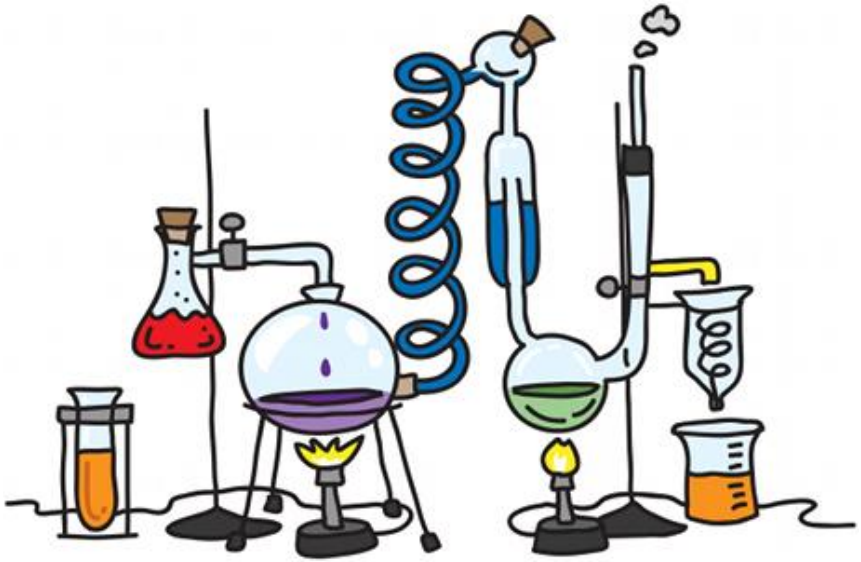
Purification of Organic Compounds



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عدد الصفحات: 110

Contents:

Introduction:

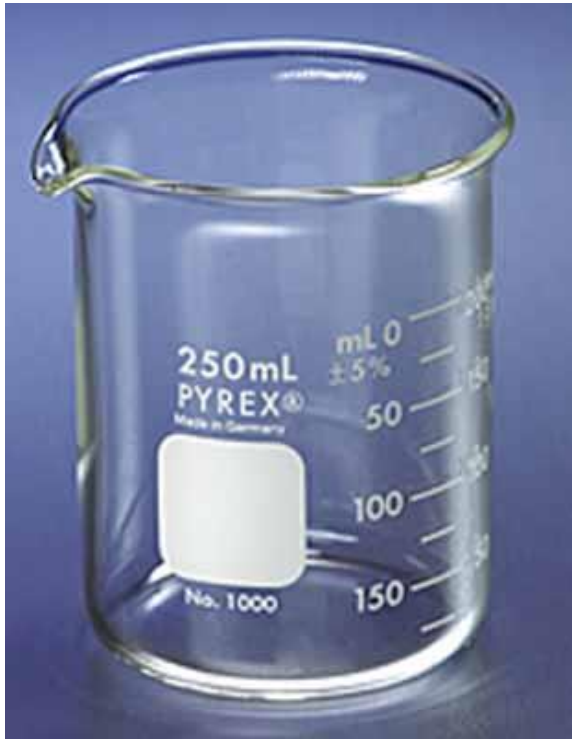
This course will focus on purification of organic compounds. Firstly, the main organic lab equipment will be presented, and then, the methods used in purification of solid organic compounds (Crystallization and Sublimation) and purifications of liquid organic compounds (Distillation, extraction, and chromatography) will be explained in some details.

Organic Compounds

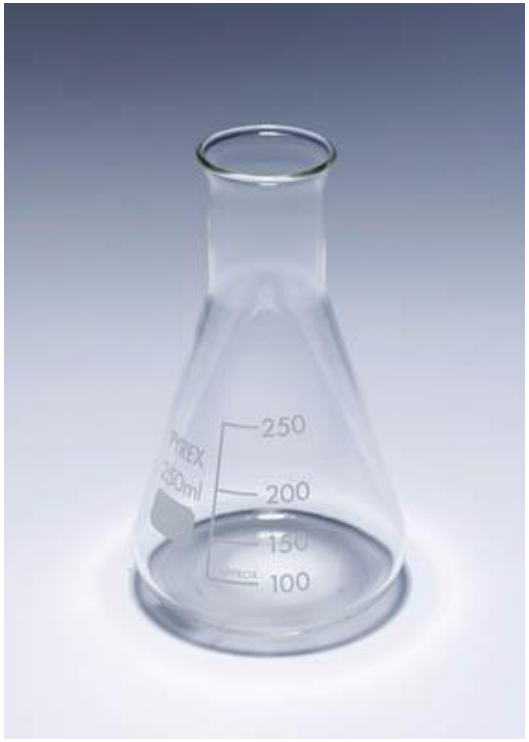
- Once the organic compounds extracted from a natural sources or synthesized in the laboratory, it's essential to purify it.

For Characterization (Full analysis)

Basic Organic Chemistry Lab Equipment



Beaker



Conical Flask

Measuring Cylinder

Basic Organic Chemistry Lab Equipment

Round bottom flask Single nick

Round bottom flask 2 nicks

Some Distillation apparatus

Basic Organic Chemistry Lab Equipment

Test tube

Test tube rake

Test tube holder

Test tube brush

bunsen burner

Basic Organic Chemistry Lab Equipment

Condenser

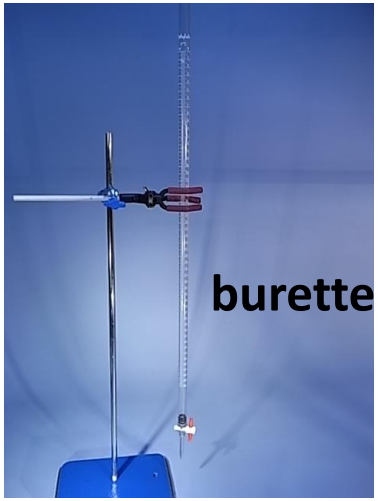
Pipette

Micro pipette

Basic Organic Chemistry Lab Equipment

Ring stand

Separatory funnel



burette

Spatulas and scoopula

Basic Organic Chemistry Lab Equipment

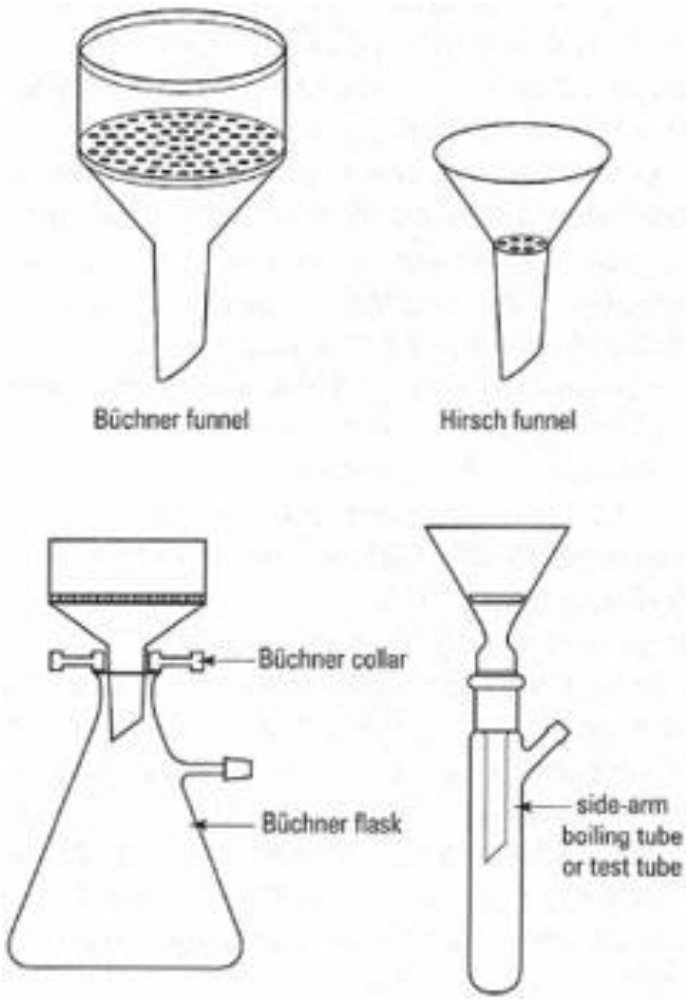
Filter funnel

Filter paper

Buchner filter funnel

Hersch filter funnel

Basic Organic Chemistry Lab Equipment



Buchner System for filtration

Basic Organic Chemistry Lab Equipment

Heat/stir plate

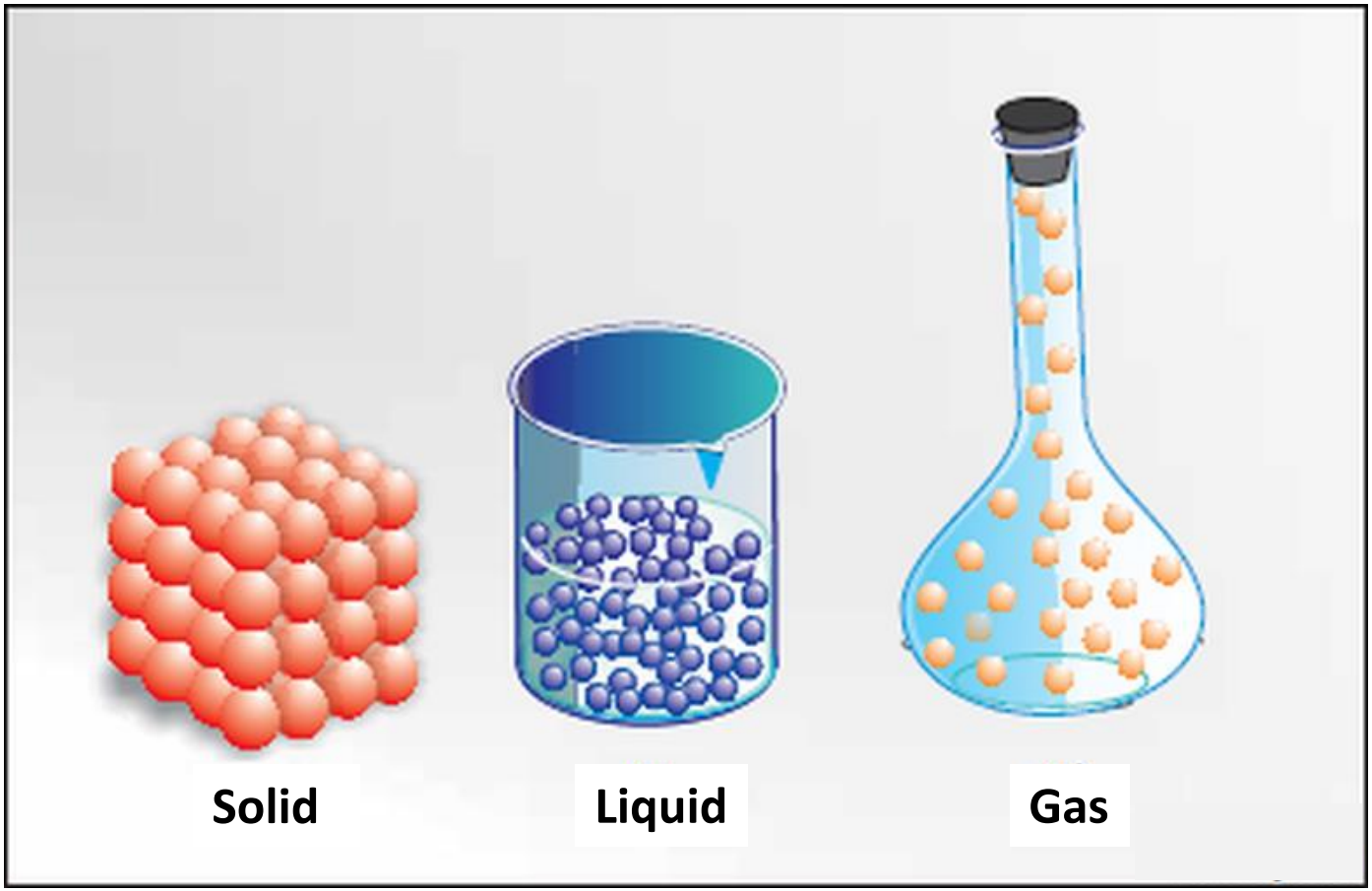
Heating mantle

Lab Oven

Melting point apparatus

Digital balance (Scale)

Organic Compounds



Methods of Purification of Organic Compounds

- Various methods used for the purification of organic compounds are based on the **nature of the compound** and **the impurities** present in it.

Purification of Solid

1- Crystallization

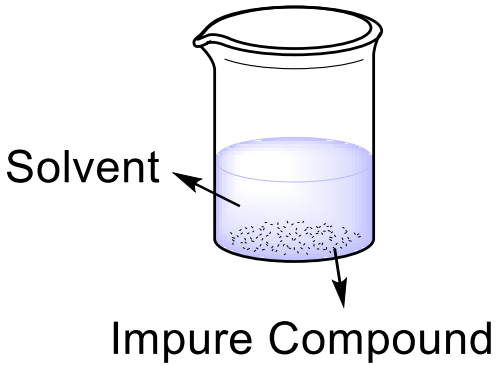
2- Sublimation

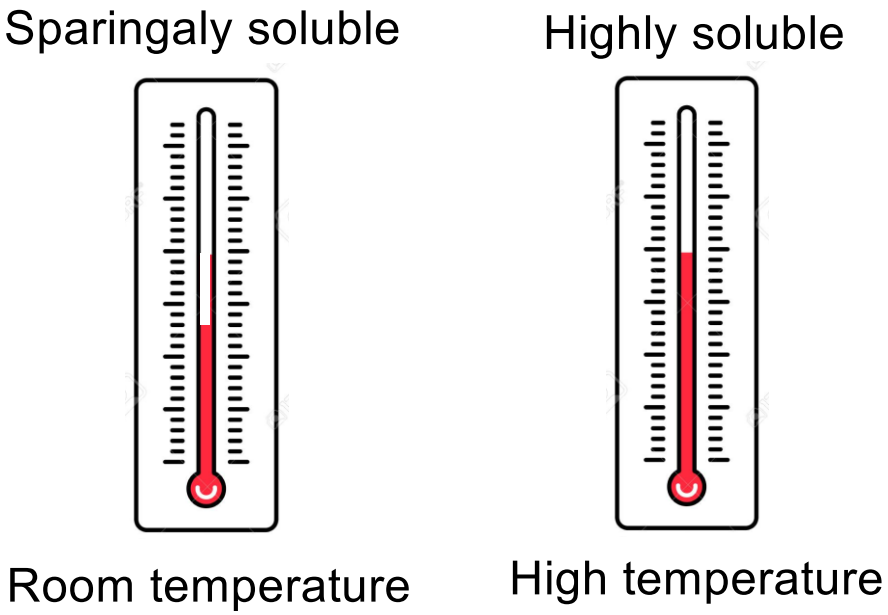
Crystallization

- Crystallization is the solidification of atoms or molecules into a highly structured form called a crystal.
- Crystallization can also refer to the solid-liquid separation and purification technique in which mass transfer occurs from the liquid solution to a pure solid crystalline phase.

Crystallization

- **The impure compound is dissolved in a solvent in which it is sparingly soluble at room temperature but more soluble at higher temperature.**

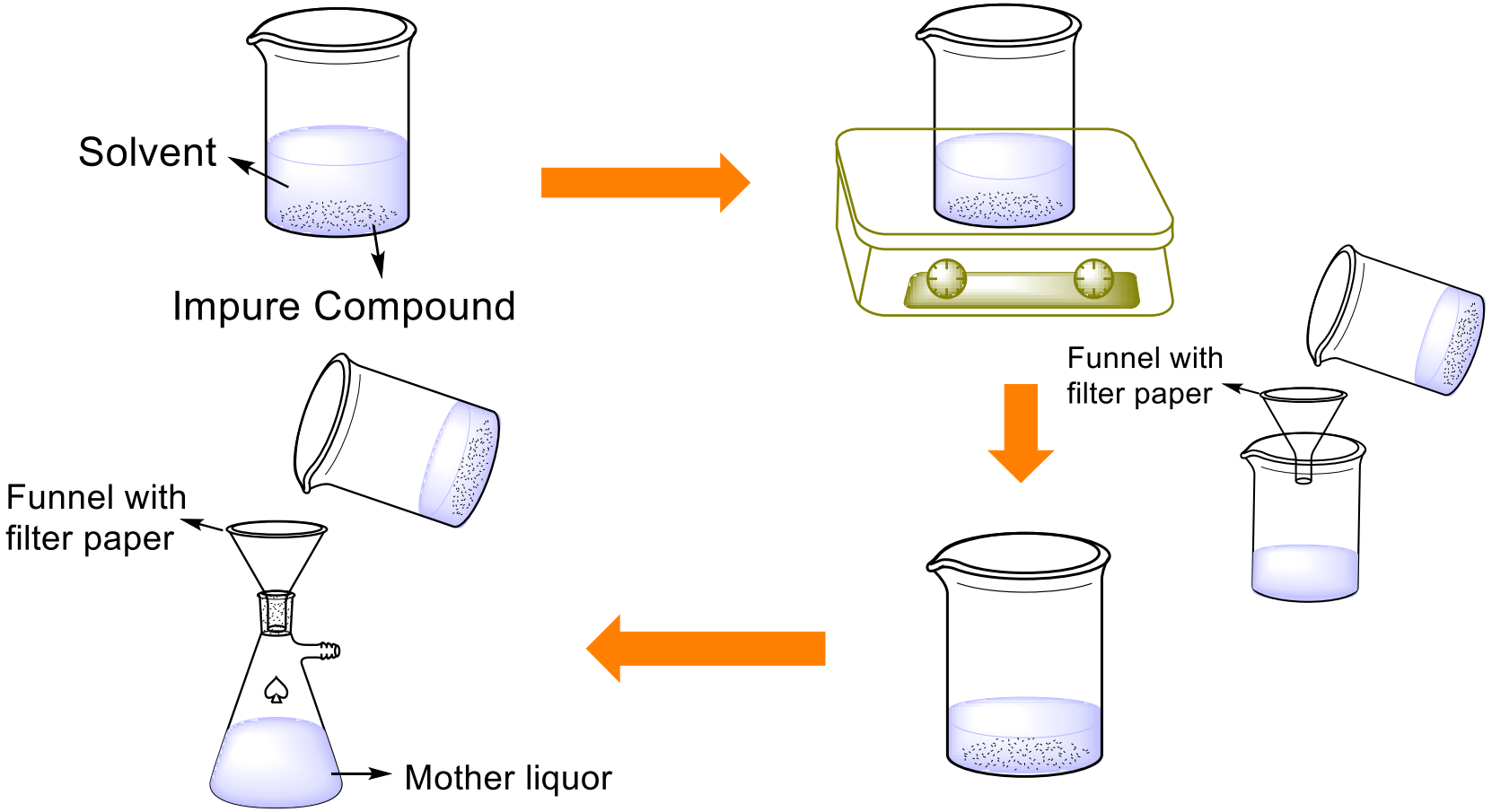




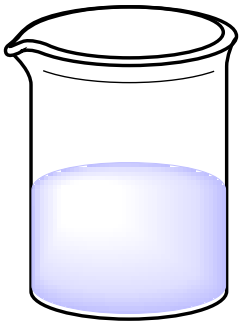
Crystallization

- The solution is concentrated to get a nearly saturated solution.
- On cooling the solution, pure compound crystallises out and is removed by filtration
- The filtrate (mother liquor) contains impurities and small quantity of the compound.
- Impurities, which impart colour to the solution are removed by adsorbing over activated charcoal

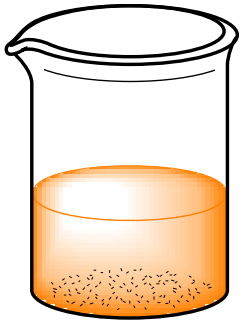
Crystallization



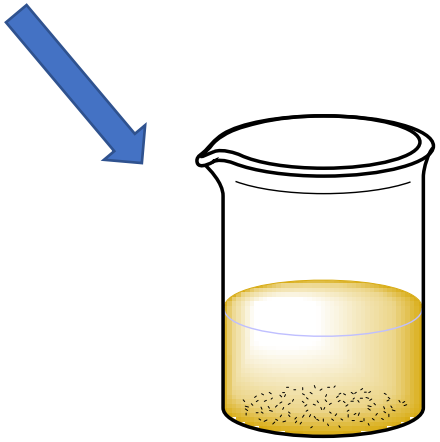
Crystallization



Highly soluble compound



Less soluble compound

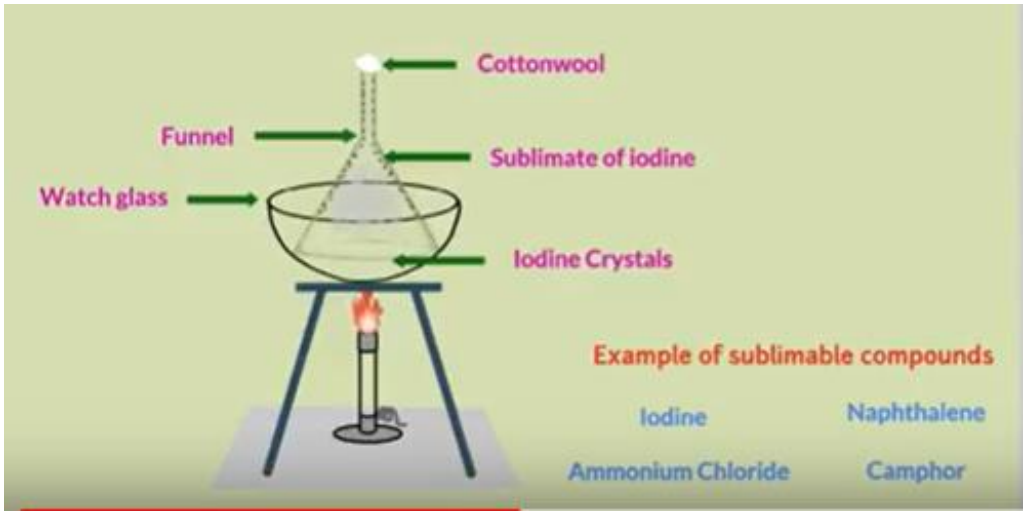


Crystalization solvent

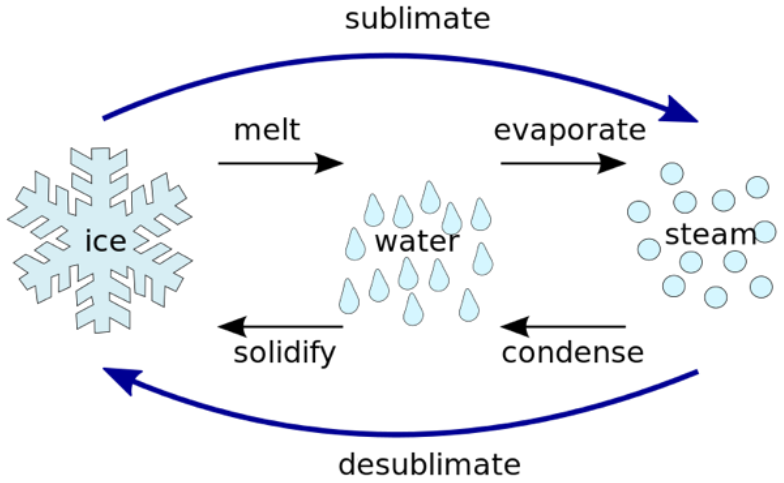
Sublimation

- **Solid substance change to vapour stat without passing through liquid state on heating.**

- **Separate sublimable compounds from non-sublimable impurities.**



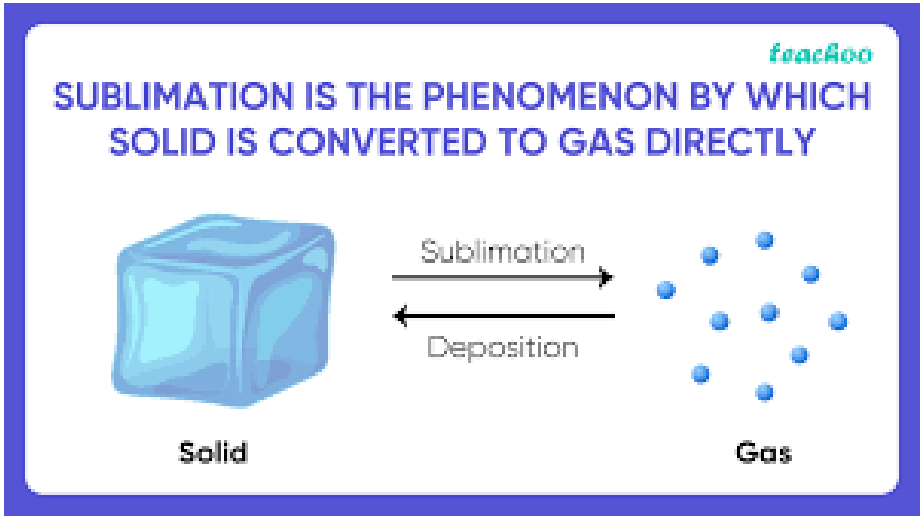
Sublimation



Sublimation is the transition of a substance directly from the solid to the gas state, without passing through the liquid state. Sublimation is an endothermic process that occurs at temperatures and pressures below a substance's triple point in its phase diagram, which corresponds to the lowest pressure at which the substance can exist as a liquid.

The reverse process of sublimation is deposition or desublimation, in which a substance passes directly from a gas to a solid phase. Sublimation has also been used as a generic term to describe a solid-to-gas transition (sublimation) followed by a gas-to-solid transition (deposition).

Sublimation



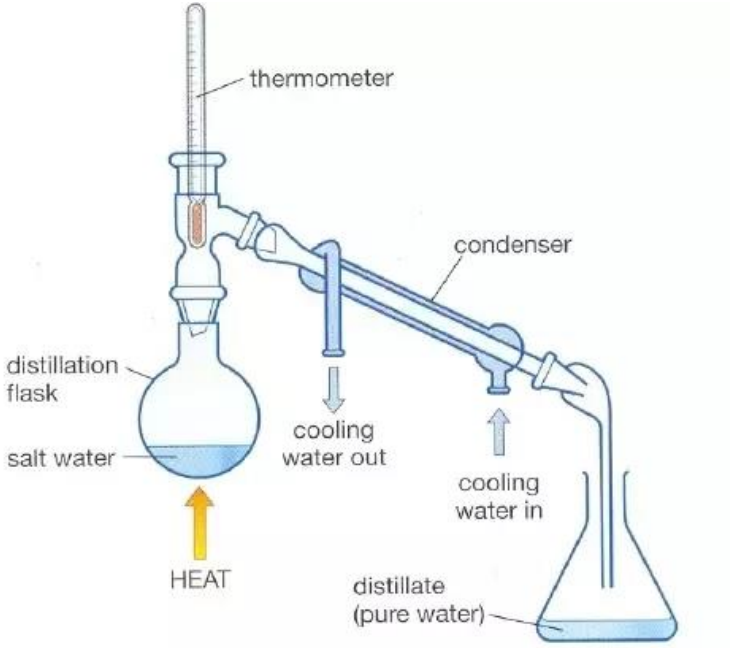
Sublimation is a technique used by chemists to purify compounds. A solid is typically placed in a sublimation apparatus and heated under vacuum. Under this reduced pressure, the solid volatilizes and condenses as a purified compound on a cooled surface (cold finger), leaving a non-volatile residue of impurities behind. Once heating ceases and the vacuum is removed, the purified compound may be collected from the cooling surface

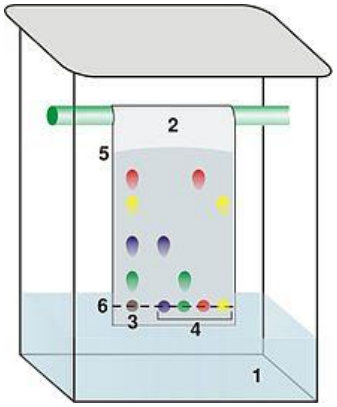
Purification of Liquids

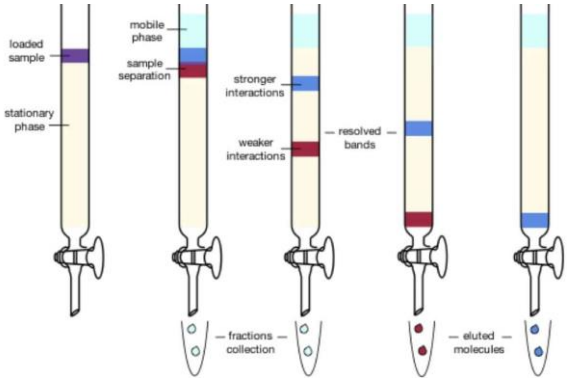
1- Distillation

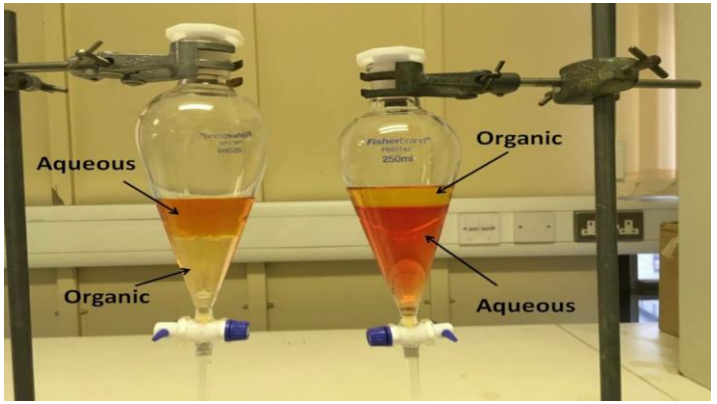
2- Differential Extraction

3- Chromatography





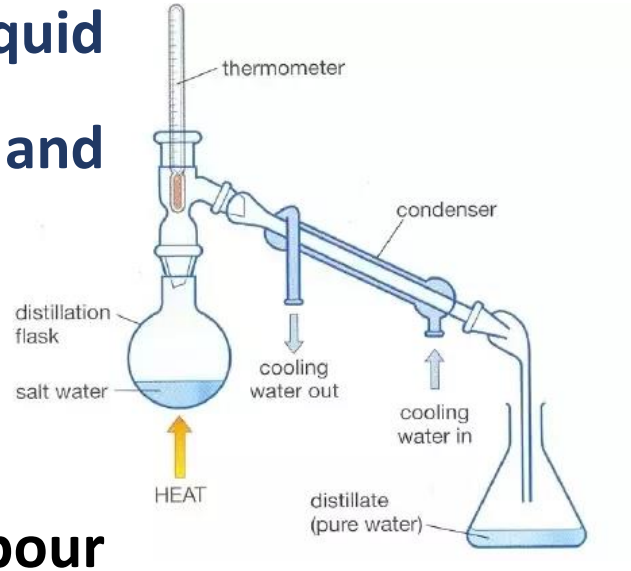




Distillation

Distillation

Is the process of separating the components or substances from a liquid mixture by using selective boiling and condensation

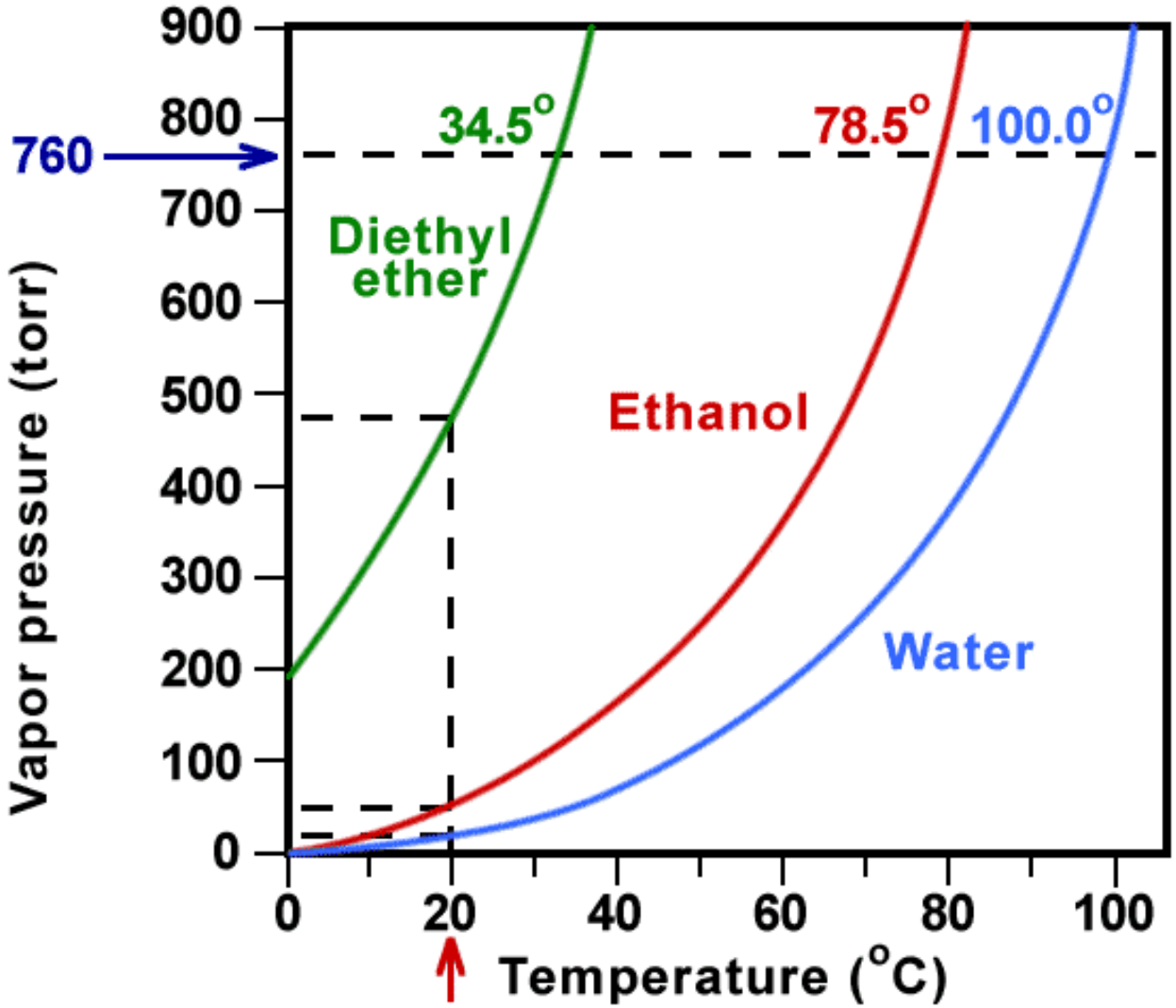


- Distillation processes based on the **vapour pressure (P_{vap})** of the mixture, which is dependant on **fraction mole** of each component

Distillation

Distillation may result in essentially **complete separation** (nearly pure components), or it may be a **partial separation** that increases the concentration of selected components in the mixture.

Relation between vapour pressure and temperature



Distillation

The Basic

- By increasing the temperature of the liquid mixture, the vapours that form will increase the pressure.
- When the vapour pressure equals the atmospheric pressure, the liquid will start boiling
- Evaporation of the liquids depending on the **Dalton's and Raoult's laws**

There are 4 types of Distillation

Simple Distillation

Fractional Distillation

Vacuum Distillation

Steam Distillation

Simple Distillation

Simple distillation is a procedure by which two liquids with different boiling points can be separated.

- **Simple distillation** can be used effectively to separate liquids that have at least (25 – 50) degrees difference in their boiling points

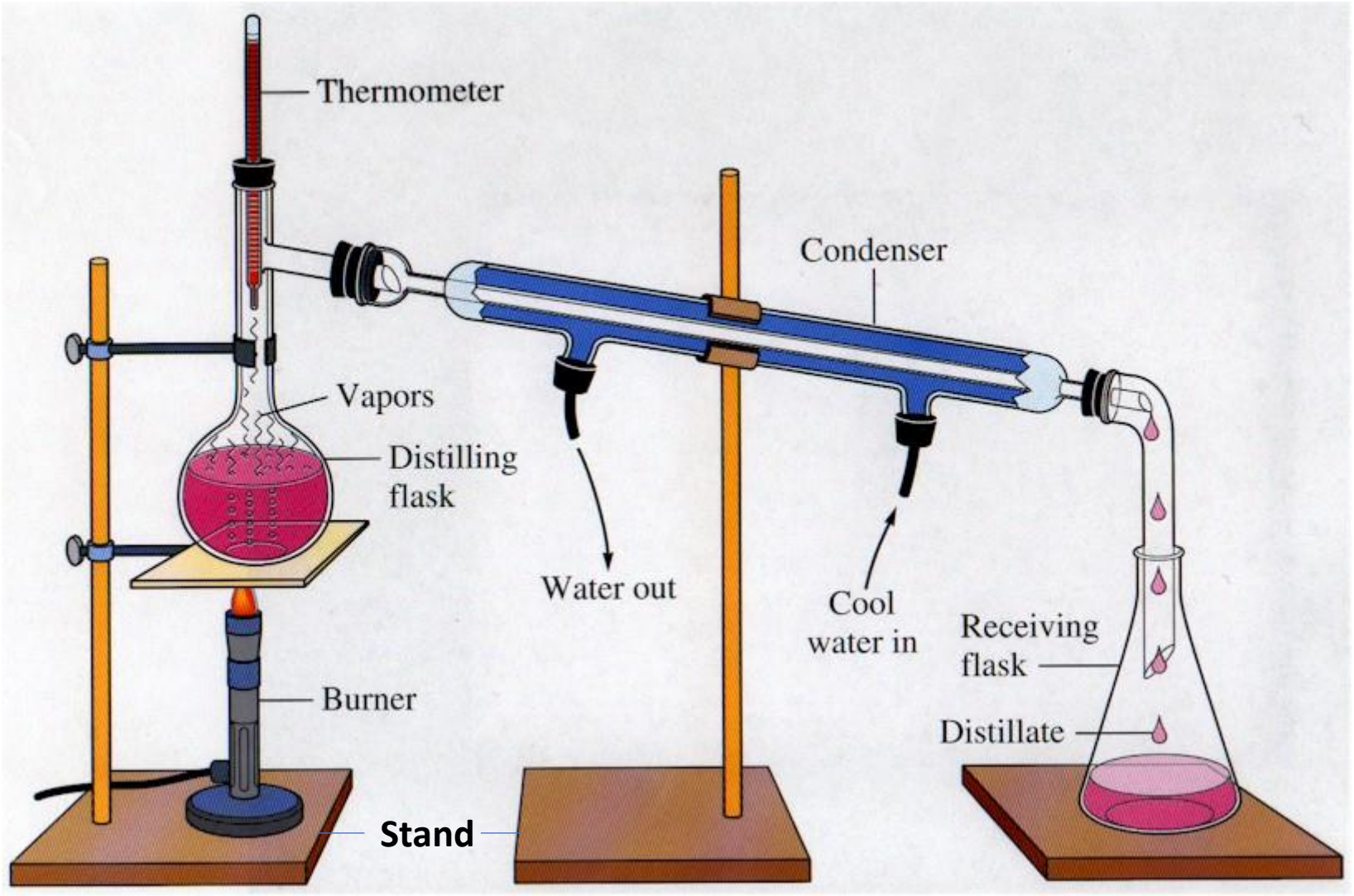
Simple Distillation

Also, It can be used to purify the liquid from solid impurities

Ex: **Water Distillation**

Separating salt water to create pure water and salt.

Simple distillation apparatus



How can you connect the simple distillation apparatus?

Raoult and Dalton's Laws

Raoult's Law

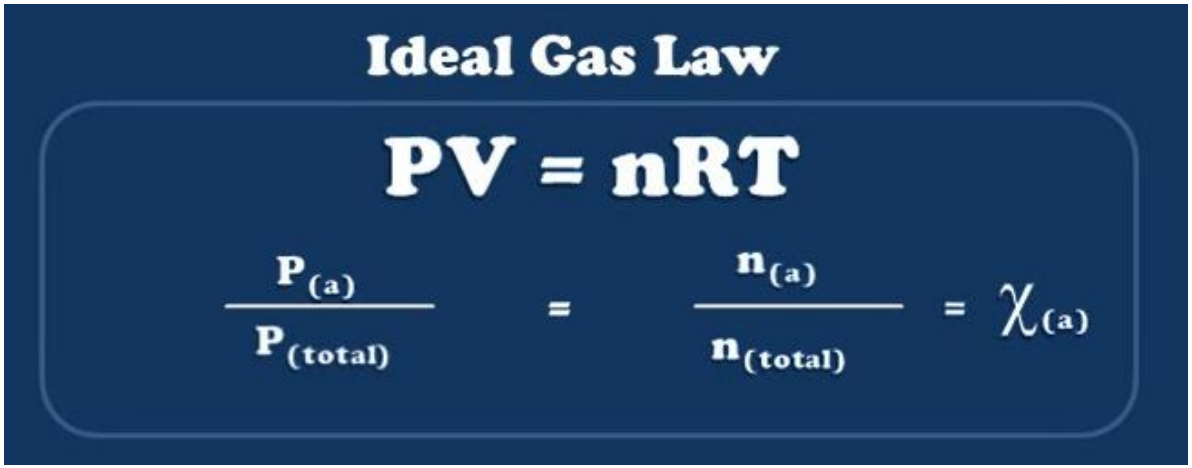
$$P_{vap} = (\chi_{liq})\, P^{o}_{vap}$$

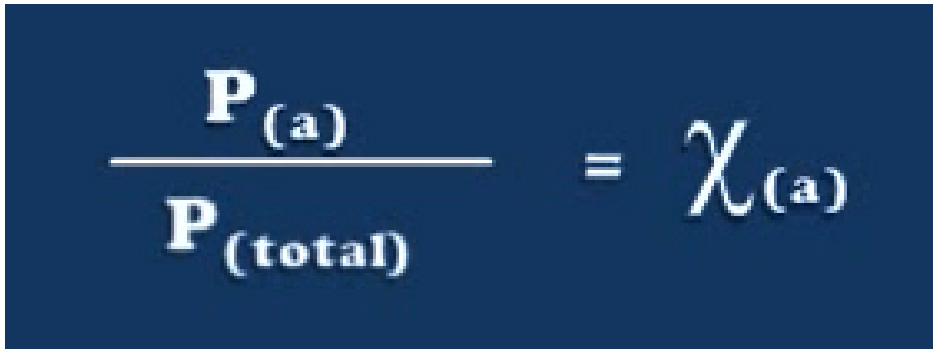
Mole fraction

Dalton's Law

$$P_{total} = P_{vap(a)} + P_{vap(b)}$$

Ideal Gas Law





Boiling a Binary Mixture

= Toluene

$P^{o}_{vap} = 300$ torr

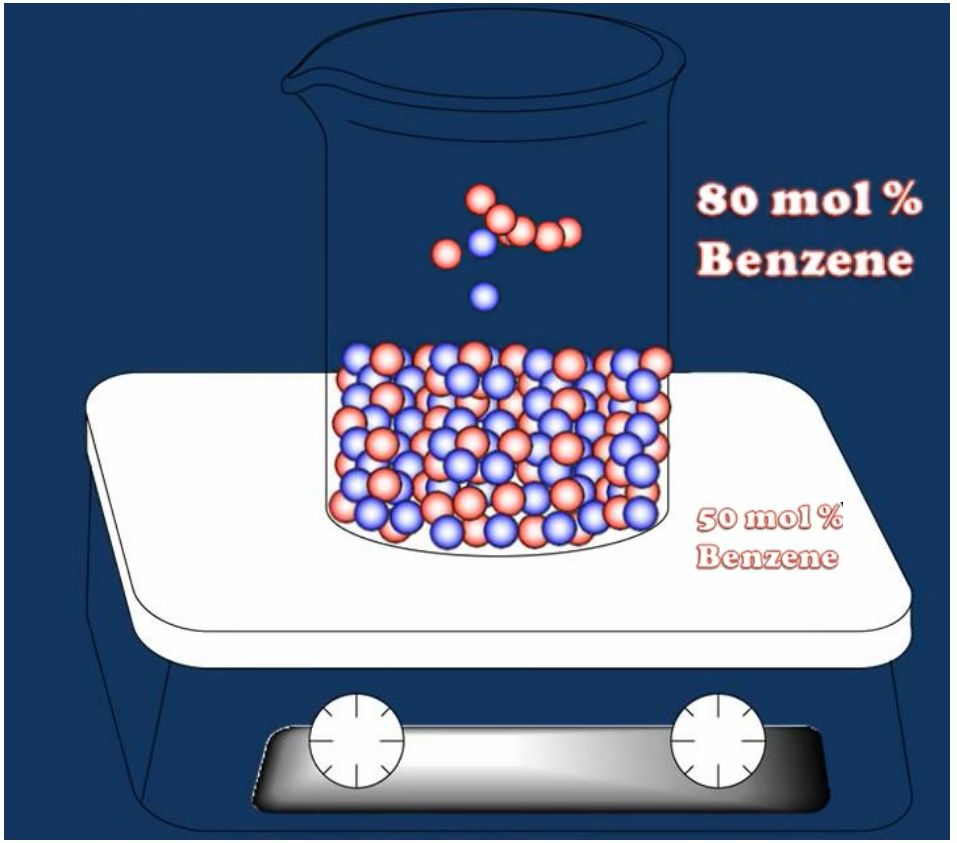
$P_{vap} = (\chi_{liq}) P^{o}_{vap}$
$P_{vap} = (0.5) * 300$ torr
$P_{vap} = 150$ torr

= Benzene

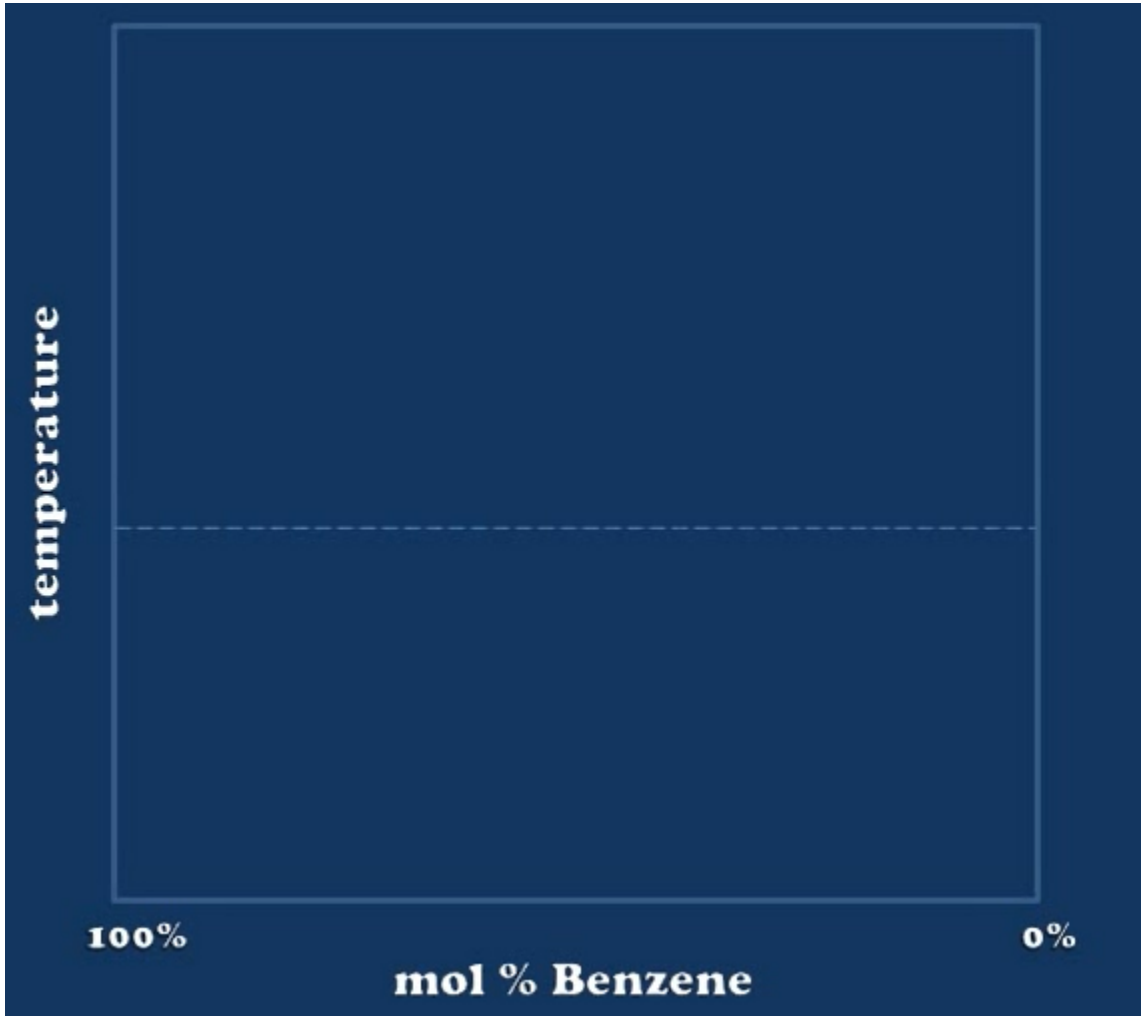
$P^{o}_{vap} = 1200$ torr

$P_{vap} = (\chi_{liq}) P^{o}_{vap}$
$P_{vap} = (0.5) * 1200$ torr
$P_{vap} = 600$ torr

$(\chi_{vap}) = P_{vap}/P_{total}$
$(\chi_{vap}) = 600$ torr$/750$torr
$(\chi_{vap}) = 0.80 = 80$ mol%



The Liquid-Vapor Composition Plot



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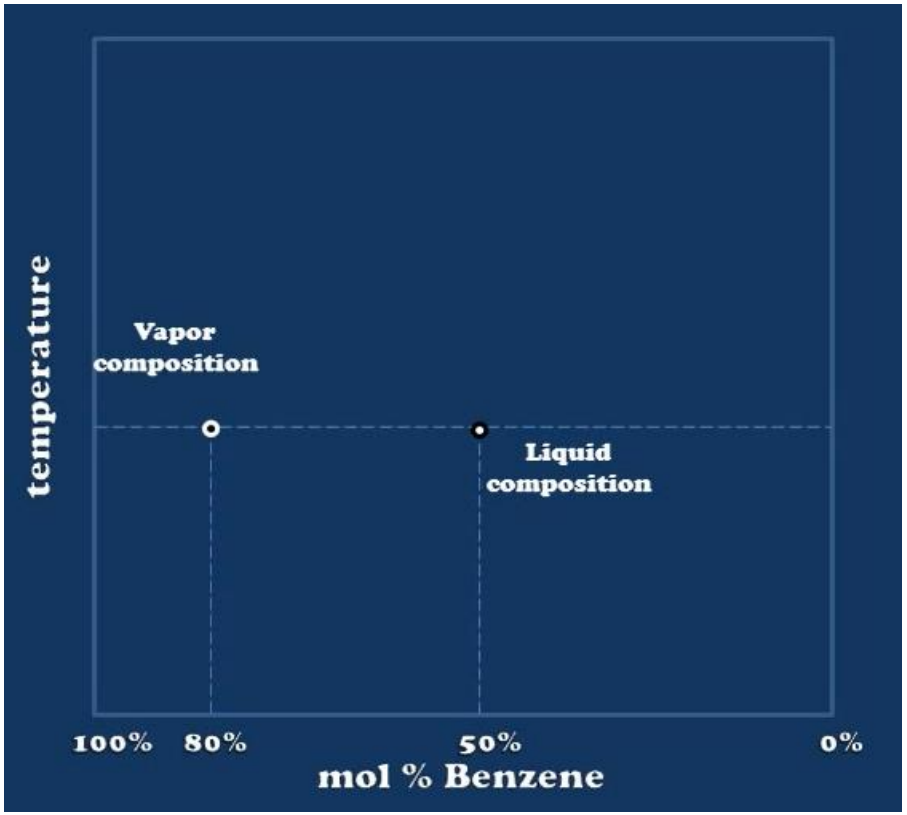
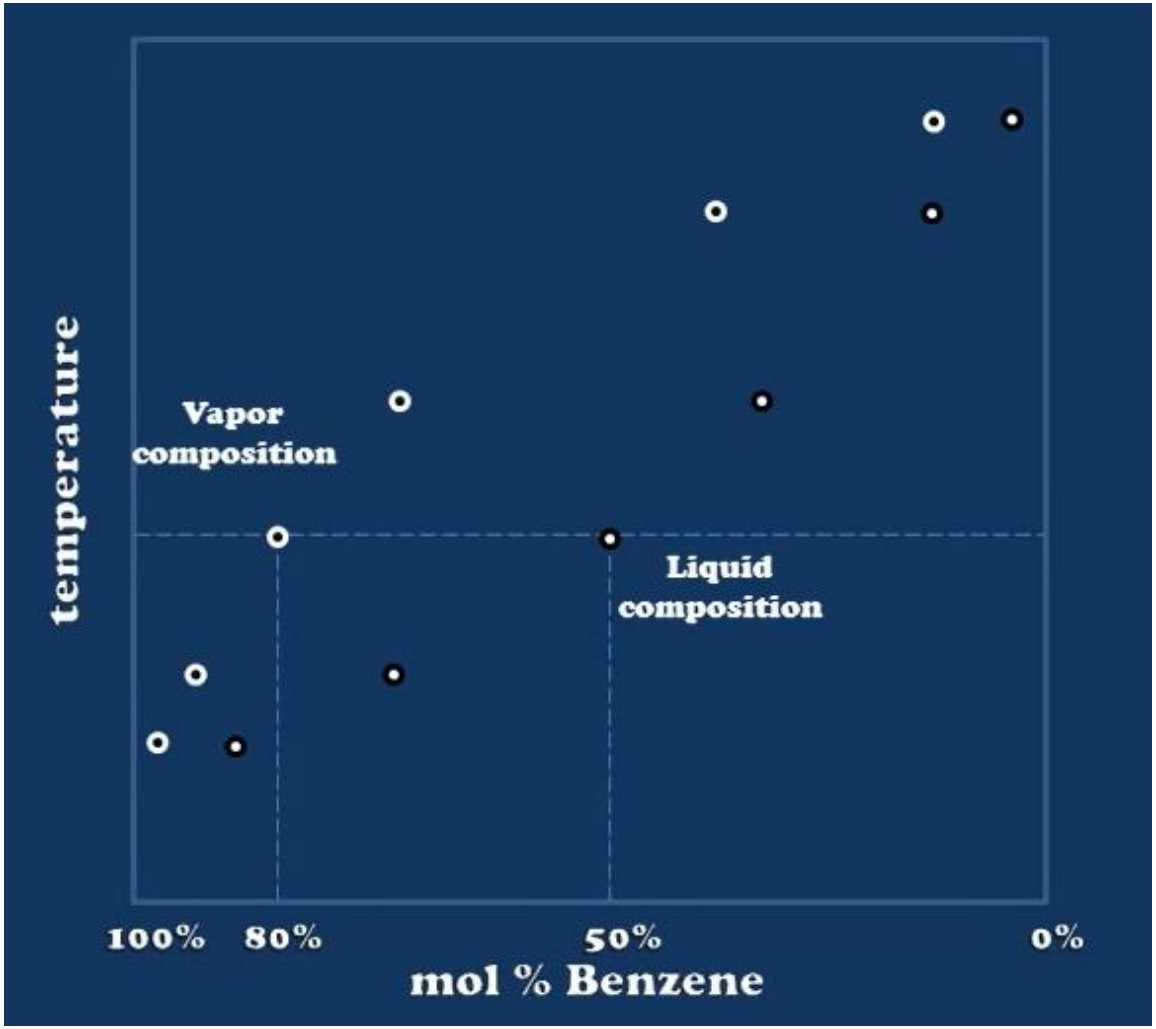
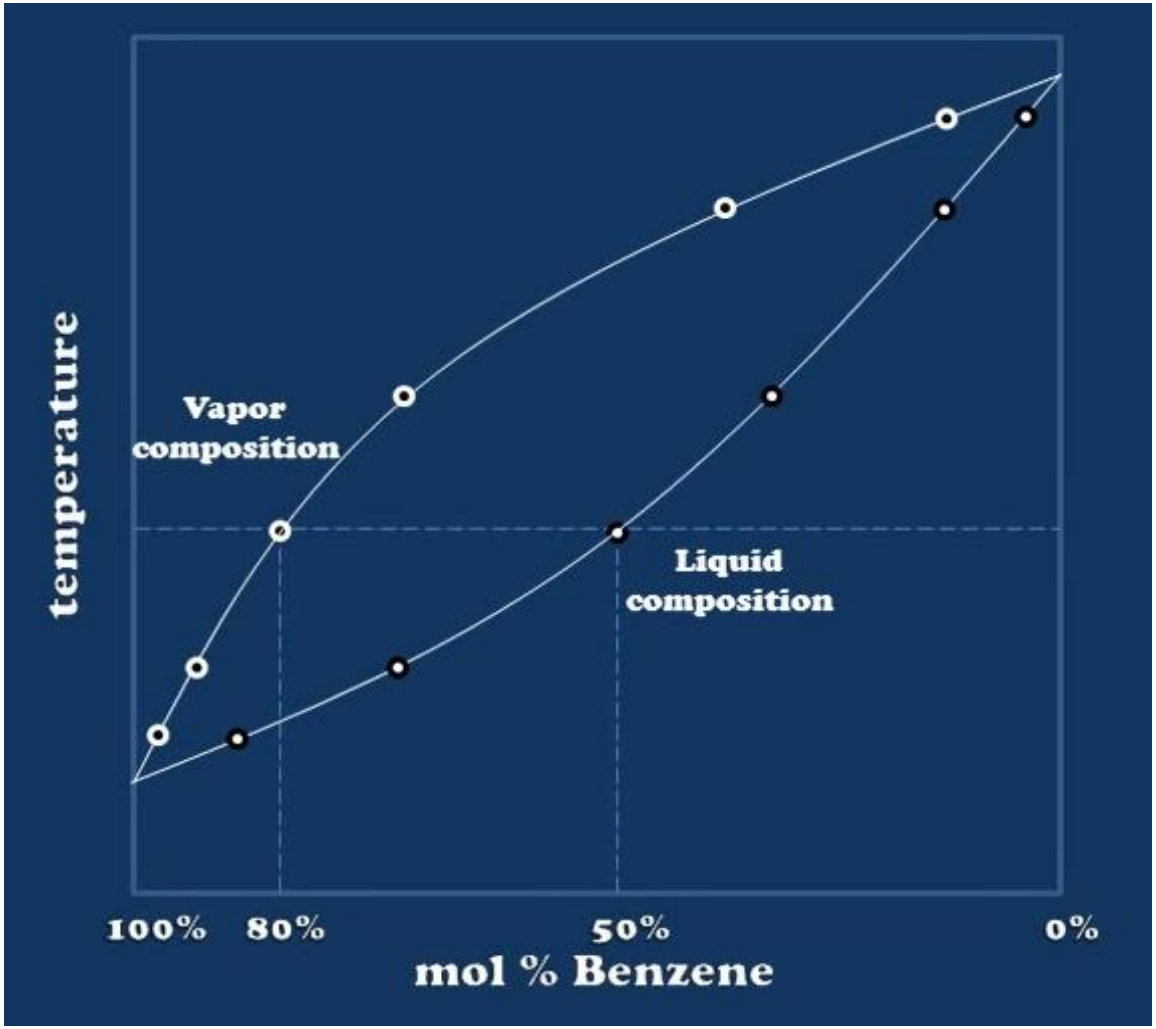


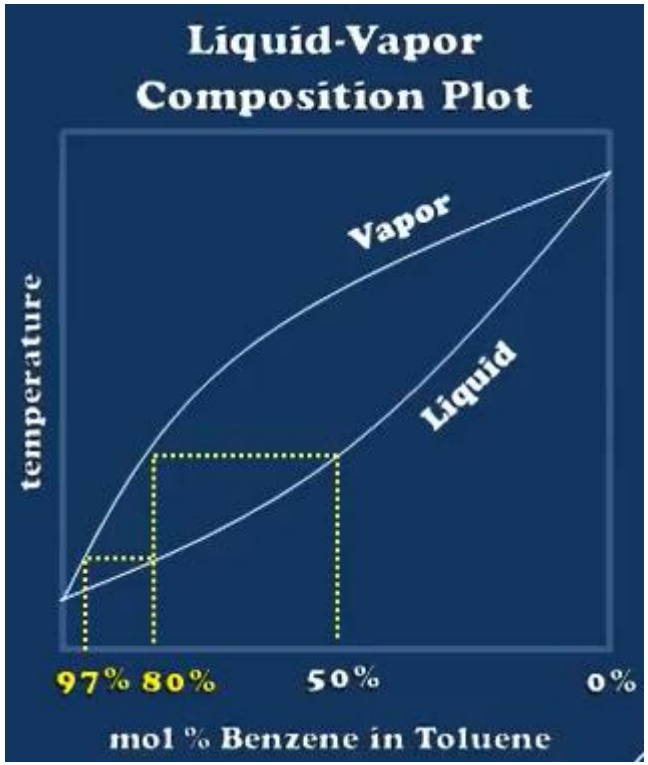
The Liquid-Vapor Composition Plot

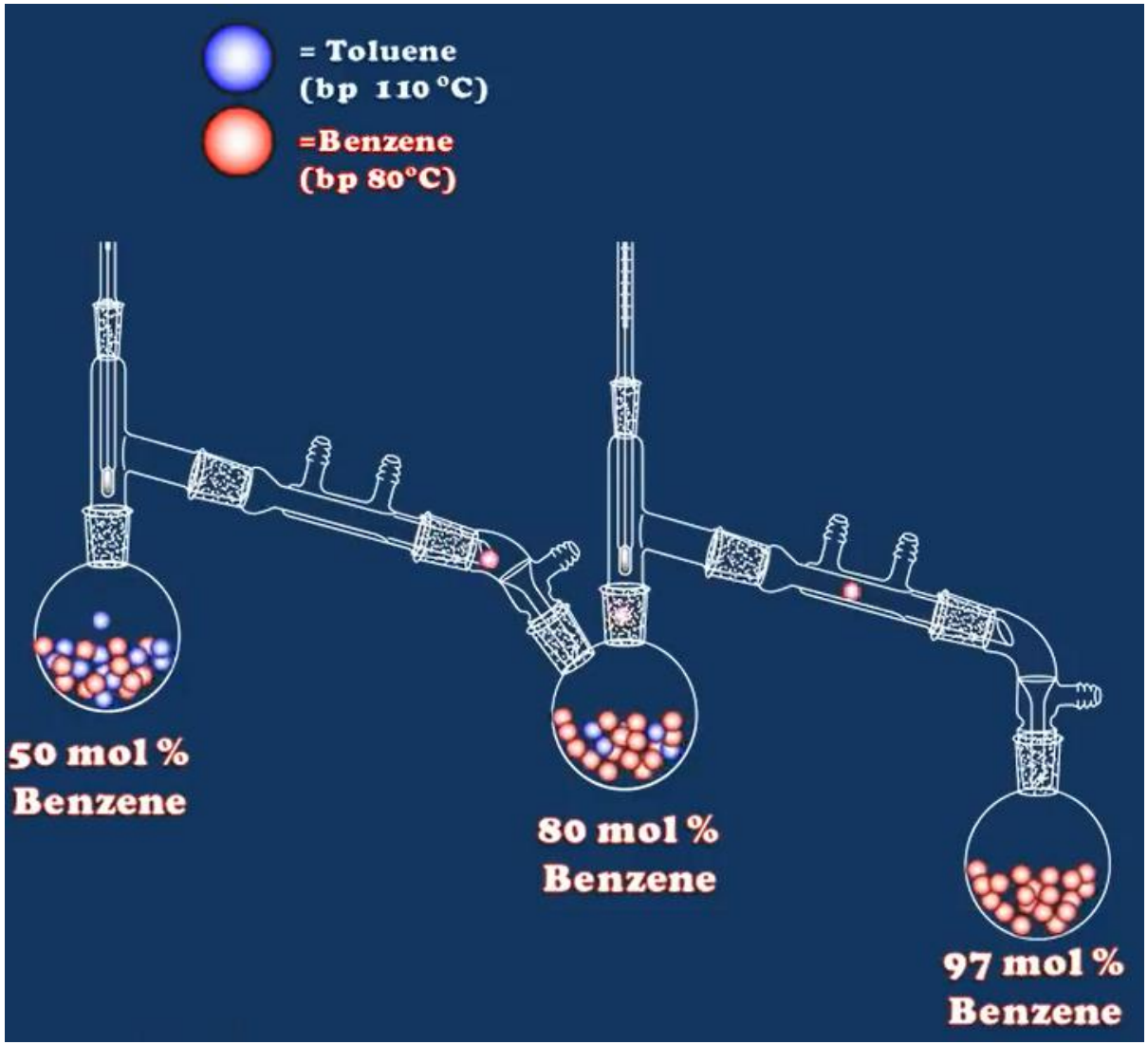


The Liquid-Vapor Composition Plot



Is it possible to have pure liquid from simple distillation?!





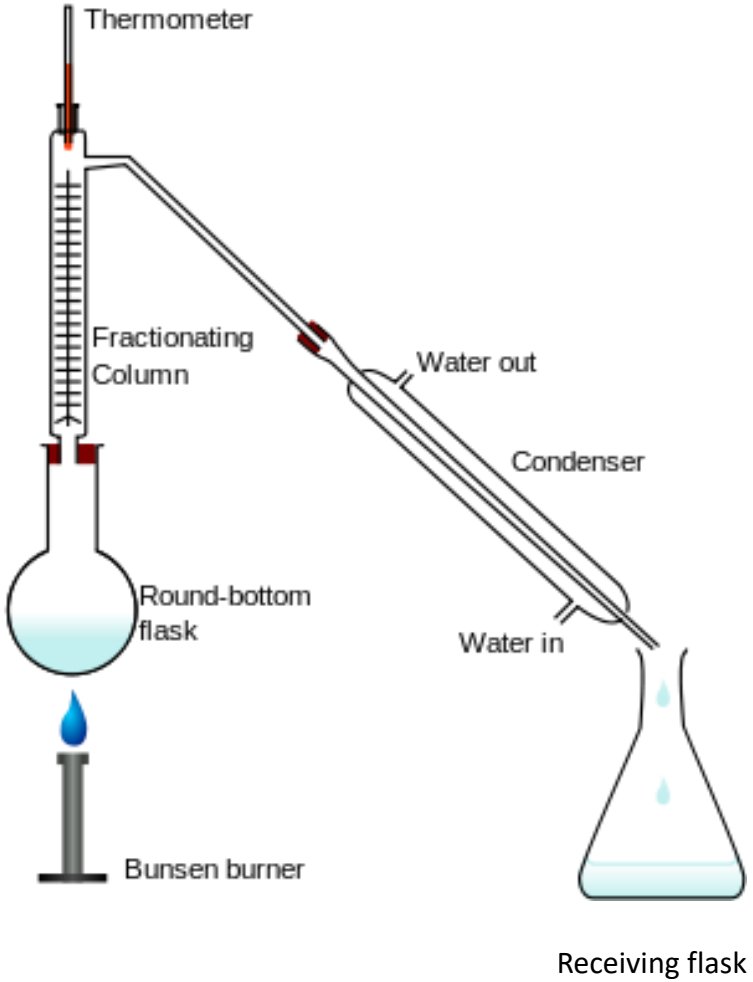
Fractional Distillation

Fractional Distillation

- Is the separation of a mixture into its component parts, or fractions.
- Chemical compounds are separated by heating them to a temperature at which one or more fractions of the mixture will vaporize.
- Generally the component parts have boiling points that differ by less than 25 °C (77 °F) from each other under a pressure of one atmosphere.

Fractional distillation apparatus

Fractional distillation is the most common form of separation technology used in petroleum refineries, petrochemical and chemical plants, natural gas processing and cryogenic air separation plants



Vacuum Distillation

Vacuum Distillation

Distillation of a liquid under reduced pressure, enabling it to boil at a lower temperature than normal

Vacuum Distillation

"low-temperature distillation"

- This technique is used when the boiling point of the desired compound is **difficult to achieve**, will cause the compound to **decompose**.
- For compounds with a normal bp above 200 ^{o}C
- To save energy in heating

Sources of Vacuum

Aspirator

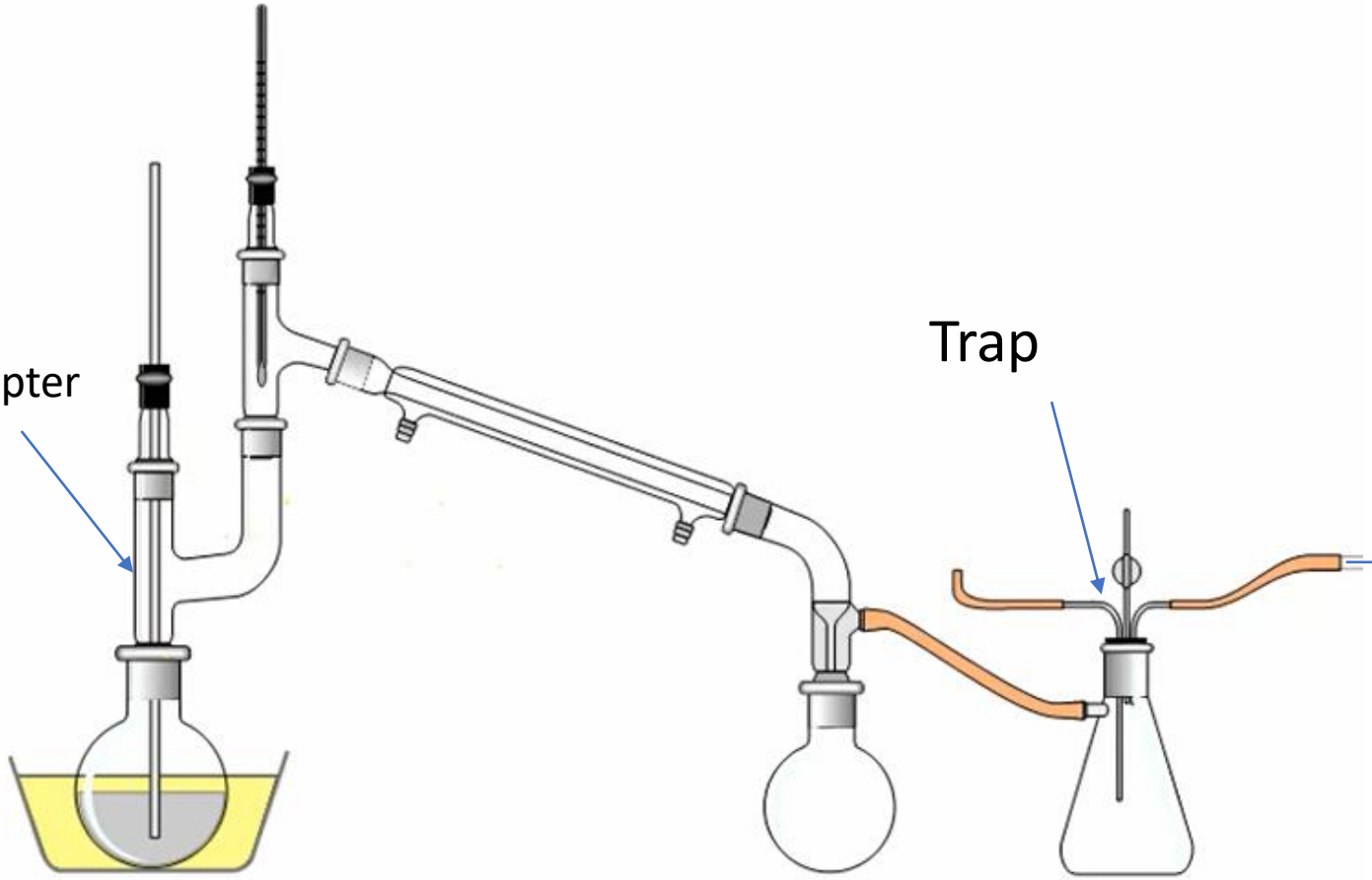
- Effective vacuum is dependent on the vapour pressure of water, which is dependent on the temperature of water
- Dependent on sufficient water pressure
- Cheap and easy
- A trap must be used

Sources of Vacuum

Vacuum pump

- Pressure dependent on the efficiency of the pump
- Pressure of < 1 mm Hg can be reached
- Expensive compared to an aspirator, but more effective

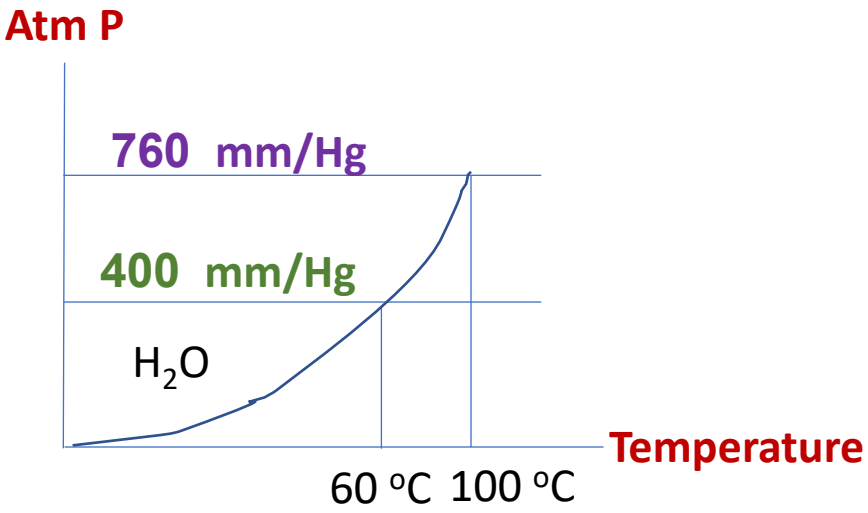
Vacuum distillation apparatus



Why the boiling point decrease by using Vacuum ?

The liquid is boil when it's
vapour pressure = atmospheric pressure

The vacuum decrease the atmospheric pressure (external pressure), so the liquid vapour pressure is decrease.



True or False?

1- Distillation is the process by which a solid forms, into a highly structured form called a crystal

2- Crystallization process is depending on the different solubility of the organic liquid compounds into a various solvents

Complete

3- Solid substance change to vapour stat without passing through liquid state on heating is called …….

$$P_{total} = P_{vap(a)} + P_{vap(b)}$$

4- This law is called …….

vapour pressure (P_{vap}) of the mixture is dependant on …… of each component

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vapour pressure (P_{vap}) of the mixture is dependant on …… of each component

Steam Distillation

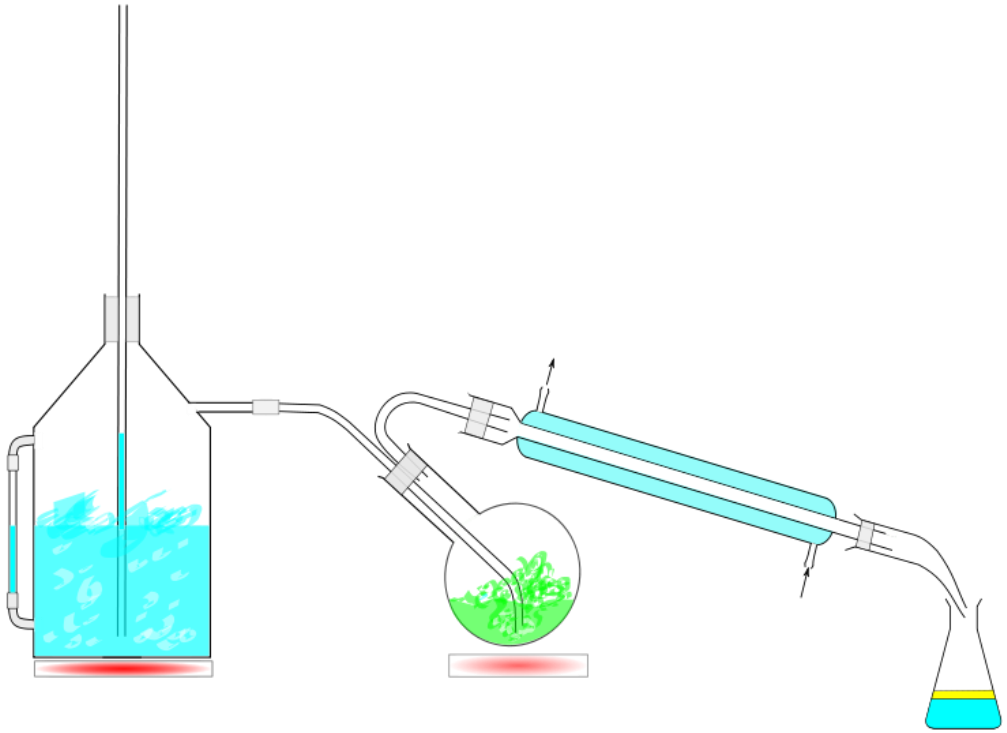
Steam Distillation

Distillation of a liquid in a current of steam, used especially to purify liquids that are **not very volatile, decomposed at their boiling points,** and are **immiscible with water**.

Steam Distillation

Steam distillation is a separation process that consists in distilling water together with other volatile and non-volatile components. The steam from the boiling water carries the vapor of the volatiles to a condenser; both are cooled and return to the liquid or solid state, while the non-volatile residues remain behind in the boiling container.

Steam distillation apparatus



Steam distillation is used in chemical laboratories as one of many substance separation methods.

تنقية الأنيلين عن طريق التقطير البخاري

Steam Distillation

Also, this method is used for extraction of **essential oil** from their original plant sources

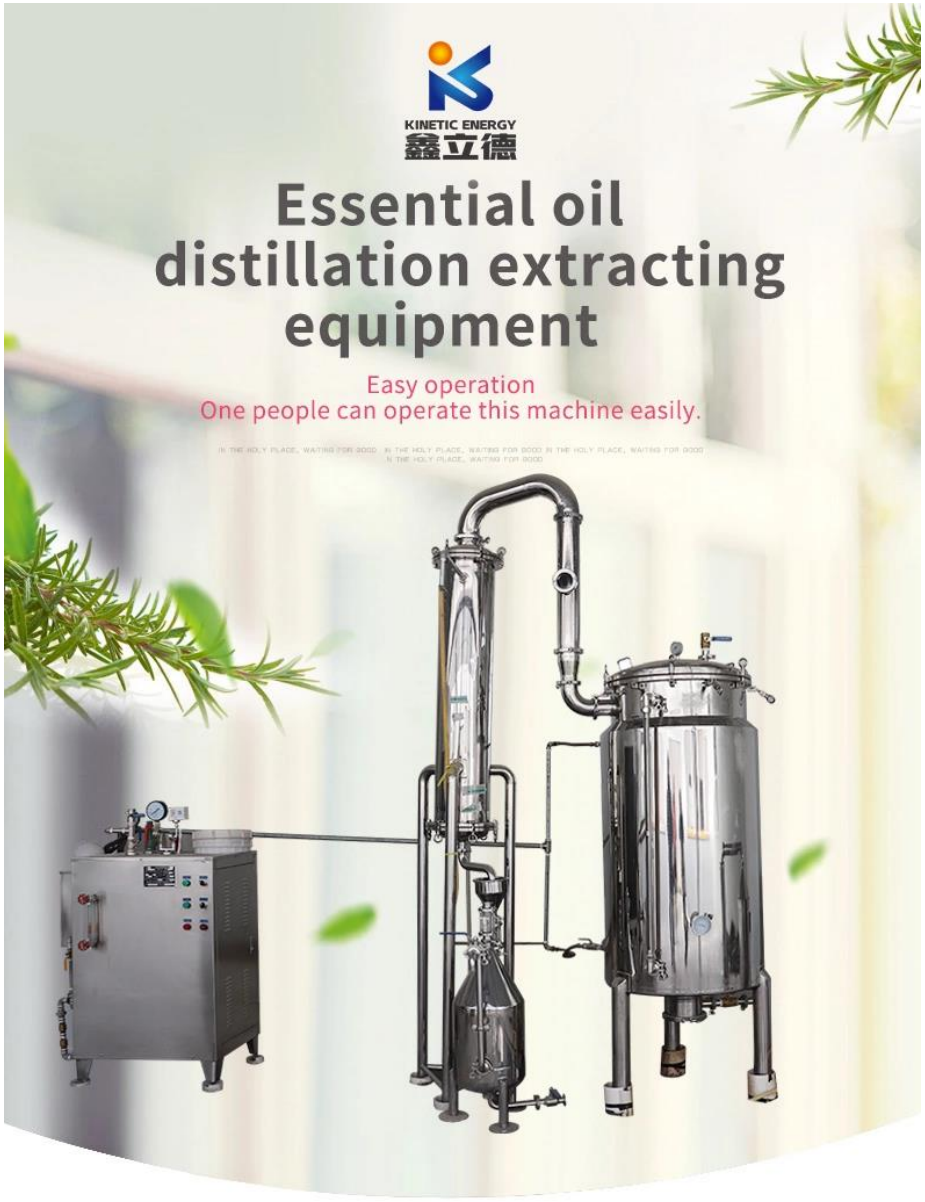
Ex:

Limonene from orang or lemon – Lavender oil – rose oil ……etc.

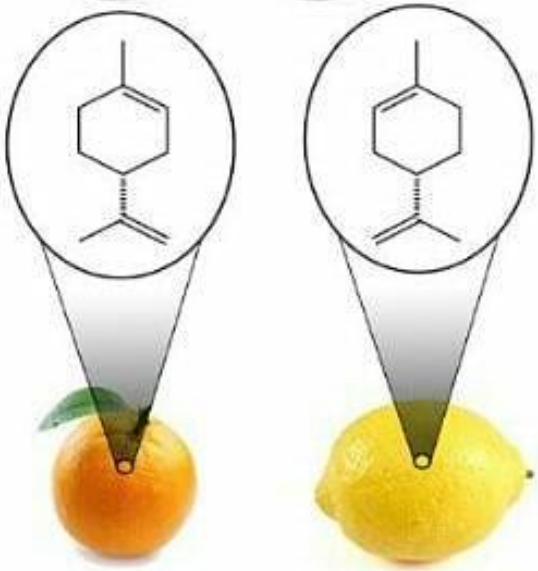
KINETIC ENERGY
鑫立德

Essential oil distillation extracting equipment

Easy operation
One people can operate this machine easily.



ليمونين
limonene



البرتقال (R)-limonene

الليمون (S)-limonene

الليمونين مركب تربيني يتواجد طبيعياً في الفواكة الحمضية كالليمون والبرتقال هذا المركب له متماكبان ضونيان هما إس-ليمونين هو المذاق المميز لليمون ، و أر-ليمونين وهو المذاق الخاص بالبرتقال. يمكن أستخلاص الليمونين من قشور الليمون أو البرتقال بأستخدام التقطير البخاري يستعمل الليمونين كمنكة في الأطعمة و في منتجات التجميل وفي صناعة معطرات الجو وغيرها.....

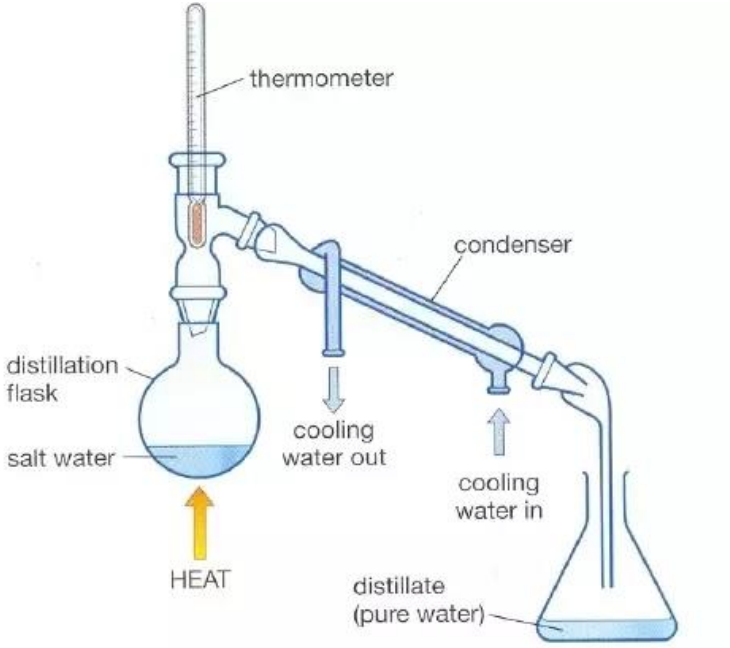
Extraction

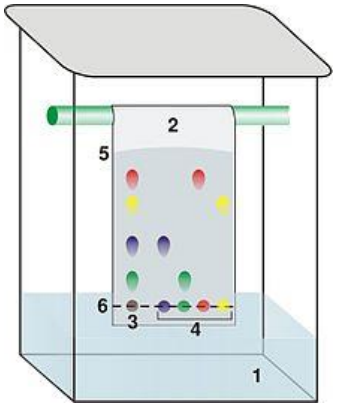
Purification of Liquids

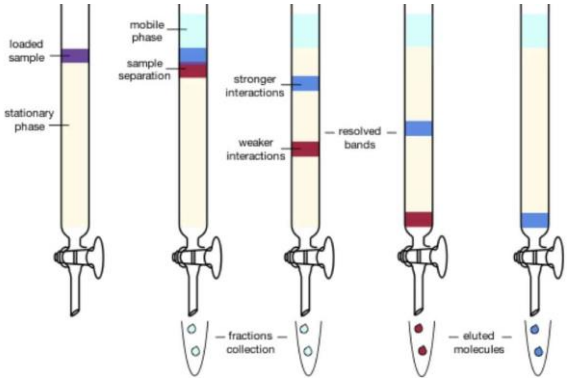
1- Distillation

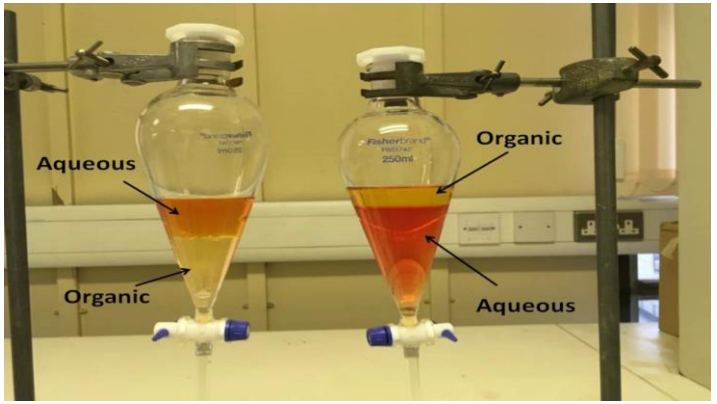
2- Differential Extraction

3- Chromatography

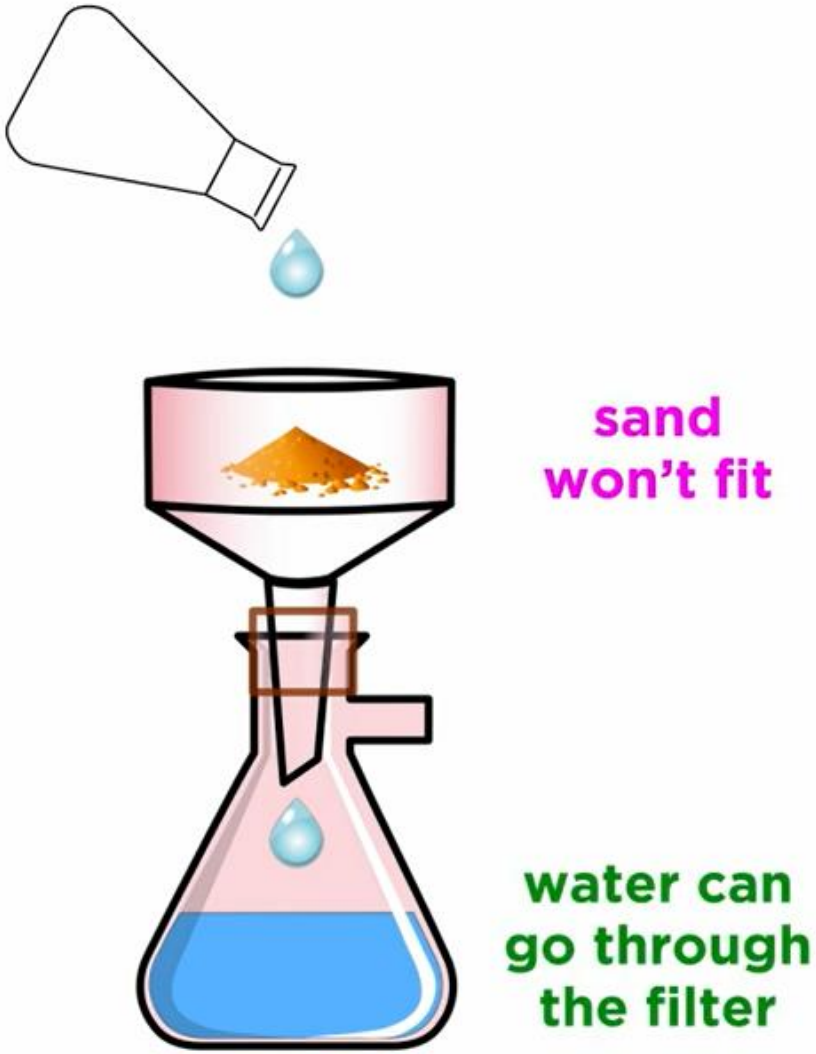




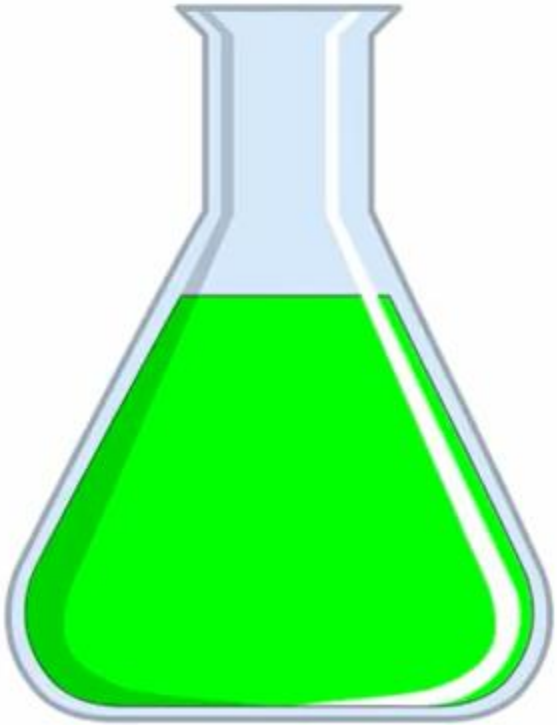




water and sand can be separated by filtration



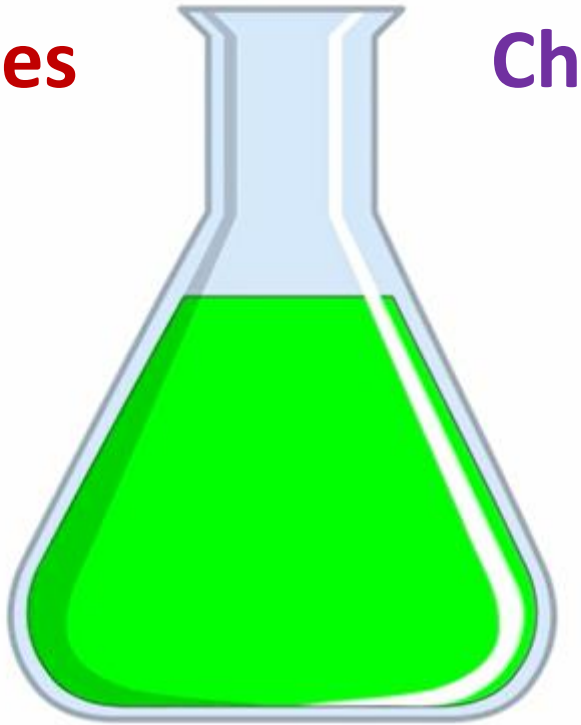
What about mixtures of only small molecules?



we will rely on solubility and reactivity

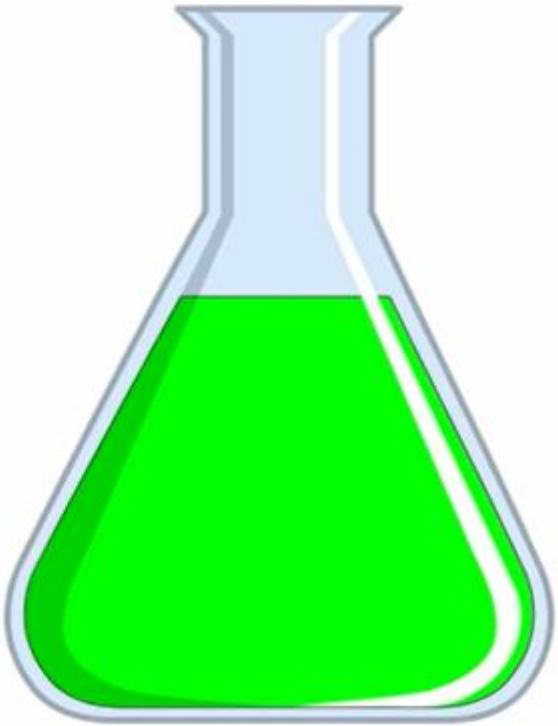
Physical properties

Chemical properties

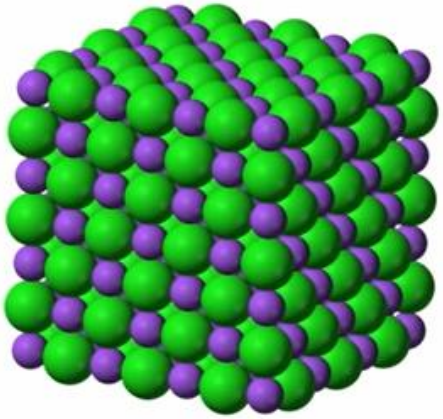


A Technik to use this is called

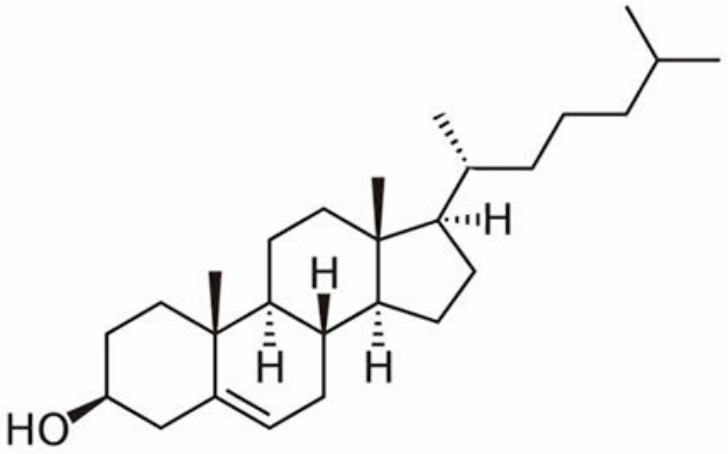
extraction



sodium chloride

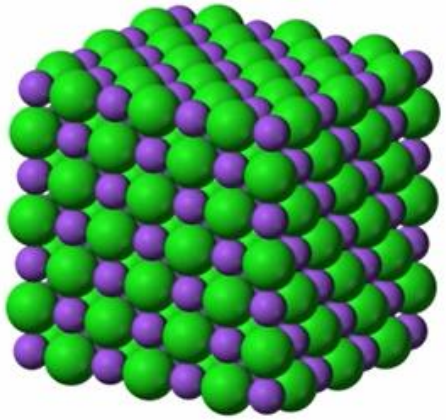


cholesterol



mixture

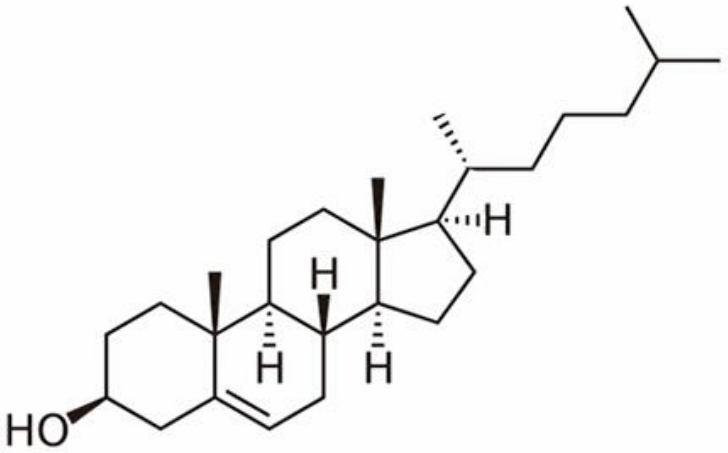
sodium chloride



ionic compound

water soluble

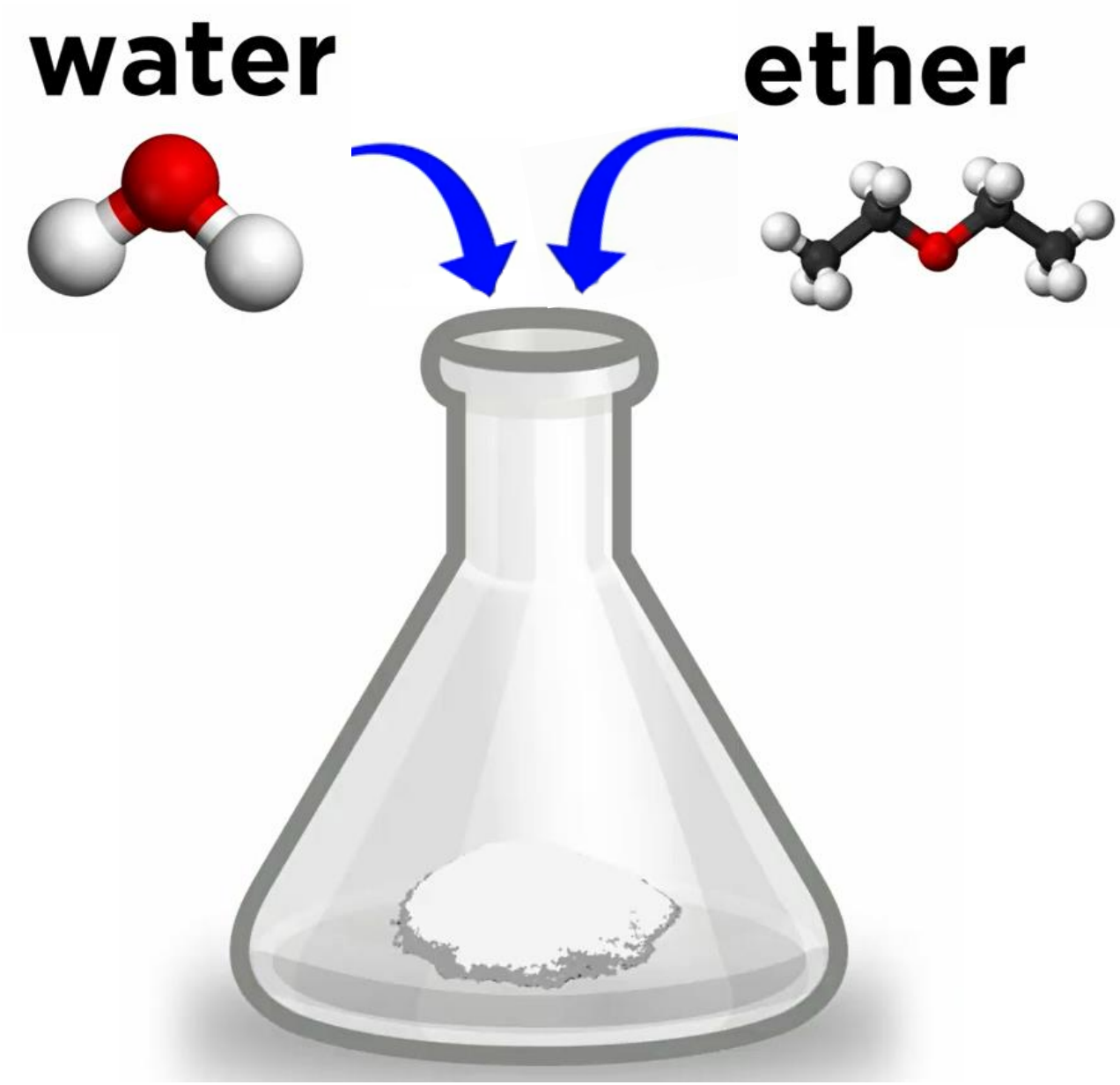
cholesterol



steroid (lipid)

water insoluble

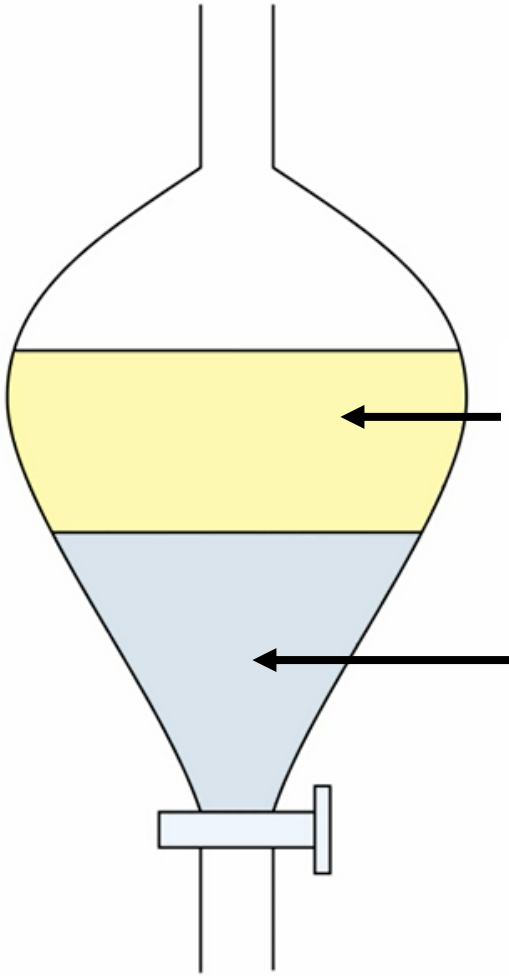
ether soluble


water
ether

separatory funnel

the solvents
are immiscible

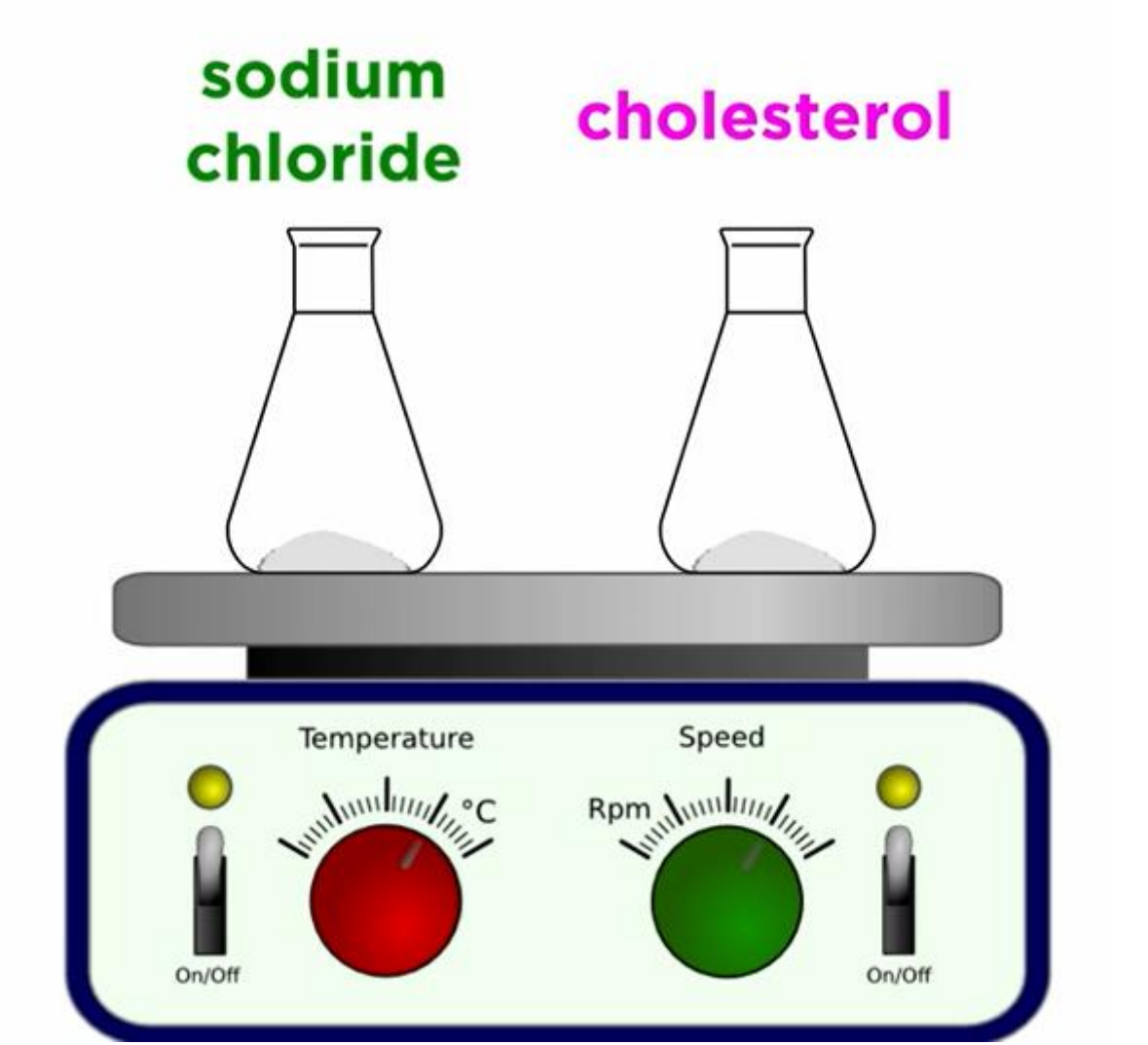
increasing
density



organic layer
(ether + cholesterol)

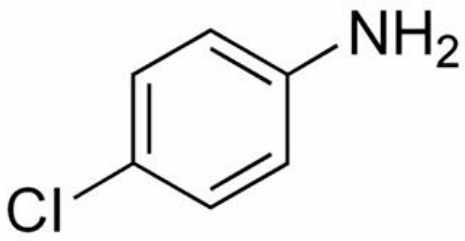
aqueous layer
(water + NaCl)

evaporate the solvents

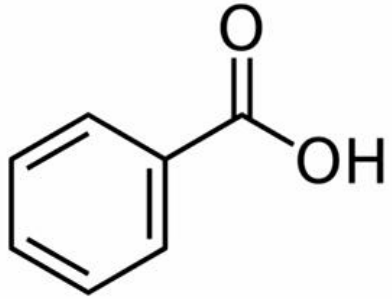


What about if you have this mixture, how can you separate them?

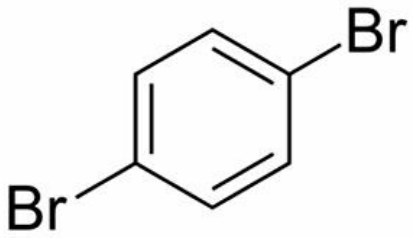
4-chloroaniline



benzoic acid

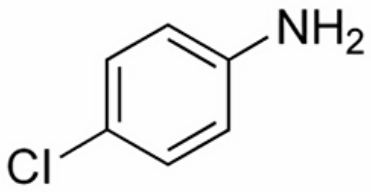


1,4-dibromobenzene

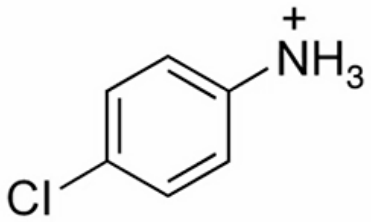


these compounds have similar solubilities

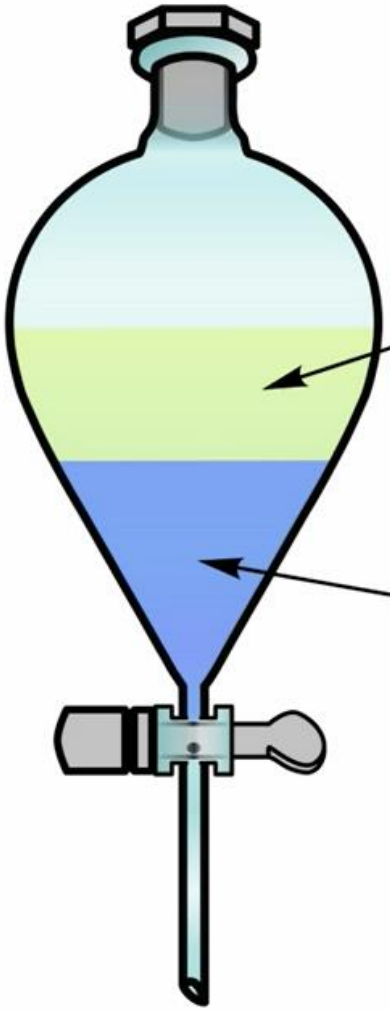
4-chloroaniline



HCl



this compound is now water soluble
(ion-dipole interactions)

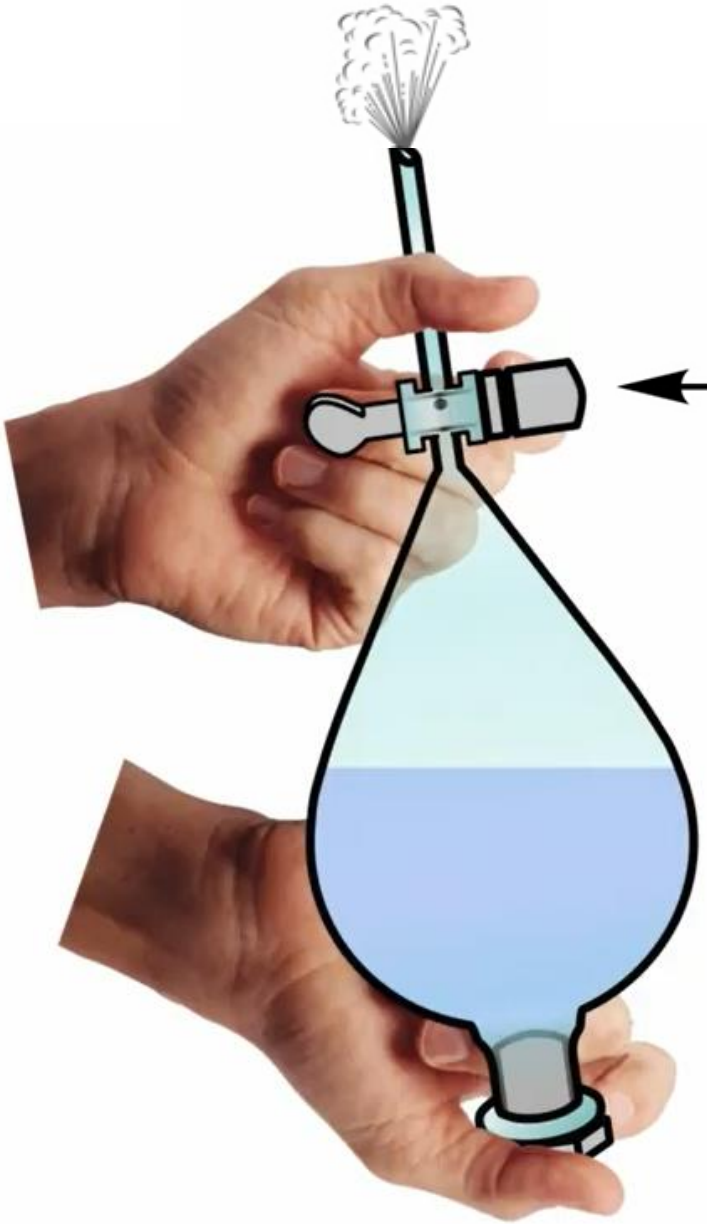


organic layer

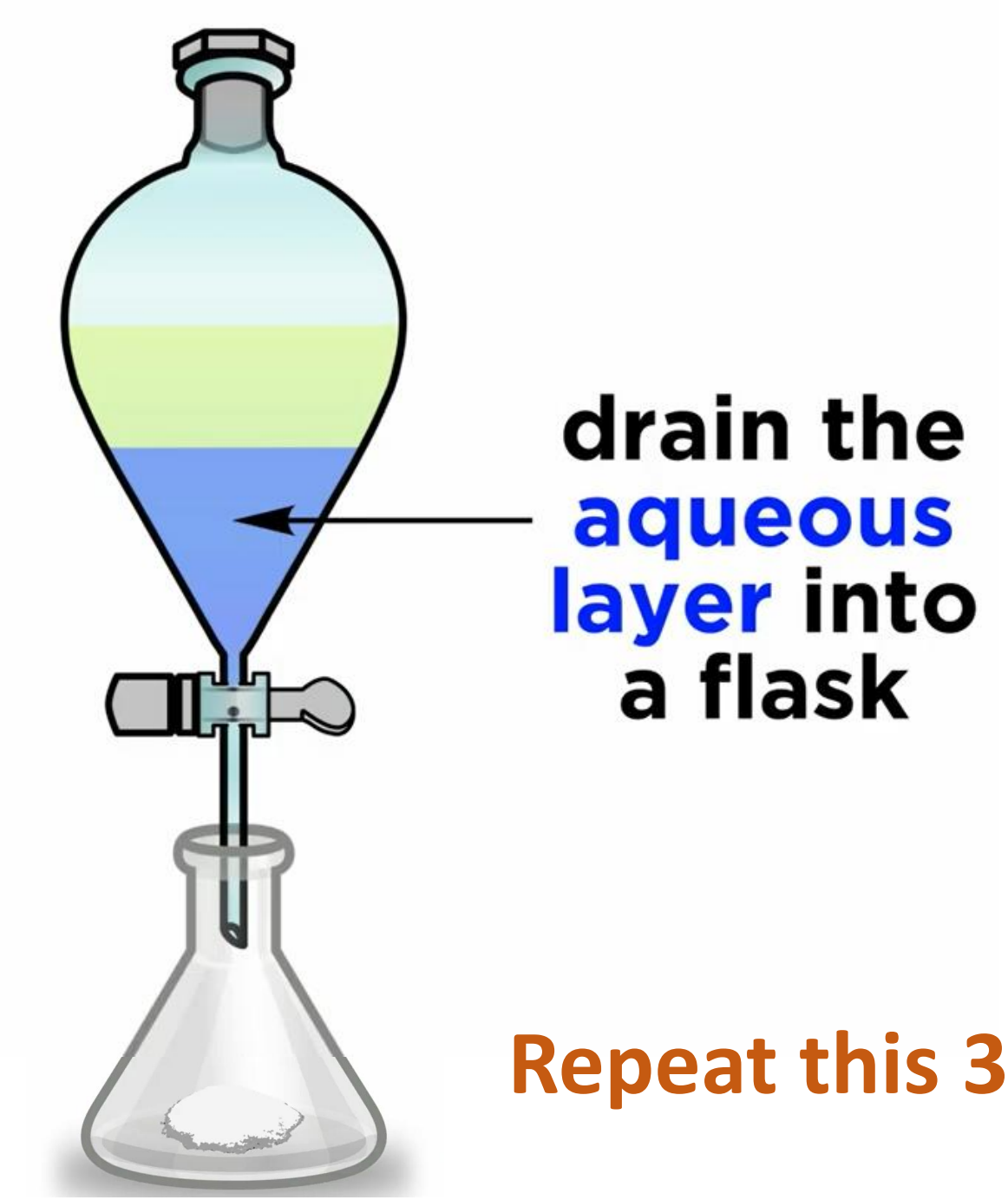
ether
benzoic acid
1,4-dibromobenzene

aqueous layer

water
4-chloroaniline salt



open the stopcock to vent the gas



Repeat this 3 times

Complete the rest of the mixture !

Q1: Choose the correct answer of the following:

Impurities, which impart colour to the solution are removed by adsorbing over …….

a) silica Gel (G)
b) silica Gel (F)
c) activated charcoal
d) aluminium

Q2: Choose true or false

The liquid is boil when it's vapour pressure equal the atmospheric pressure

a) True
b) False

Q3: If you have a binary liquid mixture **X** and **Y** with **40%mol** of **X**, and the pure vapour presser of **X = 300** and **Y = 1000** torr.

Calculate the following:

1- Vapour presser of X and Y.
2- Vapour mol fraction of X and Y.

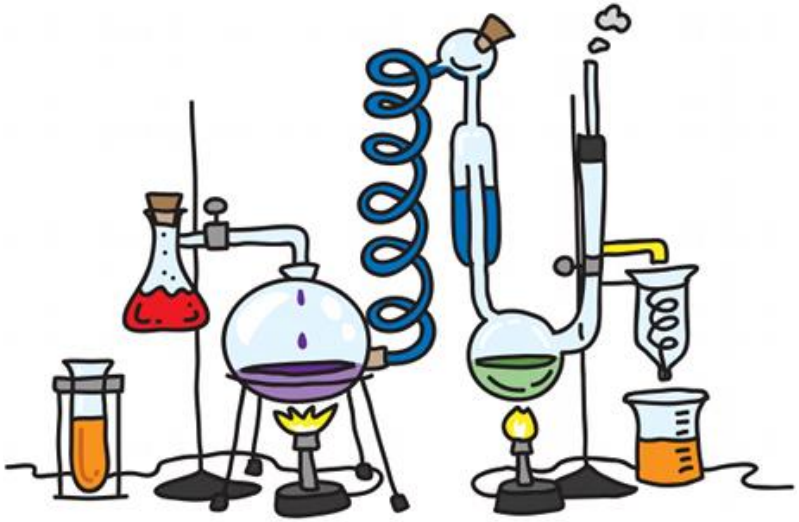
Q3: If you have a binary liquid mixture **X** and **Y** with **40%mol** of **X**, and the pure vapour presser of **X = 300** and **Y = 1000** torr.

Calculate the following:

1- Vapour presser of X and Y.

2- Vapour mol fraction of X and Y.

Purification of Organic Compounds



Dr. Mohamed Y. Mahgoub

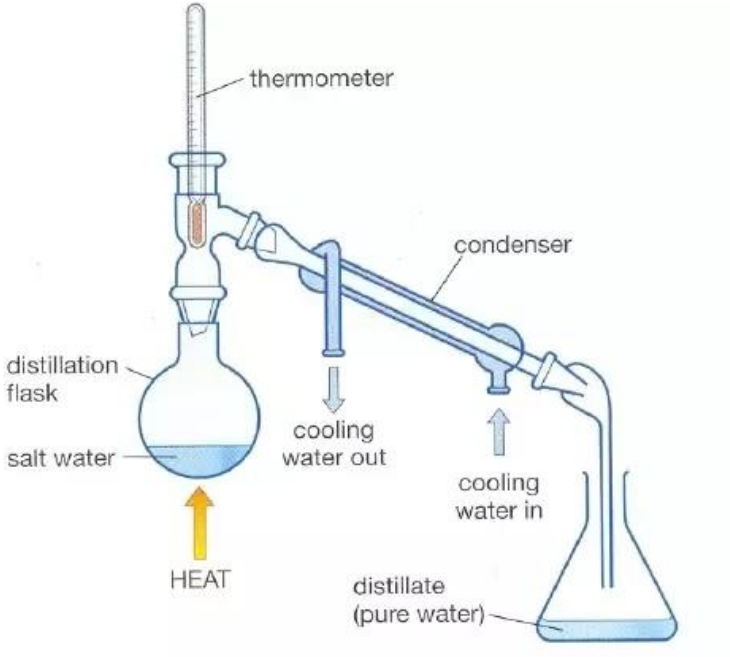
Chromatography

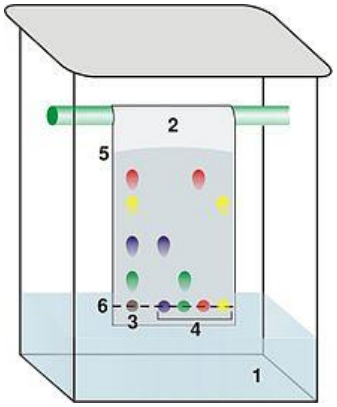
Purification of Liquids

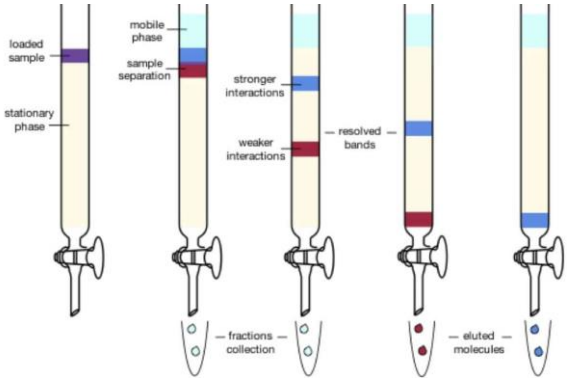
1- Distillation

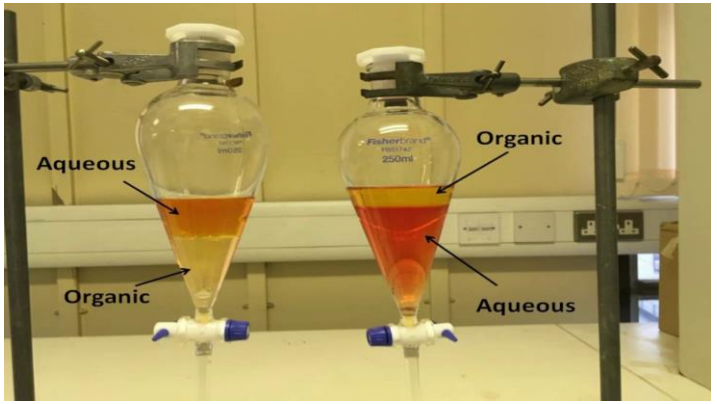
2- Differential Extraction

3- Chromatography









History

Mikhail Tswett

Russian Botanist

- He used chromatography to separate **plant pigments**
- He called the new technique chromatography because the result of the analysis was 'written in color' along the length of the adsorbent column **Chroma** means "**color**" and **graphein** means to "**write**"

Importance

Chromatography has application in every branch of the chemical, physical and biological sciences

12 Nobel prizes were awarded between 1937 and 1972 alone for work in which chromatography played a vital role

Chromatography

Is a physical method of separation in which the components to be separated are distributed between two phases one of which is stationary **(stationary phase)** while the other moves through it in a definite direction **(mobile phase).**

The chromatographic process occurs due to **differences in the distribution constant** of the individual sample components.

Chromatography

Is a technique used to separate and identify the components of a mixture.

- Works by allowing the molecules present in the mixture to distribute themselves between a stationary and a mobile medium.

- Molecules that spend most of their time in the mobile phase are carried along faster.

Classification of Chromatography

According to mobile phase

1- Liquid chromatography: mobile phase is a liquid, (**LLC, LSC**).

2- Gas chromatography : mobile phase is a gas, (**GSC, GLC**).

Classification of Chromatography

According to packing of the stationary phase

1- Thin layer chromatography (**TLC**): the stationary phase is a thin layer supported on glass, plastic or aluminium plates.

2- Paper chromatography (**PC**): the stationary phase is a thin film of liquid supported on an inert support.

3- Column chromatography (**CC**): stationary phase is packed in a glass column.

Classification of Chromatography

According to the force of separation:

1- **Adsorption chromatography** → TLC, CC

2- Partition chromatography

3- Ion exchange chromatography

4- Gel filtration chromatography

Thin Layer Chromatography (TLC)

Thin Layer Chromatography (TLC)

Is a method for identifying substances and testing the purity of compounds.

- TLC is a useful technique because it is relatively quick and requires small quantities of material.

Thin Layer Chromatography (TLC)

Separations in TLC involve distributing a mixture of two or more substances between a stationary phase and a mobile phase.

- The stationary phase: is a thin layer of adsorbent (usually **silica gel or alumina**) coated on a plate.

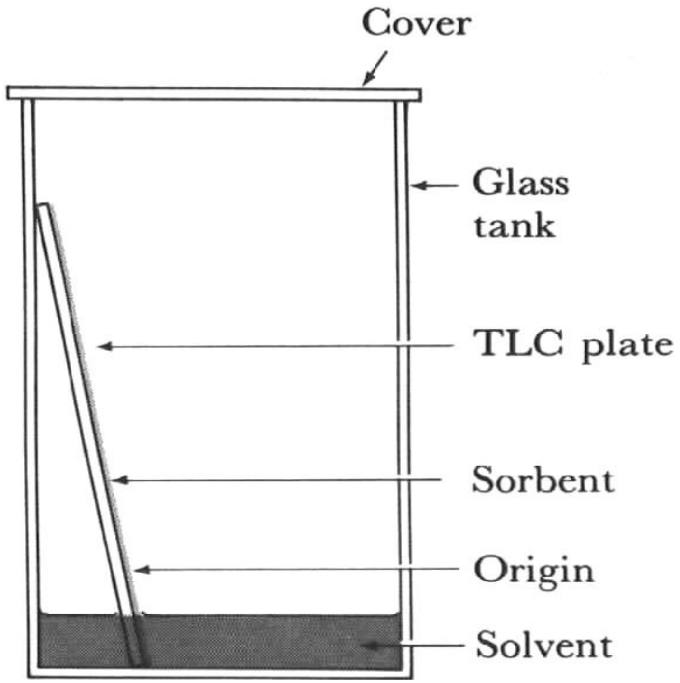
- The mobile phase: is a **developing liquid** which travels up the stationary phase, carrying the samples with it.

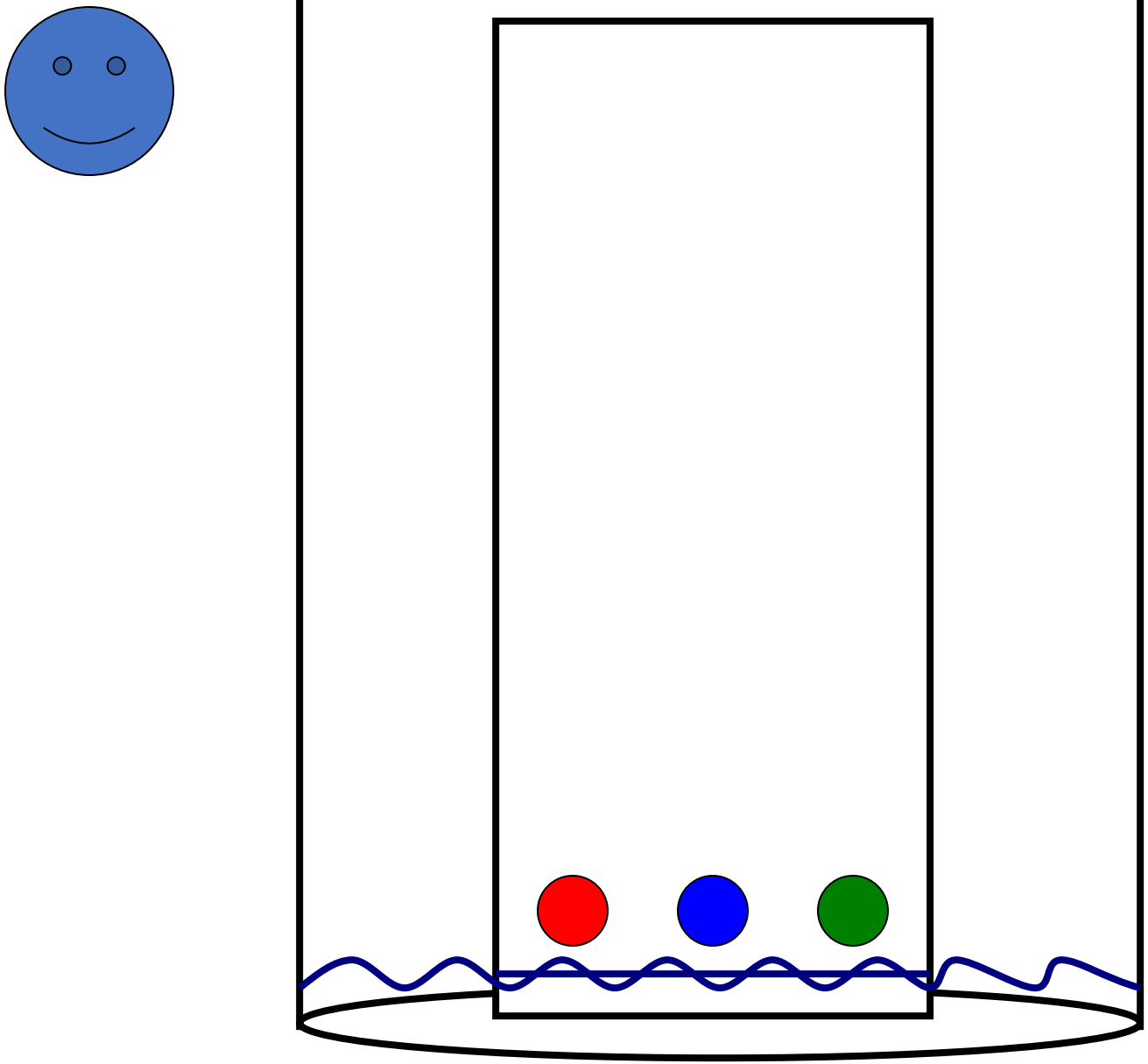
Thin Layer Chromatography (TLC)

Components of the sample will separate on the stationary phase according to

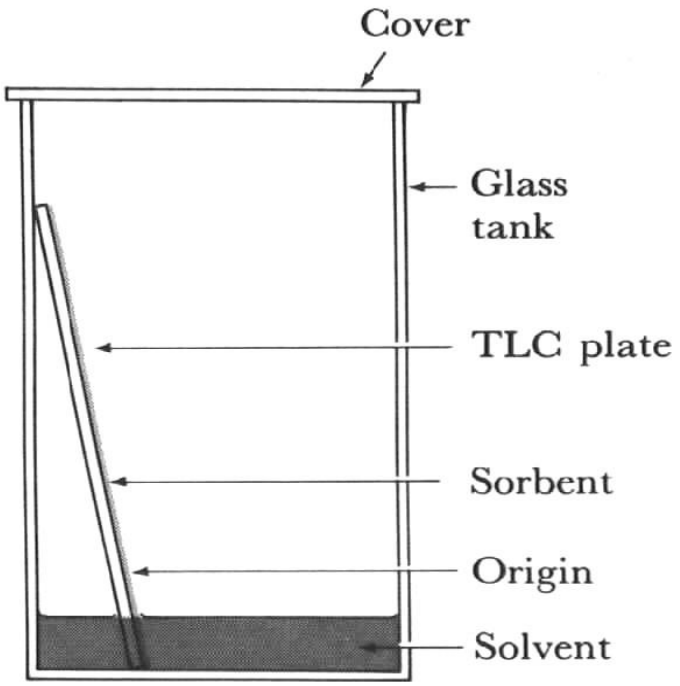
how much they adsorb on the stationary phase **versus** how much they dissolve in the mobile phase.

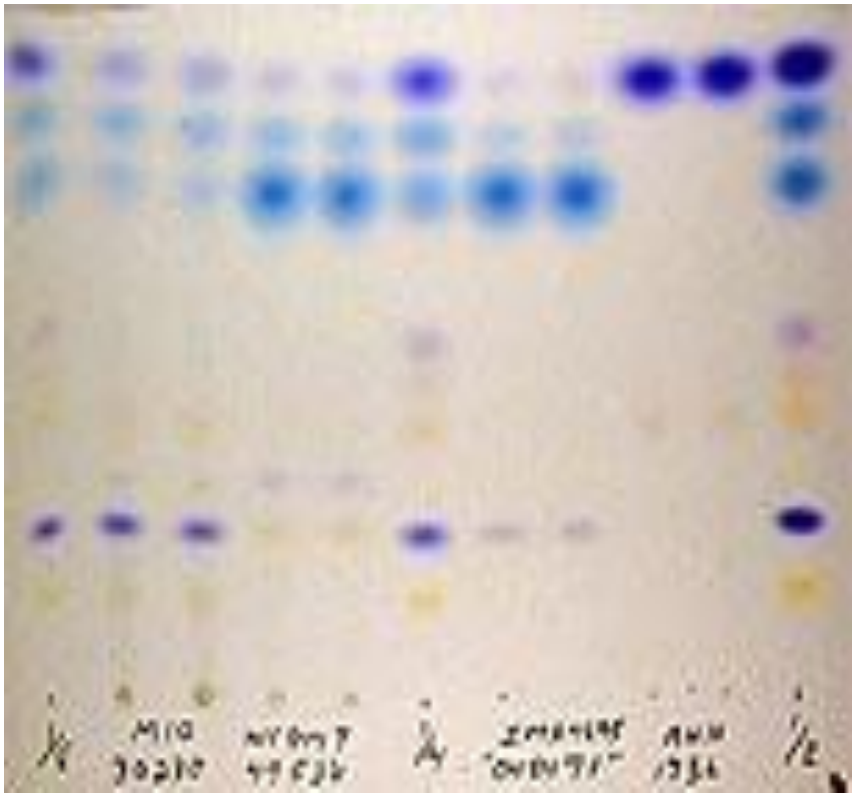
Thin Layer Chromatography (TLC)





Thin Layer Chromatography (TLC)





Applying the TLC

Step 1: Preparing the Chamber

- To a jar add enough of the appropriate developing liquid so that it is 0.5 to 1 cm deep in the bottom of the jar.

- Close the jar tightly, and let it stand for about 10 minutes so that the atmosphere in the jar becomes saturated with solvent.

Applying the TLC

Step 2: Preparing the stationary phase

A) Prepare the TLC plate:

Mix:

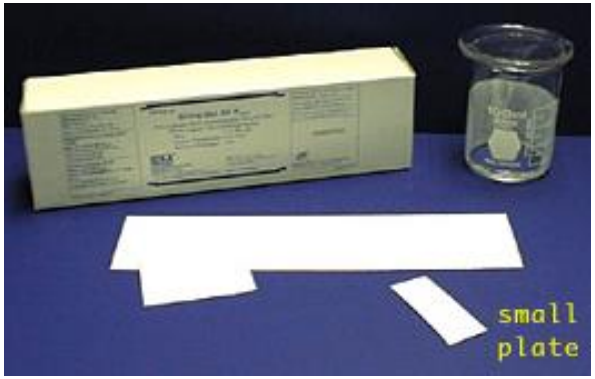
Adsorbent
Small amount of an inert binder ($CaSO_4$. $0.5H_2O$)
Water (solvent)

Spread a thin layer (no more than a few mm) of the mixture on plate

After the plate is dried, it is activated by heating in an oven for approximately 30 minutes at 110˚C

Applying the TLC

Step 2: Preparing the stationary phase

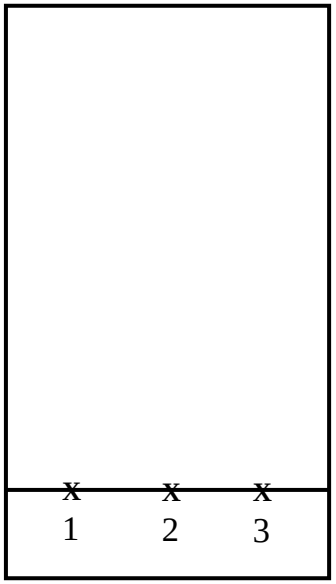


A) Prepare the TLC plate:

TLC plates are also commercially prepared and can be purchased ready for use.

B) Draw a line of origin approximately 0.5 cm from the bottom of the filter paper.

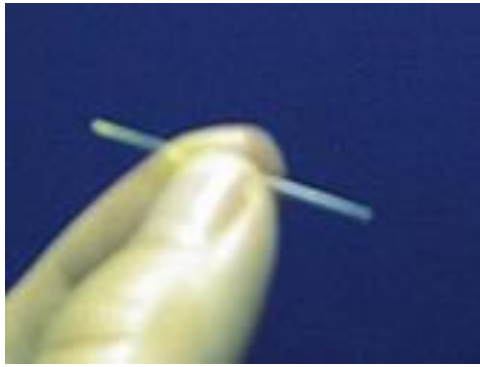
C) Indicate where each sample will be added.



Applying the TLC

Step 3: Spotting the samples

- If the sample isn't in solution, dissolve it in an appropriate solvent.



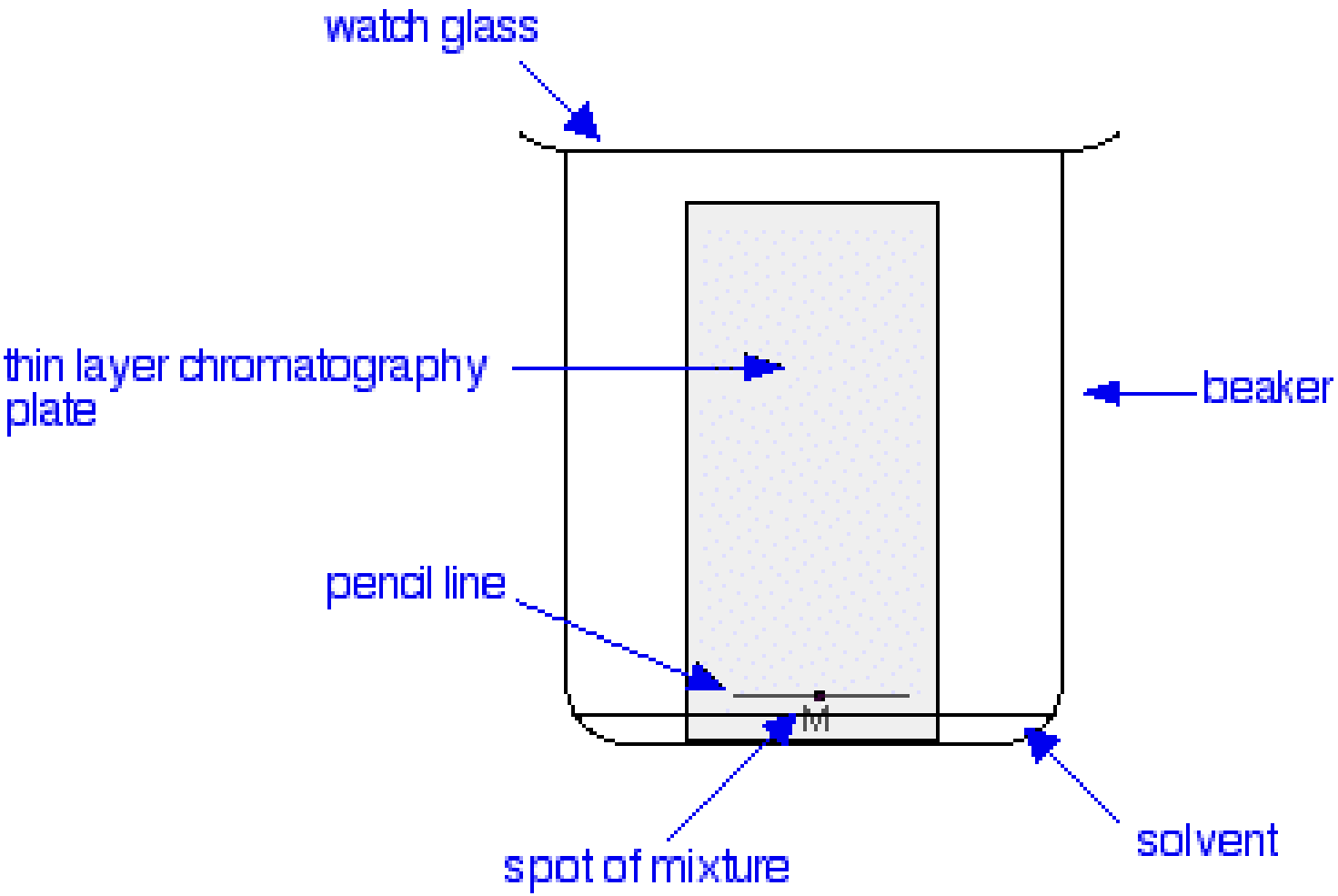
- Spot a small amount of sample onto the plate. Make sure the sample spot is dry before continuing.

Applying the TLC

Step 4: Developing the chromatograms

- When the sample spot has dried, the TLC plate is placed into the chamber containing the solvent.

- It is important that the sample spot is above the level of the solvent.


watch glass
thin layer chromatography plate
beaker
pencil line
M
spot of mixture
solvent

Applying the TLC

Step 4: Developing the chromatograms

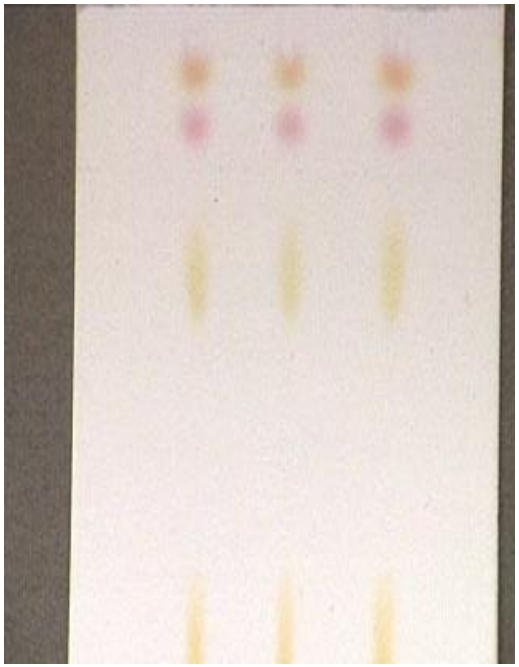
- Allow the solvent to rise until it almost reaches the top of the plate.
- Remove the plate from the chamber and mark the position of the solvent and front before it can evaporate.
- If the sample spots are visible, mark their positions.

Applying the TLC

Step 5: Identify the spots and interpret the data

If the spots can be seen, outline them with a pencil.

If no spots are obvious, the most common visualization technique is to hold the plate **under a UV lamp**.



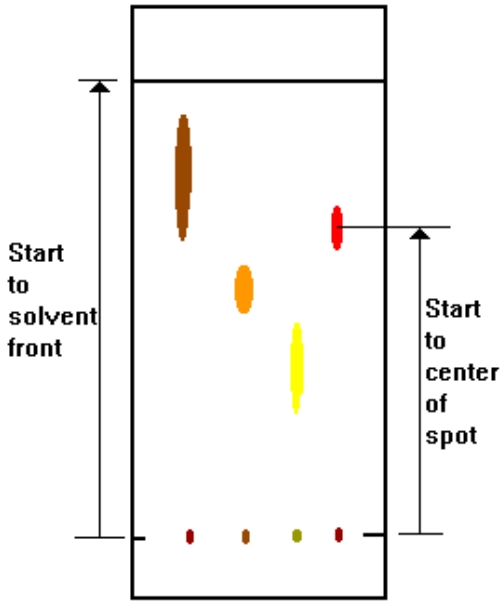
Many organic compounds can be seen using this technique, and many commercially made plates often contain a substance which aids in the visualization of compounds.

Interpreting the Data

The R_f (retention factor) value for each spot should be calculated.

It is characteristic for any given compound on the same stationary phase using the same mobile phase for development of the plates.

$$R_f = \frac{\text{Distance traveled by the compound}}{\text{Distance traveled by the solvent}}$$



R_f values are reported as relative values since they can be affected by:

- ❖ the adsorbent used
- ❖ the solvent system used
- ❖ Temperature
- ❖ the thickness of the adsorbent layer
- ❖ the amount of sample material spotted

- ➢ It can be difficult to keep all of these variables constant from experiment to experiment.

- If two substances **have the same R_f** value they may or may not be the same compound.

- If two substances **have different R_f** values they are definitely not the same compound.

TLC Applications

- ✓ Can be used to determine the number of components in a mixture.
- ✓ Can be used to identify the presence of specific compounds/ unknown compounds.
- ✓ Can be used to monitor the progress of a reaction.
  - Will show if any reactant has disappeared, if any product has appeared, and how many products are present.
  - Often used to monitor organic reactions.

TLC Applications

- Used to determine which conditions are ideal to use in column chromatography.

  Ex: which solvent system to use

- It is also used to monitor column chromatography.

- Used to quantify the amount of a component present .

  Area of the spot

  Spot extraction, then measure the amount

- Used to determine the purity of a sample.
- Can be used to isolate purified substances, and then analyse it further (MS/ IR/ NMR)

Advantages of TLC

- ✓ Low cost
- ✓ Short analysis time
- ✓ Ease of sample preparation
- ✓ All spots can be visualized
- ✓ Uses small quantities of solvents

References:

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