UNIT 1 TECHNIQUES AND APPARATUS

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1.1 INTRODUCTION

In this unit we shall describe some of the common experimental techniques which you would use for carrying out experiments in the organic chemistry laboratory. The apparatus required for various techniques will be described and the theory of some of the techniques will also be briefly discussed.

In this organic lab you will learn how to use simple laboratory techniques such as heating, cooling, stirring and filtration; as well as separation and purification techniques such as extraction, crystallisation, distillation and chromatography. Determination of the physical constants such as melting and boiling points to check the purity of organic compounds will also be discussed. Finally, we shall tell you the way you should record your work in the laboratory note book. In the next unit we shall describe various considerations you should keep in mind while planning on organic synthesis.

Objectives

After studying this unit you should be able to :

- describe basic laboratory operations such as heating, cooling, stirring and filtration,
- explain the basic concepts involved in separation and purification techniques,
- select and use appropriate apparatus and techniques for various types of organic experiments,
- state the various precautions needed in the use and cleaning of glass apparatus and for laboratory safety and
- describe how to maintain loboratory record for the experiments of the 'Organic Preparations'.

1.2 SIMPLE LABORATORY TECHNIQUES

Heating, cooling, stirring and filtration are the important operations widely used both in preparatory and quantitative organic chemistry. Let us study these simple laboratory techniques in detail.

1.2.1 Heating Methods

Heating of organic compounds is resorted to for a variety of reasons. Heating increases the rate of chemical reactions. You would recall that organic reactions are molecular reactions. Unlike most of the inorganic reactions which are ionic and often instantaneous, organic reactions are slow and imperceptible at room temperature. An organic reaction mixture has, therefore, often to be heated to make the reaction go. Heating is also required in purification of liquids by distillation and in the dissolution of solids during crystallisation as also in the determination of melting and boiling points of organic compounds for testing their purity.

In this lab course, you will use the following heating devices.

i) Direct heating on a burner
ii) Water bath
iii) Oil bath
iv) Sand bath

Since nearly all organic substances are inflammable, care and good judgement should always be exercised when considering the use of these devices.

Direct heating on a burner flame should be avoided as far as possible. However, if a burner has to be used, say, while taking a melting or boiling point, all inflammable and volatile materials should be removed away from the burner. In case direct heating has to be done, it is advisable to use a wire gauze. This makes heating more uniform.

A water bath, an oil bath or sand bath should be used to provide uniform heating. For temperatures up to 100°C, a water bath is generally employed. You may be using an electrically heated water bath or a common copper water bath which can be heated on a burner. A common type of electrically heated water bath is shown in Fig 1.1. Water bath is covered with rings, which can be adjusted according to the size of the vessel to be heated.

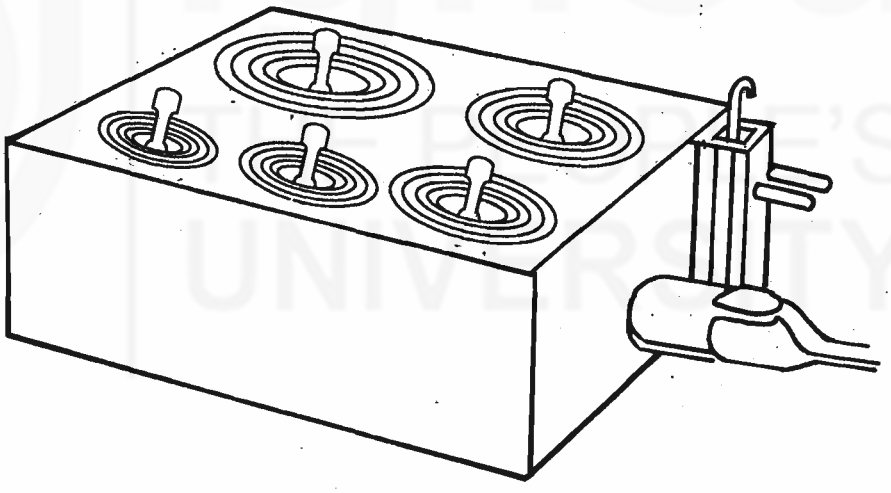


Fig 1.1 : Electrically heated water bath

An oil bath or a sand bath is used when heating is carried out above the 100°C. An oil bath can be made by filling a copper bath with a liquid like paraffin oil (Fig 1.2). A sand bath is a shallow iron plate filled with sand. Both these baths are heated by means of a burner.

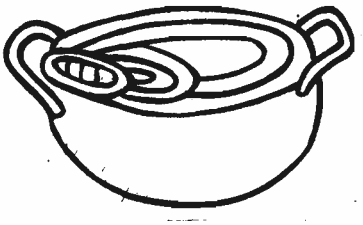


Fig 1.2 : Copper bath

1.2.2 Heating Under Reflux

A reaction mixture has to be often heated under reflux to prevent loss of volatile reagents and solvents. The reaction flask, generally a round-bottom flask, is fitted with a water condenser and heated on a water bath or an oil bath as shown in Fig 1.3. The liquid should be made to boil gently and drip back into the flask. The reaction flask should never be filled more than 1/2 to 2/3. In case of very high boiling solvents an air condenser may be used.

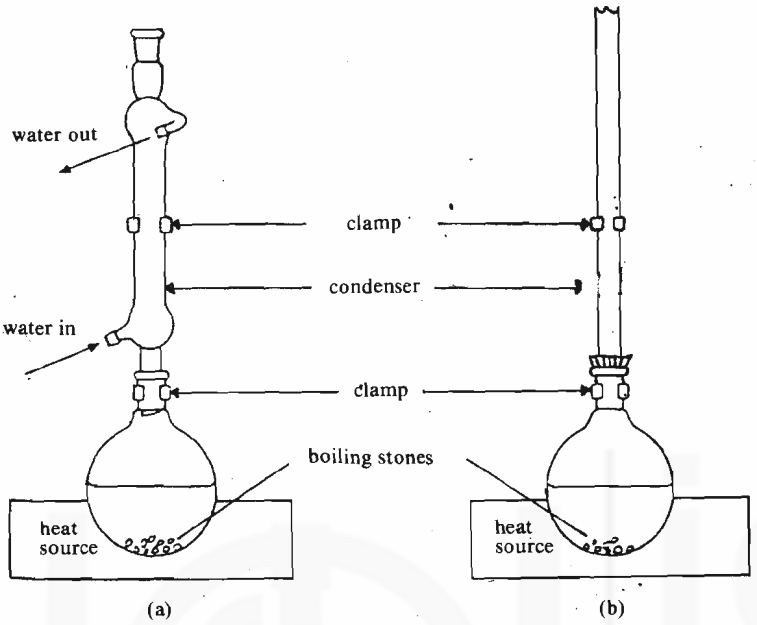


Fig 1.3 : Heating a reaction mixture under reflux :
(a) with a water condenser
(b) with an air condenser

1.2.3 Cooling Methods

Some times we have to keep temperatures below the room temperature for carrying out reactions which are strongly exothermic. Finely crushed ice is used for maintaining the temperature at 0 - 5°C. For the temperatures below 0°C, a mixture of common salt and crushed ice is used.

1.2.4 Stirring

In case of heterogeneous reaction mixtures, yields can be considerably improved by stirring. Stirring can be done with electro-mechanical or electro-magnetic stirrers. The latter may have a hotplate also, and provide both for heating and stirring (Fig 1.4).

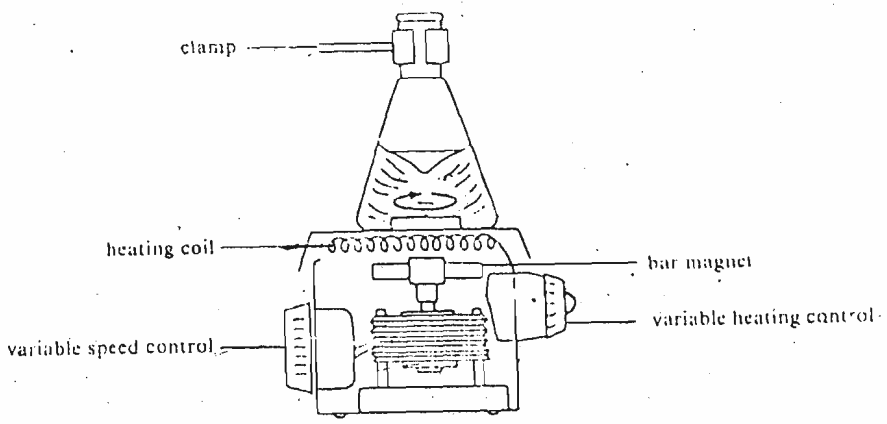


Fig 1.4 : Schematic diagram of a stirrer hotplate

1.2.5 Filtration

In an organic laboratory, filtration is a commonly used technique. Filtration can be carried out either under atmospheric pressure, (ordinary filtration) or under reduced pressure (suction filtration). Ordinary filtration is considerably accelerated when a fluted filter is used because it increases the surface area and thus the rate of filtration. We have shown in Fig 1.5 how to fold the filter paper to make it fluted.

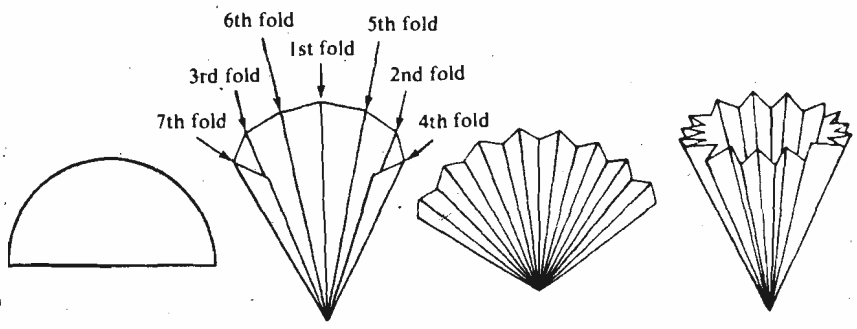


Fig 1.5 : Folding the filter paper to produce fluted filter paper.

You may also ask your counsellor to demonstrate the foldings for a fluted filter paper. The filter paper should fit the funnel snugly and before filtration it should be wetted by the pure solvent. The level of the liquid, to be filtered, should always be lower than the paper edge. For rapid filtration, we use suction filtration. In this, the filtration flask is attached to a water pump, which sucks out air, thus reducing the pressure inside the filtration flask. The liquid is forced down by the atmospheric pressure. A suction filtration unit consisting of a porcelain Büchner funnel, a filtration flask and a water pump is shown in Fig 1.6.

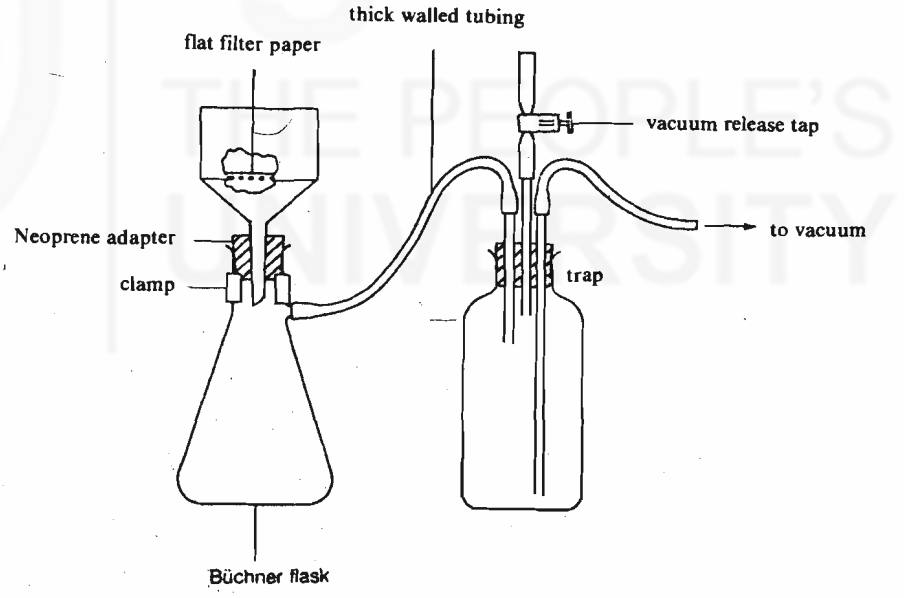


Fig 1.6 : Suction filtration using a Büchner funnel.

A filter paper circle, cut correct to size is fitted in the Büchner funnel. The filter paper is wetted with solvent, and suction put on before pouring in the solution to be filtered. The size of the funnel used in filtration, ordinary or under suction should correspond to the amount of the substance to be filtered.

1.3 TECHNIQUES OF SEPARATION AND PURIFICATION

So far we have studied common operational techniques. Organic reactions are seldom straight forward. Generally there are side reactions, leading to by-products. Because of this, a mixture of products is a rule rather than an exception. Further since organic reactions seldom go to completion, the matters get further complicated due to the presence of unreacted starting materials. So it becomes imperative to isolate and purify the desired product after carrying out a reaction. In this section, we first discuss separation and purification techniques, then we talk about some tests of purity.

1.3.1 Extraction

Extraction is based on the principle of phase distribution. An organic compound being more soluble in organic solvents will preferably go into the organic layer. For extraction, the aqueous mixture is taken in a separatory funnel. A small volume of an immiscible solvent, like diethyl ether or *n*-hexane, is added. Care should be taken that the separatory funnel is not more than 3/4 full. The funnel is stoppered and gently shaken to mix the contents thoroughly (Fig 1.7a). Since the solvents are generally volatile, it is necessary to vent the funnel by inverting it and opening the stopcock (1.7b). The funnel is then made to stand on an iron ring and the layers allowed to separate (Fig 1.7c). The aqueous layer being heavier will generally be the lower layer. It can be drawn off by opening the stopcock; and the organic layer poured off.

Chloroform and carbon tetrachloride are heavier than water, therefore, they form the lower layer in the separatory funnel.

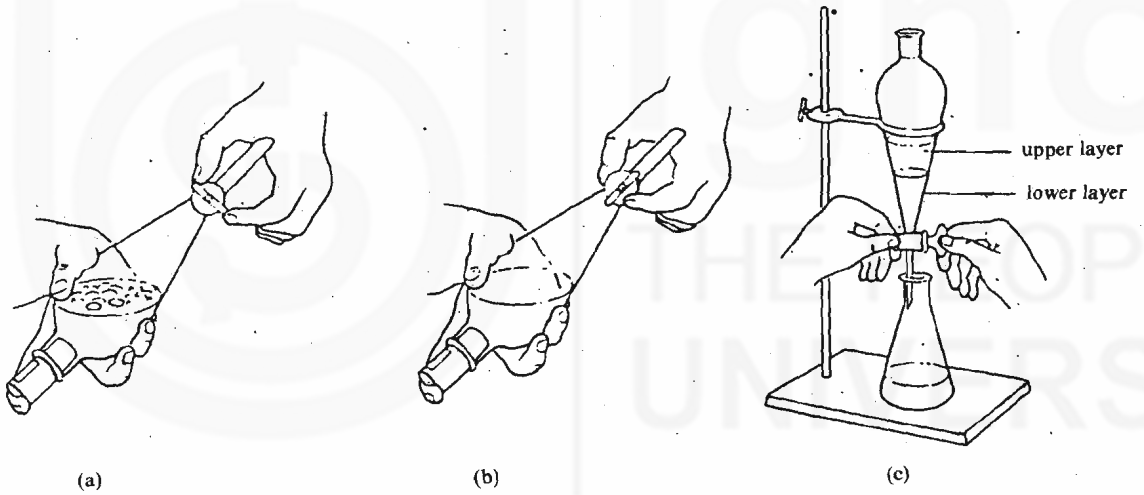


**Fig 1.7 : (a) Holding a separatory funnel during shaking;
(b) holding a separatory funnel during venting;
(c) holding a separatory funnel whilst draining the lower layer**

The process may be repeated twice and the three lots of extract combined. A larger number of extractions with small volumes of the solvent is able to extract more of the substance than a single extraction with a large volume.

It may be necessary to wash the extract with dilute acid/alkali and then with plain water before it is dried over a suitable drying agent. A larger number of extractions should be dried over a basic substance like anhydrous K_2CO_3 or solid NaOH and acid sensitive substances over Na_2SO_4. Anhydrous $MgSO_4$ is a good general purpose drying agent.

1.3.2 Crystallisation

Crystallisation is one of the most effective purification techniques for solids. It takes advantage of the fact that nearly all solids are more soluble in a hot than in a cold solvent. Before carrying out a crystallisation, it is an advantage to have an idea about the degree of purity of the substance and the nature of impurities. If the impurities in the impure solid dissolve and remain dissolved when the solution is cooled, the crystals will ideally be pure. On the other hand, the impurities may remain undissolved in the hot solution, in which

case, these can be filtered off, the solution concentrated and allowed to crystallise.

Choice of solvent

It is always better to try out on a small scale first. The following can, however, be taken as general guidelines :

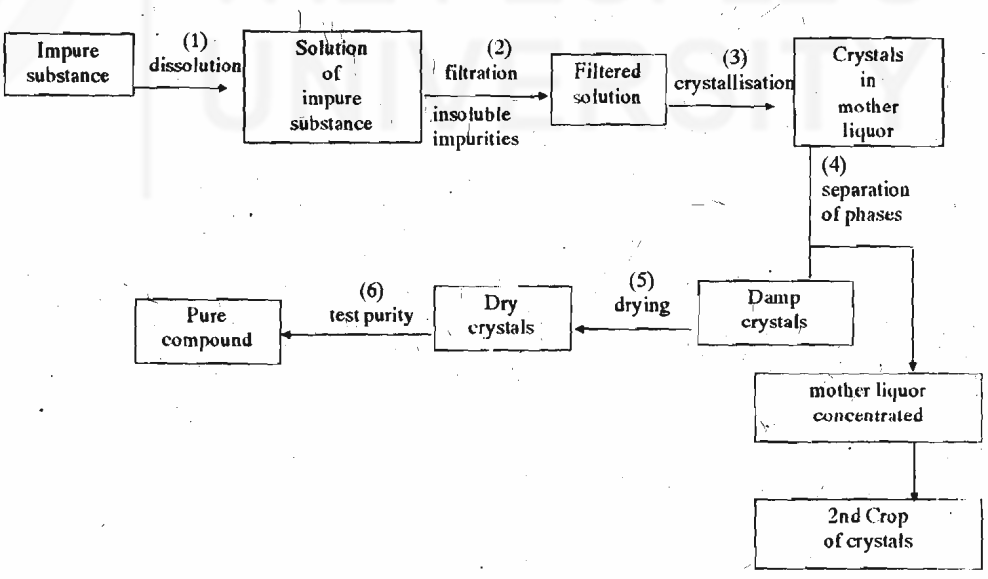
1. Substances tend to be more soluble in chemically similar solvents.
2. Good crystallisation medium would imply that the substance is very soluble in hot and insoluble in cold.
3. Very good solvents require very high concentration of solute for crystallisation.
4. Polar solvents tend to produce better crystals than hydrocarbon solvents.

Table 1.1 gives a list of common solvents arranged in order of increasing polarity and the class of compounds for which they can be used.

Table : 1.1 Some Common Solvents

Class of substance to be crystallised	Efficient Solvents	Polarity of Solvent
Hydrocarbons	pentane, hexane, petroleum ether, benzene	hydrophobic (lipophilic) non-polar
Ethers	diethyl ether, methylene chloride	
Halohydrocarbons	chloroform	
Tertiary amines	acetone	
Ketones and Aldehydes Esters	ethyl (or methyl) acetate	
Phenols Alcohols	ethanol	
Carboxylic acids	methanol	
Sulphonic acids Organic salts	water	hydrophilic polar

A general **workplan for crystallisation** can be as follows :



These steps are briefly described below :

i) Dissolution

Once the choice about a suitable solvent has been made, the impure substance is dissolved in it. It may be noted that the purer the substance and the larger the crystals, the more slowly it will dissolve. Large crystals may have to be ground before dissolving. In case the solution is strongly coloured by impurities, activated charcoal may be added to decolorise

it. For this, the material is first dissolved and then the solution heated with 2-4% of its weight of charcoal for about 10 minutes. The impure or crude substance must be weighed before dissolving, this will enable you to calculate the yield of the pure product.

ii) Filtration

Filtration serves to remove dust and insoluble impurities. A hot solution can be filtered through a fluted filter paper which has been preheated by pouring through it a small volume of the hot solvent. This is called simple or gravity filtration. To prevent premature crystallisation, a slight excess of the solvent may be used. Still if any substance is left on the filter paper, it can be eluted later.

iii) Crystallisation

Crystallisation from a super-saturated solution can be induced by :

- slowly cooling a hot saturated solution to room temperature or below in ice.
- by slowly adding a miscible poor solvent until the solution starts getting cloudy, warming to clear the turbidity and allowing it to cool slowly. This is called the mixed solvent technique, typical mixed solvents are ethanol-water, benzene-petroleum ether, etc.

Crystallisation may be facilitated :

- by addition of a seed crystal.
- by scratching the side of the vessel with a glass rod.

iv) Separation of Crystals

Crystals are separated from the mother liquor by filtration preferably under suction. Some times crystals can be removed by centrifugation, especially in case the quantity is small. The crystals are washed by cold, pure solvent to remove the sticking mother liquor.

v) Drying

Solid organic compounds must be dried because the presence of moisture or organic solvents may affect their melting point, quantitative elemental analysis and even spectra. A solid that has been crystallised from a volatile solvent can be usually dried by allowing it to air dry at room temperature. If the solid is collected on a Büchner funnel under suction, most of the solvent would be sucked off.

For more effective drying, desiccators with suitable desiccants like silica gel, phosphorus pentoxide or fused calcium chloride may be used. To remove hydrocarbon solvents, a block of solid paraffin is helpful. Samples for quantitative elemental analysis are usually dried in a vacuum desiccator. Oven drying should, if at all, be carried out at temperatures well below the melting point of the substance.

SAQ 1

List four criteria that should be used in selecting a solvent for a crystallisation.

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SAQ 2

The following solvent selection data was collected for an impure solid. Based on these results, what solvent would you use to crystalise this solid?

Solvent	Solubility at room temp.	Solubility when heated	Crystals formed when cooled
Methanol	insoluble	insoluble	...
Chloroform	insoluble	soluble	very few
Cyclohexane	insoluble	soluble	many
Toluene	insoluble	soluble	very few

1.3.3 Sublimation

Sublimation is an alternative to crystallisation for purifying some solids. The criteria for effective purification by sublimation require that :

(i) the compound to be purified must have a relatively high vapour pressure.
(ii) the impurities must have vapour pressure substantially lower than the compound to be purified.

The technique involves placing the impure solid in a sublimation chamber or dish and heating it to a temperature higher than that of the cold surface on which it is to be collected, but lower than its melting point. Under these conditions, the solid will be vaporised and the vapours will condense on the cold surface. The crystals that form on the cold surface are usually very pure, since impurities do not vaporise.

Sublimation may be carried out in a simple apparatus consisting of a china dish in which the sample is heated, and an inverted glass funnel to collect the sublimate. A piece of filter paper with a few holes ensures that the sublimate does not fall back into the dish, a loose cotton plug on the stem of the funnel prevents vapours from escaping (Fig 1.8a).

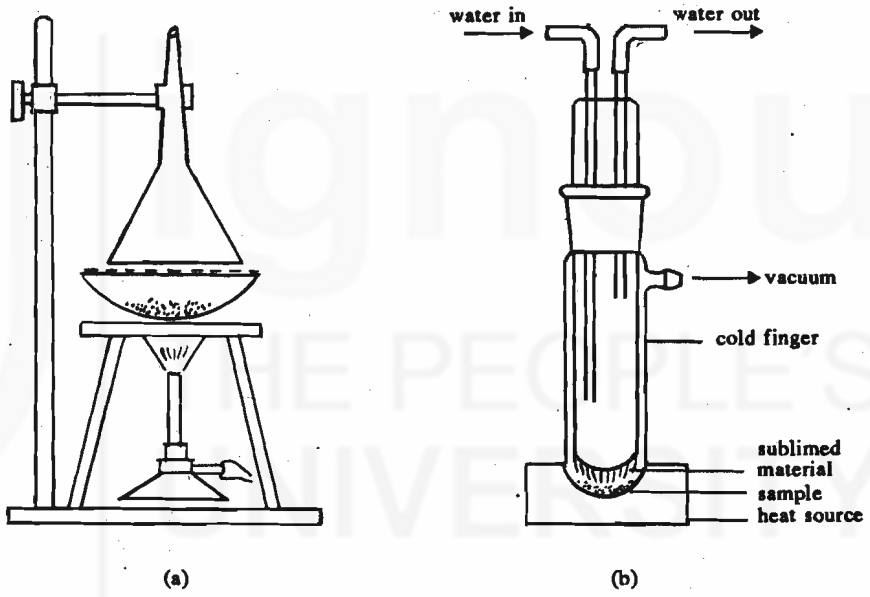

Figure 3.53. Apparatus for sublimation using
(a) purpose built sublimator (b) improvised sublimator

**Fig 1.8 : (a) Sublimation apparatus;
(b) Under Vacuum**

To increase the rate of sublimation, the process may be carried out under reduced pressure. For this purpose, a simple apparatus may be set up as shown in Fig 1.8b. The sample is put in the outer tube which is heated. Cold water is circulated through the inner tube or 'cold finger' to ensure complete condensation.

1.3.4 Distillation

Liquids can be purified by distillation, a process that consists of vaporising a liquid and condensing the vapour as a distillate. Simple distillation can help removal of non-volatile impurities or when the difference in boiling points of components is 80° or more. Fractional distillation can be used to separate components of a mixture of liquids with relatively smaller difference in boiling points. In case a liquid decomposes at or near the boiling point, distillation can be carried out under reduced pressure.

Apparatus for simple distillation is fitted as shown in Fig 1.9. For heating, a water bath (upto 100° C) or an oil bath (upto 200° C) can be used. Cold water is circulated through the condenser. To avoid bumping, boiling stones may be added to the distillation flask.

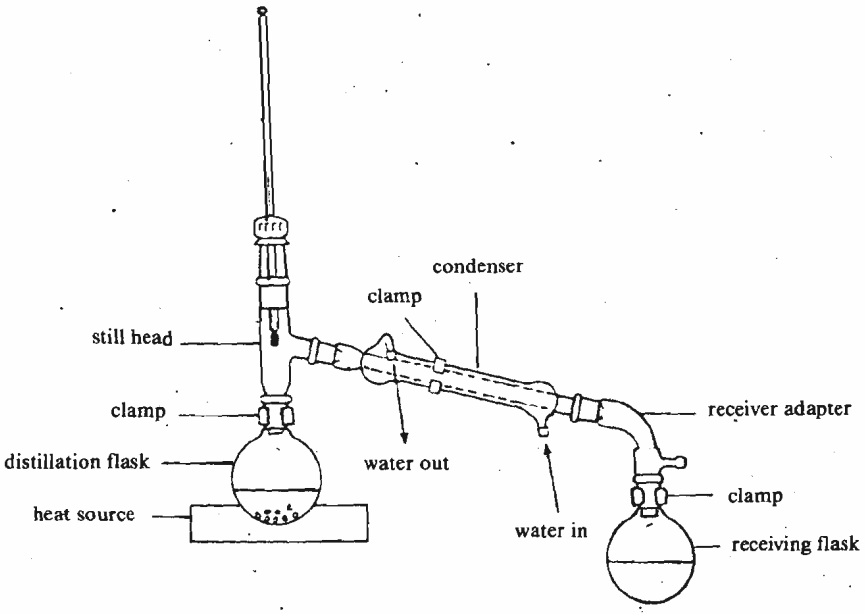

Fig 1.9 : Apparatus for simple distillation

For fractional distillation, a fractionating column is used. Various types of fractionating columns are available, which differ in their effectiveness of separation. Fig 1.10 shows the apparatus generally used for fractional distillation. For distillation under reduced pressure, the apparatus is fitted as shown in Fig 1.9 attached to a vacuum pump. A water pump generally gives a pressure of about 10-15 torr and reduces the boiling point by about 100°, an oil rotatory pump reduces the pressure to about 0.1 torr and further lowers the boiling point by 60°. A thin stream of air introduced into the distillation flask through a capillary tube prevents bumping in this case.

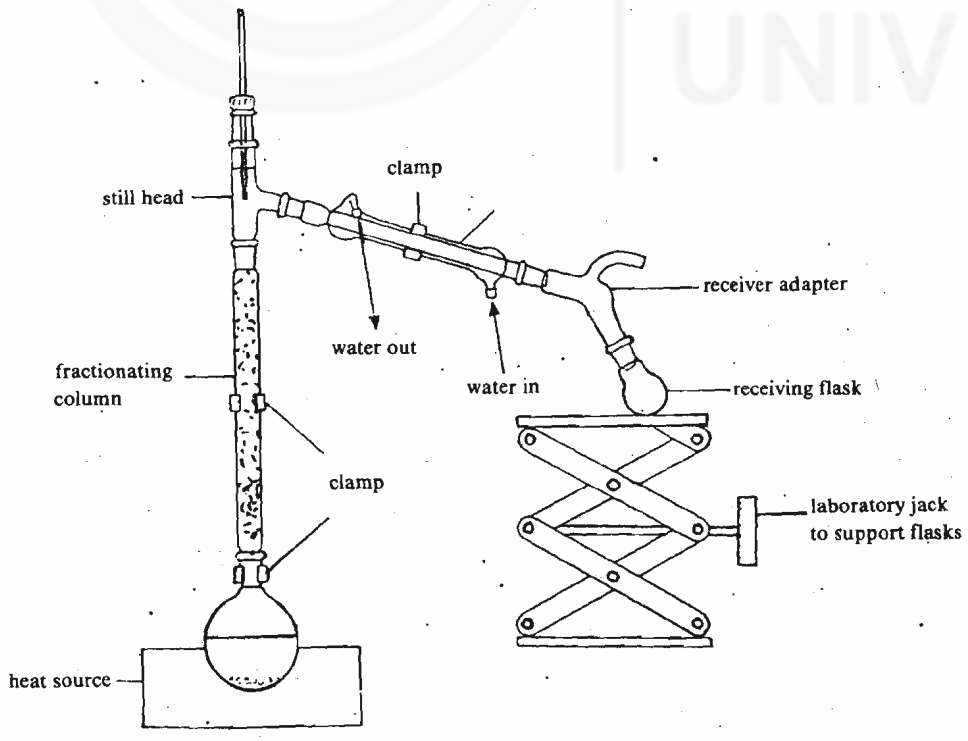

Fig 1.10 : Apparatus for fractional distillation

1.3.5 Chromatography

Chromatographic separation depends on the differences in the partition coefficients of the components of a mixture between two immiscible phases. One of these is the mobile phase which moves relative to the other, the stationary phase. The substances being separated are transported with the mobile phase.

The partition coefficient K of a substance, in such a two phase system is given by

$$K = \frac{c_s}{c_m}$$

where c_s is the concentration of the substance in the stationary phase and c_m is the concentration of the substance in the mobile phase. From the above you can see that the greater the partition coefficient of a substance, the greater would be its concentration in the stationary phase. In other words its retention in the stationary phase would be higher. Consequently its movement with the mobile phase would be slower.

According to the physical states of the mobile and stationary phases, various chromatographic methods are classified as follows :

Mobile Phase	**Stationary Phase**	**Chromatographic Technique**
Vapour	Solid	Gas chromatography (gas-solid chromatography)
	Liquid	Gas chromatography (gas-liquid chromatography)
Liquid	Solid	Adsorption chromatography
	Liquid	Liquid-Liquid partition

The stationary phase is called the **absorbent**, the mobile phase, the **eluent.** Removal of the adsorbed substance from the adsorbent by washing is known as elution. The solution, as it comes out of the chromatographic column, is called the eluate.

All the above techniques are well defined and are carried out in organic chemistry laboratories as a routine. For processes like gas chromatography, fairly sophisticated commercial instruments are available. In this course you would be mainly doing adsorption chromatography. So we shall describe this method in some detail.

1.3.6 Adsorption Chromatography

As you have read above, this entails partition between a mobile liquid and a solid stationary phase. The success of such a separation depends on the correct choice of the mobile and stationary phases.

Generally if the stationary phase is polar like kieselgel or silica gel, alumina or cellulose, etc., you would chose a mobile phase starting with non-polar going over to polar medium in order of increasing polarity, e.g., hexane→ ether→ methanol. In case the stationary phase is non-polar like nylon or polystyrene, a polar mobile phase, methanol, water or acetonitrile may be used.

i) Stationary Phases

Some of the substances which are commonly used as stationary and mobile phases are given below :

The two commonly used stationary phases are :

Kieselgel or Silica Gel

This is by far the most common substance used as a stationary phase in adsorption chromatography. Kieselgel is dehydrated, highly porous silicic acid, ground to give a particle size of 0.04 - 0.2 mm and a surface area of 200 - 400 m^2 per gram.

Alumina

Alumina is somewhat basic. Neutral alumina is prepared by neutralisation to pH 7.0, followed by activation by heating.

ii) Mobile Phases

The choice of the mobile phase depends on the nature of the substance and how strongly it is adsorbed. In Table 1.2, substances have been arranged in the order of their increasingly strong adsorption on kieselgel and alumina along with the corresponding mobile phase which can be used as an eluent. Such a series is known as eluotropic series.

Table : 1.2 Eluotropic Series

Substance	Eluent
Saturated hydrocarbons	*n*-pentane, *n*-hexane
Unsaturated hydrocarbons	cyclohexane, carbon tetrachloride, toluene
Ethers	benzene diethyl ether
Esters	chloroform
Ketones	dichloromethane
Amines	acetone (not on Al_2O_3)* ethyl acetate
Alcohols	iso-propanol ethanol
Phenols Acids	methanol
	acetic acid water
Increasingly strongly adsorbed on kieselgel or alumina	increasing eluting strength

*Acetone should not be used on Al_2O_3 as it forms addition compounds with it

Mixtures of solvents can be used as eluents. The solvents should be pure, preferably freshly distilled.

Temperature Dependence

Substances are more strongly adsorbed at lower temperatures. Chromatography in any case should be carried out in an area which is draught free and not too hot.

We are describing two experimental adsorption chromatographic techniques here, which are analytical thin layer chromatography and preparative thick layer chromatography. Others, like column chromatography will be taken up in later laboratory courses.

Analytical tlc can be used for :

- checking purity
- preliminary tests before separation
- qualitative comparison with known substances
- monitoring a reaction

Silican Gel with binder for tlc is available in market.

Procedure

(i) Preparation of the plate

Microscopic slides like the ones used in a bio-sciences laboratory can be used. The plates have to be thoroughly cleaned and dried. The stationary phase is alumina or kieselgel applied in thickness of about 0.2 mm from a slurry of the adsorbent in carbon tetrachloride (about 30 g in 100 ml of CCl_4) by dipping the plate in the slurry and allowing to drain. A binder like calcium sulphate is added to kieselgel/alumina which helps in binding the adsorbent to the glass plate. The plates are then put in a rack and activated by heating in an oven at 110°C for an hour or so.

(ii) Application of the substance

A dilute (1%) solution of the substance in the least polar, suitable, low boiling solvent is applied to the plate with a thin capillary in the form of a spot at one end as shown in Fig. 1.21a and the solvent allowed to evaporate completely.

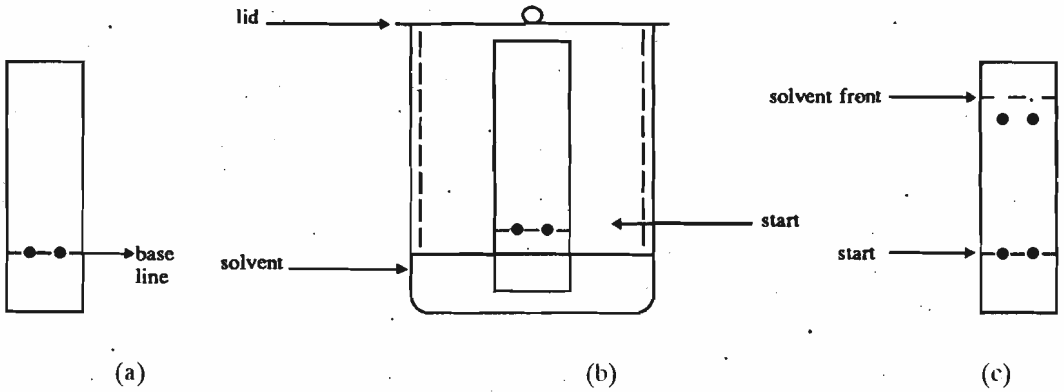

Fig 1.11 : A tlc plate spotted with the sample; tlc
a) before development
b) developing a tlc plate
c) after development

(iii) Developing the chromatogram

The plate is made to stand in a chromatographic chamber with the lower end with the spot, dipping in the eluent and allowed to develop (Fig 1.11b). The chromatographic chambers are small jars with fitting stoppers. When the solvent front has advanced a suitable distance, the plate is removed, the solvent front marked and the plate allowed to dry (Fig. 1.11c).

(iv) Detection

Coloured spots are, of course, immediately visible. Colourless spots can be made visible by :

- uv, if the substance absorbs uv, e.g., the aromatic compounds.
- standing the plate in iodine vapour in a chromatographic jar, organic compounds generally give coloured spots with I_2 ,
- spraying with 1 : 1 H_2SO_4 - water mixture and then heating strongly to carbonise the compounds. You should be careful with H_2SO_4 spray, it is preferably done in a fume hood,
- spraying with suitable reagents which give coloured spots with the substances under observation, for example ninhydrin in case of amino acids.

v) Recording

The chromatogram is recorded using a tracing paper. The starting position, solvent front and the spots are clearly marked. The details about the type of plate, eluent and method of development are also recorded.

R_f value of a substance is calculated by the relationship :

$$R_f = \frac{\text{Distance of spot centre start}}{\text{Distance of solvent front start}}$$

The R_f value depends on the conditions under which the chromatogram was run, namely, type of plate, eluent, temperature, etc. Its reproducibility is about $\pm$ 20%. However, it is best to run the probable reference compound on the same plate for comparison.

Preparative Thick Layer Chromatography

In preparative thick layer chromatography, larger samples of upto 200 mg can be handled. The plates are also bigger, 20 cm^2 or so. Since it may not be possible to get a uniform layer of the adsorbent deposited on a large plate, an applicator can be used. Commercial applicators or spreaders are available which ensure a uniform thickness of the layer, with the additional advantage that the thickness can be adjusted. After the adsorbent has been

deposited on the plate, it is activated by heating as for analytical tlc. A concentrated solution of the mixture to be separated is applied in a narrowest possible strip using a drawn out pipette. After developing the chromatogram, the separated bands are detected and scrapped off separately. These are then eluted with a solvent more polar than the eluent, filtered and the substance isolated by evaporation of the solvent.

SAQ 3

Two components, A and B, were separated by tlc. When the solvent front had moved off a distance of 10 cm above the level of the original sample spot, the spot of A was 7.0 cm and that of B was 4 cm above the original spot. Calculate the R_f for A and B.

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1.4 TESTS FOR PURITY

Efficacy of purification can be judged by any of the following criteria. These criteria can also be used for characterisation of unknown compounds.

1.4.1 Melting Point (mp)

Melting point is the most common test for purity in case of solid compounds. A pure crystalline compound has, in general, a definite and sharp melting point, i.e. the melting range or the difference between the temperature at which the collapse of crystals is first observed and the temperature at which the sample becomes completely liquid, does not exceed 0.5 - 1.0°C

Even small amounts of impurity may depress the melting point appreciably. In general, one crystallises a compound to constant melting point. It may be a good idea to crystalise it from another solvent to check whether there is any further increase in melting point. The compound should be carefully dried and finely powdered for taking a melting point.

Melting points are usually determined in capillary tubes open to the air. A capillary tube is a thin glass tube about 1-2 mm in diameter. For melting point determination, a capillary tube of about 8-9 cm long is taken and sealed at one end by holding it horizontally into the edge of a small Bunsen burner flame for a few seconds while rotating it. The molten glass would seal the capillary. Formation of large glass beads should be avoided.

The capillary tube is then filled as follows :

About 25 mg of the dry substance is placed on a clean porcelain plate and finely powdered with a metal or glass spatula forming it into a small mound. The open end of the capillary tube is pushed into the powder, when a small amount of the powder gets into the capillary tube. The solid is shaken down the tube by tapping the closed end of the tube gently on the working bench. The process is repeated until the length of the tightly packed material is about 3-5 mm. The outside of the tube is then wiped clean.

The capillary tube can be heated in a liquid bath or on an electrically heated metal block. You would be using the Thieles melting point bath, which is a tube with a closed bent side arm. On heating the bent side arm, the heated liquid circulates and raises the temperature of the sample. The tube is filled with the liquid to just above the bent side arm. No stirring is required. The bath liquid generally used is liquid paraffin, which can be safely heated upto 220°C, above this temperature it starts fuming and gets discoloured. Silicone oils, though more stable, are expensive.

The thermometer is fitted through a cork. A section of the cork is cut away, so that the thermometer scale is visible and also to allow the air to escape on heating.

The filled capillary tube is attached to the lower end of the thermometer in such a way that the substance is at the level of the middle of the mercury bulb. For this purpose, the capillary tube is moistened with the bath liquid, the surface tension of the liquid enables the capillary tube to become attached to the thermometer by capillary action. The thermometer, with the capillary tube attached, is then inserted into the bath. Care is taken

that the open end of the tube is well above the level of the liquid. Allow for expansion of the liquid on heating

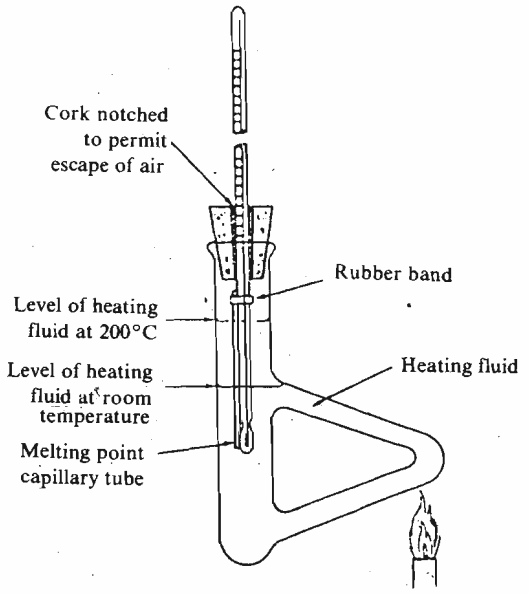

Fig 1.12 : Thiele's melting point apparatus

The melting point apparatus (Fig 1.12)is heated with a small flame; comparatively rapidly till the temperature is about 15^{o} below the melting point of the substance, and then slowly such that the rise of temperature is about 2^{o} per minute. The temperature at which the substance starts to melt and that at which it has completely liquified, i.e. the melting range is noted. As said above, for a pure compound it should not exceed 0.5^{o} - 1^{o}. Any softening, sintering, evolution of gas or any other signs of decomposition are carefully noted. In case of an unknown compound, an approximate melting point may be taken first.

Mixed Melting Point

The fact that a foreign substance lowers the melting point of a pure organic substance is utilised in mixed melting point test for the identification of organic compounds. For this, the melting point of an authentic sample of the compound is compared with that of a mixture of the authentic sample with the compound under consideration. If both are identical, there would be no depression in the melting point of the mixture. If they are different, the melting point of the mixture may get depressed by several degrees. It is often possible to attach the two tubes, one containing the authentic sample and other, the mixture on either side of the thermometer and take their melting points simultaneously.

1.4.2 Boiling Point (bp)

Boiling point can be taken as a test for the purity of a liquid. A pure liquid will have a certain definite boiling point only at a particular pressure, as the boiling point is affected both by impurities and by the ambient or external pressure. Impurities generally raise the boiling point. Since boiling point is the temperature at which the vapour pressure of a liquid becomes equal to the ambient pressure, the boiling point of a liquid will be higher at higher pressures, and the liquid will boil at a lower temperature if the pressure is reduced.

When 5 ml or more of the liquid is available, its boiling point can be determined by slowly distilling it from a small flask. For smaller quantities, a micro method has to be used. One such method which you would be using is described below.

Siwoloboff's Method

In this method, two tubes are required, one, an ordinary melting point capillary tube 90 - 110 mm long, the other, a wider tube 3-5 mm in diameter and 80 - 100 mm long. The capillary tube is sealed at one end and then another seal is made in it about 1 cm from the open end by holding it in a flame. The wider tube is also sealed at one end. The capillary tube is placed in the wider tube with open end down as shown in Fig 1.13.

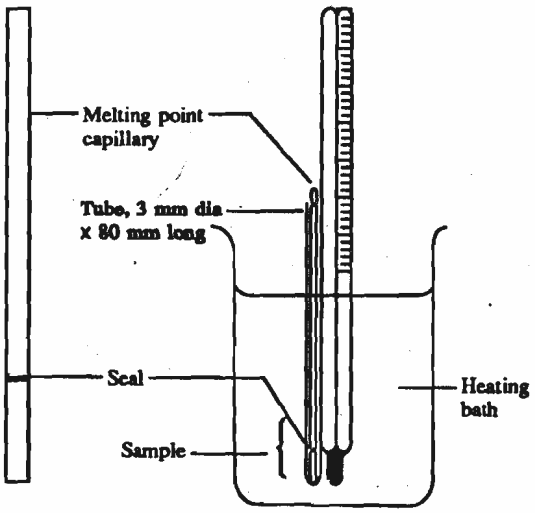

Fig 1.13 : Assembly of boiling point apparatus

Then using a pipette, the liquid, the boilding point of which has to be determined, is put into the wider tube, such that its level is about 2 mm above the seal in the capillary tube. The tube is attached to the thermometer keeping the liquid at level with the mercury bulb of the thermometer. A rubber band may have to be used for the purpose. The thermometer, with attached tubes is inserted into a heating bath. Care is taken that the rubber band is well above the level of the liquid, as rubber gets attached by liquid paraffin.

The bath is heated until a rapid and continuous stream of bubbles comes out of the capillary tube. Before this occurs, some bubbles evolving in an erratic fashion may be seen. This is due to the air trapped in the capillary tube. There would be a marked change from slow evolution of air bubbles to the rapid evolution of bubbles resulting from the liquid boiling as its boiling point is reached. However, **this is not the boiling point of the liquid.** At this stage, the heating source is removed and the bath allowed to cool slowly. As the rate of bubbling decreases, the liquid starts to rise into the capillary tube. This temperature is noted. **It is the boiling point of the liquid.** If the liquid rises sufficiently slowly, it may be possible to note the temperature at which the liquid starts to rise, and that at which the capillary is full, i.e. the boiling point range of the liquid.

The capillary tube is removed and the liquid shaken out from the small end. The capillary is then replaced in the sample tube and the process of heating and cooling repeated. A more accurate determination may be possible this time. Observed boiling points should be reproducible to within 1 - 2°.

You would like to know the physical basis of this technique. Before the liquid is heated, the capillary tube is filled with air. As the bath is heated, the air in the capillary tube is driven out and is replaced with the vapour of the liquid. On further heating until the liquid starts boiling vigorously, the actual boiling point of the liquid has been exceeded, the air in the capillary tube has been replaced completely with the vapour of the liquid. On cooling, at a particular temperature the vapour pressure of the liquid to rise in the capillary tube. This temperature is the boiling point of the liquid.

In addition to the melting and boiling points, the purity of a compound can be tested by thin layer chromatography. A pure compound would give a single spot under optimum conditions of separation. Further, the R_f value is a characteristic property of a compound under a standard set of conditions and can be used for identification of a compound.

SAQ 4

For the following melting points, indicate what might be concluded regarding the purity of the sample

a) 130° - 132° C
b) 56° - 60° C
c) 147° C (dec)
d) 173.5° - 174.5° C

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SAQ 5

Criticise the following statements by indicating whether each is true or false, and if false, explain why :

a) An impurity always lowers the melting point of an organic compound.
b) A sharp melting point for a crystalline organic substance always indicates a pure single compound.
c) If the addition of a sample of compound A to compound B does not lower the melting point of B, B must be identical to A.
d) If the addition of a sample of compound A lowers the melting point of compound B, B and A cannot be identical.

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1.5 GLASSWARE : PRECAUTIONS IN USE AND CLEANING

Organic preparations involve the use of glassware of various types. Following safety precautions may be kept in mind regarding the proper and safe use of glassware.

The cardinal rule in handling and using laboratory glassware is, **never apply undue pressure or strain to any piece of glassware.** This applies to insertion of glass tubes or thermometers into rubber or cork stoppers or fitting corks on condensers, funnels, etc. A convenient method of inserting glass into corks is to lubricate glass with a little water or water containing soap or glycerol. Glass piece must be grasped very close to the cork when trying to insert it. It is wise to wrap a piece of cloth around the glass and cork, this would prevent a serious cut even if the glass breaks.

The glassware must be washed immediately after use. Most chemical residues can be removed by washing the glassware with soap or common laboratory detergent. Common organic solvents like alcohol or acetone can be used for washing off substances insoluble in water. Stubborn residues may need more powerful cleaning solutions, like chromic acid, or a mixture of alcohol with solid potassium hydroxide, etc. We would advise you to consult your counsellor before using these strong cleaning solutions which require special care in handling.

Glassware often needs drying before it is used in an organic preparation. Glassware, other than standard or graduated glassware can be dried by a hot air blower or in a hot air oven. Graduated glassware should never be heated, it can be rinsed with alcohol or acetone and allowed to drain.

Stoppers and interchangeable joints should be properly greased in order to avoid sticking.

1.6 LABORATORY SAFETY

Chemistry laboratories are potentially dangerous because they contain inflammable liquids, poisonous chemicals and fragile glassware. Where high pressure cylinders of gases are used, they also pose a potential danger. Therefore, proper precautions must always be taken and safe experimental procedures must be followed while working in a chemistry laboratory. If this is done, a chemistry laboratory is no more dangerous than a kitchen or a bathroom.

Some important general safety considerations are given below. Any special precautions or safety measures, if required, are given in the particular experiments. You should read all these carefully and follow them faithfully.

1. The first thing is to be familiar with the layout of the laboratory especially where fire extinguishers, blankets or the first aid box is.
2. Never work alone in the laboratory
3. Check the glassware before using. It should not have any cracks or imperfections.
4. Almost all organic liquids are inflammable and therefore should never be heated on a naked flame. You may use a water or an oil bath.
5. All chemical must be handled with caution. As far as possible direct contact with skin must be avoided. Rubber or plastic gloves can be worn while handling especially toxic compounds. Avoid inhaling vapours of any compound. Never taste anything.
6. A fume hood must be used for handling dangerous substances or for carrying out reactions in which noxious gases are evolved.
7. Ask your Counsellor for safe disposal of chemicals and glassware. Never pour solvents and other chemicals into the sink, put them into special containers for waste. Also do not throw used filter papers or broken glassware into the sink, put them in dustbins.

1.7 LABORATORY NOTE BOOK

One of the most important characteristics of a scientist is the habit of keeping good record of the work that has been done. The record should reflect all the planning that has gone in as well as the observations at various stages of the experiment. A chemist must observe things like whether there was a colour change when the reactants were mixed or a reagent was added to the solution, whether a precipitate was formed or a gas evolved, was the reaction exothermic, and record them. These observations may appear insignificant but prove helpful in correct interpretation of an experimental result.

While preparing a laboratory note book, the following important features may be kept in mind.

1. Record all observations and data in the note book at the time they are obtained. Never use scraps of paper for noting things like weights of reactants taken, melting or boiling points, etc. They might get lost or mixed up.
2. The record should be so thorough and well organised that on reading it, it should be possible for any one to understand what has been done and repeat it. It may not be necessary to copy out the exact procedure, since this is given in your laboratory manual. However, results should be summarised, conclusions drawn or each experiment and explanation provided if the results vary from those expected.
3. Laboratory notebook is a complete log of all operations. Dates, times and other information must be entered regularly.
4. A bound note book should be used for laboratory record. Special laboratory note books are available, often with numbered pages, one side being blank and the other ruled.
5. All entries must be made in ink. If a mistake is made, it should be crossed out and correct data put in.
6. The first page of the note book can be used as the title page, a few pages can be left for the Table of Contents.

Types of Organic Experiments

There are two broad classes of experiments in organic chemistry. Investigative experiments like those given in Block 2 of this manual, involve qualitative organic analysis like identifying the functional group (s) in a compound or the compound itself. Preparative experiments involve conversion of one compound into another. These experiments require slightly different type of note book format. Here we will discuss the format we are going to use for preparative experiments.

Preparative Type of Experiments and Laboratory Notebook

Successful laboratory work requires preparation for the experiment in advance. You must read the theory and experimental procedure before coming to the lab, so that you understand what you are doing and are also able to plan the experiment properly; and finish it in the allotted time.

Some of the information required to be noted for preparative organic experiments is as

follows :

1. **Title**

2. **Introduction**
   Give brief description of the experiment

3. **Main Reaction (s)**

   Write equations for the conversion of starting compounds, i.e. reactants into products. The equations should be balanced so that it is possible to calculate the theoretical yield of the product.

4. **Table of Reactants and Products**

   A convenient method for summarising the amount of reactants to be taken and the products formed is setting up a Table of Reactants and Products. It may contain the following :

   (i) The name and structure of each starting material and product.

   (ii) The molecular weight of each of the above

   (iii) The weight in grams of each starting material taken

   (iv) The moles of each starting material as calculated from (ii) and (iii)

   (v) Theoretical mole ratio for the reactants and products which can be calculated from the balanced equation for the reaction.

   (vi) Physical properties of the reactants and products like melting point, boiling point, density, colour, etc.

5. **Yield Data**
   The maximum expected yield of the product, called the theoretical yield, can be calculated from the Table of Reactants and Products. In an organic preparation a reactant may sometimes be taken in excess of that indicated by the balanced equation. From the number of moles of each reactant used and the mole ratio of reactants indicated in the balanced equation, the reactant that is the limiting reagent can be determined. The reaction stops when the limiting reagent is consumed, no matter how much of the other reactants remain. This, in a way, ensures as complete a conversion of the key reactant as may be possible under the reaction conditions. The theoretical yield in such cases can be calculated from the number of moles of the product expected from the number of moles of the limiting reagent and the balanced chemical equation. The theoretical yield in grams can be calculated by multiplying the theoretical yield in moles of the product by its gram molecular weight.

Percentage yield, which is a way of expressing the efficiency of a reaction can be calculated from the actual and theoretical yield

$$\text{Per cent yield} = \frac{\text{actual yield in grams}}{\text{theoretical yield in grams}} \times 100$$

Per cent yield is often rounded off to whole numbers. Per cent yields of 80% and above are considered excellent for organic reactions.

6. **Observed Properties of the Product**
   Physical properties of the product obtained from the experiment like melting point, boiling point, colour, odour, crystalline form, etc. should be compared with ones reported.

   A sample note book formate for organic preparation experiments is given here. Preparation of acetanilide from aniline using a mixture of acitic anhydride and sodium acetate as the acetylating reagents is taken as example

   Title : Preparation of Acetanilide

   Introduction : Acetanilide is prepared by acetylation of aniline with acetic anhydride. Aniline is dissolved in diluted hydrochloric acid and acetylated with acetic anhydride in the presence of aqueous sodium acetate.

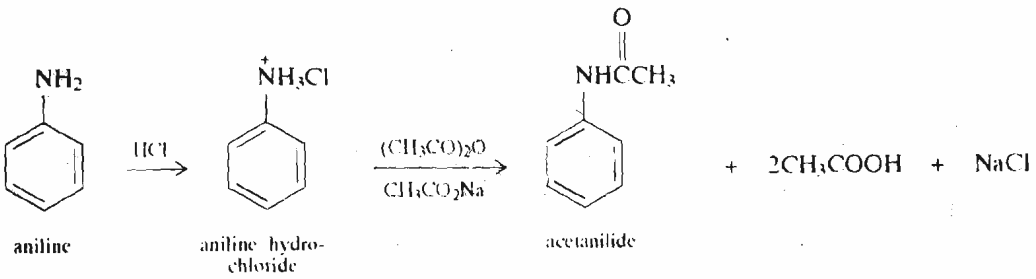

Table of Reactions and Products

Sl. No.	Compound	Mol. Wt.	Weight used	Moles used	Molar Ratio Theoritical	Other data
1.	Aniline	93	6.8 g (6.6 cm^3)	.073	1	Liquid bp 184°
2.	Conc. Hydro-chloric acid	36.5	6.1 cm^3 (1.69 *M* HCl)	0.073	1	
3.	Acetic anhydride	102	9.2 g (8.5 cm^3)	0.09	1.2	Liquid bp 139.5°
4.	Sodium acetate	82	11 g	0.134	1.8	Solid
5.	Acetanilide	135			1	

Yield

Say the yield is 6 g. From the equation it can be seen that one mole of aniline will give one mole of acetanilide, i.e., 93 g of aniline will given 135 g of acetanilide or 6.8 g should give 9.87 g.

So, the per cent yield $= \frac{6}{9.87} \times 100 = 60.8\%$

Observed Properties of the Product

Acetanilide separates out in almost pure form, mp 113°C.

1.8 ANSWERS

Self Assessment Questions

1. There are four important criteria that are used in selecting a solvent for a crystallisation.

   (i) Substance tend to be more soluble in chemically similar solvents.

   (ii) Good crystallisation would imply that the substance is very soluble in hot and insoluble in cold Solvents.

   (iii) Very good solvents require very high concentration of solute for crystallisation.

   (iv) Polar solvents tend to produce better crystals than hydrocarbon solvents.

2. Cyclohexane is a good solvent. As evident from the table that solid is very soluble in hot and insoluble in cold cyclohexane and this solvent system gives the best yield.

3. R_f value of a substance can be calculated by the relationship :

$$R_f = \frac{\text{Distance of spot on centre from start}}{\text{Distance of solvent front from start}} = \frac{l_1}{l_2}$$

In case of A, $l_1 = 7$ cm and $l_2 = 10$ cm, therefore

of A, $l_1 = 7$ cm and $l_2 = 10$ cm, therefore

$$R_f = \frac{7}{10} = .7$$

In case of B, $l_1 = 4$ cm and $l_2 = 10$ cm, therefore,

$$R_f = \frac{4}{10} = .4$$

4. As you know, a pure crystalline compound has, in general, a definite and sharp melting point, i.e., the melting range or the difference between the temperature at which the collapse of crystals is first observed and the temperature at which the sample becomes completely liquid, does not exceed 0.5 - 1.0°C. In our case only melting point 173.5° - 174.5°C is fit in this criteria. It is therefore, the melting point of pure compound.

5. a) True b) True c) True d) False

If A and B are two different compounds, the melting point of the mixture may get depressed by several degrees.