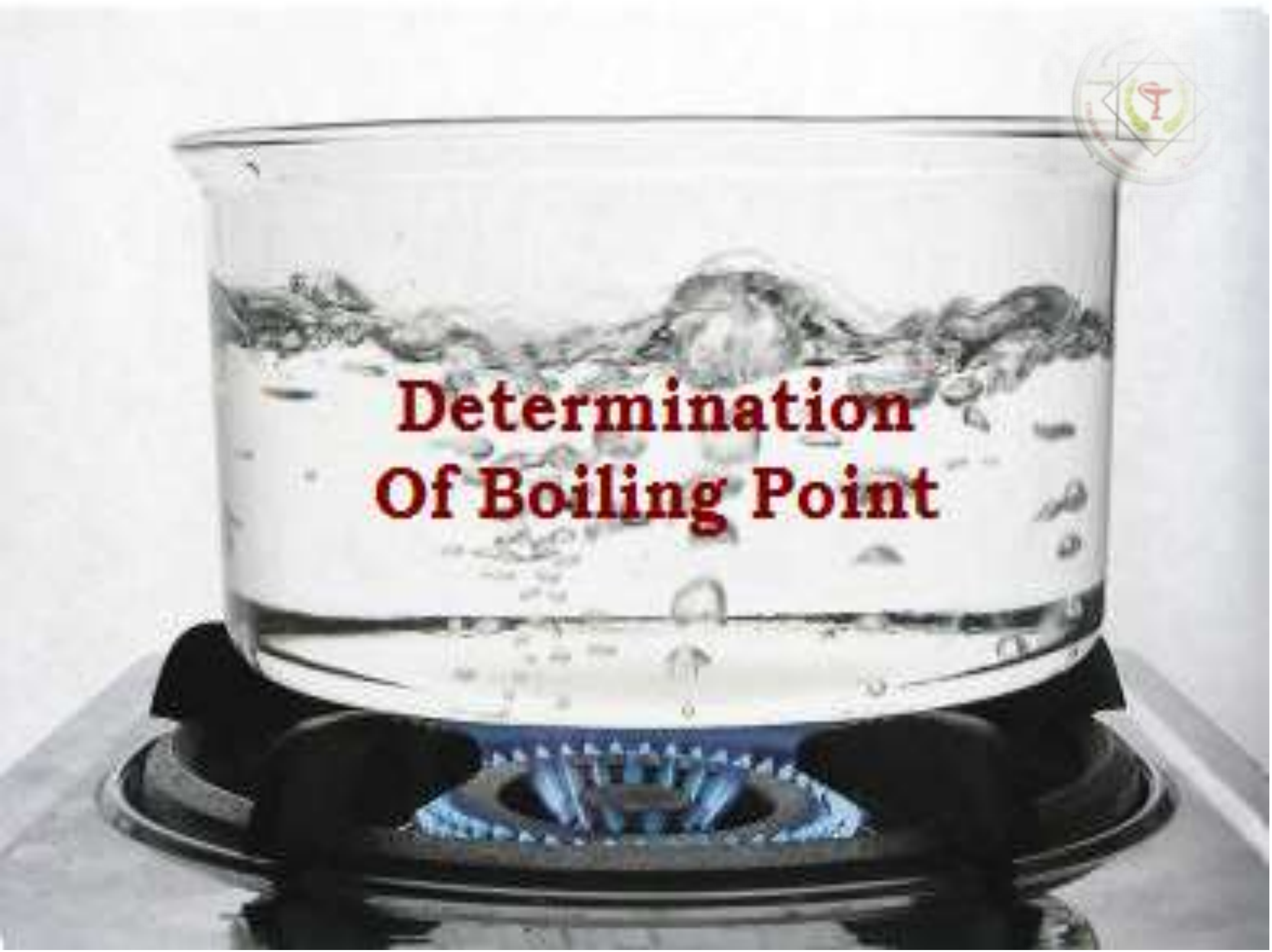
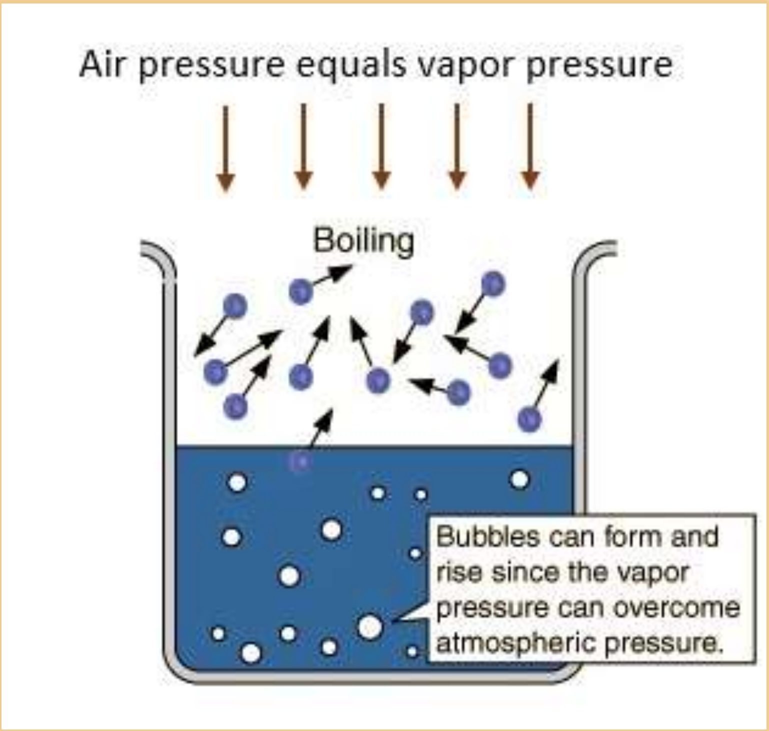


Determination Of Boiling Point

The Boiling Point of an organic liquid is the temperature at which the vapour & liquid phases are in equilibrium at a given pressure. **Or**,

It is the temperature at which the liquid's vapour pressure equals the atmospheric pressure over the liquid.

The vapour pressure of a compound is the pressure exerted by the compound's vapour above compound's surface.

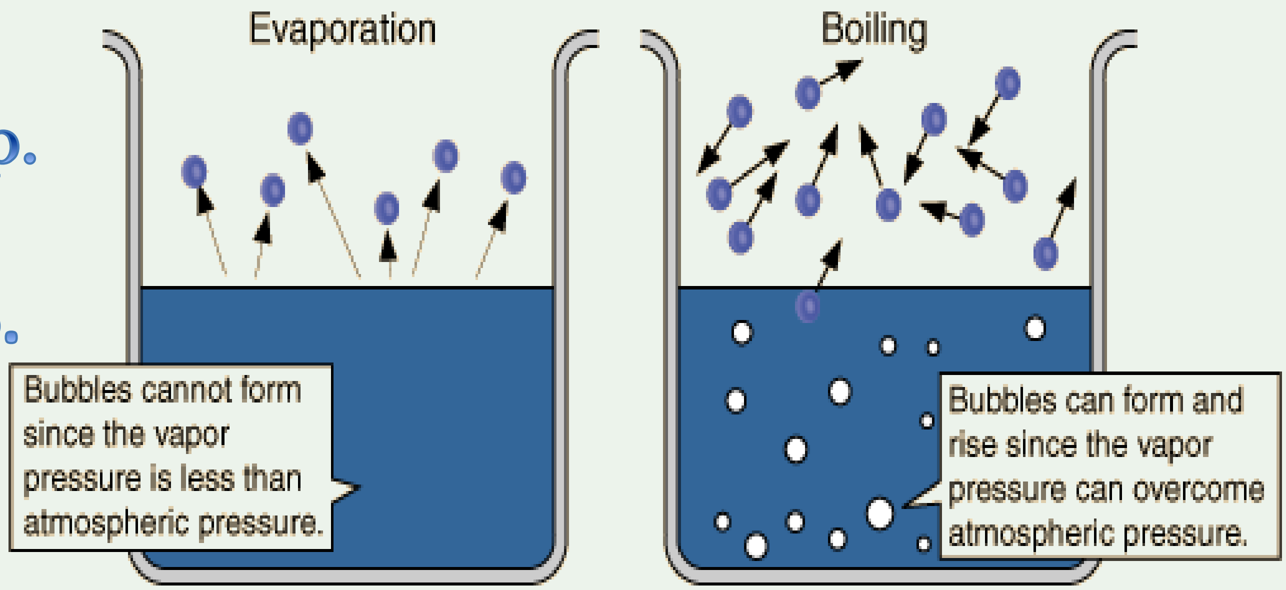


FACTORS AFFECTING THE B.P. OF A LIQUID :

1- Atmospheric pressure :

↓ pressure → ↓ b.p.

↑ pressure →↑ b.p.



Bubbles cannot form since the vapor pressure is less than atmospheric pressure.

Bubbles can form and rise since the vapor pressure can overcome atmospheric pressure.

2- Molecular weight :

For a homologous series of molecules,

↑ m.wt. → ↑ b.p.

↓ m.wt. → ↓ b.p.

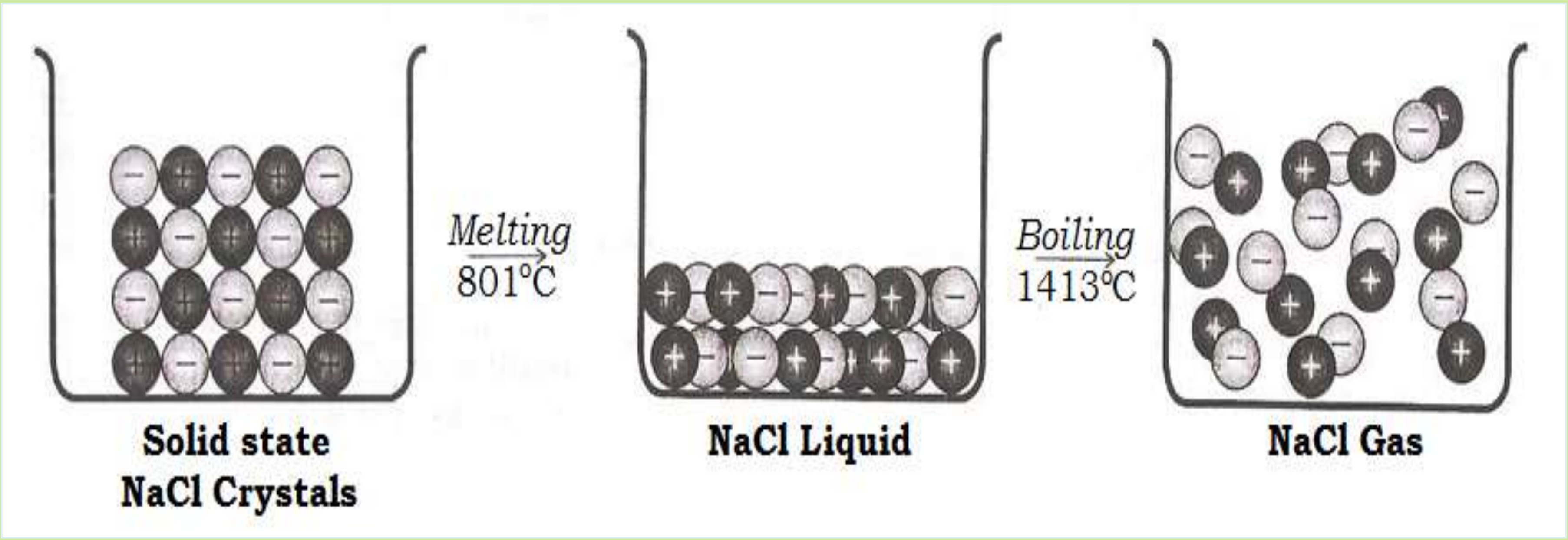
Number of Carbons in R	Boiling Points (°C)			
	R—H	R—Cl	R—OH	R—COOH
1	−160	−24	65	101
2	−89	12	78	118
3	−42	47	97	141

3- Intermolecular forces :

A- Ionic compound :

In the liquid state the units of ionic compound is ions.

Interionic forces :



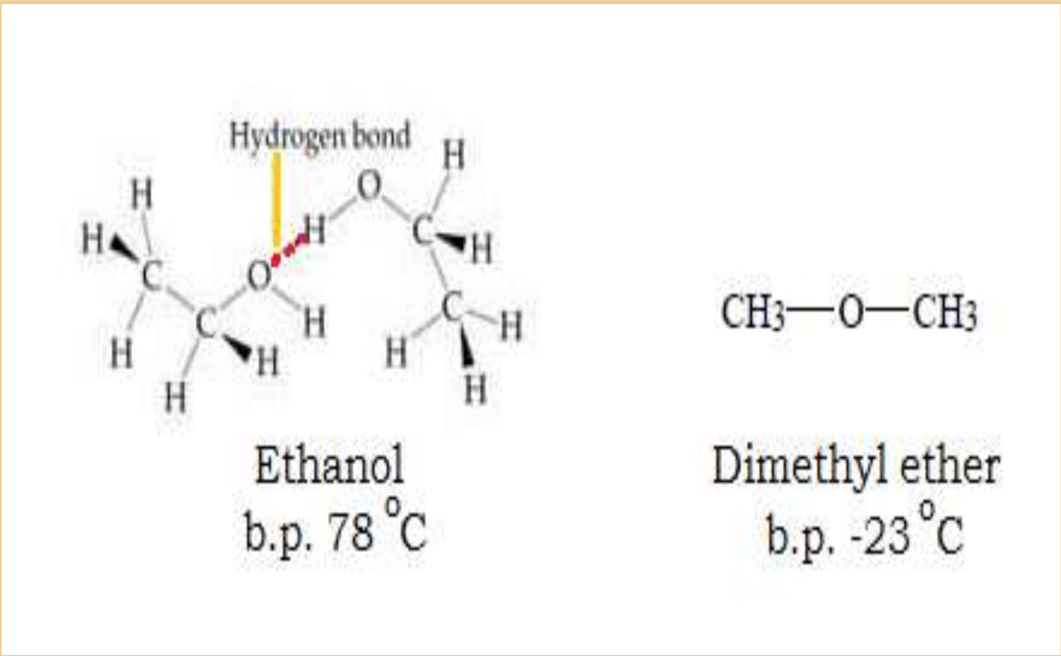
A great deal of energy is required for a pair of oppositely charged ions to break away from the liquid ; So , boiling occurs only at a very high temperature.

B- Non ionic compound :

The units of a non - ionic compound is molecules, weak intermolecular forces here :

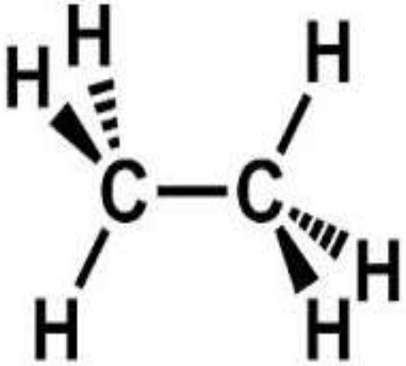
a- Intermolecular hydrogen bond :

Liquids whose molecules are held together by hydrogen bonds are called *associated liquids* . breaking these H-bonds takes a considerable energy.

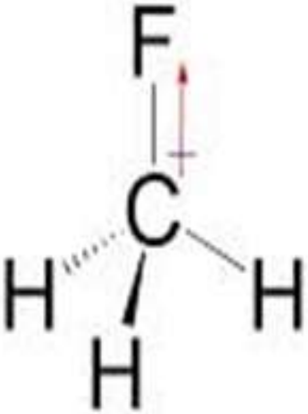


b- Dipole – dipole interaction forces :

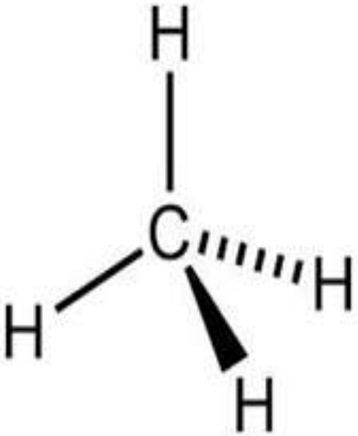
It takes place in polar molecules ; It's the attraction of the
+ ve end of one polar molecule for the - ve end of another
polar molecule



Ethane
molar mass 30.03 g/mol
m.p. -182.8°C
b.p. -88.5 °C



Flouromethane
molar mass 34.03 g/mol
m.p. -137.8 °C
b.p. -78.4 °C

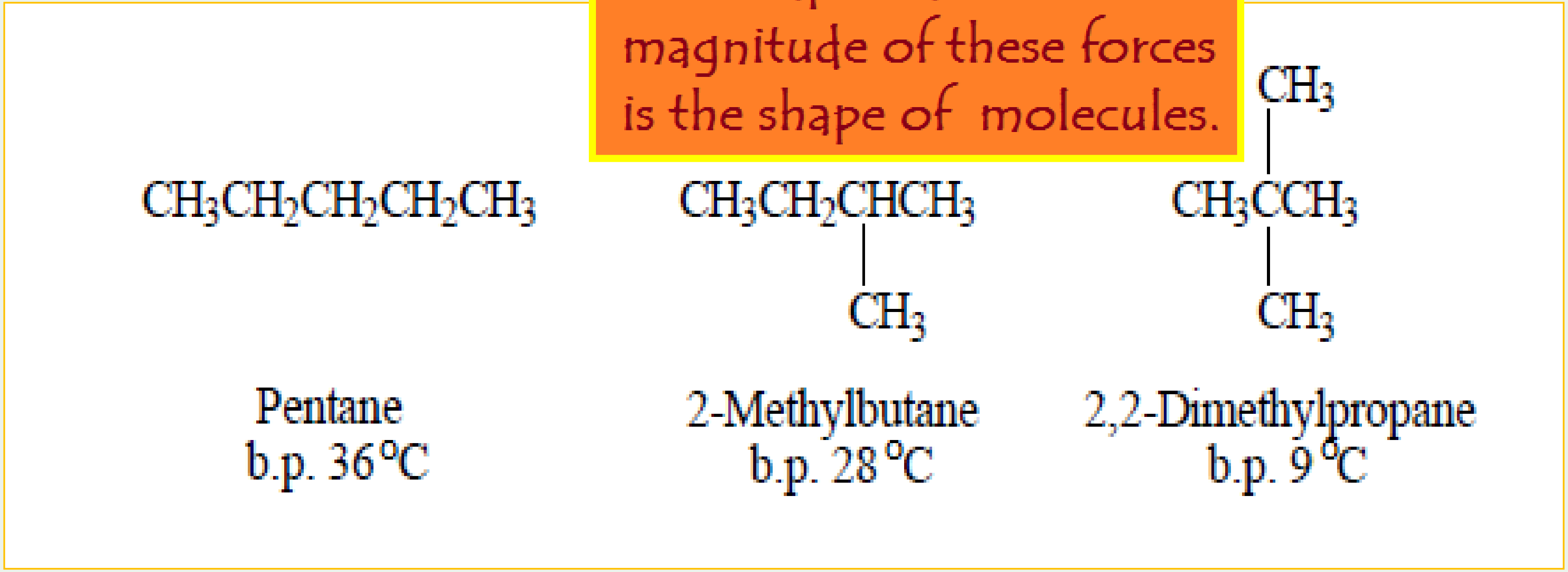


Methane
molar mass 16.04 g/mol
m.p. -182.5°C
b.p. -161.5 °C

c- Van der Waals forces:

Also called induced polarizations or induced dipoles have a very short range act between portions of different non - polar molecules that are in close contact, i.e. , between the surface of molecules.

The major factor in the magnitude of these forces is the shape of molecules.



$CH_3CH_2CH_2CH_2CH_3$

Pentane
b.p. 36°C

$CH_3CH_2CHCH_3$ with CH_3 below CH

2-Methylbutane
b.p. 28 °C

CH_3CCH_3 with CH_3 above and below C

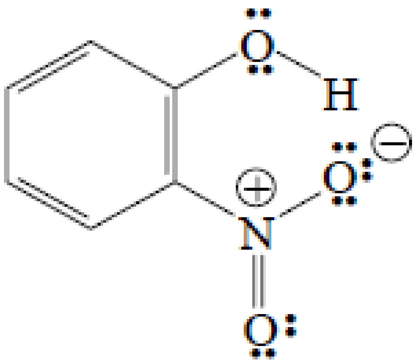
2,2-Dimethylpropane
b.p. 9 °C

↓ **Branching of molecule → ↑ S.A. → ↑ Van der Waals → ↑ b.**

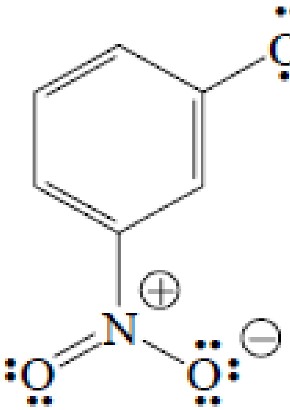
↑ **Branching of molecule → ↓ S.A. → ↓ Van der Waals → ↓ b.**

4- intramolecular hydrogen bond:

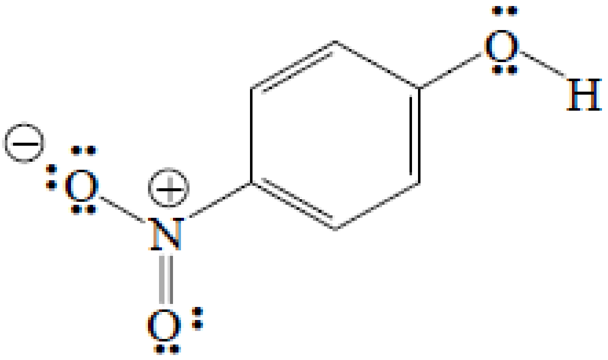
It's much more important than an intermolecular H - bond in determining the properties of the molecule.



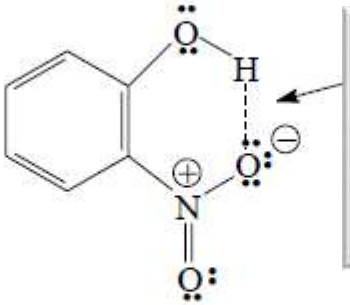
2-Nitrophenol
b.p. 215 °C



3-Nitrophenol
b.p. 263 °C



4-Nitrophenol
b.p. 279 °C



intramolecular H-bond prevents an intermole. H-bond from forming.

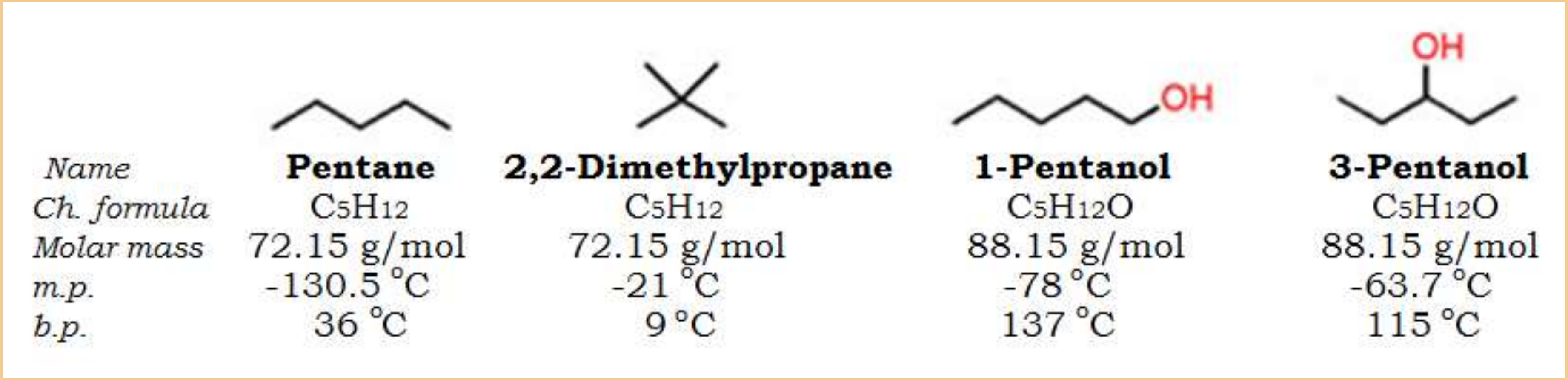
2-Nitrophenol

Thus, there are no strong intermolecular forces to be overcome in going from the liquid phase to the gas phase.

5- Branching:

In homologous series, with in the same molecular weight, as ↑ branching of the molecule → ↓ b.p.

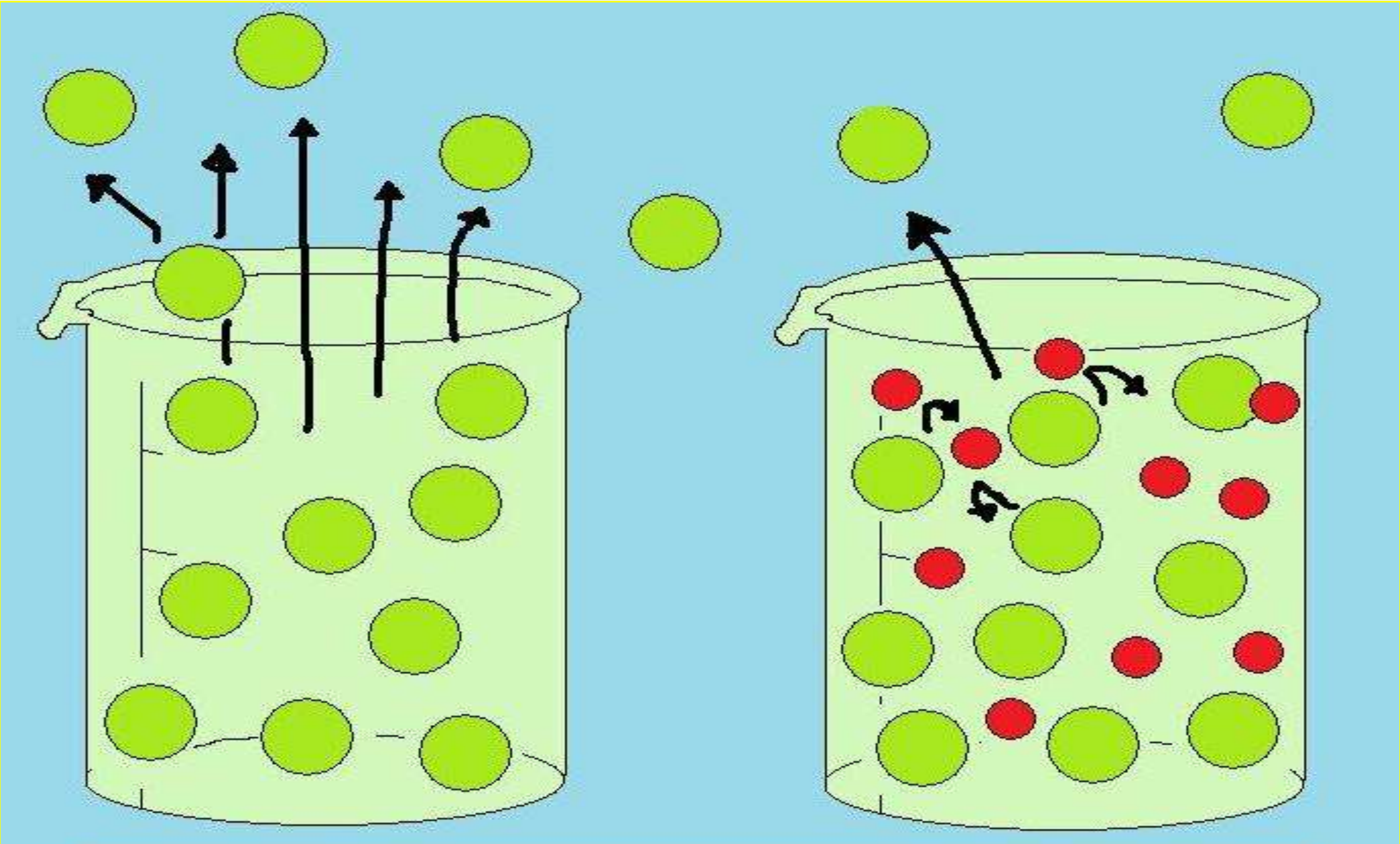
& vice versa



Name	**Pentane**	**2,2-Dimethylpropane**	**1-Pentanol**	**3-Pentanol**
Ch. formula	C_5H_{12}	C_5H_{12}	$C_5H_{12}O$	$C_5H_{12}O$
Molar mass	72.15 g/mol	72.15 g/mol	88.15 g/mol	88.15 g/mol
m.p.	-130.5 °C	-21 °C	-78 °C	-63.7 °C
b.p.	36 °C	9 °C	137 °C	115 °C

6- Presence of impurities :

Pure liquids have sharp b.p. while mixtures show a b.p. range. Presence of impurities raises the boiling point of a particular liquid.



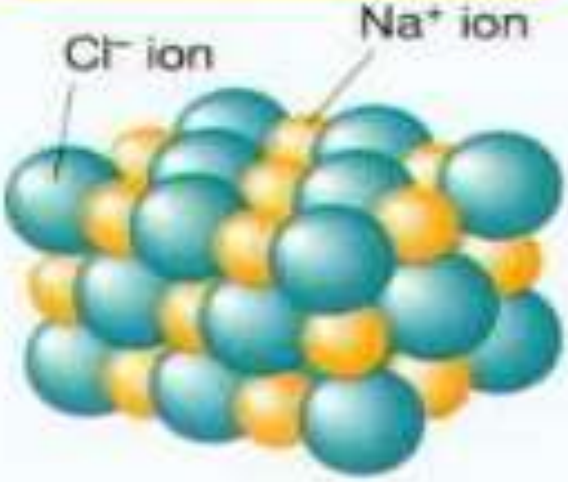
System A

In system A, the liquid particles easy shift into the gas phase at the normal boiling pressure. There are no obstacles for the liquid particles as there is in System B.

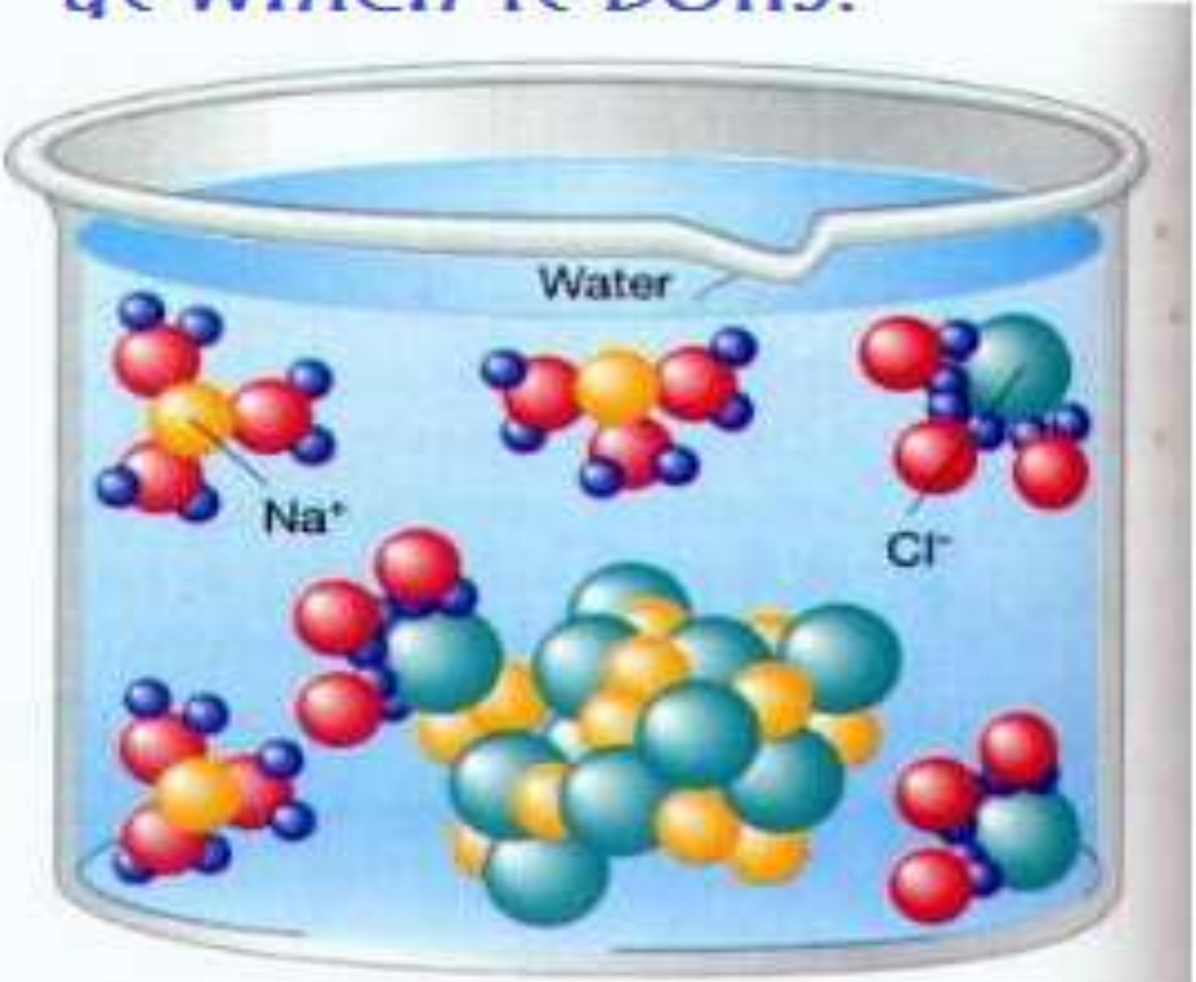
System B

In system B, the solute particles prevent the liquid particles from escaping the system to turn into gas. This requires the liquids to possess more energy to become a gas.

Adding salt to water will increase the temp. at which it boils.



Salt crystal



Number of Experiment: II

Name of Experiment: Determination of the Boiling point of an unknown sample.

Aim of Experiment:

1- Identification of an unknown cpd. using it's b.p.

2- Determination of purity of a cpd. using b.p. as a physical property.

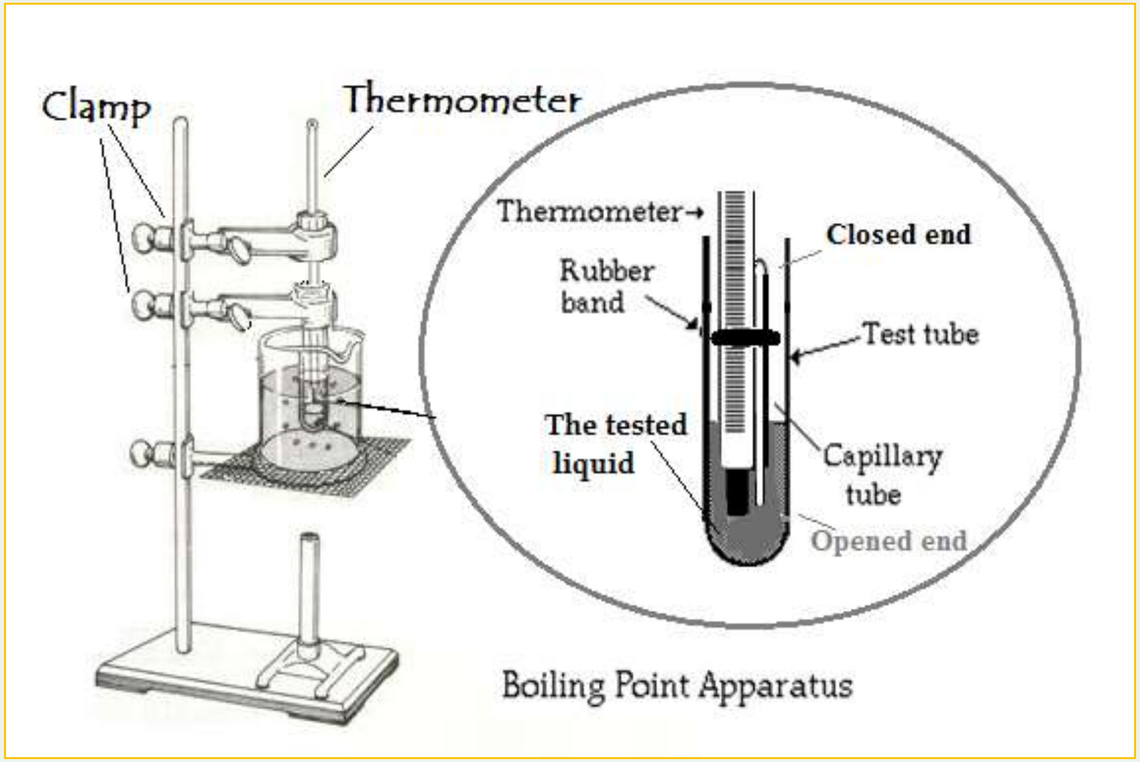
Procedure:

1- A 5 cm capillary tube closed from one end is inverted upside down & is attached to a thermometer by a rubber ring.

2- Place them in a clean & dry test tube containing a small quantity of a liquid whose boiling point is to be measured, the rubber ring should be above the surface of the liquid.

3-The whole assembly is to be placed in an oil bath.

4- Start heating with continuous stirring until a rapid stream of bubbles comes out of the capillary tube.



Boiling Point Apparatus

5- Remove the flame & allow the oil bath to cool so that the bubble stream will become slower and slower as the temperature drops until a point is reached at which bubbling ceases & the liquid starts to raise inside the capillary tube.

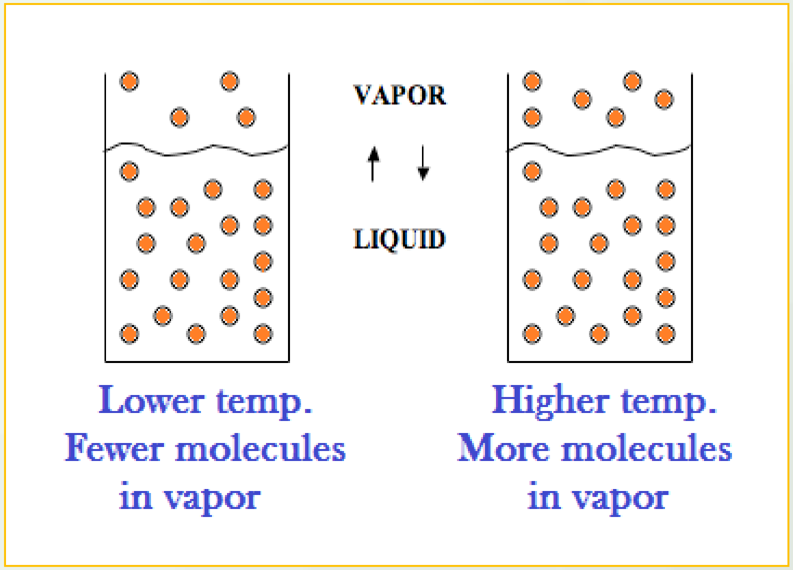
6- Record this temperature as the b.p. of the liquid.

Distillation

It is a process of separation & purification of liquid organic cpd.s by selective evaporation & condensation.

It may result in complete separation (nearly pure) , or ,a partial separation that increase the concentration of selected cpd. of the mixture.

The temp . at which a liquid distills is a definite value at a given pressure , for every pure organic cpd called boiling point.



Aim of the Distillation:

1- Purification of liquid organic cpd.
2- Determination of the boiling point.
3- Separation of liquid organic substances from each other or from a non-volatile solid cpd.s

Types of distillation:

1- Simple distillation.
2- Vacuum distillation.
3- Steam distillation.
4- Fractional distillation.
5- Reflex.

Simple Distillation:

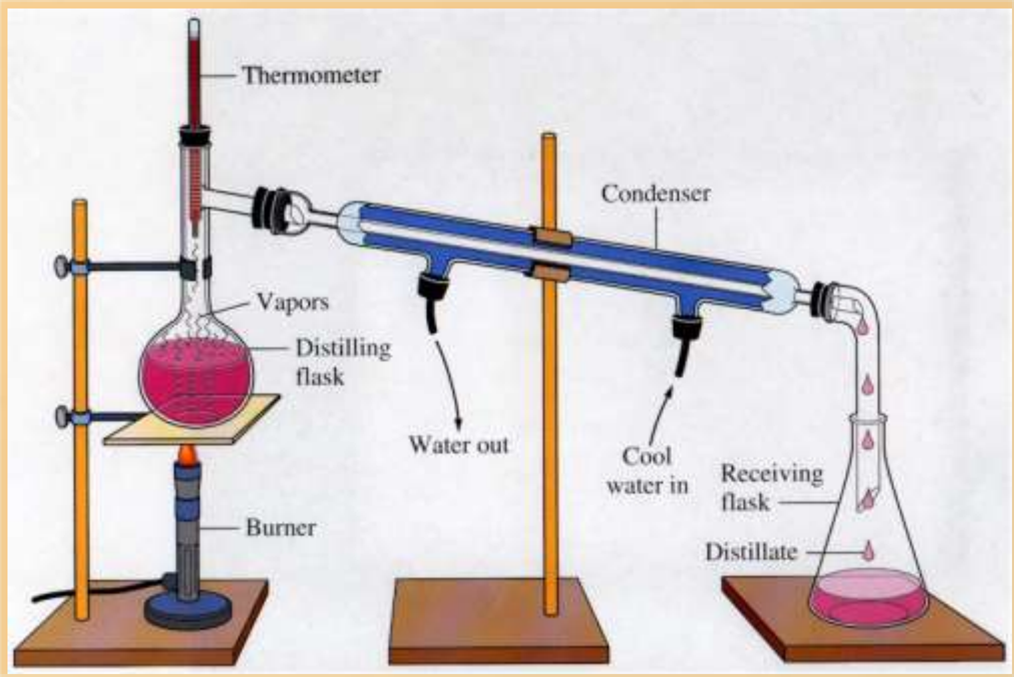
In simple distillation the vapor is immediately channeled into a condenser, so the distillate is identical to the composition of the vapors at the given temp. & pressure. That concentration follows Raoult's law.

It is effective as purification process when,

1- The liquid bp.s differ greatly (25 °C).
2- Separating liquids from non-volatile solids or oils

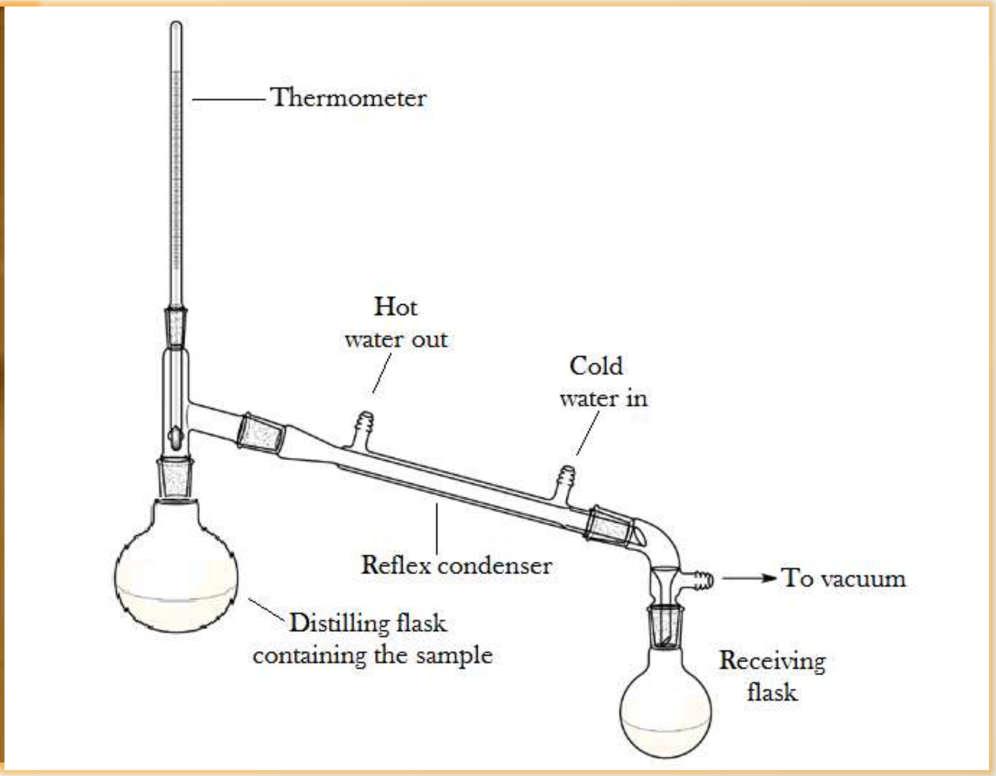
For these cases,

the vapor pressure of the components is different enough that the distillate may be sufficiently pure for it's intended purpose.

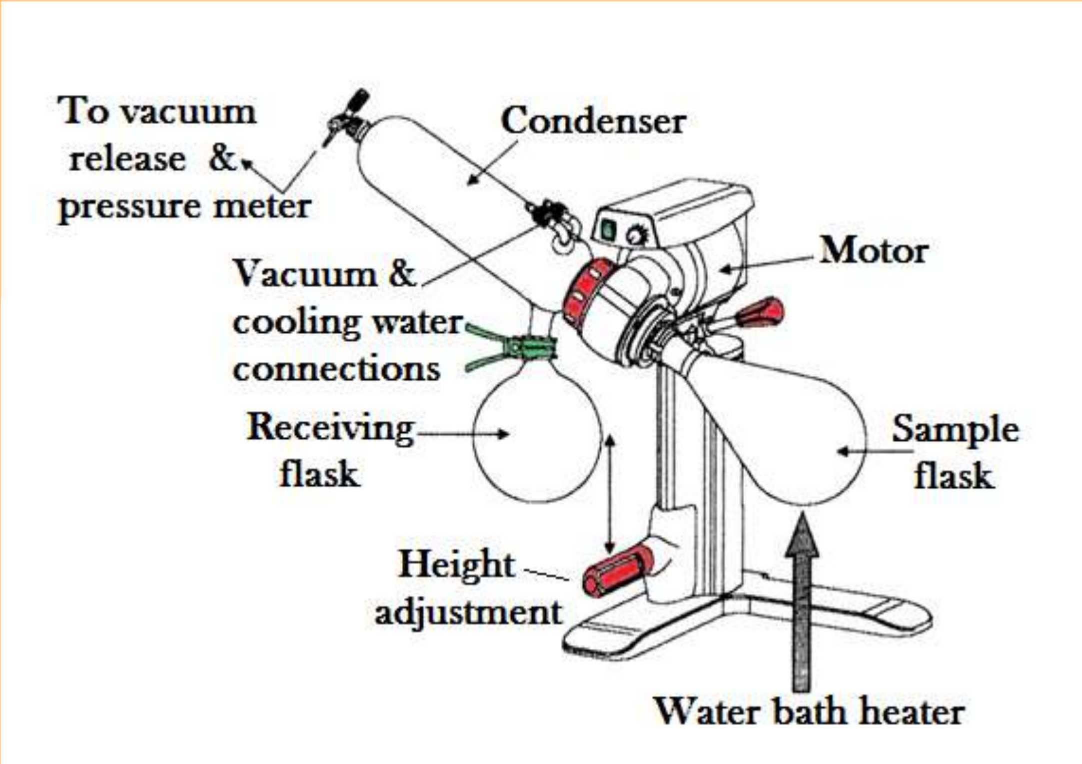


Vacuum Distillation:

Some cpd.s have very high b.p.s or unstable to heat. To boil such cpds it is better to lower the pressure at which such cpds are boiled instead of increasing the temp. Once the pressure is lowered to the vapor pressure of the cpd , at a given temp., boiling & the rest of the distillation process can commence. This technique is referred to as vacuum distillation.

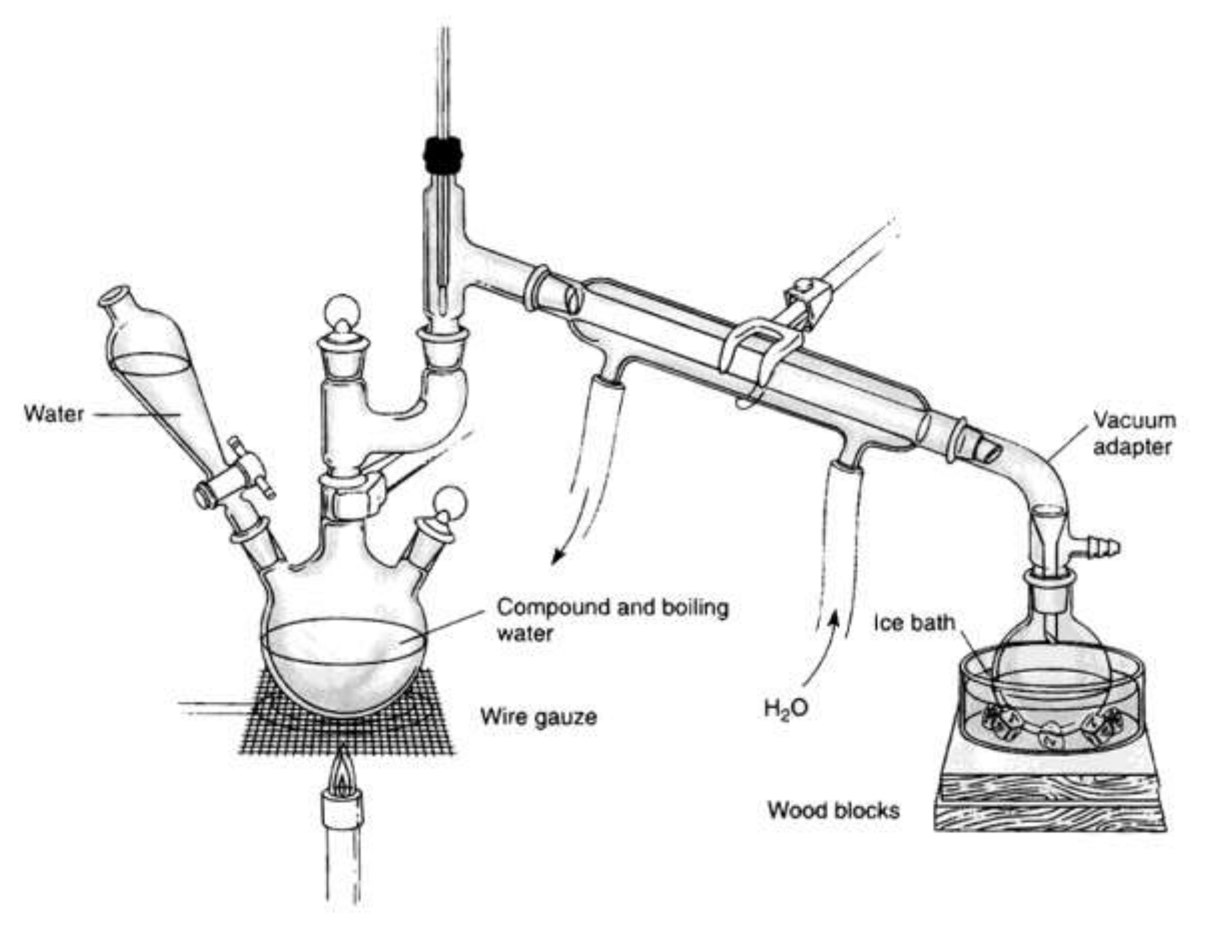


Rotary Evaporator



Steam Distillation:

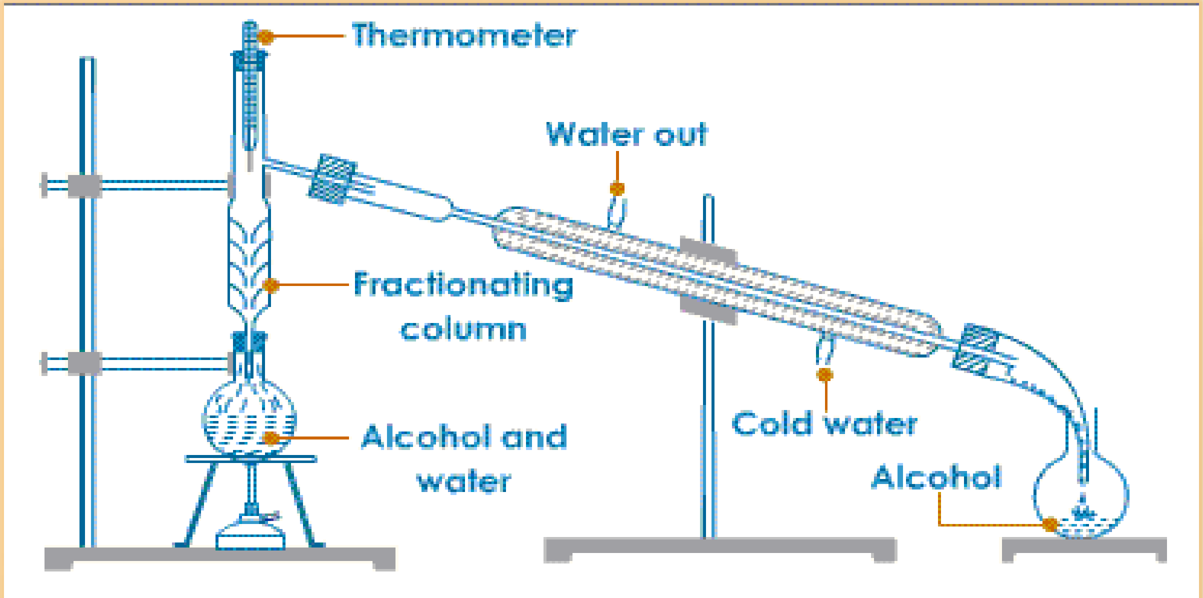
This method is used for the separation of water immiscible compound of low volatility from non- volatile tarry products which are formed as by-products in many reactions.



Fractional Distillation:

It is used to separate mixtures in which the components have boiling points that differ by only a few degrees, by employing a fractionating column in the distillation apparatus.

So, fractional distillation is a process of collecting separate fractions according to controlled boiling ranges during the distillation of a mixture of substances.



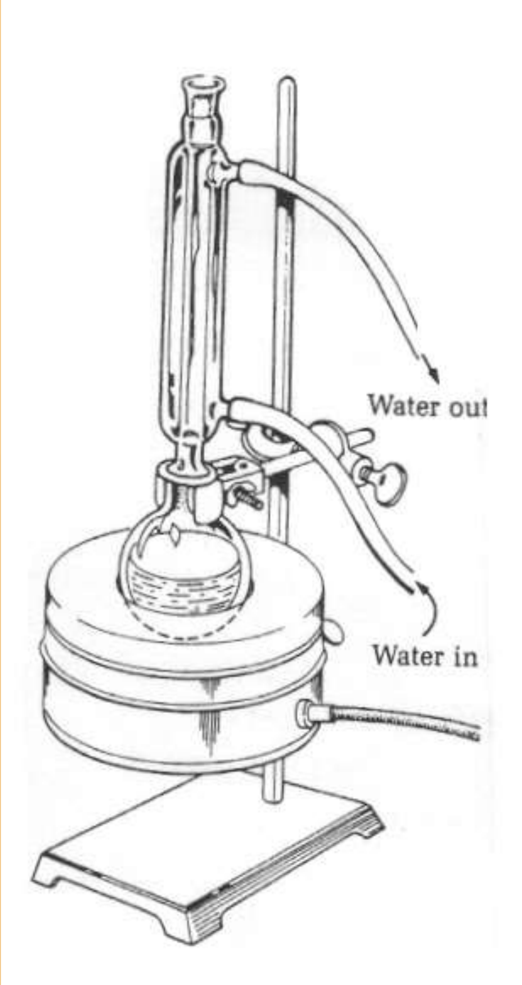
Fractional Distillation

Fractionating column
Packed column

Reflex Distillation:

Reflex is a distillation technique involves the condensation of vapors & the return of this condensate to the system from which it originated.

This method is used to keep or prevent the reactants from loss by evaporation during a reaction.



Azeotropic mixture:

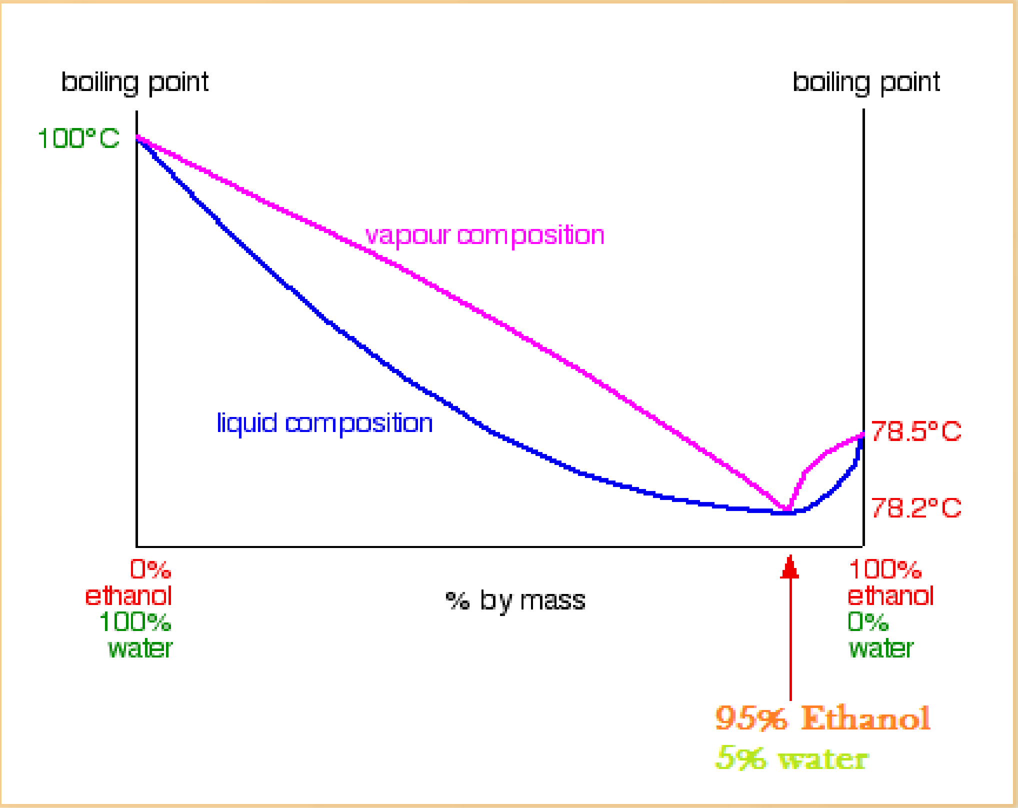
Azeotropic , a constant boiling, mixture is a mixture of two or more liquids whose proportions cannot be altered by simple distillation.

This happens because when an azeotrope is boiled, the vapor pressure has the same proportions of constituents as the unboiled mixture.

For example,

95% Ethyl alcohol & 5% water produce an Azeotropic mixture, which boils at 78.15 °C.

Ethanol , Benzene and Water azeotrope boils at 64.9 °C.



Name of experiment: **SIMPLE DISTILLATION**

Aim of experiment: Purification of Ethanol

Procedure:

1- Put 100 ml of ethanol in a boiling flask.
2- Add 2-3 pieces of boiling chips.
3- Start the water running slowly through the condenser.
4- Heat until boiling.
5- Adjust the temperature so that distillation proceeds at 2-3 drops per second. Discard the first 2-3 ml of the distillate.
6- Continue distillation until you collect 30-60 ml.
7- Record the boiling point of your liquid, Ethanol.

Discussion & Notes:

- Pue cpd.s distill over a very narrow range of temp.
- The b.p. is affected by impurities; some may increase the b.p.s, others may decrease it & some may not affect it.
- Usually the 1st few milliliters of the distillate contain water or volatile impurities, 2nd portion contains the substance.
- 2 - 3 pieces of broken porcelain chips are placed in the boiling flask with the substance to be distilled to prevent bumping by producing a constant stream of bubbles that keep the liquid in motion.
- If the liquid is volatile (low b.p.), the flask is heated by a water bath rather than by a flame.

2015 - 2016

Elemental Analysis

Assistant lecturer **Sahar M. Shakir**
Assistant lecturer **Wid Kadhim**

Elemental analysis

It is a process where a sample is analyzed for its elemental composition.

Elemental analysis can be:

1- Qualitative: determining what elements are present

2- Quantitative: determining how much of each are present.

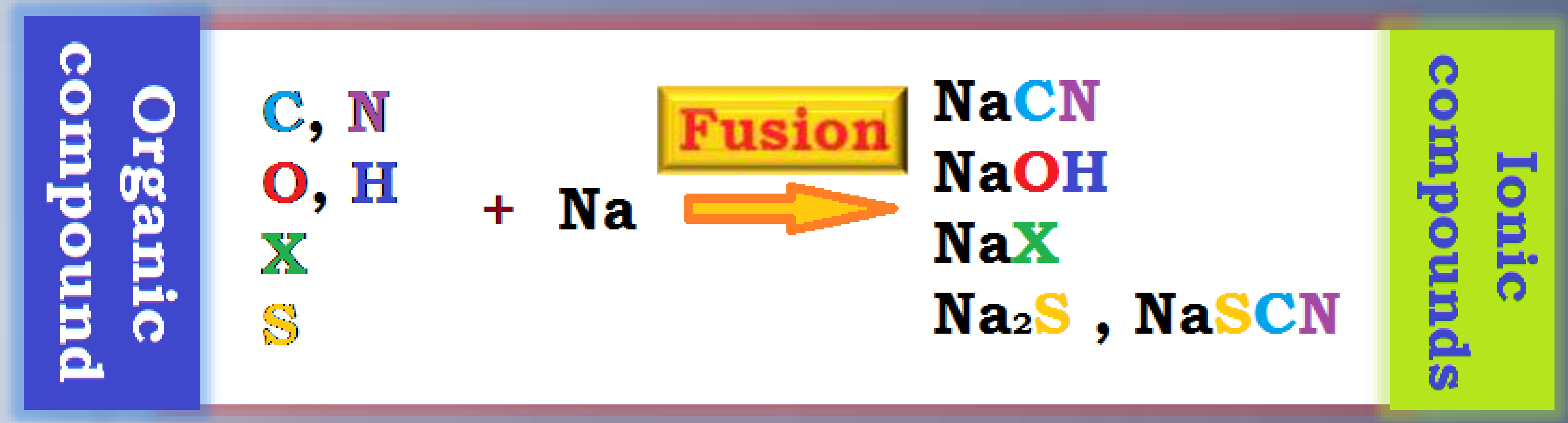
Qualitative elemental analysis:

The chief elements making up organic cpd.s are **C , H & O** for which the organic chemist do not employ chemical tests.

It is often valuable to determine the existence of other elements next in importance such as **N, halogens (Cl, Br, F & I) & S** .

Sodium fusion method:

It's used for the qualitative determination of the presence of halogens , **N** and **S** in a sample.



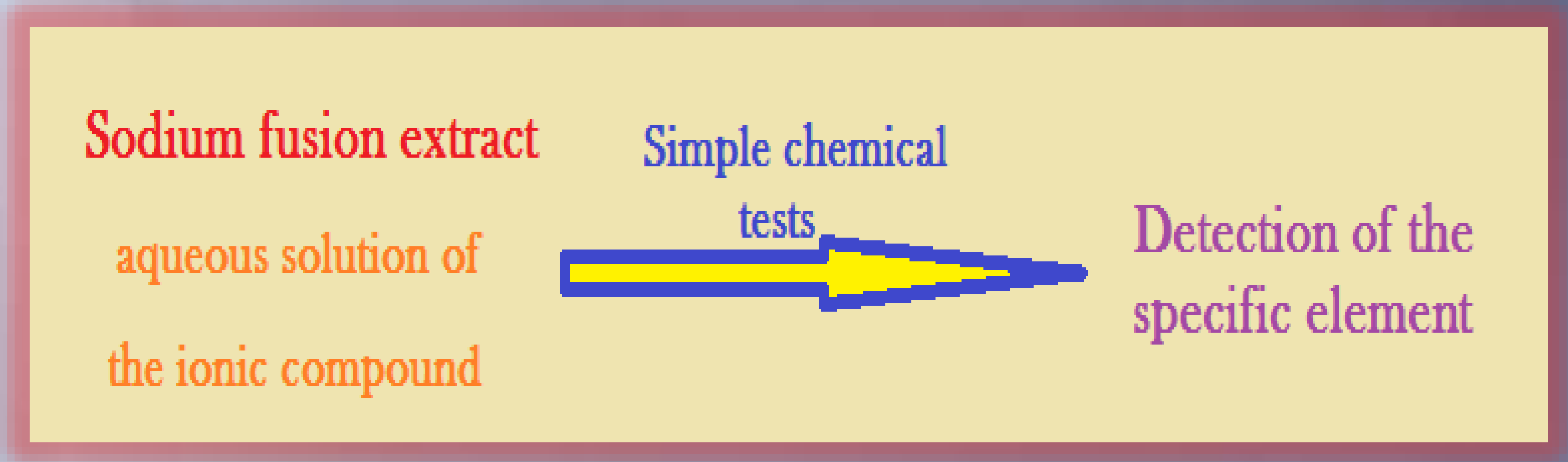
Organic compound

C, N
O, H
X
S

$$\text{C, N, O, H, X, S} + Na \xrightarrow{\text{Fusion}} NaCN,\ NaOH,\ NaX,\ Na_2S,\ NaSCN$$

NaCN
NaOH
NaX
Na_2S , NaSCN

Ionic compounds

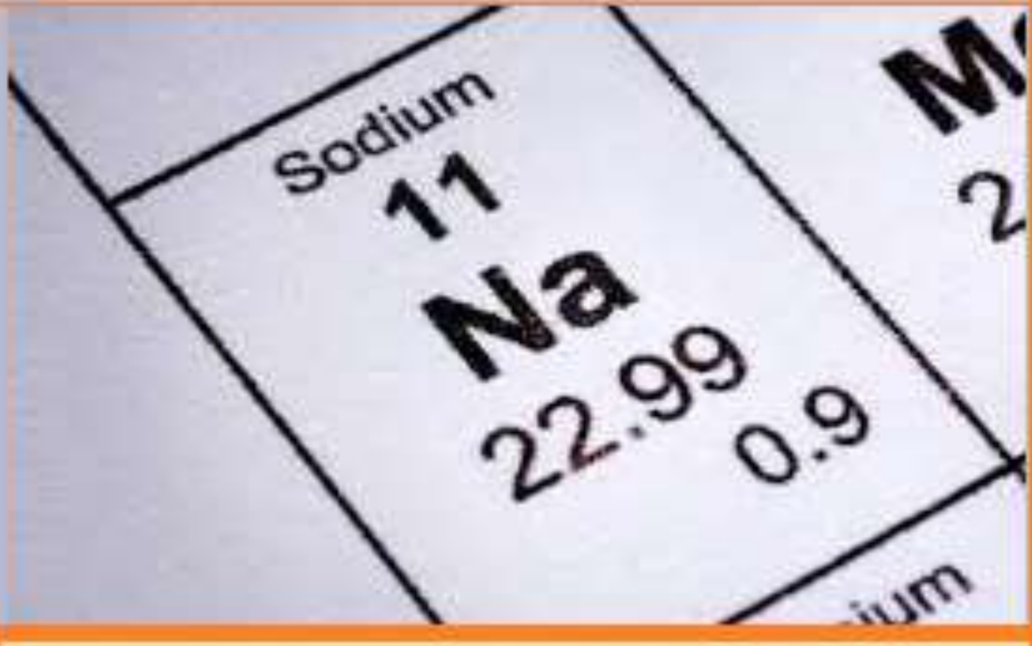


Sodium fusion extract

aqueous solution of the ionic compound

Simple chemical tests

Detection of the specific element




It is kept dipped in liquid paraffin

Bright silvery alkali metal

Cubic crystal

m.p. 97.8 °C
b.p. 882.9 °C


Sodium can be readily cut with a knife

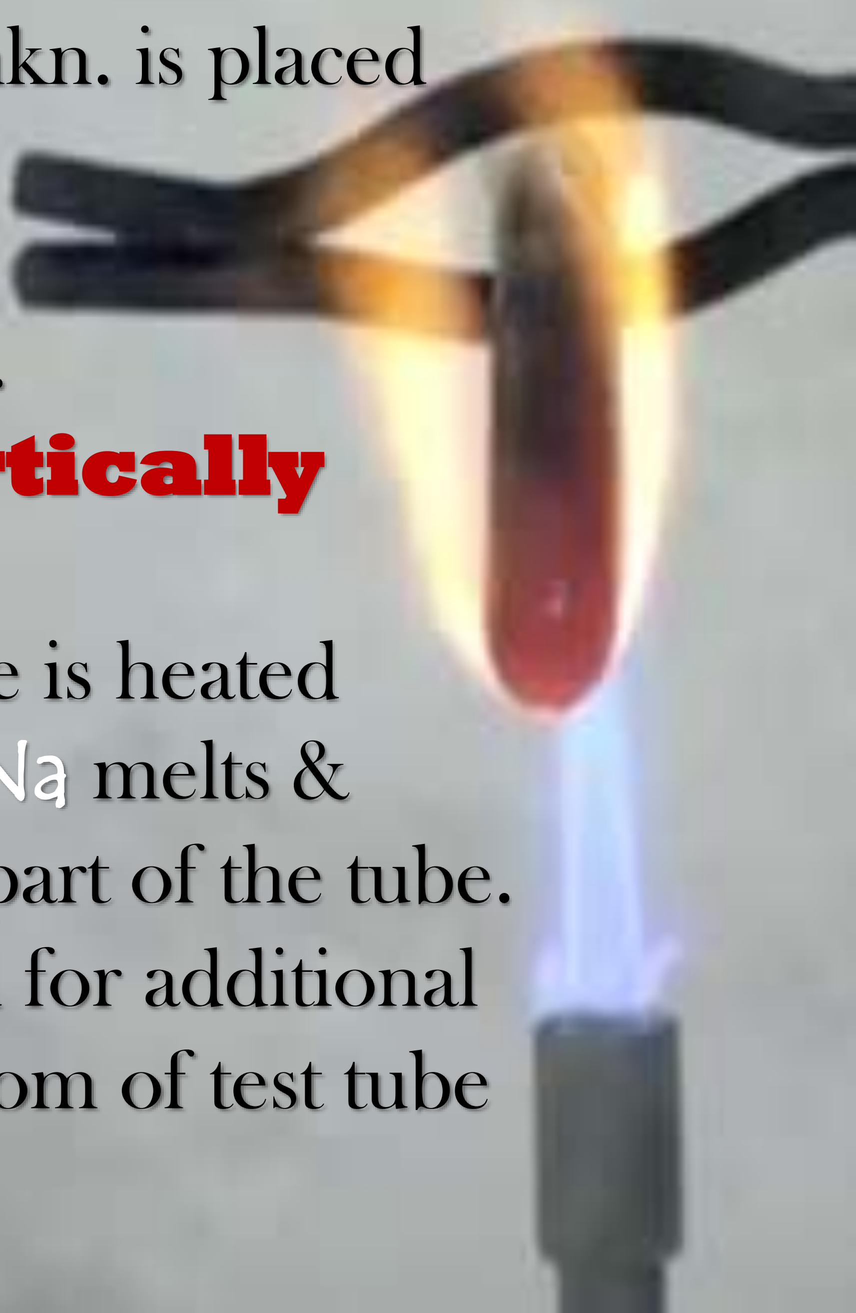
Sodium reacts **vigorously** and **Exothermically** with water

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

Free Na does not occur in nature

It must be prepared from it’s cpd.s

PROCEDURE:

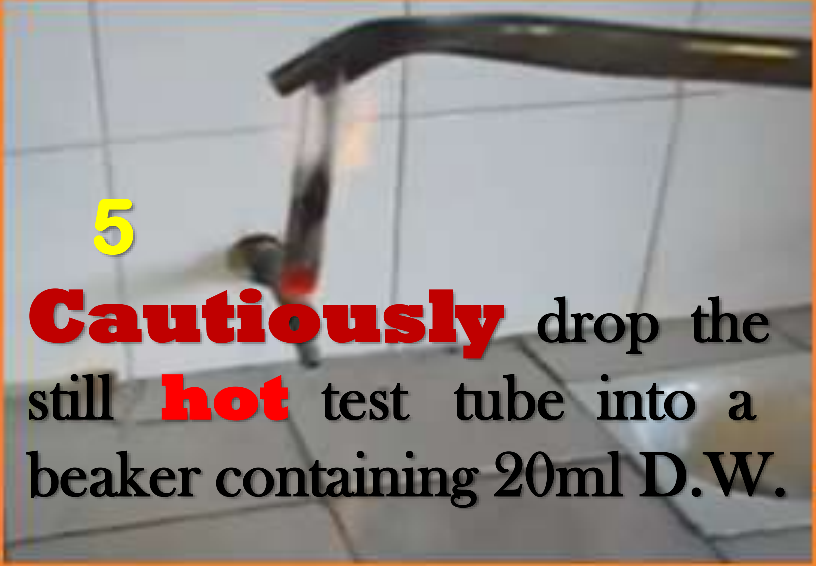


1- A small quantity of the unkn. is placed in a **clean**, **dry** test tube together with a small piece of Na metal.

2- The test tube is held **vertically** by a clamp.

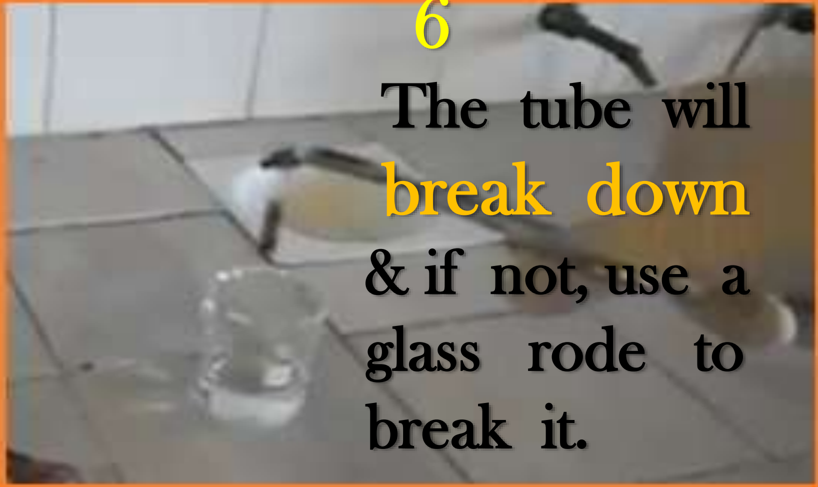
3- The lower part of the tube is heated **gradually** until the Na melts & it's vapours fill the lower part of the tube.

4- Heating is then continued for additional **5** minutes until the bottom of test tube becomes **red**.



5

Cautiously drop the still **hot** test tube into a beaker containing 20ml D.W.

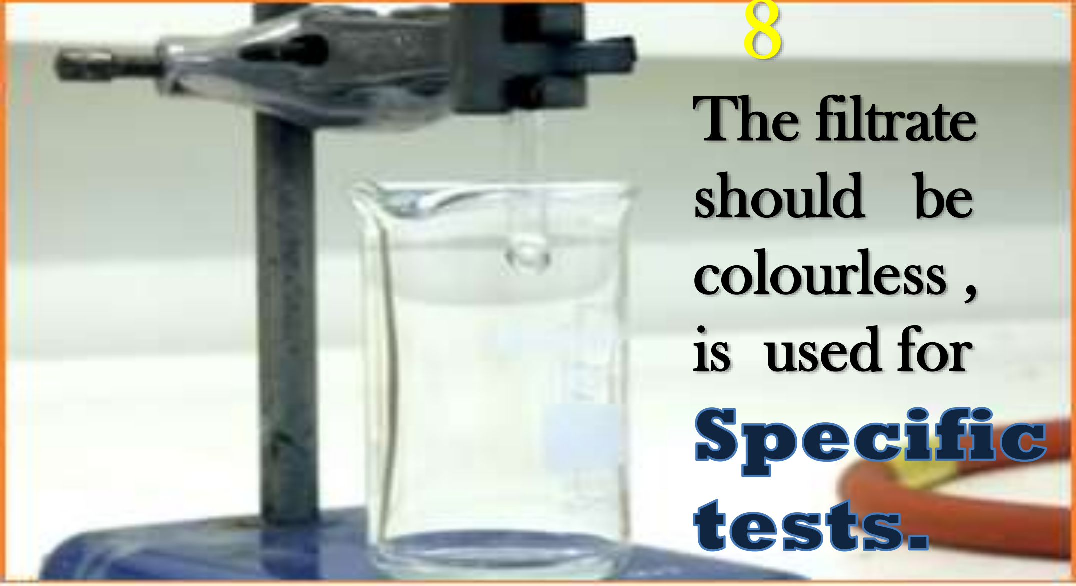


6

The tube will break down & if not, use a glass rode to break it.

7

The resulting sln. is heated to **boiling** & **filtered.**



8

The filtrate should be colourless , is used for **Specific tests.**

To remove the excess unreacted **Na** add a small quantity of **alcohol** to the test tube before breaking it with heating so that the alcohol will react
with the excess **Na** to give **sodium alkoxide**.

$Na + CH_3CH_2OH \rightarrow NaOCH_2CH_3$

Specific tests for elements

Detection of Nitrogen:

1- To a **3ml** of the filtrate add **4 drops** (0.2 gm) of **ferrous sulfate** soln.

2- Check the basicity of the soln. and make it basic by the addition of enough **NaOH** soln. (**10 %**).

3- Heat for **boiling** (**30 sec.**) .

4- Now add drops of dilute **H_2SO_4** enough to make the soln. **acidic** .

5- A **Prussian blue** precipitate indicates a **+ve** test of **N** .

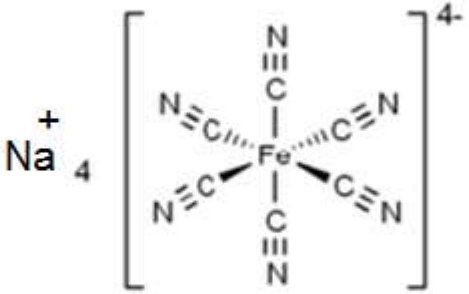
$$\mathrm{Na} + \mathrm{C} + \mathrm{N} \xrightarrow{\text{Fusion}} \mathrm{NaCN}$$

From organic compound

$$2\mathrm{NaCN} + \mathrm{FeSO_4} \xrightarrow[\text{NaOH}]{\text{Basic}} \mathrm{Fe(CN)_2} + \mathrm{Na_2SO_4}$$

$$\mathrm{Fe(CN)_2} + 4\,\mathrm{NaCN} \longrightarrow \mathrm{Na_4Fe(CN)_6}$$

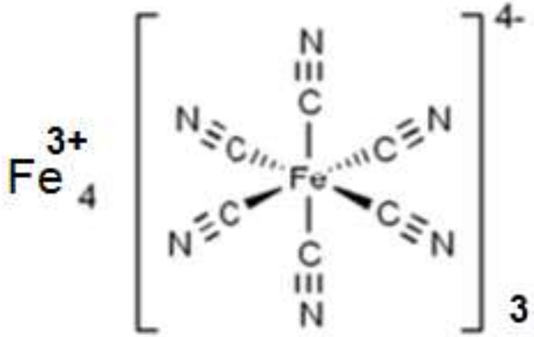
Sodium ferrocyanide



$$3\mathrm{Na_4Fe(CN)_6} + 2\,\mathrm{FeSO_4} \xrightarrow[\text{H}_2\text{SO}_4]{\text{dil.}} \mathrm{Fe_4[Fe(CN)_6]_3} + 6\,\mathrm{Na_2SO_4}$$

Ferric ferrocyanide

(Blue colour)



Detection of Sulfur :

1- **Acidify 2 ml** of the filtrate with dilute **acetic acid**.

2- Add **5 drops** of **lead acetate** soln.

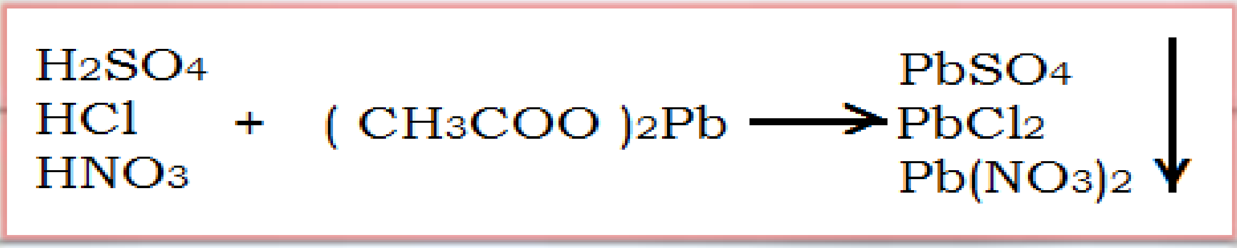
a **black** precipitate of **lead sulfide** indicates the presence of **sulfur**.

$$\underset{\substack{\text{Sodium}\\ \text{sulfide}}}{Na_2S} + \underset{\text{Lead acetate}}{(CH_3COO)_2Pb} \xrightarrow[\text{dilute}]{CH_3COOH} \underset{\substack{\text{Lead sulfide}\\ \textbf{Black ppt.}}}{PbS} + \underset{\text{Sodium acetate}}{2\ CH_3COONa}$$

Acetic acid is used in the acidification & not other acid (H_2SO_4, HCl , HNO_3)

since,

they give insoluble white ppt. by reaction with lead acetate.



$$\left.\begin{array}{l} H_2SO_4 \\ HCl \\ HNO_3 \end{array}\right. + (CH_3COO)_2Pb \longrightarrow \left.\begin{array}{l} PbSO_4 \\ PbCl_2 \\ Pb(NO_3)_2 \end{array}\right\downarrow$$

Detection of Halogen :

In case of presence of **N** and **S** in the cpd.

1- **Acidify** **3 ml** of the filtrate with dilute **HNO_3**
(add drop by drop until the soln becomes **acidic**)

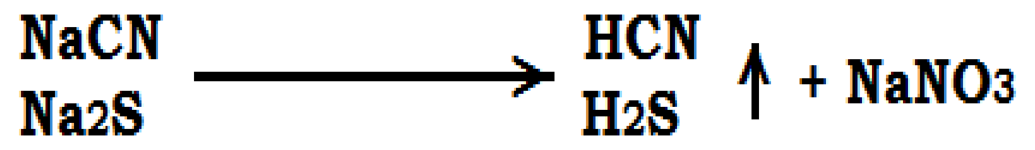
2- **Boil** for **5 minutes** & add drops of **$AgNO_3$**
White or **yellow** ppt. indicates the presence of halogens.

$NaX + AgNO_3 \rightarrow$

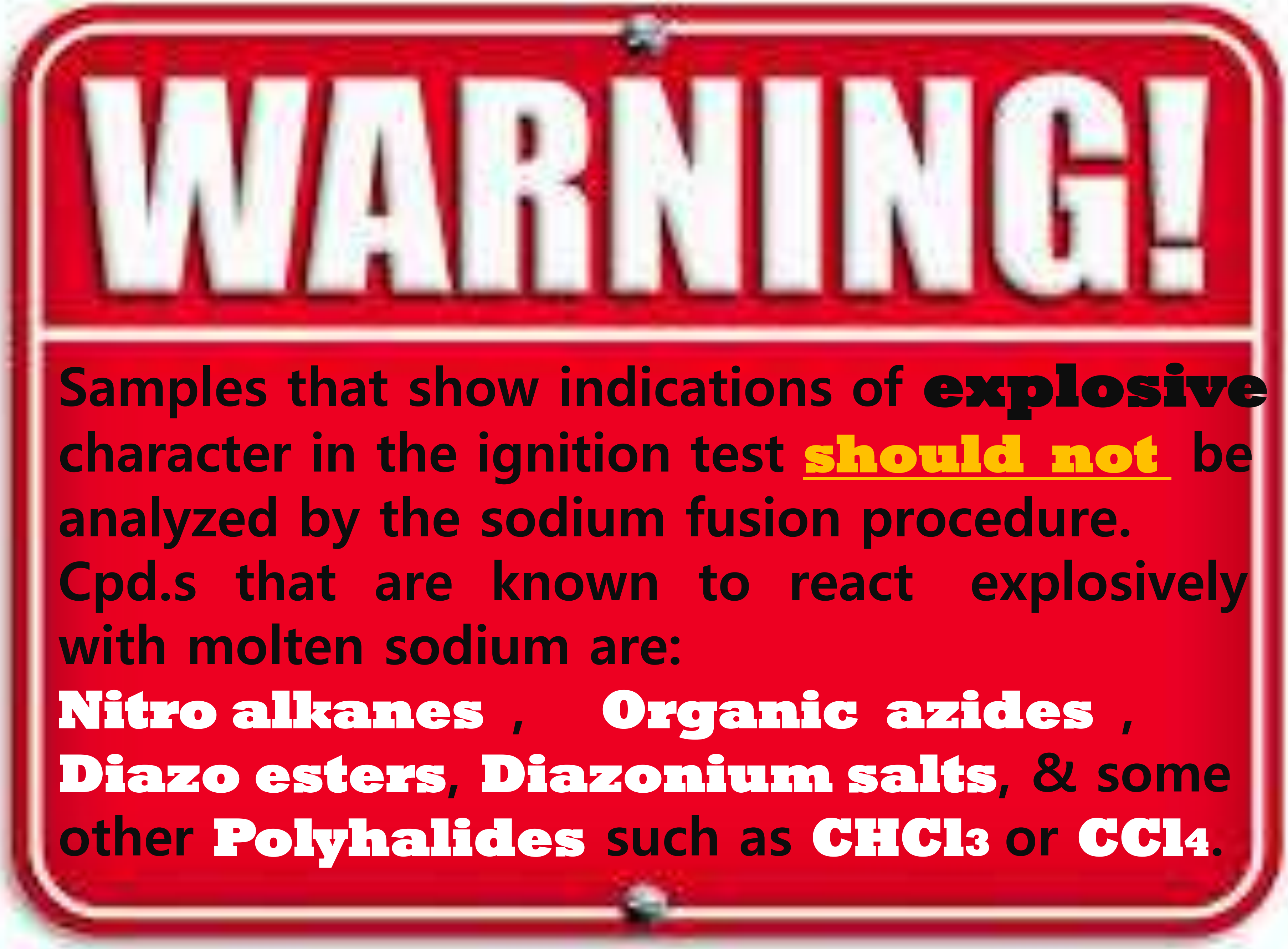
X = Cl, Br, I

AgCl **White ppt.**
AgBr **Off white ppt.**
AgI **Yellow ppt.**

Boiling for **5 min.s** is done to remove **N** & **S** present in filtrate as HCN and H_2S gases.



$$\begin{matrix}NaCN\\Na_2S\end{matrix}\longrightarrow\begin{matrix}HCN\\H_2S\end{matrix}\uparrow + NaNO_3$$



Samples that show indications of **explosive** character in the ignition test **should not** be analyzed by the sodium fusion procedure.

Cpd.s that are known to react explosively with molten sodium are:

Nitro alkanes , **Organic azides** , **Diazo esters**, **Diazonium salts**, & some other **Polyhalides** such as **$CHCl_3$** or **CCl_4**.

An unknown sample containing No halide was given to a student, then after doing his qualitative elemental analysis, the student's report read a +ve halide test (white ppt.)!! Give one possible explanation for the false result?

Answer:

There may be some drops of tap water in the glass ware used to perform halide speci. test. Tap water contain chloride ions that will react with the added silver nitrate when the student do specific halide test.

$$\underset{\text{From tap water}}{Cl^-} + AgNO_3 \longrightarrow \underset{\text{Silver chloride White ppt.}}{AgCl} + NO_3^-$$

An unknown sample containing S was given to a student, then after performing qualitative EA. the student's report read a -ve test for sulfur !!

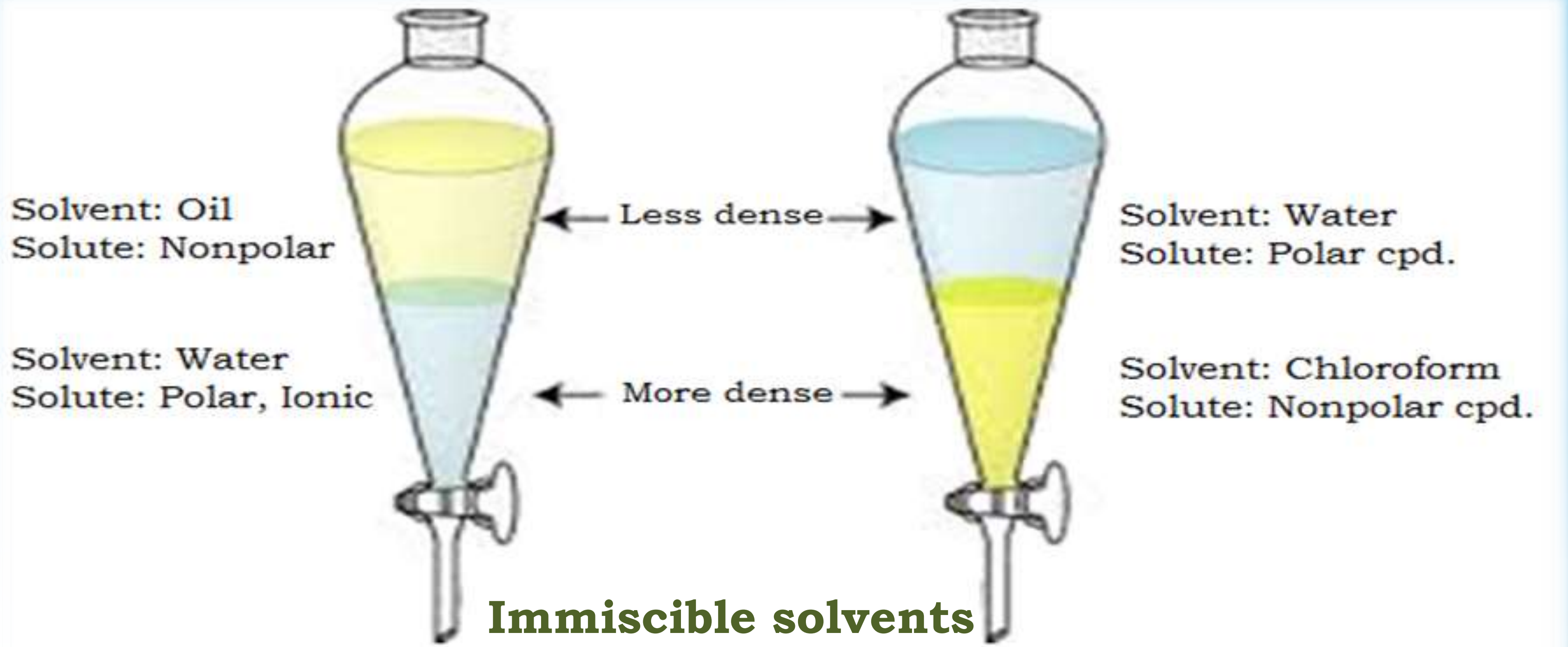
Give one possible explanation for the student's false result?

Answer:

Sulfur element may be lost as H_2S gas during fusion of the sample with sodium. (heating of the sample during fusion was not gradual)

Extraction:

It's a method of **separation** & **purification** of organic cpd.s depends on the ability of the cpd. to dissolve in two immiscible solvents, e.g., H_2O & CH_3Cl.



Immiscible solvents are mixtures of liquids Insoluble in each other

Extraction with immiscible solvents is generally employed for:

1- Isolation of dissolved cpd.s from soln.

2- Isolation of solid cpd.s from mixtures.

3- Removal of undesirable impurities From mixtures (washing).

4- Sometimes it's used in organic chemistry laboratories to remove an organic cpd. from a soln. when the use of distillation is not convenient.

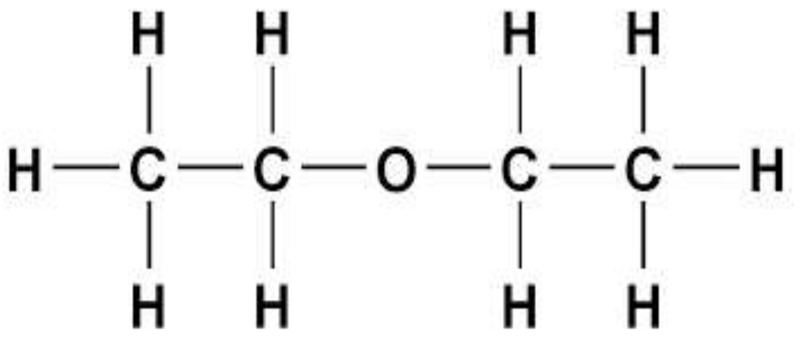
Choosing a solvent for extraction:

1- Readily dissolve the cpd. to be extracted.
2- Have a low b.p. so it can be readily removed.
3- Not react with solute or other solvent.
4- Not be flammable or toxic.
5- Show little or no water solubility (immiscible with water).
6- Be inexpensive.

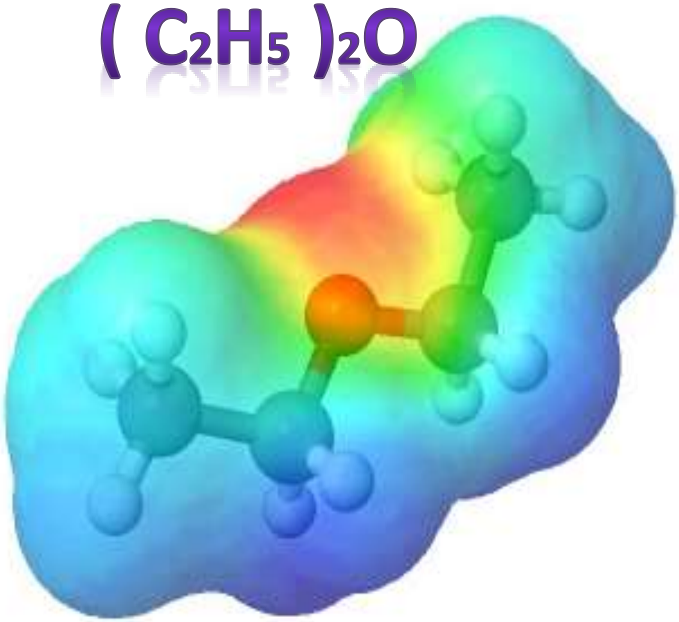
No solvent meets all these criteria,
for ex., ether,

is probably the most common solvent used for extraction but it is flammable

Diethyl ether, **Ether, $C_4H_{10}O$, Colorless liquid, Boiling point 34.6 °C , Density 0.7134 g / ml , Solubility in water 69g/L**



$(C_2H_5)_2O$



Ether:

1- Has a high solvating power for hydrocarbons & O containing cpds.

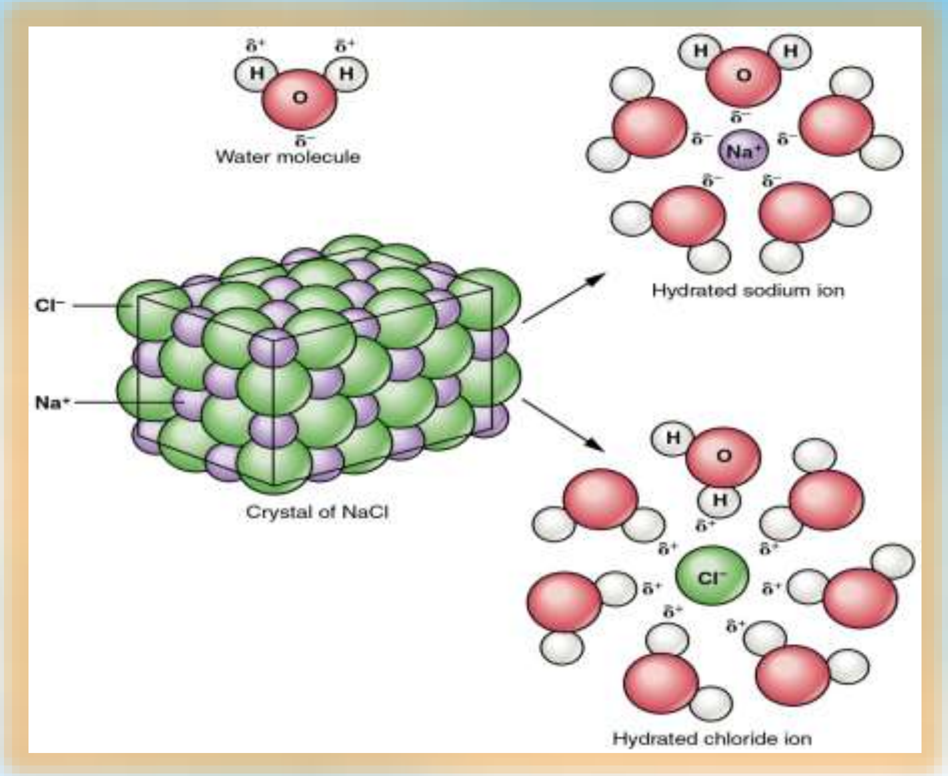
2- Is highly volatile , b.p. 34.6 °C. So that it can be easily removed from the extract at low temp. Thus even highly sensitive cpd.s are not likely to decompose.

3- Is very slightly soluble in water.

Ether, is used extensively as an extracting solvent. It's very slightly soluble in water & it's efficiency in use can be ↑ by the addition of a small amount of an ionizable salt, $NaCl$, to the water layer. This lead to an ↑ in the polarity of this soln. that result in a ↓ in the solubility of a non polar cpd. This is known as "salting out " process.

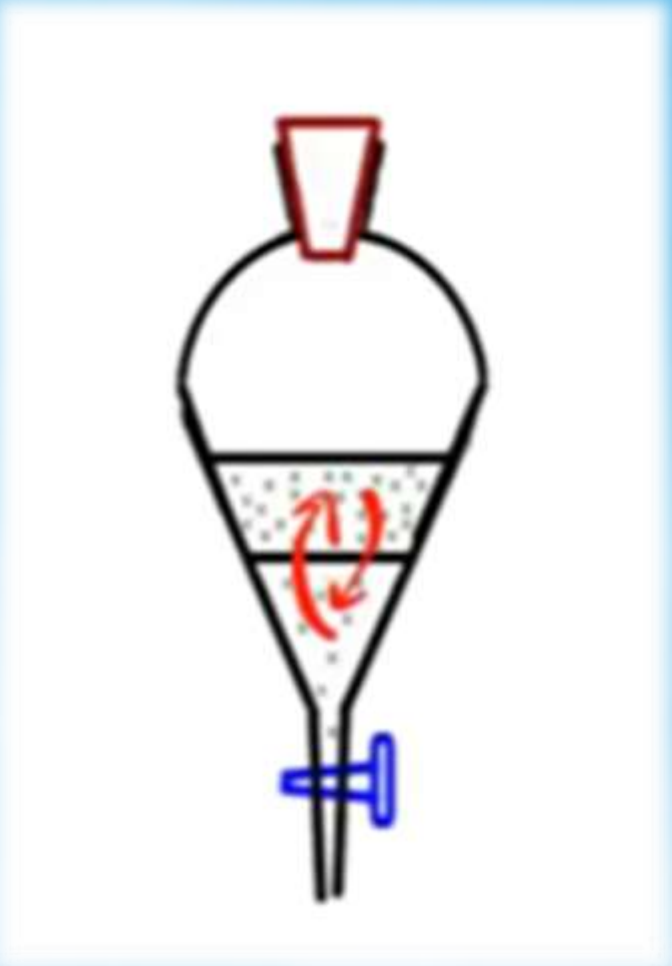
SALTING OUT ,

In aqueous soln.s of organic molecules, salt is added to separate the organic material from the salty aqueous phase.



Partition coefficient:

Partition coefficient is the ratio of concentrations of a compound in the two phases of a mixture of 2 immiscible liquids at equilibrium Normally one of the solvents is aqueous while the 2nd is organic.



$$K = \frac{\text{Conc. of compound in organic solvent}}{\text{Conc. of compound in water}}$$

$$K = \frac{\text{Solubility of compound in organic solvent } (g/100ml)}{\text{Solubility of compound in water } (g/100ml)}$$

$$K = \frac{C_{org}}{C_{w}} = \frac{Wt._{org} / V_{org}}{Wt._{w} / V_{w}}$$

Where,

C_{org} : Concentration of the solute in the organic layer.
C_{W}: Concentration of the solute in the aqueous layer.
$Wt._{org}$: Weight of the solute in the organic layer.
$Wt._{W}$: Weight of the solute in the aqueous layer.
V_{org} : Volume of the organic solvent.
V_{W}: Volume of the aqueous solvent.

Name of experiment: Solvent Extraction

Aim of experiment:

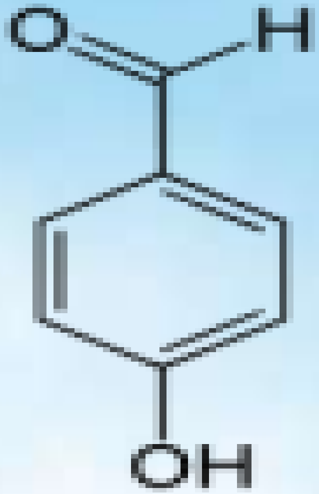
Separation of 4-hydroxybenzaldehyde from an unknown mixture containing NaCl and 4-hydroxybenzaldehyde.

Properties of the cpd.s to be separated:

4-Hydroxybenzaldehyde:

Molecular formula*: $C_7H_6O_2$, *molar mass*: 122.12 *g/mol

Yellow-tan powder, Soluble in ether, Slightly soluble in water, Sublimes.

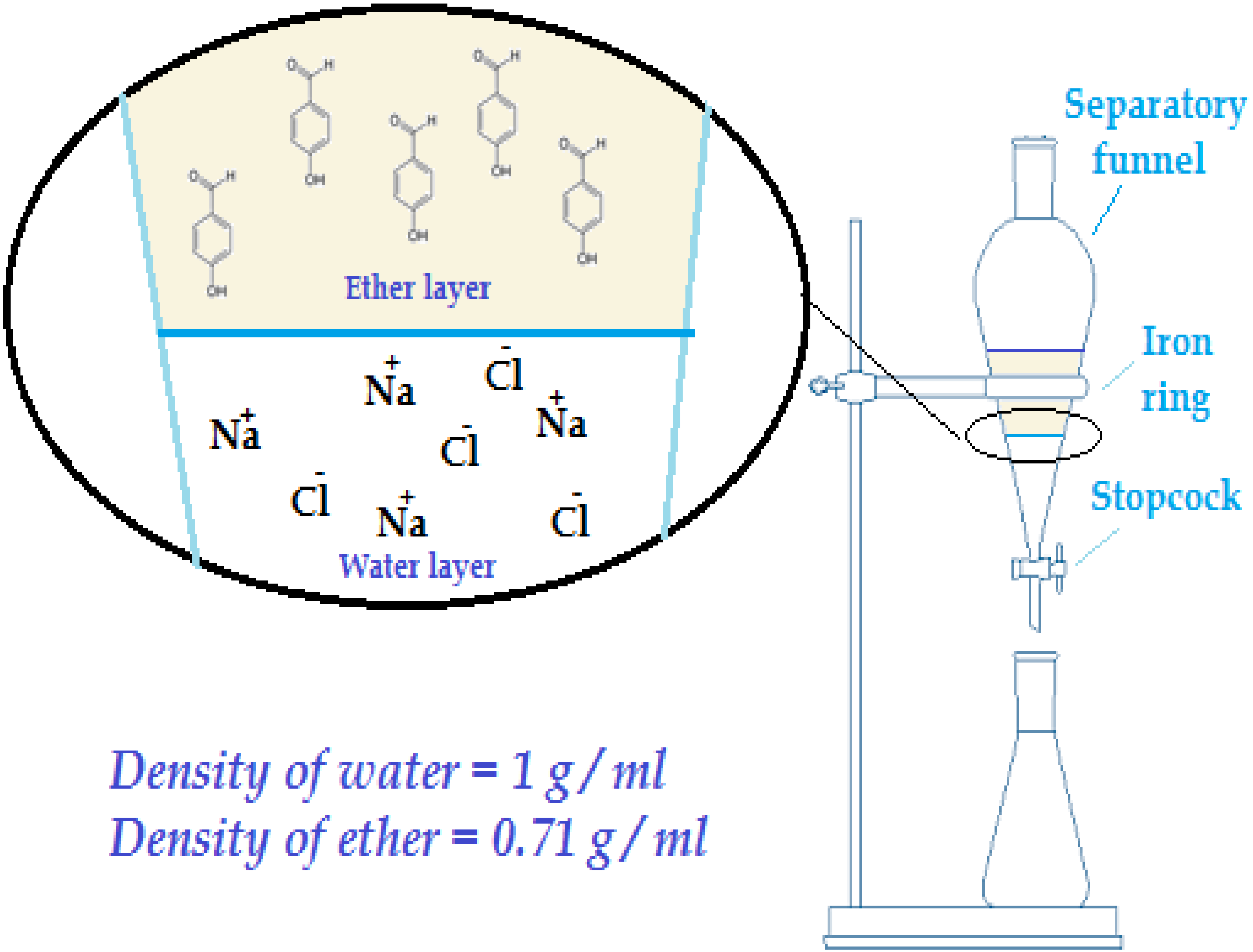


Sodium chloride:

***Molecular formula* : NaCl ,**

molar mass* :58.44 *g/mol

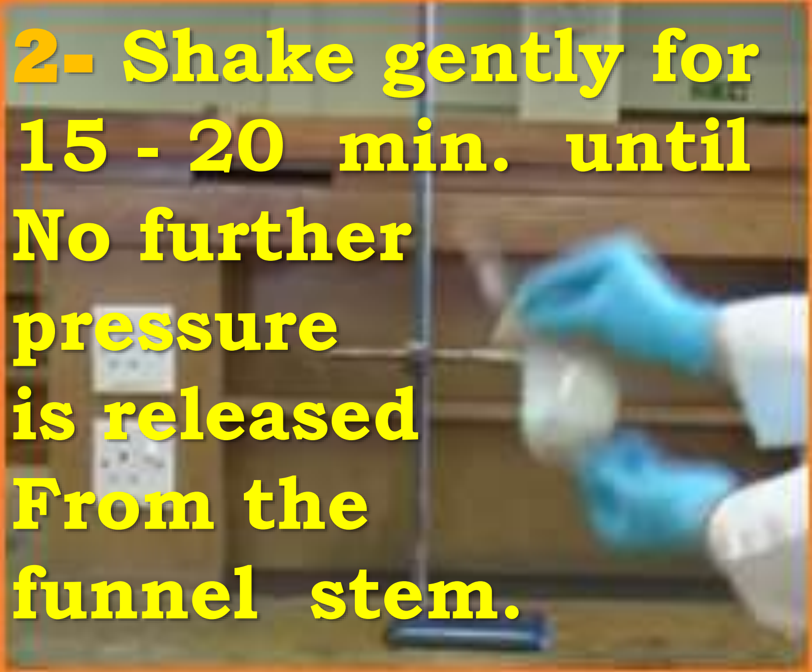
Ionic cpd, Colorless crystals, Soluble in water.



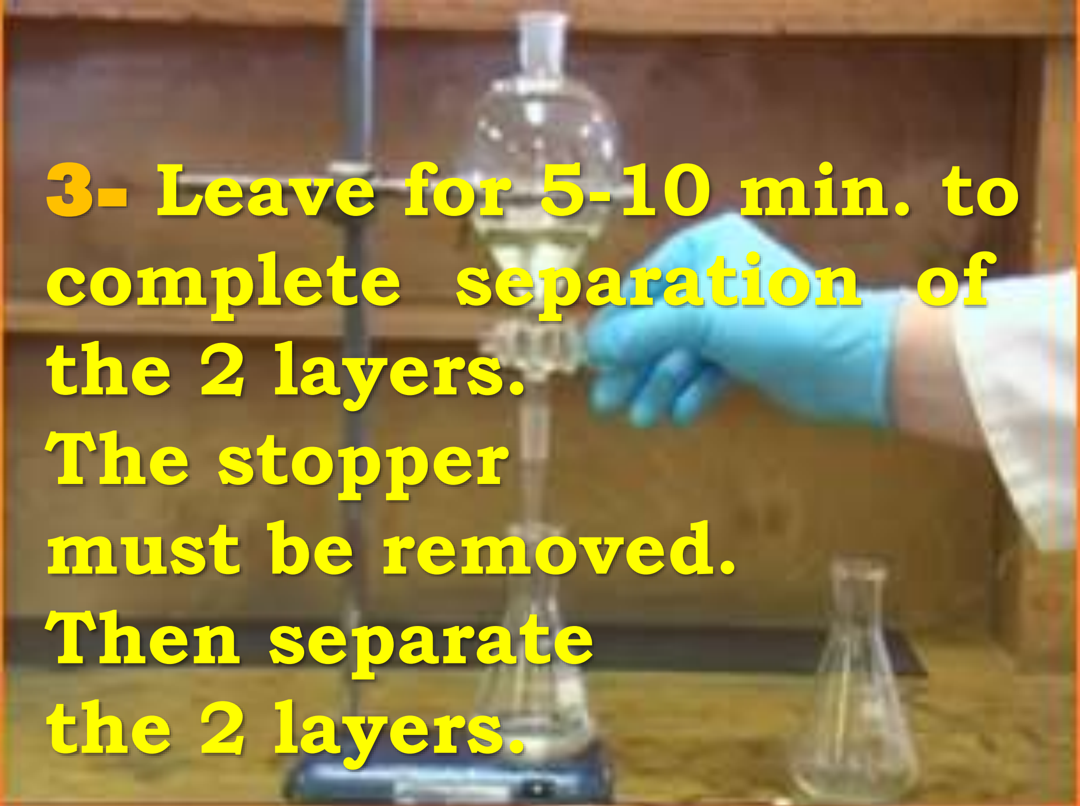
Density of water = 1 g / ml

Density of ether = 0.71 g / ml

1- Transfer an unkn. sample to a separatory Funnel ; add 20 ml ether & 20 ml of D.W.



2- Shake gently for 15 - 20 min. until No further pressure is released From the funnel stem.



3- Leave for 5-10 min. to complete separation of the 2 layers. The stopper must be removed. Then separate the 2 layers.

4- Dry the ethereal layer

DETERMINATION OF MELTING POINT

Physical Properties of Organic Compounds

The physical properties of a compound include such things as its,

Color , Odor , Refractive index, Density, Solubility, Melting point & Boiling point.

The exact values of the physical properties of a cpd. depend on its **molecular structure**.

Success in laboratory often depends on making a good prediction of physical properties from the cpd. structure.

The physical properties of a cpd. depend largely upon which kind of bonds hold it's atoms together in a molecule.

There are two kinds of bonds:

1- Ionic Bonds, formed by the transfer of electrons.

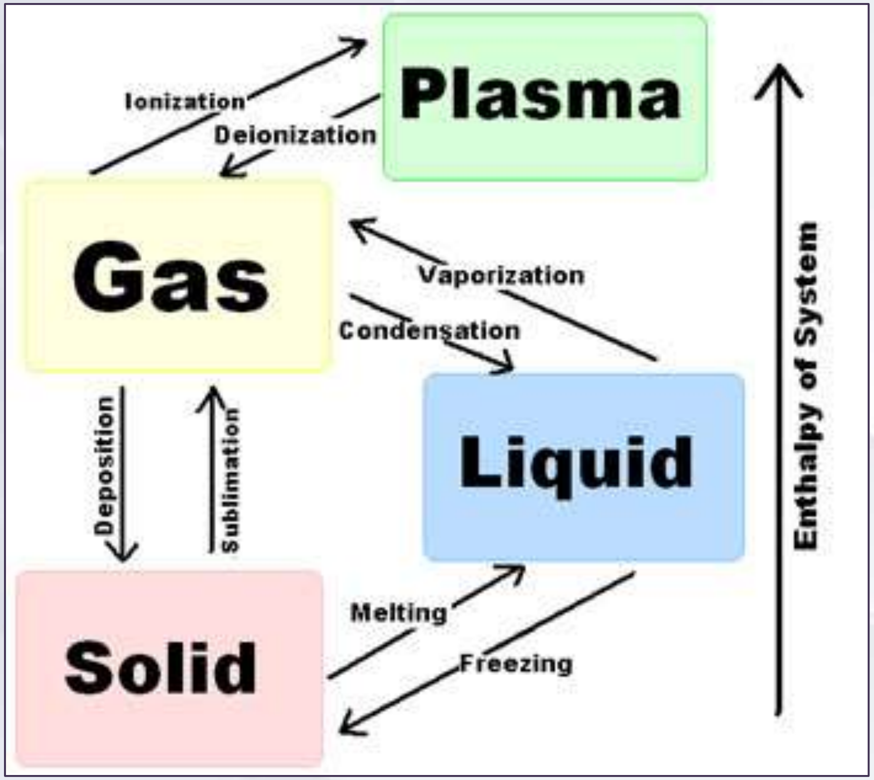
2- Covalent Bonds, formed by the sharing of electrons.

Phases of Matter

Matter ordinarily exists in four phases:
Solid , Liquid , Gas and Plasma .

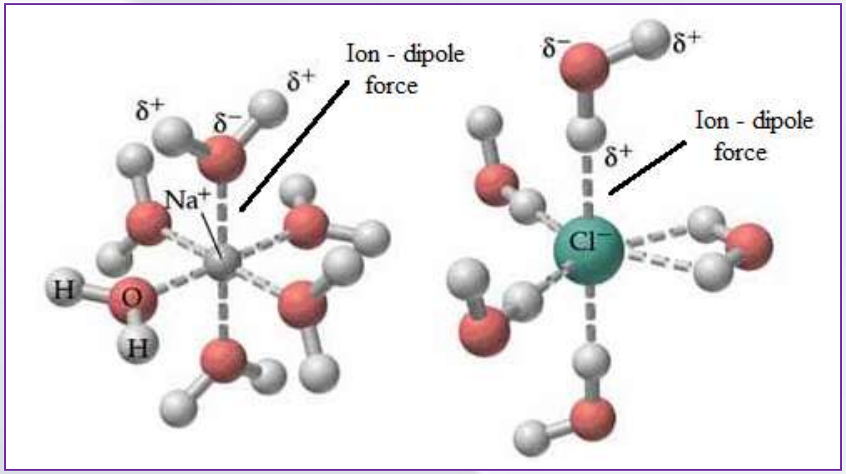
Plasma is a high – temperature phase not encountered in the typical organic chemistry laboratory.

As the environment around the materials is *changed*, for example by varying the temp. or pressure, the systems undergo a phase transition, that is the change from one state of matter into another.

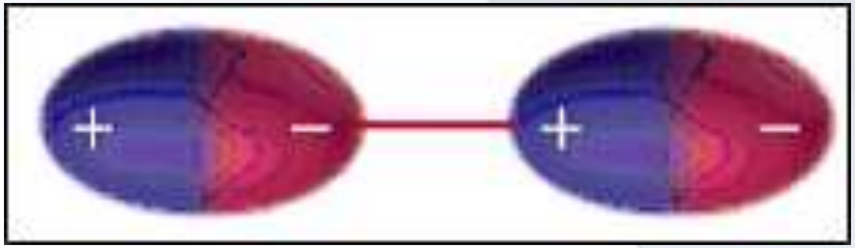


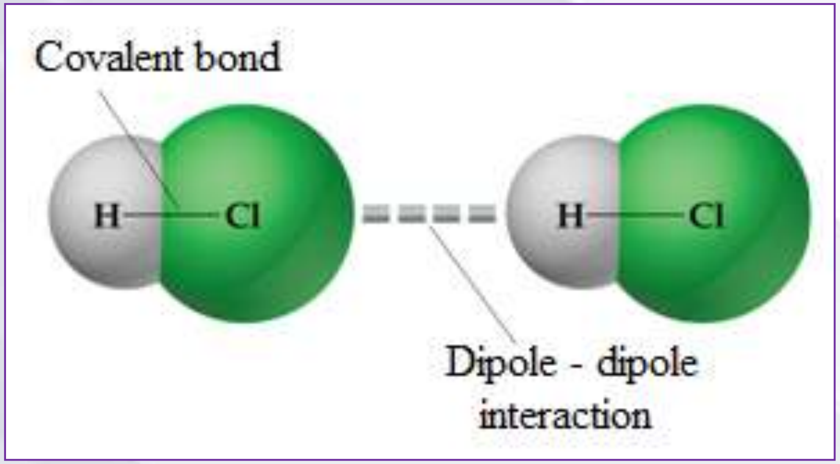
There are four Basic types of Intermolecular Forces :

1. **Ion - dipole:**
   Ion is attracted to polar molecule via this force as ex. (NaCl in water).

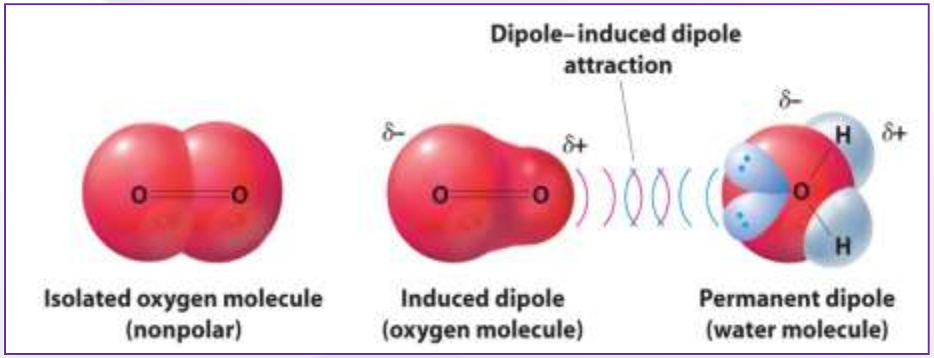


2. **Dipole – dipole:**
   Polar molecules attracted to each other as forces between HCl molecules.

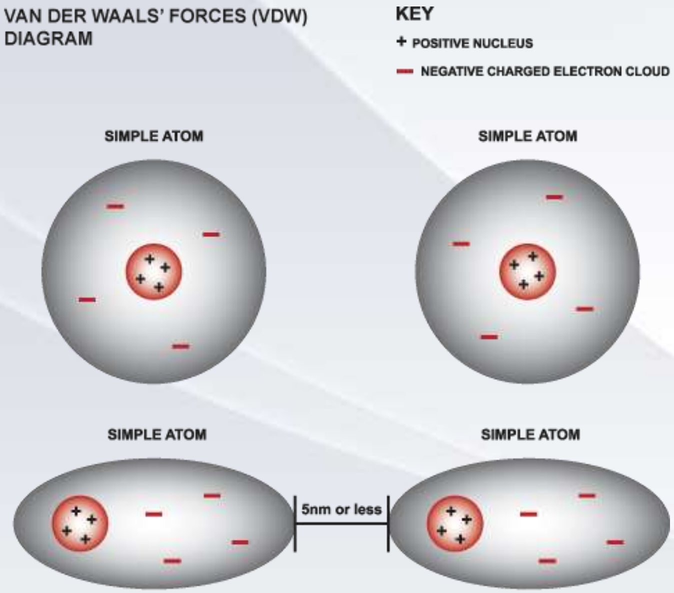




3. Dipole - induce dipole:
Polar molecules attracted to nonpolar molecules as for ex. (Oxygen in water) by dipole – induce dipole interaction .



4. Induce dipole -induce dipole:
London dispersion forces also called van der Waal's forces Nonpolar molecules attraction for each other due to electron distortion.

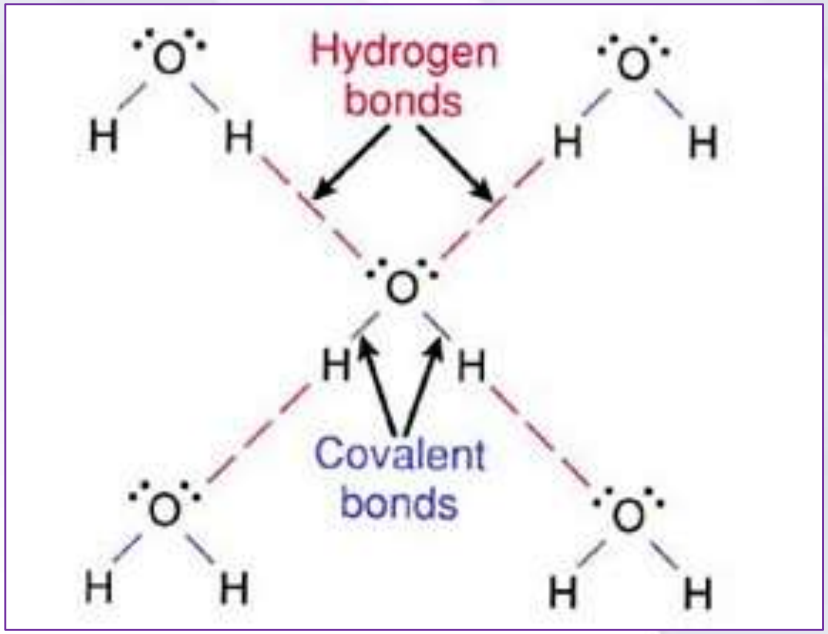


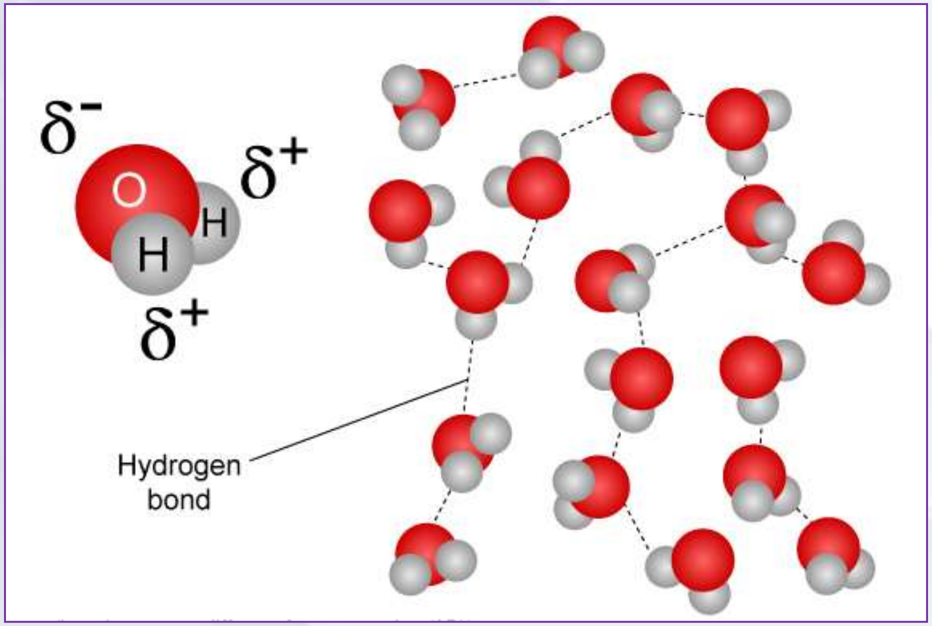
When two atoms come within 5 nanometers of each other, there will be a slight interaction between them, thus causing polarity and a slight attraction.

Hydrogen bonding :

Hydrogen bonding is an especially strong kind of dipole – dipole attraction in which a hydrogen atom serves as a bridge between 2 electronegative atoms, holding one by a covalent bond & the other by purely electrostatic forces.

For H-bonding to be important, both electronegative atoms must come from the group: F, O, N.





Melting Point:

The melting point of a solid crystalline compound is the temperature at which the solid and the liquid phase of the cpd. are in equilibrium at a certain pressure usually 1 atmosphere.

Or,

It's the temp. at which the solid begins to change into liquid under a pressure of 1 atmosphere.

The melting point range : is the difference between the temp. at which the sample begins to melt **(T_1)** & the temp. at which the sample is completely melted **(T_2)** .

Melting point rang = $T_2 - T_1$

Organic chemist used melting point to:

1- Get an indication of the purity of cpd.

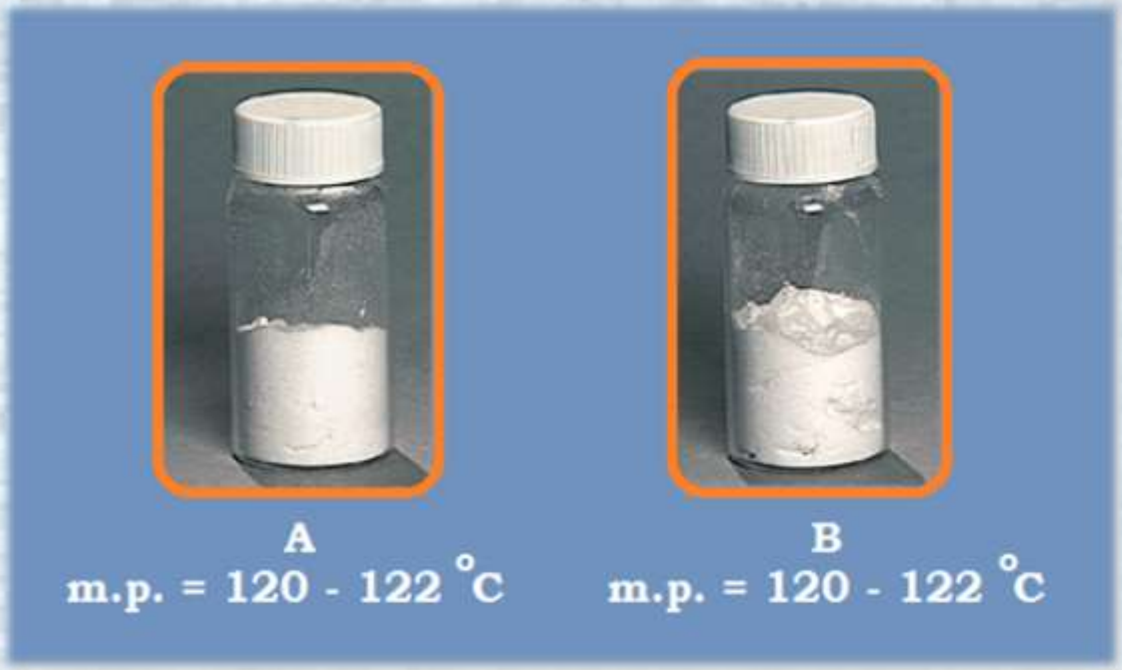
Sample	*Pure*	*Impure*	*Decomposed*
Melting point	Sharpe	Not sharpen	Not sharpen
Melting point range	0.5 – 1 ^{0}C	Wider range	Wider range

2- Help in identification of organic cpd.

Compound name	Compound formula	Compound Melting point
Sodium chloride	**NaCl**	**801 °C**
Sodium acetate	**$CH_3COO Na$**	**324 °C**
Glacial acetic acid	**CH_3COOH**	**16.6 °C**

Mixed Melting Point:

How can you know whether the 2 samples are the same or different?



Answer:

We mix them and measure the m.p. for the resultant mixture,

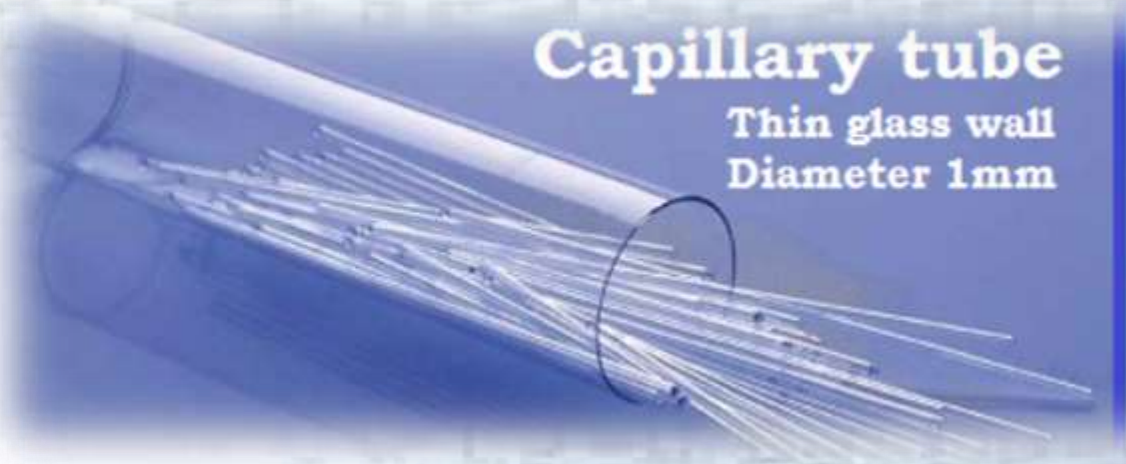
If,

m.p. of mixture < m.p. of original & wider m.p. range → different cpd.

m.p. of mixture = m.p. of original & same m.p. range → same cpd.

General Technique for m.p. Determination:

Capillary Tube method.

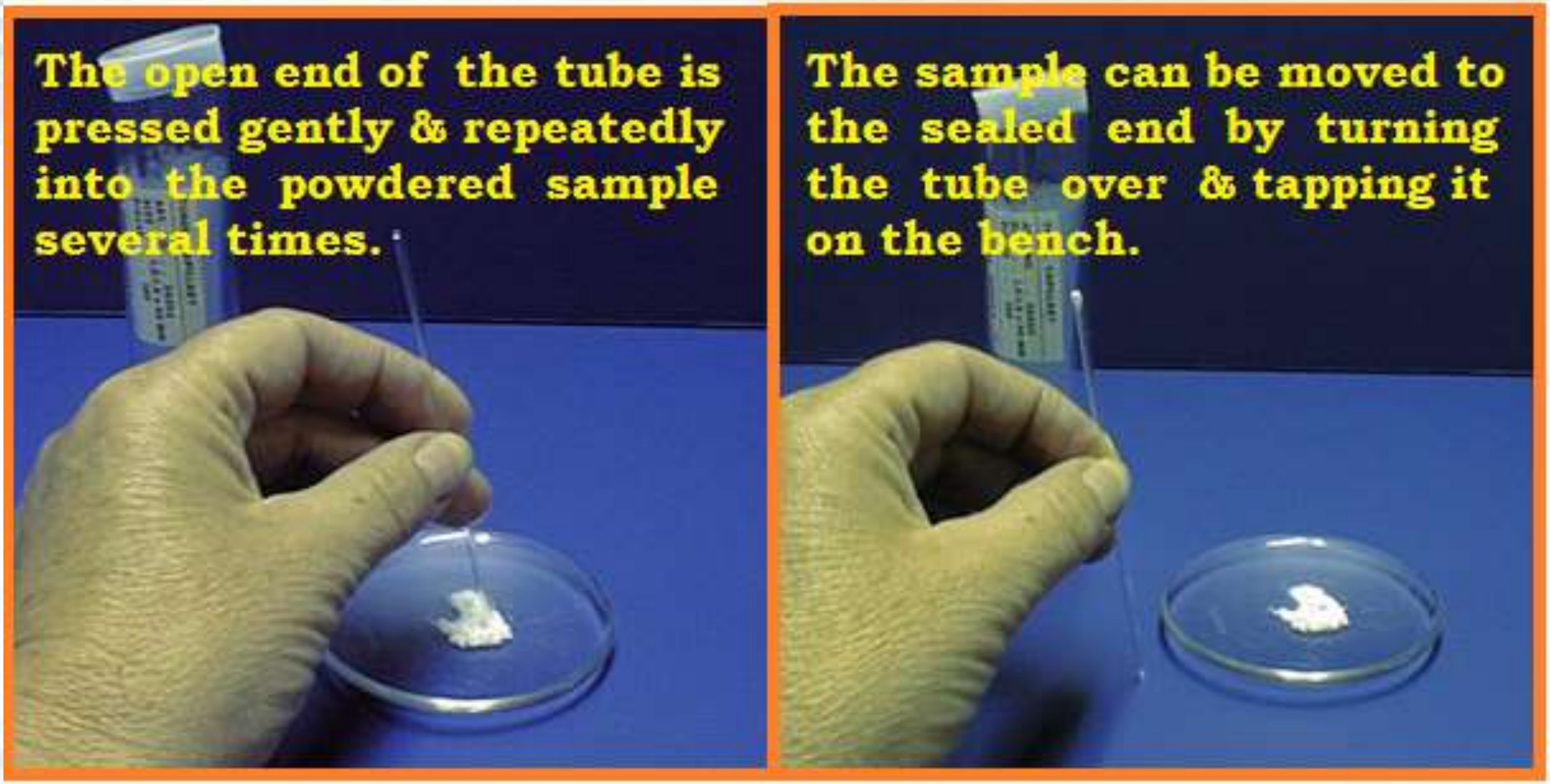


Tube tilted to prevent water condensation inside

Stages for correct sealing

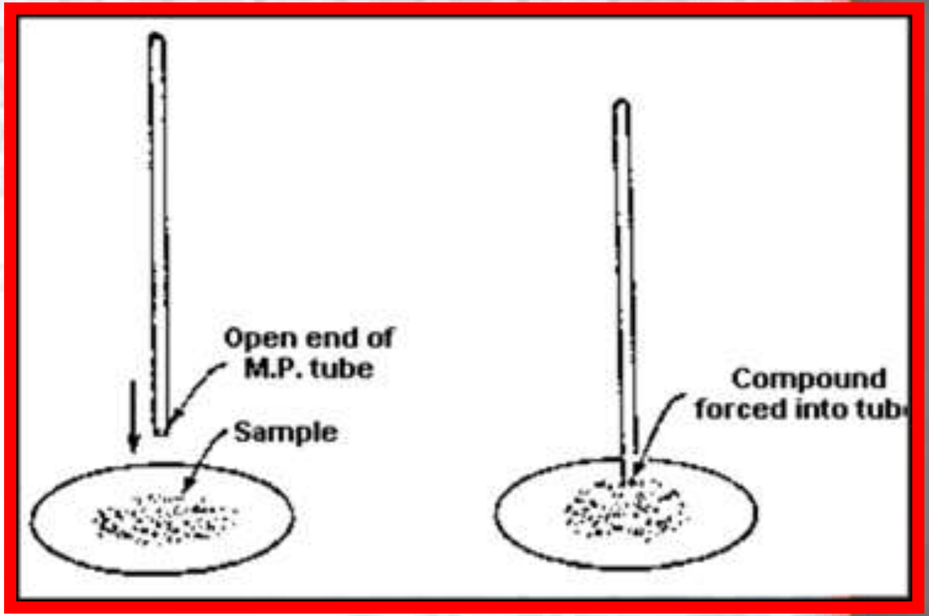
Wrong !
Tube has been overheated

Filling a capillary tube:



The open end of the tube is pressed gently & repeatedly into the powdered sample several times.

The sample can be moved to the sealed end by turning the tube over & tapping it on the bench.




A sample height of 2-3 mm in the capillary tube is recommended.

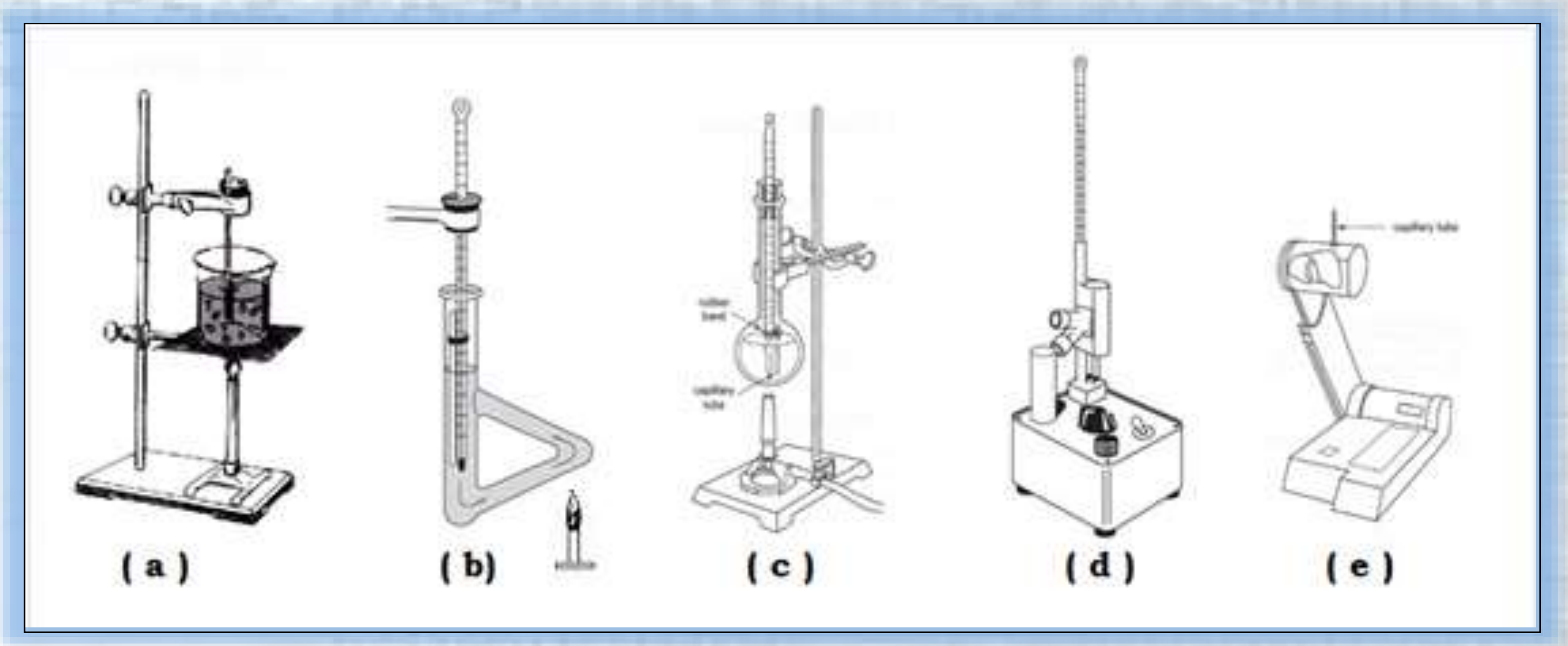
Any compound being loaded into a capillary tube <u>must be:</u>

1- Fully dried.

2- Homogeneous.

3- In powdered form.

Melting Point Apparatus:



a- Hot - oil m.p. bath.

b- Thiele apparatus.

c- Long necked flask.

d- Mel-temp apparatus.

e- Digital m.p. measuring apparatus.

Number of Experiment: **I**

Name of Experiment: **Determination of the Melting Point of an unknown sample.**

Aim of Experiment:

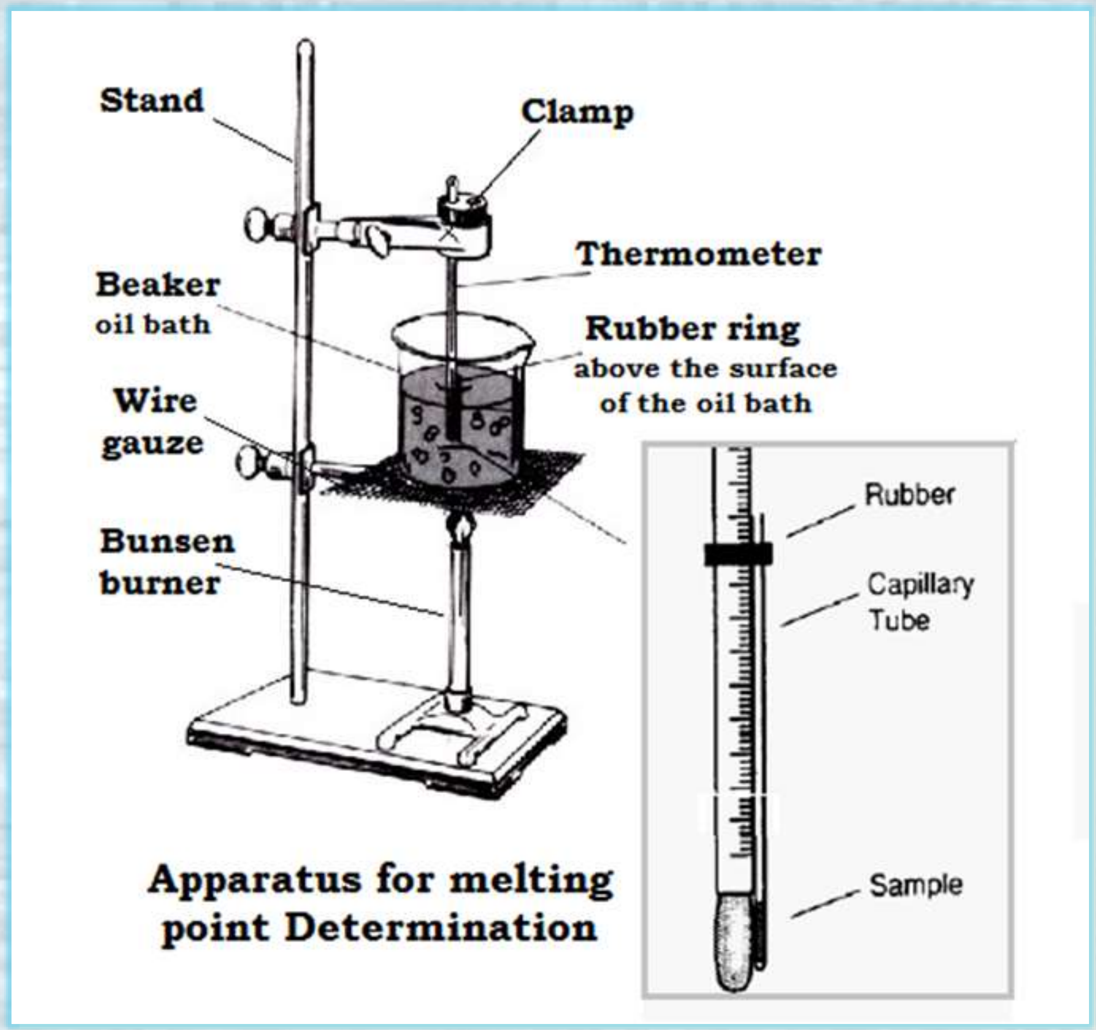
1- Identification of an unknown cpd. using it's m.p.

2- Determination of purity of a cpd. using the m.p. as a physical property.

Procedure:

1- Preparation of the unknown sample as mentioned before.

2- The capillary tube is attached to a thermometer by a rubber ring in such a way that the closed end is attached to the bottom of the thermometer's bulb.



Apparatus for melting point Determination

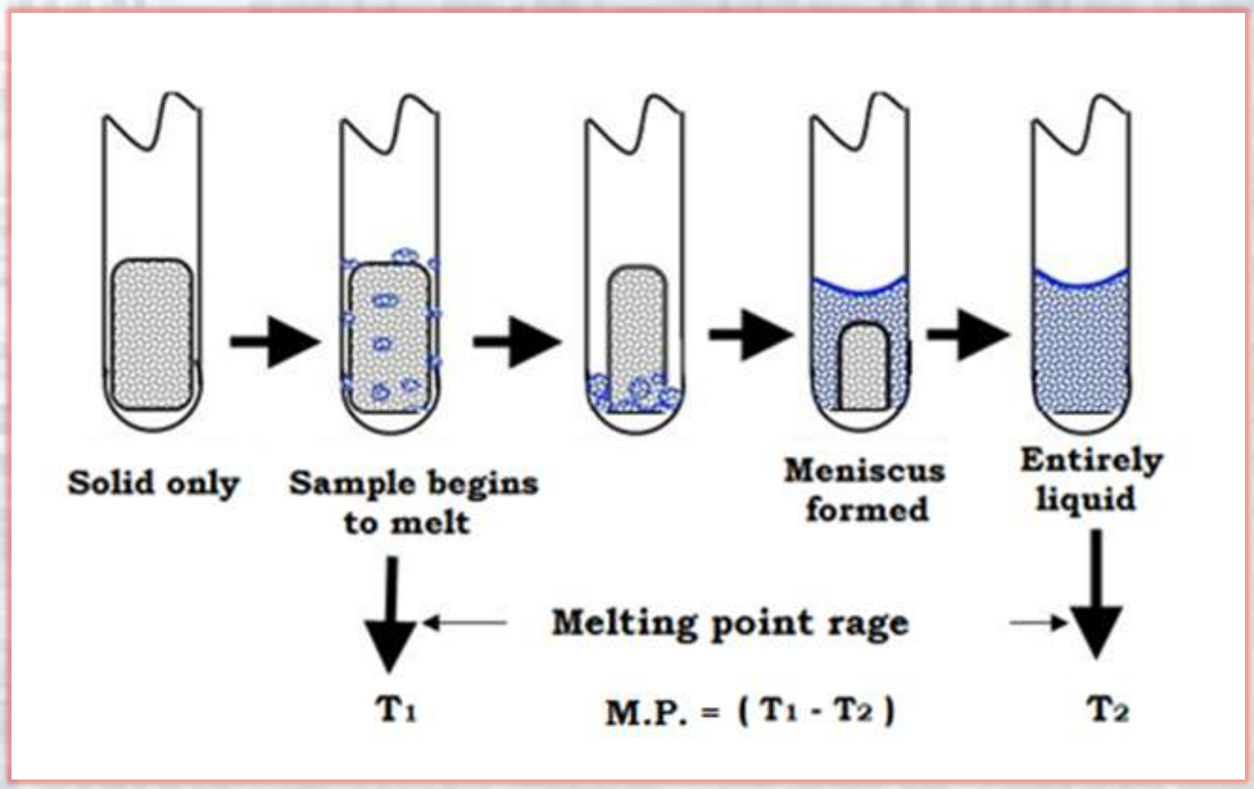
3- Then both of them are placed in an oil – bath , (the rubber ring should be above the surface of the oil - bath).

4- Heating is started gradually.

5- The range between the temperature at which the powdered solid inside the capillary tube begins to liquefy (T_1) & the temperature at which a clear liquid is observed inside the capillary tube (T_2) is recorded as the observed m.p. range.

m.p. rang = $T_2 - T_1$

m.p. = ($T_1 - T_2$)



Notes:

* For oil bath, glycerin or paraffin can be used, but glycerin is preferred since it's safer than paraffin.

* The temperature of the oil bath should rise very slowly.

* Gentle heating with continuous stirring is necessary

* After completing the experiment, the oil liquid must be allowed to cool before using it again.

Salt is added on snow covered roads?

Ice melts at ---- ?

What happens to the freezing point if salt is added?

Among these 3 samples of the same cpd. , which of them is the purest one?

m.p.
115 – 119°C

m.p.
118 – 120 °C

m.p.
121- 122°C

Two of these bottles contain benzoic acid and one m-nitrophenylacetic acid.

1

m.p.=120 –122 °C

2

m.p.=120 –122°C

3

m.p.=120 -122°C

Run mixed melting points to confirm identification :

Mixed 1 and 2 m.p. = 120 - 122°C

Mixed 1 and 3 m.p. = 114 - 117°C

Mixed 2 and 3 m.p. = 115 - 118°C

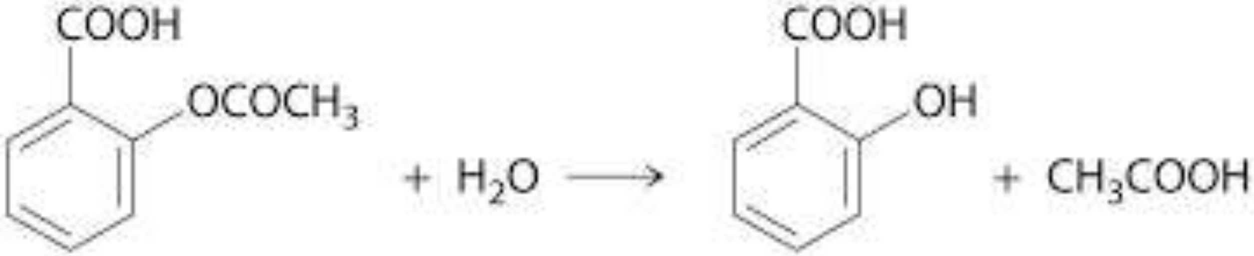
Separation & purification of organic compound is important:

1- Products of organic reactions are seldom
pure products as a result of side reactions.

2- Pure compounds are also subject to partial
decomposition on standing for some time
or on exposure to light, air, heat

m

,



acetylsalicylic acid

salicylic acid

acetic acid

acid

Methods of Separation & Purification of Organic Cpd

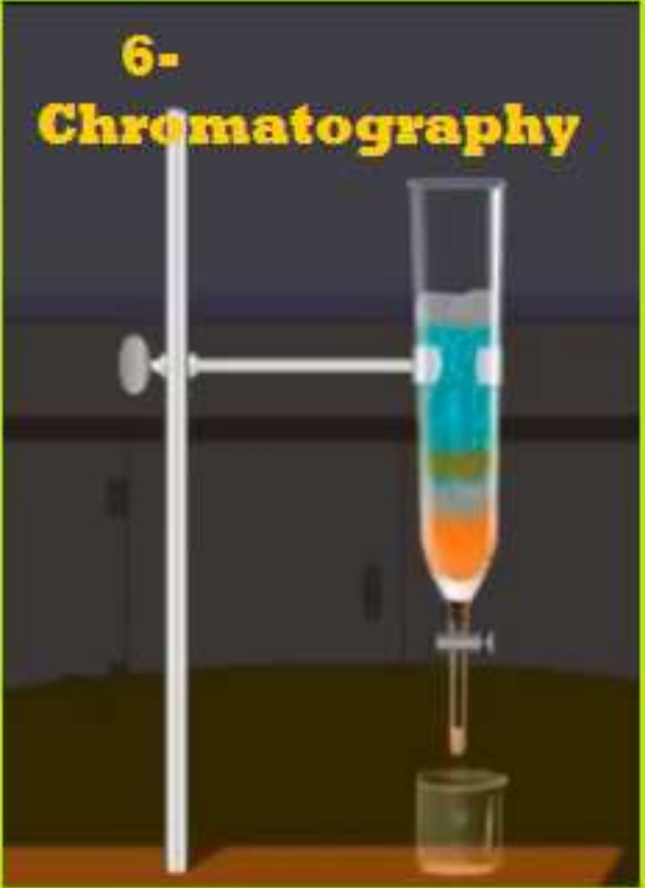

1- Solution & Filtration

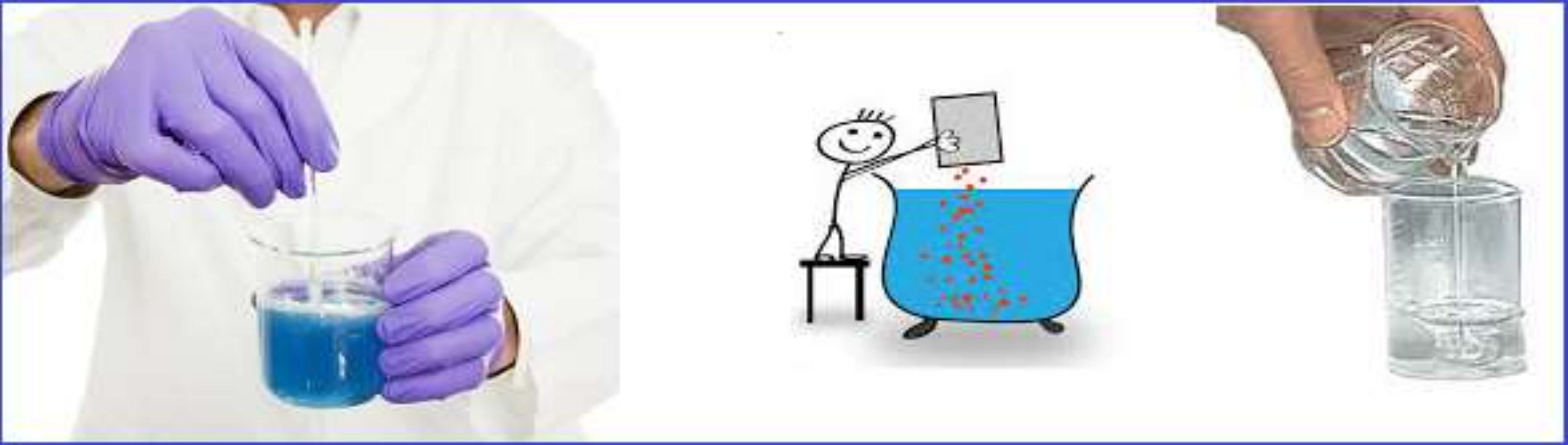

2- Extraction


3- Sublimation

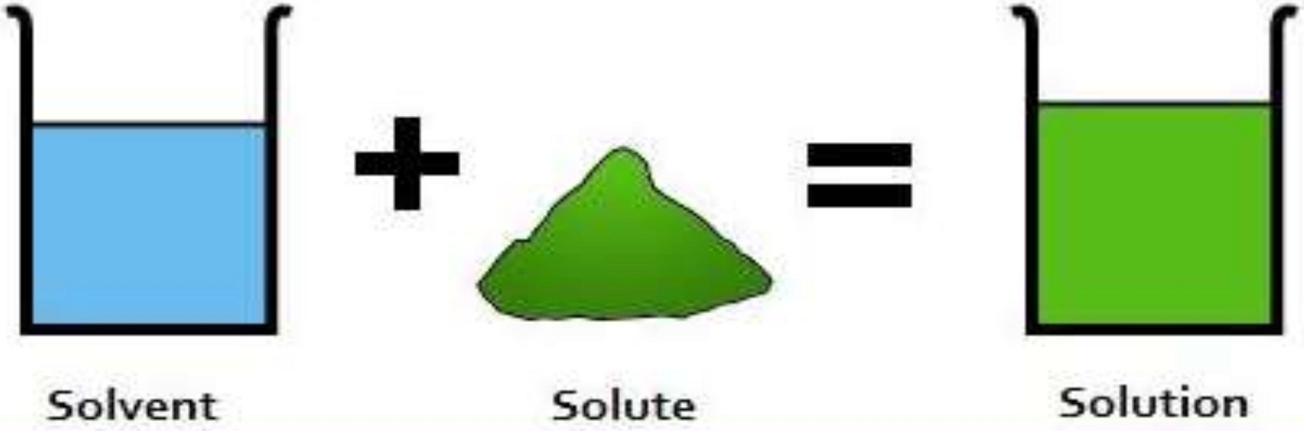

4- Recrystallisation

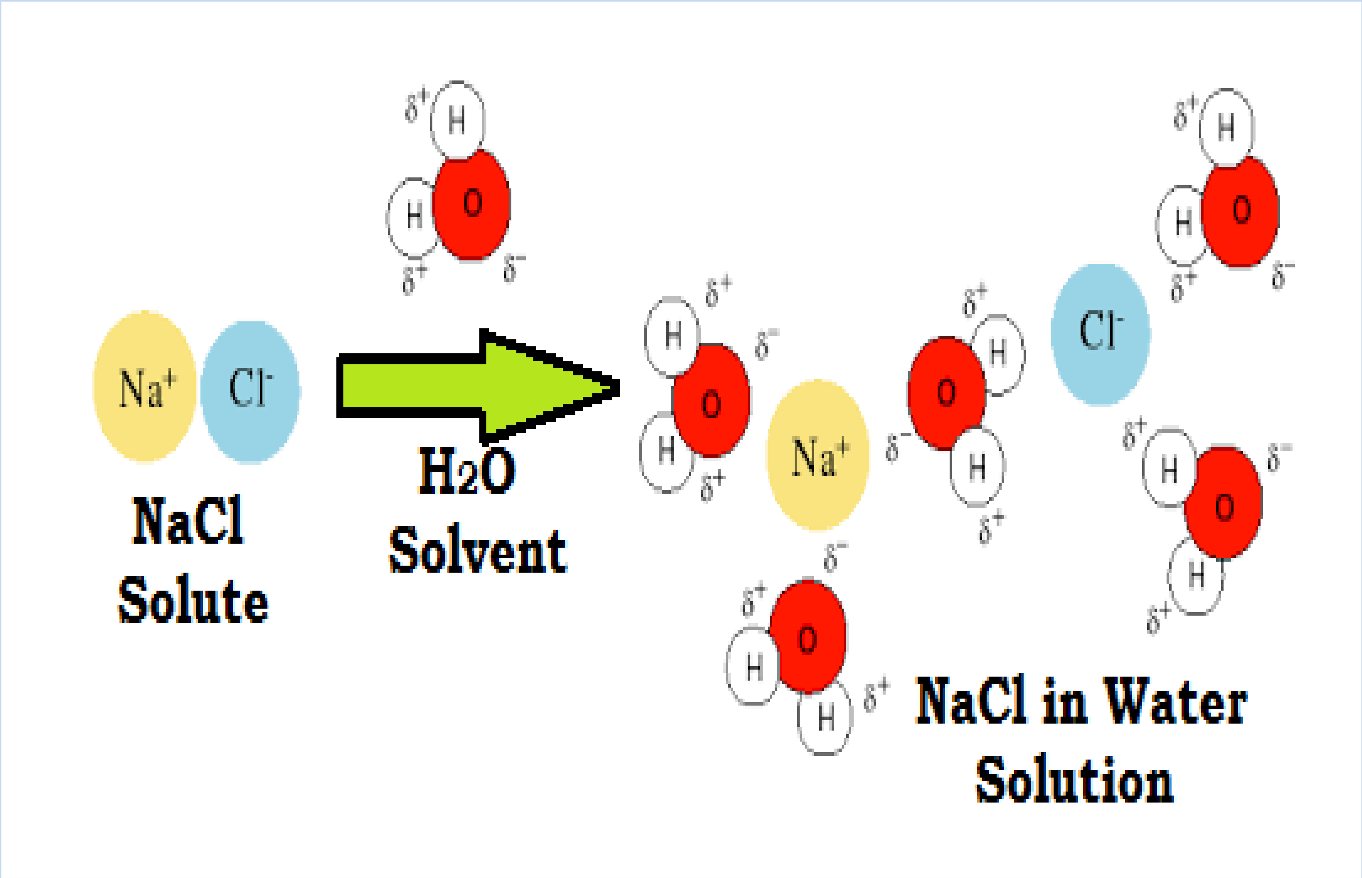

5- Distillation


6- Chromatography

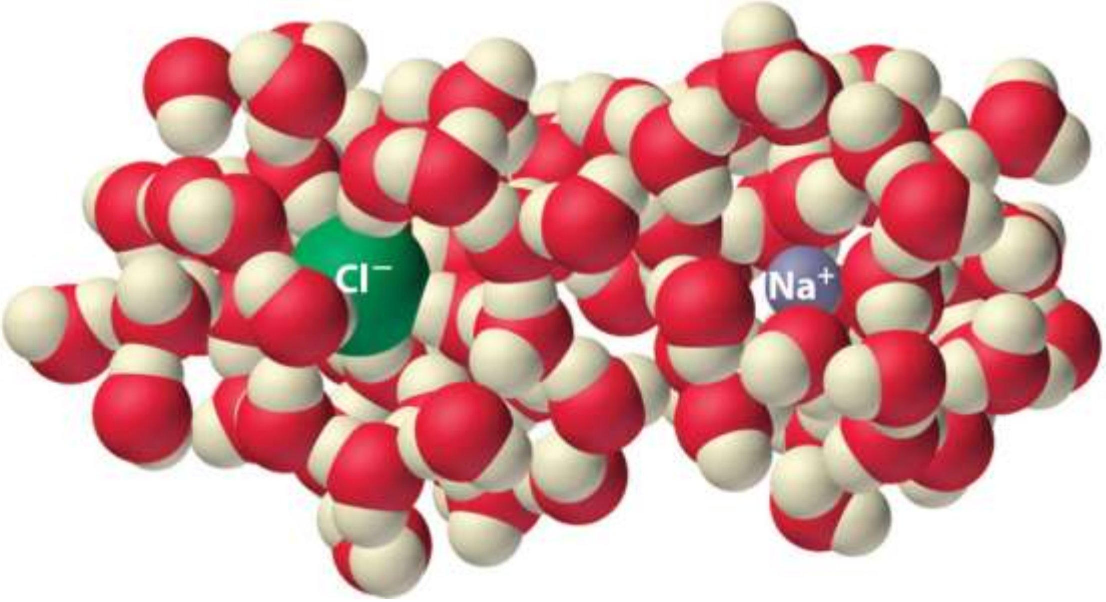


Solutions & Solubility



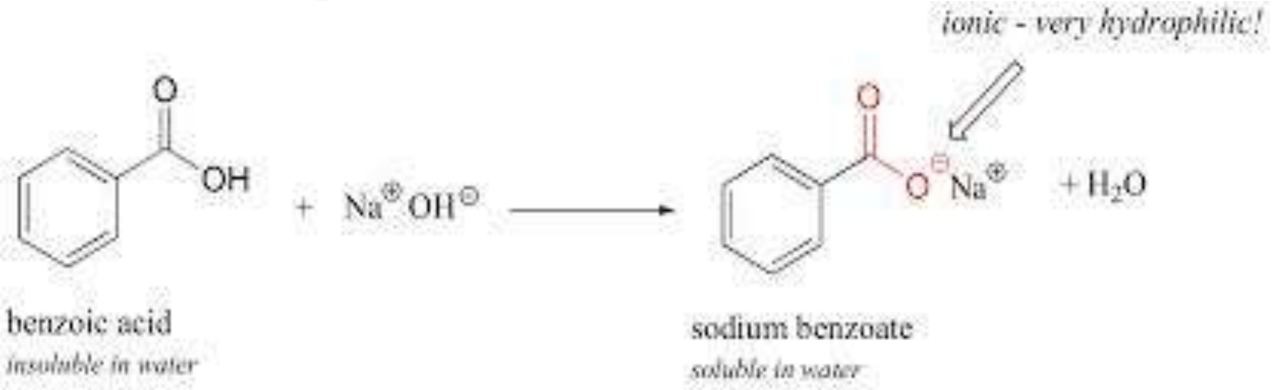


When a solid or a liquid dissolves,
the structural units (ions or molecules)
become separated from each other
and the solvent molecules occupy the
space between them

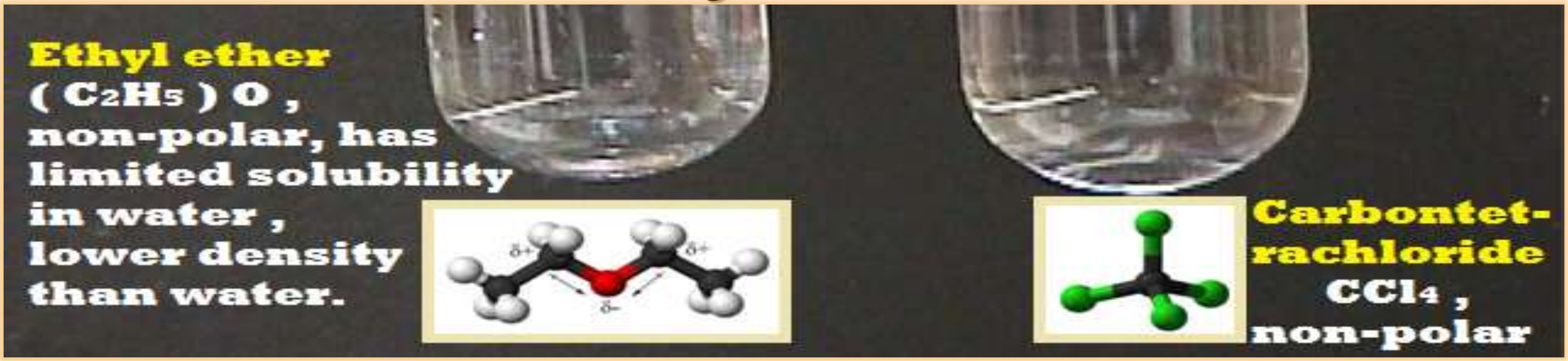

Cl⁻
Na⁺

The solubility of organic cpd. can be divided into two major types :

1- Solubility in which the chemical reaction is the driving force, ex. Acid-base reaction



2- Solubility in which only simple miscibility is involved, ex. ethyl ether in CCl_4



Ethyl ether $(C_2H_5)O$, non-polar, has limited solubility in water, lower density than water.

Carbontet-rachloride CCl_4, non-polar

Theory of Solubility:

1- Polarity effect:

" like dissolves like ".

F > O > Cl , N > Br > C , H

Decreasing electronegativity

H_2, O_2, Cl_2, Br_2 & N_2 has zero dipole moment, i.e. non polar.

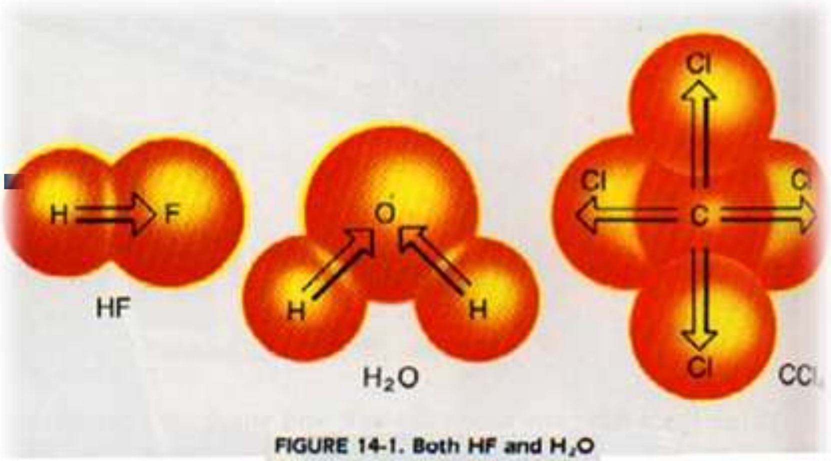


FIGURE 14-1. Both HF and H_2O are polar molecules because the arrangement of polar bonds is not symmetrical. The CCl_4 molecule is nonpolar in spite of the fact that it contains four polar bonds.

2- Dielectric constant:

D.C., is the ability of the solvent to separate ionic charges.

The D.C. of the solvent is related to it's polarity.

Water D.C. of 80 dissolves NaCl readily,

Hexane (D.C. of 1.9)

Diethyl ether (D.C. of 4.4)

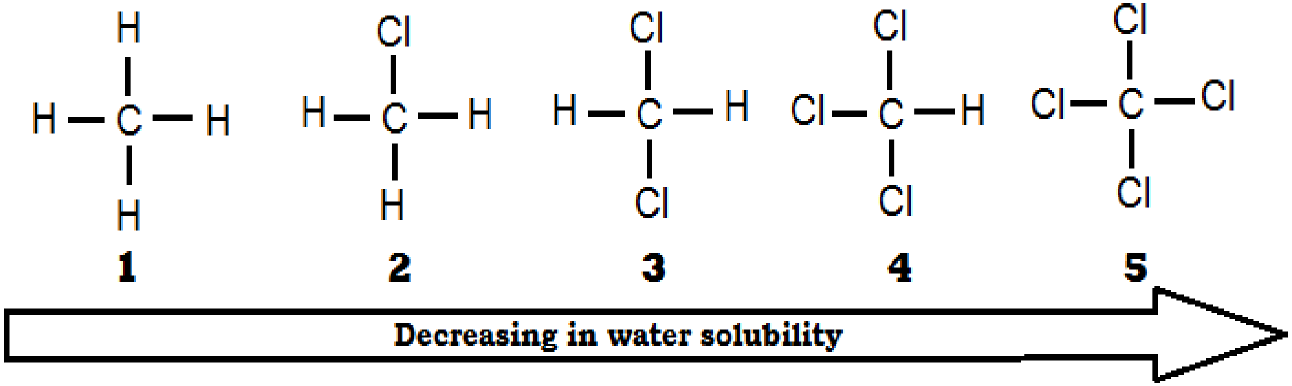
Poor solvents for ionic salts.

The effect of cpd's structure on it's water solubility :

1- Number of carbon atoms : Solubility ↑ as the no. of C atoms ≤ **5**

2- The presence of **= , ≡ , Ar. ring** ~~affect~~ **solubility**

3- As a halogen is substituted for a H, the water solubility ↓

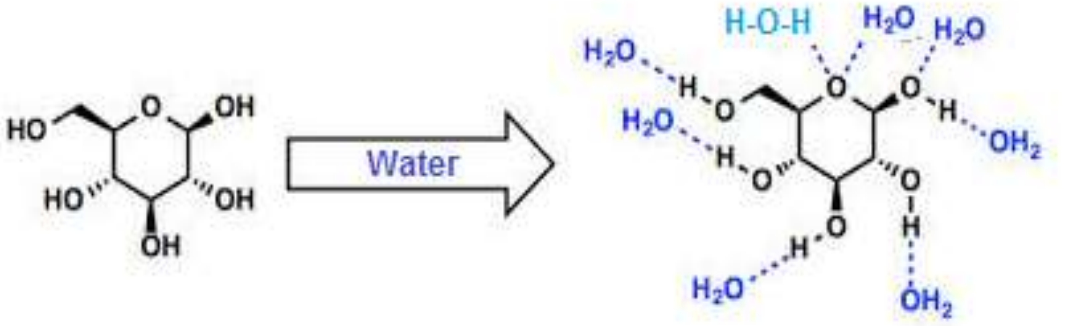


4- Acids & amines are more soluble than non polar cpds.

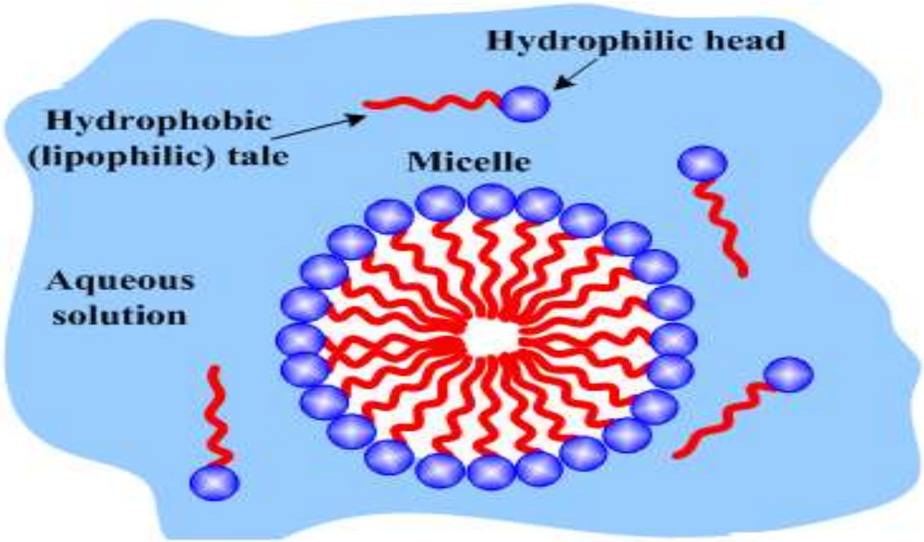
5- In a homologous series as ↑ m.wt. ⟹ Solubility ↓

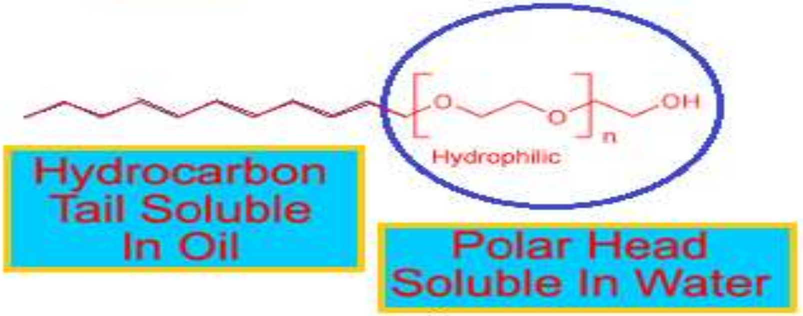
6- Saccharides,

ex. Glucose,
have many polar
- OH groups , **so**
they are water soluble.



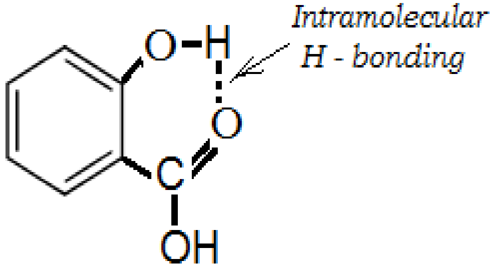
7- Compounds having both **polar** & **non polar** parts are soluble in water.



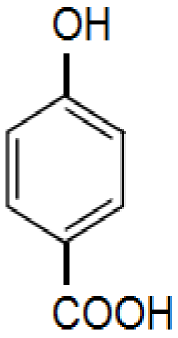


7- Intramolecular **H- bonding**

↓ water solubility.



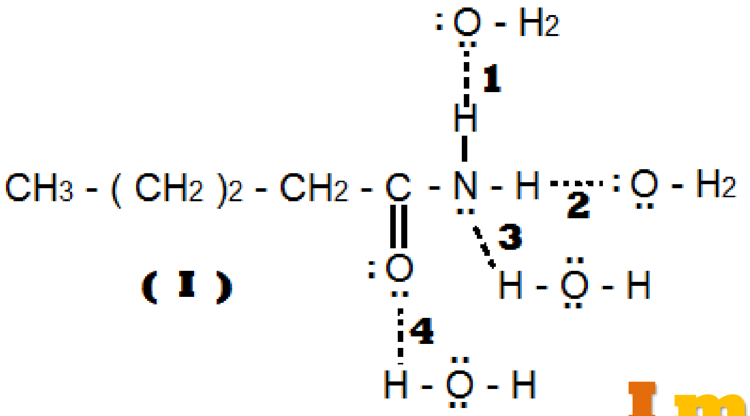
Salicylic acid
Less water solubility



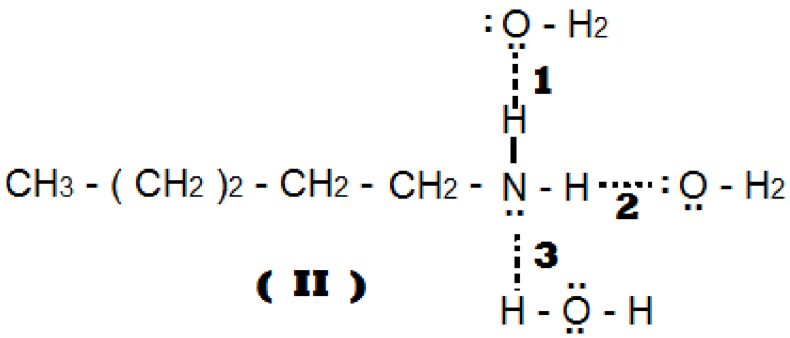
p- Hydroxybenzoic acid
More water solubility

8- Intermolecular **H – bonding** between cpd & water

↑ water solubility.



(I)



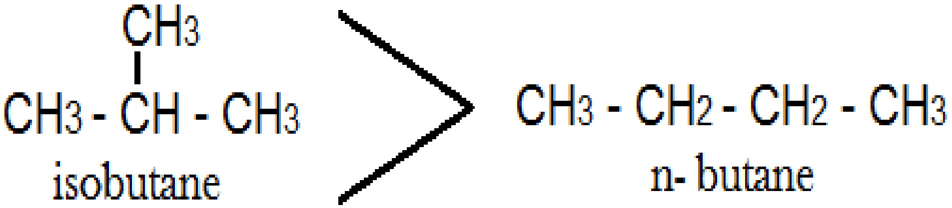
(II)

I more water soluble than II.

10- Molecular structure:

a- Branching

↑ water solubility.

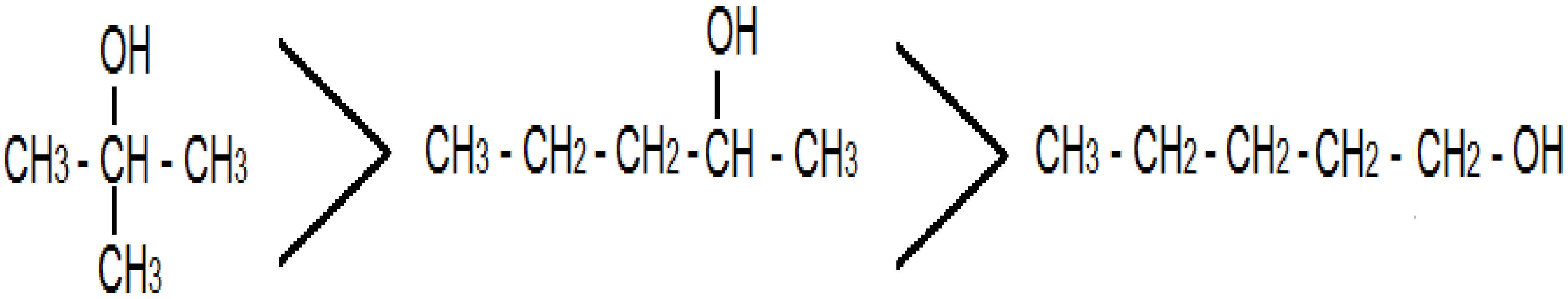


$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3 > CH_3-CH_2-CH_2-CH_3$$

isobutane

n- butane

b- Position of the functional group.



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{CH}}-CH_3 > CH_3-CH_2-CH_2-\overset{\overset{OH}{|}}{CH}-CH_3 > CH_3-CH_2-CH_2-CH_2-CH_2-OH$$

FILTRATION

Filtration:

It is an important procedure after completing the reaction either to:

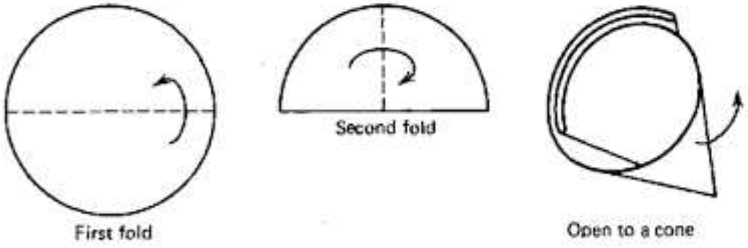
1- Separate the solid product (precipitate), or,

2- To get rid of insoluble impurities or reactant materials.

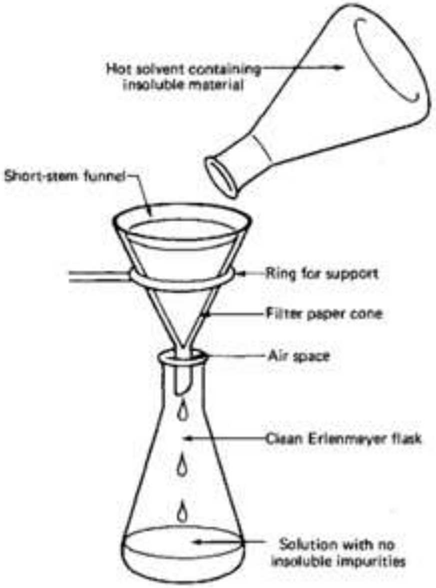
The desired soluble cpd. is recovered from the filtrate by evaporating the solvent.

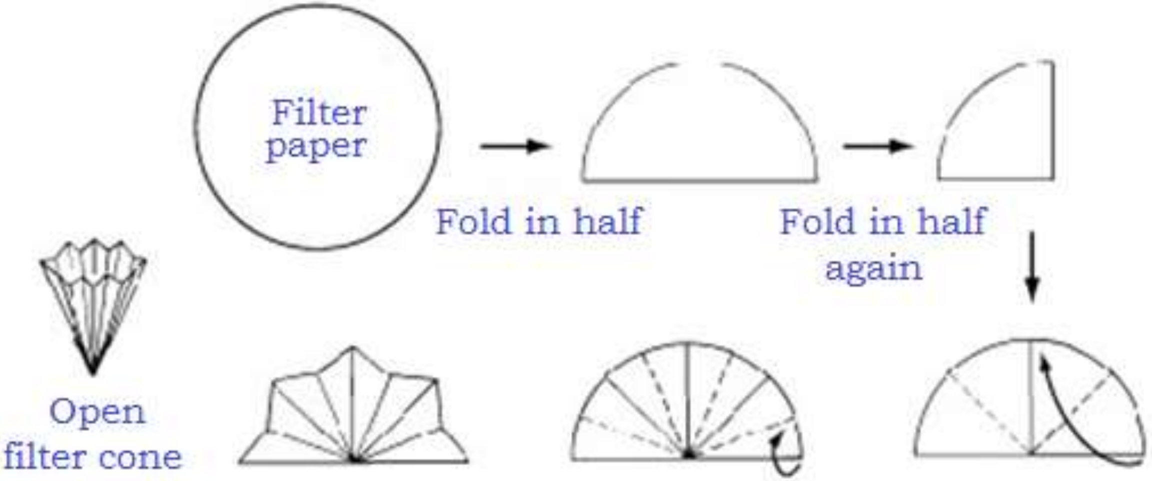
So the liquid is poured into a filter paper fitted in a funnel and either the precipitate or the filtrate that contains the desired soluble compound is collected.

Preparation of filter paper



Filter paper cone





Filter paper

Fold in half

Fold in half again

Fold to crease the quarter section

Fold to crease the eigth section

This is the "accordion" shape

Open filter cone

Recrystallization

Solid organic cpd.s when isolated from organic reaction are impure; they are contaminated with small amounts of other cpd.s produced along with the desired product.

The purification of impure crystalline compound is usually done by **Recrystallization** from a suitable solvent or a mixture of solvents.

Purification of solids by recrystallization is **based upon** differences in their solubility in a given solvent or a mix. of solvents.

Desirable solv. characteristics for Recrystallization:

1- Chemically inert toward the solute.

2- It should dissolve the solute to be purified readily at or near it's boiling point, but sparingly at the lab. temp. or below (0 – 25 °C).

3- It should dissolve the impurities readily or not at all.

4- It should be capable of easy removal from the crystals of the purified cpd., (i. e.) possess a relatively low b.p.

5- It should yield well-formed crystals of the cpd.

6- If 2 or more solvents appear to be equally suitable for recrystallization the final selection will depend up on such factors as ease of manipulation, lower toxicity, Less flammability, & Lower cost

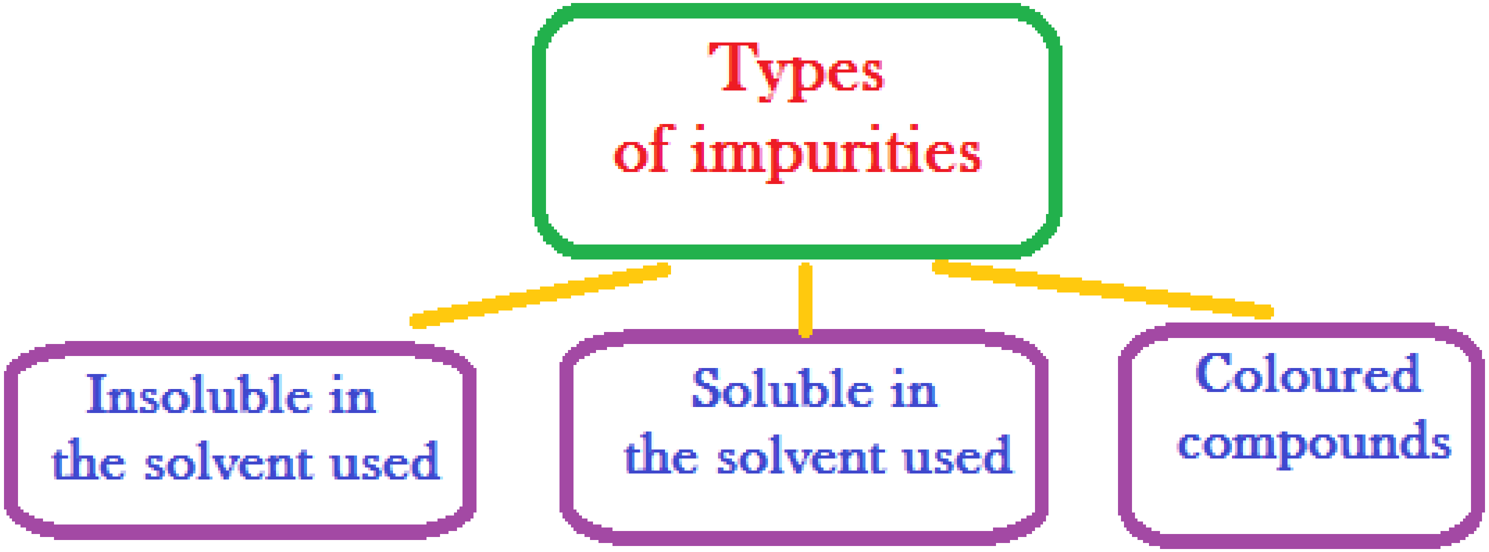
1- Dissolving the impure substance in some suitable solvent at or near the b.p.

2- Filtering the hot solution from the particles of insoluble material & dust.

3- Allowing the hot solution to cool thus causing the dissolved substance to crystallize out.

4-

so



How could we choose a good solvent :

Practically,

Take **0.1g** of a pure sample of cpd. to be purified & try to dissolve it in **1ml** of solvent,

if it;

Dissolves in the **Cold** solvent → The solvent is **Not suitable**

If it;

Dissolves in the **Hot** solvent → The solvent is **Suitable**

& If it;

Doesn't dissolve in **Hot & Cold** solvent → The solvent is **Not suitable** just an Example

Results of solubility tests for cpd. (A) are shown in table (*g/ml*).

Solvent	Water	Ethanol ✓	Diethyl ether
Cold	20	3	5
Hot	30	25	5

Which solvent will you choose to recrystalliz cpd. A?

Using Charcoal:

Samples to be purified may contain soluble colored impurities that may cause the soln.

&

the crystals to be colored.

Up on Recrystallization these impurities dissolves in the boiling solvent & adsorbs on the crystals produced up on cooling yielding a colored product.

Activated charcoal

composed of fine carbon particles with a large active surface area on which the colored impurities will be adsorbed.

Charcoal is added to the hot soln. before boiling & the soln. is kept hot at or near the b.p. for about 3 – 5 min. with shaking to wet the charcoal, the solution is then filtered through a fluted filter paper.

Notes about using activated charcoal:

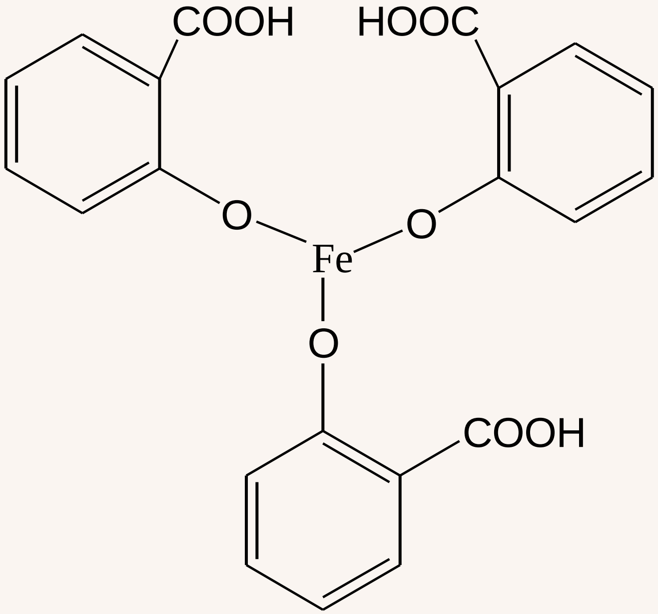
- An excessive quantity of decolorizing charcoal should be avoided since it may adsorb some of the cpd. which is being purified.

- Charcoal should not be added to a superheated solution or at the b.p. of the solvent because it's particles function as thousands of boiling chips causing the solution to boil over and foam.

- Charcoal is **Not** used for recrystallization of **phenolic cpd.s**

Because,

They contain ferric ions (Fe^{3+}) that upon heating the solution for some time it can react with the phenolic -OH forming red – violet colored complexes thus impairing the purification process.



Violet

complex

Recrystallization using mixed solvents:

It is applied when our cpd. is readily soluble in a solvent at room temp. & insoluble in other solvent, The 2 solvents must be miscible with each other as

Alcohol & water, ether & pentane

glacial acetic acid & water

Procedure :

1- The cpd. is dissolved in the solvent that is soluble in it.
2- Charcoal is used if required.
3- The solution is filtered to get rid of the insol. impurities.
4- The other solvent (in which the cpd. is insoluble), is added to the filtrate gradually until turbidity appears.
5- The mixture is then left a side to facilitate crystallization.