GENERAL CHEMISTRY

Is a branch of chemistry which deals with behaviour and characteristics of electrons.

This subtopic deals with electron occupying space in an atom. The electron occurs in the orbit/ shell at the region called orbital. The orbital is the region where there is a maximum probability of locating electron. At the same time this topic deals with electron of atom which occurs in a chemical compound. The general chemistry includes the following aspects or subtopics:-

- Atomic structure.
- Atomic spectrum/ H – spectrum.
- Wave mechanics.
- Chemical bonding.

1.0 ATOMIC STRUCTURE

Atomic structure deals with structure and component of an atom. The first scientist discovered that matter is made up of small particles called atoms. The term atom means indivisible particles. But later, different scientists put forward atomic models. These atomic models account for atomic structure. There are several atomic models which include the following:-

- Dalton’s atomic theory.
- Thompson’s atomic theory.
- Bohr’s atomic model.
- Rutherford atomic model.
- Wave particles duality nature of matter.
- Heisenberg uncertainity principle.

DALTON’S ATOMIC THEORY

Dalton’s atomic theory includes the following main points:-

i. Matter is made up of small indivisible particles called atoms.
ii. Atom is neither created nor destroyed.
iii. Atoms of the same elements are similar especially in mass.
iv. Atoms of different elements are different especially in mass.
v. Atoms of different elements when combine they do so in small ratio whole numbers.

RECENT MODIFICATION OF DALTON’S ATOMIC THEORY

Dalton’s atomic theory was modified because all points were not valid. This resulted into discover of modern atomic theory. The following include point of modern atomic theory:-

i. Matter is made up of small indivisible particles called atoms was not valid due to the existence of three particles in atom. Matter is made up of a small divisible particle called atoms.

Particle	Nature of change	symbol	mass	Position

Proton	+1	$_1^1P$	1.00	Nucleus
Neutron	0	$_0^1n$	1.00	Nucleus
Electron	-1	$_{-1}^0e$	1/1840	Shell

ii. Atom is neither created nor destroyed was not valid due to the existence of radioactivity therefore Atom can be created or destroyed by either nuclear fission or fusion.
iii. Atoms of the same elements are similar especially in mass was not valid due to the existence of isotopes. Atoms of the same elements have either same or different mass.

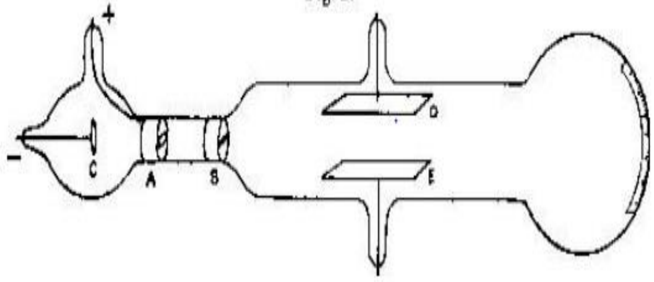
iv. Atoms of elements are different especially in mass was not valid. Atoms of different elements have either same or different mass.

v. Atoms of different elements when combine they do so in small ratio of whole number was not valid because different elements combine by using variable ratio of whole number.

THOMPSON's EXPERIMENT (DISCOVERY OF ELECTRONS)

Thompson's conducted an experiment to investigate if air conducts electricity. The following circuit was used during the experiment.

Fig. 2.



- The emission tube have electrode at each end which is connected to the external circuit. The emission tube is connected to the vacuum pump in order to maintain the low pressure in the emission tube.

The circuit is switched on which results into the following observation:-

- The bulb emitted light which indicate that the gas conduct electricity.

- There is glowing of emission tube or emission of light.

- There is fluorescence of emission tube.

- The stream of rays running from cathode to the anode. Through investigation of properties of cathode rays by using magnetic field, electric field and gold electroscope results into discover of electron. The cathode rays were the electrons.

EXPLANATION OF THOMPSON'S EXPERIMENT IN TERMS OF ATOMIC STRUCTURE

Ground state: Is lowest energetic state of an atom. Is a state when an electron filled in the lowest energy level before filling the highest energy level available. The electron filled in atom in order of increasing energy level. This state make atom to be stable.

Excited state: Is a state of an atom when electron filled in the highest energy level before filling lowest energy level available. If the electron excited jumps to the extent that the nuclear attractive force act upon it result pulling back of electrons. When return back to the ground state release all amount of energy which was absorbed inform of radiation.

RADIATION: This energy causes glowing of emission tube. When the radiation strikes the emission tube causes florescence of emission tube.

Convergent limit: Is a state of atom when an electron is removed completely from ground state to the infinite. The convergent limit occurs if atom gain high energy which result electrons to jump to the highest energy level where the nuclear attractive force cannot act up on it. This electron cannot return back to the ground state it result the atom left to positively charged. The convergent limit is a factor which causes some electrons to move from cathode to anode. These were stream of rays called cathode rays which later was electrons.

SIGNIFICANCE OF CONVERGENT LIMIT

These include the following:-

- It resulted into discover of the ionization energy. This ionization energy used in the inorganic section.

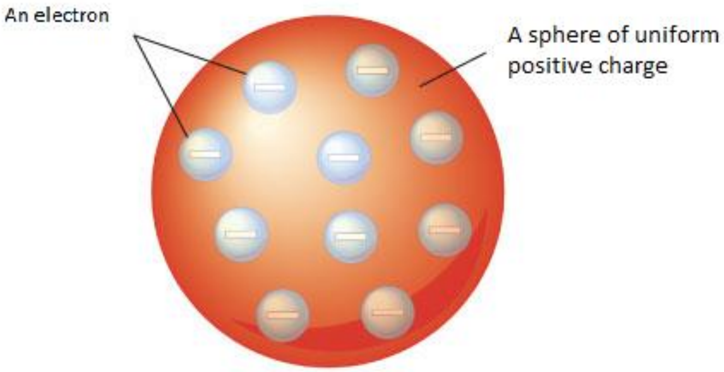
- It resulted into formation of ion particles. The ionic particle is more reactive when take part during chemical reaction.

- It resulted into production of rays. These rays are known as atomic spectrum.

THOMSON MODEL OF THE ATOM

After the discovery of electrons and protons, the next question was to know how these particles are arranged in an atom. The first simple model of the atom was proposed by J.J.Thomson in 1898.The **Thomson atomic model** is popularly known as the Thomson's **"plum-pudding"** model of the atom**.**

Thomson considered an atom to be a sphere (radius = 10^{-10} m or 10^{-8} cm) of uniform positive charge into which the negatively charged electrons were embedded. *This model is like plum-pudding dotted with raisins*



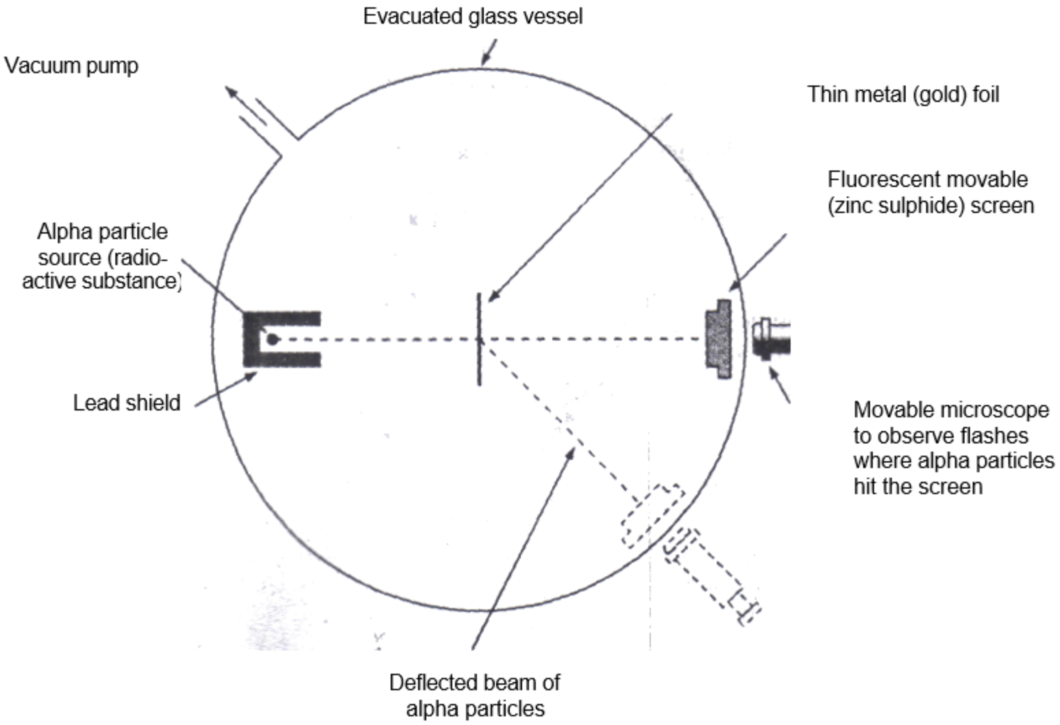
This model of an atom could not explain many experimental facts. So, it was abandoned.

RUTHERFORD'S SCATTERING EXPERIMENT

In 1911 Rutherford performed an experiment which is now known as Rutherford's scattering experiment. In this experiment, he bombarded a thin sheet (0.00006 cm thickness) of gold with alpha **α** particles. The **α**-particles were obtained from a radioactive substance. The -particles are doubly ionized helium atoms (He^{2}*).

The scattered **α** -particles produced tiny flashes on striking with the zinc sulphide screen. These tiny flashes were observed with a movable microscope. The experimental set up used in the famous **α**-scattering experiment is shown in figure below. The following observations were made from the scattering experiment.

Structure of atom

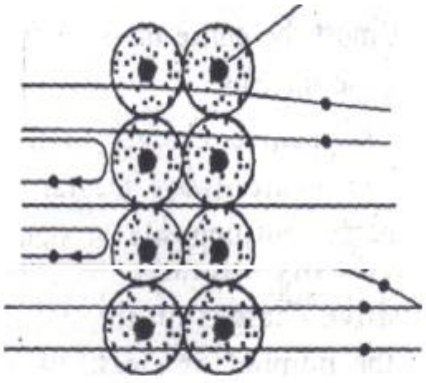


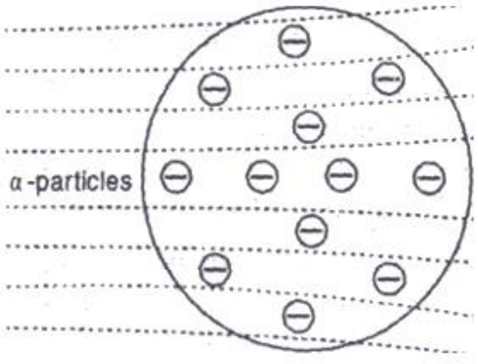
The **α** -scattering from metal foils. The -particles are produced by a radioactive source.Since lead absorbs **α** -particles a lead plate with a hole is used to obtain a beam of a particles.The **α** -particles scattered from the metal foil strike the fluorescent (zinc sulphide) screen and produce tiny flashes. A movable microscope is used to view the flashes.

i. Most of the a-particles passed through the metal foil without any change in their path *i.e. they* remained undeflected.

ii. Some of the **α** -particles deflected through small angles.

iii. Only a few of them (1 in 10,000) were actually deflected by as much as 90°, or even larger angles. One in 20,000 particles returned back suffering a deflection of 180°.





Explanation. The results of the scattering experiment could not be explained by the Thomson's atomic. Calculations showed that a charge spread over a sphere of radius 10^{-8} cm could deflect **α**

-particles only through small angles. The deflections of only**α** -particles through larger angels as observed would be possible If the positive charge in the atom is spread over a sphere of radius of about 10^{-13} cm thus, the **α**-particles scattering result could not be explained by Thomson's atomic model.

RUTHERFORD'S NUCLEAR MODEL OF THE ATOM

On the basis of **α**-particle scattering experiment, Rutherford put forwarded in 1912, his nuclei model of the atom. According to this assumptions.

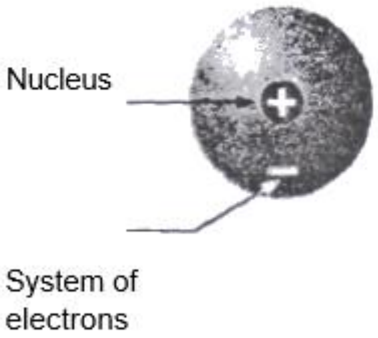
i. An atom consists of a positively charged nucleus surrounded by a system of electronics. Electrons are moving around the nucleus. The positive charge of the nucleus is due to the protons present in it.

ii. Electrons and the nucleus are held together by coulombic force of attraction,

iii. The effective volume of the nucleus is extremely small as compared to the effective volume of the atom. From the experiments, it was found that, Approximate radius of the nucleus of an atom 10^{-14}– 10^{-15} m (10^{-12} – 10^{-13} cm), Approximate radius of sphere of electrons (or the radius of an atom) 10^{-10} m (10^{-8} cm).Since, the volume varies as r^3, hence the volume occupied by the nucleus is about 10^{12} times the volume of the atom.

iv. Almost the entire mass of the atom is concentrated in the nucleus.

v. The positive charge on the nuclei of different elements are always integral multiples of the electron charge, but opposite in sign. Since, each atom is electrically neutral, hence in an atom, the number of positive charges on the nucleus of an atom is equal to the number of electrons in it. The Rutherford's model of an atom is shown in the figure below



Rutherford, in 1912, put forwarded an atomic model. According to this model an atom consists of positively charged nucleus which is surrounded by a system of electrons. The electrons and I nucleus are held together by electrostatic forces. Because of the electrostatic attraction between the nucleus and the electrons, the electrons should ultimately fall into the nucleus. But, it does not happen. In order to explain *why electrons not fall into the nucleus, Rutherford postulated that* *the electrons are not stationary, but are revolving about the nucleus in orbits.* But, this explanation did not solve the problem completely. The physicists had observed that a revolving electric charge must emit radiation and thus lose energy. Thus, *an electron revolving around a nucleus in an orbit should emit radiation and lose energy*

If so, the continuous loss of energy should slow down electrons. As a result, the electron will not be able to stand the attraction of the nucleus and gradually move towards the nucleus. The electron should, therefore, follow a spiral path and ultimately fall into the nucleus within 10^{-8}s. The atom should thus, collapse. But, it does not happen, as the atoms are stable. Thus, there must be something wrong in the Rutherford's nuclear model of the atom.

RUTHERFORD ATOMIC MODEL

(i) The atom consists of extreme denser region at center called nucleus which have positive charged particles.

(ii) The negative particles (electron(s) of atoms revolve around the nucleus in a path called orbit.

(iii) The large area of atom is empty space.

SHORT COMING OF RUTHERFORD ATOMIC MODEL.

Rutherford atomic model accounted that electron revolve around the nucleus in the path called orbit. This is an imagination because no any scientist proved occurrence but discovered that when charged particle revolve around the opposite charge reach a point when they collapse due to the attraction force occurs between the nuclear and electron(s) hence electron capture. But this proved the truth of Rutherford because no any atom discovered to collapse.

BOHR'S ATOMIC MODEL The electrons revolve around the nucleus in a path called orbits which have certain energy.

The electron when revolve in stationery state does not radiate energy.

The electrons emit or absorb energy when shift from one energy level to another.

The electronic motions are those which its angular momentum is integral multiple of where n = 1, 2, 3...

SHORT COMING OF BOHR'S ATOMIC MODEL

Bohr's accounted that electrons revolve in a single plane. But discovered that movement of electrons is not restricted in only on plane.

The Bohr's model did not explain spectral of multi-electrons atom but accounted only spectral line of uni-electron hydrogen atom.

The Bohr's model did not account for electrons which were found in a chemical bond.

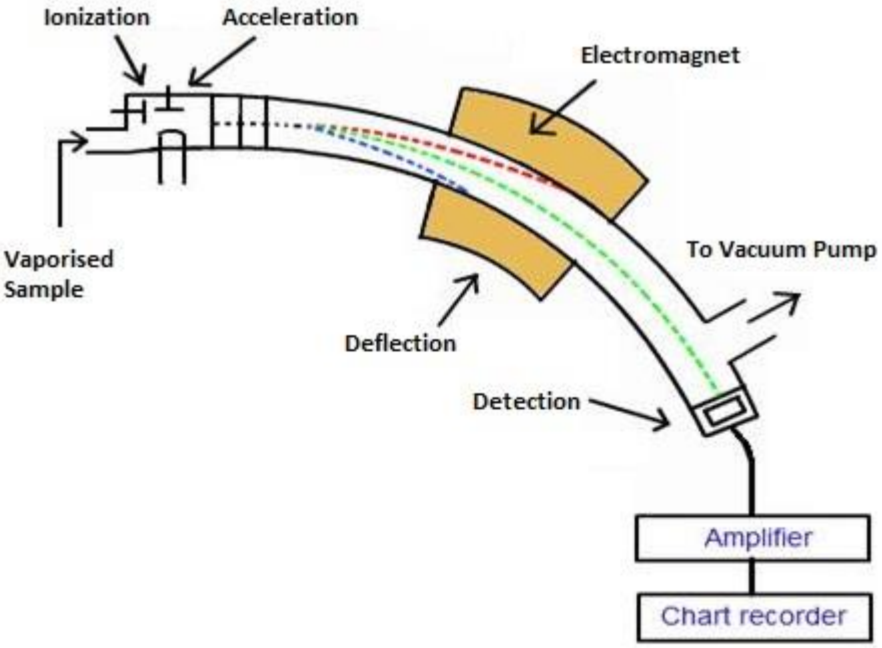
Bohr viewed an electron as being placed at a certain distance from the nucleus. However, it was proved by Weaver Heisenberg's Uncertainity Principle:–It is impossible at any movement to predict the exact position and velocity of an electron in an atom.

MASS SPECTROMETER

Is an instrument which is used to determine the relative atomic mass of an element.

Mass spectrometers have an ability to determine the relative molecular mass of a compound and formula of a compound. In a spectrographic plate.

Mass spectrograph is a plate of mass spectrometers which detect and record the relative atomic mass of an element. The spectrographic plate is a detector or recorder. The following is a diagram of mass spectrometer which has different part.



Vaporization. The instrument is evacuated in order to prevent the interference of air. The solid sample must be heated until it forms gaseous atoms and vaporized before it's introduced into the mass spectrometer.

Ionization. The vaporized sample of element is introduced in the ionization chamber. This region has electric filament which emits fast moving electrons. These electrons collide with atom of an element as a result the atom split which leave only nucleus of positive charge. The nucleus left is where mass of atom is concentrated.

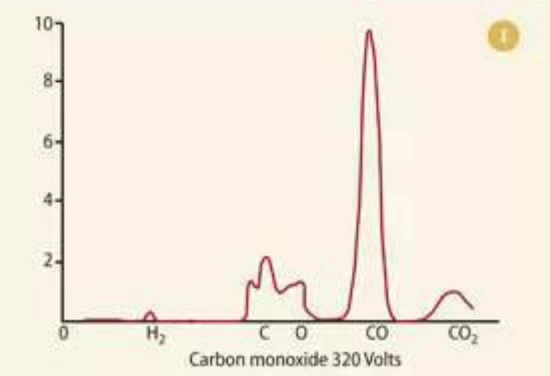
Acceleration. The ion particles formed in the ionization chamber are accelerated by two plate of negative charge toward the magnetic field. These two plates are connected to negative potential which accelerate ions as a beam of light toward the magnetic field.

Deflection. The beam of ions deflected in the magnetic field. The extent of deflection depends on the mass charge ratio m/e. The light particle deflected more than the heavy particles. The deflected ions strike on the detector. The ions at the same mass charge ratio strike on the same mass spot.

Detection. Once the ions strike the detector in the collector that converts the intensity of the ions into electric signals which is amplified by the amplifier into large electric current.

Recording. The current is used to operate a pen that moves on a paper tracing the peak of the isotope. The ion is recorded in terms of atomic mass and relative abundance. When they fall on the photographic plate they produce a mass spectrum consisting of a series of line at different point. The mass of the ions detected on the photographic plate. Relative abundance is the percentage of an isotopic atom in the element. The ions particles when strike the detector produce mass spectrum. The mass spectrum recorded as a peak.

The following include example of mass spectrum.



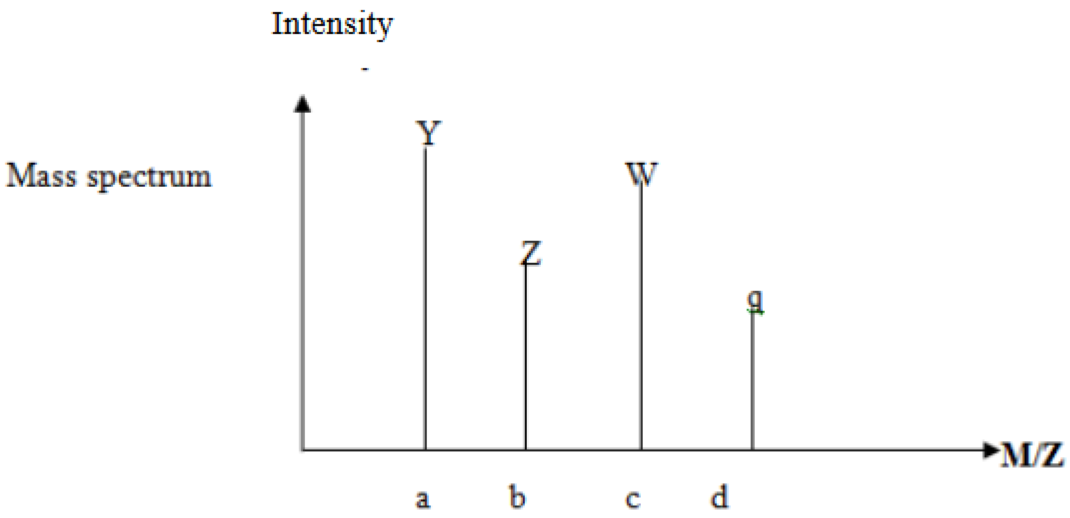
CALCULATION OF RELATIVE ATOMIC MASS

Relative atomic mass of an element is the average value of all the known isotope atomic weight relative to the proportional abundances. Relative atomic mass is more useful in chemistry than its simple atomic mass of element because simple atomic weight does not consider existence of isotopic forms of elements. The relative abundance of isotopic element is applied to determine relative atomic mass. Example isotopic element X contained Y% of ${}_z^aX$ and W% of ${}_z^bX$, the relative atomic mass of element X is determined as given below.

$$\text{RAM of X} = \left[\frac{y}{100}\ x\ a\right] + \left[\frac{w}{100}\ x\ b\right]$$

Since y + w = 100

The length of peaks of each isotopic atom applied to find the relative atomic mass. Each atom have peak due to the different mass charge ratio m/e.

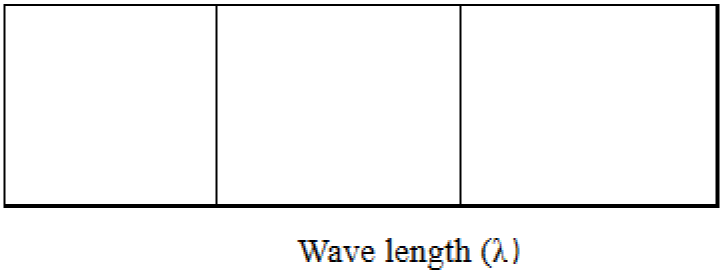


$$\text{RAM of X} = \frac{(Y \times a) + (Z \times b) + (W \times c) + (q \times d)}{(y+W+Z+q)}$$

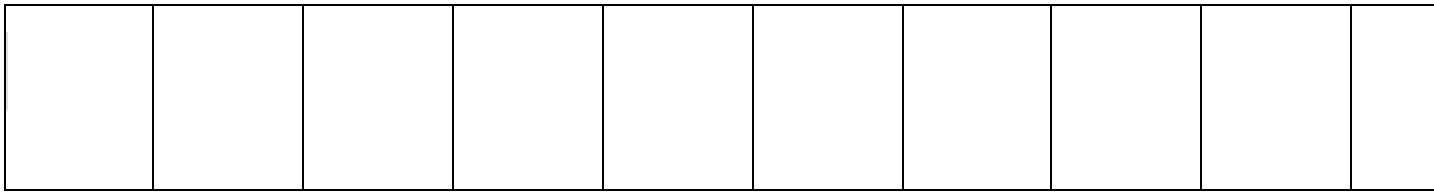
ATOMIC SPECTRUM

Definition: Are light waves which have definite line and colour because they have intermediate wave length which cannot be detected by a human eye. These spectrums have no harmful affect on human. Atomic spectrum produced once the atom gain energy which cause the electron to be excited and jump from lowest energy level. This results into an atom being unstable in order to maintain the stability these electrons return back to its group state which accompanied with release of energy inform of radiation. These radiation have wavelength which detected by a human eye of definite colour definite wave and definite line.

Continuous Spectrum: are spectrums which contain all possible frequency over wide range of energy. Continuous spectrums are colourless and have no definite line because they contain very short wave lengths which are not detected by an eye. The continuous spectrum recorded in a spectrographic plate as given below.

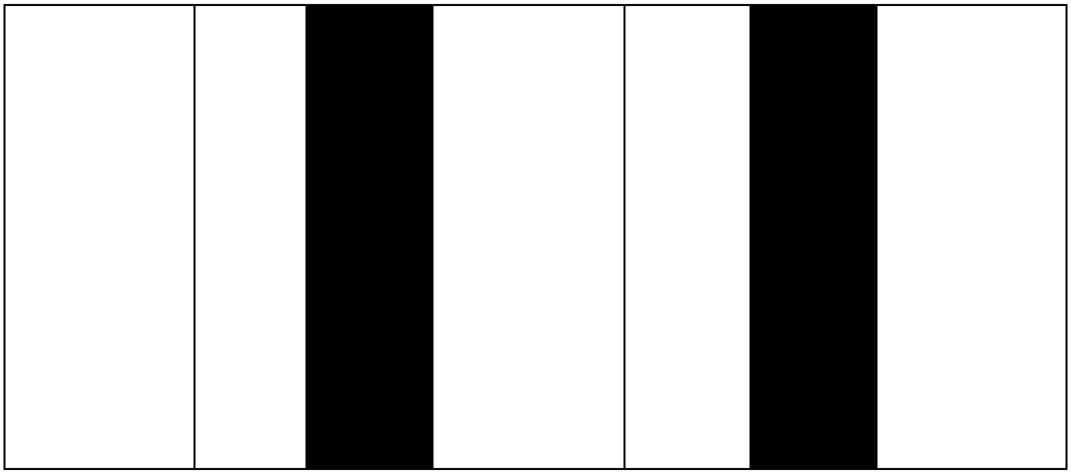


Line spectrum: is a spectrum which consists of scattered definite line. These spectrums have very long wave length. The spectrographic plate of line spectrum



Wave length (λ)

Band Spectrum: Band spectrum are spectrums which consists of a group of definite line in small bands. The spectrographic plate of band spectrum includes the following:



Wave length (λ)

BOHR-ATOMIC THEORY

(i) H - SPECTRUM

Definition:

Is a definite line and colour which resulted when electric discharge is passed through hydrogen gas in the emission tube under very low pressure. The H – spectrum recorded in the spectrographic plate. The following is a horizontal diagram of H-spectrum

UV	Violet					Infrared Red	Red	
X - ray								Radio electron

- ray								Television wave
UV – ray								
Invisible								

Note: wave length increases

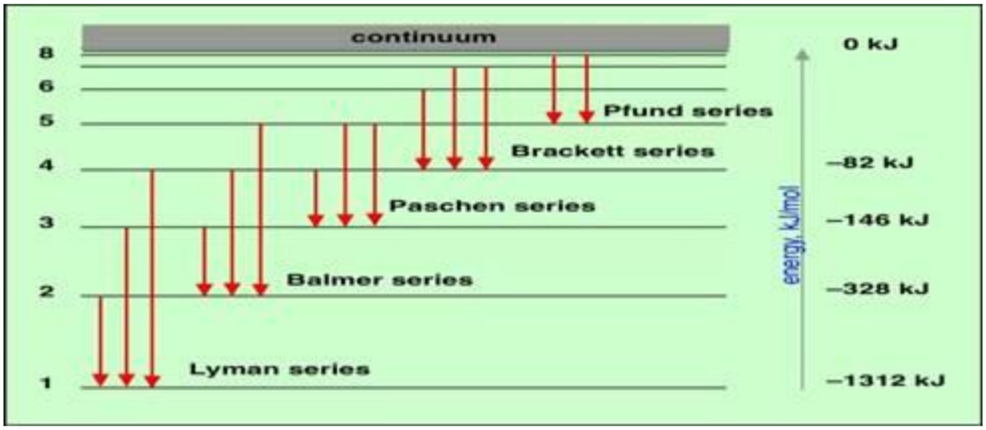
The explanation of horizontal diagram in terms of atomic structure:-

First band: is a colourless band or invisible band. These are spectrum produced by electrons which excited from the first shell. The electron from the first shell experience stronger nuclear attractive force which use high energy in order to jump toward highest energy level. When these electron returned back release high amount of energy which have shorter wave length. These wave lengths are not detected by a human eye. The radiations formed are continuous spectrum such as X – ray, sun rays etc.

Second band: is a visible band which has definite line and colour. These are line spectrum, produced by electron which excited from the second shell. The electron in the second shell need moderate energy in order to jump towards highest energy level when returned back release a normal energy which its wave length detected by a human eye.

Third band: Is invisible band. These spectrums are colourless and have no definite line.The electrons which produce these spectrum caused the scattered spectrum which appear as a colourless band. This is due to the lowest energy and highest wave length. The following include vertical diagram of H-spectrum.

The vertical diagram of Hydrogen Spectrum



Lyman series: is a series of spectrum which resulted by electron excited from the first shell (n =1). These series correspond to the invisible band or colourless band.
Balmer series: is a series of spectrum which resulted by the electron which excited from the second shell (n = 2) this corresponds with visible or violet band.
Paschen's series: is a series of spectrum which resulted with electron excited from the third shell (n = 3) etc.
Bracket series: is a series of spectrum which resulted with electron which excited from the forth shell (n = 4) etc.

p-fund series: is a series of spectrum which resulted with the electron which exited from the fifth shell (n=5).

PLANCK'S QUANTUM THEORY

Planck put forward the Planck's quantum theory. This theory has three main points which include the following;-

i. Any radiation should be association with energy.
ii. The energy is released inform of radiation, occur in small packets called quanta.
iii. The energy is directly proportion to the frequency.

$E \propto f$
$E = hf$……………………..(1)

Since h = Planck's constant
$h = 6.63 \times 10^{-34}$ JS
n= 1

Since $f = \frac{c}{\lambda}$

$E = \frac{hC}{\lambda}$ ………………….(2)

$C = 3.0 \times 10^{8}\ ms^{-1}$

REYDBERG EQUATION

Reydberg put forward a principle which applied to find wave length of spectrum. The wave length of H-spectrum determined is applied to find frequency and energy of the H- spectrum. The wave number is inversely proportional to the square of energy level differences (Δn^2).

$V \propto \frac{1}{\Delta n^2}$

$1/V = RH\ \Delta n^2$

$V = \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$ RH

Since V = $1/\lambda^{\lambda}$

$\frac{1}{\lambda} = RH\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$………………. (3)

Where λ= wave length

n_1 = lowest energy level

n_2 = highest energy level

RH = Reydberg constant RH is $1.09 \times 10^7 m^{-1}$

The value of n_1 and n_2 for H-spectrum can be obtained if given number of line and number of series. The value n_1 is equal number of series given. But the value n_2 is equal to the number of line plus the number of series. Example the value of n_1 and n_2 of third line of Balmer's series include the following:-

Number of line = Third line
Number of series = Balmer's series
n_1 = number of series = 2
n_2 = number of line + Number of series
= 3 + 2
n = 5

But: $\frac{1}{\lambda} = RH\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$= 1.09 \text{ X } 10^7 m^{-1}[1/2^2 - 1/5^2]$

$= 1.09 \text{ X } 10^7 m^{-1}[1/4 - 1/25]$

$= 1.09 \text{ X } 10^7 m^{-1}[(25-4)/100]$

$= 1.09 \text{ X } 10^7 m^{-1}[(21/100]$

$\therefore \lambda = 4.45 \times 10^{-7}$m of third line

$E = \frac{hc}{\lambda}$

$E = 6.3 \times 10^{-3}$ Js x $3.0 \times 10^8 ms^{-1}$

4.45×10^{-7}m

$E = 4.25 \times 10^{-19}$J

Also;

$$f = \frac{c}{\lambda}$$

$$f = \frac{3.0 \times 10^{8}}{4.45 \times 10^{-7}}$$

$f = 6.74 \times 10^{14} s^{-1}$

$f = 6.74 \times 10^{14}$ Hz

TRANSITION ENERGY

Is the energy which is required to shift electron from one shell to another. The energy required to shift electrons from one shell to another should be equal to the energy difference between those two shells. The energy difference between lowest energy level E_1 and highest energy level E_2 is obtained by using the following expression;-

E = E2 – E1……………… (1)

The trend of transition of electrons include the following;

$E = E_2 - E_1$ - Transition take place from $E_1 - E_2$ exactly.

$E > E_2 - E_1$ – Transition take place from E_1 toward above E_2

$E < E_2 - E_1$ – Transition take place from E1 and hang between E_1 and E_2

But if electrons gain enough energy which is equal to the ionization energy result the electron to jump completely from ground state to infinite. These electrons cannot return back instead leave atom ionized positively. The energy supplied to the atom results to be excited and electron move completely from the ground state to the infinite. The energy supplied to the electrons is used as ionization energy and as kinetic energy. The ionization energy of electrons is equal to the amount of energy associated by electron in the shell or quantum number where it belongs.

The following expression is used to find the energy associated by electrons or energy of that shell.

$1/\lambda = RH$

Let $n_1 = n$

$n_2 = \infty$

$$\frac{1}{\lambda} = RH\left[\frac{1}{n^2} - \frac{1}{\infty^2}\right]$$

$1/\lambda = RH\left[\frac{1}{n^2}\right]$ since $1/\infty = 0$

$1/\lambda = \frac{RH}{n^2}$ ……………………………..(i)

$E = hc/\lambda$

$E/hc = 1/\lambda$ ………………………..(ii)

Substitute (ii) into (i)

$$\frac{E}{hc} = \frac{RH}{n^2}$$

$$E = \frac{RHhc}{n^2}$$

$$E = \frac{13.6eV}{n^2}$$

Since R, h and C are constant

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

$1MeV = 10^{6}eV$

$1MeV = 1.6 \times 10^{-13}J$

But discovered that the energy increase from the nucleus atom toward the high energy level. The energy increases from first shell toward seventh shell. From seventh shell the energy is zero or the energy at infinite is zero. Then the energy from infinite which is zero towards the lowest shell decreases and results to be negative value of energy

n_∞ = 0.00ev

n_7 = -0.15ev

n_6 = -0.21ev

n_5 = -0.54ev

n_4 = -0.84ev

n_3 = -1.50ev

n_2 = -3.40ev

n_1 = -13.60ev

$E = E_2 - E_1$

= E – En

= 0 – En

$= 0 - \frac{13.6eV}{n^2}$

$E = \frac{-13.6eV}{n^2}$

The negative value occurs because the energy of infinite is zero. Since energy increase from nuclear towards highest energy level result the energy of each shell be negative value. This formula is used to determine energy of electron at each shell.

Example

i. Find the first ionization energy of potassium.
ii. Find the wavelength, frequency and energy of third line of Balmer's series (RH = 1.09 x 107m^{-1})
iii.If the wavelength of the first number of Balmer's series is 6563Å. Calculate Reydberg constant and wavelength of the first member of the Lyman series.
iv.Find energy associated with electrons in the quantum number 2.

Solution:

i. E = I.E
k = 2:8:8:1

$E = \frac{-13.6eV}{n^2}$

$E = \frac{-13.6 x 1.6 x 10^{-19} J}{4^2}$

$= -1.36 \text{ x } 10^{-19}$J

$E = E_2 - E_1$

$E = 0 - -1.36 \text{ x } 10^{-19}$ J

∴ $E = 1.39 \text{ x } 10^{-19}$J

ii. $n_1 = 2$
$n_2 = 3 + 1$

$$\frac{1}{\lambda} = RH\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{\lambda} = 1.097\ x\ 10^{7\left[\frac{1}{2^2}-\frac{1}{4^2}\right]}$$

$$\frac{1}{\lambda} = 1.097\ x\ 10^{7}\left[\frac{1}{4}-\frac{1}{16}\right]$$

$$\frac{1}{\lambda} = 1.097\ x\left[\frac{4-1}{16}\right]x\ 10^{7}$$

$$\frac{1}{\lambda} = 1.097\ x\ 10^{7\left[\frac{3}{16}\right]}$$

$$\lambda = \frac{16}{1.097\ x\ 10^{7}\ x\ 3}$$

∴ $\lambda = 4.86\ x\ 10^{-7}m$

iii. $\lambda = 6563A^{\circ}$

From $\frac{1}{\lambda} = RH = \left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$

$$\frac{1}{6563} = RH\left[\frac{1}{2^2}-\frac{1}{3^2}\right]$$

$$\frac{1}{6563} = RH\left[\frac{1}{4}-\frac{1}{9}\right]$$

$$\frac{1}{6563} = RH\left[\frac{9-4}{36}\right]$$

$$\frac{1}{6563} = RH\left[\frac{5}{36}\right]$$

$RH = \frac{36\ x\ 1}{5\ x\ 6563}$

$RH = 1.09\ x\ 10^{-3}\ A^{-1}$
$RH = 1.9\ x\ 10^{-3}\ x\ 1010m^{-1}$
$RH = 1.09\ x\ 10^{7}m^{-1}$

iv. E =?

n = 2

$$E = \frac{-13.6eV}{n^2}$$

$$E = \frac{-13.6 \, x \, 1.6 \, x \, 10^{-19}}{2^2} \text{ J}$$

E= -5.44 x 10^{-19}J

Example

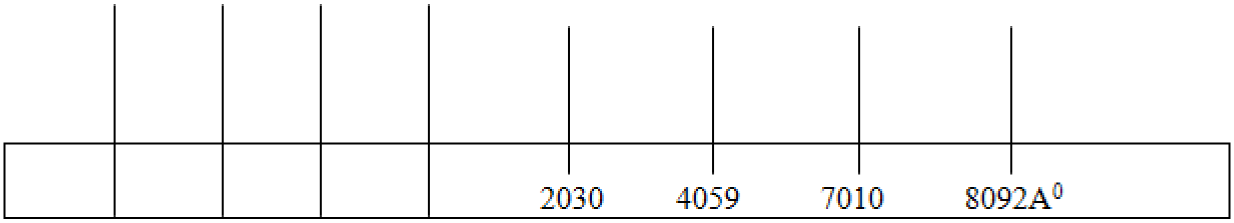
The U.V light has a wave length 2950 Å. Calculate its frequency energy 1A° = 10^{-10}M

Given $E4 \ = \ -1.36 \ x \ 19^{-19}$ J

$E2 \ = \ -5.44 \ x \ 10^{-19}$ J

If the electron dropped from E_4 to E_2: Find the frequency and wave length energy release

Given line spectrum



Wave length

i. Which line has highest frequency and energy?
ii. Which line has lowest frequency and energy?
iii. Find the energy and frequency of each line in (i) and (ii) above?

	E_5
	E_4
	E_3
e^0	E_2
	E_1

State either or not the transition of electrons would occur if energy supplied is

i. Greater than $E_4 - E_2$
ii. Equal to $E_4 - E_2$
iii. Less than $E_4 - E_2$
iv. Greater than $E_3 - E_2$ but less than $E_4 - E_2$
v. Smaller than $E_4 - E_2$

Solution:

a) $\lambda = 2950A^{\circ}$

f = c
λ

$$f = \frac{3.0x10^{8}\, m/s}{2950 \text{ x } 10^{-10}\text{ m}}$$

$f = 1.02x10^{-2}\ S^{-1}$

E= hf
$E = 6.3 \text{ x } 10^{-34}\text{Js x } 1.02 \text{ x } 10^{-2}\ S^{-1}$
$E = 6.426 \text{ x } 10^{-36}J$

b) $E_4 = -1.36 \text{ x } 10^{-19}J$
$E_2 = -15.44 \text{ x } 10^{-19}J$
$E = E_2 - E_1$
$E = E_4 - E_2$
$E = (-1.36 \text{ x } 10^{-19}) - (-5.44 \text{ x } 10^{-19})$
$E = 4.08 \text{ x } 10^{-1}$

But:

E = hf

$$f = \frac{\Delta E}{h}$$

$$f = \frac{4.08x\ 10^{-19}\, J}{6.63 \text{ x } 10^{-34}\text{ Js}}$$

$f = 6.15 \text{ x } 10^{14}\ S^{-1}$

Hence:

$$F = \frac{c}{\lambda}$$

$\lambda = \frac{c}{f}$

$\lambda = \frac{3.0 \times 10^{8} m/s}{6.15 \times 10^{14} s^{-1}}$

$\lambda = 4.88 \times 10^{-7}$m

C. i) A line of wave length 2030A°

ii) A line of wave length 8092 A°

iii) f =?

E =?

Line of 2030A°

Since $f = \frac{c}{\lambda}$

$f = \frac{3.0 \times 10^{8} m/s}{2030 \times 10^{-10} m}$

$f = 1.48 \times 10^{15} S^{-1}$

E = hf

$E = 6.3 \times 10^{-34} Js \times 1.48 \times 10^{15}$

$\therefore$ $E = 9.32 \times 10^{-19}$ J

D) Solution

i) Greater than $E_4 - E_2$ result transition of electron from E_1 and above E_4

ii) Equal $E_4 - E_2$ transition take place from E_2 to E_4

iii) Smaller than $E_4 - E_2$ result transition of electrons from E_2 but cannot reach instead hang between E_2 and E_4

iv) Greater than $E_3 - E_2$ but smaller than $E_4 - E_2$ result transition of electron from E_2 and above E_3 but cannot reach E_4

THE QUANTUM THEORY

WAVE PARTICLE DUALITY NATURE OF MATTER

States that: "Matter has particle nature as well as wave nature". This means that matter have dual properties or two properties such as particle nature and wave nature. The wave particle duality nature of matter was put forward by De Broglie scientist. De Broglie's derived an expression which applied to find the De Broglie's wave length.

De Broglie's wave length is in terms of mass and momentum.

Hence from Einstein equation;

$E = mc^2$ …………………….(i)

From Planck's equation

$E = \frac{hc}{\lambda}$ ……………… (ii)

Compare equation (i) and (ii)

$mc^2 = \frac{hc}{\lambda}$

$$\boxed{\lambda = \frac{h}{mc}}$$

$$\boxed{\lambda = \frac{h}{p}}$$

De Broglie's wave length in terms of energy

From:

$\lambda = \frac{h}{mc}$ multiply by 1/c in both side

$\lambda \frac{1}{c} = \frac{h}{mc}$ [1/c]

$\frac{\lambda}{c} = \frac{h}{mc^2}$

$$\boxed{\frac{\lambda}{C} = \frac{h}{E}}$$

Since $E = mc^2$

Example

Alpha particles emitted from radium have energy of 4.4MeV. What is the de-Broglie's wave length?

The mass of moving particles is 9.01×10^{-19}g. What is the de-Broglie's wave length?

The momentum of particles is 2.0×10^{-10}gm/s. What is the de-Broglie's wave length?

Given that:

$h = 6.63 \times 10^{-34}$ JS

$C = 3.0 \times 10^{8}$m/s

Solution

a. E = 4.4MeV

λ =?

De Broglie's

$$\frac{\lambda}{3 \text{ x } 10^8 \text{ m/s}} = \frac{6.63 \ x \ 10^{-34}}{4.4\text{MeV x } 10^6 \text{ eV x } 1.6 \text{ x } 10^{-19}\text{J}}$$

$$\lambda = \frac{6.63 \ x \ 10^{-34} \ JS \ x \ 3 \ x \ 10^{8} \ ms^{-1}}{4.4 \text{ x } 106 \text{ x } 1.6 \text{ x } 10-19\text{J}}$$

$\lambda = 4.52 \times 10^{-13}$m

b. Solution

m = 9.01 x 10-^{19}g

λ =?

De Broglie's

$$\lambda = \frac{h}{mc}$$

$\lambda = \frac{6.63 \times 10{-}34 JS}{9.01 \times 10^{-19} \times 3.0 \times 10^{8} ms^{-1}}$

$\lambda = 2.33 \times 10^{-24}m$

c. $P = 2.0 \times 10^{-10}gms$

λ =? De Broglie's

$\lambda = \frac{h}{P}$

$\lambda = \frac{6.63 \times 10^{-34} JS}{2.0 \times 10^{-10} gms^{-1}}$

$\lambda = 3.315 \times 10^{-24}Jg^{-1}m^{-1}s^{-1}$

HEISENBERG UNCERTAINITY PRINCIPLE

Heisenberg uncertainity principle state that, "It is impossible to determine position and momentum of electrons simultaneously with greater accuracy." It is impossible to determined position and momentum of electrons because;-

(i)The size of electron is very small and as such radiations of high energy extremely small wavelength are required to detect it.

(ii) Impact of these high energy photons changes both the direction and speed of the electron. Thus; the very act of measurement disturbs the position of electron. The uncertainties in the determination of these two quantities vary inversely. If one is determined fairly accurately, the other must be corresponding less accurate. The distance of electron: Is a position of electron from the nucleus and momentum of electrons is product of mass of electrons and velocity of the electron, Heisenberg put forward an expression which is used to determine uncertainity position and momentum of electrons.

Where: P – uncertainity momentum

X – Uncertainity position

$P \propto \frac{1}{\Delta X}$

$P = x \left[\frac{h}{4\pi}\right] \frac{1}{\Delta X}$

$P = \frac{h}{4\pi \Delta X}$ …………………. (1)

Since $\frac{h}{4\pi}$ = proportionality constant

Also

mc $= \frac{h}{4\pi\Delta X}$ …………………. (2)

Example

The uncertainity in the momentum of particles is 3.3 x 10^{-16}gms^{-1}. Find accuracy with which its position can be determined

$$X = \frac{h}{4\pi\Delta P}$$

$$X = \frac{6.63 \, x \, 10^{-34} J}{4 \text{ x } 3.14 \text{ x } 3.3 \text{ x } 10^{-6} \text{gms}^{-1}}$$

$= 1.59 \text{ x } 10^{-29}$m

WAVE MECHANICS

Wave mechanics deal with electron occupying space. The electrons revolve the nucleus through orbit and occur in the orbital.

Orbital:Is a region within an atomic sublevel that can be occupied by maximum two electrons that have opposite spin. Any orbital can accommodate a maximum of two electrons.

The energy level of atoms is a specific region around the nucleus electrons can occupy in atoms. A shell is defined as a complete group of orbital possessing the quantum number. The

electrons arranged in the atom starting from orbit from nucleus toward the orbit of highest energy level. The following include position of locating electrons in the atom.

i. Principal quantum number (n)

The atom shells called principal quantum number (main energy level). The electrons filled in atom in order of increasing the energy from the nucleus. Each shell have specific constant number or electrons obtained taking

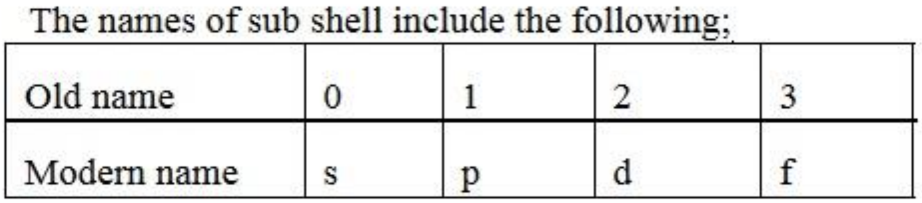
$e = 2n^2$

Old name	1	2	3	4
New name	K	L	M	N

(ii)Subsidiary quantum number (L)

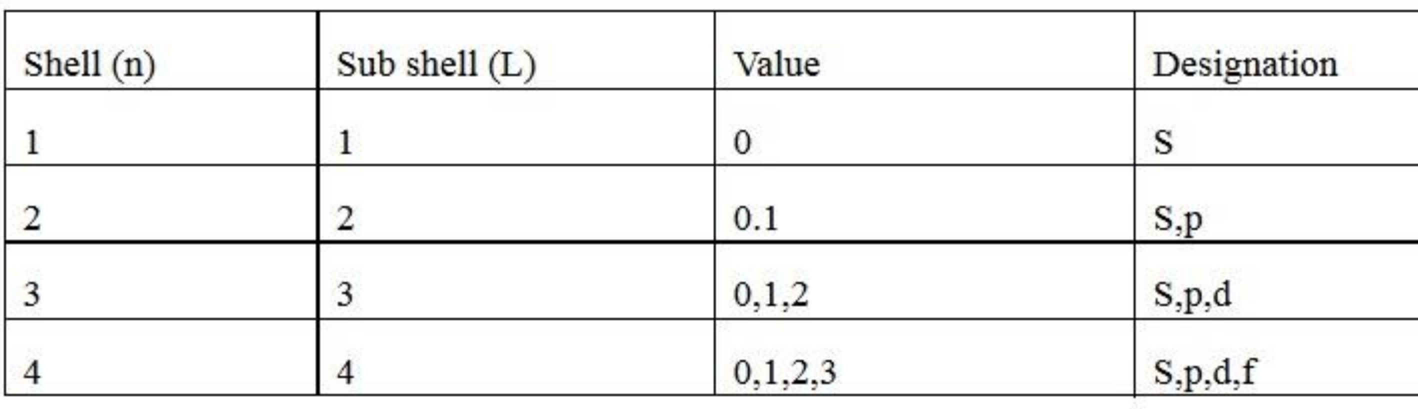
Subsidiary quantum number is a sub energy level. The sub energy level known as azimuthal quantum number, sub shell or sub energy level. The shell divides to form sub shell. The total number of sub shells in each shell is equal to the number of shell from the nucleus. This describes shapes of orbitals (sub-energy level).Values of subsidiary quantum number start from 0-------n-1

The names of sub shell include the following;



The names of sub shell include the following;

Old name	0	1	2	3
Modern name	s	p	d	f



Shell (n)	Sub shell (L)	Value	Designation
1	1	0	S
2	2	0.1	S,p
3	3	0,1,2	S,p,d
4	4	0,1,2,3	S,p,d,f

iii. Magnetic quantum number (m)

This is a quantum number which describes the orbital of each sub shell. This sub shell divided and form orbital. Each sub shells have specific number of orbital.

Sub shell	Orbital	value
s	1	☐
p	3	☐☐☐
d	5	☐☐☐☐☐
f	7	☐☐☐☐☐☐☐

(iv) Spin Quantum number (s)

These quantum numbers describe the spinning of electrons in the orbital. Maximum number of electrons in the orbital in only two which spines in opposite direction. Since each orbital has two maximum electrons result the sub shell to have constant total number of electrons which accommodated in all shells S^2, p^6, d^{10}, f^{14}, g^{18}, h^{22} and i^{26}. In order to write electrons of element consider the knowledge of all four quantum numbers.

$$S= +\frac{1}{2}\ OR -\frac{1}{2}\ OR\ \left\{ \boxed{\uparrow\downarrow}\quad \boxed{\uparrow\ \ } \right\}$$

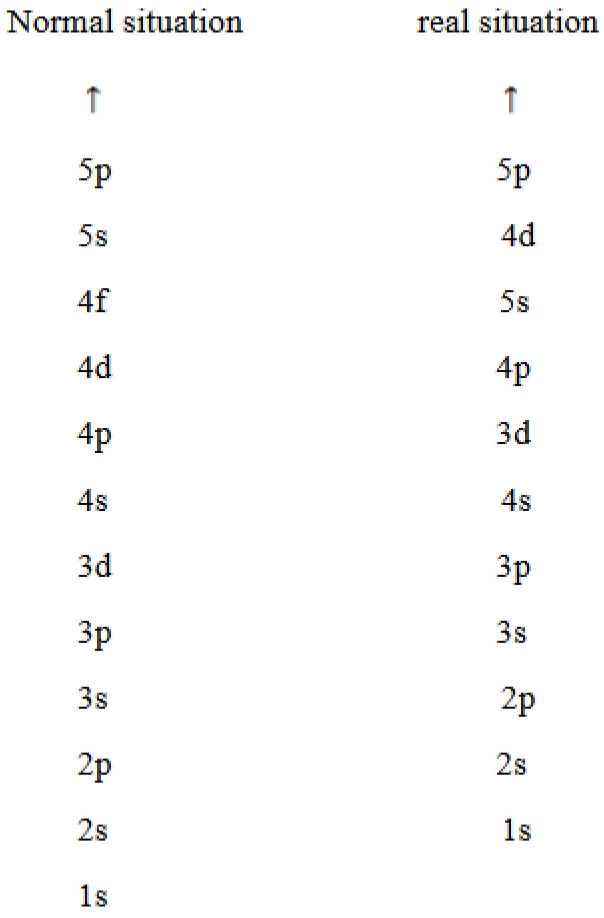
The following series of sub shell used to write the electrons structure.

1s						
2s	2p					
3s	3p	3d				
4s	4p	4d	4f			
5s	5p	5d	5f	5g		
6s	6p	6d	6f	6g	6h	
7s	7p	7d	7f	7g	7h	7i

1s	2s 2p	3s 3p	4s 3d 4p	5s 4d 5p 6s	4f 5d 6p 7s 5f 6d 7p 5g 6f 7d 6g 7f
	$_{2}He$	$_{10}Ne$	$_{18}Ar$	$_{36}Kr$	$_{54}Xe$ $_{86}Rn$

This arrangement used to write the electronic configuration.

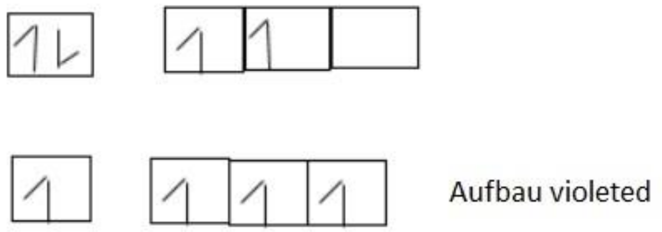
Arrangement used to write the electronic configuration has some irregularities or abnormality. This irregularity occurs because there is overlapping of orbital. The orbital of low energy jump toward highest energy level and orbital of high energy drop down towards lowest energy level. Example 4s arranged first before 3d orbital.



Normal situation	real situation
↑	↑
5p	5p
5s	4d
4f	5s
4d	4p
4p	3d
4s	4s
3d	3p
3p	3s
3s	2p
2p	2s
2s	1s
1s	

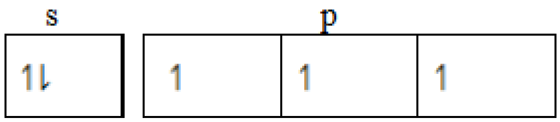
RULES WHICH GOVERN ARRANGEMENT OF ELECTRONS IN ORBITALS

1. Aufbau’s principle – State that "in the ground state of orbital the lowest energy is filled by electrons before filling orbital of the highest energy".
This means that electron filled in order of increasing energy level. The orbital of lowest energy when is full of electrons then the electron filled on the next orbital of highest energy level. Consider the following arrangement

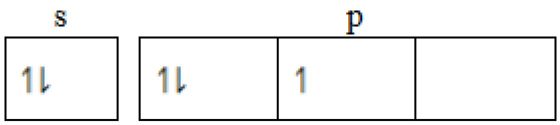


2. Hund’s rule of maximum multiplicity

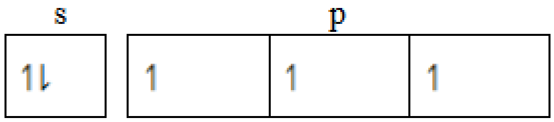
State that, “The electrons pair in the orbital of the same sub shell is allowed if all orbital of the same energy are occupied by electrons of maximum multiplicity. This means that the degenerate orbital are not allowed to pair up unless each orbital is singly occupied. The incoming pairing is done in an opposite spin. Consider a case with 5 electrons in valency shell.



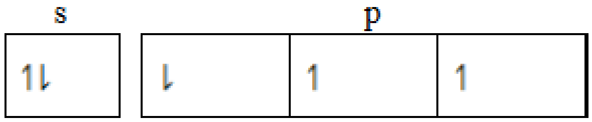
Correct w.r.t. Hundi’s rule



Incorrect w.r.t. Hundi’s rule

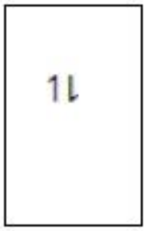


Incorrect w.r.t. Aufbau rule



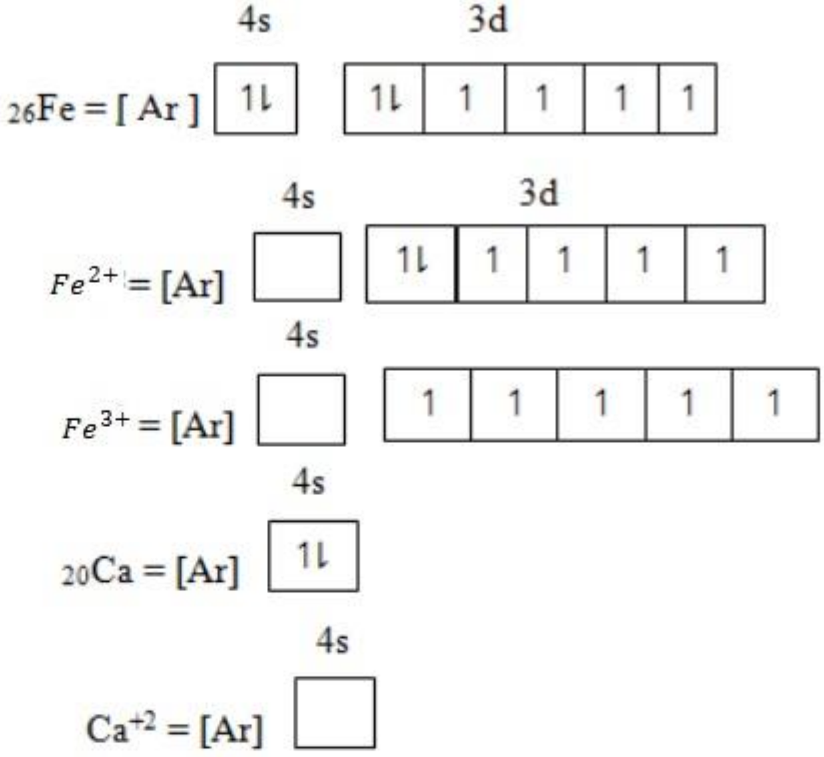
Incorrect w.r.t. Hund’s rule

3. Paul’s exclusive principle
States that, “Two electrons in an atom can never have exactly similar set of all quantum numbers.” This means that the maximum number of electrons which is occupied in the orbital is only two. Two electrons may occupy the same orbital only on condition that they have their spin in the opposite direction. Two electrons may have three quantum numbers the same; n, l and ml but the fourth, ms must be different.

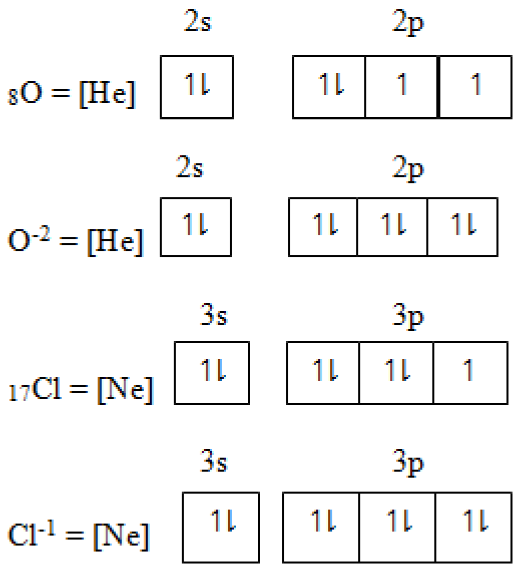


Sometimes the electrons structure or electronic diagram of ions is written according to what kind of ions given.

There are two kinds of ions which include the following;-
Cation or metallic ion is formed through losing of electrons. The electrons which are lost occur in the orbital out the of the noble gas structure. The electron removed starting from orbital of low energy toward the orbital of highest energy.



Anion or non-metallic ion – is formed by gaining electrons. Electrons which gain is added in the orbital having unpaired electrons starting from orbital of lowest energy to the orbital of highest energy level



QUANTUM NUMBER

Is a number which describe the characteristics of electrons or is a number which is used to characterize electrons as they occupy orbitals in different energy levels. The quantum number is a number which describe main energy level, orientation of orbitals and spinning of electrons.

There are four type of quantum number which includes the following:-

1.Principle quantum number (n): Is a number which specifies the location and the energy of electron. This is a number which describe the main energy level of electrons. The principle quantum number called shell orbit, main energy level and stationary state. The principle quantum number have specific name from the nucleus. K, L, M, N etc.

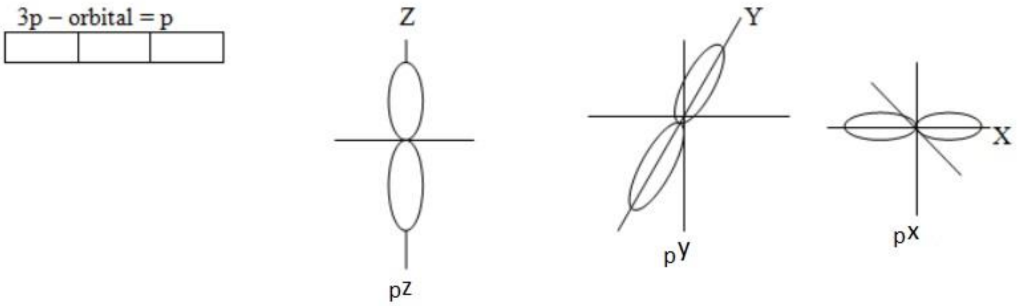
2. Subsidiary principle quantum number (L): Is a number which specifies the shape of orbitals. Subsidiary principle quantum number is a sub energy level. The sub energy level is known as azimuthal number sub shell or sub energy level. The shell is divided to form sub shell. The total number of sub shells in each shell is equal to the number of shells from the nucleus. The names of sub shells include the following; s, p, d, f, g, h, i. The value of sub energy level i.e. 0, 1, 2, …L = n - 1.The value of L must be smaller that n because L = n – 1

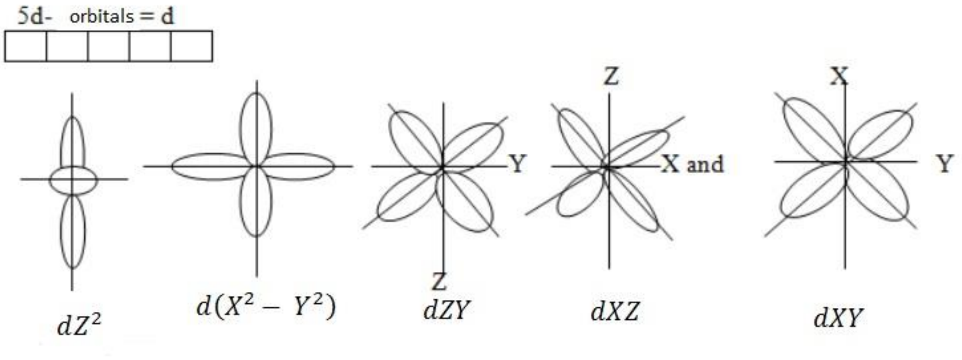
n	Value of L	Sub shell
1	0	1s
2	0, 1	2s2p
3	0, 1, 2	3sp3d
4	0, 1, 2, 3	4s4p4d4f

5	0, 1, 2, 3, 4	5s5p5d5f5f

3. Magnetic quantum number: Is a number which specifies the number of orbital present in a given value of subsidiary quantum number. This is a quantum number which describes the orientation of orbital. The magnetic quantum number is a number of orbital. When the sub shell divides form orbital, these orbitals are called Magnetic quantum number.

1s – Orbital S = X





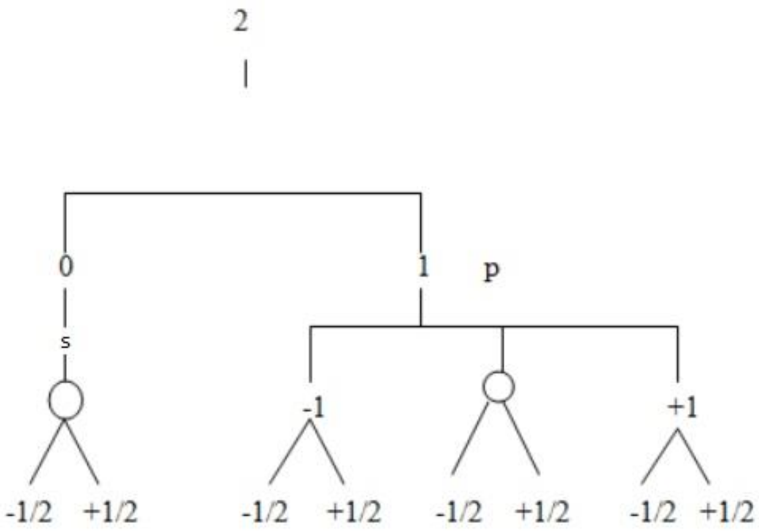
4. Spin quantum number (s) – This is a quantum number which describes the direction in which the electrons spin. There are two maximum electrons, these electrons are moving in opposite direction. They revolve clockwise + ½ and another revolve anti – clock wise – ½

APPLICATION OF QUANTUM NUMBER

Quantum number is applied to find the number of sub shell (L), number of orbital (m) and total number of electrons (s) of the given quantum number (n). There are two methods which are applied to find total sub shells, orbital and electrons.

Find total number of electrons in the principle quantum number 2.

(By using tree diagram)



Total shells = 2 (s, p)
Orbitals = 4 (0, 0, +1, -1)
Electrons = 8

Also: by using tabular form

n = 2				
L	0 s	1 p		
ml	0	-1	0	+1
ms	$-\frac{1}{2},+\frac{1}{2}$	$-\frac{1}{2},+\frac{1}{2}$	$-\frac{1}{2},+\frac{1}{2}$	$-\frac{1}{2},+\frac{1}{2}$

(b) Find the total number of electrons in the principle quantum number 3
Soln: (by using tree diagram)

n = 3										
l	0 s	1 p			2 d					
m	0	-1	0	+1	-2	-1	0	+1	+
s	$-\frac{1}{2},+\frac{1}{2}$	$-\frac{1}{2},+\frac{1}{2}$	$-\frac{1}{2},+\frac{1}{2}$	$-\frac{1}{2},+\frac{1}{2}$	$-\frac{1}{2},+\frac{1}{2}$	$-\frac{1}{2},+\frac{1}{2}$	$-\frac{1}{2},+\frac{1}{2}$	$-\frac{1}{2},+\frac{1}{2}$	−

Example
(a) The modern theory of electron behavior is based on two assumptions. State them

(b) Define the following terms
- i. Orbital.
- ii. Energy levels of atoms.
- iii A shell.
- iv. Quantum.

Solution:

(a) The modern theory of electron behavior is based on two assumptions.

(i) An electron has a dual nature i.e. it behaves both as a particle and wave.

(ii) It is practically impossible to determine simultaneously both the position and momentum of an electron with any degree of precision.

(b) (i) An Orbital is a region within an atomic sublevel that can be occupied by a maximum of two electrons that have opposite spin. There are s,p,d, and f orbitals is a volume of space surrounding the nucleus within which there is a more than 95% chances of finding electrons. Any orbital can accommodate a maximum of two electrons.

(ii) Energy level of atoms in specific region around the nucleus that electrons can occupy in atoms.

(iii) A shell is defined as a complete group of orbital possessing the same quantum number.

(iv) Quantum is the smallest countable, discrete packet or increment of radiant energy that can be absorbed or emitted.

Example

Explain the meaning of the following terms:

(a) Quantization of energy and radiation.
(b) Wave particles duality of matter.
(c) Quantum number.

Solution

(a)Light and other forms of electromagnetic radiations are not emitted continuously but in discrete "packets" called photons. Energy of an electromagnetic radiation is also not emitted continuously but in "packets" called quanta. A photon of radiation carries a quantum of energy. Energy and radiation are quantized in that electron shall fall from one energy level to another and not anywhere else in between.

(b) According to de Broglie, every sub – atomic particles has both wave and particle properties. Photons of light and other electromagnetic radiations, are regarded and wavelengths. They are regarded as waves because they have specific frequencies. Although electrons have extremely small mass, they have both velocity and momentum as particles.

(c) Quantum numbers are used to characterize electrons as they occupy orbitals in different energy levels. Each electron is characterized by four quantum numbers:-

The principal quantum number, n, which specifies the location and energy of the electron.
The azimuthal, subsidiary or angular momentum quantum number, l, which specifies the shapes of the orbitals.
The magnetic quantum number, m, which specifies the orbital orientation in space.
The spin quantum number, s, which specifies the direction in which the electron is spinning. These quantum numbers completely describe the stationary stage of the electron.

Example

(a) Distinguish between the following terms:-

(i) An orbital and orbit.
(ii) S – Orbital and P – orbital.
(iii) A quantum of light and quantization of energy.
(iv) Quantum shell and quantum number.

(b) Explain briefly the meaning of the following quantum numbers:-

(i) n
(ii) l
(iii) m
(iv) ms

(c) In a tabular form specify all the four quantum number for each electron in an atom whose n value is 2. Given all the orbitals are full of electrons.

(d) Given the value of the quantum numbers n, l and m for the electron with the highest energy in sodium atom in the ground state.

(e) Write down all the quantum number of all the electrons in the ground state of nitrogen atom.

(f) Give the values of all the four quantum number for 2p electrons in Nitrogen.

(g) Briefly explain why the following quantum numbers are not allowed.

i) $n = 1, l = 1, m = 0$
ii) $n = 1, l = 0, m = 2$
iii) $n = 4, l = 3, m = 4$
iv) $n = 0, l = -1, m = 1$
v) $n = 2, l = -1, m = 1$

Solution

(a) (i) An orbit is a well define circular path in which electrons were assumed to revolve around the nucleus. Whereas an orbital is a three dimensional region of space around the nucleus whereby there is high probability of finding an electron.

(ii) S–Orbital is spherical and hence non directional whereas p-orbital is dumbbell in shape and it is directional.

(iii) A quantum of light is a photon of radiation emitted when an electron jumps from one energy level to another whereas quantization of energy means energy emitted or absorbed following electron transition between one energy level and another is not continuous rather it is in form of small packet called quanta.

(iv) A quantum shell is the energy level of an electron in a given atom whereas quantum number refers to specifies way of defining an electron in a given atom whereas quantum number refers to specified way of defining an electron in a given orbital of an atom using n, l, m and ms values.

(b) (i) n – represents the principle quantum number;
It specifies the location and the energy of an electron.
It is a measure of the volume of the electrons cloud.
As the value of n increases or becomes less negative it means the energy levels of the electrons get further away from the nucleus n can have only integers 1, 2, 3, 4 to infinite represented by K,L,M,N etc. Also called azimuthal quantum number or subsidiary quantum number, specifies the shapes of the orbital, when n = 1 there's only l s orbital where n = 2, there's 2s and 2p orbital, thus for a given value of n, l, are all from 0, 1, 2…up to l = n - 1. Thus when n = 4 values are 0, 1, 2 and 3. Which represents 4s, 4p, 4d and 4, â„“ sub–levels m → Magnetic quantum number specifies the number of orbital present in a given value of â„“.

It specifies the orientating i.e. the direction of the orbital to magnetic field in which it's placed.

It accounts for the splitting of the spectral lines observed when an atom emitting radiation is placed in a magnetic field, ms – Refers to spin quantum number.

(i) It indicates the direction in which the electron spins.

(ii) Only two values are allowed for an electrons i.e. electrons may spin clockwise, shown as +1/2 or ↑ may spin anticlockwise as shown as ½ or ↑

(c)

Principle (n)	Azimuthal	Magnetic quantum	Spins ms
n = 1	â„“ = 0	m = 0	$^{+1}/_{2}$, $^{-1}/_{2}$
n = 2	â„“ = 0	m = 0	$^{+1}/_{2}$, $^{-1}/_{2}$
	â„“ = 1	m = -1	$^{+1}/_{2}$, $^{-1}/_{2}$
		m = 0	$^{+1}/_{2}$, $^{-1}/_{2}$
		m = 1	$^{+1}/_{2}$, $^{-1}/_{2}$
			Total of 10 electrons

(d) When n = 3 in Na atom that electron is found in s – orbital thus â„“ = 0 and also ml = 0

(e) $1s^2$ electrons:
(1st) n = 1, l = 0, m = 0, s = $+^{1}/_{2}$ (2nd) n = 1, l = 0, m = 0, s = $^{-1}/_{2}$

Electrons:
1st n = 1, l = 0, m = 0, s = $^{+1}/_2$ (2nd) n = 1, l = 0, m = 0, s = $^{-1}/_2$
2 Px; n = 2, l = 1, m = $^{+}1$, s = $^{+}1/2$ 2Py; n = 2, l = $^{-}1$, m = $^{-}1$, s = $^{+}1/2$
2Pz; n = 2, l = 1, m = 0, s = $^{+}1/2$

(f) 2P electrons, there's
2Px; n = 2, l = +1, m = +1, s = +1/2 2Py: n = 2 , l= $^{-}1$, m = $^{-}1$, s = $^{+}1/2$
2Pz: n = 2 l = 1 m = 0, s = +1/2

(g) (i) l value must be smaller than n value since l = n-1
(ii) When l = 0 value of m is only 0
(iii) For l= 3, m can range from $^{-}3$ to $^{+}3$. Thus m=$^{+}4$ is not allowed
(iv) n value cannot be equal to zero.
(v) l value cannot be a negative number.

Example

(a) briefly explain the meaning of the following quantum numbers:-

(i) ml

(ii) n
(iii) l
(iv) ms

(b) If n = 2, tabulate the values of 1, ml and ms.

(c) Give the possible values of 1 and m, for an electron with the principal quantum number, n= 3

(d) Briefly explain why an electron cannot have the quantum number n = 2, l = 2 and ml = 2

Solution

(a) (i) ml – Magnetic quantum number with values from -l to +l. These are numbers showing the number of sub – level in each energy level.

– Describes orientation

(ii) n – Principal (shell) Quantum number value of 1, 2, 3 etc theses are numbers used to represent the main energy level in which an electrons is found.

(iii) l – Azimuthal or subsidiary or Angular or orbital Quantum number. They specify the shape of orbitals.

(iv) ms – Magnetic spin Quantum number with values $^{+}1/2$ and $^{-}1/2$ shows the spinning of electrons in orbitals (clockwise and anticlockwise direction).

(a) For n = 2, the scheme below illustrates the value of 1, ml and ms.
l=0, 1
ml=-1, 0, +1, 0
ms= ±1/2, ±1/2, ±1/2, ±1/2
Therefore the total number of electrons = 8

(b) If n = 3, possible values of 1 and m are;
l = 0, 1 and 2
m = 0 for l = 0
m = $^{-}1$, 0 and $^{+}1$ for l = 1
m = $^{-}2$, $^{-}1$, 0, $^{+}1$ and 2 for l = 2
Note that: l=n-1

(c) An electrons cannot have quantum numbers, n = 2, l = 2 and m = 2. This is because when n = 2, l can be 0 and 1; then ml can be 0, $^{-}1$, 0, $^{+}1$ different values which can occupy in orbitals (i.e. they have n, l and m values the same but they must spin in opposite directions and hence have different ms values).

RULES FOR FILLING ELECTRONS IN THE ORBITALS OF AN ATOM

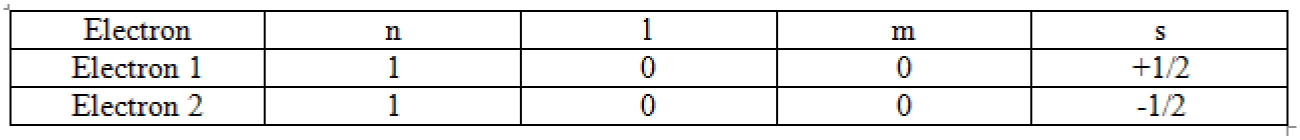
The orbitals of an atom can be filled with electrons by applying the following rules.

i)Aufbau Principle

This is also known as the building up principle. According to this principle "The electrons in an atom are so arranged that they occupy orbitals in the order of their increasing energy."
Thus, the orbital with the lowest energy will be filled first, then the next higher in energy, and so on. Since, the energy of an orbital in the absence of any magnetic field depends upon the principal quantum number *(n)* and the azimuthal quantum number (l), hence the order of filling orbitals with electrons may be obtained from the following generalizations.
a) The orbitals for which *n + I* is the lowest is filled first.
b) When two orbitals have the same values of n+l, the orbital having the lower value of *n* is filled first.
The order of filling of various orbitals with electrons obtained by this rule is given below:
1s, 2s. 2p, 3s, 3p, 4s, *3d*, *4p*, 5s, *4d*, *5p*, 6s, *4f,5d*, *6p*, *7s*, *5f…*
To remember this sequence may be a difficult task. Given a long side is a simple way of working out this order. In this method a series of arrows running from upper right to the lower left gives the order of orbitals with increasing energy.

ii) Pauli’s Exclusion principle

In 1925 Wolfgang Pauli discovered what is known as the exclusion principle. This principle is very useful in constructing the electronic configuration of atoms. According to this principle “No two electrons in an atom can have the same values for all the four quantum numbers”.
For example in 1s orbital of helium atom there are two electrons. According to the concept of quantum number and Pauli’s rule, their quantum numbers are:



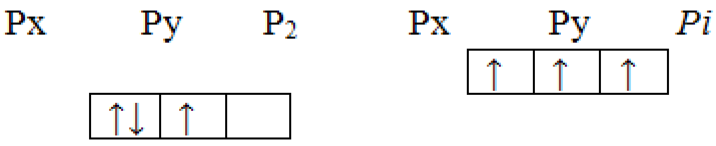
Electron	n	l	m	s
Electron 1	1	0	0	+1/2
Electron 2	1	0	0	-1/2

The + and - sign before *j* refers to the clockwise and anticlockwise spins of the electrons.
Thus, the two electrons having the same values of *n, I* and *m* could have different values *of s, i.e.,* their spins are in the opposite directions. This leads to a very significant observation that
"Each orbital can accommodate at the maximum two electrons with opposite spins."

Applications of the Pauli's exclusion principles
The Pauli's exclusion principle leads to the following conclusions:
(a) An orbital cannot have more than two electrons.
(b) In any main energy level (shell), the maximum number of electrons is twice the in number of orbitals, or is equal to $2n^2$, where *n* is the principal quantum number.

iii) Hund's Rule of Maximum Multiplicity

The rules discussed above do not give any idea for filling electrons into the orbitals having equal energies (such states are called *degenerate states).* For example, three p-orbitals, i.e. px, py and *pz,* have equal energy. How should electrons be filled into these orbitals? Let us take an example in which three electrons are to be filled into three p-orbitals. The three electrons can be filled into three *p* orbitals in two different ways as shown below.



I (wrong) II (right)

Now, which of the two is correct? The answer to this question is given by Hund's rule, Hund's rule states that, "When more than one orbitals of equal energies are available, then the electron*,] first occupy these orbitals separately with parallel spins. The pairing of electrons will | only after all the orbitals of a given sub-level are singly occupied."

According to the Hund's rule, the correct way of filling three electrons in three *p* orbitals that in which each orbital is singly occupied, (arrangement II above).
Hund's rule is also known as the *Hund's rule of maximum multiplicity.*

Explanation
Two electrons with parallel spins, tend to be as far apart as possible to minimize the electrostatic repulsion. Therefore, the electrons prefer to occupy the orbitals singly
as far as possible. When all the orbitals get singly occupied, then the incoming electron has two choices either to pair up with the other electron or to go to the next higher orbital.

When vacant orbital of suitable energy is not available, then the incoming electron will have no choice except to pair up with another
electron.

Example

(a) State the;
  - (i) Heisenberg uncertainty principle.
  - (ii) Hund's rule.
  - (iii) Paul's Principle.
  - (iv) Aufbau's Principle.

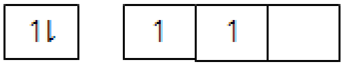
(b) Brief explain why the following sets of quantum number are NOT allowed in hydrogen atom:
  - (i) n = 1, l = 1, ml = 0
  - (ii) n = 1, 1 = 0, ml = 2
  - (iii) n = 4,1 = 3, ml = 4
  - (iv) n = 0, 1 = 0, ml = 0 and
  - (v) n = 2, 1 = $^{-}$1, ml = 1

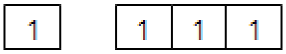
(c) How many orbitals are there in each of the following sublevel?
  - (i) 1s
  - (ii) 2p
  - (iii) 3d
  - (iv) 4f

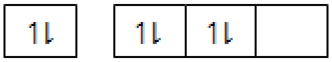
(d) How many sublevels are there in each of the following shells?
  - (i) K

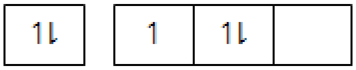
(ii) N
(iii) L

(e) Which of the following electronic configuration is correct for 14p in its ground state?

(i) [Ne]


(ii) [Ne]


(iii) [Ne]


(iv) [Ne]


State the principle violated in each case

Solution

(a) (i) The Heisenberg's uncertainly principle states that; "it is impossible to measure simultaneously the exact position and exact velocity (momentum) of an electron." Any attempt to measure one quality will distract the measurements of the other quantity

(ii) Hund's rule states that, "electron pairing is not allowed until all orbitals of the particular energy sub – level are occupied by at least one electron."

(iii) Paul's Exclusion Principle, "states that no two electrons may have all the four quantum number the same." Two electrons may have three quantum numbers of the same; the paired electrons are always in opposite direction at the same time.
(E.g. $+\frac{1}{2}$ and $-\frac{1}{2}$).

(iv)Aufbau Principle states that, "In electrons configuration, electrons are filled in order of increasing energy levels." Thus the lowest energy available must be filled up first. The orbital energy increase in the following order; is 2s, 2p, 3s, 4p, 5p etc.

(b) (i) n = 1, 1 = 1, ml = 0 this is not allowed because l must be smaller than n, in the case l = 1 which is not allowed.
(ii) n = 1, 1 = 0, ml = 2. This is not allowed because 1 = 0 and ml = 0
(iii) n = 4, 1 = 3, ml = 2. This is not allowed because for 1 = 3 can range from $^-3$, $^+3$, thus, $^+4$ is not allowed.
(iv) n = 0, l = 0, ml = 0; this is not allowed because n cannot be zero.
(v) n = 2, l = -1, ml = 1. This is not allowed because l cannot be a negative number and n can never be = 0

(c) (i) 1 s sub energy level has one – orbital (which is 1 s – orbital).

(ii) 2 p sub energy has three p – orbital (which is 1 s – orbital).

(iii) 3 d sub energy level has five d – orbital [which are 3 d (x^2 – y^2), $3dz^2$ 3dxy, 3 and 3dyz].

(iv) 4 f sub energy level has seven f – orbital [which are 4xy, 4fyz, 4fz, 4f(x^2 – y^2), 4f(x^2-z^2) and 4f (y^2 – z^2)].

(d) (i) K has one sub level (which is l s^2).

(ii) N has four sub levels (which are $4s^2$, $4p^6$, $4d^{10}$ and $4f^{14}$).

(iii) L has two sub levels (which are 2s2 and 2p6).

(e) Is the correct electronic configuration of 15p

This is correct since it obeys principle governing electron in an atom distribution

(i) [(Ne)]

(ii) [(Ne)] aufbau (building up) principle is violated as it states that electrons available as the case here.

(iii) [(Ne)]

(iv) [(Ne)] Hund's Rule of maximum that multiplicity is violated as it states electrons occupy orbital as singly as possible

Example

(a) State the rules used in filling electrons in various orbitals of an atom.

(b) By using 3 different ways for each of the following atoms write their electron configuration

(i) C

(ii) N

(iii) Ag

(c)Write the electronic configuration of Na^+ and F^- then show the other element whose electronic configuration resembles these ions. Show that electronic configurations of Cu and Cr are unusually written. Give reasons.

Solution

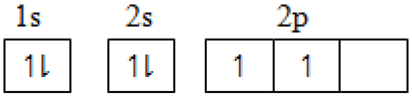
(a)(i)Paul's exclusion principle states that; "no two electrons may have all the four quantum number the same i.e. electrons may occupy the same orbital only on conditions that they have their spins in the opposite direction."

(ii) Hund's rule of maximum multiplicity states that, "when more than one orbital with equal energies are available, electrons tend occupy those orbital separately first with parallel spins and separately first with parallel spin and pairing of electrons will start only after all the orbitals of a given sub level are singly occupied."

(iii) Aufbau principle states that, "Electrons in an atom are so arranged that they occupy the orbitals in the order of their increasing energy."

(b) (i) C Atomic number 6

Using Box method:

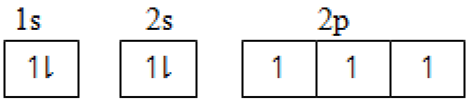


$1s^2\ 2s^2\ 2p^2$

Using noble gas structure;
[He] $2p^2$

(ii) N atomic number 7

Using box method

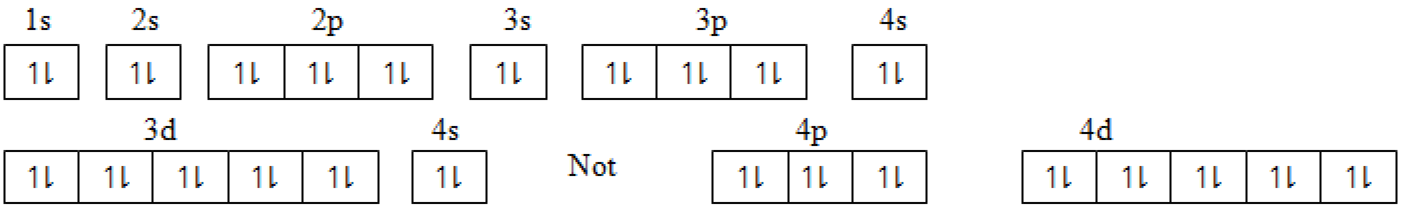


Using sub levels only;
$1s^2\ 2s^2\ 2p^3$

Using noble gas structure;
[He] $2p^3$

(iii) Ag atomic number 47

Using box method;



Note: 4d is filled first to maintain stability of full filled d – orbital before 5s is filled.

Using sub levels only;
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 4d^{10}\ 5s^1$

Using noble gas structure;
[Kr] $4d^{10}\ 5s^1$

(c)

(i) Na^+ number of electrons also 10

$1s^2\ 2s^2\ 2p^6$ resembles Ne

(ii) F – number of electrons also 10

$1s^2\ 2s^2\ 2p^6$ resembling Ne

(d) Cu Atomic number 29
e.g. [Ar] $4s^1\ 3d^{10}$

Cr Atomic number 24
e.g. [Ar] $4s^1\ 3d^5$ full filled and half filled orbitals are very stable electronic structures. The stability gained is the cause of 4s electrons to be unpaired and make 3d orbitals either full filled or half filled.

Note that: In writing the electronic configuration the atoms or orbitals of the same value are usually written together irrespective of their relation energy levels.
E.g. Cu $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$ not $1s^2\ 2s^2\ 2p^6\ 3s^2\ 2p^6\ 4s^1\ 3d^{10}$. To save time and space noble gases are often utilized e.g. sodium [Ne] $3s^1$ and Iron [Ar] $3d^6\ 4s^2$

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Definition:-chemical bond is the chemical force /force of attraction which keeps the atoms in any molecule together.

Types of the chemical bond

i) Ionic/Electrovalent bond
ii) Covalent bond
iii) Coordinate bond
iv) Polar covalent bond
v) Non-polar covalent bond
vi) Hydrogen-bonding

i) IONIC/ ELECTROVALENT BOND.

An ionic or electrovalent bond is formed by complete transfer of one or more electrons from the atom of the metal to that of a non-metal.

Note: - As a result of electron transfer the following changes occur in the reacting atom:-

(a) Both the atoms acquire stable noble gas configurations.

(b) The atoms that loses its electrons becomes positively charged ion called cation, the atom which gain this electrons becomes negatively charged ions called anion.

(c) The two oppositely charged ions .i.e. the cation and the anion are then held together by the coulombic force of attraction to form an ionic bond .

Note:- During the formation of ionic bond, a certain amount of energy is released.

e.g $Na + Cl \rightarrow Na^+cl^-$

This ionic bond may be defined as the coulombic force of attraction which holds the oppositely charged ions together.

ELECTROVALENCY

The number of electrons lost or gained by an atom of any element is termed as electrovalency. The element which gives up the electron(s) to form positive charge or ions are said to have positive valency. While the element(s) which accepts electrons to form negative ions are said to exhibit negatively valency.

Note:- Variable electrovalency of iron exist as Fe^{2+} and Fe^{3+} in ferrous sulphate and ferric sulphate .when a compound is formed by the transfer of electrons, the element that loses electron(s) is said to be oxidized and the element that gains electrons is said to be reduced. Oxidation is a process which involves loss of electrons where as reduction is the process which involves gaining of electrons.

PROPERTIES OF IONIC/ELECTROVALENT BOND
An ionic/Electrovalent bond has the following properties:-

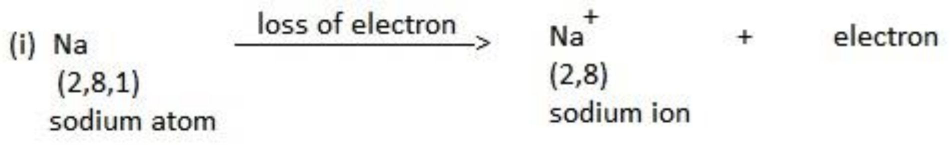
(i) An ionic bond is formed due to the coulombic attraction between the positively and negatively charged ions.

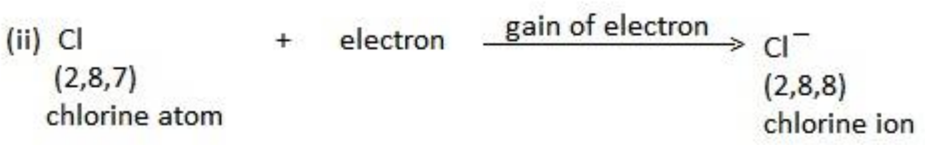
(ii) An ionic bond is non-directional, the strength of interaction between two ions depend upon distance but not the directional.

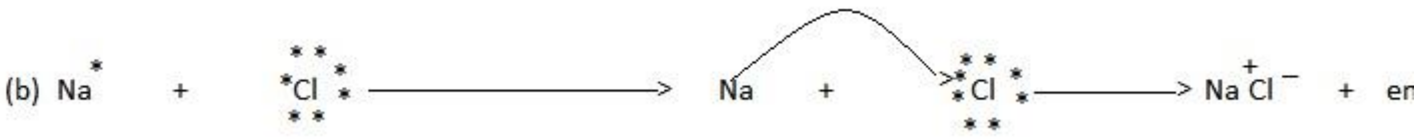
(iii) An ionic bond gets broken when the substance is dissolved in polar solvent such as water or when the substance is melted.

Typical examples of ionic bond:-

(a) $Na + Cl \rightarrow NaCl$







FACTORS INFLUENCING THE FORMATION OF IONIC BOND

The main steps involved in the formation of an electrovalent/ ionic bond are:-

(i) Removal of electrons from one atom, in this stage energy equal to the ionization energy is absorbed.

(ii) Gaining of electrons by the other atoms .In this step energy equal to the electrons affinity is released.

(iii) Combination of cation and anions. These ions are held together by coulombic force of attraction. In this step, energy equal to the lattice energy is released.

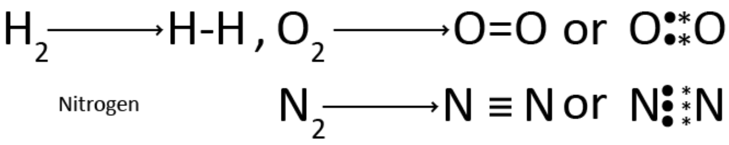
(II) COVALENT BOND

A covalent bond is formed between two atoms (similar and dissimilar) by a mutual sharing of electrons .the shared pairs of electrons are counted towards the stability of both the participating atoms.

DEFINITION: - A covalent bond is defined as the force of attraction arising due to mutual sharing of electrons between the two atoms.
When the two atoms combine by mutual sharing of electrons, then each of the atoms acquire stable configuration of the nearest noble gas.

COVALENCY

Is the number of electrons which an atom contributes towards mutual sharing during the formation of a chemical bond.
Example of the Covalency: - Covalency of hydrogen (H_2)



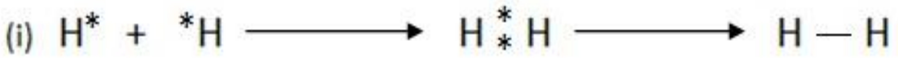
CHARACTERISTICS OF COVALENT BOND

(i) Mode of formation, covalent bond are formed due to mutual sharing of one or more pairs of electrons.

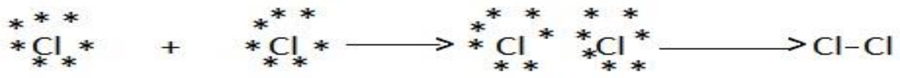
(ii) Directional character , covalent bonds are directional in nature this is because the shared electrons remains localized in a definite space between the nuclei of the two atoms.This gives a directional character to the covalent bond.

SINGLE COVALENT BOND

A covalent bond formed by mutual sharing of one pair of electrons. A single covalent bond is represented by a small line (-) between the two atoms.
E.g



(ii)



MULTIPLE COVALENT BONDS

The covalent bonds developed due to mutual sharing of more than one pairs of electrons are termed as multiple covalent bond.

The multiple covalent bonds are:-

(i) Double covalent bond
(ii) Triple covalent bond

Double covalent bond is the bond formed between two atoms due to the sharing of two electrons pairs. Its simply called Double bond

E.g. $O_2 \rightarrow O = O$

$CO \rightarrow C = O$ etc.

Triple covalent bond is the bond formed due to the sharing of three electron pairs

E.g $N_2 \rightarrow N \equiv N$,

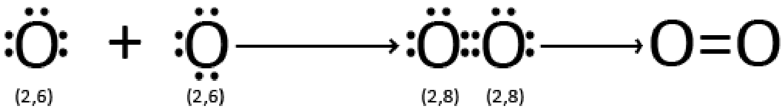
Acetylene $H - C \equiv C - H$.

(I) FORMATION OF MOLECULES HAVING DOUBLE BOND.

(i) Formation of oxygen (O_2) molecule:-

Each oxygen atom has six electrons in its outer most shell. Thus it requires two more electrons to achieve the nearest noble gas configuration.

E.g



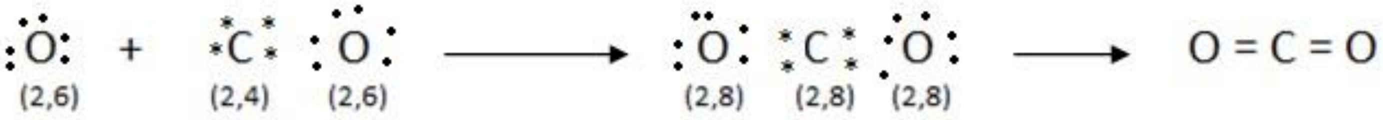
(ii) Formation of carbon dioxide(CO_2) gas

The electronic configuration of carbon and oxygen are :-

C	$1s^2\ 2s^2 2p^2$	2,4
O	$1s^2\ 2s^2 2p^4$	2,6

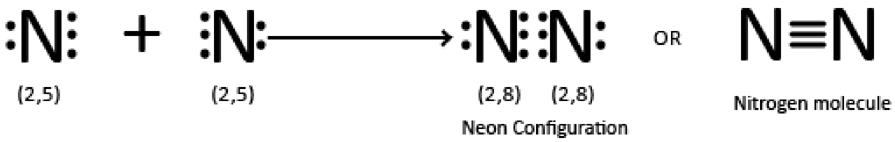
Thus each carbon atom requires four ,and each oxygen atom requires two more electrons to acquire noble gas configuration.This is achieved as follows

e.g



(iii) Formation of molecules having triple bond :-

(a) Formation of nitrogen (N_2) molecule.



COMPARISON BETWEEN SINGLE,DOUBLE AND TRIPLE COVALENT BONDS

Triple bond length < Double bond length < Single bond length.

Since a shorter bond means greater bond strength hence the energy required to separate the bonded atoms(called bond energy) follows the order

Triple bond > Double bond > Single bond

FACTORS FAVOURING THE FORMATION OF COVALENT BOND

The following are the factors that favour the formation of a covalent bond:-

(i) High ionization enthalpy (energy).

The element having higher ionisation enthalpy (energy) cannot lose electrons easily.

(ii) Nearly equal electron gain enthalpy or electron Affinity.

The atoms of the two elements which have equal or nearly equal electron gain enthalpies or electrons affinities tend to complete their outer shells by mutual sharing of electrons.

(iii) Nearly equal electronegativity.

Equal or nearly equal electronegativity of the two combining elements does not permit the transfer of electron(s) from one atom to another.

(iv) High nuclear charge and small atomic size.

High nuclear charge, and smaller atomic size of the combining elements favour covalent bond formation, because the transfer of electrons in such case will not be possible.

COORDINATE COVALENT BOND

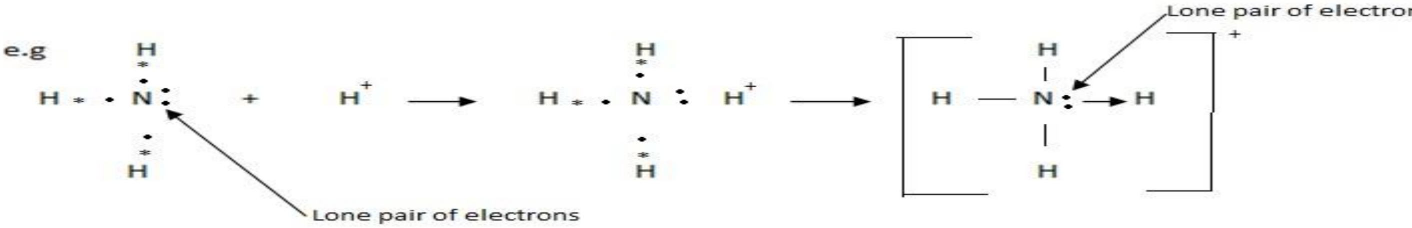
Coordinate bond is formed when the shared electron pair is provided by one of the combining atoms.The atom which provides the electron pair is termed as the donor atom ,while the other atoms which accept is termed as the acceptor atom

The bond formed when one sided sharing of electrons take place is called a coordinate or Dative bond. A coordinate bond is presented by an arrow (→) pointing towards the acceptor atom.

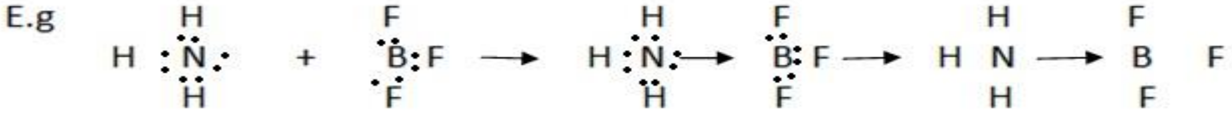
(i) Formation of coordinate bond during the formation of a molecule or molecular ion:-

(a) Formation of Ammonium (NH_4^+) ion.

During the formation of ammonium ion ,nitrogen is the donor atom while H^+ is the acceptor ion.



(b) Formation of coordinate bond between two molecules:- Two or more stable molecules combine to form a molecular complex,is such a complex molecule, the constituent molecules are held together by coordinate bond



The product above is ammonia-borontrifluoride complex

POLARITY IN COVALENT BONDS :-

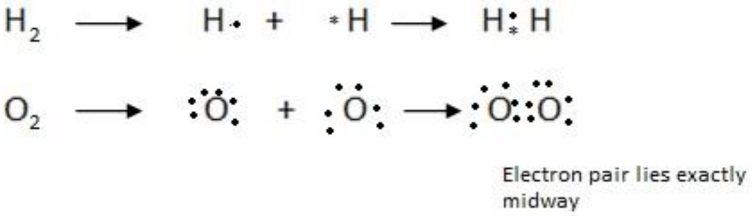
Depend upon chemical nature of the combining elements, the following two types of covalent bond are formed

(i) Non-polar covalent bond
(ii) Polar covalent bond

(i) NON-POLAR COVALENT BOND

When a covalent bond is formed between two atoms of the same element, the electrons are shared equally between the two atoms .The resulting molecule will be electrically symmetrical.

Examples are :- H_2 ,O_2 , Cl_2



(ii) POLAR COVALENT BOND

When a covalent bond is formed between two atoms of different elements, the bonding pair of electrons does not lie exactly midway between the two atoms. It lies more towards the atom which has more affinity for electrons.

The atom with higher affinity for electrons thus develops a slight negative charge and the atom with lesser affinity for electrons a slight positive charge, such molecules are called polar

molecules.The covalent bond between two unlike atoms which differ in the affinities for electrons is said to be a polar covalent bond.
Example of polar covalent bond are hydrogen chloride (H Cl) , water (H_2O)

CAUSES OF POLARITY IN BONDS
The cause of polarity in bond is due to the electronegativity difference.
Example of the electronegativity difference between hydrogen and halogen atoms is as follows:-
halogen atoms: (F,Cl,Br,I)
electronegativity differences:-

H – F	>	H – Cl	>	H – Br	>	H – I
(4- 2.1)		(3.0- 2.1)		(2.8- 2.1)		(2.5- 2.1)
1.9		0.9		0.7		0.4

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY.
The VSEPR theory was proposed by R.J Gillespie and R.S Nyholmn in 1957. This theory was developed to predict the shapes of the molecule in which the atom are bonded together with single bond only. This theory is based on the repulsions between the electron pairs in the valence shell of the atoms in the molecule. The main postulate of the vsepr theory are:-

(i) The geometry of a molecule is determined by the total number of electron pairs (bonding and non-bonding) around the central atom of the molecule.
The shape of the molecule depends upon the orientation of these electron pairs in the space around the central atom.

(ii) The electron pairs (shared or lone pairs) around the central atom in a molecule tend to stay as far away from each other as possible so as to minimize the repulsion forces between them.

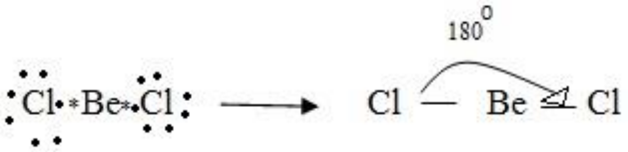
(iii) The strength of repulsion between different electron pairs follows the order.

Lone pair-lone pair > lone pair-shared pair > shared pair-shared pair
The shared pair of electrons are also called bond pair of electrons.The presence of lone pair(s) of electrons on the central atom causes some distortions in the expected regular shape of the molecules.

PREDICTING THE SHAPE OF MOLECULES ON THE BASIS OF VESPR THEORY

(i) Molecules with two bond pairs
In a molecule having two bonds pairs of electrons around its central atom, the bond pairs are located in the opposite side (at an angle of 180º) of the central atom so that the repulsion between them is minimum.

Example:-

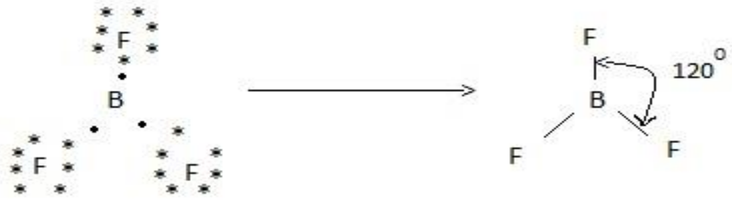


Beryllium chloride is linear shape

(ii) Molecules with three bond pair

In a molecule having three bond pairs of electrons around its central atom, the electron pair form an equilateral triangular arrangement around central atom. Thus the three bond pairs at 120º with respect of each other. Thus the molecule having three bond pairs around its central atom have trigonal planar (triangular planar shape).

Example is Boron Trifluoride

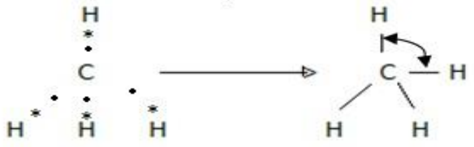


(iii) Molecules with four bond pairs

In a molecule having four bond pairs of electrons the four bond pairs are arranged tetrahedral around the central atom. Thus the four band pairs are at an angle pf 129º 28’ with respect to each other. Therefore the molecule having four bond pairs around its central atom has a tetrahedral shape.

Example of tetrahedral structure are CH_4, CCl_4,SiH_4

Methane molecule (CH_4)



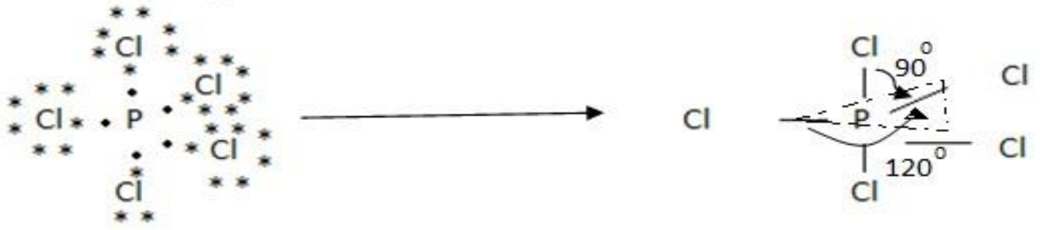
Methane molecule is tetrahedral.

(iv) Molecules with five bond pairs

Five bond pair orient themselves around the central atom in a trigonal bipyramidal way. Three bond pairs are in a plane called equatorial plane, and oriented at an angle of 120º with respect to each other.

Thus a molecule having five bond pairs around its central atom has a triangular bipyramidal shape.

Example PCl_5



PCl_5 has a Trigonal bipyramidal shape

Therefore the molecule of the type shape AB_5 are trigonal bipyramidal in shape e.g PCl_5, PF_5, $SbCl_5$.

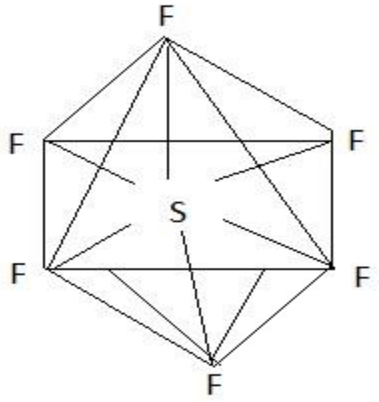
(v) Molecules with six bond pairs

Six bond pairs in a molecule are distributed octahedral around the central atom. Thus a molecule having six bond pairs around its central atom has an octahedral shape. Thus the molecules of the type AB_6 are octahedral. Thus molecules SF_6 has an octahedral

geometry

eg SF_6

SF_6 moleccules has a an octahedral shape.



SHAPES OF THE

MOLECULES HAVING BOND PAIRS AND LONE PAIR ELECTRONS.

The pair of electrons in the valence shell of an atom which is not involved in bonding is called lone pair of electrons.

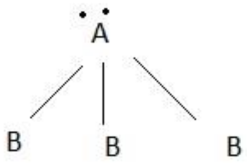
For example the nitrogen atom in ammonia molecules (NH_3) has one lone pair of electrons, the oxygen atom in water molecule (H_2O) has two lone pairs of electrons.

(i) Molecules having three bond pairs and one lone pair.

A molecule having three bond pairs and one lone pair of electrons, thus has in all four pairs of electrons around its central atom.

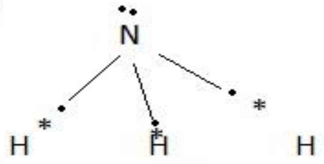
Therefore these four pairs of electrons are distributed tetrahedral around the central atom.

E.g



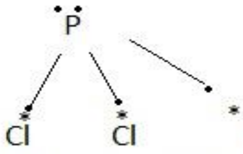
(ii) A molecule of AB_3 type has a triangular pyramidal shape
Typical molecules of this type are NH_3, NF_3,PCl_3 and H_3O^+.

(i)



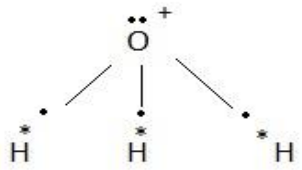
Ammonia molecule

(ii)



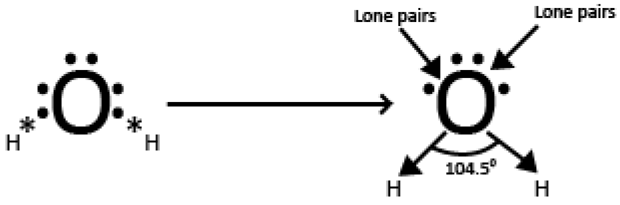
phosphorus trichloride molecule

(iii)



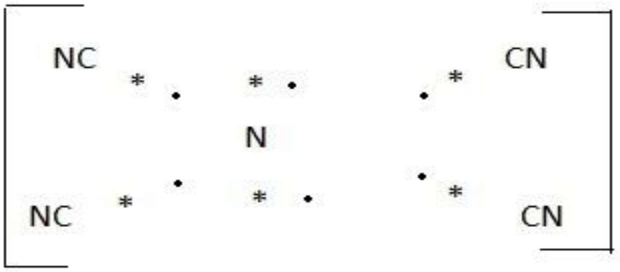
Hydronium(H_3O^+) ion

(iii) Molecules with two bond pairs and two lone pairs
The four electron pairs (two bond pair + two lone pair) are distributed tetrahedral around the central atom



The two lone pairs are the central atom repel the bond pairs slightly inward due to greater lone pair-bond pair repulsion. As a result the bond angle in such a molecule is less than the tetrahedral vale of 109º 28’
The presence of only two bond pairs is the molecules gives a bent shape (inverted V- shaped) to the molecule. Example include H_2O, H_2S, F_2O and SCl_2.
(iv) Molecules with four band pair and two lone pairs
The four bond pair are distributed in a square planar distribution. The two lone pairs are in a direction at right angles to this plane.

E.g



EXERCISE:-
(i) predict the shapes of the following molecules following the VSEPR theory.

(a)Ammonia (NH_3) molecules
(b)beryllium chloride($BeCl_3$)
(c)water (H_2O) molecule
(d)silicon tetrachloride ($SiCl_4$)

HYBRIDIZATION

Definition:- Is the process of mixing of the atomic orbitals to form new hybrid orbital.
Note:- All hybrid orbitals of a particular kind have equal energy, identical shape and are symmetrically oriented in space.

CHARACTERISTICS OF HYBRID ORBITALS

(i) The number of hybrid orbitals formed is equal to the number of the atomic orbitals participating in hybridization.
(ii) All hybrid orbitals are equivalent in shape and energy but different from the participating atomic orbitals.
(iii) A hybrid orbital which takes part in the bond formation must contain only one electron in it.
(iv) A hybrid orbital, like atomic orbital cannot have more than two electrons. The two electrons should have heir spins paired.
(v) Due to the electronic repulsions between the hybrid orbitals they tend to remain at the maximum distance from each other.

TYPES OF HYBRIDIZATION

The types of hybridization shown by an atom depends upon the requirement of the reaction.
(a) SP^3(ess-pee three) hybridization (or tetrahedral hybridization)
(b) sp^2(ess-pee two) hybridization (or trigonal hybridization)
(c) sp (ess-pee) hybridization (or linear hybridization)
(d) s,p & d) hybridization

(a) SP^3 HYBRIDIZATION

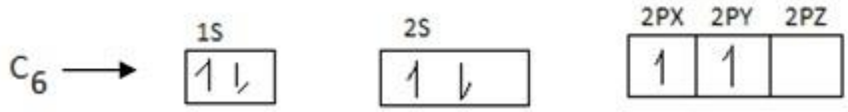
→ S + 3-P orbitals under mixing to provide new hybrid orbitals.

$$\text{e.g} \quad \underset{\text{one s- orbital}}{S} + \underset{\text{three p- orbital}}{(P_x + P_y + P_2)} \rightarrow \underset{\text{four hybrid orbital}}{SP^3}$$

Each of these hybrid orbitals has 25% S-character and 75% P-character. These four sp3 hybridized orbitals are directed along the four corner of a tetrahedron and are inclined to each other at an angle 109º 28'
Examples of sp^3 hybridization is that of methane (CH_4), the process of hybridization involves

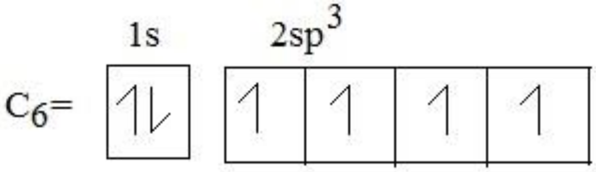
the following

$C_6 \longrightarrow 1S^2 2S^2 2P^2$ The electronic configuration of carbon at ground state before hybridisation

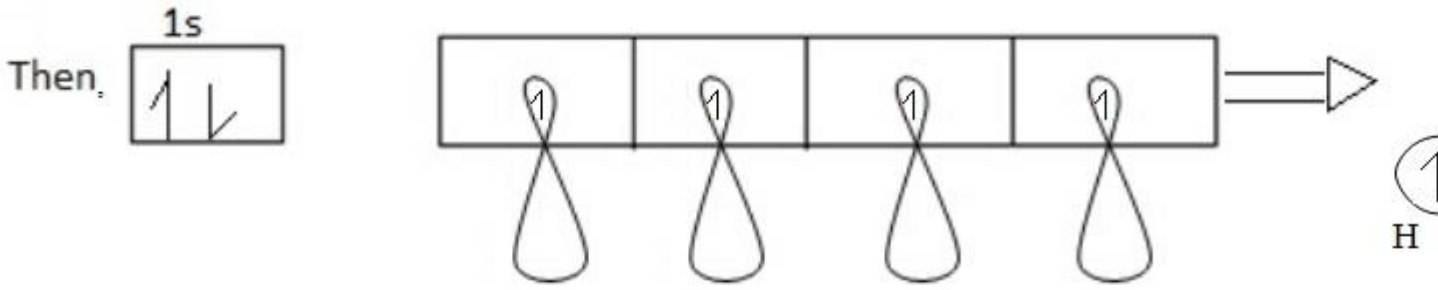


During exited state of carbon one electron is promoted from 2S to 2P orbitals .The process of promotion of an electron from 2s to 2p orbital of the carbon atom and subsequent hybridization is illustrated below.

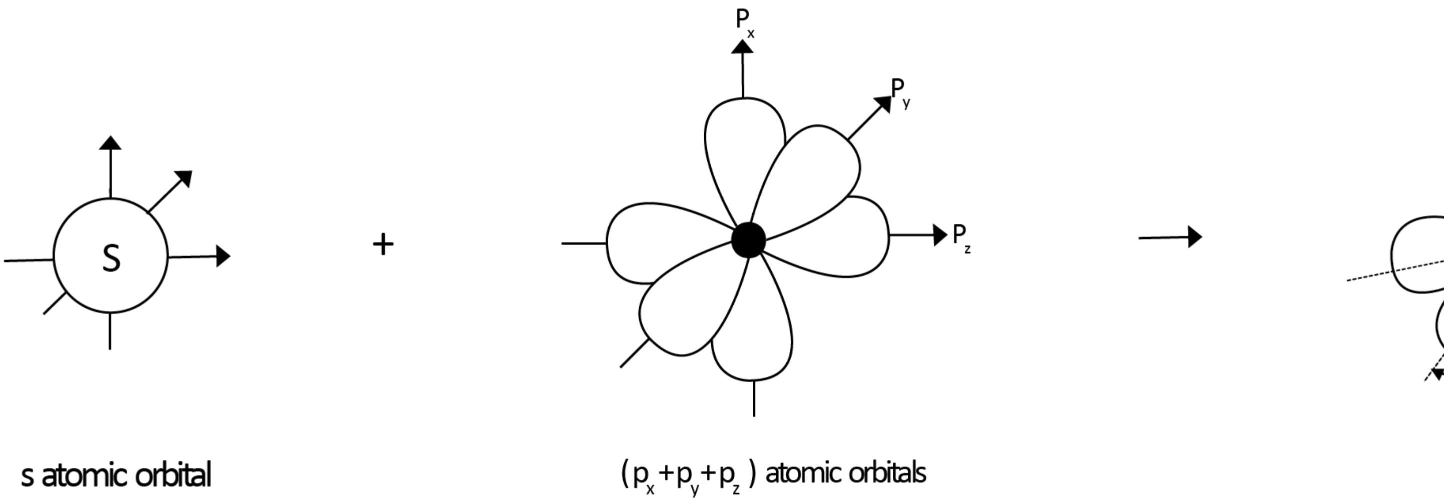
During hybridization/ During excited state ,S is promoted to P orbitals as shown below:



Shape of S is spherical and shape of p is damp bell, then S hybridized with p shape.

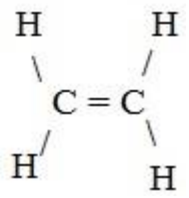


Hybrid between S + P



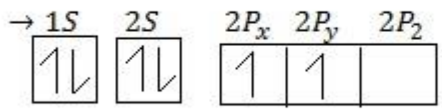
(b) SP^2 HYBRIDIZATION (trigonal hybridization)
Example of SP^2 hybrid orbital are the formation of ethane molecule(C_2H_4)
Note:- The three SP^2 hybrid orbitals are oriented in a plane along the three corners of an equilateral triangle .i.e. they are inclined to each other at an angle of 120° the third p - orbital (say P^2) remains unchanged each hybrid orbital has 33.3% s - character and 66.7% p - character

SP^2 hybridization of Ethene (C_2H_4)/Ethylene
(i) Structure of ethane.

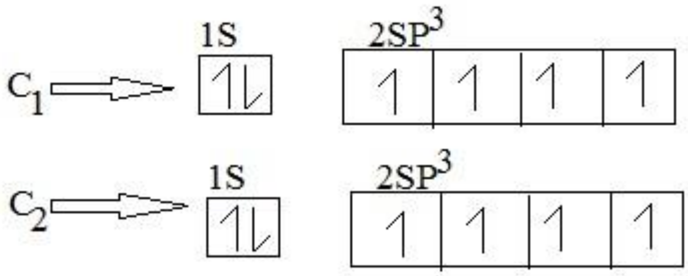


(ii) Electronic configuration of carbon.

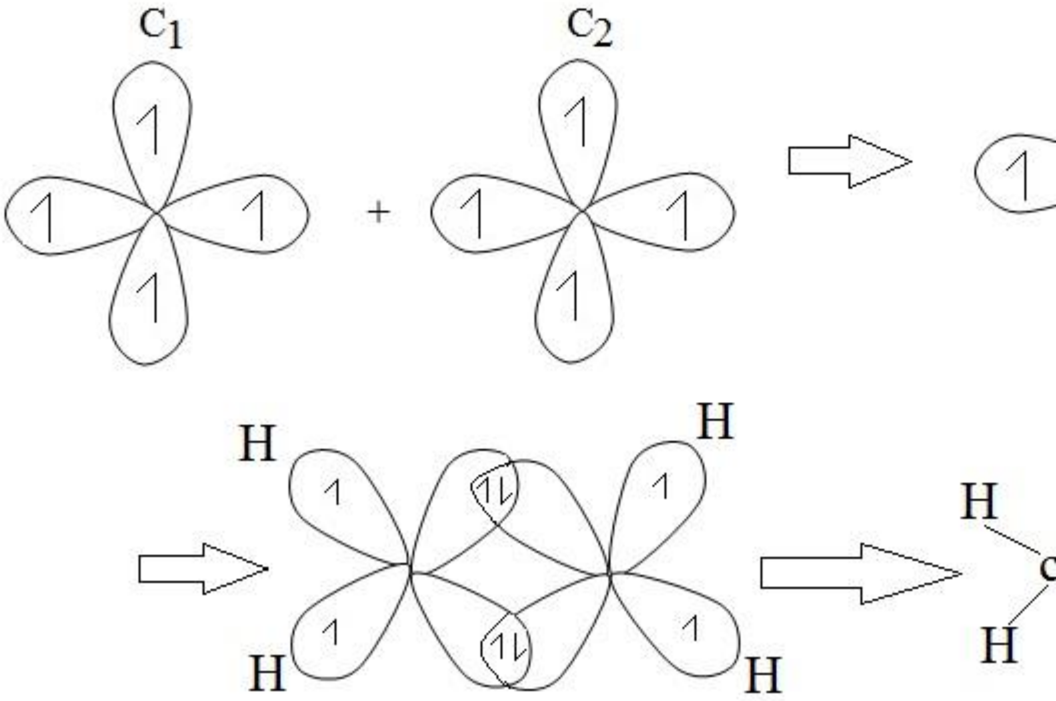
$C_6 \rightarrow 1S^2 2S^2 P^2$



(iii) During excitation hybridization takes place. Then;



Hybridised shape:-



(c) SP hybridization(or linear hybridization)

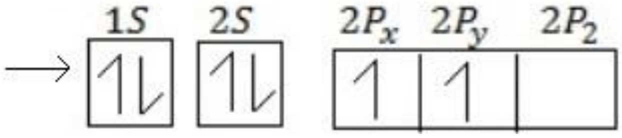
Example of SP hybridization is the formation of ethyne(acetylene) molecules(c2h2)

(i) Structure of ethyne (acetylene)molecule

E.g (i) $C_2H_2 \longrightarrow H-C\equiv C-H$

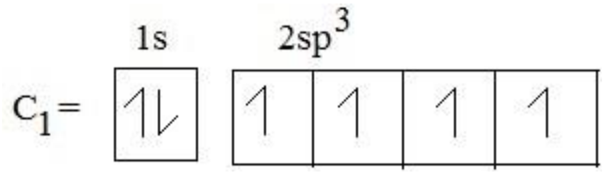
(ii) Electronic configuration of carbon from ground state.

$C_1 \rightarrow 1s^2 2s^2 p^2$

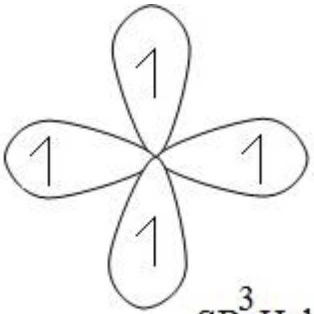


(iii) During excited state , S is promoted to P - orbital to form hybrid orbital.

(a)



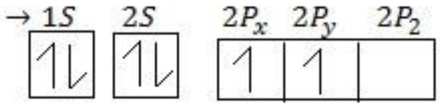
Hybrid shape for carbon 1

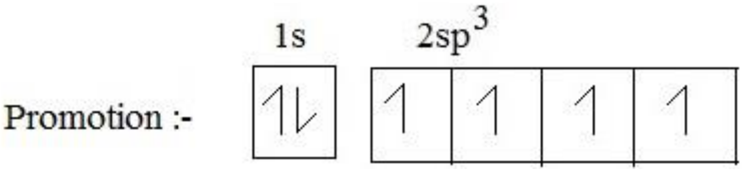


SP^3 Hybrid for Carbon 1

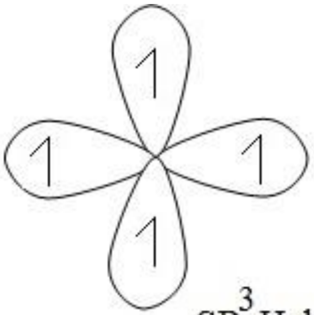
(b)

$C_2 \rightarrow 1S^2 2S^2 P^2$



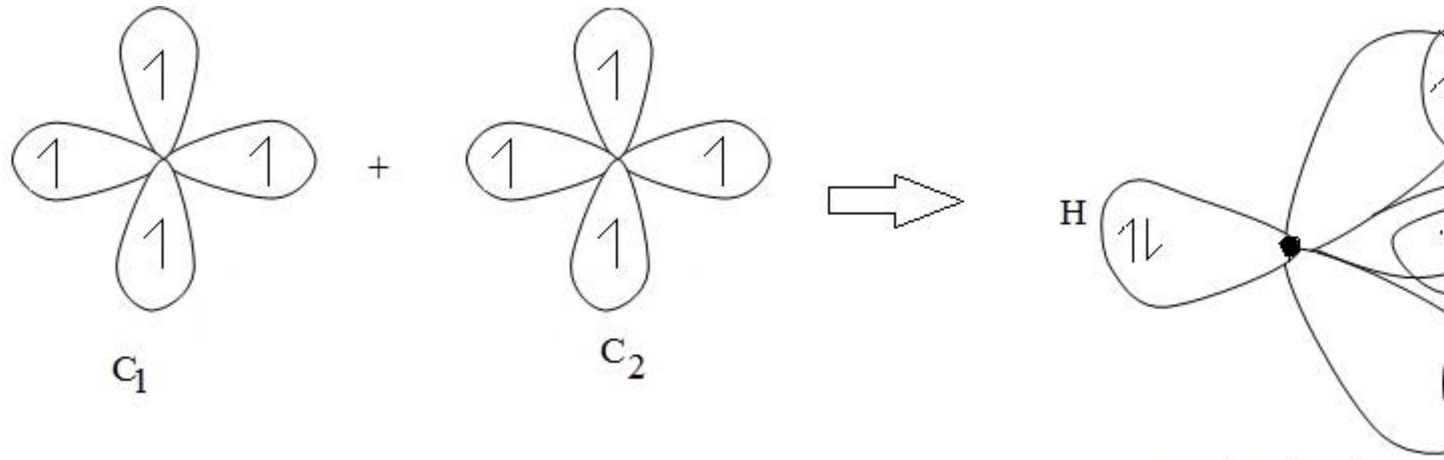


Hybrid shape for carbon 2



SP^3 Hybrid for Carbon 2

Then C_1 combine with C_2



Molecular shape o
$(H - C_1 \equiv C_2$

HYDROGEN BONDING

If a hydrogen atom is bonded to a highly electronegative element such as fluorine , oxygen, nitrogen, then the shared pair of electrons lies more towards the electronegative element. This leads to a polarity in the bond in such a way that w slight positive charge get developed on H-atom.

$H^{+\delta} : 0^{-\delta}$, $H^{+\delta} : F^{-\delta}$, $H^{+\delta} : N^{-\delta}$

The bond between the hydrogen atom of one molecule and more electronegative atom of the same or another molecule is called hydrogen bond

CONDITION NECESSARY FOR THE FORMATION OF HYDROGEN BOND

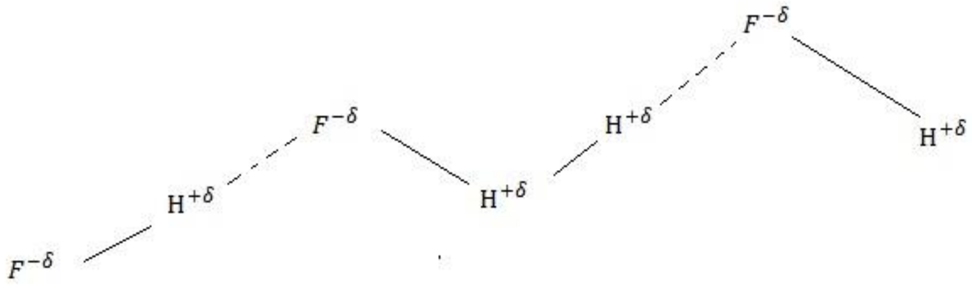
(i) Only the molecule in which hydrogen atom is linked to an atom of highly electronegative element are capable of forming hydrogen bond.

(ii) The atom of highly electronegative element should be small.

SOME TYPICAL COMPOUND SHOWING HYDROGEN BONDING

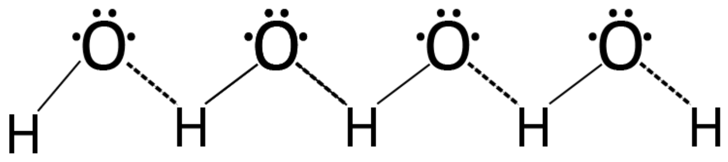
(i) Hydrogen fluoride(HF)

Structure of hydrogen fluoride:-



(ii) Water (H_2O).

Water is a typical polar compound which exhibit hydrogen bonding as shown below:-
Structure of water molecule.



Hydrogen bonding that water exist in the associated form

TYPE S OF HYDROGEN BONDING

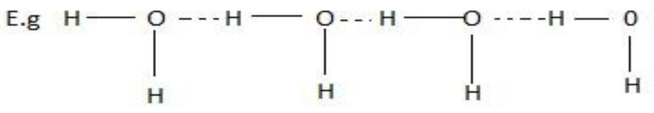
There are two types of hydrogen bonding

(i) Intermolecular hydrogen bonding
(ii) Intramolecular hydrogen bonding

(i) INTERMOLECULAR HYDROGEN BONDING.

When the hydrogen bonding is between the h-atom of one molecule and an atom of the electronegative element of another molecule.

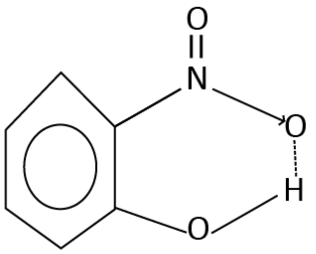
For example , hydrogen bonding in water, ammonia etc

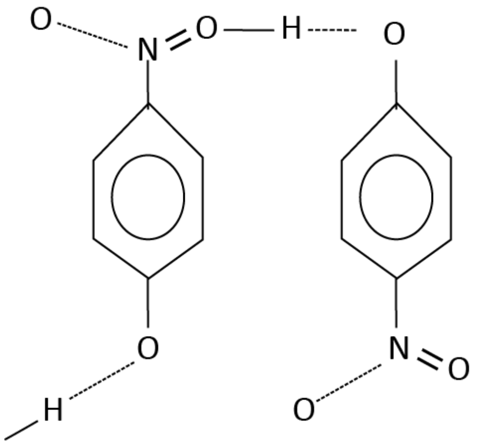


(- - - - - - - -)Represent hydrogen bonding

(ii) THE INTRAMOLECULAR HYDROGEN BONDING

Is between the hydrogen of one functional group and the electronegative atom of the adjacent functional group in the same molecule. For example the molecule of o-nitrophenol show intramolecular hydrogen bonding. The p-nitrophenol shows intermolecular hydrogen bonding.





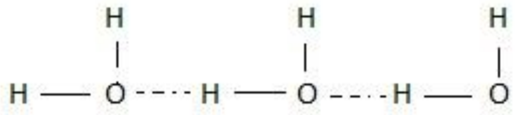
EFFECT OF HYDROGEN BONDING

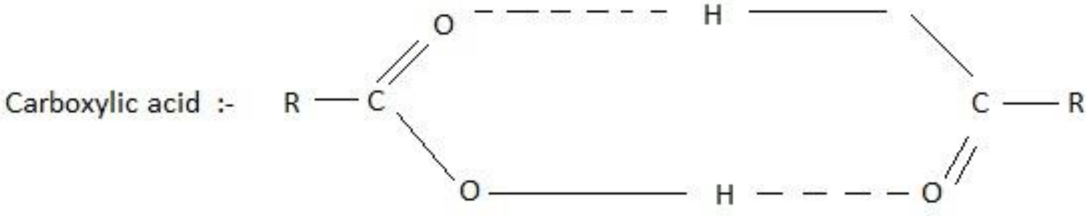
Hydrogen bonding affects the physical properties of the compound appreciable .

Some effect of hydrogen bonding are described below:-

(i) Molecular association.

Formation of aggregates containing two or more molecules due to weak electrostatic interactions such as hydrogen bonding for example ,water molecule undergoes molecular association due to hydrogen bonding.





(ii) Increase in the melting and the boiling points.

The interaction which affected the melting and boiling points of NH_3, H^2O and HF is identified to be hydrogen bonding.

COMPOUND	m.p/k	b.p/k
NH_3	195.5	239.6
PH_3	138.0	185.0
ASH_3	159.0	218.0
SbH_3	184.0	256.0

(iii) Influence on the physical state.

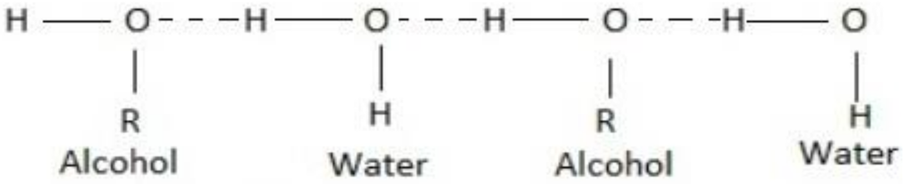
Hydrogen bonding affects the physical state of a substance also for example H_2O is liquid while H_2S is a gas under room temperature condition

(iv) Solubility of covalent compound in water

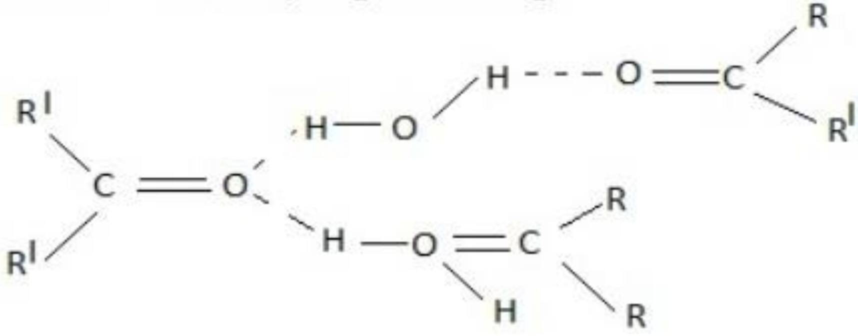
Covalent compounds generally do not dissolve in water. However the covalent compound which can form hydrogen bonds with water readily dissolved in it. For example ethanol, Ammonia, Ammine lower aldehyde and Ketones dissolve in water due to their tendency to form hydrogen bond with water.

E.g

(i)Alcohol Water hydrogen bonding



(ii)Ketone Water hydrogen bonding



REVIEW QUESTIONS

Question 31

(a) Using the electronic configuration and periodic table, give the name of the element and the number of valence electrons.

(i) $1s^2\ 2s^2\ 2p^4$

(ii) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

(b) Use Hund's rule and other information to write out electronic configuration and orbital diagram of;-

(i) Cobalt

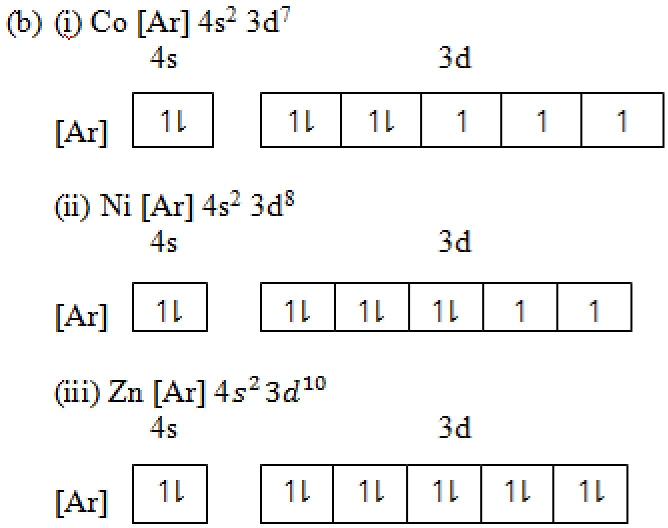
(ii) Nickel

(iii) Zinc

Solution

(a) (i) Oxygen: It has 6 valence electrons in the 2s and 2p sub levels.

(ii) Phosphorus: It has 5 valence electrons (in the 3s and 3p sub level)



(b) (i) Co [Ar] $4s^2$ $3d^7$

	4s		3d				
[Ar]	↿⇂		↿⇂	↿⇂	↿	↿	↿

(ii) Ni [Ar] $4s^2$ $3d^8$

	4s		3d				
[Ar]	↿⇂		↿⇂	↿⇂	↿⇂	↿	↿

(iii) Zn [Ar] $4s^2 3d^{10}$

	4s		3d				
[Ar]	↿⇂		↿⇂	↿⇂	↿⇂	↿⇂	↿⇂

Question 32

(a) Provide the number of orbital in each of the following shells;-

(i) 1s

(ii) 2p

(iii) 3d

(iv) 4f

(b) Howe many sub – shells are there in each of the following sub – shells? K, N and L

(c) Explain if it is possible for an electron to have the following set of quantum numbers.

n = 3, â„“ = 3; m; m = 3 and s = +1/2

(d) An electron is in a 4f orbital. What possible value for the quantum number can it have?

(e) What sub shell is found in the shell with n value = 4

(f) Write the possible value of the 4 quantum number for the outermost 2 electrons of Calcium.

(g) Write all the four quantum number for an electron added to Cl atom in forming Cl

(h) Write all the four quantum numbers for the outmost 2 electrons in Na

Question 33

(a) Write the total number of electrons possible for an atom whose n = 3. Assume that all the orbitals are full of electrons.

(b) Write electronic configuration of the following elements/ions

(i) O

(ii) K

(iii) Ni at number 28

(iv) Cu^+ (at number of Cu = 29)

(v) Mo at number 42

(vi) Cl^- (at number of Cl = 17

(c) What is the number of unpaired electrons present in the ground state of;-

(i) Fe^{+3} (At NO. of Fe = 26)

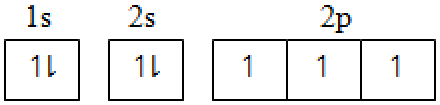
(ii) Cr^{3+} (At No. of Cr = 24)

(iii) Ni^{2+} (At No. of Ni = 28

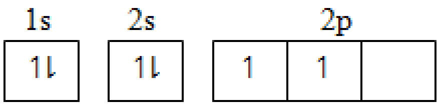
(d) Why is the electronic configuration $1s^2\ 2s^2\ 2p^2x\ 2p^0y\ 2p^0z$ not correct for the ground state of nitrogen?

(e) Mention the disobeyed law from the following arrangements;-

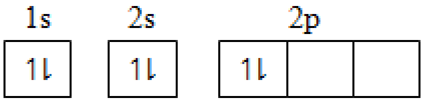
(i)



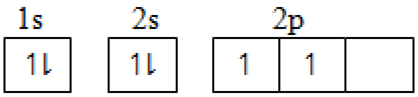
(ii)



(iii)



(iv)



Question 1

(a) State two major postulates and five short coming of Bohr's atomic models.

(b) An electromagnetic radiation was emitted in the Balmer's series as a result of electron.

Transitions between n= 2 and n= 5 calculate the;

(i) Energy of the radiation in $kJmol^{-1}$

(ii) Frequency of the radiation in hertz

(iii) Wavelength of the radiation in metres.

(c) Calculate the wavelength of a line in the Balmer Series that is associated with energy transition

E_4 E_2 ($E_4 = -1.362 \times 10^{-19}$J; E2 = -5.448×10^{-19}J; h = 6.63×10^{-34}J; C = 3×10^{-8} m/s)

Question 9

(a) The atomic spectrum in the visible is given by the following relationship: = R_H

(i) What do symbols λ, R_{H}, n_1 and n_2 represent? Show their SI units

(ii) Calculate the frequency of the third line of the visible spectrum i.e. a transit form n = 5 to n = 2 ($R_H = 1.097 \times 10^7$ M^{-1})

(b) By means of series of horizontal lines, draw an energy level diagram for visible atomic spectrum of hydrogen and indicate:

(i) The value of n for each line

(ii) By means of an arrow, show the transition which corresponds to the fourth line of emission spectrum in visible region.

(iii) By means of an arrow, indicate the transition which corresponds to the fourth ionization energy of hydrogen atom.

(c) (i) What do you understand by the term convergence limit and what is its significance?

(ii) Why are the discrete lines observed and not a continuous spectrum in Hydrogen spectrum?

Question 25

(a) Define the term electron configuration.

(b) Write down the electron configuration of these elements in their ground;

(i) Hydrogen 1p.

(ii) Beryllium.

(iii) Neon 10p.

(iv) Aluminium 13p.

(v) Calcium 20p.

(vi) Manganese 25p.

(vii) Cobalt 27p.

(viii) Zinc 30p.

(ix) Krypton 36p.

(x) Silicon 14p.

Question 18

Write electronic configuration diagram of the following;-

(a) S^{-2} (b) Na^{+} (c) Cr^{+3} (d) Cr^{+6} (e) Zn^{+2}

Question 15

Write the electronic configuration of the following;

${}_{25}V$ = [Ar] $4s^2$ $3d^3$
${}_{16}S$ = [Ar] $3s^2$ p^4
${}_{9}F$ = [He] $2s^2$ p^5
${}_{34}Cs$ = [Ar] $4s^2$ d^{10} $4p^4$
${}_{16}In$ = [Kr] $5s^2$ $4d^8$
${}_{26}Fe$ = [Ar] $4s^2$ d^6
${}_{56}Ba$ = [Xe] $6s^2$

Question 16

Provide electronic configuration of the following;

${}_{75}Pt$
${}_{80}Br$
${}_{68}I$
${}_{48}Ga$
${}_{92}Cf$
${}_{58}Te$
${}_{102}Ra$
${}_{17}Cl$
${}_{15}P$
${}_{30}Zn$

Question10

(a) All radiations are associated with the wave nature and differ from one another terms of their wavelength. Frequency, velocity and energy. Give the relationship between;

(i) Frequency and wavelength.

(ii) Energy and frequency.

(iii) Energy and wavelength.

(b) Ozone (O) protects the earth's inhabitants from the harmful effects whose wavelength is 2950A. Calculate

(i) Frequency.

(ii) Energy.
for this UV light

(c) If the wavelength of the first line of the Balmer series in a hydrogen spectrum is 6563, calculate the wavelength of the first line of Lyman series in the same spectrum. The uncertainty of the momentum of particle is 3.3×10^{-16}gms^{-1}. Find the accuracy in which its position can be determined.

Question 11

a) (i) A small object of mass 10g is thrown with velocity of 200 m/s given $h = 6.626 \times 10^{-34}$J.S. Calculate its wavelength.

(ii) Kinetic energy of a sub – atomic particles is 5.65×10^{-23}J. Calculate the frequency of the particle wave ($h = 6.626 \times 10^{-34}$)

(iii) Calculate the momentum of a particle which has a de-Broglie wavelength of 0.1nm (h = 6.6 x 10^{-34} JS).

(iv) Two particles A and B are in motion, if wavelength λ of A is 5 x 10^{-8}m. Calculate the wavelength λ of B. if its momentum is half that of A.

b) State and describe briefly Heisenberg uncertainty principle.

c) (i) Describe the concept that as the particle size gets smaller determination of its momentum and position simultaneous becomes difficult

(ii) Use the mathematical expression of the uncertainty principle to prove the validity of part c (i) above
d) (i) Calculate the uncertainty in position of an electron if uncertainty in velocity is 5.7 x 10^{5} m/s

(ii) The uncertainty in position and velocity of a particle are 1010m and 5.27 x 10^{24}ms^{-1} respectively. Calculate the mass of the particle.

Question 12

(a) Outline the postulates and weaknesses of Bohr's atomic model.

(b) Calculate the mass of a photon of sodium light having wavelength of 5894A and velocity 3 x 10^{8}m/s given h = 6.6 x 10^{-34}kgm^{2}s^{-1} and 3.7 x 10^{-36}kg.

(c) What's the wavelength of a particle mass 1 gram moving with a velocity of $200ms^{-1}$ given h = 6.626×10^{-34}J. (Answer 3.31×10^{-29}m)

(d) The mass of an oxygen molecule is 5.3×10^{-26}kg. Calculate its de Broglie wavelength if it is moving at a speed of 500m/s (Planks constant (h) = 6.626×10^{-34}Js (Answer 2.5×10^{-11}m)

Question 13

(a) Briefly explain the meaning of these terms, with the help of a diagram

(i) Wavelength

(ii) Frequency

(iii) Velocity

(iv) Amplitude

(v) Wave number

(b) Yellow light from sodium lamp has a wavelength of 5800A^{o}. Calculate the frequency and wave number of the radiations. Determine the range of frequency of visible light. The wavelength of radiations lying in the visible regions are between (3800 - 7600A^{0}).

Question 14

(a) (i) What do you understand by dual nature of matter?

(ii) How does de Broglie equation consider the dual nature of matter?

(b) (i) Calculate and compare the energies of two radiations, one with wavelength 800nm and the other with 400nm

(ii) What is the amount of radiant energy associated with atomic 6.662 x 10^{-34}Js, velocity of light 3 x 10^{8}m/s

(c) If the wavelength of a beam of light is 2.8 x 10^{-7}m. Calculate it's;-

(i) Wavelength in cm.

(ii) Frequency.

(iii) Energy of one of its photons.

(d) (i) Referring to Bohr's atomic model, what's ionization energy?

(ii) Calculate ionization energy of hydrogen. Reydberg's constant RH = 1.097 x 10^{7}m^{-1}

(e) (i) Calculate the frequency of the 3rd line of visible spectrum.

(R_H=1.097 x 10^7m, C=3 x 10^8m/s)

(ii) Given that the wavelength of the 1st line of Balmer series is 6563A. Calculate the wavelength of the 2nd line in the spectrum.

NORGANIC CHEMISTRY

Is the chemistry of all the elements and their compounds with the exception of most carbon compounds out of which only the oxides, cyanides and carbonates are considered as inorganic compound. Inorganic compound can also be defined as the study of the elements in the periodic table.

PERIODIC TABLE

Periodic table is the table of all the known elements arranged in order of increasing atomic numbers. The arrangement reflects the electronics configuration of the elements.

THE PERIODIC TABLE CLASSIFICATION OF THE ELEMENTS (MENDELEEV'S AND LOTHAR MEYER 1869)

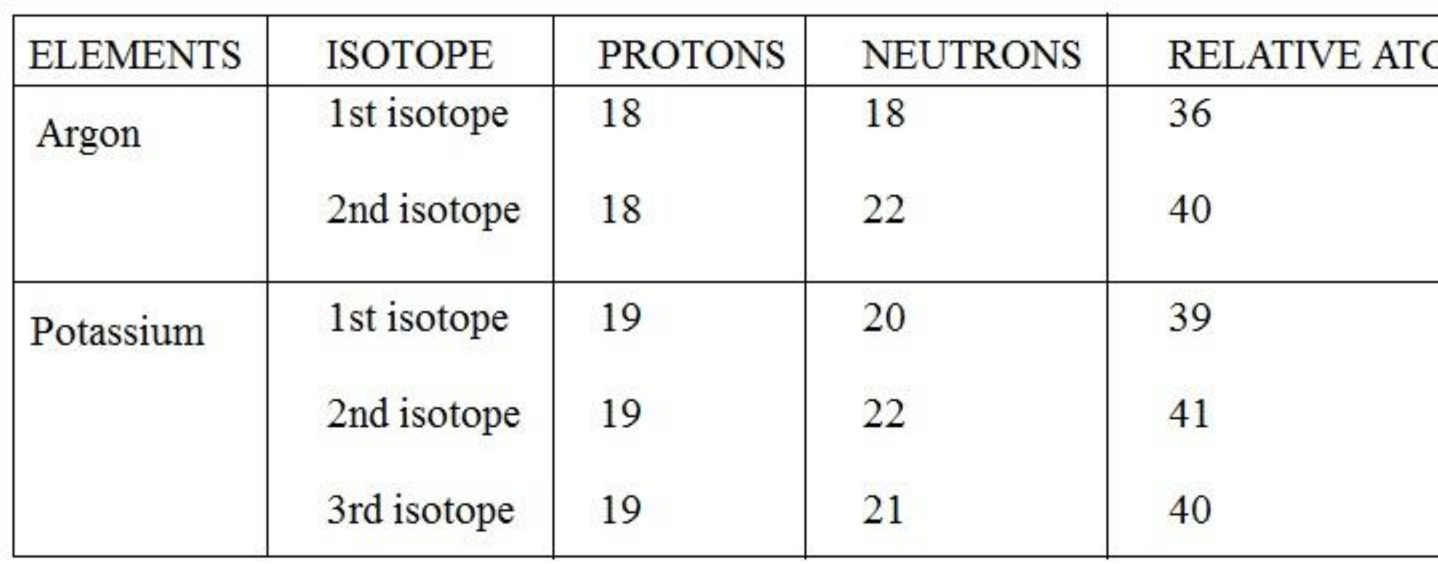
The first comprehensive classification of elements was made independently by Mendeleev's in Russia and Lothar Meyer in German in 1869.They tabulated all the known elements on the basis of relative atomic mass. The arrangement of elements in the early periodic table was according to the ordinary periodic law which states that 'The properties of elements are periodic function of their relative atomic masses'.

When elements were arranged in order of increasing atomic masses, elements with similar properties recurred at regular intervals .The recurrence or repetition of elements with similar properties of regular intervals in the periodic table is known as PERIODICITY.

Mendeleev's and Lothar Meyer placed elements in horizontal rows (periods) which caused elements with similar properties to appear in the same vertical column (group). Some element were not yet discovered and hence absent that periodic table e.g. Noble gases, gallium ,germanium etc.

On the basis of relative atomic mass three anomalies appeared in the early periodic table (Ordinary periodic table). The position of Potassium (39.1), Argon (39.9), Cobalt (58.94), Nickel (58.69), Tellurium (127.6) and Iodine (126.9) had to be reversed to bring them into correct placing on chemical grounds. The strict order of relative atomic mass would have separated the mentioned elements from closely related element. For example Potassium could have been separated from other alkali metals. These anomalies showed clearly that the relative atomic mass was not really the true basis of arranging or classifying elements in the periodic table.

The three anomalies stated above were due to *ISOTOPE.* For example both Argon and Potassium exhibit isotropy .The principal Isotopes of these elements are shown in the table below.



ELEMENTS	ISOTOPE	PROTONS	NEUTRONS	RELATIVE ATC
Argon	1st isotope	18	18	36
	2nd isotope	18	22	40
Potassium	1st isotope	19	20	39
	2nd isotope	19	22	41
	3rd isotope	19	21	40

$$R.A.M = (Mass\ of\ 1^{st} \times Abundance) + (Mass\ of\ 2^{nd} \times Abundance)$$

In the case of Argon, the heavier isotope is predominate(has higher abundance) giving an average atomic mass of 39.9,In Potassium the lighter isotope predominates giving an average atomic mass of 39.1, The explanation is similar in the case of cobalt(no isotopes) and nickel(five isotope) and tellurium(8 isotopes) and iodine(isotope)

Moseley discovered that atomic number was the proper criterion for arranging elements in the periodic table. The atomic number of an element determines the number of electronics in the atom and hence the arrangement and properties of the elements in the periodic table.

When atomic numbers are used instead of atomic masses, the anomalies observed between potassium ,Argon ,Cobalt ,Nickel Tellurium and Iodine disappears .The classification of the known elements in the periodic table is now based on the Modern Periodic law which states that " The properties of elements are periodic function of their atomic numbers"

NB: One can't use R.A.M or Atomic mass for arranging elements but atomic number is the best

STRUCTURE OF PERIODIC TABLE

The periodic table is very important in the study of inorganic chemistry. The relationship between the periodic table, atomic number and properties of elements enable us to obtain an overview of the many facts and features in Inorganic chemistry

The periodic table consist of boxes which are filled by elements .Each box contains the symbol, mass number, and atomic number of elements.

However, other data like electronegativity, boiling point, melting point, oxidation states values may be included or added. There are various lay out of the period table. The periodic table may be in the short or long form .Under this level the long form will be considered .The long form consists of all the elements of a periodic except the Lanthanide and Actinides

The elements with similar properties occur in vertical column called groups. The horizontal rows of elements in the periodic table are calling periods. The long form of the periodic table is into four major blocks according to the sub shell in which the respective elements fill their electronics. The four major blocks are S-blocks, P-blocks, d-blocks, and f- blocks.

1. S-BLOCK ELEMENTS

The S-blocks consist of elements which fills their outermost electrons in the S-sub shell. These elements use their S-sub shell electrons for bonding. The S-block is constituted by the element of Group IA and Group IIA e.g. Li, Na, K, Mg etc

2. P-BLOCK ELEMENTS

The P-blocks elements consist of elements which fills their outermost electrons in the P-sub shell. This block consist of elements of group IIIA up to VIIA example Carbon, Sulphur ,Phosphorus ,Nitrogen ,Oxygen, Chlorine, Argon ,Neon, Helium is not a P-block elements.

The S-and P-blocks elements together form main group elements .These elements use only electrons of their outermost shell for bonding .Hence there are seven main groups which constitute main group elements (example IA, IIA, III,IVA, VA, VIA and VIIA). The noble gas contains full outermost electrons S and P-sub shells. Since this configuration is very stable, the noble gases are uncreative.

However they form some compounds with strongly electronegative elements like Oxygen and Fluorine .Example of noble gases include Helium, Neon, Argon, Krypton etc

3. d-BLOCK ELEMENTS

The d-blocks consist of elements with partially or full-filled d-sub shell. They fill their electrons in the d-sub shell of the penultimate shell. They use electrons from S and d-sub shells for bonding. Example Scandium, Manganese, Iron, Radium, Nickel, Cobalt, Copper, Zinc etc

4. f-BLOCK ELEMENT

The f-block consists of elements which are called Lanthanides and Actinides. They are also known inner transition elements. These elements have two partially filled sub-shells namely (n-1)d and (n-2)f .They all belong to III B because they are so similar that it is very difficult to separate one from another example e.g. La, U, Np ,Lw, Th etc

NOTE;

I. The atoms of all elements of the same period have the same number of shells which are partially or fully occupied by electrons.

II. The number of the main groups is equal to the number of electrons in the outermost shell.

III. The number of period is equal to the principal quantum number (n) of the outermost shell and to the total number of electrons shell of the elements in a given period.

PERIODIC TRENDS IN PHYSICAL PROPERTIES

1. DOWN THE GROUP

I. I. The atomic size(Atomic Radius)

The atomic radius of an uncombined atom cannot be defined strictly because of the uncertain boundary of electron clouds .The distance between the nuclei of chemically or covalently combined atoms can be measured accurately by x-ray diffraction method

Therefore, the atomic radius is defined as half the distance between the nuclei of two similar/ identical atoms joined by a single covalent or metallic bond. There is significant regular increase in atomic radii among elements down the group .This trend is due to increase of number of electrons and number and number of shells down the group.

The newly added electrons or shell must be at greater distance from the nucleus than that of the proceeding element (i.e a noble gas). Also the added electron is shielded by the inner electrons.

Therefore the added shells and electrons reduces the attraction force between the nucleus and the outer electrons leading to increase in atomic size down the group .The following is the trend down group IA.

ELEMENT	**ATOMIC NUMBERS**	**NUCLEAR CHARGE**	**ELECTRONIC CONFIGURATION**	**ATOM**
Li	3	3^+	2,1	1.33
Na	11	11^+	2,8,1	1.57
K	19	19^+	2,8,8,1	2.03
Rb	37	37^+	2,8,18,1	2.16
Cs	55	55^+	2,8,18,18,81	2.35

II. Ionic radii

The ionic radius of the atom of an element is measured in the same way as the atomic radius. The ionic radii like atomic radii increases down the group. The reasons for this are exactly the same as those quoted for atomic radii. The radius of a cation is shorter than the radius of the parents atom (neutral atom) because electron or electrons have been removed and hence the force of attraction from the nucleus has increased e.g. Na=1.57A^0, $Na^+ =$0.97A^0

In contrast, all anions are larger than the corresponding neutral atom because electrons have been added to complete the noble gas structure. The added electrons reduces the force of attraction from the nucleus and as the result the size of an anion increase example Cl=0.99A^0 and $Cl^- =$1.81A^0. The repulsive force of inner electrons also contribute to increase in ionic size.

The table below shows the trend in ionic radii down group VIIA elements

ELEMENT	**ATOMIC NUMBER**	**ATOMIC RADIUS(nm)**	**IONIC RADIUS(nm)**	**ION**
F	9	0.072	0.136	F^-
Cl	17	0.099	0.181	Cl^-
Br	35	0.114	0.195	Br^-

I	53	0.133	0.216	I^-

NB: Ionic radius is half the distance between the nuclei of two ions in an ionic crystal

III. Ionization energy

This is the energy required to remove an electron from a gaseous atom or ion. Hence the first ionization energy of an element, M is the energy required to remove the first electron from it.

$$M_{(g)} \rightarrow M^{+}_{(g)} + e^{-}$$

The second ionization energy is the energy required to remove the second electron from a gaseous ion.

$$M^{+}_{(g)} \longrightarrow M^{2+}_{(g)} + e^{-}$$

The successive ionization energies are defined accordingly .The higher this energy the tighter the electron is bound to the atom or ion. The ionization energy decreases down the group because OR due to the increase in atomic size of the element down the group, the increase in radii downs a group correlate with the decreasing ionization energies.

The nuclear charge increases down the group but it is cancelled by shielding effect and screening effect of the electrons of the inner shells. The two effects increases down the group. Since the nuclear charge is affected by the increase of electrons, the atoms become larger down the group and therefore the outer electron(s) is easily removed as it is loosely bound. Thus for the alkali metals Li to Cs, the outer most electron is most readily removed for Cs which is the largest element in group IA. Fluorine having the smallest atomic size in group VIIA has the highest ionization energy.

IV. Electron affinity (E.A)

The electrons affinity is the energy change which occur when an electron is added to a gaseous atom or ion. The non-metallic element readily gain an electron to give a negative ion.

$$X_{(g)} + e^{-} \longrightarrow X^{-}_{(g)} \qquad \Delta H =_{KJ/mol}$$

The energy associated with this process is termed as the electron affinity. The process may either absorb or evolve energy (example endothermic and exothermic respectively). Some elements evolve large quantities of energy i.e their electron affinities are large and negative. The more negative the electron affinity, the more the electron is attracted by the nucleus. Thus the first electrons affinity is the energy change which involve the addition of the first electron to a gaseous atom

$M_{(g)} + e^{-} \longrightarrow M^{-}_{(g)}$ Negative electron affinity (in kJ$^{mol^{-}}$)

The most negative electron affinity is found in Ground VIIA elements (I.e halogens) halide ions are most easily formed as they possess high electrons affinity. There is little variation in electron affinity down the group. Also there is no simple trend of electron affinity as shown in group VIIA. However there is general decrease in electron affinity down the group

ELEMENTS	ION	ELECTRON AFFINITY
F	F^{-}	-332
Cl	Cl^{-}	-349
Br	Br^{-}	-325
I	I^{-}	-295

NB: From the table above Chlorine has higher electron affinity than Fluorine. This is probability due to the relative small atomic size of Fluorine compared to that of Chlorine. The higher electron cloud in small Fluorine atom exerts a great repulsive force to the incoming electron giving rise to a smaller value of electron affinity. Chlorine with larger atomic size has smaller repulsive force and as result an electron can easily to be added to it and hence high electron affinity. All the electron affinity valves quoted for univalent ions is negative .To add an electrons to a univalent anion may require a large amount of energy in order to overcome electrostatic repulsion between the second electron and the charge on the anion. For example the second electron affinity of oxygen is positive.

The first electron is easily accepted

$$O_{(g)} + e^{-} \longrightarrow O^{-}_{(g)} \qquad \Delta H = \text{-}148kJmol^{-}$$

The2nd electron is not easily accepted

$$O^{-}_{(g)} + e^{-} \longrightarrow O^{2-}_{(g)} \qquad \Delta H = {}^{+}850kJmol^{-}$$

More energy required to shift with to higher energy level to create space for incoming electron. Thus energy released smaller than the energy gained

IV. Electronegativity

This is the measure of the attraction which an atom exerts on the electron pairs of a covalent bond. It can also be defined as the power of an atom in a molecule to attract electron to itself. The two atoms assumed to be involved in forming a single covalent bond where shared electrons are not equally attracted by the two atoms

$$Electronegativity = \frac{Effective\ nuclear\ charge}{Covalent\ atomic\ radius}$$

Electronegativity is directly proportional to effective nuclear charge and inversely proportional to atomic radius. Small atoms with relatively large effective nuclear charge tend to have large values of electronegativity. There is general decrease in electronegativity as one goes down a group. Therefore in the first element in each group (main group element) is much more electronegative than the rest. This account for much of the differences between its properties and that of other elements e .g Li is much more electronegative compared to other numbers of the group.

The following is the trend in electronegativity down group IA

Element	*Electronegativity*
Li	1.0
Na	0.9
K	0.8
Rb	0.8
Cs	0.7

2. ACROSS THE PERIOD

I. ATOMIC RADII(ATOMIC SIZE)

The atomic radii decrease steadily across each period. There is step rise in atomic size from halogens to alkali metals.

Consider period 2 elements

Period 2 element	*Li*	*Be*	*B*	*C*	*N*	*O*	*Fe*	*Ne*
Atomic number	3	4	5	6	7	8	9	10

Nuclear charge	3^+	4^+	5^+	6^+	7^+	8^+	9^+	10^+
Electronic configuration	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8
Atomic radius	1.33	0.89	0.80	0.77	0.74	0.74	0.72	1.1

From the table above, it is observed that there is decrease in atomic radius from Li to F followed by an increase to Neon. This is probably due to the fact noble gases are mono atomic and their inter-nuclear distance is the distance between non bonded atoms held together by weak Van Der Waal's forces. The decrease in atomic size gets smaller and smaller as shown in the table above. The same trends are observed in other periods

Generally atomic size (atomic radius) continue to decrease in passing along the period, Hence the alkali metal atom has the largest atomic radius than all the element in each period.

The halogen atom has the smallest atom radius of the elements in each period except iodine which has slightly larger radius than some of the transition metals in the middle of the period.

II. IONIZATION PERIOD

On moving horizontally along the periods we find that the first ionization energy increased. This due to the increase effective nuclear charge and decrease in atomic size for a small atom the outer most electrons are firmly held by the nucleus and hence much energy is required to remove them.

Across period 2 and 3, a contractions in radius correlates with the rise in ionization energy values. Abnormally high ionization potential values in Beryllium, Magnesium, Nitrogen, and Phosphorus are explained on the basis of the extra stability associated with full S and half filled P sub shell respectively.

A break is observed between Be and B in the period 2 and between N and O in the same period. In the period 3 we observe break between Magnesium and Aluminum and age between Phosphorus and Sulphur

These breaks can be accounted as follow;

a) There is a large increase in the ionization energy as we pass from it to He. This is due to the stability of the double state of Helium

b) The break in the trend of increasing ionization energy between Be and B is due to extraordinary large ionization energy of Be

$Be = 1S^2 2S^2$

$B = 1S^2 2S^2 2P^1$

Be has two paired electrons in its 2S orbital. It needs energy first to split 2S electron pair and secondly to effect the electron removal. But for B there is only one electron in the 2P orbital which is easy to remove as it is more distant from the nucleus

A comparable explanation accounts for the break between N and O. Their electronic configurations are as follows;

$N = 1S^2 2S^2 2P^3$

$O = 1S^2 2S^2 2P^4$

For Nitrogen there is extra stability due to half-filled P-sub shell. In Oxygen the $2P_x$ sub level has a pair of electrons which shields the $2P_y$ and $2P_z$ electrons rendering them easier to remove, hence an abnormally lower ionization energy for Oxygen. We may take almost similar account for the elements in period 3 where there is break between Mg and Al and also between P and S.

$Mg = 1S^2 2S^2 2P^6 3S^2$

$Al = 1S^2 2S^2 2P^6 3S^2 3P^1$

$P = 1S^2 2S^2 2P^6 3S^2 3P^3$

$S = 1S^2 2S^2 2P^6 3S^2 3P^4$

FACTORS AFFECTING IONIZATION ENERGY

1) Effective nuclear energy; The greater the effective nuclear charge the greater the ionization energy

2) Shielding Effect and Screening Effect; The greater the shielding and screening effect, the less the ionization energy

3) Radius ; The greater the distance between the nucleus and the outer electrons of an atom, the less the ionization energy

4) Sub level; An electron from a full or half –filled sub level requires additional energy to be removed

III. IONIC RADII

Ionic radii like atomic vary periodically with atomic number. The anions are much larger than the corresponding atoms while cations are usually much smaller. The explanation of the trends in atomic radii applies also to the very similar trends in ionic radii.

Example $Na^+ = 0.095, Mg^{2+} = 0.065, Al^{3+} = 0.050, P^{3-} = 0.212, S^{2-} = 0.184, Cl^- = 0.181$

In period 4 the bivalent cation from Ti^{2+} to Z^{2+} show a d-blocks contraction similar to but larger than the corresponding contraction for atomic radius. The same is true of the Lanthanide contraction for the trivalent cations La^{3+} to Lu^{3+}in period 6

vvvvvvv

IV. ELECTRONIC AFFINITY

Electron affinity along the period can be discussed in terms of non-metal and metals. It is generally observed that non-metal have higher values of electrons affinities than metals. Non-metals have higher values because they can readily gain an electron to give negatively charged ion. The process involving addition of electrons to neutral atom is exothermic because energy must be lost in order that the formed ion is stable.

Generally there is increase of electrons affinity across the group due to the increase of electronegativity which is a result of decrease in atomic radii of the respective elements. Also increase of effective nuclear charge increases electron affinity.

V. ELECTRONEGATIVITY

Electronegativity of the main group elements increase across each period. This is due to the increase in affective nuclear charge as well as decrease in atomic size. Therefore the halogens atom in every period has the highest electronegativity value than the rest members. Alkali are the least electronegative elements in each period.

VI. MELTING POINT

The melting point of an element is the measure of the amount of energy (heat) which must be supplied to breakdown the regular arrangement of atoms or molecule in crystal.

It`s a temperature at which a substance changes from solid into liquid. There are different types of force which holds atoms and molecules together, example due to such variation in forces the melting point of the elements in a period do not change uniformity e. g Period 3 elements. Melting point increase sharply from Na^+ to Mg. Sodium atom to contribute only one electron to the metallic crystals, but Mg contributes two electrons. This accounts for the lower Melting point of Sodium compared to Magnesium.

All has three electrons in the outer valence shell but contributes only two of them to the “electrons sea”. This is why it has melting point close to that of Magnesium. The third electron is held firmly to the extent that it is not contribute to the “sea of electrons”

Silicon is non-metal with some metallic properties like luster, electric conductivity and ability to form alloy with metals. Silicon has the highest Melting point in period 3 due to its “giant covalent structure”. The silicon giant structure is comparable to that of Diamond.

Phosphorus and Sulphur have relatively low Melting point because their molecules are held together by weak Van Der Waal’s forces. Sulphur has a higher Melting point than Phosphorus due to the differences in sizes of their molecules i.e $P_4 \ and \ S_8$

Chlorine is diatomic and is a gas at room temperature. Its melting point is very low due to a very low Van Der Waal forces holding the molecules.

PERIODIC TRENDS IN CHEMICAL PROPERTIES ACROSS PERIOD THREE (Na to Ar)

Chemical properties along the period depend on the change of the elements from strongly metallic to non-metallic. Sodium and Magnesium are strongly metallic while Aluminum is weakly metallic element. Silicon, Phosphorus, Sulphur and Chlorine are non–metallic elements. Thus metallic properties decrease across the period from left side of the periodic table to the right

a) HYDRIDES

The hydrides of period 3 elements include NaH, MgH_2, AlH_3, SiH_4, PH_3, H_2S and HCl. Sodium hydride is strongly ionic while Magnesium hydride is largely ionic but the bonds are covalent. Aluminium hydride is covalent.

REACTION OF HYDRIDES WITH WATER

Sodium .Magnesium, and Aluminum yields hydrogen gas and metal hydrides, they are basic in nature because they react with water to form base

$$NaH_{(s)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + H_{2\,(g)}$$

$$MgH_{2(I)} + H_2O_{(I)} \longrightarrow Mg(OH)_{2(s)} + H_{2(g)}$$

Silicon hydride (silane) evolve hydrogen with water in alkaline medium (catalyses the reaction)

$$SiH_{4(g)} + H_2O_{(I)} + 2OH^-_{(aq)} \longrightarrow SiO_3^{2-}{}_{(aq)} + 4H_{2(g)}$$

Phosphine (PH_3) is a non–polar covalent compound and hence does not react with water. Phosphine is a non–polar covalent compound due to small difference in electronegativity values between Hydrogen and Phosphorus $(H = 2.2 \text{ and } P = 2.1)$

The hydrides of Sulphur (H_2S) and Chlorine (HCl) are polar covalent compounds. They hydrolyze in water to form acid.

$$H_2S_s + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HS^-_{(aq)}$$

$$HCl_{(l)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Therefore the hydrides of the strongly metallic elements tend to form alkaline solution with water while those of the non-metals form acidic solutions.

b) CHLORIDES

The Chlorides of period 3 elements include NaCl, ,$MgCl_2$, ,$AlCl_3$, $SiCl_4$, PCl_3, PCl_5, S_2Cl_2. The Sodium and Magnesium chlorides are ionic salts .The rest of the chlorides are covalent in nature. As metallic character decreases along the period ionic character of the chlorides decreases.

REACTION OF CHLORIDES WITH WATER

When the ionic chloride is added to water, there is an immediate attraction of polar water molecules for ions in the chlorides. The solid chloride either dissolves to form free ions example $Na^+_{aq} \text{ and } Cl^-_{(aq)}$ or react to form new substances.

The hydrolysis of chlorides varies across the period Sodium chloride is not hydrolyzed in water probability due to a large size of Na^+ ion leading to low polarizing power for water molecules. The chlorides of the rest elements have covalent characters. As metallic character decrease along the period, ionic character of the chlorides decreases as well.

The extent of hydrolysis of chlorides varies across the period. Magnesium chloride is not hydrolyzed but its hydrated crystals undergo hydrolysis when heated to give hydrogen chloride and a basic Magnesium chloride salt.

$$MgCl_2.6H_2O_{(s)} \overset{\Delta}{\rightarrow} Mg(OH)Cl_{(s)} + HCl_{(g)} \quad + 5H_2O_g$$

Aluminum chloride is easily hydrolyzed by water to produce an acidic solution. Al^{3+} ion is very small in size and it is highly charged. Thus its polarizing power is high, due to its high polarizing power it forms hydrated ions ($[Al(H_20)_6]^{3+}$). The Al^{3+} ion strongly polarizes the O-H bond of the water molecules in the $[Al(H_2O)_6]^{3+}$ ion to the extent that the bonds break to release the hydrogen protons. The solvent water molecules abstract protons from polarized water molecules to form the acidic hydroxonium ion H_3O^+, The $H_3O^{+|}$ is formed as follows

$$AlCl_{3(s)} + 6H_2O_{(l)} \longrightarrow [Al(H_2O)_6]^{3+}_{(aq)} + 3Cl^-_{(aq)}$$

$$[Al(H_2O)_6]^{3+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_5OH]^{2+}_{(aq)} + H_3O^+_{(aq)}$$

$$[Al(H_2O)_5OH]^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_4(OH)_2]^+_{(aq)} + H_3O^+_{(aq)}$$

$$[Al(H_2O)_4OH_2]^+_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_3(OH)_3]_{(s)} + H_3O^+_{(aq)}$$

$$[Al(H_2O)_3(OH)_3]_{(s)} + H_2O_{(l)} \rightleftharpoons Al(HO)_3.3H_2O_{(s)} + H_3O^+_{(aq)}$$

The chloride of Silicon Phosphorus and Sulphur hydrolyses completely in water to form acidic solution or solid

$$SiCl_{4(l)} + 2H_2O_{(l)} \longrightarrow SiO_{2(s)} + 4HCl_{(aq)}$$

$$PCl_{3(l)} + 3H_2O_{(l)} \longrightarrow H_3PO_{3(aq)} + 3HCl_{(aq)}$$

$$PCl_{5(l)} + 4H_2O_{(l)} \longrightarrow H_3PO_{4(aq)} + 5HCl_{(aq)}$$

$$S_2Cl_{2(l)} + H_2O_{(l)} \longrightarrow 2HCl_{(aq)} + H_2S_{(g)} + H_2SO_{3(aq)}$$

Note: As metallic character decreases along the period, ionic nature of the chloride decrease while the extent of hydrolysis increases

c) THE HYDROXIDES

The hydroxides in period 3 include NaOH, $Mg(OH)_2$, $Al(OH)_3$, $SiO(OH)_2$, $P(OH)_3$, $PO(OH)_3$, $SO_2(OH)_2$ and $ClO_3(OH)$, $Cl(OH)$. The hydroxides from silicon to chlorine are not true hydroxide but they are oxy–acids.

Sodium and Magnesium hydroxides are the true hydroxide. They have strong tendency of releasing the OH^- group. Aluminum hydroxide is Amphoteric.

The acidic character of non-metal hydroxides is due to the tendency of releasing or donating H^+ ion when dissolved in water. Silicon, Phosphorus, Sulphur and Chlorine are electronegative enough to withdraw electron by inductive effect from the O-H bond thus, facilitating the release of hydrogen as a proton H^+.

The acidity of the hydroxide of Si, P, S and Cl increases with the increase in the electro negativity of respective elements. Solubility decrease from NaOH to $Al(OH)_3$ due to decrease in metallic character or ion character of the hydroxides across the period

d) OXIDES

Sodium and Magnesium are strongly metallic and their oxides are ionic. Aluminum oxide is ionic but not basic as these sodium and magnesium.

The oxides of sodium and magnesium are strong bases while aluminum oxides are amphoteric. The oxides of the remaining elements are all acidic.

OXIDES	Na_2O	MgO_2	Al_2O_3	S_1O_2	P_4O_6 P_4O_{10}	SO_2 SO_3	Cl_2O_n Cl_2O_7
NATURE	Basic	Basic	Amphoteric	Acidic	Acidic	Acidic	Acidic

REACTION OF OXIDES WITH WATER

Solubility of the oxides of period 3 elements decreases along the period as metallic properties decreases. The oxides of sodium and magnesium form hydroxide with water or steam because of the protective film of oxide. The oxides of phosphorus sulphur and chlorine reacts with water to form acidic solution. Silica (SiO_2) does not react with water but it’s acidic

E.g. $$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$$

$$MgO_{(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_2$$

$$P_4O_{6(s)} + 6H_2O_{(l)} \longrightarrow 4H_3PO_{3(aq)}$$

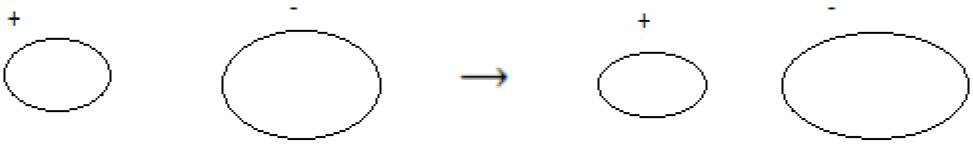
$$SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2SO_{4(aq)}$$

$$Cl_2O_{7(g)} + H_2O_{((l))} \longrightarrow 2HClO_{4(aq)}$$

DIAGONAL RELATIONSHIP BETWEEN THE ELEMENTS

The first element in every group is the smallest and has the highest electronegativity compared to the rest group member as a result the first elements have properties which differ from the rest group member but similar to those at the next lower elements diagonally. The kind of relationship in which the elements which are diagonally located in the period's table have similar properties is known as diagonal relationship.

Diagonal relationship may also be explained in terms of polarizing power of the diagonal elements .The polarizing power of an element is the ability of positive ion to polarize the negative ion .When positive and negative ions approach each other their shape are distorted. The extent by which the ion is able to undergo distortion is called polarizability. The effect is polarization is as follows;



NB; Polarization is the distortion or deformation of an electron cloud of an anion by a cation.

If polarization is quite small the ionic bond results and it is high the electrons in the anion are drawn towards the cation to the extent that a covalent bond is formed .The polarizability and polarizing power of an ion is affected by;

1. The size of the ion
2. The charge on the ion

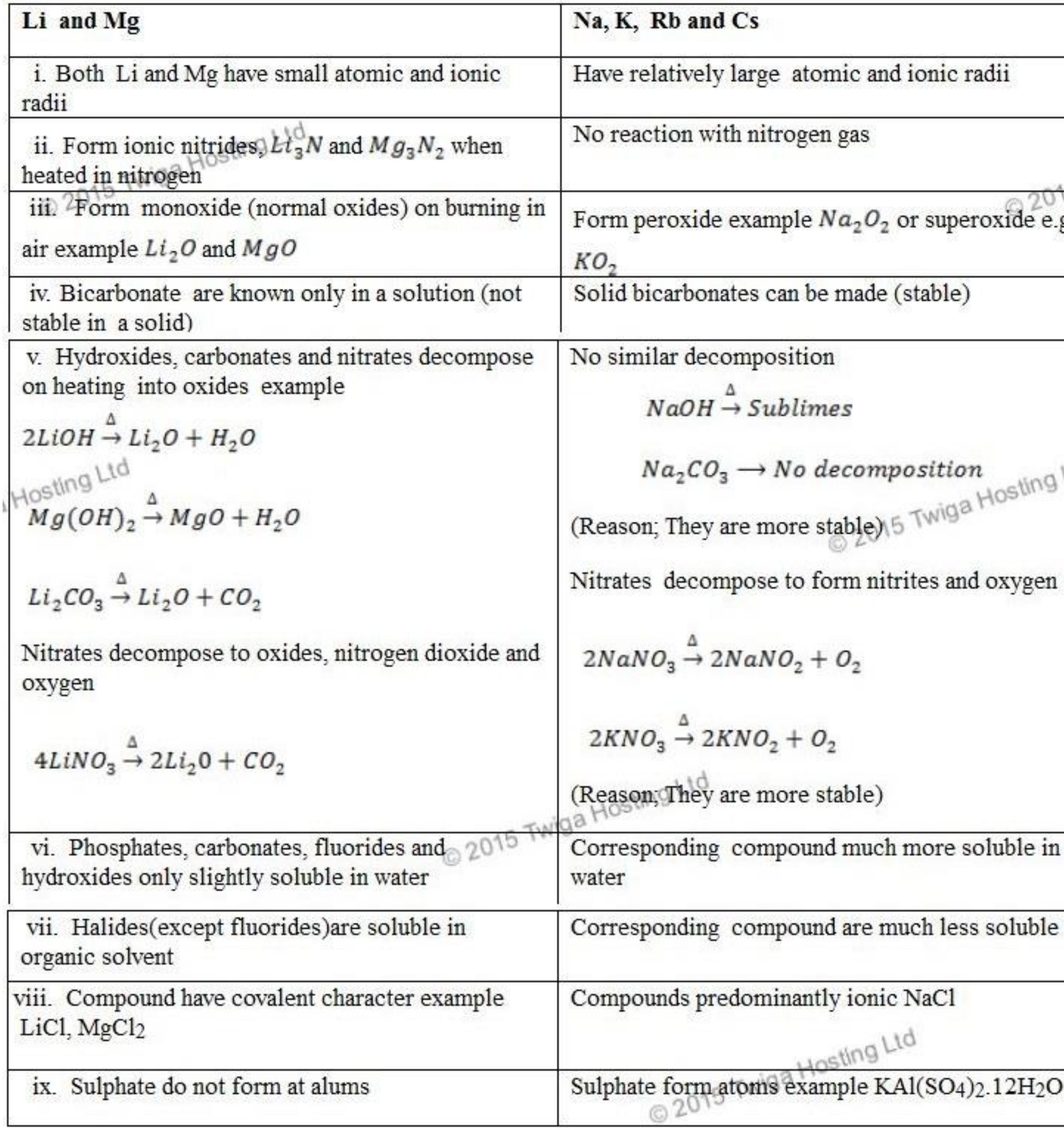
Thus polarizing power is high for a small ion which has high effective nuclear charge. On moving across a period from left to right, ionic radii decreases and effective nuclear charge increases. On descending a group ionic radii increases while the effective nuclear charge decreases. Hence the diagonal elements have similar polarizing power. Due to these elements have similar properties. The diagonal relationship can be represented as follows

Element	Li	Be	B	C	N	O	F
Electronegativity	1.O	1.5	2.0	2.5	3.0	3.5	4.0
Element	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

The relationship is most significant in the following pairs Li and Mg, Be and Al, Be and Si etc

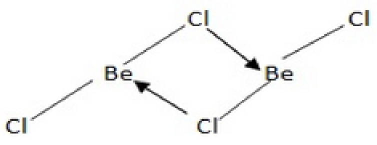
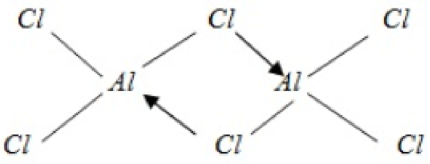
LITHIUM AND MAGNESIUM.

Lithium resembles magnesium and differs from the other alkali metals as follows;



Li and Mg	**Na, K, Rb and Cs**
i. Both Li and Mg have small atomic and ionic radii	Have relatively large atomic and ionic radii
ii. Form ionic nitrides, Li_3N and Mg_3N_2 when heated in nitrogen	No reaction with nitrogen gas
iii. Form monoxide (normal oxides) on burning in air example Li_2O and MgO	Form peroxide example Na_2O_2 or superoxide e.g KO_2
iv. Bicarbonate are known only in a solution (not stable in a solid)	Solid bicarbonates can be made (stable)
v. Hydroxides, carbonates and nitrates decompose on heating into oxides example $2LiOH \xrightarrow{\Delta} Li_2O + H_2O$ $Mg(OH)_2 \xrightarrow{\Delta} MgO + H_2O$ $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$ Nitrates decompose to oxides, nitrogen dioxide and oxygen $4LiNO_3 \xrightarrow{\Delta} 2Li_20 + CO_2$	No similar decomposition $NaOH \xrightarrow{\Delta} Sublimes$ $Na_2CO_3 \longrightarrow No\ decomposition$ (Reason; They are more stable) Nitrates decompose to form nitrites and oxygen $2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$ $2KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2$ (Reason; They are more stable)
vi. Phosphates, carbonates, fluorides and hydroxides only slightly soluble in water	Corresponding compound much more soluble in water
vii. Halides(except fluorides)are soluble in organic solvent	Corresponding compound are much less soluble
viii. Compound have covalent character example LiCl, MgCl2	Compounds predominantly ionic NaCl
ix. Sulphate do not form at alums	Sulphate form atoms example KAl(SO4)2.12H2O

BERYLIUM AND ALUMINIUM

Be and Al	**Mg, Ca , S r, and Be**
1) Compounds are mainly covalent example $BeCl_2, AlCl_3$	Main compounds are ionic, example $BaCl_2$, M
2) Metals react with concentration solutions of alkalis to form H_2 and hydro-complexes E.g. $Be_{(s)} + 2OH^-_{(aq)} + 2H_2O \longrightarrow Be(OH)^{2-}_{(aq)} + H_{2(g)}$ $Al_{(s)} + 2OH^-_{(aq)} + 6H_2O_{(l)} \longrightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)}$	No reaction
3) Oxides and hydroxides are amphoteric (example acidic and bases) As acids $Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_3O_{(l)} \rightleftharpoons 2NaAl(OH)_{4(aq)}$ $BeO_s + 2NaOH_{(aq)} + H_2O_{(l)} \longrightarrow Na_2Be(OH)_{4(aq)}$ As bases $BeO + 2HCl \longrightarrow BeCl_2 + H_2O$ $Al_2O_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$	Oxides and hydroxides are basic e.g. MgO, $Ca(OH)_2$, CaO etc
) Chlorides are readily hydrolyzed and exist as dimers (Be_2Cl_4 and Al_2Cl_6) the vapour state  Dimer of beryllium chloride  Dimer of Aluminium chloride	-Not hydrolyzed and ionic example $CaCl_2$ -The hydrated chloride of magnesium hydroly $MgCl_2.6H_2O_{(s)} \longrightarrow Mg(OH)_{2(aq)} + HCl_{(g)} +$
5) Form fluoro-complexes e.g. $[BeF_4]^{2-}$	No fluoro–complexes formed

QUESTION

outline factors that enable elements to have diagonal similarities

A. similar electronegativity
B. similar atomic and ionic sizes.
C. have ions with similar polarization power.

ANOMALOUS BEHAVIOUR OF THE FIRST ELEMENT IN A GROUP OF THE PERIODIC TABLE

The first element in every group of the period show some properties which are not shown to other elements in the respective group .The element is said to show anomalous behavior when its properties differ with those of the rest group member. The anomalous behavior of the first element in a group is due to the following factors,

A. The first element in a group has the smallest atomic and ionic size when compared with the rest group members

B. The first element in a group has the highest ionization energy

C. The first element in a group has the highest electronegativity

D. The first element in a group has the higher electronic affinity

ANOMALOUS BEHAVIOUR OF LITHIUM

I. Lithium forms covalent compounds while other alkali metals form ionic compound example LiCl is a covalence compound while NaCl is ionic

II. Lithium reacts with nitrogen gas on heating to form ionic nitride while other alkali metals do not react

$$6Li_{(s)} + N_{2(g)} \overset{\Delta}{\rightarrow} 2Li_3N_{(s)}$$

III. Lithium reacts slowly with cold water while other alkali metals react vigorously

IV. Lithium forms hydrated chloride while the rest group member form anhydrous chloride example $LiCl.2H_2O$ and NaCl (Li can polarize water due to high polarizing power)

V. When burnt in air ,lithium gives the monoxide while other alkali metals form peroxide and super oxide

$$Li_{(s)} + O_{2(g)} \xrightarrow{heat} Li_2O_{(s)}$$

Lithium monoxide

$$Na_{(s)} + O_{2(g)} \longrightarrow Na_2O_{(s)}$$

Sodium peroxide

$$K_{(s)} + O_{2(g)} \longrightarrow K_2O_{(s)}$$

Potassium peroxide

VI. Lithium does not form acetylide with ethyne (acetylene) while other alkali metals form acetylide with ethyne

$$H - C \equiv C - H_{(g)} + Na_{(s)} \overset{\Delta}{\rightarrow} Na^+C^- \equiv C^-Na^+ + H_{2(g)}$$

$$H - C \equiv C - H_{(g)} + Li_{(s)} \overset{\Delta}{\rightarrow} No\ reaction$$

VII. Lithium is only alkali metal whose salts may undergo hydrolysis

$$LiCl_{(s)} + H_2O_{(l)} \longrightarrow LiOH_{(aq)} + HCl_{(l)}$$

$$NaCl_{(s)} + H_2O_{(l)} \longrightarrow No\ reaction$$

VIII. The hydroxides of lithium decomposes on heating to monoxide and water while hydroxide of other alkali metals sublime undecomposed

$$LiOH_{(s)} \xrightarrow{heat} Li_2O_{(s)} + H_2O_{(l)}$$

$$NaOH_{(s)} \xrightarrow{heat} Sublime\ undecomposed$$

IX. Lithium nitrate decomposes on heating into Lithium monoxide, nitrogen dioxide and oxygen while the nitrates of other alkali metals decompose into nitrites and oxygen.

$$LiNO_{3(s)} \overset{\Delta}{\rightarrow} Li_2O_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

$$NaNO_{3(s)} \overset{\Delta}{\rightarrow} NaNO_{2(s)} + O_{2(g)}$$

$$KNOO_{3(s)} \overset{\Delta}{\rightarrow} KNO_{2(s)} + O_{2(g)}$$

X. Lithium carbonate decomposes gently heating into monoxide and carbon dioxide while the carbonates of other alkali metals are stable .They decompose at higher temperature.

e.g. $$Li_2CO_{3(s)} \overset{\Delta}{\rightarrow} Li_2O_{(s)} + CO_{2(g)}$$

$$Na_2CO_{3(s)} \xrightarrow[350°C]{\Delta} Na_2O_{(s)} + CO_{2(g)}$$

XI. Lithium hydroxide is less soluble in water and hence a much weak base than sodium hydroxide a and potassium hydroxide

XII. Lithium chloride is deliquescent while chloride at the rest group members aren't deliquescent

XIII. Lithium sulphate do not form alums while the sulphate of the rest group form alums

ANOMALOUS BEHAVIOUR OF BERYLIUM

1. Beryllium react with concentrated solution of alkali to form hydroxo-complexes and hydrogen gas while other alkaline earth metal do not react

E.g. $$Be_{(s)} + 2NaOH_{(aq)} + 2H_2O_{(l)} \longrightarrow NaBe(OH)_{4(aq)} + H_{2(g)}$$

$$Ca_{(s)} + NaOH_{(aq)}H_2O_{(l)} \longrightarrow No\ reaction$$

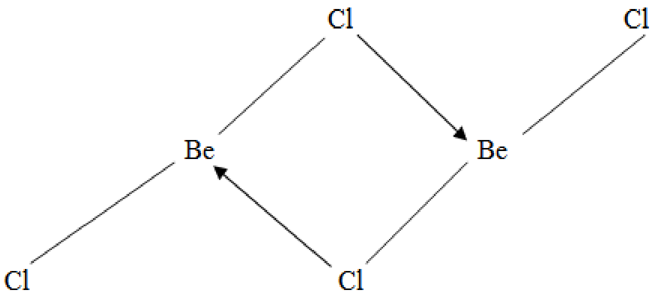
2. The oxides and hydroxides of beryllium are amphoteric while those of other alkaline earth metals are basic

3. Beryllium chlorides hydrolyze in water while the chlorides of the rest group members do not.

$BeCl_2 + H_2O \rightarrow Be(OH)_2 + 2HCl$ (Hydrolysis)

$$MgCl_2 + H_2O \longrightarrow No\ reaction$$

4. Beryllium chloride dimerize in vapour state while the chloride of the rest group member do not dimerize.



Beryllium chloride Dimer

5. Beryllium form fluoro-complexes while other alkali earth metals do not.

6. The chloride of beryllium readily dissolved in organic solvents while the chlorides of other alkali earth metals do not readily dissolved in organic solvents.

7. Beryllium do not react with water or steam while other group members can react with either cold or boiling water or steam.

8. Beryllium oxide do not react with water while the oxide of the rest group members react with water to form hydroxide.

$$CaO + H_2O \longrightarrow Ca(OH)_{2(aq)}$$

9. Beryllium do not react with either dilute or concentrated nitric acid (HNO_3) while the rest group member react with both dilute and concentrated HNO_3

10. Beryllium carbide hydrolyses in water to form methane while the carbides of other group members give ethyne

$$Be_2C_{(s)} + H_2O_{(l)} \longrightarrow BeO_{(s)} + CH_{4(g)} \quad (C^{4-}\ Oxidation\ state)$$

$CaC_{2(s)} + 2H_2O_{(cold)} \rightarrow Ca(OH)_2 + H - C \equiv C - H$ ($(C^- = C^-)^{-2}$ Oxidation state)

11. Beryllium chloride fumes in moist air while chloride of the rest group members do not.

$$BeCl_{2(s)} + H_2O_{(g)} \longrightarrow Be(OH)_{2(s)} + HCl_{(g)}$$

(From air)

The fumes are due to hydrolysis of $BeCl_2$ in water where HCl is given out.

ANOMALOUS BEHAVIOUR OF FLUORINE

Like other first elements in every group fluorine exhibit some properties which differ with the rest group members.

The anomalous behavior of fluorine is due to ;

i) Its smaller atomic and ionic size

ii) Absence of d-orbital

iii) Its highest electronegativity value

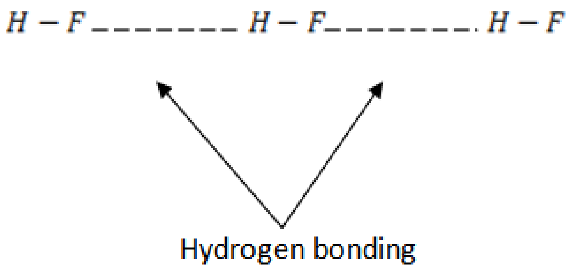
iv) Its higher electron affinity

The Anomalous behaviors of fluorine are as follows

1. Fluorine is a monovalent while other halogens show covalencies of 3 and 5. Chlorine and Iodine also show a valence of 7. Fluorine is a monovalent because it has no d-orbital while other members have d-orbital.

2. The elements in the periodic table show their highest oxidation states when combined with fluorine, example IF_7 and SF_8. This is due to highest electronegativity value of fluorine.

3. Fluorine forms hydrogen fluoride molecules which are strongly hydrogen –bonded. The hydrides of the rest halogens do not form hydrogen bonds between their molecules



4. The solubility of fluorides often differ markedly from the solubilities of other halides of the same metal, example the alkaline earth metal halides are very soluble in water except the fluorides which are insoluble .On the other hand silver fluoride is the only soluble silver halide. The fluorides of alkaline earth metal have higher lattice energies than hydration energies.

5. Metals show their highest degree of ionic character when combined with fluorine example AlF_3 and SnF_4 are ionic but AlCl_3 and SnF_4 are covalent compound.

6. Hydrogen fluoride form acidic salts containing the biflouride ion (HF_2^-). The halide of rest halogens form normal salts only, example $NaHF_2$ (Acidic salt), $NaCl, NaBr, KI$ etc.

7. Fluorine is the only halogen more electronegativity than oxygen and it often behaves differently to other halogens in reaction with oxygen containing compounds example water (F displaces O from water unlike others). Fluorine liberates oxygen from water while other halogens do not

$$2H_2O + 2F_2 \longrightarrow 4H^+ + 4F^- + O_2$$

Or

$$2H_2O + 2F_2 \longrightarrow 4HF + O_2$$

$$H_2O + Cl_2 \longrightarrow H^+ + Cl^- + HOCl$$

Or

$$H_2O + Cl_2 \longrightarrow HCl_{(aq)} + HOCl$$

8. Fluorine evolve oxygen from hot concentrated alkalis while other halogens form chloride and chlorate (v)

$$F_2 + 4OH^-_{(conc)} \overset{\Delta}{\rightarrow} 4F^- + O_2 + 2H_2O$$

$$Cl_2 + 6OH^-_{(conc)} \overset{\Delta}{\rightarrow} Cl^-_{(aq)} + ClO^-_{3(aq)} + 3H_2O_{(aq)}$$

(Chlorate ion)

$$Cl_2 + NaOH_{(aq)} \overset{\Delta}{\rightarrow} NaCl + NaClO_3 + 3H_2O$$

With cold dilute alkalis fluorine given a fluoride and difluorine monoxide while chlorine form chloride and hypochlorite.

$$F_2 + 2OH^-_{(aq)} \longrightarrow 2F^-_{(aq)} + F_2O + H_2O$$

(Difluorine monoxide)

$$Cl_2 + 2OH^-_{(aq)} \longrightarrow Cl^-_{(aq)} + ClO^- + H_2O$$

(Hypochlorite ion)

$$Cl_2 + NaOH \longrightarrow NaCl_{(aq)} + NaClO_{(aq)} + H_2O$$

9. Fluorine combines directly with carbon while other halogens have no effect on it.

SELECTED COMPOUNDS OF METALS.

(i.e COMPOUNDS OF Na, Mg, Ca, Al, Fe, Zn, Cu AND Pb)

METAL OXIDES

Definition; An oxide is binary compound made up of oxygen and other elements, example MgO, PbO, Al_2O_3, H_2O_2, NO_2, SO_2 etc

Therefore metal oxides are binary compounds made up of oxygen and metal, example PbO, FeO, , etc

NOTE: The binary oxygen – fluorine compounds are not called oxides of fluorine, but are called fluorides of oxygen since fluorine is more electronegative than oxygen (example OF_2- oxygen difluorine)

GENERAL METHODS IN PREPARATION OF METAL OXIDES.

There are two methods of preparing metal oxides

a) DIRECT METHOD

b) INDIRECT METHOD

A. DIRECT METHOD OF PREPARATION OF METAL OXIDES

In this method a metal reacts with a reagent or oxygen or air to give metallic oxide

I) A metal oxide may be prepared by burning a metal in air or oxygen

$$2Mg_{(s)} + O_{2(g)} \overset{\Delta}{\rightarrow} 2MgO_{(s)}$$

$$4Na_{(s)} + O_{2(g)} \overset{\Delta}{\rightarrow} 2Na_2O_{(s)}$$

$$4K_{(s)} + O_{2(g)} \overset{\Delta}{\rightarrow} 2K_2O_{(s)}$$

II) A metal oxide may be prepared by passing steam on red heat metal

$$3Fe_{(s)} + 4H_2O_{(g)} \overset{\Delta}{\rightarrow} Fe_3O_{4(s)} + 4H_{2(g0}$$

III) A metal oxide may be prepared by reacting a metal with an oxidizing agent like HNO_3

$$Sn_{(s)} + Conc\ 4HNO_{3(aq)} \longrightarrow SnO_{2(s)} + 4N0_{2(g)} + 2H_2O_{(l)}$$

B. INDIRECT METHOD OF PREPARATION OF METAL OXIDES

In this method, the metal oxide is obtained by heating carbonates, hydroxides and nitrates etc

Example;

$$CaCO_{3(s)} \overset{\Delta}{\rightarrow} CaO_{(s)} + CO_{2(g)}$$

$$Cu(OH)_{2(s)} \overset{\Delta}{\rightarrow} CuO_{(s)} + H_2O_{(g)}$$

$$2Pb(NO_3)_{2(s)} \overset{\Delta}{\rightarrow} 2PbO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

$$Al_2(SO_4)_{3(s)} \overset{\Delta}{\rightarrow} Al_2O_{3(s)} + 3SO_{3(g)}$$

$$FeSO_4.7H_2O_{(s)} \overset{\Delta}{\rightarrow} FeO_{(s)} + SO_{3(g)} + 7H_2O_{(s)}$$

$$MgCO_{3(s)} \overset{\Delta}{\rightarrow} MgO_{(s)} + CO_{2(g)}$$

TYPES OF METALLIC OXIDE

The metal oxides may be classified as follows:

1) BASIC OXIDE

2) ACIDIC OXIDES

3) AMPHOTERIC OXIDES

4) PEROXIDES

5) SUPEROXIDE

6) MIXED OXIDES

1. BASIC OXIDES

These are oxides which react with acids to form salt and water only. They also combine with acidic oxides to form salts. Basic oxides may be ionic or covalent

$$CuO_{(s)} + H_2SO_{4(aq)} \longrightarrow CuSO_{4(aq)} + H_2O_{(l)}$$

$$FeO_{(s)} + H_2SO_{4(aq)} \longrightarrow FeSO_{4(aq)} + H_2O_{(l)}$$

$$MgO_{(s)} + HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_2O_{(l)}$$

$$CaO_{(s)} + SiO_{2(s)} \overset{\Delta}{\rightarrow} CaSiO_{3(s)}$$

$$Na_2O_{(s)} + CO_{2(g)} \longrightarrow Na_2CO_{3(s)}$$

$$PbO_{(s)} + SO_{3(g)} \overset{\Delta}{\rightarrow} PbSO_{4(s)}$$

$$Al_2O_{3(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_2O_{(l)}$$

2. ACIDIC OXIDE

Acidic oxide are formed by metals in their higher oxidation states, example $\mathrm{CrO_3, Mn_2O_7, SnO_2, Fe_2O_3}$ etc

These oxides are generally covalent in nature. They dissolve in water to form oxy-acids and hence are called acid anhydrides.

$$SnO_2 + H_2O \longrightarrow H_2SnO_3 \quad \text{(Stannic acid)}$$

$$CrO_3 + H_2O \longrightarrow H_2CrO_4 \quad \text{(Chromic acid)}$$

$$Mn_2O_7 + H_2O \longrightarrow 2HMnO_4 \quad \text{(Permanganic acid)}$$

3. AMPHOTERIC OXIDE

These are oxides with both basic and acidic properties. They react with both acids and bases. Amphoteric oxides include ZnO, Al_2O_3, BeO, PbO, SnO_2, Cr_2O_3, Fe_2O_3, MnO_2 etc

i) AS BASES: They react with acids to form salt and water only

$$PbO_{(s)} + 2HCl_{(aq)} \longrightarrow PbCl_{2(aq)} + H_2O_{(l)}$$

$$Al_2O_{3(s)} + 6HCl_{(aq)} \longrightarrow AlCl_{3(aq)} + 3H_2O_{(l)}$$

$$Cr_2O_{3(s)} + H_2SO_{4(aq)} \longrightarrow Cr_2(SO_4)_{3(aq)} + 3H_2O_{(l)}$$

$$ZnO_{(s)} + H_2SO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + H_2O_{(l)}$$

ii) AS ACIDIC OXIDES: These react with bases to form salt and water

$$SnO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SnO_{3(aq)} + H_2O_{(l)}$$

Sodium metastannate

$$PbO_{(s)} + 2NaOH_{(aq)} \longrightarrow Na_2PbO_{2(aq)} + H_2O_{(l)}$$

$$ZnO_{(s)} + 2NaOH_{(aq)} \longrightarrow Na_2ZnO_{2(aq)} + H_2O_{(l)}$$

$$Al_2O_{3(s)} + 2NaOH_{(aq)} \longrightarrow 2NaAlO_{2(aq)} + H_2O_{(l)}$$

$$Fe_2O_{3(s)} + 2NaOH_{(aq)} \longrightarrow 2NaFeO_{2(aq)} + H_2O_{(l)}$$

Sodium ferrite

4. PEROXIDES

Peroxides are compounds containing the peroxide ion Na_2O_2 Peroxides of alkali metals and alkaline earth metals can be prepared.

a) By heating the metal in the presence of excess oxygen or air

$$2Na + O_{2(Excess)} \xrightarrow{300°C} Na_2O_2$$

b) By heating the monoxides of the metal alone or in the presence of oxygen/air.

$$2Na_2O \xrightarrow{7400°C} Na_2O_2 + 2Na_{(g)}$$

$$2BaO + O_2 \xrightarrow{500°C} 2BaO_2$$

c) By the action of oxygen or air on the metal dissolved in liquid ammonia. This method is for the preparation of K_2O_2, Rb_2O_2 and Cs_2O_2

d) By the action of H_2O_2 on metallic salt solution in the presence of an alkali.

$$BaCl_2 + H_2O_2 + 2KOH \longrightarrow BaO_2 + KCl + 2H_2O$$

PROPERTIES OF PEROXIDES

- Stability of peroxides increases with increasing of the electropositive character of the metal
- Peroxides are more stable in dry state than when they are in solution form
- Many peroxides are highly hydrated due to hydrogen bonding,

example $Na_2O_2.8H_2O$, $CaO_2.8H_2O$, $BaO_2.2H_2O$ etc

- They dissolved in water to form alkaline solution and hydrogen peroxide

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

(Ice-cold water)

- When treated with dilute mineral acids peroxides give H_2O_2

$$Na_2O_{2(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{2(aq)}$$
$$BaO_{(s)} + H_2SO_{4(aq)} \longrightarrow BaSO_{4(s)} + H_2O_{2(aq)}$$

- Peroxide give O_2 on heating and hence act as oxidizing agents

$$Na_2O_2 + 2Cr(OH)_3 \longrightarrow 2Na_2CrO_4 + 2NaOH + 2H_2O$$

NB: PbO_2 is not peroxide since this oxides does not give water when treated with mineral acids.

5. SUPEROXIDES

These are oxides of metals containing the ion the known superoxides are these of potassium (KO_2), Rubidium (RbO_2) and Caesium (Cs_2O_2)

Preparation

$$M + O_2 \xrightarrow{\Delta} MO_2 \qquad (M = K, Rb \text{ or } Cs)$$

Superoxides of K, Rb, and Cs can be prepared by burning the metal in excess of oxygen or air

PROPERTIES OF SUPEROXIDES.

- They are yellow solids

- The stability of these superoxides is in the order **KO_2 Rb CsO_2**
- They are strong oxidizing agents
- They are hydrolyzed by water forming H_2O_2 and oxygen.

$$KO_2 + H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$

Ionically;

$$2O_2^- + 2H_2O \longrightarrow 2OH^- + H_2O_2 + O_2$$

- Superoxides are paramagnetic in nature due to the presence of one unpaired electron in ion.

6. MIXED OXIDES

These are oxides composed of two simple oxides. The two simple oxides may be of the same metal or different metal in different oxidation states, example Red–Lead **(Pb_3O_4)** is combination of 2PbO and. Due to this can be written ionically

Also magnetite **(Fe_3O_4)** is a combination of **FeO** and **Fe_2O_3**

The mixed oxides with different metals are as follows;

Magnesium ferrite **($MgFe_2O_4$) $MgOFe^{3+}{}_2O_3$**

$ZnFe_2O_4$ $nOFe_2^{3+}O_3$ (Zinc ferrite)

PROPERTIES

- It is a brilliant scarlet (bright red) solid insoluble in water
- Red lead behaves chemically as if it were a loose compound of lead monoxide (PbO) and lead dioxide (PbO_2). For example it reacts with dilute HNO_3 on warming to give and water whereby PbO_2 is left with no reaction

$$2PbO.PbO_{2(s)} + 4HNO_{3(aq)} \longrightarrow 2Pb(NO_3)_{2(aq)} + PbO_{2(s)} + 2H_2O_{(l)}$$

- The reaction above is a redox reaction indicating that is a reducing agent

USES; Red-lead is used as pigment in oil plants

FERROUS –FERRIO OXIDE (Fe_3O_4) ($FeO.Fe_2O_3$)

Fe_3O_4 occurs naturally as Magnetite. It may be prepared by heating iron with oxygen or steam

$$Fe + 4H_2O_{(g)} \overset{\Delta}{\rightarrow} Fe_3O_4 + 4H_2$$

PROPERTIES

- The compound is black in color

- Very strongly ferromagnetic

- The compound is inactive chemically

- React with acids as a double oxide giving a mixture of ferrous and ferric salts in solution

$$Fe_3O_{4(s)} + 6H^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} + 4H_2O_{(l)}$$

HYDROXIDES OF THE METALS

These are compounds of metals which contains hydroxide ions (OH^-) as the only negatively charged ion, example NaOH, $Mg(OH)_2$, Zn(OH, $Fe(OH)_3$

PREPARATION OF METAL HYDROXIDES

There are two methods of preparation of metal hydroxides.

A) DIRECT METHOD OF PREPARATION OF METAL HYDROXIDES

The hydroxides which can be prepared by this method are those composed of strongly electropositive metals. Example LiOH, NaOH and $Ca(OH)_2$

Example

$$Na_{(s)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + {}^1/_2\, H_{2(g)}$$

$$Ca_{(s)} + 2H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)} + H_{2(g)}$$

B) INDIRECT METHOD OF PREPARATION OF METAL HYDROXIDES

In this method the metal hydroxide is prepared by

a) The action of water on the metal oxide;

example

$$Na_{(s)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + {}^1/_2\, H_{2(g)}$$

$$Ca_{(s)} + 2H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)} + H_{2(g)}$$
$$BaO_{(s)} + H_2O_{(l)} \longrightarrow Ba(OH)_{2(aq)}$$

NB: the metal hydroxides which are prepared by action of water on metal oxides are soluble in water.

b) Action of calcium hydroxides (milk of lime) on a solution of carbonate, example preparation of NaOH and KOH. These metal hydroxides are prepared by precipitation the unwanted ions and layering a solution of the alkali. For instance when potassium carbonates and (Ca(OH) solution are mixed and then allowed to settle, a solution of potassium hydroxides may be decanted

$$Ca(OH)_{2(aq)} + K_2CO_{3(aq)} \overset{\Delta}{\rightarrow} CaCO_{3(ppt)} + 2KOH_{(aq)}$$

c) Precipitation of a metal hydroxide by adding ammonia solution or sodium hydroxide solution to a solution of salt of the metal

$$AlCl_3 + NaOH_{(aq)} \longrightarrow Al(OH)_{3(s)} + 2NaCl_{(aq)}$$

$$AlCl_{3(aq)} + 3NH_4OH_{(aq)} \longrightarrow Al(OH)_{3(s)} + 3NH_4Cl_{(aq)}$$

$$FeSO_{4(aq)} + NaOH_{(aq)} \longrightarrow Fe(OH)_{(s)} + Na_2SO_{4(aq)}$$

$$CuCl_{2(aq)} + 2NH_4OH_{(aq)} \longrightarrow Cu(OH)_{2(s)} + 2NH_4Cl_{(aq)}$$
$$Pb(NO_3)_{2(aq)} + 2NaOH_{(aq)} \longrightarrow Pb(OH)_{2(s)} + 2NaNO_{3(aq)}$$

d) Electrolysis of a solution of the metal chloride, example preparation of NaOH. Alkali metal chlorides form conducting solutions and since these metals are highly in the electrochemical series, their ions remain in solutions during electrolysis and hydrogen evolved at the cathode. Preferential discharge of chlorides ions enable hydroxyl ions formed by ionization of the water to accumulates in the solution. As a result dilute solution of the metal hydroxide is produced

PROPERTIES OF METAL HYDROXIDES OF THE SELECTED METALS

1. ALKALI METAL HYDROXIDES (MOH)

PHYSICAL PROPERTIES

-The hydroxides of group IA metals are white crystalline solids

-They melt at moderate temperature without decomposition except (LiOH)

-They are deliquescent solids

-They are very soluble in water (form alkali solutions)

CHEMICALS PROPERTIES

-The basic strength of the alkali increases down the group, example calcium is the strongest base

-When cold and dilute alkali's reacts with chlorine to form metal chloride and hydrochlorite

$$2NaOH_{(aq)} + Cl_{2(g)} \longrightarrow NaCl + NaClO + H_2O$$

-When hot and concentrated alkali's react with chlorine to form metal chloride and chlorate (v)

$$6NaOH_{(aq)} + 3Cl_{2(g)} \longrightarrow 5NaCl_{(aq)} + NaClO_{3(aq)} + 3H_2O_{(l)}$$

$$6KOH_{(aq)} + 3Cl_{2(g)} \longrightarrow 5KCl_{(aq)} + KClO_{3(aq)} + 3H_2O_{(l)}$$

In the two reactions chlorine undergoes disproportion

- Most NaOH and KOH absorbs CO_2 from the air whereby a metal carbonates is formed

$$NaOH_{(s)} + CO_{2(g)} \longrightarrow Na_2CO_{3(s)} + H_2O_{(l)}$$

- The hydroxides of Group IA metal reacts with acids to form salts and water only, example undergo neutralization reaction

$$KOH_{(aq)} + HNO_{3(aq)} \longrightarrow KNO_{3(aq)} + H_2O_{(l)}$$

USES OF HYDROXIDES OF Na AND K

1. Owning to their highly basic character alkali metal hydroxides are used to absorb acidic gases, example CO_2
2. Alkali metal hydroxides are used in neutralization reaction.

Example

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

3. Alkali metal hydroxides are used in precipitation reaction

Example

$$Fe^{2+}_{(aq)} + 3OH^-_{(aq)} \longrightarrow Fe(OH)_{3(s)}$$

$$Zn^{2+}_{(aq)} + 3OH^-_{(aq)} \longrightarrow Zn(OH)_{3(s)}$$

4. Caustic soda (NaOH) is used in the manufacture of silk, paper and soap
5. Caustic potash (KOH) is used to manufacture soft soaps

2. ALKALINE EARTH METAL HYDROXIDES ($M(OH)_2$)

PHYSICAL PROPERTIES

- They are white crystalline solids

- Solubilities increases considerably down the group from beryllium hydroxides (Be) to barium hydroxides (Ba). Beryllium hydroxide is insoluble in water.

Solubility of calcium hydroxide decreases with rise in temperature, the others increase, magnesium slightly but strontium and barium hydroxide greatly. Increase in solubility down the group is due to the fact that lattice energy decreases faster than hydration energy (Be() is essentially covalent because of the high polarizing effect of the small

- Group IIA hydroxides are much less soluble

$$2NaOH_{(aq)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + H_2O_{(l)}$$

-The hydroxides of Na and K precipitates some metals from their soluble salts (example, Aqueous solutions of their salts) as hydroxides

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Fe(OH)_{2(s)}$$

$$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Cu(OH)_{2(aq)}$$

$$Pb^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Pb(OH)_{2(aq)}$$
$$Fe^{2+}_{(aq)} + OH^-_{(aq)} \longrightarrow Fe(OH)_{2(aq)}$$

- Both NaOH and KOH liberates ammonia gas when added to ammonium salts

$$OH^-_{(aq)} + NH^+_{4(aq)} \longrightarrow NH_{3(g)} + H_2O_{(l)}$$

$$NaOH_{(aq)} + NH_4Cl_{(s)} \longrightarrow NaCl_{(aq)} + NH_{3(g)} + H_2O_{(l)}$$

REACTION WITH AMPHOTERIC METALS

Zinc, Aluminium, Lead and Tin react with hydroxides of sodium and potassium to form complexes, example aluminate, plumbate, zincate and stumnate.

$$2Al_{(s)} + 2OH^-_{(aq)} + 6H_2O_{(l)} \longrightarrow 2[Al(OH)_4]^-_{(aq)} + 3H_{2(g)}$$

Aluminate ion

$$Zn_{(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \longrightarrow [Zn(OH)_4]^{2-}_{(aq)} + H_{2(g)}$$

Zincate ion

$$Pb_{(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \longrightarrow [Pb(OH)_4]^{2-}_{(aq)} + H_{2(g)}$$

Plumbate ion

REACTION WITH CARBONDIOXIDE

When **CO_2** is bubbled through aqueous solutions of the **NaOH** and **KOH** the carbonates are formed,With excess of the **CO_2** the hydrogen carbonates are formed.

$$NaOH_{(aq)} + CO_{2(g)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$$
$$Na_2CO_{3(aq)} + CO_{2(g)} + H_2O_{(l)} \longrightarrow NaHCO_{3(aq)}$$

Of group IA elements due to the decrease in metallic character of the elements (example Group IA elements are more electropositive than their corresponding Group IIA elements). Also the decrease in solubility may be due to decrease ionic character of the hydroxides from Group IA to Group IIA

NB; A Suspension of slaked lime(calcium hydroxide) in water is called Milk of lime

CHEMICAL PROPERTIES

1. ACTION WITH ACIDS AND ALKALIS

- Beryllium hydroxide is amphoteric. It reacts with excess sodium hydroxide forming a solution of sodium beryllate

$$Be(OH)_{2(aq)} + 2NaOH_{(aq)} \longrightarrow Na_2Be(H)_{4(aq)}$$

Sodium beryllate

The other hydroxide of group IIA metals do not react with alkalis but react with acids to form salt and water only

$$Ca(OH)_{2(aq)} + HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_2O_{(l)}$$

$$Mg(OH)_{2(aq)} + 2HNO_{3(aq)} \longrightarrow Mg(NO_3)_{(aq)} + 2H_2O_{(l)}$$

2. ACTIONS WITH CARBON DIOXIDE

- Moist hydroxides absorb CO_2 from air forming carbonates

$$Ca(OH)_{2(s)} + CO_{2(g)} \longrightarrow CaCO_{3(aq)} + H_2O_{(l)}$$

- When is bubbled through lime water ($Ca(OH)_2$) white precipitate of $CaCO_3$ are formed. This causes the lime water to turn milky. The milky colour disappears when excess CO_2 in bubbled through it. The milky colour disappears because calcium carbonates is converted into calcium hydrogen carbonate which is soluble in water

$$Ca(OH)_{2(aq)} + CO_{2(g)} \longrightarrow CaCO_{3(aq)} + H_2O_{(l)}$$

Clean solution White precipitate (milky)

$$CaCO_{3(aq)} + CO_{2(g)} + H_2O_{(l)} \longrightarrow Ca(HCO_3)_{2(aq)}$$

(Milky) (Excess) Clear solution

3. ACTION OF HEAT

The temperature at which the hydroxides begin to decompose increases down the group from about 300^{0}C for beryllium hydroxide and magnesium hydroxide to about 700^{0}C for barium hydroxide.

Example

$$M(OH)_{2(s)} \overset{\Delta}{\rightarrow} MO_{(s)} + H_2O_{(g)}$$

$$Mg(OH)_{2(aq)} \overset{\Delta}{\rightarrow} MgO_{(s)} + H_2O_{(g)}$$

4. ACTION WITH AMMONIUM SALTS

All the hydroxides except $Be(OH)_2$ react with aqueous ammonium salts to give ammonia gas. The ammonia gas is easily identified because it turn alkaline to litmus paper.

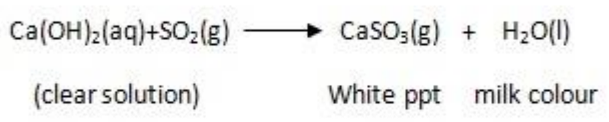
Example

$$OH^-_{(aq)} + NH^+_{4(aq)} \longrightarrow NH_{3(g)} + H_2O_{(l)}$$

$$NaOH_{(aq)} + NH_4Cl(aq) \longrightarrow NaCl_{(aq)} + NH_{3(g)} + H_2O_{(l)}$$

5. ACTION WITH SULPHUDIOXIDE

Sulphur dioxide turn lime water milky due to calcium sulphite formed. When excess SO_2 is added the milky colour disappears (example, a clear solution is formed). The milky colour disappears due to the formation of calcium bisulphite which is soluble in water.



$$\underset{\text{(clear solution)}}{Ca(OH)_2(aq)+SO_2(g)} \longrightarrow \underset{\text{White ppt}}{CaSO_3(g)} + \underset{\text{milk colour}}{H_2O(l)}$$

USES

1. Lime water is used to test for carbon dioxide.

2. A suspension of Magnesium hydroxide in water (milk of magnesium)is used as an ant-acid.

3. $Ca(OH)_2$ is used in making builders mortar (mixture of slaked lime, sand and water).

4. A mixture of $Ca(OH)_2$ is used in making bleaching powder.

5. $Ca(OH)_2$ is used for neutralizing acids in the soil.

6. A mixture $Ca(OH)_2$ and water (white wash) is used for coating walls and ceiling.

7. $Ca(OH)_2$ is used in water softening.

$$Mg(HCO_3)_{2(aq)} + Ca(OH)_{2(aq)} \rightarrow CaCO_{3(s)} + MgCO_3 + 2H_2O$$

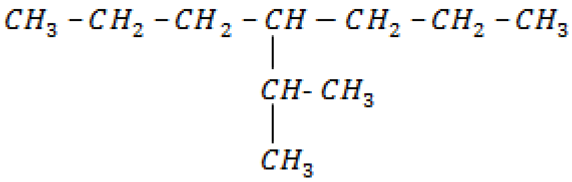
8. $Ca(OH_2)$ is used in sugar refining filtered.

ORGANIC CHEMISTRY 1

ALIPHATIC HYDROCARBONS:

Nomenclature:

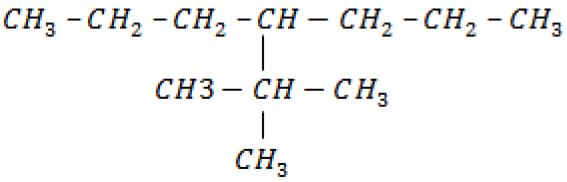
i)



$$\begin{array}{ccccccccccccc} CH_3 & - & CH_2 & - & CH_2 & - & CH & - & CH_2 & - & CH_2 & - & CH_3 \\ &&&&&& | &&&&&& \\ &&&&&& CH\text{-}\ CH_3 &&&&&& \\ &&&&&& | &&&&&& \\ &&&&&& CH_3 &&&&&& \end{array}$$

Name: 4 - (1 - methyl ethyl) heptane

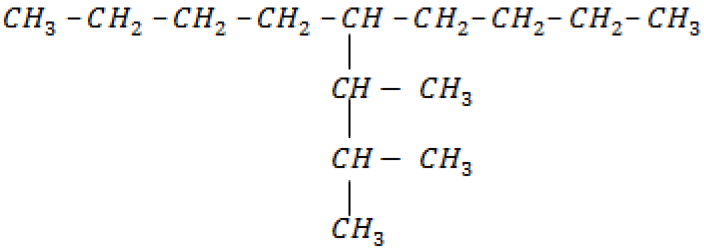
ii)



$$\begin{array}{ccccccccccccc} CH_3 & - & CH_2 & - & CH_2 & - & CH & - & CH_2 & - & CH_2 & - & CH_3 \\ &&&&&& | &&&&&& \\ &&&& CH3 & - & CH & - & CH_3 &&&& \\ &&&&&& | &&&&&& \\ &&&&&& CH_3 &&&&&& \end{array}$$

Name: 4 - (1, 1 - dimethylethyl) heptane

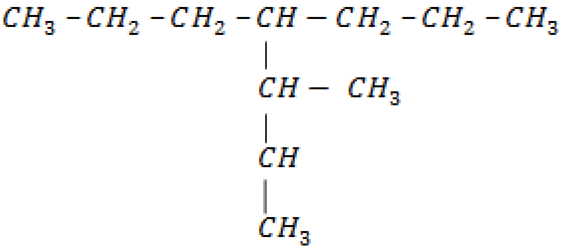
iii)



$$\begin{array}{ccccccccccccccccc} CH_3 & - & CH_2 & - & CH_2 & - & CH_2 & - & CH & - & CH_2 & - & CH_2 & - & CH_2 & - & CH_3 \\ &&&&&&&& | &&&&&&&& \\ &&&&&&&& CH & - & CH_3 &&&&&& \\ &&&&&&&& | &&&&&&&& \\ &&&&&&&& CH & - & CH_3 &&&&&& \\ &&&&&&&& | &&&&&&&& \\ &&&&&&&& CH_3 &&&&&&&& \end{array}$$

Name: 5 - (1, 2 - Dimethypropyl) nonane

iv)



$$\begin{array}{ccccccccccccc} CH_3 & - & CH_2 & - & CH_2 & - & CH & - & CH_2 & - & CH_2 & - & CH_3 \\ &&&&&& | &&&&&& \\ &&&&&& CH & - & CH_3 &&&& \\ &&&&&& | &&&&&& \\ &&&&&& CH &&&&&& \\ &&&&&& | &&&&&& \\ &&&&&& CH_3 &&&&&& \end{array}$$

METHODS OF PREPARATION OF ALKANES

(a) Hydrogenation of Alkenes and Alkynes

Alkenes and alkynes react with hydrogen in presence of catalyst eg Ni/Pt around 200°c or 300°c

From Alkenes

$$R\text{- }CH = CH_2 + H_2 \xrightarrow[300^{\circ}C]{PT} R\text{- }CH_2\,CH_3$$

$$CH_3\text{- }CH{=}\,CH\text{- }CH_3 + H_2 \ \underline{Ni}\ CH_3\,CH_2\,CH_2\,CH_3$$

ALKYNES:

E.g.

$$R\text{- }C \equiv C - H + 2H \xrightarrow[300^{\circ}C]{PT} R\text{- }CH_2\,CH_3$$

$$CH_3\,C \equiv CH + H_2 \xrightarrow[300^{\circ}C]{PT} CH_3\,CH_2\,CH_3$$

(b) Method 2 of preparation

Alkyl halide (haloalkanes)

$R - X;\ Cl, Br, I, F$

a) Reduction of alkyl halide by metal and acid

$$R - x + Zn + H^{+} \longrightarrow R - H + Zn^{2+} + X^{-}$$

$$\text{Eg. } CH_3CH_2Br + Zn + H^{+} \longrightarrow CH_3\,CH_3 + Zn^{2+} + Br^{-}$$

The hydrogen displaces Bromine. Only done in the presence of Zn metal

b) Reduction of Alkyl halide by using zinc and copper coupled with alcohol

$$R - x \xrightarrow[\text{alcohol}]{\text{zn/cu}} R - H + X^{-}$$

Note:

Both zinc and copper must be present together with alcohol.

$$\text{E.g. } CH_3\,CH_2\,CH_2\,I \xrightarrow[alcohol]{zn/cu} CH_3\,CH_2\,CH_3 + I^-$$

c) **Reduction of alkyl halide by using hydroiodic acid in the presence of red phosphorus**

$$R-X+HI \xrightarrow{red\ P} R-H\ +I^- +\ X^-$$

NOTE:

Function of red phosphorus is removing iodide so that hydrogen can react with the alkyl halide.

$$CH_3\,CH_2\,Cl + HI \xrightarrow{red\ P} CH_3\,CH_3$$

(c) Wurtz Synthesis

Alkyl halide in dry either solution react with sodium to produce alkane always the product has twice the number of carbon as that of alkyl halide.

$$2R-X+2Na \xrightarrow{dry\ ether} R-H+2NaX$$

$$2\,CH_3\,CH_2\,Br + Na \xrightarrow{dry\ ether} CH_3\,CH_2\,CH_2\,CH_3 + NaBr$$

ii) $$2\,CH_3\,I + 2Na \xrightarrow{dry\ ether} CH_3\,CH_3 + 2NaI$$

NOTE:

Dry ether is very important condition.

(d) Decarboxilation of sodium carboxilate salt

This is the reaction between carboxylic salt and sodium hydroxide in the presence of calcium oxide. The product will have 1carbon less than the reactant.

$$R - COONa + NaOH \rightarrow R - H + Na_2CO_3$$

$$Eg.\ CH_3CH_2COONa + NaOH \rightarrow CH_3CH_3 + Na_2CO_3$$

Exercise (H/W)

1. Preparation of alkanes from petroleum, coal, natural gas.

2. Read on method of preparation known as cracking. Preparation of alkanes from petroleum and natural gas.

- Petroleum is formed from the remains of tiny marine organisms that died and sank to the bottom of the sea millions of years ago.

- Petroleum is a mixture of many organic compounds, since the organic compounds are lighter than both the rock and the water they move upwards through the adjacent rock. Sometimes the organic Compound are trapped in porous rocks that are called reservoirs beneath impermeable rocks.

- Example of reservoir is limestone.

- Reservoirs from which petroleum can be extracted by drilling are referred to as oil fields.

- The petroleum obtained is referred to as a crude oil.

Fractional distillation of crude oil:

- Major components of crude oil are:-

(i) Residuals (coke, asphalt, tar).

(ii) Lubricating oils.

(iii) Fuel oils.

(iv) Diesels.

(v) Kerosene.

(vi) Naptha.

(vii) Petrol.

(viii) Petroleum gas.

The components of the crude oils are known as fractions and different fractions are separated by heating them in a process known as Fractional distillation and it is done in a distillation tower called a still.

The oil is first evaporated by heating . The vapour rises up and the tower acts as a giant heat exchanger removing heat from the gases as they rise up. Temperature falls to 20 °C by the time vapour reaches the top. The vapour condenses as they rise up.

The heavier ones i.e. those with higher boiling points condense first. Gaseous fractions pass out at the top.

Cracking

Some of the fractions obtained from the fractional distillation of the crude oil are converted into new products.

Cracking is the conversion of large molecules of organic compounds into compounds with smaller molecules.

There are two methods;-

(i) Thermal cracking.

(ii) Catalytic cracking.

In thermal cracking the large molecule organic compound is heated to a high temperature until its molecule break apart.

In catalytic cracking, a catalyst speeds up the cracking process.

(e) Preparation of Alkanes from alcohols:

By reduction of alcohols:

When alcohols are hated with concentrated hydroiodic acid and red phosphorus at 423k under high pressure, alcohols can be reduced to alkanes.

$$R - OH + HI \xrightarrow{red\ P} R - H + I_2 + H_2O\ (1)$$

Red phosphorus reacts with Iodine formed

$$CH_3\ CH_2\ OH + HI \xrightarrow{red\ P} CH_3\ CH_3 + I_2 + H_2\ O$$

Physical properties of alkanes:

(a) Boiling point and melting point:

Alkanes have low melting point and boiling point.

Reason: Since alkanes are non-polar molecules with weak Van – der - Waal forces between them then low temperature is required to break the bond hence low melting and boiling point.

$$\begin{array}{c} CH_4 \\ CH_3CH_3 \\ CH_3CH_2CH_3 \end{array} \Bigg\downarrow$$

Increase in molecular mass leading to the increase in melting & Boiling points

NB:

If you compare straight chain and branched chain of same molecular mass; straight chain has higher M.P &B.P. Branched chained isomers have lower boiling points and melting point than straight chain isomer.

Reason: Branched chains are more compact hence have less surface area. This is why they have low M.P and B.P. Straight chains have higher surface area.

(b) Solubility:

They are soluble in non polar organic solvents but insoluble in polar compounds e.g. Water.

Chemical properties of alkanes:

In general, alkanes are non reactive (inert) compared to other classes of organic compounds.

Reason:

(i) They don't have a functional group.

(ii) There bonds are quite strong i.e. c – c (strong bond). Large energy is needed to break the bond hence less reactive.

(iii) These two bounds are almost non polar and therefore neither electrophilic nor nucleophilic substitution reaction can take place. Can't react with electron - loving species or a proton loving species (Nucleophilic).

- Electrophilic reacts with a negatively charged species.
- Nucleophilic reacts with a positively charged species.

Alkanes can undergo the following reaction;-

(i) Substitution reaction.

(ii) Oxidation reaction.

(iii) Thermal decomposition (cracking).

All these reactions take place at high temperature or under the presence of light energy.

I. SUBSTITUTION REACTIONS

a) Halogenations $(X_2 - F_2, Cl_2, Br_2)$

- This is addition of halogens.
- The reaction between alkane and halogen is known as free radical substitution reaction.
- Free radical substitution reaction is the reaction in which a free radical substitutes atom/atoms in a molecule.

Q. What is a free radical?

A free radical is an atom or group of atoms which consist of unpaired electrons.

Example: $CH_4 + Cl_2 \xrightarrow{UV-light} CH_3\,Cl + HCl$

❖ Function of UV – light is to give out a free radical.

Mechanism of reaction

$$Cl - Cl \longrightarrow 2Cl$$

Homolytic sharing of electron i.e. equal sharing of electrons go to each chlorine atom

NOTE:

Free radicals are very reactive. It wants to become stable.

$$Cl + CH_4 \longrightarrow CH_3 + HCl \ [\textit{Chain initiation reaction}]$$

$$CH_3 + Cl_2 \longrightarrow CH_3\,Cl + Cl$$

$$CH_3Cl + Cl \longrightarrow CH_2\,Cl + HCl$$

$$CH_2\,Cl + Cl_2 \longrightarrow CH_2\,Cl_2 + Cl$$

$$CH_2\,Cl_2 + Cl \longrightarrow CHCl_2 + HCl$$

$$CH_2\,Cl_2 + Cl_2 \longrightarrow CHCl_3 + Cl$$

$$CHCl_3 + Cl \longrightarrow CCl_3 + HCl$$

$$CCl_3 + Cl \longrightarrow CCl_4 \ [\text{Chain termination reaction}]$$

$$CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$$

Eg2:

$$CH_3\,CH_3 + Br_2 \xrightarrow{UV-light} CH_3\,CH_2\,Br + HBr$$

$$CH_3\,CH_3 + I_2 \xrightarrow{UV-light} CH_3\,CH_2\,I + HI$$

NOTE:

With fluorine, the reaction is violet and yield hydrogen fluoride and carbon.

Eg: $CH_4 + 2F_2 \longrightarrow C + 4HF$ - Violet reaction

However, controlled fluorination in the presence of cobalt moderator the fluoral derivatives are formed.

NITRATION (With Nitric acid)

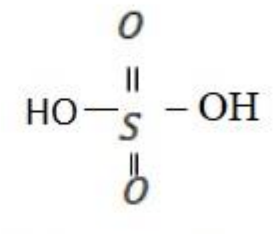
This involves the substitution of hydrogen atom in alkane with NO_2 group. This is done when a mixture of alkane and nitric acid vapour is heated at $400^{\circ}c – 500^{\circ}c$

$$R - H + HNO_3 \xrightarrow{400°C-500°C} R - NO_2 + H_2O$$

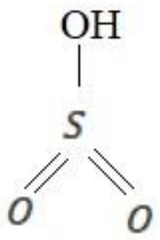
$$\underset{}{CH_3CH_3} \longrightarrow \underset{\text{Nitro ethane}}{CH_3CH_2 - No_2} + H_2O$$

<u>SULPHONATION</u> (With sulphuric acid)

Alkanes when subjected to prolonged reaction with fuming sulphuric acid one hydrogen atom of alkane is replaced with - SO_3 H group known as sulphonic group.



Sulphuric acid



Sulphonic acid

$$R - H + H_2SO_4 \longrightarrow R - SO_3H + H_2O$$

$$CH_3 + CH_3 + H_2SO_4 \longrightarrow CH_3CH_4SO_3H + H_2O$$

Oxidation Reactions:

When alkanes are ignited in the presence of excess oxygen they burn to form carbondioxide and water only.

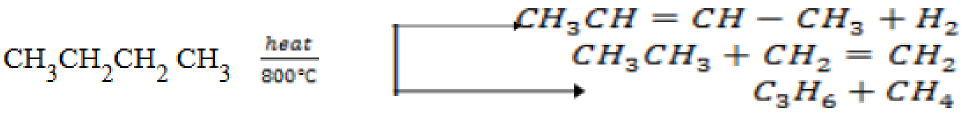
Reaction is highly exothermic:

E.g. i. $2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$

ii. $2C_4H_{10} + 13O_2 \longrightarrow 8CO_2 + 10H_2O$

Thermal decomposition (PYROLYSIS)

This is breaking down of higher alkane into lower alkane by heating alkanes in absence of air.



$CH_3CH_2CH_2CH_3 \xrightarrow[800°C]{heat}$

$CH_3CH = CH - CH_3 + H_2$

$CH_3CH_3 + CH_2 = CH_2$

$C_3H_6 + CH_4$

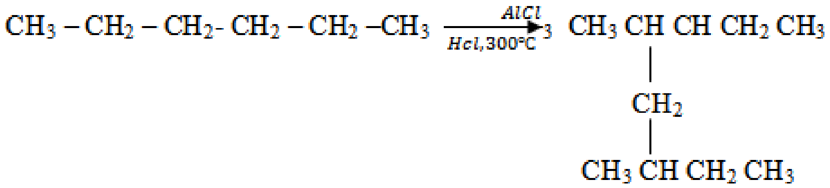
Alkane and alkene are the only possibilities.

NOTE:

No two alkenes will be formed.

Catalytic cracking (Isomerization)

When straight chains of alkanes are heated in aluminium chloride in the presence of dry hydrogen chloride at 300 °C gives a branched chain isomers. In this process there is no breaking of the *compound* but it is changed to branched chain.



$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 \xrightarrow[Hcl,300^{\circ}C]{AlCl_3} \begin{array}{c} CH_3\,CH\,CH\,CH_2\,CH_3 \\ | \\ CH_2 \\ | \\ CH_3\,CH\,CH_2\,CH_3 \end{array}$$

This process is used in petrol chemical industry. The branched chain alkane has higher octane number. Hence branched chain burns easily than straight chains.

Question:

- How to form aromatic compounds i.e. Aromatizations
- Uses of alkanes

Exercise:

Qn. How can the following conversions be achieved?

(a) Propyne to propane

(b) Hexane to 3methylpentane

(c) Ethane to butane

(d) Pentane to nitropentane

Solution:

(a) $HC \equiv C - CH_3 + H_2 \xrightarrow[\Delta]{Ni} CH_3\ CH_2\ CH_3$ (propane)

(b) By catalytic cracking:

$$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3 \xrightarrow[Hcl, 300°C]{ALCl_3} CH_3\ CH_2\ CHCH_2\ CH_3\ CH_3$$

(c) $CH_3\ CH_3 + HCl \longrightarrow CH_3CH_2\ Cl + HCl_{(g)}$

$CH_3\ CH_3 + Cl + Na \xrightarrow{dry\ ether} CH_3\ CH_2\ CH_2\ CH_3 + NaCl$ (butane)

(d) **By nitration:**

$$CH_3 + CH_2 + CH_2 + CH_2 + CH_3 + HNO_3 \longrightarrow CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ NO_2 + H_2O$$

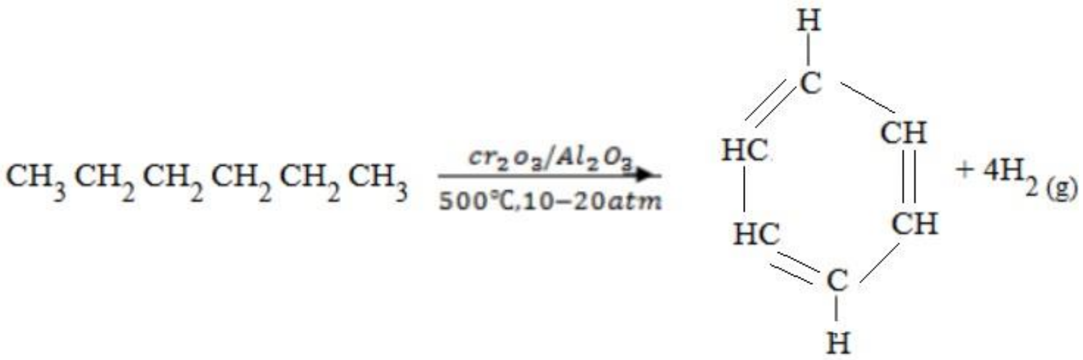
Nitropentane

AROMATIZATION

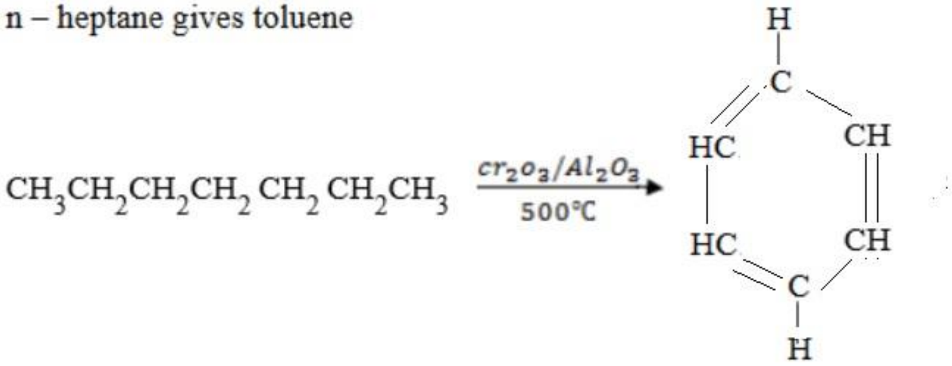
- Alkanes containing six or more carbon atoms when heated under pressure in the presence of suitable catalyst get cyclised to give aromatic compounds.

E.g.

n - hexane gives benzene



n – heptane gives toluene



USES OF ALKANES

Alkanes are the simplest organic compound containing carbon and hydrogen. Some major uses of these compounds are;

(i) Lower alkanes occurring as natural gas and lighter petroleum fractions are used as fuels.

(ii) Low – boiling liquid alkanes e.g. hexane are uses as solvents.

(iii) Heavy petroleum fractions are used as lubricants (grease) and for obtaining waxes and vaseline

(iv) The products of cracking process are generally used for producing linearalkyl benzene (LAB) used as a raw material for manufacturing detergents.

ALKENES

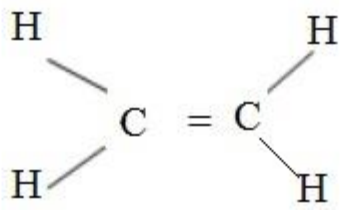
These are hydrocarbons which are unsaturated. They contain double bond between two carbon atoms.

Functional group is C = C and share the same formula with cycloalkanes (cyclalkanes) are known as fractional isomer.

General formula: $C_n H_{2n}$

Cycloalkanes: $C_n H_{2n}$

The type of hybridization is sp^2 hybridization since it is trigonal pyramidal shape.



Nomenclature:

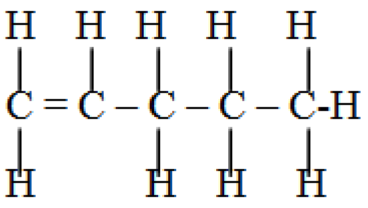
The first member is Ethane since we can't have double bond in a single carbon atom.

E.g. $C_2 H_4$ – Ethene

C_3H_6 -Propene

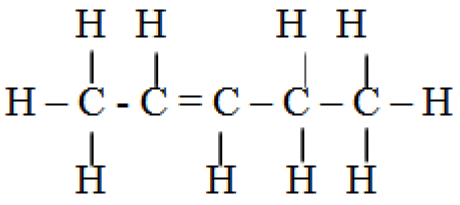
Isomerism:

$C_5 H_{10}$



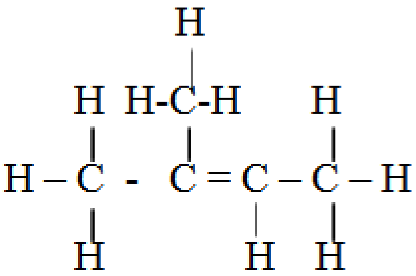
$CH_2=CH-CH_2-CH_2-CH_3$ pent – 1 – ene

2, 2 – but – 2 – ene

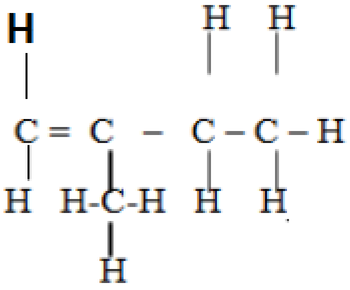


$H-CH_2-CH=CH-CH_2-CH_2-H$

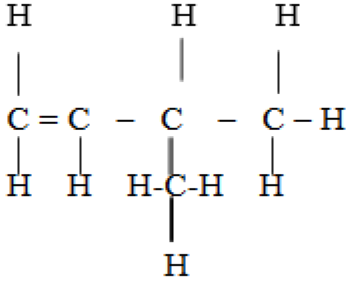
Pent-2-ene



2 – methylbut – 2 – ene



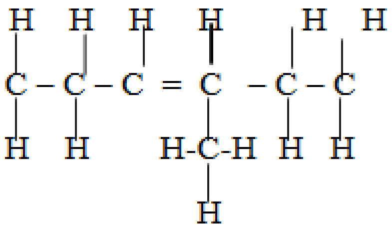
2 - methylbut – 1 – ene



3 - methylbut -1- ene

Naming of different compounds:

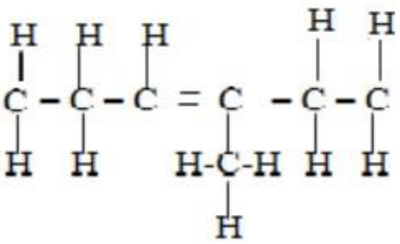
2.



3 – propylhex – 2 – ene

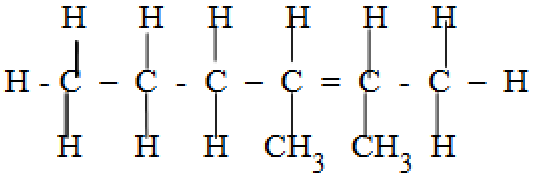
Functional isomers;- They have the same general formula but different functional group. Alkenes and cyloalkanes both have general formula $C_n H_{2n}$

2.



3 – menthlyhex – 3 – ene

3.



2, 3- dimethyl hex-2-ene

4. $CH_2 = CH\ CH_2\ CH = CH\ CH = CH_2$

If more than 1 double bond, add a prefix (a) to hept

6 – methylhepta - 1, 3, 6 – triene

Types of Isomerism in alkenes:

Alkenes show 4 types of isomerism;

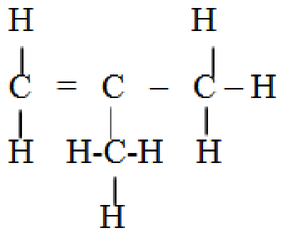
- (i) Chain isomerism
- (ii) Positional isomerism
- (iii) Geometrical isomerism
- (iv) Functional isomerism

Chain isomerism: (Skeletal isomerism)

This is due to the difference in the structure of carbon chain.

Example

$CH_2 = CH - CH_2 - CH_3$ But – 1 – ene

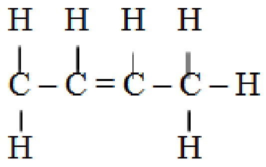


2 – methylprop – 1 – ene

Positional isomerism:

This arises from the difference in the position of the double bond.

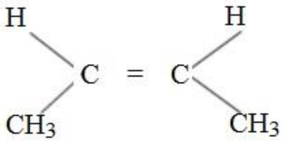
$CH_2 = CH - CH_2 - CH_3$ But – 1 – ene



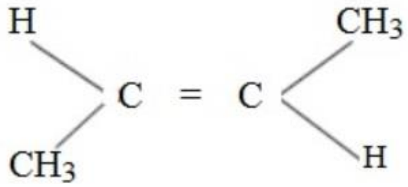
$H_3C - CH = CH - CH_3$

But –2 – ene

Geometrical isomerism:



Cis – but – 2 – ene



Trans – but – 2 – ene

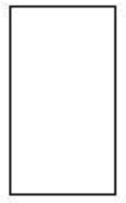
Definition:

- Is brought in the difference in the spatial arrangement of atoms or group of atoms about the double bond.

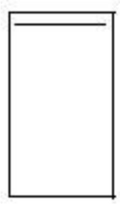
Functional isomers:

These compounds have the same general formula but difference functional group.

E.g. Alkene and cycloalkanes i.e $C_n H_{2n}$



Cyclobutane



Cyclobutene

Laboratory preparation of Alkenes:

(i) Dehydrohalogenation of haloalkanes (alkyl halides)

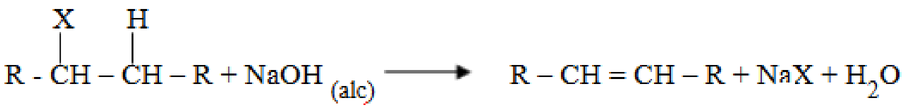
- There is elimination reaction.
- The reaction is done in alcoholic basic medium.

Note:

General formula for alky halides is R - X, X = Cl, Br, F

- When alky halide is heated with alcoholic solution of sodium hydroxide or potassium hydroxide, hydrogen and halogen will be eliminated and alkene is formed.

E.g.



$$R - \overset{X}{\overset{|}{C}}H - \overset{H}{\overset{|}{C}}H - R + NaOH_{(alc)} \longrightarrow R - CH = CH - R + NaX + H_2O$$

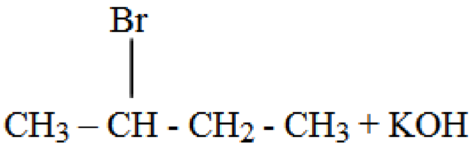
This is known as **Basic induced elimination reaction**

$$CH_3\,CH_2\,Cl + NaOH_{(alc)} \longrightarrow CH_2 = CH_2 + NaCl + H_2O$$

Chloroethane ethene

$$CH_3\,CH_2\,CH_2\,Br + NaOH \xrightarrow{alcohol} CH_2 = CHCH3 + NaBr + H_2O$$

Bromopropane propene



$$CH_3 - \overset{Br}{\overset{|}{C}}H - CH_2 - CH_3 + KOH \xrightarrow{alcohol} CH_2 = CH\,CH_2\,CH_3 + KBr + H_2O$$

H^+ is removed here according to Say tzeff's rule

Butene (minor product)

+

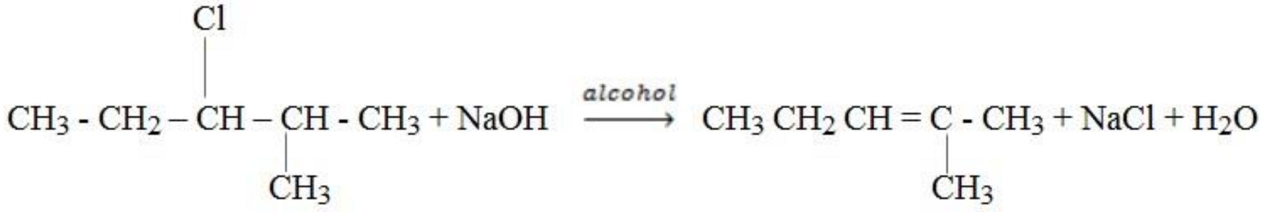
$$CH_3\,CH = CH - CH_3 + KBr + H_2O$$

(Major product)

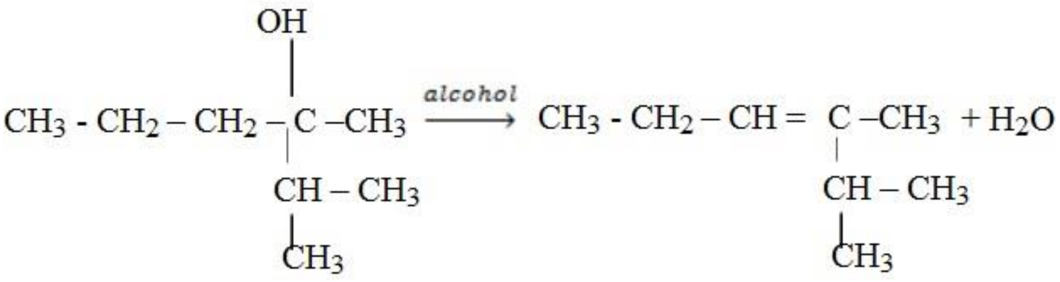
SAYTZEFF'S RULE

It states, "during elimination reaction, the electrophyl (H^+) is removed from carbon atom with fewer number of hydrogen atom.

Example of reactions which apply Saytzeff's rule;-



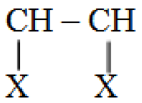
$$CH_3-CH_2-\overset{Cl}{CH}-\underset{CH_3}{CH}-CH_3+NaOH \xrightarrow{alcohol} CH_3\,CH_2\,CH=\underset{CH_3}{C}-CH_3+NaCl+H_2O$$



$$CH_3-CH_2-CH_2-\underset{\underset{CH_3}{CH-CH_3}}{\overset{OH}{C}}-CH_3 \xrightarrow{alcohol} CH_3-CH_2-CH=\underset{\underset{CH_3}{CH-CH_3}}{C}-CH_3+H_2O$$

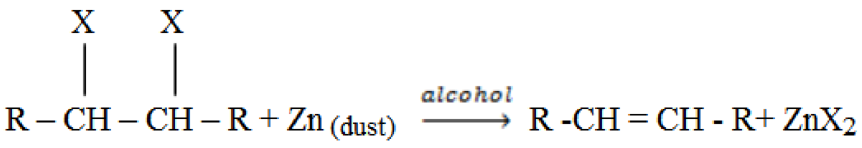
(ii) (a) Dehydration of alcohol

This is done using concentrated sulphuric acid by warming about 175 $^{\circ}C$ - 180 $^{\circ}C$. You react alcohol with conc. sulphuric acid.



$$\underset{X}{CH}-\underset{X}{CH}$$

General equation:

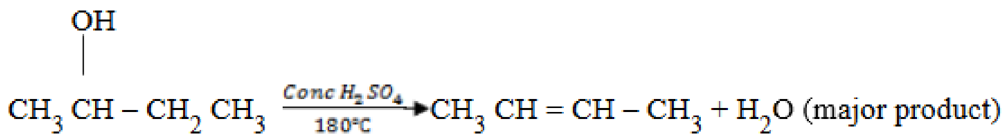


$$R-\overset{X}{CH}-\overset{X}{CH}-R+Zn_{(dust)} \xrightarrow{alcohol} R-CH=CH-R+ZnX_2$$

Note:

Temperature is very important $(175°C - 180°C.)$ this reaction is sensitive to temperature

e.g. $CH_3CH_2OH \xrightarrow[180°C]{Conc\ H_2SO_4} CH_2 = CH_2 + H_2O_{(l)}$



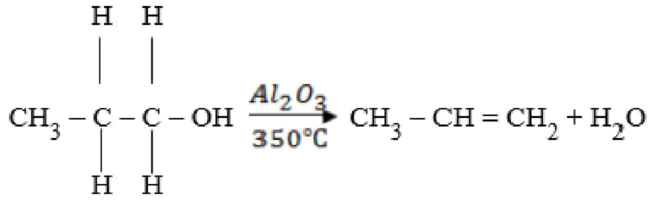
$$CH_3\overset{OH}{\overset{|}{C}H} - CH_2CH_3 \xrightarrow[180°C]{Conc\ H_2SO_4} CH_3CH = CH - CH_3 + H_2O \text{ (major product)}$$

<u>NOTE</u>:

H_3PO_4 (conc.) can be used as a dehydrating agent (373 - 383k)

(b) **Dehydration by passing the vapour of alcohol over aluminium oxide** (alumina) at 350 °C

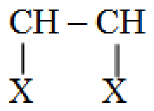
e.g. $CH_3\text{-}CH_2\text{-}CH_2OH \xrightarrow[350°C]{Al_2O_3} CH_2CH = CH_2 + H_2O$



$$CH_3 - \underset{H}{\overset{H}{C}} - \underset{H}{\overset{H}{C}} - OH \xrightarrow[350°C]{Al_2O_3} CH_3 - CH = CH_2 + H_2O$$

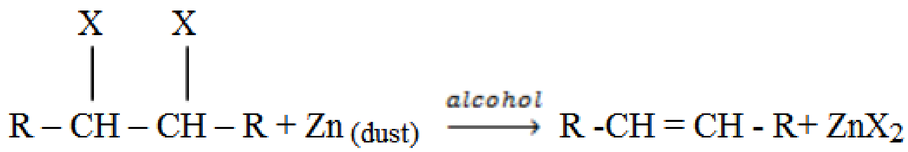
iii) Dehalogenation of vicinal dihalides

Vicinal means the halogens are on the adjacent carbon of the same carbon.



$$\underset{X}{\underset{|}{CH}} - \underset{X}{\underset{|}{CH}}$$

General equation:



$$R - \overset{X}{\overset{|}{C}H} - \overset{X}{\overset{|}{C}H} - R + Zn_{(dust)} \xrightarrow{alcohol} R\text{-}CH = CH\text{-}R + ZnX_2$$

iv) (a) **Controlled hydrogenation of alkynes**

It is done under palladium catalyst which is poisoned by calcium carbonate and quinoline and this reagent is known as Lindlers catalyst.

$$R - C \equiv C - R + H_2 \xrightarrow[Quinoline]{pd - caco_3} R - CH = CH - R \text{ - Cis}$$

Note:

Poisoned means that the palladium is not pure

(b) Sodium, Lithium and Ammonia

This is not complete hydrogenation.

$$R - C \equiv C - R \xrightarrow{Li, Na, NH_3} R - CH = CH - R$$

$$CH_3\ C \equiv C - CH_3 + H_2 \xrightarrow[Quinoline]{pd - caco_3} CH_3\ CH = CH\ CH_3$$

$$CH_3\ C \equiv C - H \xrightarrow{Li, Na, NH_3} CH_3\ CH = CH_2$$

Chemical properties of Alkenes:

NOTE: Alkenes are more reactive than alkenes due to the presence of pi bond which is relatively weak. Hence, can react easily

1. Addition of hydrogen halides (HX)

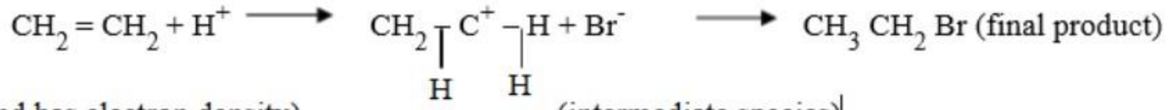
Alkenes undergo electrophilic addition reaction (electron loving/electron deficient).

Electrophilic addition reaction is the reaction in which electrophyl is added first followed by nucleophyl.

Eg. $CH_2 = CH_2 + HBr \longrightarrow CH_3\ CH_2\ Br$

Mechanism of the reaction (shows all stages)

$HBr \longrightarrow H^+ + Br^-$



$CH_2 = CH_2 + H^+ \longrightarrow CH_2 \underset{H}{-} C^+ \underset{H}{-} H + Br^- \longrightarrow CH_3\,CH_2\,Br$ (final product)

(π bond has electron density) (intermediate species)

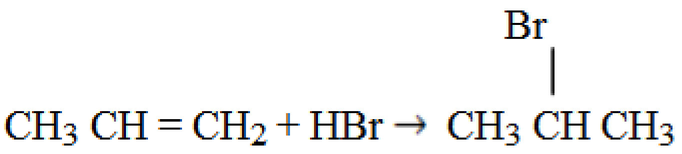
C^+ - Carbocation

Addition reaction of HBr follows a rule known as Mark KovniKov's rule

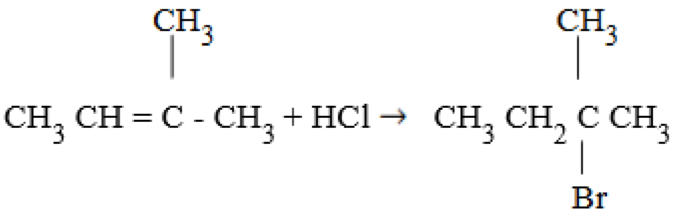
Mark KovniKov's rule:

It states, 'During the addition reaction the electrophyl (hydrogen) is added to carbon atom with more number of hydrogen atoms'.

Eg:



$CH_3\,CH = CH_2 + HBr \rightarrow CH_3\,\overset{Br}{CH}\,CH_3$



$CH_3\,CH = \overset{CH_3}{C} - CH_3 + HCl \rightarrow CH_3\,CH_2\,\underset{Br}{\overset{CH_3}{C}}\,CH_3$

Why Mark Kovni Kov's rule?

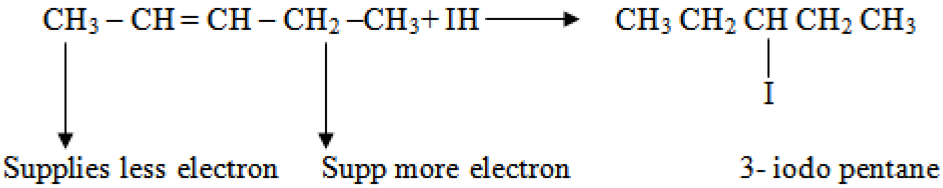
It is because of the formation of stable carbocation. Hence the rule is used so as to form a stable carbocation.

$CH_3 \longrightarrow CH - CH_2$

NOTE:

Stability of carbocation is due to the supply of electron from the alkyl group as shown above. The halogen is added to the stable carbon.

In long chains, a stable carbocation will be formed when the carbon is bounded by many alkyl groups (since the alkyl group will be supply electrons



$CH_3-CH=CH-CH_2-CH_3+IH \longrightarrow CH_3\,CH_2\,\underset{I}{CH}\,CH_2\,CH_3$

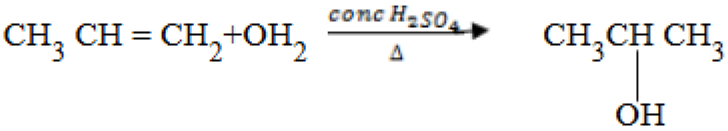
Note:

Hydrogen is added to the more stable carbon.

2. Hydration of alkenes:

Hydration means addition of water.

- This is addition of water in the presence of mineral acids. The most preferred acid is conc H_2SO_4. The mixture should be heated in order to form alcohol.



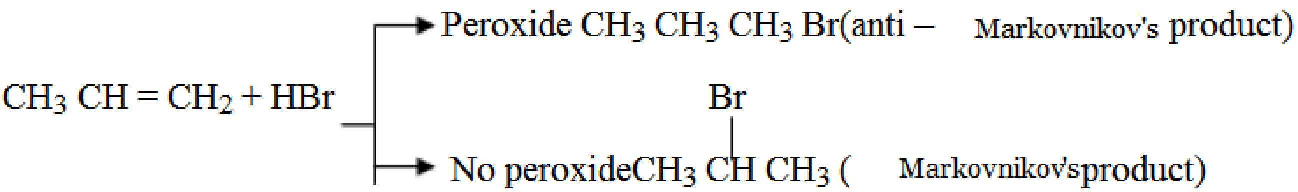
$CH_3\,CH=CH_2+OH_2 \xrightarrow[\Delta]{conc\,H_2SO_4} CH_3\underset{OH}{CH}\,CH_3$

Carbocation will be formed in CH

Home Work:

Anti - markovnikov's rule (organic peroxide HBr). In 1933 the American chemist M. S. Kharasch discovered that the addition of HBr to unsymmetrical alkenes in the presence of organic peroxide (R – O – O – R) takes a course opposite to that suggested by Markovnikovs rule.

Eg:



$CH_3\,CH=CH_2+HBr$

$\longrightarrow$ Peroxide $CH_3\,CH_3\,CH_3\,Br$(anti – Markovnikov's product)

$\longrightarrow$ No peroxide$CH_3\,\overset{Br}{CH}\,CH_3$ (Markovnikov'sproduct)

NOTE:

It is strictly works using HBr with organic peroxide.

Mechanism:

1. Peroxide dissociates to give alkoxy free radicals.

$$R - O - O - R \overset{\Delta}{\rightarrow} 2R - O$$

2. Alkoxy free radical combines with HBr to give bromine atom (a free radical).

$$R - O + HBr \longrightarrow R - OH + Br$$

3. The Bromine atom attacks propane to give a primary free radical and a secondary free radical.

$$Br + CH_3\ CH = CH_2 \longrightarrow CH_3\ CH\ \underset{|}{\overset{Br}{}}CH_2$$

(less stable 1° free radical)

$$Br + CH_3\ CH = CH_2 \longrightarrow CH_3\ \overset{Br}{\overset{|}{CH}}\ CH_2$$

(2° free radical more stable)

4. The more stable 2° free radical attacks the HBr molecule to form anti – markvnikov product and bromine atom.

$$CH_3\ CH\ CH_2\ Br + HBr \longrightarrow CH_3\ CH_2\ CH_2\ Br + Br \quad \text{(Bromopropane)}$$

Weekly Test:

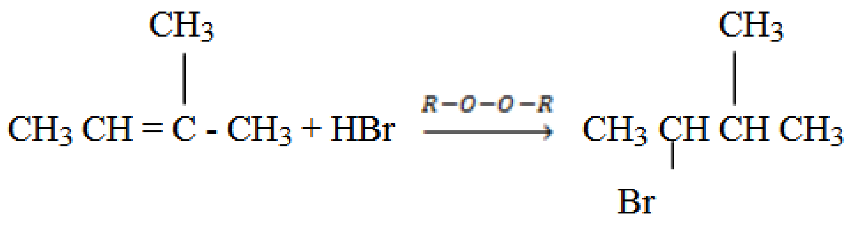
1. (b) $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

Given â^†H_r = $^-$92KJ

Since H_f you form 1mole

$H_f = \frac{\Delta H_r}{2}$

$= \frac{-92}{2}$



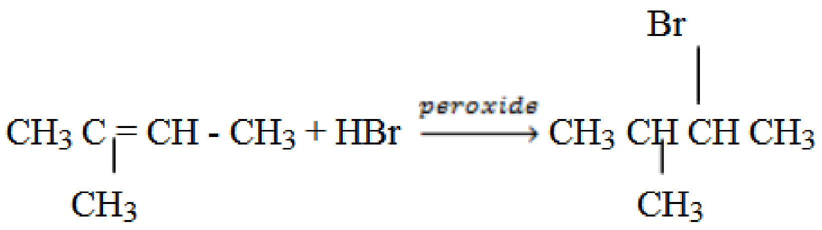
$$CH_3CH=\overset{CH_3}{C}-CH_3+HBr\xrightarrow{R-O-O-R}CH_3\underset{Br}{CH}\overset{CH_3}{CH}CH_3$$

$$H_f=\frac{\Delta H_r}{2}$$

$$=\frac{-92}{2}$$

$$H_f=-46KJmol^{-1}$$

3. (a)(ii) $CaC_2+2H_2O\longrightarrow CH_3COOH+Ca$

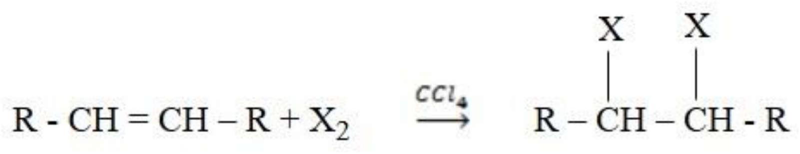


$$CH_3\underset{CH_3}{C}=CH-CH_3+HBr\xrightarrow{peroxide}CH_3\underset{CH_3}{CH}\overset{Br}{CH}CH_3$$

3. **Halogenation**

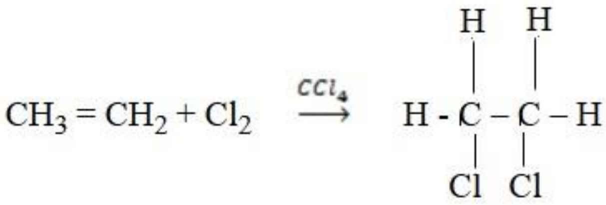
⇒Addition of halogens to alkenes

- This reaction is best carried out by simply mixing halogens in the inert solvents such as carbon tetrachloride (CCl_4)

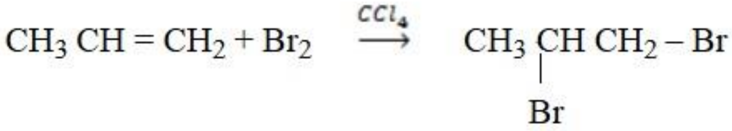


$$R-CH=CH-R+X_2\xrightarrow{CCl_4}R-\overset{X}{CH}-\overset{X}{CH}-R$$

E.g.



$$CH_3 = CH_2 + Cl_2 \xrightarrow{CCl_4} H - \underset{Cl}{\overset{H}{C}} - \underset{Cl}{\overset{H}{C}} - H$$



$$CH_3\,CH = CH_2 + Br_2 \xrightarrow{CCl_4} CH_3\,\underset{Br}{CH}\,CH_2 - Br$$

The reaction of Bromine with alkene can be used to test for the presence of double bonds.

Reason:

Addition of bromine (brown) to alkene since it makes the solution colourless. This is how we test for presence of double bonds.

Bromine tests unsaturation of hydrocarbons (alkenes and alkynes).

4. HYDROGENATION

Addition of hydrogen:

- Alkenes react with hydrogen in the presence of platinum or nickel catalyst to form alkanes.

$$R\text{- } CH = CH \text{ - } R + H_2 \xrightarrow[\Delta]{Ni} R \text{ - } CH_2 \text{ - } CH_2 \text{ - } R$$

$$CH_2 = CH_2 + H_2 \xrightarrow[\Delta]{Ni} CH_3\,CH_3$$

$$CH_2 - CH = CH\,CH_3 + H_2 \xrightarrow[\Delta]{Pt} CH_3\,CH_2 + CH_2\,CH_3$$

❖ This cannot take place without catalyst.

5. Hydration of Alkenes:

- This follows Markrnkov’s rule.

Homework on hydration of alkenes

- Find the reagent which should be added to alkene to follow Anti markornikovs rule.

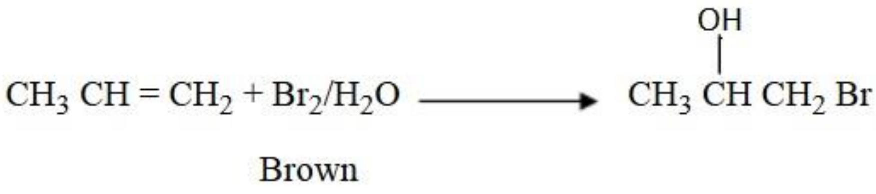
Oxidation reaction of alkenes

6. Addition of Bromine water (Br_2/H_2O)

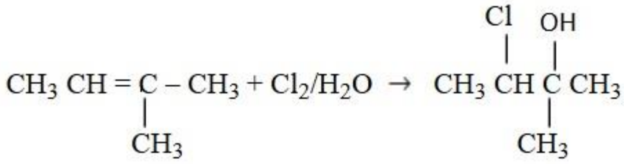
$$Br_2 + H_2O \rightleftharpoons HOBr + HBr$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

$$HOBr \longrightarrow \underset{\text{Nucleophyl}}{OH^-} + \underset{\text{Electrophyl}}{Br^+}$$



$$CH_3CH = CH_2 + \underset{\text{Brown}}{Br_2/H_2O} \longrightarrow CH_3\overset{\overset{OH}{|}}{C}H\,CH_2Br$$

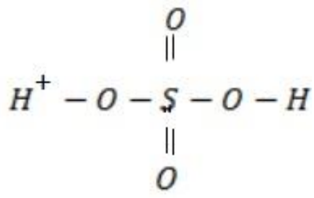


$$CH_3CH = \underset{\underset{CH_3}{|}}{C} - CH_3 + Cl_2/H_2O \rightarrow CH_3\overset{\overset{Cl}{|}}{C}H\,\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}\,CH_3$$

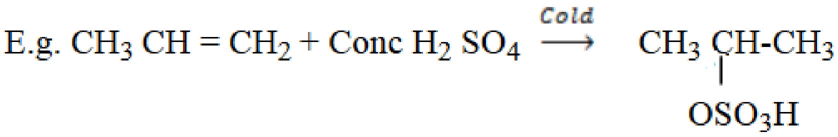
Alkenes decolourize Bromine water (Brown) apart from decolorizing Bromine solution.

Reaction with conc H_2SO_4

Structure of sulphuric acid

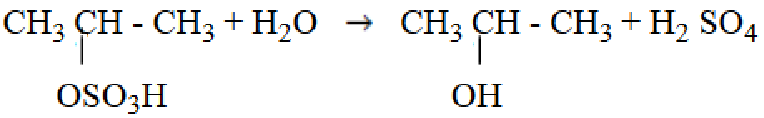


$$H^{+} - O - \overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}} - O - H$$



$$\text{E.g. } CH_3\,CH = CH_2 + \text{Conc } H_2\,SO_4 \xrightarrow{Cold} CH_3\,\underset{\underset{OSO_3H}{|}}{CH}\text{-}CH_3$$

2 - Propylhydrogensulphate

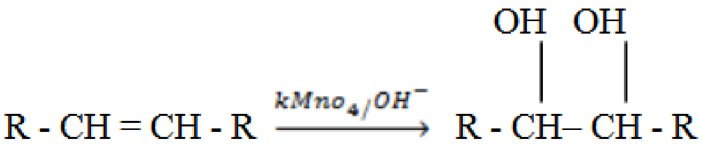


$$CH_3\,\underset{\underset{OSO_3H}{|}}{CH} - CH_3 + H_2O \rightarrow CH_3\,\underset{\underset{OH}{|}}{CH} - CH_3 + H_2\,SO_4$$

7. Oxidation reactions of Alkenes

- Alkenes react with oxidizing agent to form diols. Oxidizing agent can be either $KMnO_4$, K_2CrO_4.

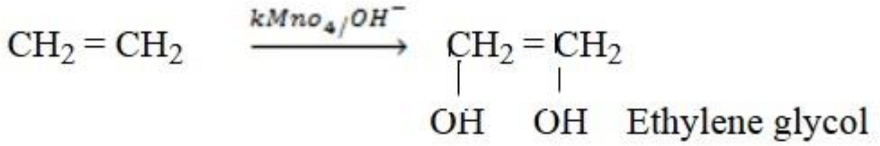
- With cold dilute $KMnO_4$ or cold alkaline$KMnO_4$ you form diols.



$$R - CH = CH - R \xrightarrow{kMno_4/OH^-} R - \underset{}{\overset{\overset{OH}{|}}{CH}} - \overset{\overset{OH}{|}}{CH} - R$$

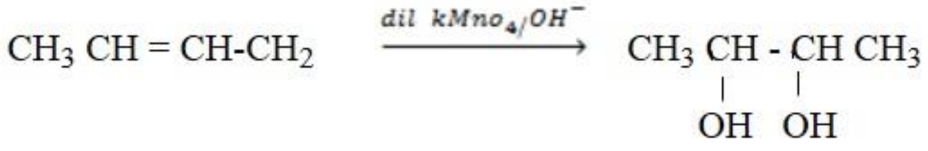
Diol

<u>NOTE:</u> Diol means two OH^-



$$CH_2 = CH_2 \xrightarrow{kMno_4/OH^-} \underset{OH}{\underset{|}{CH_2}} = \underset{OH}{\underset{|}{CH_2}}$$

Ethylene glycol

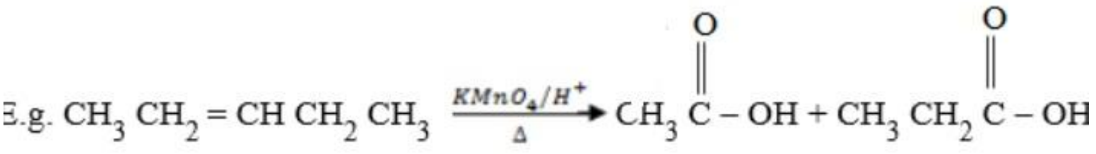


$$CH_3\,CH = CH\text{-}CH_2 \xrightarrow{dil\ kMno_4/OH^-} CH_3\,\underset{OH}{\underset{|}{CH}} - \underset{OH}{\underset{|}{CH}}\,CH_3$$

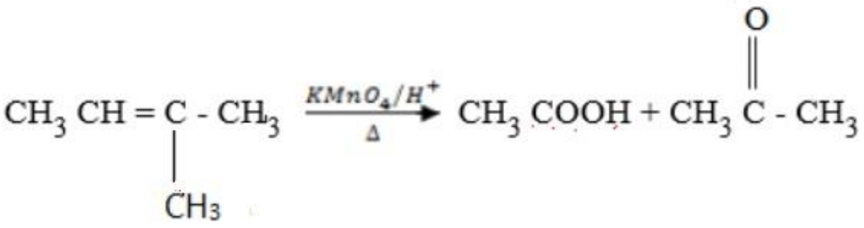
(b) When hot concentrated acidified KMnO₄ or K₂Cr₂O₄ is used. Alkenes are oxidized to carboxylic acid or oxidized to ketones or both.

$$R - CH = CH\,R' \xrightarrow[\Delta]{KMnO_4/H^+} R - C - OH + R - C - OH$$

- It is broken down to carboxylic acid.



$$\text{E.g. } CH_3\,CH_2 = CH\,CH_2\,CH_3 \xrightarrow[\Delta]{KMnO_4/H^+} CH_3\,\overset{O}{\overset{\|}{C}} - OH + CH_3\,CH_2\,\overset{O}{\overset{\|}{C}} - OH$$

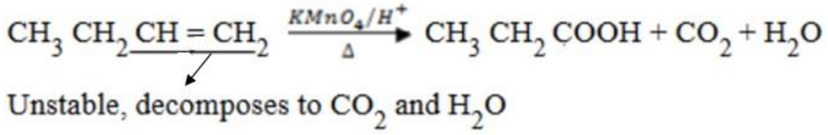


$$CH_3\,CH = \underset{CH_3}{\underset{|}{C}} - CH_3 \xrightarrow[\Delta]{KMnO_4/H^+} CH_3\,COOH + CH_3\,\overset{O}{\overset{\|}{C}} - CH_3$$

Note:

If double bond is branched, you can’t form carboxylic acid.

Terminal alkene



$$CH_3\,CH_2\,CH = CH_2 \xrightarrow[\Delta]{KMnO_4/H^+} CH_3\,CH_2\,COOH + CO_2 + H_2O$$

Unstable, decomposes to CO_2 and H_2O

<u>OZONOLYSIS</u> (O_3)Ozono ⇒ ozone

Lysis ⇒ Breaking

- This is a cleavage or breaking of carbon, carbon double bond by using ozone.
- In ozonolysis C = C is completely broken to produce aldehydes or ketones or both depending on the primary structure of alkene.

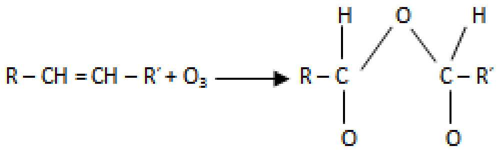
<u>NOTE:</u>

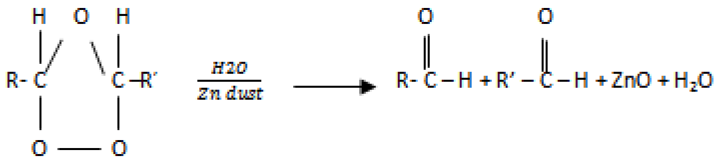
Ozonolysis is the best method of locating the position of double bond in unknown alkene.

The oxygenated carbon in carbonyl compound obtained by ozonolysis is the one that were joined by double bonds in the original alkenes.

Ozonolysis has 2 major steps:

i) 1st step:

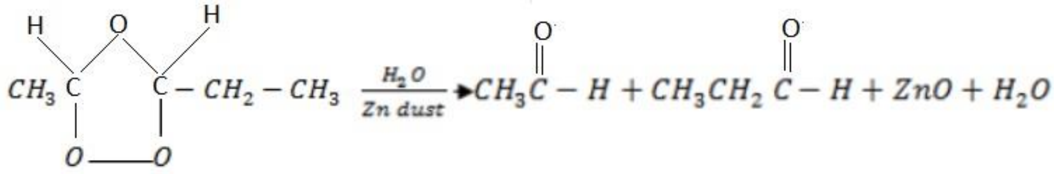


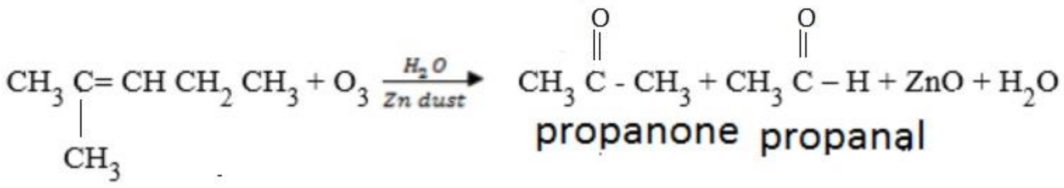


NOTE:

Zn dust is added to prevent oxidation of aldehyde to carboxylic acid.

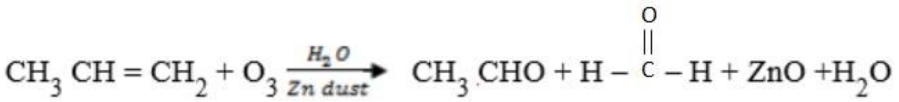
E.g.





$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH\,CH_2\,CH_3 + O_3 \xrightarrow[Zn\ dust]{H_2O} CH_3\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 + CH_3\overset{\displaystyle O}{\overset{\|}{C}}-H + ZnO + H_2O$$

propanone propanal

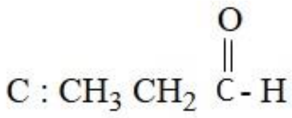


$$CH_3\,CH=CH_2 + O_3 \xrightarrow[Zn\ dust]{H_2O} CH_3\,CHO + H-\overset{\displaystyle O}{\overset{\|}{C}}-H + ZnO + H_2O$$

Questions

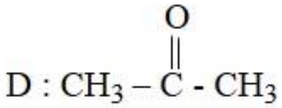
1. A certain compound A was unsaturated hydrocarbon with molecular formula C_6H_{12}. During ozonolysis of A, two compounds C and D were formed with molecular formula C_3H_6O. Compound C and compound D was ketone. Identify A, C and D.

Solution:



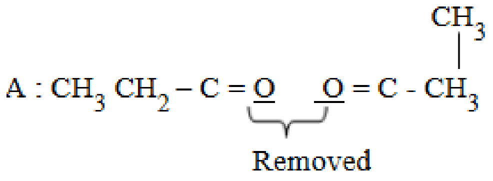
$C : CH_3\,CH_2\,\overset{\overset{O}{\|}}{C}-H$

Propanal (aldehydes)

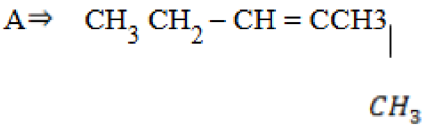


$D : CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

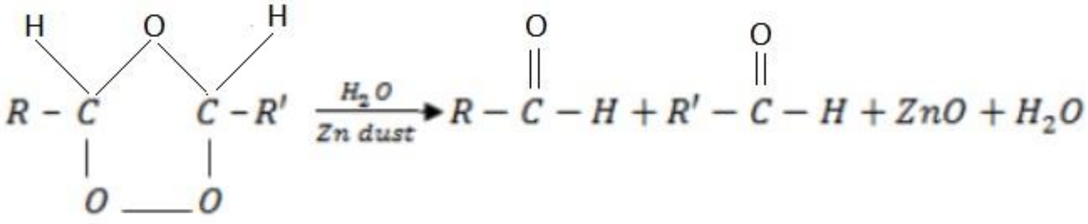
Propanone (Ketone)



$A : CH_3\,CH_2-C=\underbrace{\underline{O}\quad\underline{O}}_{\text{Removed}}=\overset{\overset{CH_3}{|}}{C}-CH_3$



$A \Rightarrow \quad CH_3\,CH_2-CH=\underset{\underset{CH_3}{|}}{C}CH3$



PHYSICAL CHEMISTRY - Gases

Is the branch of chemistry which deals with measurable quantities.

PARTS OF PHYSICAL CHEMISTRY

The physical chemistry is studied under the following sub topics. These are

1. States of matter
2. Chemical equilibrium
3. Thermochemistry/ Energetics
4. Electrochemistry
5. Chemical kinetics

1. STATE OF MATTER

This is the form in which matter do exist. There are three states of matter. These are

a) Gaseous state
b) Liquid state
c) Solid state

A. GASEOUS STATE

This is the form in which matter do exist in motion.

PROPERTIES OF GASEOUS

Properties of gases are governed by kinetic theory of gases (KTG).

THE KINETIC THEORY OF GASES

1. Kinetic theory of gases include the following points or postulates.
2. Gases contain large number of molecules which are in continuous random motion.
3. Molecules of gases are far away such that the force of attraction between individual molecules is negligible kinetic energy of the molecules is directly proportion to absolute temperature i.e the increase of temperature will causes the increases in kinetic energy of the molecules.
4. The values of individual molecules of gases is negligible compared to the volume of the container.
5. Pressure of the gas inside the container is due to the collision between molecules of the gas and the wall of the container.
6. The collision of molecules of gases are perfectly elastic that is kinetic energy is conserved (Kt before is equal to K.E after collision).

CLASSIFICATION OF GASES

Gases are categorized into two groups

These are

i) Ideal gases
ii) Real gases

i. IDEAL GASES

Ideal gases are gases which obey all assumption of kinetic theory and also they do obey the ideal gas equation

i.e $PV = nRT$.

Where by

P = Pressure of the gases

V = Volume of the gases

n = Number of moles of gases

R = Universal of gas constant

T = Temperature

ii. REAL GASES

Real gases are the gases which do not obey all the assumptions of kinetic theory of gases. Such assumptions are:

i. The volume of individual molecules of the gases is negligible compared to the volume of the container.

ii. Molecules of gases are far away such that the force of attraction between individual molecules is negligible.

From kinetic theory of gases, scientist comes up with the formula / equation that is governed by the theory the equation is

$PV = \frac{1}{3}Nm\bar{C}^2$

Where by

P = Pressure of the gas

V = Volume of the gas

N = Number of the molecules of the gas

m = Mass of molecules of the gas

$\bar{C}^2$ = Means square speed of the molecules

$\bar{C}^2$ = Is given by

$$\bar{C}^2 = \frac{C_1{}^2 + C_2{}^2 + C_2{}^3}{3}$$

DEDUCTION OF GASES LAWS FROM KINETIC THEORY OF GASES

This is the process by which gas laws are obtained or derived from kinetic theory of gases.

Such laws to be deduced are:

i. Charles's law.

ii. Boyle's laws.

iii. Graham's law of diffusion/ effusion.

iv. Dalton's law of partial pressure.

v. Avogadro's law.

1. DEDUCTION OF CHARLES' LAW

It state that " At constant pressure the volume of a fixed mass of gas is directly proportion to the absolute temperature .

$$V \propto T$$
$$V = PT$$

$$\frac{V}{T} = \text{P (Constant)}$$
$$\frac{T}{V} = \text{K}$$

i.e The ratio of volume of temperature is constant.

Thus.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = k$$

From kinetic theory of gases

PV = $\frac{1}{3}$Nm $\bar{C}^2$

For any gas to obey charle's law

$$\frac{1Nm}{3\ P} = \text{Constant (k)}$$

V = k $\bar{C}^2$

From kinetic theory of gases

$\bar{C}^2$ = T

V = KT

$\frac{V}{T} = \frac{KT}{T}$

$$\frac{\text{V}}{\text{T}} = \text{K}$$

QUESTION

a) Define the following terms

i) Real gases.

ii) Ideal gases.

b) State Charles's law.

c) Deduce Charles law from kinetic theory of gases.

2. DEDUCTION OF BOYLE'S LAW FROM KINETIC THEORY OF GASES

It state that " At constant thermodynamic volume of a fixed mass of gas is inversely proportional to pressure.

$$V \propto \frac{I}{P}$$

$$V = \frac{T}{P}$$

$$PV = T$$

$$PV = K(\text{Constant})$$

From kinetic of gases

PV = $\frac{1}{3}$Nm $\bar{C}^2$

From gas to obey Boyle's law

$$\frac{Nm}{3}\bar{C}^2 = K(\text{Constant})$$

PV = K

Hence Boyle's law deduced

3. DEDUCTION OF GRAHAM'S LAW FROM KINETIC THEORY OF GASES

Graham's rate of diffusion or effusion: It states that,

"The rate of diffusion or effusion of gaseous material is inversely proportional to the square root of its density"

If rate is represented by ***r*** and density by ρ

$$r \propto \frac{1}{\sqrt{\rho}} \qquad (k = 1)$$

$$r \propto \frac{k}{\sqrt{\rho}}$$

$$r = \frac{1}{\sqrt{\rho}}$$

For two gases which are G_1 and G_2

For Gas1

$$r_1 = \frac{1}{\sqrt{\rho_1}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

For gas 2

$$r_2 = \frac{1}{\sqrt{\rho_2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(ii)}$$

Comparison

For the ratio of their rates

$$\frac{r1}{r2} = \frac{1}{\sqrt{\rho_1}} \div \frac{1}{\sqrt{\rho_2}}$$

$$\frac{r1}{r2} = \frac{1}{\sqrt{\rho_1}} \text{ X } \frac{\sqrt{\rho_2}}{1}$$

$$\frac{r1}{r2} = \frac{\sqrt{\rho_2}}{\sqrt{\rho_1}}$$

$$\frac{r1}{r2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

In terms of their density

If the volume is constant

$$\rho = \frac{m}{v}$$

$$\frac{r1}{r2} = \sqrt{\frac{m_2}{v} \times \frac{v}{m_1}}$$

$$\frac{r1}{r2} = \sqrt{\frac{m_2}{m_1}}$$

In terms of their masses

4. DEDUCTION OF GRAHAM'S LAW

From Graham's law

$$r = \frac{1}{\sqrt{\rho}}$$

From kinetic theory of gases

$$Pv = \frac{1}{3}Nm\bar{C}^2$$

$$3PV = Nm\bar{C}^2$$

But Nm = m

$$\frac{3PV}{m} = \frac{mC^2}{m}$$

$$\overline{C}^2 = \frac{3PV}{m}$$

For *any gases to obey graham's law*

$3P = k$

constant = 1

$3P = 1$

Now,

$\bar{c}^2 = \frac{V}{m}$

$\bar{C}^2 = 1/\rho$

But,

$\bar{C}^2 = r^2$

$\sqrt{r_2} = \sqrt{\frac{1}{\rho}}$

$$r = \frac{1}{\sqrt{\rho}}$$

Hence grahams law deduced

DALTON’S LAW OF PARTIAL PRESSURE

It state that

“ The total pressure of gases which are not reacting is equal to the sum of pressure of individual gases in a container"

Consider the two gases which are;

Gas A and Gas B

Each gas will create its own pressure.

Therefore the pressure of gases will be,

P_A for gas A

P_B for gas B

From Dalton’s law of partial pressure,

$P_T = P_A + P_B$

Where by

PT is the total pressure of all gases in the container.

DEDUCTION OF DALTON’S LAW OF PARTIAL PRESSURE FROM KINETIC THEORY OF GASES

From Dalton’s law for gas A and B

$P_T = P_A + P_B$

From kinetic theory of gases

$PV = \frac{1}{3}Nm\bar{C}^2$

Since the volume is common.

For gas A

$P_{AV} = \frac{1}{3}N_A m_A \bar{c}^2\ A$

Since the volume is common.

For gas B

$P_{BV} = \frac{1}{3}\ N_B m_B \bar{c}^2\ B$

If P_t is the total pressure

V is the common volume

N_t is the total number of molecules

M is the total mass of molecules

$\bar{C}^2$ is the sum of $\bar{C}^2$ of A and B

$P_tV = \frac{1}{3}N_t\ m\ \bar{C}^2$

$N_t = \frac{3PTV}{M\bar{c}^2}$

$$N_A = \frac{3P_AV}{MA\ \bar{c}^2}$$

$$N_B = \frac{3P_BV}{MB\ \bar{c}^2}$$

But $N_t = N_A + N_B$

$$\frac{3PTV}{M\bar{c}2} = \frac{3PAV}{M_A\bar{c}2_A} + \frac{3PBV}{M_B\bar{c}2_B}$$

$$\frac{PT}{M\bar{c}2} = \frac{PA}{M_A\bar{c}2_A} + \frac{PB}{M_B\bar{c}2_B}$$

Since K. E is conserved (It is the same before and after)

$M\ \bar{c}^2 = M_A\ \overline{CA}^2 = M_B\overline{CB}^{\ 2}$

$\mathbf{P_T = P_A + P_B}$, Hence Dalton law deduced

QUESTION

Deduced the Avogadro's law from kinetic theory of gases

THE IDEAL GAS EQUATION

This is the equation which is obeyed by all ideal gases.

Formulation of ideal gas equation

The ideal gas equation is formed from the combination of two gas law . These are

i) Charles's law

ii) Boyle's law

i) Charle's law

$V \propto T$

ii) Boyle's law

$V \propto \frac{1}{P}$

Combining

$V \propto \frac{T}{P}$

$V = \frac{KT}{P}$

V = kT

k represent universal gas constant which is denoted by R.

PV = RT

This is exactly for one mole of a gas.
For n moles of the gas
PV = nRT

Where
P is the pressure of the gas
V is the volume of the gas
n is the number of the moles of the gas
R is the universal constant
T is the absolute temperature

Units for R

R can be written as;
i) R = 0.0821 atm moles $\overline{k}^{1}\ L$
ii) R = 8.314 $^{-1}$ mol $^{-1}$
Some questions need just general gas equation.
Recall

$V = \frac{KT}{P}$

$\frac{PV}{T} = K$

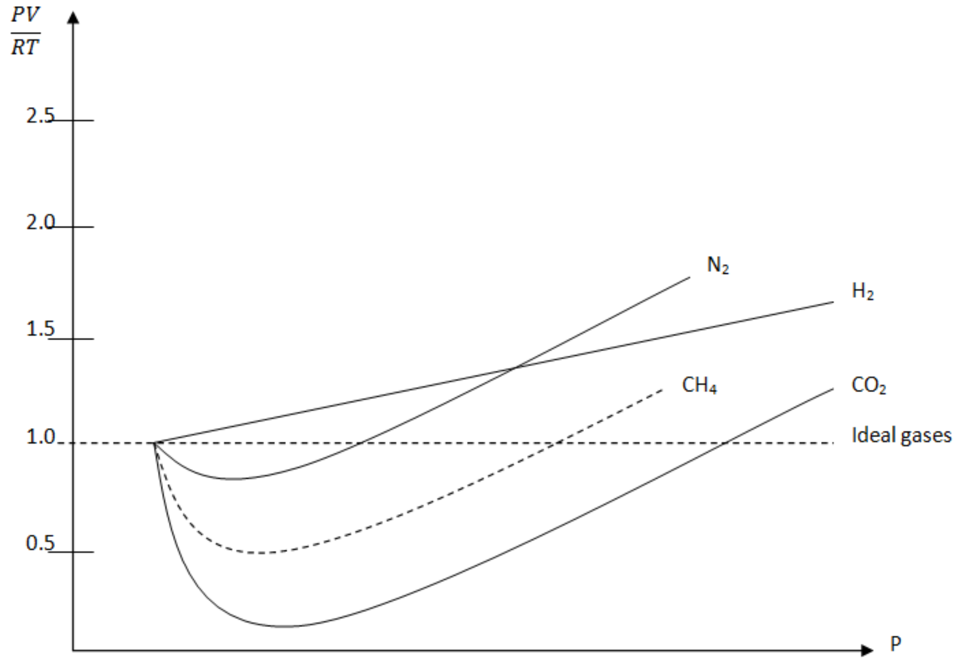
i.e $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

DEVIATION OF REAL GASES FROM IDEAL BEHAVIOUR

From kinetic theory of gases it has been observed that gases which do obey all assumption are termed

as ideal gases.
For an ideal gas PV is exactly = 1
PV = nRT
For one mole of a gas.
PV = RT
The ratio of PV to RT is exactly 1.0
$\frac{PV}{RT}$ = 1.0
Real gases do deviate from this behaviour at high pressure and low pressure.Therefore the variation of pressure cause the fluctuation on the value of $\frac{PV}{RT}$ and this bring about the deviation of real gases from ideal behaviour. This deviation is graphically represent when the graph of $\frac{PV}{PT}$ *v/s* Pressure is plotted.

The graph of $PV/_{RT}$ *v/s P (Amagat curve)*



TERMS

- Critical temperature

It is the temperature above which the gas cannot be liquified without further cooling.

- Critical pressure

It is the pressure at which the gas start to liquefy.

APPLICATION OF IDEAL GAS EQUATION

Ideal gas equation is applied in the following aspects;

1. Determination of moral mass of the gas.

From ideal gas equation

$PV = nRT$

But, n is the number of moles

$$n = \frac{M}{Mr}$$

$$PV = \frac{M}{Mr}RT \times Mr$$

$$\frac{Mr\ \ PV}{PV} = \frac{MRT}{PV}$$

$$Mr = \frac{MRT}{PV}$$

Example 1

a) Define the following terms

i) Critical pressure

ii) Ideal gas

iii) Real gas

iv) Critical temperature

b) "Some gases are ideal while other are not

c) 1.27 of sample of oxide of nitrogen believed to be either NO or NO_2 occupy the volume of 1.07 dm^3 at 25^0c and pressure of 737 mmHg. Explain what oxide is it and why? R = 0.0821 atm mol^{-1} k^{-1} L.

Solution

Mass = 1. 27g

Volume = 1.07 dm^3

Temperature = 737 mmHg

R = 0.0821

Unit conversion

1 dm^3 = 1.0 L

T = 273 + 25 = 298k

1 atm = 760 mmHg

χ = 0.97 atm

$$Mr = \frac{MRT}{PV}$$

$$Mr = \frac{1.27 \times 0.0821 \times 2981}{0.97 \times 1.07}$$

Mr = 29.9g/mol

Theoretical molar mass

$NO_2 = 14 + 32 = 46$

$NO = 30$

∴ The gas is NO because the molar mass is 30 g/mol.

2. Determination of densities of gaseous materials
From ideal gas equation

$PV = nRT$

But $n = \frac{M}{Mr}$

$PV = \frac{M}{Mr}RT$

$Mr\frac{PV}{V} = \frac{MRT}{V}$

$MrP = \frac{MRT}{V}$

But, $\frac{M}{V} = \rho$

$$\frac{MrP}{RT} = \rho$$

Example 1
At what temperature would the oxygen gas be if the pressure is kept constant at 745 mmHg . If the density of the gas is 1.00g/dm$^{3.}$ Given that
R is 0.0821 atm mol $^{-1}$ k^{-1} L

Solution
From O_2
Mr = 32
Pressure = 745
R = 0.0821
Density = 1.00g/dm^3

T = ?

$\rho = \frac{MrP}{RT}$

$T = \frac{32 \times 0.98}{1.00 \times 0.821}$

= 381.9k

∴ The temperature required = 381.9k

Example 2

What is the volume occupied by 13.7g of chlorine gas at 45°c and 745 mmHg

R = 0.0821 atom mol^{-1} k^{-1} L

Solution

M = 13.7g

T = 45°c

P = 745mmHg

R = 0.0821

Mr = 71

Conversion of units

T = 45 + 273 = 318K

P = 1 atm = 760mmHg

T = 745

P = 0.98 atm

From

$PV \times Mr = \frac{MRT}{PV} \times PV$

$\frac{MrPV}{MrP} = \frac{MRT}{MrT}$

$V = \frac{MRT}{MrT}$

$V = \frac{13.7 \times 0.0821 \times 318}{71. \times 0.98}$

V = 5.14 Liters

∴ The volume of chlorine gas is 5.14dm^3

EXAMPLES ON GAS LAWS

Example1

A certain mass of an ideal gas has a volume of 3.25dm^3 at 25^{o}c and 1.01 $\times 10^5$ NM $^{-2}$. What pressure is required to compress it to 1.88dm^3 at the some temperature.

Solution

$V_1 = 3.25$dm

$T_1 = 25^OC$

$P_1 = 1.01 \times 10^5$ NM^{-2}

$T_2 = 25^0$

$P_2 = ?$

$V_2 = 1.88$

So.

$$\frac{P_1 \quad V_1}{T_1} = \frac{P_2 \quad V_2}{T_2}$$

$$\frac{1.0 \times 10^5 \quad \times 3.25}{1.88} = \frac{P_2 \quad \times 1.88}{1.88}$$

Note:

$P_2 = 1.746 \times 10^5$NM^{-2}

1.01 10^{5}NM^{-2} = 1atm

1.01 10^{5}NM^{-2} = 760 mmHg

1 NM^{-2} = 1 P_a

Example 2.

It takes 54.4 sec. for 100cm^3 of a gas x to effuse through an aperture and 36 . 5 sec for 100cm^3 of O_2 to effuse through the same aperture

i) What is the molar mass of gas X

ii) Suggest the gas X

Solution

Rate

$$r_x = \frac{100cm^3}{54.4sec} = 2.74$$

$$rO_2 = \frac{100cm^3}{36.5sec} = 1.84$$

From Graham's law

$$\frac{r_x}{rO_2} = \sqrt{\frac{Mr_x}{MrO_2}}$$

$$\left(\frac{r_x}{rO_2}\right)^2 = \left(\sqrt{\frac{Mr_x}{MrO_2}}\right)^2$$

$$\left(\frac{r_x}{rO_2}\right)^2 = \frac{Mr_x}{MrO_2}$$

$$\left(\frac{2.74}{1.84}\right)^2 = \frac{Mr_x}{32}$$

$$\left(\frac{2.74}{1.84}\right)^2 \times 32 = Mr_x$$

$Mr_X = 70.9$

$Mr_X \approx 71$

i) The molar mass of gas X is 71g/mol

ii) The gas X is chlorine gas

Example *3*

a) Define the following terms

i. Effusion

ii) Critical temperature

b) State Grahm's law of diffusion

A certain volume of hydrogen takes 2min and 10 sec to diffuse through a porous plug and an oxide of nitrogen takes 10min 223 sec.

What is:

i) Molar mass of an oxide

ii) Give the following of an oxide

Solution

V be the volume of hydrogen

V be the volume of oxide

$$\frac{rH2}{ro} = \sqrt{\frac{M_O}{MH}}$$

$$\frac{v}{tH} \div \frac{V}{to} = \sqrt{\frac{M_O}{MH}}$$

$$\frac{V}{tH} \times \frac{to}{V} = \sqrt{\frac{M_O}{MH}}$$

$$\frac{to}{tH} = \sqrt{\frac{M_O}{MH}}$$

$$\left(\frac{to}{tH}\right)^2 = \left(\sqrt{\frac{M_O}{M_H}}\right)^2$$

$$\left(\frac{to}{tH}\right)^2 = \frac{M_O}{M_H}$$

$$\left(\frac{to}{tH}\right)^2 \times M_H = M_0$$

t_0 = 623 sec $M_H = 2$

t_H = 130 sec

$$\left(\frac{623}{130}\right)^2 \times 2 = M_O$$

$M_0 = 46$

i) The moles mass of the oxide is 46g/mol

ii) The formula of the oxide is NO_2

iii) Effusion is the escaping of a gas through a porous without molecular collision between molecules of gas.

iv) Graham's law of diffusion state that. At the same temperature and pressure the rate of diffusion of different is inversely proportional to the square roots their Mr mass.

v) Critical temperature is the temperature above which the gas cannot be liquefied without further cooling.

Example 4

a) State the kinetic theory of gases

b) Write down the equation of the gas which do obey all assumption in (a) above and define the terms

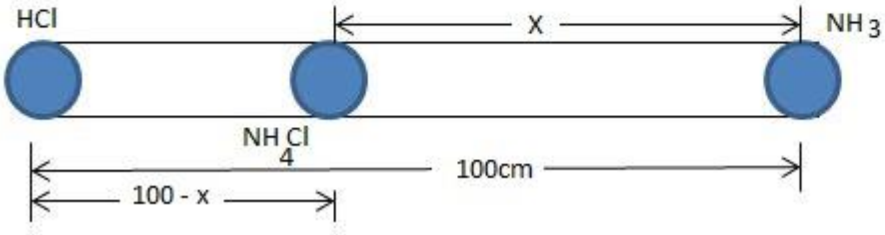
c) A plug of cotton wool one soaked in conc. Hcl where inserted into opposite ends of a horizontal glass tube

A disc of solid ammonium chloride formed in the tube plug is the 1m long how for from the ammonia plug is the deposited

Solution

Reaction

$NH_3 + Hcl \longrightarrow NH_4$



$$\frac{rHcl}{rNH_3} = \frac{dNH_3}{d}$$

$$\frac{dNH_3}{dHcl} = \sqrt{\frac{MHcl}{MNH_3}}$$

$$\left(\frac{X}{100-X}\right)^2 = \left(\sqrt{\frac{36.5}{1.7}}\right)^2$$

$$\left(\frac{X}{100-X}\right)^2 = \frac{36.5}{17}$$

$$\frac{X^2}{(100-X)^2} = 2.147$$

$$2.147\ \left(100-X\right]^2 = X^2$$

$$2.147\ \left(\ 100-X\right]^2\ X\ \left(100-X\right) = X^2$$

$$2.14\ \left(10000 - 100X - 100X + X^2\ \right] = X^2$$

$21407^{0} - 429.4X + 2.147X^2 = X^2$

$2.147X^2 - X^2 - 429.4X + 21470 = 0$

Solving quadratically

The solid deposit 59.4 cm away from N^{H_3}

a) The kinetic theory of gases states that

i) Molecules of a gas are far way such that force of attraction between the individual molecule is neglible

ii) The collision of gas molecules are perfectly elastic

iii) The pressure of a gas inside the container is due to the collision between the molecules of the gas and the wall of the container

iv) Gases container a large number of molecules which exist in continuous random motion

v) Kinetic energy of molecules is directly proportional to the absolute temperature

vi) The volume of individual molecules of the gas is negligible compared to the volume of the container.

b) Equation of the gases that obey kinetic theory of gases is as follows:
$PV = nRT$

Where by
P = Is the pressure of the gas
V = Is the volume of the gas
n = I s the number of molecules of the gas
R = is the universal constant
T = Is the absolute temperature

Example 5.
A) A certain volume of SO_2 diffuses through a porous plug in 10.0 min and the same volume of second gas takes 15.8 min. Calculate the relative molecules mass of the second gas
B) Nicked from a carbonyl, Ni (C_O) ***n*** Deduce the value of ***n*** from the fact that carbon monoxide diffuse 2.46 times faster than the carbon compound .
Solution
Let V be the volume of SO_2
V be the volume of gas x (gx)

$$\frac{rSO_2}{rgx} = \sqrt{\frac{Mrgx}{MrSO_2}}$$

Since the volume is the same

$$\left(\frac{tSO_2}{tgx}\right)^2 = \left(\sqrt{\frac{Mrgx}{MrSO_2}}\right)^2$$

$$\left(\frac{tSO_2}{tgx}\right)^2 = \frac{Mrgx}{MrSO_2}$$

$$\mathrm{tSO_2} = 600\mathrm{sec}$$

$$\mathrm{tgx} = 948\mathrm{sec}$$

$$\left(\frac{600}{948}\right)^2 = \frac{Mrgx}{64}$$

$$\left(\frac{600}{948}\right)^2 \times 64 = Mrgx$$

$$Mrgx = 25.6$$

$$\therefore The\ \ molar\ \ mass\ of\ the\ gas\ is\ 26g\,/mol$$

Solution

Mr of Ni $(C_O)n$ = 59 +(28)n

Mr of C_O = 28

Let time takes for carbonyl to diffuse = x

Time taken for carbon monoxide to diffuse = 2.46x

From Graham's law

$$\frac{RN_l CO)n}{RC_O} = \sqrt{\frac{MrC_O}{MrN_l\ \ (C_O)n}}$$

$$\frac{tN_l\ \ (C_O\ \ )n}{tC_O} = \sqrt{\frac{MrC_O}{MrN_l\ \ \ (C_O)n}}$$

$$\frac{X}{2.46X} = \sqrt{\frac{28}{28n+59}}$$

$$\left(\frac{x^2}{6.05\ x\ x^2}\right) = \left(\sqrt{\frac{28}{59+28n}}\right)^2$$

$$\frac{x^2}{6.05x^2} = \frac{28}{59+28n}$$

$$\frac{1}{6.05} = \frac{28}{59+28n}$$

28 = 9.75 + 4.62n

$$0.165 = \frac{28}{59+28n}$$

28 = 9.75 + 4.62n

$$\frac{28-9.75}{4.62} = \frac{4.62n}{4.62}$$

n = 3.9 $\approx$ 4

The volume of n in $N_l(C_O)$ is 4

MOLE FRACTION OF A GAS

Mole fraction of a gas is defined as the ratio of number of mass of such gas per total moles of gases present

The moles fraction is denoted by $\chi(\chi_l)$

Example

If there are two gas ie. Gas A and gas B in the container. Show how can you find the mole fraction each gas

Solution

Gases present

Gas **A** and gas **B**

Let **n A** be number of moles of gas A

nB be number of moles of gas B

nT = nA + nB

$$\chi_A = \frac{nA}{nT}\,\frac{nA}{nA+nB}$$

$\chi_B = \frac{nB}{nT} = \frac{nB}{nA\ +nB}$

Note

When mole are expressed in % will sum up to 100%

And when expressed in decimal will not exceed 1.00

From the example above In %

$\chi_A \quad + \ \chi_B \quad = \ 100\%$

In decimals

$\chi_A \quad + \ \chi_B \quad = 1.0$

Ie $\chi_A \quad = \quad 1 \ - \ \chi_B$

Example

The container was found to have 8g of oxygen and 4.4g of CO_2. What is the percentage composition of O_2 and CO_2 in the container

Solution

Mass of oxygen = 8g

Mass of carbon dioxide = 4.4g

No of mole of O_2 = $\frac{Mass}{molar\ mass}$

= $\frac{8}{32}$

= 0.25

No of moles of CO_2 = $\frac{4.4g}{44}$

= 0.1

Total number of moles = 0.1 + 0.25

= 0.35

% composition of m moles = $\frac{0.25}{0.35} \times \quad 100$

= 0.174 $\times$100

= 71.4%

% composition of $CO_2 = \frac{0.1}{0.35} \times 100$

$= 0.285 \times 100$

= 29%

The percentage of composition of O_2 and CO_2 in the container are 71.4% and 29%

Critical pressure is the pressure at which the gas starts to liquify

Example

A mixture of CO and CO_2 diffusion through a porous diagram in on half of the time taken for the same volume of Bromine vapour. What is the composition by volume of the mixture?

Solution

Let time taken by Br_2 be t

Time taken by the mixture $C_O + CO_2$ be $\frac{t}{2}$

Volume I is common rate of mixture = $\sqrt{\frac{Mr\ Br}{Mr\ Mixture}}$ tare of Br_2

but

$\frac{V}{\frac{t}{2}}$ = rate for mixture

$\frac{V}{t}$ = rate Br_2

Mr Br_2 = $80 \times 2 = 160$

$$\frac{V}{\frac{t}{2}} \div \frac{V}{t} = \sqrt{\frac{160}{M}}$$

$$\frac{V}{t} \times 2 \times \frac{t}{V} = \sqrt{\frac{160}{M}}$$

$$\frac{2V}{t} \times \frac{t}{V} = \sqrt{\frac{160}{M}}$$

$$2^2 = \sqrt{\frac{160}{M}}^{2}$$

$$4 = \frac{160}{M}$$

$$\frac{4M}{4} = \frac{160}{4}$$

$M = 40$

Mr of CO = 28

Mr of CO_2 = 44

χ_{CO} Mr χ_{CO_2} $+$ Mr $CO_2 = 40$

$\chi_{CO} \times 28 + \chi_{CO} + 44 = 40$

$\chi_{CO} + \chi_{CO} = 1$

$\chi_{CO_2} = 1 - \chi_{CO}$

$\chi_{CO} \times 28 + 1 - \chi CO \quad 44 \quad = \quad 40$

$28 \chi_{CO} + 44 - \chi_{CO} = 40$

$\frac{16\chi CO}{16} = 40 - 44$

$\frac{16\chi \ CO}{16} = \frac{-4}{16}$

$\chi_{CO} = 0.25$

% Of CO = 25%

% Of CO_2 = 75%

VAN DER WAAL EQUATION

The deviation of real gases from ideal behaviour has been stuglied by different scientist such as Amagat who deter minal different curves in $\frac{PVV}{RT\,S}$P

Later on van der wall explained the deviation and gave his equation which tries to work / take particle volume and attraction into account

In his equation

i) He subtracted the particle volume from the volume of the container. If the volume of container is V and that of particular be presented as "b"

Then the total volume of the system will be

$V - b$

This is called "Volume correction"

ii) He also added change in pressure which is caused by the existence of intermolecular forces of attraction among the gaseous molecules

This

$$\Delta p \propto \left(\frac{n}{v}\right)^2$$

$$\Delta P \quad \propto \quad \frac{n^2}{V^2}$$

But n = 1 for 1mole

$$\Delta P \propto \frac{1^2}{V^2}$$

$$\Delta \quad P = a\frac{1}{V^2}$$

$\Delta \quad P = \frac{a}{V^2}$ This is correction in pressure.

From ideal gas equation

PV = nRT (n = 1)

PV = RT

$$\left(P + \frac{a}{v^2}\right)(V - b) = RT$$

For one mole of the gas
Where “a” is a van der Waal constant
Note

In the van der Waal equation $\frac{a}{V^2}$ is added to the total pressure in order to cancel the effect of intermolecular forces of attraction

Expansion of the Van der waal equation

From Van der Waal’s equation

$$\left[P + \frac{a}{V^2}\right][V - b] = RT$$

PV $- Pb + \frac{a}{V} - \frac{ab}{V^2}$

PV = RT $+ Pb - \frac{a}{V} + \frac{ab}{V^2}$

The equation normally work under two assumption these is
If pressure is small then the volume is maximum

The terms Pb and $\frac{ab}{V^2}$ can be neglected

PV = RT - a/V

ii) When the pressure is very low that is **P** is approaching **O   P   O**

So V will be infinity V is ∞
We can calculate that the three term for correction can be neglected
PV = RT
This is for one mole
General conclusion
At very low pressure the real gases normally behave as ideal gases

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PHYSICAL CHEMISTRY - Two Components Liquid System

IMMISCIBLE LIQUIDS

Immiscible liquids are liquids which do not mix up to form homogeneous mixture.

When there are two immiscible liquids they form a so called immiscible pair.

Immiscible liquids form heterogeneous mixture.

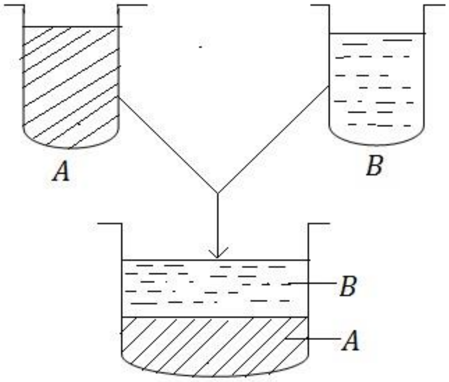
For the immiscible liquids, the intermolecular force of attraction is greater compared to intermolecular forces of attraction , that's why the liquids don’t mix up.

Since the liquids do not mix up, than their total vapor pressure (P_T) is equal to the sum of the pure vapor pressure of the components.

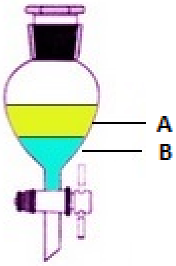
In immiscible liquids normally the denser component is found at the bottom (lower layer) while the less denser component is floating on the denser component (upper layer).

Example

Consider the immiscible pair of components A and B in which A denser than B



The immiscible pair is kept in a separating funnel in order to see them clearly.

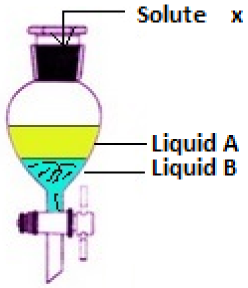


Partition law states that

"When a solute that is soluble in both liquids is added, then it will dissolve"

The ration of concentration of solute added in a pair of a immiscible liquid is constant

i.e



$$\frac{conc\ of\ x\ in\ A}{Conc\ of\ x\ in\ B} = constant$$

$$or$$

$$\frac{[x]\ in\ A}{[x]\ in\ B} = constant$$

The distribution of solute in a pair of immiscible liquid is governed by the Partition law or Distribution law.

PARTITION LAW

Partition law state that;

"In a pair of immiscible liquid, when solute which is soluble in both is added, it will distribute itself in such a way that the ratio of its concentration between the two liquid is constant."

The constant in distribution law is termed as Distribution coefficient, Distribution constant or Partition constant. It is denoted by Kd or K_D.

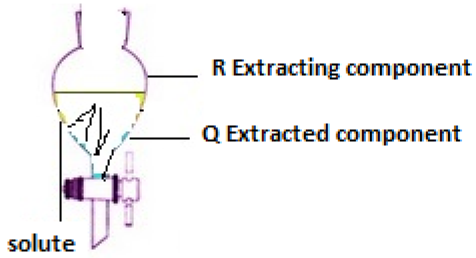
Note

The solute added in a pair of immiscible mixture can be in either of three states (liquid, gases, solid).

APPLICATION OF PARTITION LAW

One of the application is the extraction of solute from one component by mixing the solution with the second liquid that has no solute at all.

The liquid component which is removing the solute is called Extracting component and that in which the solute is removed from is called Extracted component.



In terms of Extractions

$$K_d = \frac{x \text{ in } \frac{g}{cc} \text{ in extracting}}{x \text{ in } \frac{g}{cc} \text{ in extracted}}$$

Note

Concentration is the amount of substance per unit volume.

$$K_d = \frac{Conc.of\ x\ \frac{g}{l} \text{ in extracting}}{Conc.of\ x\ \frac{g}{l} \text{ in extracted}}$$

$$K_d = \frac{Conc.of\ x\ \frac{m}{dm^3} \text{ in extracting}}{Conc.of\ x\ \frac{mol}{dm^3} \text{ in extracted}}$$

Also

$$K_d = \frac{x \text{ in } \frac{g}{cc} \text{ in extracting}}{x \text{ in } \frac{g}{cc} \text{ in extracted}}$$

NOTE

During extraction of solute the amount of solute in extracted component will be decreasing while the amount of extracting component will be increasing.

Example 1

a) State the partition law

Partition law state that;

"When a soluble solute is added in a pair of immiscible liquids, it will distribute itself in such a way that the ratio of its distribution between the two liquids is constant."

b) What does the terms "Partition coefficient" mean?

Partition coefficient is the concentration of solute in immiscible liquids.

c) An aqueous solution containing 10g per litre of solute X. This solution was shake with 100cc of ether, on shaking 6g of X was extracted. Calculate the amount of X extracted from aqueous so residue after shaking with 100cc of ether.

Solution

Given

Extracted component = 10g/ l

Volume of extracting component = 100cc

Mass of X in water (aqueous solution) = 10g

$$conc. of\ x\ in\, water = \frac{10^{-6}}{1000}$$

$$Kd = \frac{[x]\ in\ ether}{[x]\ in\ water}$$

$$Kd = \frac{[6g/1000cc]}{[4/1000cc]}$$

$$Kd = \frac{6}{100} \times \frac{1000}{4}$$

Kd = 15

Let the amount extracted be ‘a’

$$Kd = \frac{a/100}{\frac{4-9}{1000}}$$

$$Kd = \frac{a}{100}\, x \frac{1000}{4-a}$$

$$15 = \frac{10a}{4a}$$

60 - 15a = 10a

60 = 10a + 15a

60 = 25a

a = 60/25

a = 2. 4g/cc

∴ The amount of X extracted from the aqueous residue is 2. 4g/cc.

NOTE

If layers are not specified then the word "between" shows the numerator and denominator of the formula.

Example 2

A solid X is added to a mixture of benzene and water after shaking well and allowing to hand, 10ml of benzene layer was found to certain 0. 13g of X and 100ml of water layer contained 0.22g of X.

Calculate volume of distribution coefficient of solute X between benzene and water layer

Solution

Mass of solute X in benzene = 0.13g

Volume of benzene = 10ml

$$Conc.of\ x\ in\ benzene = \frac{0.13}{10}$$

$$= 0.013g/mol$$

$$Mass\ of\ solute\ x\ in\ water = 0.2$$

$$Volume\ of\ water = 100ml$$

$$Conc.of\ x\ in\ water = \frac{0.22}{100}$$

$$= 0.0022g/mol$$

$$K_d = \frac{Conc.of\ x\ in\ benzene}{Conc.of\ x\ in\ water}$$

$$= \frac{0.13}{0.0022}$$

$\therefore$ *The value of distribution coefficient is* 5.9

Example3

In the distribution of succinic acid between ether and water at 15°C , 20ml of the ethereal layer contains 0.092g of the acid. Find out the weight of the acid present in 50ml of the aqueous solution in equilibrium with it. If the coefficient kb between water and ether is (1.196g) and kd is 5.2

Solution

Mass of succinic acid in ethereal = 0.092g

Volume of ethereal = 20ml

Conc. Of succinic acid in ethereal = 0.092/20

= 4. 6 X 10^{-3} g/mol

Coefficient of succinic acid between water and ethereal

= 5.2

Volume of water = 50ml

Let X be the weight of succinic acid in water

Conc. of succinic in water = W/50

From;

$$Kd = \frac{[Succinic] in\ water}{[Succinic] in\ ether}$$

$$5.2 = \frac{\frac{w}{50}}{4.6x10^{-3}}$$

$$0.02392 = \frac{w}{50}$$

$$w = 1.196g$$

∴ The weight of the acid represent in aqueous solution 1.196g

Example 4

An aqueous solution of succinic acid at 15°C containing 0.07g in 10ml is in equilibrium with an ethereal solution which has 0.013g in mo. The acid has its normal molecular weight in both solvents. What is the concentration of the ethereal solution which is in equilibrium with aqueous solution containing 0.024g in 1oml?

(Ans: 0.00044g/ml)

Solution

Mass of succinic acid in aqueous solution = 0.07g

Volume of aqueous solution = 10mls

Concentration of succinic in ethereal = 0.013

Concentration of succinic in solution = 0.07/10

= 7 X 10^{-3}

$$Kd = \frac{[succinic]\ in\ H_2O}{[succinic]\ in\ etherial}$$

$$= \frac{7\times10^{-3}}{\frac{0.013}{10}}$$

$$= 7 \times 10^{-3} \times \frac{10}{0.013}$$

Kd = 5.38

Now

For second extraction

Mass of Aqueous solution = 0.024g

Volume of Aqueous solution = 10ml

Conc. Of succinic in aqueous solution = 0.024/10

= 2.4 X 10^{-3}

Volume of ethereal = 10ml

Let X be the concentration of succinic acid in ethereal

$$kd = \frac{[succinic]\ in\ H_2O}{[succinic]\ in\ etherial}$$

$$5.38 = \frac{2.4\times10^{-3}}{x/10}$$

$$5.38 = 2.4 \times 10^{-3} \times \frac{10}{x}$$

$$x = \frac{2.4\times10^{-3}\times10}{5.38}$$

$$x = 4.46 \times 10^{-3}$$

∴The Conc. of succinic acid in the ethereal solution is 0.0044g/ml.

For more than one extraction we normally use the following formula;

$$Ar_e = \left(\frac{Va}{Va+k+Vb}\right)^n w_o$$

Where by;

Ar_e is the amount of solute remain

Va is the volume of extracted solution

V_b is the volume of extracting solution

K is the constant of distribution

W_o is the original weight of the solute

From the formula, the amount extracted can be calculated as (A ex)

$A_{ex} = W_o - Ar_e$

$$A_{ex} = w_o - \left(\frac{Va}{Va+V_b\,k}\right)^n x\ w_o$$

If the amount extracted and amount remained are known, then their respective percentages can be calculated.

i.e

$$\%\,remained\ = \frac{Amount\ remained}{Original\ amount} \times 100\%$$

$$\%\,remained\ = \frac{Are}{w_o} \times 100\%$$

For extracted %

$$\%\,Extracted\ = \frac{Aex}{w_o} \times 100\%$$

Example 1

Solute the partition law

Calculate the amount of solute extracted by shaking 1 litre of aqueous solution containing 11g of Q with;

i) 100ml of ether (10g)

ii) Two successive volume of 50ml of ether (kd = 100) (10. 69g)

Answer

The partition law states that;

“When a soluble solute is added in a pair of immiscible liquid, it will distribute itself in such a way that, the ration of its distribution in the liquid is constant"

Data given

Mass of solute Q = 11g

Volume of aqueous solution = 1 litre = 1000cc

Conc. Of Q in aqueous solution

Let X be the amount extracted

$$\text{Kd} = \frac{[Q]\ in\ ether}{[Q]\ \ in\ H_2O}$$

$$100 = \frac{{}^{x}/_{100}}{11-{}^{x}/_{100}}$$

$$100 = \frac{x}{100} \times \frac{1000}{11-x}$$

$$100 = \frac{1000x}{1100-x}$$

$$100 = \frac{10x}{11-x}$$

10*x* = 1100 - 100x

110x = 1100

x = 10g.

∴ The solute extracted is 10g.

b) (ii) Number of extraction = 2

volume of ether (Vb) = 50ml.

volume of water (Vb) = 1000ml.

kd = 100

Wo = 11g

$$\text{Amount remained } \mathrm{Ar_e} = \left(\frac{V_a}{V_b + KV_b}\right)^n$$

$$= \left(\frac{1000}{1000 + 100 \times 50}\right)^2 \times 11$$

= 0.30556

Again

Aex = Wo - Are

= 11 - 0.3556

= 10.69g

∴ The solute extracted is 10.69g.

Example 2

a) Explain the principle of solvent extractions.

b) What is the condition necessary for solvent extraction?

Answer

b) The conditions of solvent extraction;

(i) The liquid to be mix must form immiscible solution.

(ii) the solute that is added to the extracted component must be soluble to the extracting component like wise.

a) The principles of solvent extraction;

i) Division of the volume of extracting components

So as the extraction to be efficient the extracting components can be divided into two or more partitions.

ii) When a liquid A (extracting component) mixed with liquid B (extracted component) must form the immiscible liquid with layer between them.

iii) The solute should be soluble in both liquid component hence it will allow its distribution such pair of immiscible liquid.

Example 3

a) State the partition law

Two form five girls each were given a solution which contains 10g of solute A in 900cc of solvent C. The first girl used 900cc of solvent B to extract solute from C. The second girl decided to use 300cc of B for the three extractions.

The distribution coefficient of solute A between C and B is 8.

i) Calculate the percentage of A left in C by the first girl.

ii) Calculate the percentage of A left in C by the second girl.

iii) Comment on the result obtained by the two girls.

Solution

a) Partition law states that:

“When a soluble solute is added in a pair immiscible liquid it will distribute itself in such a way that, the ratio of concentration of it in each component is constant".

b) Solution

Mass of solute Wo = 10g

Volume of extracted = 900cc

Volume of extracting Vb = 900cc

Distribution constant Kd = 8

Amount remained $Ar_e = \left(\frac{Va}{Va+kV_b}\right)^n w_o$

$$= \left(\frac{Va}{900 + 8x900}\right)^1 x10$$

= 1.11g

% remained = 1.11/10 X 100 = 11%

ii) % remained by the second girl

$$\text{Amount remained } \mathrm{Ar_e} = \left(\frac{V_a}{V_b+KV_b}\right)^n \times w_o$$

$volume\ of\ extracting = 300$

$n = 3$

$$= \left(\frac{900}{900+8\times300}\right)^3 \times 10$$

$= 0.2g$

$= \frac{0.2}{10} \times 100$

= 2%

∴ The percentage of A left inn C by the second girl is **2%**.

iii) For a successful extraction, the extracting liquid component must be divided into small portion as possible.

Example 4

Find out the principles of solvent extraction 100cm^3 of there is available for extracting the solute X from 100cm^3 of water. The partition coefficient of X between ether and water is 4.

i) Calculate the fraction of X extracted by using 100cm^3 of ether all at once.

ii) Calculate the fraction of X extracted by using 4 (If aqueous solution contains 8g of X)

Answer

The principles of solvent extraction.

i) The solute that is added in the immiscible mixture must be soluble to both liquids

So as the extraction to be perfect the extracting liquid must be divided into small portions as possible.

ii) When the extracted liquid is mixed with the extracting liquid, they should form immiscible mixture.

Solution

i) X extracted

given:

volume of extracting Vb = 100cm^3

volume of extracted Va = 100cm^3

Distribution constant k = 4

mass of solute X = 8g

from

$$Kd = \frac{[x]\ in\ ether}{[x]\ in\ water}$$

$$Kd = \frac{[x/100]}{[8-x/100]}$$

$$4 = \frac{8}{100} \times \frac{100}{8-x}$$

$$32 - 4x = x$$

$$32 = 5x$$

$$x = \frac{32}{5}g$$

∴The fraction of X extraction is

ii) Fraction of X extracted by using two 50cm3

$$Amount\ remained\ Ar_e = \left(\frac{Va}{Va+V_b k}\right)^n xw_o$$

$$= \left(\frac{100}{1000 \times 4 \times 50}\right)^2 \times 8$$

= 8/9

Amount extracted = 8 - 8/9

= 64/9 g

∴ The amount of X extracted by using 2, 50cm^3 is 64/9 g.

Example 5.

The Mogul oil company is disturbed by the presence of impurity M In its for star petrol. 1 litre of petrol contains 5g of M. In an effort to decrease the concentration of M in a petrol, Mogul has discovered the secret of solvent S and the partition coefficient of M between petrol and S is 0.01.

a) What is meant by the term partition?

b) Explain the principle of solvent extraction

c) Calculate the total mass m of M removed in by using

i) One portion

ii) Two 50cm^3 portion of solvent

Solution

a) Partition is the distribute of solvent in a pair of immiscible mixture.

b) i. The principle of solvent extraction;

"When the two components are added (extracted and extracting) they should form immiscible mixture."

ii. The solute that is used must be soluble in both extracting and extracted component.

iii. The extracting component should be divided in small portions so as the experiment to be perfect.

c) **Given**

Volume of petrol Va = 1 litre = 1000cm^3

Mass of M X = 5g

Distribution constant kd = 0.05

Volume of solvent S Vb = 100cc

i)

$$kd = \frac{[M]\ in\ petrol}{[M]\ in\ solvent}$$

$$0.01 = \frac{{}^{-x+5}/_{100}}{{}^{x}/_{100}}$$

$$0.01 = \frac{5-x}{1000} \times \frac{100}{x}$$

$$x(10 \times 0.01) = 5 - x$$

$$0.1x = 5 - x$$

$$0.1x + x = 45$$

$$1.1x = 5$$

$$x = 4.55g$$

∴ The mass removed is 4.55g

$$ii)\ Amount\ remained = \left(\frac{100}{100 + (10.0^{-1})x50}\right)^2 x\ 5$$

= 0.138g

∴ The amount removed is 5 - 0.138g = 4.86g.

SEPARATION OF IMMISCIBLE LIQUID

Immiscible liquids are separated by the process of steam distillation.

Steam distillation.

This is the process of separating immiscible liquids of different boiling points by passing super heated steam through

Condition necessary for steam distillation

In order for steam distillation to be feasible, the following conditions are;

i) The two liquids should have different B.P.

ii) The two liquids should be immiscible.

iii) There should be no volume change.

iv) The total vapor pressure of the liquids should be equal to the sum of the components vapor pressure.

APPLICATION OF STEAM DISTILLATION

Steam distillation can be used to determine the molar mass of unknown liquid.

Let the two liquids A and B form an immiscible pair

And

$n_A = a$

$n_B = b$

Since the two liquids are immiscible then, their distillation process can be explained in terms of their proportions or compositions (mole fraction).

From the number of moles of components the total number of moles can be obtained

i.e $n_T = n_A + n_B$

$n_T = a + b$

If n_T is known then mole fraction or composition can be calculated

i.e

$$X_A = \frac{n_A}{n_T}$$

$$X = \frac{a}{a+b}$$

$$Also$$

$$X_B = \frac{n_B}{n_T}$$

$$= \frac{a}{a+b}$$

For immiscible liquids , the ratio of their compositions is equal to the ratio of their vapor pressure.

$$\frac{X_A}{X_B} = \frac{P_A}{P_B}$$

$$\frac{a}{a+b} \, x \, \frac{b+a}{b} = \frac{P_A}{P_B}$$

$$\frac{a}{b} = \frac{P_A}{P_B}$$

But

$$a = \frac{mass\ of\ A}{Molar\ mass\ of\ A}$$

$$a = \frac{m_A}{M_A}$$

and

$$b = \frac{mass\ of\ B}{Molar\ mass\ of\ B}$$

$$b = \frac{m_B}{M_B}$$

$$\frac{m_A}{M_A} \div \frac{m_B}{M_B}$$

$$\frac{m_A}{M_A} \, x \, \frac{M_B}{m_B} = \frac{P_A}{P_B}$$

$$\boxed{\frac{M_B m_A}{M_A m_B} = \frac{P_A}{P_B}}$$

Where:

M_B is the molar mass of B

M_A is the molar mass of A

m_A is the mass of A

m_B is the mass of B

P_A is the vapor pressure of A

P_B is the vapor pressure of B

Example 1.

A solution of 6gm of substance X in 50cm^3 of aqueous solution is in equilibrium at room temperature with an ether solution of X containing 108gm of X in 100cm^3 . Calculate what weight of X could be extracted by shaking 100cm^3 of an aqueous liquids containing 10gm of X with;

i) 100cm$^{3\ \text{ether}}$

ii) 50cm^3 of ether twice at room temperature.

Solution

Concentration of X in H_2O = 6 g/50 cm^3

Concentration of X in ethereal = 108/100

$$Kd = \frac{[x]\ in\ extracting}{[x]\ in\ extracted}$$

$$= \frac{(108/100)}{(6/50)}$$

K = 9

Now

(i) $A_{ex} = w_o - \left(\frac{V_a}{V_b+KV_b}\right)^n \times w_o$

$$= \left(\frac{100}{1000+9\times100}\right)^1 \times 10$$

$$= \underline{9\text{g}}$$

$\therefore$ The amount extracted is $\underline{9\text{g}}$

(ii) $Aex = 10 + \left(\frac{100}{100+9\times50}\right)^2 \times 10$

$$= \underline{9.7\text{g}}$$

$\therefore$ The amount extracted is $\underline{9.7\text{g}}$

Example 2.

What is steam distillation?

State the four conditions necessary for steam distillation.

A organic liquid distills in steam, the partial pressure of the two liquids at the boiling point are 5.3 k pa for organic liquid and 96 k pa for water. The distillate contains the liquids in the ratio of 0.48g organic liquid to 1g of water. Calculate the molar mass of organic liquid.

Answer

a) Steam distillation Is the process of separating immiscible liquids of different boiling points by passing super heated steam through it.

b) The conditions necessary for steams distillation are;

i) The liquids must form immiscible solution.

ii) The total vapor pressure is equal to the sum of the vapor pressure of the components.

iii) There should be no change in volume.

iv) The liquids should have different boiling point.

Solution

P_o = 5.3kpa

m_o = 0.48

M_o = ?

P_w = 96 kpa

M_w = 18

m_w = 1g

$$\frac{M_o m_w}{M_w m_o} = \frac{P_w}{P_o}$$

$$M_o = \frac{M_w m_o P_w}{P_o m_w}$$

$$= \frac{18\ x\ 0.48\ x\ 96}{5.3\ x\ 1}$$

$$= 156.498$$

$$\therefore\ The\ molar\ mass\ of\ organic\ compound\ is\ \ 156\, g/mol$$

Note

Unit conversion

i) $1\ N/m^2 = 1$ pa

ii) 1 atm = 760 mmHg

iii) 1 atm = 1.01×10^5 Pa

iv) 1 atm = $1.01 \times 10^5\ N/M^2$

Example 3.

a) Differentiate between thermal distillation and steam distillation.

b) Bronbenzene (C_6H_5Br) distills in steam at 95°C the vapor of Bromobenzene and water are $1.39 \times 10^4\ N/M^2$ and $8.5 \times 10^4\ N/M^2$ .Calculate the percentage by mass of bromobenzene.

(c =12 Br =80 O = 16 H = 1) Note mass of H_2O =24g

Solution

a) Thermal distillation is the process of separating immiscible mixture by the use of thermal energy (heat) while

Steam distillation is the process of separating immiscible liquids by having different boiling points by passing super heated steam through it.

Data

$P_B = 1.39 \times 10^4\ N/M^2$

$P_w = 8.5 \times 10^4\ N/M^2$

$M_B = 157$

$M_w = 18$

$m_w = 24g$

from

From

$$\frac{M_B m_w}{M_w m_B} = \frac{P_w}{P_B}$$

$$m_B = \frac{M_B m_w P_B}{M_w P_w}$$

$$= \frac{157 \ x \ 24 \ x \ 1.39 \ x \ 10^4}{18 \ x \ 8.5 \ x \ 10^4}$$

$$= 34.23$$

$$Total\ mass = 34.23 + 24$$

$$= 58.23$$

$$\%\ by\ mass\ of\ B = \frac{34.23}{58.23}\ X\ 100$$

$$= 58.78\%$$

$$\therefore\ The\ percentage\ by\ mass\ of\ bromobenzene\ is\ 58.78\%$$

Example 4.

An organic liquid Q which do not mix with water distills in steam at 96°C under the pressure of 1.01 $\times 10^5 \ N/M^2$. The pressure of water at 96°C is 8.77 $\times 10^4$ N/M^{-2} . The distillate contains 51% by mass Q . Calculate the molar mass of Q.

Solution

Atmospheric pressure $P_{atm} = 1.01 \times 10^5$ N/M^2

$PQ = P_{atm}$ ¯ Pw

$P_w = 8.77 \times 10^4$

Now

$P_Q = 1.01 \times 10^5 - 8.77 \text{ X } 10^4$

$= 1033 \times 10^4$

$M_Q = ?$

$M_w = 18$

Mass of Q $m_B = 51g$

Mass of W $m_w = 49$

From

$$\frac{M_Q m_w}{M_w m_Q} = \frac{P_w}{P_Q}$$

$$M_Q = \frac{M_w m_Q P_w}{m_w P_Q}$$

$$= \frac{18 \; x \; 51 \; x \; 8.77 \; x \; 10^4}{49 \; x \; 1.33 \; x \; 10^4}$$

$$= 123.54 g/mol$$

$$\therefore \; The \; molar \; mass \; of \; Q \; is \; 123.54 g/mol$$

Example 5.

i) Define the term steam distillation.

ii) State the conditions necessary for steam distillation.

Calculate the molar mass of the compound B whose mixture with water distills at 95°C. At this temperature the pressure of compound B and water are 119mmHg and 64mmHg. The ratio of B to water is 1.61 : 1

Answer

i) Steam distillation is the process of separating immiscible mixture by passing super heated steam through it.

ii) The condition necessary for steam distillation are

There should be no change in volume

The liquid must form immiscible solution

The liquids should have different boiling point

The total vapor pressure is equal to the sum of pressure in the mixture.

Solution

P_B = 119mmHg

P_W = 64 mmHg

M_B = 1.61g

m_w = 1g

M_B = ?

M_w = 18g/mol

From

$$\frac{M_B m_w}{M_w m_B} = \frac{P_w}{P_B}$$

$$M_B = \frac{M_w m_B P_w}{P_B m_w}$$

$$M_B = \frac{18\ x\ 1.61\ x\ 64}{119}$$

$$= 15.59 g/mol$$

$$\therefore\ The\ molar\ mass\ of\ B\ is\ 15.59 g/mol$$

Example 6.

At a pressure of 760 mmHg, a mixture of nitrobenzene ($C_6H_5NO_2$) and water boils at 99^oC. The vapor pressure at this temperature is 733 mm. Find the proportion of water and nitrobenzene in the distillate obtained by steam distillation of pure $C_6H_5NO_{2.}$

Solution

Atmospheric pressure p_{atm} = 760

Pressure of H_2O P_w = 733

Pressure of nitrobenzene p_n = P_{atm} - Pw

= 760‾ 733

Pn = 27

M_w = 18

$M_n = (12 \times 6) + 5 + 14 (16 \times 2)$

$M_n = 123$

From

$$\frac{M_w m_n}{M_n m_w} = \frac{P_n}{P_w}$$

$$Multiply\ by\ \frac{M_n}{M_w}\ both\ sides$$

$$\frac{\cancel{M_n}}{\cancel{M_w}}\ x\ \frac{\cancel{M_w} m_n}{\cancel{M_n} m_w} = \frac{P_n}{P_w}\ x\ \frac{M_n}{M_w}$$

$$\frac{m_n}{m_w} = \frac{P_n}{P_w}\ x\ \frac{M_n}{M_w}$$

$$\frac{m_n}{m_w} = \frac{27}{733}\ x\ \frac{123}{18}$$

$$= \frac{3321}{13194}$$

$$= 0.25$$

$$= 1{:}\,4$$

$$\therefore\ The\ proportion\ of\ water\ to\ nitrobenzene\ is\ 1{:}\,4$$

Example 7.

A mixture of water and bromobenzene (C_6H_5Br) distills at 95^oC and the distillate contain 1.6 times as much C_6H_5Br as water by mass. At 95^OC the vapor pressure of water and C_6H_5Br are 640mmHg and 120mmHg respectively. Calculate the molecular weight of bromobenzene.

Solution

P_W = 640mmHg

P_B = 120mmHg

Mw = 18g/mol

MB = ?

Let X be the mass of water (Mw).

1.6X will be the mass of C_6H_5Br (MB).

From

From

$$\frac{M_B m_w}{M_w m_B} = \frac{P_w}{P_B}$$

$$M_B = \frac{M_w m_B P_w}{P_B m_w}$$

$$= \frac{18 \ X \ 1.6x \ X \ 640}{120 \ X \ x}$$

$$= 153.6$$

$$\therefore \textit{ The molecular weight of bromobenzene is } 153.6g/mol$$

COLLIGATIVE PROPERTIES

What is colligative properties?

Definition

Colligative properties are properties of the liquid which change depending on the number of particle of solute added, but not on the nature of the solute.

Mainly there are 4 colligative properties:

i) Lowering of vapor pressure.

ii) Boiling point elevation.

iii) Freezing point elevation.

iv) Osmotic pressure.

Assumptions of colligative properties:

i) The solute should not react with solvent

ii) The solute should be not volatile compared to solvent

iii) The solute should not dissociate or associate in the solvent

1. LOWERING OF VAPOR PRESSURE

Vapor pressure is the pressure exerted by vapor against the atmospheric pressure.

Lowering of vapor pressure: Is the difference between the original pressure of liquids solvent (P^o) and the pressure of the solution.

Effect of solute on the vapor pressure of the solvent

When solute particles are added in the solvent, the vapor pressure of the solution is lowered.

When solute particles dissolve in a given solvent normally they collide with the solvent molecule and hence prevent / decrease the number of solvent molecules that escape from liquid phase to vapor phase. This causes the decrease amount of vapor above the solution and normally causes the decrease in vapor pressure.

Relative lowering of vapor pressure

Relative lowering of vapor pressure is the ratio lowering vapor pressure to the vapor pressure the solvent.

RAOULT'S LAW OF VAPOR PRESSURE

It states that “The relative lowering of vapor pressure is proportional to the mole fraction of the solute added"

Mathematically

Let **P^o** be the vapor pressure of the solvent

P be the vapor pressure of solution

X_s be the mole fraction of solute

From Raoult's law of vapor pressure

$$\frac{P^{\circ}-p}{p^{\circ}} \propto X_s$$

$$\frac{P^{\circ}-p}{p^{\circ}} = KX_s \ \ where\ K = 1$$

$$\frac{P^{\circ}-p}{p^{\circ}} = X_s$$

For mole fraction of solute

Let **n** be number of mole solute

N be number of mole solvent

$$X_s = \frac{n}{n+N}$$

$$\frac{P^{\circ}-p}{p^{\circ}} = \frac{n}{n+N}$$

$$For\ dilute\ solution\ (n <<< N)\ \ n\ is\ very\ small$$

$$\therefore n \approx 0$$

The molar mass of solute can be determined

$$N\left(\frac{P^{\circ}-p}{p^{\circ}}\right) = n$$

$$But\ n = \frac{m}{Mr}$$

$$Mr \times N\left(\frac{P^{\circ}-p}{p^{\circ}}\right) = \frac{m}{Mr} \times Mr$$

$$Mr \times N\left(\frac{P^{\circ}-p}{p^{\circ}}\right) = m$$

$$Mr = \frac{m}{N\left(\frac{P^{\circ}-p}{p^{\circ}}\right)} = m$$

Example 1.

What do you understand by the term “ Colligative property”?

Colligative property is the property of a liquid which change depending on the number of properties of solute added but not on the nature of the solute.

A solution is prepared from 90g of water and 10.6g of non – volatile solute. If the vapor pressure of the solution at 60°C was found to be 0.1867 atm. Calculate the relative molecular mass of solute. Given that V. P of H_2O at 60°C was 0.1966 atm

Solution

Mass of water (solvent) = 90g.

Mass of non – volatile solute = 10.6g.

Vapor pressure of solution (P) = 0.1867 atm.

Vapor pressure of solvent Po = 0.1966 atm.

Recall

$$\frac{P^{\circ}-p}{p^{\circ}} = \frac{n}{N}$$

$$\text{But } n = \text{number of moles of solute}$$
$$N = \text{number of moles of solvent}$$

$$\frac{P^{\circ}-p}{p^{\circ}} = \frac{\text{mass of solute}}{\text{molar mass}} \div \frac{\text{mass of solvent}}{\text{molar mass}}$$

$$\frac{0.1966-0.1867}{0.1966} = \frac{10.6}{Mr} \div \frac{90}{18}$$

$$0.05 = \frac{190.8}{90Mr}$$

$$90Mr \times 0.05 = 190.8$$

$$\frac{4.5Mr}{4.5} = \frac{190.8}{4.5}$$

$$Mr = 42.4g/mol$$

$$\text{The molar mass of solute is } 42.4g/mol$$

Example 2.

When 114g of sucrose are dissolved in 1000g at water the vapor pressure was lowered 0.11mmHg . Calculate the relative molecular mass of sucrose if the vapor pressure of water at 20°C was 17.54 mmHg.

Solution

Mass of solute = 114g

Mass of solvent = 1000g

Lower vapor pressure = 0.11mmHg (P^o - P)

Vapor pressure of solvent = 17.54mmHg

Recall

$$\frac{P^{o}-p}{p^{o}} = \frac{n}{N}$$

$$But\ n = number\ of\ moles\ of\ solute$$
$$N = number\ of\ moles\ of\ solvent$$

$$\frac{P^{o}-p}{p^{o}} = \frac{mass\ of\ solute}{Mr\ of\ solute} \div \frac{mass\ of\ solvent}{Mr\ of\ solvent}$$

$$\frac{0.11-0.1867}{17.54} = \frac{114}{Mr} \div \frac{1000}{18}$$

$$6.27 \times 10^{-3} = \frac{114 \times 18}{1000Mr}$$

$$\frac{6.27Mr}{6.27} = \frac{2052}{6.27}$$

$$Mr = 327.3g/mol$$

$$The\ relative\ molecular\ mass\ of\ sucrose\ is\ 327.3g/mol$$

Example 3.

Calculate the vapor pressure lowering caused by the addition of 100g of sucrose of molar mass 342g/mol to 1000g of water if the vapor pressure of pure water at 25^{o}C is 23.8 mmHg.

Solution

Mass of solute = 100g

Mass of solvent = 1000g

Molar mass of solute = 342g/mol

Molar mass of solvent = 18g/mol

Vapor pressure of solvent = 23.8mmHg

$Recall$

$$\frac{P^0 - P}{P^0} = \frac{n}{N}$$

$But\ n = Number\ of\ moles\ of\ solute$

$N = Number\ of\ moles\ of\ solvent$

$$\frac{mass\ of\ solute}{Mr\ of\ solute} \div \frac{mass\ of\ solvent}{Mr\ of\ solvent}$$

$$\frac{P^0 - P}{23.8} = \frac{100}{342} \div \frac{1000}{18}$$

$$\frac{P^0 - P}{23.8} = \frac{100}{342} \div \frac{18}{1000}$$

$$P^0 - P = 23.8\left(\frac{100}{342} \div \frac{18}{1000}\right)$$

$$P^0 - P = \frac{42{,}840}{342{,}000}$$

$$P^0 - P = 0.125mmHg$$

$\therefore The\ lowering\ vapour\ pressure\ is\ 0.125mmHg$

Example 4.

The vapor pressure of ether (molar mass 74g/mol) is 442mmHg at 293k. If 3g of compound A are dissolved in 50g of ether at this temperature, the vapor pressure falls to 426mmHg. Calculate the molar mass of A assuming that the solution of A in ether is very dilute.

Solution

Mass of solute = 3g

Mass of solvent = 50g

Vapor pressure of solution P = 426mmHg

V.p of solvent P^o = 442mmHg

Mr of solvent = 74g/mol

Recall

$$\frac{P^0 - P}{P^0} = \frac{n}{N}$$

But n = Number of moles of solute

N = Number of moles of solvent

$$\frac{P^0 - P}{P^0} = \frac{mass\ of\ solute}{Mr\ of\ solute} \div \frac{mass\ of\ solvent}{Mr\ of\ solvent}$$

$$\frac{442 - 426}{442} = \frac{3}{M_r} \div \frac{50}{74}$$

$$\frac{16}{442} = \frac{3\ x\ 74}{50 M_r}$$

$$M_r = \frac{3\ x\ 74\ x\ 442}{16\ x\ 50}$$

$$Rmm = 122.6g/mol$$

$\therefore$ The molar mass of compound $A = 122.6g/mol$

Example 5.

18. 2g of urea is dissolved in 100g of water at 50^oC . The following of vapor pressure produced is 5mmHg. Calculate the molecular mass of urea if the vapor pressure of water at 50^oC is 92mmHg.

Solution

Mass of solute = 18.2g

Mass of solvent = 100g

Lowering vapor pressure (P^o - P) = 5mmHg

V . p of solvent (P^o) = 92mmHg

Required to find Mr of solute

$Recall$

$$\frac{P^0 - P}{P^0} = \frac{n}{N}$$

$But\ n = Number\ of\ moles\ of\ solute$

$N = Number\ of\ moles\ of\ solvent$

$$\frac{P^0 - P}{P^0} = \frac{mass\ of\ solute}{Mr\ of\ solute} \div \frac{mass\ of\ solvent}{Mr\ of\ solvent}$$

$$\frac{5}{92} = \frac{18.2}{M_r} \div \frac{100}{18}$$

$$\frac{5}{92} = \frac{18.2\ x\ 18}{100M_r}$$

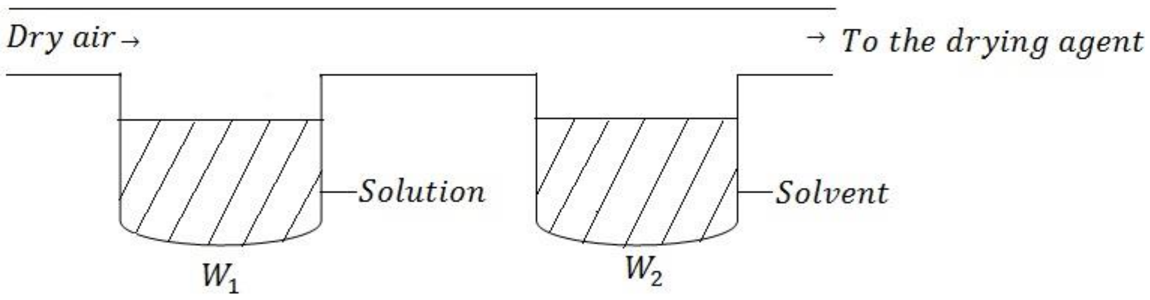
$$M_r = \frac{18.2\ x\ 18\ x\ 92}{500}$$

$$= 60.27g/mol$$

$\therefore\ The\ molecular\ mass\ of\ urea = 60.27g/mol$

EFFECT OF SOLUTE ON VAPOR PRESSURE BY OSWALD'S METHOD

Consider the solution made by dissolving solute in a given solvent. Then the dry air being passed through the two component



The passage of dry air cause the loss in mass (weight).

Let:

W_1 be loss in mass of solution.

W_2 be loss in mass of solvent.

Also the **P^o** is be the vapor pressure of solvent

P be the vapor pressure of solution

$W_1 \alpha \; P$

$W1 \; \alpha \; P^0 - P$

$W_1 = KP$ But $k = 1$

$W_1 = p$ ------------(i)

$W_2 = k(P^o - P) \quad k = 1$

$W_2 = P^o - P$ ---------(ii)

Now

Add the two equations

$W_1 + W_2 = P^o - P + P$

$W_1 + W_2 = P^o$

From Raoults,

Relative lowering of

$$V.p = \frac{P^0 - P}{P^0}$$

But $P^o - P = W_2$ and $P^o = W_1 + W_2$

Hence;

$$\frac{P^o - p}{p^o} = \frac{W_2}{W_{1+W_2}}$$

Where

P^o is the V.p of solvent

P is the V.p of solution

W_1 is the loss in mass of solution

W_2 is the loss in mass of solvent

Example 6

A current of dry air was passed through a solution of 2.64g of benzoic acid in 30g of ether ($C_2H_5OC_2H_5$) and then through pure ether. The loss in weight of the solution was 0.64g and that of ether was 0.0345g. Calculate the molecular mass of benzoic acid (122g/mol).

Solution

Weight of solution W_1 = 0. 645g

Weight of solvent W_2 = 0.0345g

Mass of solution m = 2.64g

Mass of solvent M = 30g

Mr of ether ($C_2H_5OC_2H_5$) = 74g/mol

But

$$\frac{P^{\circ}-p}{p^{\circ}} = \frac{W_2}{W_{1+W_2}}$$

$$= \frac{W_2}{W_{1+W_2}} = \frac{n}{n+N}$$

$$\frac{0.0345}{0.645+0.0345} = \frac{2.64/_{Mr}}{2.64/_{Mr}+{}^{30}/_{74}}$$

$$30 = \frac{n}{n+0.405}$$

$$0.0508n + (0.0508 \times 0.405) = n$$

$$0.0508n + 0.0206 = n$$

$$0.0206 = n - 0.0508n$$

$$n = 0.0217$$

$$But\ n\ is\ the\ number\ of\ moles\ of\ solute$$

$$n = \frac{Mass}{Molar\ mass}$$

$$n = \frac{2.64}{Molar\ mass}$$

$$Mr = \frac{2.64}{0.0217}$$

$$= 121.6$$

$$The\ molar\ mass\ of\ benzoic\ acid\ is\ 121.6g/mol\ \approx\ 122g/mol$$

Example 7

A stream of dry air was passed through a bulb containing a solution of 7.5g of aromatic compound in 75cm^3 of water and through another globe containing pure water. The loss in mass in the first globe was 2.81g and in the second globe was 0.054g. Calculate the Molar mass of aromatic compound 93.6.

Solution

Mass of solution = 7.5g

Mass of solvent = 75g

Loss in mass of solution = W_1 = 2.81g

Loss in mass of solvent = W_2 = 0.054g

From Oswald's law;

$$\frac{P^0 - P}{P^0} = \frac{W_2}{W_1 + W_2}$$

$$\frac{W_2}{W_1 + W_2} = \frac{n}{n + N}$$

$$Where \quad N = \frac{m}{M_r}$$

$$N = \frac{75}{18}$$

$$\frac{0.054}{2.81 + 0.054} = \frac{n}{n + \frac{75}{18}}$$

$$0.018855 = \frac{n}{n + 4.1667}$$

$$n = 0.018855n + 0.07856$$

$$n - 0.018855n = 0.07856$$

$$0.98115n = \frac{0.07856}{0.98115}$$

$$n = 0.08007$$

$$Now$$

$$M_r = 7.5 \div 0.08007$$

$$= 93.67g/mol$$

Example 8

In a experiment air was drown successively through a solution of sugar (38.89g per 100g H_2O) and the distilled water, and then through anhydrous calcium chloride. It was found that water lost was 0.0921g and the calcium chloride globe gained 110g. Calculate the molar mass of sugar

Solution

Mass of sugar = 38.89g, $W_1 + W_2$ = 5.16g

Mass of water 100g, $W_2 = 0.0921$g

$$\frac{P^0 - P}{P^0} = \frac{W_2}{W_1 + W_2} = \frac{n}{n + N}$$

$$\frac{W_2}{W_1 + W_2} = \frac{n}{n + N}$$

$Where$

$$N = \frac{m}{M_r}$$

$$N = \frac{100}{18}$$

$$\frac{0.0921}{5.16} = \frac{n}{n + \frac{100}{18}}$$

$$0.0178 = \frac{n}{n + 5.56}$$

$$n = 0.0178(n + 5.56)$$

$$n = 0.0178n + (0.0178\ x\ 5.56)$$

$$n = 0.0178n + 0.098968$$

$$n - 0.0178n = 0.098968$$

$$n(1 - 0.0178) = 0.098968$$

$$0.9822n = 0.098968$$

$$n = \frac{0.098968}{0.9822}$$

$$n = 0.1007$$

$$M_r = \frac{38.89}{0.1007}$$

Now

$$M_r = 386.2g/mol$$

2. BOILING POINT ELEVATION

What is boiling point?

Boiling point is the temperature at which liquid boils where by the vapor pressure of that liquid is equal to the atmospheric pressure.

Effect of solute(impurities) to the boiling point of the liquid.

When solute particles are added to the liquid, the solution formed. The boiling point of the solution formed is increased by some ^{o}C. The boiling point is elevated due to the increase in collision of solute molecules and liquid molecules. Finally the temperature being raised.

The difference between the boiling point of the solution and the boiling point of the liquid is what we call **Boiling point elevation**

The boiling point is denoted by ΔT

$\Delta T = T_2 - T_1$

Where by;

$\mathbf{T_2}$ is the boiling point of solution

$\mathbf{T_1}$ is the boiling point of solution

Note

ΔT is always positive.

The relationship between boiling point elevation and the amount of solute added

This relationship can be explained by two laws which are;

i) Blagden's law

ii) Raoult's law

i) **BLAGDEN’S LAW**

It states that;

“The change in temperature caused by addition of solute is directly proportional to the amount of solute being added”

If the amount is represented by m

From Blagden’s law

$$\Delta T \propto m$$

$$\Delta T = km \text{ (m expressed in moles)}$$

ii) **RAOULT’S LAW OF BOILING POINT ELEVATION**

It state that;

“The change in temperature caused by the addition of solute particles is inversely proportional the molecular weight of the solute added"

From Raoult's law

$$\Delta T\ \alpha\ \frac{1}{Mr}$$

$$\Delta T = \frac{K}{Mr}$$

Where we combine the two Laws

$$\Delta T\ \alpha\ \frac{m}{Mr}$$

$$\Delta T = \frac{Km}{Mr}$$

$$\text{Where by } \frac{m}{Mr} \text{ is equal to the MOLALITY of the solution and is denoted by } M_L$$

What is Molality?

Molality is the number of moles of solute per 1kg of the solvent.

$$\Delta T = kMl$$

$$But$$

$$Ml = \frac{n_x}{m_s}$$

Where

m_s mass of solvent in **kg**

n_x number of moles of solute

If **m_s** is given in **'g'**

Then it has to be converted to kg

$$\Delta T = \frac{kn_x}{m_s\ x\ 10^{-3}}$$

But

K is called boiling point elevation constant or ebullioscopic constant (k)

$$\Delta T = K_b \frac{nx}{Ms \times 10^{-3}}$$

K_b *is also known as molar elevation constant*

Definition

Molar elevation constant is the boiling point elevation produced when 1 mole of solute is dissolved in 1kg of the solvent.

$$\Delta T = K_b \frac{nx}{Ms \times 10^{-3}}$$

But

$$nx = \frac{mx}{Mx}$$

$$\Delta T = \frac{K_b mx}{Mx \times ms \times 10^{-3}}$$

Or

$$\Delta T = \frac{K_b mx \times 1000}{Mx \times ms}$$

Example 1

a) Define the following

i) Boiling point

ii) Boiling point elevation constant

iii) Ebullioscopic constant

Answer

i) **Boiling point** is the temperature at which liquid boils where by the vapor pressure of that liquid is equal to the atmosphere pressure.

ii) **Boiling point elevation** constant is the temperature change when 1 mole of solute is dissolved 1kg of the solvent.

iii) **Ebullioscopic constant** is the boiling point elevation obtained when 1 mole of solute is dissolved in 1kg of the solvent.

b) What is the boiling point of the solution containing 3moles of sugar in 1000g of water (Kb for H_2O is 0.52).

Solution

Number of moles of solute $n_x = 3$

Kb = 0.52

Mas of solvent = 1000g

$$\Delta T = K_b \frac{nx}{Ms \times 10^{-3}}$$

But

$$nx = \frac{mx}{Mx}$$

$$\Delta T = \frac{K_b nx}{Ms}$$

$$= \frac{0.52 \times 3}{1}$$

$$\Delta T = 1.56$$

$$\Delta T = T_2 - T_1$$

$$\Delta T + T_1 = T_2$$

$$1.56 + 100 = T_2$$

$$T_2 = 101.56°c$$

$$The\ boiling\ point\ of\ the\ solution\ is\ 101.56°c$$

Example 2

When 1g of solute was added in 10g of water the boiling point elevation was 1.2^{o}C. Calculate the molar mass of solute if the ebullioscopic constant of water is 0.52

Solution

Mass of solute m_x = 1g

Mass of solvent = 1og

B.P elevation T = 1.2^oC

Kb of solvent = 0.52.

$$\Delta T = \frac{K_b mx \times 1000}{Mr \times ms}$$

$$\Delta T = \frac{0.52 \times 1 \times 1000}{Mr \times 10}$$

$$Mr = 520 \div 12$$

$$Mr \ = 43.3 g/mol$$

$$The\ molar\ mass\ of\ solute\ is\ 43.3g/mol$$

Example 3.

A solution containing 18.4g glycerine per 100g of water boil at 101.04^oC. Calculate the molar mass of glycerine .

Kb for 0.52^oC kgmol^{-1}

Solution

Mass of solute mx = 18.4g (T_1 = B.P of H_2O)

Mass of solute m_s = 100g

B.P of solution T_2 = 101.04^oC

Kb of solvent = 0.52

$$\Delta T = \frac{K_b mx \times 1000}{Mrx \times ms}$$

$$T_2 - T_1 = \frac{K_b mx \times 1000}{Mrx \times ms}$$

$$101.04 - 100 = \frac{0.52 \times 18.4 \times 1000}{Mr \times 100}$$

$$\frac{1.04Mr}{1.04} = \frac{95.68}{1.04} = 43.3g/mol$$

$$Mr = 92g/mol$$

$$The\ molar\ mass\ of\ gycerine\ is\ 92g/mol$$

Example 4

The boiling point of a solution containing 0.2g of substance X in 20g of ether is 0.17k higher than that of the pure ether . Calculate the molecular mass of X . The boiling point constant of ether per 1kg is 2.16k (127. 8g/mol).

Solution

Mass of solute = 0.2g

Mass of solvent = 20g

B .P elevation ΔT = 0.17k

Kb of ether (solvent) = 2.16

$$\Delta T = \frac{K_b mx \times 1000}{Mr \times ms}$$

$$0.17 = \frac{2.16 \times 0.2 \times 1000}{20Mr}$$

$$Mr = \frac{2.16}{0.17}$$

$$Mr = 127.06g/mol$$

Example 5

Acetone boils at 56.38°C and a solution of 1.41g of an organic solid in 20g of acetone boils at 56.88°C . If k for acetone per 100g is 16.7°C . Calculate the mass of one mole of the organic solid.

Solution

B .P of solvent T_1 = 56.38°C

B.P of solution T_2 = 56.88°C

Mass of solute = 1.41g

Mass of solvent = 20g

Kb of solvent = 1.67

$$\Delta T = \frac{K_b mx \times 1000}{Mr \times ms}$$

$$T_2 - T_1 = \frac{K_b mx \times 1000}{Mr \times ms}$$

$$56.88 - 56.38 = \frac{1.67 \times 1.41 \times 1000}{Mr \times 20}$$

$$0.5Mr = 117.735$$

$$Mr = 235.47g/mol$$

$$Now\ for\ 1\ mole$$

$$n = \frac{m}{Mr}$$

$$1 = \frac{m}{235.47g}$$

$$The\ mass\ of\ ome\ mole = 235.47g$$

3. FREEZING POINT DEPRESSION

What is freezing point?

Is the temperature at which liquid change into solid state /freeze.

Effect of solute on the freezing property of the liquid

When solute is added to a certain liquid, the freezing point of the liquid is lowered. This is because the solute particles disturb the intermolecular forces between the molecules of the liquids.

The difference between the freezing point of the solvent (pure liquid) and that of solution is what we call freezing point

Depression

Freezing point depression is denoted by ΔT

$\Delta T = T_2 - T_1$

Where;

T_1 is the freezing point of solvent

T_2 is the freezing point of solution

The freezing point depression (T) is related to the amount of solute added by the following expression

Note

The some derivation as in boiling point elevation

$$\Delta T = K_f \frac{nx}{Ms \times 10^{-3}}$$

$$\Delta T = K_f \frac{mx \times 1000}{Mrx \times Ms} \qquad If\ Ms\ is\ in\ 'g'$$

Definition

Freezing point depression equation;

Kf is freezing point constant or Cryoscopic constant.

Definition

Cryoscopic constant is the temperature expressed when the molar weight of solute dissolved in a kg of solvent.

Example 1

Ethanoic acid has the freezing point of 16.63^oC on adding 2.5g of solute to 40g of the acid, The freezing point was lowered to 11.48^oC. Calculate the molar mass of the solute if kf is 3.9^oC kgmol^{-1}

Solution

F.P of ethanoic T_1 = 16. 63^oC

Mass of solute = 2. 5g

Mass of solvent = 40g

Lowered F.P T_2 = 11.48^oC

K_f of the solvent = 3.9^oC kgmol^{-1}

$\Delta T = T_2 - T_1$

$= 11.48 - 16.63^o$

$= -5.15^0C$

Now

$$\Delta T = K_f \frac{n \times 1000}{Ms}$$

$$5.15 = \frac{3.9 \times n \times 1000}{40}$$

$$206 = 3900n$$

$$n = 0.0528$$

$$But$$

$$Mr = \frac{2.5}{0.0528}$$

$$= 47.3g/mol$$

Example 2

When 0.946g of organic substance was added in 15g of water resulting into the solution which was found to have the freezing point of -0.651^oC (k_f is 3.9).

i) Calculate the molar mass of solute (179.2)

ii) What is the molecular formula of solute (mf) if its empirical formula is CH_2O?

Solution

Mass of solute = 0.946g

Mass of solvent = 15g

F. P of solution = -0.651°C

K_f of solvent = 1.86

F.P of solvent = 0°C

$T = T_2 \; T_1$

$T = 0.651 - 0$

$T = {}^{-}0.651$

$$(i)\quad \Delta T = \frac{K_f \; X \; M_x \; X \; 1000}{M_r \; X \; m_s}$$

$$0.651 = \frac{1.86 \; X \; 0.946 \; X \; 1000}{M_r \; X \; 15}$$

$$M_r = \frac{1.86 \; X \; 0.946 \; X \; 1000}{15 \; X \; 0.651}$$

$$= 180.2g/mol$$

$$\therefore The\ molar\ mass\ of\ solute = 180.2g/mol$$

$$(ii)\ Molecular\ formular$$

$$(CH_2O)_n = 180.2$$

$$\frac{30n}{30} = \frac{180.2}{30}$$

$$Now$$

$$= (CH_2O)_6$$

$$= C_6H_{12}O_6$$

$$\therefore The\ molecular\ formular\ is\ \ C_6H_{12}O_6$$

Example 3

Define the following terms

i) Boiling point.

ii) Freezing point.

iii) Freezing point depression.

iv) Cryoscopic constant.

Answers

i) **Boiling point** Is the temperature st which liquid boils where by the vapor pressure of that liquid is equal to the atmospheric pressure.

ii) **Freezing point** Is the temperature at which liquid change into solid state. e.g f.P of water is O°C.

iii) **Freezing point depression** Is the difference between the freezing point of the solution and that of the solvent (pure liquid).

iv) **Cryoscopic constant** Is the temperature depressed when the molar weight of solute is dissolved in a kilogram of solvent.

b) 7.85g of the compound Y having the empirical formula of C_5H_4 was dissolved in 310g of benzene (C_6H_6) . If the freezing point of the solution is 1.05°C below that of pure benzene.

i) Determine the molecular mass Y.

ii) Find the molecular formula of Y if Kf for C_6H_6 is 5.12°C kg mol^{-1}

4. OSMOTIC PRESSURE

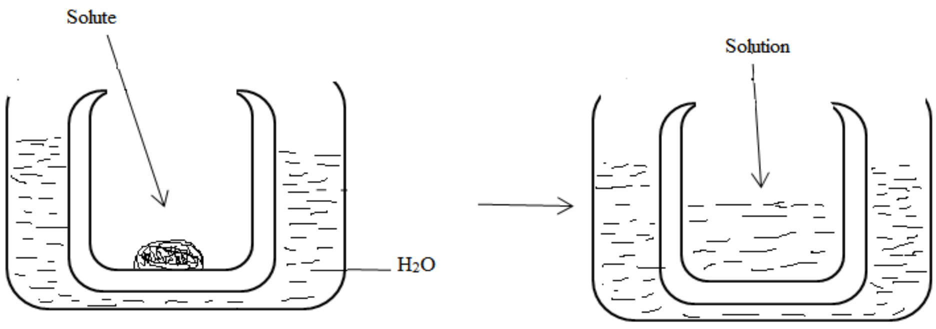
What is osmotic pressure ?

Osmotic pressure: Is the force per unit area which occur as the results of solvent to flow From low concentration to the high concentration of solute through a semi permeable membrane .

Osmotic pressure causes the osmosis to take place.

Osmosis: Is the tendency of solvent molecular to migrate from the region of low concentration to the region of high concentration of solute.

Consider the simple experiment below



Factors affecting the Osmotic pressure of the substance

The Osmotic pressure of the substance affected by the two factors

i) Concentration or volume of the solvent.

ii) Temperature

i) CONCENTRATION OR VOLUME OF THE SOLVENT

The osmotic pressure of the substance varies directly proportional to the concentration and inversely proportional to the volume .

i.e An increase in concentration of the solution will cause an increase in osmotic pressure of the solution.

Also increases in osmotic pressure cause the decrease in volume.

ii) TEMPERATURE

The temperature varies directly proportional to the osmotic pressure as long as the temperature do not exceed the optimum temperature of the semi permeable membrane.

The effect of two factors above are explained by Vant- hoff's laws of osmotic pressure.

VANT – HOFF'S LAWS OF OSMOTIC PRESSURE

Vant – hoff tried to put forward his laws which explain the variation of osmotic pressure with concentration and temperature.

There are two laws developed, These are:

i) Vant- hoff"s first law of osmotic pressure.

ii) Vant – hoff's second laws of osmotic pressure.

i) VANT – HOFF’S FIRST LAW OF OSMOTIC PRESSURE

It states that;

“The osmotic pressure of the solution is inversely proportional to its volume"

Let the osmotic pressure be denoted by π

From 1st law

$$\pi \ \alpha \ \frac{1}{V}$$

$$\pi = \frac{K}{V} \underline{\qquad} (i)$$

ii) VANT – HOFF’S SECOND LAW OF OSMOTIC PRESSURE

It states that;

“The osmotic pressure of the solution is directly proportional to temperature”

From 2nd law

$$\pi \ \alpha \ T$$

$$\pi = KT \underline{\qquad} (ii)$$

By combining the two laws

$$\pi = \frac{kT}{v}$$

$$\pi = kT$$

$$But \ \ k = R \ (in \ Joules)$$

$$\pi v = RT$$

This is for 1 mole, But for ‘n’ mole the formula will be

$$\boxed{\pi v = nRT}$$

Example1

7.85g of the compound Y having the empirical formula of C_5H_4 was dissolved in 301g of Benzoic (C_6H_6) . If the freezing point of the solution is 1.05°C below that of pure benzene.

i) Determine the molecular mass of Y

ii) Find the molecular formula of Y if kf for C_6H_6 is 5.12°C kg mol^{-1}

Solution

Mass of solute = 7.85g

Mass of solvent = 301g

F . P depression ΔT = 1.05°C

Kf of solvent = 5.12°C kgmol^{-1}

$$(i)\ \ \Delta T = \frac{K_f\ X\ M_x\ X\ 1000}{M_r\ X\ m_s}$$

$$1.05 = \frac{5.12\ x\ 7.85\ x\ 1000}{M_r\ x\ 301}$$

$$\frac{\cancel{316.05}M_r}{\cancel{316.05}} = \frac{40192}{316.05}$$

$$M_r = \frac{40192}{316.05}$$

$$M_r = 127.2$$

$$\therefore\ The\ molar\ mass\ of\ Y\ is\ 127.2g/mol$$

$$(ii)\ (C_5H_4)_n = M_r$$

$$(64)_n = 127.2$$

$$\frac{64n}{64} = \frac{127.2}{64}$$

$$n = 1.987$$

$$n \approx 2$$

$$But$$

$$m.f = (C_5H_4)_n$$

$$= (C_5H_4)_2$$

$$\therefore The\ molecular\ formular\ is\ \ C_{10}H_8$$

Example 2

Calculate the molar mass of solute given that 35g of solute dissolved in $1dm^3$ has osmotic pressure of 5.51 N/M^2 at 20^oC. ($R = 8.314\ Jmol^{-1}k^{-1}$)

Solution

Mass of solute = 35g

Volume of solution = $1dm^3$

Osmotic pressure $\pi = 5.51$

Temperature T = $20^oC + 273k$

= 293k

$\pi v = nRT$

$$M_r \; x \; \pi v = \frac{m}{M_r} RT \; x \; M_r$$

$$M_r = \frac{mRT}{\pi v}$$

$For \; volume \; v,$

$$1m^3 = 10dm^3$$

$$x = 1dm^3$$

$$x = 10^{-3}m^3$$

Now

$$M_r = \frac{mRT}{\pi v}$$

$$= \frac{35 \; x \; 8.314 \; x \; 293}{5.51 \; x \; 10^5 \; x \; 10^{-3}}$$

$$= \frac{85260.07}{551}$$

$$= 154.74 g/mol$$

$\therefore The \; molar \; mass \; of \; solute = 154.74 g/mol$

Example 3

a) Define

i) Osmosis

ii) Osmotic pressure

b) Differentiate between osmosis and diffusion

Answers

a) i. **Osmosis** : Is the tendency of a solvent molecules to move from the region of law concentration to the region of high concentration of solute.

ii. **Osmotic pressure** : Is the force per unit area which occur as the result of solvent to flow from low concentration to the high concentration of solute through a membrane.

b) **Osmosis** is the movement of solvent molecules from the region of low concentration to the region of high concentration of solute through a semi- permeable membrane **while Diffusion** is the movement of gases molecules from the region of high concentration to a region of low concentration .

c) Calculate the osmotic pressure of the following solution at 25^{o}C

i) Sucrose solution of concentration 0.213M (527.72 N/m^2)

ii) A solution of glucose ($C_6H_{12}O_6$) made by dissolving 144g/dm^3 . (1.1982 x 10^6 N/m^2)

c) Solution

Temperature T = 25^{o}C + 273

= 298k

Molarity = 0.213M

$$(i)\ Molarity = \frac{n}{v}$$

$$\pi v = nRT$$

$$\pi = \frac{n}{v}RT$$

$$\pi = 0.213\ x\ 8.314\ x\ 298$$

$$\pi = 527.72Nm^{-2}$$

$$\therefore The\ osmotic\ pressure\ of\ the\ solution\ is\ \ 527.72Nm^{-2}$$

(ii) Molar mass of glucose = 180

Concentration = 144g/dm^3 = 144000g/m^3

$$Molarity = \frac{C0nc.}{M_r}$$

= 144000 ÷ 180

= 800M

Osmotic pressure π = MRT

$= 800 \times 8.314 \text{ X } 298$

$= 1.982 \text{ X } 10^6 N/M^2$

∴ The osmotic pressure of a solution = $1.982 \text{ X } 10^6$ N/M^2

Example 4

Calculate the osmotic pressure of the solution containing 12g of $C_6H_{12}O_6$ in 300g of water at 20^{o}C.

R = 8. 314 Jmol $^{-1}$k^{-1}(54.13 X 102 N/m^{-2})**.**

Solution

Mass of solute = 12g

Mass of water = 300g hence volume = 300cm^3

Temperature T = 20^o + 273
= 293k

But
1m = 100cm

1m^3 = 100^{3}cm^3

$$X = \frac{300cm^3}{100^3}$$

X = 3 X 10 $^{-4}$

$For\ Osmotic\ pressure,$

$$\pi v = nRT$$

$$\pi = \frac{n}{v}RT$$

But

$$n = \frac{12}{180}$$

$$\pi = \frac{\frac{12}{180}\ x\ 8.314\ x\ 293}{3\ x\ 10^{-4}}$$

$$= 54.13\ x\ 10^{2} Nm^{-2}$$

Example 5

Calculate the osmotic pressure of 10% glucose solution at 50^{o}C R= 8.314 Jmol^{-1}k^{-1}

Solution

Temperature T = 50^{o}C + 273

= 323k

Mass = 10% glucose

Molar mass of glucose = $C_6H_2O_6$

= 180

$$mass = \frac{10}{100} x\ 180$$

$$= 18g$$

$$n = \frac{mass}{M_r}$$

$$n = \frac{18}{180}$$

$$= 0.1$$

Now,

$$\pi v = nRT$$

$$\pi = \frac{nRT}{v}$$

$$\pi = \frac{0.1\ x\ 8.314\ x\ 323}{1\ x\ 10^{-3}}$$

$$= 2.685\ x\ 10^5 Nm^{-2}$$

$\therefore$ *The osmotic pressure of the solution is* $2.685\ x\ 10^5 Nm^{-2}$

Example 6

37.44g of haemoglobin, the protein of red blood cell which carries the oxygen in the blood, were dissolved in a dm^3 of water.

The solution formed had an osmotic pressure of 1.37 kPa at body temperature of 37^oC.

Determine the molar mass of haemoglobin.

Solution

Mass of solute = 37.44g

Volume = 1 dm^3

Temperature = 37^oC + 273k

=310k

Osmotic pressure = 1.37 kPa X 1000

= 1370Pa

$$\pi = \frac{nRT}{v}$$

$$\pi = \frac{mRT}{M_r v}$$

$$M_r = \frac{mRT}{\pi v}$$

$$M_r = \frac{37.44\ x\ 8.314\ x\ 310}{1370\ x\ 1\ x\ 10^{-3}}$$

$$= 70.4g/mol$$

$$\therefore The\ molar\ mass\ of\ haemoglobin = 70.4g/mol$$

Example 7

A solution containing 10g of solute A in 300. Of water has an osmotic pressure of 375mm of 25^{o}C. What will be the osmotic pressure be dissolving 2.55g of solute A in 50g of water? R = 0.0821 atm mol^{-1} k $^{-1}$ L.

Solution

Mass of solute A M_A =10g

Volume of solvent = 300cm^3 = 0.3m^3

Osmotic pressure = 375mmHg

1 atm = 760mmHg

X = 375mmHg

$$X = \frac{375}{760}$$

= 0.49

Temperature T = 25^{o}C + 273k

= 298k

$$M_r = \frac{mRT}{\pi v}$$

$$M_r = \frac{10 \ x \ 0.0821 \ x \ 298}{0.49 \ x \ 0.3}$$

$$= 1664g$$

$$But\ mass\ of\ solute = 2.55g$$

$$Volume = 0.05l$$

$$\pi = \frac{nRT}{v}$$

$$\pi = \frac{2.55 \ x \ 0.0821 \ x \ 298}{1664 \ x \ 0.05}$$

$$= 0.749 \approx 0.75atm$$

$$\therefore The\ osmotic\ pressure\ is\ 0.75atm$$

COLLIGATIVE PROPERTIES OF ASSOCIATIVE AND DISSOCIATIVE SOLUTE

Colligative properties depends on vant hoff's factor . Vant hoff factor is the ratio of observed colligative properties to that of calculated colligative property.

OR

Vant hoff factor is the ratio of experimental colligative property to that of theoretical colligative property.

VANT HOFF FACTOR

Vant hoff's factor is denoted by ‘g’ or ‘l’ and therefore

$$g = \frac{Observed\ colligative\ property}{Calculated\ colligative\ property}$$

$$OR$$

$$i = \frac{Experimental\ colligative\ property}{Theoretical\ colligative\ property}$$

Vant's hoff factor is obtained when the solute added is not completely ionized (dissociated). Also some solutes, when added in the solvent tend to associate.

The phenomena of associating or dissociating of solute is explained in terms of degree (degree of association or dissociation).

The degree of dissociation is

Define:

The degree of dissociation is the percentage or fraction of moles of ions which have gone into the solution.

It is denoted by α

The degree of dissociation is related to Vant hoff's factor and the number of ions formed by the solute dissolved.

$i.e$

$$\alpha = \frac{g - 1}{N - 1}$$

Where by;

α is the degree of dissociation

g is the Vant hoff's factor

N is the number of ions

But

$$g = \frac{o.c.p}{c.c.p}$$

$$\alpha = \frac{\frac{o.c.p}{c.c.p} - 1}{N - 1}$$

Example 1.

Calculate the N values for the ionization of the following compounds

Solution

i) Al (OH)3

Ionization equation

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$

$N = 1 + 3$

$= 4$

ii) FeCl3

Ionization equation

$FeCl_3 \rightleftharpoons Fe^{3+} + 3Cl^-$

$N = 3 + 1$

$= 4$

iii) BaCl2

Ionization equation

$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$

$N = 1 + 2$

$= 3$

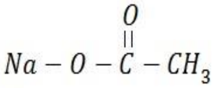
iv) NaCl

Ionization equation

$NaCl \rightleftharpoons Na^+ + Cl^-$

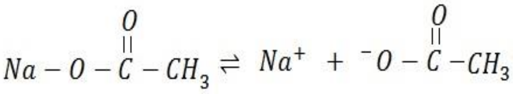
$N = 1 + 1$

$= 2$



v) $Na - O - \overset{\overset{O}{||}}{C} - CH_3$

Ionization equation



$Na - O - \overset{\overset{O}{||}}{C} - CH_3 \rightleftharpoons Na^+ + {}^-O - \overset{\overset{O}{||}}{C} - CH_3$

$N = 1 + 1$

$= 2$

NOTE

The degree of dissociation can be expressed terms of

i) Percentage%

ii) Decimals

When it is expressed in percentage it cannot exceed 100% and

When it is expressed in decimal it cannot exceed 1.00

Also when solute is ionizing completely its degree of dissociation become 100% OR 1.00

Example 2.

What will be the boiling point of the solution containing 2.4g NaCl in 250cm^3 of water . it an aqueous solution of NaCl is 70% Dissociation.

(kb water = 1.86)

Solution

Mass of solute m_x = 2.4g.

Mass of solvent m_s = 250g.

Kb = 1. 86.

α = Degree of elevation 70% or o.7http://192.168.137.101/tz/cexam.php?MASTexam=586

M_{rx} = NaCl

= 23 + 35.5

= 58.5 g/mol

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$N = 1 + 1$$

$$= 2$$

$$\Delta T = \frac{Kb \times m \times 1000}{m_s \times Mr_x}$$

$$= \frac{1.86 \times 2.4 \times 1000}{250 \times 58.5}$$

$= 0.305^oC$

c.c.p $= 0.305^oC$

$$\alpha = \frac{g-1}{N-1}$$

$$(N-1)\alpha = g-1$$

$$(N-1)\alpha + 1 = g$$

$$(2-1)0.7 + 1 = g$$

$$g = 1.7$$

$$g = \frac{o.c.p}{c.c.p}$$

$$1.7\ x\ 0.305 = o.c.p$$

$$\Delta T = 0.519$$

$$T = 100 + 0.519$$

$$= 100.519^0C$$

$$\therefore The\ boiling\ point\ of\ solution\ is\ \ 100.519^0C$$

PHYSICAL CHEMISTRY - Energetics

THERMOCHEMISTRY

This is also termed as Energetics.

Definition

Is the branch of physical chemistry which deals with energy changes that occurs during the chemical reaction.

The energy change during the chemical reaction is either positive or negative.

It is denoted by ΔH.

ENTHALPY OF REACTION/HEAT OF REACTION

Definition

Enthalpy is the energy change which takes place during chemical reaction.

THE COMMON ENTHALPIES OF REACTIONS

The following are the common Enthalpies of reactions:-

1. STANDARD ENTHALPY OF COMBUSTION

This is the heat energy given out when 1mole of a certain substance is completely burnt in a given moles of oxygen at standard state.

If ΔH for combustion reaction is negative i.e. The reaction is exothermic.

Example of combustion reaction

i. $C + O_2 \longrightarrow CO_2 \; \Delta H = -Ve$

ii. $S + O_2 \longrightarrow SO_2 \; \Delta H = -Ve$

iii. $CS + O_2 \longrightarrow CO_2 + SO_2 \; \Delta H = -Ve$

iv. $H_2 + O_2 \longrightarrow H_2O \quad \Delta H = -Ve$

v. $CH_4 + O_2 \longrightarrow CO_2 + H_2O \quad \Delta H = -Ve$

vi. $CH_3 - CH_3 + O_2 \longrightarrow O_2 + H_2O \quad \Delta H = -Ve$

vii. $CH_3CH_2OH + O_2 \longrightarrow CO_2 + H_2O \quad \Delta H = -Ve$

HOW TO BALANCE THE COMBUSTION REACTIONS

In balancing the combustion reactions we normally balance the other materials apart from hydrogen and oxygen first.

Secondly balance hydrogen then finally oxygen.

Example

i. $H_2 + O_2 \longrightarrow H_2O$

$H_2 + {}^1/_2O_2 \longrightarrow H_2O$

ii. $CH_3\ CH_2\ CH_3 + O_2 \longrightarrow CO_2 + H_2O$

$CH_3\ CH_2\ CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

iii. $CH_3\ (CH_2)_2\text{-}CH_3 + O_2 \longrightarrow CO_2 + H_2O$

$CH_3(CH_2)_2CH_3 + {}^{13}/_2O_2 \longrightarrow 4CO_2 + 5H_2O$

iv. $C_2H_5OH + O_2 \longrightarrow CO_2 + H_2O$

$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$

v. $CH_3COOH + O_2 \longrightarrow CO_2 + H_2O$

$CH_3COOH + 2O_2 \longrightarrow 2CO_2 + 2H_2O$

vi. $C_6H_{14} + O_2 \longrightarrow CO_2 + H_2O$

$C_6H_{14} + O_2 \longrightarrow 6CO_2 + 7H_2O$

2. STANDARD ENTHALPY OF FORMATION

This deal with the formation of compounds. It is donated by ΔH°f.

Definition

Standard enthalpy of formation is the heat change which occur when 1mole of substance is formed from its element at standard state. Standard enthalpy of formation can be positive or negative.
ΔH°f may be +Ve or -Ve.

ΔH°f = +Ve Endothermic.

or
ΔH°f = -Ve Exothermic.

Example

Standard enthalpy of formation of CO_2.
$C + O_2 \rightarrow CO_2$ ΔH°f.
ΔH°f of CO_2 = ΔH comb of C

Example

ΔH°f of CH_3COOH

$$2C + 2H_2 + O_2 \xrightarrow{\Delta H°f} CH_3COOH$$

Example

ΔH°f of $CH_3 - O - CH_3$

$$2C + 3H_2 + {}^1/_2O_2 \xrightarrow{\Delta H°f} CH_3 - O - CH_3$$

3. STANDARD ENTHALPY OF NEUTRALIZATION (E_N)

Definition

This is the heat energy given out when one mole of water is formed from the reaction between acid and base at standard state. Or
This is the Enthalpy change which take place when one mole of water is formed from reaction between acid and base at standard condition.

Example

$HCl + NaOH \rightarrow NaCl + H_2O$ $\Delta H = -$ Ve

4. ATOMIZATION ENERGY

Definition

Atomization energy is the energy absorbed when a molecule or electron is converted to gaseous atoms. Atomization energy applied for non-compound and ΔH is positive.
Atomization of energy is denoted by "Eat".

Example

$$\underset{\text{Gaseous molecule}}{Cl_2(g)} \xrightarrow{Eat} \underset{\text{Gaseous atom}}{2Cl(g)}$$

$$Br_{2\,(g)} \xrightarrow{Eat} 2Br_{(g)}$$

$$O_{2(g)} \xrightarrow{Eat} 2O_{(g)}$$

5. SUBLIMATION ENERGY (Es)

It is also known as dissociation energy.

Definition

Sublimation energy is the energy absorbed when one mole of solid atom is converted into gaseous atom.

Sublimation energy is applied for metallic atom and ΔH is positive.

Sublimation energy is denoted by ‘Es’.

Example

$$\underset{\text{Solid atom}}{Na_{(s)}} \xrightarrow{Es} \underset{\text{Gaseous atom}}{Na_{(g)}}$$

$$Al_{(s)} \xrightarrow{Es} Al_{(g)}$$

$$Mg_{(g)} \xrightarrow{Es} Mg_{(g)}$$

$$Ca_{(s)} \xrightarrow{Es} Ca_{(g)}$$

6. IONIZATION ENERGY (E_I)

Is the energy used to remove an electron from the outer most shell of an atom, gaseous atom or ions to form an ion(s).

It is denoted by “E_I”.

Ionization energy can be categorized as first 1st, 2nd and 3rd depending on the nature of stable ions that can be formed from an atom.

ΔH is positive.

Example1

$$\underset{\text{Gaseous atom}}{Ca_{(g)}} \xrightarrow{EI^{1st}} \underset{\text{Ion}}{Ca^{+}} + \bar{e}$$

$$Ca^{+}_{(g)} \xrightarrow{EI^{2nd}} Ca^{2+} + \bar{e}$$

Example 2

$$Al_{(g)} \xrightarrow{EI^{1st}} Al^{+} + \bar{e}$$

$$Al^{+} \xrightarrow{EI^{2nd}} Al^{2+} + \bar{e}$$

$$Al^{+} \xrightarrow{EI^{3rd}} Al^{3+} + \bar{e}$$

7. ELECTRON AFFINITY (E_{aff})

Definition

Is the energy required when one mole of non- metallic gaseous atom combine with one mole of electron.

It is denoted by E_{aff}.

Example

$$Cl_{(g)} + \bar{e} \xrightarrow{Eaff} Cl^{-}$$

$O_{(g)} + \bar{e} \xrightarrow{Eaff} O^-$

8. LATTICE ENERGY (E_L)

Definition

Is the energy given out when one mole of ionic compound is formed from its ions.

It is denoted by E_L.

Example

$Na^+ + Cl^{-1} \xrightarrow{EL} NaCl$

$Al^{3+} + 3Cl^{-1} \xrightarrow{EL} AlCl3$

$Mg^{2+} + 2Br^- \xrightarrow{EL} MgBr2$

$\Delta H = -ve$

9. STANDARD ENTHALPY OF SOLUTION

Definition

Is the heat change when one mole of a compound is dissolved in a given moles of water at standard conditions.

$Na\,Cl + Aq \xrightarrow{\Delta H} NaCl\,(aq)$

10. STANDARD ENTHALPY OF FORMATION

Is the heat change which occur when one mole of a substance is formed from its element at standard conditions.

eg. $C + O_2 \rightarrow CO_{2(g)}$ $\Delta Hf = -393 KJmol^{-1}$.

11. HEAT OF DILUTION

Is the heat change when one mole of a substance is dissolved in a given mole of water

METHODS OF FINDING HEAT OF FORMATION OF A GIVEN COMPOUNDS

The calculation in thermochemistry are categorized in the following;-

(i). Calculation based on combustion Data.

(ii). Calculation based on bond energies.

(iii). Calculation based on atomization Data.

(iv). Calculation based on calorimetry information.

(v). Determination of molecular formular by combustion Data.

(vi). Calculation based on Born–Haber cycle.

CALCULATIONS BASED ON COMBUSTION DATA

Calculations involving combustion data has got the following Steps:-

(i). Identify the required equation.

(ii). Data presentation.

(iii). Data manipulation.

(iv). Conclusion.

Example 1

a) With one example in each briefly define the following terms;-

(i). Standard enthalpy of combustion.

(ii). Sublimation energy.

(iii). Standard enthalpy of formation.

(iv). Atomization energy.

(v). Lattice energy.

Solution

(i). *Standard enthalpy of combustion:* is the heat energy given out when 1mole of a certain substance is completely burnt in a given moles of oxygen at standard state.

(ii). *Sublimation energy:* Is the energy absorbed when one mole of solid atom is converted to gaseous atom.

(iii). *Standard enthalpy of formation:* is the heat change which occur when 1 mole of substance is formed from its element.
eg. $C + O_2 \rightarrow CO_{2\,(g)}$ $\Delta H°f = -393\ KJmol^{-1}$

(iv). *Atomization energy:* is the energy absorbed when a given molecule or element is converted into gaseous atom.

(v). *Lattice energy:* Is the energy given out when 1 mole of ionic compound is formed from it ions.
eg. $Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl$

b) Calculate the enthalpy of formation of methane given that,

Enthalpy of combustion are;-

i. Carbon 394 $KJmol^{-1}$.

ii. Hydrogen 286 $KJmol^{-1}$.

iii. Methane 891 $KJmol^{-1}$.

Solution

Required equation

$$C + 2H_2 \xrightarrow{\Delta\ H\ °F} CH_4$$

Data presentation	KJ mol $^{-1}$
i. $C + O_2 \longrightarrow CO_2$	- 394
ii. $H_2 + {}^1/_2\, O_2 \longrightarrow H_2O$	- 286
iii. $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$	891

Data manipulation $KJmol^{-1}$

i. $C + O_2 \longrightarrow CO_2$ - 394

ii. $H_2 + {}^{1}/_{2}O_2 \longrightarrow H_2O$ - 286) × 2

$2H_2 + O_2 \longrightarrow 2H_2O$ - 572

iii. $2H_2 + O_2 \longrightarrow CH_4 + 2O_2$ 891

$C + 2H_2 \xrightarrow{\Delta H °F} CH_4$ - 75

∴ The enthalpy of formation of methane is -75 $KJmol^{-1}$.

Example 2

Calculate the standard enthalpy of formation of ethane given that enthalpy of combustion.

i) C = -394 $KJmol^{-1}$

ii) hydrogen = -216 $KJmol^{-1}$

iii) Ethane = -1561 $KJmol^{-1}$

Solution

Required equation

$2C + 3H_2 \xrightarrow{\Delta H°F} C_2H_6$

Given $KJmol^{-1}$

$(C + O_2 \longrightarrow CO_2$ -394

$H_2 + {}^{1}/_{2}O_2 \longrightarrow 2CO_2$ - 788

$C_6H_6 + 7/2\ O_2 \longrightarrow 2CO_2 + 3H_2O$ -1561

Data Manipulation

$(C + O_2 \longrightarrow CO_2$ -394 $)\times 2$

$2C + 2O_2 \longrightarrow 2CO_2$ -788

$(H_2 + {}^{1}/_{2}O_2 \longrightarrow H_2O$ $-216)\times 3$

$3H_2 + {}^{3}/_{2}O_2 \longrightarrow 3H_2O$ -648

$2CO_2 + 3H_2O \longrightarrow CH_3CH_3 + {}^{7}/_{2}O_2$ 1561

$2C + 3H_2 \longrightarrow C_2H_6$ $+125$

$\therefore$ The standard enthalpy of formation of C_2H_6 is 125 $KJmol^{-1}$.

Example 3

a) Define;-

i.Heat of combustion

Is the heat given out when one mole of a substance is completely burnt in given moles of O_2 at standard state.

ii. Heat of neutralization

Is the heat energy given out when one mole of water is formed the reaction between acid and base at standard state.

iii.Heat of dilution

Is the heat change when one mole of a compound is dissolved in a given moles of water.

b) Calculate the heat of formation of ethanoic acid , if the enthalpy of combustion are C = -394 H_2 = - 284 ethanoic acid -876 (All in KJ mol^{-1}).

Solution

Required equation

$2C + 2H_2 + O_2 \longrightarrow CH_3COOH$

Data presentation	KJ mol^{-1}
$C + O_2 \longrightarrow CO_2$	-394
$H_2 + {}^{1}/_{2}O_2 \longrightarrow H_2O$	-284
$CH_3 + 2O_2 \longrightarrow 2CO_2 + 2H_2O$	-876

Data manipulation

$2C + 2O_2 \longrightarrow 2CO_2$	- 788
$2H_2 + O_2 \longrightarrow 2H_2O$	- 568
$2CO_2 + 2H_2O \longrightarrow CH_3COOH + 2O_2$	876

The equation obtained

$2C + 2H_2 + O_2 \longrightarrow CH_3COOH$ -480

∴ The heat of formation of ethanoic acid is -480 KJmol^{-1}.

Example 4

From the following Thermodata at 298k.

(i) $H_2 + {}^{1}/_{2}\,O_2 \longrightarrow H_2O \quad -288\ KJmol^{-1}$

(ii) $CH_3(CH_2)_2 - CH_3 + {}^{13}/_{2}\,O_2 \longrightarrow 5H_2O + 4CO_2 \quad -287\ KJmol^{-1}$

(iii) $CH_3CH_2CH = CH_2 + 6O_2 \longrightarrow 4H_2O + 4CO_2 \quad -271\ KJmol^{-1}$

Calculate ΔH for the reaction

$CH_3CH_2CH = \ CH_2 + H_2 \longrightarrow CH_3CH_2CH_2 - CH_3$

Solution

Required equation

$CH_3CH_2 = CH_2 + CH_2 \longrightarrow CH_3CH_2CH_2 - CH_3$

Data presentation

$H_{2+} \, {}^1/_2 \, O_2 \longrightarrow \quad H_2O \qquad -288 \ KJmol^{-1}$

$CH_3(CH_2)_2 - CH_3 + {}^{13}/_2 \, O_2 \longrightarrow 5H_2O + 4CO_2 \qquad -287 \ KJmol^{-1}$

$CH_3CH_2CH = \ CH_2 + 6O_2 \longrightarrow 4H_2O + 4CO_2 \quad -271 \ KJmol^{-1}$

Data manipulation

$5H_2O + 4CO_2 \longrightarrow CH_3(CH_2)_2 - CH_3 + {}^{13}/_2 \, O_2 \qquad 287$

$CH_3CH_2CH = \ CH_2 + 6O_2 \longrightarrow 4H_2O + 4CO_2 \quad -271$

$H_{2+} \, {}^1/_2 \, O_2 \longrightarrow \quad H_2O \qquad - 288$

$CH_3CH_2CH = \ CH_2 \longrightarrow CH_3(CH_2)_2 - CH_3 \qquad -272$

$\therefore \boldsymbol{The \ \ \Delta H}$ **For the reaction is** $\boldsymbol{-272 \ KJmol^{-1}}$

Example 5

Calculate the enthalpy change for the reaction.

$C_2H_5OH \longrightarrow CH_3 - O - CH_3$

Given

Enthalpies of combustions are;-

$C_2H_5OH \quad -276\ KJmol^{-1}$

$(CH_3)_2O \quad -1456\ KJmol^{-1}$

$C \quad -394\ KJmol^{-1}$

Heat of formation of water is $-286\ KJmol^{-1}$

Solution

Required equation

$C_2H_5OH \longrightarrow CH_3 - O - CH_3$

Data presentation $\boldsymbol{KJmol^{-1}}$

$C_2H_5OH + O_2 \longrightarrow CO_3 + H_2O \quad -276$

$(CH_3)_2O + 3O_2 \longrightarrow 2CO_2 + 3H_2O \quad -1456$

$C + O_2 \longrightarrow CO_2 \quad -394$

Data manipulation

$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O \quad -276$

$2CO_2 + 3H_2O \longrightarrow (CH_3)_2O + 3O_2 \quad -1456$

$C_2H_5OH \longrightarrow (CH_3)_2O \quad 1180$

$\therefore \textbf{The enthalpy change is} \quad \mathbf{1180\ KJmol^{-1}}$

Example 6

Calculate the enthalpy change for the reaction.

$CH_3CH_2OH \longrightarrow CH_3 - O - CH_3$

Given

Heat of combustion of CH_3CH_2OH $-276\ KJmol^{-1}$

Heat of combustion of H_2O $-286\ KJmol^{-1}$

Heat of combustion of C $-394\ KJmol^{-1}$

Heat of combustion of $CH_3 - O - CH_3$ $-1456KJmol^{-1}$

Solution

Required equation

$CH_3CH_2OH \longrightarrow CH_3 - O - CH_3$

Data presentation

$CH_3CH_2OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O \quad -276\ KJmol^{-1}$

$H_2 + {}^1/_2\,O_2 \longrightarrow H_2O \quad -286\ KJmol^{-1}$

$C + O_2 \longrightarrow CO_2 \quad -394\ KJmol^{-1}$

$CH_3 - O - CH_3 + 3O_2 \longrightarrow 2CO_2 + 3H_2O \quad -1456\ KJmol^{-1}$

Data manipulation

$CH_3CH_2OH + 3O_2 \longrightarrow \quad 2CO_2 + 3H_2O \quad -276\ KJmol^{-1}$

$2CO_2 + 3H_2O \longrightarrow \quad CH_3-O-CH_3 + 3O_2 \quad -1456\ KJmol^{-1}$

$CH_3CH_2OH \longrightarrow \quad CH_3-O-CH_3 \quad 1180\ KJmol^{-1}$

$\therefore \boldsymbol{The\ \ enthalpy\ change\ is \quad 1180\ KJmol^{-1}}$

Example 7

(a) Define the following terms;-

(i) Enthalpy of sublimation.

Is the energy absorbed when one mole of solid atom is converted to gaseous atom.

(ii) Enthalpy of atomization.

Is the energy absorbed when a certain molecule or element is covered into gaseous atom.

(iii) Standard enthalpy of combustion.

Is the head given out when one mole of a substance is burnt in a given moles of Oxygen.

(b) The combustion of carbon disulphide is exothermic and the enthalpy of combustion of the compound is 1180 $KJmol^{-1}$.

Given that carbon dioxide and sulphur dioxide are exothermic compounds with enthalpies of formation of 405 and 293 $KJmol^{-1}$ respectively.

(i) Calculate the heat of formation of carbon disulphide.

(ii) comment on the stability of this compound at various temperature considering the results obtained in the light of Le-chaterlier`s principle.

Solution

Required equation

2S + C $\longrightarrow CS_2$

Data presentation $KJmol^{-1}$

$CS_2 + 3O_2 \longrightarrow CO_2 + 2SO_2$ - 1108

C + $O_2 \longrightarrow CO_2$ -405

S + $O_2 \longrightarrow SO_2$ -293

Data manipulation

$2SO_2 + CO_2 \longrightarrow CS_2 + 3O_2$ 1108

$C + O_2 \longrightarrow CO_2$ -405

$2S + 2O_2 \longrightarrow 2SO_2$ -586

$2S + C \longrightarrow CS_2$ 117

∴The heat of formation of CS_2 is 117 $KJ\ mol^{-1}$

ii) In high temperature the compound will be move stable.

Example 8

Given the following reaction;-

$Fe_2 + 3CO \longrightarrow 2Fe + 3CO_2$ $-28KJ\ mol^{-1}$

$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$ $-59\ KJmol^{-1}$

$Fe_3O_3 + CO \longrightarrow 2Fe + 3CO_2$ $38\ KJmol^{-1}$

Calculate the enthalpy change for the reaction $FeO + CO \longrightarrow FeO + CO_2$

Solution

Required manipulation $KJ\ mol^{-1}$

$^1/_2\ (Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2\ -28)$

$^1/_6\ 2Fe_3\,O_4 + CO_2 \longrightarrow 3Fe_2O_3 + CO\quad 59$

$^1/_3\,(3Feo + CO_2) \longrightarrow Fe_3O_4 + CO\quad -38$

$^1/_2\,Fe_2O_3 + {}^3/_2\,CO \longrightarrow Fe + {}^3/_2\,CO_2\quad -14$

$^1/_3\,Fe_3O_4 + {}^1/_6\,CO_2 \longrightarrow {}^1/_2\,Fe_2O_3 + {}^1/_6\,CO\quad 9.83$

$Feo + {}^1/_3\,CO_2 \longrightarrow {}^1/_3\,Fe_3O_4 + {}^1/_3\,CO\quad -12.67$

$Feo + CO \longrightarrow Fe + CO_2\quad -16.84$

$\therefore$ ***The enthalpy change is*** $\mathbf{16.84KJmol^{-1}}$

2. CALCULATION OF ENTHALPIES

BASED ON BOND ENERGIES

BOND ENERGIES

Is the energy change which is obtained when one mole covalent bond is formed or broken of an atom.

Any reaction involves bond breaking and bond formation. Reactants bonds are normally broken while products bonds are formed.

Since the bonds energies are known then ΔH of the reaction can be calculated as the difference between broken bond energies and formed bond energies.

ΔH = B.B.E - F.B.E

Where by;-

ΔH Is the heat change of reaction.

B.B.E is the broken bond energies.

F.B.E is the formed bond energies.

Example 1

(a) Define

(i) Bond energy.

Is the energy which is obtained when one mole of covalent bond is formed or broken of an atom.

(ii) Enthalpy of neutralization.

Is the heat given out when one mole of water is formed from the reaction between acid and base at standard state.

(b) Calculate the heat of formation of ethane given that:

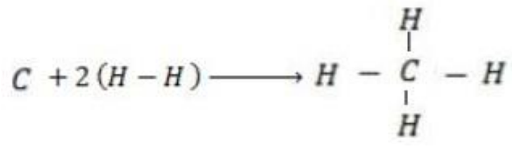
$C - H = 413\ KJmol^{-1}$

$H - H = 436\ KJmol^{-1}$

Solution

Required equation

$$C + 2H_2 \xrightarrow{\Delta H^\circ F} CH_4$$



$$C + 2(H - H) \longrightarrow H - \underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}} - H$$

Broken bond energies

$= 2(H - H)$

$= 2\,X\,436$

$= 872\ KJmol^{-1}$

$= 4\,(C - H)$

$= 4\,X\,413$

$= 1652\ KJmol^{-1}$

$\Delta H°F = BBE - FBE$

$= 872 - 1652$

$= \ -780\ KJmol^{-1}$

$\therefore The\ heat\ of\ fprmation\ of\ methane - 780KJmo\,l^{-1}$

Example 2

Calculate the enthalpy of hydrogenation of ethane to ethane.

Given

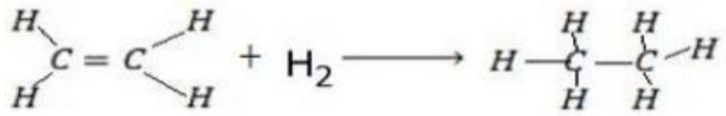
$(i)\ C = C \quad = 612\ KJmol^{-1}$

$(ii)\ C - H \quad = 416\ KJmol^{-1}$

$(iii)\ H - H \quad = 436\ KJmol^{-1}$

$(iv)\ C - C \quad = 348\ KJmol^{-1}$

Solution



B.B.E

$= 4(C - H)$

$= 4\ x\ 416$

$= 1664$

$= (H - H) = 348$

$= 436$

$= (C = C)$

$= 612$

F.B.E

$6(C - H)$

$= 6\ x\ 416$

$= 2496$

$C - C$

= 348

Total FBE = 2496

$\underline{348 +}$

= 2844

Total BBE = 436

612 + 1664

= 2712

ΔH = BBE – FBE

= 2712 – 2844

$\underline{= -132\ KJmol^{-1}}$

Example 3

Calculate the enthalpy of hydrogenation of prop -1 – yne to saturated if mean bond energies are: -

$(i)\ C \equiv C \quad = 837\ KJmol^{-1}$

$(ii)\ C = C \quad = 612KJmol^{-1}$

$(iii)\ C - C \quad = 348\ KJmol^{-1}$

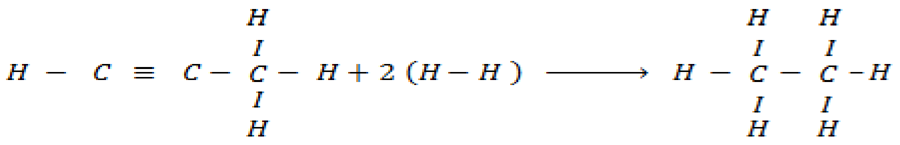
$(iv)\ C - H \quad = 416\ KJmol^{-1}$

$(v)\ H - H \quad = 436\ KJmol^{-1}$

Solution

Required equation

$C_3H_4 + 2H_2$



$$H - C \equiv C - \overset{\overset{H}{I}}{\underset{\underset{H}{I}}{C}} - H + 2\,(H - H) \longrightarrow H - \overset{\overset{H}{I}}{\underset{\underset{H}{I}}{C}} - \overset{\overset{H}{I}}{\underset{\underset{H}{I}}{C}} - H$$

BBE

$4\ \ (H - C \ = \ 4 \ \times \ 416$

$=$1664

$1\ \ (C \ \equiv \ C) \ = \ 837$

$C \ - \ C \quad = \quad 348$

$2\ \ (\ H - \ H \quad = \ 2 \times \ 436)$

$= \ 872$

Total BBE = $(1664 + \ 872 \ + \ 837 + 348)$

= 3721

FBE

$8\ (C - H\ = 8 \times 416)$

$= 3328$

$2\ (C - C) = 2 \times 348$

$= 696$

Total FBE $= 3328 + 696$

$= 4024$

Then,

$\Delta H = BBE - FBE$

$= 3721 - 4024$

$= -303\ KJ\, mol^{-1}$

$\therefore\ The\ entalpy\ of\ hydrogenation\ of\ prop - 1 - yne\ is - 303\ KJ\ mol^{-1}$

Example 4

Benzene under harsh condition undergoes hydrogenation recitation. Calculate the heat of hydrogenation of benzene if mean bond energies are;-

i) $C = C \quad 612\ KJ\ mol^{-1}$

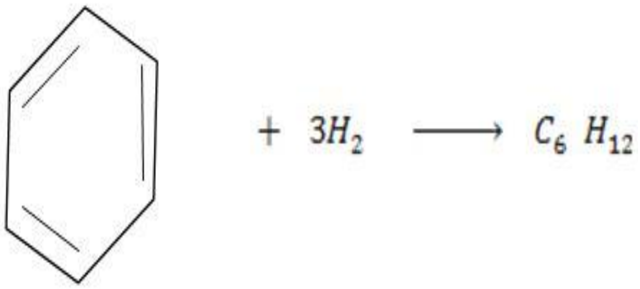
$C - C \quad 348KJ\ mol^{-1}$

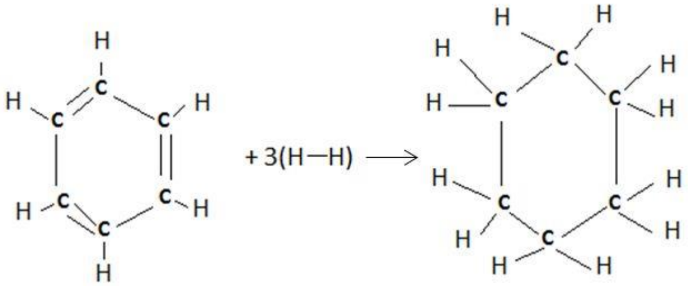
$H - H \quad 436\ KJ\ mol^{-1}$

$C - H \quad 416\ KJ\ mol^{-1}$

Solution

$$C_6 + 3H_2 \longrightarrow C_6 H_{12}$$





BBE	FBE
$3\,(C = C)$	$6\,(C - C)$
$3\,(C - C)$	$12\,(C - H)$
$6\,(C - H)$	
$3\,(H - H)$	

Therefore,

$$3\,(C = C) = 3 \times 612 = 1836$$

$$3\,(H - H) = 3 \times 436 = 1308$$

FBE

$$3\,(C - C) = 3 \times 348 = 1044$$

$6\ (C-H)\ = 6\ \times 416\ = 2496$

Heat of formation

$\Delta H°F\ \ =\ BBE\ -\ FBE$

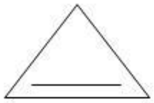
$=\ 3144 - 3540$

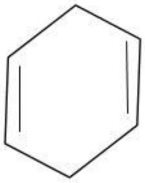
$=\ \ \ -396$

Example 5

Use the data in example 4 above to calculate the enthalpy of hydrogenation of the following compounds.

i) 

(iii) 

ii) 

(iv) 

Solution

i)  $+\ 2\,H_2\ \longrightarrow$ 

BBE

$2\ (C = C) = 2 \times 612 = 1224$

$1\ (C - C) = 1 \times 348$

$6\ (C - H) = 6 \times 416 = 2496$

$2\ (H - H) = 2 \times 436 =$ 872

BBE $= 1224 + 348 + 2496 + 872$

$= 4940\ KJ\ mol^{-1}$

FBE

$8(C - H) = 8 \times 416 = 3328$

$3\ (C - C) = 3 \times 348 = 1044$

F B E $= 3328 + 1044$

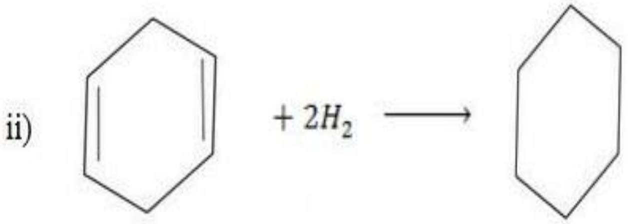
$= 4372\ KJ\ mol^{-1}$

$\Delta H°H = BBE - FBE$

$= 4940 - 4372$

$= 568\ KJmol^{-1}$

$\therefore$ *The heat of hydrogrnation of such compound is* $568\ KJ\ mol^{-1}$

ii) 

BBE

$2(C = C) = 2 \times 612$

$= 1224$

$4(C - C) = 4 \times 348 = 1392$

$8(C - H\ ) = 8 \times 416 = 3328$

$2(H - H) = 2 \times 436$

$= 872$

$BBE = 872 + 1392 + 1224 + 3328$

$= 3488 KJmol^{-1}\ \ + 3328$

F.B.E

$6(C - C) = 6 \times 358$

$= 2088$

$12\ (C - H) = 12 \times 416$

$= 4992 + 2088$

$7080 KJmol^{-1}$

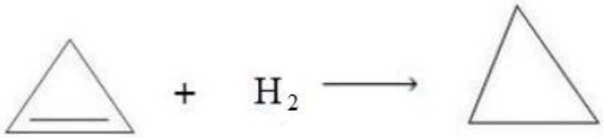
$\Delta H°\mathrm{F}\ = BBE - FBE$

$= 6816\ - 7080$

$=\ -264 KJmol^{-1}$

$\therefore The\ heat\ of\ hydrogenational\ of\ such\ \ compound\ is - 264\ KJmol$

iii)



BBE

$(C = C) = 612$

$2(C - C)\ 2 \times 348$

$= 696$

$4(C - H) = 4 \times 416$

$= 1664$

$2\ (H - H) = 436$

$BBE\ = 436 + 696 + 1664 + 612$

$= 3408KJmol^{-1}$

FBE

$3(C - C) = 3 \times 348$

$= 1044$

HESS`S LAW OF CONSTANT HEAT SUMMATION

It State that,

“The total heat change of a chemical reaction is independent of the route taken".

BORN HABER CYCLE

Is the cycle which is used to determine the heat of formation of a given compounds.

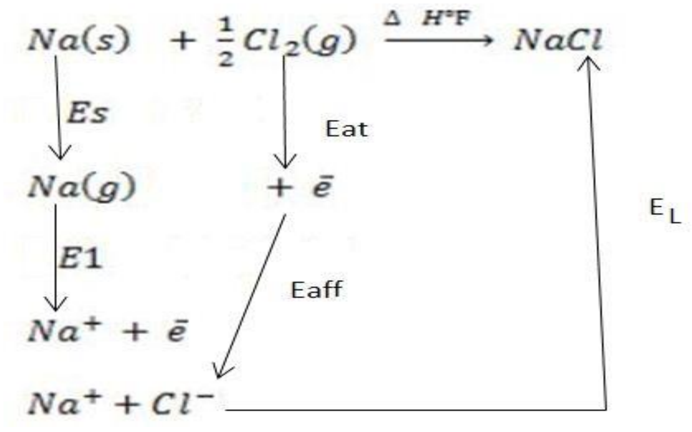
Example 1

a) Draw the born haber cycle for the formation of the following compounds;-

i) $NaCl$ ii) $MgCl_2$

Solution

(i)



$\therefore\ \Delta H^\circ f = E_s + E_I + E_{at} + E_{aff} + E_L$

Where by,

E_s is the sublimation energy.

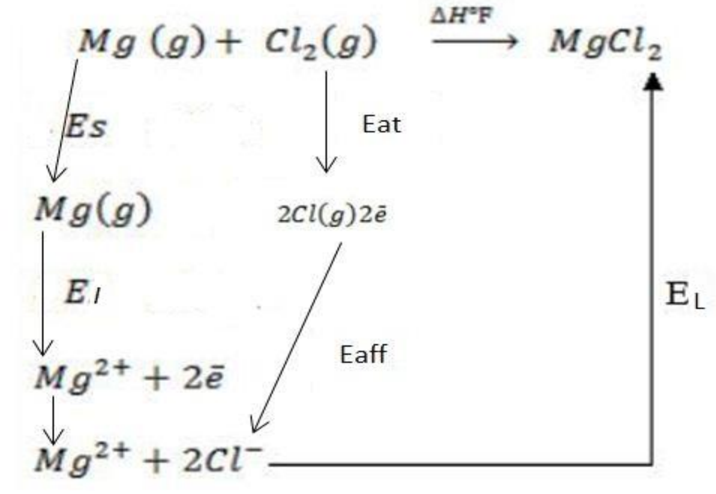
E_I is the Ionization energy.

E_{at} is the Atomization energy.

E_{aff} is the Electronic affinity energy.

E_L is the lattice energy.

(ii)



$\therefore\ \Delta H°f = E_s + E_I + E_{at} + E_{aff} + E_L$

Where by,

E_s is the sublimation energy.

E_I is the Ionization energy.

E_{at} is the Atomization energy.

E_{aff} is the Electronic affinity energy.

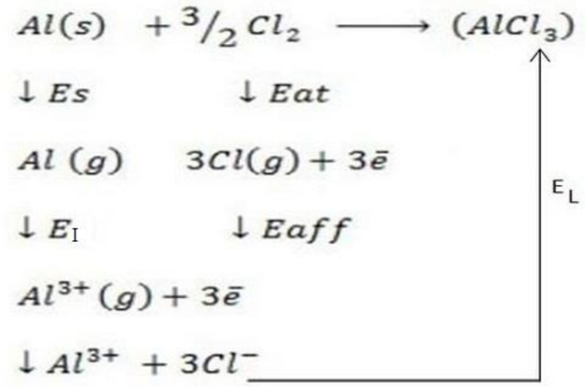
E_L is the lattice energy.

Example 2

Draw the born Haber cycle for the formation of the following;-

i) Aluminium Chloride ($AlCl_3$).

Solution



∴ $\Delta H°f = E_s + E_I + E_{at} + E_{aff} + E_L$

Where by,

E_s is the sublimation energy.

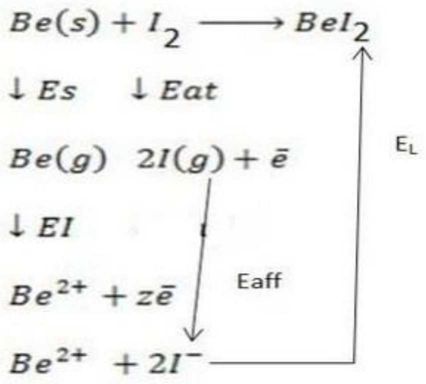
E_I is the Ionization energy.

E_{at} is the Atomization energy.

E_{aff} is the Electronic affinity energy.

E_L is the lattice energy.

ii) Beryllium iodide (BeI_2)



∴ $\Delta H°f = E_s + E_I + E_{at} + E_{aff} + E_L$

Where by,

E_s is the sublimation energy.

E_I is the Ionization energy.

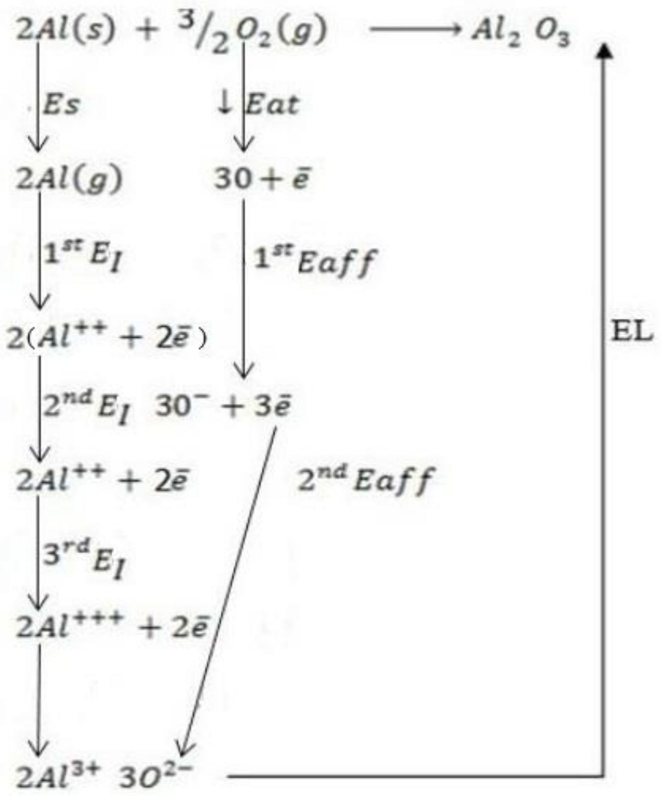
E_{at} is the Atomization energy.

E_{aff} is the Electronic affinity energy.

E_L is the lattice energy.

(iii) Aluminium oxide (Al_2O_3).

Solution



$\therefore \ \Delta H^\circ f = E_s + E_I + E_{at} + E_{aff} + E_L$

But, $E_I = 1^{st} E_I + 2^{nd} E_I + 3^{rd} E_I$

$E_{aff} = 1^{st} E_{aff} + 2^{nd} E_{aff}$

Where by,

E_s is the sublimation energy.

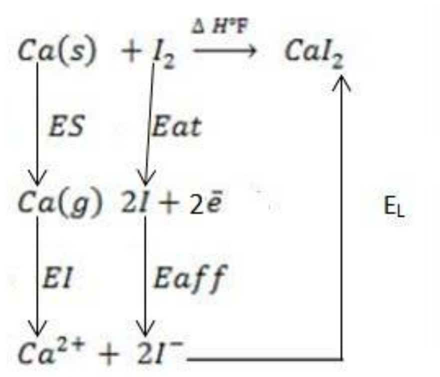
E_I is the Ionization energy.

E_{at} is the Atomization energy.

E_{aff} is the Electronic affinity energy.

E_L is the lattice energy.

iv) Calcium iodide (CaI_2).



$\therefore$ $\Delta H^\circ f = E_s + E_I + E_{at} + E_{aff} + E_L$

Where by,

E_s is the sublimation energy.

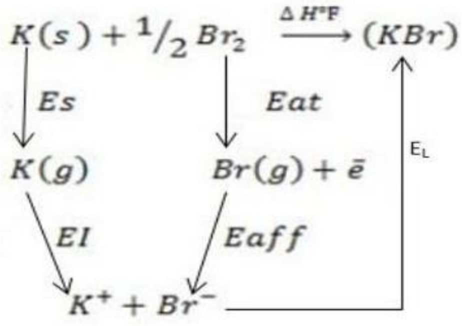
E_I is the Ionization energy.

E_{at} is the Atomization energy.

E_{aff} is the Electronic affinity energy.

E_L is the lattice energy.

v) Potassium Bromide (KBr).



$\therefore\ \Delta H°f = E_s + E_I + E_{at} + E_{aff} + E_L$

Where by,

E_s is the sublimation energy.

E_I is the Ionization energy.

E_{at} is the Atomization energy.

E_{aff} is the Electronic affinity energy.

E_L is the lattice energy.

Example 3

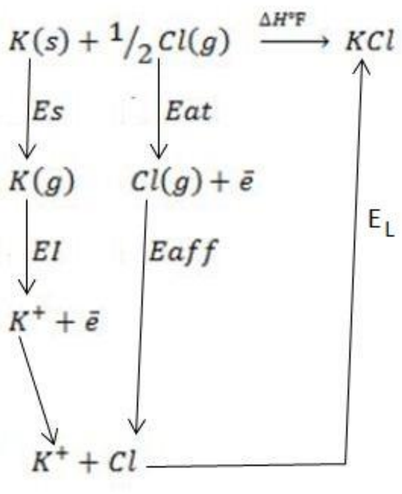
a) What is "Born Haber cycle" as applied in energetic?

Solution

Born Haber cycle is the cycle which is used to determine the heat of formation of ionic compound which involves intermediate changes.

b) Construct born haber cycle for the formation of KCl.

solution



∴ $\Delta H°f = E_s + E_I + E_{at} + E_{aff} + E_L$

Where by,

E_s is the sublimation energy.

E_I is the Ionization energy.

E_{at} is the Atomization energy.

E_{aff} is the Electronic affinity energy.

E_L is the lattice energy.

(c) Using data below calculate the heat of formation of KCl.

$$K(s) \longrightarrow K(g) \quad 90KJmol^{-1}$$

$$K(s) \longrightarrow K^+ + \bar{e} \quad 418KJmol^{-1}$$

$$Cl_2(g) \longrightarrow 2Cl(g)\ 244KJmol^{-1}$$

$$Cl + \bar{e} \longrightarrow Cl - 348KJmol^{-1}$$

$$K^+ + Cl \longrightarrow KCl\ -718\ KJmol^{-1}$$

∴ $\Delta H°f = E_s + E_I + E_{at} + E_{aff} + E_L$

Given that,

$$Es \quad = \quad 90KJmol^{-1}$$

$$EI \ = 418 \ KJmol^{-1}$$

$$Eat = \quad (244KJ \ mol^{-1}) \div 2 \ = 122KJmol^{-1}$$

$$Eaff \quad = -344KJmol^{-1}$$

$$EL \quad = -718 \quad KJmol^{-1}$$

∴ $\Delta H°f = E_s + E_I + E_{at} + E_{aff} + E_L$

$$= 90 + 418 + 1222 + (-344) + (-718)$$

$$= 630 + (-1062)$$

$$630 - 1062$$

$$= \ -432$$

$$\therefore The \ heat \ of \ formation \ of \ KCl \quad = \ -342KJmol^{-1}$$

Example 4

(a) Define the following;-

(i) Atomization energy.
Atomization energy is the energy absorbed when a certain molecule or element is converted to gaseous atom.

(ii) Ionization energy.
Ionization energy is the energy required by the gaseous atom to release electron from its outer most shell.

(iii) Electron affinity.
Electron affinity is the energy requires when 1 mole of gaseous atom combine with one mole of electron.

(b) Use the following data and calculate the electron affinity of chlorine.

$Ca(s) \longrightarrow Ca(g) 190 \quad KJmol^{-1}$

$Ca(g) \longrightarrow Ca^{+}(g) + \bar{e} \; 480 \; KJmol^{-1}$

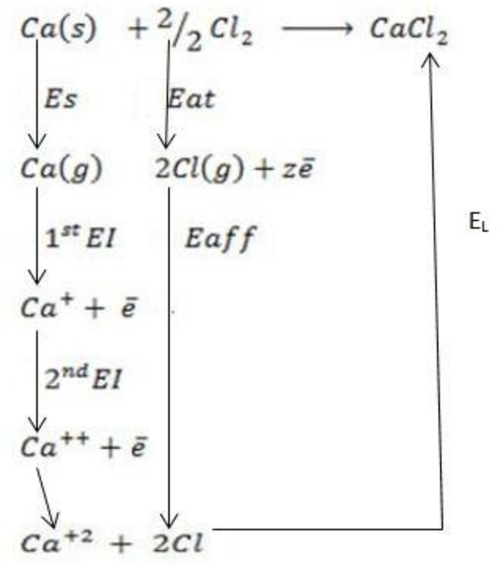
$Ca^{+}(g) \longrightarrow Ca^{++} \bar{e} \; 1240 \quad KJmol^{-1}$

${}^{1}/_{2}\, Cl(g) \longrightarrow Cl(g) \; 121 \; KJmol^{-1}$

$Ca \; (s) + Cl_2 \longrightarrow \quad CaCl_2 - 795 \; KJmol^{-1}$

$Ca^{+2} + \; 2Cl \longrightarrow CaCl_2 - 2184 \quad Kjmol^{-1}$

Solution



∴ $\Delta H°f = E_s + 1^{st} E_I + 2^{nd} E_I + E_{at} + E_{aff} + E_L$

Where

$Es \quad = \quad 190$

$1^{st} \; EI \; = 480$

$2^{nd} EI \; = 1240$

$Eat \quad = 2\,(121) \;\; = 242$

$Eaff \ = ?$

$EL \ = -2184$

$\Delta H°\mathrm{F} \ = \ -795$

From,
∴ $\Delta H°f = E_s + 1^{st} E_I + 2^{nd} E_I + E_{at} + E_{aff} + E_L$

$E_{aff} = \Delta H°f - (E_s + 1^{st} E_I + 2^{nd} E_I + E_{at} + E_L)$

$= -795 - (190 + 1720 + 242) + 2184$

$= 827 \ KJ \ mol^{-1}$

$\therefore The\ electron\ affinity\ energy\ of\ cholorine\ is\ 827\ KJmol^{-1}$

(d) Account for the differences in energies between;-

$Ca(g) \longrightarrow Ca^{+} + \bar{e} \quad 480KJmol^{-1} \quad and$

$Ca^{+} \longrightarrow Ca^{2+} + \bar{e} \ \ 1240KJmol^{-1}$

Answer

The difference in energies is due the fact that when the first electron is removed, the force of attraction becomes greater in second electron. Finally greater energy is needed to remove it from the atom. The energy is greater so as to overcome the force of attraction between the electron and the nucleus.

Example 5

1. (a) Define the following terms;-

i) Bond dissociation energy.

Bond dissociation energy is the e required to remove electron from the outer must shell of an atom.

ii) Enthalpy of dilution.

Enthalpy of dilution is the heat change when one mole of a compound dissolved in a given moles of water.

iii) Lattice energy.

Lattice energy is the heat given out when one mole of ionic compound is formed from its respective ions.

2. (a) Enthalpy of atomization.

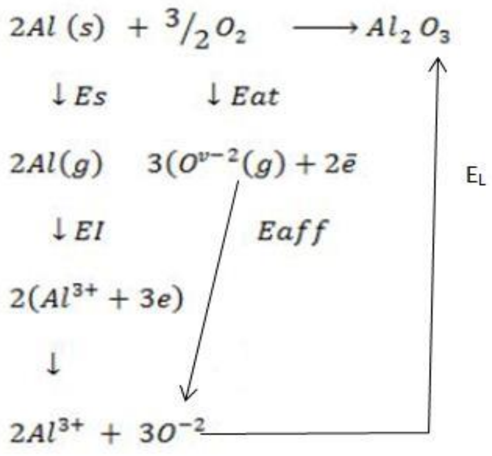
Enthalpy of atomization is the energy absorbed when a certain gaseous molecule or elements converted to gaseous ions.

(b) State Hess`s law of constant heat summation.

It state that,

“If the reaction can take place in more than on rout, then the overall heat change is the same for which ever rout may be taken”.

(c) (i) Draw a well labeled born Haber cycle for the reaction of formation of (Al_2O_3).



$\therefore\ \Delta H°f = E_s + E_I + E_{at} + E_{aff} + E_L$

Where by,

E_s is the sublimation energy.

E_I is the Ionization energy.

E_{at} is the Atomization energy.

E_{aff} is the Electronic affinity energy.

E_L is the lattice energy.

(ii) Calculate the heat of formation of (Al_2O_3) from the following;-

$Atomization\ of\ Aluminum\ is\ 560KJmol^{-1}$

$1^{st}\ EI\ \ of\ Aluminium\ \ is\ 455KJmol^{-1}$

$2^{nd}\ EI\ \ of\ Aluminium\ \ is\ 695\ KJmol^{-1}$

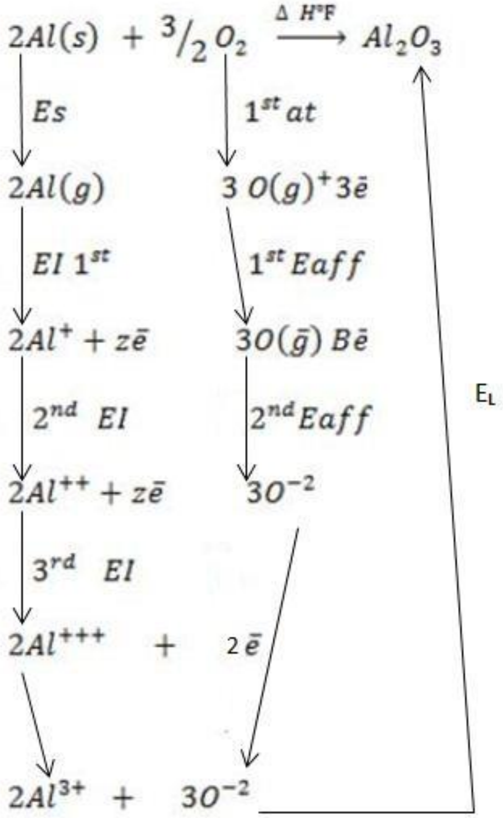
$3^{rd}\ \ EI\ \ of\ Aluminium\ \ is\ 1990\ KJmol^{-1}$

First electron affinity of oxygen is -$550KJmol^{-1}$

Second electron affinity of oxygen is $850KJmol^{-1}$

Lattice energy of $Al_2\ O_3$ is $-1200\ KJmol^{-1}$

Atomization energy of oxygen is $720KJmol^{-1}$



∴ $\Delta H^\circ f = E_s + E_I + E_{at} + E_{aff} + E_L$

Where,

$Es = 560 \times 2 = 1120$

$$EI = 1^{st} EI + 2^{nd} EI + 3^{rd} EI$$

$$= (455 + 965 + 1990) \times 2$$

$$= 6280$$

$$Eaff = (-550 + 850)3$$

$$= 900$$

$$\Delta H^\circ F = 1120 + 6080 + 2160 + 900(-1200)$$

$$= 9260 KJmol^{-1}$$

(d) Draw a born cycle for the formation of Al_2Cl_6 and calculate ΔH for the process.
$2Al + 3Cl_3 \rightarrow Al_2Cl_6 \quad \Delta H = ?$

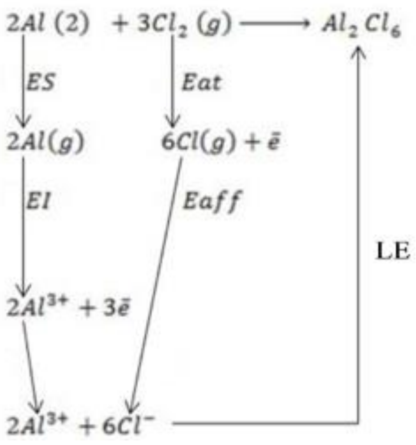
Given that,

i) $2Al_s + 6HCl(aq) \longrightarrow 2AlCl_3 + H_2 \quad -1003KJ\,mol^{-1}$

ii) $H_2\,(g) + Cl_2(g) \longrightarrow 2HCl(g) \quad -184\,KJmol^{-1}$

iii) $HCl\,(g) + aq \longrightarrow HCl + aq \quad -724KJmol^{-1}$

iv) $Al_2Cl_6 + aq \longrightarrow 2AlCl_3 \quad -643KJmol^{-1}$



∴ $\Delta H°f = E_s + E_I + E_{at} + E_{aff} + E_L$

From the data,

$$2Al(s)\ + 6HCl(aq) \longrightarrow 2AlCl_3 + 3H_2 \quad -1033KJmol^{-1}$$

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \quad -184\ KJmol^{-1}$$

$$HCl\ \ + aq \longrightarrow HCl + aq \quad -724\ KJmol^{-1}$$

$$Al_2Cl_6 + aq \longrightarrow 2AlCl_3 \quad -643\ KJmol^{-1}$$

Data manipulation

$$2Al(s)\ + 6HCl°C99) \longrightarrow 2AlCl3 + 3H_2 \quad -1003KJmol^{-1}$$

$$3H_2(g)\ + 3Cl_2(g) \longrightarrow 6HCl\ (g) \quad -552\ KJmol^{-1}$$

$$2AlCl3 \longrightarrow AlCl_6 + aq \quad 643\ KJmol^{-1}$$

$$6HCl(g) + aq \longrightarrow 6HCl(aq) \quad -4344\ KJmol^{-1}$$

Req eqn.

$$2Al(s) + 3Cl_2(g) \longrightarrow Al_2\ Cl_6 \quad -5256\ KJmol^{-1}$$

CALCULATIONS OF ENTHALPIES BY USING ATOMIZATION DATA

During the reaction reactants are atomization (changed to atoms) while the product energy. Calculate from bond energy.

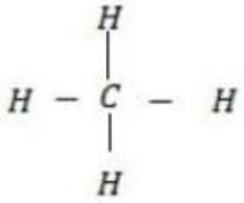
$\Delta H \quad of\ reaction \quad = Eat - F.B.E$

Example1

$$\begin{tikzcd}
Cl(s) \arrow[d] & + & 2H_2 \arrow[d] \arrow[r, "\Delta H^\circ F"] & CH_4 \\
C & + & 4H \arrow[ur] &
\end{tikzcd}$$

$$\Delta H^\circ F = \quad Eat\ of\ \ C + Eat\ of\ H) - \quad FBE$$

But. $FBE =$



$$H - \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}} - H$$

$= 4(C-H)$

Example 2

Calculate the following of formation of CH_4 given that,

Enthalpy of atomization of carbon = $715\ KJmol^{-1}$

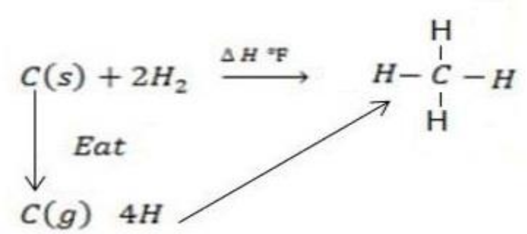
Enthalpy of atomization of hydrogen $= 218\ KJmol^{-1}$

$C - C = 348\ KJmol^{-1}$

$C - H = 416\ KJmol^{-1}$

$H - H = 436\ KJmol^{-1}$

Solution



$Eat\ = 715 + 4(128)$

$= 1587\ KJmol^{-1}$

$FBE = 4(C - H)$

$= 4 \times 416$

$= 1664$

$\Delta\ H°\mathrm{F}\ = Eat - FBE$

$= 1587 - 1664$

$=\ -77KJmol^{-1}$

Example 3

Use the information provided in the above example. Then calculate the heat of formation of ethane.

Solution

$2C_{(g)} +\ 3H_2 \quad \longrightarrow \quad CH_3\,CH_3$

$Eat = 2(715) + 6(218)$

$= 1430 + 1308$

$= 2730$

F.B.E

$1(C-C)=348$

$6(C-H)=6\times 416$

$=2496$

$\Delta H°F\ =Eat-F.B.E$

$2730-(2496+348)$

$=\ -144KJmol^{-1}$

Example 4

The energy required to atomize 6g of carbon is 357.5 KJ. Calculate the energy required to atomize hydrogen atom. If the heat of formation of methane is $-77KJmol^{-1}$ given that,

$C-H\ =416\ KJmol^{-1}$

Solution

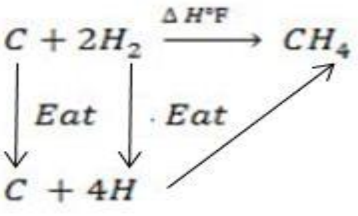
$1\ mole\ \ C=12g$

$6g\ \ =357.5KJ$

$12g=x$

$x\ =\frac{12\times 357.5}{6}$

$=\ \ 715KJmol^{-1}$



$\Delta H°F=Eat-FBE$

$-77=715+4X-4(416)$

$-77 = 715 + 4X - 1664$

$-77 + 949 = 4X$

$872 = 4X$

$X = 218KJmol^{-1}$

$\therefore$ *The haet reqiured is* $218KJmol^{-1}$

CALCULATION OF ENTHALPIES BY CALORIMETRY

Calorimetry Is the method determined the heat change reaction by the using calorimeter.

Example of enthalpies that can be determined by calorimetry method;-

i) Enthalpy of hydrogen.

ii) Enthalpy of neutralization.

DETERMINATION OF ENTHALPIES OF NEUTRALIZATION BY CALORIMETRY

What is neutralization reaction?

Neutralization reaction is the reaction between acid and base to give salt and water.

Example

$HCl + NaOH \longrightarrow NaCl + H_2O$

$KOH + H_2SO_4 \longrightarrow K_2SO_4 + H_2O$

$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O$

In this method the density of salt solution formed is assumed to be equal to the density of water.

$\rho_w = \rho_{\text{salt solution}}$

But, $\rho = 1g/m^3$

$1 = \frac{m}{v}$

$$\frac{m}{v} = \frac{m}{v}$$

$$\therefore Mass\ in\ (g) = volume\ \ in\ cm^3$$

Quantity of that in this method can be calculate by using heat capacity (C)and by using specific heat capacity (c) .

Let the quantity of heat be Q.

By using heat capacity

$$\boldsymbol{Q = C\,\Delta\theta}$$

C = heat capacity.

By using specific heat capacity.

$$\boldsymbol{Q = mc\,\Delta\theta}$$

Where by $\Delta\ Q$ is change in temperature.

c = specific heat capacity.

If quantity of heat calculated is the same and $\Delta\theta$ is also the same, then the relationship between c and C can be,

$$Q_1 = C\Delta\theta$$

$$Q_2 = mc\Delta\theta$$

$$Q_1 = Q_2$$

$$\frac{C\Delta\theta}{\Delta\theta} = \frac{mc\Delta\theta}{\Delta\theta}$$

$$\boldsymbol{C = mc}$$

Enthalpy of neutralization is calculate with respect to the number of moles of water producer.

Reaction.

$H + OH^- \longrightarrow H_2O$

But number of moles of water depends on the moles of limiting reagent

QUESTION
What is limiting reagent?

Limiting reagent is the reactant compound in the neutralization reaction which have small number of moles.

Example 1

250cm^3 of NaOH of 0.4M were added to 250cc of the HCl of 0.4M in a calorimeter. The temperature of the two solutions and the calorimeter was 17.05^oC. The mass of calorimeter was 50g and its specific heat capacity was $400KJg^{-1}K^{-1}$. after the reaction the temperature rose to 19.5$5^oC$

Assuming the specific heat capacity of all the solution is $4200JKg^{-1}k^{-1}$. Calculate the standard enthalpy of neutralization.

Solution

Data

$Vb \quad = \; 250$

$Mb \; = \; 0.4M$

$Va \quad = 250$

$Ma \; = 0.4M$

$Q_1 \quad = \; 17.05$

$Q_2 \; = \; 19.55$

$\Delta Q \; = \; 19.55 - 17.05$

$\qquad = \; 2.5kg$

$Mcal \ = 50a \ \ = \ \ 0.05kg$

$C\ cal \ = 400JKg^{-1}K^{-1}$

$C\ sol \ = 4200JKg^{-1}K^{-1}$

$Msol \ = 0.5kg\ (3OO + 250 + 500g)$

Reaction

$HCl \ + NaOH \ \longrightarrow \ NaCl + H_{2O}$

Limiting reagent

Base

$0.4\ mole \ \equiv \ \ 1000cc$

$x \ \equiv \ \ 250cc$

$x = \ \ \ \frac{250 \times 04}{1000}$

$= 0.1\ mol$

Acid

The same 0.1 mol

Both are limiting reagent.

Moles of water produced

$1\ HCl = \ \ 1.H_2O$

$0.1\ mol \ = \ \ x$

$moles\ of\ H_2O = 0.1$

$\Delta\ H\ \ of\ reacton \ \ = Heat\ gained\ by\ solutin + Heat\ gained\ by\ calorimeter$

$= \ \ MC\Delta\theta + mC\ \Delta\theta$

$$= \quad 0.5kg \times \frac{4\propto 200J}{kgK} \quad 2.5k + 0.05kg \times \frac{400J}{kgK} \quad 2.5$$

$$= \quad 5300J$$

$$= \; 5.3\ KJ$$

$$Per\ mole \;= \frac{5.3KJ}{0.1mol}$$

$$= \; 53KJ\ mol^{-1}$$

$$\therefore \quad The\ standard\ enthalpy\ of\ neutralization\ is\ 53KJmol^{-1}$$

Example 2

Define

i) Heat of neutralization.

Is the heat given out when one mole of water is formed from the reaction between base and acid at standard state.

ii) Heat of Ionization.

Is the heat energy required to remove an electron from the outer most shell of a gaseous atom.

iii) Heat of sublimation.

Is the heating absorbed when one mole solid atom is converted to gaseous atom.

iv) Limiting reagent.

Is the reacted compound in the neutralization reaction which have small number of moles.

b) State Hess`s Law of heat summation.

It state’s that,

“If a reaction take place by more than are route the overall heat change is the same for which ever route may be taken”.

Question

$50cm^3\ of\ 0.5M\ NaOH\ requires\ 20cm^3\ of\ 0.5M\ H_2SO_4$ For neutralization. The reading was absorbed to rose temperature of both the calorimeter and the solution by 3.4k. Calculate the standard enthalpy of neutralization of $NaOH\ \ and\ H_2SO_4$. Given that capacity of calorimeter is $39JK^{-1}$ and specific heat capacity of the solution was 4.2$Jg^{-1}K^{-1}$.

PHYSICAL CHEMISTRY - Relative Molecular Masses in Solutions

SOLUTIONS

What is a solution homogeneous?

A solution is a uniform mixture of two or more substances.

The substance which are mixed to form solution are also termed as components

Example of solution

The solution formed can be

i) Solution of liquid in liquid

ii) Solution of solid in liquid

iii) Solution of gas in liquid

iv) Solution of gas in gas

SOLUTION OF LIQUID IN LIQUID

This is the solution formed when two or more liquids are mixed to form a uniform homogeneous mixture.

When the solution of liquid in liquid is formed the liquids are to be miscible.

When the solution is formed the saturated vapour pressure depends on the composition of the components.

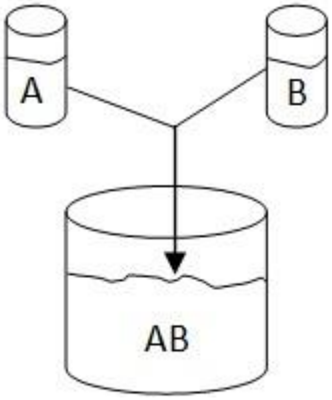
The composition of the components is also depends on the mole fraction of such component.

Example

What is mole fraction

Mole fraction Is the ratio of number of a liquid to the total number of moles of all liquid present in the container.

Consider the solution formed by mixing liquid A and B



Then

Let : n_A be number of moles of liquid A

n_B be number of moles of liquid B

Total number of moles = $n_A + n_B$

$$n_T = n_A + n_B$$

Then to get mole fraction:
X_A = mole fraction of A
X_B = mole fraction of B

Also

$$X_A = \frac{n_A}{n_{A+}n_B}$$

$$X_B = \frac{n_B}{n_A + n_B}$$

i.e.

$$X_A + X_B = 1$$

$$\frac{n_A}{n_{A+}n_B} + \frac{n_B}{n_A + n_B} = 1$$

When expressed in decimal

$$\frac{n_A}{n_{A+}n_B} + \frac{n_B}{n_A + n_B} = 100\%$$

When expressed in percentage

The mole fraction can also be calculated interns of partial pressure ie If the liquid to be mixed are A and B

$$X_A = \frac{P'A}{P_T}$$

$$X_B = \frac{P'B}{P_T}$$

RAOULT'S LAW OF PARTIAL PRESSURE

The Raoult’s law of partial pressure states that

"The saturated vapour pressure of each component in a mixture is equal to the product of mole fraction of that component and its pure vapour pressure"

ASSUMPTIONS OF RAOULT’S LAW

For the Raoult’s law to be feasible the following assumptions are to be considered.

i) Intermolecular forces of attraction should be equal to the intermolecular forces of attraction.

ii) After mixing the component there must be no change in volume.

iii) There must be No change in temperature.

iv) The liquids must be miscible.

v) The liquid should not react.

CONCLUSION

The solutions that do obey all assumption of Raoult's law are called IDEAL SOLUTION. While the liquid which deviate from the assumption of Raoult's law are termed as NON – IDEAL SOLUTION/REAL SOLUTION.

IDEAL SOLUTION

In an Ideal solution the cohesive forces between its molecules. In an ideal or perfect solution, the cohesive forces would be just the same as those existing in the separate components of the solution. A solution made from A and B would only be ideal if the forces existing in the solutions of A and B were just the same as those existing in pure A and pure B.
Ideal solutions are rare, but they are most likely same to occur with mixtures of two almost identical chemicals e.g. hexane and heptane. Most solutions deviate considerably from the ideal because the interactions within the solution are different from those in the pure liquids.

Ideal solution depends on:

1) Vapour pressure of Ideal solution

2) Boiling point of Ideal solution

1. VAPOUR PRESSURE OF IDEAL SOLUTIONS OF TWO LIQUIDS

The vapour in equilibrium with a mixture of two liquids is a mixture of two vapours, and the total vapour pressure is the sum of the two partial vapour pressure. All three pressures vary with temperature and with the composition of the solution.
The change with the composition for ideal solution at a fixed temperature, is describe by Raoult's law (1886) which state that the partial vapour pressure of A in a solution, at a given temperature, is equal to the vapour pressure of pure A, at the same temperature, multiplied by the mole fraction of A in the solution.

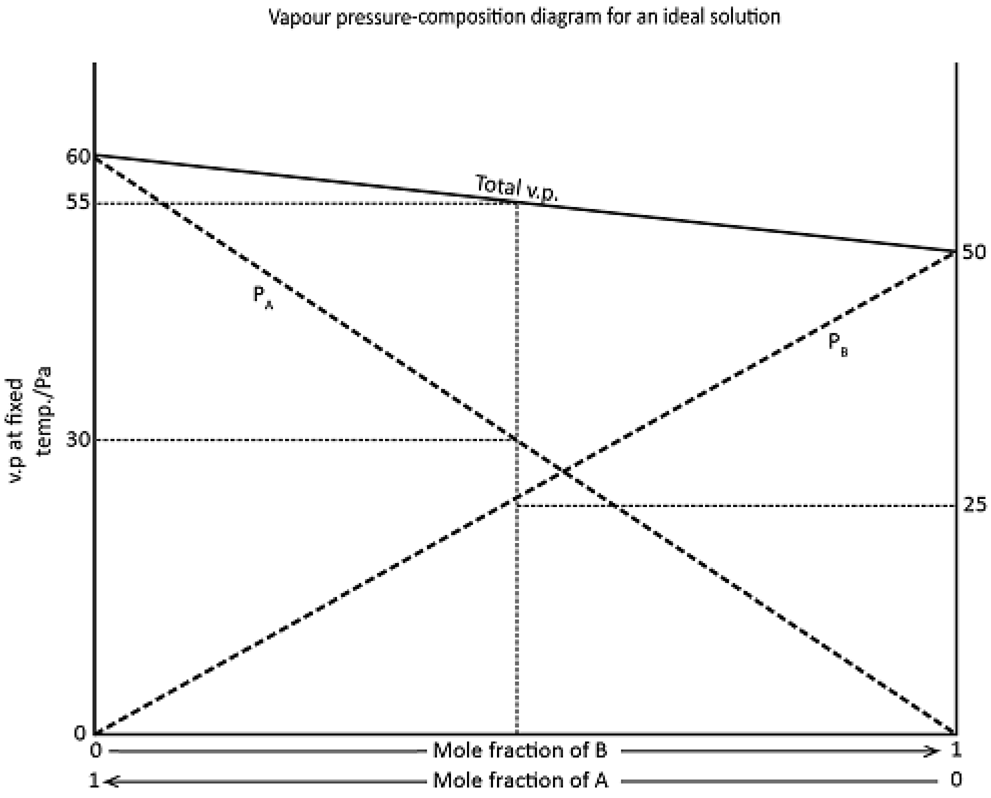
In an Ideal solution components A and B will have just the same tendency to pass into the vapour phase as they have in pure A and pure B because the internal forces within the pure liquids and the solution are like.

There will however be relatively fewer particles of A in a solution containing both A and B than in a pure A, so that the partial vapour pressure of A above the solution might be expected, ideally to be proportional to the mole fraction of A in the solution. Similarly the partial vapour pressure of B above the solution would be proportional to the mole fraction of B.

The total vapour pressure above the solution would be equal to the sum of the partial vapour pressures of A and B.

This is illustrated in the figure below. The vapour pressure of pure B is 50 but it is only 25 when the mole fraction of B in a solution with A, is 0.5.

Similarly the vapour pressure of a pure A is 60, but only 30 at a mole fraction of 0.5. The total vapour pressure of a mixture of A and B at a mole fraction of 0.5 will therefore be 25 plus 30, i.e 35, Numerical result of this type are given only by ideal solutions eg. hexane and heptane or bromoethane and idoethane.



VAPOUR PRESSURE COMPOSITION DIAGRAM FOR NON – IDEAL SOLUTION

What is non ideal solution?

Non ideal solution is the solution which do not obey some or not all assumption of Raoult’s law

Non Ideal solution are of two types:

i) Positive deviation from Raoult’s law

ii) Negative deviation from Raoult’s law

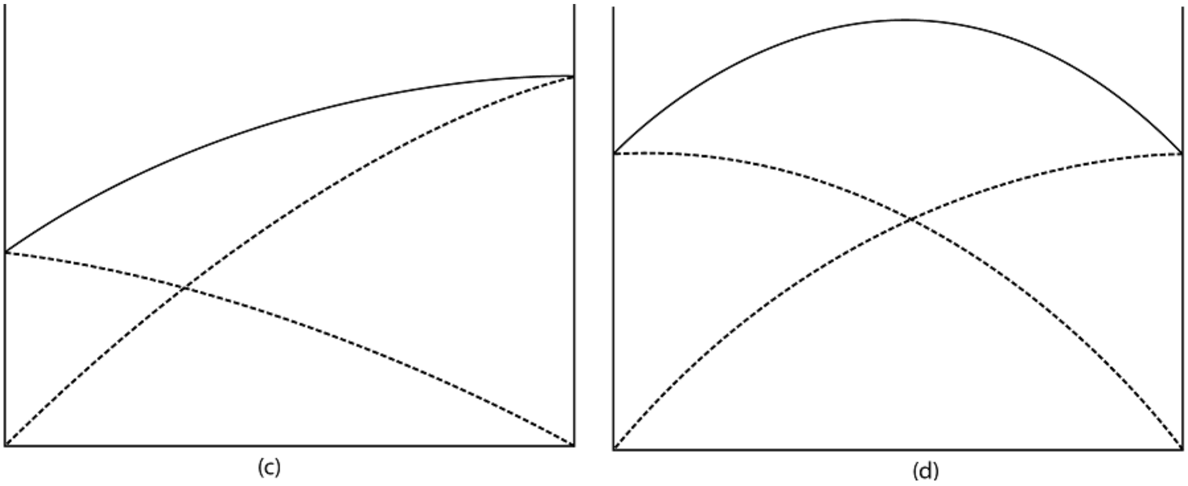
i) POSITIVE DEVIATION FROM RAOULT'S LAW

The positive deviation is observed when the saturated vapour pressure of the solution is greater than the expected one (ideal).

This is due to the large number of molecules that escape from liquid phase to vapour phase.

The large number of molecules escape is due to the fact that intramolecualar forces of attraction is greater than intermolecular forces of attraction.

Vapour pressure composition diagram/positive deviation from Raoult's law.



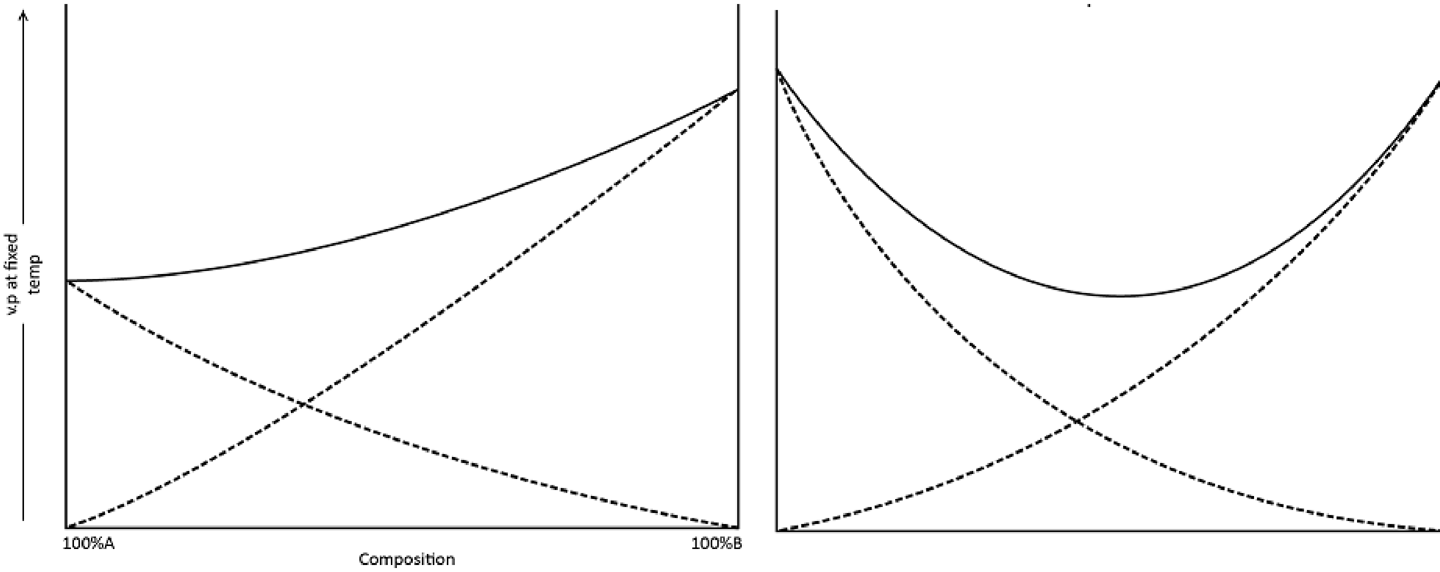
ii) NEGATIVE DEVIATION FROM RAOULT'S LAW

The negative deviation is observed when the saturated vapour pressure of the solution is less than the expected one (ideal)

This is due to the less number of molecules that escape from liquid phase to vapour phase

The small number of molecule that escaped is due to the fact that intermolecular forces of attraction is less than the intramolecular forces of attraction

Vapour pressure composition diagram/negative deviation from Raoult's law



(a) (b)

(2) BOILING POINT COMPOSITION DIAGRAM

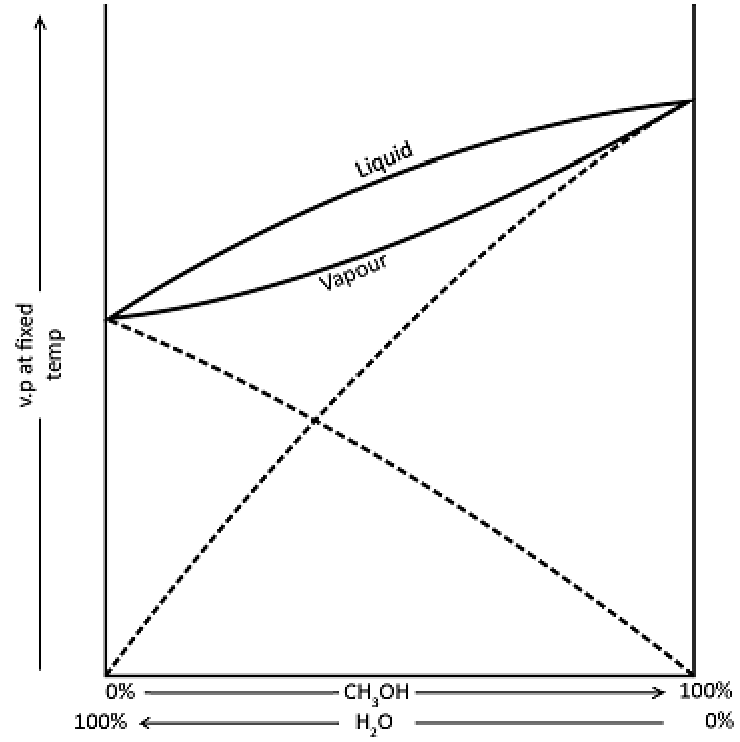
The shape of the boiling point diagram depends on the nature and the degree of deviation from Raoult's law of the two liquids concerned. There are three important type of diagram:

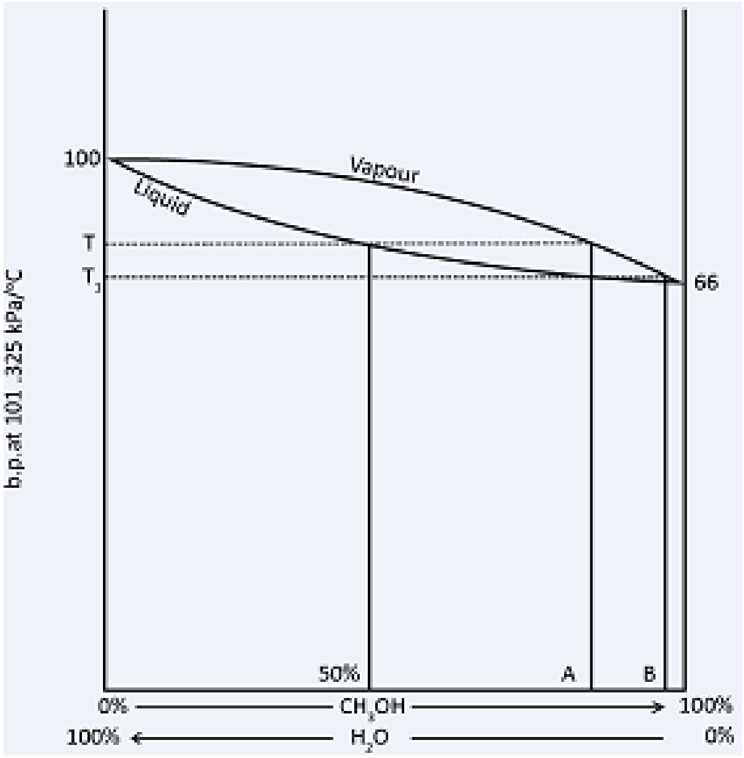
i) No maximum or minimum
This type corresponds with the vapour pressure composition diagrams. Any deviation from Raoult's law is relatively small.

ii) A maximum boiling point
Corresponding with vapour pressure composition diagrams and a large negative deviation from Raoult's law.

iii) A minimum boiling point
Corresponding with vapour pressure composition diagrams and a large positive deviation from Raoult's law.

Boiling point composition diagrams with no maximum or minimum

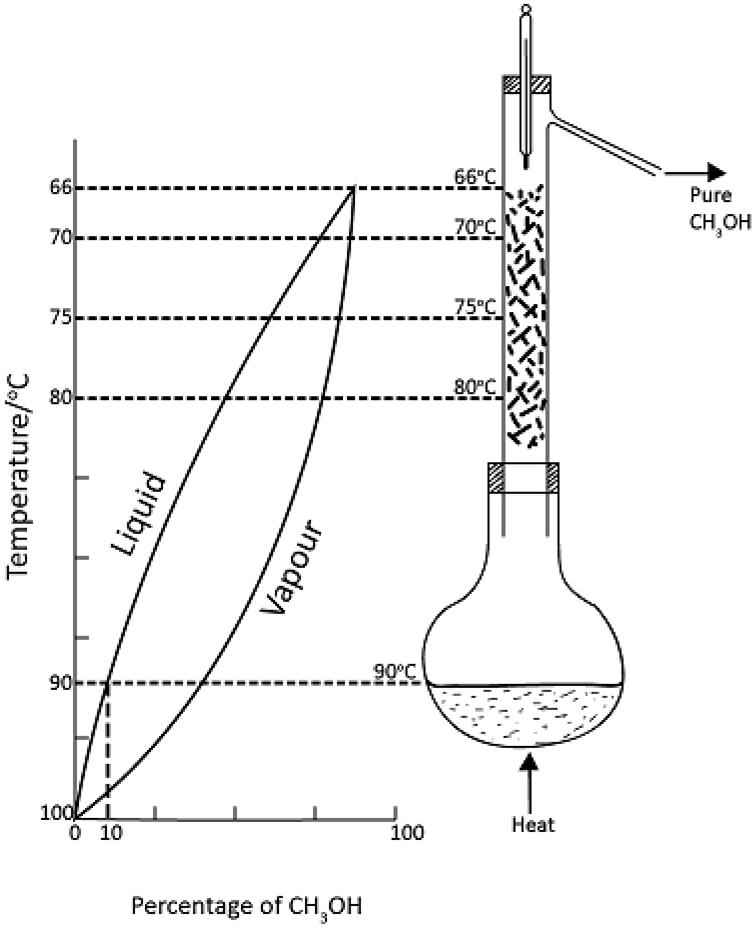




Boiling point composition diagram with no maximum or minimum

A diagram of this type is given by methanol water mixtures. The liquid line shows the way in which

boiling point of methanol water mixture varies with composition at fixed pressure.
For liquid mixture of any one composition the water vapour with which it is in equilibrium will be richer in the more volatile component i.e. in methanol. The liquid line has therefore an associated vapour line. The vapour pressure composition diagram corresponding with this Boiling point composition diagrams as shown above.
When a mixture of methanol and water containing 50 per cent of each is boiled, it will boil at temperature T. The vapour coming from it will have a composition represented by A, and on condensing, this liquid is boiled again, it will now boil at temperature t_1, giving a vapour of a composition B, and this will condense into a liquid whose composition is also B. By repeating this boiling condensing boiling point process, pure methanol could be obtained, but the method would be tedious, and the same result can be obtained in one operation by fractional distillation using a fractionating column.

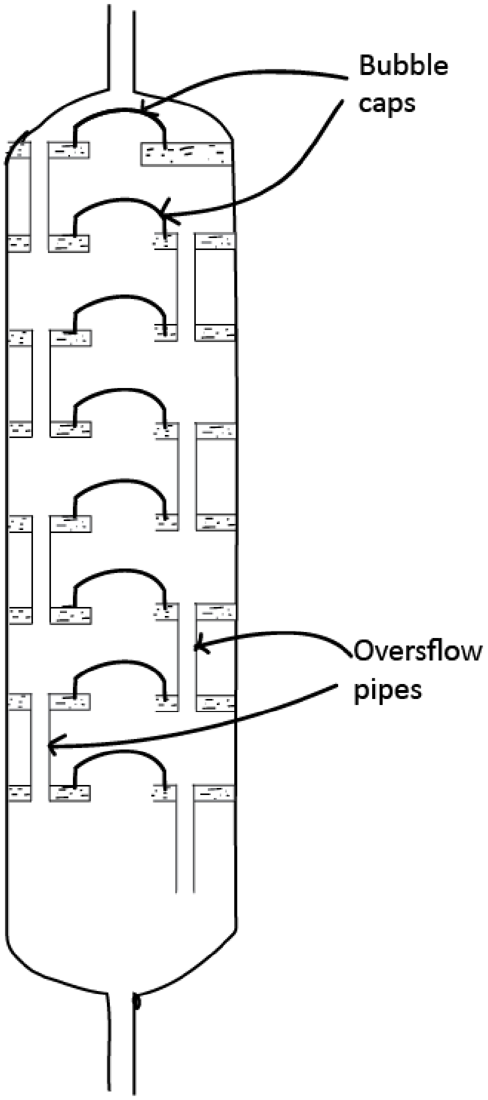


Idealized and simplified representation of the fractional distillation of a mixture of methanol 10% and water 90% using fractionating column.

A simple and effective column for laboratory use consists of along glass tube packed with short lengths of a glassing tubing, glass beads or specially made porcelain rings. The aim is to obtain a large surface area, and there are many patent designs of column. Industrially, a fractionating tower is used. Such a tower is divided into a number of compartments by means of trays set one above the other. These trays contain central holes, covered by bubbles caps, to allow vapour to pass up the tower and overflow pipes

to allow liquids to drop down.
At each point in a column or at each plate in a tower, an equilibrium between liquid and vapour is setup and this is facilitated by an upward flow of vapour and downward flow of liquid, a large surface area slow distillation. It also preferable to maintain the various levels of the column or tower at a steady temperature so that external lagging or an electrical heating jacket is often used.

A fractionating tower



These state of affairs existing in an idealized and simplified distillation of a mixture of a methanol and water, containing 10 per cent by mass of methanol as shown in the figure above. The figure shows five liquid vapour equilibria which are setup at different temperatures in the fractionating column.
The purpose of the fractionating column is to facilitate the setting up of this equilibria.
Mixtures of varied compositions can be drawn off from different points on the column or tower as is done, for instance in the fractional distillation of crude oil in a refinery.

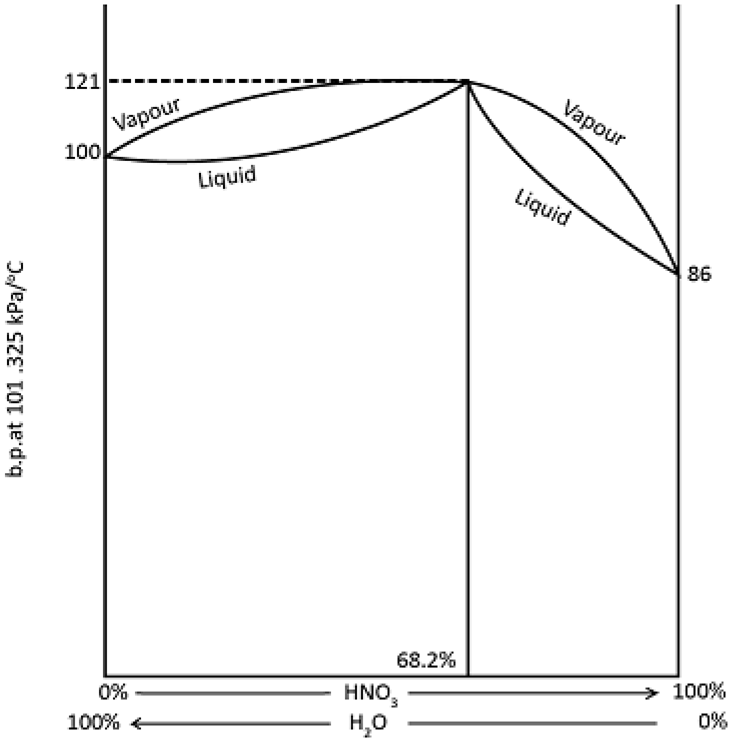
BOILING POINT COMPOSITION DIAGRAM WITH MAXIMUM

The vapour pressure composition diagram for nitric acid water mixtures shows a minimum and the corresponding boiling point composition diagram, with a maximum is shown.

On distilling a mixture of nitric acid and water containing less than 68.2 per cent nitric acid, the distillate will consist of pure water and the mixture in the flask will become more and more concentrated until it contain 68.2 per cent nitric acid . At this stage, the liquid mixture will boil at a constant temperature because the liquid and the vapour in equilibrium with it have the same composition, i.e. 68.2 per cent nitric acid.

Mixtures containing more than 68.2 percent nitric acid will give a distillate of a pure nitric acid until the residue in the flask reaches the 68.2 percent nitric acid.

Boiling point-composition diagram at fixed pressure for nitric acid-water mixture



Thereafter the distillate will 68.2 percent nitric acid be as before. A mixture with this type of boiling point composition curve cannot be completely separated by the fractional distillation. It can only be separated into a one component and what is known as the constant boiling mixture, maximum boiling point mixture, or azeotropic mixture.

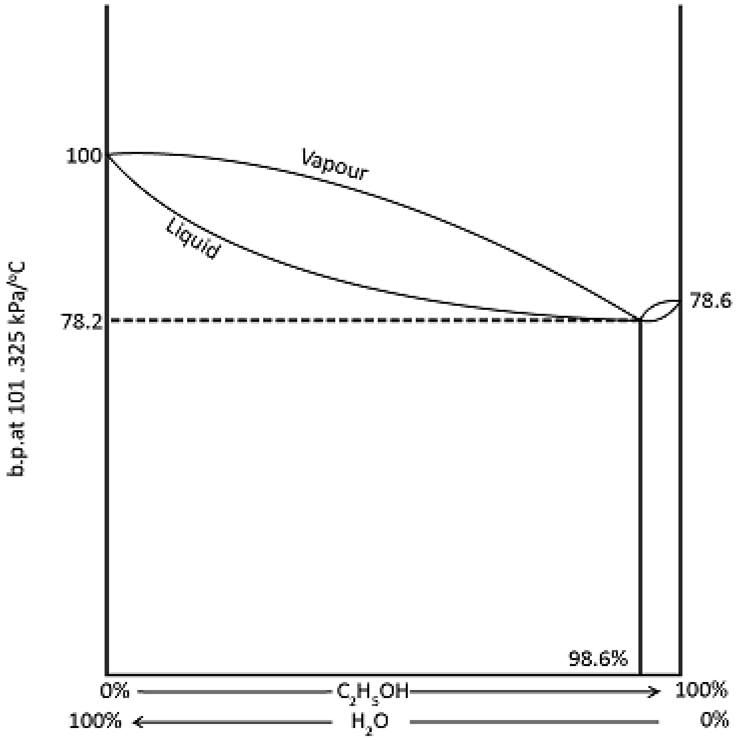
Maximum boiling point of mixtures are also obtain from mixtures of water with hydrofluoric, hydrobromic, hydrochloric, sulphuric and methanoic acids.

BOILING POINT COMPOSITION DIAGRAM WITH A MINIMUM

Ethanol and water give a vapour pressure composition diagram with a maximum. The corresponding boiling point composition diagram, with a minimum is shown in figure below. It is not possible to get a complete separation of ethanol and water by fractional distillation. A mixture containing more than 95.6 percent ethanol can be separated into pure ethanol and a minimum boiling point mixture, with a composition of 96.5 percent ethanol. A mixture containing less than 96.5 percent ethanol can be separated int pure water and the same water and the same boiling point mixture.

Water with propanol or pyridine and ethanol with tri-chloromethane or methyl benzene, also give minimum boiling point mixtures.

Boiling point-composition diagram at fixed pressure for ethanol acid-water mixture



SEPARATION OF AZEOTROPIC MIXTURES

An azeotropic mixture may have either a maximum or a minimum boiling point but at any one pressure, it has a fixed composition.

It is a unusual for this composition to correspond with that of any sample chemical formula for the mixture, and there is definitely no compound formation because the composition of the mixture does not depend on pressure.

Moreover, the mixture can be separated into its component parts fairly easily. Such separation can be brought about by the following methods.

a) By distillation with a third component

The azeotropic mixture of ethanol and water contains 95.6 percent of alcohol at normal atmospheric pressure. If benzene is added distillation yields, first a ternary azeotropic mixture of ethanol, water and benzene, then a binary azeotropic mixture of ethanol and benzene, and finally absolute ethanol.

b) By chemical methods
Quicklime may be used to remove the water from an azeotropic mixture of ethanol and water. Concentrated sulphuric acid will remove aromatic or unsaturated hydrocarbons from mixtures with saturated hydrocarbons in the refining of petrols and oils.

c) Absorption
Charcoal or silica gel may absorb one of the components.

d) Solvent extraction
One component can be extracted by a solvent.

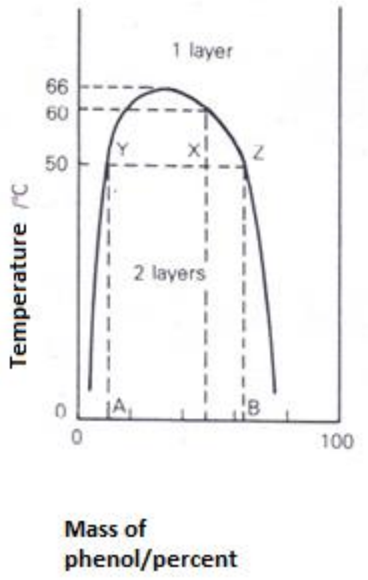
PARTIALLY MISCIBLE LIQUIDS

Critical Solution temperature.

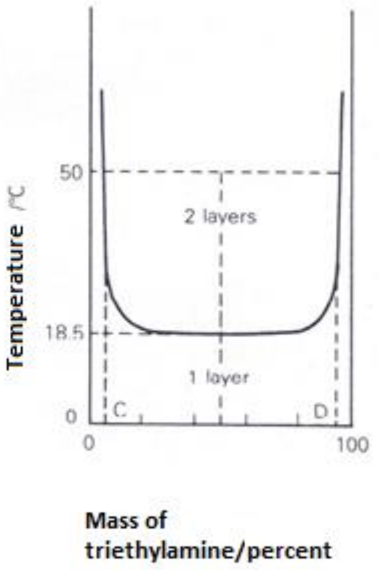
Phenol and water are completely miscible, forming one solution, above 66°C, but two immiscible solutions may from below that temperature, depending on the composition of the mixture. One of the solutions will be a solution of phenol in water, the other a solution of water in phenol.

They called conjugate solutions

The effect of composition and temperature is shown in a temperature-composition diagram below. The temperature above which phenol and water are always completely miscible is known as the upper critical solution temperature. At any point above the curve there will only be one layer, i.e. one solution. Below the curve, two layers will-always form and the curve will give the compositions of the two conjugate solutions making up the two layers. A mixture of 50 per cent phenol and 50 per cent water, for example, at 50 °C, will form two layers whose compositions are given by *A* and *B.* The line YZ is known as a tie-line. The ratio YX/XZ is equal to the ratio of the mass of the phenol layer (of composition *B)* to that of the mass of the aqueous layer (of composition *A).*



(a)



(b)

The complete miscibility of phenol and water with increasing temperature comes about because their mutual solubilities increase as the temperature does. The curve in Fig.(a) can be regarded as made up of two halves, one being the solubility curve of water in phenol and the other the solubility curve of phenol in water.

With triethylamine and water the mutual solubilities decrease as the temperature is increased. This leads to a temperature-composition diagram with a lower critical solution (or consolute) temperature of I8,5°C (Fig. (b)). A 50:50 mixture will be completely miscible at 10 °C but will separate into two layers, with compositions *C* and *D*, at 50 °C.

Mixtures of nicotine and water are very unusual as they have both an upper (208 °C) and a lower (61 °C) critical solution temperature.

Conjugate solutions have the same total vapour pressure and the same vapour composition; that is why they can coexist together.

REVIEW QUESTIONS

1. Some solution are ideal while others are not briefly explain what do you understand by this statement

2. How do ideal gases differ from ideal solution?

3. Define the following

i) Mole fraction of that liquid

ii) Ideal solution

iii) Briefly explain how Raoult’s law becomes feasible

4. Vapour pressure of methyl alcohol and ethyl alcohol at 20ºc are 94 mmHg and 44mmHg respectively. If 20g of ethyl alcohol and 100g of ethyl alcohol are mixed. Calculate

a) Partial pressure of each in a mixture

b) Total pressure of the mixture

c) % composition of each alcohol in a mixture

5. Define the following terms

i) Vapour pressure

ii) Partial Vapour pressure

6.a) Define the following

i) Ideal solution

ii) Non ideal solution

b) State the Raoult’s law partial pressure

Answer

a) i) Ideal solution are these solution that do obey all assumption of Raoult’s law of partial pressure

ii) Non ideal solution are these solution that do not obey some or all assumption of Raoult’s law of partial pressure

b) i) Raoult’s law of partial pressure states that "The saturated vapour pressure of each component in a mixture is equal to the product of mole fraction of that component and its pure vapour pressure"

7.a) ii) Raoult’s law

ii) Partition law

b) The ideality of a solution is approached when it is made more dilute explain

c) 10 g of methanol give an ideal solution when mixed with 50g of ethanol. If the vapour pressure of methanol and ethanol at the same temperature are 6265 Pa and 2933 Pa respectively

Calculate

i) The partial pressure exerted by each component in the mixture

ii) The component of the vapour

8.a) State

i) Boyl's law

ii) Charles's law

iii) Avogadros law

b) SO_2 used in manufacture of sulphuric acid is obtained from sulphide ore

$4\ Fe_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8\ SO_2(g)$

Find the mass of oxygen in grams reacting when 75 litres SO_2 is produced at 100^0C and 1.04 atm.

9. What is azeotropic mixture?

Azeotropic mixture is the mixture of two different components with constant vapour pressure and boiling point and it cannot be separated by fractional distillation.

10. What is azeotropic point

Azeotropic point is the point in temperature composition graphic which shows the azeotropic temperature and its composition

11. What is azeotropic temperature?

Azeotropic point is the temperature is the temperature at which azeotropic mixture tend to boi

The temperature composition graph of non ideal solution shows some deviations from ideal behaviour deviation

i) Positive deviation

ii) Negative deviation

iii) Boiling point composition diagram which undergo Positive deviation

12. a) Define the following terms

i) Azeotropic mixture

ii) Azeotropic point

iii) Boiling point

iv) Azeotropic composition

b) Liquid Q and R from a non ideal solution. If liquid Q boil at 100°C and R boil at 43% less than that of Q. On boiling the azeotropic mixture was formed at 56% composition by mass liquid Q and boil at 51°C

i) Plot the temperature composition graph

ii) What type of deviation is shown by your graph?

13. a) What do you understand by the following terms

i) Non ideal solution

ii) Azeotropic solution

b) How does non ideal solution deviate from ideal solution?

c) The mixture container the following water and nitric acid which boil at 86°C . The composition of azeotropic is 68% by mass nitric acid

i) Plot the boiling point curve which represent above data

ii) Account for the distillated and residue on distilling the mixture contain 50% by mass water

iii) Account for the distillated and residue on distilling the mixture contains 78% by mass HNO_3. If azeotropic temperature is 12°C

iv) Is the deviation positive or negative? Why?

v) 20% by mass HNO_3 . Account for the distillated at the point.

14. i) Raoult's law states that

The saturated vapour pressure of a component in a mixture is equal to the product of mole fraction of that components and its partial vapour pressure

ii) Partition law state that

When a solute is added to two immiscible solvents it distribute itself between the two solvent until the ratio of concentration of solute in one solute to another is constant, provided that solute remains in the same molecular state in both solvent and temperature is constant

b) The ideality of a solution is approached when it is made more dilute because the attractive or repulsive forces between solvent and solute molecules become weaker and cause the gas to obey assumption Raoult's law .

As a solution become more dilute

* In start stronger forces, grater deviation from Raoult's law , solution become more constant

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ORGANIC CHEMISTRY 2

AROMATIC COMPAOUNDS (ARENES)

These are organic compounds with benzene ring as functional group.

Molecular formula of benzene is $C_6 H_6$.

-It is highly unsaturated molecule but it does not undergo reaction readily and it tends to undergo substitution reaction.

STRUCTURES OF BENZENE

Structure of benzene can be expressed (shown) by using;

i. Kekule structure

ii. Resonance structure

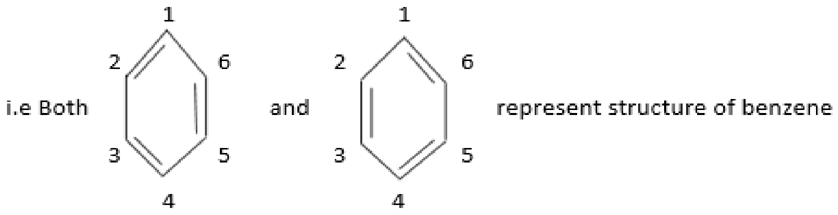
I. KEKULE STRUCTURE (1865)

According to kekule;

-Structure of benzene is hexagonal (It is cylic structure with six carbon atoms).

-In structure of benenze carbon-carbon double bond alternate carbon – carbon single bond.

-The structure of benzene is interconvertable.



STRENGTH OF KEKULE STUCTURE

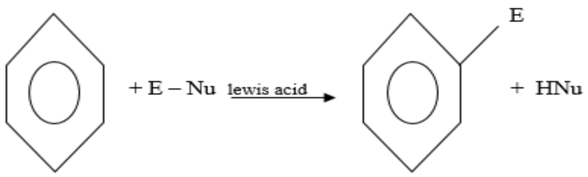
-It gives correct molecular formula of benzene which is C_6H_6.

-It is true that C-H bond in benzene are all alike. (This can be seen though x-ray diffraction).

WEAKNESS OF KEKULE STRUCTURE

-It fails to explain why benzene does not undergo addition reaction readily and it tends to undergo substitution reaction in steady.

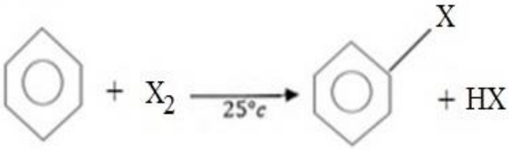
-Through x-ray diffraction it can be seen that carbon – carbon bond are equal throughout the benzene the fact which can not be explained to by Kekule structure (According to kekule structure there is C=C and C-C so it was expected that bond length of c=c to be shorter than that of c-c).

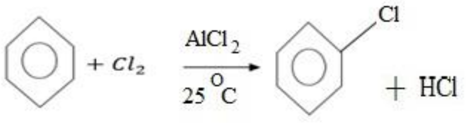


EXAMPLES OF ELECTROPHILIC SUBSTITUTION REACTIONS IN BENZENE

a) (a) HALOGENATION

Generally

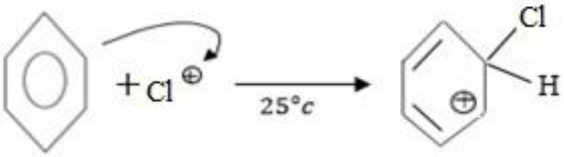




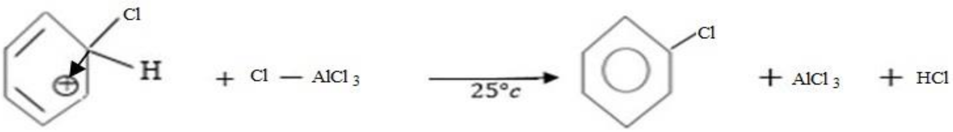
MECHANISM

i. Formation of an electrophile.

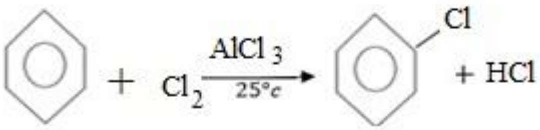
ii. Formation of intermediate carbonium ion.



iii. Formation of product and regeneration of catalyst.



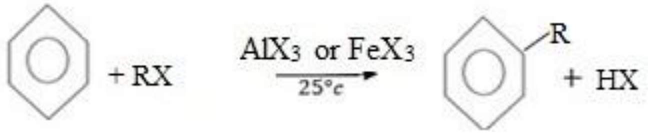
Thus, Overall reaction is



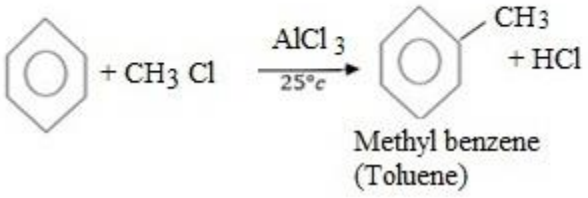
(b) ALKYLATION (FRIDEL CRAFT ALKYLATION)

Craft alkylation is the electrophilic substitution reaction between Benzene and haloalkane under presence of lewis acid catalyst to give alkylbenzene.

Generally;



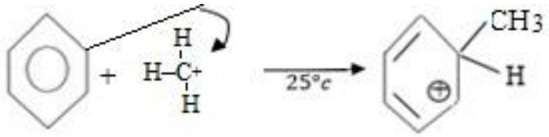
Example.



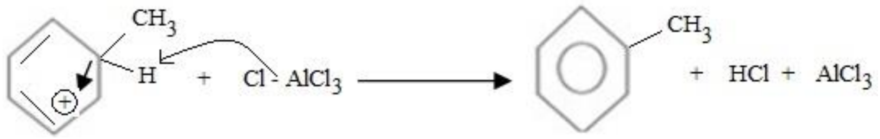
MECHANISM

i. i Formation of an electrophile.

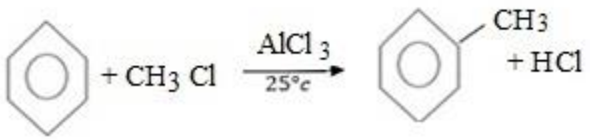
ii. Formation of intermediate carbonium ion.



iii. Formation of product and regeneration of catalyst.



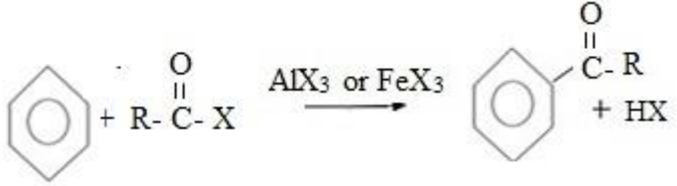
Hence, overall reaction.

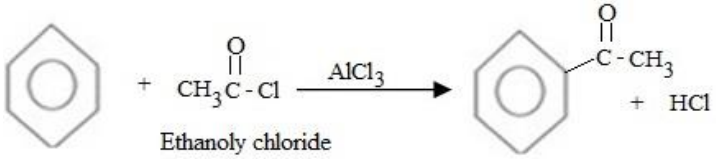


(c) ACYLATION (FRIDEL CRAFT ACYLATION)

Fridel crafit acylation is the electrophilic substitution reaction between benzene and acyl compounds under presence of lewis acid catalyst aromatic ketone.

Generally;

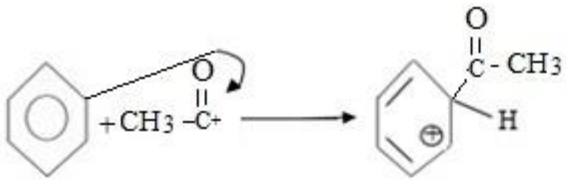




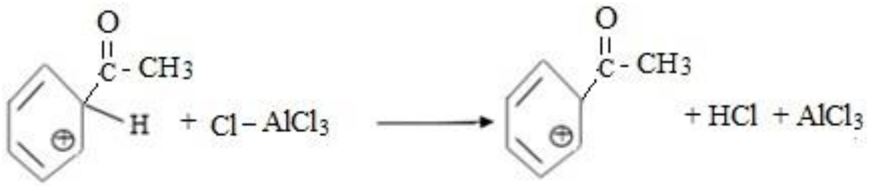
MECHANISM

i.Formation of an electrophile.

ii. Formation of intermediate carbonium ion.

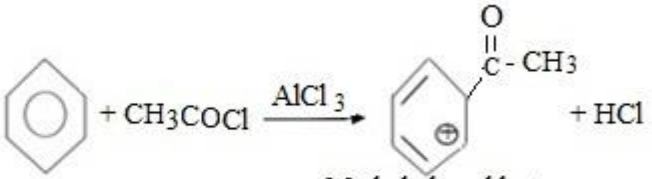


iii. Formation of product and regeneration of catalyst.



iv.

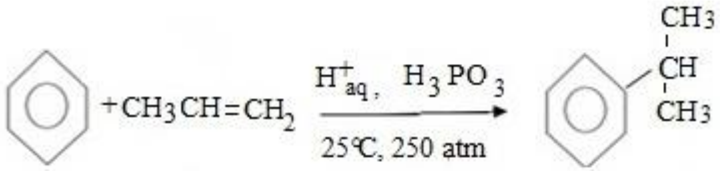
Thus, overall reaction is



Methyl phenyl ketone

(d) CUMENE FORMATION

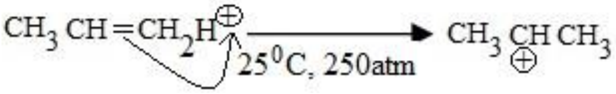
Bnzene react with propene under presence of acid medium to give isopropyl benzene (cumene)



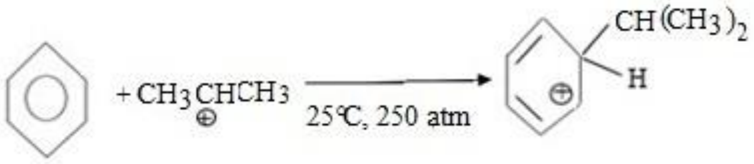
Cumene (Isopropyl benzene)

MECHANISM

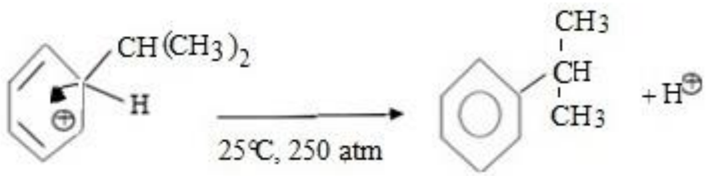
i.Formation of an electrophile.



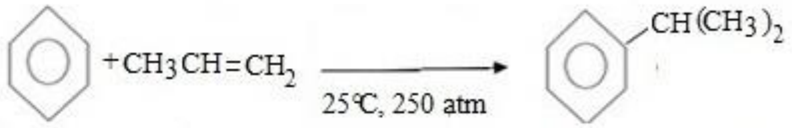
ii. Formation of intermediate carbonium ion.



iii. Formations of product and regeneration of catalyst.



Thus, overall reaction is

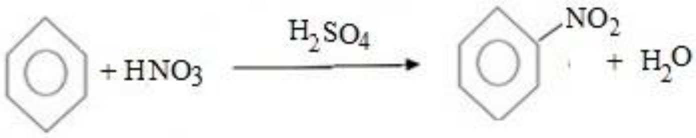


Cumene (Isopropyl benzene)

(e) <u>NITRATION</u>

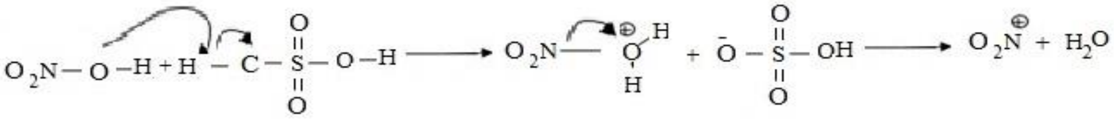
Benzene react with Nitric acid under presence of sulphuric acid yielding nitrobenzene.

i.e

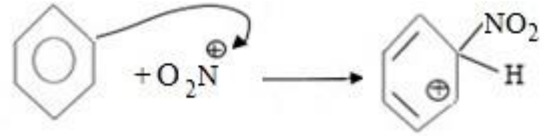


MECHANISM

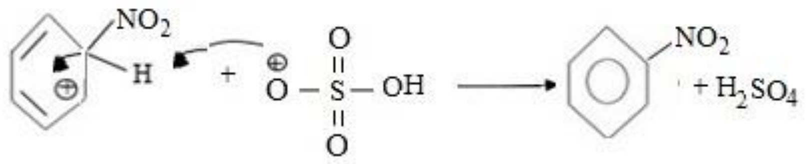
i. Formation of an electrophile.



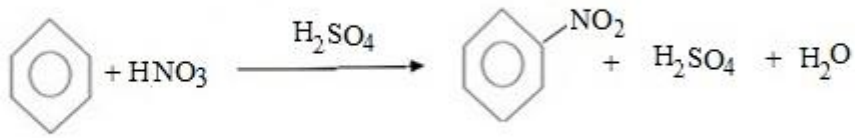
ii. Formation of intermediate carbonium ion.



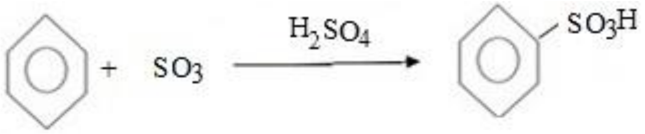
iii. Formation of product and generation of catalyst.



Hence, overall reaction is

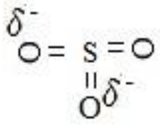


Benzene react with sulphur trioxide (or concentrated sulphuric acid) to give sulphobenzene (Benzene sulphoric acid).



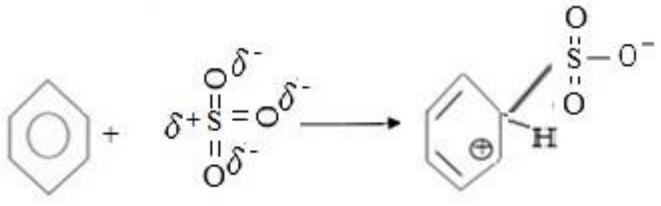
MECHANISM

i. Formation of an electrophile.

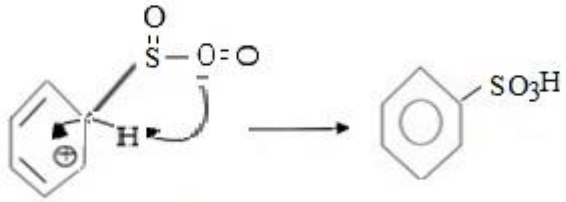


Itself is good electrophile.

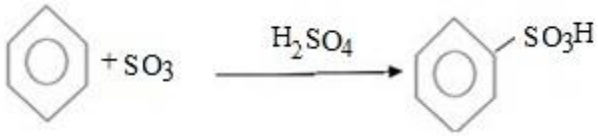
ii. Formation of intermediate carbonium ion.



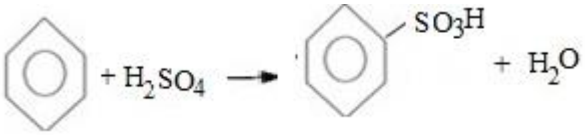
iii. Formation of product.



Thus, overall reaction is



<u>Also.</u>



Above reaction sulphuric acid Itself is good lewis acid (There is need of another lewis acid catalyst).

<u>DIRECT EFFECT IN MONOSUBSTITUETED BENZENE</u>

<u>ACTIVATOR AND DEACTIVATOR</u>

- Reactivity of benzene towards electrophile (in eletrophilic substitution reaction of benzene) depend on the electrons density in benzene ring.
- If the electron density is high then benzene will be more reactive towards electrophile and if it is low than the benzene will be less reactive toward an electrophile.
- When substitutients in benzene increase electron density in benzene ring, then the substituents in said to increase reactivity of benzene towards an electrophile.
- So any factor which affect the electron density in benzene ring is said to affect reactivity of benzene towards an electrophile.
- When substituents in benzene increase electron density in benzene ring, Then the substituents is said to increase reactivity of benzene towards an electrophile. i.e it is said to activate electrophilic substitution reaction of benzene and hence the substituent is known a <u>ACTIVATOR.</u>

· On other hand if the substituents decrease electron density in benzene ring, then the substituents is said to decrease reactivity of benzene towards an electrophile. i.e It said to deactivate electrophilic substitution reaction of benzene and hence the substituent is known as <u>DEACTIVATOR.</u>

Qn. How we can recognize the substituents is activator or Deactivator?

ANS

Before studying recognisation of activators and deactivators. It is better to study first effect which cause activation and deactivation in benzene.

There are two effect which cause activation in benzene.

i. Positive Inductive effect (+I).

ii. Positive mesomeric effect (+M).

i. POSITIVE INDUCTIVE EFFECT (+I)
This is the effect which arise in the organic compounds as a result of partial movement of electron pair towards the functional group. (In this case benzene ring).

ii. POSITIVE MESOMERIC EFFECT (+M)

This is the effect which arise in the organic compounds as a result of total movement of an electron pair towards the functional group (in case benzene ring) and move back again to its original position within the same molecule. Thus +M to activation in benzene substituents which cause +M (in benzene) are those with atoms possessing pair or negatively charged atom and It self directly bonded to another atom by sigma (δ)bond.

Example

OH^-, NH_2^-, RO^-, X.

Other hand there are two effects which cause deactivation in benzene.

i. Negative Inductive effect (-I).

ii. Negative mesomeric effect (-M).

i. NEGATIVE INDUCTIVE EFFECT (-I)

This is the effect which arise in organic compound as result of partial withdraw of an electron pair from functional group. (in this case benzene ring).

Inductive effect do deactivate of the benzene by partial withdraw of electron pair from benzene ring.

Substituent which cause **(-I)** are strong electronegative atom or electron attracting radicals.

Examples. OH^-, X, etc.

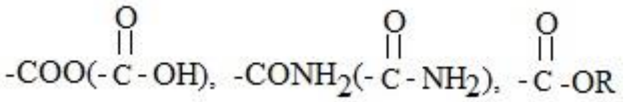
ii. NEGATIVE MESOMERIC EFFECT (-M)

This is the effect which arise in organic compounds as a results of partial withdraw of an electron pair from functional group (in this case benzene ring) and then moving back again to the original position within the same molecule.

- So -M do deactivation in benzene by withdraw of an electron pair from benzene ring.

- Substituents which cause –**M** are those with atoms possessing pair or negatively charged electron and itself is bonded to atom by π-bond.

Example:



$-COO(-\overset{\overset{O}{||}}{C}-OH),\ -CONH_2(-\overset{\overset{O}{||}}{C}-NH_2),\ -\overset{\overset{O}{||}}{C}-OR$

- There is the case where there is competition between mesomeric effect and Inductive effect. i.e the same substituent cause negative inductive and positive mesomeric effect (+M).

- When this occur in most cases mesomeric effects tends to outweighs Inductive effects i.e when the same species cause –I and then the effect at which will be considered is +M and these will be ACTIVATOR (Not deactivator).

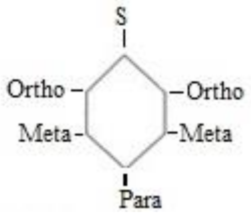
- Halogens are exceptional of above explanations i.e In halogens Inductive effects tends to outweighs mesomeric effects why?

REASONS

- Halogens are strongest electronegative element among all substituent of benzene as result of their smallest atomic size. This make halogens to exert strongest negative inductive effect.
- On other hand Halogens have maximum number of lone pair electron, thus making less available in participation of mesomerism thus make Halogens to exert weakest mesomeric effect among all substituents.
- So while Halogens exert strongest negative Inductive effect it also weakest effect (-M) hence in halogens Inductive effect weighs mesomeric effect.
- Generally we can conclude that all substituents which cause positive inductive effect and those which cause positive mesomeric exceptional of halogens are ACTIVATOR. And all substituents which cause negative mesomeric effect with addition of Halogens (which –I) are DEACTIVATOR.

DIRECTING EFFECT

Carbons in benzene with only one substituent group can be formed as follow;



The subustituent is activated, then it tends to direct incoming electrophile substituent at Ortho and para position i.e All activators are Ortho – para directors.

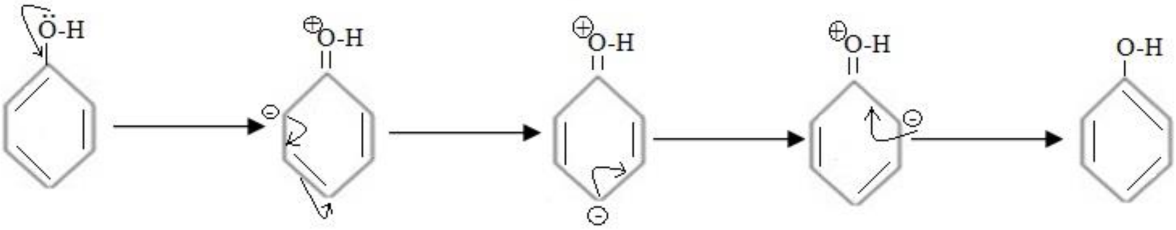
This can be explained considering;

i.Position of carbonium ion.

ii.Stability of intermediate carbonium ion.

I. POSITION OF CARBONIUM ION

Understand this consider mesomerism of phenol in which OH^- activator is directly attached to benzene ring.

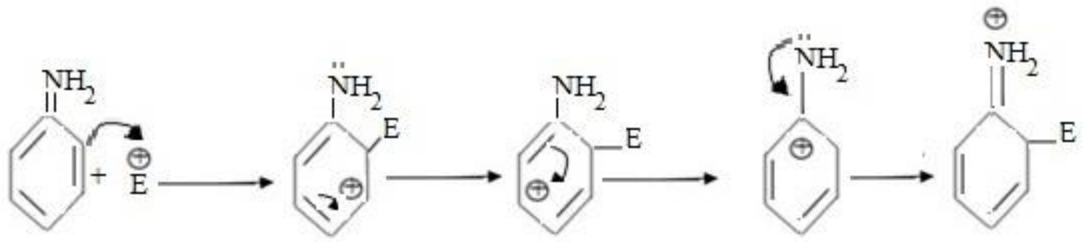


Above mesomerism (+M). It can be seen that despite the fact OH^- (activator) increase electron density through out the benzene ortho, para positions are more effected and hence ortho and para, carbons become better site for incoming electrophile.

II. STABILITY OF INTERMEDIATE CARBONIUM ION

1st CASE

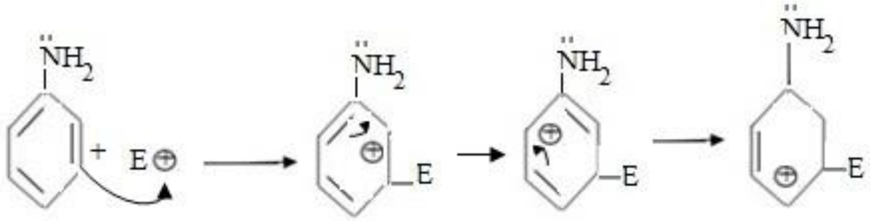
Incoming electrophile attach at ortho position. Consider electrophilic substitution reaction in aniline



Mecomerism it is clearly understood that intermediate carbonium ion is stabilised by lone pair electrons in nitrogen of amino group (-NH_2) and hence it is more stable

2nd CASE

If incoming electrophile attaches (substitute) at meta position consider the same reaction in aniline.

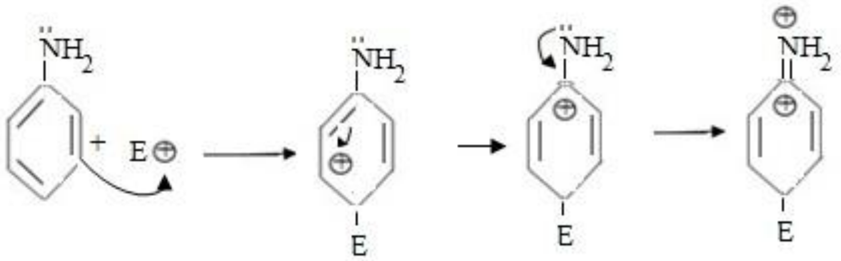


- In this case intermediate carbonium is not stabilised by lone electrons of nitrogen in amino group and hence it is less stable.

3rd CASE

If incoming electrophile substituents are at para position.

. Consider the same reaction in aniline.



· . In this case carbonium ion is stabilised by lone pair of nitrogen in group amino hence it is more stable.

CONCLUSION

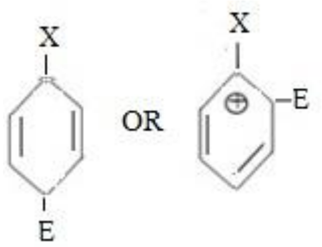
Since carbonium ions formed in 1st and 3rd case are more stable than that formed in 2nd case. Ortho and para positions are prefered sites for incoming electrophile.

NOTE:

- Alkyl group act as ortho-para directon by doing partial neutralization of positive charge formed on the adjustment carbon

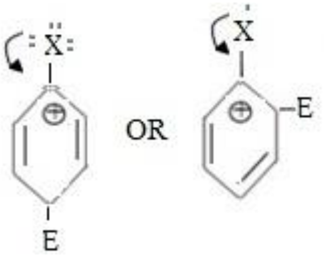
(The partial neutralization is done by positive inductive effect exerted by alkyl groups). Hence ortho - para directing of alkyl groups is simply explained by considering stability intermediate carbonium ion like in (ii) above.

i.e.



Are ortho - para directors due to stability intermediate carbonium ion. This is simply because despite the fact that lone pairs in halogens have not good participation in mesomerism for reason which has explained, but in presence of positive charge on adjacent carbon lone pair electrons participate in neutralizing positive charge on the carbon.

i.e.



- Among the two products (ortho product and para product in most cases para product is major product why?

Reason

Due to steric hinderance exerted by the substituent originally present in benzene, ortho carbons which are closer to the substituents experience the effect strongly and hence incoming electrophile is more favoured to substitute at para carbon which is far from the substituent.

But if the substituent in halogen, ortho product become major product why?

Reason

Halogens like Cl have very small atomic size, Thus they exert very small steric hinderance thus make incoming electrophile to substitute first at ortho carbons (for every two ortho) carbons there is only one para carbon).

Deactivators with exceptional of halogens directs incoming eletrophile at meta position i.e. Deactivator (with exceptional halogens) are meta directors.

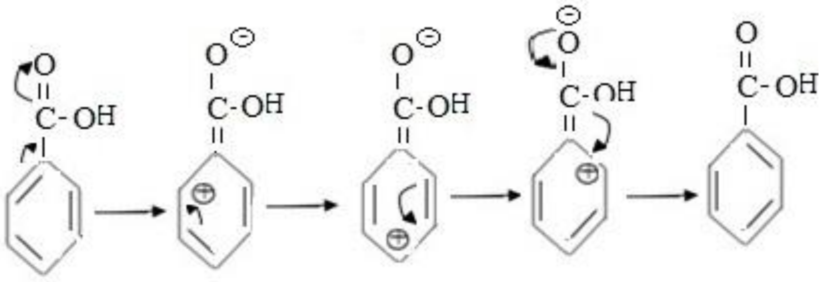
This can be explained by considering

i. Position of carbonium ion

ii. Stability of intermediate carbonium ion.

I. POSITION OF CARBONIUM ION

- To understand this consider mesomerism (-M) in benzoic acid



From the above shown mesomerism it can be seen that despite the fact that carboxylic group (-COOH) deactivate the whole benzene ring ortho and para positions are more effected and hence meta carbon somehow become pereferd position for incoming eletrophile.

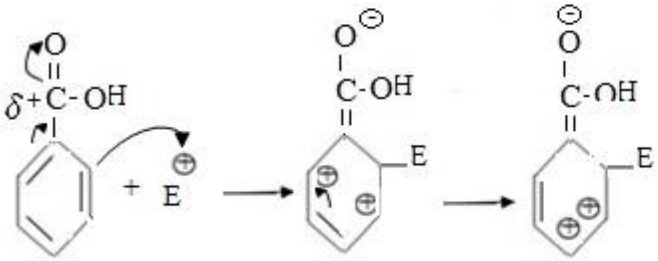
II. STABILITY OF INTERMEDIATE CARBONIUM ION

- Consider the electrophilic substitution reactions in benzoic acid.

1st CASE

If incoming electrophile substitute of ortho position.

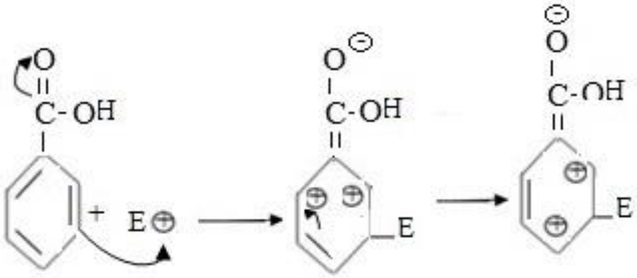
i.e.



- Intermediate carbonium is not stable as result of very large repulsion force between closer positively charged ions in adjacent carbons.

2nd CASE

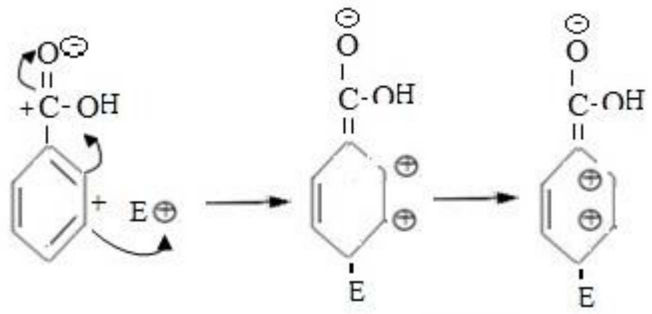
If incoming eletrophile substitute of meta position.



- Carbonium ion formed in this case is somehow more stable as a result of comparable small repulsion force between position charged carbons which are not adjacent.

3rd CASE

If incoming electrophilic substitutes at para position. Also Intermediate carbonium ion formed is not stable as a result of very large repulsion force between closer positively charged ions in adjacent carbons.
i.e.



CONCLUSION

Intermediate carbonium ion formed in second case is more stable than in 1st case and 3rd case and hence meta position is better site for incoming electrophile.

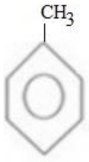
SUMMARY ON DIRECTING EFFECT

ORDHO- PARADIRECTORS		META DIRECTORS
ACTIVATORS	DEACTIVATORS	DEACTIVATORS
OH NH_2 RO^- R R is the alkyl group.	X (Halogens) E.g F Cl Br etc.	$-\overset{O}{\overset{\|}{C}}-OH$ $-\overset{O}{\overset{\|}{C}}-NH_2$ $-\overset{O}{\overset{\|}{C}}-OR$ $C\equiv N$ $-NO_2$ $(-N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$ $-SO_3H\,(-\underset{\underset{O}{\|}}{\overset{\overset{OH}{\|}}{S}}=O$ $-\overset{O}{\overset{\|}{C}}-$ etc.

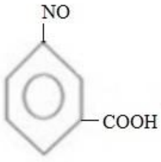
SOLVED PROBLEMS

QN 1. Arrange the following compounds in order of reactivity towards.

i. Nucleophile.



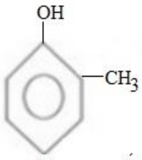
A



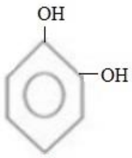
B

C

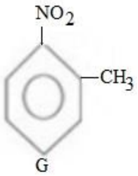
D



E



F



G

<u>ANS</u>

I. F< E <A <D <G <C <B
$\longrightarrow$
Increase in reactivity towards nucleophile

II. B< C< G< D< A< E< F
$\longrightarrow$
Increase in reactivity towards electrophile

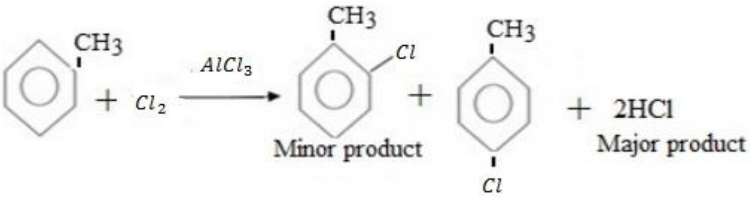
Qn. 2. Explain why alkylation of nitrobenzene is much slaver that of methy l benzene?

<u>ANS</u>

Alykylation in given compounds is electrophile substitution reaction so presence of nitro group which is an electron withdrawing (deactivator) in nitrobenzene deactivate. Its reaction towards electrophile while presence of methyl group which is electron receptor group (activator) in methyl benzene activate its reaction towards electrophile and hence alkylation of nitrobenzene become less than that of methyl benzene.

Qn. 03. Complete the following organic reactions.

i.



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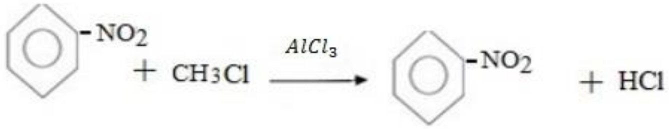
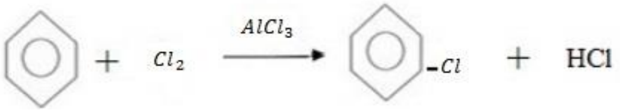
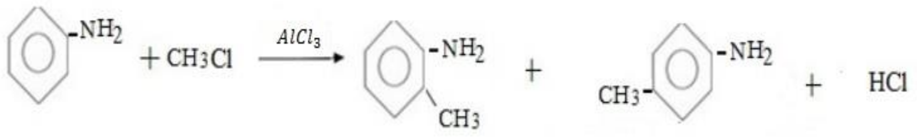


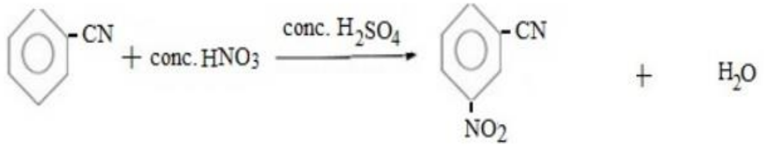
iii.



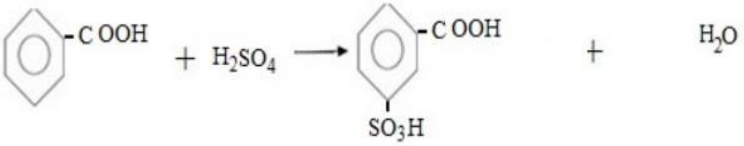
iv.



v.



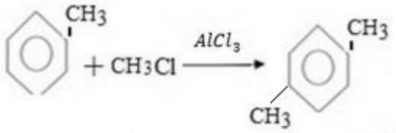
vi.



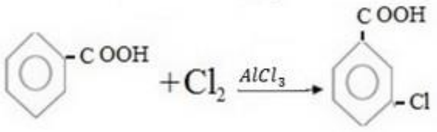
Qn. 04. NECTA 1994

Write structural formula of main substitutional product in the following organic reactions.

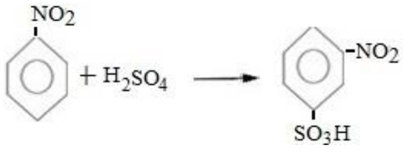
i.



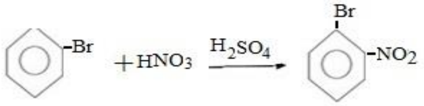
ii.



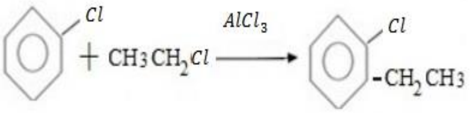
iii.



iv.



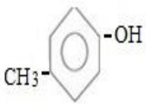
v.



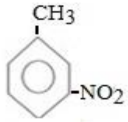
Qn 05. NECTA 1993

Which substituent entered first in the following organic compounds giving reasons.

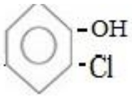
i.



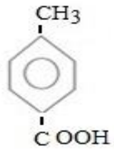
ii.



iii.



iv.



ANS

i. Either of the two substituents entered first.

<u>Reason</u>

In given compound OH and CH_3 are para related and OH^- and CH_3 are ortho –para directors forming para product as a major product and hence either of the two entered first so as to direct incoming substituent at para position.

ii. NO_2 entered first

<u>Reason</u>

In given compound CH_3 and NO_2 are meta related so being meta director it must be entered first so as to direct the incoming CH_3 group at meta position.

iii.Cl entered first

<u>Reason</u>

In given compound OH and Cl are ortho related and OH and Cl are orth-para directors, OH^- forming product a major product (as result of its large steric hinderance while Cl form ortho product as major product (as result low steric hinderance) and Cl^- must be entered first so direct at ortho position.

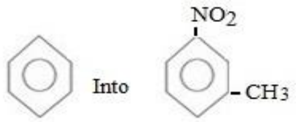
<u>Reason</u>

In given compound CH_3 and COOH are para related, CH_3 being ortho –para product forming para product as major product must be entered first so as to direct incoming – COOH at para position.

Qn 6.

Show how the following conversions can be achieved.

i.



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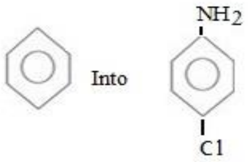

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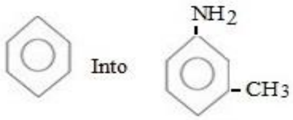

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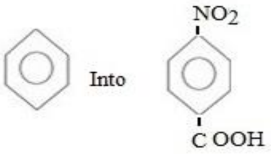
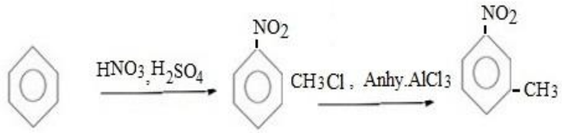


ANS

i.



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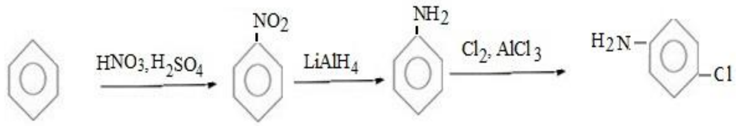

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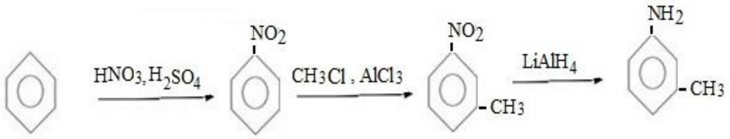

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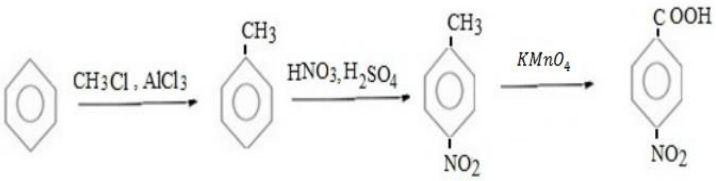


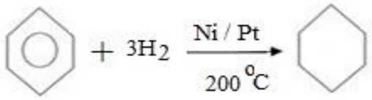
FURTHER CHEMICAL REACTIONS OF BENZENE
Apart from electrophilic substitution reactions benzene can undergo the following reactions.

i. ADDITION REACTIONS

- Under vigorous condition benzene can undergo addition reaction.

eg.
(a) HYDROGENATION

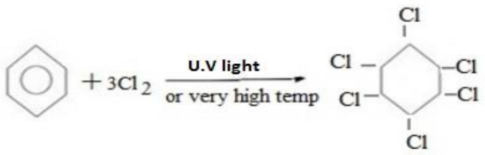
Benzene can react with hydrogen under presence of nickel or platinum catalyst yielding cyclohexane.
i.e.



(b) CHLORINATION

- Under presence of U.V a very high temperature benzene react with chlorine to give 1,2,3,4,5,6-hexachlorocyclohexane.

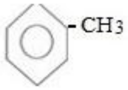
i.e.



TOLUENE (METHYL BENZENE)

- Toluene is the aromatic compound which is formed when one halogen atom of benzene is replaced by methyl group.

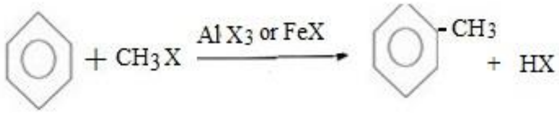
i.e. Structure of toluene is ;-



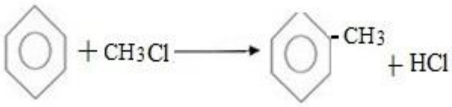
PREPARATION OF TOLUENE

(a) METHYLATION OF BENZENE

Generally;

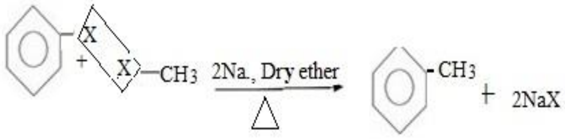


Example:

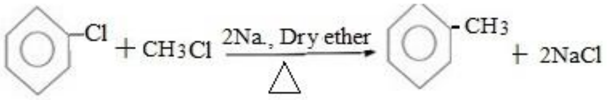


(b) Reaction between halobenzene and halomethane under;
Presence of sodium and dry ether.

Generally.



Example;



PHYSICAL PROPERTICES OF TOLUENE

- It is more denser than water.
- It is solube in non-polar solvents like organic solvent (Toluene itself is good organic solvent)
- It melts at temperature of -95^{0}C and boils at 111^{0}C
- Its vapour density is large than that of the air
- It is colourless liquid at room temperature.

In most cases toluene is used as organic solvent instead of benzene because it is less toxic.

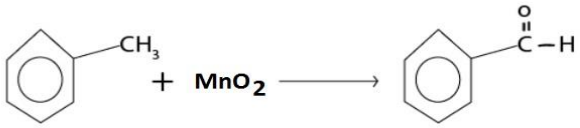
CHEMICAL REACTION OF TOLUENE

Commonly toluene undergo the following chemical reactions
i. Side chain chemical reactions
ii.Electrophilic substitutions in benzene ring

I. SIDE CHAIN CHEMICAL REACTIONS
Under this heading toluene undergo the following
a)Oxidation
b)Free radical substitution reactions.

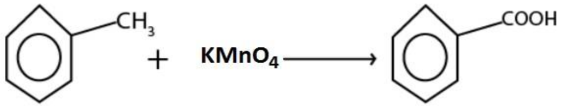
A) OXIDATION
With milder oxidizing like MnO_2 agent benzaldehyde is med.

i.e



But with strong oxidizing agent like kmno$_4$ and $K_2Cr_2O_7$ ie acid is formed

eg.

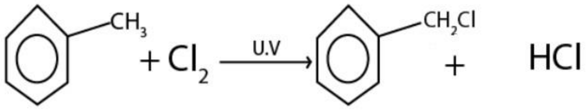


B) FREE RADICAL SUBSTITUTION REACTION

· With halogens under presence of U.V or very high temperature tends to undergo side chain radical substitution reactions.

Example

i/



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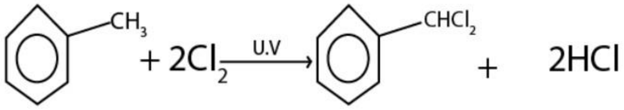
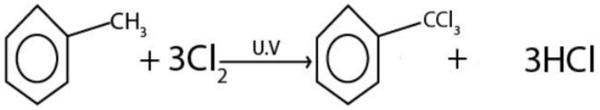


iii/

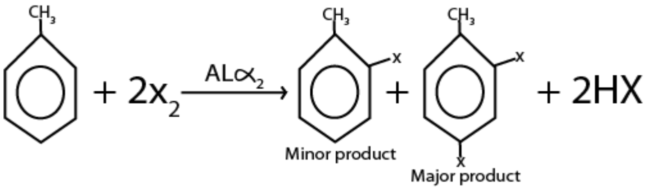


II. ELECTROPHILIC SUBSTITUTIONS IN BENZENE RING

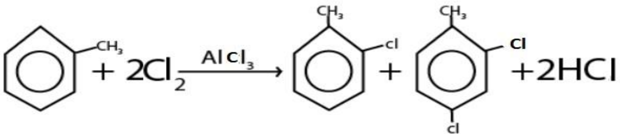
Consider this heading toluene undergo similar chemical reaction as those of benzene. The only difference is that methyl group in toluene act as ortho director forming para product as major product Example of electrophilic substitution reactions of Toluene

i. HALOGENATION

Generally

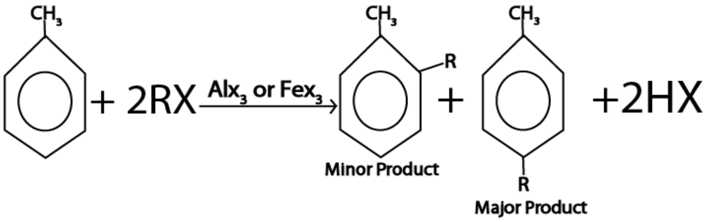


Example

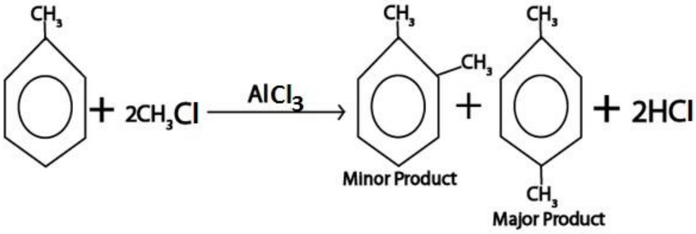


ii. ALKYLATION

Generally

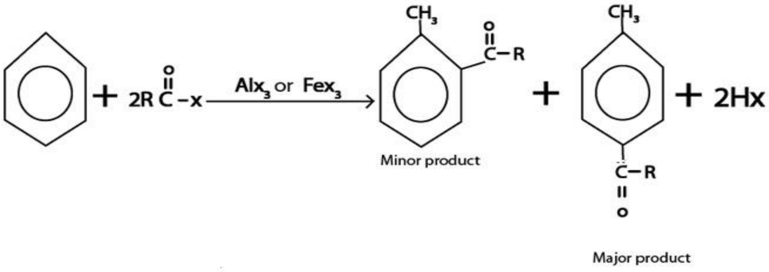


Example

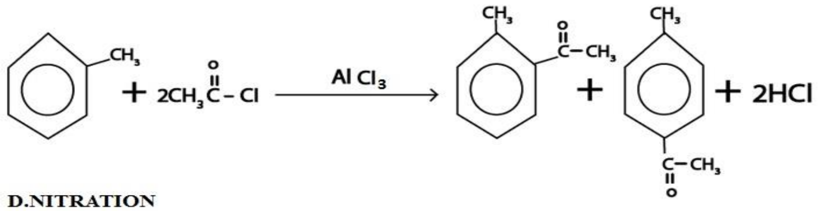


iii. ACYLATION

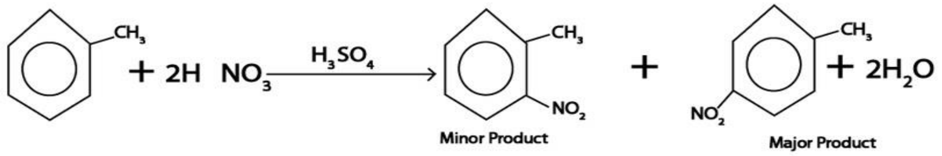
Generally



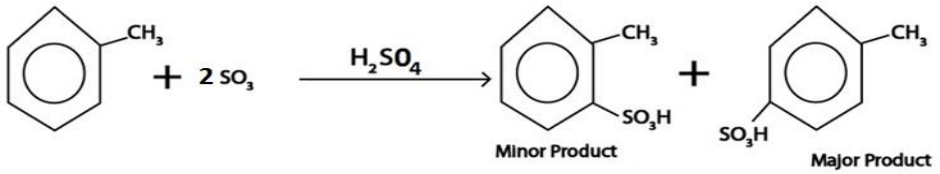
Example



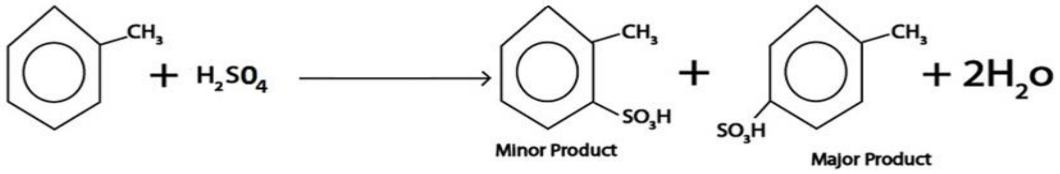
D.NITRATION



E .SULPHONATION

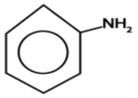


OR



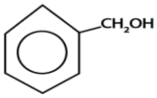
SOME STRUCTURE OF AROMATIC COMPOUNDS $ THEIR COMMON NAME

i/



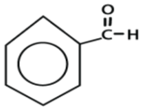
Aniline

ii/



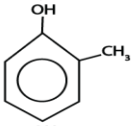
Benzyl alcohol

iii/



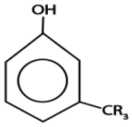
Benzal dehyde

iv/



O-cresol

v/

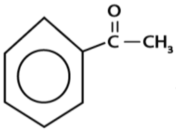


M-cresol

vi/

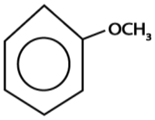
P-cresol

vii/



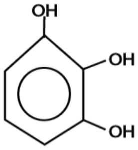
Acetophenone

viii/



Anisole

ix/

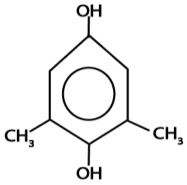


Pyrogallol

x/

Hydroxyquinone

xi/

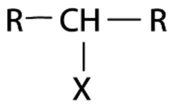


Dettol

II. SECONDARY (2^0) HALOALKANE

These are haloalkanes where by a carbon with halogen is directly bonded to two alkyl groups

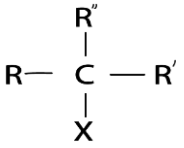
Thus for haloalkane with only one halogen the carbon with halogen is also directly bonded to only one hydrogen atom.



$$R-\underset{X}{\underset{|}{CH}}-R$$

III. TERTIARY (3^{O}) HALOALKANES

These are haloalkanes where by a carbon containing halogen directly bonded to three alkyl groups. Thus in tertiary haloalkanes there is no hydrogen atom which is directly bonded to carbon with halogen.



$$R-\overset{R''}{\overset{|}{\underset{X}{\underset{|}{C}}}}-R'$$

Haloalkanes are named by naming halogen as substituent of alkanes.

PREPARATIONS OF HALOALKANES

a). FREE RADICAL SUBSTITUTION REACTION OF ALKANES

Generally.

$$RH + x_2 \xrightarrow{U.V} Rx + Hx$$

Example.

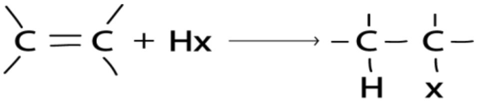
$$CH_3CH_3 + Cl_2 \xrightarrow{U.V} CH_3CH_2Cl + HCl$$

In above reaction chlorine must be present in limited amount so as to prevent further chlorination of the product otherwise

$$CH_3CH_3 + \underset{(excess\ Cl_2)}{6Cl_2} \longrightarrow Col_3Col_3 \quad + 6HCl$$

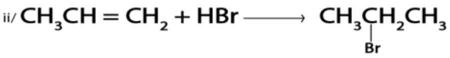
b). HALOGENATION OF ALKANES

Generally



Example

i/ $CH_2 = CH_2 + HCl \longrightarrow CH_3CH_2Cl$



ii/ $CH_3CH = CH_2 + HBr \longrightarrow CH_3\underset{Br}{\underset{|}{C}}HCH_3$

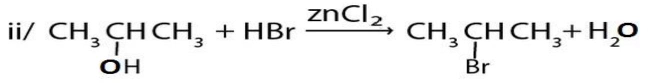
C). HALOGENATION OF ALCOHOL

1. By using hydrogen halide

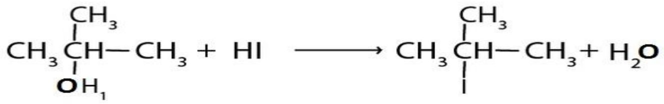
Alcohol reacts with hydrogen halide to give haloalkanes

Example

i/ $CH_3CH_2OH + HCl \xrightarrow{znCl_2} CH_3CH_2Cl + H_2O$

ii/ 

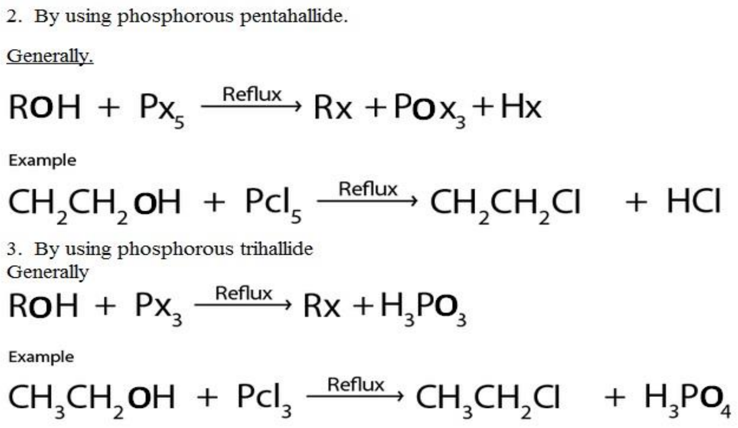
$CH_3\underset{OH}{CH}CH_3 + HBr \xrightarrow{znCl_2} CH_3\underset{Br}{CH}CH_3 + H_2O$

iii/ 

$CH_3\overset{CH_3}{\underset{OH_1}{CH}}-CH_3 + HI \longrightarrow CH_3\overset{CH_3}{\underset{I}{CH}}-CH_3 + H_2O$

2. By using phosphorous pentahallide.

Generally.



2. By using phosphorous pentahallide.

Generally.

$ROH + Px_5 \xrightarrow{Reflux} Rx + POx_3 + Hx$

Example

$CH_2CH_2OH + Pcl_5 \xrightarrow{Reflux} CH_2CH_2Cl + HCl$

3. By using phosphorous trihallide

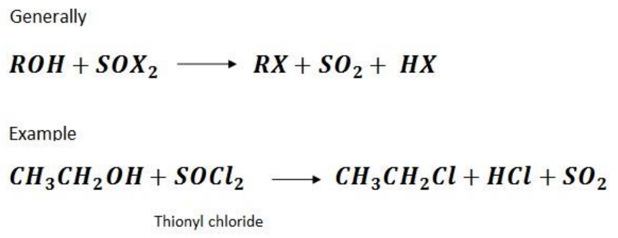
Generally

$ROH + Px_3 \xrightarrow{Reflux} Rx + H_3PO_3$

Example

$CH_3CH_2OH + Pcl_3 \xrightarrow{Reflux} CH_3CH_2Cl + H_3PO_4$

4. Reaction by using thionylchloride



Generally

$ROH + SOX_2 \longrightarrow RX + SO_2 + HX$

Example

$CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + HCl + SO_2$

Thionyl chloride

PHYSICAL PROPERTIES OF HALOALKANES

Melting and boiling point of haloalkane are greater than those of corresponding members of alkanes(alkane whose moleculer mass do not differ with those of haloalkanes) as a result of highly polarity of C-X bond

eg $C^{\delta+} — Cl^{\delta-}$

Haloalkanes are soluble in organic solvent (haloalkanes themselves are good organic solvent i.e they tend to form miscible with another organic solvent) but are almost insoluble in water .

CHEMICAL REACTIONS OF HALOALKANES.

Haloalkanes undergo the following chemical reactions

a) Nucleophilic reaction
b) Elimination reaction
c) Reaction which leads to formation of Grignard reagent
d) Wurtz/coupling/fillings reactions
e) Reduction

A) NUCLEOPHILIC SUBSTITUTION REACTION

Nucleophilic substitution reaction in Haloalkane undergo two types of mechanism namely:

i) SN mechanism
ii) SN^2 mechanism

i. SN. MECHANISM

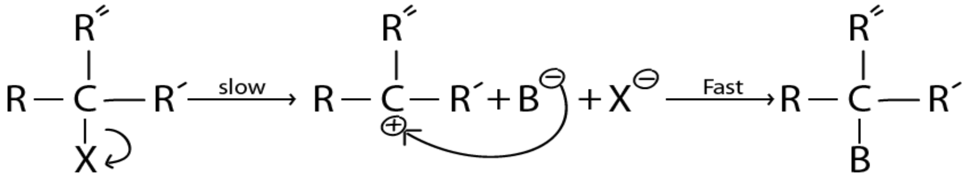
This is nucleophilic substitution reaction where by there is only one molecule which is involved in rate determining

Definition of Rate dertermining step

This is the lowest step in reaction mechanism

SN. Mechanism is more common in tertiary haloalkanes as a result of high stability brought by strong positive active effect exerted by three alkyl groups

Illustration.



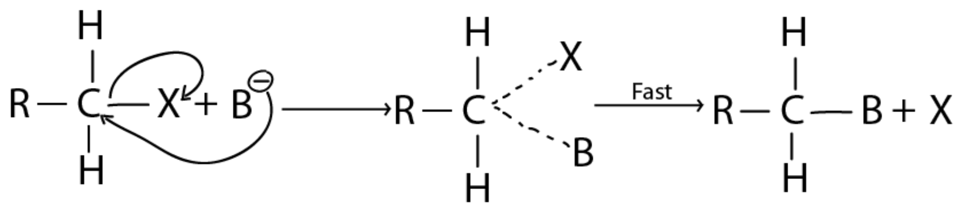
where:-

$B^{\ominus}$ Is lewis base

ii. SN^2 MECHANISM

This is the Nucleophilic substitution reaction mechanism which by there are two molecules in rate determining step.

It is more common in primary haloalkanes (also in secondary haloalkanes)



where:-

$B^{\ominus}$ Is lewis base

Generally reactivity of haloalkanes towards nucleophile follow the following

3° haloalkanes, 2° haloalkanes, 1° haloalkanes →

Decrease in ability of undergo nucleophilic substitution reaction

Haloalkanes

i. Formation of alcohol

Haloalkanes reacts with alkaline solution like $NaOH_{(aq)}$ yielding alcohol

Generally

$$Rx + NaOH_{(aq)} \xrightarrow[25^{\circ}c]{} ROH + Nax$$

(K can be used instead of Na)

Example

$$CH_3CH_2Cl + NaOH_{(aq)} \xrightarrow[25^{\circ}c]{} CH_3CH_2OH + Nacl$$

To avoid formation of elimination product, moist silver oxide is used. i.e

$$CH_3CH_2CL + Ag_2O \xrightarrow{H_2O} CH_3CH_2OH + Agcl$$

ii. Formation of amines.

Haloalkanes react with ammonia yielding amines

Generally.

$$Ag - x \boxed{x + H} - NH_2 \xrightarrow[\triangle]{} R - NH_2 - Hx$$

Example

$$CH_3CH_2Cl + NH_3 \xrightarrow[\triangle]{} CH_3CH_2NH_2 + HCl$$

iii. Formation of nitroalkanes

Generally

$$Rx + MNO_2 \xrightarrow[\triangle]{} RNO_2 + Mx$$

Where:
M is g, Na, k e.t.c

<u>Example</u>

i/ $CH_3CH_2Br + AgNo_2 \xrightarrow[\triangle]{} CH_3CH_2No_2 + AgBr$
ii/ $CH_3CH_2Cl + NaNo_2 \xrightarrow[\triangle]{} CH_3CH_2No_2 + Nacl$

iv. Formation of Ester

$$R\overset{O}{\overset{\|}{C}}-o\boxed{Ag + x}-R' \longrightarrow R-\overset{O}{\overset{\|}{C}}-o-R' + Agx$$

Example

$$CH_3CH_2COOAg + CH_3CH_2Cl \longrightarrow CH_3CH_2COOCH_2CH_3 + AgCl$$

V. Formation of Ether

<u>Generally.</u>

$$RO\boxed{Ag + x}-R' \longrightarrow ROR' + Nax$$

Example

$$CH_3CH_2Cl + \underset{\text{sodium methoxide}}{NaOCH_3} \longrightarrow CH_3CH_2OCH_3CH_3 + Nacl$$

vi. Formation of Nitrile

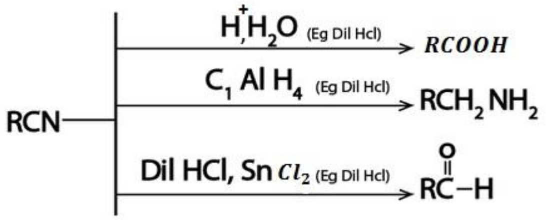
<u>Generally</u>

$$R-x + KCN \xrightarrow{\text{Reflux}} \underset{\text{Nitrile}}{RCN} + Kx$$

Example

$$CH_3CH_2Cl + KCN \xrightarrow{\text{Reflux}} CH_3CH_2CN + KCl$$

Nitrile is used to synthesize various organic compound



So the reaction (formation of nitrile) is very important in dealing with conversion problems which show that number of carbons have increase by one.

Example

Show how the following conversion can be

i/ CH_3CH_2OH into $CH_3CH_2CH_2OH$
ii/ CH_3CH_2Cl into $CH_3CH_2CH_2I$
iii/ CH_3CH_2OH into CH_3CH_2COOH
iv/ CH_3CH_3 into $CH_3CH_2CH_3$
v/ $CH_2 = CH_2$ into $CH_3CH = CH_2$

ANS.

i/ $CH_3CH_2oH \xrightarrow[\text{reflux}]{Pcl_5} CH_3CH_2 \xrightarrow[\text{reflux}]{KCN} CH_3CH_2CN \xrightarrow{H^+,H_2o} CH_3CH_2CooH \xrightarrow{liAlH_4} CH_3CH_2CH_2oH$

ii/ $CH_3CH_2Cl \xrightarrow[\text{reflux}]{KCN} CH_3CH_2CN \xrightarrow[H_2o]{\text{Dil HCl}} CH_3CH_2CooH \xrightarrow{liALH_4} CH_3CH_2CH_2oH \xrightarrow{HI} CH_3CH_2CH_2I$

iii/ $CH_3CH_2oH \xrightarrow[\text{reflux}]{Pcl_5} CH_3CH_2Cl \xrightarrow[\text{reflux}]{KCN} CH_3CH_2CN \xrightarrow{\text{Dil HCl}} CH_3CH_2CooH$

iv/ $CH_3CH_3 \xrightarrow[\text{U.V}]{Cl_5} CH_3CH_2Cl \xrightarrow[\text{reflux}]{KCN} CH_3CH_2CN \xrightarrow{\text{Dil HCl}} CH_3CH_2CooH \xrightarrow[\text{reflux}]{Pcl_5} CH_3CH_2CH_2Cl \xrightarrow[\triangle]{H_2/N_2} CH_3CH_2CH_3$

v/ $CH_2 = CH_2 \xrightarrow{HCl} CH_3CH_2Cl \xrightarrow[\text{reflux}]{KCN} CH_3CH_2CN \xrightarrow{\text{Dil HCl}} CH_3CH_2CooH \xrightarrow[\text{reflux}]{Pcl_5} CH_3CH_2CH_2Co \xrightarrow[\triangle]{KoH,CH_2CH_2OH} CH_2 = CH_3CH_2$

Replacement by another halogen

- Halogen in haloalkane can be replaced by another halogen which is more nucleophilic.
- The strength of nucleophilic character of halogen follow the following order.

$I^- > Br^- > CL^- > F^-$

Most nucleophilic — Least nucleophilic

B). ELIMINATION REACTIONS.

Elimination and nucleophilic substitution reactions in haloalkane are competitive reactions.

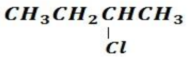
Conditions which favour elimination reactions are

- The reaction should under taken in non-aqueous solution (in this case the reaction is undertaken inpresence of alcohol)
- Presence of strong and concentrated base like conc. KOH
- The reaction should be undertaken at hight temperature
- Tertiary haloalkane

Formation of major product in elimination reaction (if there is ability of forming more than one product) is governed by saytzeff's rule which. States that. "The alkane with great number of alkyl group is more stable.

- So according to saytzeff's rule if there is possibility of forming more than one elimination product, the major product is the alkene with greater number of alkyl groups

· Elimination product of



$CH_3CH_2\underset{Cl}{\underset{|}{C}}HCH_3$ is ether

i. $CH_3CH{=}CHCH_3$ or

ii. $CH_3CH_2CH{=}CH_2$, so according to saytzeff's rule (i) is <u>Major PRODUCT</u>

·There are two types of mechanism of elimination reaction in haloalkane namely

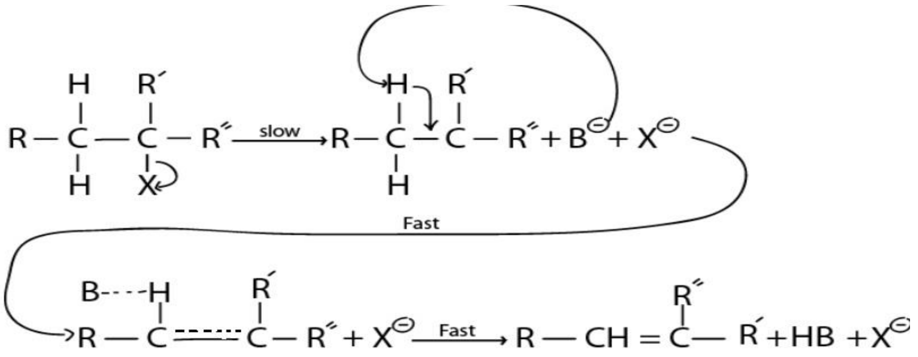
a) E_1 mechanism

b) E_2 mechanism

A. E_1 MECHANISM

·This is mechanism of elimination reaction where by there is only one molecule which is involved in rate determining step

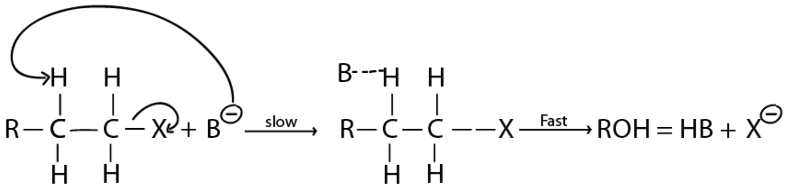
- It is more common in tertiary haloalkane as result of high stability of intermediate carbonium ion which is brought by very strong positive inductive effect from three alkyl groups.



B. E_2 MECHANISM

·This is the elimination reaction mechanism where by there are two molecules which are involved in rate determining step.

- It is more common in primary haloalkane (also in secondary haloalkane) due to instability of intermediate carbonium ion which could be formed if it undergo mechanism as a result of weak ^{+}I exerted by one alkyl group.



Examples of elimination reaction in haloalkanes are

i/ $CH_3CH_2CH_2CL + \text{Conc. } KOH \xrightarrow[\triangle]{} CH_3CH = CH_2 + KCL + H$

ii/ $CH_3CH_2\underset{\displaystyle CL}{\underset{|}{C}}HCH_2 + \text{Conc. } NaoH \xrightarrow[\triangle]{\text{Alcohol}} CH_3CH = CHCH_2 + NaoH + H_2O$

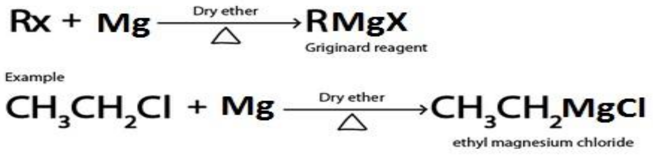
NOTE:

Possibility of haloalkanes to undergo elimination reactions follow the following trend
Tertiary haloalkanes>Secondary haloalkanes > Primary haloalkanes

C. GRIGINARD REAGENT FORMATION

- Grignard reagent is alkylmagnesium halide (RMgx)
- Haloalkane react with magnesium under presence of dry ether yielding Grignard reagent.

Grignard reagent.



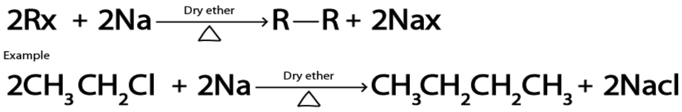
$$Rx + Mg \xrightarrow[\Delta]{\text{Dry ether}} \underset{\text{Griginard reagent}}{RMgX}$$

Example

$$CH_3CH_2Cl + Mg \xrightarrow[\Delta]{\text{Dry ether}} \underset{\text{ethyl magnesium chloride}}{CH_3CH_2MgCl}$$

D. WURTZ REACTION.

Generally



$$2Rx + 2Na \xrightarrow[\Delta]{\text{Dry ether}} R—R + 2Nax$$

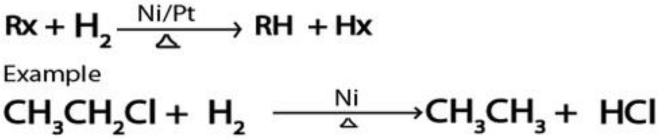
Example

$$2CH_3CH_2Cl + 2Na \xrightarrow[\Delta]{\text{Dry ether}} CH_3CH_2CH_2CH_3 + 2Nacl$$

E. REDUCTION.

· With hydrogen gas under presence of nickel or plantinum catalystal heat alkananes formed from haloalkanes.

Generally



$$Rx + H_2 \xrightarrow[\Delta]{Ni/Pt} RH + Hx$$

Example

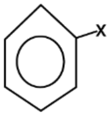
$$CH_3CH_2Cl + H_2 \xrightarrow[\Delta]{Ni} CH_3CH_3 + HCl$$

HALOARENE

This is the halohygrocarbon which is formed when atleast one hydrogenation of benzene is replaced by halogen.

- The simplest one is formed when only one hydrogen atom of benzene is replace by halogen.

i.e

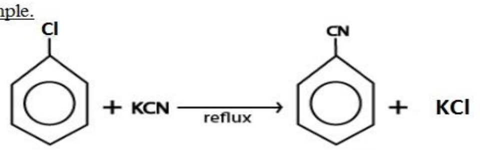


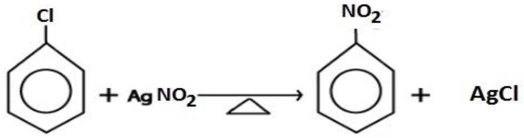
Chemical reactions of haloarenes include.

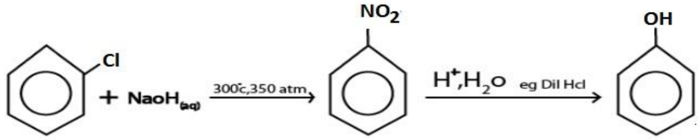
i. Nucleophilic substitution reaction
ii. Grignard reagent formation
iii. Wurtz/Fitting/coupling reaction.
iv. Reduction
v. Electrophilic substitution reaction

I. NUCLEOPHILIC SUBSTITUTION REACTION

Example.

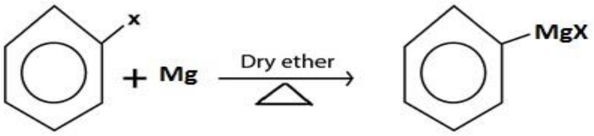
i/


ii/


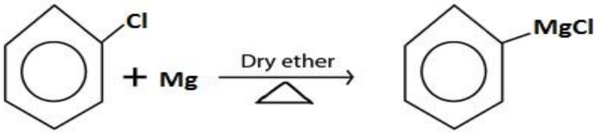
iii/


II. GRIGINARD REAGENT FORMATION

Generally

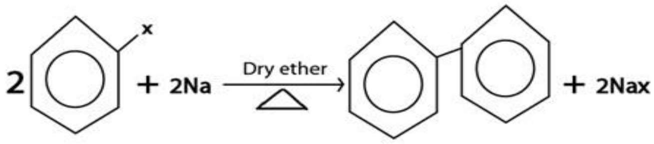


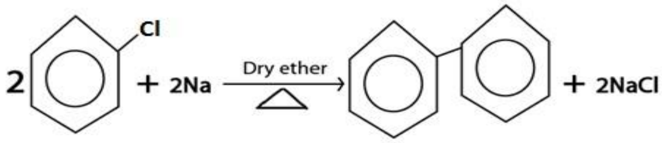
Example



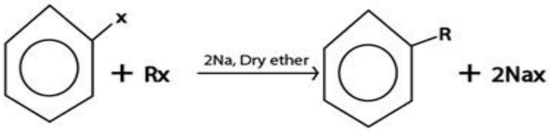
III. WURTZ REACTION

Generally



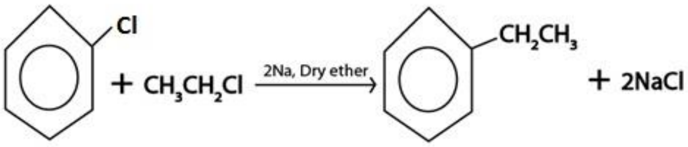


Similary

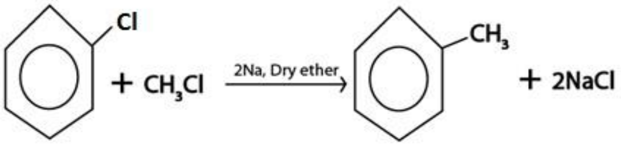


Example

i/

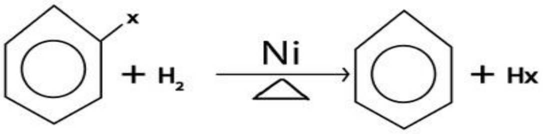


ii/

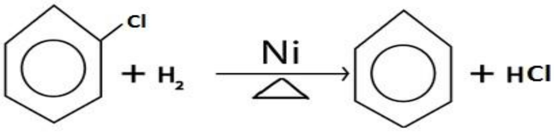


IV. REDUCTION

Generally



Example



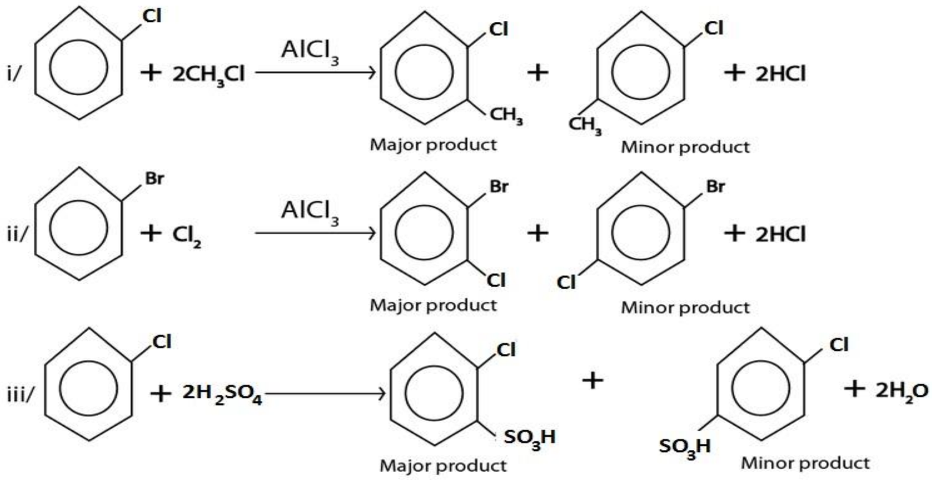
NOTE:

When hydrogen present in excess, cyclohexane if formed.

V. ELECTROPHILIC SUBSTITUTION REACTIONS

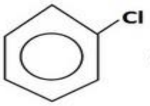
Under this heading haloarene undergo similar reactions as those of benzene, the only difference is that halogen present in haloarene directs incoming electrophile at ortho and para position forming ortho product as major product.

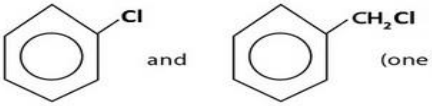
Example



Qn:

Give chemical tests to distinguish each of the following pairs of organic compounds.

i/ CH_3CH_2Cl and  (one test)

ii/  (one test)

iii/  (one test)

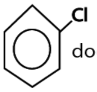
iv/ CH_3CH_2Br and CH_3CH_2Cl (one test)

v/  (one test)

vi/ Chloroform and carbon tetrachloride (one test)

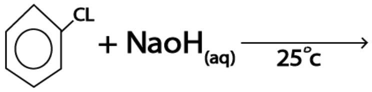
ANS.

i/ With **NaoH(aq)** at room temperature (laboratory condition) followed by

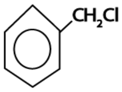
Ag No_3**(aq) .** CH_3CH_2Cl give white ppt of **Ag Cl .** while  does not

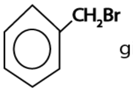
i.e $CH_3CH_2Cl + NaoH_{(aq)} \xrightarrow[25°c]{} CH_3CH_2oH + Nacl$

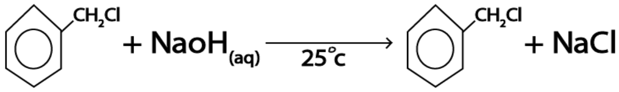
then $Nacl + AgNo_3 \xrightarrow[\circ]{} NaNo_3 + AgCl$

While  No reaction (No formation of white ppt of **AgCl**

ii/ With **NaoH(aq)** at room temperature followed by addition of

Ag No_3**(aq) .**  give white ppt of **AgCl** while

 give yellow ppt of **AgBr**

i.e 

then $Ag\ No_3 + NaCl \longrightarrow Na\ No_3 + AgCl$ White ppt

With NaOH$_{(aq)}$ at room temperature followed by addition of $AgNO_3\ CH_2Cl\,CH = \ CH_2$ give white ppt of $Agcl\ while\ CH_2CH = CH_2$ does not.

i.e

$CH_2Cl = CH_2 + NaOH \xrightarrow[25°C]{} OHCH_2CH = CH_2 + Na\,cl$

Then,

$Nacl + AgNO_2 \longrightarrow NaNO_3 + Agcl$

While

$CH_3CH{=}CH_2 + NaOH_{(aq)} \rightarrow$ No reaction

iv) With NaOH$_{(aq)}$ at room temperature and $AgNO_3,\ CH_3CH_2Br$ gives yellow ppt of $AgBr$ while CH_3CH_2cl gives white ppt of $Agcl$

i.e $CH_3CH_2Br + NaOH_{(aq)} \xrightarrow[25°C]{} CH_3CH_2OH + NaBr$

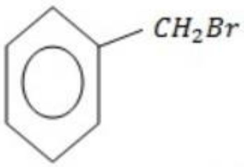
Then, $NaBr + AgNO_3 \longrightarrow AgBr + NaNO_3$

While, $CH_3CH_2cl + NaOH_{(aq)} \xrightarrow[25°C]{yellow\ PPt} CH_2CH_3OH + Nacl$

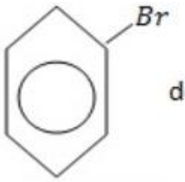
Then, $Nacl + AgNo_3 \longrightarrow Agcl + NaNo_3$

White ppt

v) With $NaOH_{(aq)}$ at room temperature followed by addition of $AgNO_{3(aq)}$

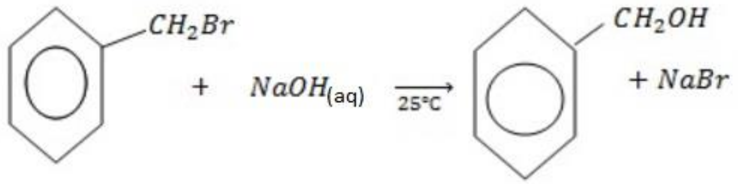


Give yellow ppt of $AgBr$ white



does not

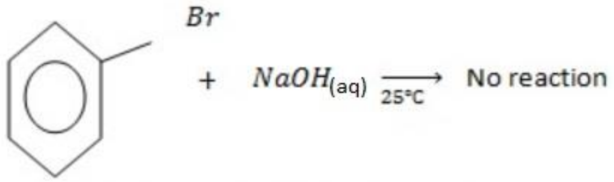
i.e.



Then $NaBr + AgNo_3 \longrightarrow NaNo_3 + AgBr$

Yellow

While



vii) Qn $CH_3CH = CH_2$ and $CH_2ClCH = CH_2$

Ans

With $NaOH_{(aq)}$ at room temperature followed by addition

$AgNo_3$ $CH_2\ cl\ CH = CH_2$ give white ppt of $Agcl$ while $CH_3\ CH = CH_2$ does not

i.e $CH_2C\ lCH = CH_2 + NaOH_{(aq)} \xrightarrow[25°C]{} OHCH_2CH = CH_2 + Nacl$

Then

$$Nacl + AgNo_3 \longrightarrow NaNo_3 + \underset{\text{White PPt}}{Agcl}$$

While

$CH_3CH{=}CH_2 + NaOH_{(aq)} \rightarrow$ No reaction

ALCOHOL AND PHENOL

- These are organic compounds with hydroxyl group (OH^-) as functional group.
- Alcohols and phenol are formed when at least one hydrogen atom of hydrocarbons is replaced by hydroxyl group.
- When the hydrogen atom is **replaced** from aliphatic hydrocarbon the resulting compound is known as **alcohol.**
- When the hydrogen atom is replaced from benzene then the resulting compound is known as **phenol**.
- Most of properties of alcohol resembles with those of phenol due to similarity in their functional group but some properties are different due to difference in their structure.

CLASSIFICATION OF ALCOHOLS

- Like in haloalkanes, according to number of alkyl groups which are directly bonded to a carbon OH^-, alcohols can be classified into three categories.

i. Primary (1^0) alcohols
ii. Secondary (2^0) alcohols
iii. Tertiary (3^0) alcohols

i. PRIMARY (1^0) ALCOHOLS

- These are alcohols where by a carbon with hydroxyl group is also directly bonded to one alkyl group only.
- Thus far alcohols with one hydroxyl group, the carbon with OH^- is also directly bonded to two hydrogen atoms.

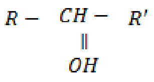
i.e. $RCH_2OH\ R$ where alkyl group only

ii. SECONDARY (2^0) ALCOHOLS

- These are alcohols where by a carbon with hydroxyl group is also directly bonded to two alkyl groups.

- Thus for alcohol with one hydroxyl group, the carbon with OH^- is also directly bonded to one hydrogen atom only.

i.e



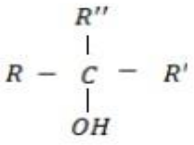
$$R - \underset{OH}{\underset{\|}{CH}} - R'$$

iii. TERTIARY (3^0) ALCOHOL

- These are alcohols where by a carbon with hydroxyl group is also directly bonded to three alkyl groups.

- Thus there is no hydrogen which is directly bonded to the carbon with (OH^-).

i.e



$$R - \overset{R''}{\overset{|}{\underset{OH}{\underset{|}{C}}}} - R'$$

NOMENCLATURE OF ALCOHOLS

• Rules of naming alcohols are the same as those alkanes with the following modifications

i. The parent chain must contain hydroxyl group (OH^-)

ii. In numbering carbons start at the end closer to hydroxyl group.

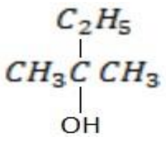
iii. Position of hydroxyl group should be indicated by using Arabic numerals.

iv. In giving a name of alcohol, the name must end with suffix ol (after removing e from corresponding name of hydrocarbon)

Example

Give systematic (IUPAC) name of the following organic compounds.

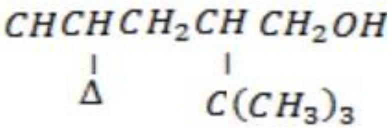
i.



$$CH_3\overset{C_2H_5}{\overset{|}{\underset{OH}{\underset{|}{C}}}}CH_3$$

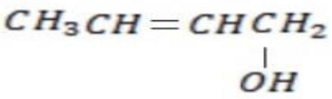
i. 2- Methylbutan -2- ol OR (2 methyl -2- butanol)

ii.



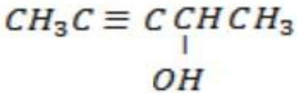
4 - Cyclopropyl- 2 tertbutylpentanol.

OR (4- Cyclopropyl - 2- terbuty-pentan-1-ol

iii. 

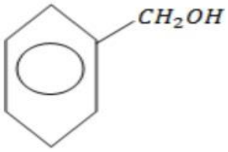
$CH_3CH=CH\underset{\substack{|\\OH}}{C}H_2$

Pent – 3 con 1- 01
OR (3 - pentanol).

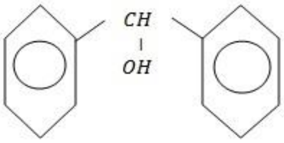
iv. 

$CH_3C\equiv C\underset{\substack{|\\OH}}{C}HCH_3$

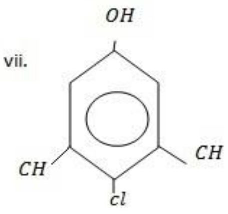
Pent – 3 – yn – 2- ol.

v. 

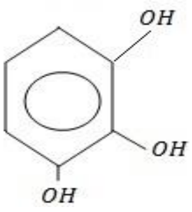
1 - Pheny methanol.

vi. 

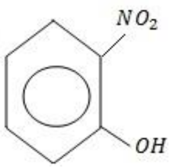
vi. 1, 1 - diphenylmethanol.

vii. 

vii. 4 - chloro - 3, 5 - dimethylphenol

viii. 

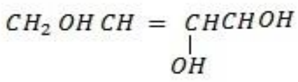
2,3 - dihydroxyl phenol OR (1,2,3,- trihydroxylbenzene) ix.



2 - nitrophenol.

x. $CH_2OHCH_2CH_2OH$ X. propane - 1, 3 - diol

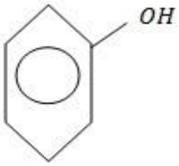
xi.



$CH_2\,OH\,CH = \underset{OH}{\underset{|}{C}}HCHOH$

xi. but -2- ene -1, 2, 4- triol

xii.



xii. Hydroxyl benzene

PREPARATION OF ALCOHOLS

a) REACTION BETWEEN MOIST SILVER OXIDE AN HALOALKANE.

Generally

$$R - X + Ag_2O \xrightarrow{H_2\,O} ROH + AgX$$

Example

$$CH_3CH_2cl + Ag_2O \xrightarrow{H_2\,O} CH_3CH_2OH + Ag\,cl$$

b) REACTION BETWEEN HALOALKANE AND ALKALINE SOLUTION.

- Haloalkane react with alkaline solution like NaOH and KOH yielding alcohol

E.g. In case of NaOH

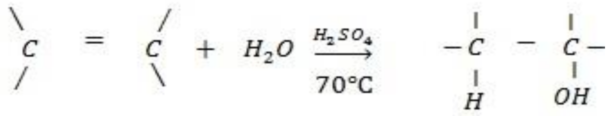
$$RX + NaOH \xrightarrow[25°C]{} HOH + NaX$$

Example

$$CH_3CH_2Cl + Ag_2O \xrightarrow{H_2\,O} CH_3CH_2OH + Ag\,Cl$$

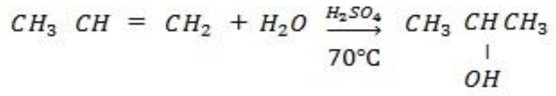
c) ACIDIC HYDROLYSIS OF ALKENE (REACTION BETWEEN ALKENE AND WATER UNDER PRESENCE OF SULPHURIC ACID).

Generally



$$\rangle C = C\langle + H_2O \xrightarrow[70°C]{H_2SO_4} -\underset{H}{\overset{|}{\underset{|}{C}}} - \underset{OH}{\overset{|}{\underset{|}{C}}}-$$

Example



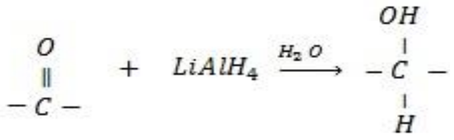
$$CH_3\ CH = CH_2 + H_2O \xrightarrow[70°C]{H_2SO_4} CH_3\ \underset{OH}{\underset{|}{CH}}CH_3$$

$$CH = CH_2 + H_2O \xrightarrow[70°C]{H_2SO_4} CH_3\ CH_2OH$$

d) REDUCTION OF CARBONYL COMPOUNDS

- Carbonyl compounds react with reducing agent like $LiAlH_4$ alcohols.

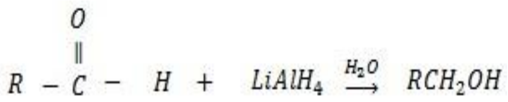
Generally



$$-\overset{O}{\overset{\|}{C}}- + LiAlH_4 \xrightarrow{H_2O} -\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-$$

- Aldehydes give primary alcohol.

i.e

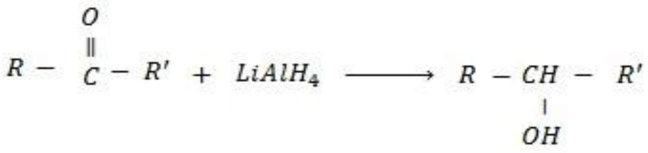


$$R - \overset{O}{\overset{\|}{C}} - H + LiAlH_4 \xrightarrow{H_2O} RCH_2OH$$

While

- Ketones give secondary alcohol.

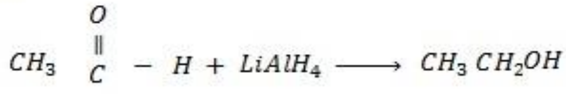
i.e



$$R - \overset{O}{\overset{\|}{C}} - R' + LiAlH_4 \longrightarrow R - \underset{OH}{\underset{|}{CH}} - R'$$

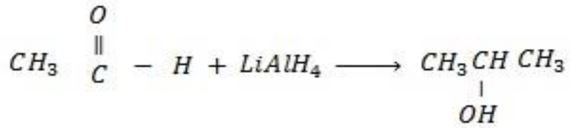
Example

i.



$$CH_3\ \overset{O}{\overset{\|}{C}} - H + LiAlH_4 \longrightarrow CH_3\ CH_2OH$$

ii.



$$CH_3\ \overset{O}{\overset{\|}{C}} - H + LiAlH_4 \longrightarrow CH_3\underset{OH}{\underset{|}{CH}}\ CH_3$$

e) REDUCTION OF CARBOXYLIC ACID

- Carboxylic acids react with strong reducing agent like $LiAlH_4$ forming primary alcohols.

$ROCCOH + LiAlH_4 \longrightarrow R\,CH_2OH$

Example

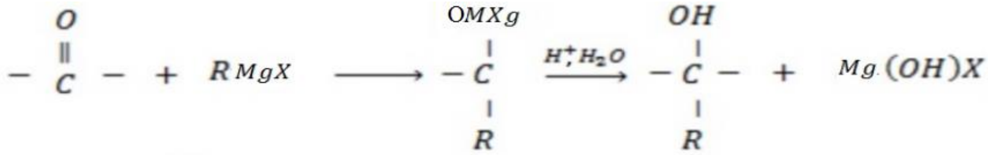
$CH_3COOH + LiAlH_4 \longrightarrow CH_3CH_2OH$

NOTE

In above reaction if $LiAlH_4$ is in limited amount (or weak reducing agent is used instead of $LiAlH_4$) aldehyde is formed instead of alcohol.

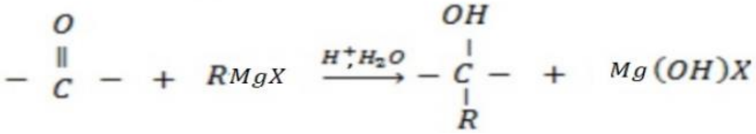
f) REACTION BETWEEN GRIGINARD REAGENT AND CARBOXYLIC COMPOUNDS ACID FOLLOWED BY ACIDIC HYDROLYSIS

Generally



$$-\overset{O}{\overset{\|}{C}}- + RMgX \longrightarrow -\underset{R}{\overset{OMXg}{C}} \xrightarrow{H^+, H_2O} -\underset{R}{\overset{OH}{C}}- + Mg(OH)X$$

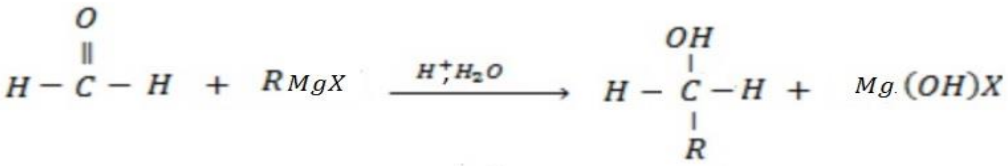
OR



$$-\overset{O}{\overset{\|}{C}}- + RMgX \xrightarrow{H^+, H_2O} -\underset{R}{\overset{OH}{C}}- + Mg(OH)X$$

- If the aldehyde used is methanol, primary alcohol is formed.

i.e

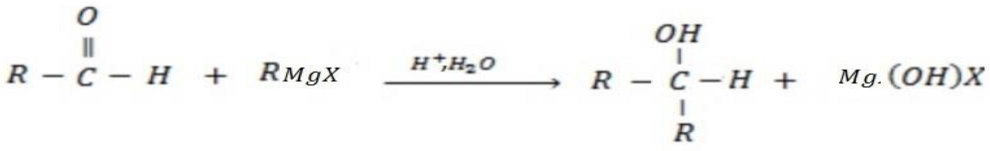


$$H-\overset{O}{\overset{\|}{C}}-H + RMgX \xrightarrow{H^+, H_2O} H-\underset{R}{\overset{OH}{C}}-H + Mg(OH)X$$

Eg. $HCHO + CH_3CH_2MgCl \xrightarrow{H^+, H_2O} CH_3CH_2OH + Mg(OH)Cl$

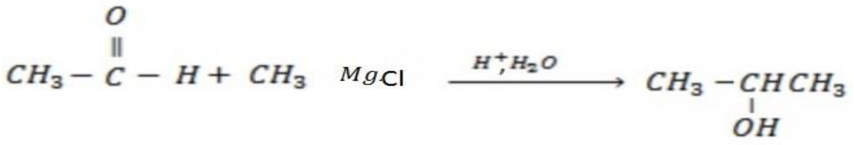
- If higher member of aldehyde is used, secondary alcohol is formed.

i.e



$$R-\overset{O}{\overset{\|}{C}}-H + RMgX \xrightarrow{H^+,H_2O} R-\underset{R}{\overset{OH}{C}}-H + Mg.(OH)X$$

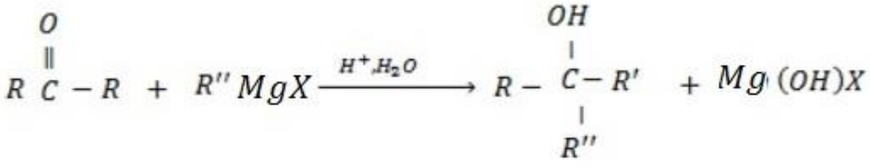
Example



$$CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3\ MgCl \xrightarrow{H^+,H_2O} CH_3-\underset{OH}{CH}CH_3$$

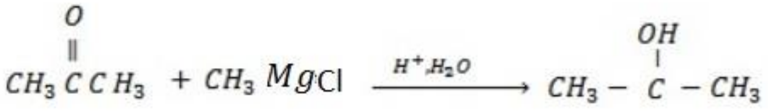
- If the carbonyl compound which is used is Ketone, tertiary alcohol is formed.

i.e



$$R\ \overset{O}{\overset{\|}{C}}-R + R''MgX \xrightarrow{H^+,H_2O} R-\underset{R''}{\overset{OH}{C}}-R' + Mg(OH)X$$

Example



$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + CH_3\ MgCl \xrightarrow{H^+,H_2O} CH_3-\overset{OH}{C}-CH_3$$

PHYSICAL PROPERTIES OF ALCOHOLS

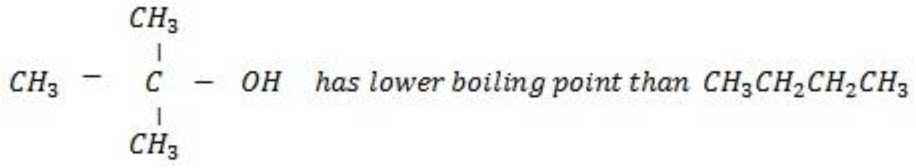
- Boiling point of alcohol increase with an increase of number of carbon (As number of carbon increase the molecular weight also increase)

E.g

Boiling point of $CH_3CH_2CH_2OH$ is large than the CH_3CH_2OH

- The less branched alcohol has higher boiling point than that alcohol which is more branched.

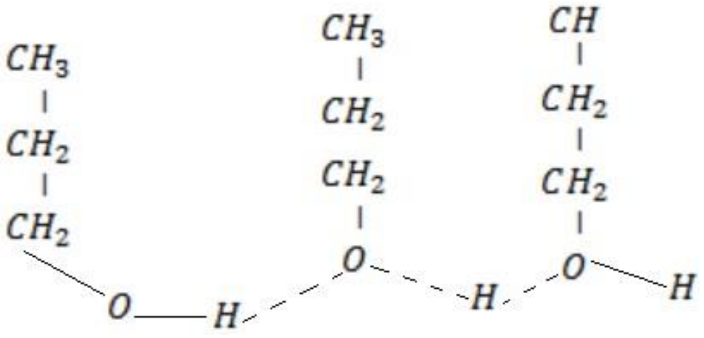
Example



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \text{ has lower boiling point than } CH_3CH_2CH_2CH_3$$

- The more branched has lower boiling point due to the following reason,
    i. Poor package of carbon atoms
    ii. Minimum surface area as it attain more spherical shape hence heating become easier

-In comparison to alcohol and corresponding carbon member of alkene (with approximately the same molecular weight) alcohol have higher boiling due to presence of hydrogen bond in alcohol.



- For polyhydric alcohols. Alcohol with more than one OH^- group has the boiling point increase, with number of hydroxyl groups due to increase in position of making hydrogen bond.

Example.

Explain the following the B.P (boiling point) of ethyl glycol is highest among the compound given below although is little in the molecular weight.

compound	**Formula**	**Molecular weight**	**Boiling point in °c**
Ethylene glycol	$OHCH_2CH_2OH$	62	197
Propanol	$CH_3CH_2CH_2OH$	60	97
Butane	$CH_3CH_2CH_2CH$	58	-0.5

ANS

Boiling point of alcohol increase with an increase in number of OH group.
(for polyhydric alcohol) due to increase in number of position of making hydrogen bonding, ethylene glycol has two OH groups so compare to 1- propanol which has only one OH group. Ethylene glycol, have many position of making hydrogen bonding and hence the boiling will be higher, in case of butane it has group, there is no hydrogen bonding at all that is why has lowest boiling point compound.

Solubility of alcohol in water decrease with an increase hydrophobic group (increase number of carbons due to an increase of non polar covalent character).

In increase of polyhydric alcohols solubility increase with an increase in number of OH group as a result of increasing number of position of making hydrogen bonding.

Example. NECTA 1993 PP1
Explain the solubility of alcohol increase with order

$$CH_3\ CH_2\ CH_2OH\ <\ CH_2OHCHOH\,CH_2\ OH < CH_2OH\ CH\ OH\ CH_2OH$$

For Polyhydric alcohol solubility increase with an increase in number of position of making hydrogen bonding that is why solubility of given compound increase in that order (i.e the longer the number of group the higher the solubility will be).Alcohol exist as coloured liquid compound because hence easily exposed

EXPLANATION ON COMPARISON OF ACIDIC STRENGTH IN ALCOHOLS AND PHENOLS

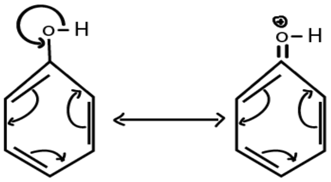
Phenol is stronger acid than alcohol due to following reason

1. Easier of releasing hydrogen proton
2. Stability of phenoxide ion formed after releasing hydrogen proton

1. EASIER OF RELEASING HYDROGEN ATOM

Lone pair electrons in oxygen of OH groups in phenol are localized they are involved in mesomerism (+M) i.e they are delocalized.

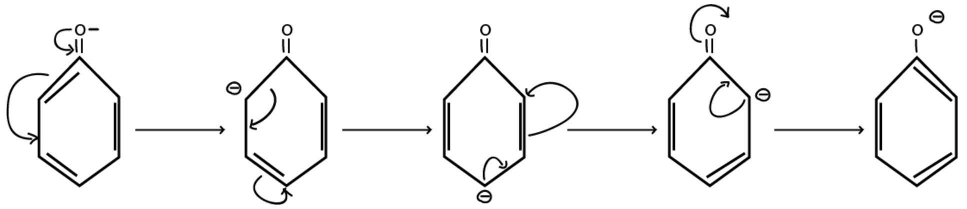
The delocalization of lone pair electron tends to form +ve charge in oxygen atom of OH group thus making easier to releasing oxygen proton.



There is no such occasion in alcohol

2. STABILITY OF PHENOXIDE ION FORMED AFTER RELEASING HYDROGEN PROTON

Consider



From above mechanism in phenoxide ion, it clearly understood negative charged electrons in oxygen atom of phenoxide is delocalized thus stabilizing the negative charge formed releasing hydrogen proton i.e (it can exist on its own with combining with hydrogen proton). There is no such occusion alcoxide ion RO^- formed in alcohol after releasing hydrogen proton.

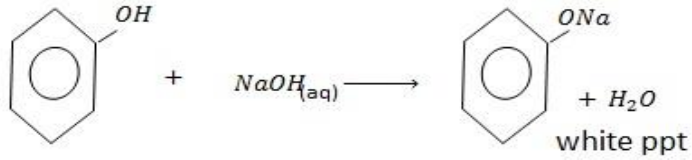
ACIDIC THAN ALCOHOL

A. a) REACTION WITH ALKALINE SOLUTION

With alkaline solution like NaOH phenol tend to react with them

Example with $NaOH$ phenol form sodium phenoxide.

i.e



But

There is no such reaction with alcohol indicating that alcohol has basic character and hence phenol is more acidic than alcohol

Alcohol+ alkaline solution $\longrightarrow$ No reaction

Note

The reaction is very important in separating phenol from other class of alcohol.

Qn. Without using the distillation explain how would you separate the following pair of organic compounds

i. Phenol and 1- hexanol

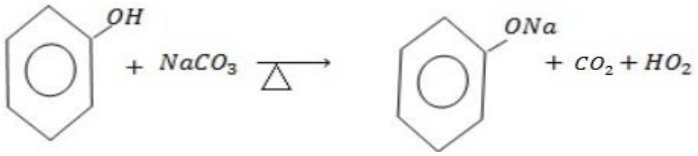
ii. Phenol and benzene

B.

b) REACTION WITH SODIUM CARBONATE

Acids react with carbonate to form carbon dioxide gas phenol like other acids react with sodium carbonate to evolve a gas.

Phenol like other acid react with sodium carbonate evolve a gas which turns lime water milky.



But

$$Alcohol + Na_2Co_3 \xrightarrow[\Delta]{} \text{No reaction}$$

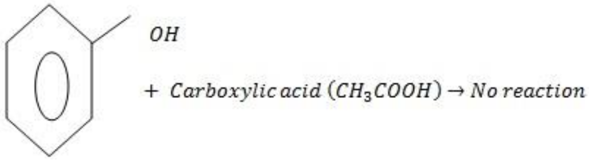
c) REACTION WITH CARBOXYLIC ACID

Alcohol react with carboxylic acid in presence of sulphuric to form ester and water.
i.e.

$$ROH + RCOOH \xrightarrow{H_2SO_4} \underset{\text{ester}}{RCOOR} + H_2O$$

This verify that alcohol has basic character in this case phenol it does not react with carboxylic acid either in presence or in absence of suplhuric acid. This verify that phenol some alcohol character and hence phenol has higher strength than alcohol.

i.e



CHEMICAL REACTION OF ALCOHOL

Ø Chemical reaction of alcohol can be classified into the following

a. Reaction which involve replacement of whole OH^- group

b. Reactions which involve replacement of H from OH^- group

c. Reactions which involve OH^- group and β- hydrogen

d. Oxidation

A. REACTION WHICH INVOLVE REPLACEMENT OF HYDROGEN ATOM

- Under this heading alcohol react with strong alkaline metals like Li, Na, K to form alkoxide and hydrogen gas is
- Generally

$$2ROH + 2M \longrightarrow 2ROM + H_2$$

$$M = Alkaline, Metal\ like\ Li, Na, K$$

Example

$$2CH_3CH_2OH + 2Li \longrightarrow 2\,CH_3CH_2OLi + H_2$$

- The main reaction under this heading is halogenations of alcohol.

Examples

$$\text{i. } ROH + PCl_5 \xrightarrow[\text{reflux}]{} Rx + POX_3 + Hx$$

$$\text{Eg : } CH_3CH_2OH + PCl_5 \xrightarrow[\text{reflux}]{} CH_3CH_2Cl + POCl_5 + HCl$$

Hcl involved in the above reaction produce denser white fumes with ammonia so that reaction is used as test of presence of OH^- group in the compound.

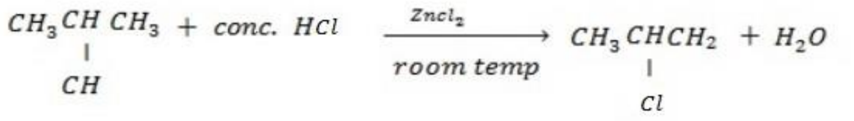
ii/ $ROH + SO\ X_2 \longrightarrow RX + SO_2 + HX$

Example

$$CH_3CH_2OH + SO\ Cl_2 \longrightarrow CH_3CH_2Cl + SO_2 + HCl$$

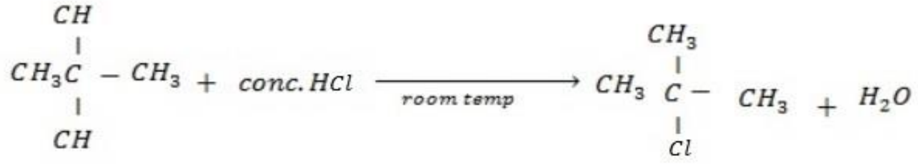
iii/ $CH_3CH_2CH_2OH + conc.HCl \xrightarrow[25°C,300atm]{Zncl_2} CH_3CH_2CH_2Cl + H_2O$

iv/



$$CH_3\underset{\substack{|\\CH}}{CH}CH_3 + conc.\ HCl \xrightarrow[room\ temp]{Zncl_2} CH_3\underset{\substack{|\\Cl}}{CH}CH_2 + H_2O$$

v/

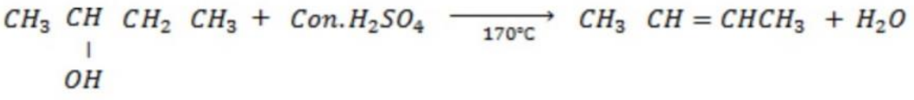


$$CH_3\underset{\substack{|\\CH}}{\overset{\substack{CH\\|}}{C}} - CH_3 + conc.HCl \xrightarrow[room\ temp]{} CH_3\ \underset{\substack{|\\Cl}}{\overset{\substack{CH_3\\|}}{C}} - CH_3 + H_2O$$

B. REACTION WHICH INVOLVE OH$^-$ GROUP AND B- HYDROGEN.

Under this heading alcohol undergo elimination reaction to from alkene.

Example



$$CH_3\ \underset{\substack{|\\OH}}{CH}\ CH_2\ CH_3 + Con.H_2SO_4 \xrightarrow[170°C]{} CH_3\ CH = CHCH_3 + H_2O$$

$$CH_3CH_2OH + Con.H_2SO_4 \xrightarrow[170°C]{} CH_2 = CH_2 + H_2O$$

But

$$CH_3CH_2OH + Con.H_2SO_4 \xrightarrow[140°C]{} CH_3CH_2OCH_2CH_3 + H_2O$$

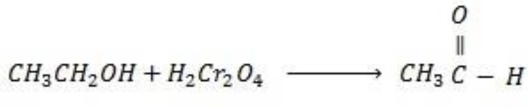
$$CH_3\ CH_2\ OH + OH\ CH_2\ CH_3 \xrightarrow[140°C]{Con.H_2O} CH_3CH_2OCH_2CH_3 + H_2O$$

The production of either in above reaction is more favoured when H_2SO_4 is dilute and cold.

C. OXIDATION

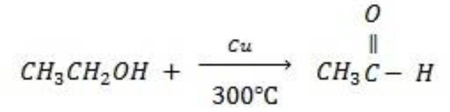
- Ø With weak oxidation agent like $H_2\ Cr_2\ O_4$ primary alcohol tend to form aldehyde.

Example



$$CH_3CH_2OH + H_2Cr_2O_4 \longrightarrow CH_3\,\overset{\overset{O}{\|}}{C}-H$$

Also



$$CH_3CH_2OH + \xrightarrow[300^\circ C]{Cu} CH_3\overset{\overset{O}{\|}}{C}-H$$

With strong oxidizing agent like $K_2Cr_2O_7$ $KMnO_4$ carboxylic acid is formed.

Example

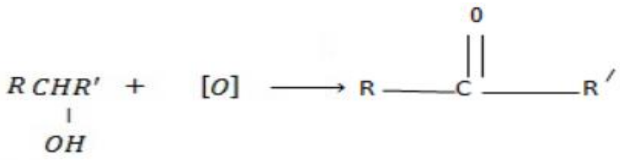
$$CH_3CH_2OH + K_2Cr_2O_7 \longrightarrow CH_3COOH + Cr^{3+}$$

Orange Green

$$CH_3CH_2OH + KMnO_4 \longrightarrow CH_3COOH + MnO_2$$

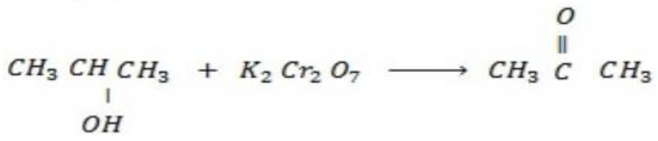
-With either weak oxidizing or strong oxiding agent secondary (2°)alcohol from Ketone.

Generally



$$R\,\underset{\underset{OH}{|}}{C}HR' + [O] \longrightarrow R-\overset{\overset{0}{\|}}{C}-R'$$

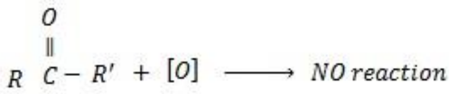
Example



$$CH_3\,\underset{\underset{OH}{|}}{CH}\,CH_3 + K_2Cr_2O_7 \longrightarrow CH_3\,\overset{\overset{O}{\|}}{C}\,CH_3$$

NOTE

Tertiary alcohol remit oxidation since there is no hydrogen to be removed.



$$R\overset{\overset{O}{\|}}{C}-R' + [O] \longrightarrow NO\ reaction$$

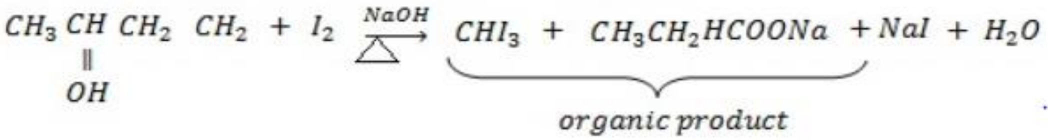
IODOFORM TEST

- This is the chemical test for presence of terminal methyl group which is directly bonded to carbon with OH^- group or (to carbonyl group in the case of carbonyl compounds) by giving yellow ppt of trichloromethane (Iodoform) CHI_3.

- When compounds with terminal methyl group bonded to carbon with OH group is heated with 1_2 in presence of NaOH they give yellow ppt of Iodoform.

Example

$$i.\ CH_3CH_2OH + 2I_2 \xrightarrow[\triangle]{NaOH} \underbrace{CHI_3}_{\text{Yellow PPt}} + HCOONa + NaI + H_2O$$



$$\underset{\underset{OH}{\|}}{CH_3\,CH}\,CH_2\ \ CH_2 + I_2 \xrightarrow[\triangle]{NaOH} \underbrace{CHI_3 + CH_3CH_2HCOONa}_{organic\ product} + NaI + H_2O$$

CHEMICAL TEST TO DISTINGUISH BETWEEN PRIMARY, SECONDARY AND TERTIARY ALCOHOLS.

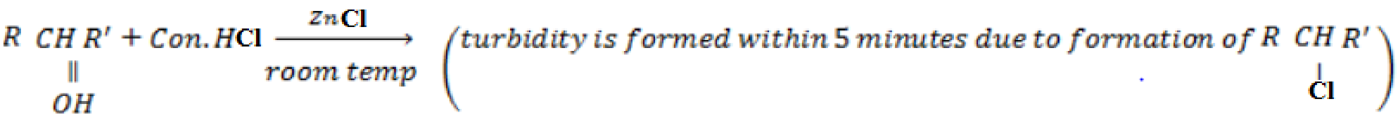
- Three classes of alcohol can be distinguished by using Lucas reagent.

- Lucas reagent is the mixture of concentrated HCl and ZnCl mixed at equal proportion.

- With Lucas reagent at room temperature, primary alcohol do not form cloudness or turbidity (insoluble substance) at all.

i.e $2CH_3OH + Con.\mathrm{HCl} \xrightarrow[Room\ temp]{Zn\mathrm{Cl}} No\ reaction\ (No\ formation\ of\ turbidity\ ie\ insoluble\ substance)$

- Secondary alcohol tends to form turbidity (insoluble substance which is chloroalkane within 5 minutes).



$$R\ \underset{\underset{OH}{\|}}{CH}\ R' + Con.HCl \xrightarrow[room\ temp]{ZnCl} \left(turbidity\ is\ formed\ within\ 5\ minutes\ due\ to\ formation\ of\ R\ \underset{\underset{Cl}{|}}{CH}\ R'\right)$$

- Tertiary alcohol, tend to form turbidity immediately.

$$R\ \overset{\overset{R'}{|}}{\underset{\underset{OH}{|}}{C}} - R + Conc.HCl \xrightarrow[Room\ temp]{ZnCl_2} \left[Turbidity\ is\ formed\ immediately\ due\ to\ formation\ of\ R - \overset{\overset{R''}{|}}{\underset{\underset{Cl}{|}}{C}} - R'\ which\ is\ insolbuble\right]$$

Example

Qn. Gave chemical test to distinguish between

i. Ethanol and propanol (I test)

ii. Butan – 1-ol and butan – 2- ol (2 test)

iii. Butan -2- ol and 2- methyl propan - 2-ol (2 test apart from using Lucas reagent)

ANS

i. Ethanol gives positive Iodoform test while propanol give negative Iodoform test.

i.e

$$CH_3CH_2OH + I_2 \xrightarrow[\triangle]{NaOH} yellow\ PPt\ of\ CHI_3\ (Iodoform)$$

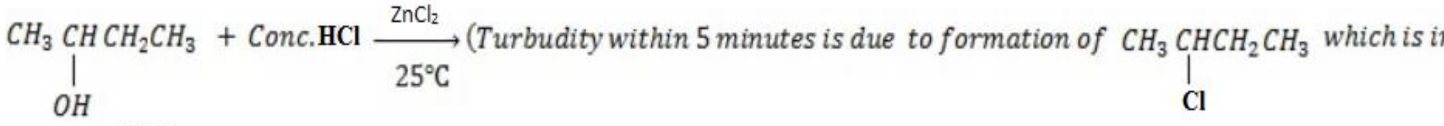
$(Ethanol)$

While

$$CH_3CH_2CH_2OH + I_2 \xrightarrow[\triangle]{NaOH} No\ reaction\ ie\ No\ formation\ of\ yellow\ PPt$$

ii. 1st TEST

With Lucas reagent at room temperature butan -2-ol give turbidity (cloudness) within 5 minutes while butan -1-ol do not give turbidity at all.



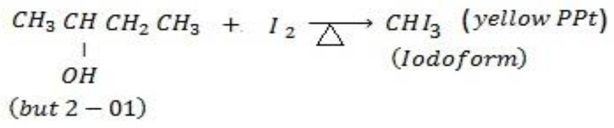
$CH_3CH(OH)CH_2CH_3 + Conc.HCl \xrightarrow[25°C]{ZnCl_2}$ (Turbudity within 5 minutes is due to formation of $CH_3CH(Cl)CH_2CH_3$ which is i

While

$CH_3\ CH_2\ CH_2\ CH_3\ OH + Conc.HCl \xrightarrow{ZnCl_2}$ No reaction (No formation of turbidity)

2nd TEST (Iodoform Test)

Butan -2- ol give positive iodoform test while but-1-ol give negative iodoform test.



$CH_3CH(OH)CH_2CH_3 + I_2 \xrightarrow{\triangle} CHI_3$ (yellow PPt) (Iodoform)

(but 2 − 01)

While

$CH_3\ CH_2\ CH_2\ CH_2\ OHl_2 + I_2 \xrightarrow[\triangle]{NaOH_{(aq)}}$ No formation of yellow PPt

iii.1st TEST

When butan -2- ol is mixed with $K_2\,Cr_2\,O_7$ solution the orange colour of $K_2Cr_2O_7(Cr_2O_7^{2-})$ is changed to green while 2- methylpropan- 2 - ol do not show any change.

i.e

Butan $-2-nol + Cr_2O_7{}^{2-} \longrightarrow$ butan one Cr^{3+}

(orange) (Green)

While

2- Methylpropan $-2-ol+\ Cr_2O_7{}^{2-} \longrightarrow$ No reacton

2nd TEST

Butan $-2-ol$ decolourise $KMnO_4$ with black ppt appearing at the bottom of the beaker which is deep purple while 2-methylpropan $-2-ol$ do not.

i.e.

Butan $-2-ol + MnO_4 \longrightarrow$ Butanone $+ Mn^{2+}$

(Deep purple) (Colorless) (Black ppt)

While

2 - Methylpropan $-2-ol \longrightarrow$ NO reaction

NECTA 2006 PP₂ QN. 8(a)

Organic compound $C_4H_{10}O$ reacts with PCl_5 to form an organic compound "Q" In organic compound "N" and gas 'R' which produce denser white fumes with a aqueous ammonia "P" also react with a mixture of Iodine and NaOH forming a sodium salt "W" and triodomethane.

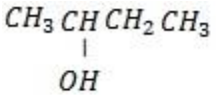
i. Identify and write the structural formula Q, R and W.
ii. Write an equation of each of the above reaction.

ANS:

The molecular formula $C_4H_{10}O$ confirm general molecular formula of $C_nH_{2n+2}O$

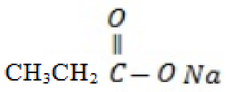
- Thus P is either alcohol or ether.
- A gas which produce dense white fumes with aquous ammonia is HCl
- So since the reaction "P" and PCl_5 produce HCl then there is OH group in P.
- Hence compound "P" reacts with mixture of iodine and NaOH to give triodemethane then compound "P" give positive Iodoform.
- Hence in "P" there is terminal methyl groups bonded to carbon with OH^- group. This "P" is butan -2-ol.

Its structure is



$$CH_3\underset{\displaystyle OH}{\underset{|}{CH}}CH_2CH_3$$

- Q is 2 - chlorobutane
- Its structure is
- N is $PoCl_3$
- R is HCl
- W - is sodium propanoate
- Its structure is



$$CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}-ONa$$

CHEMICAL REACTIONS OF PHENOL

Generally chemical reactions of phenol can be divided into two types;

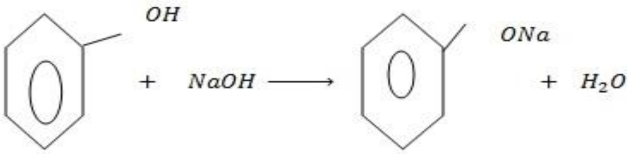
i. Electrophilic substitution reactions inside OH^- group.
ii. Electrophilic substitution reactions in benzene ring.

1. ELECTROPHILIC SUBSTITUTION REACTION INSIDE OH^- GROUP

a) REACTION WITH ALKALINE SOLUTION

Unlike Alcohol, phenol react with alkaline soluble NaOH

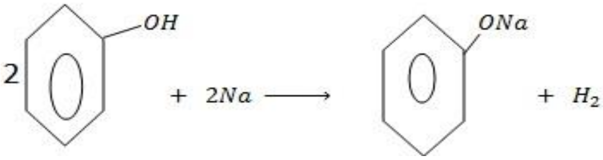
i.e. Alcohol + Alkaline solution. e.g, $\xrightarrow{NaOH}$ No reaction



The reactions give one of the differences between alcohol and phenol

b) REACTION WITH ALKALING METALS

Phenol reacts, with alkaline metals like Na, K, Li etc to form phenoxide and hydrogen gas is involved.



The reaction show one of the similarities between alcohol and phenol.

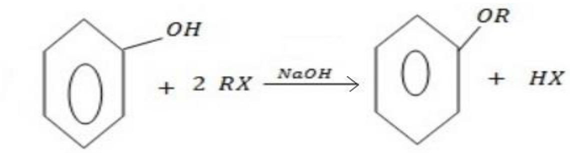
i.e

Alcohol + alkaline metal $\longrightarrow$ Allcoxide + Hydrogen gas.

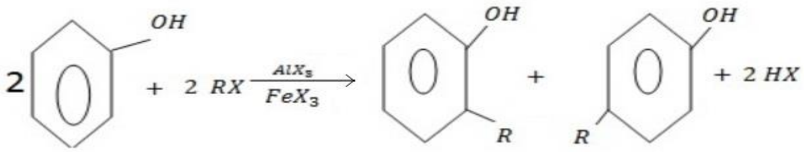
c) FORMATION OF ETHER

Phenol react with haloalkane in presence of acqueous sodium hydroxide to form ether.

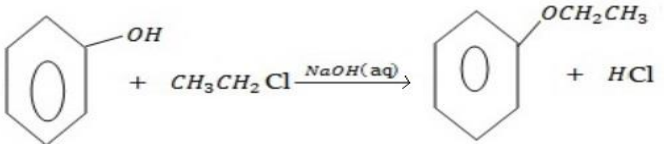
Generally



But



Example



The reaction show another similarity between alcohol and phenol although in alcohol there is no need of $NaOH$.

i.e

$$ROH + R'X \longrightarrow ROR' + HX$$

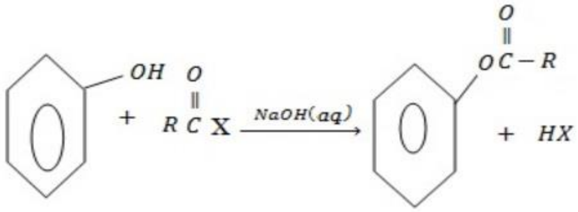
Example

$$CH_3CH_2OH + CH_3\,Cl \longrightarrow CH_3CH_2OH_3 + H\,Cl$$

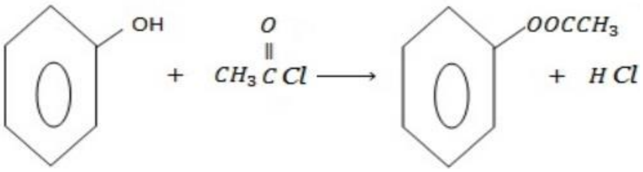
d) FORMATION OF ESTER

Phenol reacts with acyl compounds in presence of NaO to form ester.

i.e



Example



and phenol i.e alcohol also reacts with acyl compounds to form ester although in alcohol there is no need of $NaOH_{(aq)}$.

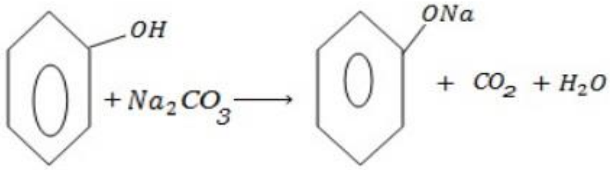
i.e.

$$ROH + R'\overset{\overset{O}{\parallel}}{C}-X \longrightarrow R'\overset{\overset{O}{\parallel}}{C}-OR + HX$$

e) REACTION WITH SODIUM CARBONATE.

Phenol reacts with sodium carbonate to form phenoxide and the gas which turn lime water milky i.e. CO_2 gas is evolved.

i.e.



- The reaction show another difference between alcohol and phenol i.e. Alcohol reacts with Na_2Co_3.

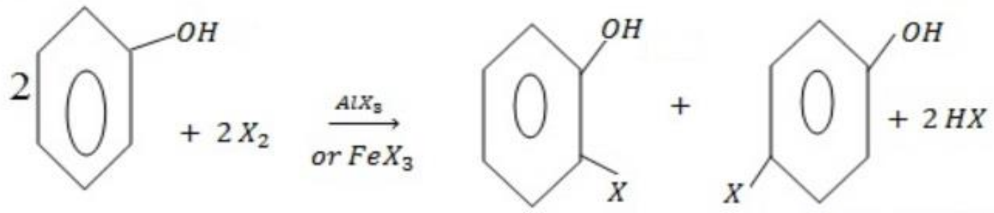
i.e. Alcohol + $Na_2\,CO_3 \longrightarrow$ No reaction

II. ELECTROPHILIC SUBSTITUTION REACTION IN BENZENE RING

- Under this heading phenol reacts like benzene the only difference is that OH^- group in phenol directs incoming electrophile at ortho and Para position.

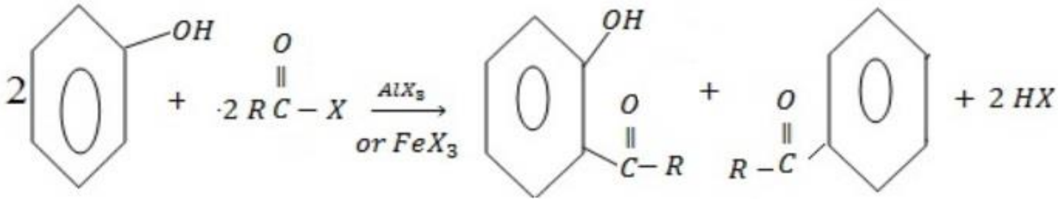
Example

i.



Major product

ii.

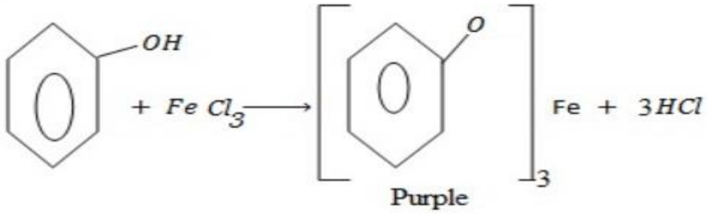


TESTS OF PHENOL

Phenol turns blue litmus paper into red

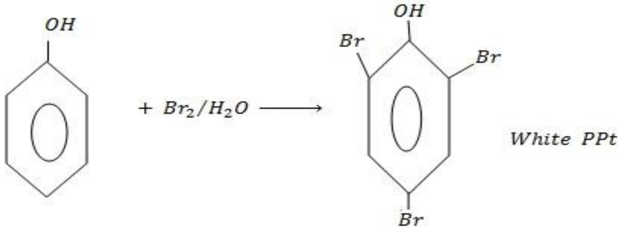
- With ion (III) Chloride phenol tends to form purple violet color of ion(III) phenoxide.

i.e.



- With bromine water phenols tend to form white ppt of 2-tribomophenol.

i.e.



SOME DIFFERENCES BETWEEN ALCOHOL AND PHENOL

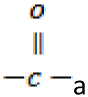
	ALCOHOL	PHENOL
1.	Undergo oxidation easily (for primary and secondary alcohol)	Do not undergo oxidation easily
2	Do not react with bromine water	Form white ppt of 2, 4, 6 – tribomophenol with bromine water.
3	Do not react with $FeCl_3$	Form purple colouration with ion(III) chloride.

4	Form ester (has fruity smell)	Do not react with carboxylic acid
5	Do not react with sodium hydroxide solution	Form white ppt of sodium phenoxide with $NaOH_{(aq)}$.
6	Do not react with sodium carbonate	Form white ppt of sodium phenoxide and gas which turns lime water milky (i.e CO_2 is evolved).

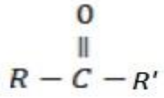
SIMILARITIES BETWEEN ALCOHOL AND PHENOL

- Evolve hydrogen gas with alkaline metals.
- They form ether with haloalkane.
- They form ester with acyl compound.
- They reacts with hydrogen halide.

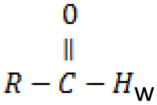
CARBONYL COMPOUND

These are organ compounds with Carbonyl group  $-\overset{O}{\overset{\parallel}{C}}-$ as functional group

If the carbonyl compound is directly bonded to two alkyl groups two aryl groups or one group and one aryl group, the resulting carbonyl compound known as KETONE.

I.e. General structure of kenton can be represented as ( $R-\overset{O}{\overset{\parallel}{C}}-R'$)where R and R' can be alkyl or aryl group

If the carbonyl compound is directly bonded to at least one hydrogen atom, the resulting carbonyl compound is known as ALDEHYDE

I.e. General structure of aldehyde is  $R-\overset{O}{\overset{\parallel}{C}}-H$ where R is alky group, aryl group or hydrogen atom

Both aldehyde and Ketone (carbonyl compound) have general molecular formula 0f C_n,H_{2n} 0, thus aldehyde and Ketone are isomeric (exhibit position isomerism)
Most of properties of aldehyde are the same as those of ketone. But there is some differences in their properties due to differences in their structures.

NOMENCLATURE OF CARBONYL COMPOUNDS

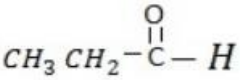
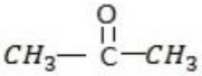
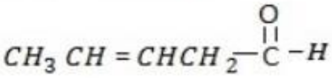
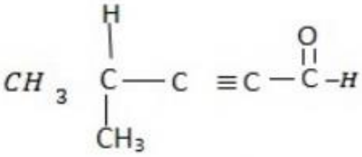
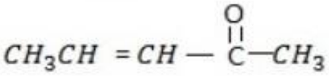
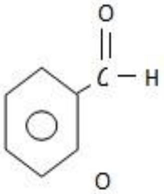
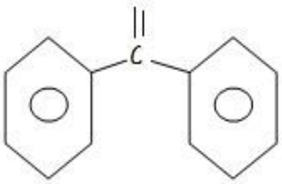
The parent chain in must contain carbonyl group  $\left(-\overset{O}{\overset{\parallel}{C}}-\right)$

i.e.The parent chain is the longest continuous carbon chain with carbonyl group Numbering of carbons is done as follows

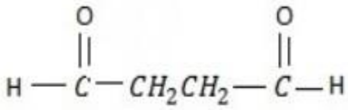
For aldelhyde the carbon in carbonyl group must be kept first position
For ketone numbering must state at the end closer in carbonyl
For ketone with more than four carbons, position of carbonyl must be indicated by using Arabic numerals

In naming aldehyde leave the suffix -e from the corresponding hydrocarbon and the end with suffix- al and naming ketone leave the suffix e from name of corresponding hydrocarbon and then end with suffix one
Other rules are the same as those of alkanes rule
Example.

Qn.Name the following organic compounds.

(i)	 $CH_3CH_2-\overset{\overset{O}{\|}}{C}-H$	i) Propanal
(ii)	 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$	ii) Propanone
(iii)	 $CH_3CH=CHCH_2-\overset{\overset{O}{\|}}{C}-H$	iii) Pent -3- enal
(iv)	 $CH_3-\underset{CH_3}{\overset{H}{C}}-C\equiv C-\overset{\overset{O}{\|}}{C}-H$	iV) 4 – methypent-2-ynal
(v)	 $CH_3CH=CH-\overset{\overset{O}{\|}}{C}-CH_3$	v) pent -3 en-2- one
(vi)		vi) Cyclopropanone
(vii)		vii) 2- vinylcyclobutanone
(viii)		viii) Phenulmethanal
ix)		Ix) Diphenylmethanone

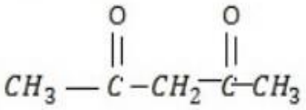
x)



$H-\overset{\overset{O}{\|}}{C}-CH_2CH_2-\overset{\overset{O}{\|}}{C}-H$

x) butane -1, 4- dial

xi)

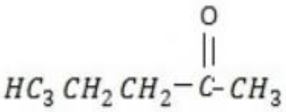


$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

xi) Hexane -2, 4- dione OR

(2,4- hexanedione)

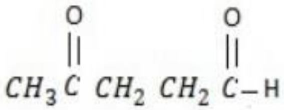
xii)



$HC_3\,CH_2\,CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

xii) Pentane- 2- one OR (2- oxopentanone)

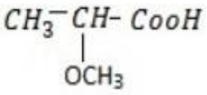
xiii)



$CH_3\overset{\overset{O}{\|}}{C}\ CH_2\ CH_2\ \overset{\overset{O}{\|}}{C}-H$

Xiii) 4- oxopentanal

xiv)



$CH_3-\underset{\underset{OCH_3}{|}}{CH}-CooH$

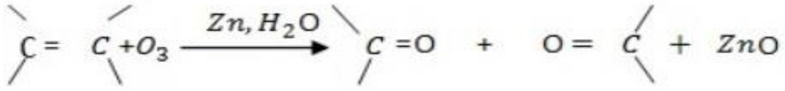
xiv) Methoxypropanoic

PREPARATION OF CARBONYL COMPOUNDS

a) a) REDUCTIVE OZONOLYSIS OF ALKENES

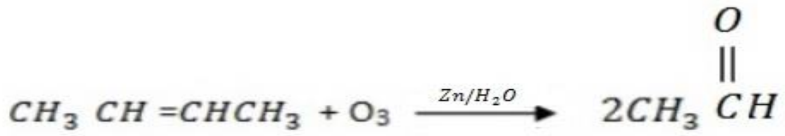
Alkene reacts with ozone followed by reductive hydrolysis done by Zn under presence of H_2O yielding carbonyl compound.

Generally:



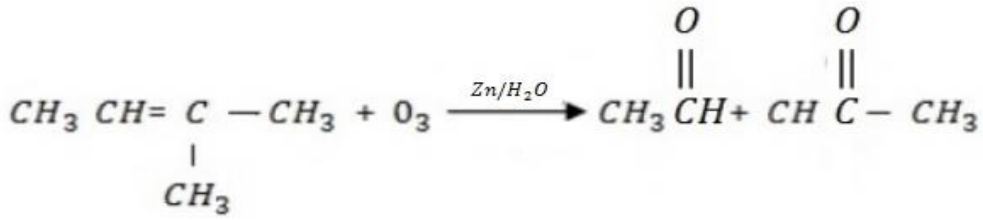
If there is at least one hydrogen atom at each carbon with double, bond aldehyde is formed

Example:



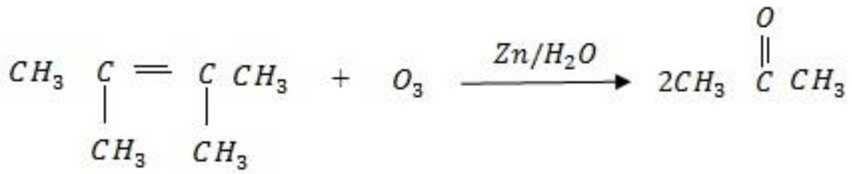
$$CH_3CH{=}CHCH_3 + O_3 \xrightarrow{Zn/H_2O} 2CH_3\overset{\overset{O}{\|}}{C}H$$

If one carbon with double bond has at least one hydrogen atom and another carbon has no hydrogen atom , aldehyde and ketone are formed



$$CH_3CH{=}\underset{\underset{CH_3}{|}}{C}-CH_3 + O_3 \xrightarrow{Zn/H_2O} CH_3\overset{\overset{O}{\|}}{C}H + CH\overset{\overset{O}{\|}}{C}-CH_3$$

If there is no hydrogen atom which is directly bonded to carbon with double bond, ketone is formed



$$CH_3\underset{\underset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}CH_3 + O_3 \xrightarrow{Zn/H_2O} 2CH_3\overset{\overset{O}{\|}}{C}CH_3$$

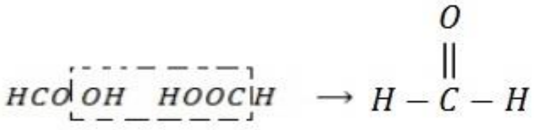
b) HEATING OF CARBOXYLIC ACIDS

When carboxylic acid is heated to temperature about 300^0 C under presence of manganese (iv) Or (MnO_2) carbonyl compound is formed heating of methanoic acid produce methanal (aldehyde)

I.e.

$$2HCooH \xrightarrow[300^0c]{mno_2} HCOH + CO_2 + H_2O$$

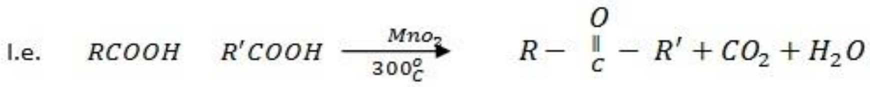
Memorizing



$$HCO\boxed{OH \quad HOOC}H \rightarrow H-\overset{\overset{O}{\|}}{C}-H$$

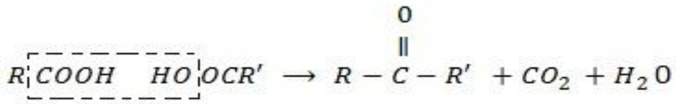
.

Heating higher members of carboxylic acids produces



I.e. $$RCOOH \quad R'COOH \xrightarrow[300^0_C]{Mno_2} R-\overset{\overset{O}{\|}}{C}-R' + CO_2 + H_2O$$

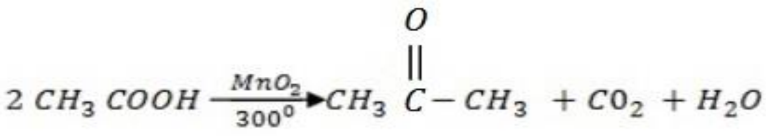
Memorizing



$$R\boxed{COOH\quad HO}OCR' \longrightarrow R-\overset{\overset{O}{\parallel}}{C}-R' + CO_2 + H_2O$$

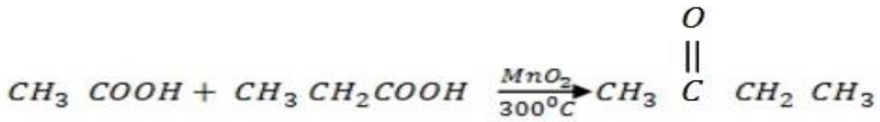
Example

(i)



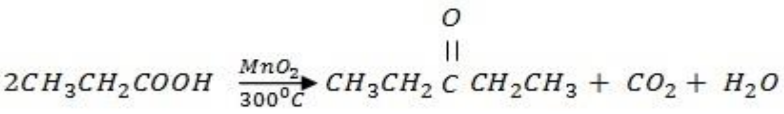
$$2\,CH_3\,COOH \xrightarrow[300^0]{MnO_2} CH_3\,\overset{\overset{O}{\parallel}}{C}-CH_3 + CO_2 + H_2O$$

(ii)



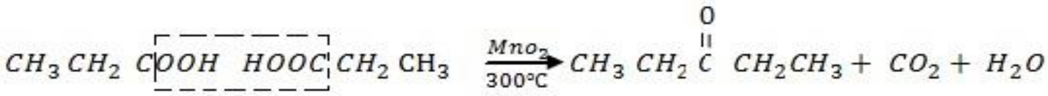
$$CH_3\ COOH + CH_3\,CH_2COOH \xrightarrow[300^0C]{MnO_2} CH_3\ \overset{\overset{O}{\parallel}}{C}\ CH_2\ CH_3$$

iii)



$$2CH_3CH_2COOH \xrightarrow[300^0C]{MnO_2} CH_3CH_2\,\overset{\overset{O}{\parallel}}{C}\,CH_2CH_3 + CO_2 + H_2O$$

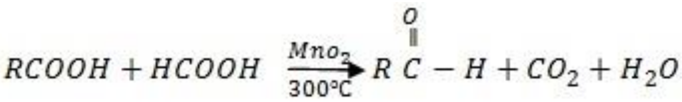
Memorizing



$$CH_3\,CH_2\,C\boxed{OOH\quad HOOC}CH_2\,CH_3 \xrightarrow[300°C]{Mno_2} CH_3\,CH_2\,\overset{\overset{O}{\parallel}}{C}\,CH_2CH_3 + CO_2 + H_2O$$

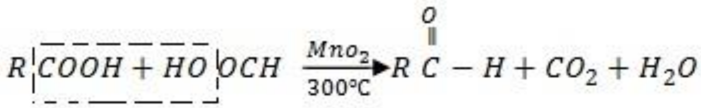
- Heating methanoic acid and higher member of carboxylic acids produce aldehyde

I.e.



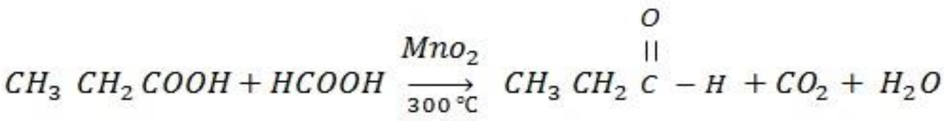
$$RCOOH + HCOOH \xrightarrow[300°C]{Mno_2} R\,\overset{\overset{O}{\parallel}}{C}-H + CO_2 + H_2O$$

Memorizing



$$R\boxed{COOH + HO}OCH \xrightarrow[300°C]{Mno_2} R\,\overset{\overset{O}{\parallel}}{C}-H + CO_2 + H_2O$$

<u>Example</u>



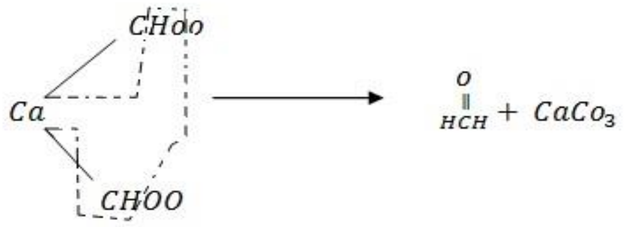
$$CH_3\ CH_2\,COOH + HCOOH \xrightarrow[300\,°C]{Mno_2} CH_3\ CH_2\ \overset{\overset{O}{\parallel}}{C}-H + CO_2 + H_2O$$

c) HEATING OF CALCIUM CARBOXYLATES

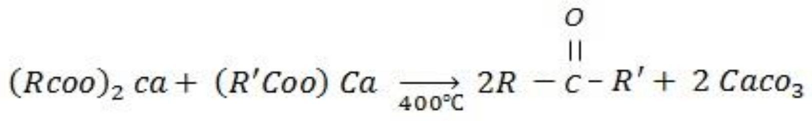
When calcium carboxylates are heated to temperature of about 400 °C ,carbonyl compounds are formed. Heating calcium methanoate produce methanal

$$(Hcoo)_2Ca \xrightarrow[400^\circ C]{} HCHO + CaCo_3$$

Memorizing



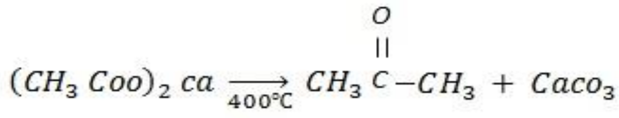
Heating higher members of calcium carboxylates produce Ketones



$$(Rcoo)_2\ ca + (R'Coo)\ Ca \xrightarrow[400^\circ C]{} 2R - \overset{\overset{O}{||}}{C} - R' + 2\ Caco_3$$

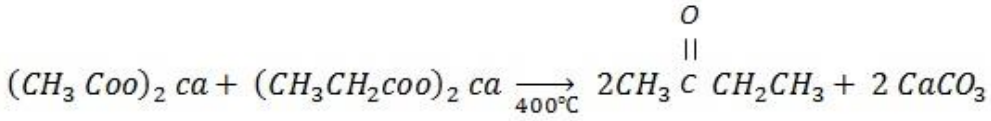
Example

i)



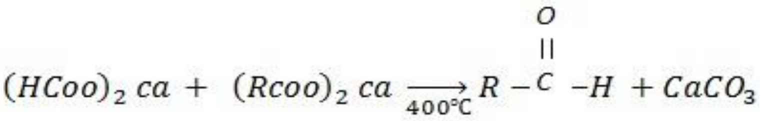
$$(CH_3\ Coo)_2\ ca \xrightarrow[400^\circ C]{} CH_3\ \overset{\overset{O}{||}}{C} - CH_3 + Caco_3$$

ii)



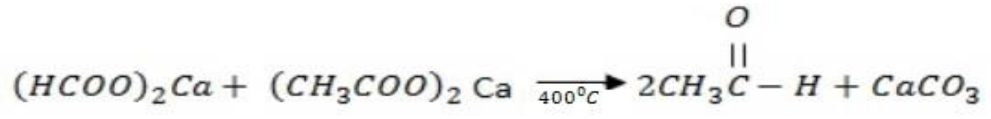
$$(CH_3\ Coo)_2\ ca + (CH_3CH_2coo)_2\ ca \xrightarrow[400^\circ C]{} 2CH_3\ \overset{\overset{O}{||}}{C}\ CH_2CH_3 + 2\ CaCO_3$$

Heating calcium methanoate and higher member of calcium calylates produce aldehyde i.e



$$(HCoo)_2\ ca + (Rcoo)_2\ ca \xrightarrow[400^\circ C]{} R - \overset{\overset{O}{||}}{C} - H + CaCO_3$$

Example

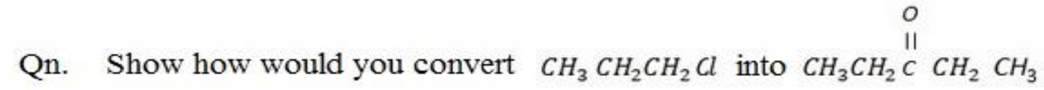


$$(HCOO)_2Ca + (CH_3COO)_2\,Ca \xrightarrow[400^0C]{} 2CH_3\overset{\overset{O}{||}}{C}-H + CaCO_3$$

Note

Reactions used in preparations of carbonyl compounds in (b) and show an increase in number of carbon form n to 2n-1 in these which the same type of acid is applied so reactions are very weak which is dealing with conversions problems which show that number of carbons has increased from n to 2n -1

<u>Example:-</u>

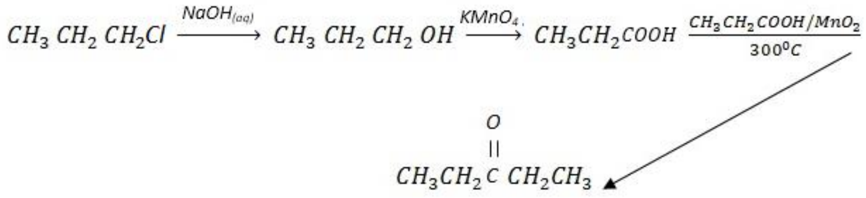


Qn. Show how would you convert $CH_3CH_2CH_2Cl$ into $CH_3CH_2\overset{\overset{O}{||}}{C}CH_2CH_3$

<u>ANS.</u>

$$CH_3CH_2CH_2CL \xrightarrow{NaOH_{(aq)}} CH_3CH_2CH_2OH \xrightarrow{KMnO_4} CH_3CH_2COOH \xrightarrow[400^\circ C]{CaO} CH_3$$

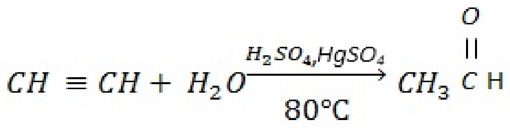
<u>Alternative</u>.



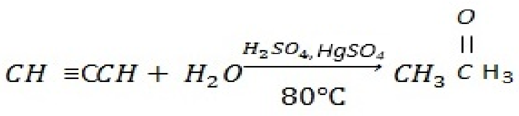
$$CH_3CH_2CH_2Cl \xrightarrow{NaOH_{(aq)}} CH_3CH_2CH_2OH \xrightarrow{KMnO_4} CH_3CH_2COOH \xrightarrow[300^0C]{CH_3CH_2COOH/MnO_2} CH_3CH_2\overset{\overset{O}{||}}{C}CH_2CH_3$$

(d) ACID AND MERCURY SULPHATES

Examples



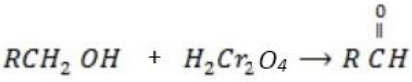
$$CH \equiv CH + H_2O \xrightarrow[80^\circ C]{H_2SO_4, HgSO_4} CH_3\overset{\overset{O}{||}}{C}H$$



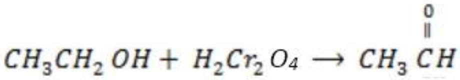
$$CH \equiv CCH + H_2O \xrightarrow[80^\circ C]{H_2SO_4, HgSO_4} CH_3\overset{\overset{O}{||}}{C}H_3$$

(e) OXIDATION OF ALCOHOL

Primary alcohols give aldehyde (the oxidizing agent must be weak like $H_2cr_2O_2$ oxidation of aldehyde to carboxylic acid)

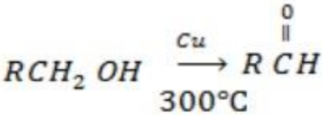


$$RCH_2\,OH + H_2Cr_2O_4 \longrightarrow R\overset{0}{\overset{\|}{C}}H$$

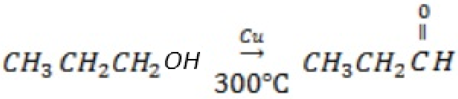


$$CH_3CH_2\,OH + H_2Cr_2O_4 \longrightarrow CH_3\,\overset{0}{\overset{\|}{C}}H$$

The more appropriate method of preparing aldehyde which ensures higher yield percentage of formation of aldehyde rather than carboxylic acid is heating alcohol under the presence of copper pirates catalyst.

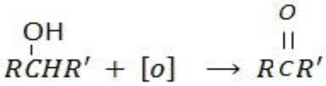


$$RCH_2\,OH \xrightarrow[300°C]{Cu} R\,\overset{0}{\overset{\|}{C}}H$$

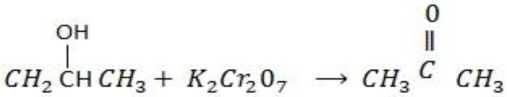


$$CH_3\,CH_2CH_2OH \xrightarrow[300°C]{Cu} CH_3CH_2\overset{0}{\overset{\|}{C}}H$$

Oxidation of secondary alcohol yield Ketones



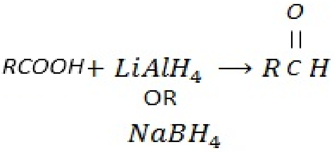
$$R\overset{OH}{\overset{|}{C}}HR' + [o] \longrightarrow R\overset{O}{\overset{||}{C}}R'$$



$$CH_2\,\overset{OH}{\overset{|}{C}}H\,CH_3 + K_2Cr_20_7 \longrightarrow CH_3\,\overset{0}{\overset{\|}{C}}\,CH_3$$

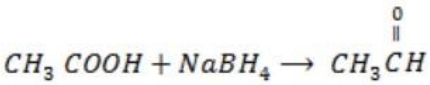
f) REDUCTION OF CARBOXYLIC ACID

Carboxylic acids can be reduced to aldehyde



$$RCOOH + \underset{NaBH_4}{\underset{OR}{LiAlH_4}} \longrightarrow R\overset{O}{\overset{||}{C}}H$$

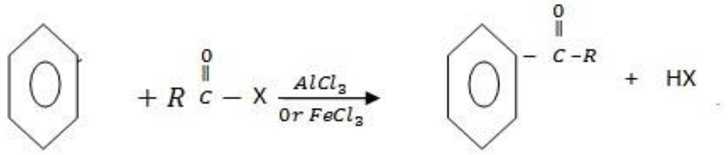
Example



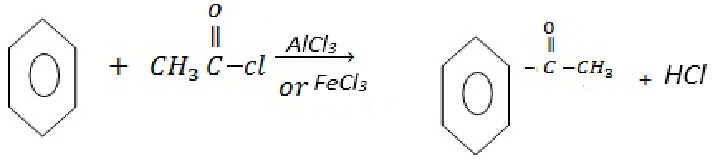
$$CH_3COOH + NaBH_4 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}H$$

In above reaction reducing agents (Li AlH_4 Or Na BH_4) must be limited amount so as to prevent further reduction of aldehyde alcohol.

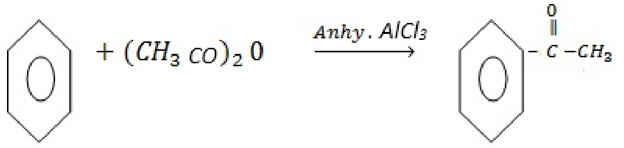
Benzene reacts with acyl compounds yield aromatic ketone
i.e



Example

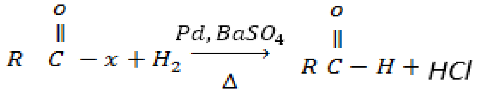


Analogously



h) REDUCTION OF ACYL COMPOUNDS (ROSENMUND REACTION)

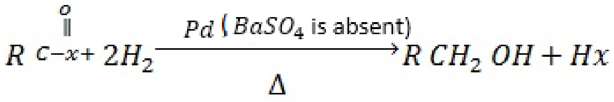
Acyl compounds react with hydrogen gas under the presence Palladium Catalyst poisoned with sulphur containing catalyst (mainly $BaSO_4$) is used to form aldehyde
I.e.



$$R\overset{o}{\overset{\|}{C}} - x + H_2 \xrightarrow[\Delta]{Pd,BaSO_4} R\overset{o}{\overset{\|}{C}} - H + HCl$$

In above reaction the use of $BaSO_4$ (Sulphur containing) is to poison palladium catalyst so as to preview reduction of aldehyde to alcohol

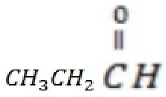
I.e.



$$R\overset{O}{\overset{\|}{C}}-x + 2H_2 \xrightarrow[\Delta]{Pd\ (BaSO_4\text{ is absent})} R\,CH_2\,OH + Hx$$

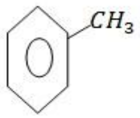
Show how would you convert

i) CH_3CH_2Cl into

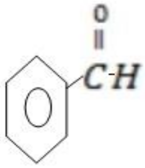


$$CH_3CH_2\overset{O}{\overset{\|}{C}}H$$

ii)

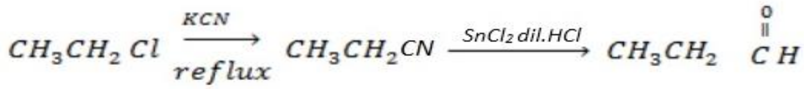


Into



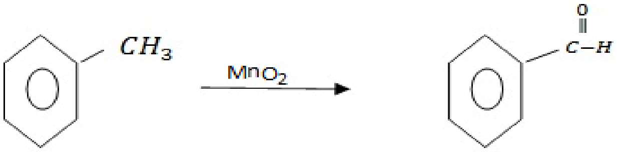
ANS

i)



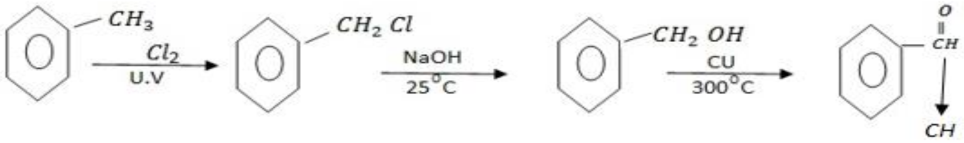
$$CH_3CH_2\,Cl \xrightarrow[reflux]{KCN} CH_3CH_2CN \xrightarrow{SnCl_2\ dil.HCl} CH_3CH_2\overset{O}{\overset{\|}{C}}H$$

ii)



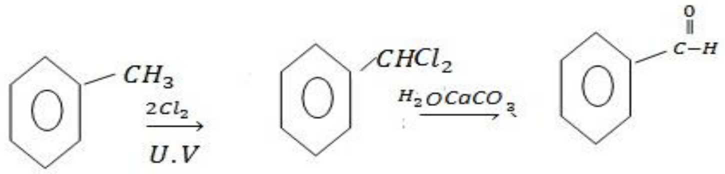
(One step)

Alternatively



(3 steps)

Alternatively



(2 step)s

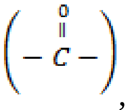
PHYSICIAL PROPERTIES OF CARBONYL COMPOUNDS

In comparison to alcohol carboxylic acids carbonyl and compound have lower boiling point due to limited hydrogen bonding present in them (There is weaker hydrogen binding existing between molecules of carbonyl compounds than that present in alcohol and carboxylic acid)

Among carbonyl compounds themselves boiling point increase with an increase in number of carbon atoms in the compounds Carbonyl compounds are slightly soluble in water due to their ability of forming hydrogen bonding with water molecules but are more soluble in organic solvents

CHEMICAL REACTIONS OF CARBONYL COMPOUNDS

a) a) NUCLEOPHILIC ADDITION REACTIONS

i. In Carbonyl group  $\left(-\overset{O}{\overset{\|}{C}}-\right)$,)Oxygen being more electronegative than carbon, Oxygen is negatively polarized and C is positively polarized is

Thus in carbonyl group is electrophilic and hence it becomes a good site for incoming nucleophile.

Yet there is π- bond in carbon of carbonyl group (functional) then carbonyl compounds are more likely to undergo addition reactions i.e. nucleophilic addition reactions.
Ability of carbonyl compound to undergo nucleophilic addition reactions depend on the amount of partial positive charge present in carbon if the carbon is more positively, polar than the compound will be more likely to undergo nucleophilic reaction and versa.
On another hand the amount of partial positive charge. Present in the carbon is determine by the strength of positive inductive effect which is exerted than the carbonyl will be less positively polarized and vice-versa

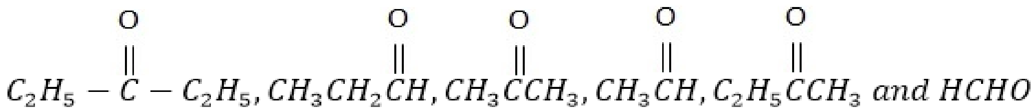
This explain why higher member of aldehyde are less reactive towards nucleophile than lower member because the strength positive inductive effect increase with an increase in length on chain of alkyl group.

The strength of positive inductive effect also explain why aldehydes are more reactive than keteones because while in positive inductive effect is exerted by one alkyl groups from two directions. In ketonepositive inductive effect s exerted by alkyl group from two direction, thus carbonyl group experience stronger positive inductive effect than in aldehyde.

Another reason of low reactivity of Ketone compaired to aldehyde is the fact that: (carbonyl group in ketone) experience large steric hindrance from the alkyl and aryl groups aldehyde there is only one alkyl group and this can also used to explain why carbonyl group with large alkyl group is less to explain why carbonyl group with large alky group is less reactive towards nuclephile (in nuclephilic addition reaction) because steric hindrance with increase with increase in size of alkyl group.

Example

Qn. Arrange the following organic compounds according to ability of undergoing nucleophilic addition reactions.

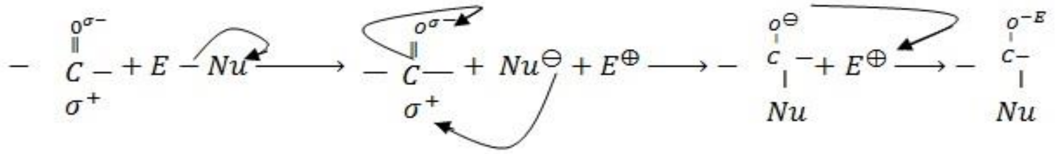


$$C_2H_5-\overset{\overset{O}{||}}{C}-C_2H_5, CH_3CH_2\overset{\overset{O}{||}}{C}H, CH_3\overset{\overset{O}{||}}{C}CH_3, CH_3\overset{\overset{O}{||}}{C}H, C_2H_5\overset{\overset{O}{||}}{C}CH_3 \text{ and } HCHO$$

ANS

$$\xrightarrow[\text{Decreases in ability of undergoing Nucleophilic addition reaction}]{HCHO > CH_3CHO > CH_3CH_2\,CHO > CH_3COCH_3\ > C_2H_5\,COCH_3 > C_2H_5COC_2H_5}$$

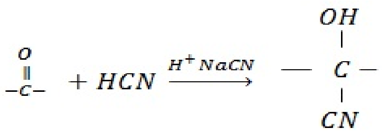
Generally carbonyl compounds follow the following mechanism in nucleophilic addition reaction



Examples of Nucleophilic addition reaction

i)Reaction with hydrogen cyanide (HCN)
Carbonyl compounds react with HCN under presence of sodium cyanide and strong acidic medium like HCl yielding cyanic hydrin

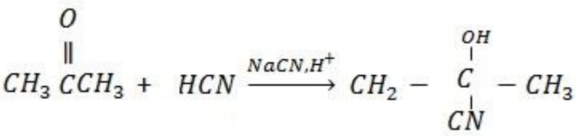
Generally:



$$\overset{O}{\overset{\|}{-C-}} + HCN \xrightarrow{H^+ NaCN} -\overset{OH}{\overset{|}{\underset{CN}{\underset{|}{C}}}}-$$

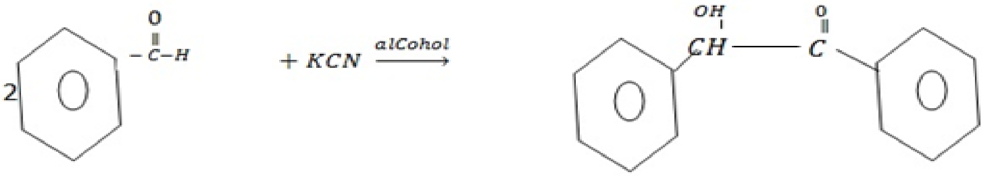
Cynohydrin

Example



$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + HCN \xrightarrow{NaCN,H^+} CH_2 - \overset{OH}{\overset{|}{\underset{CN}{\underset{|}{C}}}} - CH_3$$

But

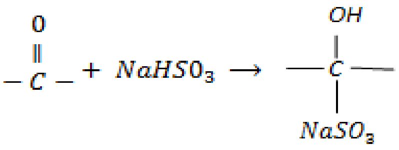


1,2 -----phenyl-2-hydroxyethanone

ii)Formation of bisulphite

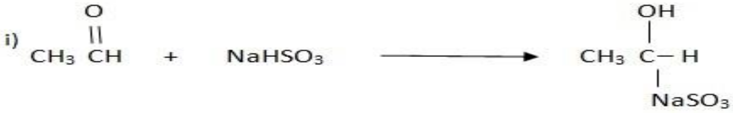
Carbonyl compound react with $NaHS0_3$ resulting to formation of bisulphite

Generally:-



$$-\overset{0}{\overset{\|}{C}}- + NaHS0_3 \longrightarrow -\overset{OH}{\overset{|}{\underset{NaSO_3}{\underset{|}{C}}}}-$$

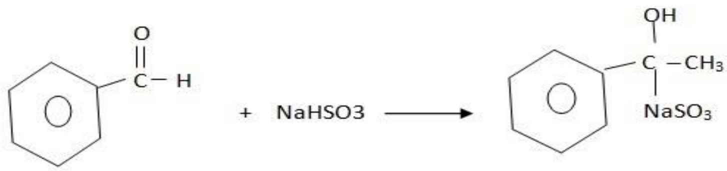
Examples



i) $$CH_3\overset{O}{\overset{\|}{CH}} + NaHSO_3 \longrightarrow CH_3\overset{OH}{\overset{|}{\underset{NaSO_3}{\underset{|}{C}}}}-H$$

(ii) $$CH_3\overset{O}{\overset{\|}{C}}CH_3 + NaHSO_3 \longrightarrow CH_3\overset{OH}{\overset{|}{\underset{NaSO_3}{\underset{|}{C}}}}-CH_3$$

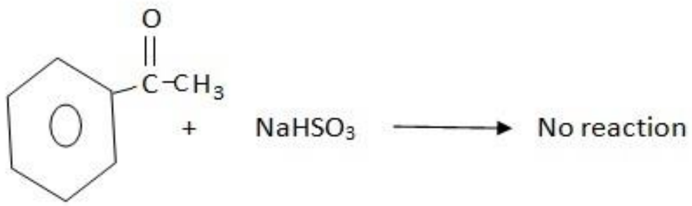
iii)

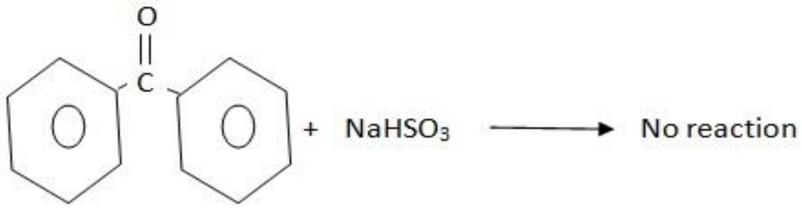


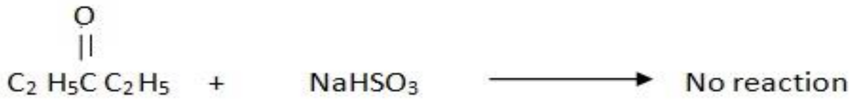
NOTE

Thus reaction involved an introduction (addition) of $NaHSO_3$ is very large molecule so there is large steric hinderancially in aromatic, ketones the reaction will not occur

e.g





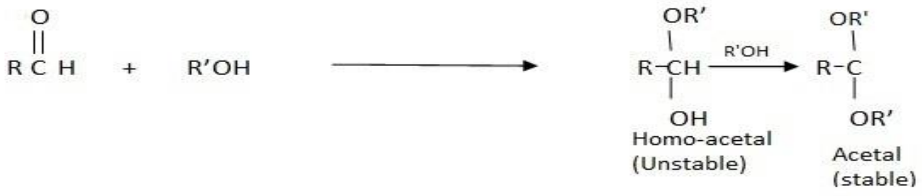


$C_2H_5\overset{O}{\overset{||}{C}}C_2H_5 + NaHSO_3 \longrightarrow$ No reaction

iii)Reaction with alcohols

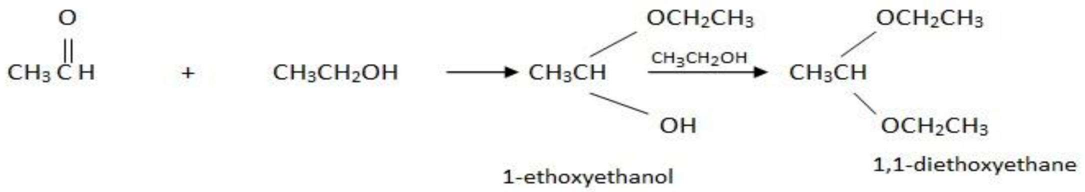
Aldehyde reacts with alcohol to form homo- acetal which is unstable but if alcohol present in excess a stable acetal is formed

Generally:-

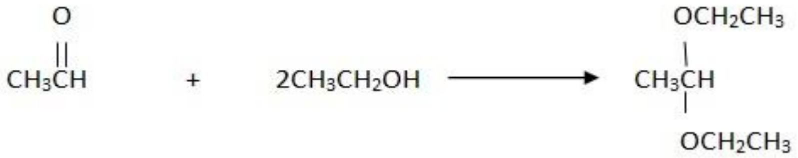


Hemo-acetal Acetal

Example



Thus overall reaction can be written as



$$CH_3\overset{O}{\overset{\|}{C}}H + 2CH_3CH_2OH \longrightarrow \underset{OCH_2CH_3}{\overset{OCH_2CH_3}{CH_3CH}}$$

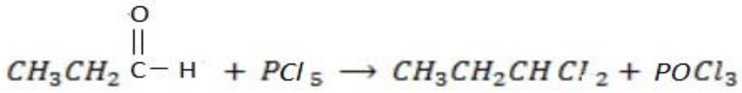
b)

b) NEUCLEOPHILIC SUBSTITUTION REACTION

When carbonyl compounds is heated with halogenating agents like Pcl_5 Oxygen in carbonyl group is replaced by halogens

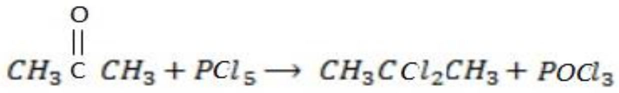
Example.

i)



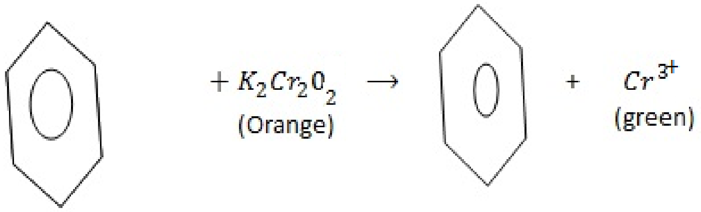
$$CH_3CH_2\overset{O}{\overset{\|}{C}}-H + PCl_5 \longrightarrow CH_3CH_2CHCl_2 + POCl_3$$

ii)

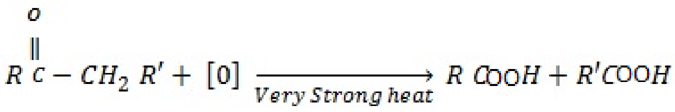


$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + PCl_5 \longrightarrow CH_3CCl_2CH_3 + POCl_3$$

In above example the reaction is similar to that in alcohol difference is that HCl is not evolved (like in alcohol) there is no OH group



- Ketones resist oxidation but they can undergo oxidation under very vigorous condition i.e

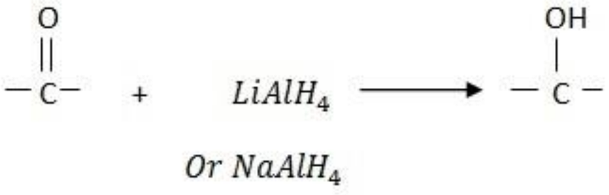


$$R\overset{O}{\overset{\|}{C}}-CH_2R' + [0] \xrightarrow[\text{Very Strong heat}]{} RCOOH + R'COOH$$

c) FORMATION OF ALCOHOL (REDUCTION)

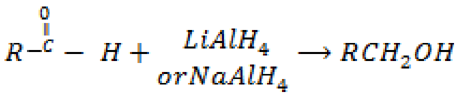
Carbonyl compound react with reducing agents like $LiAlH_4$ and $NaBH_4$ to form alcohol

Generally:-



$$-\overset{O}{\overset{\|}{C}}- + \underset{\text{Or } NaAlH_4}{LiAlH_4} \longrightarrow -\overset{OH}{\overset{|}{C}}-$$

Aldehyde form primary alcohol
i.e

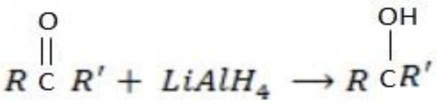


$$R-\overset{O}{\overset{\|}{C}}-H + \underset{or NaAlH_4}{LiAlH_4} \longrightarrow RCH_2OH$$

Example:-

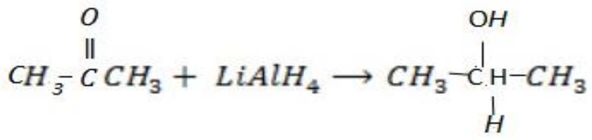
$$CH_3\overset{O}{\overset{\|}{C}}-H + LiAlH_4 \longrightarrow CH_3CH_2OH$$

Ketones from secondary alcohol



$$R\overset{O}{\overset{\|}{C}}R' + LiAlH_4 \longrightarrow R\overset{OH}{\overset{|}{C}}R'$$

Example



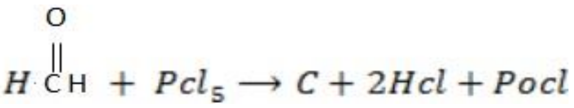
$$CH_3-\overset{\overset{O}{\|}}{C}CH_3 + LiAlH_4 \longrightarrow CH_3-\underset{H}{\overset{OH}{\overset{|}{\underset{|}{C}}}}H-CH_3$$

e) FURTHER EXAMPLES ON REDUCTION

- **Formation of alkane** .

Carbonyl compound reacts with hydroiodic acid in presence of red phosphorus at temperature of 150°C to form alkane

BUT



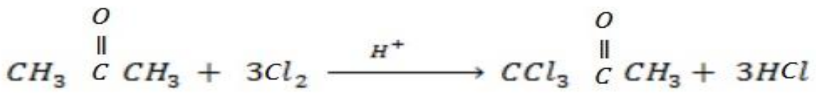
$$H\overset{\overset{O}{\|}}{C}H + Pcl_5 \longrightarrow C + 2Hcl + Pocl$$

NOTE

Carbonyl compound with alkyl group directly bonding carbonyl compound can react with halogen in the presence of acidic medium.

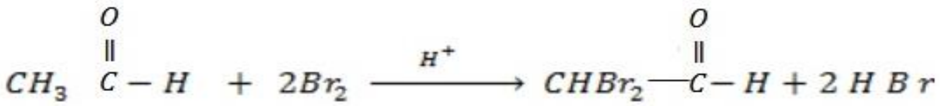
Example

i)



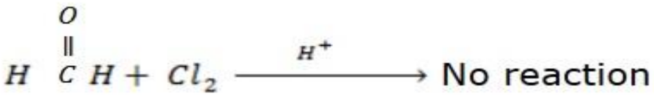
$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + 3Cl_2 \xrightarrow{H^+} CCl_3\overset{\overset{O}{\|}}{C}CH_3 + 3HCl$$

ii)



$$CH_3\overset{\overset{O}{\|}}{C}-H + 2Br_2 \xrightarrow{H^+} CHBr_2-\overset{\overset{O}{\|}}{C}-H + 2HBr$$

iii)



$$H\overset{\overset{O}{\|}}{C}H + Cl_2 \xrightarrow{H^+} \text{No reaction}$$

NOTE:

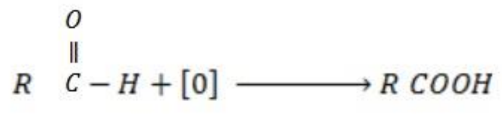
Similary

$$CH_3\overset{\overset{O}{\|}}{C}H + SOCl_2 \longrightarrow CH_3CHCl_2 + SO_2$$

c) OXIDATION

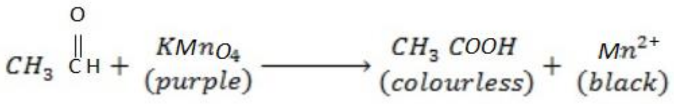
Aldehyde are good reducing agents. Ie. They oxidised to carboxylic acid

Generally.



$$R\ \overset{\overset{O}{\|}}{C} - H + [0] \longrightarrow R\ COOH$$

Example



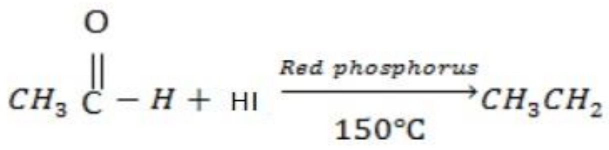
$$CH_3\overset{\overset{O}{\|}}{C}H + \underset{(purple)}{KMnO_4} \longrightarrow \underset{(colourless)}{CH_3COOH} + \underset{(black)}{Mn^{2+}}$$

Generally

$$-\overset{\overset{O}{\|}}{C}- + HI \xrightarrow[150^\circ C]{Red\ phosphorus} CH_2-$$

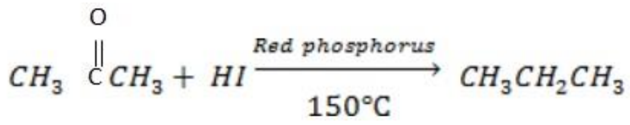
Example

i)



$$CH_3\overset{\overset{O}{\|}}{C} - H + HI \xrightarrow[150^\circ C]{Red\ phosphorus} CH_3CH_2$$

ii)

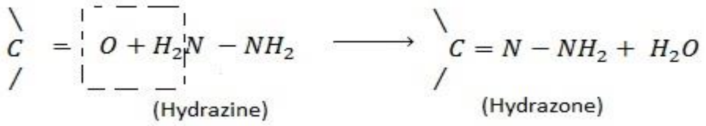


$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + HI \xrightarrow[150^\circ C]{Red\ phosphorus} CH_3CH_2CH_3$$

2) REACTION WITH HYDRAZINE

Carbonyl compound reacts with hydrazine to form hydrazone

Generally

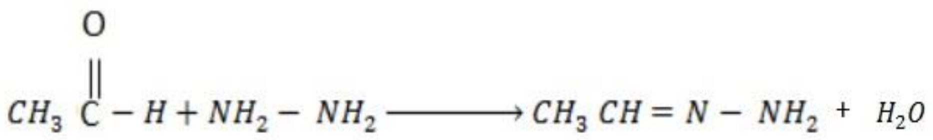


$$\rangle C = \boxed{O + H_2}N - NH_2 \longrightarrow \rangle C = N - NH_2 + H_2O$$

(Hydrazine) (Hydrazone)

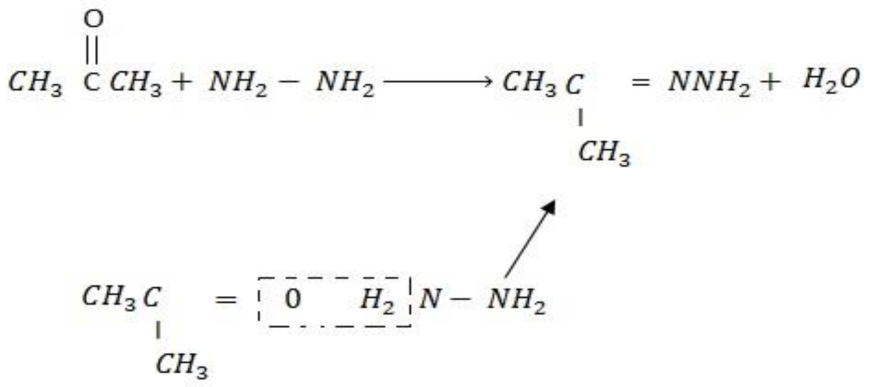
Example

i)



$$CH_3\overset{\overset{O}{\|}}{C} - H + NH_2 - NH_2 \longrightarrow CH_3\,CH = N - NH_2 + H_2O$$

ii)



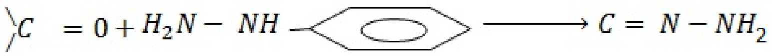
$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + NH_2 - NH_2 \longrightarrow CH_3\underset{\underset{CH_3}{|}}{C} = NNH_2 + H_2O$$

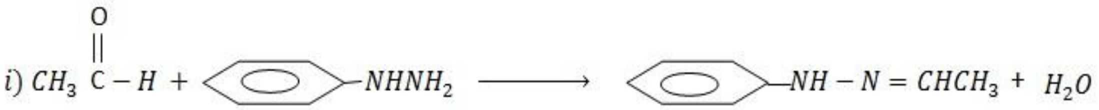
$$CH_3\underset{\underset{CH_3}{|}}{C} = \boxed{0 \quad H_2}N - NH_2$$

3) REACTION WITH PHENYL HYDRAZINE

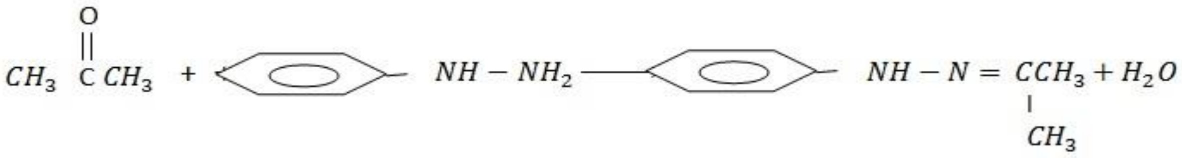
Carbonyl compound reacts with phenyhydrazine to form hydrazone

Generally

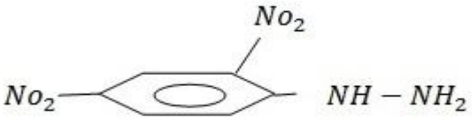




ii)



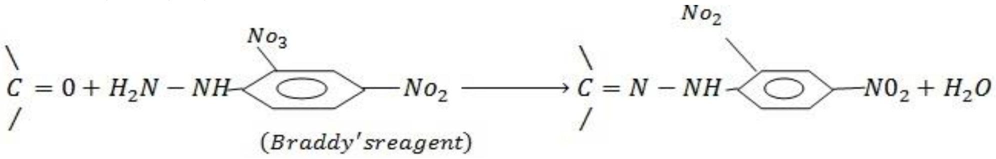
4) REACTION WITH 2,4 –dinitrophenylhydrazine (BRADDY'S REAGENT)



(Braddy's reagent)

[2,4 – dinitrophenyl hydrazine]

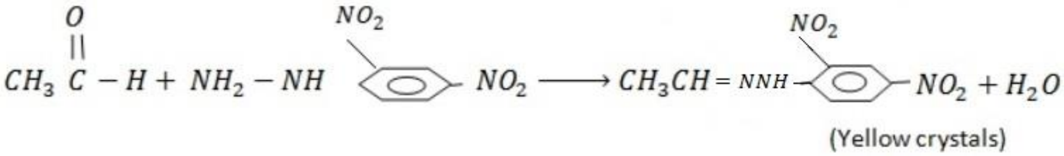
Carbonyl compound react with braddy's reagent to form yellow crystalline product(appear as yellow ppt) of 2,4-dinitrophenylhydrazone)



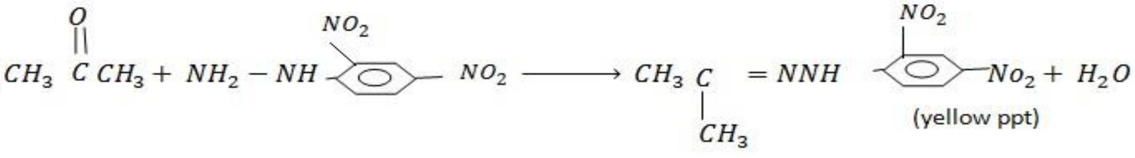
The reaction is used as chemical test of presence of carbonyl group in the compound.

Example:

i)



ii)



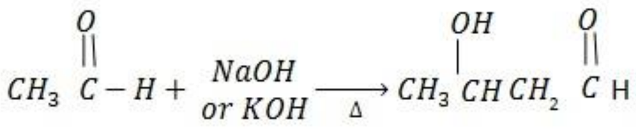
<u>OTHER REACTION OF CARBONYL COMPOUNDS</u>

i)Alde – condensation reaction

This is the reaction between carbonyl compound with hydrogen and alkane solution to form new compound both hydroxyl group and carbonyl group in the same compounds

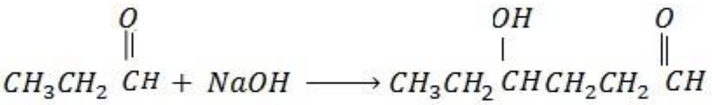
Example:

i)



$$CH_3\overset{O}{\overset{\|}{C}}-H + \frac{NaOH}{or\ KOH}\xrightarrow[\Delta]{} CH_3\overset{OH}{\overset{|}{C}}H\,CH_2\overset{O}{\overset{\|}{C}}H$$

ii)

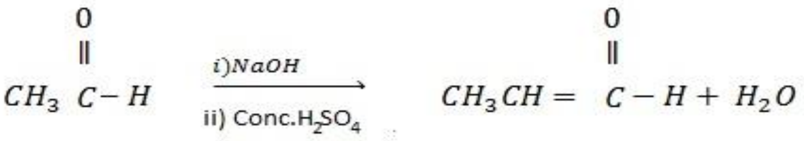


$$CH_3CH_2\overset{O}{\overset{\|}{C}}H + NaOH \longrightarrow CH_3CH_2\overset{OH}{\overset{|}{C}}H\,CH_2CH_2\overset{O}{\overset{\|}{C}}H$$

When the product is passed through acidic medium like conc. H_2SO_4 unsaturated carbonyl compound is formed.

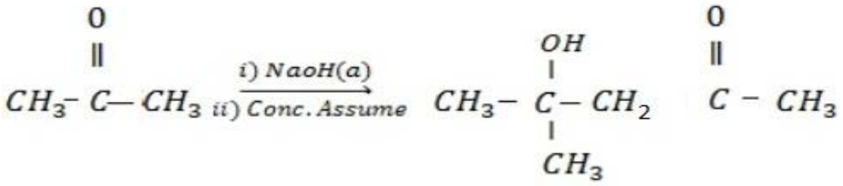
i.e

i)



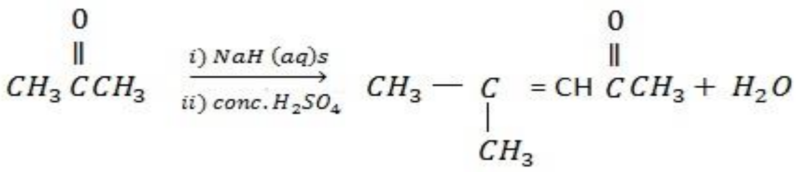
$$CH_3\overset{0}{\overset{\|}{C}}-H \xrightarrow[ii)\ Conc.H_2SO_4]{i)NaOH} CH_3CH = \overset{0}{\overset{\|}{C}}-H + H_2O$$

ii)



$$CH_3-\overset{0}{\overset{\|}{C}}-CH_3 \xrightarrow[ii)\ Conc.Assume]{i)\ NaoH(a)} CH_3-\overset{OH}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_2\ \overset{0}{\overset{\|}{C}}-CH_3$$

iii)



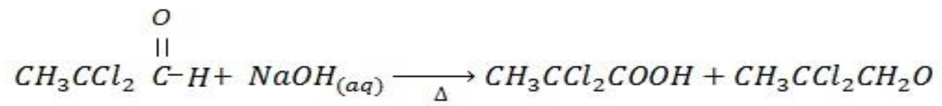
$$CH_3\overset{0}{\overset{\|}{C}}CH_3 \xrightarrow[ii)\ conc.H_2SO_4]{i)\ NaH\ (aq)s} CH_3-\underset{\underset{CH_3}{|}}{C} = CH\,\overset{0}{\overset{\|}{C}}CH_3 + H_2O$$

b) **Cannizaro reation**

This is the disproportionation reaction which occur between hyde $\propto$- hydrogen and alkane solution to form carbonic acid and alcohol.

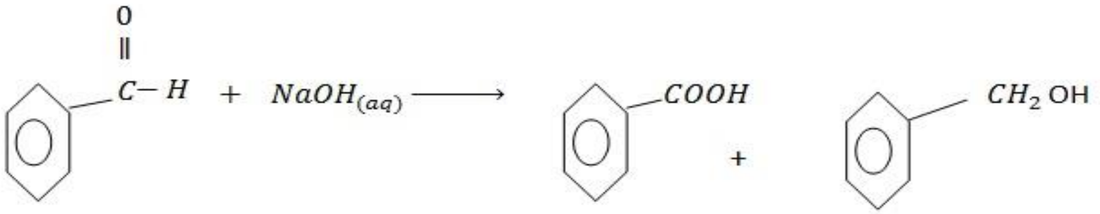
Example.

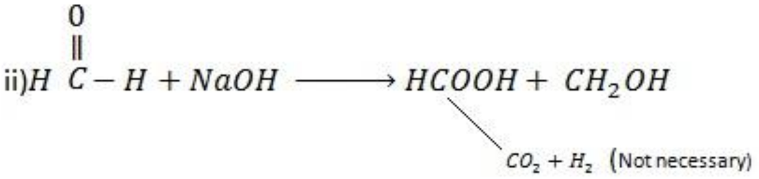
i)



$$CH_3CCl_2\overset{\overset{O}{||}}{C}-H + NaOH_{(aq)} \xrightarrow[\Delta]{} CH_3CCl_2COOH + CH_3CCl_2CH_2O$$

ii)





$$\text{ii)}H\ \overset{\overset{0}{||}}{C}-H + NaOH \longrightarrow HCOOH + CH_2OH$$

$CO_2 + H_2$ (Not necessary)

CHEMICAL TESTS TO DISTINGUISH BETWEEN ALDEHYDE AND KETONE

Aldehyde and Ketone may be distingushed using the fact that aldehyde is good reducing agent ie. it can be oxidised easily while ketone cannot be oxidised

There are two solutions which are commonly used to distinguish aldehyde and ketones

i) Fehlings/ Benedict solutions which consist of Cu^{2+}

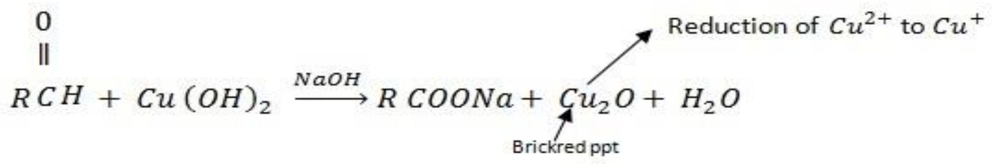
ii) Tollen's reagents which consist of $[Ag\ (NH_3)_2\ ]$(silver mirror test)

1) BY USING FEHLINGS / BENEDICT SOLUTION

- With fehlings or Benedict solution aldehyde give brick red ppt of copper (I) oxide (copper II) is reduced to copper(I)
- Ketones being poor reducing agent give negative test i.e it does not reduce Cu^{2+},to Cu^{+} and hence there is no formation of brick red ppt

Example:-

I)

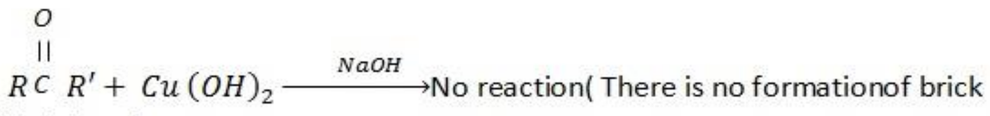


$$R\overset{\overset{O}{\parallel}}{C}H + Cu(OH)_2 \xrightarrow{NaOH} R\,COONa + Cu_2O + H_2O$$

Reduction of Cu^{2+} to Cu^{+}

Brickred ppt

ii)

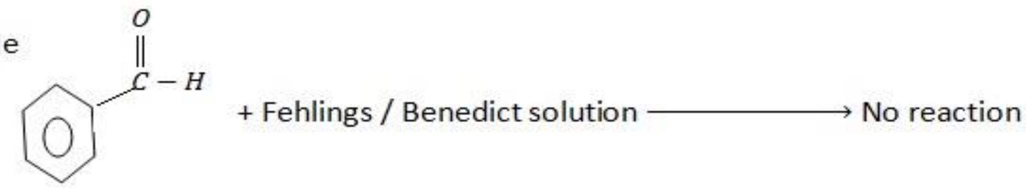


$$R\overset{\overset{O}{\parallel}}{C}R' + Cu(OH)_2 \xrightarrow{NaOH} \text{No reaction(There is no formationof brick}$$

red brick ppt)

NOTE.
Benzaldehyde do not react with Benedict/ Fehlings solution

Ie

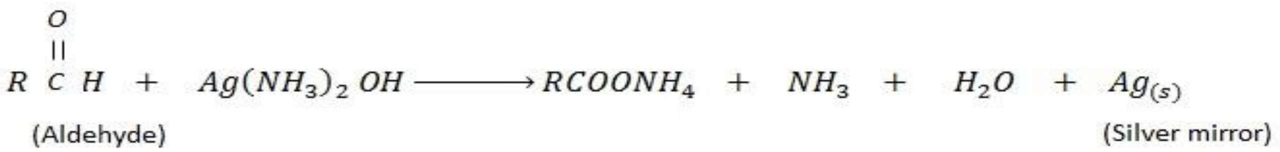


+ Fehlings / Benedict solution ⟶ No reaction

2) **BY USING TOLLEN'S REACTION**(silver mirror test)

With tollen's reagents aldehyde being reducing agent reduce Ag^+ to Ag ie precipitate of $Ag_{(s)}$which appear as silver mirror hence the name mirror test) Aldehyde react with tollen's (Ammoniacal silver nitrate) form white ppt of silver which appear like mirror
Ketones being poor reducing Agent give negative mirror test

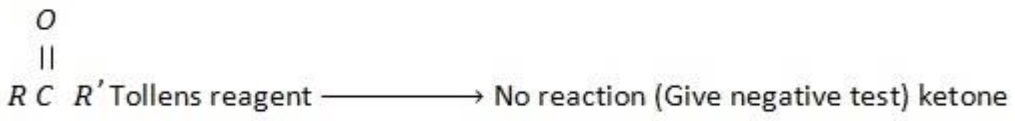
I.e



$$R\overset{\overset{O}{\parallel}}{C}H + Ag(NH_3)_2\,OH \longrightarrow RCOONH_4 + NH_3 + H_2O + Ag_{(s)}$$

(Aldehyde) (Silver mirror)

WHILE



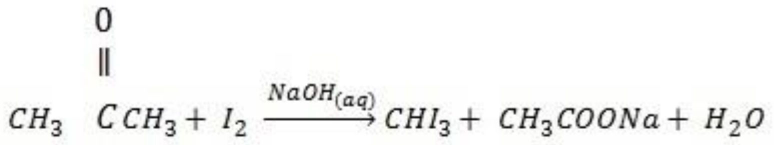
$$R\overset{\overset{O}{||}}{C}\ R'\ \text{Tollens reagent} \longrightarrow \text{No reaction (Give negative test) ketone}$$

OTHER CHEMICAL REACTION.

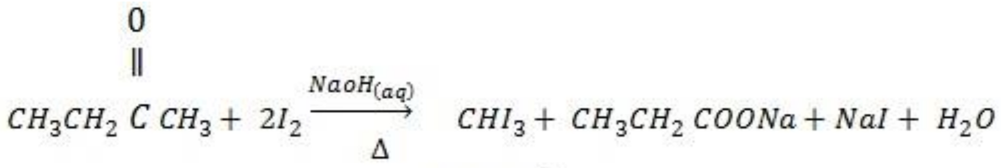
IODOFORM TEST.

- This is the test for presence of terminal methyl group is directly bonded to carbonyl group by giving yellow ppt of iodoform CHI_3
- For aldehyde only ethanal give iodoform test.

Example

i) 

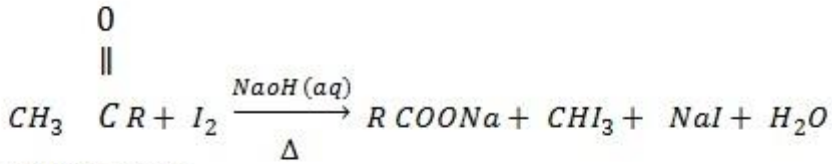
$$CH_3\ \overset{\overset{0}{\|}}{C}CH_3 + I_2 \xrightarrow{NaOH_{(aq)}} CHI_3 + CH_3COONa + H_2O$$

ii) 

$$CH_3CH_2\ \overset{\overset{0}{\|}}{C}\ CH_3 + 2I_2 \xrightarrow[\Delta]{NaoH_{(aq)}} CHI_3 + CH_3CH_2\ COONa + NaI + H_2O$$

(Yellow ppt)

Generally



$$CH_3\ \overset{\overset{0}{\|}}{C}R + I_2 \xrightarrow[\Delta]{NaoH\ (aq)} R\ COONa + CHI_3 + NaI + H_2O$$

(Methylketone)

NECTA 2000 PP$_1$ QN 14 (a)

QN. Compound A which has an unbranched carbon chain, react methyl magnesium bromide to give after hydrolysis compound B. chromic acid oxidation of B gives C ($C_5H_{10}O$) or which gives crystal product with 2, 4- dinitrophenylhydrazine and a positive iodoform test.

i)Give the formula of A, B, C and equation for all reaction mentioned.

ii) Give the formula of possible Isomer of A that would give the same result as A in the above transformation (5 marks)

ANSWER

Molecular formula $C_5H_{10}O$ confirm general molecular formula of $C_nH_{2n}O$

This C is either aldehyde or Ketone.

Formation of crystalline product with 2,4 dinitrophenyl hydrazine confirm that there is a Group in C (it either aldehyde or ketone)

Since C give positive Iodoform test then there is terminal methyl group which is directly bonded to carbonyl group in C.

A compound which gives carbonyl compound on oxidation is alcohol $(1^{\circ} \quad and \ \ 2^{\circ} \quad alcohol)$

This B is either primary (1°)or secondary

Carbonyl compound which give secondary (2°)alcohol with griginard reagent (in this case methyl magnesium bromide) are higher member of aldehyde rather than methanol which give primary (1°) alcohol .

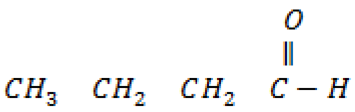
This A is either methanol or higher member of aldehyde .

Product formed after reaction between methyl magnesium bromine followed by hydrolysis indicate that there are 4 carbon in A

so A must be aldehyde with A - carbons and B must be secondary (2°)alcohol with 5 carbons

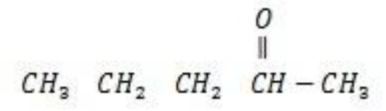
Since A is unbranched

Structure formula of A



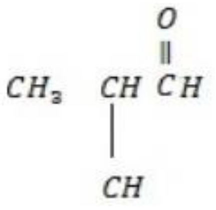
$$CH_3 \quad CH_2 \quad CH_2 \quad \overset{\overset{O}{\|}}{C} - H$$

Structure formula of B is



$CH_3 \ CH_2 \ CH_2 \ \overset{\overset{O}{\|}}{CH} - CH_3$

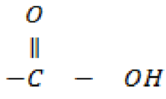
ii) Possible Isomers is



$CH_3 \ \underset{\underset{CH}{|}}{CH} \ \overset{\overset{O}{\|}}{CH}$

CARBOXYLIC ACID AND ITS DERIVATIVES

These are organic compound with carboxylic group $-COOH$ as functional group.
They can be aliphatic or aromatic



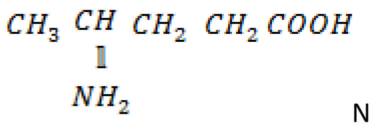
Carboxylic group $\overset{\overset{O}{\|}}{-C} - OH$ result after mixing carbonyl group and hydroxyl group.

NOMENCLATURE OF CARBOXYLIC ACIDS

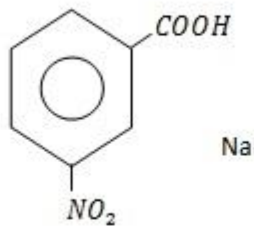
Example

i) $CH_3 \ CH_2 \ COOH$ Name Propanoic acid

ii) $CH_3 \ CH = CH \ CH_2COOH$ name 3 – Pentanoic acid **Or** Pent -3-enoic acid



iii) $CH_3 \ \underset{\underset{NH_2}{\|}}{CH} \ CH_2 \ CH_2 \ COOH$ Name: 4 – aminopentanoic acid iv)

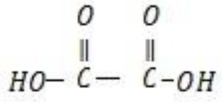


Name : 3 - nitro benzoic acid

v) $HCOOH$ Name: Methanoic acid (Common name formic acid)

vi) CH_3COOH Name : Ethanoic acid (Common name Acetic acid)

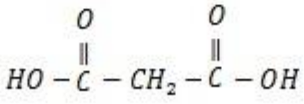
vii)



$$HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

Name: Ethanedioie acid (Common name Oxalic acid)

viii)



$$HO-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

Name: Propane -1, 3 –dioic acid

OR (simply propane dioic acid)

PREPARATION OF CARBOXYLIC ACID

i). OXIDATION

a) Oxidation of alcohol

Alcohol can be oxidised by strong oxidising agent like $K_2\,Cr_2\,O_7$ andKMnO₄ to give carboxylic acid.

$$RCH_2OH \xrightarrow{[O]} RCOOH$$

Where $[O]$ is a strong oxidising agent

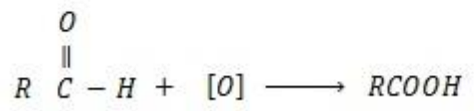
EXAMPLE

$$CH_3CH_2OH + KMnO_4 \text{ (excess)} \longrightarrow CH_3COOH$$

If oxidising agent is weak or is in limited amount aldehyde is formed.

b/ Oxidation of carbonyl compound

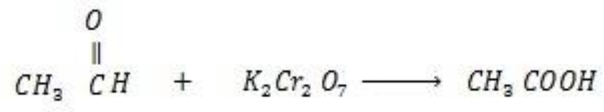
Aldehyde can be oxidised easily to give carboxylic acids
i.e



$$R\overset{\overset{O}{\|}}{C}-H + [O] \longrightarrow RCOOH$$

Where $[O]$ is oxidising agent

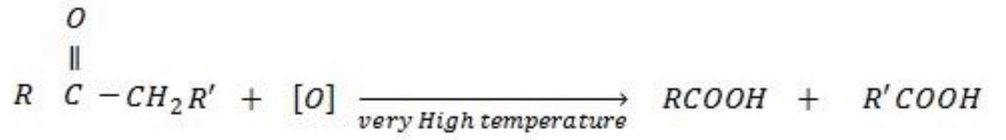
Example



$$CH_3\overset{\overset{O}{\|}}{C}H + K_2Cr_2O_7 \longrightarrow CH_3COOH$$

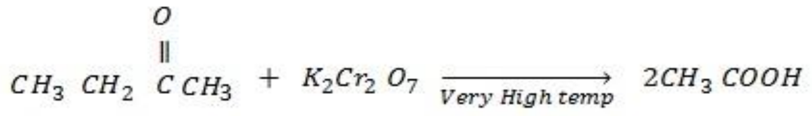
Ketones resist oxidation but under drastic (vigorous) condition it can form carboxylic acid

I.e.



$$R\overset{\overset{O}{\|}}{C}-CH_2R' + [O] \xrightarrow[\text{very High temperature}]{} RCOOH + R'COOH$$

Example



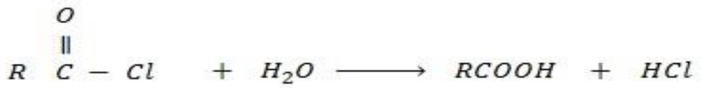
$$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3 + K_2Cr_2O_7 \xrightarrow[\text{Very High temp}]{} 2CH_3COOH$$

NOTE
Methanoic acid cannot be prepared by this method (Oxidation method) . Since it can farther oxidised to CO_2 and H_2O

ii) HYDROLYSIS

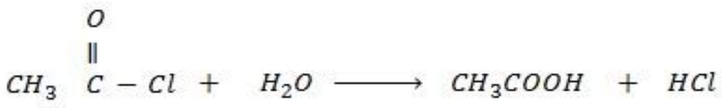
Acyl compound can be hydrolysed to give carboxylic acid

E.g.



$$R\overset{\overset{O}{\|}}{C}-Cl + H_2O \longrightarrow RCOOH + HCl$$

Example



$$CH_3\overset{\overset{O}{\|}}{C}-Cl + H_2O \longrightarrow CH_3COOH + HCl$$

Ethanol chloride

b/ Acidic hydrolysis of Nitrile

Generally

$$RNC + H_2O \xrightarrow{H^+} RCOOH + other\ products$$

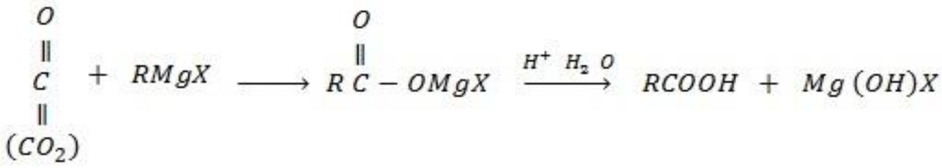
Example

$$CH_3CH_2CN + dil.HCl \longrightarrow CH_3CH_2COOH$$

III FORM GRIGINARD REAGENT

Carbon dioxide reacts with Grignard reagent followed by acidic hydrolysis to form carboxylic acid.

Generally:-



$$\underset{\underset{(CO_2)}{\|}}{\overset{\overset{O}{\|}}{C}} + RMgX \longrightarrow R\overset{\overset{O}{\|}}{C}-OMgX \xrightarrow{H^+\ H_2\ O} RCOOH + Mg(OH)X$$

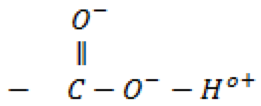
Example

$$CO_2 + CH_3CH_2MgCl \xrightarrow{H^+\ H_2O} CH_3CH_2COOH + Mg(OH)Cl$$

PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

Carboxylic acid has highest boiling point among alcohol phenol carbonyl compound or easy other hydrocarbons with comparable molecular weight due to stronger hydrogen bonding existing between molecules of carboxylic acids.

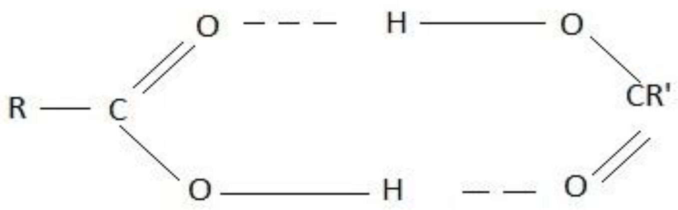
Alcohol phenol carbonyl compound or any other hydrocarbons because they come capable of making strong hydrogen bonding with water and high polarity of carboxylic group.
I.e



$$- \overset{\overset{O^-}{\|}}{C} - O^- - H^{o+}$$

Carboxylic acid is capable of undergoing dimerisation when it is in the hydrocarbon solvent it or any other similar solvent without hydrogen bonding

I.e



Dimer

ACIDIC BEHAVIOUR OF CARBOXYLIC ACID

Carboxylic acids have higher acid strength than alcohol and phenol.

For aliphatic carboxylic acids strength depend on:-

i/ length of carbon chain

ii/ Type of substituent in carboxylic acid

The acidic strength decrease with increase in length of carbon chain due to strong positive effect exerted by longer alkyl group.

When substituent carboxylic acid is stronger electronegative element like halogens which exert –I acidic strength is increase due to following reason:-

i/ Negative inductive effect weakens OH bond by reducing electron density in bond . Thus making easier to release hydrogen proton.

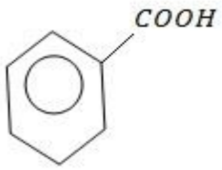
ii/ Negative inductive effect stablised the carboxylate ion formed after releasing hydrogen proton by withdrawing (partial withdraw) - Very charged electron.

In aromatic acid the acidic strength depend on whether the substituent in benzene ring is activator or deactivator

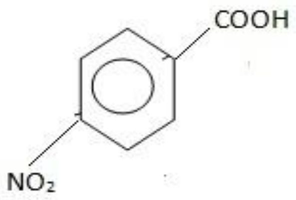
When the substituent is activator the acidic strength with decrease and if it is deactivator the acidic strength will increase.

Example

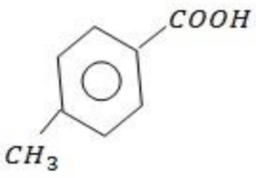
Qn. Starting with less acidic arrange the following organic compound according to increase in acidic strength.



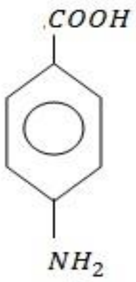
A



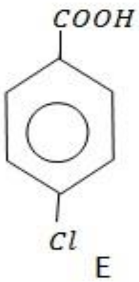
B



C



D



E

ANS.

$$\begin{array}{c} D < C < A < E < B \\ \xrightarrow{\qquad\qquad\qquad\qquad} \\ \text{Increase in acidic strength} \end{array}$$

CHEMICAL REACTION OF CARBOXYLIC ACIDS

I. REACTION WHICH INVOLVE – COOH (CARBOXYLIC GROUP)

a/ Reaction with sodium bicarbonate (sodium hydrogen carboxylic acid reacts with sodium bicarbonate to give solid carbonate and bubble of Co_2 are formed.

Generally:-

$$-COOH + NaHCO_3 \longrightarrow -COONa + CO_2 + H_2O$$

Example

i) 

ii) $CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$

The reaction showed one of the differences between carboxylic acid on one side and alcohol and phenol on another. Ie alcohol and phenol do not react with $NaHCO_3$

b) Reaction with alkali

Under this heading carboxylic acid reacts with alkali like
$NaOH \text{ and } Na_2CO_3 \text{ to form carboxylic salt}$

Generally

$$-COOH + NaOH \longrightarrow -COONa + H_2O$$

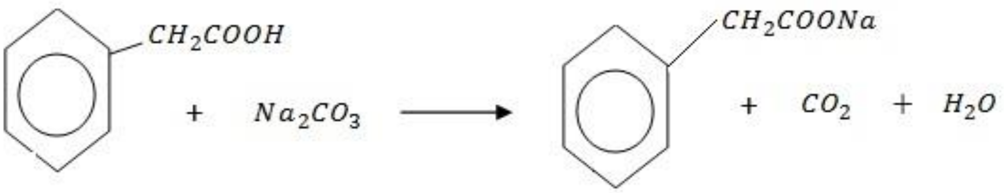
And

$$-COOH + NaCO_3 \longrightarrow -COONa + CO_2 + H_2O$$

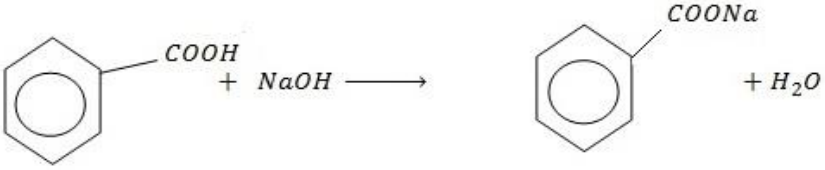
Example

i) $-CH_3 + COOH + NaOH \longrightarrow CH_3COONa + H_2O$

ii)



iii)



- Phenol reacts with $\underline{Na_2CO_3}$ and $\underline{NaOH}$ in the some way so the reaction gives of one of the similarities between alcohol and phenol.

c) Reaction with strong metals

- Carboxylic acid react with strong metals to give carboxylic salt and hydrogen gas is evolved.
- Generally
- $2-COOH+2M \longrightarrow 2-COOM\ +H_2$

Where M is the strong metal

Example

i/ $2CH_3COOH+2Na \longrightarrow 2CH_3\ COONa+H_2$

ii/ $2CH_3COOH+Ca \longrightarrow (CH_3\ COO)_2\ Ca+H_2$

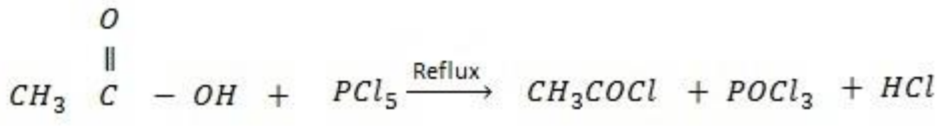
Alcohol and phenol also react with strong alkaline metals

II. REACTIONS WHICH REPLACE OH^- FROM CARBOXYLIC GROUP $(-\ COOH)$

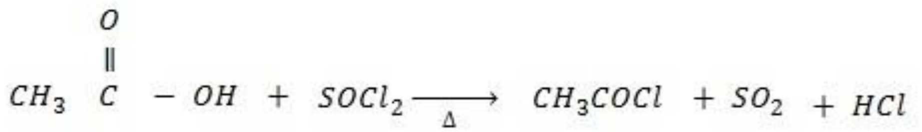
a) HALOGENATION

Carboxylic acid react with halogenating agent like PX_5, PX_3 and SOX_2 to form acyl halide

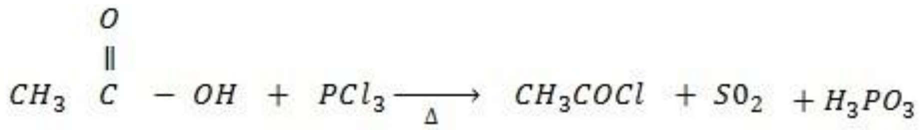
Example

i) 

$$CH_3\overset{\overset{O}{\|}}{C}-OH + PCl_5 \xrightarrow{\text{Reflux}} CH_3COCl + POCl_3 + HCl$$

ii) 

$$CH_3\overset{\overset{O}{\|}}{C}-OH + SOCl_2 \xrightarrow[\Delta]{} CH_3COCl + SO_2 + HCl$$

iii) 

$$CH_3\overset{\overset{O}{\|}}{C}-OH + PCl_3 \xrightarrow[\Delta]{} CH_3COCl + SO_2 + H_3PO_3$$

b) Reaction with alcohol (Ester formation)

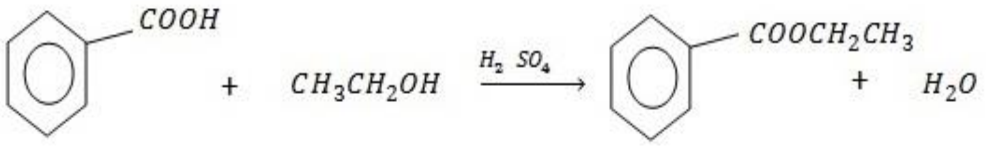
Carboxylic acid reacts with alcohol in presence of acidic medium like sulphuric acid to form ester.

Generally:-

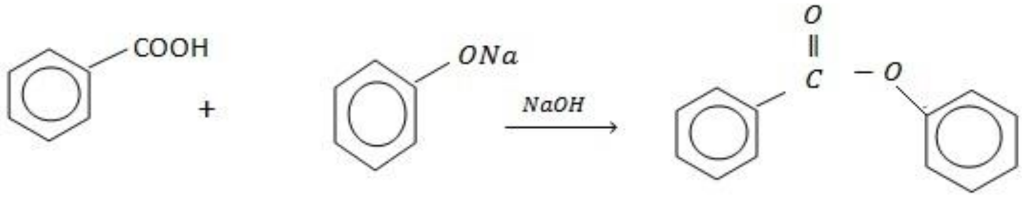
$$RCOOH + R'OH \xrightarrow[H_2So_4]{H^+\ eg} RCOOR' + H_2O$$

Example

i) $CH_3CH_2COOH + CH_3CH_2OH \xrightarrow{H_2\ SO_4} CH_3CH_2COOCH_2CH_3$

ii) 

BUT



CHEMICAL TEST OF CARBOXYLIC ACIDS

a/ REACTION WITH ALCOHOL

Carboxylic acid reacts with alcohol in presence of acid

$$RCOOH + R'OH \xrightarrow{H_2\ SO_4} RCOOR' + H_2O$$

The reaction is very important in distinguishing carboxylic acid from phenol is phenol do not react with alcohol verifying that carboxylic acid is more acidic than phenol

b/ REACTION WITH SODIUM BICSRBONATE

Carboxylic acid reacts with sodium bicarbonate to give effervescence of carbon dioxide gas which turn lime water milky

$$-COOH + NaHCO_3 \longrightarrow -COONa + \underset{\text{Turn lime water milky}}{CO_2} + H_2O$$

The reaction gives another difference between carboxylic acid and phenol as phenol do not give effervescence acidic than phenol.

c/ REACTION WITH $Fecl_3 (Iron(III)\ chloride)$Ferric chloride test

carboxylic acid reacts with $Fecl_3$ to give Iron (III) carboxylic (alkanoate) which appear as buff colourled compound i.e. $3\,RCOOH + FeCl \longrightarrow \underset{\text{Buff coloured}}{(RCOO)_3Fe} + 3HCl$

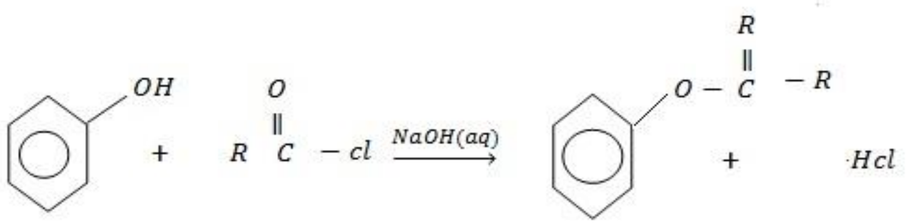
The reaction is important in distinguish between alcohol, phenol and carboxylic acid

- Alcohol give no change indicating that there is no reaction between alcohol and Iron (III) chloride $(Fecl_3)$
- Phenol give purple/violet coloured compound
- Carboxylic give buff coloured compound
-

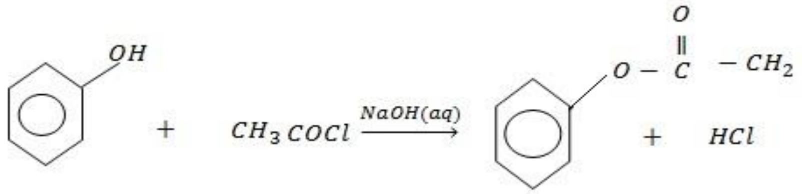
f/ FORMATION OF ESTER

Acyl chloride reacts with phenol in presence of $NaoH$ to form ester

I.e.



Example

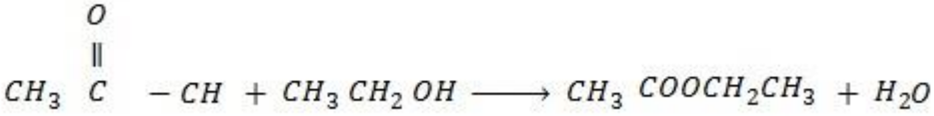


Acyl chloride also reacts with alcohol to form ester although with alcohol there is no need of $NaOH_{(aq)}$

I.e.

$$RCOCl + R'OH \longrightarrow RCOOR' + HCl$$

E.g.



$$CH_3\overset{\overset{O}{\|}}{C} - CH + CH_3CH_2OH \longrightarrow CH_3\ COOCH_2CH_3 + H_2O$$