\frac{\Delta T_2}{\Delta T_1}=\frac{\Delta P_2}{\Delta P_1}$$

$$\Delta T \propto \Delta P$$

From Raoult's law

$\Delta P \propto \frac{w_B}{m_B \times w_A}$ w_B = weight of solute, m_B = molecular weight of solute, w_A = weight of solvent

$\Delta P \propto m$ (molality of the solution)

OR

$$\Delta T \propto \frac{w_B}{m_B \times w_A}$$

$\Delta T \propto m$ (molality of the solution)

$\Delta T = K_b\, m$ (K_b = molal elevation constant or ebullioscope constant)

- Molal elevation constant be defined as the elevation in boling point when the molality of solution is unity

$$\Delta T = K_b \times \frac{w_B}{w_A \times m_B} \times 1000$$

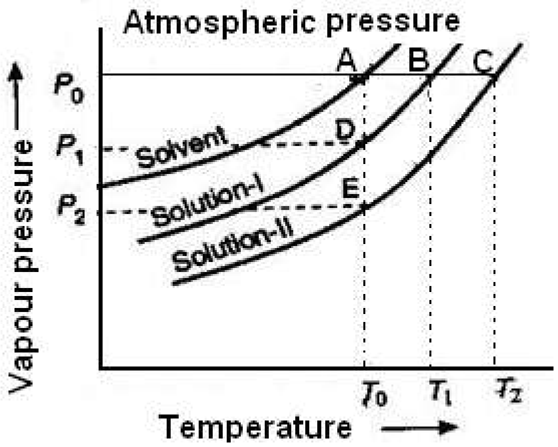
Here formula for K_b

$$K_b=\frac{RT_b^2}{1000L_v}$$

R = gas constant , T_b : Boiling point of solvent in Kelvin, L_v = latent heat of vapourisation of solvent in calories per gram

DEPRESSION IN FREEZING POINT (CRYOSCOPY)

- Freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to vapour pressure of the corresponding solid
- Since, the addition of a non-volatile solute always lowers the vapour pressure of a solvent therefore, it will be in equilibrium with solid phase at a lower pressure and hence at a lower temperature. The difference between the freezing points of a pure solvent and its solution is called depression in freezing point.
  Depression in freezing point ΔT = freezing point of the solvent – freezing point of the solution.
- This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and two solutions solution I and solution II. CFB is a curve for the solid solvent. The solvent, solution I, solution II respectively. The vapour pressure at temperatures and solution II are thus P_O, P_1 and P_2 respectively.



- For very dilute solutions, the curves FD and CE is also nearly a straight line. The ΔBEC and ΔBDF are similar so,

$$\frac{EC}{DF} = \frac{BE}{BD}$$

$$\frac{T_0 - T_2}{T_0 - T_1} = \frac{P_0 - P_2}{P_0 - P_1}$$

$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

$$\Delta T \propto \Delta P$$

From Raoult's law

$\Delta P \propto \frac{w_B}{m_B \times w_A}$ w_B = weight of solute, m_B = molecular weight of solute, w_A = weight of solvent

$\Delta P \propto m$ (molality of the solution)

OR

$$\Delta T \propto \frac{w_B}{m_B \times w_A}$$

$\Delta T \propto m$ (molality of the solution)

(i) The depression in freeing point of a solvent is directly proportional to molal concentration of solution

(ii) Equimolal quantities of different substances dissolved in the same quantity of solvent bring out the same depression in freezing point of the solvent under ideal conditions. So, depression in freezing point is a colligative property.
$\Delta T \propto m$
$\Delta T = K_f m$ (K_f = molal depression constant or cyroscopic constant)

- Molal depression constant , K_f may be defined as depression in freezing point of a solvent when one mole of a solute is dissolved in 1000 g of the solvent. It is expressed as K_{f1000}
$$\Delta T = K_f \times \frac{w_B}{w_A \times m_B} \times 1000$$
Here formula for K_f
$$K_f = \frac{RT_f^2}{1000L_f}$$
R = gas constant , T_f : Freezing point of solvent in Kelvin, L_f = latent heat of fusion of solvent in calories per gram

Ebullioscope and Cryoscopic methods are effective to determine molecular weight when:

(i) Solutions are dilute. Solutions obey Raoult's law
(ii) The solute is non-volatile
(iii) There is no association of solute molecules in the solution
(iv) Solute does not form a solid solution with solvent in frozen state, i.e., only solvent separates in solid state on freezing the solution

OSMOTIC PRESSURE

- The phenomenon of the passage of pure solvent from a region of lower concentration of solution to a region of higher concentration of solution through a semi-permeable membrane is called osmosis.
- The driving force of osmosis is known as osmotic pressure. It is the difference in the pressure between the solution and the solvent system or it is the excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semi-permeable membrane. Once osmosis is completed the pressure exerted on the semi-permeable membrane is same.
Osmotic pressure
$$\pi = \frac{n}{V}RT = CRT$$
π = Osmotic pressure
V = Volume of solution
n= number of molecules of solute = w_B/m_B
R = Gas constant
T = Temperature
C= concentration
w_B = weight of solute
M_B = molecular weight of solute
$$\pi = \frac{w_B}{m_B V}RT$$

- When height is involved π = hdg here h = height; d= density; g = gravitational acceleration
- The two solutions having same osmotic pressure and hence same molar concentration at the same temperature are called isotonic or iso-osmotic solutions

For isotonic solutions, at constant temperature

$$\frac{n_1}{v_1} = \frac{n_2}{v_2}$$

If one of the solution is of lower osmotic pressure, it is called hypotonic solution with respect to more concentrated solution.

The more concentrated solution with higher osmotic pressure is known as hypertonic solution with respect to dilute solution

- When the pressure applied on the solution is more than osmotic pressure then solvent will start flowing from the solution to the solvent through semi-permeable membrane. This process is called reverse osmosis. It is used in the desalination of eater.

VAN'T HOFF FACTOR

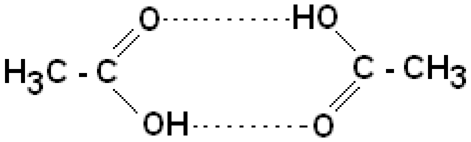
- Colligative properties depend upon the number of particles of the solute in the solution. In some cases, where the solute undergoes association or dissociation in solution, abnormal results for molecular masses are obtained.
- Van't Hoff Factor (i)
  Van't Hoff , in order to account for extent of association or dissociation of solute in solution introduced a factor "i" known as the van't Hoff factor. It is defined as the ratio of experimental value of colligative property to the calculated value of that colligative property

$$i = \frac{observed\ colligative\ property\ (actual)}{theoritical\ colligative\ property\ (expected)}$$

$$i = \frac{Calculated\ molecular\ mass\ (M_C)}{observed\ (experimental) molecular\ mass\ (M_O)}$$

$$i = \frac{Number\ of\ molecules\ actually\ present}{Number\ of\ molecules\ expected\ to\ be\ present}$$

- Association
  There are many organic solutes which in non-aqueous solutions undergo associated, that is two or more molecules of solute associate to form a one bigger molecule. Thus, the number of effective molecules decreases and consequently the colligative property become less than expected value which depend upon the number of solute molecules. Example : acetic acid in benzene and chloroacetic acid in naphthalene



- Degree of association α

$$\alpha = \frac{Nunber\ of\ molecules\ associated}{Total\ number\ of\ molecules\ taken}$$

Suppose n simple molecules combine to form an associated molecules

$nA \leftrightarrows (A)_n$

initial concentration 1 0

Final concentration 1- α α/n

Total number of effective moles after dissociation = 1 – α + α/n

$$i = \frac{1 - \alpha + \frac{\alpha}{n}}{1}$$

$$i = 1 - \alpha\left(1 - \frac{1}{n}\right)$$

$$\alpha = \frac{(1 - i)n}{n - 1}$$

Here $i = \frac{Calculated\ molecular\ mass\ (M_C)}{observed\ (experimental) molecular\ mass\ (M_O)}$

$$\alpha = \frac{M_O - M_C}{M_O}\frac{n}{n-1}$$

$M_O > M_C$

Thus $i < 1$

Observed colligative property < Calculated value

- Dissociation

  Inorganic acids, bases and salts in aqueous solutions undergo dissociation that is, the molecules break down into ions. In such cases, the number of effective particles increases and value of colligative property becomes higher than expected one (which depends upon number of solute particles
- Degree of dissociation α

$$\alpha = \frac{Nunber\ of\ molecules\ dissociated}{Total\ number\ of\ molecules\ taken}$$

Consider a molecule of an electrolyte dissolved in a solvent dissociated to give n ions

$(A)_n \leftrightarrows A$

initial concentration 1 0

Final concentration 1- α n α

Total number of effective moles after dissociation = 1 – α + nα

$i = 1 - \alpha + n\alpha$

$= 1 - \alpha (n - 1)$

$\alpha = \frac{i-1}{n-1}$

$$i = \frac{M_C}{M_O}$$

$$\alpha = \frac{M_C - M_O}{M_O}\frac{1}{n-1}$$

$M_C > M_O$: $i > 1$

Observed colligative property > Calculated value of colligative property

1. Relative lowering of vapour pressure

$$\frac{P_1^O - P_S}{P_1^O} = iX_2$$

   X_2 = mole fraction of solute
2. Osmotic pressure $\pi = i\ CRT$
3. Elevation in boiling point $\Delta T_b = i \times K_b \times$molality
4. Depression in freezing point $\Delta T_f = i \times K_f \times$molality

SOLVED NUMARICAL

Q1) The mole fraction of methanol in an aqueous is 0.02 and its density is 0.994 g/ml. Determine the molarity of the solution.

Solution:

Let volume of solution be 1 L . From density of solution weight of solution = 994 gm

N = Number of moles of water (solvent) ; n = number of moles of solute (methanol)

Molecular weight of methanol = 32; molecular weight of water = 18

Now 994 = n(32) + N(18) --- eq(1)

From the formula of mole fraction $X = \frac{n}{n+N}$

$\therefore n = \frac{XN}{1-X} \ldots \ldots . eq(1)$

Substituting value of n in equation 1

$$994 = \left(\frac{XN}{1-X}\right)32 + 18N$$

$$994 = \left(\frac{0.02}{1-0.02}\right)32N + 18N$$

994 = (0.65 + 18) N

N = 53.29

Substituting value of N in equation 2 we get n = 1.08

According to definition of molarity volume is taken 1 litre therefore molarity = 1.08

Q2) 100g water contains 1.0 g urea and 2.0 g sucrose at 298 K. The vapour pressure of water at 298K is 0.03167 bar. Determine the vapour pressure of the solution.

Solution :

$$\frac{P^0 - P_S}{P^0} = \frac{n_2}{n_1}$$

$$\frac{\Delta P}{P^0} = \frac{n_2}{n_1}$$

$$\frac{\Delta P}{0.03167} = \frac{\frac{1}{60} + \frac{2}{242}}{\frac{100}{18}}$$

$$\Delta P = 0.00014$$

$$P^0 - P_S = \Delta P$$

$$P_S = P^0 - \Delta P$$

$$P_S = 0.03167 - 0.00014 = 0.03153 \text{ bar}$$

Q3) The boiling point of a solution of 0.105g of substance in 15.84 g of ether was found to be 0.1°C higher than that of pure ether. What is molecular weight of solute? Given:K_b(ether) = 21.6K mole^{-1} per 100 g.

Solution

$\Delta T_b = 0.1^oC$

$$m = \frac{w \times 1000}{M_0 \times W} = \frac{0.105 \times 1000}{M_0 \times 15.84}$$

$\Delta T_b = K_b \times m$

K_b is for 100g , must be converted for 1000g . Therefore value of ΔT_b will be 21.6/10

$$0.1 = \frac{21.6}{10} \times \frac{0.105 \times 1000}{M_0 \times 15.84}$$

M_0 = 143.18 gm/mol

Q4) Calculate the mole fraction, molal and molar concentration of a solution containing 20% acetic acid by mass in water, if the density of the solution at 20^{O}C is 1.026 g cm^{-3}.

Solution:

	$ZnSO_4$ ⇄	Zn^{2+} +	SO_4^{2-}
Initial concentration	1	0	0
Final concentration	(1-α)	α	α

Now i =1- α + 2α

$= 1 + \alpha$

Now

$$\frac{P^0 - P_S}{P^0} = i\frac{n_2}{n_1}$$

$$\frac{750 - 740}{750} = i\frac{0.5}{55.55}$$

i=1.482

1+α=1.482

α=0.482

% dissociation = 48.2%

Q5) Calculate the amount of ice that will separate out on cooling a solution containing 50g of ethylene glycol in 200g water to -9.3°C. Given K_f for water = 1.86 K mol^{-1}kg

Solution:

$\Delta T_f = K_f \times m$

m= 9.3 /1.86

For the formula of molality

$$\frac{50 \times 1000}{62 \times W} = \frac{9.3}{1.86}$$

W=161.29

Weight of water converted in to ice = 200 – 161.29 = 38.71 g

Q6) A solution contains 0.011 kg of barium nitrate in 0.1 kg of water boils at 100.46°C. Calculate the degree of ionization of salt. Given K_b(water) = 0.52 K kg mol^{-1}

$\Delta T_b = i \times K_b \times m$

$$i = \frac{\Delta T_b}{K_b \times m}$$

Molecular weight of barium nitrate = 261, weight of solvent = 0.1 , weight of solute 11, molality

$$m = \frac{11}{261 \times 0.1}$$

Thus

$$i = \frac{0.46 \times 261 \times 0.1}{0.52 \times 11} = 2.098$$

$Na(NO_3)_2 \rightleftarrows Ba^{2+} + 2NO_3^-$

Final concentration 1 α 2α

i= (1-α) + 3α =1+2α

2.098 = 1 + 2α

α = 0.55

Q7) if boiling point of an aqueous solution is 100.1°C, what is its freezing point? Given latent heat of fusion and vaporization of water are 80 cal g^{-1} and 540 cal g^{-1} respectively

Solution

$$K_f = \frac{RT_0^2}{1000L_f} = \frac{2 \times (273)^2}{1000 \times 80} = 1.8632$$

$$K_b = \frac{RT_0^2}{1000L_v} = \frac{2 \times (273)^2}{1000 \times 540} = 0.5153$$

$\Delta T_b = K_b \times m$

$0.1 = 0.5153 \times m$

Therefore m = 0.194 mol/kg

$\Delta T_f = K_f \times m$

$\Delta T_f = 1.8632 \times 0.194 = 0.361^\circ C$

Freezing point of pure water is 0°,

Therefore freezing point of solution = 0 -0.361 = -0.361°C

Q8) Find the molarity and molality of a 15% solution of H_2SO_4 (density H_2SO_4 = 1.020 g/cc)

Solution:

15% solution of H_2SO_4 means 15g of H_2SO_4 have been dissolved in 100 g of solution i.e.

Weight of H_2SO_4 = 15 g and weight of water = 85

Molarity

Volume of solution = mass/density = 100/1.02 = 98.04 ml

$$M = \frac{W \times 1000}{M_0 \times V} = \frac{15 \times 1000}{98 \times 100} = 1.56M$$

Molality

$$m = \frac{W \times 1000}{M_0 \times mass\ of\ solvant} = \frac{15 \times 1000}{98 \times 85} = 1.8m$$

Q9) A 500g tooth pate sample has 0.2g fluoride concentration. What is the concentration of fluorine in terms of ppm level?

Solution

$$ppm = \frac{mass\ of\ solute}{mass\ of\ solution} \times 10^6 = \frac{0.2}{500} \times 10^6 = 400ppm$$

Q10) The vapour pressure of pure benzene and tolune at 40^{o}C are 184.0 torr and 59.0 tor respectively. Calculate the partial pressures of benzene and toluene, the total vapour pressure of the solution and mole fraction of benzene in the vapour phase above the solution, if mole fraction of benzene in solution is 0.40. Assume that the solution is ideal

Solution: subscript B denote Benzene and T denote Toluene

In Solution X_B = 0.40 and Hence X_T= 0.6

$P_B = X_B P_B^O = 0.40\times 184.0 = 73.6$ torr

$P_T = X_T P_T^O = 0.6 \times 59.0 = 35.4$ torr

$P_{TOTAL} = P_B + P_T = 73.6 + 35.4 = 109.0$ torr

$$X_B = \frac{P_B}{P_{TOTAL}} = \frac{73.6}{109} = 0.675$$

Q10) The vapour pressure of benzene and toluene are 75 mmHg and 22mmHg respectively. 23.4g of benzene and 64.4 g of toluene are mixed. If the two form an ideal solution, calculate the mole fraction of benzene in the vapour phase if the vapours are in equilibrium with the liquid mixture at the same temperature.

Solution

Number of moles of benzene n_B = 23.4 /78 = 0.3

Number of moles of toluene n_T = 64.4/92 = 0.7

Mole fraction of Benzene

$$X_B = \frac{0.3}{0.3 + 0.7} = 0.3$$

Then mole fraction of toluene X_T = 1 -0.3 = 0.7

$P_{TOTAL} = P_{benzen} + P_{toluene}$

= 75×0.3 + 22×0.7 = 37.9

Mole fraction of benzene in vapour phase = $P_{benzene}$ / P_{TOTAL}

$$= \frac{75\times0.3}{37.9} = 0.59$$

Q11) Vapour pressure of a pure liquid A is 10.0 torr at 270°C. the vapour pressure is lowered to 9.0 torr on dissolving one gram of B in 20g of A. If molar mass of A is 200 then calculate molar mass of B

Solution

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A}$$

$$\frac{10-9}{9} = \frac{w_B}{M_B}\times\frac{M_A}{w_A} = \frac{1}{M_B}\times\frac{200}{20}$$

$M_B = 100$

Q12) Calculate the molecular weight of glycerine if its solution containing 10.2 g of glycerine per litre is isotonic with solution of glucose.

Solution:

For being isotonic

$$\pi_{glycerine} = \pi_{flucose}$$

$$\frac{n_1}{V_1}RT = \frac{n_2}{V_2}RT$$

Number of moles = weight/molecular weight,

2% solution means 2 gram glucose in 100g solution, density of water = 1g/cm^3

$$\frac{W_{glycerine}}{M_{glycerine}}\times\frac{1}{V_1} = \frac{W_{glucose}}{M_{glucose}}\times\frac{1}{V_2}$$

$$\frac{10.2}{M_{glycerine}}\times\frac{1}{1000} = \frac{2}{180}\times\frac{1}{100}$$

$M_{glycerine} = 91.8$

Q13) A 5% aqueous solution by mass of a volatile solute boils at 100.15°C. Calculate the molar mass of the solute K_b = 0.52 K Kg mol^{-1}

Solution

Normal boiling point of water = 100°C

∴ Increase in boiling point of water = 100.15 -100 = 0.15°C

The solution contains 5% by mass of the solute that is 5 g solute in 100 g of solvent

∴ Mass of solvent = 100 – 5 = 95g

From the formula for elevation in boiling point

$$\Delta T = K_b \times \frac{w_B}{w_A \times m_B} \times 1000$$

$$m_B = K_b \times \frac{w_B}{w_A \times \Delta T} \times 1000$$

$$m_B = 0.52 \times \frac{5}{95 \times 0.15} \times 1000 = 21.6$$

Q14) What weight of glycerol have to be added in 500g of water in order to lower its freezing point by 20°C? $K_f = 1.86$°C

Solution

From the formula for depression in freezing point

$$\Delta T = K_f \times \frac{w_B}{w_A \times m_B} \times 1000$$

Molecular weight of glycerol m_B is 92

$$w_B = \frac{\Delta T \times w_A \times m_B}{K_f \times 1000} = \frac{20 \times 92 \times 500}{1.86 \times 1000} = 495g$$

Q15) In 100g of naphthalene, 2.423 g of S was dissolved. Melting point of naphthalene = 80.1°C. ΔT_f= 0.661°C L_f = 35.7 cal/g of naphthalene. Determine the molecular formula of sulphur added

Solution

From the formula

$$K_f = \frac{RT_f^2}{1000L_f}$$

And formula for depression in freezing point

$$\Delta T_f = K_f \times \frac{w_B}{w_A \times m_B} \times 1000$$

$$\Delta T_f = \frac{RT_f^2}{1000L_f} \times \frac{w_B}{w_A \times m_B} \times 1000$$

$$m_B = \frac{RT_f^2}{1000L_f} \times \frac{w_B}{w_A \times \Delta T_f} \times 1000$$

$$m_B = \frac{2 \times (353.1)^2}{1000 \times 35.7} \times \frac{2.423}{0.661 \times 100} \times 1000 = 256$$

(value of R taken as 2 in calories)
If molecular formula of S is S_x then
X = 256/32 = 8
Thus substance is S_8

Q16) The freezing point of a solution of acetic acid (mole fraction = 0.02) in benzene 277.4 K. Acetic acid exists partly as dimer $2A \leftrightarrows A_2$. Calculate equilibrium constant for dimerisation. Freezing point of benzene is 278.4K and K_f for benzene is 5 K kg mol^{-1}

Solution

Let acetic acid = A, Benzene = B

Assume α part of A forms dimer

$2A \rightleftharpoons A_2$

1-α α/2 moles after dimer is formed

I = (1-α) + α/2 = 1 –α/2 ---- eq(1)

Mole fraction of A = X_A = 0.02

Mole fraction of B = X_B = 1-0.02 = 0.98

Molality of A in B

$$m = \frac{X_A \times 1000}{X_B \times M_B} = \frac{0.02 \times 1000}{0.98 \times 78} = 0.262 molkg^{-1}$$

(Molecular weight of benzene =78)

Since $\Delta T_f = K_f \times i \times$molality
278.4-277.4 = 5× i ×0.262
$i = 0.763$
Thus from equation 1
0.763 = 1 – α/2
A = 0.48
Hence the molality of A after dimer is formed = (1-α)×initial molality
= (1-0.48)×0.262 = 0.13624
Anad the lolaity of A_2 after dimer is formed = (α/2) × molality =0.24 ×0.262 =0.06288
The equilibrium constant

$$K_{eq} = \frac{[A_2]}{[A_1]^2} = \frac{0.06288}{(0.13624)^2} = 3.39\ kgmol^{-1}$$

Q17) A solution of monobasic acid (3×10^{-2}m) has a freezing point depression of 0.06°C. Calculate pK_a for the acid [Mola depression constant 1.86°C/m for water]

Solution

We know that $\Delta T_f = K_f \times i \times$molality
$0.06 = 1.86 \times i \times 3\times10^{-2}$

$i = 1.07526$

Let acid is MH

$MH \rightleftharpoons M^- + H^+$

Initial concentration C 0 0

Final concentration C(1-α) Cα Cα

$K_a = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = C\alpha^2$

Now

$$i = \frac{total\ moles\ after\ disociation}{initial\ mole}$$

$$i = \frac{C(1-\alpha) + C\alpha + C\alpha}{C} = 1 + \alpha$$

$\alpha = i - 1 = 1.07526 - 1 = 0.07526$

$K_a = 1.6992 \times 10^{-4}$

$pK_a = -\log K_a = -\log(1.6992 \times 10^{-4})$

$pK_a = +3.769$

ATOMIC MODEL AND ELECTROMAGNETIC WAVE THEORY

Dalton in 1808 proposed that matter was made up of extremely small indivisible particles called ATOM. But in early 20th century various experiments established that atom was not the smallest indivisible particle but made up of still smaller few fundamental particles like electrons, protons and neutrons.

FUNDAMENTAL PARTICLES

Electron, proton and neutron are regarded as the fundamental particles.

Electrons

Electron was discovered in cathode-ray experiment.

The charge on an electron (-1.602×10^{-19} coulomb or $- 4.8 \times 10^{-10}$ esu) was determined by R.A. Millikan with his oil drop experiment.

Charge/mass *(elm)* ratio of the electron was determined by J. J. Thomson as

elm = 1.76×10^{8} coulombs/g.

The *elm* ratio of electron was found to be independent of nature of gas and electrodes used.

Mass of electron is calculated as : 9.11×10^{-28} g

This is the rest mass of electron and it is 1 /1837 times mass of a hydrogen atom.

The mass of electron moving with velocity v is given as

$$m = \frac{m_{rest}}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

Where c is the velocity of light

Mass of one mole of electrons is nearly 0.55 mg

Charge of electron (1.6×10^{-19} coulomb) is the smallest measurable quantity and is called one unit.

Radius of electron = 42.8×10^{-15} m

Density of electron = 2.17×10^{17} g/cm^3

Charge on one mole of electron ≈ 96500 coulomb or I Faraday

Protons

Proton was discovered in anode-ray experiment. Anode rays also called as canal rays or positive rays discovered by E. Goldstein contain positive ions produced as a result of knock out of electrons from the gaseous atom or molecule.

When hydrogen gas is taken in the discharge tube the positive particles (H^+) produced in the anode rays are called protons. Mass of proton was found to be 1.673×10^{-24} g

The magnitude of charge on a proton was found to be same as that on the electron but with opposite sign (positive) *i. e.* $e = +1.6 \times 10^{-19}$ coulomb. Charge/mass *(elm)* ratio of proton was found to be 9.58 x 10^4 coulombs per gram

Mass of 1 mole of protons = 1.007 g"

Charge on 1 mole of protons'" 96500 coulombs or 1 Faraday

Neutrons

Neutron was discovered in scattering experiment by James Chadwick in 1932.

Mass of neutron was found to be 1.675 x 10^{-24} g or 1.008665 amu. It is slightly heavier (0.18%) than proton.

Neutron is a neutral particle with density = 1.5 x 10^{14} g/cm^3 Mass of one mole of neutron is 1.0087 g

Besides these three fundamental particles 35 different subatomic particles are also known like positron, neutrino, antineutrino, mesons, etc.

Cathode rays consist of negatively charged electrons with negligible mass. These are emitted from cathode itself.

Where as ***anode rays*** consist of positively charged ions *produced by the removal of one or more electrons from the gaseous atom or* molecule*.* It shows that anode rays are not emitted from anode but produced in the space between the anode and cathode. Thus *elm* of anode rays depends on the nature of gas taken in discharge tube whereas *elm* of cathode rays is constant and independent of nature of gas and electrodes.

RUTHERFORD'S ATOMIC MODEL (NUCLEAR MODEL)

Rutherford explained the structure of atom on the basis of his scattering experiment in which thin foil of metals like gold, silver, platinum, etc. was bombarded with fast moving a-particles. Various postulates of this model are:

Atom is spherical and consists of two parts, nucleus and extranuclear part.

Nucleus is very small in size. It is a positively charged highly dense central core in which entire mass of the atom is concentrated.

Extra nuclear part is an empty space around nucleus where *electrons* are *revolving* in a *circular orbit with very high* speed. This nuclear model is comparable to our solar system in which planets are revolving around sun. This model however fails to explain the stability of atom and line spectrum of hydrogen.

Atomic Number

Number of protons present in an atom is known as its atomic number. In a neutral atom,

Atomic number = Number of protons (n_p) = Number of electrons present

It is represented as *'Z'.*

Mass Number

Mass of an atom is concentrated in centrally located nucleus only. The sum of number of protons and neutrons in an atom is known as its mass number.

Mass number = Number of protons (n_p) + Number of neutrons (n_e)

Since it is the sum of number of protons and number of neutron in nucleus, mass number is always a whole number. It is represented by *'A'.*

An element *X* is represented as : ${}_{Z}^{A}X$

Different types of atomic species

(i) Isotopes

Atoms of same element having same atomic number but different mass number are called isotopes. *e.g.* : ${}_{1}^{1}H$ and ${}_{1}^{2}H$, ${}_{15}^{30}P$ and ${}_{15}^{31}P$

(ii) Isobars

Atoms of different elements having same mass number but different atomic number are called isobars. *e.g.* ~ ${}_{19}^{40}K$ and ${}_{6}^{14}C$ and ${}_{7}^{14}N$

(Hi) Isotones

Atoms of different elements having same number of neutrons are called isotons

e.g ${}_{6}^{14}C$ and ${}_{8}^{16}O$, ${}_{19}^{39}K$ and ${}_{20}^{40}Ca$

(iv) Isoelectronics

The chemical species having same number of electrons are called isoelectronics. *e.g.* 0^{2}-, F^-, Na^+, Mg^{2+}, etc.

(v) Isodiaphers

The chemical species having same isotopic number

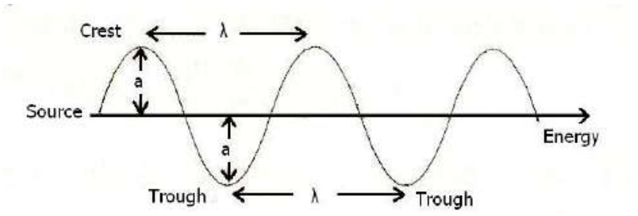
i.e. Number of neutrons - Number of protons (n_n - n_p) are called isodiapher

${}_{92}^{235}U$ and ${}_{90}^{231}Th$

ELECTROMAGNETIC WAVE THEORY

According to electromagnetic wave theory, energy is emitted continuously from a source in the form of radiation (or wave) and is called radiant energy. The radiations consist of both electric and magnetic field oscillating perpendicular to each other and to the direction of propagation. These radiations associated with both electric and magnetic field possess wave character and travel with speed of light. Hence these are known as *electromagnetic radiations* or *electromagnetic wave.* Electromagnetic waves do not require a *material* medium for propagation.

Characteristics of a wave



(i)Wavelength (λ)

Distance between two consecutive crests or troughs is known as wavelength. It is expressed in centimetres, nanometres (nm) or angstrom (Å)

$1\text{nm} = 10^{-9}\text{m} = 10^{-7}$ cm $1\ \text{Å} = 10^{-10}$ m,= 10^{-8} cm

(ii) Frequency (v)

It is the number of waves passing through a given point in one second. It is expressed as cycles per second or hertz (Hz).

1 Hz = 1 cps.

Frequency is inversely proportional to wavelength of the wave

i.e. $\nu \propto 1 / \lambda$ or $c = \quad \lambda$

where c is velocity of the wave.

(iii) Velocity *(c)*

It is defined as the distance travelled by a wave in one second.

Electromagnetic radiations travel with velocity of light *i. e.* $c = 3 \times 10^8$ *m/s.*

(iv) Wave Number (k) or $\bar{v}$

It is the number of waves present in one cm length. *i.e.* $\bar{v} = 1 / \lambda$

(v) Amplitude *(a)*

It is defined as the height of crest or depth of trough. It gives the intensity or brightness of the beam of light.

PLANCK'S QUANTUM THEORY

According to this theory, emission or absorption of radiant energy is not a continuous process but takes place discontinuously in the form of small discrete packets of energy. Such packets of energy are called ' quanta' , in case of light they are known as 'photons' Energy of each quantum is directly proportional to the frequency of radiation it is given by equation $E = h\upsilon$ where h is constant of proportionality known as Planck's constant. Its value = 6.626×10^{-34} J-sec or 6.626×10^{-27} erg-sec

The total amount of energy emitted or absorbed is measured in terms of number of quanta. *i.e.* Total energy, $E = nh\upsilon$

where *n* is number of quanta (any integer).

PHOTOELECTRIC EFFECT

It is the ejection of electrons from metal surface when a beam of light of certain minimum frequency is allowed to strike the metal surface in vacuum. The electrons so ejected are called as photoelectrons.

Energy of photoelectron ∝ Frequency of incident radiation and

Number of photoelectrons ∝ Intensity of incident radiation emitted per second

Few important facts about photoelectric

i) Only radiation striking the metal surface with certain minimum frequency have certain minimum energy are able to eject the electron. This minimum value of frequency known as Threshold Frequency v_0> If frequency is less than threshold frequency , no electron is ejected

(ii) The minimum energy required to eject the called the work function (ϕ).

(iii) If the frequency of incident light is more than threshold frequency then some of the energy gets consumed to eject the electron from atom and the extra energy enders the electron with kinetic energy $\frac{1}{2} mv^2$

i.e. Total energy $(E) = I.E. + K.E.$

where *I.E.* is the ionisation energy require to knock out the electron and *K.E.* is the kinetic energy of electron It can be written as

$hv = h\ v_0 + \frac{1}{2} mv^2$

by substituting value of v from equation $c = v\lambda$ we can get above equation in terms of λ

iv)The number of photoelectrons ejected is proportional to intensity of incident radiation *i.e.* an increase in intensity of incident radiation increases the rate of energy of photoelectrons. Not the energy of photo electrons

v) Alkali metals having lower ionization energy readily show the photoelectric effect. Caesium having lowest ionization energy, shows this effect in a best way. Hence it is used in photoelectric cells.

Compton effect

When monochromatic X-rays are allowed to fall on lighter elements like carbon, they suffer an increase in wavelength after scattering, *i.e.*

Wave length of scattered X-rays > Wave length of incident X-rays

Thus Energy of scattered X-rays < Energy of incident X-rays

or Frequency of scattered X-rays < Frequency of incident X-rays

This phenomenon of increase in wavelength of X-rays after scattering from the surface of lighter elements is known as *Compton effect.* The scattering of X-rays is due to interaction of photon (X-rays) and electrons.

BOHRS MODEL AND HYDROGEN SPECTRUM

When a radiation is analysed through the prism it produces particular pattern on photographic film. This pattern of radiation is known as spectrum. Spectra are classified in two types

1)Emission Spectra: When an excited electron returns back from higher energy level to ground state, it emits energy in the form of radiations. The spectrum produced by these emitted radiations is known as Emission Spectrum. It is further of two types

i) Continuous spectra. It consist of continuous bans of radiations corresponding to different wave length

ii) Line spectra

This spectrum consists of isolated coloured lines on photographic plate separated from each other by dark space.

2) Absorption Spectra

When white light from a source is first passed through a solution of a chemical substance, then radiation of particular wave length is absorbed by the solution of a particular wavelength is absorbed by the solution depending upon the nature of chemical substance. Now if the light coming out from the solution is analyzed by spectroscope, we get some dark lines in the otherwise continuous spectrum corresponding to the absorbed wavelength. It is observed that these dark lines appear at the same place where colored lines appeared in the emission spectrum of same substance. Absorption spectrum is always a discontinuous spectrum consisting of dark lines

HYDROGEN SPECTRUM

When electric discharge is passed through hydrogen gas taken in a discharge tube at low pressure, some radiations are emitted. These radiations on spectroscopic analysis give emission spectrum of hydrogen. The spectrum consists of number of lines in UV, visible and Infra red region each line corresponds to very particular wave length. These lines are grouped into fivr different series named after the discoverers.

Though a large number of lines appear in the hydrogen spectrum, their wave length can be measured by calculating their wave number given by Rydberg Formula

$\bar{\nu} = \frac{1}{\lambda} = R\left[\frac{1}{n^2} - \frac{1}{m^2}\right]$ n and m are the energy levels involve din transition

Here energy of energy level m > energy of energy level n

R is a constant known as Rydberg constant value is 13.6eV

By using equation c = νλ we can get above equation in terms of ν

BOHR'S ATOMIC MODEL

To explain the stability of atom and line spectrum of hydrogen, Neil Bohr in 1913 proposed a model of atom. His theory was based on Planck's quantum theory and some postulates of classical physics. The various postulates of the model are as follows :

(i) An atom consists of highly dense positively charged nucleus at the centre and electrons revolving around nucleus in circular orbits.

(ii) Angular momentum of an electron in an atom is quantized.

$mvr = nh/2\pi$

where m = mass of electron, v = velocity of electron

r = radius of orbit, n = number of orbit in which electron is present

Out of numerous possible circular orbits, an electron can revolve only in that orbit for which n is a whole number.

(iii) Orbits in which electrons are revolving have fixed value of energy. These orbits are called *energy levels* or *stationary states.* As long as electrons are revolving in these orbit, they neither lose nor gain energy and hence explain the stability of atom. The energy of a stationary state of hydrogen atom is given as

$E_n = -\frac{2\pi^2 me^4}{n^2h^2}$ where n is the n^{th} energy level

Putting the value of m and e

$E_n = -\frac{21.8\times10^{-19}}{n^2}$- J/ atom OR $E_n = -\frac{13.6}{n^2}$ eV/atom OR $E_n = -\frac{1312}{n^2}$ kJ /mole

Energy of n^{th} orbit of other hydrogen-like one electron species is given as

$E_n = -\frac{2\pi^2 me^4}{n^2h^2}Z^2$

$= -\frac{1312}{n^2}Z^2$kJ / mol

$= -\frac{13.6}{n^2}Z^2$eV / atom

$= -\frac{21.8\times10^{-19}}{n^2}Z^2$ J / atom where Z is atomic number

iv) Lowest energy state of electrons in an atom is the most stable state and is known as *Ground state or Normal state.* Electrons keep on revolving in this state without absorption or emission of energy.

v) Absorption or emission of energy takes place during the transition of electron from lower to higher energy level or vice-versa respectively. Energy absorbed or released in an electronic transition is given as

$\Delta E = E_2 - E$

where ΔE is energy absorbed or emitted E_2 is energy at final state E_1 is energy at initial state of transition

On the basis of Bohr's Theory, radius of *nth* orbit of anyone electron system with atomic number Z is derived as

$r = \frac{n^2h^2}{4\pi^2 mZe^2k}$ here k = 1/4πε$_0$, ε$_0$ is absolute permittivity of vacuum.

Its value is 9×10^9 Nm^2 / C^2,

Substituting values of h, m, e, etc we get radius of electron of hydrogen atom

r = 0.529 × n^2 Å

For nth orbit of any one electron species with atomic number Z

$R_n = \frac{0.529 \times \mathrm{n2}}{Z}$

Velocity of an electron in an orbit

Velocity with which an electro is revolving in an orbit is calculated using Bohr's theory as v $= \frac{2\pi e^2}{nh}Z$ substituting value of e , h ,п we get

$V = \frac{2.19\times10^6}{n}Z$ m/s

We can observe from above equation that velocity decreases at higher energy lelvels

Velocity of electron in 1st orbit is also known as Bohr's velocity. It is calculated that Bohr's Velocity = 1/138 of velocity of light

Advantages of Bohr's Theory

i) It explain the stability of atom

ii) Line spectrum of hydrogen can be explained with Bohr's theory

iii) Using the concept of Bohr's theory radius and velocity of electron in various orbits can be calculated

Drawbacks of Bohr's Theory

i) Bohr's theory donot explain the spectrum of multielectron atom. It can only explain the spectrum of single electron species like H-atom He$^+$, Li^{2+}

ii) It does not explain the splitting of spectral lines under the influence of magnetic effect.

iii) Bohr's theory does not justify the principle of quantization of angular momentum

iv) Bohr's theory gave two dimensional model of atom by saying that electron revolves in circular orbit around nucleus in one plane. Whereas it is now established that atom has three dimensional structure

v) Bohr's Model fails to explain de Broglie concept of duel character and Heisenberg's principle of uncertainty.

CONCEPT OF DUAL CHARACTER

According to de Broglie's concept, moving matter *i.e.* moving material objects possess dual character *viz.* wave nature and particle nature (like radiations). de Broglie wavelength of material particles is given as

$\lambda = \frac{h}{mv}$

This concept of dual character gave rise to the wave mechanical theory according to which electrons, protons and even atoms possess wave properties in motion.

This concept of duality is applicable only in case of microscopic particles like atom, electron, etc. The wave character associated with macroscopic objects is of no significance.

This concept justify the quantization of angular momentum.

Construction of electron microscope and study of surface structure of solids by electron diffraction are few important applications of this concept.

de-Broglie's wavelength can also be calculated from kinetic energy of the particle using following expression

$\lambda = \frac{h}{\sqrt{2mE}}$ here E is the kinetic energy

de-Broglie concept applies quantitatively to the particles in force-free environment. Therefore, it cannot be applied directly to an electron in an atom, where the electron is subjected to the attractive forces of the nucleus.

HEISENBERG"S UNCERTAINTY PRINCIPLE

The principle states that, "it is impossible to measure position and momentum of any microscopic particle (subatomic particles) simultaneously with absolute accuracy". It has been seen that product of uncertainty in position (Δx) and uncertainty in momentum (Δp) is always constant and is equal to or greater than $h/4\pi$ i.e $\Delta x\ \Delta p \geq h/4\pi$ value of $h/4\pi$ is 5.25×10^{-35}

ATOMIC ORBITALS AND ELECTRONIC CONFIGURATION

QUANTUM NUMBERS

Quantum numbers are the set of four numbers which explain the state of electron *i.e.* location, energy, type of orbital, orientation of orbital, etc. in an atom. Various quantum numbers are as follows:

1. Principal Quantum Number *(n)*

It represents the principal shell of an atom. It can have integral values except zero like 1, 2, 3, ... also denoted as *K, L, M,* .... etc.

Maximum number of electrons in a principal shell can be $2n^2$ where n is principal quantum number.

This quantum number gives information about

distance of electron from nucleus *i.e.* size of electron cloud·

energy of electron in any shell

$E_n = \frac{1312}{n^2} Z^2$ kJ mol^{-1} where Z is atomic number and n is principle quantum number

Azimuthal or Subsidiary or Angular Quantum Number (I)

Azimuthal quantum number represents the subshell or sub energy shell in an atom.

This quantum number renders following information's:

The number of subshells present in a principal shell:

For a principal shell *'n', 'l'* can have values starting from 0 to $(n - I)$ *i.e.* a total of n values where n is principal quantum number.

Subshell notations *ares,p, d,fetc.*

for'l' values 0, 1, 2, 3 respectively.

Values of'n'	Values of'/'	Subshell notation
1	0	s
2	0 1	s *P*
3	0 1 2	s *p* *d*
4	0 1 2 3	s *p* *d* f

The maximum number of electrons present in a subshell is given by $2(2l + 1)$.

Subshell	l	Number of electrons
s	0	2
P	1	6
d	2	10
f	3	14

Orbital angular momentum of electron is given as

$$= \sqrt{l(l+1)}\frac{h}{2\pi}$$

Value of l gives an idea about shape of orbital.

Relative energy of different subshells belonging to same principal shell is $s < P < d < f$

3) **Magnetic Quantum Number *(m)***

It was given by Lande. Magnetic quantum number represents the orbital's present in a subshell. In a given sub-shell values of m are $(2l + 1)$ ranging from $- l$ to $+ l$ including zero. Each value of m corresponds to an orbital. Splitting of spectral lines in magnetic field (Zeeman effect) or in electric field (Stark effect) can be explained with this quantum number.

Subshell	/	*m*
s	0	0
P	1	-1,0,+1
d	2	-2,-1,0,+1,+2
/	3	-3,-2,-1,0, + 1, +2,

Thus we can say that

s-subshell has only one orbital,

p subshell has 3 orbitals P_X P_Y and P_Z

d-subshell has 5 orbitals d_{XY}, d_{YZ}, d_{xz}, dz^2 $d(z^2-y^2)$ and

f subshell has 7 orbitals.

In general, for p-subshell

m = 0 is taken for P_z and m = ± 1is taken for Px and Py

Similarly, for d-subshell

m = 0 is taken for dz^2

m = ± 2 is taken for $d(z^2-y^2)$ and d_{XY}

and m = ± 1 is taken for d_{xz} and d_{YZ}

Magnetic quantum number gives information about

Orientation of orbital in space around the nucleus.

Maximum number of electrons in an orbital can be two.

Number of orbitals in a shell = n^2.

4) **Spin Quantum Number *(s)***

It was given by Uhlenbeck and Goldschmidt. Spin quantum number gives information about spinning of electron on its own axis in an orbital. Electron in an orbital can spin either clockwise or anti clock wise. Thus an electron can have only two possible values of this quantum number, either +1/2 or -1/2 respectively.

Spin angular momentum (S) of an electron is given as

$$= \sqrt{l(l+1)}\frac{h}{2\pi}$$

A spinning electron acts like a micromagnet with a definite magnetic moment. In an orbital containing two electrons the two magnetic moments oppose each other and thus cancelled out. Thus in an atom if all the electrons are paired, the net magnetic moment is zero and the substance is known as *diamagnetic* (repelled by external magnetic field). However if any unpaired electron is present, the atom has a net magnetic moment and substance is known as *paramagnetic* (attracted by external magnetic field).

Net magnetic moment of an atom is given as $\mu = \sqrt{n(n+2)}$ where n is number of unpaired electrons.

Filling of Orbitals/Rules for writing electronic Configuration

There are few rules governing the filling of electrons in various orbitals which ultimately give electronic configuration.

1. Aufbau Principle

According to this rule, "orbitals are filled in the increasing order of their energies starting with the orbital of lowest energy". Energy of various orbitals are compared with *(n +l)* rule. The orbital having lower value of *(n + l),* has lower energy.

e.g. *3p* and *3d*

$n=3$	$n=3$
$l=1$	$l=2$
$n+l=4$	$n+l=5$

Thus, energy of *3p* is lower than that of *3d.*

If value *of(n + I)* is same for two orbitals, then orbital with lower value of *'n'* would have lower energy and filled first.

e.g.	*4p*	and	*3d*
	$n=4$		$n=3$
	$l=1$		$l=2$
	$n+l=5$		$n+l=5$

3d with lower value of *'n'* would be having lower energy than *4p.*

Increasing order of energy of various orbitals is given as

Is < 2s < *2p* < 3s < *3p* < 4s < *3d* < *4p* < 5s < *4d* < *5p* < 6s < *41*< *5d* < *6p* < 7s < 5/< *6d* and so on.

2. Pauli's exclusion Principle

The principle states that, "no two electrons in an atom can have same set of four quantum numbers". This shows that no two electrons in an atom are alike or an orbital can accommodate a maximum of two electrons that too with opposite spin.

3. Hund's Rule

According to this rule, "pairing of electrons in an orbital can not take place until each orbital of the same sub-shell is occupied by a single electron with parallel spin".

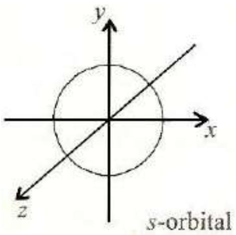
However some exceptions are found to this rule like Cr ($3d^5$) and Cu ($3d^{10}$ $4s^l$), etc. owing to the extra stability of half- filled and full-filled orbitals.

SHAPES OF ORBITALS

Shape of an orbital is given by total probability density \jf2 including both radial part as well as angular part.

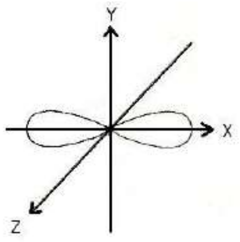
Shape of s-orbital

Shape of s-orbital must be spherical since probability of finding electron is equal in all directions at a distance from nucleus.

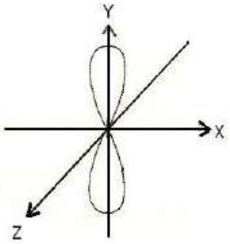


Shape of p-orbitals

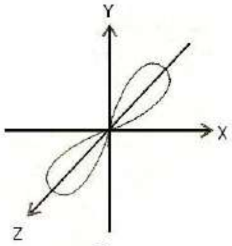
The probability of finding *p-electron* is maximum in two dumb bell type lobes on the two opposite sides of nucleus. Thus, p-orbital has dumb-bell shape. In the three *p-orbitals* ,p_X,p_Y and p_Z the probability lies maximum along x-axis, y-axis and z-axis respectively. p-orbitals possess one nodal plane passing through the nucleus.



P_x



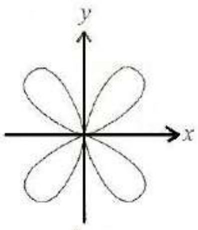
P_y



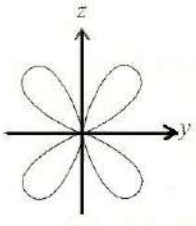
P_z

Shape of d-orbitals

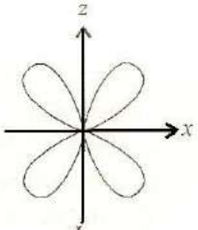
Depending on the probability, d-orbitals have clover-leaf shape. There are five d-orbitals, d_{XY}, d_{YZ}, d_{xz}, dz^2 $d(z^2 - y^2)$. dz^2 has exceptionally doughnut shape. Each d-orbital has two nodal planes.



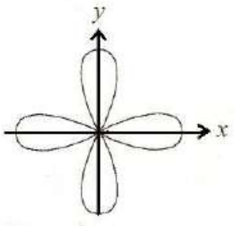
d_{xy}



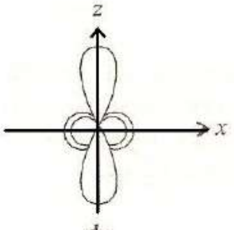
d_{yz}



d_{xz}



$d_{x^2-y^2}$



d_{z^2}

Number of radial node for orbit = (n- l -1)

Qualitative Analysis Test for and identify organic functional groups

Functional group	Test method	Observation	Comments
Alkene or Alkyne	Bubble gas through or add Bromine solution in hexane or water	The orange /brown bromine rapidly decolourises, as a saturated colourless organic bromo-compound is formed	$R_2C = CR_1 \rightarrow BrR_2C – CR_2BR$ $RC \equiv CR + 2Br_2 \rightarrow Br_2RC\text{-}CRBr_2$ Here R is H, alkyl or aryl Saturated alkane do not reacts with bromine
Hydroxy group –OH chemical test in alcohol and phenols (in dry conditions) The first 3 tests (i) (ii) (iii) given on right are quit general for most alcohol	(i) Mix it with a few drops of ethanoyl chloride, test fumes with litmus and silver nitrate (* note ethanoyl chloride reacts with water, phenols and amines too!). (ii) Mix it with a little phosphorus(V) chloride and test as above. (iii) Warm with a little ethanoic acid and a few drops of conc. sulphuric acid. Pour into water.	(i) Litmus turns red and a white precipitate with silver nitrate$_{(aq)}$(drop on end of glass rod), if the mixture is poured into water you may detect a 'pleasant' ester odour, can test for HCl but water and amines produce it too! (ii) as for (1) but no ester smell! (iii) You should get a 'pleasant' characteristic smell of an ester.	(i) $R–OH + CH_3COCl \rightarrow CH_3COOR + HCl$ An ester and hydrogen chloride are formed (ii) $R–OH + PCl_5 \rightarrow R–Cl + POCl_3 + HCl$ a chloro compound and hydrogen chloride are formed. (i) and (ii) $Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$ from the hydrogen chloride fumes dissolved in water. (iii) $CH_3COOH + ROH \rightarrow CH_3COOR + H_2O$
Primary alcohol chemical test RCH_2OH, R = H, alkyl or aryl (NOT a phenol). (ii) is not a good test on its own, since so many other readily reducible organic compounds will give the same reaction, though following it up by testing for an aldehyde gives it much more validity	(i) Lucas test – shake a few drops with cold zinc chloride in conc. $HCl_{(aq)}$ (ii) Distil with potassium dichromate(VI) and mod. conc. $H_2SO_{4(aq)}$	(i) Solution remains clear. (ii) If product distilled off immediately an aldehyde odour can be detected and the solution colour changes from orange to green.	(i) Not usually reactive enough to form a primary halogenoalkane. (ii) $R–CH_2OH + [O] \rightarrow R–CHO + H_2O$ or the full works! $3R–CH_2OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3R–CHO + 7H_2O$ The orange dichromate(VI) ion is reduced to thegreen chromium(III) ion. If the organic product is collected you could test for an aldehyde.

Qualitative Analysis Test for and identify organic functional groups

Functional group	Test method	Observation	Comments
Secondary alcohol chemical test R_2CHOH, R = alkyl or aryl. (ii) is not a good test on its own, since so many other reducible organic compounds will give the same reaction, though following it up by testing for a ketone gives it much more validity.	(i) Lucas test. (ii) Distil with $K_2Cr_2O_7/H_2SO_{4(aq)}$	(i) Solution may cloud very slowly or remains clear (hit and miss) (ii) If product distilled off immediately ketone odour can be detected and the solution colour changes from orange to green	(i) May be reactive enough to slowly form an insoluble secondary halogenoalkane: $R_2CHOH + HCl \rightarrow R_2CHCl + H_2O$ (ii) $R_2CHOH + [O] \Rightarrow R\text{–}CO\text{–}R + H_2O$ or the full works! $3R_2CHOH + Cr_2O_7^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3R\text{–}CO\text{–}R + 7H_2O$ The orange dichromate(VI) ion is reduced to thegreen chromium(III) ion. If the organic product is collected you could test for an aldehyde.
Tertiary alcohol chemical test R_3COH, R = alkyl or aryl.	(i) Lucas test. (ii) Distil with $K_2Cr_2O_7/H_2SO_{4(aq)}$	(i) Goes cloudy very quickly. (ii) No aldehyde or ketone readily formed	(i) Reactive enough to immediately form an insoluble tertiary halogenoalkane $R_3COH + HCl \Rightarrow R_3CCl + H_2O$ (iii) Stable to modest oxidation.
Phenols(OH group is attached directly to aromatic ring)chemical test. R–OH, where R is aryl e.g. C_6H_5OH	Add a few drops of iron(III) chloride solution to little of the phenol in water	Usually gives a purple colour	(See also test for primary aromatic amines –use it in reverse starting with a known primary aromatic amine)
Carboxylic acids chemical test RCOOH	Mix the carboxylic acid with water and add a little sodium hydrogencarbonate solid or solution	Fizzing, colourless gas gives white precipitate with lime water	$RCOOH + NaHCO_3 \rightarrow$ $RCOONa + H_2O + CO_2$ (see also salts of aliphatic carboxylic acids below)

Qualitative Analysis Test for and identify organic functional groups

Functional group	Test method	Observation	Comments
Salts of aliphatic carboxylic acids e.g. $RCOO^-Na^+$or $(RCOO^-)_2Mg$ etc.	Add a little hydrochloride/ sulphuric acid to a suspected salt of an aliphatic carboxylic acid	The solid or solution have no stronger odour, but after adding the mineral acid you should get a pungent odour of the original aliphatic acid. If it's the salt of an aromatic carboxylic acid, you get little odour and maybe white crystalline precipitate	The stronger acid, HCl/H_2SO_4 displaces the weaker aliphatic carboxylic acid which have strong–pungent characteristic odours e.g. ethanoic acid from an ethanoate salt *(smell of acetic acid, vinegar)* and butanoates release butanoic acid*(butyric acid, rancid odour).*
Acid or Acyl Chloride chemical test RCOCl Fumes in air forming $HCl_{(g)}$	(i)Add a few drops to water, test with litmus and silver nitrate solution. (ii) Add to a little ethanol and pour the mixture into water.	(i) Litmus turns red and a white precipitate with silver nitrate. (ii) As above and you may detect a 'pleasant' ester odour.	(i) $RCOCl + H_2O \rightarrow RCOOH + HCl$ The acid chloride is hydrolysed to form HCl acid (chloride ions) and the original carboxylic acid. (ii) $CH_3CH_2OH + RCOCl \rightarrow RCOOCH_2CH_3 + HCl$ an ethyl ester and hydrogen chloride are formed
Acid Amide chemical test $RCONH_2$	Boil the suspected amide with dilute sodium hydroxide solution, see in inorganic for ammonia tests	Ammonia evolved on boiling (no heat required to form ammonia, if it was an ammonia salt)	$RCONH_2 + NaOH \rightarrow RCOONa + NH_3$
Aliphatic amines (primary, where R = alkyl) chemical test $R–NH_2$ e.g. $CH_3CH_2CH_2–NH_2$	(i) Lower members soluble in water but a very fishy smell! test with red litmus and conc. HCl(aq) fumes. (ii) If a suspected salt of an amine, then add sodium hydroxide solution to free the amine	(i) A fishy odour , litmus turns blue, white clouds with HCl. (ii) The above is not observed until after adding the alkali.	(i) Unless its a liquid or solid, only the more fishy odour distinguishes it from ammonia.(ii) The reaction is e.g. $R–NH_3^+ + OH^- \Rightarrow R–NH_2 + H_2O$

Qualitative Analysis Test for and identify organic functional groups

Aliphatic amines	Test method	Observation	Comments
(Primary,secondary and tertiary)	(i)Sub+dil.HCl+$NaNO_2$ cool to 0^0-5^0C (ii) Sub+dil.HCl+$NaNO_2$ cool to 0^0-5^0C+NaOH (iii) Sub+dil.HCl+$NaNO_2$ cool to 0^0-5^0C+ β-naphthol in NaOH	Yellow ppt Green ppt Red azo dye	(i) Secondary amine (ii)Tertiary amine (iii)primary amine
Aldehydes chemical test (R–CHO, R = H, alkyl or aryl) to distinguish from ketones ($R_2C=O$, R = alkyl or aryl) and also reducing sugars. Note (1) Test (b)(i) and (ii) can be used to distinguish aldehydes (reaction) and ketones (no reaction). (2) Aromatic aldehydes do NOT give a positive result with (b)(ii)Benedict's or Fehling's reagent). (3) Reducing sugars may also give a positive test with (b)(i)/(ii)reagent e.g. glucose (aldohexose) but not fructose? (ketohexose)?	(a) Add a few drops of the suspected carbonyl compound by Brady's reagent (2,4-dinitrophenylhydrazine solution)	(a) A yellow – organge precipitate forms with both types of carbonyl compound	The aldehyde or ketone 2,4–dinitrophenylhydrazone is formed $R_2C=O$ + $(NO_2)_2C_6H_3NHNH_2$ ==> $(NO_2)_2C_6H_3NHN=CR_2$ + H_2O (R = H, alkyl or aryl) This tells you its an aldehyde or ketone, but can't distinguish them, read on below!
	(b)(i) warm a few drops of the compound withTollens' reagent[ammoniacal silver nitrate] (b)(ii) simmer withFehling's or Benedictssolution [a blue complex of $Cu^{2+}_{(aq)}$]	(b) Only the aldehyde produces(i) A silver mirror on the side of the test tube. (ii) A brown or brick red ppt	Aldehydes are stronger reducing agents than ketones and reduce the metal ion and are oxidised in the process i.e. RCHO + [O] → RCOOH (i) reduction of silver(I) ion to silver metal $RCHO + 2Ag^+ + H_2O \rightarrow RCOOH + 2Ag + 2H^+$ (ii) reduction of copper(II) to copper(I) i.e. the blue solution of the Cu^{2+} complex changes to the brown/brick red colour

			of insoluble copper(I) oxide Cu_2O. $RCHO + 2Cu^{2+} + 2H_2O \rightarrow RCOOH + Cu_2O + 4H^+$ With (b)(i)/(ii) no reactions with ketones.
Aromatic amines chemical test (where R = aryl with the amine or amino group directly attached to an aromatic ring) $R–NH_2$ e.g. $C_6H_5–NH_2$	(i) Dissolve the primary aromatic amine in dilute hydrochloric acid at 5ºC and mix with sodium nitrite solution. (ii) Add a phenol dissolved in dilute sodium hydroxide.	(i) It should be a clear solution with few, if any, brown fumes. (ii) A coloured precipitate [red – brown – yellow etc.]	(i) If a primary aromatic amine, a 'stable' diazonium salt is formed. Diazonium salts from aliphatic amines decompose rapidly evolving colourless nitrogen. (ii) An azo dyestuff molecule is formed in a coupling reaction e.g. $C_6H_5–N=N–C_6H_4–OH$
Halogenoalkanes (haloalkanes)chemical test R–X where R = alkyl, X = Cl, Br or I . The halide is covalently bound (C–X bond), so the halogen X cannot react with the silver ion to form the ionic $Ag^+X^-_{(s)}$precipitate until it is converted to the 'free' X^- ionic form. Note that aromatic halogen compounds where the X is directly attached to the ring, do NOT readily hydrolyse in this way and no AgX ppt. will be seen. Aromatic C–X is a stronger bond than aliphatic C–X.	(i) Warm a few drops of the haloalkane with aqueous ethanolic silver nitrate solution, the ethanol increases the solubility of the immiscible haloalkanes. (ii) Gently simmering a few drops with aqueous NaOH (may need to add ethanol to increase solubility and reaction rate). Add dilute nitric acid followed by aqueous silver nitrate solution.	(i) Observe colour of precipitate and the effect of ammonia solution on it (for rest of details see the (i) notes for chloride bromide and diodide tests above in inorganic) (ii) see the (i) notes as above for more details.	i) $AgNO_3 + RX ==> R–NO_3? + AgX_{(s)}$ (ii) The sodium hydroxide converts the halogen atom into the ionic halide ion in a hydrolysis reaction. $RX_{(aq)} + NaOH_{(aq)} ==> ROH_{(aq)} + NaX_{(aq)}$ then $Ag^+_{(aq)} + X^-_{(aq)} \rightarrow AgX_{(s)}$ The addition of dilute nitric acid prevents the precipitation of other silver salts or silver oxide (e.g. Ag_2O forms if solution alkaline)

Qualitative Analysis Test for and identify organic functional groups

Functional group	Test method	Observation	Comments
Esters chemical test RCOOR' R = H, alkyl or aryl R' = alkyl or aryl There is no simple test for an ester. Usually a colourless liquid with a pleasant 'odour'.	The ester can be reacted with saturated ethanolic hydroxylamine hydrochloride + 20% methanolic KOH and gently heated until boiling. Then mixture acidified with 1M $HCl_{(aq)}$ and $FeCl_{3\ (aq)}$ added dropwise.	Deep read or purple colour formed. The test depends on the formation of a hydroxamic acid R-C(=NOH)OH which forms coloured salts with $Fe^{3+}_{(aq)}$ ion	The reaction is also given by acid chlorides and acid anhydrides and phenols gives a purple colour with iron(III) chloride, so frankly, the test is not that good. This test is not to be expected .
Iodoform test The formation of CHI_3, triiodomethane(or old name '*iodoform*'.	$NaOH_{(aq)}$ is added to a solution of iodine in postassium iodide solution until most of the colour has gone. The organic compound is warmed with this solution	A yellow solid is formed with the smell of an antiseptic CHI_3, tri-iodomethane melting point 119°C	This reaction is given by the alcohol ethanol CH_3CH_2OH and all alcohols with the 2–ol structure –CHOH–CH_3 and the aldehyde ethanal CH_3CHO and all ketones with the 2–one structure R–CO–CH_3 *('methyl ketones')* It's a combination of halogenation and oxidation and is not a definitive test for anything, it just indicates a possible part of a molecules structure.

Equilibrium is that state of a process in which the concentration of reactants and products becomes constant until the conditions of temperature and pressure are unchanged. It can be a physical equilibrium or chemical equilibrium based on the type of process. It can be physical equilibrium or chemical equilibrium based on the type of process.
If the opposing process involves only physical change, the equilibrium is called physical equilibrium and if the process involves only chemical change, the equilibrium is called chemical equilibrium.

Equilibrium in physical processes

When there is a change in the state of occurrence of matter, then a physical transformation is said to have occurred. The equilibrium concepts are also applicable to physical state transformations of matter.

(i) Solid-liquid equilibria

Here, the solid and the liquid forms of a substance co exist at characteristic temperature and pressure. At 1 atm and at the melting point of a substance, there is a solid-liquid equilibrium existing. For example, the solid-liquid equilibrium of water at 0°C,

water(l) $\rightleftharpoons$ ice(s)

occurs at 1 atm pressure. Here, both the liquid and ice exist together. Also, at melting point of ice or freezing point of water, the rate of melting of ice equals with rate of freezing of water. With change in pressure the temperature at which this equilibrium onsets changes.

(ii) Liquid-vapour equilibrium

Here the vapour and the liquid forms of a substance exist simultaneously at a characteristic temperature called as boiling point and at 1 atm pressure. For example at 100°C which is the boiling point of water, and 1 atm pressure,

Water(l) $\rightleftharpoons$Steam(g)

both liquid water and water vapour (steam) exist simultaneously, provided the vapour does not escape.

(iii) Solid-solid equilibrium

When a substance existing in a particular crystalline solid transforms to another crystalline form retaining its solid nature at a characteristic temperature called the transition temperature with both the solid forms coexisting, at 1 atm pressure then it is said to be in solid-solid equilibrium.
For example, solid sulphur exhibits equilibrium with rhombic to monoclinic forms at its transition temperature.

S(rhombic) $\rightleftharpoons$ S(monoclinic)

(iv) Solid-Gas equilibrium

Some solid substances on heating directly change into vapour state. Only those solids sublime which attain the vapour pressure of 1 atm at temperature lesser than their triple point

Dissolution if solid in liquid

After the arrival of saturation point the amount of un dissolved solid solute and the concentration of solid solute in the solution remains constant At equilibrium

‛Rate of dissociation = Rate of precipitation

(v) Dissolution of gases in liquid

Dissolution of gasses in water is always exothermic. As dissolution is spontaneous(takes place on its own) ΔG = -ve, entropy decreases in the process of dissolution ΔS = -ve. Therefore ΔH has be negative i.e. exothermic. The amount of gas dissolved is given by Henry’s law

Henry’s law

The law states that the mass of gas dissolved in a given mass of solvent at a given temperature is directly proportional to the partial pressure of the gas above the solution

$m \propto P$ or $m = kP$

Where k is constant or proportionality known as Henry’s constant

Chemical equilibrium

Chemical reactions are broadly divided into two categories

(i) irreversible reaction (ii)Reversible reaction

(i)Irreversible reaction

These are the reaction in which products do not react back to give the reactant. i.e. reaction can not be retraced at any point

E.g. $AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$

$SnCl_2 + 2FECl_3 \rightarrow SnCl_4 + 2FeCl_2$

Free energy change (ΔG) for irreversible reaction $\neq 0$

(ii)Reversible reaction

A reaction in which reactants are formed back by the reaction of products with each other at the given conditions of reaction. These reactions if carried out in closed vessel do not go to completion

e.g. $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

$N_2(g) + 3H_2(g) \rightleftharpoons 2HMH_3(g)$

Free energy change ΔG for reversible reaction is zero, $\Delta G = 0$

State of equilibrium

Chemical equilibrium is that state of reaction at which the rate of forward reaction is equal to rate of backward reaction .

The concentration of reactant and product becomes constant. At the stage of equilibrium, the reaction seems to be static, but actually it is not so. Only forward and backward reactions takes place at the same rate, so that composition of chemical system remains constant

Characteristics of chemical equilibrium

(i)Equilibrium state is attended only when reaction is carried out in closed vessel (system) (ii)At equilibrium, concentration of all reactants and products becomes constant

(iii)Equilibrium is dynamic in nature i.e. reaction seems to be static because no change in concentration of reactants or product, but actually reaction takes place in both the directions with same speed

(iv)Catalyst does not affect the equilibrium, it only fastens the chemical reaction to attain the state of equilibrium

(v) Chemical equilibrium can be attended in either direction

(vi) Change in conditions like temperature, pressure or concentration disturb the equilibrium and shift the equilibrium in one direction to attend new equilibrium

(vii) at the stage of equilibrium free energy change is zero $\Delta G = 0$

Homogenous equilibrium

If the reactants and the products in a system are in same phase, the equilibrium is said to be homogeneous

For example $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (represents a homogeneous equilibrium in gaseous phase)

$CH_3COOH (l) + C_2H_5OH (l) \rightleftharpoons CH_3COOC_2H_5 (l) + H_2O (l)$ (represents a homogeneous equilibrium in liquid phase)

A phase is homogeneous (same composition and property throughout) part of a system, separated from other phase (or homogeneous parts) by bounding surface

(i)Any number of gases constitute only one phase

(ii) In liquid system, the number of phases = number of layers in the system. Completely miscible liquids such as ethanol and water constitute a single phase. On the other hand, benzene water has two layers and so two phase

(ii) Each solid constitutes a separate phase, except in the case of solid solutions. [A solid solution e.g. lead and silver, forms homogenous mixture]

Heterogeneous equilibrium

If more than one phase is present in a chemical equilibrium, it is said to be heterogeneous equilibrium

For example $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

Represents a heterogeneous equilibrium involving solid phase and gaseous phase

Law of chemical equilibrium and equilibrium constant

Law of Mass action

Two Norwegian Chemists, Guldberg and Waage, studied experimentally a large number of equilibrium reactions. In 1864, they postulated a generalisation called the **Law of Mass action**. It states that:

"the rate of a chemical reaction is proportional to the active masses of the reactants". By the term `active mass', it is meant the molar concentration i.e., number of moles per litre. According to this law, rate of reaction is directly proportional to the product of the molae concentration (active mass) of reactants with each concentration term raised to the power equal to its stoichiometric coefficient as represented by the balanced chemical equation

For example $aA + bB \rightleftharpoons cC + dD$

According to law of active mass action

Rate of forward reaction $r_f \propto [A]^a [B]^b$

Rate of backward reaction $r_b \propto [C]^c [D]^d$

Active mass of a substance is simply number of moles dissolved per litre of the solution. Active mass of a gas or liquid is equal to its pressure or molar concentration, where as active mass of solid is constant and is taken as unity

Law of Mass Action based on the Molecular Collision theory

We assume that a chemical reaction occurs as the result of the collisions between the reacting molecules. Although some of these collisions are ineffective, the chemical change produced is proportional to the number of collisions actually taking place. Thus at a fixed temperature the rate of a reaction is determined by the number of collisions between the reactant molecules present in unit volume and hence its concentration, which is generally referred as the active mass.

Equilibrium constant and equilibrium law

Let us consider a general reaction

$aA + bB \rightleftharpoons cC + dD$

According to law of mass action

Rate of forward reaction $\propto [A]^a+[B]^b = k_f [A]^a+[B]^b$

Rate of backward reaction $\propto [C]^c+[D]^d = k_f [C]^c+[D]^d$

Here k_f and k_b are rate constant for forward reaction and rate constant for backward reaction respectively

At equilibrium

Rate of forward reaction = rate of backward reaction

$k_f [A]^a[B]^b = k_f [C]^c[D]^d$

$$K_{eq} = \frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Since k_f and k_b are constants k_{eq} is also constant called as equilibrium constant

Above expression is called law of chemical equilibrium

If concentration is measured in moles/lit then $K_{eq} = K_c$ and if concentration is measured in pressure then $K_{eq} = K_p$

The distinction between K_{eq} and K_c is that the expression of K_{eq} involves all species (whether they are pure solids, pure liquids, gases, solvents or solutions) while the K_c expression involves only those species whose concentration is a variable (like pure solids and pure liquids) and solvents

Relation between K_c and K_p

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} \quad ----eq(1)$$

From ideal gas equation PV = nRT

$$P = \frac{nRT}{V}$$

Since Volume and temperature for all reactant and product is same

$$P_A = \frac{aRT}{V}, \quad P_B = \frac{bRT}{V}, \quad P_C = \frac{cRT}{V}, \quad P_D = \frac{dRT}{V}$$

Now a/v = concentration = [A] similarly

b/v = [B]. c/V = [C] and d/V = [D]

Thus

$$P_A = [A]RT, \quad P_B = [B]RT, \quad P_C = [C]RT, \quad P_D = [D]RT,$$

$$K_p = \frac{([C]RT)^c([D]RT)^d}{([A]RT)^a([B]RT)^b}$$

$$K_p = \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{c+d-a-b}$$

$$K_p = K_c(RT)^{\Delta n_g}$$

Here Δn_g is change in number of gaseous molecules

Since, partial pressure are generally noted in atm and concentrations are measured in (moles/litre) , so valur of R used in the given expression should be litre-atm per mole per Kelvin = R =0.082 litre-atm per mole per Kelvin

Case

(i) If $\Delta n_g = 0$ then $K_p = K_c$

(ii) If $\Delta n_g < 0$ then $K_p < K_c$

(iii) If $\Delta n_g > 0$ then $K_p > K_c$

Equilibrium constant in terms of mole fraction (K_x)

$$K_X = \frac{X_C^c X_D^d}{X_A^a X_B^b}$$

Here X_A, X_B, X_C, X_D are mole fraction of A, B, C, D respectively, K_X depends upon pressure temperature and volume of the chemical system

$$K_p = K_X(RT)^{\Delta n_g}$$

Solved numerical

Q) The K_P value for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ at 460°C is 49. If the initial pressure of H_2 and I_2 is 0.5atm respectively, determine the partial pressure of each gas at equilibrium

Solution

	H_2	+	I_2	$\rightleftharpoons$	$2HI$
Initial pressure	0.5		0.5		0
At equilibrium	(0.5 – x)		(0.5-x)		2x (from stoichiometry of equation)

$$K_P = \frac{P_{HI}^2}{P_{H_2} \times P_{I_2}}$$

$$49 = \frac{(2x)^2}{(0.5-x)^2}$$

$$X = 0.39 \text{ atm}$$

∴ Pressure of H_2 and I_2 at equilibrium = (0.5-x) = 0.11 atm

Q) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$; $K_1 = 1.8 \times 10^{-5}$

$2H_2O \rightleftharpoons H_3O^+ + OH^-$, $K_2 = 1\times10^{-14}$

Calculate equilibrium constant for reaction

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$

Solution

Equilibrium constant for the reaction

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

$$K_1 = \frac{[\mathrm{CH_3COO^-}][H_3O^+]}{[\mathrm{CH_3COOH}][\mathrm{H_2O}]}$$

Equilibrium constant for the reaction

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

$$K_2 = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Taking the ratio of K1 and K_2

$$\frac{K_1}{K_2} = \frac{[\mathrm{CH_3COO^-}][H_3O^+]}{[\mathrm{CH_3COOH}][\mathrm{H_2O}]} \times \frac{[H_2O]^2}{[H_3O^+][OH^-]}$$

$$\frac{K_1}{K_2} = \frac{[\mathrm{CH_3COO^-}][H_2O]}{[\mathrm{CH_3COOH}][\mathrm{OH^-}]}$$

Above ratio is the equilibrium constant of the reaction

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$

$$\therefore K = \frac{K_1}{K_2} = \frac{1.8\times10^{-5}}{1\times10^{-14}} = 1.8\times10^{9}$$

Q) For the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta H = -46\ kJmol^{-1}$

Calculate the value of K_P. Given $K_C = 0.5\ lit^2mol^{-2}$ at 400^OC

Solution:

$K_P = K_C (RT)^{\Delta n}$

$\Delta n = 2-4=-2$

$K_P = 0.5(0.082\times673)^{-2} = 1.641\times10^{-4}$

Q) Determine the amount of ester present under equilibrium when 3 mol of ethyl alcohol react with 1mole of acetic acid, when equilibrium constant of the reaction is 4

Solution

	CH_3COOH	+	C_2H_5OH	$\rightleftharpoons$	$CH_3COOC_2H_5$	+	H_2O
At equilibrium	1-x		3 –x		x		x

$$K_C = \frac{x\times x}{(1-x)(3-x)}$$

$$4 = \frac{x\times x}{(1-x)(3-x)} = \frac{x^2}{3-4x+x^2}$$

$3x^2 -16x +12 = 0$

X = 0.903 or 4.73 (inadmissible)

∴ Amount of ester at equilibrium = 0.903 mole

Predicting the direction of attainment of equilibrium

The reaction quotient is defined as the ratio of concentration of the reaction species at any point of time other than the equilibrium stage.

It is represented by Q. Thus, inserting the starting concentrations of reactant and product in the equilibrium constant expression gives

$$Q = \frac{[C_0]^c[D_0]^d}{[A_0]^a[B_0]^b}$$

Here A_0, B_0, C_0 and D_0 are the concentration before equilibrium is reached

To determine the direction in which the net reaction will proceed to achieve equilibrium, we compare the values of Q and K_C. The three possible cases are as follows

(a) $Q > K_C$; for such a system, products must be converted to reactants to reach equilibrium. The system proceeds from right to left to reach equilibrium

(b) $Q = K_C$; The initiall concentrations are equilibrium concentrations. So, the system is already at equilibrium

(c) $Q < K_C$; For such a system., reactants must be converted to products to reach equilibrium. The system proceeds from left to right to attain equilibrium

Mode of writing a chemical equation

The values of K_P and K_C also depends on the method of representing a chemical equation for example

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

i) When the equilibrium reaction is reversed

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

$$K'_C = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{K_C}$$

ii) When the equation for a reaction is divided by a factor 'n' the value of new equilibrium constant becomes equal to nth root of the previous equilibrium constant k'

$A+B \rightleftharpoons C+D$

$$\frac{1}{n}A + \frac{1}{n}A \leftrightharpoons \frac{1}{n}C + \frac{1}{n}D$$

$$K' = \sqrt[n]{K_c}$$

iii) If the equation for reaction is multiplied by a factor 'n' then new equilibrium constant K' becomes K^n

$A+B \rightleftharpoons C+D$

$nA+nB \rightleftharpoons nC+nD$

$K' = K_C^n$

iv) If the equation is written in number of steps, then its equilibrium constant will be the multiple of the equilibrium constant of each step

Example $A+B \rightleftharpoons C+D$

If above reaction takes placed in two steps

$$A+B \overset{K_1}{\rightleftharpoons} X+Y$$

$$X+Y \overset{k_2}{\rightleftharpoons} C+D$$

Then $K = K_1 \times K_2$

Characteristics of equilibrium constant

(i)The value of equilibrium constant is independent of initial concentration or volume of the reactants

(ii)Its value is not influenced by the presence of catalyst

(iii)Equilibrium constant is not affected by pressure or nature of reactant (iv)The value of the equilibrium constant of a particular reaction is always constant depending upon the temperature of the reaction and is independent of the direction from which the equilibrium is attained

(v)Equilibrium constant is not changed by the inert material added to the system

(v) The value of the equilibrium constant depends on the stoichiometry of reactants and products at the equilibrium

Effect of temperature on equilibrium constant

The value of equilibrium constant for a particular reaction is constant at a given temperature. In case of endothermic reversible reaction, equilibrium constant, increases with the increase in temperature where as incase of exothermic reaction, equilibrium constant decreases with the increase in temperature. Variation of equilibrium constant with temperature is explained with the help of following equation

$$log\frac{K_2}{K_2} = \frac{\Delta H^0}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

Where K_2 and K_1 are equilibrium constant at temperature T_2 and T_1 respectively

ΔH^O is the enthalpy of reaction and R is the gas constant

If $\Delta H^O = 0$, no heat is absorbed or evolved in the reaction

$$log\frac{K_2}{K_2} = 0 \ or \ K_2 = K_1$$

i.e equilibrium constant does not change with temperature

If $T_2 > T_1$ and ΔH^O is positive (endothermic reaction) then $K_2 > K_1$

But if $T_2 > T_1$ and ΔH^O is negative (exothermic reaction) then $K_2 < K_1$

Significance of equilibrium constant

(1) Magnitude of equilibrium constant gives an idea about the extent of reaction

–Greater value of equilibrium constant ($>10^3$) implies the greater concentration of products in comparison to that of reactants. It means reaction is favourable in forward direction i.e. towards product side

- Smaller value of equilibrium constant ($<10^{-3}$) implies the greater concentration of reactants as compared to that of products. It shows that reaction is favourable in backward direction i.e. towards reactant side
- Intermediate value of equilibrium constant (10^{-3} to 10^3) implies the comparable concentration of reactant

(2) Value of equilibrium constant also explains the thermodynamic stability of products. Greater the value of K, greater will be the stability of products and instability of reactants.

(3) Equilibrium concentration of reactants and products can be calculated with the help of equilibrium constant

Units of equilibrium constant

Concentration of a substance is measure in terms of moles/litre, therefore unit of

K_C is (mol $L^{-1})^{\Delta n}$

Similarly partial pressure is measured in terms of atmosphere, hence unit of K_P is (atm) $)^{\Delta n}$, where Δn is the difference in number of moles of products and reactant

If Δ n = 0, both K_C and K_P has no units

If Δ n > 0, unit of K_C = (mol $L^{-1})^{\Delta n}$, unit of K_P = $(atm)^{\Delta n}$

If Δ n < 0, unit of K_C = (L $mol^{-1})^{\Delta n}$, unit of K_P = $(atm^{-1})^{\Delta n}$

Equilibrium constant and standard free energy change

We know that free energy change (ΔG) is related to ΔG^O as follows

$\Delta G = \Delta G^O + 2.303RT\log Q$

But at equilibrium Q = K and ΔG = 0

$\therefore \Delta G^O = -2.303RT\log K$

If K > 1, then ΔG^O is negative. reaction in forward direction is spontaneous

If K < 1, then ΔG^O is positive , reaction is spontaneous in backward direction

Le-Chatelier's principle

A statement of Le Chatelier's Principle

- If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change.

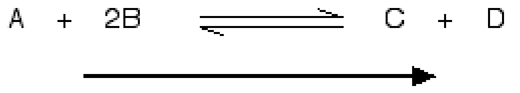
Using Le Chatelier's Principle with a change of concentration

Suppose we have an equilibrium established between four substances A, B, C and D.

$$A + 2B \rightleftharpoons C + D$$

What would happen if concentration of A is increased?

According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the concentration of A decreases again - by reacting it with B and turning it into C + D. The position of equilibrium moves to the right.

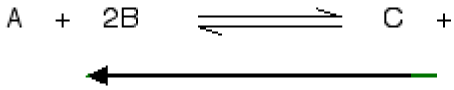


The position of equilibrium moves to the right if we increase concnetration of A

This is a useful way of converting the maximum possible amount of B into C and D. You might use it if, for example, B was a relatively expensive material whereas A was cheap and plentiful.

What would happen if we changed the conditions by decreasing the concentration of A?

According to Le Chatelier, the position of equilibrium will move so that the concentration of A increases again. That means that more C and D will react to replace the A that has been removed. The position of equilibrium moves to the left.



$$A + 2B \rightleftharpoons C + D$$

The position of equilibrium moves to the left if we decrease the concnetration of A

This is essentially what happens if we remove one of the products of the reaction as soon as it is formed. If, for example, you removed C as soon as it was formed, the position of equilibrium would move to the right to replace it. If you kept on removing it, the equilibrium position would keep on moving rightwards - turning this into a one-way reaction.

Using Le Chatelier's Principle with a change of pressure

This only applies to reactions involving gases:

$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

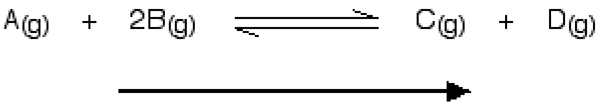
What would happen if we changed the conditions by increasing the pressure?

According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the pressure is reduced again.

Pressure is caused by gas molecules hitting the sides of their container. The more molecules you have in the container, the higher the pressure will be. The system can reduce the pressure by reacting in such a way as to produce fewer molecules.

In this case, there are 3 molecules on the left-hand side of the equation, but only 2 on the right. By forming more C and D, the system causes the pressure to reduce.

Increasing the pressure on a gas reaction shifts the position of equilibrium towards the side with fewer molecules.

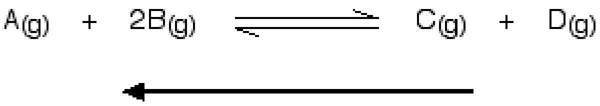


$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

The position of equilibrium moves to the right if we increase the pressure on the reaction

What would happen if you changed the conditions by decreasing the pressure?

The equilibrium will move in such a way that the pressure increases again. It can do that by producing more molecules. In this case, the position of equilibrium will move towards the left-hand side of the reaction.



$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

The position of equilibrium moves to the left if we decrease the pressure on the reaction

What happens if there are the same number of molecules on both sides of the equilibrium reaction?

In this case, increasing the pressure has no effect whatsoever on the position of the equilibrium. Because you have the same numbers of molecules on both sides, the equilibrium can't move in any way that will reduce the pressure again.

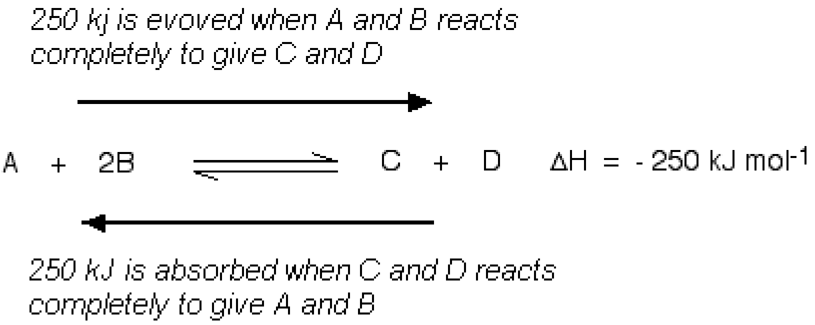
Using Le Chatelier's Principle with a change of temperature

For this, you need to know whether heat is given out or absorbed during the reaction. Assume that our forward reaction is exothermic (heat is evolved):

$$A + 2B \rightleftharpoons C + D \quad \Delta H = -250 \text{ kJ mol}^{-1}$$

This shows that 250 kJ is evolved (hence the negative sign) when 1 mole of A reacts completely with 2 moles of B. For reversible reactions, the value is always given as if the reaction was one-way in the forward direction.

The back reaction (the conversion of C and D into A and B) would be endothermic by exactly the same amount.

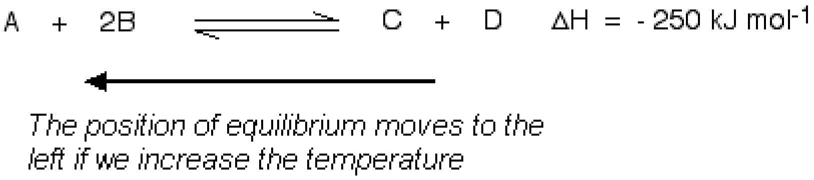


What would happen if you changed the conditions by increasing the temperature?

According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the temperature is reduced again.

Suppose the system is in equilibrium at 300°C, and you increase the temperature to 500°C. How can the reaction counteract the change you have made? How can it cool itself down again?

To cool down, it needs to absorb the extra heat that you have just put in. In the case we are looking at, the *back reaction* absorbs heat. The position of equilibrium therefore moves to the left. The new equilibrium mixture contains more A and B, and less C and D.



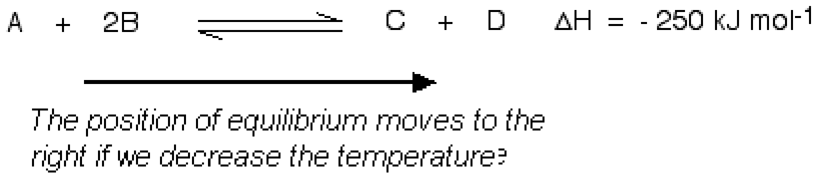
If you were aiming to make as much C and D as possible, increasing the temperature on a reversible reaction where the forward reaction is exothermic isn't a good idea!

What would happen if you changed the conditions by decreasing the temperature?

The equilibrium will move in such a way that the temperature increases again.

Suppose the system is in equilibrium at 500°C and you reduce the temperature to 400°C. The reaction will tend to heat itself up again to return to the original temperature. It can do that by favouring the exothermic reaction.

The position of equilibrium will move to the right. More A and B are converted into C and D at the lower temperature.



The position of equilibrium moves to the right if we decrease the temperature?

Le Chatelier's Principle and catalysts

Catalysts have sneaked onto this page under false pretences, because *adding a catalyst makes absolutely no difference to the position of equilibrium,* and Le Chatelier's Principle doesn't apply to them.

This is because a catalyst speeds up the forward and back reaction to the same extent. Because adding a catalyst doesn't affect the relative rates of the two reactions, it can't affect the position of equilibrium. So why use a catalyst?

For a dynamic equilibrium to be set up, the rates of the forward reaction and the back reaction have to become equal. This doesn't happen instantly. For a very slow reaction, it could take years! A catalyst speeds up the rate at which a reaction reaches dynamic equilibrium.

Ionic equilibrium

When an ionic compound is dissolved in water or melted, it gets split into its ions. The process is known as ionization or dissociation.

Degree of dissociation

Degree of dissociation of a substance is the fraction of the total number of molecules dissociated into simpler molecules at a particular temperature

$$Degree\ of\ dissocaiation(\alpha) = \frac{Numer\ of\ moles\ dissociated}{Total\ number\ of\ moles\ taken}$$

For example

Let the equilibrium reaction is the dissociation equilibrium of NH_3 into N_2 and H_2

$NH_3(g) \rightleftharpoons (1/2)\ N_2(g) + (3/2)H_2(g)$

Let the initial moles of NH_3 taken be 1 and the moles of NH_3 dissociated at equilibrium be ‘x’

Then

	$NH_3(g)$	⇌	$(1/2)\ N_2(g)$	+	$(3/2)H_2(g)$
Moles initially	1		0		0
Moles at equilibrium	1-x		x/2		3x/2

Here, x represents the degree of dissociation (α). If we would have stated with 'a' moles of NH_3 and moles of NH_3 dissociated is taken as 'x', then degree of dissociation of NH_3 will not be 'x' but would be x/a

The degree of dissociation is defined only for those equilibrium in which dissociation takes place. For example the degree of dissociation cannot be defined for reverse reaction in which N_2 and H_2 combine to give NH_3 · Degree of dissociation is proportional to temperature

Solved numerical

Q) A sample of HI was found to22% dissociated when equilibrium was reached. What will be the degree of dissociation if hydrogen is added in the proportion of 1 mole for every mole of HI originally present, the temperature and volume of the system is kept constant

Solution

The degree of dissociation (α) is the fraction of 1mole of HI that has dissociated under the given conditions. If the % dissociation of HI is 22, the degree of dissociation is 0.22

	2HI	⇌	H_2	+	I_2
At equilibrium	(1- α)		α/2		α/2
	1-0.22 =0.78			0.11	0.11

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.11 \times 0.11}{(0.78)^2} = 0.0199$$

Now adding 1 mole of hydrogen at equilibrium. Let x be the degree of dissociation thus

	2HI	⇌	H_2	+	I_2
At equilibrium	(1- x)		[(x/2) +1]	x/2	

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{\left(\frac{x}{2}+1\right)\left(\frac{x}{2}\right)}{(1-x)^2} = 0.0199$$

X=0.037 or -2.4 (not admissible)

Degree of dissociation = 0.037

% of dissociation = 3.7

Note :Introduction of H_2 suppresses the dissociation of HI

Q) A vessel at 1000K contains carbon dioxide at a pressure of 0.5 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of K, if the total pressure is 0.8atm

Solution

$$CO_2 + C_{graphite} \rightleftharpoons CO$$

Let the decrease in pressure of CO_2 after reaction be p atm

Then, increase in pressure due to CO after reaction = 2p atm

Final pressure = (0.5 –p) +2p = 0.8 atm

Therefore p = 0.3atm

Thus after reaction, P_{CO2} = 0.5 -0.3 = 0.2 atm

P_{CO} = 2p = 2×0.3 = 0.6 atm

Equilibrium constant K

$$K = \frac{(0.6)^2}{(0.2)} = 1.8\ atm$$

Q) The equilibrium constant K_P for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 467^{O}C is found to be 636 mm Hg. If the pressure of the gas mixture is 182mm, calculate the percentage dissociation of N_2O_4. At what pressure will it be half dissociated

Solution

Let dissociation of 1 mole of N_2O_4 be α then

NO_2 formed at equilibrium will be= 2α

N_2O_4 at equilibrium will be = (1- α)

Total moles at equilibrium = (1- α)+2 α = 1+ α

If P_T is total pressure at equilibrium then

Pressure of N_2O_4 at equilibrium

$$\left(\frac{1-\alpha}{1+\alpha}\right)\times P_T$$

Pressure of NO_2 at equilibrium

$$\left(\frac{2\alpha}{1+\alpha}\right)\times P_T$$

Now

$$K_P = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{\left(\frac{2\alpha}{1+\alpha}\times P_T\right)^2}{\frac{1-\alpha}{1+\alpha}\times P_T} = \frac{4\alpha^2 P_T}{1-\alpha^2}$$

Thus

$$636 = \frac{4\alpha^2\times 182}{1-\alpha^2}$$

α = 0.6829

% dissociation of N_2O_4 = 68.29

When the gas is half dissociated α =0.5 , Let the total pressure be P’

$$636 = \frac{4\times 0.5^2\times 182}{1-0.5^2}\times P'$$

P’=477mm

Electrolyte and Non-electrolyte

A compound whose aqueous solution or melt conducts electricity is known as electrolyte, where as non-electrolyte is the compound whose neither aqueous nor melt conducts electricity

Strong and weak electrolytes

Electrolytes which dissociate almost completely into ions in aqueous solution are known as strong electrolytes. E.g. NaCl , HCl, NaOH, H_2SO_4 etc. They are good conductors of electricity Whereas those electrolytes which dissociate only partally into ions in aqueous solution are known as weak electrolytes. E.g. CH_3COOH, NH_4OH etc.

They have conductivity smaller than that of strong electrolytes. Their value of degree of dissociation is much smaller than one i.e $\alpha < 1$. An equilibrium is setup in case of partially ionized weak electrolytes between ions and unionized electrolyte

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

Ostwald's Dilution law

The molecules of an electrolyte in solution are constantly splitting up into ions and the ions are constantly reuniting to form unionized molecules. Therefore, a dynamic equilibrium exists between ions and unionized molecules of the electrolyte in solution. It was pointed out by **Ostwald** that like chemical equilibrium, law of mass action van be applied **to** such systems also.

Consider a binary electrolyte AB which dissociates into A^+ and B- ions and the equilibrium state is represented by the equation:

$$AB \leftrightarrow A^+ + B^-$$

	AB	A^+	B^-
Initially t = 0	C	0	0
At equilibrium	C(1-α)	Cα	Cα

So, **dissociation constant** may be given as

$$K_{eq} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$K_{eq} = \frac{C\alpha^2}{(1-\alpha)} \quad ----eq(i)$$

For very weak electrolytes,

$\alpha <<< 1, \ (1 - \alpha) = 1$

$\therefore \quad K_{eq} = C\alpha^2$

$$\alpha = \sqrt{\frac{K_{eq}}{C}} \quad ----eq(ii)$$

Concentration of any ion = $C\alpha = \sqrt{(CK)}$.

From equation (ii) it is a clear that degree of ionization increases on dilution.

If 1mole is present in 'V' litres of solution , C = 1/V

$$K_{eq} = \frac{\alpha^2}{V(1-\alpha)}$$

Is another expression for Ostwald's dilution law

$$\alpha = \sqrt{K_{eq} \times V}$$

Thus, **degree of dissociation** of a weak electrolyte is proportional to the square root of dilution.

Ostwald's dilution law is applicable to weak electrolytes, not strong electrolytes.

The Arrhenius concept

An acid is a substance which in aqueous solution gives hydrogen ion as the only cation (This definition excludes acid salt.

$HCl \rightleftharpoons H^+ + Cl^-$

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

A base is a substance which in aqueous solution gives hydroxyl (OH^-) ions as the only anions

$NaOH \rightleftharpoons Na^+ + OH^-$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Neutralization is nothing but combination of H^+ ions of the acid and OH^- ions of the base to form unionized water

Limitations of Arrhenus concept

(i) It does not explain the acidic character of certain compounds like CO_2, SO_2, $AlCl_3$ etc and basic character of some compounds like Na_2CO_3, NH_3 etc. which does not give H^+ and OH^- ions respectively

(ii) It does not explain the behavior of acids and base in absence of water

(iii) It does not explain the nature of H^+ and OH^- ions in water

Bronsted Lowry Concept of Acid and Base

This concept defines the acids and base in terms of proton donor and proton acceptor. An acid is defined as a substance which can give / donate a proton (H^+) where as base is a substance which can accept a proton (H^+). This called a protonic theory of acid and base.

In case of acid base reaction, the reverse reaction is also acid base reaction. Every acid forms a conjugate base by loss of proton while every base forms a conjugate acid by the gain of proton (H^+). A conjugate pair of acid and base differ by a proton only For example

Donar Acid		Acceptor base		conjugate acid		conjugate base
HCl	+	H_2O	⇌	H_3O^+	+	Cl^-
CH_3COOH	+	H_2O	⇌	H_3O^+	+	CH_3COO^-
H_2O	+	NH_3	⇌	NH_4^+	+	NO_3^-
H_2O	+	CO_3^-	⇌	HCO_3^-	+	OH^-

- A strong acid gives a weak conjugate base and vice versa
- If two acids (with respect to water) are mixed together the weak acid will act as base with respect to strong acid
- Acid base reaction always proceed in the direction from the stronger to weaker acid base combination
- For example

  $H_2SO^4 + NH_3 \rightarrow NH_4^+ + HSO^4-$ (both the products are weak)

Lewis concept of acid and Base

According to this concept, an acid is a substance which can accept a pair of electrons, whereas a base is a substance which can donate a pair of electrons. i.e. acids are electron acceptors and bases are electron donors

Chemical species which can acts as Lewis acid

(i) Electron deficient neutral compounds i.e. molecules in which central atoms has incomplete octatae eg. BF_3, $FeCl_3$, $AlCl_3$ etc

(ii) All simple cation e.g. H^+, Mg^{2+}, Ag^+, Fe+3+ ^{etc}

(iii) Molecules having multiple bond between atoms of different electro-negativities e.g. SO_3, CO_2 etc

(iv) In coordination complexes, metal atoms acts as Lewis acid

(v) Molecules having a central atom with empty d-orbital's, e.g SiF_4, $SnCl_4$

Chemical species which can act as Lewis base

(i)Electron rich neutral compound i.e. molecules with least one lone pair of electrons eg.

$\ddot{N}H_3$, $R\text{-}\underset{\cdot\cdot}{\ddot{O}}\text{-}H$, $R-\ddot{N}H_2$

ii) All negatively changed ions e.g. CN^-, OH^-, Cl^- etc

iii) In coordinate compounds, the ligands acts as Lewis base. For CO acts as Lewis base in $Ni(CO)_4$

Summary of concept to acid and base

Concept	Acid	Base
Arrhenius	H^+ donor	OH^- donor
Bronsted-Lowry	H^+ donor	H^- acceptor
Lewis	e^- pair acceptor	e^- pair donor

Strength of acids and bases

Strength of acid in terms of H^+ produced i.e. greater the number of H^+ produced in aqueous solution, stronger is the acid. Whereas strength of base is measured in terms of OH^- produced i.e. greater the number of OH^- produced in aqueous solution, stronger is the base

HA + water $H^+(aq) + A^-(aq)$

Acid

$$k_a = \frac{[H^+][A^-]}{[HA]} \quad or \ K_a \propto \ [H^+]$$

Where K_a is the dissociation constant of acid HA.

Similarly for base $K_b \propto [OH^-]$ where K_b is the dissociation constant of a base BOH

It means greater the value of dissociation constant (K_a or K_b), greater is the amount of H^+ aqueous or OH^- produced and stronger is the acid or base respectively.

Relative strength of acid and bases

Degree of dissociation is considered as measure of strength of an acid, for equimolar acids

$$\frac{Strength\ of\ HA_1}{Stregth\ of\ HA_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a1}}{K_{a2}}}$$

Similarly for equimolar weak base

$$\frac{Strength\ of\ BOH_1}{Stregth\ of\ BOH_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b1}}{K_{b2}}}$$

Polybasic acids and polyacidic base

Acids which have more than one ionisable proton per molecule of the acid are known as polybasic or polyprotic acids. For example oxalic acid $(COOH)_2$, Sulphuric acid H_2SO_4, phosphoric acid H_3PO_4, carbonic acid (H_2CO_3 are considered as dibasic acid

$$H_2A_{(aq)} \xrightleftharpoons{K_{a1}} H^+ + HA^-$$

$$HA^- \xrightleftharpoons{K_{a2}} H^+ + A^{2-}$$

The ionization constant K_{a1} and K_{a2} are given as

$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} \quad , K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]}$$

It is observed that $K_{a1} > K_{a2} > K_{a3}$

The reason behind the decrease in the dissociation constant of successive stages is that in the first dissociation, a neutral molecule give proton (H^{+}), while in the second stage of dissociation, the proton is coming from the negatively changed molecule and in the third step of dissociation, a doubly negative charged molecule is giving a proton which in turn is more difficult than first two

Similarly, polyacidic bases also ionize in steps For any polyacidic base

` $K_{b1} > K_{b2} > K_{b3}$

Solved Numerical

Q) Ionization constant of equimolar solution of HF, HCOOH and HCN at 298K are 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. What is the order of their acidic strength?

Solution

We know that acidic strength ∝ $\sqrt{R_a}$

Since the ionization constant are in the order

HF>HCOOH > HCN, order of acidic strength is HF>HCOOH>HCN

Q) Compare the strength of HCN ($K_a = 4.9\times10^{-10}$) with 0.01M aquesius solution of formic acid which it is 14.5% dissociated

Solution

Applying

$$\frac{stregth\ of\ formic\ acid}{strength\ of\ HCN} = \sqrt{\frac{K_a(formic\ acid)}{K_a(HCN)}}$$

Degree of dissociation = 14.5% = 0.145

From formula K_a (HCOOH) = $C\alpha^2 = 0.01\times(0.145)^2 = 2.1\times10^{-4}$

Thus

$$\frac{stregth\ of\ formic\ acid}{strength\ of\ HCN} = \sqrt{\frac{2.1\times10^{-4}}{4.9\times10^{-10}}} = 6.5\times10^{2}$$

i.e Formic acid is 6.5×10^2 times stronger than HCN

Effect of solvent on acid strength

Strength of acid depends on the nature of solvent

A leveling solvent is defined as the solvent in which all strong acids dissociate to some extent so that their relative strength cannot be compared

All acids stronger than H_3O^+ appears equally strong in aqueous solution, thus water is known as leveling solvent, this phenomenon is known as leveling effect

Differentiating solvents

These are the solvents in which strong acids and strong base ionize to different extent, so their relative strength can be compared

For example: Acetic acid (CH_3COOH) is a weak base and has a little tendency to accept proton from strong acids alike HCl, HBr, HNO_3, H_2SO_4 ,$HClO_4$

On the basis of equilibrium constant the strength of the above mentioned acids is found in order $HClO_4 > H_2SO_4 > HI > HBr > HCl > HNO_3$

Liquid ammonia has a such strong tendency to accept proton that even weak acid like acetic acid dissociate to a considerable extent and behave as strong acid

Strong bases also depends on the nature of solvent. Bases ionize to a different extent in a solvent which is weakly acidic in nature like H_2O and their relative strength can be compared

Types of solvent

(i)Protophilic solvents : Solvents which have trendency to accept protons are called protophilic solvents e.g. H_2O, C_2H_5OH, liquid NH_3 etc

(ii) Protogenic solvents: Solvents which have tendency to donate protons are called protogenic solvents e.g. HCl, CH_3COOH, H_2O etc

(iii)Amphiprotic solvents: Solvents which can act both as proton acceptor as well as proton donor are called amphiprotic solvents e.g. H_2O, NH_3, C_2H_5OH etc

Aprotic solvents: Solvents which neither donate nor accept protons are call aprotic solvents e.g. CCl_4, Benzene etc

Ionic product of water

Ionic product of water is the product of molar concentration of H_3O^+ ions and OH^- ions in pure water or in any acidic or basic solution. It is a constant at particular temperature

At 298 K

$K_W = [H_3O^+] [OH^-] = 1\times10^{-14}$ mol^{2}litre^{-2}

In pure water

$H_2O + H_2O \rightleftharpoons H_3O^- + OH^-$

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

Thus at 298K, $[H_3O^-] = [OH^-] = 1\times10^{-7}$ mole litre^{-1}

With increase in temperature, degree of dissociation increases, so more of H_2O dissociates into H_+ and OH^- and hence ionic product increases

Relation between the ionization constants of acid and their conjugate bases

The equilibrium reaction of acetic acid with water is written as

$$CH_3COOH\ (aq) + H_2O \rightleftharpoons CH_3COO^-(aq) + H_3O^+$$

$$K_{eq} = \frac{[CH_3COO^-] + [H_3O^+]}{[CH_3COOH][H_2O]}$$

$$K_a = K_{eq}[H_2O] = \frac{[CH_3COO^-] + [H_3O^+]}{[CH_3COOH]} \quad ----eq(1)$$

The conjugate base of acetic acid CH_3COO^- acts as base in its reaction with water as

CH_3COO^- (aq) + $H_2O \rightleftharpoons$ CH_3COOH(aq) + OH^-

$$K_b = K_{eq}[H_2O] = \frac{[CH_3COOH] + [OH^-]}{[CH_3COO^-]} \quad ------eq(2)$$

Eq(1) × eq(2)

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

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

As we know that $K_W = [H^+]\ [OH^-]$ Thus

$$K_w = K_a \times K_b$$

Thus stronger the , weaker the baseacid

Acidity and pH scale

pH is a convenient method to represent hydrogen ion concentration. pH of s olution is defiend as negative logarithm of hydrogen ion concentration

pH = -loh[H^+] or pH = - loh [H_3O^+]

Similarly, negative logarithm of hydroxyl ion concentration is called pOH

pOH = = -loh [OH^-]

pH-Scale: A solution is classified as acidic , basic or neutral based on pH value

(i) If pH = pOH = 7 , then solution is neutral

(ii) If pH < 7 or pOH >, then solution is acidic

(iii) IF pH > 7 or [pOH] < 7, then solution is basic

pH scale varies from 0 to 14

Relation between pH and pOH

We know that $K_W = [H^+]\ [OH^-] = 10^{-14}$ at 298K

Taking log on both soides

log K_W = log[H^+] + log[OH^-] = log10^{-14}

-log K_W =- log[H^+] - log[OH^-] = -log10^{-14}

pK_W = pH +pOH = 14

Thus pH + pOH = 14

And pK_W = pH + pOH

- Higher the concentration of H^+ ions, lower the pH by one unit to tenfold increase of H^+ion concentration

- pH value decreases on heating since H^+ ion concentration increases
- We know that $K_w = K_a \times K_b$ thus $pK_w = pK_a + pK_b$

Salt Hydrolysis

Salt hydrolysis is a process in which a salt reacts with water to give acid and the base

$$\underset{\text{Salt}}{BA} + H_2O \rightarrow \underset{\text{acid}}{HA} + \underset{\text{base}}{BOH}$$

In other words, we can say that hydrolysis is the reverse of neutralization

On the basis of strength of acid and base produing salts, the salts are classified into four categories

1)Salt of strong acid and strong base

Examples NaCl, KCl, K_2SO_4, Na_2SO_4, KNO_3, $NaNO_3$ etc

Consider the hydrolysis of KCl

$KCl + H_2 \rightarrow KOH + HCl$

Or $K^+ + Cl^- + H_2O \rightarrow K^+ + OH^- + Cl^- + H^+$

Thus sch salts only ionize and do not hydrolyse. It is obvious from the reaction that $[H^+] = [OH^-]$ i.e solution is neutral

In other words, we can say that salts of strong acid and strong base do not undergo hydrolysis and give a neutral resultant solution

2)Salts of weak acid and strong base

Examples CH_3COONa, Na_3PO_4, K_2CO_3, Na_2CO_3 etc

Consider the hydrolysis of $CH_3COONa + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$

Such salts undergo anionic hydrolysis since anion reacts with water to give base solution

Hydrolysis constant of such salts

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

Where Ka is dissociation constnatof weak acid and KW is ionic product of water

Degree of hydrolysis

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

$$h = \sqrt{\frac{K_W}{K_a C}}$$

And

$$pH = \frac{1}{2}[pK_W + pK_a + logC]$$

3) Slats of strong acid and weak base

Examples NH_4Cl, $CuSO_4$, $CaCl_2$, $AlCl_3$ etc

$BA + H_2O \rightleftharpoons BOH$ + HA

Salt weak base strong acid

Or $B^- + A^- + H_2O \rightleftharpoons BOH + H^+ + A^-$

$B^+ + H_2O \rightleftharpoons BOH + H^+$

These salts undergo cationic hydrolysis since cation reacts with water to give acidic solution

Hydrolysis constant

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

Where K_b is dissociation canostant of weak base

Degree of hydrolysis

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

$$h = \sqrt{\frac{K_W}{K_b C}}$$

And

$$pH = \frac{1}{2}[pK_W - pK_a - logC]$$

4) Salts of weak acid and weak base

Examples CH_3COONH_4, $AlPO_4$, $(NH_4)^2CO_3$ etc

$BA + H_2O \rightleftharpoons BOH$ + HA

Salt weak base weak acid

Or $B^{+6} + A^- + H_2O \rightleftharpoons BOH + HA$

These salts involves both cationic and anionic hydrolysis to give almost neutral solution since both acid and base produced are weak

Hydrolysis constant

$$K_h = \frac{K_W}{K_a \times K_b}$$

Degree of hydrolysis $h = \sqrt{(K_h)}$ or

$$h = \sqrt{\frac{K_W}{K_a \times K_b}}$$

and

$$pH = \frac{1}{2}[pK_W + pK_a - pK_b]$$

Solved Numerical

Q) Calculate OH^- ion concentration in 5.82M aqueous solution of ammonia, K_a for $NH_4^+ = 5.0\times10^{-10}M$

Solution

$NH_3 + H_2O \rightarrow NH_4OH$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

At equilibrium $C(1-\alpha)$ $C\alpha$ $C\alpha$

Now

$$K_b = \frac{C\alpha\times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Since aqueous solution of ammonia is weak base $1-\alpha \approx 1$

$$K_b = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_b}{C}}$$

At equilibrium $[OH^-] = C\alpha$

$$[OH^-] = C\sqrt{\frac{K_b}{C}} = \sqrt{K_bC}$$

But $K_a\times K_b = K_W$

$$\therefore K_b = \frac{K_W}{K_a}$$

$$[OH^-] = \sqrt{\frac{K_W}{K_a}C}$$

$$[OH^-] = \sqrt{\frac{10^{-14}}{5\times10^{-10}}\times5.82} = 1.079\times10^{-2}$$

Q) Calculate the pH of $10^{-6}M$ HCl solution if 1ml of it is diluted to 100ml, $K_W = 1\times10^{-14}$

Solution

Concentration of HCl after dilution = $10^{-6}/100 = 10^{-8}M$

Hence $[H^+] = 10^{-8}$ M

Since concentration of H+ ions is very low, concentration of H+ from water is also taken into account

$[H^+]$ from water = 10-7 M

Total $[H^+] = (10^{-8} + 10^{-7}) = 1.1\times10^{-7}M$

$pH = -\log[H^+] = -\log(1.1\times10^{-7})$

$pH = 7 - \log 1.1 = 6.95$

Q) What will be the resultant pH when 200ml of an aqueous solution of HCl (pH =2.) is mixed with 300ml of an aqueous solution of NaOH (pH = 12.0)?

Solution

HCl	NaOH
pH = -log[H^+] = 2	pH = -log[H^+] =12
H^+] = 10^{-2}M	[H^+] = 10^{-12}M
	[OH^-] = 10^{-2}M
Millimoles of H^+	Millimoles of OH^-
10^{-2}×200 = 2	=10^{-2} × 300 = 2

2 millimoles of H^+ will be neutralized with 2 millimoles of OH^-. Thus, the resulting solution contains 1millimole of OH^- in 500ml

Concnetration of [OH^-] left = = 1/500 = 2×10^{-3} M

pOH = -log[OH^-] = -(log2×10^{-3}) = 2.69

pH = 14 –pOH = 14-2.69 v= 11.31

Q) Calculate the approximate pH of a 0.1M aqueous H_2S solution, K_1 and K_2 of H_2S are 1.00×10^{-7} and 1.3×10^{-13} respectively at 25^{O}C

Solution:

Since K_1 >> K^2 we can neglect second dissociation and all H^+ ion concentration can be considered from 1st dissociation only

$H_2S \rightleftharpoons H^+ + HS^-$

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]}$$

As [H^+] = [HS^-]

$$K_1 = \frac{[H^+]^2}{[H_2S]}$$

$$[H^+] = \sqrt{K_1 \times [H_2S]}$$

$$[H^+] = \sqrt{10^{-7} \times 0.1} = 10^{-4}$$

Hence pH = -log[H^+] = -log10^{-4} =4.

Q) What is the pH of 0.5M aqueous NaCN solution pK_b of CN^- is 4.7

Solution

NaCN + H_2O $\rightleftharpoons$ NaOH + NHCN

$Na^+ + CN^- + H_2O \rightleftharpoons Na^+ + OH^{-+\ +\ HCN}$

i.e. $CN^- + H_2O \rightleftharpoons OH^- + HCN$

$$K_b = \frac{[HCN][OH^-]}{[CN^-]}$$

Since at equilibrium [OH^-] = [HCN]

$$K_b = \frac{[OH^-]^2}{[CN^-]}$$

Taking log on both sides

$$-\log K_b = -2\log[OH^-] + \log [CN^{-+}]$$

$$2\log[OH^-] = \log 0.5 - pK_b$$

$$\log[\mathrm{OH}^-] = \frac{-.3010 - 4.7}{2} = -2.5$$

pOH = 2.5

pH = 14-pOH = 14-2.4 = 11.5

Ionic product

Ionic product of an electrolyte is the product of concentrations of the ions in solution, each raised to the power equal to number of ions produced on dissociation of one mole of the electrolyte, at specific temperature

$P_xQ_y \rightleftharpoons xP^{y+} + yQ^{x-}$

Ionic product = $[P^{y+}]^x [Q^{x-}]^y$

For example $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

Ionic product = $[MG^{2+}] [OH^-]^{2+}$

Solubility product

Solubility product of a sparingly soluble salt at a given temperature is defined as the product of molar concentration of its ions in a saturated solution, with each concentration term raised to the power equal to number of ions present in the chemical equation representing the equilibrium of dissociation of one molecule of the salt. It is represented as K_{SP}

$A_xB_y \rightleftharpoons xA^{y+} + yB^x$

Solubility product $K_{SP} = [A^{y+}]^x [B^{x-}]^y$

For example

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$, $K_{SP} = [Al^{3+}] [OH^{-+}]3$

Application of solubility product

1.Predicting precipitate formation

If the ionic product of a sparingly soluble salt exceeds solubility product, then excess of ions combine to form precipitates i

If ionic product > K_{SP} precipitation takes place

If ionic product < K_{SP} no precipitation takes place

2. Predicting solubility of sparingly soluble salt

Solubility of a sparingly soluble salt can be calculated from its solubility product at a given temperature

	XY	⇌	X^+	+	Y^-
Let solubility be	S		S		S

$K_{SP} = [X^+]\,[Y^-] = (S)(S) = S^2$

$s = \sqrt{(K_{SP})}$

3. Precipitation of common salt

When HCl gas is passed through a saturated solution of impure common salt, the concentration of Cl^- increases due to ionization of HCl

$NaCl \rightleftharpoons Na^+ + Cl^-$, $HCl \rightleftharpoons H^+ + Cl^-$

Thus ionic product $[Na^+][Cl^-]$ exceeds solubility product and pure NaCl precipitates out

4.Salting out of soap

Soap are sodium salt of long chain fatty acids. When some NaCl is added to soap solution, concentration of Na^+ increases due to ionization of NaCl

$RCOONa \rightleftharpoons RCOO^- + Na^+$

$NaCl \rightleftharpoons Na^+ + Cl^-$

Thus ionic prodct $[RCOO^-][[Na^+]$ exceeds solubility product of soap and soap precipitates out from the solution

5. Qualitative analysis

Various basic radicals are identified and separated by the principle of solubility product and common ion effect

Common ion effect

Common ion effect is defined as the suppression of ionization of weak electrolyte by addition of strong electrolytes having an ion common to weak electrolyte.

For example weak base NH_4OH ionizes to a small extent

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

When a strong electrolyte like NH_4Cl or NaOH is added to this solution, a common ion NH_4^+ and OH^- respectively is furnished so that the equilibrium is shifted to the right, according to Le-Chatelier's principle

$$\begin{array}{lcl} NH_4OH \rightleftharpoons & NH_4^+ & +OH^- \\ NH_4Cl \rightleftharpoons & NH_4^+ & +Cl^- \\ & \text{common ion} & \end{array}$$

Thus, degree of dissociation of an electrolyte decreases by common ion effect but dissociation constant of the electrolyte remains same

Isohydric solutions

The solution of weak electrolytes are said to be isohydric if both have equal concentration of common ion present in them. On mixing such solutions no change in the degree of dissociation of either of the electrolytes occurs. For two isohydric solutions

$$\frac{\alpha_1}{V_1} = \frac{\alpha_2}{V_2}$$

Where V_1 and V_2 are the diluting solution (1) and (2) respectively. And α_1 and α_2 are their degree of dissociation at respective dilution

Solved Numerical

Q) The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6}M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8

Solution

$Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^-$

S S 2S

S = 6.7×10^{-6}M

$K_{SP} = [Pb^{2+}][OH^-]^2$

$K_{SP} = (6.7\times10^{-6})(2\times6.7\times10^{-6})^2 = 1.2\times10^{-15}$

In the solution of pH = 8, $[H^+] = 10^{-8}$M

As $[H^+][OH^-] = K_W$

$$[OH^-] = \frac{K_W}{[H^+]} = \frac{10^{-14}}{10^{-8}} = 10^{-6}$$

K_{SP} of salt remains constant at a particular temperature

Again $K_{SP} = [Pb^{2+}][OH^-]^2$

$1.2\times10^{-15} = [Pb^{2+}][10^{-6}]^2$

$$[Pb^{2+}] = \frac{1.2\times10^{-15}}{10^{-12}} = 1.2\times10^{-3}M$$

i.e. Solubility = 1.2×10^{-3} mol litre^{-1}

Q) A sample of AgCl was treated with 5.0 ml of 1.5M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contains 0.0026g of Cl^- per litre. Calculate the solubility product of AgCl (K_{SP} for $Ag_2CO_3 = 8.2\times10^{-12}$)

Solution

$Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$

$K_{SP} = [Ag^+]^2 [CO_3^{2-}]$

Given $[CO_3^{2-}]$ from Na_2CO_3 = 1.5M

$$\therefore [Ag^+] = \sqrt{\frac{K_{SP}}{CO_3^{2-}}} = \sqrt{\frac{8.2\times10^{-12}}{1.5}} = 2.34\times10^{-6}M$$

Now molar concentration of Cl^- = $[Cl^-]$ = 0.0026/35.5 (atomic mass of Cl = 35.5)

K_{SP} for AgCl = $[Ag^+][Cl-]$

$\therefore K_{SP}$ for AgCl

$$K_{SP} = (2.34\times10^{-6})\left(\frac{0.0026}{35.5}\right) = 1.71\times10^{-10}$$

Buffer Solutions

Buffer solution is defined as a solution which resists the change in its pH value when small amount of acid or base is added to it or when the solution is diluted. Buffer solution has a definite pH value at specific temperature and it does not change on keeping for long time.

Types of buffers

1. Simple buffer

   These are the solutions of salt of weak acid and weak base.

   For example Ammonium acetate (CH_3COONH_4)

2. Mixed buffers

These are the mixtures of two solutions. These are further of two types

9i) Acidic buffers

These are the solutions of mixture of weak base and salt of this weakbase with strong acid. For example $CH_3COOH + CH_3COONa$. They have pH value less than 7 i.e pH <7

(ii) Basic buffers

These are the solutions of mixture of weak base and salt of this weak base with strong acid. For example $NH_4OH + NH_4Cl$. They have pH value more than 7 i.e. pH > 7

pH of buffer solution

pH value of buffer solution is given by Henderson-Hasselbalch equation

(i) Acidic buffer :

$$pH = pK_a + log\frac{[salt]}{[acid]}$$

Where K_a is dissociation constant of acid and pK_a = -lonK_a , [salt] and [acid] are molar concentration of salt and acid respectively

(ii) Basic buffer

$$pOH = pK_b + log\frac{[salt]}{[base]}$$

Where K_a is dissociation constant of acid and pK_b = -lonK_b , [salt] and [base] are molar concentration of salt and base respectively

Blood as buffer solution

Blood acts as a buffer solution and maintains a pH level of about 7.1. Any change in pH of blood can produce illness or even cause death

Solved Numerical

Q) A buffer solution with pH = 9 is to be prepared by mixing NH_4Cl and NH4OH. Calculate the number of moles of NH_4Cl that should be added to one litre of 1.0 M NH_4OH ($K_b = 1.8\times10^{-8}$)

Solution

Weak base (NH_4OH) + salt of weak base with strong acid (NH_4Cl) = Base buffer

For basic buffer

$$pOH = pK_b + log\frac{[salt]}{[base]}$$

pOH = 14 –pH

pOH = 14 – 9 = 5

and $pK_b = -logK_b = -log(1.8\times10^{-5}) = 4.7447$

[Base] = [NH_4OH] = 1.0M

Thus

$$5 = 4.7447 + log\frac{[salt]}{1}$$

Log[salt] = 0.2553

On taking antilog

[salt] = 1.8 mol $litre^{-1}$

NOMENCLATURE OF ORGANIC COMPOUND

Classification of organic compounds

Organic compounds are broadly classified into following to classes

1) Acyclic compounds

These are the compounds in which carbon atoms are linked to form open chain (straight or branched). These compounds may be saturated(all single bonds) or unsaturated (multiple bonds)

Example

Propane $CH_3 – CH_2 – CH_3$ is saturated as it contains single bond between two carbon atoms

Propyne $CH_3 – CH = CH_2$ is unsaturated as it contains double between tow carbon atoms

2)Cyclic compounds/ close chain/ ring compounds

These are the compounds which contains one or more closed ring in their molecule. These are further of two types

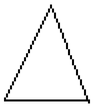
(a) Homocylic compounds

These are the cyclic compounds in which ring is made of only one type of atoms. These are further divided into two sub-classes

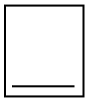
These are the cyclic compounds in which ring is made of only one type of atoms. These are further divided into two sub-classes

(i)Alicyclic compounds

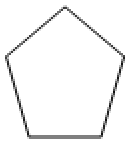
These are the carbocylic compounds which resemble corresponding acyclic compounds in their properties e.g.



Cyclopropane



Cyclobutene



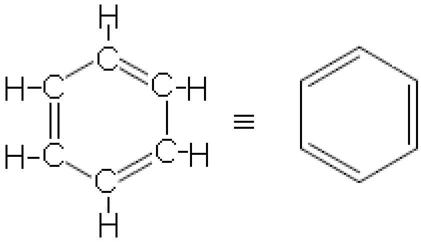
Cyclopentane

(ii)Aromatic homocyclic compounds

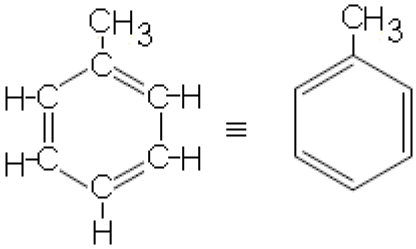
These are the compounds which contains one or more fused or isolated benzene ring. These are also called benzenoid compounds e.g.

Monocyclic

benzene

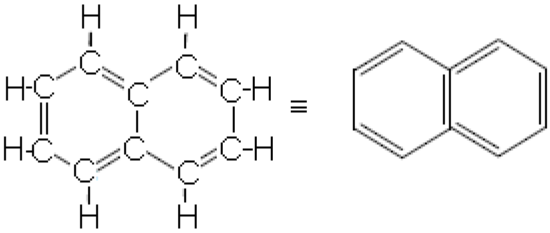


toluene

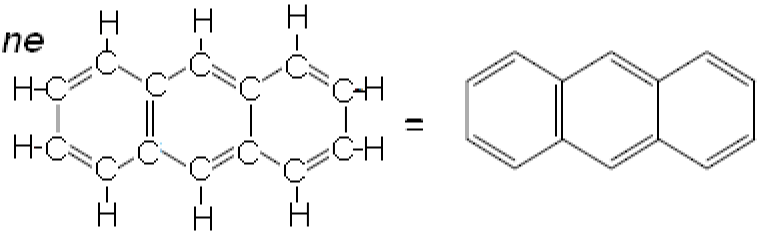


Polycyclic

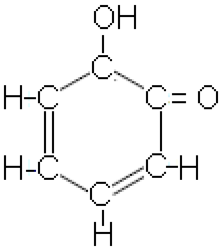
naphthalene



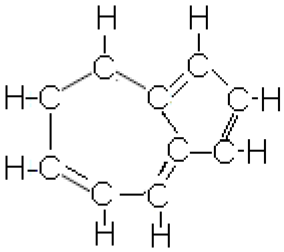
anthracene



There are some other aromatic homocyclic compounds which do not contain benzene ring. Such compounds are known as non-benzenoid compound



Tropolone

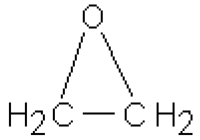


Azulene

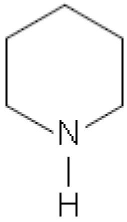
(b)Heterocyclic compounds

These are the cyclic compounds which contains one or more heteroatoms (atoms other than C and H) in the ring. These are further divided into two subclasses (i)Alicyclic heterocyclic compounds

The heterocyclic compounds which resemble the corresponding aliphatic compound in most of the property is known as alicyclic heterocyclic compounds examples



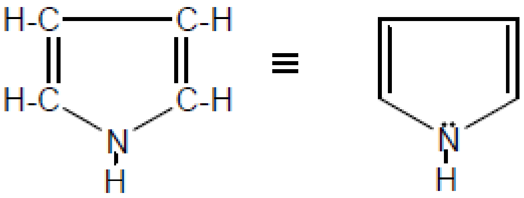
Oxirane or epoxy ethane



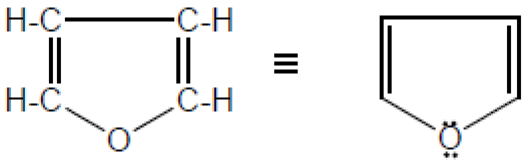
Piperidine

(ii) Aromatic heterocyclic compounds

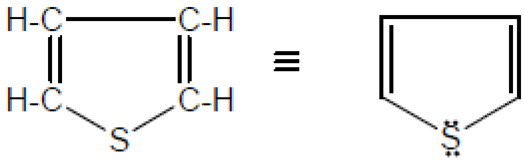
These are the heterocyclic compounds which posses aromaticity and resemble corresponding aromatic compounds in most of their property. These are also called non-benzenoid aromatic compounds. Examples



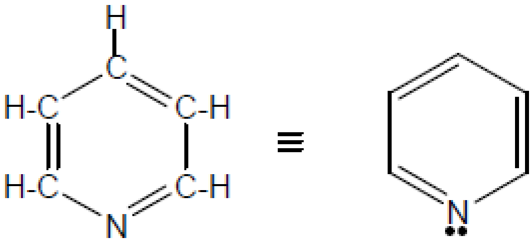
pyrrole



furan



thiophene



pyridine

Homologous series

It is a series of compounds in which the adjacent members differ by a $–CH_2-$ unit. All the members of such a series have same general formula, same functional group, same chemical properties and show regular gradation in physical properties e.g. members of homologous series of alkenes have general formula C_nH_{2n},

Two successive members differ by $–CH_2-$ unit. Individual members of such series are called homologues and the phenomenon is called as homology.

Functional group

It is an atom or group of atoms that decides the chemical nature of an organic compound . For example -OH (hydroxyl), $-NH_3$(amine) etc

NOMENCALATURE OF ORGANIC COMPOUND

The world wide accepted system for naming organic compounds is IUPAC system of nomenclature (International Union of Pure and Applied Chemistry) according to which all organic compounds are considered as derivative of saturated hydrocarbons. The IUPAC name of an organic compounds consists of three parts: word –root, suffix and prefix

(i)Word root

Word root gives the idea about principle carbon chain. Word root is given according to number of carbon atoms in a carbon chain

Number of carbons	Word root	Number of carbon	Word root
1	Meth-	7	Hept-
2	Eth-	8	Oct-
3	Prop-	9	Non-
4	But-	10	Dec-
5	Pent-	11	Undec
6	Hex-	12	Dodec-

(ii)Suffix

There are two type of suffixes

(a)Primary suffix

It gives the idea about saturation and un-saturation of the organic compound. It is always added to the word root. Primary suffix for various saturated and unsaturated carbon chains as follows

Type of carbon chain	Suffix	IUPAC
Saturated, C – C	-ane	Alkane
Unsaturated, C = C	-ene	Alkene
Unsaturated, C≡C	-yne	Alkyne

If the parent chain contains two or more multiple bonds then numerical prefixes such as di (for two), tri (for three), tetra (for four) etc. are added to the primary suffix

Examples

Organic compound	Word root	Primary suffix	IUPAC name
$CH_2CH_2CH_3$	Prop	ane	Propane
$CH_2 = CH_2$	Eth	ene	Ethane
$CH_3C \equiv CH$	Prop	yne	Propyne
$CH_2 = CH - CH = CH_2$	But	dine	Butadiene

(b) Secondary suffix

Secondary suffix gives the idea about nature of the functional group present in the compound. It is added after primary suffix. Secondary suffix for some common functional groups are as follows

Class of compounds	Functional group	Secondary suffix
Alcohols	-OH	-ol
Aldehydes	-CHO	-al
Ketones	>C = O	-one
Carboxylic acids	-COOH	-oic acid
Acid amides	$-CONH_2$	-amide
Acid chloride	-COCl	-oyl chloride
Esters	-COOR	-oate
Nitriles	-CN	-nitrile
Amine	$-NH_2$	-amine
Thioalcohol	-SH	-thiol
Sulphonic acid	$-SO_3H$	-sulphonic acid

Examples

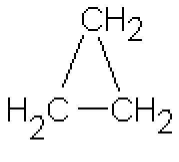
Organic compound	Word root	Primary suffix	Secondary suffix	IUPAC name
$HC \equiv C-CHO$	Prop	yne	Al	Propynal
$CH_3CH_2CH_2CN$	But	ane	Nitrile	Butane nitrile
$CH_2 =CHOH$	Eth	ene	ol	Ethenol
CH_3CH_2COOH	Prop	ane	Oic acid	Propanoic acid

(iii)Prefix

Prefixes are of two types

(a)Primary prefix

Primary prefix is used to give idea about cyclic or acyclic nature of the compound. For carbocyclic compounds a primary prefix cyclo is added before word root whereas in case of acyclic compounds no prefix is used Example



Cyclo + Prop + ane = Cyclopropane

Types of carbon atoms

(i)Primary or 1^{O} carbon atom

A carbon atom attached to one (or no) other carbon atom

(ii)Secondary or 2^{O} carbon atom

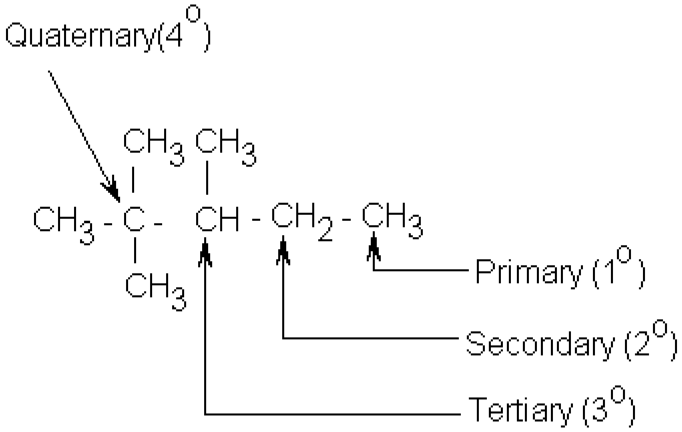
It is the carbon atom attached to two other carbon atoms

(iii)Tertiary or 3^{O}carbon atom

It is the carbon atom attached to three other carbon atoms

(iv)Quaternary or 4^{O} carbon atom

It is the carbon atom attached to four other carbon atoms

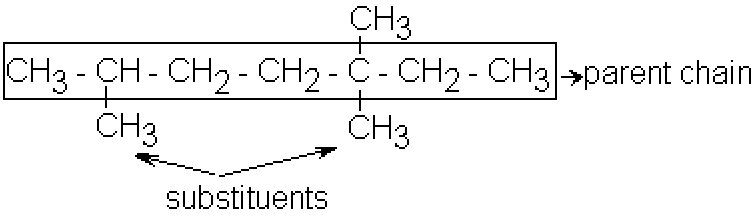


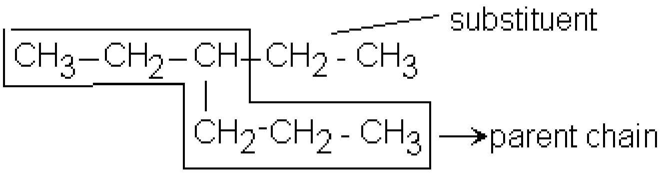
Hydrogen atom attached to 1°, 2°, 3° carbon atoms are called primary (1°), secondary (2°) and tertiary(3-o_) hydrogen atoms respectively.

Rules for nomenclature of organic compounds

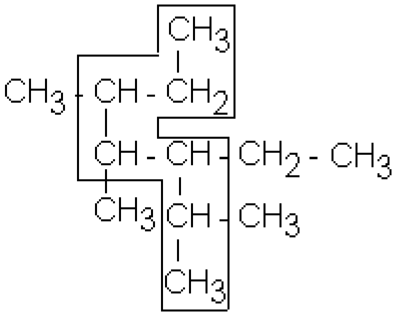
1.Longest chain rule

(i)Select the longest continuous chain of carbon atoms in the molecules. The longest continuous chain, containing the maximum number of carbon atoms, is taken as the parent chain and other part which are not included in parent chain are identified by substituents or branched chain

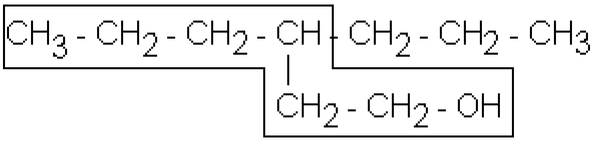




(ii) If two different chain of equal lengths are possible, the chain with maximum number of side chains of alkyl group is selected

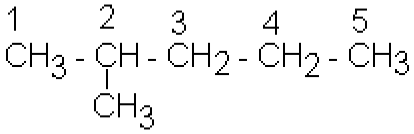


(iii) If the compound contains one functional group or multiple bonds or substituent then select the longest chain of carbon atoms containing functional group and maximum number of multiple bonds as parent chain

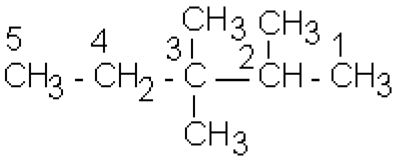


2.Numbering of the principal chain

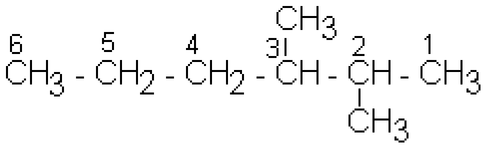
(i)Number the carbon atoms in the parent chain as 1,2,3. ….etc starting from end which gives smaller number to the carbon atoms carrying the substituent



(ii) When the parent chain has two or more substituent's, numbering should be done in such a way that sum of locants on the parent chain is lowest possible number.



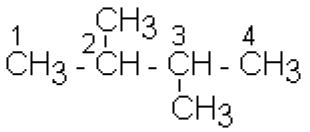
Set of locant = 2, 3, 3 (2+3+3 =8)



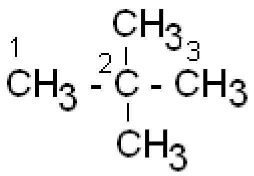
Set of locants = 2, 3 (2+3 = 5)

3. Presence of more than one same substituent

If the same substituent occurs more than once on the parent chain, it is indicated by the prefixes such as di, tri, tetra, etc to 2, 3, 4 etc. same substituent



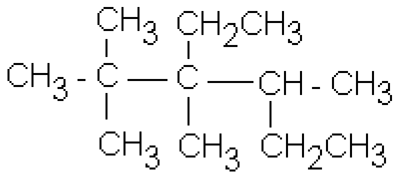
2, 3 - Dimethylbutane



2,2 -Dimethylpropane

4.Naming different substituent

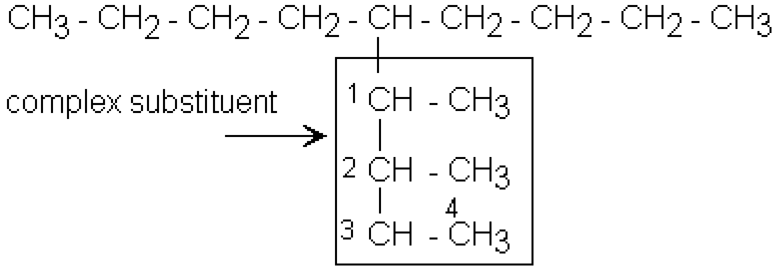
If two or more substituent are present on the parent chain, they are named in the alphabetical order along with their appropriate position



3, 4 - Diethyl - 2, 2, 4 - Trimethyl pentane

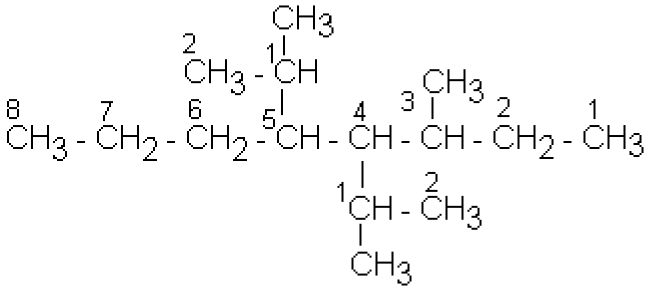
5.Naming the complex substituent

If the substituent on the parent chain is complex (i.e. it is branched) it is named as a substituted alkyl group by numbering the carbon atom of this group attached to the parent chain as 1. The name of such substituent is written in bracket in order to avoid any confusion with the numbering of the parent chain



Complex substituent : 1,2 - Dimethyl propyl

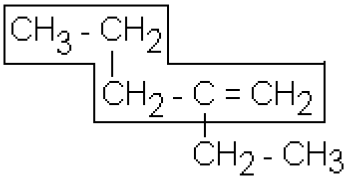
If the same complex substituent is repeated twice or thrice in the compound then prefixes bis(for two), tris (for three), tetrakis (for four) etc. are used before the name of complex substituent



3 - Methyl - 4,5 - bis(1-methyl ethyl) octane

6.Nomenclature of unsaturated hydrocarbons (Containing double or triple bond)

i)Select the longest continuous chain containing the carbon atom involved in the multiple bonds



ii) While writing the name of the alkene or alkyne, the suffix ‘ane’ of the corresponding alkane is replaced by ‘ene’ or ‘yne ‘ respectively

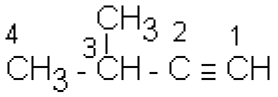
iii)IF the multiple bond occurs twice in the parent chain the alkene and alkyne are called diene and diyne respectively

iv) The numbering of atoms in parent chain is done in such a way that the carbon atom containing the double or triple bond gets the lowest number

$$\overset{1}{CH_3} - \overset{2}{CH} = \overset{3}{CH} - \overset{4}{CH_2} - \overset{5}{CH_3}$$

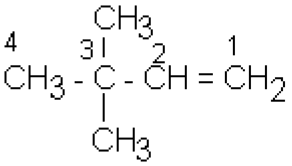
Pent - 2 - ene

v) All the rules for naming the side chains or substituent are then follows



$$\overset{4}{CH_3} - \overset{3}{\underset{}{CH}}(CH_3) - \overset{2}{C} \equiv \overset{1}{CH}$$

3 -methyl but - 1 - yne



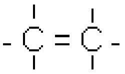
$$\overset{4}{CH_3} - \overset{3}{C}(CH_3)_2 - \overset{2}{CH} = \overset{1}{CH_2}$$

3, 3 - Dimethyl but - 1 - ene

7. Functional group and their nomenclature

i)Alkene

Functional group



$$- \overset{|}{\underset{|}{C}} = \overset{|}{\underset{|}{C}} -$$

Replace ane of alkane by ene

$$\overset{1}{CH_2} = \overset{2}{CH} - \overset{3}{CH_2} - \overset{4}{CH_3}$$

But - 1 - ene

ii)Alkyne

- C ≡ C –

Replace ane of alkane by yne

$$\overset{1}{CH} \equiv \overset{2}{C} - \overset{3}{CH_2} - \overset{4}{CH_3}$$

But - 1 - yne

iii)Alcohol

- OH

Relace e of alkane by ‘ol’

$\overset{1}{CH_3} - \overset{2}{CH_2} - \overset{3}{CH_2} - \overset{4}{CH_2} - OH$

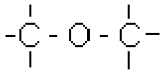
Butan -1 -ol

$\overset{4}{CH_3} - \overset{3}{CH} = \overset{2}{CH} - \overset{1}{CH_2} - OH$

But - 2 -en - 1 -ol

Note : if parental chain contain single bond, double bond or triple bond then 'e' from ane, ene or yne will be dropped only if it is followed by 'a', 'i' 'o', 'u' , 'y'

iv)Ether



$-\underset{|}{\overset{|}{C}} - O - \underset{|}{\overset{|}{C}} -$

These are written as alkoxy alkanes, if chain is unsymmetric then '-oxy' is attached to lower carbon chain

$CH_3 - CH_2 - O - CH_2 - CH_3$

Ethoxy ethane

$CH_3 - O - CH_3 - CH_2 - CH_3$

methoxy propane

v) Alkyl halides

F , Cl, Br, I

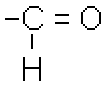
Prefix fluoro, chloro, bromo, iodo is used for F, Cl, Br and I respectively

These are named as haloalkanes

$CH_3 - CH_2 - CH_2 - CH_2 - Br$

1 - Bromobutane

vi) Aldehydes



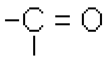
$-\underset{\underset{H}{|}}{C} = O$ OR $- CHO$

Replace 'e' of alkane by –al

$CH_3 - CH_2 - CH_2 -CHO$

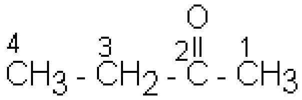
Butanal

vi)Ketones



$-\underset{|}{C} = O$

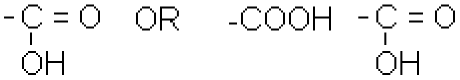
Replace 'e' of alkane by one



$\overset{4}{CH_3} - \overset{3}{CH_2} - \overset{\overset{O}{\|}}{\underset{2}{C}} - \overset{1}{CH_3}$

But - 2 - one

vii)Caboxylic acid



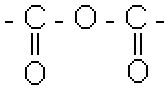
$-\underset{OH}{\underset{|}{C}}=O$ OR $-COOH$ $-\underset{OH}{\underset{|}{C}}=O$

Replace e of alkane by –oic acid

$CH_3-CH_2-CH_2-COOH$

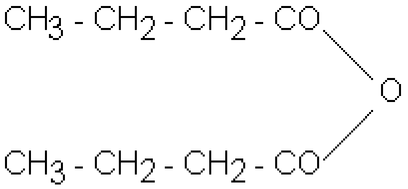
Butanoic acid

viii) Acid anhydride



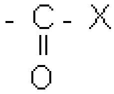
$-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-$

Replace ‘e’ of alkane by oic anhydride



Butanoic anhydride

ix) Acid halide



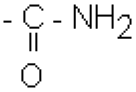
$-\underset{O}{\underset{\|}{C}}-X$ (X = F, Cl, Br, I)

Replace oic acid of corresponding acid by oyl halide

$CH_3CH_2CH_2\ COCl$

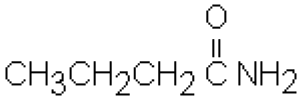
Butanoyl chloride

x) Amide



$-\underset{O}{\underset{\|}{C}}-NH_2$

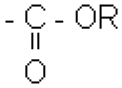
Replace oic acid of corresponding acid by amide



$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}NH_2$

Butamide

xi)Ester



$-\underset{O}{\underset{\|}{C}}-OR$

Naming the alkyl group (R) and change oic acid of acid by one

$C_3H_7COOCH_3$

methyl butanoate

xii)Nitro

$-NO_2$

Naming as nitroalkane

$CH_3CH_2CH_2CH_2NO_2$

1 -nitrobutane

xiii) Nitride

- $C{\equiv}N$

$CH_3CH_2\ CH_2C \equiv N$ Butanenitride or cyanopropane (Note if cyano is used Carbon with nitrogen is not counted)

xiv) carbylamines

$-C \overset{\rightarrow}{\equiv} N$

$CH_3CH_2CH_2-C \overset{\rightarrow}{\equiv} N$

Propane carbylamine

xv) Amine

- NH_2

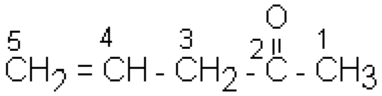
  $CH_3CH_2CH_2CH_2 - NH_3$

  1 – Butanamine

8.Nomenclature of compounds having functional groups, multiple bonds, side chains/ substituent

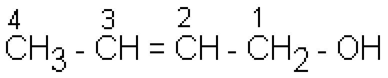
(i)If the organic compounds contains a functional group, multiple bond, side chain or substituent, the order of preference is

Functional group > Double bond > Triple bond > substituent



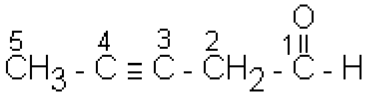
$$\overset{5}{C}H_2 = \overset{4}{C}H - \overset{3}{C}H_2 - \overset{2}{\underset{}{\overset{\overset{O}{\|}}{C}}} - \overset{1}{C}H_3$$

Pent - 4 - en - 2 -one



$$\overset{4}{C}H_3 - \overset{3}{C}H = \overset{2}{C}H - \overset{1}{C}H_2 - OH$$

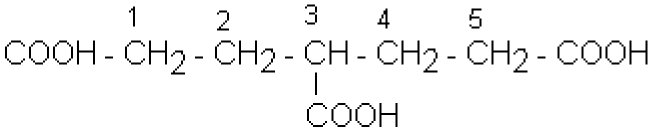
But - 2 - en - 1 - ol



$$\overset{5}{C}H_3 - \overset{4}{C} \equiv \overset{3}{C} - \overset{2}{C}H_2 - \overset{1}{\overset{\overset{O}{\|}}{C}} - H$$

Pent - 3 - yn - al

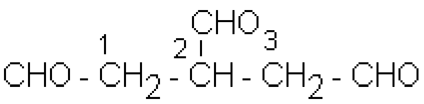
9. Compound containing more than two like functional groups



$$COOH - \overset{1}{C}H_2 - \overset{2}{C}H_2 - \overset{3}{\underset{\underset{COOH}{|}}{C}}H - \overset{4}{C}H_2 - \overset{5}{C}H_2 - COOH$$

Pentane - 1,3,5 - tricarboxylic acid

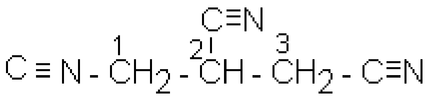
Note : since word carb used carbon in functional group –COOH is not counted



$$CHO - \overset{1}{C}H_2 - \overset{\overset{CHO}{|}}{\overset{2}{C}}H - \overset{3}{C}H_2 - CHO$$

Propane - 1,2,3 tricarbaldehyde

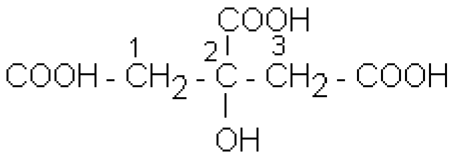
Note : since word carb



$$C\equiv N-\overset{1}{C}H_2-\overset{2}{C}H(C\equiv N)-\overset{3}{C}H_2-C\equiv N$$

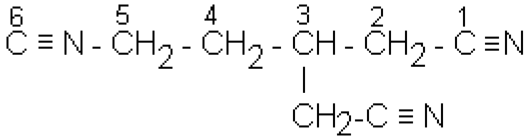
Propane - 1,2,3 - tricarbonitride

Note : since word carb is used carbon in functional group –C≡N is not counted



$$COOH-\overset{1}{C}H_2-\overset{2}{C}(COOH)(OH)-\overset{3}{C}H_2-COOH$$

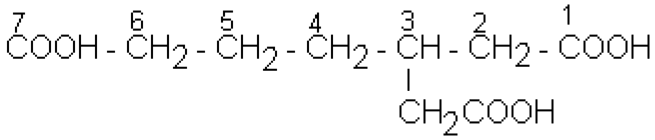
2 - Hydroxy propane - 1, 2, 3 - tri-carboxylic acid



$$\overset{6}{C}\equiv N-\overset{5}{C}H_2-\overset{4}{C}H_2-\overset{3}{C}H(CH_2-C\equiv N)-\overset{2}{C}H_2-\overset{1}{C}\equiv N$$

3 - (cyanomethyl) heptane - 1,7 dioic acid

Note : since carb word is not used carbon in C≡N is also counted



$$\overset{7}{C}OOH-\overset{6}{C}H_2-\overset{5}{C}H_2-\overset{4}{C}H_2-\overset{3}{C}H(CH_2COOH)-\overset{2}{C}H_2-\overset{1}{C}OOH$$

3 - (carboxy methyl) heheptane - 1,7 dioic acid

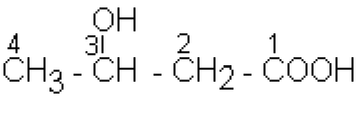
10. Nomenclature of poly – functional organic compounds

When an organic compound contains two or more functional groups, one group is treated as principal functional group and other group is regarded as the secondary functional group and may be treated as substituent

The order of for the preference of principal functional group is given below

Carboxylic acid > sulphonic acid > anhydrides> esters > acid chloride > acid amides > nitriles > aldehydes > ketones> alcohols> phenol > thiols > amine > ethers > alkene > alkynes > halo , nitro, alkyl

All other functional groups halo (fluoro, chloro, bromo, iodo) nitro (-NO_2), nitroso (- NO) and alkoxy (-OR) are always treated as substituent groups

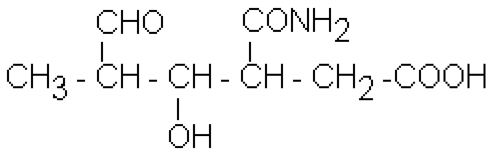


$$\overset{4}{C}H_3-\overset{3}{C}H(OH)-\overset{2}{C}H_2-\overset{1}{C}OOH$$

-COOH is principal functional group

- OH is substituent

3 - Hydroxybutan - 1 -oic acid



$CH_3 - \overset{CHO}{\overset{|}{C}H} - \underset{OH}{\underset{|}{C}H} - \overset{CONH_2}{\overset{|}{C}H} - CH_2 - COOH$

-COOH is principal functional group

-CHO, -OH, -CONH2 are substituent group

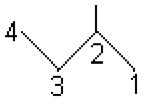
3 -carbamoyl - 5 - formyl - 4 - hydroxyhexan - 1 - oic acid

The names of secondary groups which are used as prefixes are given below

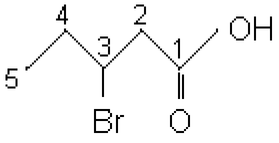
- COOH : Carboxy
-COOR : Alkoxy carbonyl or carbalkoxy
-COCl : Chloroformyl
$-CONH_2$: Carbamoyl
-CN : Cyano
-OR : R –oxy
$-SO_3H$: Sulpho
-CHO : Formyl
>CO : Oxo or keto
-OH : Hydroxy
-SH : mercapto
$-NH_2$: amino
=NH : Imino
R-CH = CH – :alkenyl
R – C ≡ C - : Alkynyl

11. Bond line notations

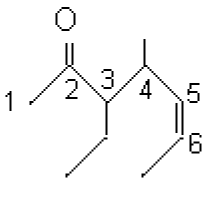
In this type of structural formulas, carbon-carbon bond is represented by a line drawn in zig-zig fashion, in which the line ends and intersections represents the carbon atom. A single bond is represented, by a single line (-) , a double bond by two parallel lines (=)and triple bond by three parallel lines (≡). Carbon and hydrogen atoms are not shown on a bond line structural formula but other atoms are shown by their usual symbols



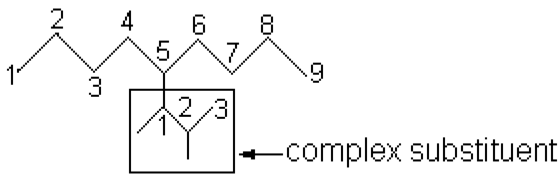
2-methyl butane



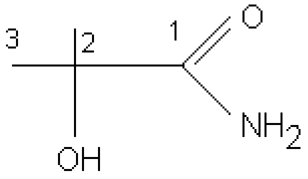
3 - bromopentan-1-oic acid



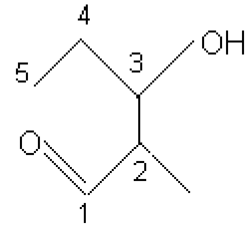
3-ethyl-4,methyl hept -5-ene-2-one



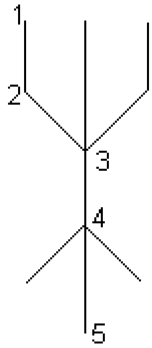
5-(1,2 - dimethyl propyl) nonane



2-Hydroxy - 2- methyl propanamide



3-Hydroxy-2-methylpentan-1-al

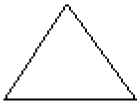


3 -ethyl - 3,4,4 trimethylpentane

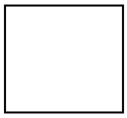
12. Nomenclature of alicyclic compounds

Following rules are generally followed for naming of alicyclic compounds

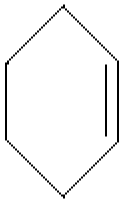
i) In the naming of such compound a prefix cyclo is added to the word root



Cyclopropane

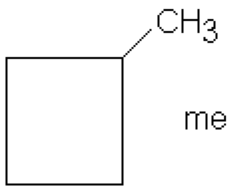


Cyclobutane



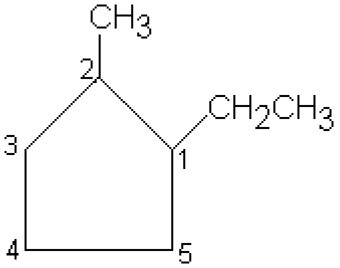
Cyclohexene

ii) If only one substituent is present on the ring, then it is not required to give its position

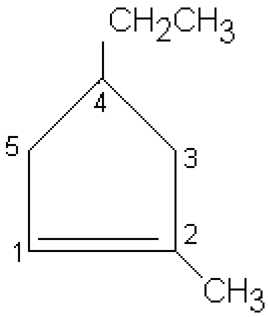


methyl cyclo butane

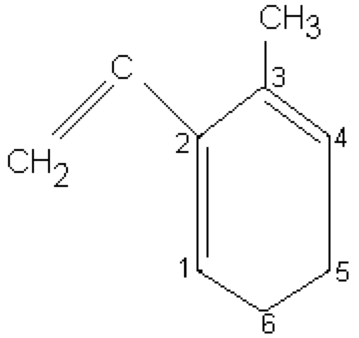
If two or more substituent are present in the ring, their positions is done by numbering of ring according to lowest set of locants rule



1 - ethyl - 2 - methylcyclopentane

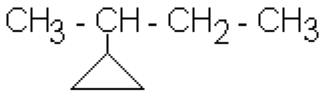


4-ethyl-2-methyl cyclopent-1-ene



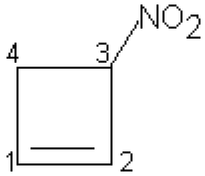
2-ethyl-3-methylcyclohexa-1,3-deine

iii) If the ring contains lesser number of carbon atoms than that of alkyl group attached to it, the compound is named as derivative of alkane and the ring is considered as a substituent group to the alkane, otherwise it is named as derivative of cycloalkane.

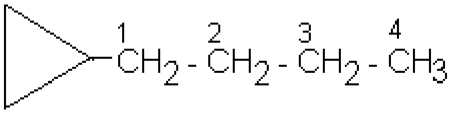


$CH_3 - \underset{\triangle}{CH} - CH_2 - CH_3$

2 - cyclopropylbutane

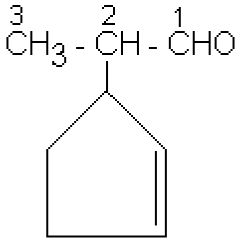


3 - nitrocyclobut-1-ene

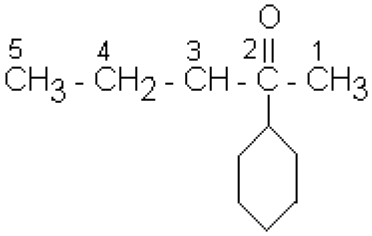


1 - cyclopropyl butane

iv) If the side chain contains a multiple bond or a functional group, then alicyclic ring is treated as the substituent irrespective of the size of the ring and/ or alicyclic ring contains multiple bonds or not

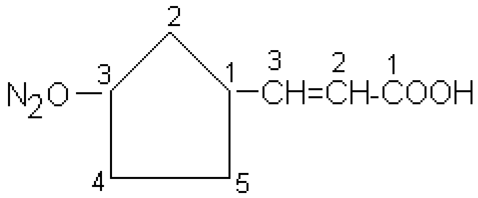


2 -cyclopentyl propanal

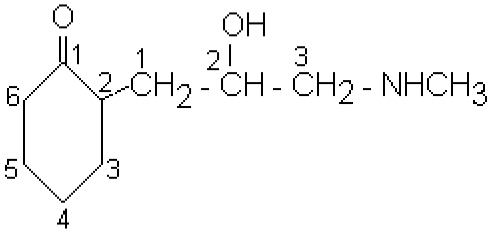


3 - cyclohexyl pentan - 2 -one

v) if both the rings as well as side chain contain the functional group, then parent hydrocarbon is then parent hydrocarbon is decided on the basis of principal functional group which is further based on preferential order of functional groups

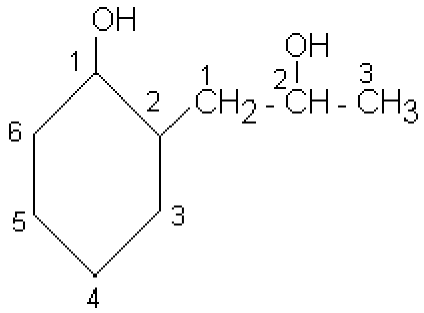


3 - (3 - Nitrocyclopentyl) prop - 2 - en - 1 - oic acid

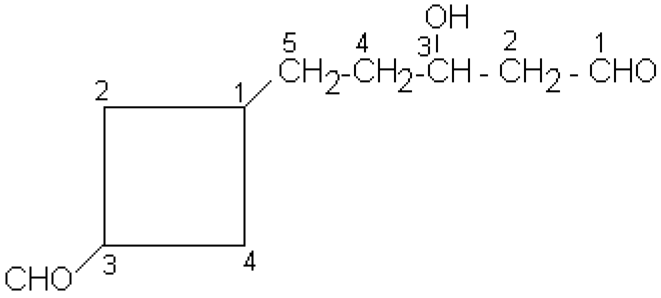


2 - (3 aminomethyl - 2 - hydroxypropyl) cyclohexan - 1 - one

vi) If both alicyclic ring and the side chain contains same functional group, the parent hydro-carbon is selected on the basis of number of carbon – atoms in the ring and side chain

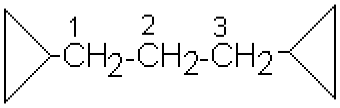


2 - (2-Hydroxypropyl) cyclohexane - 1 - ol

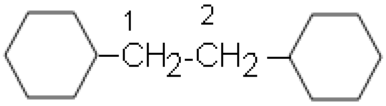


5-(3-formylcyclobutyl)-3-methyl pentanal

vii) If more than one alicyclic rings are attached to the single chain of carbon atom, the compound is named as a derivative of alkane and alicyclic rings are treated as substituent irrespective of the number of carbon atoms in the ring or chain

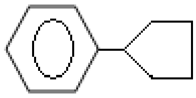


1, 3 - dicyclopropyl propane

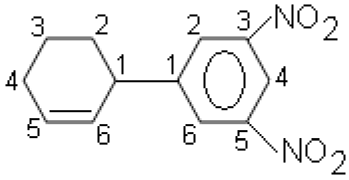


1, 2 - dicyclohexylethane

viii)If the alicyclic ring is attached to the benzene ring, the compound is named as a derivative of the benzene

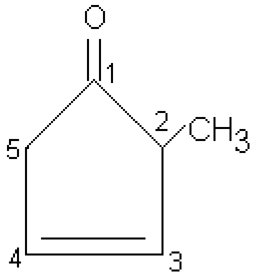


Cyclopentyl benzene

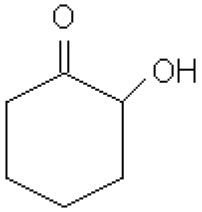


1-(2-methylcyclohex-2-ene-1-yl)-3,5-dinitrobenzene

ix) If the alicyclic ring has a functional group along with some substituent on the ring, then appropriate prefixes and suffix are used and numbering is done in such a way that the functional group gets the lowest possible number

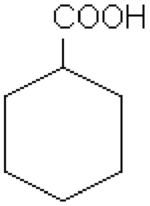


2 - methyl cyclopent-3-en-1- one

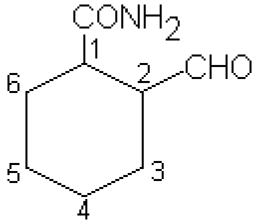


3-amino - 2-hydroxycyclohexan-1-one

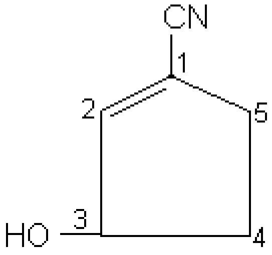
x) If an alicyclic ring is directly attached to a carbon, containing functional group, the carbon – atom of the functional group is not counted for word root rather appropriate suffix (use carb-) are used to represent such group.



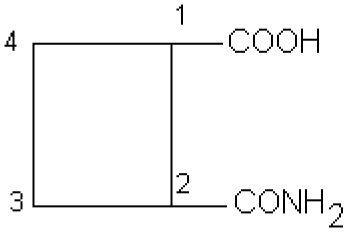
Cyclohexanecarboxylic acid



2-Formyl cyclohexane - 1 - carboamide



3-hydroxy cyclopent-1-en-1-carbonitrile



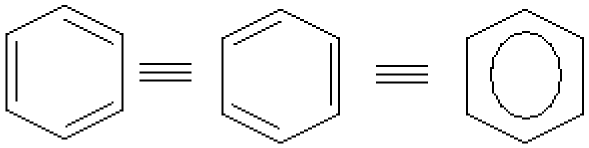
2-carbamoyl cyclobutane-1-carboxylic acid

13.Nomenclature of aromatic compounds

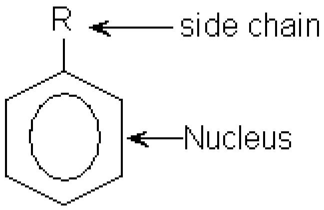
An aromatic compound consists of two parts i.e. nucleus and side chain

(a)Nucleus

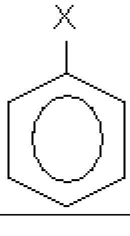
The benzene ring present in aromatic compound is called nucleus. It is represented as follows



(b) side chain



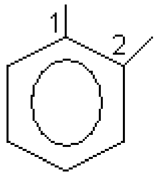
Alkyl or any other aliphatic group attached to benzene nucleus by replacing one or more hydrogen



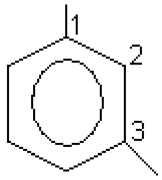
monosubstituent derivative

If only one hydrogen atom of ring is replaced by some other group, then it is called as mono substitute derivative

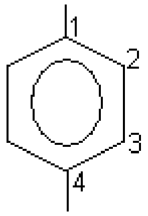
If more than one hydrogen atom of benzene ring is replaced by some other atom or group, then their position is mentioned by numbering,. In +++++case of distribution respective position of two groups can also be mentioned as follows



(1, 2) ortho
(adjacent)

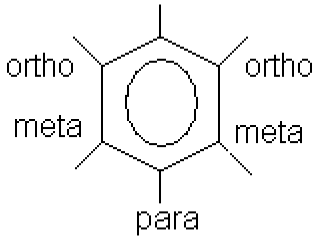


(1, 3) meta
(alternate)



(1, 4) para
(opposite)

With respect to a particular group the three positions can be represented as



Aromatic compounds are basically of two types

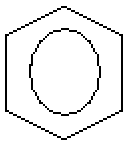
i) Nuclear substituted aromatic compounds

These are the compounds in which functional group is directly attached to benzene ring are named as derivative of benzene

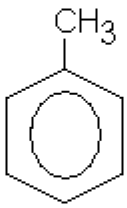
ii)Side chain substitute aromatic compounds

these are the compounds in which functional group is present in the side chain of the benzene ring. These are named as phenyl derivatives of the corresponding aliphatic compounds

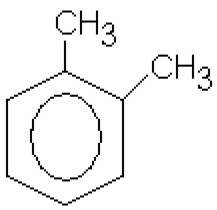
(A)Aromatic compounds



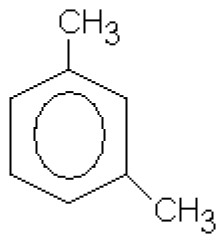
Benzene



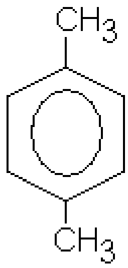
Toluene



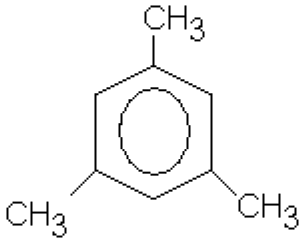
1,2 - dimethyl benzene
(o- xylene)



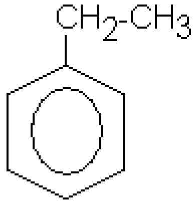
1, 3 - Dimethyl benzene
(m-xylene)



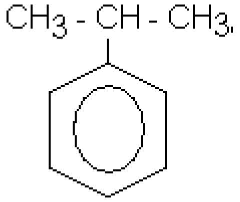
1, 4 - Dimethyl benzene
(p -xylene)



1, 3, 5 - trimethyl benzene
(mesitylene)

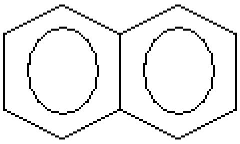


Ethyl benzene

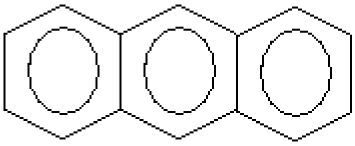


2-propyl benzene

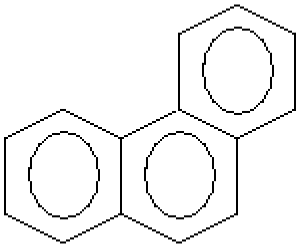
Iso-propyl benzene
or cumene



Naphthalene



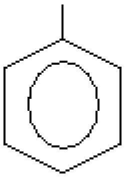
Anthracene



Phenanthere

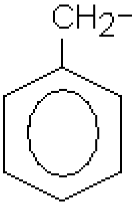
(B) Aryl groups

The radical obtained by removal of one or more hydrogen atoms of the aromatic hydrocarbon molecules are known as aryl group.

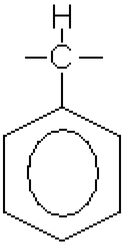


or C_6H_5-

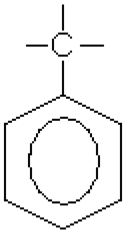
Phenyl



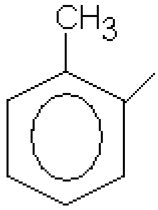
Benzyl



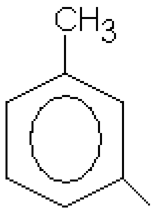
Benzal



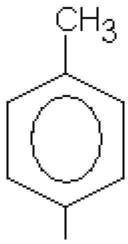
Benzo



O - tolyl or
2 -tolyl



m- tolyl or
3 -tolyl

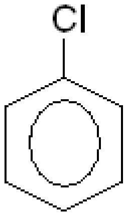


p- tolyl or
4-tolyl

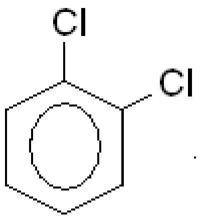
C) Halogen derivatives

(a)Nuclear substitute

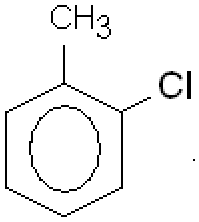
These are the compounds in which substitution on benzene ring with halogen takes place



Chloro benzene



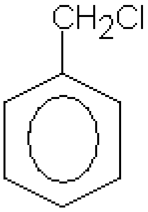
1,2 - Dichlorobenzene
(o-dichlrobenzene)



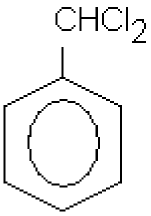
1,2 - Dichlorotoluene
(o-dichrlorotoluene)

(b)Side chain substitute

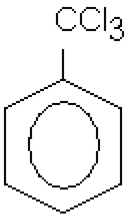
In these compounds, the side chain of the aromatic compound get substituted with halogen e,g.



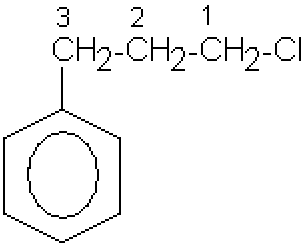
Phenyl chloromethane
(Benzyl chloride)



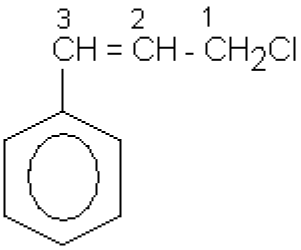
Phenyl dichloromethane
(Benzal dichloride)



Phenyl trichloromethane
(Benzo trichloride)



1-chloro-3-phenyl propane

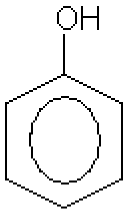


3-chloro-1-phenylprop-1-ene

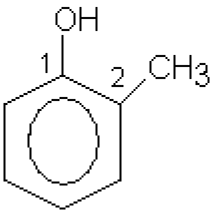
D) Hydroxy derivatives

(a)Nuclear substitute

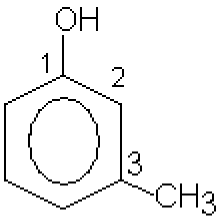
When one or more H-atom of benzene ring get substituted with –OH group we get nuclear substitute aromatic hydroxyl derivative. Which are also known as phenols



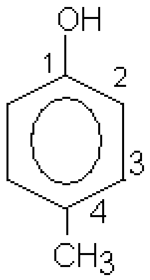
phenol



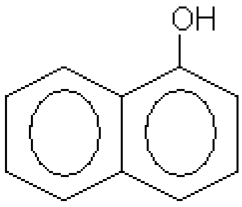
2 - methyl phenol



3 - methyl phenol

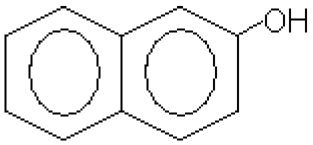


4-methyl phenol



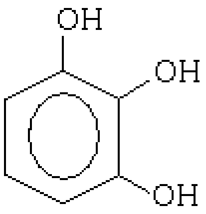
Naphth - 1 -ol

α -Naphthol



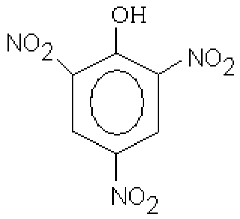
Naphth - 2 -ol

β -Naphthol



Benzene - 1,2,3-triol

Pyrogallol

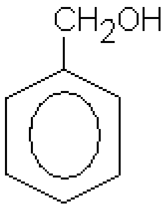


2,4,6 - Trinitrophenol

(Picric acid)

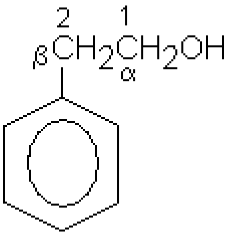
(b) Side chain substituted

In these compounds one or more H-atom of the side chain get substituted with _OH group. These compounds are called aromatic alcohol



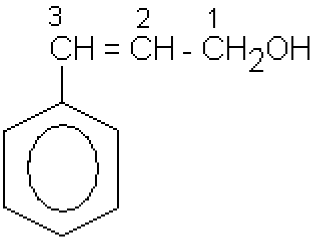
Phenyl methanol

(Benzyl alcohol)



2-Pheyl ethan -1 -ol

β – phenyl ethyl alcohol



3-Phenyl prop-2-en-ol