وزارة التعليم العالي والبحث العلمي
جامعة الموصل
كلية العلوم
قسم الأدلة الجنائية

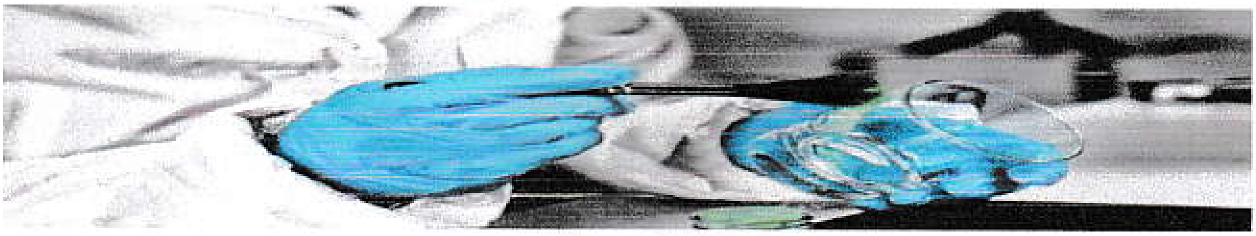
مادة

الكيمياء العضوية

العملي

المرحلة الاولى

الكورس الثاني



مدرس المادة

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(I)

(Rules for personal safety)

The chemicals employed in the organic laboratories are usually flammable, irritating, and may possess known or as yet undetermined toxic characteristics . More over working with glassware carelessly may lead to injuries which are sometimes permanent or even fatal . Therefore basic safety must be followed rigidly to ensure personal safety .

Some of these rules include :

1-Wear safety glasses or other eye protection in the laboratory all times .

2-Never work alone in the laboratory .

3-Acts of carelessness, including those done in jest endanger the safety of laboratory and are strictly prohibited .

4-Eating, drinking or smoking in the laboratory is prohibited.

5-Unplug electrical equipment and turn off water and gas outlets when not in use.

6-Avoid skin contact with chemicals.

7-Never heat a closed system of any kind.

8-Do not use flames in an unventilated laboratory area and never produce a flame near containers of flammable compounds.

9- Do not heat flammable compounds directly, and heat it by using water, oil, or sand bath .

10-Do not smell or taste any chemicals .

11-Treat out, heat burns and chemical burns as follow:

Cuts :- if the cut is not serious, wash the affected area with water and dilute soup solution. If bleeding is serious , apply direct pressure with a clean, sterile dressing and contact the physician .

Heat burns :- minor burns, where the tissue is not charred, can be treated by flushing with cold water , serious burns should be treated by physician.

Chemical burns :- Chemicals on the skin or in the eyes should be flushed with a large amount of water and physician should be contacted immediately .

(Cleaning and drying of glassware)

Cleaning :- glassware is best cleaned with a brush , water , and soap or detergent. Tarry and mucky organic materials can be removed easily by dissolving it in a few milliliters of acetone or sometimes chromic acid is recommended for their removal .

Drying :- Glassware that has been rinsed with ether, water, or acetone will dry upon storage . If it is necessary to quickly dry an item of glassware it should be first rinsed with acetone and then dried in the furnace or with a towel .

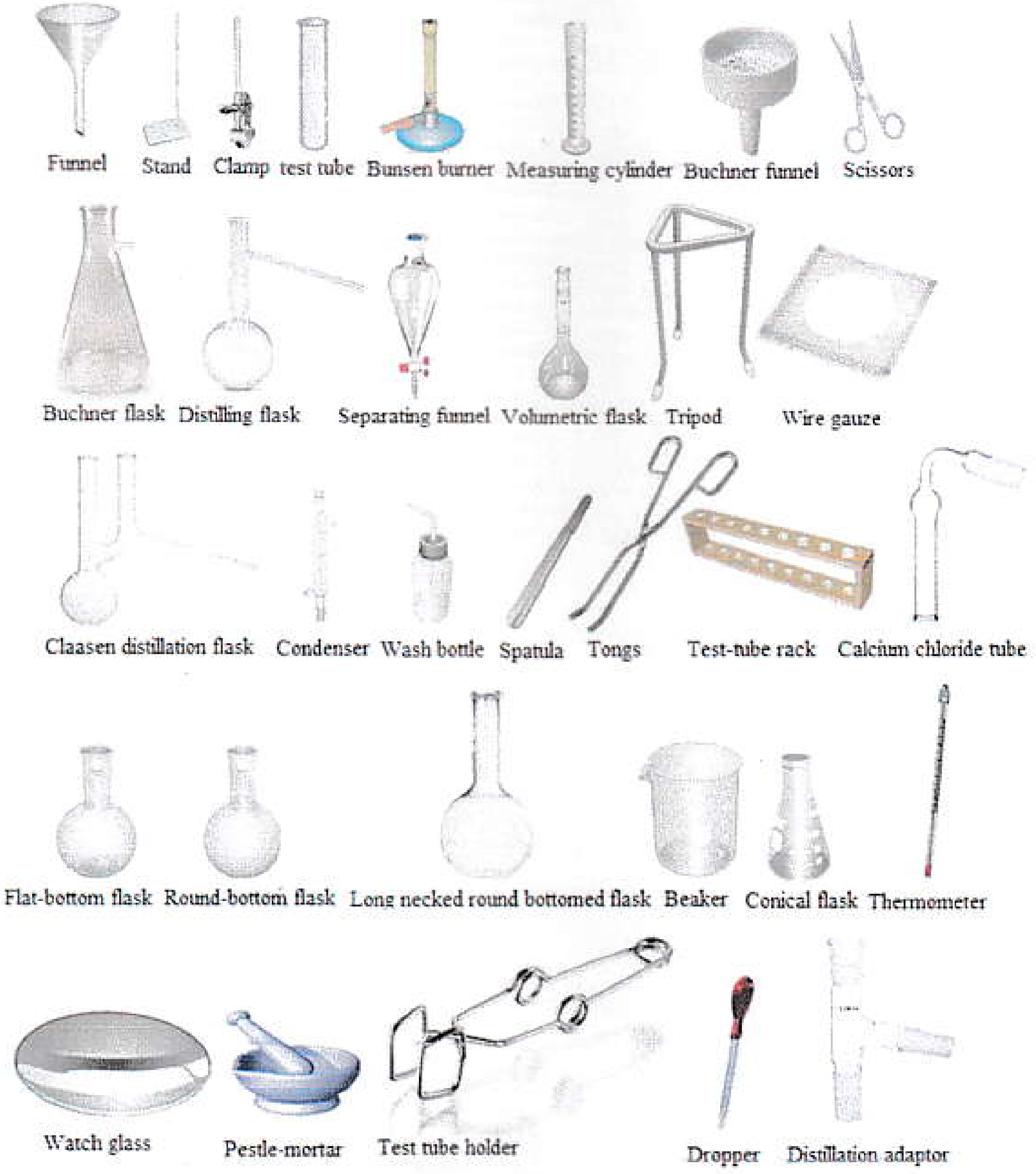


Fig. (1): Some glassware used in the organic chemistry laboratories.

(Determination of melting point)

(First experiment)

Theory :

The melting point of a pure compound is defined as the temperature at which the liquid and solid phases of that compound are in equilibrium at one atmospheric pressure .

$$\text{Solid phase} \xrightleftharpoons{\text{Temp.=m.p}} \text{Liquid phase}$$

The melting point is usually reported as two temperatures between which the sample was observed to melt (melting range).

Solid State Properties:

1. highly attractive forces and no intermolecular between the molecules.
2. no free rotation because found Vander Waais force.
3. highly lattice energy.

The thermal energy that is exerted on a pure solid is always consumed to overcome the lattice energy that binds together the molecules of the crystal, or in other wards it is required for the transition from the ordered molecular arrangement in the crystalline lattice (solid) to the disordered condition of the fluid (liquid).

The lattice energy and consequently melting point depends on :

1. molecular weight (directly proportional) melting point increase with increasing molecular weight.
2. symmetry of the molecules (directly proportional).
3. polarity of the molecules (directly proportional).

Uses of melting point:

1. Identify organic solid compound.
2. Determine the degree of purity of the organic solid compound.

Since a pure crystalline organic compound usually has a sharp and characteristic melting point while the presence of a very small amounts of impurities will produce depression of the melting point and an increase in the melting point range (melting range of 1°C or less is considered as a sharp melting).

Melting range (1-2)°C consider as normal melting point and the compound is pure. Melting range >2°C is consider broad melting point and the compound is impure.

Paraffin oil is used in the experiment because it has :

1. highly boiling point more than 230°C.
2. non-toxic.
3. inflammable and cheap.
4. low specific gravity, low heat capacity .

Procedure:

1. close one end of a capillary tube (6cm. long and about 1 mm. in diameter) by the flam of Bunsen burner.
2. place a small amount of dry finely powdered organic sample (benzoic acid) inside the capillary tube by pressing the open end in to a small heap of the substance turning the capillary open end up and vibrating it to rattle the substance down in to the bottom.
3. Attach the capillary tube to a thermometer by means of a small rubber ring.
4. Immerse the thermometer and the capillary tube inside beaker filled with paraffin as shown in down (fig. 2)

5. Start to heat as pointed in (fig. 2),and put in your mind that, the rate of heating should be very low (1 degree per minute) as the melting point is approached. Otherwise, the temperature of the mercury in the thermometer bulb and the temperature of the crystals in the capillary will be below the temperature of the paraffin and not equal to each other, and this is because of the slowness with which heat energy is transferred by conduction.
6. Report the temperature of the thermometer as soon as the crystals begin to melt and the temperature at which melting is completed, as shown in (fig. 3).

   NOTE: If the approximate temperature at which the sample will melt is not known, a preliminary melting point determination should be made in which the temperature of the paraffin is raised quickly.

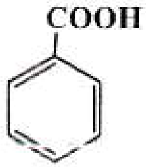
Mixed milting point:

Unknown compound can be identified by comparing its melting point with that of known compounds, but some some times many known compounds have melting points identical with that of unknown, and in order to identify the unknown we have to determine the melting point of the mixture (unknown compound + one of the known compounds) any depression in the m.p. means that, the two compounds are not identical and vice versa (if there is no depresstion this means that the two compounds are identical.

Results:

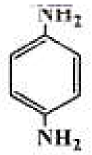
The chemical used in the experiment is benzoic acid

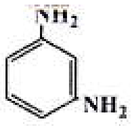
m.p of benzoic = (-   )°C.



Discuss :

1. which compound has the highest melting point ?





2. Thermometer and capillary tube must be in the same level, why?.
3. Why we use paraffin oil and do not use water bath?
4. The flame of Bunsen burner must be law, why?
5. What is the effect of humidity on the melting point of solid organic compound.

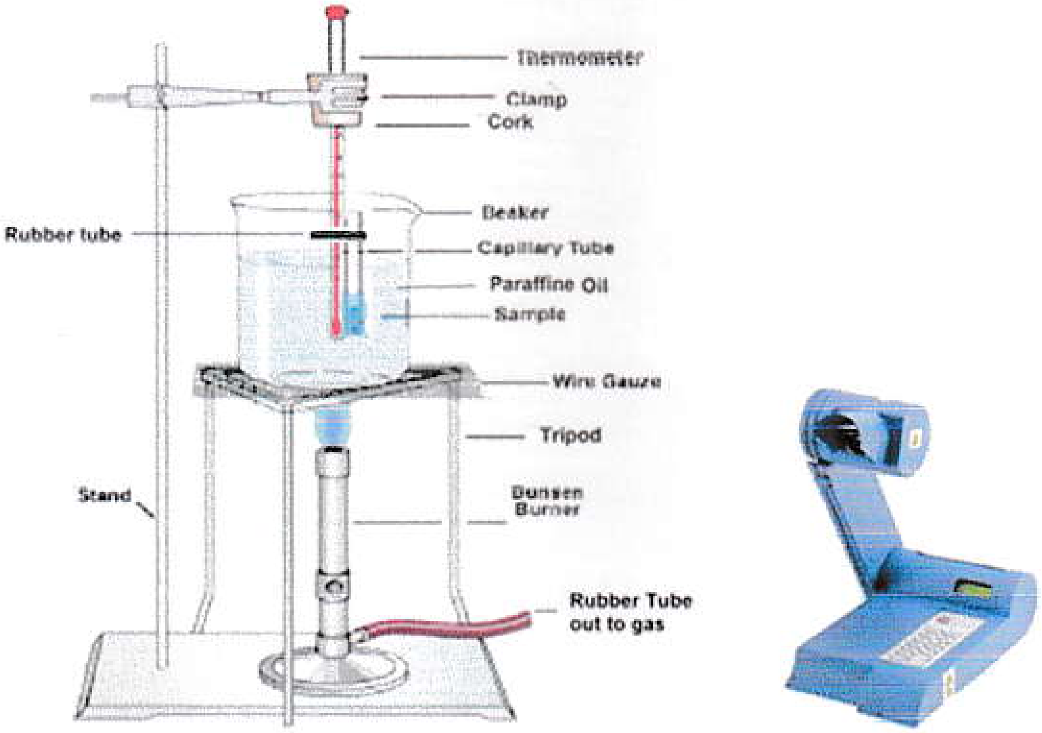


Fig. (2): Determination of melting point

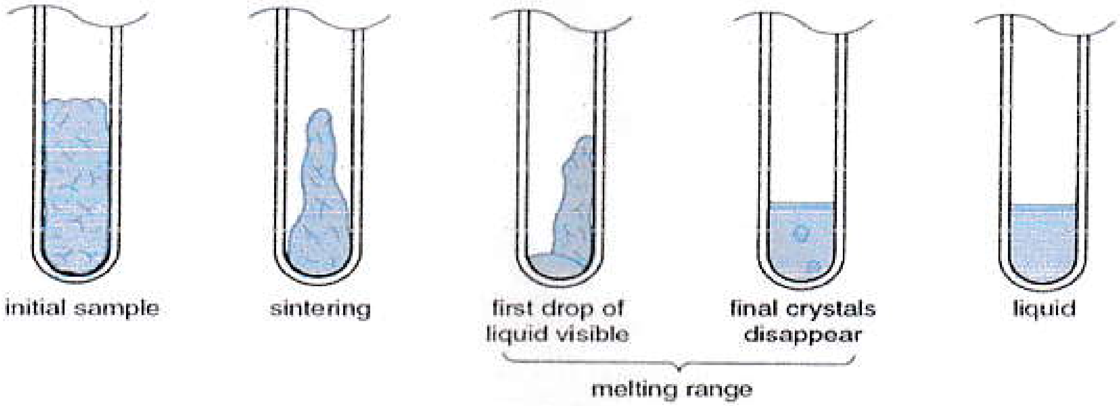


Fig. (3): Typical changes in the appearance of sample in the region of its melting point.

(Determination of Boiling Point)

(Second experiment)

Theory:

Boiling point is one of the physical constant of the liquid and is defined as the temperature at which the Vapor pressure (the tendency of molecules on the surface of the liquid to pass into the Vapor state) equal with atmospheric pressure (760mmHg).

Boiling point is used to identify liquid organic compound and to estimate its purity. If sufficient material available, the boiling point may be determined by distillation otherwise are small scale may be used.

The heat of Vaporization is a measure of the amount of energy required to separate the liquid molecules and to overcome the intermolecular attractive forces between them .the stronger the intermolecular forces, the higher the heat of vaporization.

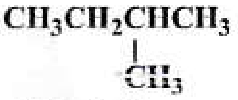
The kind of intermolecular forces between liquid molecules include:

1- Vander Waal's forces (increase with increasing molecular weight in the same series of compounds, and decrease with branching).

$CH_3CH_2CH_2OH$ > CH_3CH_2OH

Propanol **Ethanol**

$CH_3CH_2CH_2CH_2CH_3$ >



$$\underset{\displaystyle CH_3}{CH_3CH_2\underset{|}{C}HCH_3}$$

n-Pentane **2-Methyl butane**

2- Dipole - dipole forces. (Directly proportional).
3- Induced dipolar forces. (Directly proportional).
4- Hydrogen - bonding forces. (Directly proportional).

Boiling point of liquid is inversely proportional with its vapor pressure and directly proportional with pressure exerted on it. Impurities always rise the boiling point of the liquid.

Procedure:

1- Place (2 - 3) drops of the liquid sample into a Sodium fusion tube (tube 4 cm. long and 4 mm in diameter) by dropper.
2- Immerse one end closed capillary tube inside the liquid with the sealed end up.
3- Attach the sodium fusion tube to a thermometer by means of rubber band.
4- Clamp the apparatus as in fig. (4)
5- Start and continue heating until a very rapid steady of bubbles comes out from the capillary end.
6- Stop heating and let the paraffin cool slowly .
7- The temperature at which bubbles just fails to come out of the capillary and the liquid starts to enter it is taken as the boiling point of the liquid.as shown in fig. (5).

Results:

Chemical used is (ethanol).
Boiling point of ethanol = ( )° C

Discuss:

1- What is the effect of the impurities on the boiling point ?
2- Why the boiling point for n- hexane is higher than isohexane ?
3- What is the relationship between b.p and atmospheric pressure ?
4- Boiling point of R-OH higher than R-H ,Why ?

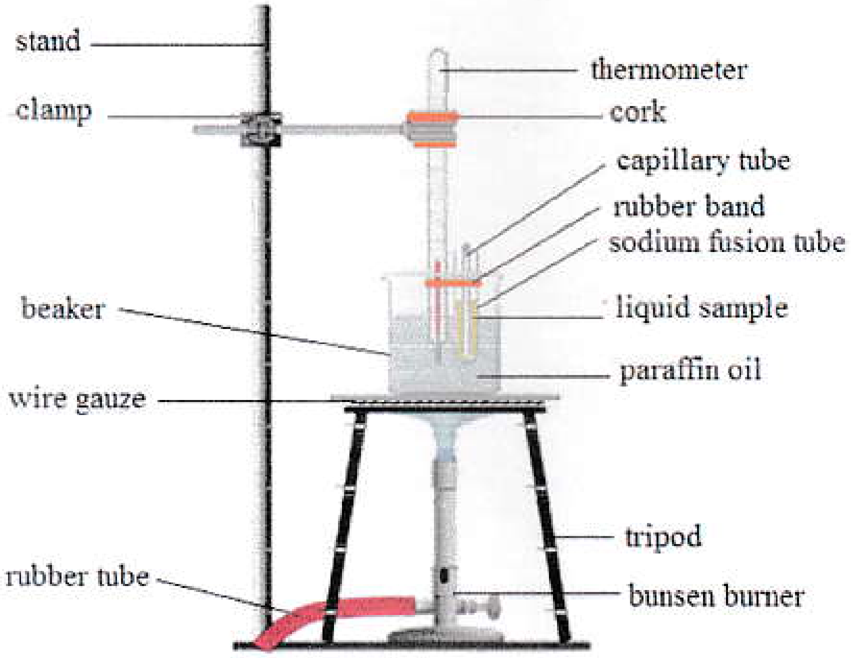


Fig. (4): Determination of boiling point apparatus .

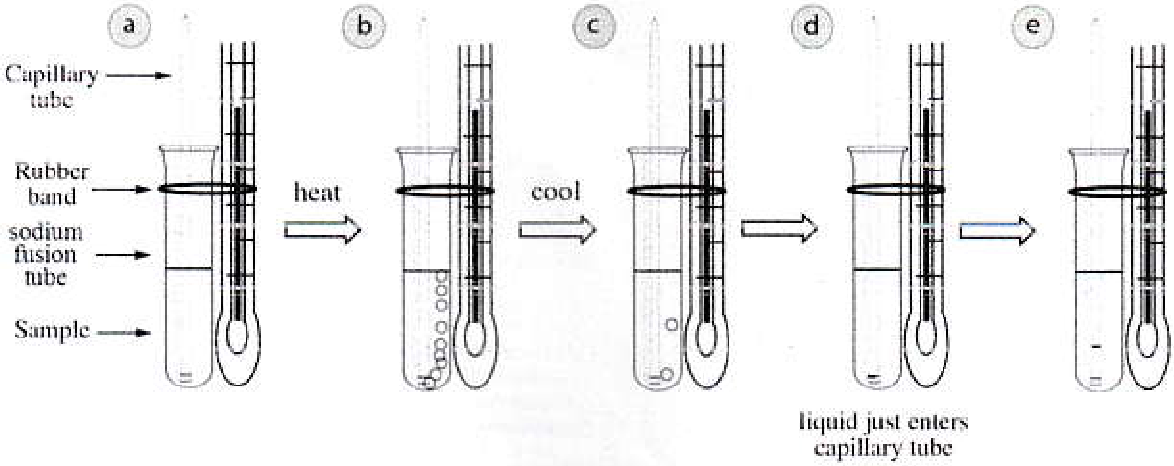


Fig. (5): Determination of boiling point step by step .

Distillation

(Simple Distillation)

(third experiment)

Theory:

The process of distillation consist of heating a liquid to a temperature at which it is converted to vapour, and then condensing the vapour back a liquid in another part of the apparatus.

There are four types of distillation:

1) Simple distillation.
2) Fractional distillation
3) Steam distillation.
4) Vacuum distillation.

Simple distillation is the most commonly used method for:

1) Purification of a liquid from non-volatile solids.
2) Separation of two or more miscible liquid compounds, provided that their boiling points are differ by at least 50 °C or more.
3) Determination of true boiling point.

At a given temperature the vapour pressure of a liquid in the simple distillation apparatus is constant and independent on the total pressure exerted on the surface of the liquid. The vapour pressure increases upon heating the liquid with a flame until it becomes equal to the atmospheric pressure where the liquid begins to boil and converted to vapour which rises in the apparatus and flows down through the condenser.

The cool walls of the condenser remove heat of the vapour and recondense it to liquid form. The distillation should be conducted slowly and steadily and at a rate such that, the thermometer bulb always carries a drop of the condensed, where in such case the liquid and the vapor are in equilibrium and the temperature of thermometer indicates to the true boiling point . However if excessive heat is applied to the walls of the distilling flask, the vapor become superheated, the drop will disappear from the thermometer and the temperature of the vapor rises above the boiling point.

Types of heating methods:

Heating methods depended on the type of liquid so that there are two types of heating.

1) **Direct heating:** Used for inflammable liquids (B. P >100 °C), distil by using Bunsen burner or heater.
2) **Indirect heating:** Used for flammable liquids, distil by using:
    a- Water bath (B. P <100 °C)
    b- Oily bath (B. P >100 °C)
    c- Sand bath (B. P >100 °C)

Types of condenser:

1) Air condenser (B.P > 150 °C)
2) Water condenser (B.P 100-130 °C)
3) Ice water condenser (B.P <100 °C)

Procedure:

1) Set up the apparatus as shown in fig. (6).
    a) Clamp a distilling flask (which is frequently one and half the volume of the liquid to be distilled) to a stand and directly over a tripod covered with a wire gauze.
    b) Attach the condenser to the side arm of the distilling flask.
    c) Attach the rubber tubes to the inlet (bottom) and outlet (top) of the condenser. Be sure that the tubing is secure. Turn the water on slowly. Chek to be sure that the water is flowing through the condenser in slow stream.
    d) Stopper the head of the distilling flask by a cork through which a thermometer is inserted. Adjust the height of the thermometer so that the bulb is just below the side-arm of the distilling flask.
2) Remove the thermometer with the cork and by means of a funnel, introduce 10 ml of dirty water into the distilling flask. Also, add 2-3 pieces of boiling stones (boiling chips) to prevent local super heating which in turn cause bumping.

3) Return the cork with the thermometer to its position and start heating the distilling flask.
4) Adjust the flame of the burner so as to maintain a drop at the condensate of the thermometer bulb throughout all distillation.
5) Discard the first few drops of distillate and collect the rest.
6) Do not distil to dryness.
7) Record the temperature at which the distillation is collected, and the volume of the distillate.

Note: Boiling stones are used to prevent local super heating which in turn cause bumping. Since the tiny air bubbles trapped in the pores of these stones provide nuclei for bubble formation, that prevent local superheating.

Results:

Boiling point = ( ) °C

Volume of impure liquid = 10 ml

Volume of pure liquid = ( ) ml

$$\% = \frac{\text{Pure liquid}}{\text{Impure liquid}} \times 100\%$$

Discuss:

1) The thermometer bulb always carries a drop of the condensed liquid.
2) Addition of (2-3) pieces of boiling stones (chips).
3) You have a liquid has boiling point (120 °C), suggest a way to heat it.
4) Why should the thermometer bulb be near the side arm of the distillation flask?

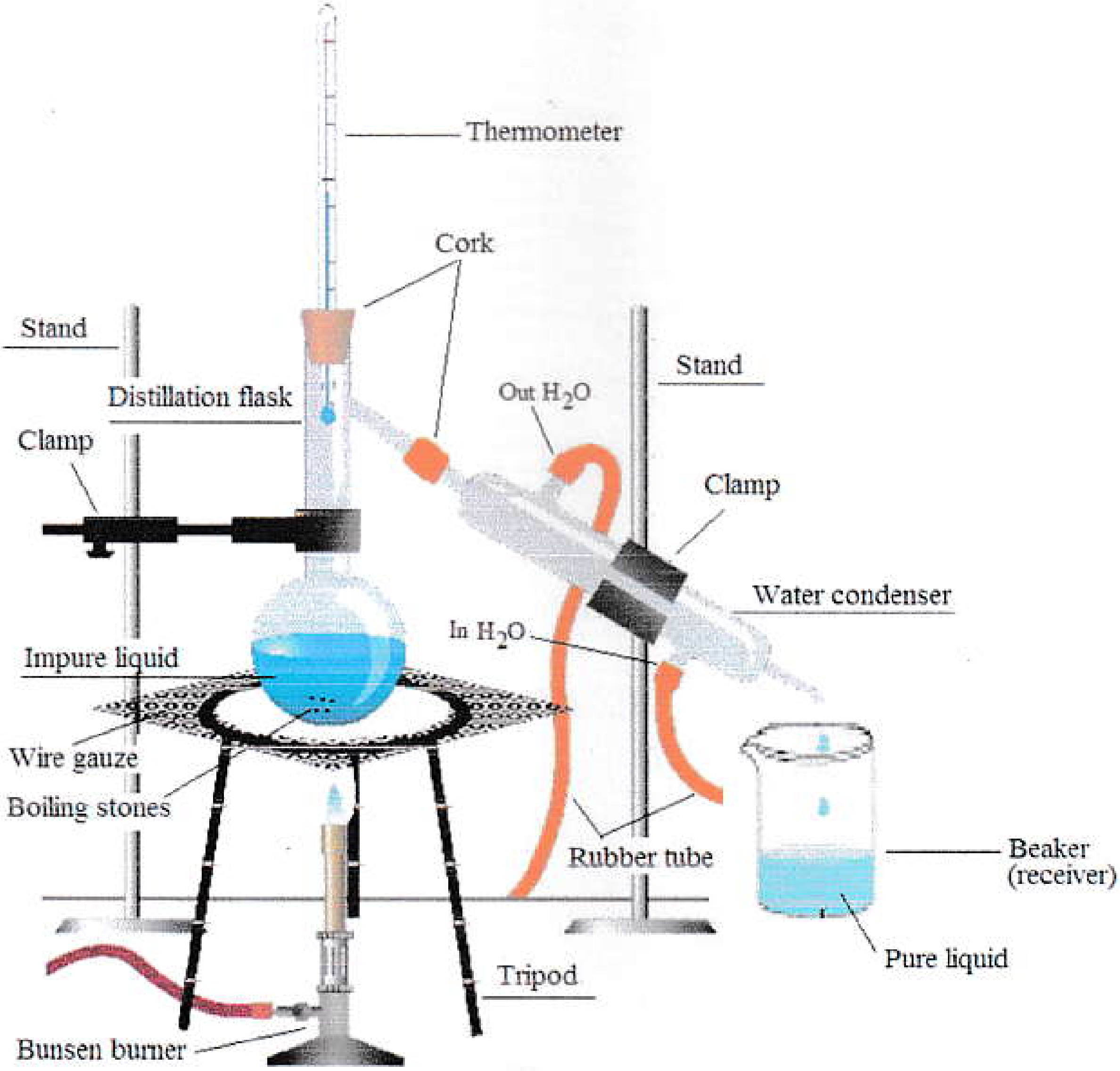


Fig.(6): Simple Distillation Apparatus

(Fractional Distillation)

(Fourth Experimental)

Theory:

Fractional distillation is employed for the separation of miscible liquids whose boiling points differ by less than 50°C.

As predicted by Raoult's law "which state that, the vapor pressure of one pure component in the mixture is equal to its vapor pressure when its pure multiplied by its mole fraction in the liquid mixture". The composition of the vapor above a boiling ideal mixture differs from the composition of the liquid. For example, the composition of A and B in a mixture consists only of these two components it's given by:

$$X_A + X_B = 1$$

X_A = mole fraction of A in the mixture.

X_B = mole fraction of B in the mixture.

In the vapor, the relationship between total pressure and mole fraction is:

$$P_{total} = P^{\circ}_A X_A + P^{\circ}_B X_B$$

Where: P_{total} = total vapor pressure of the mixture

P°_A = vapor pressure of pure A

P°_B = vapor pressure of pure B

$$x_A = \frac{n_A}{n_{A+B}}$$

$$x_B = \frac{n_B}{n_{A+B}}$$

$$n = \frac{Wt}{M.Wt}$$

That is ,the composition of the vapor is dependent on the mole fraction of the solution components as well as on the partial pressure of the pure compounds, consequently, the more volatile compound in the mixture will be concentrated in the vapor phase more than the other compound which is less volatile.

The relationship between the boiling point and the composition of the liquid and vapor phase for a binary mixture such as benzene / toluene is represented in (fig. 7a) since the lower curve represents the boiling points of all mixtures of toluene and benzene, while the vapor curve describes the composition of the vapor phase at the same temperature . From (fig. 7a) it is obvious that if we start to distill a mixture that was 0.2 mole fraction in benzene, the vapor which is in equilibrium with the mixture would be about 0.4 mole fraction in benzene and this would be the composition of the first part of distillation . If this part of the distillate were then redistilled , the vapor in equilibrium with it would be approximately 0.6 mole fraction in benzene and this would be the composition of the second distillate . About five-step process of this type could produce a fairly well purified benzene .

However , this process would be too inefficient to be practical and a more practical process, is to introduce a fractionating column to the simple distillation apparatus as shown in (fig. 7).

The significant feature of a fractionating column is that it is built up of units called **theoretical plates**, on which and due to the temperature gradient that was issued along the column at the beginning of the distillation , occur efficient exchange of heat and material between the condensate flowing down the column and the vapor flowing up . In other words, the material finally coming out of the top of the column as a vapor will be subjected to multiple condensation and evaporation on the way up , each of which serves to enrich the vapor in the more volatile component. A good column can produce a distillation in which the enrichment corresponds between 25 and 100 steps like the five in (fig. 7a).

The vapor pressure of miscible liquids less than each liquid alone .

The liquid begins to boil when the sum of the vapor pressure of the two

The efficiency of a fractionating column for a particular distillation depend on:-

1- Number of theoretical plates
2- Column hold up
3- HETP (Height Equivalent Theoretical Plate)
4- Through put
5- Reflux ratio = distilling material / condensing material

Procedure:

1-Assemble the glassware as in (fig. 7).

2-Intraduce 50 ml of ethanol – water mixture into the round bottom flask ,also add 2-3 fragments of boiling stones.

3- Start heating the mixture with very small flam. Carefully protected from draughts to ensure a uniform supply of heat. It is also essential that the initial heating of the mixture should not be hurried , because the column may choke by the considerable extra condensation that may occur while the column is warming up.

4- When thermal equilibrium established between the column and its surroundings (when the distillation started). adjust the heating until the distillate is coming out from the side arm of the column not faster than about 1 drop per (4-5)second.

5- Collect the first fraction (ethanol) and record the temperature rang at which it is collected.

6- When the thermometer temperature increase, change the receiver and collect the second fraction (water) and record the temperature range of distillation .

7- Also you can collect a mixture in between the two distillates.

Results:

1- Volume of CH_3CH_2OH at (78-80)$^{\circ}$C = (   ) ml

$$\% = \frac{\text{Volume of EtOH}}{15} \times 100 = (\ \ )\%$$

2- Volume of ($CH_3CH_2OH+H_2O$)at (80-95)$^{\circ}$C=(   )ml

$$\% = \frac{\text{Volume of Mix}}{15} \times 100 = (\ \ )\%$$

3- Volume of H_2O at (96-100))$^{\circ}$C=(   )ml

$$\% = \frac{\text{Volume of } H_2O}{15} \times 100 = (\ \ )\%$$

Discuss :

1-You have miscible two liquids one of these has b.p = 100 °C and the other has b.p = 38 °C, how can you separation them?

2- What different between simple distillation and fractions distillation?

3-The vapor pressure of miscible liquids less than each liquid alone ,why?

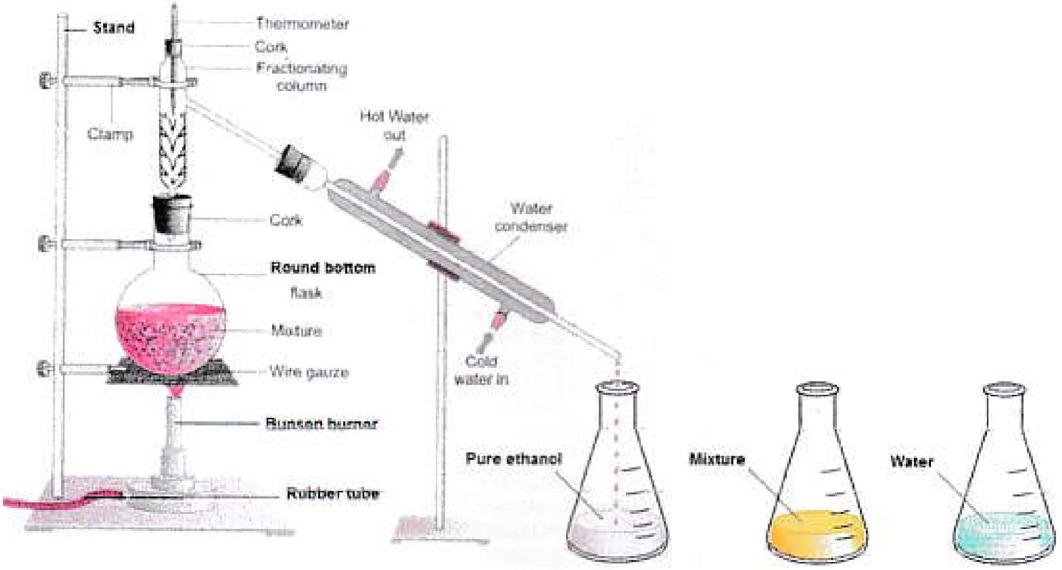
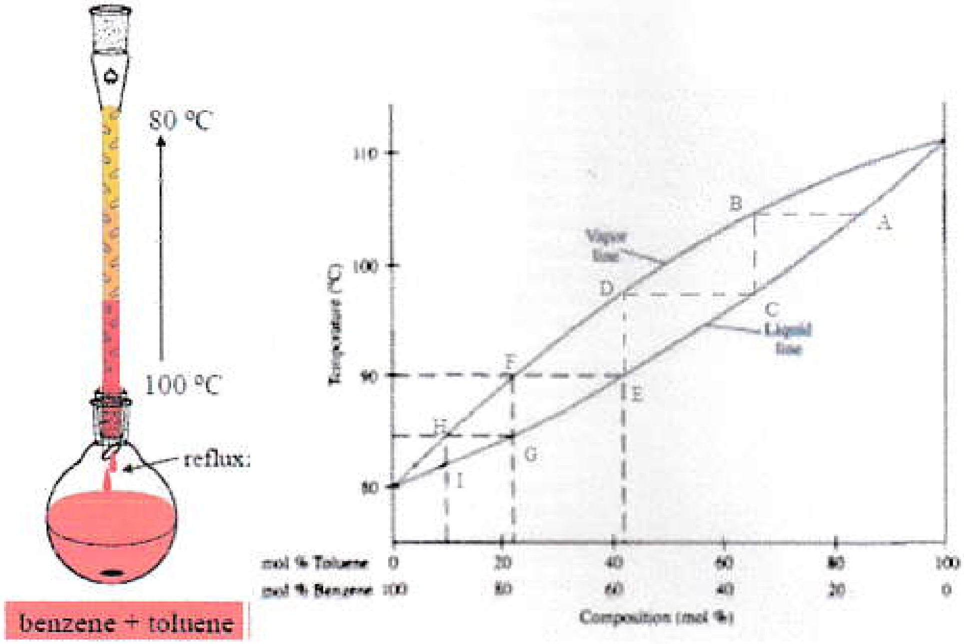


Fig. (7): Fractional Distillation apparatus



(Fig. 7a): The Temperature/Composition Diagram Of A Benzene/Toluene Mixture.