

EXPERIMENTAL TECHNIQUES

1.1 Safety Precautions

The handling of many chemicals in a laboratory is attended with considerable hazards unless proper precautions are observed. It is the duty of all members of laboratory staff to co-operate in the prevention of accidents. In addition to the welfare of the staff of the laboratory there is concern for preservation of the building, equipment furnishing and apparatus. It is the duty of the employing authority to provide safe working conditions in the form of adequately ventilated laboratories with suitable equipment such as benching with non-absorbent creak-free surfaces, fume cabinets, protective clothing and facilities for hand washings. It is recommended that a senior member of staff is appointed as a safety officer and that he should have responsibility for the accident book in which all accidents and their after effects are recorded shortly after they occur. Most of the dangers encountered in laboratories start from inferior material, prone chemicals fire, faulty electric wiring, faulty apparatus and last but not the least, careless working.

One of the most important aspects of concern in the organic chemistry laboratory is the handling of inflammable materials. The precautions to be observed cannot be over emphasized.

It is essential that each chemistry laboratory is to be provided with a first aid box, fire alarm, fire extinguishers, waste disposable bins, showers and eye washers etc.

The laboratory work will be concerned with the principles involved as well as the acquisition of the techniques. Thus it is mandatory that each student study each experiment prior to undertaking any laboratory procedure.

Chemical Hazards

Most compounds are highly toxic when ingested orally. Many chemicals also poisonous, corrosive, carcinogenic or explosive. Corrosive chemicals such as acids and alkalis are stored in low shelves and opened with care. Dangerous chemicals obtained from commercial sources usually carry a warning printed on the bottle. These warnings should be followed. Certain substances, can produce serious burns upon contact with the skin. One should never taste any compound and odour of substances should be detected with extreme care.

Mouth pipetting is always potentially dangerous and some form of safety pipette must be used instead. Procedures involving boiling solvents, toxic gases and vapours must be carried out in an efficient fume cupboard.

Sensitive tissues, for example, the eyes should not be needlessly exposed to vapours. One should never place his/her face directly over a reaction mixture. In case of any chemical get his/her into the eyes, they should be flooded immediately with copious amounts of water. In order to decrease any possibility of damage to the eyes, all students will be required to wear safety glasses while working in the laboratory.

Fire

Fire is one of the most serious and most likely hazards to occur in a laboratory. All the staff should know where the fire extinguishers are and how to use them. The most generally useful fire extinguisher in the laboratory is the carbon dioxide cylinder which can be safely used with most chemicals and electric equipment, and is clean. Dry powder extinguishers, like sand, are also useful but are messy in use. Asbestos blankets are useful for smothering small fires and burning clothing.

Most organic compounds are combustible. Those with low boiling points and high vapor pressure at room temperatures may present a serious fire hazard. Ether, which has a boiling point of 35°C may be ignited by a flame removed by sixteen feet. Hence, it is never permissible to heat over an open flame any substance in an open vessel containing such volatile liquids. Steam bath is ideal for this purpose.

Summary of safety precautions: The following simple rules have been drawn up for your own and others protection. Read them before starting on practical work:

1. No smoking is allowed in chemical laboratories.
2. Every student must wear protective eye shields at all times in the laboratory. This is to protect you from your neighbour's mistakes as well as your own.
3. Report any accident immediately to a demonstrator (even if it does not involve personal injury, as in spillage of chemicals or breaking of glasses).
4. Carryout experiments which produce toxic chemicals or vapours, and / or are likely to be violent, in a fume cupboard.
5. Fire is a serious hazard in the laboratory and is usually caused by the careless handling of organic solvents. These must not be heated using a Bunsen burner.
6. Be familiar with the placing of fire extinguishers in the laboratory.
7. Do not point a test tube which is being heated, or in which a reaction is occurring, at any person in the neighbourhood.

8. Do not peer into the mouth of a test tube which is being heated or in which a reaction may be occurring.
9. If the clothing is splashed by a corrosive liquid, strip the clothing and treat the skin immediately. As a first treatment washing with water is generally appropriate, call a demonstrator to assist you.
10. Wear a laboratory coat at all times in the practical laboratory to protect your cloths.
11. Always carry a small towel to the laboratory to assist you in handling hot objects in addition to tongs.
12. Bunsen burners may only be used in the fume cupboard or keep it away from the inflammable solvents.

1.2 Risk Assessment of Some General Reagents

No.	Compound	Hazard	Spillage	Disposal
1.	Acids (All)	Corrosive, toxic	Wash off with Plenty of water	Pour down sink with a lot of water
2.	Bases	Corrosive, toxic	-do-	-do-
3.	Benzil	Irritant	-do-	Return to teacher
3a.	Benzene	Toxic, avoid inhalation carcinogenic	-do-	-do-
4.	Bromine	Serious burns upon contact with the skin	-do-	Pour down sink with a lot of water
5.	Benzoyl chloride	Corrosive lachrymatory, avoid inhalation	-do-	Return to teacher
6.	Bromine in acetic acid	Corrosive wear gloves	-do-	use volume specified in manual
7.	Chloroform	Toxic, avoid inhalation	-do-	Place in waste solvent bottle for halogenated solvents.
8.	Dichloro-methane	Toxic, avoid inhalation	-do-	Solvents
9.	Concentrated ammonia soln	Corrosive irritant wear gloves	-do-	Pour down sink with lot of water

Table contd...

No.	Compound	Hazard	Spillage	Disposal
10.	Conc. Sulphuric acid	Corrosive, toxic, wear gloves	-do-	-do-
11.	Cyclohexane	Flammable	-do-	Use waste bottle provided
12.	2-Chloro Phenol	Toxic, corrosive, causes burns	-do-	Pour NaOH soln., down sink with a lot of water
13.	H ₂ O ₂ soln.,	Oxidiser, irritant	-do-	Pour down sink with water
14.	Iodine	Irritating to eyes, skin	-do-	Neutralise with sodium thiosulphate
15.	Naphthalene	Flammable, irritant	-do-	Return to demonstrator
16.	Benzaldehyde	Toxic, irritant	-do-	Wash test soln., down sink with water
17.	Benzyl amine	Corrosive, lachrymatory	-do-	-do-
18.	Brady's reagent	Flammable, corrosive	-do-	-do-
19.	2-Naphthol solution	Irritant	-do-	-do-
20.	t-Butanol	Flammable, corrosive	-do-	-do-
21.	Ethanol	Flammable	-do-	-do-
22.	Petroleum ether	Flammable	-do-	Place residue in waste bottle
23.	Nitrobenzoic acid	Irritant	-do-	Return used sample to the teacher
24.	Sodium dichromate soln.,	Cancer suspect agent	-do-	Pour down sink with water
25.	Sodium nitrite	Toxic	-do-	-do-
26.	Phenolphthalein in ethanol	Toxic, flammable	-do-	-do-
27.	Starch soln., (under toluene)	Flammable	-do-	-do-
28.	2-Naphthol solution	Irritant	-do-	-do-
29.	Silver nitrate solution	Toxic	-do-	-do-
30.	Unknown amines	Irritant, toxic	-do-	Return unused sample to teacher

Table contd...

No.	Compound	Hazard	Spillage	Disposal
31.	Ethanoic anhydride	Corrosive, lachrymatory	-do-	-do-
32.	2,4-Dichloro Phenol	Corrosive, wear gloves	-do-	Return the sample to the teacher
33.	Phenols amines, acetanilide and ethanoic acid	Corrosive toxic wear gloves	-do-	-do-

1.3 Glass and Plastic Laboratory Ware

Borosilicate glass is now almost exclusively used for the manufacture of apparatus they will be used for conducting a chemical reaction or be used for measuring volumes. This glass consists of about 80% silica and 13% boric oxide with the oxides of sodium, aluminium and other metals. It is more resistant to thermal shock than ordinary soda glass but should not be abused to the extent, for example, heating beakers containing liquid in flame without the protection of a gauze or plunging hot glass into cold water.

Generally, volumetric glassware is calibrated for use at 20°C (27°C for use in tropical countries).

1.4 Apparatus

Pipettes: The undesirability of pipetting by mouth has been increasingly recognised in recent years. This has led to the introduction of various devices to fill and empty conventional pipettes and of disposable-pipettes. The pipette fillers include rubber bulbs and various valve-operated designs. Only the most commonly used pipettes are described below, there are, of course, many other designs of pipettes available.

- 1 (a) **One-mark pipettes:** Also referred to as volumetric or transfer pipettes. These pipettes are governed by BS1583. The capacity is defined as the volume of water at 20°C delivered by the pipette when used in the prescribed manner.
- (b) **Graduated pipettes:** They consist of pipettes calibrated for delivery from zero down to any graduation line.
- (c) **Pasteur pipettes:** These are uncalibrated pipettes that can easily be made in the laboratory or obtained commercially.
- (d) **Disposable-tip pipettes:** A number of pipetting systems have been made using disposable plastic tips. They eliminate the necessity of mouth pipetting and are quicker to use than conventional pipettes. Fixed - or variable-volume patterns are available.

(e) **Dispensers:** For the repeated dispensing of fixed volume of solution, the advantage of using them include speed of operation, reproducibility and safety.

- Burettes:** Burettes with PTFE (polytetrafluoroethylene) stopcocks are recommended particularly when alkalis are to be used. PTFE stopcocks require no lubrication and do not seize up.
- Graudated measuring cylinders:** Measuring cylinders can have spouts or be stoppered. Cylinders are not accurate, they should not be used in making solutions where a moderate degree of accuracy is required.
- Volumetric flasks:** Volumetric flasks to hold 5 ml, 10 ml, 50 ml, 100 ml, 250 ml, 500 ml and 1 litre of solutions are commonly used.
- Conical (Erlenmeyer) flasks:** These are useful when making solutions, particularly when boiling is required. They are commonly used in titration.
- Buchner (Filter) flasks:** These are similar to conical flasks but have a side arm which can be attached to a vacuum pump. A Buchner funnel has a sintered glass platform or a wire-mesh platform used for supporting filter paper.
- Filter funnels:** The ordinary conical filter funnel can have plain or fluted sides.
- Separating funnels:** Separating funnels may be spherical, conical or cylindrical. Separating funnels are used in extraction procedures and to separate immiscible liquids. When mixing the contents during an extraction procedure, the pressure that builds up should be released occasionally by inverting the funnel and slowly opening the stop cock. After extraction is complete, clamp the funnel in a vertical position and allow the fluids to separate. Remove the stopper and drain out the lower liquid.

Care should be taken to avoid the formation of emulsions when using a separating funnel; gentle inversions will be found preferable to shaking.
- Thermometers:** There are greater variety of thermometers designed for particular purposes over various temperature ranges.
- Filter pumps:** Filter (Venturi) pumps are available in glass, metal and plastic. Depending, of course, upon the water pressure available, an ultimate vacuum of about 15 torr is possible with this type of pump.
- Desiccators:** Glass and plastic desiccators are available, may be of vacuum or non-vacuum type. The non-vacuum type can be used to maintain a dry atmosphere in which chemicals that have been previously dried can be kept. The vacuum type can be used to dry solids.

Commonly used desiccants are a) phosphorus pentoxide, very powerful but use only if strictly necessary b) Silicagel, reusable, safe, incorporates an indicator; normally blue changing to pink when wet and reusable after

- heating in a oven. c) Anhydrous calcium chloride, satisfactory for storage of dehydrated chemical.
12. **Plastics:** Most of the apparatus described here, as well as many other items used in the laboratory, can now be manufactured in plastic.
 13. **Condensers:** The condensers are used for refluxing and ordinary distillation. The air condenser is employed if the liquid distilling has a very high boiling point.
 14. **Flasks:** These are common type of flasks for a variety of purposes. Round bottomed flasks are employed for refluxing and distillation purpose. The Erlenmeyer (conical) flask is useful when making solutions and titrations.

1.5 Cleaning Glass Apparatus

It is very important that clean glassware must be used for carrying out any type of reaction. Presence of impurities may have an undesirable effect on the particular reaction as well as the purity of the final end compound.

- (A) **Chromic acid cleaning method:** Glass is soaked in a solution of sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) 7 g; concentrated sulphuric acid 100ml. This solution should be prepared and used **with care** and stored in a glass bottle. The glass-ware is soaked overnight in the cleaning fluid, then rinsed **several times** in distilled water. The apparatus is then dried, open-end down or in a hot-air oven. Acid washing is particularly good for removing silicone grease and certain organic compounds.
- (B) **Washing laboratory glass-apparatus with detergents:** A number of detergents are available commercially which for most purposes are (at least) as efficient as acid, safer to use and often cheaper. The glassware should be soaked in an aqueous solution of the detergent. After soaking, the glassware is brushed (if necessary), washed with tap water and then rinsed with distilled water and dried.

1.6 Purification of Solvents

Commercially available grades of organic solvents are of adequate purity for use in many reactions provided that the presence of small quantities of water is not harmful to the course of the reaction (unless the reaction needs dry conditions), and also the presence of other impurities (e.g., ethanol in diethyl ether and thiophene in benzene) is unlikely to cause undesirable side reactions. The commercially available solvents for general use are often accompanied by specifications indicating the amount and nature of the impurities present in it. When the levels of impurities, including moisture or water content, are not acceptable for a particular reaction, it is more economic to purify the commercial grade than to purchase the more expensive analar grade solvent.

Common drying agents

- (i) For Alcohols: Anhydrous potassium carbonate, calcium sulphate or magnesium sulphate, calcium oxide.
- (ii) For Saturated and aromatic hydrocarbons and ethers: Anhydrous calcium chloride, calcium sulphate phosphoric acid.
- (iii) For Aromatic Aldehydes, Anhydrous calcium, magnesium and sodium sulphates

Ketones

- (iv) For Amines: Solid potassium or sodium hydroxide, calcium and barium oxide
- (v) For Organic acids: Anhydrous calcium, sodium & magnesium sulphates

The preliminary treatment is in fact essential for the vast majority of organic solvents, unless it is certain that the water content is very low, before using the more powerful drying agents (such as a reactive metal, e.g., sodium or a metal hydride, e.g., calcium hydride, lithium aluminum hydride. Attention should be drawn to the considerable fire or explosion hazards of these highly reactive drying agents, particularly at the end of a solvent distillation when residual material has to be disposed of.

It is often convenient to remove final traces of water with the aid of a molecular sieve and store the dried solvent in the presence of the sieve. The term, molecular sieve, applies to a group of dehydrated synthetic sodium and calcium aluminosilicate adsorbent (Zeolites). Currently four principal types are available in the market, namely types 3A, 4A, 5A and 13A, representing an effective pore diameter of approximately 0.3, 0.4, 0.5 and 1.0 mm respectively.

Note: Almost all organic solvents are flammable. Apart from taking the obvious precautions of avoiding all flames in the vicinity of a solvent distillation, it must be remembered that faulty electrical connections or even contact with hot metal surface may ignite the vapour of volatile solvents. It is advisable to use double surface condensers in many cases for solvent distillation.

Purification of commercial ether ($C_2H_5OC_2H_5$): The commercial ether is usually contaminated with water and ethanol. Furthermore, when ether is allowed to stand for sometime in contact with air and exposed to light slight oxidation occurs with the formation of the highly explosive diethyl peroxide (Et_2O_3). If present, the peroxide may be removed by shaking 1 litre of ether with 10-20 ml of concentrated solution of an iron (III) sulphate, prepared by dissolving 60 g of iron (II) sulphate in a mixture of 6 ml conc. sulphuric acid and 110 ml of water. Remove the aqueous solution and pour the ether portion in a clean winchester bottle and add 50-100 g of anhydrous calcium chloride. Allow the mixture to stand for 24 hrs with occasional shaking; the water and ethanol are largely removed during this period.

Finally the ether should be redistilled. Filter it through a large fluted filter paper into a 500 ml round bottomed flask, add two or three anti-bumping granules, and arrange the flask for distillation by passing cold water through condenser. Note that the end of the condenser must lead into a flask surrounded by ice. The ether is most suitably distilled by placing the distilling flask on (but not in) an electrically heated constant-head water-bath, collecting the fraction boiling between 34° and 38°C.

Benzene (C₆H₆): Benzene has been identified as a carcinogen (CAUTION). Commercial grade benzene may contain thiophene (b.p. 84°C), which cannot be separated by distillation. The commercial benzene is shaken two or three times with about 15 percent of its volume of conc. sulphuric acid (i.e., 15 ml per 100 ml of benzene) in a stoppered separating funnel (Alternatively, the mixture may be stirred mechanically for 20-25 minutes) until the acid layer is colourless or very pale yellow on standing. After each shaking, the mixture is allowed to settle and the lower layer is drawn off. Next, the benzene is shaken twice with water and once with 10% sodium carbonate solution in order to remove most of the acid and finally dried with anhydrous calcium chloride. After filtration, the benzene is distilled and the fraction, b.p. 80-81°C, collected. The distilled benzene may either be stored over sodium wire or left in the presence of a type 5A molecular sieve. Pure benzene has b.p. 81°C / 760 mmHg. and m.p. 5.5°C.

Chloroform (CHCl₃): Chloroform is a suspect carcinogen, wherever possible it should be replaced by dichloromethane as an alternative solvent. The commercial grade may contain upto 1% of ethanol which is added as a stabiliser. The ethanol may be removed by either one of the following procedures.

- (a) The chloroform is shaken with about half its volume of water, then dried over anhydrous calcium chloride for at least 24 hours, and distilled.
- (b) The chloroform is passed through a column of basic alumina (10 g per 14 ml of solvent). This procedure removes not only traces of water but also acid and eluate may be used directly.

Dichloromethane (CH₂Cl₂): Commercial grade is purified using 5% sodium carbonate solution and water. It is dried over anhydrous calcium chloride and then distilled. The fraction b.p. 40-41°C is collected. Dichloromethane is a useful substitute for diethyl ether in extraction process.

***t*-Butyl alcohol (C₄H₉OH):** This and other higher alcohols may be purified by drying with anhydrous potassium carbonate or with anhydrous calcium sulphate and fractionated after filtration. The fraction with the boiling point 81-83°C is to be collected.

Acetone (CH₃COCH₃): The commercial grade usually contains appreciable quantities of methanol, acetic acid and water. Commercial acetone is heated and refluxed with solid potassium permanganate until the violet colour

remains. It is further dried by keeping the solvent overnight, with anhydrous potassium carbonate, filtered and redistilled. Pure acetone distills at 56.5°C / 760 mmHg.

Acetonitrile (CH_3CN): Some commercial grades of acetonitrile is usually contaminated with water, acetamide and ammonium acetate. Water may be removed with activated silica gel or type 4A molecular sieves. [Further, this partially dried solvent is stirred with phosphorus pentoxide until hydrogen evolution stops. The solvent is decanted from the solid and fractionally distilled at atmospheric pressure. The pure acetonitrile has b.p. $81\text{--}82^{\circ}\text{C}/760$ mmHg.

Dimethyl sulphoxide (DMSO, $\text{Me}_2\text{S}=\text{O}$): The commercial grade may be purified by standing overnight over freshly activated alumina, barium oxide or calcium sulphate. The filtered solvent is then fractionally distilled over calcium hydride under reduced pressure (12 mmHg) and stored over type 4A molecular sieve. The pure solvent has b.p. 189°C .

N,N-Dimethylformamide (DMF) (Me_2NCHO): Dimethyl formamide can be purified first by drying over anhydrous calcium sulphate or type 3A molecular sieve for 72 hours, followed by distillation under reduced pressure. The pure solvent has b.p. 153°C .

Ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$): Commercial grade usually contains water, ethanol and acetic acid as impurities. A mixture of ethyl acetate (1000 ml), acetic anhydride (100 ml) and concentrated sulphuric acid (10 drops) is heated under reflux for 4 hours and then distilled. It is further dried by shaking with 20-30 g of anhydrous potassium carbonate; filtered and redistilled. Pure ethyl acetate has b.p. $77^{\circ}\text{C}/760$ mmHg.

Dioxane (1,4-dioxane, diethylene dioxide, $(\text{CH}_2\text{CH}_2\text{O})_2$): The commercial grade dioxane contains small quantities of acetaldehyde and glycol acetate. A mixture of 1 litre technical grade dioxane, 14 ml of conc. hydrochloric acid and 100 ml of water is refluxed for 6-12 hours; while a slow stream of nitrogen is bubbled into the solution to remove acetaldehyde formed. After cooling to the room temperature, it is treated with excess potassium hydroxide pellets until some remain undissolved and the strongly alkaline aqueous layer is separated from the dioxane. Dioxane layer is decanted and refluxed with excess sodium metal for 8-12 hours. Finally, the dioxane is distilled over the fractionating column and receiving flask being covered with black paper. The pure compound has b.p. $101.5^{\circ}\text{C}/760$ mmHg.

Removal of any peroxide present as impurity on storage, can be eliminated by passing the above distilled dioxane through a column of basic activated alumina (100 g for 300 ml of dioxane).

Ethyl alcohol (Et OH): Ethanol is used as a solvent/reagent in a wide variety of reactions. Alcohol is a mixture consisting of 95.6% by weight of ethanol and the remainder being water. This is known as rectified spirit. Ethyl alcohol of a high degree purity is frequently required in many organic preparations. Absolute alcohol of 99.5 percent grade may be purchased or it may be conveniently prepared by the dehydration of rectified spirit with calcium oxide. In the laboratory, the alcohol is heated to reflux with calcium oxide (quicklime) for 6 hours and distilled. It is very hygroscopic and precautions have to be taken to guard against the absorption of water during the distillation and subsequent storage. The distillate, which still contains about 0.5% water, is known as absolute alcohol. The last traces of water can be removed by refluxing with magnesium. Pure absolute alcohol b.p. 78°C.

Methanol (MeOH): The methanol now available in the market is suitable for most purposes without purification. Synthetic methanol may contain a small amount of acetone and may be removed by the following procedure.

A mixture of 250 ml methanol, 12.5 ml furfural and 30 ml of 10% sodium hydroxide solution is refluxed in a 1 litre round bottomed flask, fitted with a double surface condenser, for 6 to 10 hours. A resin is formed during heating which removes all the acetone present. The alcohol is then distilled. Pure methyl alcohol has b.p. 65°C.

Petroleum ether: The fractions of petroleum, which are commonly used, have b.p. 40-60, 60-80, 80-100 and 100-120°C. They contain some unsaturated hydrocarbons (chiefly aromatic) and may be removed by shaking with 10% conc. sulphuric acid. The solvent is then shaken with a mixture of a concentrated solution of KMnO_4 in 10% sulphuric acid to remove oxidizable impurities. The solvent is washed with sodium carbonate and thoroughly with water, dried over anhydrous calcium chloride and distilled.

Pyridine ($\text{C}_6\text{H}_5\text{N}$): Pyridine of analytical reagent grade is satisfactory for most purposes. If it is desired to get the dry product, it is heated under reflux over calcium hydride, potassium or sodium hydroxide pellets or over barium oxide and then distilled with careful exclusion of moisture. Pure pyridine has b.p. 115°C/760 mmHg. It is highly hygroscopic and should be stored over calcium hydride or type 4A molecular sieve.

Tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$): The commercial grade solvent contains water and peroxide as impurities. Peroxide, if present, may be removed by running through column of alumina. It is purified by distillation over calcium hydride or lithium aluminium hydride. Pure tetrahydrofuran has b.p. 65-66°C. It should not be stored for more than a few days unless an anti-oxidant is added.

1.7 Recrystallisation

Recrystallisation is a process of purification and always involves a separation of the solid that is wanted from the liquid that contains unwanted material of course the liquid may contain some wanted material too, but loss of this is the price that is paid for the purity of the remainder.

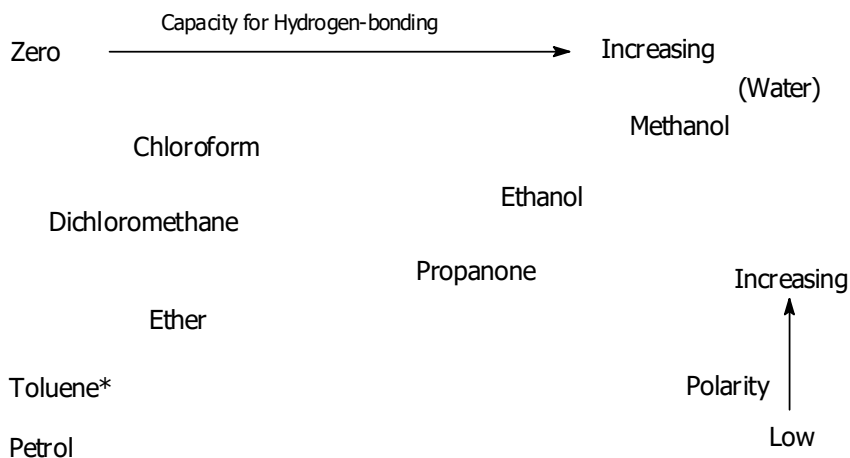
Learning to choose a suitable solvent for recrystallisation is part of the course. It is convenient to class solvents by polarity, and by capacity for hydrogenbonding, as shown in the diagram below. Generally, solvents near to foot of the diagram are useful for non-polar materials, while those higher up will dissolve a wider range of substances. Solids whose molecules can participate in hydrogen bonds are generally more soluble in solvents that also can form hydrogen bonds than in solvents that lack this capacity.

Size of apparatus

Generally, chemicals are easiest to handle if the container is about one-third full, or less for narrow items like test tubes. thus, for 10 ml of liquid, a 25 ml flask is more appropriate than either a 10 ml flask (risk of spillage) or a 100 ml flask (loss due to wetting the surface of the container). The same principle applies when collecting a solid on a filter; choose a funnel of suitable size for the solid to be collected.

If the quantity of liquid is small-say less than 5 ml, it is often easier to transfer the liquid using a pipette, rather than by pouring it. By extration, filtration on this scale can be avoided by removing the liquid with a pipette, leaving behind the solid which should then be washed with fresh solvent.

Selected solvents, classified by polarity (vertical scale) and by capacity for hydrogen-bonding (horizontal scale).



* Boiling point 110°C; cannot be removed on a steam bath at atmospheric pressure. Propanone and the solvents to the right of it are miscible with water.

1.8 Determination of Boiling Point on a Semi-Micro Scale

Using a small flame, draw out the centre part of a melting-point capillary so that the diameter is reduced to about $\frac{1}{3}$ of the original. Cut the tube into two at the narrowest point and seal the larger end of each tube. You should have two tubes looking like (1) below.

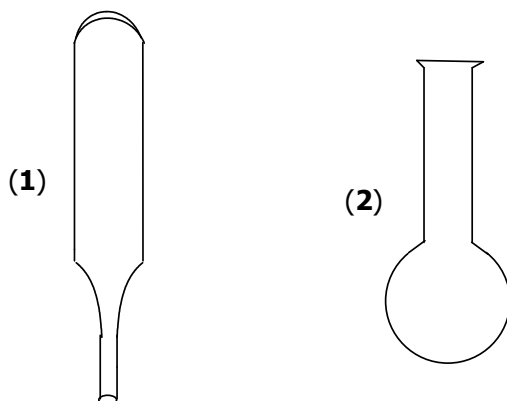


Fig. 1.1

Prepare a heating bath by taking a long-necked flask like (2) which must be dry and adding liquid paraffin till the level is about 5 mm ($\frac{1}{4}$ ") below the shoulder. Fit a cork to a thermometer and, using a file, cut a notch in the side of the cork to allow air to flow past it.

Put 1 or 2 drops, no more, of liquid in a small (5 mm x 25 mm) test tube and insert the prepared capillary, open end down. Join the test tube to the thermometer with a nylon clip so that the sample of liquid is beside the bulb. Using a tripod and gauze, and a Bunsen with a small flame, heat the bath. As the temperature rises bubbles of air escape from the capillary. When the bubbling becomes rapid, remove the flame and allow the temperature to fall till liquid re-enters the capillary. Note the temperature, t_1 . Heat the bath again gently till a rapid stream of bubbles issues from the capillary, at temperature t_2 . The boiling point can be taken as half-way between t_1 and t_2 . If the values lie more than 10° apart, repeat the cycle of heating and cooling.

1. Choose for practice one of the following:

Toluene,	b.p.	110°C
Methanol	b.p.	68°C
Ethanol	b.p.	78°C

2. Obtain an unknown from a demonstrator.
3. No liquid unknown you will do in this exercise has a b.p. higher than 260°C .

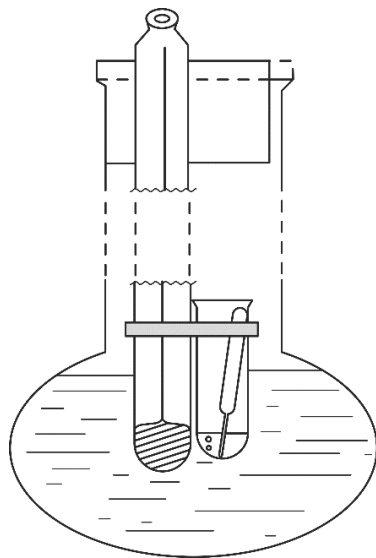


Fig. 1.2 Boiling point apparatus

1.9 Melting Point Determination

The melting point is the property of an organic solid which is most frequently used as a criterion of purity. A pure compound has a sharp m.p. (i.e., melts over a narrow temperature range).

- (a) **Determination:** Crush a small amount of the sample on a filter paper with a small spatula. Introduce a little of the powder into the open end of a capillary tube and shake it down to the closed end by gentle stroking with a file. The column of solid should be no more than 3 mm in length and should be tightly packed.

Place the sample in a melting point apparatus, heat, and note the temperature at which melting occurs. This is the **approximate** melting point of the sample. Prepare a new sample and repeat the melting point measurement, this time allowing the temperature to rise by only **approximately** 2°C per min., as the melting point is approached. Record the temperature at which melting begins, and the temperature at which the last traces of solid disappear. This is the melting point range of the sample, normally expressed in the form, e.g., sample x, m.p. = 125–128°C. You will not obtain accurate melting points if the sample is heated too rapidly.

- (b) **Melting point of a pure sample:** Obtain small samples of two unknown solids y and z. using the above method. Determine their melting points, and record your values. If in doubt about your technique, check with your demonstrator that your values are acceptable.

1.10 Identification of an Unknown Sample by Mixed Melting Points

Theory: If one mixes two solids, melting points A and B, than the melting point of the mixture will be lower than either A or B. For example, 2 solids with m.p.'s 100°C and 105°C will, when mixed, give a sample of melting point well below 100°C . This phenomenon, called melting point depression, is very useful for distinguishing between solids of a very similar point. A mixture of two compounds not only melts at a temperature below either of the pure compounds but also over a greater temperature range.

The following compounds will be available:

Benzamide	(A)
Cinnamic acid	(B)
Urea	(C)

Determine the melting point of each of these compounds, thus showing that their melting points lie too close together to enable any one compound to be identified by a simple melting point determination.

An unknown compound (**U**) will be supplied that is one of the members of this series. It should be identified by mixed melting point determination.

Suppose the compounds each have m.p. $132\text{-}135^{\circ}$ and the unknown compound is found to have m.p. 132°C . Mix a small amount of **U** with a small amount of **A** and determine the m.p. of the mixture. Suppose the mixture has m.p. $121\text{-}127^{\circ}$, then **U** has lowered the m.p. of **A** and so **U** is not identical with **A**. Now mix **U** with **B** and find the m.p. of the mixture. If this is $132\text{-}134^{\circ}$, then **U** has not lowered the melting point of **B**. So **U** must be identical with **B**. Confirm by determining the m.p. of a mixture of **U** and **C** and if you are correct should be lower than 132° .

Conclusion: **U** is identical with **B**

1.11 Purification of Organic Compounds by Recrystallisation

Crystallisation is a very efficient method for the purification of solid organic substances. It is first necessary to find a suitable solvent, i.e., one which will readily dissolve the material when hot, but only to a small extent when cold.

The technique of recrystallisation thus involves dissolving the pure organic material in the minimum volume of hot solvent. Insoluble impurities, which will not dissolve in the hot solvent, are filtered off. The filtrate is then allowed

to cool. The organic material crystallises out of solution leaving any soluble impurities in the solution. The crystals are then filtered off using a Buchner funnel. It is important to free the crystals from their mother liquors by washing with a little cold solvent and by sucking dry.

The solvents normally used for recrystallisation are:

	b.p. (°C)	
Distilled water	100	Non-inflammable
Acetone	56	Inflammable
Ethyl alcohol (industrial spirit)	78	Inflammable
Benzene	81	Inflammable
Light petroleum	60-80	Inflammable
Acetic acid	118	Not readily Inflammable
Chloroform	61	Non-inflammable

- (a) **Solubility and Crystallisation:** Test the solubility of 0.1 g samples of the following compounds in water, ethanol, and benzene noting the solubility in the cold and hot solvent and also how well the compound crystallises when a hot solution is cooled.

Salicylic acid

Benzanilide

- (b) **Purification Exercise:** Apparatus required: Conical flask (25, 50 and 100ml), Filter funnel, Buchner funnel and flask

Obtain from the demonstrator the sample of impure material and carry out small scale solubility tests in a small test tube to determine the best recrystallising solvent as above. Weigh out about 2.0 g of the material into a suitable flask, add a small quantity of the selected solvent and a boiling stone and heat to boiling point.

N.B. If an inflammable solvent is being used the flask should be fitted with a condenser and the heating carried out on the steam bath, solvent being added down the inside of the condenser. If only a small quantity of solvent has been added initially the solid will not be completely soluble even at b.p. Therefore add more solvent a little at a time (using a dropper) until the main bulk of the solid just dissolves completely in the minimum volume of boiling solvent. It is now necessary to filter the hot solution to remove insoluble impurities.

The filtration is being carried out rapidly either through a 'fluted' filter paper or through a Buchner funnel using the water pump. The material in solution is always liable to crystallise out during the filtration thus blocking the funnel. To avoid this, it is best to preheat the funnel in the oven immediately before use. The filtrate is set aside to cool. Slow cooling promotes the growth of large crystals; rapid cooling (under tap) gives small crystals. When crystallisation is complete, collect the crystals by suction filtration using a Hirsch or Buchner funnel, wash with a little cold solvent, allow to dry, and determine m.p. and weight of dry crystals.

Ideally the material should be recrystallized until the m.p. remains constant and is not altered by further crystallization.

Write a brief account of the process in your lab notebook and submit this report together with the dry recrystallized material (in a labelled sample tube) to the demonstrator.

(c) Solubility test: Test the solubility of the impure material in the following solvents - chloroform, light petroleum (b.p. 68-80°), methanol, and water. Place about 0.02 g (a small spatula tip full) of the compound in a small test tube and add about 0.5 ml of the solvent to be tested. Shake and observe the solubility of the compound in the cold solvent. If the compound is not appreciably soluble in the cold solvent, warm the test tube on a steam bath and observe its solubility (use a low Bunsen flame in a fume cupboard when water is used as the solvent). (N.B. A good solvent is one in which the compound is fairly soluble in hot solvent but only sparingly soluble in cold solvent). Record your observation and deduce which of the solvent(s) you have used are suitable for recrystallization.

1.12 Purification of a Liquid by Fractional Distillation

Fractional Distillation

Distillation and recrystallisation are the two chief methods of purifying organic compounds. Several kinds of distillations are possible, including simple distillation, fractional distillation, and steam distillation. This experiment is concerned with the separation, by fractional distillation, of two miscible liquids, methylene chloride and carbon tetrachloride.

It will be seen from the diagram below (curve A) that it is not possible to separate these liquids completely by simple distillation. Use of fractionating column, however, results in an efficient separation of the two components (curve B). In the following experiment the efficiency of the separation is checked by gas-liquid chromatography (G.L.C.).

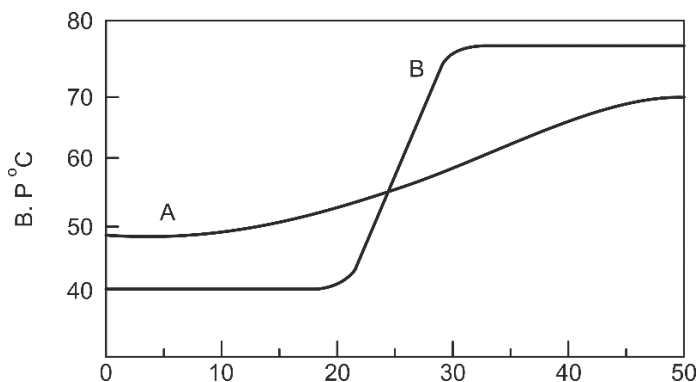


Fig. 1.3 Volume of distillate (ml.)

Distillation curve for 50 ml. of a 1:1 mixture of methylene chloride and carbon tetrachloride: (A) – simple distillation (B) fractional distillation.

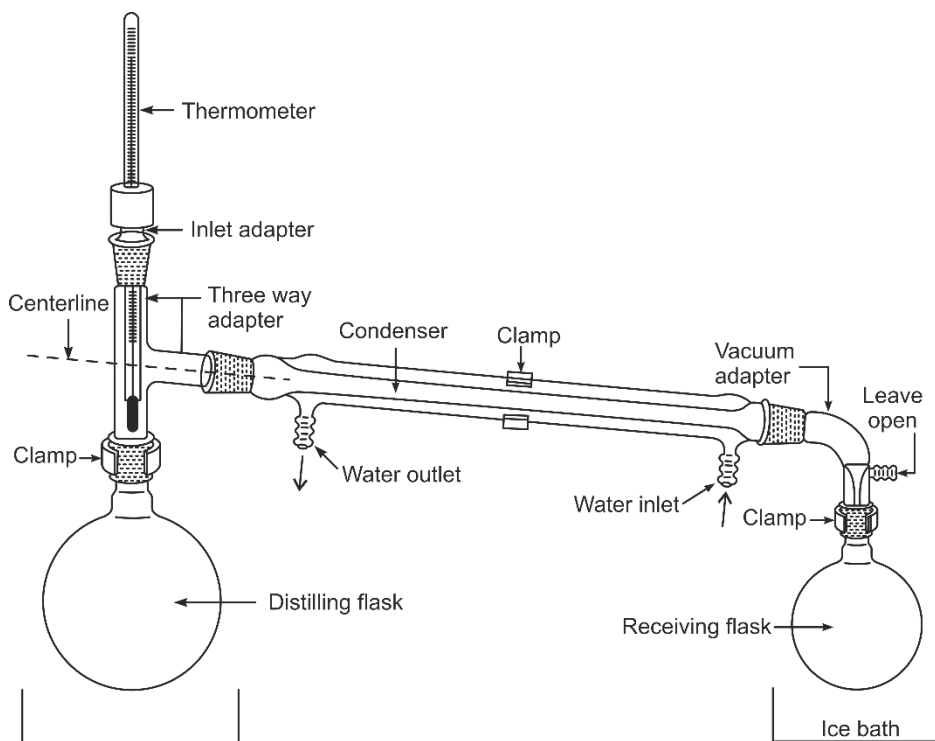


Fig. 1.4 Simple distillation apparatus

Fractional Distillation

Place 50 ml of the given mixture in the distilling flask and add a small boiling stone (to prevent super heating and to facilitate even boiling). Connect the flask to the apparatus and heat it gently with a small non-luminous Bunsen flame.

The slower the distillation, the better will be the separation. Collect the 5 ml fraction of the distillate in a small measuring cylinder and note the temperature at which each fraction distils. Transfer each fraction to a clean, dry, numbered test-tubes; stopper the test-tubes and set them aside for subsequent g. l. c. examination.

Plot a graph of the volume of distillate against the boiling point.

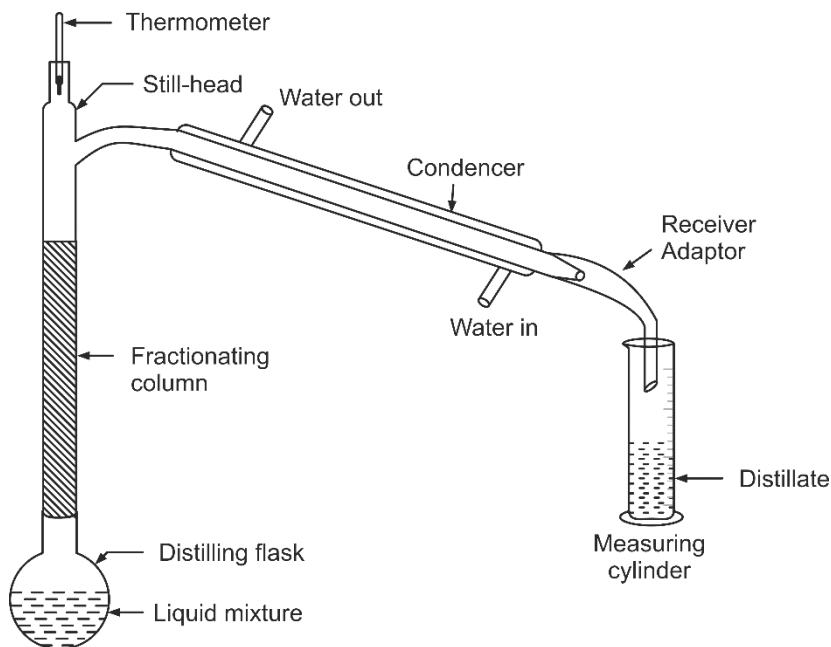


Fig. 1.5 Fractional distillation apparatus

1.13 Vacuum Distillation (Distillation at Reduced Pressure)

High boiling liquids, or those which decompose at or normal boiling point, are generally distilled at lower temperature under reduced pressure.

Use a round bottom flask as the distillation pot. The size of the flask depends on the volume to be distilled, but ideally it should be between one quarter and one half full – and no more. In order to prevent the *extremely bad bumping* that occurs with *every* vacuum distillation, the liquid should be stirred with a magnetic stirrer bar. The distillation pot is then fitted with a still head, quickfit thermometer (see demonstrator), condenser and a pig (3-way receiver adaptor) with 3 round bottom flasks (see diagram below).

Place the liquid in the distillation pot and assemble the apparatus, all the ground glass joints should be lightly greases, with vacuum grease not Vaseline. Remember to support the collection flasks, until the system is under

vacuum, gravity rules! Start stirring vigorously but do not heat. Turn the tap for the water pump on full before connecting the tubing to the system. Once connected, use the stopcock on the trap to carefully apply the vacuum. Ensure that the contents of the pot do not froth over and contaminate the collection flasks. If this happens, dismantle the apparatus and start again. Only when the apparatus is fully evacuated can the heater be switched on.

Therefore, if you purify a sample by distillation at reduced pressure, it is acceptable to quote the boiling range at which you collected the sample as long as you quote the pressure. With a water pump a pressure of 10-20 mmHg can be obtained, under these conditions, boiling points are reduced by approximately 100°C .

Vigorous stirring is maintained throughout the distillation and fractions are collected by rotation of the pig at the appropriate point. When distillation is complete, turn off the heating and allow the apparatus to cool. Then, holding the collecting flasks, release the vacuum by opening the stopcock on the trap. Do not switch the water pump off before releasing the vacuum.

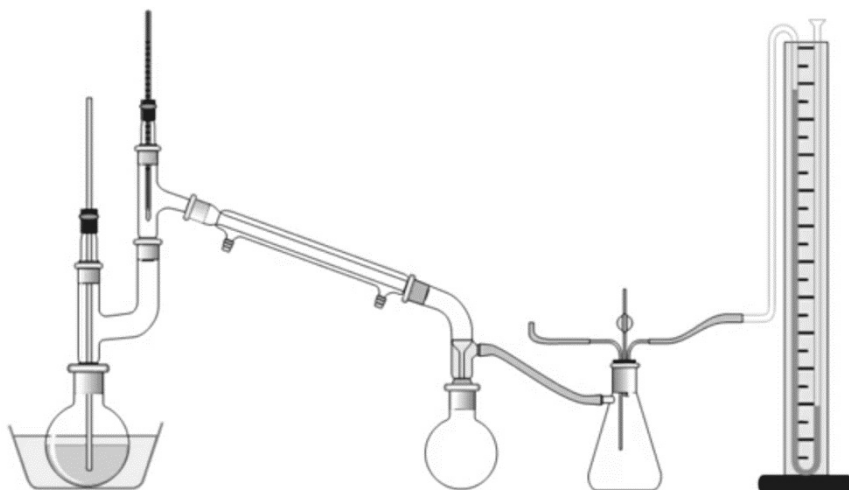


Fig. 1.6 Vacuum distillation set-up