CHAPTER II

EXPERIMENTAL TECHNIQUE

II,1. COMMON ORGANIC LABORATORY APPARATUS

It will be useful at the very outset to introduce the student to the apparatus that is commonly employed in the organic laboratory. Whether he will personally handle all the types of apparatus to be described will, of course, depend (i) upon the duration of the course in practical organic chemistry and (ii) upon the facilities provided by the laboratory. Nevertheless, it is deemed advantageous that the student should, at least, know of their existence.

Flasks. Various types of flasks are shown in Fig. *II, 1*, 1, *a–e*.

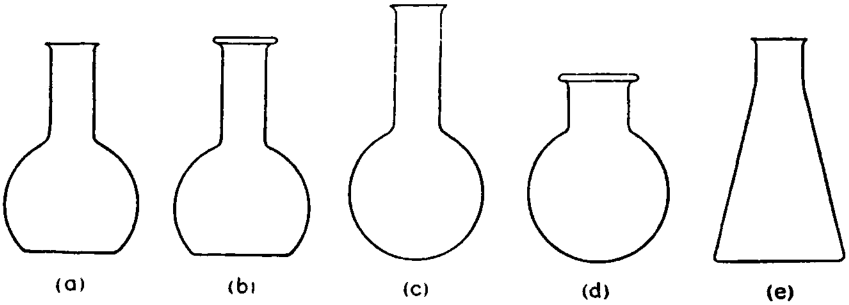


Fig. *II, 1*, 1.

(*a*) Flat-bottomed flask (the so-called Florence flask) with vial mouth. The sizes vary between 50 ml. and 40 litres.

(*b*) This is similar to (*a*) except that it is provided with a ring neck, which increases the mechanical strength, prevents breakage when a stopper is inserted, and provides a means for wiring a stopper in place. The upper rim is ground flat.

(*c*) Round-bottomed flask. The common sizes range between 25 ml. and 50 litres.

(*d*) Round-bottomed flask with short ring neck (the so-called bolt-head flask). This is widely used, particularly in advanced work, and possesses the advantages given under (*b*). The common sizes range between 50 ml. and 20 litres.

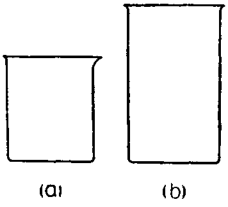


Fig. *II, 1*, 2.

(*e*) This is the familiar Erlenmeyer or conical flask. The common sizes range between 25 ml. and 6 litres.

Beakers. The usual Griffin form with spout, Fig. *II, 1*, 2, *a*, are widely used. Sizes between 30 ml. and 6 litres are available. The tall form without spout (Fig. *II, 1*, 2 *b*) occasionally finds application in organic laboratories.

Distilling flasks. Fig. *II*, *1*, 3, *a* is the ordinary distilling flask. The sizes vary between 25 and 5,000 ml.

(*b*) is the so-called **Claisen flask,** a distilling flask with two necks; the thermometer is placed in the neck carrying the side arm. Sizes vary between 25 ml. and 2,000 ml. It is of particular value in distillations where foaming or bumping occurs, and is widely employed in distillations under diminished pressure.

(*c*) is identical with (*b*) except that it is provided with a second long and indented neck (which is essentially a Vigreux column—see Section **II,15**). It is sometimes termed a Claisen flask with fractionating side arm.

In (*d*) the side arm outlet extends a short distance into the long neck of the flask, thus preventing any vapour which has been in contact with cork or rubber stoppers from condensing and flowing down the side arm. It is usually employed for those liquids which attack cork or rubber stoppers.

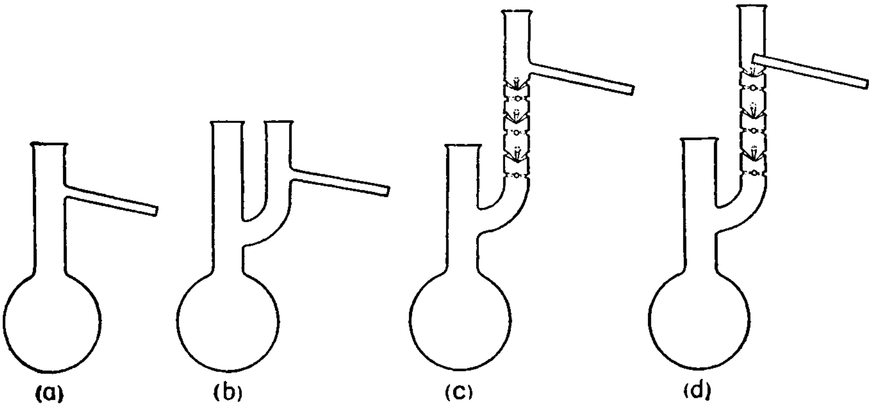


Fig. *II*, *1*, 3.

Condensers. The various types in common use are shown in Fig. *II*, *1*, 4, *a–h*.

(*a*) is a typical **Liebig condenser,** which consists of an inner glass tube surrounded by a glass jacket through which water is circulated. The inner jacket is fitted into the outer jacket by means of rubber stoppers; rubber tubing, formerly used, is less durable and is not recommended.

(*b*) is an all-glass Liebig condenser of similar design to (*a*); the jacket is sealed to the condenser tube. Two convenient sizes of condensers, suitable for general use, have jackets of 20 and 40 cm. length.

In the Pyrex glass **West** condenser greater efficiency of cooling is obtained by having a light-walled inner tube and a heavy-walled outer tube with a minimum space between them.

(*c*) is the inner tube of a Liebig condenser. It is used as an **air-condenser** when the boiling point of the liquid is above 140–150°.

(*d*) is an all-glass **Allihn** condenser. The condensing tube is made with a series of bulbs; this increases the condensing surface and lessens the resistance to the passage of vapours when the condenser is employed for refluxing, *i.e.*, for condensing the vapours issuing from the flask so that the liquid continuously flows back again.

(*e*) is a typical **double surface condenser** (Davies type). It is far more efficient than any of the preceding types and the jacket is usually shorter.

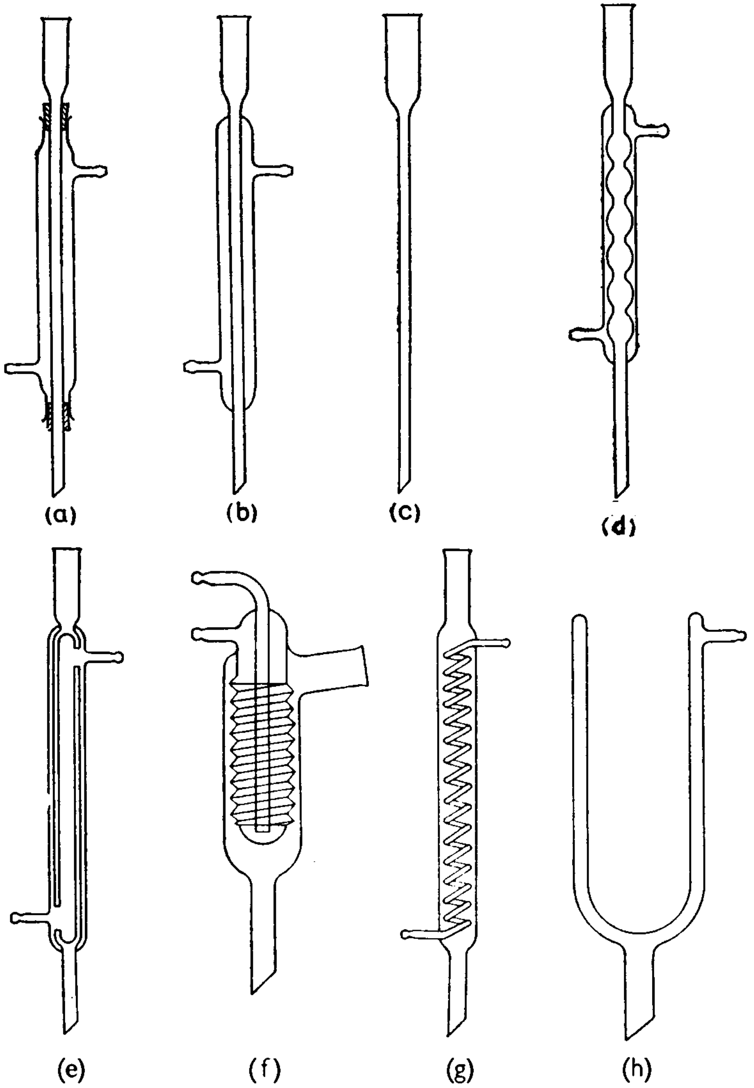


Fig. *II*, *1*, 4.

(*f*) is an efficient spiral condenser of the **Friedrich type**. The hot vapours can be introduced either at the side or the bottom, thus permitting the use of the condenser either for condensing vapours from another reaction vessel or for ordinary reflux purposes.

(*g*) is a **coil condenser** provided with an internal glass coil or spiral. In a modification there is both an internal spiral as well as an outer cooling jacket.

(*h*) is a Dewar type of reflux condenser. It is usually charged with a freezing mixture, *e.g.*, Dry Ice mixed with alcohol or acetone.

Funnels. Various kinds of funnels are depicted in Fig. *II*, *1*, 5, *a–f*.

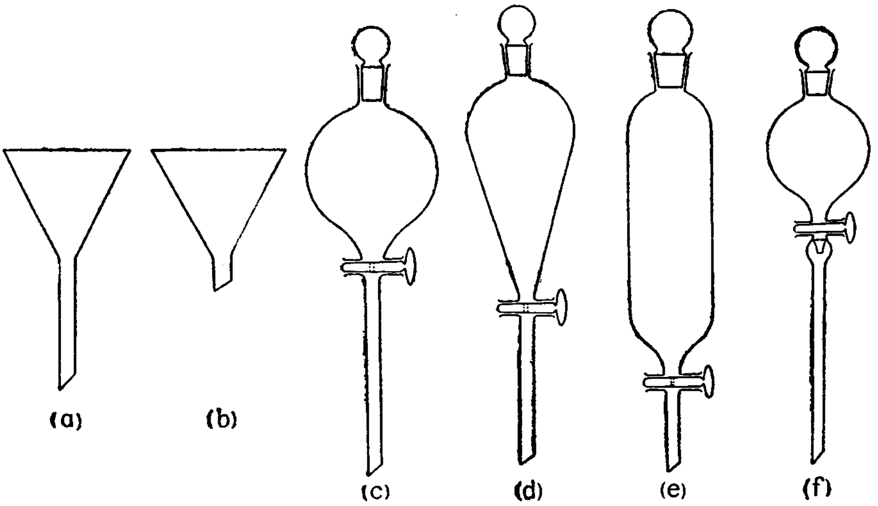


Fig. *II*, *1*, 5.

(*a*) is the ordinary 60° filtration funnel. It is convenient in many operations to employ funnels with a short stem (0·5–1 cm. long) as in (*b*).

(*c*), (*d*) and (*e*) are examples of separatory funnels. Type (*c*) is the globular form and is the most widely used ; (*d*) and (*e*) are the Squibb (pear-shaped) and cylindrical separatory funnels respectively. The funnel (*f*) is similar to (*c*) except that it is provided with a device immediately below the tap which enables the liquid to be added dropwise, the rate of addition being visible even when the stem of the funnel is immersed in a liquid : it is termed a **dropping funnel.**

Hot water funnels. Three varieties of hot water funnel are illustrated in Fig. *II*, *1*, 6. Type (*a*) consists of a double-walled copper jacket to

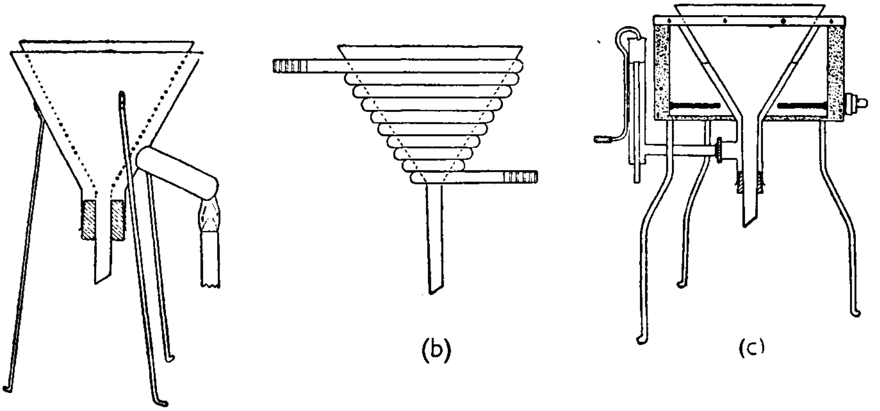


Fig. *II*, *1*, 6.

house the funnel; it is mounted on a tripod. The space between the walls is almost completely filled with water, and the water may be heated to any desired temperature below 100° by directing the flame of a Bunsen burner on to the side tube. Type (*b*) consists of a coil made of copper or lead tubing of about 10 mm. diameter forming a 60° cone; this will therefore accommodate any funnel. Hot water or steam is passed through the coil, hence it is very suitable for the filtration of inflammable liquids. The funnel may also be used for "cold filtrations" by circulating cold water through the coil. Type (*c*) is an electrically heated funnel and is provided with a constant level device. Electric heating mantles (see Section **II, 57**) for both 60° glass funnels and Buchner funnels are commercial products.

Funnels for filtration by suction. These are illustrated in Fig. *II, 1,* 7, *a–g*.

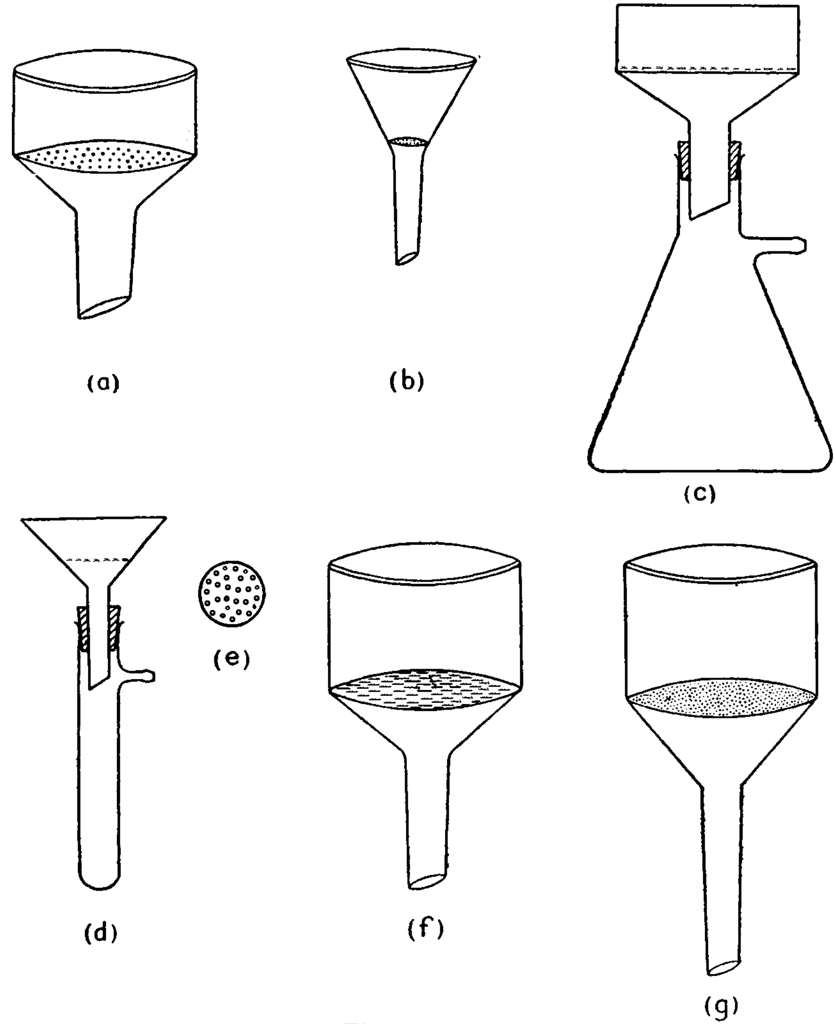


Fig. *II, 1,* 7.

(*a*) is a **Buchner funnel**; it is made of porcelain and has a perforated porcelain plate to support a filter paper. A Buchner funnel (and other funnels described below) is used in conjunction with **a filter or suction flask,** into which it is fitted by means of a rubber stopper as in (*c*); the flask is attached by means of thick-walled rubber tubing ("pressure tubing") to a water suction pump.

(*b*) is a modification known as a **Hirsch funnel.** This has sloping sides and is designed to deal with a smaller amount of precipitate than the Buchner funnel. The smallest size will accommodate filter papers 3–4 mm. in diameter.

(*d*) is a substitute for the Hirsch funnel. It consists of an ordinary glass funnel fitted with a **Witt plate** (*e*), which is a perforated porcelain plate 1–4 cm. in diameter, upon which a filter paper can rest. The great advantage of (*d*) is that it is possible to see whether the apparatus is clean; with porcelain funnels it is impossible to inspect the lower side of the perforated plate.

(*f*) is a **"slit sieve" funnel.** It is constructed entirely of glass (Jena or Pyrex) and therefore possesses obvious advantages over the opaque (porcelain) Buchner or Hirsch funnel.

(*g*) is a sintered glass funnel, and is available in a number of porosities (coarse, medium and fine).

Multi-necked flasks. Fig. *II*, *1*, 8, *a*, illustrates a typical three-necked flask. This has numerous applications in organic chemistry; for many operations, the central aperture carries a mechanical stirrer, and the two side apertures a dropping funnel and a reflux condenser respectively.

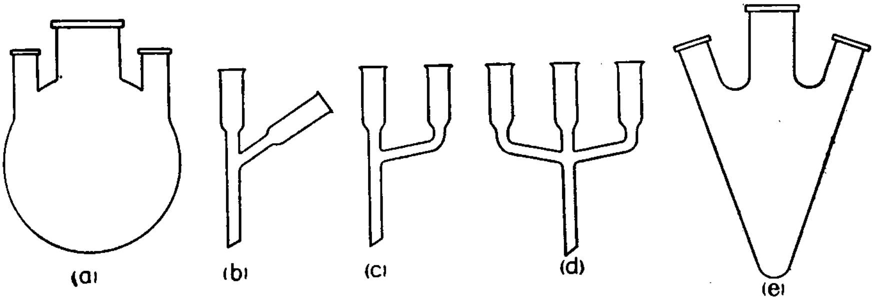


Fig. *II*, *1*, 8.

(*b*) and (*c*) are alternative forms of two-way addition tubes. These normally have an overall length of 16–20 cm., and the openings have an internal diameter of 24–25 mm.

(*d*) is a three-way addition tube. The addition tubes are usually inserted into wide-necked flasks (*e.g.*, bolt-head flasks).

(*e*) is a special form of three-necked flask (sometimes termed a Grignard flask), which is particularly suitable for any reaction (*e.g.*, the Grignard reaction) where components of widely different densities are to be mixed.

Spatulas. Stainless steel, nickel and porcelain spatulas are available commercially. Some of these are shown in Fig. *II*, *1*, 9; (*a*) is a spatula with a flexible stainless steel blade and is provided with a wooden handle; (*b*) is a nickel spatula and has a turned-up end to facilitate the handling of small quantities of material; (*c*) is the scoop-type of nickel spatula *; and (*d*) is a spatula in porcelain.

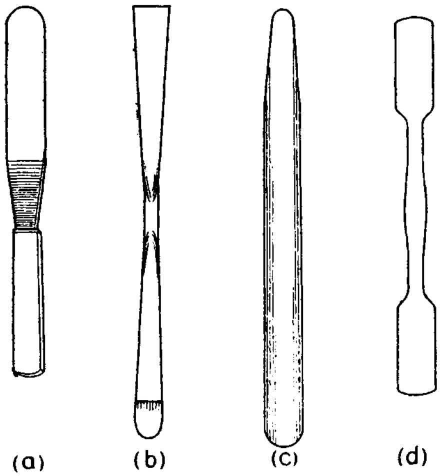


Fig. *II*, *1*, 9.

Miscellaneous apparatus. Two forms of **adapters** (or **adapter tubes**) are illustrated in Fig. *II*, *1*, 10, *a* and *b*; these are generally used to facilitate the delivery of a distillate from a condenser to a receiver. Two forms of the so-called **calcium chloride tubes** (also termed drying tubes, straight form) are shown in (*c*) and (*d*); these are filled with anhydrous calcium chloride or with cotton wool (previously dried at 100°), and are attached by means of a stopper to a flask or apparatus containing substances from which moisture is to be excluded.

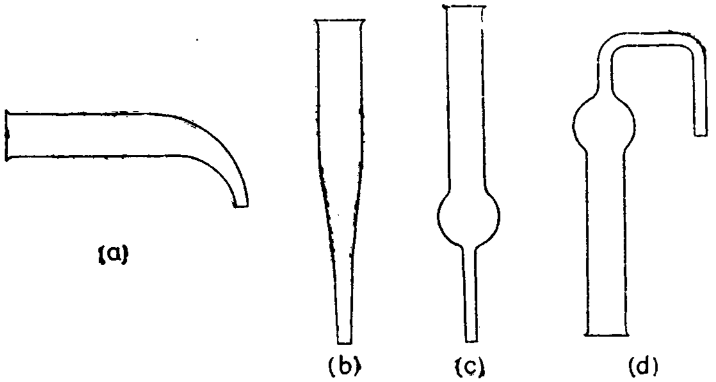


Fig. *II*, *1*, 10.

---

* Supplied by the Fisher Scientific Company.

II,2. CLEANING AND DRYING OF GLASSWARE

All glassware should be scrupulously clean and, for most purposes, dry before being employed in preparative work in the laboratory. It is well to develop the habit of cleaning all glass apparatus immediately after use; the nature of the " dirt " will, in general, be known at the time, and, furthermore, the cleaning process becomes more difficult if the dirty apparatus is allowed to stand for any considerable period, particularly if volatile solvents have evaporated in the meantime.

The simplest method, when access by a test-tube brush is possible, is to employ a commercial household washing powder containing an abrasive which does not scratch glass (*e.g.*, " Vim," " Glitto," etc.). The washing powder is either introduced directly into the apparatus and moistened with a little water or else it may be applied to the dirty surface with a wet test-tube brush which has been dipped into the powder; the glass surface is then scrubbed until the dirt has been removed. The operation should be repeated if necessary. Finally, the apparatus is thoroughly rinsed with distilled water. If scrubbing with the water-washing powder mixture is not entirely satisfactory, the powder may be moistened with an organic solvent, such as acetone.

Excellent results are obtained with warm 15 per cent. trisodium phosphate solution to which a little abrasive powder, such as pumice, has been added. This reagent is not suitable for the removal of tars.

The most widely used cleansing agent is the **" chromic acid " cleaning mixture.** It is essentially a mixture of chromic acid (CrO_3) and concentrated sulphuric acid, and possesses powerful oxidising and solvent properties. Two methods of preparation are available :—

(1) Five grams of sodium dichromate are dissolved in 5 ml. of water in a 250 ml. beaker; 100 ml. of concentrated sulphuric acid are then added slowly with constant stirring. The temperature will rise to 70–80°. The mixture is allowed to cool to about 40° and then transferred to a dry, glass-stoppered bottle.

(2) One hundred ml. of concentrated sulphuric acid, contained in a 250 ml. Pyrex beaker, are cautiously heated to about 100°, and 3 grams of sodium or potassium dichromate gradually added with stirring. Stirring should be continued for several minutes in order to prevent the resulting chromic acid from caking together. The mixture is allowed to cool to about 40°, and transferred to a dry, glass-stoppered bottle. The chromic acid mixture prepared by shaking excess of sodium dichromate or of finely-powdered potassium dichromate with concentrated sulphuric acid at the laboratory temperature is not as efficient as that prepared by method (1) or (2); it is, however, useful for cleaning glassware for volumetric analysis. The mixture has powerful oxidising and solvent properties; its exhaustion is readily recognised by the change in colour from reddish-brown to green.

Before using the chromic acid mixture for cleaning, the vessel should be rinsed with water to remove organic matter and particularly reducing agents as far as possible. After draining away as much of the water as practicable, a quantity of the cleaning mixture is introduced into the vessel, the soiled surface thoroughly wetted with the mixture, and the main quantity of the cleaning mixture returned to the stock bottle. After standing for a short time with occasional rotation of the vessel to spread the liquid over the surface, the vessel is thoroughly rinsed successively with tap and distilled water. If a black solid, probably consisting largely of carbon produced by overheating the contents of the apparatus, remains after the above treatment, it is recommended that a small volume of the reagent be introduced into the flask and the latter gently and evenly heated with a free flame until the acid commences to fume.. Under these conditions, most carbonaceous matter is oxidised.

The procedure whereby a *little* alcohol is *rapidly* added to the vessel, supported in the fume chamber and containing some concentrated nitric acid, although generally preceded by a short period of induction, may be extremely dangerous and should not be used. Under no circumstances should concentrated nitric acid be added to ethyl alcohol—a violent explosion may result.

Satisfactory cleaning may often be achieved by rinsing the vessel with a few ml. of benzene, draining well, thoroughly wetting the soiled surface with concentrated sulphuric acid, then pouring out and washing well with distilled water.

It must be emphasised that there is no universal cleaning mixture. The student must take into account the nature of the substance to be removed and act accordingly. Thus if the residue in the flask is known to be basic in character, dilute hydrochloric or sulphuric acid may dissolve it completely; similarly, dilute sodium hydroxide solution may be employed for acidic residues. If the residue is known to dissolve in a particular inexpensive organic solvent, this should be employed.

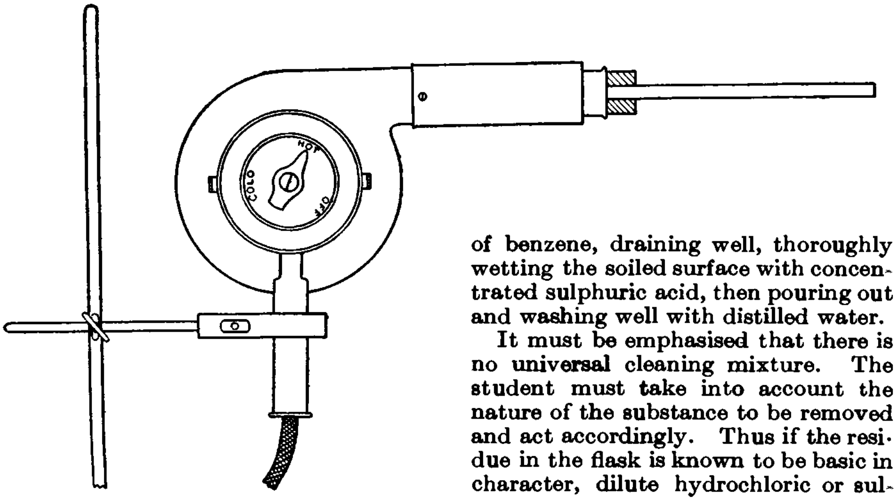


Fig. *II*, *2*, 1.

Small glass apparatus may be dried by leaving it in a steam oven or in an electrically-heated oven maintained at 100–120° for one to two hours. Most organic apparatus is too bulky for oven drying and, moreover, is generally required soon after washing : other methods of drying are therefore used. All these methods depend upon the use of a current of air, which should preferably be warm. If the apparatus is wet with water, the latter is drained as completely as possible, then rinsed with a little methylated spirit, followed, after draining, with a little ether; alternatively, the apparatus may be rinsed with a little acetone. It is convenient to have two bottles labelled *METHYLATED SPIRIT FOR WASHING* and *ETHER FOR WASHING* if the alcohol-ether method of drying is used for rinsing out the apparatus. If acetone rinsing is employed, the bottle should be labelled *ACETONE FOR WASHING.* After rinsing with the organic solvent, the subsequent drying is most conveniently done with the aid of the warm air blower shown in Fig. *II,2*, 1. It consists of an inexpensive commercial hair drier * mounted on a retort stand; a cork carrying a wide glass tube (about 10 mm. in diameter) is fitted into the air orifice and securely wired into position. The air blast is controlled by a three-way combination switch : with one setting of the switch the apparatus blows air at the laboratory temperature, with another setting it blows hot air, and with a third setting the blower is switched off. The apparatus, moist with organic solvent, is held (or supported) over the glass tube and cold air is first passed through for a minute or two, and this is soon followed by hot air until the apparatus is thoroughly dry.

A less satisfactory method of drying after the washing with the organic solvent is to pass a stream of air from a blowpipe bellows (foot or electrically operated) into the vessel through a long wide glass tube. When most or all of the solvent has evaporated, a length of the glass tube may be heated in a flame, thus introducing warm air into the vessel to complete the drying.

II,3. USE OF CORK AND RUBBER STOPPERS

Two points must be borne in mind when selecting a cork stopper. In the first place, the cork should be examined for freedom from flaws; unless corks of the highest quality are employed, they are liable to have deep holes, which render them useless. In the second place, the cork should originally fit as shown in Fig. *II*, *3*, 1, *a* and not as in *b*. It should then be softened by rolling in a cork press or by wrapping it in paper and rolling under the foot.

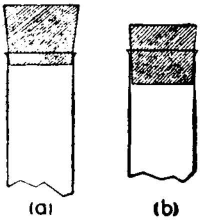


Fig. *II*, *3*, 1.

To bore a cork, a borer should be selected which gives a hole only very slightly smaller than that desired. The cork borer is moistened with water or alcohol or best with glycerine; it is convenient to keep a small bottle (*ca.* 25 ml. capacity) containing glycerine, Fig. *II*, *3*, 2, for this purpose. The borer is held in the right hand and the cork in the left hand. The hole is started at the narrow end with a continuous rotary motion. Beginners should bear in mind that the borer is a cutting instrument and not a punch, and on no account should it be allowed to burst its way through the cork because the borer, upon emerging, will almost invariably tear the surface of the cork. It is a good plan to examine the borer from time to time as it advances through the cork to see that it is cutting a straight hole. Boring should be stopped when it is half through the cork † and the tool removed from the hole. The cork plug is pushed out with the aid of the solid metal rod supplied with the set of borers, and the remainder of the hole is bored from

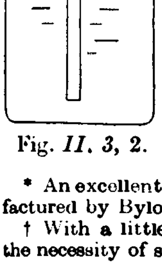


Fig. *II*. *3*, 2.

---

* An excellent and inexpensive hot air drier ("A.M. Industrial Type Blower") is manufactured by Bylock Electric Ltd., Ponders End, Enfield, Middlesex.

† With a little experience this can usually be accomplished in one operation without the necessity of stopping to see whether a straight hole is being cut.

the other end. If the holes are carefully aligned, a clean cut hole is obtained. Experienced laboratory workers frequently complete the whole boring operation from one side, but beginners usually tear the edges of the cork by this method, which is therefore not recommended. A well-fitting cork should slide over the tube (side arm of distilling flask, thermometer, lower end of condenser, etc.) which is to pass through it with only very moderate pressure. The bored cork should be tested for size ; if it is too small, the hole should be enlarged to the desired diameter with a small round file. When the correct size is obtained, the tube is held near the end and inserted into the cork. The tube is then grasped *near* the cork and cautiously worked in by gentle twisting. Under no circumstances should the tube be held too far from the cork nor should one attempt to force a tube through too small an opening in a cork; neglect of these apparently obvious precautions may result in a severe cut in the hand from the breaking of the glass tube.

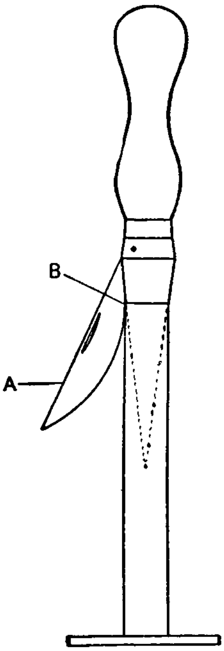


Fig. *II, 3,* 3.

For consistently successful results in cork boring, a sharp cork borer must be used. The sharpening operation will be obvious from Fig. *II, 3,* 3. The borer is pressed gently against the metal cone, whilst slight pressure is applied with the " cutter " *A* at *B* ; upon slowly rotating the borer a good cutting edge will be obtained. If too great pressure is applied either to the borer or to the " cutter," the result will be unsatisfactory and the cutting circle of the borer may be damaged. To maintain a cork borer in good condition, it should be sharpened every second or third time it is used.

Rubber stoppers are frequently employed in the laboratory in " vacuum distillation " assemblies (compare Section **II,19**); for distillations under atmospheric pressure bark corks are generally used. Many organic liquids and vapours dissolve new rubber stoppers slightly and cause them to swell. In practice, it is found that rubber stoppers which have been previously used on one or two occasions are not appreciably attacked by most organic solvents, owing presumably to the formation of a resistant surface coating. **To bore a rubber stopper,** it is essential to employ a very sharp cork borer of the same size as the tube to be inserted into the hole. The borer is lubricated with a little glycerine (Fig. *II, 3,* 2) and steadily rotated under only very slight pressure. The operation requires a good deal of patience and time and frequent lubrication may be necessary ; if too much pressure be exerted on the borer, a hole of irregular shape and diminishing size will result.

The insertion of a glass tube into a rubber stopper or into rubber tubing is greatly facilitated by moistening the rubber with a little glycerine. After some use rubber may stick to glass and great care must be taken not to break the glass tube when removing it. Frequently the exertion of gentle pressure on the rubber stopper by means of the two thumbs whilst the end of the tube (or thermometer) rests vertically on the bench will loosen the stopper; this operation must, however, be conducted with great care. Another method is to slip the smallest possible cork borer, lubricated with a little glycerine, over the tube, and to gradually rotate the borer so that it passes between the stopper and the glass tube without starting a new cut.

II,4. CUTTING AND BENDING OF GLASS TUBING

Many students tend to forget the practical details learnt in elementary courses of chemistry; they are therefore repeated here. **To cut a piece of glass tubing,** a deep scratch is first made with a triangular file or “glass knife.” The tubing is held in both hands with the thumbs on either side of the scratch, but on the side opposite to it. The tubing is then “ pulled ” gently as though one wanted to stretch the tube and also open the scratch. A break with a clean edge will result. The cut edge must then be rounded or smoothed by **fire polishing.** The end of the tube is heated in the Bunsen flame until the edges melt and become quite smooth; the tube is steadily rotated all the time so as to ensure even heating. Overheating should be avoided as the tube will then partially collapse.

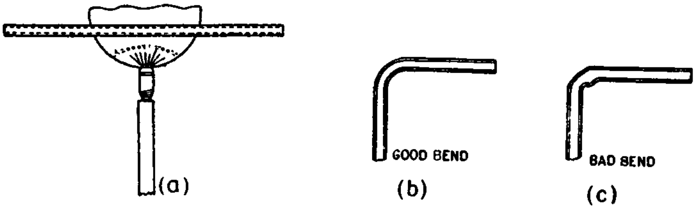


Fig. *II*, *4*, 1.

A “ batswing ” or “ fish-tail ” burner is generally used for the **bending of glass tubing.** The tube is held with both hands in the length of the flame (Fig. *II*, *4*, 1, *a*) so that 5–8 cm. are heated: the tube must be slowly rotated about its axis so as to heat all sides equally. As soon as the glass is felt to be soft, it is bent to the required shape. This is best done by removing it from the flame and allowing one end to fall gradually under its own weight, whilst being guided so that it is in the same plane as the rest of the tube. The glass must never be forced, otherwise a bad bend with a kink will be obtained as in Fig. *II*, *4*, 1, *c*.

II,5. HEATING BATHS

For temperatures up to 100°, a **water bath** or **steam bath** is generally employed. The simplest form is a beaker or an enamelled iron vessel mounted on a suitable stand; water is placed in the vessel, which is heated by means of a flame. This arrangement may be used for non-inflammable liquids or for refluxing liquids of low boiling point. Since numerous liquids of low boiling point are highly inflammable, the presence of a naked flame will introduce considerable risk of fire. For such liquids a steam bath or an electrically-heated water bath, provided with a constant-level device, must be used. If the laboratory is equipped with a steam service, it is convenient to have a number of baths, fitted with a series of concentric copper or lead rings in order to accommodate various sizes of flasks, mounted on lead-covered benches; the steam supply enters near the bottom of the bath and is controlled by a cock outside it. If the laboratory has no external steam supply, the electrically-heated water bath, depicted in Fig. *II*, *5*, 1, is equally serviceable. The bath is of copper, has a diameter of 20–25 cm., and is fitted with an all-metal constant-level device. It is heated by means of a hot plate * in which is incorporated a three-heat (" high," " medium " and " low ") switch. Any size flask may be supported with the aid of the set of concentric copper or lead rings. The temperature of the water in *A* is controlled by the three-way switch on the hot plate and by the rate at which water is allowed to enter the bath *A* ; it is recommended that the thick-walled rubber tubing connecting the water tap with the constant level device *B* be securely fixed at both ends with a turn or two of copper wire.

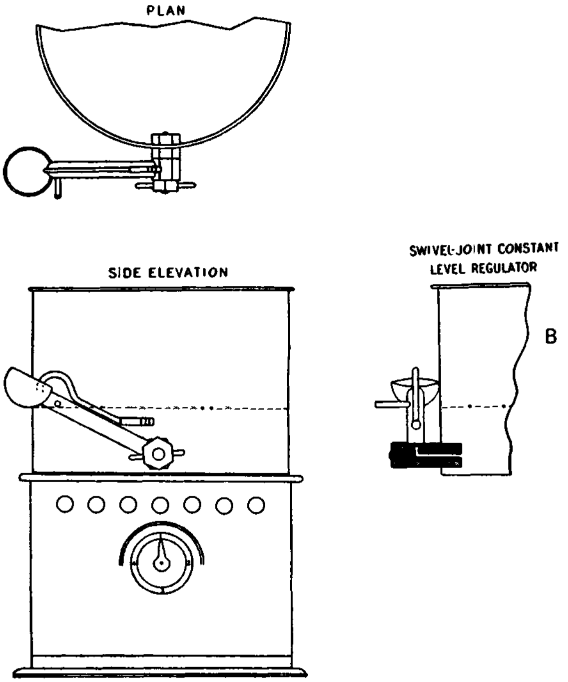


Fig. *II*, *5*, I.

For temperatures above 100°, **oil baths** are generally used. Medicinal paraffin may be employed for temperatures up to about 220°. Glycerol and di-*n*-butyl phthalate are satisfactory up to 140–150° ; above these temperatures fuming is usually excessive and the odour of the vapours is unpleasant. For temperatures up to about 250° " hard hydrogenated " cotton seed oil, m.p. 40–60°, is recommended : it is clear, not sticky and solidifies on cooling ; its advantages are therefore obvious. Slight discoloration of the " hard " oil at high temperatures does not affect its

* A suitable enclosed-type hot plate (" boiling ring ") is supplied by Belling and Co. Ltd.

value for use as a bath liquid. The Silicone fluids, *e.g.*, MS 550 *, are probably the best liquids for oil baths, but are at present too expensive for general use. The MS 550 fluid may be heated to 250° without appreciable loss and discoloration. Oil baths should be set up in the fume cupboard wherever possible. A thermometer should always be placed in the bath to avoid excessive heating. Flasks, when removed from an oil bath, should be allowed to drain for several minutes and then wiped with a rag. Oil baths are generally heated by a gas burner. Some form of internal electrical heating may be employed by advanced students ; a commercial heater embedded in ceramic material and sealed in metal may be supported near the bottom of the bath : the heat input is conveniently controlled by a variable transformer.

Higher temperatures may be obtained with the aid of **baths of fusible metal alloys**, *e.g.*, **Woods metal**—4 parts of Bi, 2 parts of Pb, 1 part of Sn, and 1 part of Cu—melts at 71° ; **Rose's metal**—2 of Bi, 1 of Pb and 1 of Sn—has a melting point of 94° ; a eutectic mixture of lead and tin, composed of 37 parts of Pb and 63 parts of Sn, melts at 183°. Metal baths should not be used at temperatures much in excess of 350° owing to the rapid oxidation of the alloy ; this oxidation may be reduced by employing a small commercial glue pot (Fig. *II*, *5*, 2), the outer pot containing the metal alloy. Before heating, the beaker should be held in a large luminous flame until it is covered with a deposit of carbon, which prevents the fused metal from adhering to the beaker ; the same result is obtained by coating the beaker with graphite. The beaker and thermometer should be removed from the metal bath before the latter solidifies. Metal baths have the advantage that they do not smoke or catch fire ; they are, however, solid at the ordinary temperature and are usually too expensive for general use.

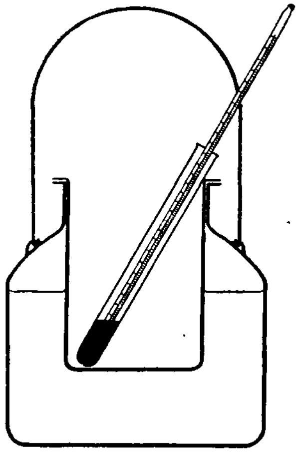


Fig. *II*, *5*, 2.

A satisfactory bath suitable for temperatures up to about 250° may be prepared by mixing four parts by weight of 85 per cent. ortho-phosphoric acid and one part by weight of meta-phosphoric acid ; the mixed components should first be heated slowly to 260° and held at this temperature until evolution of steam and vapours has ceased. This bath is liquid at room temperatures. For temperatures up to 340°, a mixture of two parts of 85 per cent. ortho-phosphoric acid and one part of meta-phosphoric acid may be used : this is solid (or very viscous) at about 20°.

A shallow metal vessel containing sand, the so-called **sand bath**, heated by means of a flame, was formerly employed for heating flasks and other glass apparatus. Owing to the low heat conductivity of sand, the temperature control is poor ; the use of sand baths is therefore not

---

* Supplied by Midland Silicones Ltd., 19 Upper Brook Street, London, W. 1 ; also by Imperial Chemical Industries Ltd., 149 Park Lane, London, W. 1. An equivalent product is available from Dow-Corning, U.S.A.

recommended for routine work in the laboratory. It may occasionally be employed where high temperatures are required, *e.g.*, in thermal decomposition ; as a rule, graphite or nickel shot is preferable for this purpose.

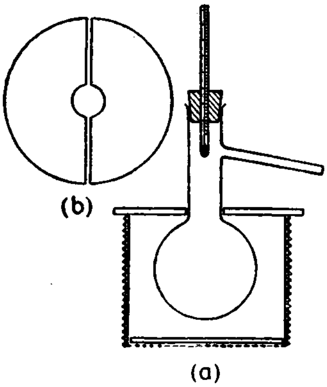


Fig. *II*, *5*, 3.

An air bath may be readily constructed by the student from a commercial circular tin can (that from tinned fruit or food is quite suitable), and is very satisfactory for most work involving the heating of liquids of boiling point above 80° (or below this temperature if the liquid is non-inflammable). The top edge of the can is first smoothed and any ragged pieces of metal removed. A series of holes is then punched through the bottom, and a circular piece of asbestos (about 2–3 mm. thickness) of the same diameter as the can inserted over the holes. The body of the can is then wrapped with asbestos cloth which is bound securely in position by two wires near the top and bottom of the can respectively. A piece of asbestos board (2–4 mm. thickness) of diameter slightly larger than the top of the can is then obtained and a hole of suitable diameter made in its centre ; the asbestos is then cut diametrically. The two halves, which constitute the cover of the air bath, will have the shape shown in Fig. *II*, *5*, 3, *b*. The diameter of the hole in the asbestos lid should be approximately equal to the diameter of the neck of the largest flask that the air bath will accommodate. The air bath, supported on a tripod, is heated by means of a Bunsen burner : the position of a distilling flask, which should be clamped, is shown in Fig. *II*, *5*, 3, *a*. The flask should not, as a rule, rest on the bottom of the bath. The student is recommended to construct three air baths for flasks of 50, 100 and 250 ml. capacity. The advantages of the above air bath are : (1) simplicity and cheapness of construction ; (2) ease of temperature control ; (3) rapidity of cooling of the contents of the flask effected either by removing the asbestos covers or by completely removing the air bath ; and (4) the contents of the flask may be inspected by removing the asbestos covers.

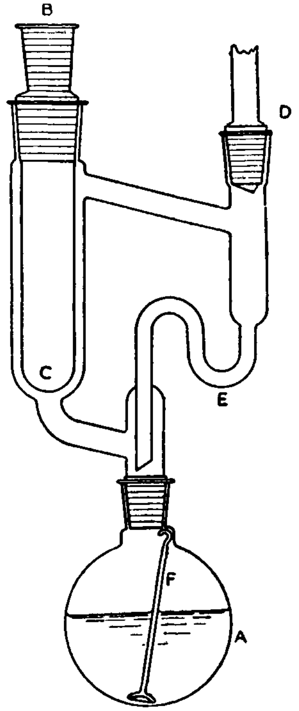


Fig. *II*, *5*, 4.

One of the disadvantages of oil and metal baths is that the reaction mixture cannot be observed easily ; also for really constant temperatures, frequent adjustment of the source of heat is necessary. These difficulties are overcome, when comparatively small quantities of reactants are involved, in the apparatus shown in Fig. *II*, *5*, 4 (not drawn to scale). A liquid of the desired boiling point is placed in the flask *A*. The liquid in *A* is boiled gently so that its vapour jackets the reaction tube *BC* ; it is condensed by the reflux condenser at *D* and returns to the flask through the siphon *E*. Regular ebullition in the flask is ensured by the bubbler *F*. The reaction mixture in *C* may be stirred mechanically. It is convenient to have a number of flasks, each charged with a different liquid ; changing the temperature inside *C* is then a simple operation. A useful assembly consists of a 50 ml. flask *A* with *B*19 joint, a vapour jacket about 15 cm. long, a *B*34 joint at B, and a *B*19 or *B*24 joint at *D*.

The following liquids may be used (boiling points are given in parentheses) :— chlorobenzene (132–3°) ; bromobenzene (155°) ; *p*-cymene (176°) ; *o*-dichlorobenzene (180°) ; aniline (184°) ; methyl benzoate (200°) ; tetralin (207°) ; ethyl benzoate (212°) ; 1 : 2 : 4-trichlorobenzene (213°) ; *iso*propyl benzoate (218°) ; methyl salicylate (223°) ; *n*-propyl benzoate (231°) ; diethyleneglycol (244°) ; *n*-butyl benzoate (250°) ; diphenyl (255°) ; diphenyl ether (259°) ; dimethyl phthalate (282°) ; diethyl phthalate (296°) ; diphenylamine (302°) ; benzophenone (305)° ; benzyl benzoate (316°).

Electric hot plates may also be employed for heating. These should be of substantial construction and be provided with three-way switches. The diameter of the heavy cast-iron top may vary between 5″ and 10″. It is usually advisable to interpose a sheet of asbestos board between the metal top and the vessel to be heated, particularly if the contents of the latter are liable to "bump."

II,6. COOLING BATHS

It is often necessary to obtain temperatures below that of the laboratory. Finely-crushed ice is used for maintaining the temperature at 0–5° : it is usually best to use a slush of crushed ice with sufficient water to provide contact with the vessel to be cooled and to stir frequently. For temperatures below 0°, the commonest freezing mixture is an intimate mixture of common salt and crushed ice : a mixture of one part of common salt and three parts of ice will theoretically produce a temperature of about — 20° but, in practice, the ice salt mixtures give temperatures of — 5° to — 18°. Greater cooling may be obtained by the use of crystalline calcium chloride ; temperatures of — 40° to — 50° may be reached with five parts of $CaCl_2,6H_2O$ and 3·5–4 parts of crushed ice.

If ice is temporarily not available, advantage may be taken of the cooling effect attending the solution of certain salts or salt mixtures in water. Thus a mixture produced by dissolving 1 part of NH_4Cl and 1 part of $NaNO_3$ in 1–2 parts of water causes a reduction in temperature from 10° to — 15° to — 20° ; 3 parts of NH_4Cl in 10 parts of water from 13° to — 15° ; 11 parts of $Na_2S_2O_3,5H_2O$ in 10 parts of water from 11° to — 8° ; and 3 parts of NH_4NO_3 in 5 parts of water from 13° to — 13°.

Solid carbon dioxide (Dry Ice, Drikold) is employed when very low temperatures are required. If it is suspended in solvents, such as alcohol or a mixture of equal volumes of chloroform and carbon tetrachloride, temperatures down to — 50° can be easily attained. Lower temperatures still are reached if intimate mixtures of solid carbon dioxide and organic solvents are employed : with ethyl alcohol, — 72° ; with diethyl ether, — 77° ; and with chloroform or acetone, — 77° (compare Section **I,19**).

In order to keep a freezing mixture for hours or overnight, it is transferred to a glass or copper “ thermos ” flask ; the test-tube or small flask may then be immersed in the mixture. When it is desired to keep larger vessels at about 0°, an ice box (a metal, usually galvanised iron, container, filled with ice, well insulated by thick cork slabs and surrounded by a wooden box) is generally employed. A large commercial refrigerator, suitably adapted, serves the dual purpose of supplying ice for the requirements of the laboratory and as a cold chamber.

II,7. MECHANICAL AGITATION

Mechanical stirring is not necessary in work with homogeneous solutions except when it is desired to add a substance portion-wise or dropwise so as to bring it as rapidly as possible into intimate contact with the main bulk of the solution. This applies particularly in those cases where a precipitate is formed and adsorption may occur, or where heat is generated locally which may decompose a sensitive preparation. In such cases the solution must be continuously agitated by manual shaking or, preferably, by mechanical stirring. When large quantities of material are to be dealt with, it is much easier and very much more efficient to employ mechanical stirring. The importance of mechanical agitation cannot be over-estimated where heterogeneous mixtures are involved. In many preparations the time required for completion of the reaction is shortened, temperatures are more readily controlled, and the yields are improved when mechanical agitation is employed. No apology is therefore needed for discussing this subject in some detail.

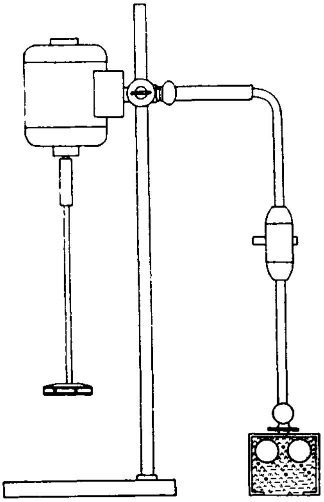


Fig. *II*, *7*, 1.

Stirring in open vessels, such as beakers or flasks, can be effected with the aid of a stirrer attached directly to a small electric motor by means of a chuck or a short length of “ pressure ” tubing. Excellent stirring units are available commercially. Only two of these, which the author has found satisfactory, will be described. Fig. *II*, *7*, 1[*] illustrates a general purpose stirrer, equipped with a $\frac{1}{16}$ h.p. motor, which can be fitted to any retort stand : glass stirrers may be attached with a short length of heavy-wall rubber tubing, whilst stainless steel stirrers (compare Fig. *II*, *7*, 6) are fitted into position by means of a screw. The stirrer unit shown in Fig. *II*, *7*, 2[†] is particularly useful : the motor is $\frac{1}{30}$ h.p. It is mounted on a heavy enamelled iron base (55 × 30 cm.),

---

[*] “ Kestner Laboratory Stirrer ” supplied by Kestner Evaporator and Engineering Co. Ltd.

[†] A slightly smaller unit but fitted with only one resistance control mounted on a box below the base is marketed by L. Mitchell, Ltd.

the vertical rod (2 cm. diameter and 72 cm. long) is hollow and is connected at the lower end beneath the base with a " rotating arm " resistance (housed in a water-tight box) and at the upper end with a switch and rotary control for the resistance. This serves as a coarse control for the speed of the stirrer. A finer control is given by the variable resistance (500 ohms ; 0·5 amp.) fixed to the base. The special type of clamp, illustrated in Fig. *II*, *7*, 2, which will accommodate rods up to 2 cm. in diameter and fix them in any position, is noteworthy.

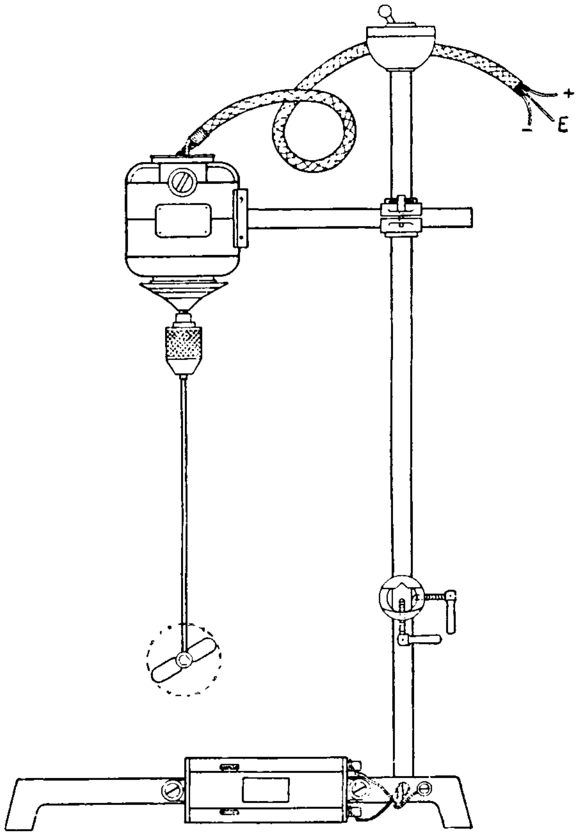


Fig. *II*, *7*, 2.

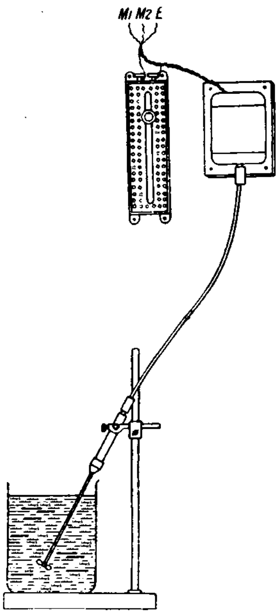


Fig. *II*, *7*, 3.

A powerful stirrer, driven by a flexible driving shaft between the motor ($\frac{1}{8}$ h.p.) and the stirrer, is depicted in Fig. *II*, *7*, 3.* The motor may be placed at a distance from the stirrer head and reaction vessel, thus enabling the assembly to be used for inflammable, corrosive or fuming liquids without damage to the motor. Furthermore, any laboratory retort stand and clamp may be used since the stirrer head weighs only about 250 grams. A variable speed control (500–2000 r.p.m.) is provided.

---

* The " Flexo-Mix Stirrer Unit " supplied by Kestner Evaporator and Engineering Co. Ltd.

Stirrers are usually made of glass, but those of monel metal, stainless steel or Teflon (a polyfluoroethylene) also find application in the laboratory. An important advantage of a stirrer with a Teflon blade is that it is comparatively soft and merely bends if it hits the glass even at high speed; furthermore, it can be shaped to fit the bottom of the vessel, thus rendering the stirring of small volumes of liquid in a large flask possible. A few typical glass stirrers are collected in Fig. *II*, 7, 4; some of these can easily be constructed by the student from glass rod. Types (v) and (vi) are recommended; they possess the advantage that they may be inserted through a narrow neck. A stirrer with a half-moon shaped Teflon blade is illustrated in Fig. *II*, 7, 5; it may be employed for stirring in a round-bottomed or flat-bottomed vessel (the latter by turning the blade over). Two typical stirrers in stainless steel (Kestner) are depicted in Fig. *II*, 7, 6: (*b*) is a vortex stirrer and in use gives the effect shown in (*c*).

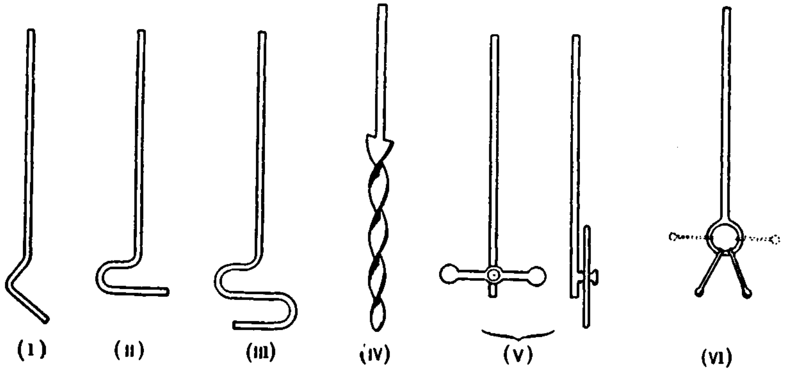


Fig. *II*, 7, 4.

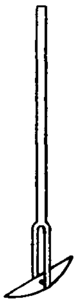


Fig. *II*, 7, 5.

A useful stirrer—sometimes termed a **Hershberg stirrer**—for efficient agitation in round-bottomed vessels, even of pasty mixtures, is presented in Fig. *II*, 7, 7. It consists of a hollow glass tube to which a glass ring is sealed; the glass ring is threaded with chromel or nichrome or tantalum wire (about 1 mm. diameter). By

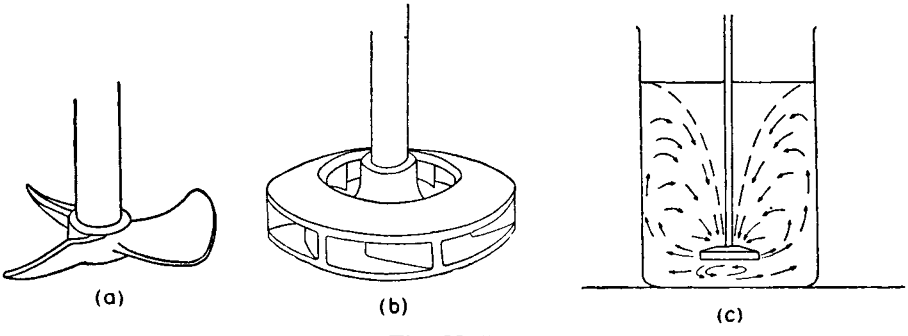


Fig. *II*, 7, 6.

sealing another glass ring at right angles to the first and threading this with wire, better results will be obtained; this is usually unnecessary. The stirrer is easily introduced through a narrow opening, and in operation follows the contour of the flask; it is therefore particularly valuable when it is desired to stir a solid which clings obstinately to the bottom of a round-bottomed flask.

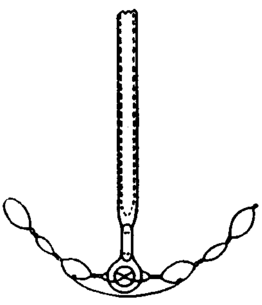


Fig. *II*, *7*, 7.

A stirrer, known as a **Vibro Mixer**,* and of particular value for closed systems, is illustrated in Fig. *II*, *7*, 8 fitted into the central neck of a three-necked flask. The enclosed motor, operating on alternating current, vibrates the stirrer shaft at the same frequency (as the a.c. mains), moving up and down in short, powerful strokes. A control knob at the top of the stirrer housing is provided for adjusting the stroke length from gentle strokes (0·2 mm.) to powerful strokes (*ca.* 2 mm. in thrust). As it is a non-rotating stirrer, a hermetic seal with the reaction flask can be made easily. Several types of stirrer blades are available; two "plate" stirrers are shown in Fig. *II*, *7*, 8, *A* and *B*. In *A* the holes taper upward; the liquid will (on the downstroke) flow up through the wide lower orifices to be violently expelled through the narrower orifices at the top. The principle involved is similar to what happens when water flowing through a pipe suddenly enters a narrower pipe; the speed of flow is greatly increased. In *B* the holes taper downward; excellent mixing is thus obtained for solids etc. at the bottom of the vessel. These "plate" stirrers are useful for intimately mixing liquids in a separatory funnel. For reactions in which gas is passed into the reaction mixture, a hollow shaft is supplied and the gas enters the liquid under the blade and is dispersed into extremely fine bubbles. A special "hydrogenation" stirrer is also marketed: this incorporates a gas circulating device that sucks gas from above the liquid down into the liquid. The base of the stand upon which the stirrer is mounted rests upon sponge rubber or thick felt sheets in order to reduce vibration to a minimum. No guide for the stirrer shaft is necessary; the stirring is very efficient.

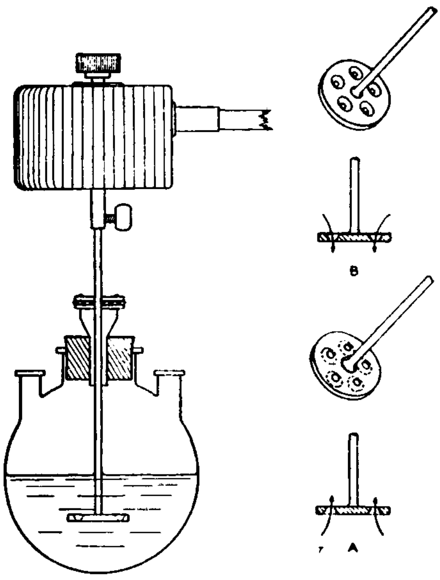


Fig. *II*, *7*, 8.

---

* Manufactured by A.G. für Chemie-Apparatebau, Zürich 6, Ottikerstr. 24; also supplied by the Fisher Scientific Company. Model E 1 is recommended for general laboratory purposes.

Mercury-sealed stirrers are used in the following operations: (1) simultaneous stirring and refluxing of a reaction mixture; (2) stirring the contents of a closed vessel; (3) agitation with prevention of the escape of a gas or vapour; and (4) stirring in an inert atmosphere, such as nitrogen or hydrogen. Three forms of mercury-sealed stirrers are shown in Fig. *II*, *7*, 9, *a–c*; mercury is poured into the space between the outer tube and the inner bearing tube. In (*b*) the lower rubber stopper is replaced by a glass seal, and thus eliminates the danger of possible leakage of mercury through the stopper. Trap (*c*) incorporates an additional stopper and glass bearing, and is a slight improvement upon (*a*): the spattering of mercury during the operation of the stirrer, particularly at high speeds, and the spilling of mercury when the seal is disconnected are thus prevented. The bearings may be lubricated with a little glycerine.

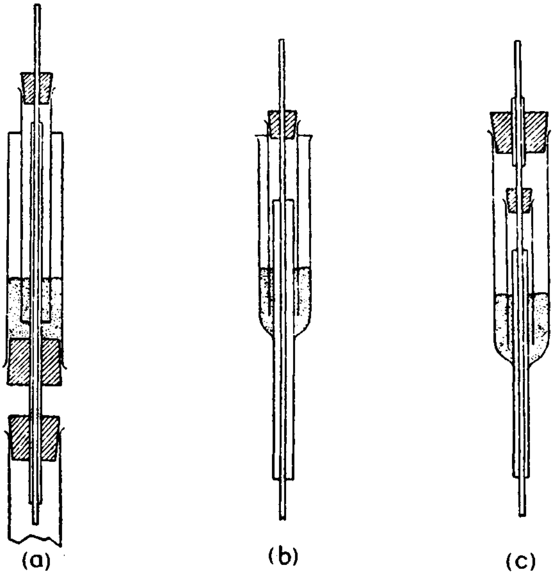


Fig. *II*, *7*, 9.

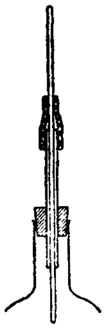


Fig. *II*, *7*, 10.

A simple substitute for a mercury-sealed stirrer is illustrated in Fig. *II*, *7*, 10. The upper, fire-polished end of a 8–10 cm. length of 10 mm. glass tubing, projecting through a stopper which fits into the flask, is fitted with a 2 cm. length of 6 mm. heavy-wall rubber tubing so that it projects 5–8 mm. beyond the end of the glass tube; this projecting portion fits tightly to form a seal round an 8 mm. stirrer shaft running through the glass tubing. Glycerine (or Silicone grease) is applied to the point of contact of the glass and rubber to act as a lubricant and sealing medium. The seal, sometimes known as the Kyrides seal, can be used with reduced pressure down to 10–12 mm. of mercury.* The above dimensions are not

---

* This stirrer is not dependable for stirring operations lasting several hours; the rubber tubing may stick to the shaft and may also be attacked by the organic vapours causing it to swell and allow the escape of vapours.

rigid, but are given as an indication of the relative sizes of the tubes to be employed in the construction of the stirrer, which will be termed a **glycerine-sealed stirrer.** It has also been named a **Kyrides stirrer.**

A common operation in practical organic chemistry is for stirring, refluxing, and addition of a liquid from a dropping funnel to be carried on simultaneously. The most convenient apparatus for this purpose is a three-necked flask, fitted as in Fig. *II*, *7*, 11, *a*. If a three-necked flask is not available, the three-way adapter inserted into a bolt-head flask (Fig. *II*, *7*, 11, *b*) may be used. A further simplification, suitable for elementary students, is to employ a two-way adapter as in Fig. *II*, *7*, 11, *c* ; the stirrer passes through a closely-fitting glass sleeve which is extended well into the liquid so that the liquid itself serves to seal the stirrer. The dropping funnel is supported by means of a cork, into which a V-cut has been made to allow for the expansion of the air, at the top of the condenser. The mercury-sealed stirrer in (*a*) may be replaced by the glycerine-sealed stirrer illustrated in (*b*).

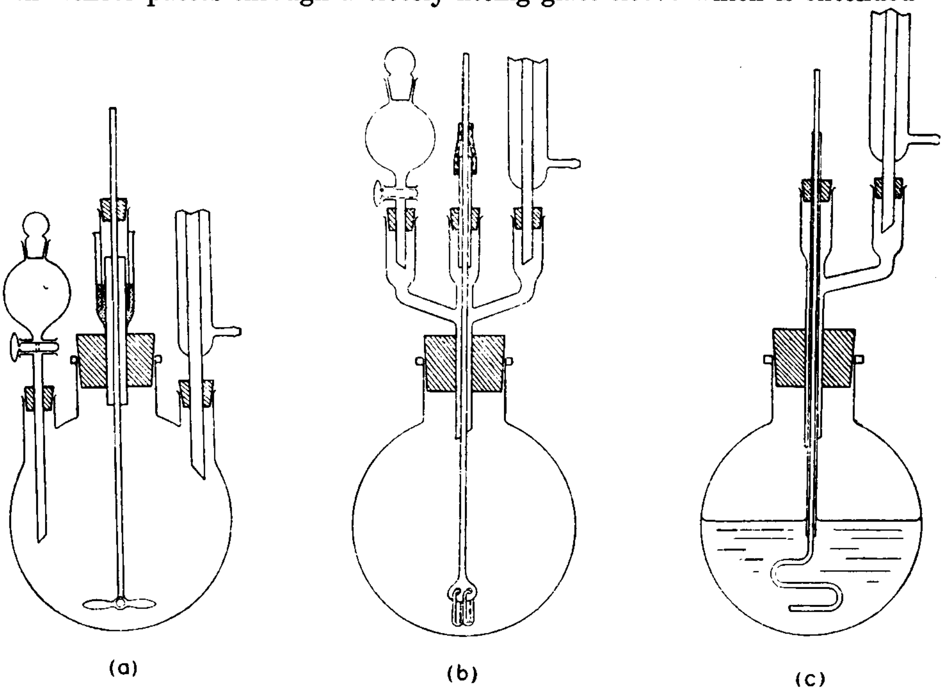

(a) (b) (c)

Fig. *II*, *7*, 11.

If it is desired to carry out the combined operations of stirring, refluxing, and addition of a liquid in a stream of gas, the apparatus of Fig. *II*, *7*, 12, *a* may be used : the side tube for the gas is sealed on to the separatory funnel. For the passage of a gas into a stirred liquid, the aperture carrying the modified separatory funnel may be fitted with the device shown in Fig. *II*, *7*, 12, *b* ; the glass rod inside the tube is held in position by a short length of heavy-wall rubber tubing and is employed to clear the lower end of the gas delivery tube, should it become blocked with solid reaction product.

If a solid reagent, which is affected by moisture in the atmosphere (*e.g.*, anhydrous aluminium chloride), is to be added in small portions to a reaction mixture which is being refluxed and/or stirred, one aperture of the three-necked flask is fitted with a length of wide, thin-walled rubber tubing (say, a 12 cm. length of 20 mm. tubing) and a 100 or 250 ml. conical flask containing the reagent is inserted into the other end of the tubing (Fig. *II*, *7*, 12, *c*). The solid is readily added in portions by raising the flask; the latter can be cut off from the reaction mixture by kinking the rubber tube. An alternative device for adding a solid intermittently to a stirred reaction mixture in a multi-necked flask is depicted in Fig. *II*, *7*, 12, *d*, and is almost self-explanatory. It may be constructed, if desired, from a small Pyrex Erlenmeyer flask and a broken pipette. The solid is charged into the conical reservoir; by raising the plunger to the appropriate height, any desired amount of the solid may be made to flow into the reaction vessel, and the flow can be completely stopped by merely twisting down the plunger until the rubber ring seals the opening. The rubber ring should be, say, 3 mm. thick and 5 mm. wide; if solvents which attack rubber are present, a neoprene gasket may be used. The rubber tubing at the top is lubricated with glycerine or castor oil (Kyrides seal) to make an air-tight joint which will allow free movement of the plunger. The hopper may be recharged during a reaction without breaking the seal by lifting the stopper while holding down the pipette.

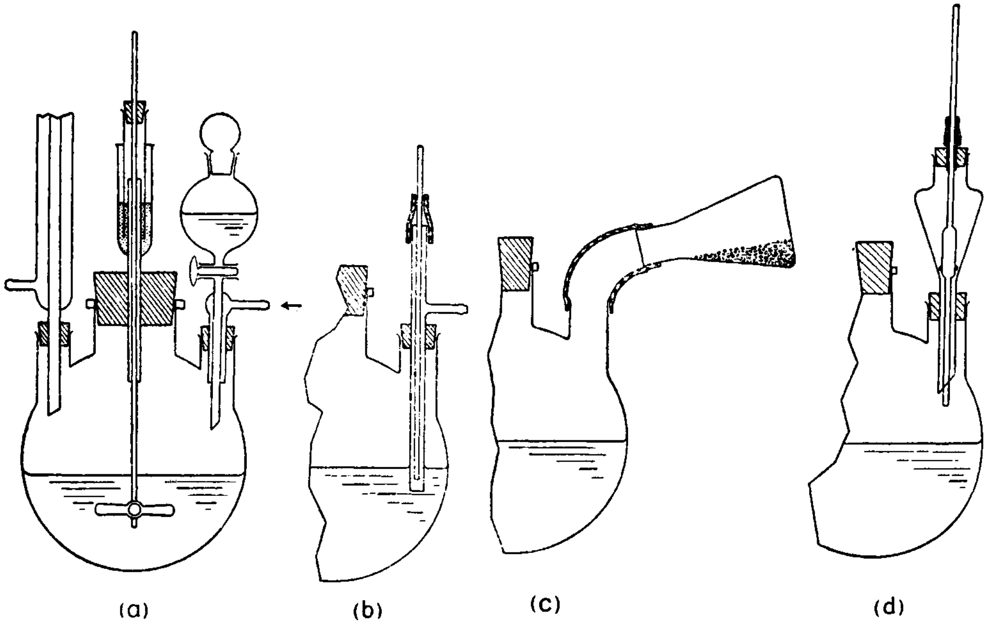


Fig. *II*. *7*, 12.

It is sometimes necessary (*e.g.*, in reactions involving organolithium compounds or in certain Grignard preparations) to carry out a reaction in an atmosphere of an inert gas, such as nitrogen. A suitable set-up is shown in Fig. *II*, 7, 13. Dry nitrogen is introduced at the top of the condenser and initially can be allowed to sweep through the apparatus and escape at the mouth of the dropping funnel: it will be noted that the latter has a pressure-equalising side tube. The mercury valve permits a slight pressure of gas. When the funnel is closed a slight positive pressure is maintained at the nitrogen cylinder, as indicated by the level of the mercury in the escape valve. This arrangement is economical in nitrogen and is to be preferred to the use of a continuous stream of inert gas since it obviates the evaporation of the solvent. The mercury-sealed stirrer is of the Hershberg type made of tantalum wire.

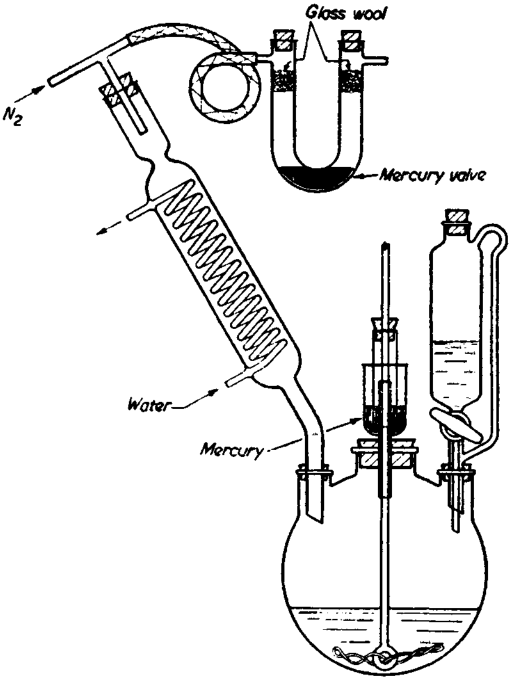


Fig. *II*, 7, 13

The mechanical shaking machine is employed for automatic mixing of heterogeneous systems and finds many applications in the organic chemistry laboratory. Numerous forms are available, but these are generally expensive.* A simple, efficient but inexpensive shaking machine, which can easily be constructed by a competent mechanic, is illustrated in Fig. *II*, 7, 14. It is mounted on a heavy teak base (115 × 50 × 2·5 cm.). A 1/6 H.P. motor,† coupled with pulleys of

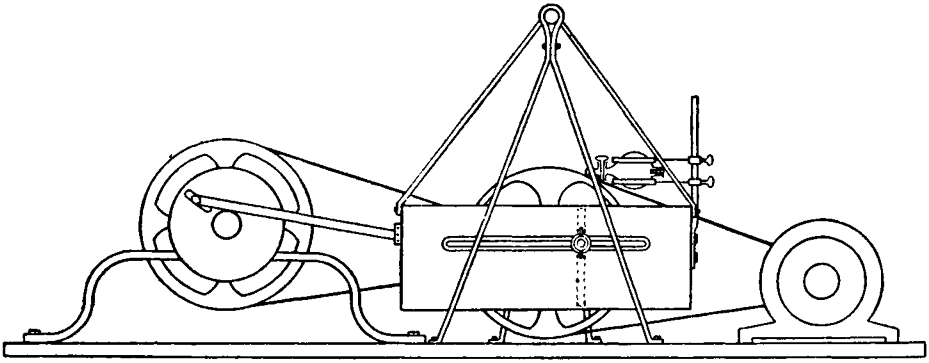


Fig. *II*, 7, 14.

---

* The "Super Shaker," manufactured by A. Gallenkamp and Co. Ltd., is excellent.

† For example, a "capacitor motor," 1,425 r.p.m., supplied by British Thomson Houston Co. Ltd., Rugby, England.

suitable diameter and incorporating a V-belt to minimise slipping, shakes the wooden box (40 × 16 × 10 cm.), which will accommodate a "Winchester quart" bottle. The speed of shaking may be simply controlled by varying the size of pulley on the motor shaft. Any size of bottle may be securely held in the box by means of felt-covered wooden wedges, which are fixed by means of wing nuts passing through the metal slides fitted into the sides of the box. A rod is bolted to one side of the box to permit the clamping of flasks and separatory funnels; the latter are held in position by two retort rings covered with rubber (made by cutting rubber "pressure" tubing along its length).

Mention must also be made of magnetic stirring. A rotating field of magnetic force is employed to induce variable speed stirring action within either closed or open vessels. The stirring is accomplished with the aid of small permanent magnets sealed in Pyrex glass or in Polythene. The principle of magnetic stirring will be evident from Fig. *II*, 7, 15. A permanent bar magnet, mounted horizontally, is attached to the shaft of an electric motor: the whole is mounted in a cylindrical housing with flat metal top and heavy cast metal base. A resistance (which is frequently incorporated in the housing) is provided to control the rate of stirring. To use the apparatus, the rheostat, which is initially in the off-position, is slowly rotated (this increases the motor speed) until the required rate of stirring is attained. When the experiment is complete, the rheostat is returned to the zero position, the "stirrer" allowed to come to rest and removed with the aid of a pair of forceps. Magnetic stirring has many obvious applications, but the most important are probably to stirring in closed systems, *e.g.*, (*a*) where gas volume changes must be observed as in catalytic hydrogenations, (*b*) where exclusion of air is desirable to prevent oxidation, (*c*) where reactions are to be carried out in an anhydrous environment, and (*d*) where small containers are used and the introduction of a propeller shaft is inconvenient.

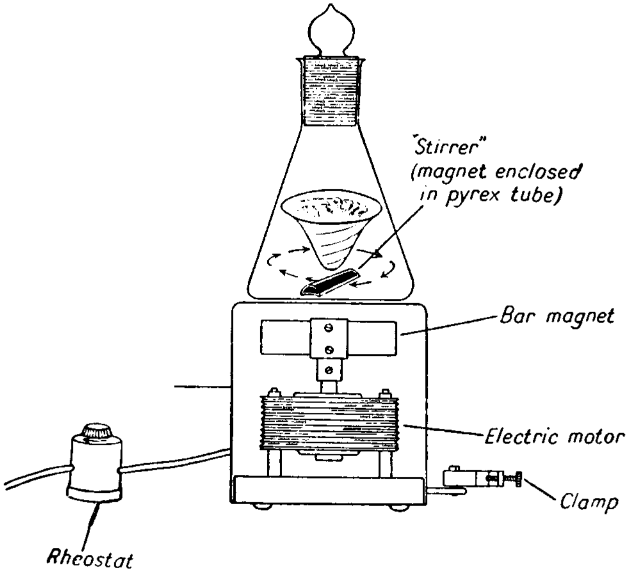


Fig. *II*, 7, 15.

Many forms and sizes of magnetic stirring apparatus are available commercially. These include those fitted with an electric hot plate attached to the flat top; the hot plate is controlled by an energy regulator or variable transformer (Variac).

II,8. GAS ABSORPTION TRAPS

The gas traps depicted in Fig. *II*, *8*, 1, *a* and *b* are used when limited quantities of gas are to be absorbed. For larger volumes of gas, or where the gas is rapidly evolved, the gas traps shown in Fig. *II*, *8*, 1, *c* and *d* are eminently satisfactory. In (*c*) the gas is passed into a wide tube in which a stream of water (usually from a reflux condenser) flows into a large filter flask and overflows at constant level, which is above the lower end of the wide tube ; a water seal is thus provided which prevents the escape of the gas into the atmosphere, and the heat of solution of the gas (*e.g.*, hydrogen chloride or hydrogen bromide) is dissipated. A convenient size for (*d*) is a tube 80–100 cm. long and about 25 mm. diameter.

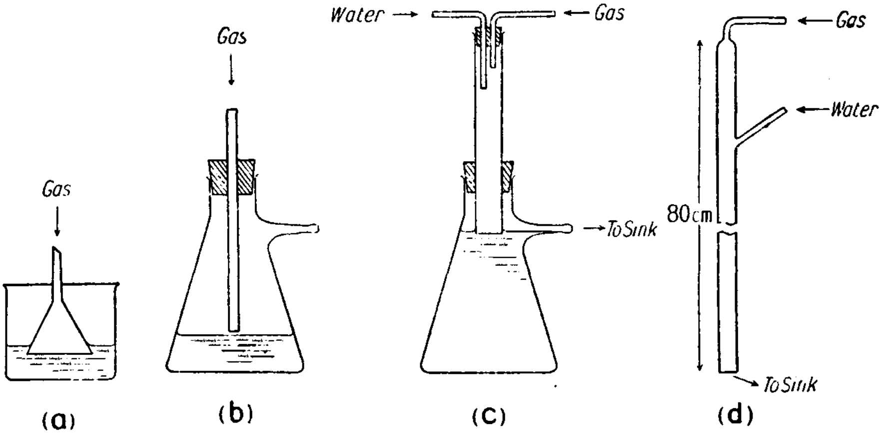


Fig. *II*, *8*, 1.

A highly efficient gas-absorption apparatus * is depicted in Fig. *II*, *8*, 2. The over-all length is about 15″ ; two inlets for obnoxious gases are provided, but one can be readily closed if not required. The waste water from a water condenser may be employed. The water enters in the middle of the apparatus and passes up the outer annulus, spraying out at the top of the tower on to $\frac{3}{8}''$ Raschig or similar rings. It then passes down the column and through the water trap at the bottom of the apparatus to waste through a side tube fitted with a siphon-breaking device. The contaminated gas enters at either side of the two inlet connexions and is absorbed by the water passing down the column.

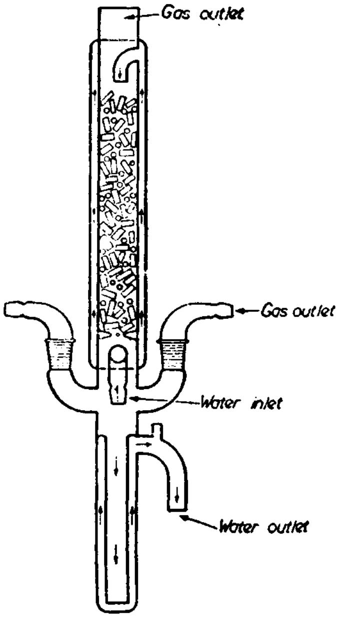


Fig. *II*, *8*, 2

---

* Designed in the Research Laboratories of May and Baker Ltd., Dagenham.

II,9. CALIBRATION OF THERMOMETERS

The comparatively inexpensive long-scale thermometer, widely used by students, is usually calibrated for complete immersion of the mercury column in the vapour or liquid. As generally employed for boiling point or melting point determinations, the entire column is neither surrounded by the vapour nor completely immersed in the liquid. The part of the mercury column exposed to the cooler air of the laboratory is obviously not expanded as much as the bulk of the mercury and hence the reading will be *lower* than the true temperature. The error thus introduced is not appreciable up to about 100°, but it may amount to 3–5° at 200° and 6–10° at 250°. The error due to the column of mercury exposed above the heating bath can be corrected by adding a **stem correction**, calculated by the formula :

$$\textit{Stem correction} \text{ (in degrees)} = KN(t_1 - t_2)$$

where K = the apparent expansion coefficient of mercury in glass ;
N = the length, measured in degrees, of the part of the thermometer not heated to the temperature of the bulb, *i.e.*, the length of the exposed column ;
t_1 = the observed temperature ; and
t_2 = the mean temperature of the exposed mercury column (determined on an auxiliary thermometer placed alongside with its bulb at the middle of the exposed thread).

The value of K for normal glass is 0·000158 from 0° to 150° ; 0·000159 at 200° ; 0·000161 at 250° ; and 0·000164 at 300°. For borosilicate (Pyrex) glass the values of K are : 100°, 0·000164 ; 150°, 0·000165 ; 200°, 0·000167 ; 250°, 0·000170 ; 300°, 0·000174 ; 350°, 0·000178 ; 400°, 0·000183 ; and 450°, 0·000188. Owing to the difficulty of determining t_2 with any accuracy, the above correction cannot be applied with any degree of precision, but is sufficiently accurate for all ordinary purposes.

In addition to the error due to the exposed stem, ordinary chemical thermometers of low cost are subject to errors due to irregularities in the bore and sometimes the scale graduations may not be very accurate.* It is therefore essential to check the thermometer at several temperatures against the melting points of pure solids or the boiling points of pure liquids as described below. The application of an exposed stem correction will of course be unnecessary if the thermometer is calibrated in this way. A calibration curve may then be drawn upon " graph " paper from the data thus obtained. Temperatures at intervals of about 20° are marked as abscissae and the corrections to be added or subtracted as ordinates ; the points thus obtained are then connected by a smooth curve. The thermometer correction at any temperature may be read directly from the curve.

The stem correction may be avoided by employing a thermometer with a short scale (sometimes termed an *Anschütz thermometer*) and of such size that the entire column of mercury is immersed in the vapour or in the liquid. In practice, it is generally more convenient to use thermometers which have been graduated for *partial immersion* for a short and con-

---

* For advanced work, it is advisable to use a thermometer of better quality and which is provided with a small mercury bulb ; the latter rapidly attains the temperature of the bath or vapour. Satisfactory small bulb thermometers are manufactured *inter alia* by H. J. Elliott Ltd. and by Short and Mason Ltd.

venient length of the stem. A special mark is usually etched on the stem to indicate the depth of immersion and, provided that this is approximately adhered to, no serious error due to exposed stem will be present in the resulting reading of the thermometer. A thermometer which is to be used for distillation is usually graduated for 7·5 or 8 cm. immersion, whilst that for melting points may be graduated for 25 or 35 mm. immersion.

Table II, 9, A.—Reference Substances for the Calibration of Thermometers by the Melting Point Method

Water — ice	0·0° *
α-Naphthylamine, A.R.	50°
Benzylidene aniline	52°
Diphenylamine, A.R.	53·5°
p-Dichlorobenzene	54°
Phenyl benzoate	69°
Phenylacetic acid	76°
8-Hydroxyquinoline, A.R.	76°
Vanillin, A.R.	82°
m-Dinitrobenzene	89·5°
Benzil	95°
α-Naphthol, A.R.	96°
Catechol	104°
Resorcinol, A.R.	112°
Acetanilide	114°
Benzoic acid, A.R.	122°
β-Naphthol, A.R.	123°
Urea	132°
Phenylurea (mono)	148°
Benzilic acid	150°
s-Diphenylthiourea	154° *
Salicylic acid, A.R.	159°
Hydroquinone	170°
p-Tolylurea (mono)	181°
Succinic acid, A.R.	185°
3 : 5-Dinitrobenzoic acid	205°
p-Nitrobenzoic acid	239°
p-Chlorobenzoic acid	239°
s-Diphenylurea	242°
Cinchonine	264°
s-Di-*p*-tolylurea	268°
s-Di-α-naphthylurea	298°
Diacetyl-*p*-phenylenediamine	303°
NN-Diacetylbenzidine	317°
Fluorescein (for spot tests)	330°

---

* These compounds are unsuitable for use in the hot plate method, *cf.* Section II,11, Fig. *11, 11*, 1.

Full experimental details for the determination of melting and boiling points are given in Sections **II,10** and **II,11** respectively. The Tables **II, 9, A** and **II, 9, B** list suitable substances for the calibration of thermometers by melting point or boiling point determinations respectively. Substances which are " bracketed " are alternative to each other. It need hardly be emphasised that only compounds of the highest purity should be employed.

TABLE II, 9, B.—REFERENCE SUBSTANCES FOR THE CALIBRATION OF THERMOMETERS BY THE BOILING POINT METHOD

COMPOUND	BOILING POINT (°C) AT 760 MM.	Δt/10 MM. (°C) *
Carbon disulphide . . .	46·3°	0·42
Acetone	56·1°	0·39
Benzene	80·2°	0·43
Water	100·0	0·37
Toluene	110·8°	0·42
Ethylene dibromide. . .	131·7°	0·48
Chlorobenzene . . .	132·0°	0·49
Bromobenzene . . .	156·2°	0·53
Aniline	184·4°	0·51
Nitrobenzene . . .	210·9°	0·48
Naphthalene	217·9°	0·58
Quinoline	237·5°	0·59
Diphenyl	255·5°	0·6
Benzophenone . . .	305·9°	0·6

* Change in boiling point for every 10 mm. mercury pressure at 760 ± 20 mm.

The zero point is best determined with an intimate mixture of distilled water and pure ice made from distilled water. About 20 ml. of distilled water are placed in a boiling tube (150 × 25 mm.) and frozen partially by immersion in an ice-salt mixture ; during the freezing the mixture is stirred with a glass rod until a thick slush is obtained. The boiling tube is then removed from the freezing mixture, the thermometer immersed in the slush so that the zero point is just visible ; the mixture is stirred gently with the thermometer and the reading taken after the temperature has become constant (2–3 minutes).

The most satisfactory and the most accurate method for the calibration of a thermometer is to compare it directly with short-scale thermometers, each of limited range, which have been standardised at the National Physical Laboratory.† The comparison should be made as far as possible under the same conditions as the thermometer is to be used. For experiments demanding the highest precision (*e.g.*, in research work), it is a good plan to have two similar sets of short-scale thermometers, one of which has been standardised at the N.P.L. ; the unstandardised set is

---

† The Bureau of Standards in the U.S.A., etc.

directly compared with the certified set and employed for all routine operations. The standardisation should be made at least once a year.

II,10. EXPERIMENTAL DETERMINATION OF THE MELTING POINT

The theory of melting and freezing has been discussed in Sections **I,10–I,18**. A pure crystalline organic compound has, in general, a definite and sharp melting point, that is, the melting point range (the difference between the temperature at which the collapse of the crystals is first observed and the temperature at which the sample becomes completely liquid) does not exceed about 0·5°. The presence of small quantities of miscible, or partially miscible, impurities will usually produce a marked increase in the melting point range and cause the commencement of melting to occur at a temperature lower than the melting point of the pure substance. The melting point is therefore a valuable criterion of purity for an organic compound.

A sharp melting point is usually indicative of the high purity of a substance. There are, however, some exceptions. Thus a eutectic mixture of two or more compounds (Section **I,12**) may have a sharp melting point, but this melting point may be changed by fractional crystallisation from a suitable solvent or mixture of solvents. The number of exceptions encountered in practice is surprisingly small, hence it is reasonable to regard a compound as pure when it melts over a range of about 0·5° (or less) and the melting point is unaffected by repeated fractional crystallisation.

In addition to the use of a melting point determination as a criterion of purity, an equally valuable application is for the identification of organic compounds. If the melting point is known within one degree, the major proportion of possible substances is immediately eliminated from consideration. The study of the general chemical properties of the compound and a mixed melting point determination (Section **I,17**) will largely establish the identity of the compound.

The experimental method in most common use is to heat a small amount (about 1 mg.) of the substance in a capillary tube attached to a thermometer which is immersed in a suitable bath of liquid, and to determine the temperature at which melting occurs. **The capillary melting point tubes are prepared** either from soft glass test-tubes or from wide glass tubing (*ca.* 12 mm. diameter).* A short length of glass tubing or glass rod is firmly fused to the closed end of the test-tube. The test-tube (or wide glass tubing) must first be thoroughly washed with distilled water to remove dust, alkali and products of devitrification which remain on the surface of the glass, and then dried. The closed end of the test-tube is first heated whilst being slowly rotated in a small blowpipe flame : the glass rod or tube is simultaneously heated in the same manner (Fig. *II, 10,* 1, *a*). When the extremities of both pieces of glass are red hot, they are firmly fused together, twisting of the joint being avoided, and then

---

* Pyrex glass is preferable, but this requires an oxy-coal gas blowpipe for manipulation. Suitable melting point tubes may be purchased from dealers in scientific apparatus or chemicals. It is, however, excellent practice, and an essential part of his training, for the student to learn to prepare his own capillary tubes.

removed momentarily from the flame until the seal is just rigid enough that no bending occurs. The test-tube is then immediately introduced into a large " brush " flame (Fig. *II, 10,* 1, *b*) so that a length of about 5 cm. is heated, and the tube is rotated *uniformly* in the flame. When the heated portion has become soft and slightly thickened as the result of the heating, the tube is removed from the flame and, after a second or two, drawn, slowly at first and then more rapidly, as far apart as the arms will permit (or until the external diameter of the tube has been reduced to 1–2 mm.). If the operation has been successfully performed, a long capillary of regular bore throughout most of its length will be obtained. The long thin tube is then cut into lengths of about 8 cm. by touching it *lightly* with a file and then tapping gently with the flat portion of the file ; after a little practice, no difficulty should be experienced in dividing the long capillary into suitable lengths without crushing the fragile tubing. It will be found that a short length of tubing ("glass spindle"), sufficiently rigid to act as a holder, will remain attached to the test-tube after the long capillary has been cut off. The operation may then be repeated. When the test-tube becomes too short to be handled at the open end, a piece of glass tubing or rod may be fused on, in the manner previously described, to act as a convenient handle. In this way a large number of capillary tubes may be prepared from one test-tube. One end of each of the capillary tubes should be sealed by inserting it horizontally into the extreme edge of a small Bunsen flame for a few seconds, and the capillary tube rotated meanwhile ; the formation of a glass bead at the end of the tube should be avoided. The prepared capillary tubes should be stored either in a large specimen tube or in a test-tube closed with a cork.

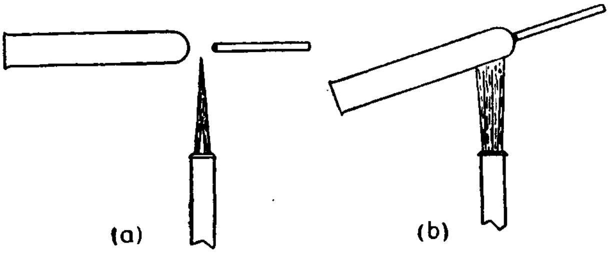
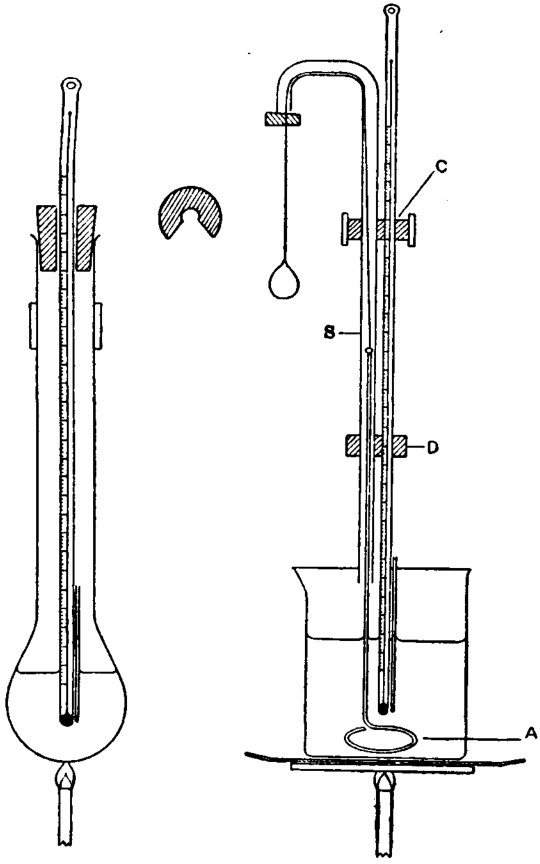


Fig. *II, 10,* 1.

The capillary tube is then filled as follows. About 0·1 gram of the dry substance is placed on a glass slide or upon a fragment of clean porcelain plate and finely powdered with a clean metal or glass spatula, and then formed into a small mound. The open end of the capillary tube is pushed into the powder, " backing " the latter, if necessary, with a spatula. The solid is then shaken down the tube by tapping the closed end on the bench or by gently drawing the flat side of a triangular file (a pocket " nail file " is quite effective) along the upper end of the tube. The procedure is repeated until the length of lightly-packed material is 3–5 mm. Any substance adhering to the outside of the tube must be wiped off so that it will not discolour the bath.

The filled melting point tube is now attached to the lower end of a thermometer in such a way that the substance is at the level of the middle of the mercury bulb (which has previously been wetted with the bath liquid); the moistened capillary is then slid into position. Advantage is taken of the surface tension of the bath liquid to hold the melting point tube in position by capillary attraction; the use of a thin rubber band, prepared by cutting narrow rubber tubing, to attach the capillary tube near the open end to the thermometer is not recommended. The thermometer, with the tube attached, is inserted into the centre of the bath; the melting point tube should extend about as far along above the liquid as it does in the liquid in order to ensure that the capillary force will be large enough to hold it to the thermometer.



(a) (b)

Fig. *11*, *10*, 2.

Two convenient forms of bath are shown in Fig. *11*, *10*, 2, *a* and *b*. The former consists of a long-necked, round-bottomed flask (a long-necked Kjeldahl flask of 100 ml. capacity is quite satisfactory) supported by means of a clamp near the upper part of the neck. The thermometer is fitted through a cork, a section of the cork being cut away (see inset) so that the thermometer scale is visible and also to allow free expansion of the air in the apparatus. The bulb is about three-quarters filled with concentrated sulphuric acid.* The apparatus of Fig. *II*, *10*, 2, *b* consists of a small Pyrex beaker (*e.g.*, of 250 ml. capacity) containing the bath liquid, which may be stirred by means of a small glass stirrer *A* so placed that its shaft is in the glass tube *B*. The thermometer and glass tube are held together by passing through holes in the corks *C* and *D*. The stirrer is connected by a length of string through the tube *B* as shown, and is prevented from falling to the bottom of the beaker by a small cork or knot at the extreme end. This melting point apparatus is supported on a gauze-covered ring attached to a retort stand, which also holds the thermometer and tube in a clamp round the cork *C*. Stirring of the bath liquid is effected by suitable manipulation of the string, and should be conducted at a regular rate throughout the heating.

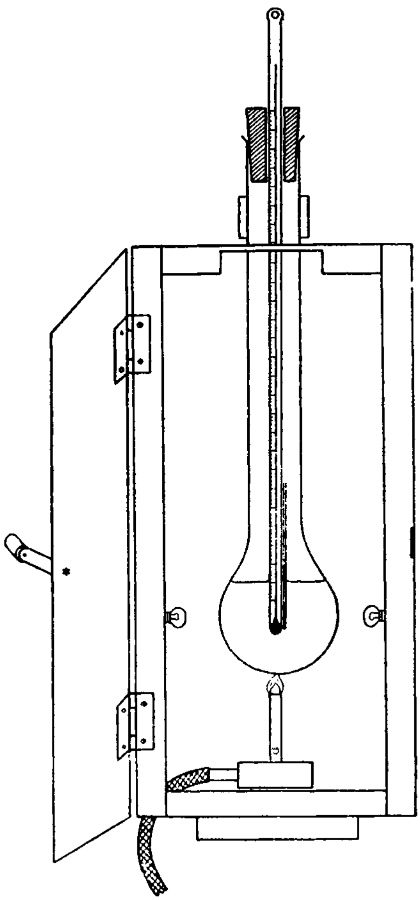


Fig. *II*, *10*, 3.

Fig. *II*, *10*, 3, depicts a " housing " for the apparatus of Fig. *II*, *10*, 2, *a* ; it is easily constructed from lengths of " angle iron " and asbestos board. If desired, " torch " bulbs may be fixed in the appropriate holders in the walls, and connected with a dry battery or accumulator in order to provide illumination of the melting point apparatus. The electric bulb immediately behind the apparatus should be connected to an independent micro-switch. Alternatively,

---

* The bath liquid generally employed is concentrated sulphuric acid : this may be heated to a temperature of 250–280° in the apparatus of Fig. *II*, *10*, 2, *a*, but only to 200–220° in the open beaker heating bath owing to the excessive fuming above this temperature range. By boiling together in a fume cupboard either 70 parts by weight of concentrated H_2SO_4 and 30 parts by weight of K_2SO_4 or 55 parts by weight of concentrated sulphuric acid with 45 parts by weight of $KHSO_4$ until the solid has dissolved (5–10 minutes), a bath liquid, possessing the consistency of glycerine and which does not fume badly, is obtained : this may be employed in an open beaker for temperatures between 220° and 320° (Mulliken). If the sulphuric acid becomes discoloured, the addition of a few crystals of sodium or potassium nitrate will restore the original colour.

Another convenient heating liquid is medicinal paraffin ; it has a low specific heat, is non-inflammable and is non-corrosive, but it can only be safely heated to about 220°; above this temperature it begins to decompose slightly.

A mixture of equal parts of cottonseed oil and castor oil, containing about 1 per cent. of hydroquinone as an anti-oxidant, is a useful bath liquid which can be heated up to about 250°.

The highly stable and heat-resistant Silicone oils are very satisfactory. Midland Silicone or Dow-Corning fluid 550 or 500 (or the equivalent I.C.I. product) is recommended. Their only drawback is their high cost.

the melting point capillary may be illuminated by holding a small electric "torch" in front of the bulb of the flask. The clamp supporting the flask is outside the "housing" and is attached to a retort stand which forms the base of the apparatus. The flask is heated by means of an "arsenic" or micro burner.

The melting point apparatus is heated comparatively rapidly with a small flame until the temperature of the bath is within 15° of the melting point of the substance, and then slowly and regularly at the rate of about 2° per minute until the compound melts completely. The temperature at which the substance commences to liquefy and the temperature at which the solid has disappeared, *i.e.*, the melting point range, are observed, For a pure compound, the melting point range should not exceed 0·5–1°; it is usually less. Any sintering or softening below the melting point should be noted as well as any evolution of gas or any other signs of decomposition.* If the approximate melting point is not known, it is advisable to fill two capillaries with the substance. The temperature of the bath may then be raised fairly rapidly using one capillary tube in order to determine the melting point approximately; the bath is then allowed to cool about 30°, the second capillary substituted for the first and an accurate determination made.

It should be noted that a second determination of the melting point should not be made as the bath liquid cools by observing the temperature at which the molten material in the capillary tube solidifies, or by reheating the bath after the solidification has occurred. This is because, in many cases, the substance may partially decompose, and, in some instances, it may undergo a change into another crystalline form possessing a different melting point. A freshly-filled capillary tube should always be employed for each subsequent determination. Substances which sublime readily are sometimes heated in melting point capillaries sealed at both ends. For compounds which melt with decomposition, difficulties sometimes arise in the melting point determination; it is best to insert the capillary tube into the bath when the temperature is only a few degrees below the melting and decomposition point of the material. This avoids decomposition, with consequent lowering of the melting point, during the time that the temperature of the bath liquid is being raised.

After the melting point has been determined, the thermometer reading is corrected by reference to the calibration chart of the thermometer. Methods for calibrating a thermometer are described in Section **II,9.**

The melting point of a substance which melts either slightly above or below the laboratory temperature is conveniently determined in the apparatus illustrated in Fig. *II, 10,* 4. It consists of a test-tube supported in a slightly larger test-tube by means of a cork (thus forming an air jacket and preventing too rapid a change of temperature) and cooled in a suitable bath, *e.g.*, of crushed ice. The inner test-tube is provided with a thermometer and a stirrer (preferably of glass), and is supported by means of a clamp. Sufficient substance is introduced to cover the bulb of the thermometer when completely molten. The compound is

---

* A substance which commences to soften and pull away from the sides of the capillary tube at (say) 120°, with the first appearance of liquid at 121° and complete liquefaction at 122° with bubbling, would be recorded as m.p. 121–122° (decomp.), softens at 120°.

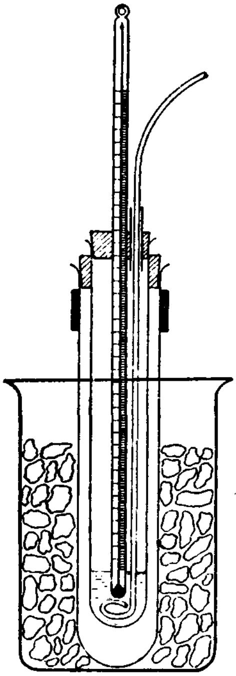


Fig. *II*, *10*, 4.

first melted, *e.g.*, by immersing the tube in warm water, the apparatus set up as in the figure, and the appropriate cooling mixture placed in the beaker (cold water, ice or a freezing mixture, according to the melting point of the substance) so that the rate of cooling is about 0·5° per minute. Both the liquid substance and the cooling bath are kept well stirred, and temperature readings are taken at half-minute or one minute intervals ; this is continued until the compound has fully solidified. Upon plotting temperatures (ordinates) against time (abscissae), a horizontal portion will be obtained in the cooling curve, if the substance is pure (compare Section **I,13**) ; this corresponds to the **freezing (or setting) point.** It is advisable to determine the melting point also. The cooling bath is removed and replaced, if the substance melts above room temperature, by a bath of warm water. Stirring is continued as before and temperatures are observed at regular intervals until the substance is completely fluid. Upon plotting the temperature-time graph (heating curve), the break in the curve (horizontal portion for a pure substance) takes place at the **melting point.** For pure compounds the melting point and freezing point are identical. It must be emphasised that the above method applies only to substances which melt without decomposition.

II,11. MISCELLANEOUS FORMS OF MELTING POINT APPARATUS

Several forms of apparatus employing electrical heating will be described. A simple form may be readily constructed from a domestic " electric iron " of 400–500 watts rating. The handle is removed, and two holes of 8 mm. diameter are drilled through the base (*ca.* 11 mm. thick) so that they meet in the centre of the block. One hole is for a 360° thermometer (small bulb) ; the other hole is spare and can be used for comparison with a standard thermometer. The heater is mounted on a sheet of thick asbestos board which is fixed to an appropriate wooden base. The wires from the heating unit are connected to two insulated terminals fitted on the board (Fig. *II*, *11*, 1). The rate of heating is controlled by either of the following methods :

(i) A rheostat (*e.g.*, a Zenith double-tubular sliding adjustable resistance type D with lead-screw motion, 230 ohms resistance to carry 2·8 amperes, is suitable).

(ii) A variable voltage transformer (*e.g.*, a Variac transformer, enclosed model, type 200-CMH, is satisfactory ; a compact assembly is thus obtained).

With a little experience, the correct setting for any desired rate of heating (from rapid heating to about 1° per minute) may be obtained.

The area immediately over the bulb of the thermometer has a uniform temperature, and is employed for melting point determinations. The exact size of the uniform temperature area is determined by spreading a solution of a substance possessing a conveniently low melting point (*e.g.*, urea) over the surface of the plate, and evaporating the solution by raising the temperature of the hot plate slightly. A thin coating of the substance remains on the surface. The temperature is then raised rapidly until within 5–10° of the melting point, after which the heating is adjusted to give a temperature rise of about 1° per minute. The area inside which the substance melts within 0·5° of the melting point (132° for urea) is noted; it is convenient to mark this first (temporarily) with chalk and later (permanently) with a diamond. The process may be repeated, if desired, with other substances of different melting points, but substantially the same result will be obtained. To determine the melting point of a substance, a small quantity of the substance is finely powdered and placed in the centre of the area of constant temperature. The temperature is raised comparatively rapidly to within 3° or 4° of the melting point and then the temperature rise is reduced to 0·5–1° per minute. The moment an instantaneous fusion is observed, the temperature is read and is recorded as the melting point of the substance. The apparatus is allowed to cool somewhat, and the surface of the heater is wiped with glass wool or, cautiously, with a damp cloth.

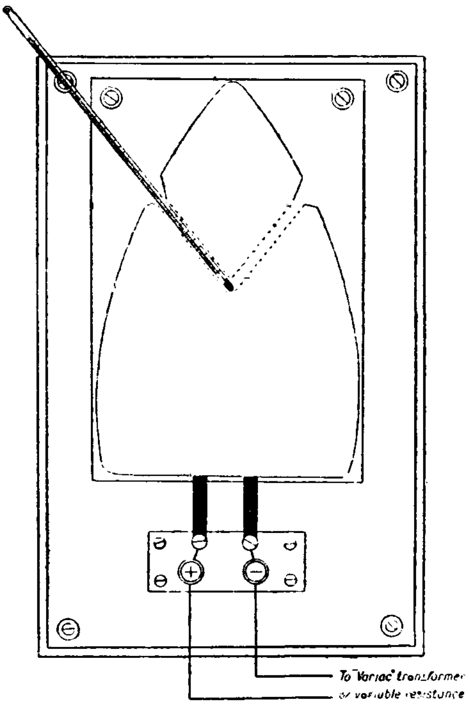


Fig. *II*, *11*, 1.

The advantages of the above "electric hot plate method" for the determination of melting points are obvious; these include :—

(1) The elimination of the liquid baths and, in consequence, the absence of burns due to accidental breakage of the ordinary glass apparatus.

(2) No glass melting point capillaries need be prepared.

(3) The wide temperature range covered (room temperature to 360° and even higher, if necessary).

(4) Several melting points can be simultaneously determined; the substances must of course be placed in separate minute heaps in the constant temperature area on the surface of the apparatus.

The only disadvantage is that the procedure does not give accurate results if the compound sublimes: the capillary tube method should be used in such cases, and it may be necessary to employ a sealed capillary tube. This apparatus should find a place in every laboratory. It is strongly recommended as a desirable alternative to that involving the use of a liquid bath and a capillary tube. Possible improvements for precision work are (*a*) replacement of the chromium-plated surface by a plating of a noble metal or alloy in order to increase its resistance to the action of liquid organic compounds, and (*b*) a purpose-made internal resistance so designed as to increase the area of constant temperature.

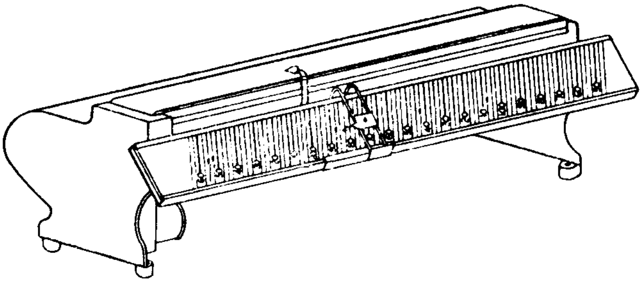


Fig. *II*, *11*, 2

The **Kofler hot bench**,[*] illustrated in Fig. *II*, *11*, 2, consists of a metal alloy band with chromium-plated surface, 36 cm. long and 4 cm. wide, heated electrically at one end, the other end remaining unheated. It is claimed that a moderate and constant temperature gradient is thus produced. Fluctuations in the mains voltage are compensated for by a built-in stabiliser. At any point from the heated end, there is a definite and constant temperature. The graduations cover the range 50° to 260° C. in 2°. Provision is made for variations in room temperature by adjustment on the reading device moving over the scale. The current must be switched on at least one hour before the apparatus is required and the latter should be surrounded by a screen to protect it from draughts. The hot bench should be calibrated before use with the aid of several of the substances supplied by the manufacturers. The test substances include:—azobenzene, m.p. 68°; benzil, m.p. 95°; acetanilide, m.p. 114°; phenacetin, m.p. 135°; benzanilide, m.p. 163°; salophene (acetylaminosalol), m.p. 190°; and saccharin, m.p. 228°. The melting point is

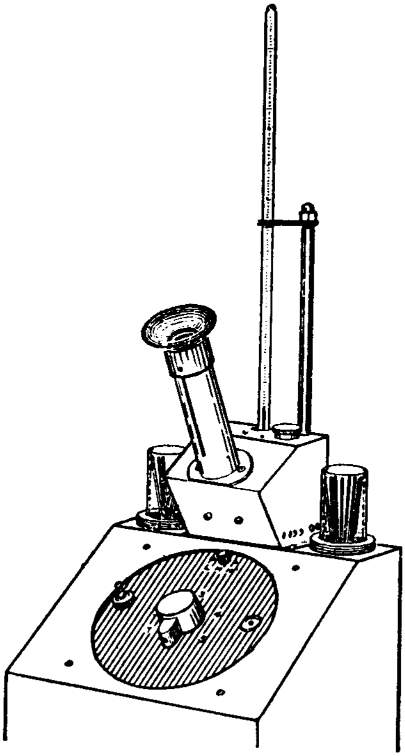


Fig. *II*, *11*, 3.

---

[*] Manufactured by C. Reichert Akt., Wien xvii, Austria. It is available from Shandon Scientific Company, 6 Connaught Place, London, S.W. 7.

readily determined by sprinkling a few small crystals of the substance on the hot bench; these may be moved along the bench by the brass lancet attached to the reading device. Usually a sharp division occurs between the solid and liquid, and the temperature corresponding to the line of demarcation is read off on the scale. For maximum accuracy, the apparatus should be recalibrated with two test substances with melting points close to that of the unknown. The procedure is clearly rapid and is very useful for substances which tend to decompose upon gradual heating. It is important not to allow any of the molten substance to remain on the chromium-plated surface for long periods; it should be wiped away with clean filter paper immediately after the experiment. It is an advantage to platinise the surface of the heating bar; possible attack by organic substances is thus avoided.

A commercial form of electrically-heated melting point apparatus,* designed for the simultaneous observations of two *capillary tubes*, is shown in Fig. *II*, *11*, 3. A copper block, bored with holes for the capillaries and the thermometer, is wound with glass-covered resistance wire; special provision is made for various rates of heating by the incorporation of a specially tapped transformer. There is a central hole for viewing the capillaries, but this hole terminates near the central thermometer opening; the capillaries are illuminated by reflected light from a 6-volt lamp passing down a solid glass rod in an opening on the same level as the viewing hole but at an angle to it.

II,12. EXPERIMENTAL DETERMINATION OF THE BOILING POINT

The theory of the process is discussed in Sections **I,1–I,3**. The apparatus of Fig. *II*, *12*, 1 may be used when moderate quantities of the substance are available. *A* is a 50 ml. distilling flask attached by a cork to a Liebig condenser *B*, upon the end of which an adapter *C* is fitted: *D* is a receiver for collecting the distillate. The thermometer *E* is fitted into the neck of the distilling flask by means of a well-bored cork; the bulb of the thermometer should be in the centre of the neck of the flask and slightly below (*ca.* 5 mm.) the level of the side tube. The flask may be heated on a wire gauze with asbestos centre or preferably in an air bath (Fig. *II*, *5*, 3).

The following hints on the setting up of the apparatus will be useful for beginners.

1. All corks should fit tightly, since the apparatus may be used for inflammable liquids.
2. All clamps holding glass apparatus should be lined with cork, attached by means of glue or "seccotine", or with asbestos paper; this will reduce the danger of fracture if excessive pressure is exerted on the clamp.
3. The flask, condenser and receiver should be set up independently with such clamps as are necessary and arranged at the back of the apparatus in as nearly the correct position as possible.

---

* This is the "Reflected Light Melting Point Apparatus" marketed by Townson and Mercer Ltd., Croydon, England.

4. The size of the flask to be employed depends upon the quantity and nature of the liquid to be distilled ; it should be one half or at most two-thirds full. If too large a flask is used, superheating and, sometimes, decomposition may occur.

5. The upper outlet for water from the condenser should be above the jacket so as to ensure that the condenser is full of water. If the rubber tube, which carries the waste water to the sink, tends to kink, a short copper spiral, made by winding a length of copper wire round a glass tube, may be slipped over the end attached to the condenser.

The liquid should be poured into the distilling flask, preferably through a funnel the stem of which extends below the side arm, and a few fragments of unglazed porous porcelain (" porous pot," see Section **I,2**) added, and the thermometer placed in position. The " porous pot " will promote regular ebullition in the subsequent heating ; they should ***never*** be added to the hot liquid. The flask is heated on a wire gauze or in an air bath. Heating may be rather rapid until boiling commences ; the flame must then be decreased and adjusted so that the distillate is collected at the rate of one or two drops per second. It must be borne in mind that at the commencement of the distillation it takes an appreciable time for the vapour to heat the upper part of the flask and the thermometer. The distillation should not be conducted too slowly, for the thermometer may momentarily cool from lack of a constant supply of fresh vapour on the bulb, and an irregular boiling point will result ; on the other hand, the flame should not be too large for it may heat directly a part of the vapour as well as the liquid, and superheating may occur.

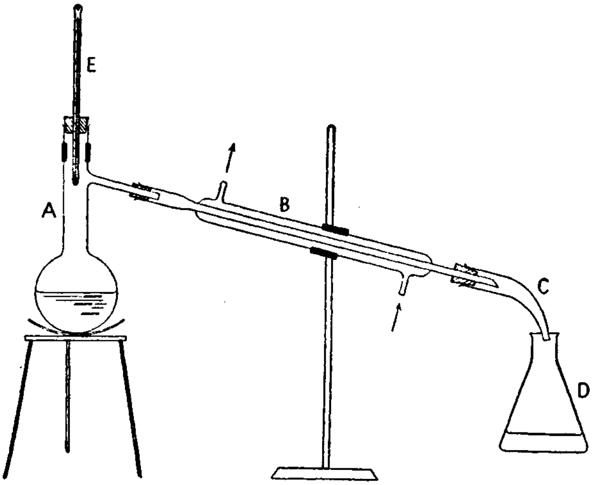


Fig. *II, 12,* 1.

It will be found that the temperature will first rise rapidly until it is near the boiling point of the liquid, then slowly, and finally will remain practically constant. It is a good plan to watch for the ring of condensing vapour in the neck of the flask and to attempt to hold this at least about one cm. above the side arm of the flask by appropriately controlling the flame. The distillation should be continued until only a small volume of liquid remains in the flask ; the temperature is noted at regular intervals. If the liquid is pure, most of it will pass over at constant temperature (within 0·5°) ; this constant temperature is **the boiling point of the liquid.** Towards the very end of the distillation the temperature may rise slightly owing to superheating. The necessary correction to the thermometer, as determined from the calibration chart, should be applied in order to obtain the correct boiling point.

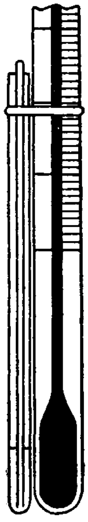
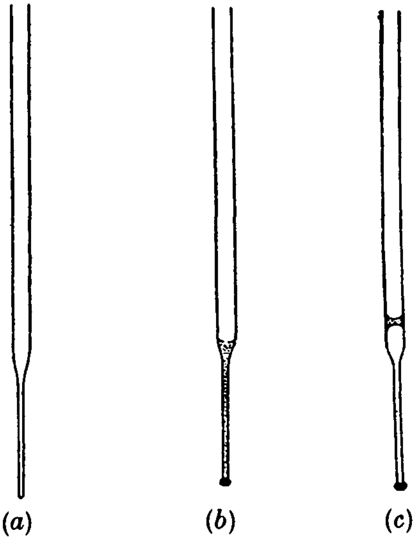


Fig. *II*, *12*, 2.

When the boiling point of the liquid is above 140–150°, an air condenser (Fig. *II*, *4*, 1, *c*) may replace the water condenser. If the liquid is inflammable, the conical flask may be replaced by a filter or suction flask (see Fig. *II*, *1*, 7, *c*), and a length of rubber tubing leading to the sink is attached to the side tubulure.

When only minute quantities of liquid are available, either of two **micro methods for the determination of the boiling point** may be used.

Method 1 (**Siwoloboff's method, 1886**).—Two tubes, closed at one end, are required ; one, an ordinary melting point capillary, 90–110 mm. long and 1 mm. in diameter, and the other, 80–100 mm. long and 4–5 mm. in diameter. The latter may be prepared from 4–5 mm. glass tubing and, if desired, a small thin bulb, not exceeding 6 mm. in diameter, may be blown at one end. A small quantity of the liquid, 0·25–0·5 ml. (depending upon the boiling point), is placed in the wider tube, and the capillary tube, with sealed end uppermost, is introduced into the liquid. The tube is then attached to the thermometer by a rubber band (Fig. *II*, *12*, 2), and the thermometer is immersed in a bath of a melting point apparatus (see Fig. *II*, *10*, 2). As the bath is gradually heated there will be a slow escape of air bubbles from the end of the capillary tube, but when the boiling point of the liquid is attained, a rapid and continuous escape of air bubbles will be observed. The reading of the thermometer when a rapid and continuous stream of air bubbles first emerges from the capillary tube is the boiling point of the liquid. Unless the temperature is raised very slowly in the vicinity of the boiling point of the liquid, the first determination may be slightly in error. A more accurate result is obtained by removing the source of heat when the rapid stream of bubbles rises from the end of the capillary tube ; the speed at which bubbles are given off will slacken and finally,



(*a*) (*b*) (*c*)

Fig. *II*, *12*, 3.

when the last bubble makes its appearance and exhibits a tendency to suck back, the thermometer is read immediately. This is the boiling point of the liquid because it is the point at which the vapour pressure of the liquid is equal to that of the atmosphere. As an additional check on the latter value, the bath is allowed to cool a few degrees and the temperature *slowly* raised; the thermometer is read when the first continuous series of air bubbles is observed. The two thermometer readings should not differ by more than 1°.

Method 2 (Emich's method).—A capillary tube about 10 cm. long and of about 1 mm. bore is used. One end is drawn out by means of a micro flame into a capillary with a very fine point and about 2 cm. long as in Fig. *II, 12,* 3, *a*. Such a capillary pipette may also be constructed by suitably drawing out soft glass tubing of 6–7 mm. diameter. The tube (*a*) is then dipped into the liquid of which the boiling point is to be determined; the liquid will rise slowly by capillary attraction, and the tube is removed when the liquid has filled the narrow conical portion. The capillary end is then sealed by merely touching with a minute flame. A small air bubble is formed in the point of the capillary; it should be examined with a lens to make sure that it is not too large. A convenient size is 1–3 mm. long (Fig. *II, 12,* 3, *b*). The prepared capillary tube is then attached to a thermometer as in a melting point determination (Section II,10) and slowly heated in an open bath, which is kept well stirred. The capillary is best observed with a lens. When the bubble enlarges (as in Fig. *II, 12,* 3, *c*) and begins to exhibit signs of upward motion, the flame is removed or considerably lowered. The temperature at which the bubble reaches the surface of the bath liquid is the boiling point of the liquid. The bath is allowed to cool about 10° below the first observed boiling point, then *slowly* heated again, and a second determination of the boiling point is made.

II,13. TYPICAL ASSEMBLIES OF APPARATUS FOR DISTILLATION AND REFLUXING

In order to avoid duplication of diagrams in the actual description of preparations given in Chapters III *et seq.*, the set-up of apparatus involving the processes of distillation or refluxing will be collected in this section. Heating in all cases may be on an asbestos-centred wire gauze, in a water or oil bath, or, best, by means of an air bath (Fig. *II, 5,* 3): the manner of heating the vessel (distilling flask, flask, etc.) will therefore not be shown in the diagrams. Adapters may be employed, as in Fig. *II, 13,* 3, where the receiver cannot be conveniently supported at the end of the condenser.

Fig. *II, 13,* 1 illustrates a distillation unit when it is desired to protect the distillate from moisture in the atmosphere. The "drying tube" may be filled with anhydrous calcium chloride held in position by loose plugs of glass wool or with a loose plug of cotton wool. Fig. *II, 13,* 2 depicts the use of an air condenser for liquids of boiling point above 140–150°.

In Fig. *II, 13,* 3 the distillation is conducted from a flask. This apparatus is used when it is desired to distil the product of a reaction which has been conducted in a round-bottomed flask. It is not recommended when a distilling or Claisen flask can be used. The apparatus may also be employed for the distillation of inflammable or other solvents from a solution; here the receiver should be a filter flask as in Fig. *II*, *13*, 4.

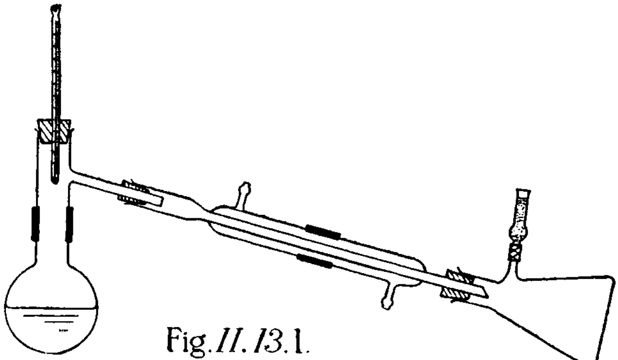


Fig. *II*. *13*.1.

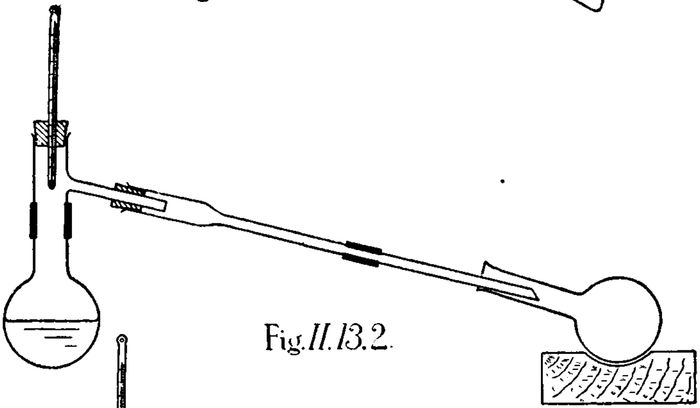


Fig. *II*. *13*.2.

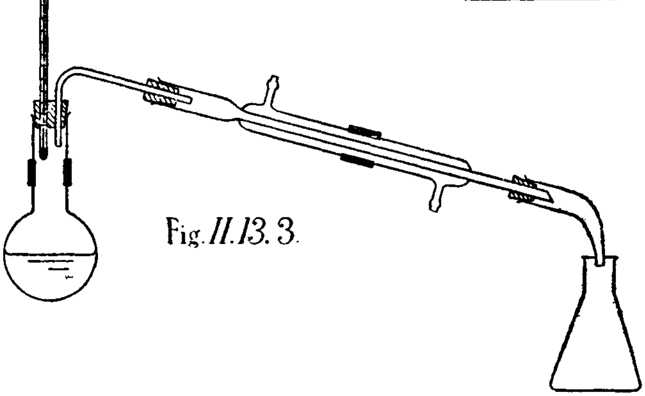


Fig. *II*. *13*. 3.

In certain circumstances it may be necessary to introduce a short fractionating column between the flask and the condenser; the thermometer is then inserted at the top of the column.

Fig. *II*, *13*, 4 shows an assembly which is useful *inter alia* for distilling off solvents from solutions. The solution is placed in the separatory funnel and is allowed to drop into the flask, initially about half-full with the solution, at approximately the same rate as that at which the solvent distils into the receiver. The use of a large flask for distilling the solution is thus rendered unnecessary. The distilling flask (alternatively, a Claisen flask or Claisen flask with fractionating side arm, see Figs. *II*, *13*, 6 and *II*, *13*, 5, may be used, particularly if the residue is to be ultimately distilled under diminished pressure) should have a capacity of about twice the estimated volume of the residue after the removal of the solvent. The adapter may be omitted, if desired, and the end of the

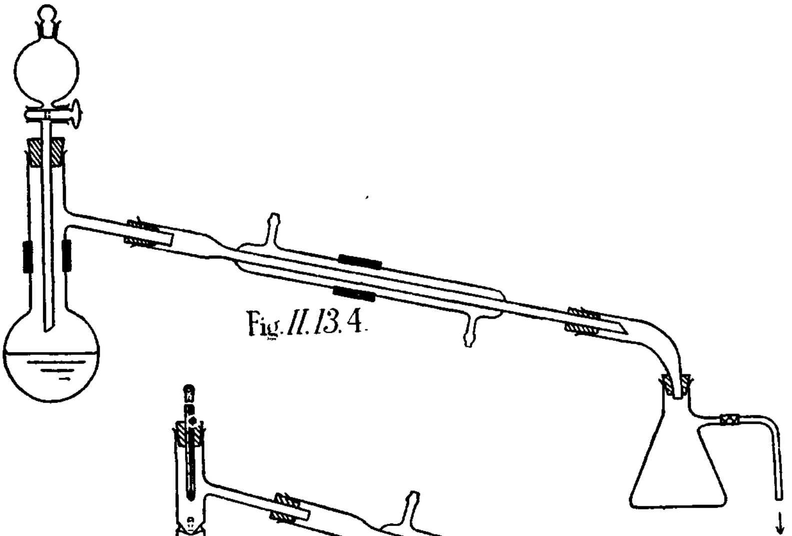


Fig. *II*. *13*. 4.

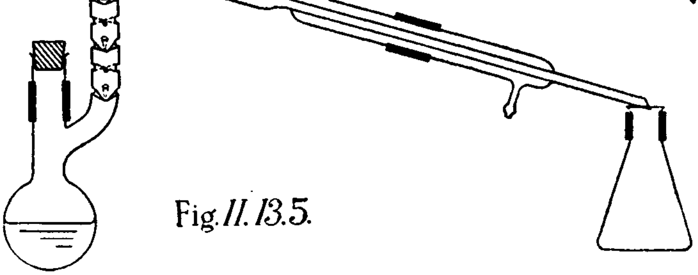


Fig. *II*. *13*. 5.

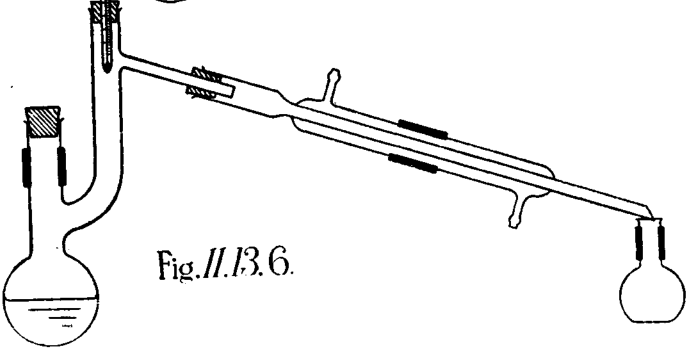


Fig. *II*. *13*. 6.

condenser fitted directly into the filter flask. The removal of the solvent in this manner is sometimes termed **flash distillation.**

Figs. *II*, *13*, 5 and *II*, *13*, 6 illustrate the use of a Claisen flask with fractionating side arm and an ordinary Claisen flask respectively.

Figs. *II*, *13*, 7 and *II*, *13*, 8 depict various set-ups which involve the refluxing of a liquid ; the Liebig condenser may, of course, be replaced by a double-surface condenser. In Fig. *II*, *13*, 7 a " calcium chloride " guard protects the contents of the flask from ingress of moisture. The device at the top of the condenser in Fig. *II*, *13*, 8, *a* is for the absorption of a water-soluble gas (hydrogen chloride, hydrogen bromide or sulphur dioxide) : it should be noted that the tube is just *above* the level of the liquid in the flask. Alternatively, an inverted funnel (Fig. *II*, *13*, 8, *b*) may be employed for the absorption of gases.


Fig. *II*, *13*, 7.

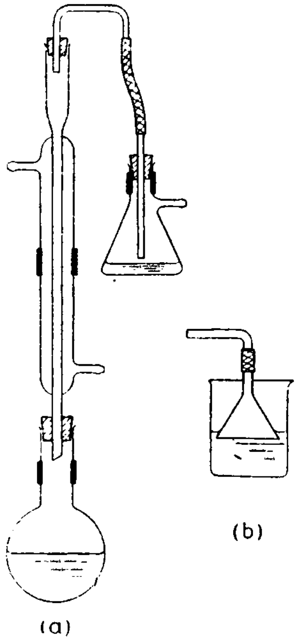


Fig. *II*, *13*, 8.

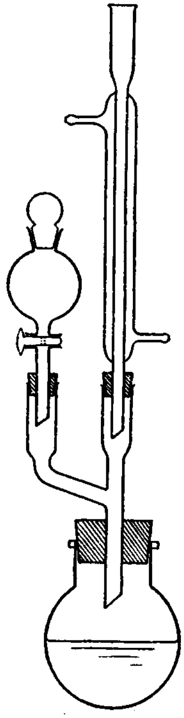


Fig. *II*, *13*, 9.

Fig. *II*, *13*, 9 depicts the use of a two-way adapter arranged for simultaneous addition of a reagent from a dropping funnel and refluxing. An equivalent result may, of course, be obtained by inserting a long-necked, suitably-bent separatory funnel and a condenser through a cork into a flask. The two-way adapter is convenient when a comparatively narrow-necked flask is employed.

Apparatus permitting the use of stirring combined with refluxing and/or the addition of a reagent is described in Section **II,7** (Figs. *II*, *7*, 11 and *II*, *7*, 12).

II,14. FIRE HAZARDS ATTENDING THE DISTILLATION OF INFLAMMABLE SOLVENTS

The inflammable solvents most frequently used for reaction media, extraction or recrystallisation are diethyl ether, petroleum ether (b.p. 40–60° and higher ranges), carbon disulphide, acetone, methyl and ethyl alcohols, di-*iso*-propyl ether, benzene, and toluene. Special precautions must be taken in handling these (and other equivalent) solvents if the danger of fire is to be more or less completely eliminated. It is advisable to have, if possible, a special bench in the laboratory devoted entirely to the recovery or distillation of these solvents ; no flames are permitted on this bench.

Ether. The most satisfactory method for the removal of (diethyl) ether is either on a steam bath fed from an external steam supply or by means of an electrically-heated, constant-level water bath (Fig. *II*, *5*, 1). If neither of these is available, a water bath containing hot water may be used. The hot water should be brought from another part of the laboratory ; under no circumstances should there be a free flame under the water-bath. It cannot be too strongly emphasised that no flame whatsoever may be present in the vicinity of the distillation apparatus : a flame 10 feet away may ignite diethyl ether if a continuous bench top lies between the flame and the still and a gentle draught happens to be blowing in the direction of the flame.

Carbon disulphide. It is best to use a water bath maintained at a temperature of 60°–80°.

Solvents with boiling points below 90–95°. A steam bath or water bath should be employed. Alternatively, the apparatus of Fig. *II*, *13*, 3, but with a filter flask as receiver, may be used; the end of the rubber tubing attached to the tubulure is either placed in the sink or allowed to hang over the bench. If a distillation is ultimately to be conducted in the flask from which the solvent is removed, the apparatus depicted in Fig. *II*, *13*, 4 is recommended : the distilling flask may be replaced by a Claisen flask or a Claisen flask with fractionating side arm, particularly if the subsequent distillation is to be conducted under diminished pressure.

It must be borne in mind that in spite of the fact that the solvents have normal boiling points below 90–95°, they cannot always be completely removed by heating on a steam or water bath when they form part of mixtures with less-volatile liquids. Simple distillation may lead to mixtures with higher boiling points than the individual solvents, so that separation of the latter may not be quite complete. In such cases the distillation should be completed with the aid of an air bath (Fig. *II*, *5*, 3) or an oil bath ; the fire hazard is considerably reduced since most of the solvent will have been removed.

Solvents with boiling points above 90–95°. The apparatus of Fig. *II*, *13*, 3 (with closed filter flask and rubber lead-off tube) or of Fig. *II*, *13*, 4 (see discussion in previous paragraph but one) should be utilised with an air bath or oil bath as the source of heat. Heating on a wire gauze is not recommended.

II,15. FRACTIONAL DISTILLATION. DISTILLATION WITH A FRACTIONATING COLUMN

An account of the elementary theory of fractional distillation is given in Section **I,4**. Fractionating columns suitable for both elementary and advanced work will be described in the following pages.

A fractionating column of moderate efficiency is the **Vigreux column**, shown in Fig. *II 15*, 1. This column is made by indenting a glass tube so that the points of a pair of indentations almost touch each other: the indentations should have a slight downward slope when the tube is vertical. It is essential to arrange the pairs of indentations so that they form a spiral of glass inside the tube; it should not be possible for the vapour to pass directly through the whole length of the tube without meeting at least one indentation.

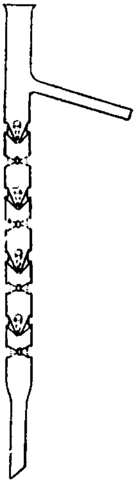


Fig. *II*, *15*, 1.

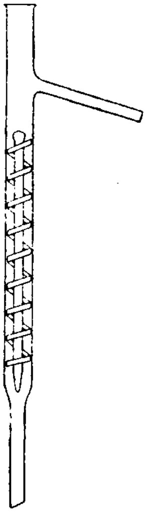


Fig. *II*, *15*, 2.

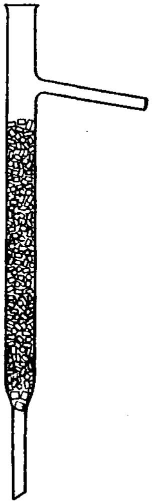


Fig. *II*, *15*, 3.

Fractionating columns of greater efficiency than the simple Vigreux column are illustrated in Figs. *II*, *15*, 2, *II*, *15*, 3 and *II*, *15*, 5. The **all-glass Dufton column** (Fig. *II*, *15*, 2) is a plain tube into which a solid glass spiral, wound round a central tube or rod, is placed. The spiral must fit tightly inside the tube in order to prevent leakage of any appreciable amount of vapour between the walls of the column and the spiral; this is best ensured by grinding the edges of the spiral into the tube. Typical dimensions are: spiral, 15–30 cm. long fitted inside a tube of 20 mm. diameter; hollow tube, sealed at both ends and round which the spiral is tightly wound, 13 mm. external diameter; turns of glass spiral, 10–13 mm. apart. The **Hempel column** (Fig. *II*, *15*, 3) is a simple glass tube, 30–40 cm. long and 15–25 mm. diameter, filled to within 5 cm. of the side arm with a suitable packing. For general use $\frac{1}{4}'' \times \frac{1}{4}''$ hollow glass rings (or a smaller size, if available) are quite satisfactory. Excellent packings for columns may be purchased * either in

---

* Supplied *inter alia* by the Hydronyl Syndicate Ltd. More expensive column packings, such as Fenske helices, are described in Section **II,17**.

the form of hollow rings (sometimes termed **Raschig rings**) (Fig. *II*, *15*, 4, *a*) or as hollow rings with a central partition (**Lessing rings**) (Fig. *II*, *15*, 4, *b*). The Lessing rings consist of hollow cylinders of approximately equal height and diameter with a central partition when made of porcelain; when constructed of metal, there is a gap in the circumference and a more or less diametrical partition connected on one side with the cylinder but out of touch on the opposite side (Fig. *II*, *15*, 4, *c*). The provision of the central partition increases the efficiency of the packing material by adding to the contact surface available and enhancing the drainage capacity. For most purposes $\frac{3}{16}''$ Lessing rings of porcelain may be used; plain porcelain rings $\frac{1}{8}''$ diameter are somewhat more efficient. If the substances being distilled do not attack aluminium, $\frac{1}{8}''$ Lessing rings of this metal afford the most efficient packing of general utility. No difficulty is experienced in filling a Hempel column (15–20 mm. diameter) with hollow cylinders of $\frac{1}{4}''$ or $\frac{3}{16}''$ size; the column is laid on its side, about one quarter filled with the packing material, and the column rapidly turned to the vertical position. It will be found that the promiscuous arrangement of the hollow cylinders will be such as to prevent them falling through the somewhat narrower lower end of the column. The column may then be filled to within 4–5 cm. of the side arm. Indentations may be made, if desired, in the lower portion of the column, but this is usually unnecessary. For packing of $\frac{1}{8}''$ size (and occasionally for the $\frac{3}{16}''$ size), two or three $\frac{1}{4}''$ cylinders of the same material as the smaller size will be found to provide a suitable support.

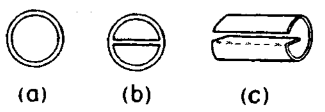


Fig. *II*, *15*, 4.

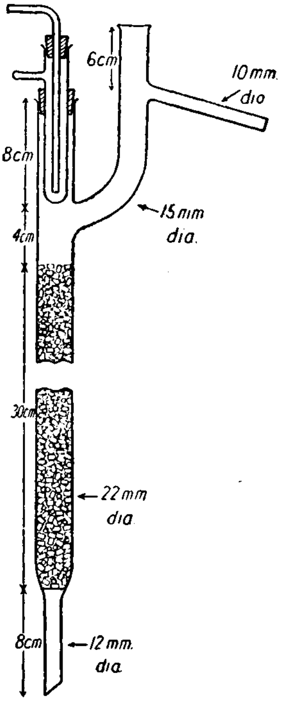


Fig. *II*, *15*, 5.

A modified Hempel column, which incorporates a small reflux condenser ("cold finger" or "cold spot condenser"), is shown in Fig. *II*, *15*, 5. The partial condenser can be raised or lowered to decrease or increase the amount of refluxing liquid, and further control is provided by the rate at which cold water is passed through the "cold finger." The reflux condenser thus controls the volume of liquid returned to the column and therefore permits the effective use of the whole length of the column for the fractionation. The **reflux ratio** is the quotient of the amount of liquid returning through the column to the amount collected in the receiver during the same interval of time. The efficiency of separation of a mixture can be improved by increasing the reflux ratio (say, from 1 : 1 to 10 : 1 or even higher), but care must be taken to avoid flooding the column with liquid. Flooding will diminish the contact area between the vapour and the liquid, and the pressure of the rising vapour may force the liquid upwards in the column. Flooding may be avoided by suitable insulation and control of the rate of heating. The column may be charged with $\frac{1}{4}''$ × $\frac{1}{4}''$ (or smaller) glass rings or with any of the packing materials described in the previous paragraph.

It is desirable to surround all the fractionating columns described above either by a glass jacket (held in position by split corks) or by a layer or two of asbestos cloth (held in place by turns of stout copper wire). The insulation will reduce the effect of draughts, and will improve the performance of the column. For liquids of boiling point above 100°, lagging of the column and of the side tube with at least two thicknesses of asbestos cloth is essential. In order to obtain improved results for liquids of high boiling point, the column should be heated electrically to a temperature only a few degrees below the boiling point of each component of the mixture. This is most easily done by winding electric heating tape of $\frac{1}{2}''$ diameter round the column : a thermometer, with scale exposed, is embedded in the windings. Alternatively, the heating tape may be covered with asbestos cloth and a thermometer held in position between the heating tape and the layer of asbestos cloth. The tape is connected to the mains through an adjustable resistance, energy regulator or a variable transformer (Variac).

II,16. SIMPLE APPARATUS FOR FRACTIONATION

Fig. *II, 16,* 1 illustrates a set-up for simple fractionation : a Hempel column is shown, but it may be substituted by a modified Hempel, a Vigreux or an all-glass Dufton column. The Hempel column may be filled with $\frac{1}{4}''$ glass rings, $\frac{3}{16}''$ porcelain Lessing rings, or with $\frac{1}{8}''$ porcelain rings. The mixture to be fractionated is placed in a bolt-head flask of convenient size (it should be one third to one half full), a few fragments of porous porcelain added, the column fixed in position, and a water condenser attached to the side arm. The distillate is collected in small flasks or in test-tubes. The bulb of the thermometer should be just below the level of the side arm. It is advisable to lag the column by wrapping asbestos cloth round it ; this will minimise the effect of draughts in producing excessive cooling. Lagging of the column is essential if the boiling point of any of the components exceeds 100°

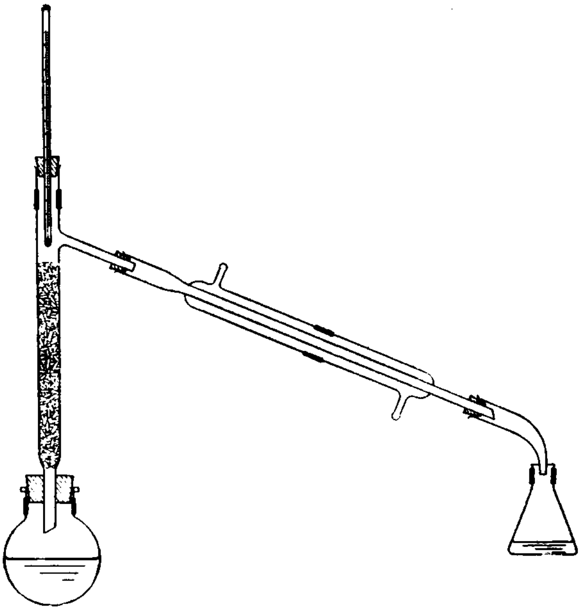


Fig. *II, 16,* 1.

(compare previous paragraph). The flask is then heated with a small flame, protected from draughts so as to ensure a uniform heating ; an air bath (Fig. *II*, *5*, 3) gives better results. The initial heating must not be hurried as owing to the considerable extra condensation which occurs whilst the column is warming up, the latter may easily choke with liquid. Once distillation has commenced, the size of the flame is adjusted so that the liquid passes over at the rate of one drop every two or three seconds. Under these conditions fairly efficient fractionation should be obtained. When the low boiling point fraction has passed over, distillation should cease. The heating is then slowly increased, and a sharp rise in boiling point should occur as the second fraction commences to distil ; it is assumed, of course, that the fractionating system is capable of effecting a sharp fractionation of the components of the mixture. If the set-up is inefficient, a relatively large intermediate fraction may be obtained. It is desired to emphasise the fact that the distillation must be conducted slowly ; no time is usually saved by distilling rapidly since a second fractionation will then be necessary.

II,17. IMPROVED APPARATUS FOR FRACTIONAL DISTILLATION

A detailed discussion of the theory underlying modern developments in fractional distillation is outside the scope of this volume,* but a brief description of the terms used in discussing fractionating columns and the chief *desiderata* of efficient columns will be given. The **capacity** of a column is a measure of the quantity of vapour and liquid which can be passed counter-current to each other in a column without causing it to choke or flood. The **efficiency** of a column is the separating power of a definite length of the column ; it is measured by comparing the performance of the column with that calculated for a theoretically perfect plate column under similar conditions. A **theoretical plate** is defined as a section of a distilling column of such length that the vapour comes to equilibrium with the liquid, *i.e.*, the vapour leaving the " plate " has the same composition as the vapour entering it and the vapour ascending from the " plate " is in equilibrium with the liquid descending from it. The number of theoretical plates cannot be determined from the dimensions of the fractionating column ; it is computed from the separation effected by distillation of a liquid mixture (*e.g.*, benzene and toluene ; benzene and carbon tetrachloride ; benzene and dichloroethane ; *n*-heptane and methyl*cyclo*hexane), the vapour and liquid compositions of which are accurately known.† An ordinary one cm. tube one metre long might be equivalent to only one theoretical plate, whilst the same tube filled with a suitable packing can give the equivalent of 20 or more theoretical plates. A column with 12 theoretical plates is satisfactory for the practical separation of a mixture of benzene and toluene. The effectiveness of a column depends upon the height as well as upon the

---

* See, for example, A. Weissberger (Editor), *Technique of Organic Chemistry*, Volume IV. *Distillation*, 1951 (Interscience).

† For experimental details, see, for example, Daniels, Matthews and Williams, *Experimental Physical Chemistry*, 4th Edition, 1949, p. 95 (McGraw-Hill).

packing or internal construction, hence the efficiency is frequently expressed in terms of the **height equivalent per theoretical plate (H.E.T.P.)**. It is obtained by dividing the height by the number of theoretical plates, and is usually stated in cm. For the comparison of the relative efficiencies of fractionating columns, the operating procedure should be standardised.

The ideal fractionation yields a series of sharply defined fractions, each distilling at a definite temperature. After each fraction has distilled, the temperature rises rapidly, no liquid being distilled as an intermediate fraction. If the temperature is plotted against the volume of the distillate in such an ideal fractionation, the graph obtained is a series of alternate horizontal and vertical lines resembling a staircase. A more or less sloping break reveals the presence of an intermediate fraction and the amount of such fraction can be used as a qualitative criterion of the performance of different columns. The ultimate aim in the design of efficient fractionating columns is to reduce the proportion of the intermediate fractions to a minimum. The most important factors which influence the separation of mixtures into sharp fractions are the following :

(1) **Thermal insulation.** Even slight heat losses considerably disturb the delicate equilibrium of an efficient column, and almost perfect thermal insulation is required for the separation of components with boiling points only a few degrees apart. Theoretically, the greatest efficiency is obtained under adiabatic conditions. If the components boil below 100°, a silvered vacuum jacket is satisfactory ; the efficiency of such a jacket will depend upon the care with which it is cleaned, silvered and exhausted. In general, the most satisfactory insulation is provided by the application of heat to balance the heat loss. An electrically-heated jacket is fitted round the column ; the temperature of the jacket, which should be controlled by means of an external resistance or a variable voltage transformer (Variac), should be adjusted within 5° of the temperature of the vapour condensing at the upper end of the column.

(2) **Reflux ratio.** This is defined as the ratio between the number of moles of vapour returned as refluxed liquid to the fractionating column and the number of moles of final product (collected as distillate), both per unit time. The reflux ratio should be varied according to the difficulty of fractionation, rather than be maintained constant ; a high efficiency of separation requires a high reflux ratio.*

Otherwise expressed, the number of theoretical plates required for a given separation increases when the reflux ratio is decreased, *i.e.*, when the amount of condensed vapour returned to the column is decreased and the amount distilled off becomes greater.

(3) **Hold-up of column.** The hold-up of liquid should be reduced to a minimum compatible with scrubbing effectiveness and an adequate column capacity. The ratio of charge of the still to the hold-up of the

---

* The more difficult the fractionation, the greater the reflux ratio to be employed. Thus for compounds differing only slightly in boiling point, this may be as high as 50 to 1 ; for liquids of wider boiling point range, thus permitting of fairly easy separation, a reflux ratio of 5 or 10 to 1 may be used.

Beyond certain limits increase of the reflux ratio does not appreciably increase the separating power or efficiency of the column. As a rough guide, if the column has an efficiency of n plates at total reflux, the reflux ratio should be between $2n/3$ and $3n/2$.

column should be as large as possible ; in general, the still charge should be at least twenty times the hold-up.

(4) **Packing.** The column should spread the returning liquid over a considerable surface so that the exchange with the vapour is facilitated.

(5) **Time of distillation.** For any column there is always an optimum time of distillation below which accuracy is sacrificed and above which the slightly improved separation does not justify the extra time taken. For most laboratory columns this will vary between 1 hour and 8–10 hours.

An electrically-heated jacket is easily constructed from two pieces of Pyrex glass tubing of such a length as to extend from the bottom of the head to just above the lower end of the column—the latter may carry a ground joint. The inner tube may be of 35 mm. bore and the outer tube of 55 mm. bore : this allows room for the column with attached thermometer inside the inner tube (compare Fig. *II, 17,* 2). The narrow tube is wound with ½" electric heating tape ; heat input is controlled by a resistance, energy regulator or a variable transformer. The ends of the jacket are closed with asbestos or other insulating board of convenient size and shape.

The efficient fractionating columns in general use may be divided into two main groups :—

(*a*) Those incorporating metal spirals or coils (Dufton, Podbielniak) or glass spirals (all-glass Dufton, Widmer).

(*b*) Columns filled with various packings, *e.g.*, conical disc type of fine stainless steel gauze (Stedman columns), hollow rings in glass, porcelain and various metals (Raschig rings), hollow rings with partition in centre made of porcelain and various metals (Lessing rings), small gauze rings in " staybrite " steel (Dixon rings), and helices in glass (Fenske rings), stainless steel, monel metal, nichrome and nickel.

Examples from each group will now be given with especial reference to those columns which are comparatively inexpensive. A brief description will also be given of two highly efficient fractionating columns, which are available commercially ; these, as well as the Podbielniak and Stedman types, although giving excellent results, are too expensive for the average laboratory.

An **all-glass Dufton column** has been described in Section **II,15** (Fig. *II, 15,* 2). A disadvantage is that for temperatures above 100° the column may choke unless it is well lagged or surrounded by an electrically-heated jacket. For higher temperatures it is advisable to have the inner spiral at least 20 mm. in diameter ; the length may vary between 15 and 30 cm. and the " pitch " should be not less than 10–12 mm. The **Widmer column,** shown diagrammatically in Fig. *II, 17,* 1, constitutes an improvement on the all-glass Dufton column. It consists of three concentric glass tubes, *C, D* and *E,* so constructed that the vapours rise between *E* and *D,* descend between *D* and *C,* and then rise round the spiral in *C.* In this manner the inner spiral, around which almost, if not, all the fractionation occurs, is kept warm by the vapours which surround it ; the condensate in the column is returned to the still through a trap *F.* The glass spiral *B* is tightly fitted round a central glass tube sealed at both ends ; the outside of the helix is ground so that it fits snugly into the tube *C.* The column should be surrounded with an air jacket, held in position by split corks, for the fractionation of liquids of boiling point below 100° in order to prevent excessive condensation. For liquids distilling above 100°, an electrically-heated jacket should enclose the column. Further details concerning the Widmer and other columns will be found in Section **II,57**.

A number of excellent packings for distilling columns are available commercially. The simplest, cheapest, and yet highly effective packing consists of hollow glass rings of $\frac{1}{8}''$, $\frac{3}{16}''$ and $\frac{1}{4}''$ height and diameter; $\frac{1}{8}''$ hollow porcelain rings (Raschig rings) are almost equally effective. Lessing rings (see Section **II,15**) of porcelain ($\frac{3}{16}''$ size) and, where no chemical action occurs between the vapour of the liquid and the metal, of aluminium ($\frac{1}{8}''$), of copper ($\frac{1}{8}''$) and of nickel ($\frac{1}{8}''$) give excellent results; aluminium rings, where applicable, constitute a particularly efficient packing medium. The merits of the above contact rings for laboratory fractionating columns appear to have been overlooked. They are comparatively inexpensive and are applicable to most problems of fractional distillation encountered in the organic chemistry laboratory. Some idea of their efficiency may be obtained from the fact that one fractionation of a mixture of 50 ml. of benzene and 50 ml. of toluene through a simple Hempel column filled with $\frac{1}{8}''$ Raschig porcelain rings or with $\frac{1}{8}''$ Lessing aluminium rings (the column packing was 35 cm. long and 18 mm. in diameter) gave 43–47 ml. of pure benzene and 44–46 ml. of pure toluene.

Glass helices (Fenske rings) are an alternative packing for fractionating columns. A convenient size for single turn helices is 4·0 mm. external diameter and 0·50 mm. rod thickness: one pound of these occupies approximately 900 ml. There can be little doubt that Fenske rings possess many desirable properties as a packing for columns but, for routine use, they are somewhat expensive. For many purposes satisfactory results can be obtained by the use of the small Raschig or Lessing rings already described. However, where small quantities of liquids are involved, a column filled with glass helices will probably give the best results and the cost will not be unduly high. Rings in stainless steel and other metals can be purchased in sizes from $\frac{1}{16}''$ to $\frac{1}{4}''$.

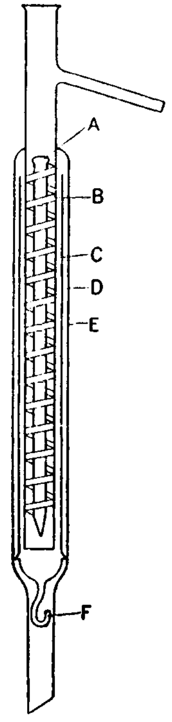


Fig. *II, 17*, 1.

An excellent but expensive packing for columns consists of **Dixon gauze rings.*** They are small gauze rings of Lessing shape made of "Staybrite" (stainless steel) gauze. A useful size is $\frac{1}{16}'' \times \frac{1}{16}''$; one pound of these occupies about 750 ml.

Fig. *II, 17*, 2 illustrates a fractional distillation unit † for use with glass helices. The column is provided with an electrically-heated jacket; the resistance shown in the Figure may be replaced by a variable transformer. The still head is of the total-condensation variable take-off type; all the vapour at the top of the column is condensed, a portion of the condensate is returned to the column by means of the special stopcock (permitting of

---

* Supplied by Griffin and George Ltd.

† Supplied by J. W. Towers and Co. Ltd.

fine adjustment of the reflux ratio) and the remainder is collected in the receiver. The advantages of the still head are :—

(1) True equilibrium conditions can be established before any distillate is collected; this is particularly important when the jacket temperature must be controlled.

(2) Reflux is more easily controlled, since careful adjustment of the reflux condenser is unnecessary.

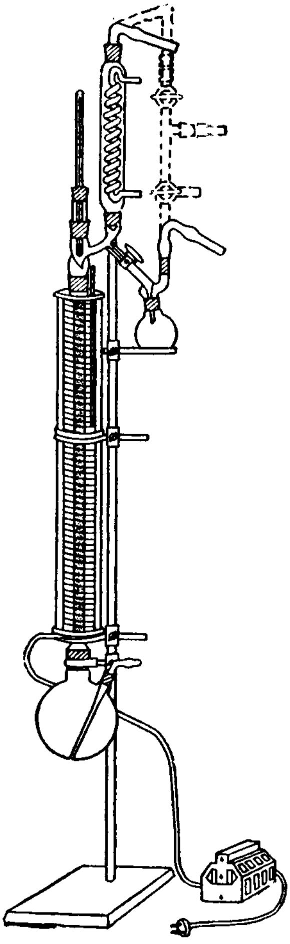


Fig. *II*, *17*, 2.

(3) Changing from a lower to a higher boiling point fraction is comparatively easy. The stopcock is closed and the liquid is allowed to reflux until the thermometer records the lowest temperature possible; at this point the column is effecting its maximum degree of separation and an equilibrium condition is reached. The tap is then partially opened and the distillate is collected in the receiver until the temperature begins to rise. The stopcock is then closed and equilibrium conditions again established, and a further fraction is removed. In this way sharper separations may be obtained. Further improvement results from the use of a capillary tube to drain the condensate into the receiver. The reflux ratio may be measured approximately by counting the number of drops of liquid which fall back into the column as compared with the number of drops which fall into the receiver flask (the liquid drops falling off the slanting ends of the drip tubes are readily observable).

The dotted line in Fig. *II*, *17*, 2 refers to the modification of the apparatus for use in fractional distillation under reduced pressure: a Perkin triangle or equivalent receiver device ("vacuum distilling adapter") is generally employed for collection of the various fractions.

A very efficient and versatile laboratory fractional distillation assembly* and the essential parts are shown in Fig. *II*, *17*, 3. The main feature of the apparatus is that the fractional distillation is conducted under virtually adiabatic conditions with complete visibility to all parts of the apparatus. This is achieved by means of a "staggered dual heating unit," which enables the temperature gradient to be varied along the entire length of the column, so as to be substantially the same as the internal temperature gradient which is determined solely by the mixture being fractionated. Thermometers are fixed inside the heating jacket surrounding the column at such positions that the temperatures at the top and bottom can be determined. The "staggered heating unit" consists of two independent heating units (top and bottom) which extend over the entire length of the jacket and are overlapped or

---

* Supplied by the Todd Scientific Company.

staggered in the middle third of the column. The upper and lower heating units are insulated from each other and are connected to slide wire rheostats mounted on a separate control panel. By means of these rheostats the heater jacket temperature can be varied from room temperature to about 360° C. All that is necessary in practice to secure adiabatic conditions is to observe the "overhead" vapour temperature and adjust the top external heating unit to this temperature: the vapour temperature in the still pot is also noted and the lower external heating unit is adjusted approximately to this temperature. The other features of the assembly are :—

(i) Three interchangeable fractionating columns, length **90** cm. each, internal diameters 5, 12 and 25 mm. respectively, are available. The packing for the 5 mm. column consists of a Monel metal rod of 1·5 mm. diameter wound with wire of the same diameter into a spiral with 2·2 turns per cm. The packing for the other columns consists of 4 mm. glass helices.

(ii) The fractionation charges for the three columns are 2–75 ml., 75–250 ml. and 250–5,000 ml. respectively; materials boiling from room temperature to 360° C. may be distilled.

(iii) Fractional distillation may be carried out at atmospheric or under reduced pressure. The receiver has a capacity of 50 ml. and is graduated in 0·1 ml.

(iv) The still head is of compact design enabling it to be enclosed in the heating jacket. The use of an "automatic still head" and an "automatic still head timer" permit the automatic maintenance of constant reflux ratios at atmospheric or reduced pressure, regardless of the rate of distillation.

(v) The fractionation efficiency is 42 to 60 theoretical plates at total reflux. Mixtures with components whose boiling point differences are as little as 6° apart can be readily separated.

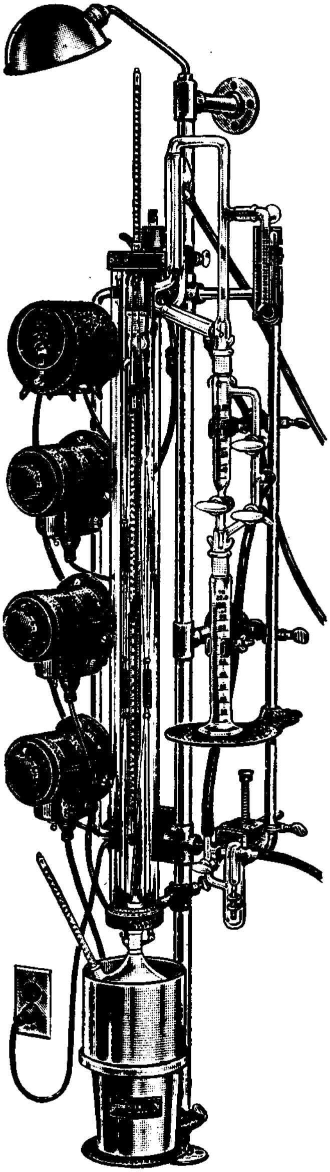


Fig. *II*, *17*, 3.

(vi) Heating of the still pot is effected with a special aluminium alloy pot heater with low temperature lag; a highly polished, parabolic aluminium reflector is incorporated which concentrates the radiant heat energy from the coil uniformly on the bottom of the still pot. The heater is controlled by a variable transformer.

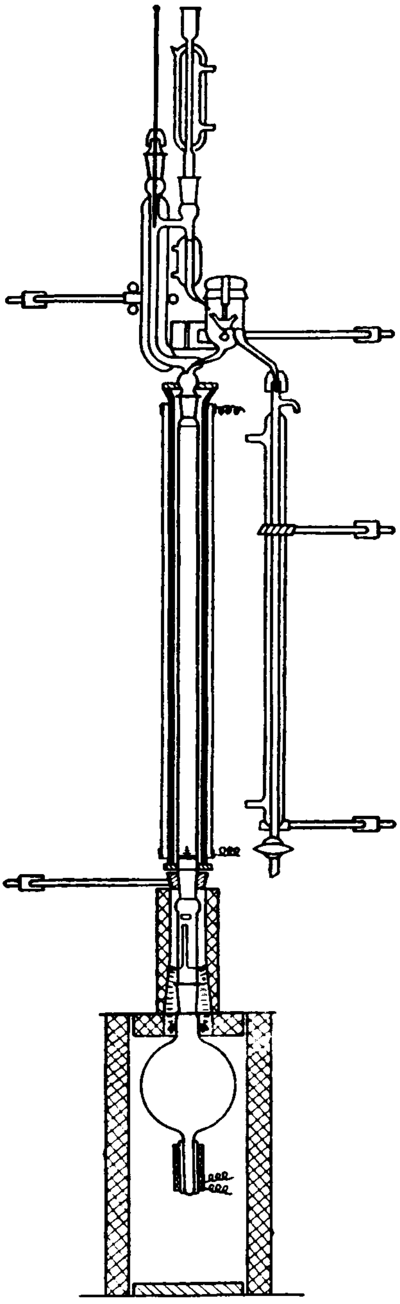


Fig. *II*, *17*, 4.

Another precision fractional distillation apparatus * is depicted in Fig. *II*, *17*, 4. The main features, worthy of special mention, are :—

(*a*) Two sizes of column, *viz.*, 45 cm. × 17 mm. and 150 cm. × 20 mm., are available; only the former is illustrated and described.

(*b*) The packing consists of stainless steel Dixon gauze rings $\frac{1}{16}''$ × $\frac{1}{16}''$, or of 4 mm. glass helices.

(*c*) Two types of column head are supplied, one for manual and the other for automatic operation. Both allow constant reflux ratios to be attained. The automatic column head is of the "tipping bucket" type and is electromagnetically controlled.

(*d*) A reflux meter is incorporated in the base of the column for the measurement of the boil-up (or reflux) rate ; it also incorporates a flooding device.

(*e*) The column is surrounded by a removable, silvered vacuum jacket with an electrically-heated lagging shield.

(*f*) The flask (150, 250 or 500 ml.) is provided with a cylindrical extension at the bottom forming a boiling tube : the latter is heated electrically and the heat input is controlled by a resistance or variable transformer.

(*g*) The apparatus may be operated at reduced pressure by the addition of a manometer, manostat, vacuum pump and appropriate receiver system.

Notes on the operation of a precision fractionating column. The following notes on the technique of conducting a fractionation under diminished pressure may be of value to the student : their adaptation to fractionation at atmospheric pressure should not present any difficulty.

1. Attach the flask containing the mixture, with capillary in position, to the column : make sure that the Perkin triangle (or "vacuum distilling adapter") and receiver are in place. See that the oil pump is functioning

---

* Designed by the staff of the Sunbury Research Station of the British Petroleum Company, and marketed by Griffin & George Ltd.

satisfactorily, adjust the pressure in the system to the desired value and control this with the aid of a manostat. Set the still head for total reflux and heat the flask until the material begins to reflux into the column. Then heat the column very slowly until the refluxing liquid reaches the top of the column and the boiling point registers on the thermometer. Adjust the temperature in (or near the top of) the jacket, as recorded on the thermometer adjacent to the column, until it is just below (*i.e.*, within 5°) the boiling point recorded in the vapour. With random packings, such as glass helices or gauze rings, the column should first be flooded in order to coat the packing completely with liquid; it is then operated under total reflux until equilibrium is attained (about 1 hour per 10 theoretical plates). A small forerun (*e.g.*, a low boiling water azeotrope resulting from traces of moisture in the liquid) can be removed before the column is brought to equilibrium.

2. When the column has reached equilibrium, adjust the head to give the desired reflux ratio, change the receiver and collect the lowest boiling point component over an appropriate distillation range, say, 1–2°. During the distillation, maintain as high a rate of reflux as possible consistent with prevention of flooding the column ; under these conditions the reflux ratio is controlled by the rate of take-off. As the lowest boiling point component is removed, the proportion of it in the distillation flask gradually decreases and eventually a mixture of two components reaches the top of the column, and this will be indicated by a slight rise in boiling point. When this occurs, gradually increase the reflux ratio, *i.e.*, decrease the rate of take-off: this will make it possible to collect the lowest boiling point fraction over a narrow range ; eventually a point will be reached when even with a high reflux ratio the boiling point rises. At this stage, change the receiver and commence the collection of the intermediate fraction.

3. During the distillation of the intermediate fraction, keep the rate of take-off very slow. The boiling point will rise and eventually either remain constant or increase very slowly. At this point, change the receiver, adjust the temperature of the heating jacket again, and collect the second fraction over a narrow distillation range—rapidly so long as the temperature remains essentially constant, then more slowly until finally the second intermediate fraction is reached again whilst distilling very slowly. Change the receiver, collect the intermediate fraction, and proceed as before for the third component, etc.

The following general comments upon situations which may arise during fractionation may be helpful :—

(*a*) The sharper the fractionation, the smaller, of course, is the intermediate fraction. If the difference in boiling points of the components being separated is considerable, the separation will be so facile that practically all the lower boiling point component will be removed whilst the boiling point remains essentially constant. Eventually the upper part of the column will begin to run dry, distillation will slow up and finally stop, whilst the reflux at the bottom of the column will be heavy. The vapour temperature may begin to fall until it is below the temperature at the top of the heating jacket. Mere increase of the bath temperature may result in the flooding of the column : the power input to the heating jacket must be gradually increased until reflux again reaches the top of the column, the boiling point begins to rise and eventually becomes constant; the temperature in the jacket is maintained just below the boiling point of the vapour.

(*b*) As the rate of take-off is reduced near the end of a fraction, a slight lowering of the bath temperature may be necessary to avoid flooding of the column. Also as the boiling point rises during the collection of the intermediate fraction, the power input to the jacket must be increased in order to hold its temperature just below the boiling point.

(*c*) If the column is flooding near the top and there is little reflux at the bottom, the jacket temperature is too high. If there is normal heavy reflux at the bottom of the column and there is flooding at the top, the bath temperature is probably too high. If the column is flooding near the bottom and there is little reflux near the top, the jacket temperature is too low.

(*d*) If it is desired to collect the liquid remaining in the column at the end of the fractionation (constituting the " hold up "), the column may be stripped by the addition of a " chaser " at the beginning of the fractional distillation in a quantity somewhat greater than the estimated " hold up." The boiling point of the " *chaser* " should be at least 20° higher than the final boiling point of the material being fractionated. For this operation the bath temperature is kept sufficiently high to distil the end component, and the jacket temperature is carefully and slowly raised above the boiling point of the component. " Chasers " should be chemically inert, inexpensive, and should not form azeotropic mixtures; examples are :—*p*-cymene, b.p. 175°; diphenyl, b.p. 254°; acenaphthene, b.p. 277°; and phenanthrene, b.p. 340°.

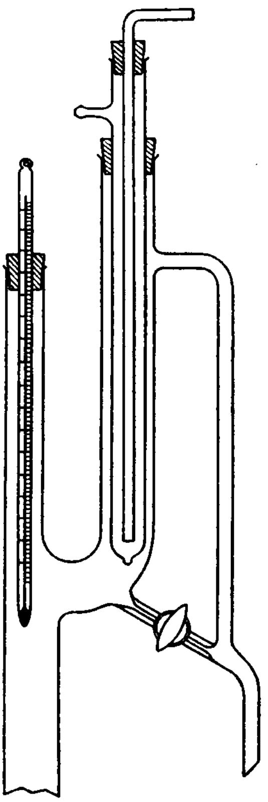


Fig. *II, 18,* 1.

II,18. STILL HEADS FOR FRACTIONATING COLUMNS

It is generally agreed that for efficient fractionation a large percentage of the vapours which pass through the length of the column must be condensed and returned. Two types of still head are employed for this purpose, known respectively as the **partial condensation** and the **total condensation variable take-off types.** In the former, first referred to in connexion with the modified Hempel column (Fig. *II, 15,* 5), a portion of the vapour is condensed by a reflux condenser (" dephlegmator ") and returned to the column, whilst the remainder passes through to the receiver. The heat interchange in the dephlegmator is controlled by adjusting the water inlet with stopcocks or screw-clips, by varying the depth to which the condenser is immersed in the vapour stream or by other means. In the total-condensation variable take-off still head, all the vapour is condensed, a portion of the condensate is returned to the fractionating column, and the remainder collected in the receiver. The advantages of this still head are pointed out in the previous Section. The main features will be evident from Fig. *II, 18,* 1. More complex types of total-condensation variable take-off still heads are described and illustrated in Section **II,17.**

II,19. DISTILLATION UNDER DIMINISHED PRESSURE ("VACUUM" DISTILLATION)

Many organic substances cannot be distilled satisfactorily under atmospheric pressure because they undergo partial or complete decomposition before the normal boiling point is reached. By reducing the external pressure to 1–30 mm. of mercury, the boiling point is considerably reduced and the distillation may usually be conducted without danger of decomposition.

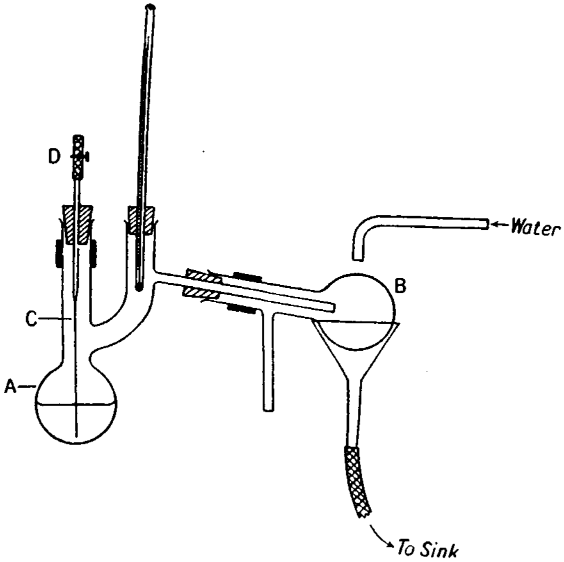


Fig. *II, 19,* 1.

A simple arrangement for distillation under diminished pressure is shown in Figs. *II, 19,* 1 and *II, 19,* 2. Well-fitting and well-bored rubber stoppers (see Fig. *II, 3,* 1) and heavy-walled rubber tubing ("pressure" tubing) are employed in distillations under reduced pressure. *A* is a Claisen flask (the two necks considerably reduce the danger of mechanical contamination of the distillate from violent bumping or frothing) and *B* is a distilling flask to act as a receiver. The right-hand neck of the flask is fitted with a thermometer with the bulb just (1–2 mm.) below the level of the side arm, whilst the left-hand neck carries a stout capillary tube *C*, which is closed at the upper end by a short piece of pressure tubing and a screw clip *D*.* The capillary tube *C* should always be prepared by drawing out a length of thick-walled capillary tube of 3–5 mm. external bore

---

* After some experience it will be found that a drawn-out capillary tube of the correct size may be prepared; the rubber tubing and the screw clip *D* are then omitted.

If pressure tubing is used, it is advisable to insert a short length of thin metal wire (*e.g.*, copper wire, 22 gauge) to prevent the tubing being closed completely by the screw clip.

(dependent upon the size of the Claisen flask): the length of the fine drawn-out capillary is adjusted so that it reaches 1-2 mm. from the bottom of the flask. Ordinary glass " quill " tubing should not be used for the preparation of *C*, since the resulting capillary will be very fragile and may snap during the course of the distillation. The side-arm of the Claisen flask is then fitted so that it projects well into the bulb of the distilling flask *B* in order that condensation of the vapours should be as complete as possible. For liquids of boiling point below 140-150°, the bulb of the receiver *B* is cooled with a stream of cold water, the waste water being collected by a funnel below and carried to the sink by rubber tubing. For liquids of higher boiling point adequate cooling is usually obtained by surrounding the receiver with a vessel containing cold water.

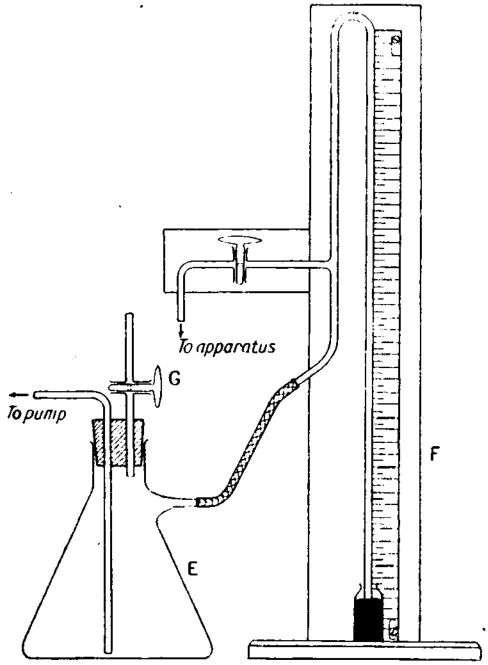


Fig. *II*, *19*, 2.

The distilling flask *B*, acting as a receiver, is connected by means of rubber " pressure " tubing to a filter flask *E* (which, *inter alia*, serves as a reservoir to equalise the pressure and the latter to a manometer and water pump. The glass tube connecting the suction flask *E* with the pump should extend to the bottom of the flask in order that any water which may flow back owing to unequal pressure in the water main may be sucked out as soon as the water pressure returns; if the flow back of the water is appreciable, it may be checked by opening the stop-cock *G* until the original water pressure is restored. The manometer illustrated is easily constructed and is particularly suitable for elementary students. Two slots are provided on the meter scale (graduated in mm.) so as to enable accurate adjustment of the zero to the level of the mercury in the small reservoir; the adjustment is best made when the manometer is connected to a pump and the mercury has risen to a height of about 750 mm.

The pressure is reduced by means of a high capacity water pump, preferably constructed of metal; * the lowest pressure that can be attained is that of the vapour pressure of water at the particular temperature (for a detailed discussion, see Section **II,21**). In winter when the temperature of the water may be 6-8° the vapour pressure of water is 7-8 mm., but in summer when the temperature of the water may reach 22°, the corresponding vapour pressure is 20 mm. Thus the " vacuum "

---

* A particularly good metal pump, which operates on a comparatively small head of water is made by Edwards High Vacuum Ltd.

produced by an efficient water pump normally varies between 7 and about 20 mm., depending upon the temperature of the tap water. If lower pressures are required, an oil pump should be used (see following Section).

As already pointed out, bumping is prevented (or minimised) by the passage of a *fine* stream of air bubbles through the capillary tube in the Claisen flask when the apparatus is under reduced pressure. The introduction of a vapour phase tends to prevent a delay in the appearance of that phase and thus to prevent superheating (compare Section I,3). The volume of air introduced in the form of minute bubbles is small so that the effect of the partial pressure upon the boiling point will usually be negligible. Bumping is also minimised by the use of a water, oil or air bath; heating on a wire gauze or by means of a free flame should not be employed.* Bumping is said to be entirely prevented by packing enough glass wool into the flask to rise about 5 mm. above the surface of the liquid.

To carry out a distillation, the liquid is poured into the Claisen flask so that it is about one-half full, and the apparatus is completely assembled as in Figs. *II*, *19*, 1–2. The barometric pressure is read. The flask is heated either by means of an air bath (Fig. *II*, *5*, 3) or by means of a water or oil bath; in the latter case the bulb of the flask is immersed at least two-thirds into the bath, which should contain a thermometer. The water pump is then turned on to its maximum capacity and the screw clip *D* almost fully closed.† The latter is then adjusted so that a fine stream of air bubbles passes through the liquid; when the mercury in the manometer ceases to rise, the reading (in mm.) is taken on *F* and this value is subtracted from the atmospheric pressure in order to obtain the pressure within the system. If the pressure thus obtained does not differ by more than 10 mm. from that expected from the temperature of the tap water, the set-up may be regarded as satisfactory. If the pressure is unsatisfactory, the apparatus must be carefully tested for leaks and these eliminated before the distillation can be commenced: special attention should be paid to ensure that all the stoppers are firmly in position and all the rubber " pressure " tubing fits tightly over the glass tubing. The cooling water for the receiver is first turned on, and, when the mercury level on the gauge is more or less steady, heating is commenced. (For high boiling point liquids, it is advantageous to wrap linen cloth or, better, asbestos cloth or string round the neck of the flask below the outlet tube.) If an air bath is employed, the temperature is slowly raised until the liquid commences to distil, and the heating is

---

* Experienced laboratory workers sometimes employ a large free flame for liquids which tend to froth considerably; by directing the flame for the most part at approximately the level of the surface of the liquid and heating the circumference evenly with a " rotating " flame, the frothing may be reduced and the distillation carried out with comparative safety. Boiling points which are slightly high may be obtained by the use of a free flame unless the liquid is distilled slowly.

† If the material in the flask contains traces of volatile solvents, it is advisable to allow the passage of a comparatively large volume of air through the liquid while warming the flask slightly: this drives off the last traces of volatile solvents, which are carried down the water pump. If this is not done, the pressure obtained when testing out the apparatus will be above the real capacity of the pump and the student will erroneously assume either that the pump is not functioning efficiently or that leaks are present in the apparatus. When all traces of volatile solvents have been removed, the screw clip *D* is almost completely closed or otherwise adjusted.

maintained at this intensity so that the liquid distils at the rate of 1–2 drops per second. With an oil bath, the temperature of the latter should be 20–25° above the boiling point of the liquid. The readings on the thermometer and gauge are taken frequently during the course of the distillation. For a pure compound the boiling point will not rise more than a degree or two during the whole of the distillation, even when the bath temperature must be raised considerably towards the end to drive off the last ml. or so of liquid. If the initial distillate boils at a lower temperature than that expected, the heating is continued until the thermometer records a temperature near that anticipated, and the receiver is changed in the manner described below ; this procedure is also employed if it is desired to remove a fraction. The flame beneath the bath is first removed, and the Claisen flask is allowed to cool slightly either by removing the asbestos covers on the air bath or by lowering the bath (an equivalent result is obtained by raising the flask, etc.). The " vacuum " is gradually released by opening the stop-cock *G* on the filter flask *E*, and the screw clip on *D* is fully opened (this will prevent any liquid entering the capillary). The receiver is then replaced by a clean distilling flask, care being taken that all joints are tight. The system is then again evacuated, the air flow through the capillary regulated and, when the pressure is steady, the heating is recommenced.

If the pressure during the distillation is not exactly that given in the recorded boiling point, it may be estimated *very approximately* for the working pressures of a water pump (10–25 mm.) by assuming that a difference of 1 mm. in pressure corresponds to one degree difference in the boiling point. A more accurate method is described in Section **I,2.** Table *II, 19* may be found useful as a guide to the *approximate* boiling point under diminished pressure when the boiling point under atmospheric pressure is known : it will enable the student to select and adjust the thermometer employed in the distillation.

Table II, 19. Approximate Boiling Points (°C) at Reduced Pressures

Pressure (mm. Hg)	Water	Chlorobenzene	Benzaldehyde	Ethyl salicylate	Glycerol	Anthracene
760	100	132	179	234	290	354
50	38	54	95	139	204	225
30	30	43	84	127	192	207
25	26	39	79	124	188	201
20	22	34·5	75	119	182	194
15	17·5	29	69	113	175	186
10	11	22	62	105	167	175
5	1	10	50	95	156	159

Distillation of solids under reduced pressure.—The apparatus shown in Fig. *II, 19,* 1 may be employed for the distillation under diminished pressure of solids possessing comparatively low melting points;

water cooling of the receiver is generally unnecessary. Any tendency to solidify in the side arm of the Claisen flask may be overcome by conducting the distillation fairly rapidly, and by warming the side arm of the Claisen flask and the neck of the receiver with a luminous flame from time to time.

A more satisfactory apparatus is depicted in Fig. *II*, *19*, 3. With this all-glass apparatus, the whole side arm may be heated directly with a flame, thus enabling materials melting as high as 200° to be distilled with ease. A liquid forerun may be removed with a bulb pipette. A solid forerun may be melted and similarly removed; the receiver may then be rinsed with a little solvent and dried. If the distillate must be left in the receiver, the side arm may be cut a few cm. from the receiving flask and a new receiver sealed to the side arm.

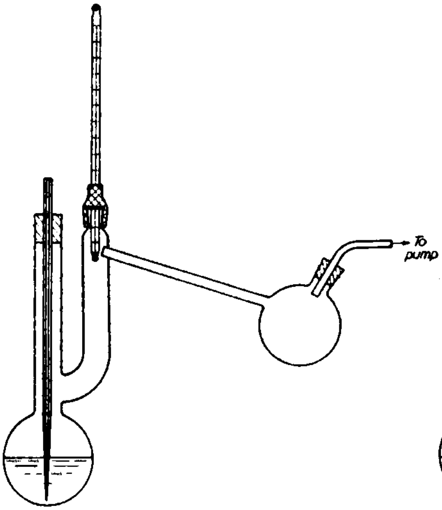


Fig. *II*, *19*, 3.

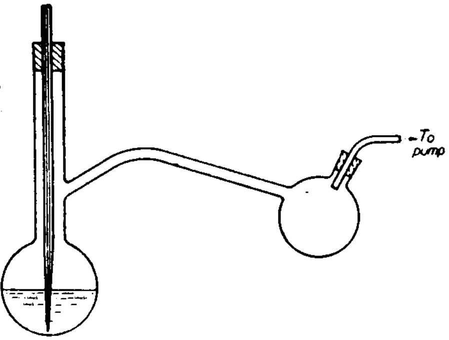


Fig. *II*, *19*, 4.

Frequently, the object of distillation of a solid under reduced pressure is to remove foreign colouring matter, tar and other non-volatile solids without appreciable loss of material—a process which is generally more effective and more economical than several crystallisations from a solvent; the purity of the distillate may be more easily ascertained by a melting point determination. In such circumstances, a thermometer is unnecessary and the two-bulb flask, depicted in Fig. *II*, *19*, 4, may be employed; rubber stoppers are used, and both the solid and the apparatus must be dry. It is usually advisable to heat the flask with a rather large free flame and to maintain a rotary motion round the walls; less bumping occurs than when the flask is heated from the bottom. If there is considerable frothing at the start, the flame should be directed at the upper walls and neck of the flask. If the solid tends to solidify in the side arm, it may be melted by the application of a free flame. When the distillation is complete, air is allowed to enter the apparatus, the contents of the receiving bulb are melted and poured out into a convenient receptacle.

II,20. FRACTIONAL DISTILLATION UNDER DIMINISHED PRESSURE

The chief disadvantage of the simple "vacuum-distillation" set-up shown in Fig. *II, 19,* 1 is that, if more than one fraction is to be collected, the whole process must be stopped in order to change the receiver *B*. It is of value, however, for the distillation of solids of low melting point; the distillate can easily be removed from the receiver by melting and pouring out. For routine work, involving the collection of several fractions under reduced pressure, the most convenient receiver is the so-called **Perkin triangle**; the complete apparatus for "vacuum distillation" is depicted in Fig. *II, 20,* 1. The Claisen flask *A* is fitted to a short water condenser *B*, which passes through the usual rubber stopper into the main receiver *C* * of the Perkin triangle. The latter has "two-way" taps at *D* and *E* and one "three-way" tap *F*, which are connected together with glass to glass joints by short lengths of rubber "pressure" tubing. All the glass parts of the triangle may be fused together thus dispensing with the rubber connexions, but in the author's experience an all-glass Perkin triangle is too fragile for students' use; rubber connexions possess the additional advantage that broken parts may be easily replaced at reasonable cost. The receiver *G* consists of a round-bottomed flask † or a test-tube and is fitted to a rubber stopper on the double-walled tube

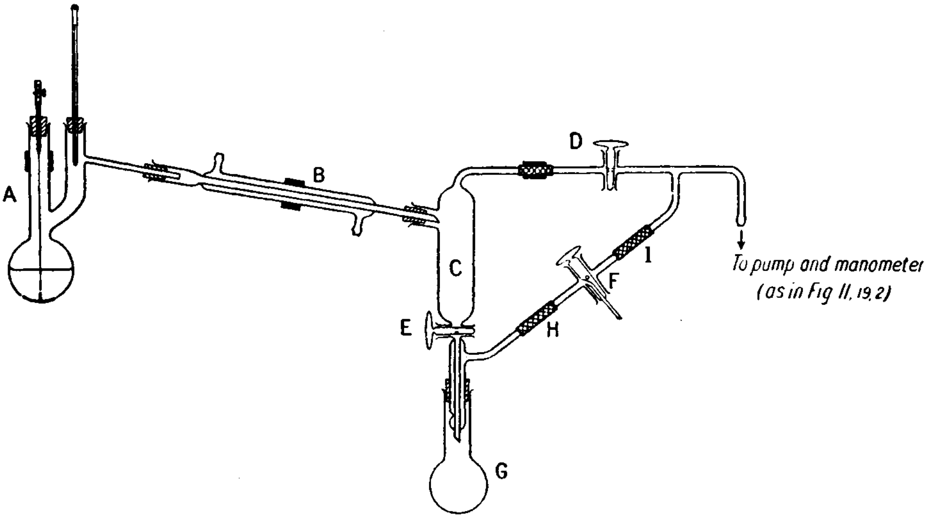


Fig. *II, 20,* 1.

---

* For general work in the laboratory, *C* should have a capacity of about 35 ml. and the opening should accommodate a 15 mm. stopper (narrow end) and be inclined at an angle of 105–110° to the body of *C*. It is an advantage to have *C* graduated by the manufacturers. Alternatively, it may be graduated at 2 or 5 ml. intervals by the student with the aid of a burette; a scale is pasted on the outside of *C* and rendered permanent by covering it with a thin layer of varnish or paraffin wax.

† Flat-bottomed vessels should not be employed in "vacuum distillation" because of the possible danger of collapse under diminished pressure.

leading from tap *E* ; the inner tube provides direct access from *C* through the tap *E* to receiver *G*, whilst the outer (annular) tube connects *G* with the " three-way " tap *F* through several small holes situated at the lower end below the stopper. The " three-way " tap *F* permits, by suitable rotation, the connection of : (i) the receiver *G* with the pump system, (ii) the receiver *G* with the atmosphere (tap *E* is, of course, closed), whilst the main apparatus is under " vacuum " thus allowing an easy change of the receiver, and (iii) the gradual entrance of air into the whole apparatus in order to restore the atmospheric pressure (tap *E* is then open).

In order to carry out a distillation, the apparatus is completely assembled, the water pump turned on to its maximum capacity, and the screw clip on the capillary tube in the Claisen flask adjusted so that a gentle stream of air bubbles through the liquid (see Section **II,19** for details of the preparation of the capillary tube). The barometric pressure is read, and if the resulting " vacuum " determined from the reading on the manometer is satisfactory (as estimated from the temperature of the tap water), the flask may be heated in an air (Fig. *II*, *5*, 3), water or oil bath. At the commencement of the distillation stop-cocks *D* and *E* are open and the " three-way " stop-cock *F* is turned so as to connect *H* and *I*. The first fraction therefore runs from *C* into *G* ; the latter may then be detached in the manner previously described and a new receiver fitted. If a highly efficient pump is being used, it is sufficient to turn *F* so as to connect *H* and *I*, thus rapidly exhausting the new receiver ; after a few moments to allow for the equalisation of pressure, the second fraction may be run into the new receiver by opening the tap *E*. If the pump has a small capacity or is somewhat inefficient, the sudden admission of air into the apparatus may cause a slight rise in pressure and distillation may cease temporarily. It is then advisable to remove the flame from beneath the bath (with an air bath the removal of the asbestos covers will suffice) and not to recommence heating until the previous pressure has been restored. This operation of changing the receiver for the collection of different fractions may be repeated as often as is necessary.

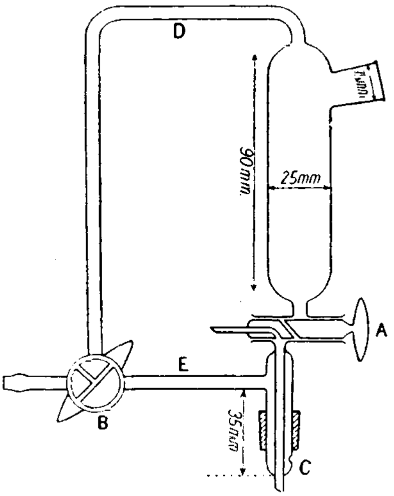


Fig. *II*, *20*, 2.

A modification of the Perkin triangle (Kon, 1930) is shown in Fig. *II*, *20*, 2. It has two stopcocks (both "three-way ") *A* and *B* instead of the three in the conventional form. Another advantage is that when air is admitted through the tap *A* to the lower portion of the apparatus in order that the receiving flask may be changed, the last few drops of distillate remaining in the tube *C* are blown out into the receiver, thus minimising waste and also reducing contamination of the various fractions. The " three-way " tap *B* enables connexion to be made between the pump with either or with both halves of the apparatus. It is, of course, possible to construct this vacuum receiver with two rubber " pressure " tubing glass to glass joints at *D* and *E*, but the all-glass apparatus is generally preferred. The method of use of the Kon vacuum receiver will be obvious from the description already given for the Perkin triangle.

II,21. WATER PUMPS

The high-pressure water supply service is employed for the operation of the ordinary " filter pump," which finds so many applications in the laboratory. A typical all metal " filter pump " is illustrated in Fig. *II, 21,* 1.* It is an advantage to have a non-return valve fitted in the side arm to prevent " sucking back " if the water is turned off or if the water pressure is suddenly reduced. Theoretically, an efficient filter pump should reduce the pressure in a system to a value equal to the vapour pressure of the water at the temperature of the water of the supply mains. In practice this pressure is rarely attained (it is usually 4–10 mm. higher) because of the leakage of air into the apparatus and the higher temperature of the laboratory. The vapour pressures of water at 5°, 10°, 15°, 20° and 25° are respectively 6·5, 9·2, 12·8, 17·5 and 23·8 mm. respectively. It is evident that the " vacuum " obtained with a water pump will vary considerably with the temperature of the water and therefore with the season of the year; in any case a really good " vacuum " cannot be produced by a filter pump.

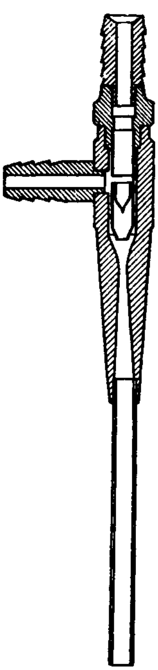


Fig. *II, 21,* 1.

II,22. OIL PUMPS

Water pumps are not always satisfactory, particularly in the summer or if the pressure on the water mains is not too high; they are sometimes erratic in action and cannot be used if low pressures are required. Motor-driven oil pumps now find extensive use either as individual units or as a large capacity unit connected through lead pipes to points situated at convenient positions in the laboratory.† These pumps may evacuate to about 0·1 mm. of mercury, but a vacuum of 5–10 mm. is quite satisfactory for most purposes. Indeed, it has been pointed out by Hickman (1932–37) that however low the pressure produced by the pump, it is rarely possible to obtain a vacuum better than about 5 mm. above the surface of the boiling liquid owing to the pressure required (1–8 mm.) to drive vapours from the distilling surface through the neck and side arm (usually 4–5 mm. diameter) of the ordinary flask; to take advantage of the low pressure produced by a good oil pump, the use of a wide side arm situated just above the bulb of the flask is recommended.

---

* The metal pump illustrated has given excellent results in the author's laboratory, and is made by Edwards High Vacuum Ltd.

† Satisfactory vacuum installation units are supplied by Edwards High Vacuum Ltd.

In order to protect the oil in the oil pump from contamination, some form of trap must be interposed between the distillation apparatus and the pump in order to prevent vapours from the distilling flask, etc. passing

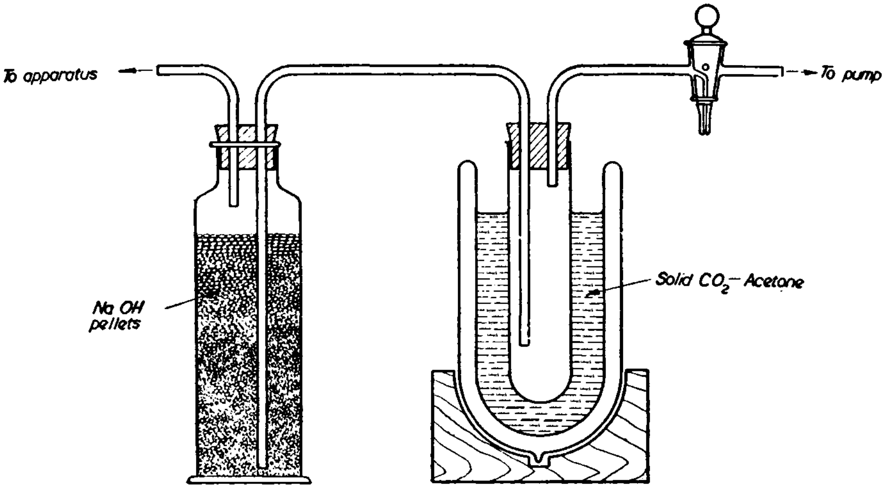


Fig. *II*, *22*, 1.

into the pump. The trap may consist of a bottle charged with sodium hydroxide pellets, followed by a wide empty tube immersed in a Dry Ice - acetone (or Dry Ice - alcohol) mixture contained in a Dewar vessel, as in Fig. *II*, *22*, 1 ; the three-way stopcock enables air to be admitted into the apparatus whilst avoiding entry of corrosive vapours into the pump. Rubber stoppers must be used throughout. Solvents of low boiling point must also be prevented from contaminating the oil in the pump: it is usually best to remove these solvents by warming gently under the vacuum of a water pump and allowing the flask to cool before connecting to the oil pump.

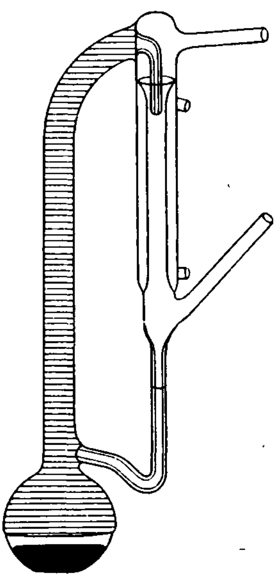


Fig. *II*, *22*, 2.

The so-called " hydro-vac " pump,* shown in Fig. *II*, *22*, 2 (the upper half of the mercury reservoir and the column above it are insulated by a layer of asbestos), is an inexpensive, all-glass, mercury diffusion pump, which can be used in series *either* with an oil pump *or* with a water filter pump (compare Fig. *II*, *21*, 1) capable of producing a "vacuum" of at least 2 mm. It is accordingly of particular value in the organic laboratory for " vacuum " distillations, fractionations, sublimations and pyrolyses as well as for " molecular " distillations (see Section **II,26**). The " hydro-vac " pump, unlike an oil pump, may be used in operations which evolve moisture and non-condensable or corrosive vapours. In use the pump is clamped in a vertical

---

* Supplied by the Todd Scientific Company.

position, the lower outlet tube is connected by means of rubber "pressure" tubing through a suitable safety trap to the water filter pump, whilst the upper inlet side arm is connected through another safety trap to the apparatus to be evacuated. The filter pump is turned on and when the pressure in the system is below 25 mm., the diffusion pump is started as follows. Water is passed through the condenser and the mercury reservoir is heated either with a Fisher burner or by an electric heating mantle (compare Figs. *II*, *57*, 1–2): the burner or electric heater is adjusted so that the mercury is maintained essentially (± 5 mm.) at the calibration mark in the side arm. Under ideal conditions an ultimate vacuum of 0·00001 mm. of mercury is claimed; the pump has evidently ample capacity for most organic operations. To stop the pump, the source of heat under the mercury reservoir is removed, air is admitted to the evacuated system and the water pump is turned off. If the apparatus should become appreciably contaminated after prolonged use, the mercury is removed and is easily cleaned by washing with dilute nitric acid and then rinsed with water.

II,23. MANOMETERS AND MANOSTATS

A simple mercury manometer has already been described (see Fig. *II*, *19*, 2). Another type that is frequently employed is the U-tube manometer illustrated in Fig. *II*, *23*, 1. It consists of a U-tube filled with mercury and mounted on a wooden stand. The scale *B*, graduated in

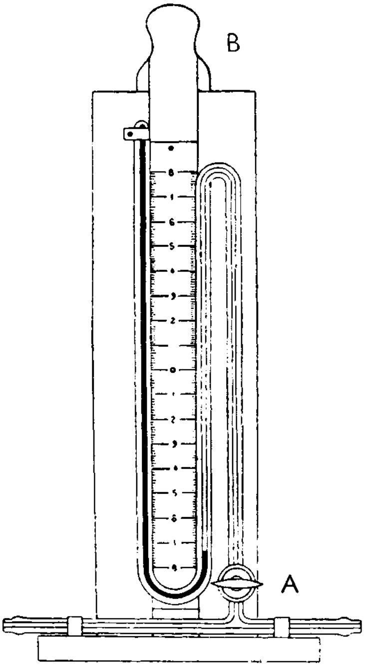


Fig. *II*, *23*, 1.

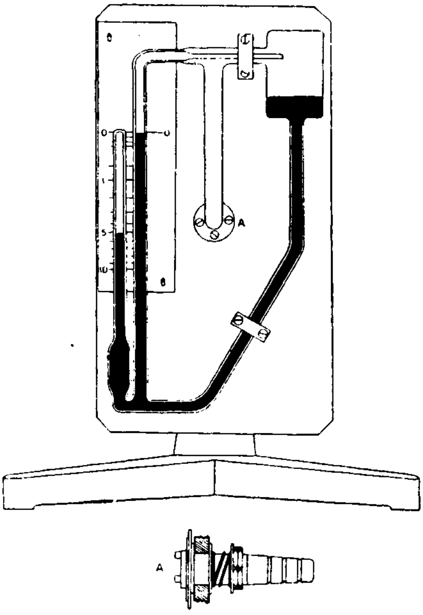


Fig. *II*, *23*, 2.

mm.,* between the two arms of the U-tube, is movable; this enables adjustment of one of the mercury levels to a convenient point on the scale to be made, thus facilitating the reading of the difference in height of the mercury in the two arms. The pressure is obtained directly, and it is unnecessary to know the barometric pressure. A tap is usually provided so that the manometer may be isolated from the distillation apparatus when required. Great care should be exercised when using this manometer: if air is allowed to enter the exhausted apparatus rapidly and tap A is open, the mercury may rise to the top of the closed end with sufficient velocity to break it. It is advisable, therefore, to close stopcock A when the gauge is not being used, and to open it *slowly* after the pressure in the "vacuum" distillation apparatus has been restored to that of the atmosphere.

The "**vacustat**"† (Fig. *II*, *23*, 2) is another useful gauge; it covers the range 10 to 0·01 mm. of mercury and is usually employed in conjunction with an oil pump. It is direct reading, compact, and is charged with only about 8 ml. of mercury. The gauge must be swivelled to the vertical position when a reading of the pressure is required; it does not automatically record a variable pressure.

The **Zimmerli vacuum gauge** ‡ covers a wide range of pressure (0–100 mm. Hg) and is depicted in Fig. *II*, *23*, 3. It is an improvement of the U-tube gauge (Fig. *II*, *23*, 1). The chief disadvantages of the latter are: (i) the necessity for boiling the mercury to remove the air from the closed reference tube when filling the gauge, (ii) the tendency for air to enter the closed limb after a period of time, and (iii) the difficulty of precision reading due to the capillary action in the narrow tube and the facile fouling of the mercury surface in the narrow tube. In the Zimmerli gauge A and B are the limbs of a U-tube each having a diameter of 16 mm. Tube A is the indicating limb; tube B, the reference limb, is not sealed at the top but is connected to a capillary tube C, which is in turn joined to a wide tube D: both A and D are connected to the vacuum line at E. Thus the indicating limb and the reference limb are both connected to the same vacuum line; this facilitates the filling of the gauge and its maintenance in perfect working condition. The gauge is filled with mercury as shown in the figure; the levels in A and D should be about 2 cm. above the bottom so as to form an effective seal.

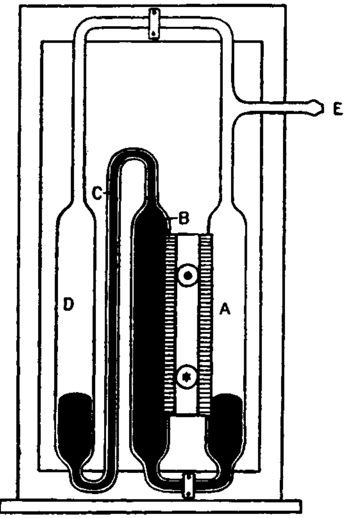


Fig. *II*, *23*, 3.

When the manometer is connected to the apparatus in which the

---

* This is sometimes made of mirror glass in order to eliminate the error due to parallax.

† Manufactured by Edwards High Vacuum Ltd. This is essentially a form of McLeod gauge.

‡ Supplied by the Scientific Glass Apparatus Company; a precision model, reading to 0·1 mm., is also marketed.

pressure is to be measured, it will be found that as soon as the pressure is reduced to a value corresponding to the difference in height of the mercury levels in *A* and *B* (or *C* and *D*) the mercury will separate at the top of the bend (between *B* and *C*), and as the pressure diminishes each part will recede in *B* and *C* until the levels become constant. The difference in height of the mercury levels in *A* and *B*, read on the scale between *A* and *B*, indicates the absolute pressure.

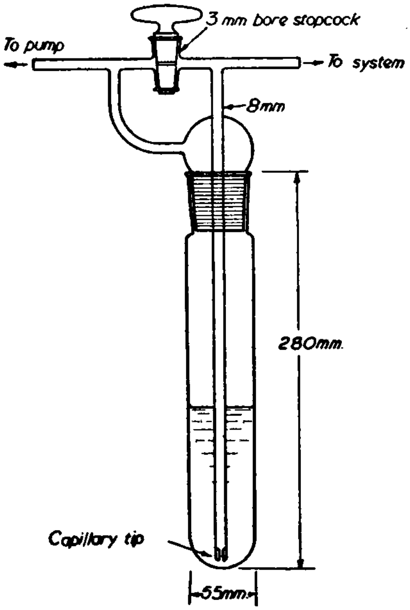


Fig. *II*, *23*, 4.

The reading of the pressure gauge is improved by providing blackened metal sleeves which can be moved up and down over the limbs *A* and *B*; when viewed against diffused light, the lower edges of the sleeves and the meniscus of the mercury show up against a white background as sharply defined straight and curved lines. When the sleeves are adjusted so that they seem to touch the top of the mercury columns, the absolute pressure is represented by the difference in height between the edges of the sleeves.

The maintenance of a constant pressure in a system during distillation under diminished pressure is of great practical importance if trustworthy boiling points are desired. Devices which maintain a constant pressure in a system that is higher than the minimum pressure that the pump will give are termed manostats. A simple manostat, due to M. S. Newman, is illustrated in Fig. *II*, *23*, 4. The underlying principle is that the gas in the system whose pressure is to be controlled must overcome the pressure of a column of liquid before it can be pumped out. When the pump is first started the bulk of the air in the system is removed through the open stopcock. When the pressure, as measured on a mercury manometer, has almost reached the desired value, the stopcock is closed thus forcing the remaining gas to be pumped through the head of liquid in the manostat. The end of the gas inlet tube is constricted (say, to 1–1·5 mm.) so that when the system has reached equilibrium, the constant leaks therein (including the distillation capillary) cause a steady stream of bubbles instead of the more intermittent larger bubbles that result if a capillary is absent. Before admitting air when the distillation has been completed, the stopcock is opened in order to avoid violent splashing of

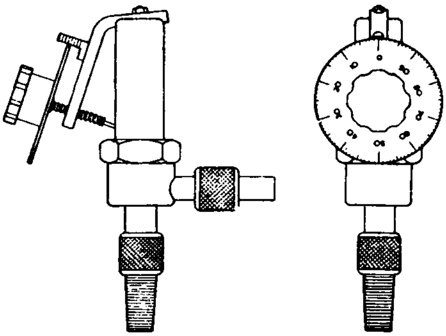


Fig. *II*, *23*, 5.

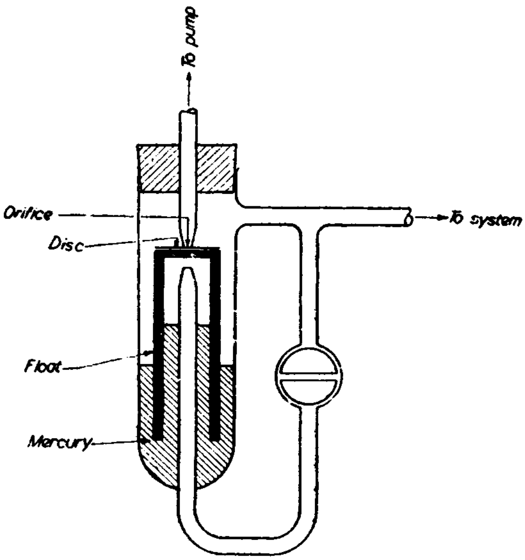


Fig. *11*, *23*, 6.

the liquid in the pressure regulator. The device is essentially one for maintaining a constant pressure differential between the pump system and the distillation system; the difference in pressure is equal to the head of liquid in the regulator. The liquid in the regulator may be di-*n*-butyl phthalate; this permits a pressure range of 1 mm. to 15 mm. of mercury to be covered, provided of course that the minimum pressure delivered by the pump is less than 1 mm. If higher pressures are desired, it is more convenient to use two or more of these regulators in series than to employ a longer one; alternatively, the manostat may be charged with a suitable volume of mercury, in which case the base should be of the Drechsel bottle type.

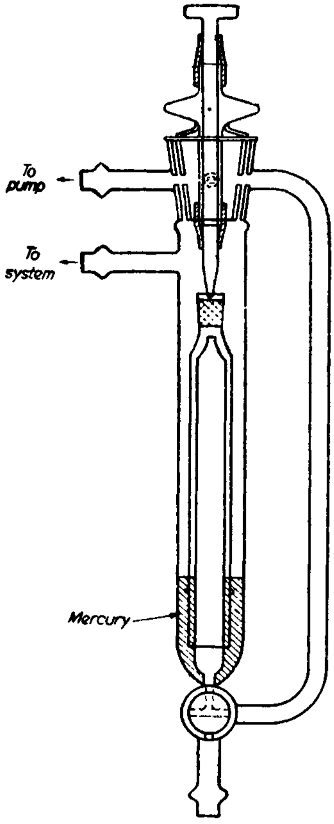


Fig. *11*, *23*, 7.

A mechanical device embodying a bellows-sealed needle valve with a lever reduction movement for fine control * is shown in Fig. *11*, *23*, 5. The needle is of stainless steel. This fine control valve assembly is useful for pressures ranging from 20 to 100 mm. of mercury when used in conjunction with a good water pump.

An excellent manostat, based on the Cartesian diver principle, is marketed under the name of **Cartesian manostat**.

The action of the manostat may be explained with the aid of Fig. *11*, *23*, 6. Mercury is introduced into the container until the disc of the float just makes contact with the orifice, when the pressure is equalised inside and outside the float. The device is connected to the pump and to the system by way of a large reservoir and a manometer. With the stopcock open, the pressure in the system is reduced by way of a by-pass between the pump and the system until the desired value as read on the manometer is reached, then both the stopcock and by-pass are

---

* Supplied by Edwards High Vacuum Ltd.

closed; the device will automatically maintain the desired pressure. If the system is vacuum tight, the pressure will maintain itseif; a slight leak, which may be introduced intentionally, will cause the pressure to rise slightly. This will produce a displacement of the mercury level downward outside the float and a corresponding displacement upward inside the float; the buoyant force on the float is consequently diminished and when this reduction in buoyancy becomes sufficient to overcome the suction force at the orifice due to the pressure differential, the disc will break away from the orifice and permit the pump to evacuate sufficient gas from the system to restore the original pressure. When the original pressure is restored, the disc will return to its former position and seal off the orifice. The cycle is repeated indefinitely, if the size of the leak in the system does not exceed the capacity of the gas flow that is possible through the orifice and the pump is of sufficient rating to carry the load.

The commercial form of Cartesian manostat,* model 7A, is depicted in Fig. *II*, *23*, 7; it is normally charged with mercury except for very low pressures when di-*n*-butyl phthalate is employed. The manostat is highly sensitive in its action; furthermore, once the pressure has been set in the instrument, the system may be shut down without disturbing the setting.

II,24. REFINEMENTS IN THE TECHNIQUE OF DISTILLATION UNDER DIMINISHED PRESSURE

A criticism that is sometimes levelled at distillation under diminished pressure when rubber stoppers are used is that contact of the hot vapour with the rubber frequently contaminates the distillate. In the author's experience, the contamination is of comparatively rare occurrence except for substances of fairly high boiling point, particularly if the stoppers have been previously used on one or two occasions. If, however, attack

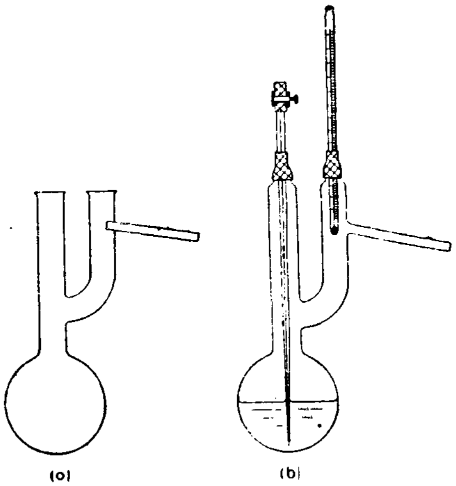


Fig. *II*, *24*, 1.

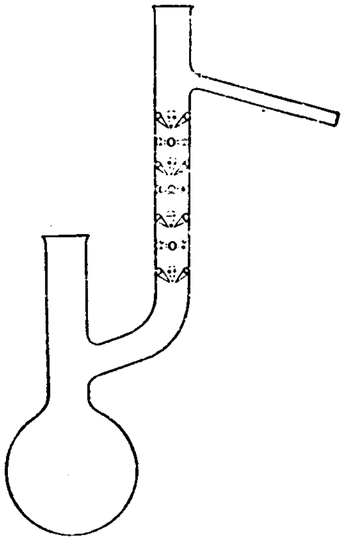


Fig. *II*, *24*, 2.

---

* Supplied by The Emil Greiner Co. of New York and by Edwards High Vacuum Ltd.; an all-metal Cartesian manostat is also marketed.

of the rubber stoppers is suspected, two types of flask (Fig. *II*, *24*, 1, *a* and *b*) may be utilised instead of the conventional Claisen flask. In the former (*a*) the side arm outlet is extended a short distance into the neck, thus preventing any liquid which has been in contact with the rubber stopper at the top from running down the side arm into the receiver. In the latter (*b*) the necks of the flask are constricted; here the capillary and the thermometer are held in place by short lengths of rubber "pressure" tubing slipped over the necks (this is facilitated by coating the inside of the rubber with a thin film of glycerine). If the substance is not extremely destructive to rubber, the neck carrying the capillary may be of normal diameter; filling and cleaning the flask will thus be comparatively easy. Either or both of these modifications may be introduced into the flasks shown in Figs. *II*, *24*, 2–3. The difficulty mentioned above may, of course be surmounted by substituting ground glass joints (see Section **II,55** *et seq.*) for rubber stoppers or tubing.

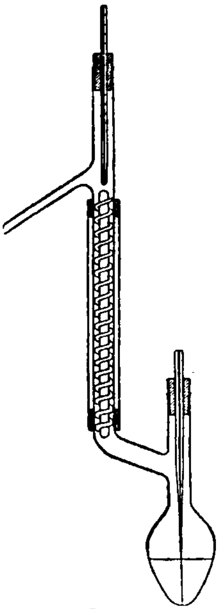


Fig. *II*, *24*, 3.

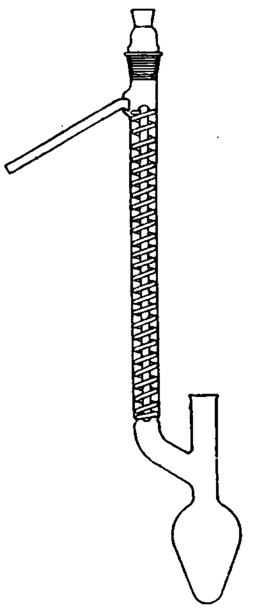


Fig. *II*, *24*, 4.

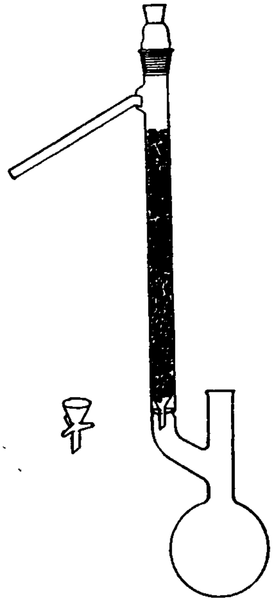


Fig. *II*, *24*, 5.

For routine fractional distillation under reduced pressure, either of the flasks shown in Figs. *II*, *24*, 2–3 finds many applications in the laboratory. The **Claisen flask with fractionating side arm** (Vigreux type; Fig. *II*, *24*, 2) has the long neck indented like a Vigreux column; great care must be taken in making these indentations (see Section **II,15**). In the **Widmer flask** (Fig. *II*, 24, 3) the long neck carries a closely-fitting glass spiral * wound tightly round a glass tube sealed at both ends or round a glass rod. This neck is generally surrounded by an air jacket for liquids of boiling point up to about 100°; for higher temperatures, it is recommended that the long neck be lagged with several thicknesses of asbestos cloth or better wound with electric heating tape, the heat input to which is controlled by a

---

* The spiral should preferably be ground into the inner walls of the long neck—compare the all-glass Dufton column, Section **II,15**.

variable transformer. The Widmer flask is superior to the Claisen flask with Vigreux type fractionating side arm.

The flasks depicted in Figs. *II*, *24*, 4 and *II*, *24*, 5* give excellent results in routine distillations at atmospheric and under diminished pressure. Pear-shaped bulbs are used for flasks of 25 and 50 ml. capacity, whilst spherical bulbs are employed for capacities of 100 and 175 ml. and larger. Each flask is provided with a *B*19 socket and an adapter carrying a *B*19 lower cone and an unground *B*10 or *B*14 socket; if required, the upper socket in the adapter may be a ground *B*10 or *B*14 and a thermometer with a ground *B*10 or *B*14 cone used in conjunction with it, but this refinement is generally unnecessary. The adapter is incorporated in the design of the flasks in order to permit the removal of the glass spiral from the necessarily wide neck and, particularly, to ensure the minimum contact with organic vapour of the rubber stopper holding the thermometer. The packing (Fig. *II*, *24*, 5) may consist of either Fenske helices or Dixon gauze rings ($\frac{1}{16}'' \times \frac{1}{16}''$); it will be noted that the packing is supported upon a glass funnel (the upper diameter of which is slightly less than that of the internal diameter of the long neck) which rests by means of three glass "feet" upon a slight constriction in the base of the "column." The long necks of both flasks are wound with $\frac{1}{2}''$ (or narrower) electric heating tape and the latter is covered by asbestos cloth; power input to the heating tape is controlled by a variable transformer, and a thermometer is inserted between the electric heating tape and the asbestos cloth. Attention is drawn to the fact that the long arm in Fig. *II*, *24*, 4 is constricted slightly at the lower end; this is in order that it may be used as in Fig. *II*, *24*, 5 by removing the glass spiral.

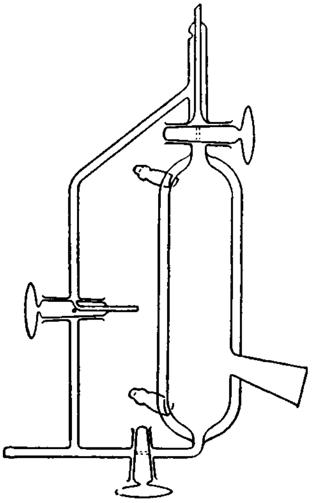


Fig. *II*, *24*, 6.

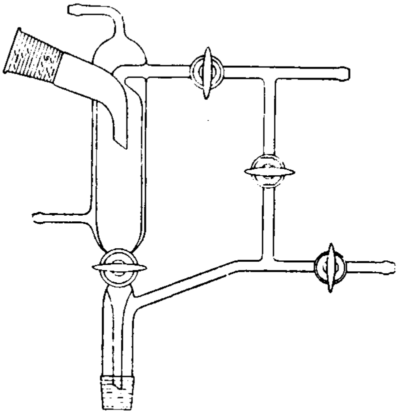


Fig. *II*, *24*, 7.

The following dimensions of the small flasks may be found useful. The internal seal must be inside the line of the long neck to enable the glass spiral to be inserted or removed easily. The mouth of the flask is preferably an unground *B*10 or *B*14 socket.

---

* Supplied by H. J. Elliott Ltd.

25 and 50 ml. flask. Side arms 10 cm. long and 4 mm. internal diameter; shorter neck 16 mm. internal diameter; long neck 14 mm. internal diameter to accommodate a 15 cm. spiral with 18 turns; total length to side arm 18–20 cm. When used with Fenske helices or Dixon gauze rings, the length of the filled column will be 10–12 cm.

100 and 175 ml. flask. Side arms 10 cm. long and 5 mm. internal diameter; shorter neck 17 mm. internal diameter; long neck 14 mm. internal diameter to accommodate a 20 cm. spiral with 24 turns; total length to side arm 23–25 cm. This will give a 15–17 cm. packed column.

In addition to the Perkin triangle and the Kon vacuum receiver already described (see Figs. *II*, 20, 1 and *II*, 20, 2), there are two modifications which are sometimes employed. The apparatus shown in Fig. *II*, 24, 6 * is a standard form of all-glass Perkin triangle but with a water cooling jacket outside the receiver; that in Fig. *II*, 24, 7 † has a similar function and four " two-way " stopcocks are utilised in its construction. Both of the last-named receivers are designed for use with low boiling point liquids, and are also useful for the distillation of small volumes of liquids since the side arm of the Claisen flask, etc., may be fitted directly into the adapter. Another application is to the distillation of solids of low melting point; warm water is then circulated through the glass jacket. It will be noted that a simple vacuum distillation receiver results if the apparatus of Fig. *II*, *24*, 7 is constructed without the internal water jacket.

II,25. PRECISION FRACTIONAL DISTILLATION UNDER DIMINISHED PRESSURE

An elementary account of the subject has been given in the previous Section. For the fractional distillation under diminished pressure of liquids differing only slightly in boiling point, a fractionating column (see Sections **II,15** and **II,17**) must be used. Provision must, of course, be made for the insertion of a capillary tube into the flask containing the mixture. This can be done by any of the following methods:—

1. If a bolt-head flask is used and a rubber stopper is permissible, there is ample room for the insertion of a capillary tube and the fractionating column in the wide neck.

2. A flask is provided with a long side neck (Fig. *II*, *25*, 1) through which a capillary is inserted and attached externally by a short length of rubber " pressure " tubing. With this type of connexion there is essentially no contact of hot vapours with the rubber and little or no contamination results. The neck of the flask is preferably fitted with a standard ground joint if attack of the organic vapours on the rubber stopper is likely to occur.

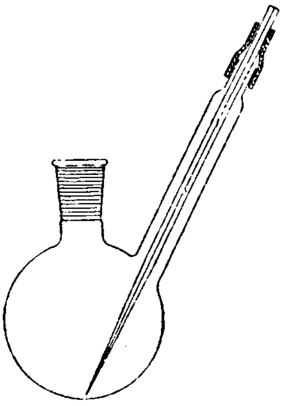


Fig. *II*, 25, 1.

---

* Marketed by Baird and Tatlock (London) Ltd.

† Marketed by the Scientific Glass Apparatus Company.

3. A two-necked flask (compare Fig. *II, 56,* 13), with the wide neck for the fractionating column and the small neck for the capillary tube, is widely employed.

Any of the fractionating columns previously described may be used. Precision fractionating columns, which find application under diminished pressure, are shown in Figs. *II, 17,* 2–4.

Claisen flasks with fractionating side arms (see Figs. *II, 24,* 2–5) may be employed for comparatively small volumes of liquid.

II,26. MOLECULAR DISTILLATION

In molecular distillation, the permanent gas pressure is so low (less than 0·001 mm. of mercury) that it has very little influence upon the speed of the distillation. The distillation velocity at such low pressures is determined by the speed at which the vapour from the liquid being distilled can flow through the enclosed space connecting the still and condenser under the driving force of its own saturation pressure. If the distance from the surface of the evaporating liquid to the condenser is less than (or of the order of) the mean free path of a molecule of distillate vapour in the residual gas at the same density and pressure, most of the molecules which leave the surface will not return. The mean free path of air at various pressures is as follows :—

Pressure (mm. of Hg) .	1·0	0·1	0·01	0·001
Mean free path (cm.) .	0·0056	0·0562	0·562	5·62

The mean free path of large organic molecules is shorter ; it is evident, therefore, that the condenser must be quite close to the evaporating surface. Strictly speaking, a molecular still may be defined as a still in which the distance between the evaporating surface and the cold condensing surface is less than the mean free path of the molecules. The escaping molecules will, for the most part, proceed in a straight path to the condenser ; by maintaining the temperature of the latter comparatively low, the amount of reflection of molecules from the condensing surface is reduced. The great advantage of distillation under a high vacuum is that the "boiling point" is considerably reduced—in some cases by as much as 200–300°—thus rendering possible the distillation of substances which decompose at higher temperatures, of substances which are very sensitive to heat, and also of compounds of very high boiling point and large molecular weight.

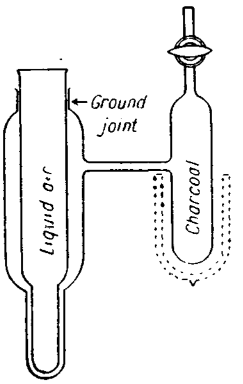


Fig. *II, 26,* 1.

A simple form of apparatus is that in which a cooled condensing surface is supported a few cm. above a shallow, heated pool of liquid, and the whole is enclosed in a highly evacuated chamber (compare Fig. *II, 26,* 1) ; this offers the least hindrance to the flow of vapour from the evaporating to the condensing surface. The rate of distillation is then determined by the rate at which the liquid surface is able to produce vapour. When the evaporating liquid is a chemical individual, the rate of evaporation will be pc/s grams per square cm. per second, where p is the density of the saturated vapour at the given temperature, c is the mean molecular velocity, and s the mean free path of a distillate molecule. If the liquid is a mixture, the rate of evaporation of the rth component will be $p_r c_r/s$ grams per square cm. per second. The separation obtained in a molecular distillation thus depends upon the quantity $p_r c_r$, unlike the separation obtained in ordinary distillation, where the vapour is in equilibrium with the liquid, which depends upon p_r. Since c_r is inversely proportional to the square root of the molecular weight, and the magnitude of p_r is, in general, greatest for the components of least molecular weight, $p_r c_r$ is greatest for constituents of least molecular weight. Molecular distillation (sometimes termed *evaporative distillation*) is the only method by which substances of high molecular weight can be distilled without decomposition. According to Langmuir (1917) the theoretical rate of distillation can be written in the form :

$$w = p\sqrt{\frac{1}{2\pi MRT}}$$

where w is the weight of substance evaporating per square cm. of liquid surface per second, M is the molecular weight of the liquid, R the gas constant, and T the absolute temperature. In practice, lower values are obtained because of the reflection of molecules from the condensing surface.

Some simple apparatus, suitable for high vacuum distillation, are collected in Figs. *II*, *26*, 1–4. Fig. *II*, *26*, 1 represents an apparatus, which is particularly well adapted for solids ; the ground glass joint must be lubricated with a grease of negligible vapour pressure. Hickman's vacuum still * is shown in Fig. *II*, 26, 2 ; it is about 60 mm. in diameter, 45 mm. high and will hold about 40 ml. of liquid. The roof of the still is filled with ice water or any appropriate freezing mixture. A modification, which permits continuous flow of cooling liquid over the roof of the still, is shown in Fig. *II*, *26*, 3. A very simple still for liquids is depicted in Fig. *II*, *26*, 4. The horizontal flask contains the liquid to be distilled. The special receiver (" four-point-star rotating receiver ") permits the collection of various fractions, but any other vacuum receiver may be employed. As a very rough approximation, the temperature of the distillation may be taken as that of the bath.

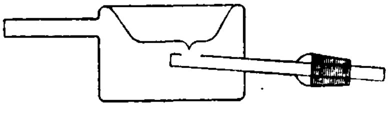


Fig. *II*, *26*, 2.

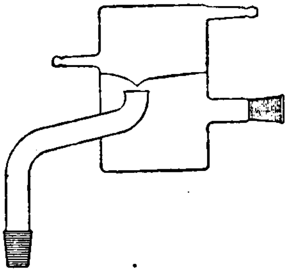


Fig. *II*, *26*, 3.

---

* Supplied, for example, by the Scientific Glass Apparatus Co. and by Midland Silicones Ltd.

The low pressure required for molecular distillation is usually produced by coupling a "backing" pump (*e.g.*, a Cenco Hyvac or Edwards Speedivac pump) with *either* a multi-stage mercury diffusion pump in quartz or metal (these two are combined in certain pumps, *e.g.*, Cenco Hypervac 4) *or* an oil-vapour diffusion pump * (the oils used include amyl and butyl sebacate, amyl phthalate, di-2-ethylhexyl sebacate and phthalate, Apiezon B, Dow-Corning Silicone Nos. 702 and 703). The advantages of the latter are :—(i) the highly purified oils have vapour pressures of about one hundredth of that of mercury and consequently produce lower pressures without the use of traps, and (ii) no contamination from mercury is possible. A McCleod gauge is generally utilised for measuring the low pressure.

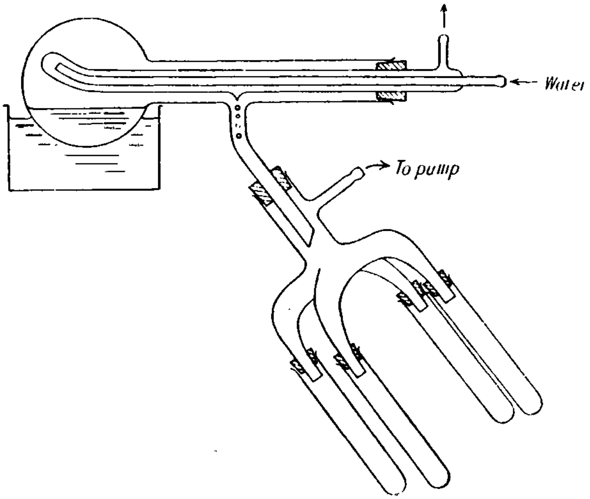


Fig. *II*, *26*, 4.

The purification of solids by low pressure sublimation is described in Section **II,45**.

II,27. PURIFICATION OF SOLID ORGANIC COMPOUNDS BY CRYSTALLISATION

GENERAL CONSIDERATIONS

Solid organic compounds when isolated from organic reactions are seldom pure ; they are usually contaminated with small amounts of other compounds ("impurities") which are produced along with the desired product. The purification of impure crystalline compounds is usually effected by crystallisation from a suitable solvent or mixture of solvents. Attention must, however, be drawn to the fact that direct crystallisation of a crude reaction product is not always advisable as certain impurities may retard the rate of crystallisation and, in some cases, may even prevent the formation of crystals entirely ; furthermore, considerable loss of

---

* Supplied, for example, by the Scientific Glass Apparatus Co.

material may occur. It is therefore, desirable, if possible, to adopt other methods of preliminary purification {*e.g.*, steam distillation (Section **II,40**); distillation under diminished pressure (Section **II,19**); fractional distillation (Section **II,15**); extraction in a Soxhlet or equivalent apparatus (Section **II,44**) } before crystallisation.

The purification of solids by crystallisation is based upon differences in their solubility in a given solvent or mixture of solvents. In its simplest form, the crystallisation process consists of: (i) dissolving the impure substance in some suitable solvent at or near the boiling point, (ii) filtering the hot solution from particles of insoluble material and dust, (iii) allowing the hot solution to cool thus causing the dissolved substance to crystallise out, and (iv) separating the crystals from the supernatant solution (or mother liquor). The resulting solid, after drying, is tested for purity (usually by a melting point determination, Section **II,10**) and if found impure, it is again recrystallised from fresh solvent. The process is repeated until the pure compound is obtained; this generally means until the melting point is unchanged.

The theory underlying the removal of impurities by crystallisation may be understood from the following considerations. It is assumed that the impurities are present in comparatively small proportion—usually less than 5 per cent. of the whole. Let the pure substance be denoted by A and the impurities by B, and let the proportion of the latter be assumed to be 5 per cent. In most instances the solubilities of A (S_A) and of B (S_B) are different in a particular solvent: the influence of each compound upon the solubility of the other will be neglected. Two cases will arise for any particular solvent: (i) the impurity is more soluble than the compound which is being purified ($S_B > S_A$) and (ii) the impurity is less soluble than the compound ($S_B < S_A$). It is evident that in case (i) several recrystallisations will give a pure sample of A, and B will remain in the mother liquors. Case (ii) can be more clearly illustrated by a specific example. Let us assume that the solubility of A and B in a given solvent at the temperature of the laboratory (15°) are 10 g. and 3 g. per 100 ml. of solvent respectively. If 50 g. of the crude material (containing 47·5 g. of A and 2·5 g. of B) are dissolved in 100 ml. of the hot solvent and the solution allowed to cool to 15°, the mother liquor will contain 10 g. of A and 2·5 g. (*i.e.*, the whole) of B; 37·5 g. of pure crystals of A will be obtained.

The most desirable characteristics of a solvent for recrystallisation are: (*a*) a high solvent power for the substance to be purified at elevated temperatures and a comparatively low solvent power at the laboratory temperature or below; (*b*) it should dissolve the impurities readily or to only a very small extent; (*c*) it should yield well-formed crystals of the purified compound; and (*d*) it must be capable of easy removal from the crystals of the purified compound, *i.e.*, possess a relatively low boiling point. It is assumed, of course, that the solvent does not react chemically with the substance to be purified. If two or more solvents appear to be equally suitable for the recrystallisation, the final selection will depend upon such factors as ease of manipulation, inflammability and cost.

The common solvents available for recrystallisation are collected in the Table *II, 27.*

TABLE II, 27. COMMON SOLVENTS FOR RECRYSTALLISATION

SOLVENT	B.P.	REMARKS
Water (distilled) . . .	100°	To be used whenever suitable.
Diethyl ether . . .	35°	Inflammable; avoid wherever possible.
Acctone	56°	Inflammable; should preferably be dried before use.
Chloroform	61°	Non-inflammable; vapour toxic.
Methyl alcohol . . .	64·5°	Inflammable; poisonous.
Carbon tetrachloride . .	77°	Non-inflammable; vapour toxic
Ethyl acetate . . .	78°	Inflammable.
Methylated (industrial) spirit	77–82°	Inflammable.
Rectified spirit (95 % C_2H_5OH)	78°	Inflammable.
Ethyl alcohol (absolute) .	78°	Inflammable.
Benzene	80°	Inflammable.
Light petroleum (petroleum ether)	40–60°	Inflammable.*
Acetic acid (glacial) . .	118°	Not very inflammable; pungent vapours.

The use of ether as a solvent for recrystallisation should be avoided wherever possible, partly owing to its great inflammability and partly owing to its tendency to creep up the walls of the containing vessel, thus depositing solid matter by complete evaporation instead of preferential crystallisation. Carbon disulphide, b.p. 46°, should never be used if an alternative solvent can be found; it has a dangerously low flash point and forms very explosive mixtures with air.

Less commonly used solvents include methyl ethyl ketone, b.p. 80°; ethylene chloride, b.p. 84°; dioxan (diethylene dioxide), b.p. 101° (vapours are toxic); toluene, b.p. 110°; pyridine, b.p. 115·5°; chlorobenzene, b.p. 132°; cellosolve (ethylene glycol monoethyl ether), b.p. 134·5°; di-*n*-butyl ether, b.p. 141°; *s*-tetrachloroethane, b.p. 147°; nitrobenzene, b.p. 209·5°; and ethyl benzoate, b.p. 213°.

Fig. *II, 27,* 1.

The choice of solvent cannot usually be made on the basis of theoretical considerations alone (see below), but must be experimentally determined, if no information is already available. About 0·1 g. of the powdered substance is placed in a small test-tube (75 × 11 or 110 × 12 mm.) and the solvent is added a drop at a time (best with a calibrated dropper, Fig. *II, 27,* 1) with continuous shaking of the test-tube. After about 1 ml. of the solvent has been added, the mixture is heated to boiling, due precautions being taken if the solvent is inflammable. If the sample dissolves easily in 1 ml. of cold solvent or upon gentle warming, the solvent is unsuitable. If all the solid does not dissolve, more solvent is added in 0·5 ml. portions, and again heated to boiling after each addition. If 3 ml. of solvent is added and the substance

---

* Other fractions available are b.p. 60–80°, 80–100°, and 100–120°: when the boiling point exceeds 120°, it is usually called "*ligroin*."

does not dissolve on heating, the substance is regarded as sparingly soluble in that solvent, and another solvent should be sought. If the compound dissolves (or almost completely dissolves *) in the hot solvent, the tube is cooled to determine whether crystallisation occurs. If crystallisation does not take place rapidly, this may be due to the absence of suitable nuclei for crystal growth. The tube should be scratched below the surface of the solution with a glass rod ; the fine scratches on the walls (and the minute fragments of glass produced) may serve as excellent nuclei for crystal growth. If crystals do not separate, even after scratching for several minutes and cooling in an ice-salt mixture, the solvent is rejected. If crystals separate, the amount of these should be noted. The process may be repeated with other possible solvents, using a fresh test-tube for each experiment, until the best solvent is found ; the approximate proportions of the solute and solvent giving the most satisfactory results should be recorded.

If the substance is found to be far too soluble in one solvent and much too insoluble in another solvent to allow of satisfactory recrystallisation, **mixed solvents or " solvent pairs "** may frequently be used with excellent results. The two solvents must, of course, be completely miscible. Recrystallisation from mixed solvents is carried out near the boiling point of the solvent. The compound is dissolved in the solvent in which it is very soluble, and the hot solvent, in which the substance is only sparingly soluble, is added cautiously until a slight turbidity is produced. The turbidity is then *just* cleared by the addition of a small quantity of the first solvent and the mixture is allowed to cool to room temperature ; crystals will separate. Pairs of liquids which may be used include : alcohol and water ; alcohol and benzene ; benzene and petroleum ether ; acetone and petroleum ether ; glacial acetic acid and water.

The following rough generalisations may assist the student in the selection of a solvent for recrystallisation, but it must be clearly understood that numerous exceptions are known (for a more detailed discussion. see Section XI,4) :

1. A substance is likely to be most soluble in a solvent to which it is most closely related in chemical and physical characteristics.
2. In ascending a homologous series, the solubilities of the members tend to become more and more like that of the hydrocarbon from which they may be regarded as being derived.
3. A polar substance is more soluble in polar solvents and less soluble in non-polar solvents.

II,28. EXPERIMENTAL DETAILS FOR RECRYSTALLISATION

It is assumed that the best solvent and the approximate proportions of solute and solvent have been determined by preliminary tests as described in the previous Section or have been obtained from reference

---

* If the crude substance contains an insoluble impurity, difficulty may be experienced at a later stage in estimating how much solute has crystallised from the cold solution. The hot solution should therefore be filtered into another tube through a *very small* fluted filter paper contained in a small short-stemmed funnel. The solution must always be clear before cooling is attempted.

books containing solubility data.* The solid substance is placed either in a small bolt-head flask or conical flask and slightly less than the required quantity of solvent is added together with a few fragments of porous porcelain or, better, a boiling tube (Fig. *I*, *3*, 1) ; a reflux condenser is then fitted to the flask (Fig. *II*, *13*, 7). If the solvent is not inflammable, toxic or expensive, the reflux condenser is not essential and may be replaced by a funnel with a short stem. The mixture is boiled and more solvent is added down the condenser (or directly into the flask if a condenser is not employed) until a clear solution, apart from insoluble impurities,† is produced. If the boiling point of the solvent is below 80°, a water bath (Fig. *II*, *5*, 1) or steam bath is satisfactory ; for solvents of higher boiling point an air bath (Fig. *II*, *5*, 3), electric hot plate, or asbestos-centred wire gauze should be used.

Filtration of the hot solution. The boiling or hot solution must be rapidly filtered before undue cooling has occurred. (If an inflammable solvent has been used, all flames in the vicinity must be extinguished.) This is usually done through a fluted filter paper (for preparation, see Section **II,29**) supported in a relatively large funnel with a short wide stem : separation of crystals in and clogging of the stem is thus reduced to a minimum. It is often advantageous to warm the funnel in the steam oven before filtration is started. The funnel is supported in a conical flask of sufficient size to hold all the solution ; alternatively, the funnel may be clamped or supported in a stand and the filtrate collected in a beaker, but the use of a conical flask is preferable. If the operation has been successfully carried out, very little material will crystallise on the filter : any solid that does separate must be scraped back into the first flask, redissolved and refiltered. The filtered solution is covered with a watch or clock glass, and then set aside to cool undisturbed. If large crystals are desired, any solid which may have separated from the filtered solution should be redissolved by warming (a reflux condenser must be used for an inflammable solvent), the flask wrapped in a towel or cloth, and allowed to cool slowly. If small crystals are required, the hot saturated solution should be stirred vigorously and cooled rapidly in a bath of cold water or of ice.

If crystallisation commences as soon as the solvent cools or if large quantities of hot solution are to be filtered, the funnel (and fluted filter paper) should be warmed externally during the filtration (hot water funnel). Three types of hot water funnel are illustrated in Fig. *II*, *1*, 6 ; no flames should be present whilst inflammable solvents are being filtered through the funnel of Fig. *II*, 1, 6, *a*. Alternatively, the funnel may be surrounded by an electric heating mantle (see Section **II,57**) ; the heat input may be controlled by a variable transformer. When dealing with considerable volumes of aqueous or other solutions which do not deposit crystals rapidly on cooling, a Buchner funnel may be used for filtration (see detailed account in Section **II,1** and Fig. *II* *1*, 7, *c*). The filter paper

---

* For example, Lange, *Handbook of Chemistry*, Ninth Edition (1956) (Handbook Publishers, Sandusky, Ohio) ; Seidell, *Solubilities of Inorganic and Organic Substances*, Third Edition (1941–1952) (Van Nostrand).

† The undissolved material will be readily recognised if preliminary solubility tests have been made (Section **II,27**).

should be of close-grained texture and should be wetted with the solvent before suction is applied ; the solution may then be poured on to the filter.

The experimental details for recrystallisation from mixed solvents (or solvent pairs) will be evident from the account already given ; the best proportions of the two solvents are determined by preliminary small-scale experiments.

II,29. PREPARATION OF A FLUTED FILTER PAPER

The filter paper is first folded in half and again in quarters, and opened up as shown in Fig. *II, 29,* 1, *a.* The edge 2,1 is then folded on to 2,4 and edge 2,3 on to 2,4, producing, when the paper is opened, new folds at 2,5 and 2,6. The folding is continued, 2,1 to 2,6 and 2,3 to 2,5, thus producing folds at 2,7 and 2,8 respectively (Fig. *II, 29,* 1, *b*) ; further 2,3 to 2,6 giving 2,9, and 2,1 to 2,5 giving 2,10 (Fig. *II, 29,* 1, *c*). The final operation consists in making a fold in each of the eight segments —between 2,3 and 2,9, between 2,9 and 2,6, etc.—in a direction *opposite* to the first series of folds, *i.e.*, the folds are made outwards instead of inwards as at first. The result is a fan arrangement (Fig. *II, 29,* 1, *d*), and upon opening, the fluted filter paper (Fig. *II, 29,* 1, *e*) is obtained.

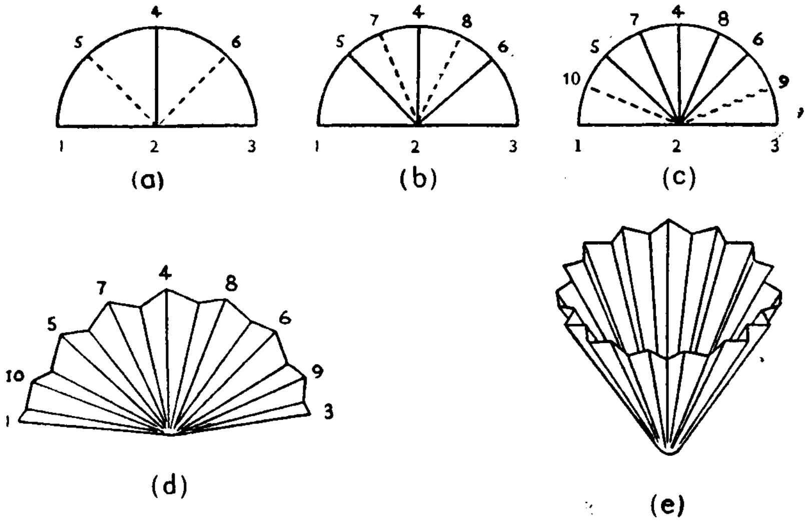


Fig. *II, 29,* 1.

II,30. REMOVAL OF TRACES OF COLOURING MATTER AND RESINOUS PRODUCTS
USE OF DECOLOURISING CARBON

The crude product of an organic reaction may contain a coloured impurity. Upon recrystallisation, this impurity dissolves in the boiling solvent and is partly adsorbed by the crystals as they separate upon cooling, yielding a coloured product. Sometimes the solution is slightly turbid owing to the presence of a little resinous matter or a very fine suspension of an insoluble impurity, which cannot always be removed by simple filtration. These impurities can be removed by boiling the substance in solution with a little decolourising charcoal for 5–10 minutes, and then filtering the solution while hot as described in Section **II,28.** The decolourising charcoal adsorbs the coloured impurity and holds back resinous, finely-divided matter, and the filtrate is usually free from extraneous colour, and therefore deposits pure crystals. The decolourisation takes place most readily in aqueous solution, but can be performed in almost any organic solvent; the process is least effective in hydrocarbon solvents. It must be pointed out that boiling in a solvent with decolourising carbon is not always the most effective method of removing the colour: if boiling is only partially effective, it is often worth while to pass the cold solution of the substance (preferably in an organic solvent such as ether) through a small amount of decolourising carbon supported on a wad of cotton wool in the stem of a funnel—this is effectively a chromatographic procedure.

An excessive quantity of decolourising agent must be avoided, since it may also adsorb some of the compound which is being purified. The exact quantity to be added will depend upon the amount of impurities present; for most purposes 1–2 per cent. by weight of the crude solid will be found satisfactory. If this quantity is insufficient, the operation should be repeated with a further 1–2 per cent. of fresh decolourising charcoal. Sometimes a little charcoal passes through the close-grained filter paper: the addition, before filtration, of a little asbestos fibre, filter paper pulp, high grade infusorial or diatomaceous earth will give a clear filtrate. Attention is directed to the fact that the decolourising charcoal should not be added to a superheated solution as the latter may foam excessively and boil over.

The most widely known form of decolourising carbon is animal charcoal (also known as bone black or bone charcoal); it is the least expensive, but by no means the best. It has limited adsorptive power, and contains a large proportion of calcium phosphate and other calcium salts; it should not be used with acidic solutions, particularly if the desired compound is to be subsequently obtained by a process of neutralisation. This difficulty may be overcome, and all risk of the introduction of impurities into the hot solution avoided, by boiling the commercial animal charcoal with dilute hydrochloric acid (1 : 1) for 2–3 hours. The mixture is then diluted with hot distilled water, filtered through a fine-grained filter paper supported on a Buchner funnel, and washed repeatedly with boiling distilled water until the filtrate is no longer acid. It is then well drained, and dried in an evaporating basin (or casserole) over an electric hot plate or a sand bath. Acid-washed decolourising charcoal is also available commercially.

On the whole it is better to employ the activated decolourising charcoal prepared from wood. Excellent decolourising carbons are marketed under the trade names "*Norit*" * (from birch wood), "*Darco*" * and "*Nuchar.*" *

---

* Obtainable, for example, from Eastman Kodak Company.

II,31. DIFFICULTIES ENCOUNTERED IN RECRYSTALLISATION

The separation of a second liquid phase, commonly known as an "oil," instead of the expected crystalline solid, sometimes occurs during recrystallisation. The oil often solidifies on standing, although at times a considerable period may elapse before crystallisation occurs. The resulting crystals will probably occlude some of the mother liquor, and the purity will therefore not be high. If the substance has a low melting point, it must not be assumed that this apparently abnormal behaviour is due to the presence of impurities ; it is probably an example of a system in which the solid phases consist of the pure components and the components are only partially miscible in the liquid state (see Section **I,18**). The separation of the oil may be avoided by diluting the solution considerably, but this will lead to large losses. It is probably best to re-heat the mixture until a clear solution is obtained, and allow it to cool spontaneously ; immediately the oil commences to separate, the mixture is vigorously stirred so that the oil is well dispersed in the solution. Eventually, crystals will separate and these will grow in the bulk of the solution and not in a pool of oil, so that occlusion of the mother liquor is considerably reduced. When all the oil has disappeared, stirring may be stopped and the crystals allowed to accumulate. Sometimes the addition of a minute quantity of the crude compound in order to "seed" the solution may facilitate the initial crystallisation.

Occasionally substances form supersaturated solutions from which the first crystals separate with difficulty ; this is sometimes caused by the presence of a little tar or viscous substance acting as a protective colloid. The following methods should be tried in order to induce crystallisation :—

1. By scratching the inside of the vessel with a glass rod. The effect is attributed to the breaking off of small particles of glass which may act as crystal nuclei, or to the roughening of the surface, which facilitates more rapid orientation of the crystals on the surface.

2. By inoculating ("seeding") the solution with some of the solid material or with isomorphous crystals, crystallisation frequently commences and continues until equilibrium is reached. The "seed crystals" may be obtained by cooling a very thin film of liquid to a low temperature. Several drops of the solution are placed in a test-tube or beaker and spread into a thin film by rotating the container ; the latter is then cooled in a mixture of ice and salt or in some other suitable freezing mixture. A better procedure, which avoids the necessity of subsequently scraping the surface to remove the "seed crystals" and the attendant melting if the compound is impure or of low melting point, is to moisten a small glass bead with the supersaturated solution, place it in a test-tube, cool the latter in a freezing mixture and thus form crystals on the surface of the bead. The glass bead can then be rolled out of the tube into the vessel containing the main bulk of the solution.

3. By cooling the solution in a freezing mixture (ice and salt, ice and calcium chloride, or solid carbon dioxide and ether). It must be borne in mind that the rate of crystal formation is inversely proportional to the temperature ; cooling to very low temperatures may render the mass very viscous and thus considerably hinder crystallisation. In the latter case, the mixture should be allowed to warm slowly so that it may be given the opportunity to form crystals if it passes through an optimum temperature region for crystal formation. Once minute crystals have been formed, it is very probable that their size will be increased by keeping the mixture at a somewhat higher temperature.

4. By adding a few lumps of solid carbon dioxide ; this produces a number of cold spots here and there, and assists the formation of crystals.

5. If all the above methods fail, the solution should be left in an ice chest (or a refrigerator) for a prolonged period. The exercise of considerable patience is sometimes necessary so as to give the solution every opportunity to crystallise.

The product of a chemical reaction, isolated by solvent extraction and subsequent removal of the solvent, which should normally be crystalline, is sometimes an oil, due to the presence of impurities. It is usually advisable to attempt to induce the oil to crystallise before purifying it by recrystallisation. Methods *1* and *2* (previous paragraph) may be applied ; method *2* cannot always be used because of the difficulty of securing the necessary seed crystals, but should these be available, successful results will usually be obtained. Another procedure is to add a small quantity of an organic solvent in which the compound is sparingly soluble or insoluble, and then to rub with a stirring rod or grind in a mortar until crystals appear ; it may be necessary to continue the rubbing for an hour before signs of solidification are apparent. Another useful expedient is to leave the oil in a vacuum desiccator over silica gel or some other drying agent. If all the above methods fail to induce crystallisation, direct recrystallisation may be attempted : the solution should be boiled with decolourising carbon as this may remove some of the impurities responsible for the difficulty of crystal formation. Occasionally, conversion into a simple crystalline derivative is applicable ; subsequent regeneration of the original compound will usually yield a pure, crystalline solid.

II,32. FILTRATION WITH SUCTION

The technique of the filtration of hot solutions has already been described in Section **II,28.** The filtration of cold solutions will now be considered ; this operation is usually carried out when it is desired to separate a crystalline solid from the mother liquor in which it is suspended. When substantial quantities of a solid are to be handled, a Buchner funnel of convenient size is employed. The ordinary Buchner funnel (Fig. *II*, *1*, 7, *a*) consists of a cylindrical porcelain funnel carrying a fixed, flat, perforated porcelain plate. It is fitted by means of a rubber stopper or a good cork into the neck of a thick-walled filtering flask (also termed **filter flask, Buchner flask** or **suction flask**) (Fig. *II*, *1*, 7, *c*), which is connected by means of thick-walled rubber tubing (rubber " pressure " tubing) to a similar flask or safety bottle, and the latter is attached by rubber " pressure " tubing to a filter pump ; the safety bottle or trap is essential since a sudden fall in water pressure may result in the water "sucking back." The use of suction renders rapid filtration possible and also results in a more complete removal of the mother liquor than filtration under atmospheric pressure. A filter paper * is selected (and trimmed, if necessary) of such size that it covers the entire perforated plate, but its diameter should be slightly less than the inside diameter of the funnel; the filter paper should never be folded up against the sides of the funnel. The filter paper is moistened with a few drops of the solvent used in the recrystallisation (or with a few drops of the clear supernatant liquid), and the suction of the pump is applied; the filter paper should adhere firmly to, and completely cover, the perforated plate of the funnel and thus prevent any solid matter from passing under the edge of the paper into the flask below. The mixture of crystals and mother liquor is then immediately filtered through the funnel under gentle suction. Gentle suction is often more effective in filtration than powerful suction, since in the latter case the finer particles of the precipitate may reduce the rate of filtration by being drawn into the pores of the filter paper. If crystals remain in the vessel when all the liquid suspension has been filtered, a little mother liquor is returned to the vessel,† well stirred to remove any crystals adhering to the sides, and again filtered. This operation may be repeated until all the solid material has been transferred to the filter. The suction is continued until most of the mother liquor has passed through: the removal of the mother liquor is facilitated by pressing the crystals down with a wide glass stopper.

If the filtrate is of value, it should be transferred to another vessel immediately the crystals have been drained. Frequently, the mother liquor may be concentrated (suitable precautions being, of course, taken if it is inflammable), and a further crop of crystals obtained. Occasionally, yet another crop may be produced. The crops thus isolated are generally less pure than the first crystals which separate, and should be recrystallised from fresh solvent; the purity is checked by a melting point determination.

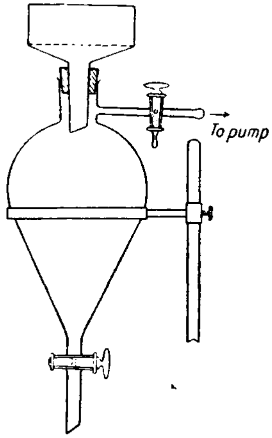


Fig. *II*, *32*, 1.

When the volume of mother liquor is large and the amount of crystals small, the apparatus of Fig. *II*, *32*, 1 ‡ may be used. The large pear-shaped receiver is supported on a metal ring attached to a stand. When the receiver is about two-thirds full, atmospheric pressure is restored by suitably rotating the "three-way" stopcock; the filtrate may then be removed by opening the tap at the lower end. The apparatus is again exhausted and the filtration continued.

After the main filtrate has been removed, the crystals should be washed in order to remove the mother liquor which, on drying, would contaminate the crystals. The wash liquid will normally be the same solvent as was used for recrystallisation, and must be used in the smallest possible

---

* Two thicknesses of filter paper are desirable for aqueous solutions and, on occasion, for certain finely-divided solids.

† The filter flask must be disconnected from the pump before the latter is turned off.

‡ Supplied in capacities of 1, 2 and 4 litres by the Scientific Glass Apparatus Company.

amount in order to prevent appreciable loss of the solid. With the suction discontinued, the crystals are treated with a small volume of the solvent and cautiously stirred with a spatula or with a flattened glass rod (without loosening the filter paper) so that the solvent thoroughly wets all the crystals. The suction is then applied again, and the crystals are pressed down with a wide glass stopper as before. The washing is repeated, if necessary, after connexion to the filter pump has been broken.

If the solvent constituting the crystallisation medium has a comparatively high boiling point, it is advisable to wash the solid with a solvent of low boiling point in order that the ultimate crystalline product may be easily dried; it need hardly be added that the crystals should be insoluble or only very sparingly soluble in the volatile solvent. The new solvent must be completely miscible with the first, and should not be applied until the crystals have been washed at least once with the original solvent.

II,33. DRYING OF THE RECRYSTALLISED MATERIAL

In order to dry the crystals, the Buchner funnel is inverted over two or three thicknesses of "drying paper" (*i.e.*, coarse-grained, smooth-surfaced filter paper) resting upon a pad of newspaper, and the crystalline cake is removed with the aid of a clean spatula; several sheets of drying paper are placed on top and the crystals are pressed firmly. If the sheets become too soiled by the mother liquor absorbed, the crystals should be transferred to fresh paper. The disadvantage of this method of rapid drying is that the recrystallised product is liable to become contaminated with the filter paper fibre.

Another method, which is especially suitable for low melting point solids or solids which decompose at low temperatures, is to place the material on a porous plate or pad of "drying paper," and to cover the latter with another sheet of filter paper perforated with a number of holes or with a large clock glass or sheet of glass supported upon corks. The air drying is continued until the solvent has been completely eliminated.

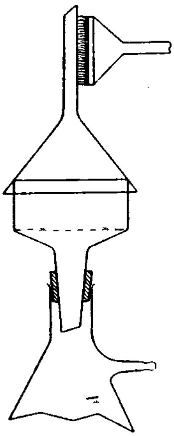


Fig. *II*, *33*, 1.

For solids which melt above 100° and are stable at this temperature, drying may be carried out in a steam oven. The crystals from the Buchner funnel should then be placed on a clock glass or in an open dish. The substance may sometimes be dried in the Buchner funnel itself by utilising the device illustrated in Fig. *II*, *33*, 1. An ordinary Pyrex funnel is inverted over the Buchner funnel and the neck of the funnel heated by means of a broad flame (alternatively, the funnel may be heated by a closely-fitting electric heating mantle); if gentle suction is applied to the filter flask, hot (or warm) air will pass over the crystalline solid.

The best method of drying, if time permits, is to place the crystals in a desiccator containing an appropriate substance (usually anhydrous calcium chloride, silica gel, or concentrated sulphuric acid) to absorb the solvent. More efficient and more rapid drying is obtained with the aid of a vacuum desiccator (see Section **II,38** and Fig. *II*, *38*, 1).

Before attempting a melting point determination as a check on the purity, care must be taken to ensure a perfectly dry sample of the compound since traces of solvent may lower the melting point appreciably.

II,34. FILTRATION OF SMALL QUANTITIES OF MATERIAL WITH SUCTION

For the suction filtration of small quantities (less than 5 g.), a small conical Buchner funnel, known as a **Hirsch funnel** (Fig. *II*, *1*, 7, *b*), is employed ; the filtrate is collected either in a small filter flask or in a test tube with side arm. A useful arrangement, utilising an ordinary filter funnel, is shown in Fig. *II*, *1*, 7, *d*. A small **Witt filter plate** with bevelled edges * is inserted in the funnel and a circle of filter paper 1–2 mm. larger than the diameter of the plate is placed upon it. The filter paper is moistened with the solvent and fitted closely to the funnel by pressing and rubbing out the small folds with a glass rod. The loose perforated plate has the advantage that its cleanliness on both sides can be checked in contrast with the fixed plate in the opaque Hirsch funnel. A small sintered glass funnel or "slit-sieve" funnel (see Section **II,35**) may also be employed. The procedure for filtration is similar to that already given for the Buchner funnel (Section **II,32**).

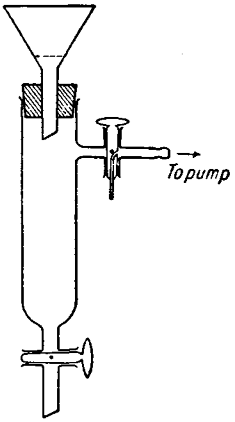


Fig. *II*, *34*, 1.

The apparatus depicted in Fig. *II*, *34*, 1, intended for advanced students, may be used for the filtration of a small quantity of crystals suspended in a solvent ; either a Hirsch funnel or a glass funnel with Witt filter plate is employed. The mixture of crystals and mother liquor is filtered as usual through the funnel with suction. Rotation of the "three-way" tap will allow air to enter the filter cylinder, thus permitting the mother liquor to be drawn off by opening the lower tap. The mother liquor can then be applied for rinsing out the residual crystals in the vessel, and the mixture is again filtered into the cylinder. When all the crystals have been transferred to the funnel and thoroughly drained, the mother liquor may be transferred to another vessel ; the crystals may then be washed as already described (Section **II,32**).

II,35. MISCELLANEOUS APPARATUS FOR FILTRATION WITH SUCTION

The chief disadvantages of a Buchner funnel for filtration are : (i) it is impossible to see whether the underside of the perforated plate is perfectly clean, and (ii) the larger sizes are "top-heavy." The first drawback is absent in the Jena "slit-sieve" funnel (Fig. *II*, *1*, 7, *f*) ; this is an all-glass funnel provided with a sealed-in transparent plate, perforated by a series of angular slots, upon which the filter paper rests. The sintered glass

---

* A Gooch perforated porcelain plate may also be used.

funnel (Fig. *II*, *1*, 7, *g*) is a cylindrical all-glass funnel carrying a plate of porous sintered glass ; it is marketed in many sizes and in a number of porosities. A slight drawback is the difficulty of completely removing all the material from the sintered glass surface of the funnel.

Both disadvantages of the Buchner funnel are overcome in the "**Minifilter**"* ; this constitutes an important development for the filtration of relatively large quantities of materials. The upper portion, carrying a fixed perforated filter plate, fits into the cylindrical base by a ground centre joint, and the filtrate is drawn off from the enclosed chamber below through a vacuum connexion. The "Minifilter" sits firmly on the bench and is perfectly stable ; the ground centre joint enables the apparatus to be readily taken apart for cleaning. The complete assembly is illustrated in Fig. *II*, *35*, 1 ; the filtrate is collected in the filter flask nearest the "Minifilter," and the second flask acts as a trap.

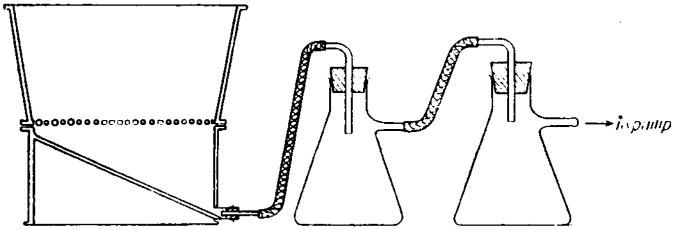
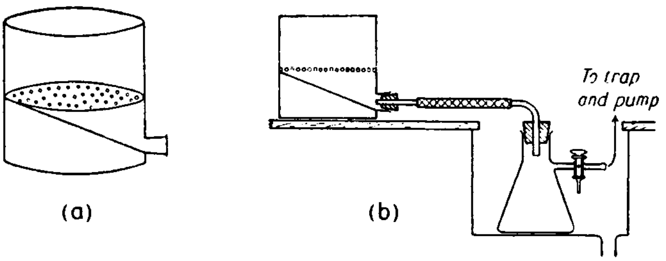


Fig. *II*, *35*, 1.

A similar apparatus, but without the advantage of the central ground joint is marketed under the name "**Buechner stable filter**"† (Fig. *II*, *35*, 2, *a*) ; one method of use is shown in Fig. *II*, *35*, 2, *b*. The "Buechner stable filter" is made of porcelain ; the filtrate is drawn off through a vacuum chamber below the perforated plate, the whole apparatus is supported by a cylindrical base, and sits firmly on the bench. The sizes of perforated plate available are 56, 91, 111, 126, 186, 241 and 308 mm. diameter respectively, and it would appear that these will eventually largely displace the old type of Buchner funnel for general laboratory work.



(a) (b)

Fig. *II*, *35*, 2.

---

* Made by Hathernware Ltd. for filter papers of 185 and 270 mm. diameter.

† Supplied by the Fisher Scientific Company ; a product of the Coors Porcelain Company.

Filtration of corrosive liquids with suction. A strongly alkaline or acid suspension is best filtered through a sintered glass funnel. Alternatively, glass wool or asbestos may be plugged into the stem of a glass funnel or supported upon a Witt plate in a glass funnel.

II,36. RECRYSTALLISATION IN AN ATMOSPHERE OF INERT GAS

Substances which decompose (or otherwise change) in contact with air must be recrystallised in an indifferent atmosphere, such as carbon dioxide, nitrogen or hydrogen. The apparatus of Fig. *II, 36,* 1 is almost self-explanatory; two ground glass joints are used, but these may be replaced by rubber stoppers, if desired. The crude substance is placed in the flask *A*. Stopcocks *1* and *2* are closed, and the apparatus is exhausted through tap *3*; the indifferent gas is then allowed to enter the apparatus to atmospheric pressure. The evacuation and filling with inert gas are repeated several times. The solvent is added through the tap funnel *B*. The flask *A* is heated in a suitable bath until all the solid has dissolved; a stream of inert gas may be passed through the apparatus during this operation. The flask is allowed to cool in order that the compound may crystallise out. By inclining the flask *A*, applying suction at *3* and connecting *1* to a source of inert gas, the mother liquor may be drawn into the sintered glass funnel *C* without the crystals blocking the end of the tube *D*. The crystals remaining in the flask *A* may again be recrystallised if necessary. Finally, the suspension of mother liquor and crystals is transferred to the sintered glass plate in *C* by applying suction and maintaining a stream of indifferent gas through the apparatus. In an alternative method of filtration, the sintered glass funnel is replaced by a tube carrying a sintered glass disc at the lower end inside the flask (*i.e.*, at *D*); the crystals will then remain in the flask *A*.

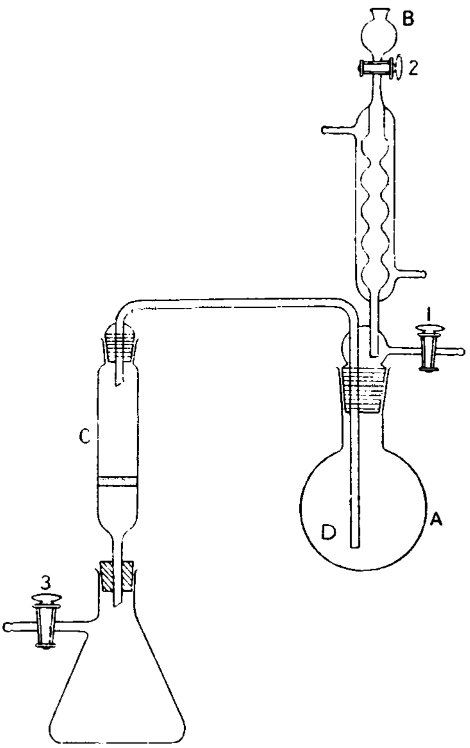


Fig. *II, 36,* 1.

II,37. EVAPORATION OF THE SOLVENT

It is frequently necessary to concentrate a filtrate in order to obtain a further crop of crystals, or it may be necessary to concentrate a solution to a smaller volume. If the solvent is water and the substance is not volatile in steam, simple evaporation on a large dish on a steam or water bath is satisfactory. If more rapid evaporation is required or if organic solvents are involved, use may be made of either of the following assemblies.

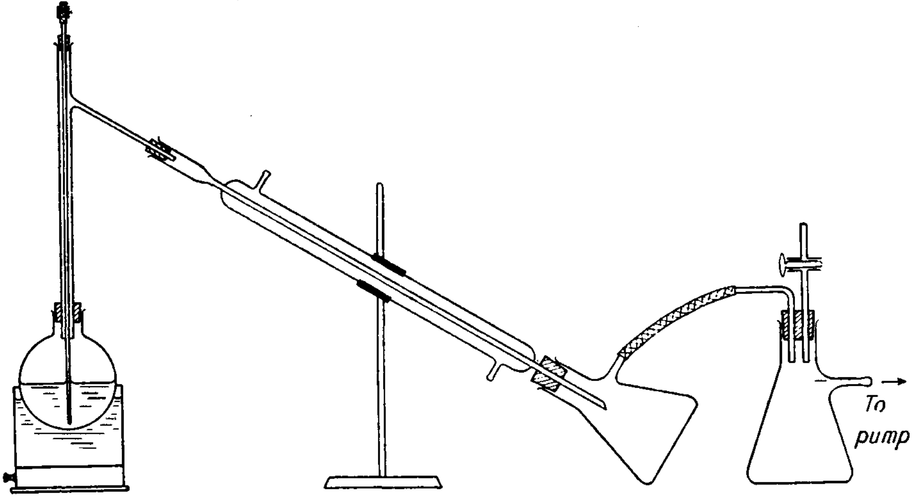


Fig. *II*, *37*, 1.

Fig. *II*, *37*, 1 illustrates a convenient set-up for concentrating a large volume of solution. The solution is placed in a large bolt-head flask, the special head is introduced and connected to a condenser, a filter flask as receiver, and another filter flask acting as a trap. Rubber stoppers must be used throughout. The flask should never be more than half full, so that foaming of the contents into the condenser may be avoided. Heating is carried out in a water bath, and the pressure is reduced by means of a water pump.

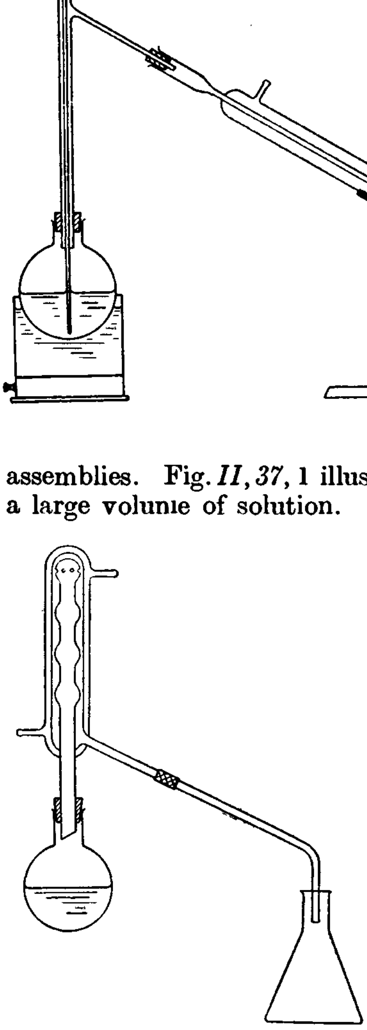


Fig. *II*, *37*, 2.

Fig. *II*, *37*, 2 depicts the apparatus for dealing with comparatively small volumes of liquid. The essential feature is the special condenser with a take-off tube. A few small pieces of porous porcelain are introduced and the flask is heated either on a water bath or upon an electric hot plate. The assembly is also useful in the recrystallisation of compounds which dissolve slowly ; excess of solvent may be employed, and the excess of solvent subsequently removed by distillation.

II,38. DRYING OF SOLID ORGANIC COMPOUNDS

The theory of the action of drying agents has been considered in Section **I,20**. We are now concerned with the practical methods for the removal of water from organic solids and liquids and from solutions of these in organic solvents. The present Section will be devoted to the drying of solids.

A solid, moist with water or a volatile organic solvent, may be dried in the open air by spreading it in thin layers on several layers of absorbent filter paper ; the whole should be covered by a sheet of glass, clock glass or absorbent paper resting upon corks in order to protect it from dust (compare Section **II,33**). This method is rather time-consuming if water is to be completely removed. More effective drying may be secured by placing the substance in thin layers upon clock glasses in a steam oven or in a thermostatically-controlled, electrically-heated oven ; the temperature of the drying oven must be below the melting or decomposition point of the compound, and it is recommended that a preliminary test be made with a small sample.

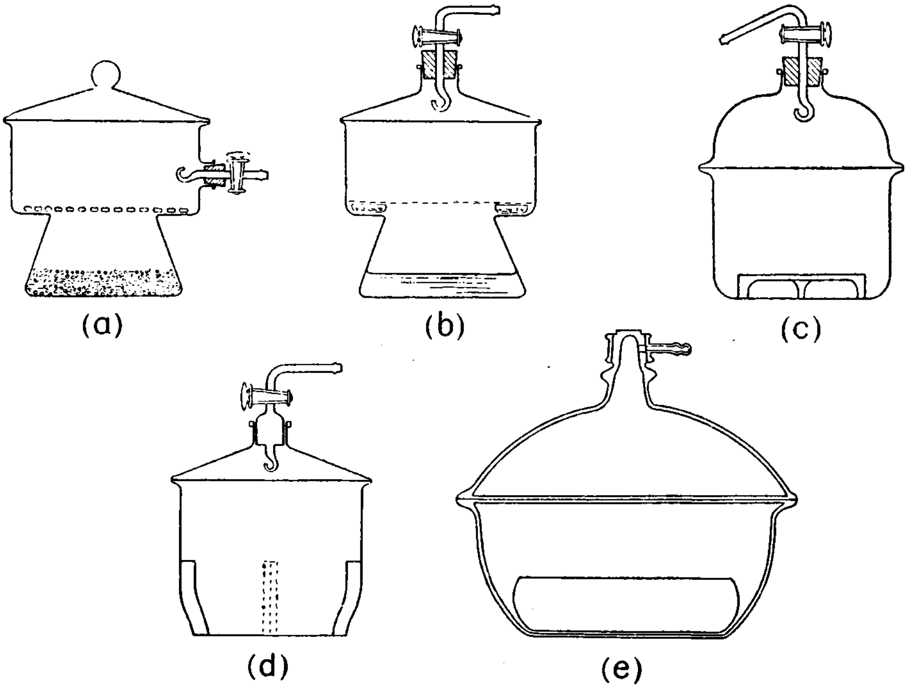


Fig. *II, 38,* 1.

Small quantities of solids may be spread upon unglazed porcelain plates. The chief disadvantage of this method is the comparatively high cost of the porous plates, since they cannot be conveniently cleaned nor can the same area be used for different substances. However, a plate may be broken and used for small amounts of material.

The best method for removing water (and also solvents of relatively low boiling point) adhering to solids is drying under reduced pressure.* A **vacuum desiccator** is used for this purpose ; several forms are shown in Fig. *II, 38,* 1. These are fitted {with the exception of (*e*)} either with

---

* The ordinary desiccator (as in Fig. *II, 38,* 1, *a*, but without tubulure) may be used. The drying at atmospheric pressure is, however, slow. A vacuum desiccator should be employed, if available.

a ground-in stopcock or with a rubber stopper carrying the stopcock; the latter is more economical since the tap may be readily replaced if broken. Fig. *II, 38,* 1, *a* and *b* are the so-called Scheibler forms of desiccator with tubulure in the side and lid respectively; (*c*), the dome form, is constructed with heavy walls and has a relatively large internal volume; (*d*) is a heavy wall Pyrex desiccator; (*e*) is a Pyrex desiccator especially designed for a high vacuum.* In order to render the desiccators air-tight, the ground surfaces of the cover and body are lightly smeared with pure vaseline or with a mixture of pure vaseline and resin stearate.†

When exhausting desiccators, a filter flask trap (see Fig. *II, 19,* 2) should always be inserted between the desiccator and the pump. The "vacuum" should be applied gradually and should not exceed about 50 cm. of mercury for models (*a*), (*b*) and (*d*). These desiccators may withstand lower pressures, but it is generally considered unsafe to exhaust below this pressure unless the precaution be taken of surrounding the desiccator by a cage of fine-mesh steel wire; collapse of the desiccator will then do no harm.‡ Models (*c*) and (*e*) may be exhausted to about 20 mm. of mercury; a steel wire cage must be provided for this low pressure.

The charge of the desiccator will naturally depend upon the exact nature of the substance to be absorbed. An effective "universal" filling is obtained by placing concentrated sulphuric acid § in the lower half and flake sodium hydroxide || in the inverted glass collar supported on the shoulders of the desiccator, the collar being then covered with a zinc gauze or a glazed porcelain perforated plate (as shown in Fig. *II, 38,* 1, *b*). If ether, chloroform, carbon tetrachloride, benzene, toluene and similar vapours are to be absorbed, some freshly cut shavings of paraffin wax should be placed on the sodium hydroxide. Alternatively, granular calcium chloride may be placed in the bottom of the desiccator and silica gel in the shallow porcelain container (Fig. *II, 38,* 1, *c*); if acid vapours are likely to be present, the latter may be charged with flake or pellet sodium hydroxide.

---

* The distinguishing features are: (i) the special stopcock is constructed to turn easily under a high vacuum; (ii) a moulded arrow on the stopcock indicates the "open" position, and a quarter turn from this position closes the desiccator; and (iii) a special liquid container of the non-spill type.

† Many other lubricants are available commercially. "Cello-Seal," designed by Dr. K. Hickman and having a castor oil base, and "Cello-Grease," a similar lubricant intended for stopcocks and ground glass joints, are marketed by the Fisher Scientific Company. "Silicone" stopcock grease (Midland Silicones Ltd.; I.C.I. Silicones Ltd.; Dow-Corning) may also be used; it is said to be applicable over the range −40° to 240°.

‡ The "Desiguard," supplied by the Fisher Scientific Company, is a commercial form of perforated guard for desiccators. It is 12 inches in diameter, 11 inches high, and the upper opening is 3 inches in diameter.

§ If a solution of 18 g. of barium sulphate in one litre of concentrated sulphuric acid is employed, a precipitate of barium sulphate will form when sufficient water has been absorbed to render it unfit for drying: recharging will then, of course, be necessary.

|| This dual filling permits the absorption of both acid and basic vapours which may be evolved. Thus an amine hydrochloride, which has been recrystallised from concentrated hydrochloric acid, may be readily dried in such a desiccator. If concentrated sulphuric acid alone were used, so much hydrogen chloride would be liberated that the pressure inside the desiccator would rise considerably, and the rate of drying would be reduced. With sodium hydroxide present, however, the hydrogen chloride is removed, and the water is absorbed in the normal manner by the reagents but largely by the acid.

When using a vacuum desiccator, the vessel containing the substance (clock glass, etc.) should be covered with an inverted clock glass. This will protect the finer crystals from being swept away should the air, accidentally, be rapidly admitted to the desiccator. In actual practice the tube inside the desiccator leading from the stopcock is bent so that the open end points in the direction of the lid, hence if the tap is only slightly opened and air allowed to enter slowly, there is little danger of the solid being blown from the clock glass or other receptacle.

Frequently the water or other solvent is so firmly held that it cannot be completely removed in a vacuum desiccator at the ordinary temperature. These substances are dried in a vacuum oven at a higher temperature. A convenient laboratory form of vacuum oven is the so-called "**drying pistol**" (*Abderhalden vacuum drying apparatus*) (Fig. *II*, *38*, 2). The vapour from a boiling liquid in the flask *A* rises through the jacket surrounding the drying chamber *B* (holding the substance), and is returned by the condenser. The drying chamber *B* is connected by means of a ground glass joint to the vessel *C* containing the drying agent: *C* is attached to a suction pump. The liquid in *A* is selected according to the temperature desired, *e.g.*, chloroform (62°), trichloroethylene (86°), water (100°), perchloroethylene (120°), *s*-tetrachloroethane (146°), etc. The charge in *C* consists of phosphorus pentoxide distributed on glass wool when water is to be removed, of potassium hydroxide flakes or pellets for removal of acid vapours, and of silica gel or thin layers of paraffin wax for removal of organic solvents, such as chloroform, carbon tetrachloride, benzene and toluene.

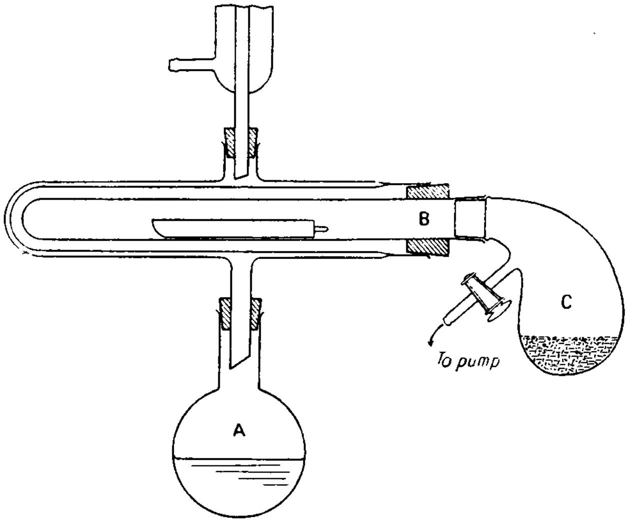


Fig. *II*, *38*, 2.

II,39. DRYING OF LIQUIDS OR OF SOLUTIONS OF ORGANIC COMPOUNDS IN ORGANIC SOLVENTS

Liquids or solutions of organic substances in organic solvents are usually dried by direct contact with a solid inorganic drying agent. The selection of the desiccant will be governed by the following considerations :—(i) it must not combine chemically with the organic compound ; (ii) it should have a rapid and effective drying capacity ; (iii) it should not dissolve appreciably in the liquid ; (iv) it should be as economical as possible ; and (v) it should have no catalytic effect in promoting chemical reactions of the organic compound, such as polymerisation, condensation reactions, and auto-oxidation. The various common drying agents are discussed in detail below ; their relative efficiencies will depend upon the vapour pressure of the system, water : drying agent (see Section **I,20**).

It is generally best to shake the liquid with small amounts of the drying agent until no further action appears to take place : too large an excess is to be avoided in order to keep absorption losses down to a minimum. If sufficient water is present to cause the separation of a small aqueous phase (*e.g.*, with calcium chloride), this must be removed and the liquid treated with a fresh portion of the desiccant. If time permits, the liquid, when apparently dry, should be filtered and left overnight in contact with fresh drying agent. The desiccant should, in general, be separated by filtration (best through a fluted filter paper) before the distillation of the liquid. This is particularly necessary with many reagents whose drying action depends upon the formation of hydrates (*e.g.*, sodium sulphate, magnesium sulphate, and calcium chloride) : at higher temperatures the vapour pressures above the salts become appreciable and unless the salts are removed, much, if not all, of the water may be returned to the distillate. However, with some desiccating agents (sodium, quicklime, baryta, phosphorus pentoxide), the reaction products with water are quite stable and filtration is not essential.

A list of the common drying agents with their practical limitations and their important applications follows.

" Anhydrous " calcium chloride. This reagent is widely employed because of its high drying capacity and its cheapness. It has a large water-absorption capacity (since it forms $CaCl_2,6H_2O$ below 30°) but is not very rapid in its action ; ample time must therefore be given for desiccation. The slowness of the action is attributed to the blanketing of the particles of calcium chloride with a thin layer of the solution formed by the extraction of the water present ; on standing, the water combines forming a solid lower hydrate, which is also a desiccating agent. The industrial process for preparing the reagent usually permits a little hydrolysis to occur, and the product may contain a little free calcium hydroxide or basic chloride. It cannot therefore be employed for drying acids or acidic liquids. Calcium chloride combines with alcohols, phenols, amines, amino-acids, amides, ketones, and some aldehydes and esters, and thus cannot be used with these classes of compounds.

Anhydrous magnesium sulphate. This is an excellent, neutral desiccating agent and is inexpensive. It is rapid in its action, chemically inert and fairly efficient, and can be employed for most compounds including those (esters, aldehydes, ketones, nitriles, amides, etc.) to which calcium chloride is not applicable.

Granular magnesium sulphate is prepared by heating the heptahydrate gently (at 150–175°) in an oven until most of the water of hydration has been evolved, and then heating to redness. A product of less attractive appearance is obtained more rapidly by heating the crystallised salt in a thin layer in an evaporating dish or casserole over a wire gauze; the solid will melt partially and steam will be copiously evolved. The residue (granules and powder) is powdered in a glass mortar, and preserved in a tightly-corked, wide-mouthed bottle. If the crystallised salt is stirred with a glass rod during heating, a dry powder is ultimately obtained directly.

Anhydrous sodium sulphate. This is a neutral drying agent, is inexpensive, and has a high water-absorption capacity (forming $Na_2SO_4,10H_2O$ below 32·4°). It can be used on almost all occasions, but the drying action is slow and not thorough. The desiccant is valuable for the preliminary removal of large quantities of water. Sodium sulphate is an inefficient drying agent for solvents, such as benzene and toluene, whose solubility in water is slight: anhydrous copper sulphate is preferable. Anhydrous sodium sulphate is useless as a desiccant above 32·4°, the decomposition temperature of the decahydrate.

Anhydrous calcium sulphate. When the dihydrate $CaSO_4,2H_2O$ or the hemihydrate $2CaSO_4,H_2O$ is heated in an oven at 230–240° for about three hours, anhydrous calcium sulphate is obtained; much material may be regenerated by the same process. It is sold commercially under the name of "*Drierite*" (not to be confused with "Dehydrite," which is magnesium perchlorate). The reagent is extremely rapid and efficient in its action, is chemically inert, and is insoluble in organic solvents; it may therefore be used with most organic compounds. The only disadvantage is its limited capacity for absorption of water since it passes into the hemihydrate $2CaSO_4,H_2O$, and should theoretically absorb only 6·6 per cent. of its weight of water to retain its maximum efficiency: where extreme desiccation is not essential, the porous commercial product may absorb up to about 10 per cent. of its weight of water. This desiccant is more expensive than magnesium and sodium sulphates, but it can easily be regenerated as indicated above. It is recommended that the substance be subjected to a preliminary drying with magnesium or sodium sulphate, the latter filtered off, and the "Drierite" applied.

The great efficiency of anhydrous calcium sulphate is due to the fact (see Section I,20) that the vapour pressure of the system:

$$2CaSO_4 + H_2O \rightleftharpoons 2CaSO_4,H_2O$$

is only 0·004 mm. at about 25°, and the change with rise of temperature up to about 100° is small. Organic solvents with boiling points below 100° may

COMPOUND	$d_{4^\circ}^{25^\circ}$ (found)	$d_{4^\circ}^{25^\circ}$ (accepted)
Methyl alcohol . .	0·7891 (22°)	0·7898
Ethyl alcohol . .	0·7851	0·7851
Diethyl ether . .	0·7138 (20°)	0·7135
Acetone . . .	0·7844	0·7844
Formic acid . .	1·2202	1·2212
Acetic acid . .	1·051 (20°)	1·0498

therefore be dried by direct distillation from the reagent. The efficiency of its own action will be apparent from the Table on p. 141, which the densities of a few compounds dried by distillation over anhydrous calcium sulphate are compared with the accepted values.

Anhydrous potassium carbonate. This drying agent possesses a moderate efficiency and drying capacity (the dihydrate is formed). It is applied to the drying of nitriles, ketones, esters and some alcohols, but cannot be employed for acids, phenols and other acidic substances. It also sometimes replaces sodium or potassium hydroxide for amines, when a strongly alkaline reagent is to be avoided. Potassium carbonate frequently finds application in salting-out water-soluble alcohols, amines and ketones, and as a preliminary drying agent. In many cases it may be replaced by anhydrous magnesium sulphate.

Sodium and potassium hydroxides. The use of these efficient reagents is generally confined to the drying of amines (soda lime, barium oxide and quicklime may also be employed): potassium hydroxide is somewhat superior to the sodium compound. Much of the water may be first removed by shaking with a concentrated solution of the alkali hydroxide. They react with many organic compounds (*e.g.*, acids, phenols, esters and amides) in the presence of water, and are also soluble in certain organic liquids so that their use as desiccants is very limited

Calcium oxide. This reagent is commonly used for the drying of alcohols of low molecular weight; its action is improved by preheating to 700-900° in an electric furnace. Both calcium oxide and calcium hydroxide are insoluble in the medium, stable to heat, and practically non-volatile,* hence the reagent need not be removed before distillation. Owing to its high alkalinity, it cannot be used for acidic compounds nor for esters; the latter would undergo hydrolysis. Alcohols dried by distillation over quicklime are not completely dry; the last traces of moisture may be removed by distillation over aluminium or magnesium amalgam or by treatment with a high boiling point ester and a little sodium (see Section **II,47**,*5* and *6*).

Aluminium oxide. The commercial material, "activated alumina," is made from aluminium hydroxide; it will absorb 15–20 per cent. of its weight of water, can be re-activated by heating at 175° for about seven hours, and does not appreciably deteriorate with repeated use. Its main application is as a drying agent for desiccators.

Boric anhydride. This is a powerful and efficient desiccant and will absorb up to about 25 per cent. of its weight of water. It is useful for drying formic acid.

Phosphorus pentoxide. This is an extremely efficient reagent and is rapid in its reaction. Phosphoric oxide is difficult to handle, channels badly, is expensive, and tends to form a syrupy coating on its surface after a little use. A preliminary drying with anhydrous magnesium

---

* Some finely divided particles of solid may be carried over during the distillation from quicklime. It is recommended that the head of the distillation assembly leading to the condenser be a wide tube filled with purified glass wool in order to retain the finely-divided solid. The purified glass wool is prepared by boiling commercial glass wool with concentrated nitric acid for about 15 minutes, washing thoroughly with distilled water, and drying at 120°.

sulphate, etc., should precede its use. Phosphorus pentoxide is only employed when extreme desiccation is required. It may be used for hydrocarbons, ethers, alkyl and aryl halides, and nitriles, but not for alcohols, acids, amines and ketones.

Metallic sodium. This metal is employed for the drying of ethers and of saturated and aromatic hydrocarbons. The bulk of the water should first be removed from the liquid or solution by a preliminary drying with anhydrous calcium chloride or magnesium sulphate. Sodium is most effective in the form of fine wire, which is forced directly into the liquid by means of a sodium press (see under *Ether*, Section **II,47,*1***) : a large surface is thus presented to the liquid. It cannot be used for any compound with which it reacts or which is affected by alkalis or is easily subject to reduction (due to the hydrogen evolved during the dehydration), *viz.*, alcohols, acids, esters, organic halides, ketones, aldehydes, and some amines.

CAUTION. Sodium must be handled with great care and under no circumstances may the metal be allowed to come into contact with water as a dangerous explosion may result. Sodium is stored under solvent naphtha or xylene ; it should not be handled with the fingers but with tongs or pincers. Waste or scrap pieces of sodium should be placed in a bottle provided for the purpose and containing solvent naphtha or xylene : they should never be thrown into the sink or into the waste box. If it is desired to destroy the scrap sodium, it should be added in small portions to rather a large quantity of methylated spirit.

Concentrated sulphuric acid. The only well-known use for this reagent is for drying bromine, with which it is immiscible. The bromine is shaken in a separatory funnel with small quantities of concentrated sulphuric acid until no further action takes place. The reagent is, however, widely used for desiccators.

Absorbent cotton (cotton wool). This material is an excellent drying agent for use in the so-called " calcium chloride tubes," *i.e.*, drying tubes, placed at the top of dropping funnels, reflux condensers, etc., to exclude moisture. It is more convenient than calcium chloride, and should preferably be dried in an oven at 100° before use.

The common drying agents that are suitable for various classes of organic compounds are listed in Table **II**, 39.

Drying by distillation. In most cases the distillation of organic preparations before drying is regarded as bad technique, but in a number of instances of solvents or liquids, which are practically insoluble in water, the process of distillation itself effects the drying. In short, advantage is taken of the formation of binary and ternary mixtures of minimum boiling point (compare Section **I,4,** and also the theory of steam distillation in Section **I,6**). Thus if moist benzene is distilled, the first fraction consists of a mixture of benzene and water (the constant boiling point mixture, b.p. 69·3°, contains 29·6 per cent. of water) ; after the water has been removed, dry benzene distils. Other solvents which may be dried in this manner include carbon tetrachloride, toluene, xylene, hexane, heptane, petroleum ether, and ethylene dichloride. The dry solvent should not be collected until after about 10 per cent. of the main bulk has passed over, since it is necessary to eliminate also

TABLE II, 39. COMMON DRYING AGENTS FOR ORGANIC COMPOUNDS

Alcohols	Anhydrous potassium carbonate ; anhydrous magnesium or calcium sulphate ; quicklime.
Alkyl halides *Aryl halides*	Anhydrous calcium chloride ; anhydrous sodium, magnesium or calcium sulphate ; phosphorus pentoxide.
Saturated and aromatic hydrocarbons *Ethers*	Anhydrous calcium chloride ; anhydrous calcium sulphate ; metallic sodium ; phosphorus pentoxide.
Aldehydes	Anhydrous sodium, magnesium or calcium sulphate.
Ketones	Anhydrous sodium, magnesium or calcium sulphate ; anhydrous potassium carbonate.
Organic bases (amines)	Solid potassium or sodium hydroxide ; quicklime ; barium oxide.
Organic acids	Anhydrous sodium, magnesium or calcium sulphate.

the moisture adsorbed by the walls of the flask and the condenser. If moist aniline (b.p. 184°) or moist nitrobenzene (b.p. 210°) is distilled, the moisture is rapidly removed in the first portion of the distillate and the remainder of the liquid passes over dry. Sometimes a moist liquid preparation, which is sparingly soluble in water, is dried by admixture with a solvent (usually benzene) immiscible with water, and the resulting mixture is distilled. Thus when a mixture of *n*-valeric acid, water and benzene is distilled, the mixture of benzene and water passes over first (b.p. 69·3°), this is followed by dry benzene (b.p. 80°), and finally by dry *n*-valeric acid (b.p. 186°). This method has been used for the drying of commercial preparations of *iso*-valeric, *n*-caproic, *iso*-caproic, capric acids, etc. by distillation with about 40 per cent. of the weight of benzene until the temperature of the vapours reaches 100°. The dehydration of crystallised oxalic acid by distillation with carbon tetrachloride (see also pinacol from pinacol hydrate, Section **III,77**) is sometimes regarded as another example of the use of a binary mixture for the removal of water.

The use of a ternary mixture in the drying of a liquid (ethyl alcohol) has been described in Section **I,5** ; the following is an example of its application to the drying of a solid. Laevulose (fructose) is dissolved in warm absolute ethyl alcohol, benzene is added, and the mixture is fractionated. A ternary mixture, alcohol-benzene-water, b.p. 64°, distils first, and then the binary mixture, benzene-alcohol, b.p. 68·3°. The residual, dry alcoholic solution is partially distilled and the concentrated solution is allowed to crystallise : the anhydrous sugar separates.

Drying by hydrolysis. The production of extremely dry (99·9+ per cent.) ethyl alcohol from commercial " absolute " alcohol (99+ per cent.) is possible by taking advantage of the fact that the hydrolysis of an ester consumes water. Thus if the " absolute " alcohol is treated with a little sodium in the presence of an ester of high boiling point (*e.g.*, ethyl phthalate or ethyl succinate) and the mixture is distilled from a water or steam bath, extremely dry alcohol will pass over :

$$RCOOC_2H_5 + NaOC_2H_5 + H_2O = RCOONa + 2C_2H_5OH$$

(see Section **II,47,*5***).

II,40. TECHNIQUE OF STEAM DISTILLATION

Steam distillation is a means of separating and purifying organic compounds. Essentially the operation consists in volatilising a substance, which is insoluble or sparingly soluble in water, by passing steam into a mixture of the compound and water. Provided the organic compound has an appreciable vapour pressure (at least 5–10 mm. at 100°), it will distil with the steam ; it can be readily separated from the distillate since it is immiscible with water. Steam distillation takes place at a temperature below the boiling point of water (for theory, see Section **I,6**) and hence, in numerous cases, well below the boiling point of the organic substance. This renders possible the purification of many substances of high boiling point by low temperature distillation, and is particularly valuable when the substances undergo decomposition when distilled alone at atmospheric pressure. It is also of importance in the separation of the desired organic compound :

(i) from non-volatile tarry substances which are formed as by-products in many reactions ;

(ii) from aqueous mixtures containing dissolved inorganic salts ;

(iii) in those cases where other means of separation might lead to difficulties (*e.g.*, the direct ether extraction of aniline, produced by the reduction of nitrobenzene by tin, etc., leads to troublesome emulsion formation owing to the alkali and the tin compounds present) ;

(iv) from compounds which are not appreciably volatile in steam (*e.g.*, *o*-nitrophenol from *p*-nitrophenol) ; and

(v) from certain by-products which are steam volatile (*e.g.*, diphenyl and excess of unreacted starting materials from the non-volatile triphenylcarbinol, Section **IV,202**).

The student should be familiar with the theory of steam distillation, given in Section **I,6**, before carrying out the operation in the laboratory.

A simple apparatus for steam distillation is shown in Fig. *II*, *40*, 1, *a*. The steam is generated in the steam can *A*,* which is provided with a long glass safety tube dipping well below the surface of the water, and passes into the round-bottomed flask *B* by a tube bent as shown. The steam distillation flask is inclined at an angle so as to prevent the solution in *B* from being splashed into the entrance of the outlet tube and thus being blown over mechanically into the condenser. A tube of comparatively wide bore (5–8 mm.), with one end just below the cork in the flask, connects the flask with a Liebig condenser. The distillate is collected in the flask *D* ; *E* is a glass adapter which facilitates the collection of the distillate, but may be omitted if desired. The flask *B* is heated on an asbestos-centred wire gauze, supported on a tripod. If the laboratory

---

* Alternatively, a flask (capacity one litre or more), fitted with a two-holed cork carrying a long safety tube and a short right-angled bend, may be used. A large distilling flask will serve the same purpose.

possesses an external steam supply, the trap (Fig. *II*, *40*, 1, *b* or *c*) replaces the steam can ; it will remove foreign matter and also the water present in the steam ; the screw clip is opened from time to time to allow the accumulated water to run to the sink.

To carry out a steam distillation, the solution (or mixture or the solid with a little water) is placed in the flask *B*, and the apparatus is completely assembled. Steam is passed into the flask *B*, which is itself heated by means of a small flame to prevent too rapid an accumulation of water, at such a rate that it is completely condensed by the condenser *C*. The passage of steam is continued until there is no appreciable amount of water-insoluble material in the distillate. If the substance crystallises in the condenser and tends to choke it, the water should be run out of the condenser for a few minutes until the solid material has been melted and carried by the steam into the receiver ; the water should then be cautiously re-admitted to the hot condenser. To discontinue the distillation, the rubber connexion between the steam can and the flask is first removed ; this will prevent any liquid from the flask *B* passing into *A*. The flames are then extinguished. The method of isolation of the pure organic compound from the distillate will depend upon its physical state and upon its solubility in water. Examples will be found in Chapters III and IV.

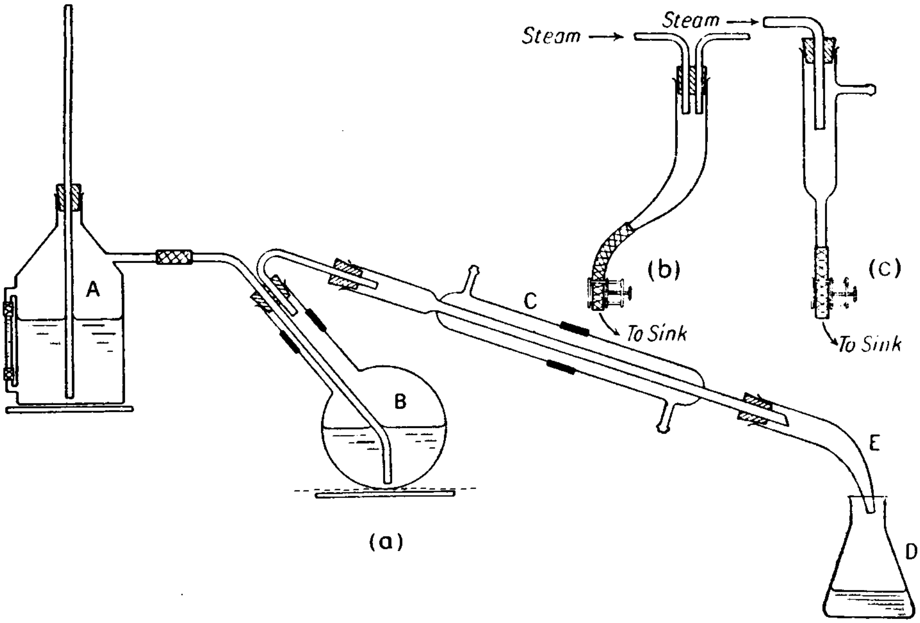


Fig. *II*, *40*, 1.

II,41. MODIFICATIONS OF THE STEAM DISTILLATION APPARATUS

It is frequently convenient to carry out the steam distillation from the flask in which the chemical reaction has taken place ; losses due to transfer to another vessel are thus avoided and much time may be saved. Two types of suitable apparatus are illustrated in Figs. *II*, *41*, 1 and *II*, *41*, 2 ; the former is for a three-necked flask and the latter for a bolt-head (or other wide-necked) flask.

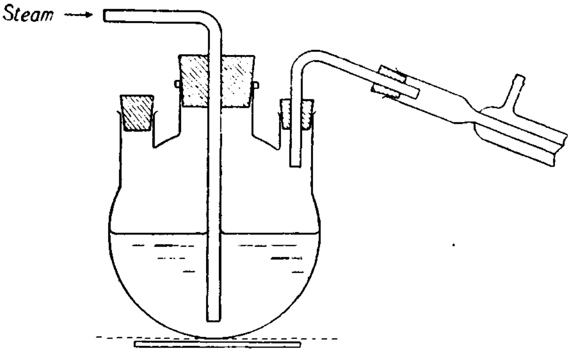


Fig. *II*. *41*. 1.

The set-up of Fig. *II*, *41*, 3 ensures the complete condensation of the steam when a rapid flow of steam is necessary for satisfactory results, and is useful in the distillation of large volumes of liquids of low vapour pressure, such as nitrobenzene. Thus the flask *A* containing the mixture may be of 3-litre capacity and *B* may be a 1-litre flask ; the latter is cooled by a stream of water, which is collected in a funnel and conducted to the sink. The receiver *C* must be of proportionate size ; all stoppers should be wired into place. When a rapid current of steam is passed into the flask *A* (which should be heated on an asbestos-centred gauze by means of a small flame), some vapour is soon condensed in receiver *B* and the resulting liquid forms a liquid seal at the exit tube. Vapour cannot escape into the second condenser. The effect of uncondensed vapour in *B* is to force the liquid over into *C* as soon as sufficient pressure

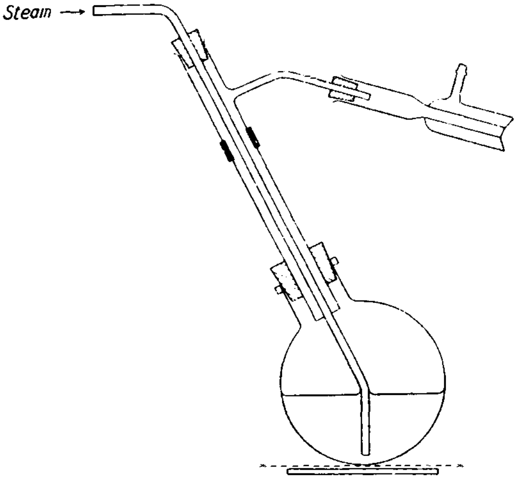


Fig. *II*, *41*, 2.

develops. To determine when the distillation is complete, the supply of cooling water for flask *B* is temporarily turned off; this results in the emptying of the intermediate receiver and permits the inspection of the condensed liquid in the second condenser.

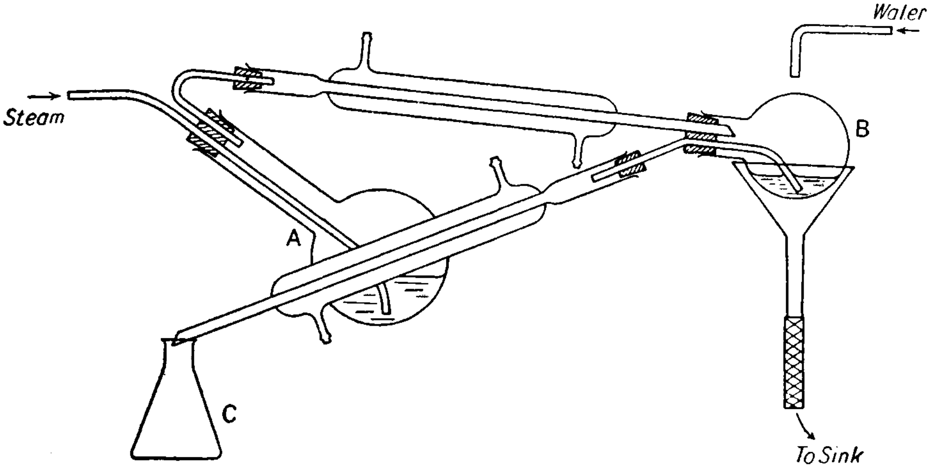


Fig. *II*, *41*, 3.

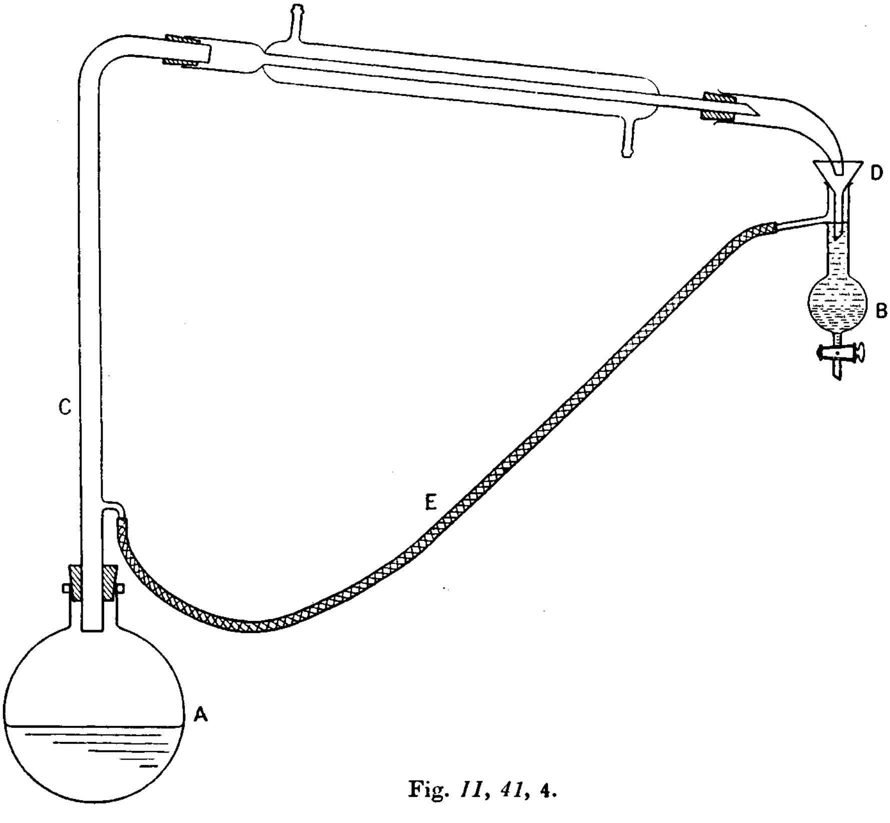


Fig. *II*, *41*, 4.

Fig. *II*, *41*, 4 is an apparatus for **the continuous steam distillation of a liquid which is heavier than water.** The aqueous mixture is placed in the flask *A* of relatively large capacity ; the receiver *B* consists of a distilling flask (provided with a stopcock at the lower end), the capacity of which is less than the volume of the liquid in *A*, and is placed several inches higher than the opening in the wide vertical tube *C*. The lower end of the funnel *D* must be below the side arm of the receiver in order to prevent bubbles of the heavy liquid from collecting on the surface of the steam distillate and being carried back to the flask *A*. The rubber tube *E* for the returning aqueous liquor must at some point be lower than the entrance to the tube *C* so that a trap of liquid will be formed and prevent the vapours from *A* entering the side tube. Sometimes an air bubble enters the tube *E* and prevents the regular flow of liquid from *B*; the air bubble is easily removed by shaking the rubber tube. The flask *A* is heated (*e.g.*, by a ring burner) so that distillation proceeds at a rapid rate ; the process is a continuous one. If the liquid to be steam distilled is lighter than water, the receiver must be modified so that the aqueous liquors are drawn off from the bottom (see *Continuous Extraction of Liquids*, Section **II,44**).

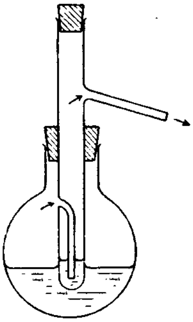


Fig. *II*, *41*, 5.

The steam distillation of small quantities of material may be conducted in the apparatus of Fig. *II*, *41*, 5. The substance to be distilled is placed in the small inner tube (a specially constructed test-tube) and water is boiled in the outer bolt-head flask. The volume of the liquid in the inner tube does not increase appreciably since it is immersed in the hot liquid in the flask.

The theory of, and the apparatus for, **distillation with superheated steam** are described in Section **I,7**.

II,42. TECHNIQUE OF EXTRACTION WITH SOLVENTS

A common operation in practical organic chemistry is the separation of an organic compound from a solution or suspension in a liquid by shaking with a second solvent in which the organic compound is soluble and which is immiscible (or nearly immiscible) with the liquid containing the substance. The liquid is generally water, so that the subsequent discussion will be concerned with extraction from this medium. The solvents generally employed for extraction are diethyl ether, di-*iso*-propyl ether, benzene, chloroform, carbon tetrachloride, and petroleum ether. The solvent selected will depend upon the solubility of the substance to be extracted in that solvent (compare Section **I,22**) and upon the ease with which the solvent can be separated from the solute. Diethyl ether, owing to its powerful solvent properties and its low boiling point (35°) thus rendering its removal extremely facile, is very widely used ; its chief disadvantage lies in the great fire hazard attending its use, but this may be reduced to a minimum by adopting the precautions given in Section **II,14**. The fire hazard is reduced also by employing di-*iso*-propyl ether (b.p. 67·5°), but this solvent is much more expensive than diethyl ether.

The theory of extraction with solvents has been discussed in Section **I,22**, and it has been shown that for a given volume of solvent several extractions with aliquot parts give better results than a single extraction with the total volume of the solvent. By way of illustration, the technique of the extraction of an aqueous solution with diethyl ether * will be described. A separatory funnel (globular or pear-shaped with a short stem, see Figs. *II*, *1*, 5, *c* and *d*) is selected of about twice the volume of the liquid to be extracted, and is mounted in a ring on a stand with a firm base. The barrel and plug of the stopcock are dried with a linen cloth, and lightly treated with a suitable lubricant (vaseline, etc.; see third footnote in Section **II,38**). A new well-fitting cork is selected for closing the mouth of the funnel; alternatively, the ground glass stopper, supplied with the separatory funnel, may be used. The solution and the extraction solvent (usually about one third of the volume of the solution, but see Section **I,22**) are introduced into the funnel, and the latter stoppered. All naked flames in the immediate vicinity should be extinguished. The funnel is then shaken *gently* (so that the excess vapour pressure † will be developed slowly), inverted, and the stopcock opened in order to relieve the excess pressure. The stopcock is again closed, the funnel again shaken, and the internal pressure released. When the atmosphere inside the funnel is saturated with ether vapour, further shaking develops little or no additional pressure. At this stage, the funnel is vigorously shaken for 2-3 minutes to ensure the maximum possible transfer of the organic substance to the ether layer, and then returned to the stand in order to allow the mixture to settle. When two sharply defined layers have formed, the lower aqueous layer is run off and separated as completely as possible. The residual ethereal layer is then poured out through the upper neck of the funnel; contamination with any drops of the aqueous solution still remaining in the stem of the funnel is thus avoided. The aqueous solution may now be returned to the funnel and the extraction repeated, using fresh ether on each occasion until the extraction is complete. Not more than three extractions are usually required, but the exact number of extractions will naturally depend upon the partition coefficient (Section **I,22**) of the substance between water and ether. The completeness of the extraction can always be determined by evaporating a portion of the last extract on the water bath and noting the amount of residue. The combined ethereal solutions are dried with an appropriate reagent (Section **II,39**), and the ether removed on a water bath (Sections **II,5**, **II,13** and **II,14**). The residual organic compound is purified, depending upon its properties, by distillation or by recrystallisation.

Occasionally **emulsions** are formed in the extraction of aqueous solution by organic solvents, thus rendering a clean separation impossible. Emulsion formation is particularly liable to occur when the aqueous

---

* Diethyl ether will be abbreviated throughout the book to *ether*. The ether should be reasonably free from "peroxides," see Section **II,47**,*1*.

† When ether is poured into a funnel containing an aqueous solution, a two liquid-phase system is formed (compare Section **I,6**). If the funnel is stoppered and the mixture shaken, the vapour pressure of the ether (300-500 mm., according to the temperature) is ultimately added to the pressure of the air (about 760 mm.) plus water vapour, thus producing excess of pressure inside the funnel. Hence the necessity for shaking gently and releasing the pressure from time to time until the air has been expelled.

solution is alkaline, but the emulsion may be broken by the addition of dilute sulphuric acid, if this is permissible. Various devices which are employed to break up emulsions include :—

1. Drawing a stream of air over the surface by inserting a tube, connected to a water pump, above the mixture.
2. Saturating the aqueous phase with sodium chloride.
3. Addition of a few drops of alcohol or other suitable solvent (this is generally undesirable).

In general, however, satisfactory separation will be obtained if the mixture is allowed to stand for some time.

In the isolation of organic compounds from aqueous solutions, use is frequently made of the fact that the solubility of many organic substances in water is considerably decreased by the presence of dissolved inorganic salts (sodium chloride, calcium chloride, ammonium sulphate, etc.). This is the so-called **salting-out effect.*** A further advantage is that the solubility of partially miscible organic solvents, such as ether, is considerably less in the salt solution, thus reducing the loss of solvent in extractions.

II,43. EXTRACTION BY CHEMICALLY ACTIVE SOLVENTS

This type of extraction depends upon the use of a reagent which reacts chemically with the compound to be extracted, and is generally employed either to remove small amounts of impurities in an organic compound or to separate the components of a mixture. Examples of such reagents include dilute (5 per cent.) aqueous sodium or potassium hydroxide solution, 5 or 10 per cent. sodium carbonate solution, saturated sodium bicarbonate solution (*ca.* 5 per cent.), dilute hydrochloric or sulphuric acid, and concentrated sulphuric acid.

Dilute sodium hydroxide solution (and also sodium carbonate solution and sodium bicarbonate solution) can be employed for the removal of an organic acid from its solution in an organic solvent, or for the removal of acidic impurities present in a water-insoluble solid or liquid. The extraction is based upon the fact that the sodium salt of the acid is soluble in water or in dilute alkali, but is insoluble in the organic solvent. Similarly, a sparingly soluble phenol, *e.g.*, β-naphthol, $C_{10}H_7.OH$, may be removed from its solution in an organic solvent by treatment with sodium hydroxide solution.

Dilute hydrochloric or sulphuric acid finds application in the extraction of basic substances from mixtures or in the removal of basic impurities. The dilute acid converts the base (*e.g.*, ammonia, amines, etc.) into a water-soluble salt (*e.g.*, ammonium chloride, amine hydrochloride). Thus traces of aniline may be separated from impure acetanilide by shaking with dilute hydrochloric acid : the aniline is converted into the soluble salt (aniline hydrochloride) whilst the acetanilide remains unaffected.

Cold concentrated sulphuric acid will remove unsaturated hydrocarbons present in saturated hydrocarbons, or alcohols and ethers present in alkyl halides. In the former case soluble sulphonated products are formed, whilst in the latter case alkyl hydrogen sulphates or addition complexes, that are soluble in the concentrated acid, are produced.

---

* For a detailed discussion, see, for example, Glasstone, *Text Book of Physical Chemistry*, 1947, p. 729 (Van Nostrand ; Macmillan).

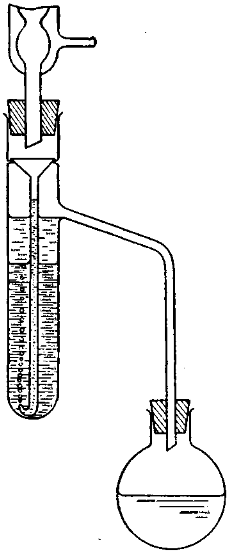


Fig. *II*, *44*, 1.

II,44. CONTINUOUS EXTRACTION OF LIQUIDS OR SOLIDS BY SOLVENTS

When the organic compound is more soluble in water than in the organic solvent (*i.e.*, the distribution coefficient between the organic solvent and water is small, compare Section **I,22**), very large quantities of organic solvent must be employed in order to obtain even a moderate extraction. This may be avoided by the use of an apparatus for continuous extraction; only relatively small volumes of solvent are required. Two types of apparatus are used for the extraction of aqueous solutions according as to whether the organic solvent is heavier or lighter than water. Figs. *II*, *44*, 1 and 2 illustrate two forms of **apparatus for the extraction of a heavier liquid by a lighter one,** *e.g.*, an aqueous solution by means of ether. The assembly of Fig. *II*, *44*, 1 is suitable for the extraction of relatively small volumes of solutions; the lower end of the funnel may carry a sealed-in sintered glass disc to improve the circulation of the lighter solvent or it may be sealed

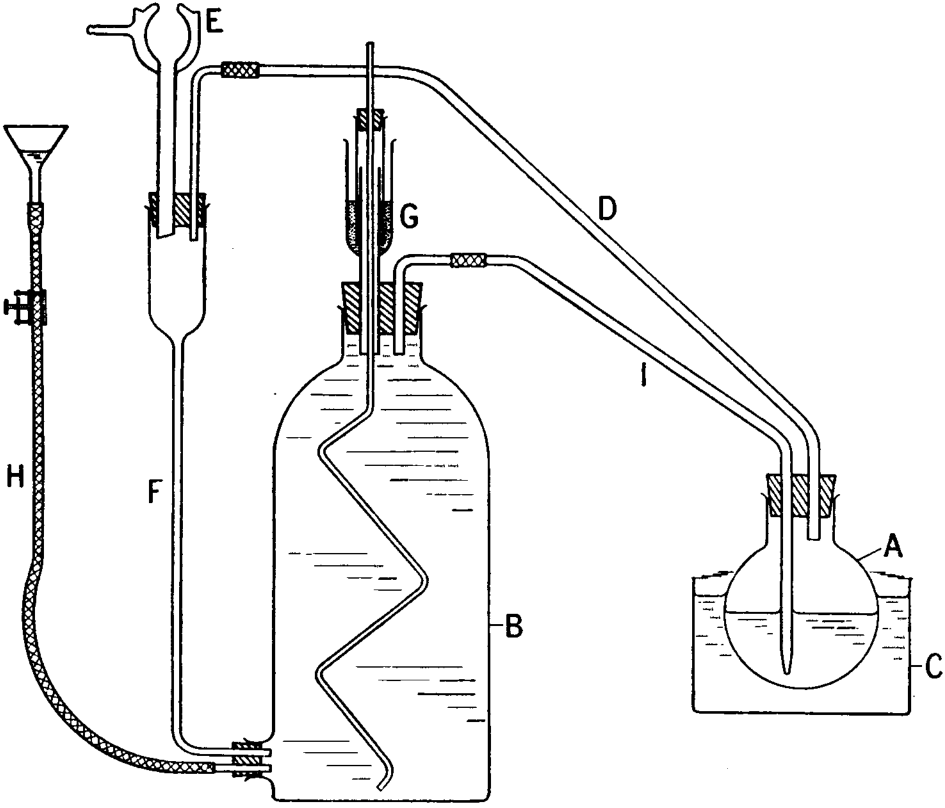


Fig. *II*, *44*, 2.

completely in the form of a small bulb with three 1 mm. holes blown near the bottom. The set-up of Fig. *II*, *44*, 2 is preferable where comparatively large volumes of solutions are involved. Two-thirds of the solvent to be used for the extraction are placed in the flask *A* and the remainder in the wide-mouthed bottle *B*, which should be just large enough to hold the aqueous solution and the solvent (ether). The flask is heated on a steam or water bath *C* ; the ether vapour passes through the tube *D* into the condenser (preferably of the double surface type) *E*. The condensed ether flows through *F* into the bottle *B*, the contents of which are mechanically stirred by the mercury-sealed stirrer *G* in order to ensure efficient contact of the liquids. The tube *H*, carrying the screw clip, enables the bottle to be filled or emptied without disconnecting the apparatus. If the solution in *A* becomes too concentrated and consequently so hot that ether cannot flow back through the tube *I* owing to its rapid vaporisation, the contents of the flask *A* must be removed and replaced by fresh solvent.

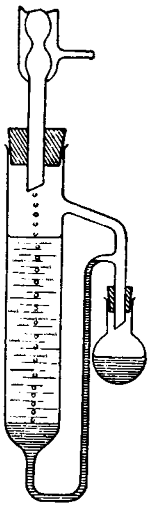


Fig. *II*, *44*, 3.

Fig. *II*, *44*, 3 depicts an apparatus for the continuous extraction of a liquid with a heavier liquid, for example, an aqueous solution by chloroform or carbon tetrachloride. The apparatus of Fig. *II*, *44*, 2 can easily be adapted for the same purpose by arranging for the removal of the solvent from the *bottom* of the extraction bottle *B* and returning it to the flask *A*.

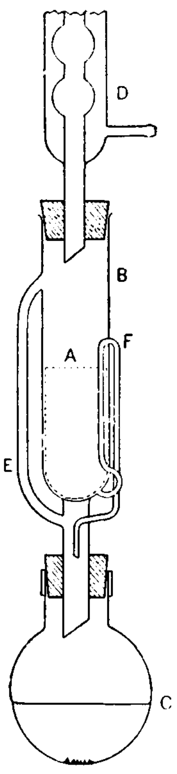


Fig. *II*, *44*, 4.

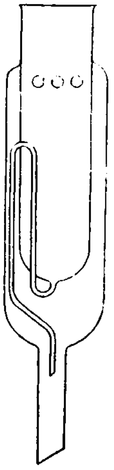


Fig. *II*, *44*, 5.

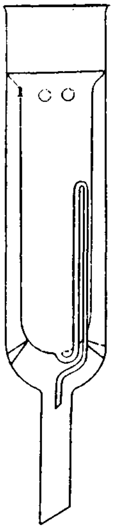


Fig. *II*, *44*, 6.

For the continuous extraction of a solid by a hot solvent, the *Soxhlet extraction apparatus*, shown in Fig. *II*, *44*, 4, is usually employed. The solid substance is placed in the porous thimble *A* (made of tough filter paper) and the latter is placed in the inner tube of the Soxhlet apparatus. The apparatus is then fitted to a bolt-head flask *C*, containing the solvent, and to a reflux condenser *D* (preferably of the double surface type). The solvent is boiled gently; the vapour passes up through the tube *E*, is condensed by the condenser *D*, and the condensed solvent falls into the thimble *A* and slowly fills the body of the Soxhlet.* When the solvent reaches the top of the tube *F*, it siphons over into the flask *C*, and thus removes that portion of the substance which it has extracted in *A*. The process is repeated automatically until complete extraction is effected. The extracted compound may be isolated from its solution in *C* by any of the usual methods. One minor disadvantage of this apparatus is that the temperature of the liquid in *A* differs considerably from the boiling point of the solvent; extraction is thus effected by the lukewarm liquid and is therefore relatively slow, particularly if the solubility of the substance increases markedly with temperature. This disadvantage is absent in the modifications illustrated in Figs. *II*, *44*, 5 and 6, in which the part of the apparatus housing the extraction thimble is surrounded by the vapour of the solvent: extraction is accordingly effected by the hot solvent. In Fig. *II*, *44*, 5 the inner wide tube carrying the siphon tube is fused to the outer jacket, and the vapour of the solvent enters through the series of small holes near the top. In Fig. *II*, *44*, 6 the inner tube rests on small glass supports situated at the bottom of the outer jacket.

II,45. TECHNIQUE OF SUBLIMATION

The theory of sublimation, *i.e.* the direct conversion from the vapour to the solid state without the intermediate formation of the liquid state, has been discussed in Section **I,19**. The number of compounds which can be purified by sublimation under normal pressure is comparatively small (these include naphthalene, anthracene, benzoic acid, hexachloroethane, camphor, and the quinones). The process does, in general, yield products of high purity, but considerable loss of product may occur.

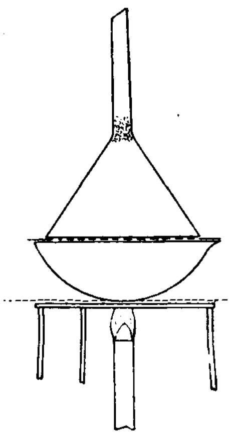


Fig. *II*, *45*, 1.

The simplest form of apparatus consists of a small porcelain evaporating dish covered with a filter paper which has been perforated with a number of small holes; a watch glass of the same size, convex side uppermost, is placed on the filter paper. The substance is placed inside the dish, and the latter heated with a minute flame on a wire gauze or sand bath. The sublimate collects in the watch glass, and the filter paper below prevents the sublimate from falling into the residue. The watch glass may be kept cool by covering it with several pieces of damp filter

---

* For solids of low density, the top of the porous thimble *A* should be above the siphon tube *F*, otherwise the solid may tend to float out of the thimble and pass down the siphon tube.

paper, and moistening these from time to time. Another form of apparatus suitable for somewhat larger quantities of material, is shown in Fig. *II*, *45*, 1. The crude substance is placed in an evaporating dish and a narrow ring of Pyrex glass or asbestos board is fitted near the rim. The latter supports a filter paper or thin asbestos paper pierced with a number of small holes, and an inverted glass funnel, with a plug of glass wool in the stem, is supported upon the asbestos or glass ring. Upon heating the dish gently, the pure compound collects on the upper surface of the filter (or asbestos) paper or on the walls of the funnel ; the heating is stopped when most of the material in the dish has vaporised. Care must be taken that the supply of heat is adjusted so that the funnel does not become more than lukewarm. Excellent results may be obtained by using a funnel surrounded by a water jacket or with a coil of copper tubing wound into a 60° cone and through which water is circulated (compare the hot water funnel of Fig. *II*, *1*, 6, *b*). An alternative procedure, which is particularly valuable for substances which sublime at a comparatively high temperature, is to use a large crucible, preferably of silica, which is fitted into a hole in a thick asbestos board so that about half of the crucible projects beneath the board. Two nested funnels are inverted over the crucible, the larger funnel having a plug of glass wool in the neck. The crucible is then heated to the required temperature with an open flame.

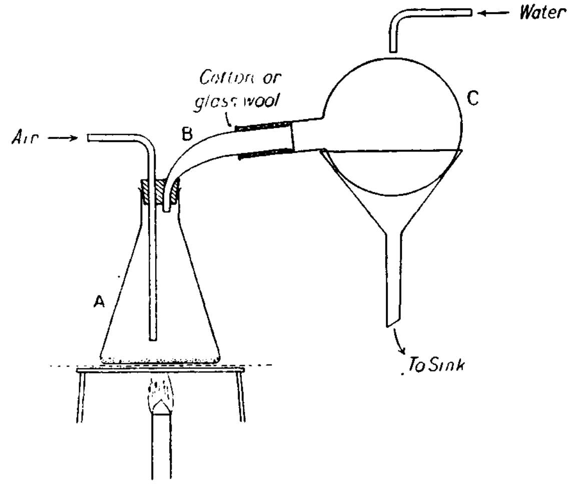


Fig. *II*, *45*, 2.

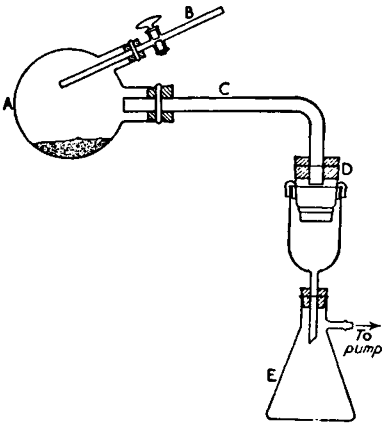


Fig. *II*, *45*, 3.

A simple apparatus for sublimation in a stream of air or inert gas is shown in Fig. *II*, *45*, 2. *A* is a wide-necked conical flask provided with a two-holed cork carrying a delivery tube for the supply of air (or inert gas) and an adapter *B*; the latter fits loosely into a round-bottomed flask *C*, the mouth of which is plugged with glass or cotton wool. The flask *C* is cooled by a stream of cold water, which is collected in the funnel below and the waste water is run to the sink. Upon heating the crude substance in the flask *A*, the pure material collects on the walls of *C*.

A simple apparatus for sublimation in a stream of air or of inert gas is shown in Fig. *II*, *45*, 3. *A* is a two-necked flask equipped with a narrow inlet tube *B* with stopcock and a wide tube *C* 12–15 mm. in diameter. The latter is fitted to a sintered glass crucible and the usual adapter and suction flask *E*. A well-fitting filter paper is placed on the sintered glass filter plate to collect any sublimate carried by the gas stream.

Sublimation under reduced pressure. The so-called "vacuum sublimation" may be carried out in the apparatus of Fig. *II*, *45*, 4. The "cold finger" is fitted into the larger tube by means of a rubber stopper and carries a disc slightly smaller in diameter than the outer tube; the pressure may be reduced by a water or oil pump. The impure material is placed in the wider tube, and the apparatus is exhausted. Upon heating gently (preferably by immersion in a bath of liquid), the pure substance collects on the cold surface and on the disc. The apparatus is available commercially in all-glass form, with a ground glass joint replacing the rubber stopper (Fig. *II*, *45*, 5) *; this is intended for dealing with quantities of a few milligrams up to about 1 gram. It is recommended that the apparatus be heated in an oil bath : a direct flame may lead to decomposition, due to too high a temperature.

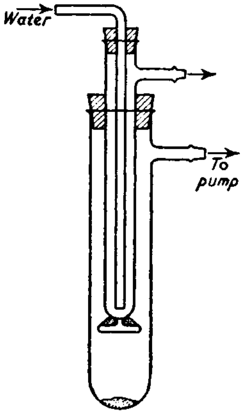


Fig. *II*, *45*, 4.

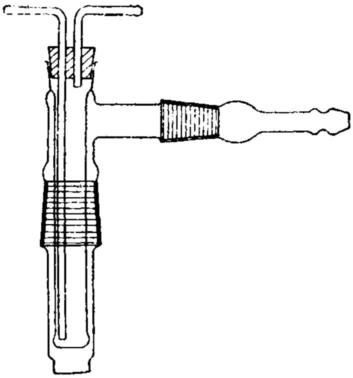


Fig. *II*, *45*, 5.

II,46. CHROMATOGRAPHIC ADSORPTION

Chromatography is based upon the selective adsorption from solution on the active surface of certain finely divided solids. Closely related substances exhibit different powers of adsorption, so that separations, which are extremely difficult by ordinary chemical methods, may be effected by this means. When, for example, a solution of leaf pigments

---

* Supplied by J. W. Towers and Co. Ltd.

in an organic solvent (*e.g.*, a mixture of light petroleum, b.p. 60–80°, and benzene), is passed slowly through a tube packed with a white adsorbent, such as alumina, the individual pigments tend to be retained in different coloured zones, the most strongly adsorbed components being retained at the top, and those with less affinity for the adsorbent at lower levels. The initial separation of the different coloured layers is usually not very distinct, but by passing a fresh portion of the original solvent or of another solvent through the tube, the zones become more sharply defined and may spread over the length of the whole column. The banded column of adsorbent is termed a **chromatogram**, and the operation is spoken of as the **development of the chromatogram**. The appearance of the chromatogram of spinach leaves is shown diagrammatically in Fig. *II*, *46*, 1 ; the tube is packed with alumina (bottom), calcium carbonate and sugar. The resolution into chlorophyll-*b* (yellowish-green), chlorophyll-*a* (bluish-green), xanthophyll (yellow) and carotene (yellow) is clearly visible. Two procedures may be adopted in order to recover the constituents of the mixture. The column of adsorbent may be pushed out of the tube, the various zones cut with a knife at the boundaries, and the coloured components extracted with a suitable solvent: this recovery is called **elution**. Alternatively, the column may be washed with more solvent, now termed the **eluent** (the solvent is not necessarily identical with that used as the developer), and each component collected separately as it reaches the end of the column and is released.

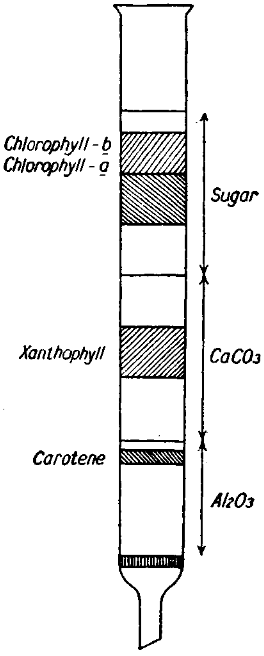


Fig. *II*, *46*, 1.

Column chromatography was first developed by the American petroleum chemist D. T. Day in 1900. M. S. Tswett, the Polish botanist, in 1906 used adsorption columns in his investigations of plant pigments. It was not until about 1930 that the method was used extensively by chemists. The most startling results have been obtained in the fields of plant pigments and natural products, but chromatography has also many applications in ordinary laboratory practice. A substance need not be highly coloured to give a visible adsorption band ; it must be remembered that the material retained in a zone of the column is in a concentrated form. Thus a pale yellow reaction product may be resolved by chromatography into a yellow component and a colourless one, and the latter may pass through into the filtrate. Frequently, a colour which cannot be removed by repeated recrystallisation nor by treatment with decolourising carbon in the usual way is thus readily separated by adsorption analysis. This method of purification is assisted by the general tendency of coloured substances to be adsorbed more strongly than related substances, which are less highly coloured or less unsaturated. Furthermore, certain colourless substances exhibit a bright fluorescence in ultraviolet light, and the passage of such a substance through a column of adsorbent material can be followed with the aid of a quartz mercury vapour lamp in a partially darkened room. Methods which have been developed for processing colourless and non-fluorescent compounds include:

1. The conversion of the compounds under investigation into coloured derivatives (*e.g.*, the separation of carbonyl compounds by conversion into their 2 : 4-dinitrophenylhydrazones, etc.; of hydrocarbons through their picrates; of alcohols through their 3 : 5-dinitrobenzoates; of glucose, fructose and other simple sugars through their *p*-phenylazobenzoyl esters).

2. The use of an indicator or marking substance, which is adsorbed on the column in a position in known relation to that of the colourless substance (*e.g.*, Sudan **III** for isolation of Vitamin D upon alumina).

3. The brush method; here the substances to be separated give a colour test with a reagent. The developed column is extruded from the tube and streaked lengthwise with a brush dipped in the test reagent; the colours appearing on the surface of the column at the place touched by the reagent indicate the position of the zones: that part of the adsorbent containing the colour test can be readily shaved off so that it may be discarded.

The chief uses of chromatographic adsorption include: (i) resolution of mixtures into their components; (ii) purification of substances (including technical products from their contaminants); (iii) determination of the homogeneity of chemical substances; (iv) comparison of substances suspected of being identical; (v) concentration of materials from dilute solutions (*e.g.*, from a natural source); (vi) quantitative separation of one or more constituents from a complex mixture; and (vii) identification and control of technical products. For further details, the student is referred to specialised works on the subject.*

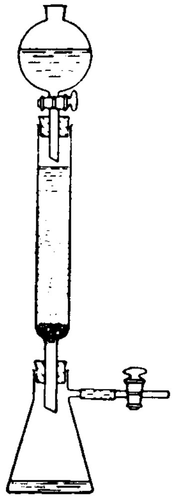


Fig. *II*, *46*, 2.

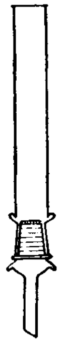


Fig. *II*, *46*, 3.

Apparatus. The essential part of the apparatus consists of a long narrow tube (20–30 cm. long and 1–3 cm. diameter); this holds 50–100 g. of adsorbent and may retain several grams of the adsorbate, although the amount is usually somewhat smaller. Fig. *II*, *46*, 2 illustrates a simple form of apparatus; the adsorbent is supported on a plug of cotton or glass wool; for wide tubes a perforated disc, covered by a pad of cotton or glass wool, may be used. Fig. *II*, *46*, 3 depicts a column fitted with a ground glass joint and a perforated glass plate or fritted glass disc is sealed into the lower part of the ground joint †; the removal of the column

---

* See, for example, A. Weissberger (Editor), *Technique of Organic Chemistry*. Volume V. *Adsorption and Chromatography*. Interscience (1951); H. H. Strain, *Chromatographic Adsorption Analysis*, Interscience (1945).

† Supplied by the Scientific Glass Apparatus Co. and, in larger sizes, by Quickfit and Quartz Ltd.

from the tube is a simple process. Fig. *II*, *46*, 4 illustrates a simple assembly* with standard ground glass joints. On occasion substances have to be handled which are readily oxidised in air : a simple apparatus, which permits the replacement of air by an inert gas, is shown in Fig. *II*, *46*, 5. The solution is run through the column with gentle suction (*ca.* 680 mm.), if necessary ; a high vacuum results in the tight packing of the adsorbent and also in the evaporation of the solvent in the lower end of the column. Pressure filtration may also be employed ; the upper end of the column is connected through a large bottle to a rubber bulb or other means of exerting a slight pressure.

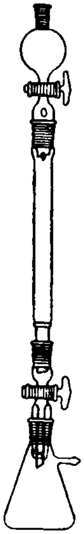


Fig. *II*, *46*, 4.

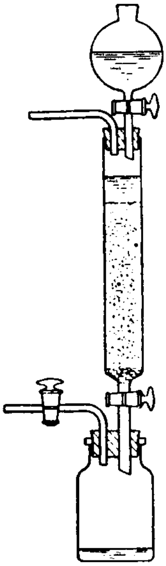


Fig. *II*, *46*, 5.

Adsorbents. The most widely used adsorbent is activated aluminium oxide, and commercial products are available which combine high activity with regular grain size. Other adsorbents include magnesium oxide, magnesium carbonate, magnesium trisilicate, calcium carbonate, barium carbonate, calcium hydroxide, calcium sulphate, silica gel, glucose, lactose, inulin, starch, cellulose and Fuller's earth. They are all employed in the form of uniform white powders : the inorganic compounds may usually be improved by heating at 200–230°. Diatomaceous earth filter aids (sold under various trade names—Filter Cel, Super-Cel, Clara-Cel, etc.), although sometimes employed as adsorbents, find their main application for improving the solvent flow rate through columns of other adsorbents : for this purpose they are mixed with the finely-powdered adsorbent in a suitable ratio ; uniform packing of the column is also facilitated by their use. Table *II*, *46*, 1, due largely to Strain, gives a list of adsorbents in increasing order of adsorption.

---

* Supplied by Quickfit and Quartz Ltd.

TABLE II, 46.1. GRADED SERIES OF ADSORBENTS

1. Sucrose, starch.
2. Inulin.
3. Talc.
4. Sodium carbonate.
5. Calcium carbonate.
6. Calcium phosphate.
7. Magnesium carbonate.
8. Magnesia.
9. Lime.
10. Activated silicic acid.
11. Activated magnesium silicate.
12. Activated alumina.
13. Fuller's earth.

Formation of an adsorption column. In order to obtain satisfactory results, the tube must be uniformly packed with the adsorbent. Uneven distribution leads to the formation of cracks and channels. If there is any doubt concerning the uniformity of the adsorbent powder, it should be sifted before use. The necessary support for the column (glass wool or cotton wool plug; perforated porcelain plate, or sintered glass plate, with filter paper circle, etc.) is placed in the tube, the latter is clamped or held vertically, and the adsorbent added portionwise. The first portion should be about twice the size of those that follow. For tubes up to one cm. diameter, the individual portions are pressed down with a flattened glass rod. For wider tubes, a cylindrical wooden pestle (walnut wood is recommended), slightly convex in the centre (Fig. *II*, *46*, 6), is used; the area of the conical end should be two-thirds to three-quarters of that of the tube. The adsorbent is pressed down by a short vigorous tapping from a height of 3 to 6 cm. With certain adsorbents, a slight vacuum is created as the pestle is raised and a cloud of fine powder may be formed; this is avoided if a slight rotary movement is given to the pestle as it is raised, or by slightly turning the glass tube with the left hand each time the pestle is lifted. From one-fifth to one-third of the tube should be left empty. The amount of adsorbent is usually generous compared with the quantity of material to be adsorbed.

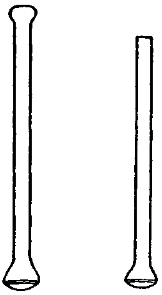


Fig. *II*, *46*, 6.

Another method of filling the column consists in placing the adsorbent and solvent in a separatory funnel, fitted with an efficient stirrer (*e.g.*, Fig. *II*, *56*, 31, *a*, a "link" type), and allowing the resulting slurry to flow through the tap into the clean, dry column. The adsorbent settles fairly rapidly under gravity, and the process may be assisted by gently tapping the tube. A packing, free from air bubbles, is thus obtained.

When the adsorbent has been introduced into the tube, the latter is fitted into a filter flask (see Fig. *II*, *46*, 2) to which a pump is attached; the pump is run slowly and the column is again pressed down gently with the wooden pestle. The circumference of the upper surface is gently and uniformly tapped, especially where it is in contact with the glass surface, for about one minute; air bubbles and channels are thus avoided when the solution is poured in. Some workers place a loose plug of cotton wool or a circle of filter paper at the top of the column in order to protect the solid from disturbance when the liquid is introduced.

Another procedure, which is sometimes adopted, consists in adding a suspension of the adsorbent in petroleum ether (b.p. *ca.* 60–80°) in small portions to the tube, fixed vertically and connected to the pump through a stopcock. After each addition, suction is applied, first gently and then somewhat more strongly ; the surface of the column must at all times be covered with petroleum ether.

Selection of solvents. The choice of solvent will naturally depend in the first place upon the solubility relations of the substance. If this is already in solution, for example, as an extract, it is usually evaporated to dryness under reduced pressure and then dissolved in a suitable medium ; the solution must be dilute since crystallisation in the column must be avoided. The solvents generally employed possess boiling points between 40° and 85°. The most widely used medium is light petroleum (b.p. not above 80°) ; others are *cyclo*hexane, carbon disulphide, benzene, chloroform, carbon tetrachloride, methylene chloride, ethyl acetate, ethyl alcohol, acetone, ether and acetic acid.

It is important to appreciate clearly the function of solvents in chromatographic adsorption. Whereas in any one analysis only one adsorbent will normally be employed, several solvents may be used. Solvents have a triple role :—

(i) They serve to introduce the mixture to the column.

(ii) They effect the process of development by which the zones of the chromatogram are separated to their fullest extent. When used for this purpose, the solvents are termed **developers**.

(iii) They remove the required content of each zone from the mechanically separated parts of the column, or from the column as a whole, the passage of the zone through the column being followed by physical methods (colour, fluorescence in ultraviolet light, etc.). Solvents utilised for removing the various components of a mixture as separated on a column are called **eluents**.

While the same solvent may serve throughout, it is often necessary to use different solvents at different stages of the chromatographic separation.

Reference has already been made to the choice of solvent for introducing the mixture to the column. Generally speaking, adsorption takes place most readily from non-polar solvents, such as petroleum ether or benzene, and least from highly polar solvents such as alcohols, esters and pyridine. Frequently the solvent for introducing the mixture to the column and the developer are so chosen that the same solvent serves the dual purpose.

The developer is generally a solvent in which the components of the mixture are not too soluble and is usually a solvent of low molecular weight. The adsorbent is selected so that the solvent is adsorbed somewhat but not too strongly ; if the solvent is adsorbed to some extent, it helps to ensure that the components of the mixture to be adsorbed will not be too firmly bound. Usually an adsorbate adheres to any one adsorbent more firmly in a less polar solvent, consequently when, as frequently occurs, a single dense adsorption zone is obtained with light petroleum and develops only slowly when washed with this solvent, the development may be accelerated by passing to a more polar solvent. Numerous adsorbates are broken up by methyl alcohol, ethyl alcohol or acetone. It is not generally necessary to employ the pure alcohol ; the addition from 0·5 to 2 per cent. to the solvent actually used suffices in most cases.

The choice of an eluent is governed by a few simple and obvious rules. It should be a liquid which is a good solvent for the components to be eluted. The eluent may be well adsorbed itself, so that its solvent action is assisted by its displacing action at the interface ; or one may add to the eluent some strongly adsorbed substance to promote this displacement. The eluent should be easily removable from the desorbed component ; low-boiling eluents may be used to elute high-boiling substances ; basic or acidic solvents may be employed to elute stable neutral compounds, or neutral solvents to elute acidic or basic substances. The following Table of a graded series of eluents may be found useful.

TABLE II, 46.2. GRADED SERIES OF ELUENTS

1. Petroleum ether, b.p. 30–50°.
2. Petroleum ether, b.p. 50–70°.
3. Carbon tetrachloride.
4. *Cyclo*hexane.
5. Benzene.
6. Ether (absolute).
7. Acetone (anhydrous).
8. Chloroform.
9. Ethyl acetate.
10. Ethanol.
11. Methanol.
12. Ethyl acetate.
13. Pyridine.
14. Glacial acetic acid.

The value of a graded series of eluents is that if one member of the series succeeds in desorbing a portion of an adsorbate, then another more powerful eluent should remove a further portion of the adsorbate. By mixing the eluents in various proportions, a finer gradation may be obtained, *e.g.*, petroleum ether ; benzene and petroleum ether ; benzene and ether ; ether and acetone, etc.

Introducing the solution. The top of the column is covered with a circle of filter paper or a loose plug of cotton wool and is washed with some of the solvent ; the rate of flow is observed under slight suction (Fig. *II*, *46*, 2) or under slight pressure. The solvent should percolate at the rate of 4–10 cm. per minute in a 2 cm. tube, and about 20–40 cm. per minute in a 5 cm. tube. The solution is added through a funnel or, better, through a tap funnel. The upper surface of the column must remain covered with liquid from the introduction of the first liquid to the end of the development ; if this precaution is not observed, the column may, in some circumstances, dry so quickly as to shrink and this may sometimes lead to the oxidation of the adsorbate. When suction is applied (Fig. *II*, *46*, 2), the stopcock of the filter flask should be closed after a suitable pressure has been established in order to avoid evaporation and to maintain a steady suction. As the last portion of the solution enters the column, the tap funnel is filled with the developing solution. After filtration is complete, the contents are dried in air or oxygen. The adsorbent may be pushed out completely with the wooden pestle or plunger (Fig. *II*, *44*, 6) and the zones cut with a knife or scalpel, or the coloured zones may be separated as they leave the tube. The individual homogeneous portions of the column are broken up, immediately dropped into the eluent, and stirred ; the suspension is filtered on a sintered glass funnel, and the filter cake is washed. Control of homogeneity is best carried out by repeating the chromatographic adsorption.

In another procedure, the column of adsorbent is not removed from the glass tube. The developed chromatogram is treated either with a single eluent or with a succession of solvents having increasingly powerful eluent actions. The various portions of the adsorbate are thus driven through the column, and the separate fractions of the filtrate are collected in different receivers. The series of filtrates constitutes the **liquid chromatogram.** The process is frequently applied to complex mixtures: the filtrates thus obtained can sometimes be passed again through a column.

II,47. PURIFICATION OF THE COMMON ORGANIC SOLVENTS

Reasonably pure solvents are required for many organic reactions and for recrystallisations; methods for obtaining these from commercial products will accordingly be described. Frequently, the pure solvent (*e.g.*, the analytical reagent) can be purchased, but the cost is usually high, particularly if comparatively large volumes are required. Furthermore, it is excellent practice for the student to purify inexpensive commercial solvents.

1. **Absolute diethyl ether.** The chief impurities in commercial ether (sp. gr. 0·720) are water, ethyl alcohol, and, in samples which have been exposed to the air and light for some time, "ethyl peroxide." **The presence of peroxides may be detected** either by the liberation of iodine (brown colouration or blue colouration with starch solution) when a small sample is shaken with an equal volume of 2 per cent. potassium iodide solution and a few drops of dilute hydrochloric acid, or by carrying out the "perchromic acid" test of inorganic analysis with potassium dichromate solution acidified with dilute sulphuric acid. **The peroxides may be removed** by shaking with a concentrated solution of a ferrous salt, say, 5–10 g. of ferrous salt (≡ 10–20 ml. of the prepared concentrated solution) to 1 litre of ether. The concentrated solution of ferrous salt is prepared either from 60 g. of crystallised ferrous sulphate, 6 ml. of concentrated sulphuric acid and 110 ml. of water or from 100 g. of crystallised ferrous chloride, 42 ml. of concentrated hydrochloric acid and 85 ml. of water.* Peroxides may also be removed by shaking with an aqueous solution of sodium sulphite (for the removal with stannous chloride, see Section **VI,12**).

In practice, it is best to purify a quantity, say one Winchester quart bottle, of technical 0·720 ether to cover the requirements of a group of students. The "Winchester quart" of ether is divided into two approximately equal volumes, and each is shaken vigorously in a large separatory funnel with 10–20 ml. of the above ferrous solution diluted with 100 ml. of water. The latter is removed, the ether transferred to the Winchester bottle, and 150–200 g. of anhydrous calcium chloride is added. The mixture is allowed to stand for at least 24 hours with occasional shaking. Both the water and the alcohol present are thus largely removed. The ether is then filtered through a large fluted filter paper into another clean dry Winchester bottle (*CAUTION*: all flames in the vicinity must be

---

* Traces of aldehyde are produced. If ether of a high degree of purity is required, it should be further shaken with 0·5 per cent. potassium permanganate solution (to convert the aldehyde into acid), then with 5 per cent. sodium hydroxide solution, and finally with water.

extinguished). Fine sodium wire (about 7 g.) is then introduced directly into the ether with the aid of a **sodium press** (Fig. *II*, *47*, 1).* The latter consists of a rigid metal framework, which can be attached to the bench by means of a single bolt (as in the Figure). An adjustable bottle stand is provided so that bottles up to a capacity of one Winchester quart can be used and their necks brought up to the underside of the mould. The plunger is of stainless steel as is also the one piece mould and die. (A number of dies of various sizes, thus giving sodium wire of different diameters, are usually available for alternative use.) The die is nearly filled with lumps of sodium, then placed in position in the press, and the plunger slowly screwed down. As soon as the sodium wire emerges from the die, the Winchester bottle containing the ether is held immediately beneath the die, and the plunger is gradually lowered until all the sodium has been forced as a fine wire into the ether. The Winchester bottle is then closed by a rubber stopper carrying a drying tube filled loosely with cotton wool or with calcium chloride (to exclude moisture and permit the escape of hydrogen), and the ether is allowed to stand for about 24 hours. The steel die must be removed from the press after use, any residual sodium destroyed with methylated spirit, and then thoroughly dried, preferably in the steam oven ; the plunger should also be swabbed with a rag or filter paper soaked in methylated spirit. If, on the following day, no bubbles of hydrogen rise from the sodium in the ether and the latter still possesses a bright surface, the Winchester bottle is closed by its own ground glass stopper or by a rubber stopper, and preserved in the dark (to check the formation of peroxides as far as possible) in a cool place remote from flames. If, however, the surface of the sodium wire is badly attacked, due to insufficient drying with the calcium chloride, the ether must be filtered through a fluted filter paper into another clean, dry Winchester bottle and the treatment with sodium repeated. The **absolute diethyl ether**

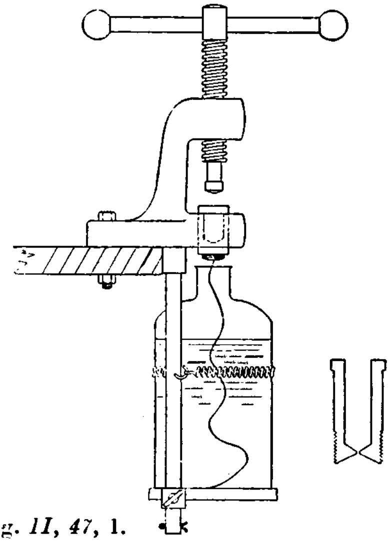


Fig. *II*, *47*, 1.

---

* Supplied by Griffin and George Ltd., Ealing Road, Alperton, Wembley, Middlesex.

thus prepared is suitable for use in the Grignard reaction. If a fresh supply of high-grade ether, *e.g.*, ether for anaesthesia, sp. gr. 0·720, or of analytical reagent quality, is available, the treatment with ferrous salt solution may be omitted.

When ether is allowed to stand for some time in contact with air and exposed to light, slight oxidation occurs with the formation of the highly explosive diethyl peroxide, $(C_2H_5)_2O_2$. The danger from this unstable compound becomes apparent at the conclusion of the distillation of impure ether, when the comparatively non-volatile peroxide becomes concentrated in the distillation flask ; a serious explosion may result if an attempt be made to evaporate the ether to dryness. In the extraction of an organic compound with ether and the subsequent removal of the solvent, the presence of the residual compound seems largely to eliminate the danger due to traces of peroxides. Nevertheless, ether, which has been standing for several months in a partially filled bottle exposed to light and air, should be tested for peroxides and, if present, should be eliminated by treatment with an acid solution of a ferrous salt or with a solution of sodium sulphite, as described in the previous paragraph. Peroxide formation takes place with all ethers, but particularly with di-*iso*-propyl ether.

Attention is directed to the fact that ether is highly inflammable and also extremely volatile (b.p. 35°), and great care should be taken that there is no naked flame in the vicinity of the liquid (see Section **II,14**). Under no circumstances should ether be distilled over a bare flame, but always from a steam bath or an electrically-heated water bath (Fig. *II*, *5*, 1), and with a highly efficient double surface condenser. In the author's laboratory a special lead-covered bench is set aside for distillations with ether and other inflammable solvents. The author's "*ether still*" consists of an electrically-heated water bath (Fig. *II*, *5*, 1), fitted with the usual concentric copper rings ; two 10-inch double surface condensers (Davies type) are suitably supported on stands with heavy iron bases, and a bent adaptor is fitted to the second condenser furthermost from the water bath. The flask containing the ethereal solution is supported on the water bath, a short fractionating column or a simple bent still head is fitted into the neck of the flask, and the still head is connected to the condensers by a cork ; the recovered ether is collected in a vessel of appropriate size.

2. **Di-*iso*-propyl ether.** The commercial product usually contains appreciable quantities of peroxides ; these should be removed by treatment with an acidified solution of a ferrous salt or with a solution of sodium sulphite (see under *Diethyl ether*). The ether is then dried with anhydrous calcium chloride and distilled. Pure di-*iso*-propyl ether has b.p. 68·5°/760 mm.

3. **Di-*n*-butyl ether.** Technical *n*-butyl ether does not usually contain appreciable quantities of peroxides, unless it has been stored for a prolonged period. It should, however, be tested for peroxides, and, if the test is positive, the ether should be shaken with an acidified solution of a ferrous salt or with a solution of sodium sulphite (see under *Diethyl ether*). The ether is dried with anhydrous calcium chloride, and distilled through a fractionating column : the portion, b.p. 140–141°, is collected. If a fraction of low boiling point is obtained, the presence of *n*-butyl alcohol is indicated and may be removed by shaking twice with an equal volume of concentrated hydrochloric acid (see, however, Section **III,57**), followed by washing with water and drying. Pure di-*n*-butyl ether has b.p. 141°/765 mm.

4. **Absolute ethyl alcohol.** Ethyl alcohol of a high degree of purity is frequently required in preparative organic chemistry. For some purposes alcohol of *ca.* 99·5 per cent. purity is satisfactory; this grade may be purchased (the "absolute alcohol" of commerce), or it may be conveniently prepared by the dehydration of rectified spirit with quicklime. **Rectified spirit** is the constant boiling point mixture which ethyl alcohol forms with water, and usually contains 95·6 per cent. of alcohol by weight. Wherever the term rectified spirit is used in this book, approximately 95 per cent. ethyl alcohol is to be understood.

Dehydration of rectified spirit by quicklime. It is convenient to work with one Winchester quart bottle of rectified spirit (2–2·25 litres); considerable time is saved and sufficient of the product is obtained for the requirements of a large group of students. The quicklime should be freshly prepared by strongly heating lumps of clean marble in a muffle furnace (preferably electrically-heated) for 3–6 hours; the product must be stored, directly it cools, in a well-stoppered bottle, although, wherever possible, it should be used immediately after its preparation. If commercial quicklime is employed, it should be similarly heated in a muffle furnace for 1–2 hours immediately before use. The contents of one Winchester bottle of rectified spirit (2–2·25 litres) are poured into a 3–4 litre round-bottomed Pyrex flask, about 500 g. of freshly-burnt quicklime are introduced, and the flask fitted with a double surface condenser carrying a drying tube (this may be filled with cotton wool or with anhydrous calcium chloride between plugs of glass wool placed at either end of the tube) on top (see Fig. *II*, *13*, 7). The mixture is gently refluxed on a water bath for 6 hours, and allowed to stand overnight. In the meantime, **purified glass wool** is prepared by boiling a little glass wool with concentrated nitric acid for 30 minutes, washing thoroughly with distilled water in order to remove adhering acid, and drying in the steam oven. The purified glass wool is packed tightly into a wide glass tube, bent as shown in Fig. *II*, *47*, 2, and the complete apparatus is assembled. The glass wool will completely retain any finely-divided lime which tends to pass over with the alcohol; alternatively, a splash head—as for ammonia distillation—may be used. The receiver consists of a clean, dry Winchester bottle in which the "absolute" alcohol will subsequently be stored. The special adapter shown is easily prepared by sealing a short length of glass tubing to the ordinary form of adapter and attaching a drying tube containing cotton wool or anhydrous calcium chloride. Rubber stoppers should be used throughout. The flask is heated on a water or steam bath, and the first 10–15 ml. of distillate are discarded. When most of the alcohol has passed over, the rate of distillation will slacken appreciably even on a boiling water bath; a cloth or towel should then be wrapped round the flask, when the rate of distillation will increase. The alcohol obtained in this way is very hygroscopic, and the bottle should be closed by a well-fitting, ground glass stopper or by a tightly-fitting rubber stopper. A bark cork is not recommended as this may contain an appreciable quantity of water unless it has been previously dried at about 120°. The product is generally termed " absolute " ethyl alcohol, although it usually still contains about 0·5 per cent. of water. The exact water content may be computed from a density determination or by the critical solution temperature procedure described in Section **I,9**.

5. **Extremely dry (or " super-dry ") ethyl alcohol.** The yields in several organic preparations (*e.g.*, malonic ester syntheses, reduction with sodium and ethyl alcohol, veronal synthesis) are considerably improved by the use of alcohol of 99·8 per cent. purity or higher. This very high grade ethyl alcohol may be prepared in several ways from commercial " absolute " alcohol or from the product of dehydration of rectified spirit with quicklime (see under *4*).

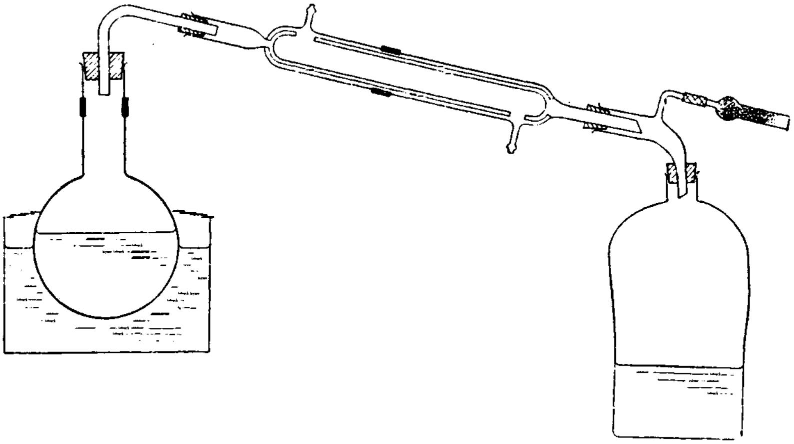


Fig. *II*, *47*, 2.

Method 1 (Lund and Bjerrum, 1931). The procedure depends upon the reactions :

$$Mg + 2C_2H_5OH = H_2 + Mg(OC_2H_5)_2 \qquad (1);$$
$$Mg(OC_2H_5)_2 + 2H_2O = Mg(OH)_2 + 2C_2H_5OH \qquad (2).$$

Reaction (1) usually proceeds readily provided the magnesium is activated with iodine and the water content does not exceed one per cent. Subsequent interaction between the magnesium ethoxide and water gives the highly insoluble magnesium hydroxide ; only a slight excess of magnesium is therefore necessary.

A dry 1·5 or 2 litre round-bottomed Pyrex flask is fitted with a double surface condenser and a drying tube (the latter may contain either cotton wool or anhydrous calcium chloride between plugs of glass wool). Five grams of clean dry magnesium turnings and 0·5 g. of iodine are placed in the flask, followed by 50–75 ml. of the 99+ per cent. alcohol. The mixture is warmed until the iodine has disappeared : if a lively evolution of hydrogen does not set in, a further 0·5 g. of iodine is added. Heating is continued until all the magnesium is converted into the ethylate. Nine hundred ml. of the " absolute " alcohol are then added, and the mixture is refluxed for 30 minutes. The alcohol is distilled off directly into the vessel in which it is to be stored, using an apparatus similar to that of Fig. *II*, *47*, 2. The purity of the alcohol exceeds 99·95 per cent., provided adequate precautions are taken to protect the distillate from atmospheric moisture. The super-dry alcohol is exceedingly hygroscopic.

If the alcohol is required for conductivity or other physico-chemical work and traces of bases are objectionable, these may be removed by redistillation from a little 2 : 4 : 6-trinitrobenzoic acid. This acid is selected because it is not esterified by alcohols, consequently no water is introduced into the alcohol.

Method 2 (E. L. Smith, 1927). Sodium alone cannot be used for the complete removal of water in ethyl alcohol owing to the equilibrium between the resulting sodium hydroxide and ethyl alcohol :

$$NaOH + C_2H_5OH \rightleftharpoons C_2H_5ONa + H_2O \qquad (3).$$

If, however, the sodium hydroxide is removed by allowing it to react with excess of an ester of high boiling point, such as ethyl succinate or ethyl phthalate, super-dry ethyl alcohol may be obtained :

$$C_2H_4(COOC_2H_5)_2 + 2NaOH = C_2H_4(COONa)_2 + 2C_2H_5OH \qquad (4).$$

The ethyl alcohol is easily removed from the excess of ester by distillation through a short column.

The apparatus consists of a 1·5 or 2 litre round-bottomed Pyrex flask fitted with an Allihn condenser (Fig. *II*, *1*, 4, *d*). The upper end of the latter carries a short still head to which is attached a Liebig condenser set for downward distillation ; the last-named is connected to a modified adapter and receiver as in Fig. *II*, *47*, 2. The apparatus must be perfectly dry ; rubber stoppers are used throughout. One litre of " absolute" alcohol of approximately 99·5 per cent. strength, together with 7 g. of clean dry sodium, are placed in the flask. When the sodium has reacted, 25 g. of pure ethyl succinate or 27·5 g. of pure ethyl phthalate are introduced, and the mixture gently refluxed for 2 hours whilst a rapid stream of water is passed through the Allihn condenser. The water in the reflux condenser is then allowed to run out, and the mixture is distilled from a water or steam bath ; the first 25 ml. of alcohol are rejected. The water content of the resulting ethyl alcohol should not exceed 0·05 per cent. and, if moisture has been rigidly excluded, may be as low as 0·01 per cent. The super-dry alcohol must be kept in a tightly stoppered bottle owing to its extremely hygroscopic character.

If preferred, the following alternative procedure may be adopted. The " absolute " alcohol is placed in a 1·5 or 2 litre three-necked flask equipped with a double surface reflux condenser and a mercury-sealed mechanical stirrer ; the third neck is closed with a dry stopper. The sodium is introduced and, when it has reacted completely, the ester is added and the mixture is gently refluxed for 2 hours. The reflux condenser is then rapidly disconnected and arranged for downward distillation with the aid of a short still head or " knee tube." The other experimental details are as above except that the mixture is stirred during the distillation ; bumping is thus reduced to a minimum.

Method 3 (F. Adickes, 1930). The experimental procedure is similar to that described in *Method 2* except that excess of ethyl formate (b.p.

54°/760 mm.) is employed to remove all the sodium hydroxide in the equilibrium of equation (3) :

$$HCOOC_2H_5 + NaOH = HCOONa + C_2H_5OH \qquad (5).$$

The sodium formate is sparingly soluble in ethyl alcohol and therefore separates out. The residual ethyl formate is catalytically decomposed in the presence of sodium ethoxide at the boiling point of the ethyl alcohol, *i.e.*, by refluxing the mixture :

$$HCOOC_2H_5 = CO + C_2H_5OH \qquad (6).$$

One litre of commercial " absolute " alcohol (or any ethyl alcohol of 99 per cent. purity or better) is treated with 14 g. of clean, dry sodium ; when the sodium has completely reacted, 40 g. of pure ethyl formate are added. The mixture is refluxed for 2–3 hours, and the dry alcohol is distilled off as in *Method 2* : the first 25 ml. of distillate are discarded. The super-dry alcohol contains about 0·03 per cent. of water.

6. **Absolute methyl alcohol.** The synthetic methanol now available is suitable for most purposes without purification : indeed, some manufacturers claim a purity of 99·85 per cent. with not more than 0·1 per cent. by weight of water and not more than 0·02 per cent. by weight of acetone. Frequently, however, the acetone content may be as high as 0·1 per cent. and the water content 0·5–1 per cent.

Water may be removed, if necessary, by treatment with quicklime as detailed under *Ethyl alcohol* (*4*), but the method is wasteful and is not generally employed unless the water content is comparatively high, say above 3–4 per cent. An excellent method of particular value in recovering the alcohol, consists in fractionating through a highly efficient column (compare Sections **II,15** and **II,17**) ; no constant boiling point mixture is formed as with ethyl alcohol. The boiling point of the pure methyl alcohol is 65°/760 mm. Methyl alcohol is highly inflammable and adequate precautions against fire must be taken (compare Section **II,14**).

Genuine absolute methyl alcohol may be readily prepared from the 99+ per cent. product (the usual commercial " absolute " methanol) by treatment with magnesium activated by iodine ; the dehydration is due essentially to the magnesium methylate formed (compare *Method 1* in *5*). Five grams of clean, dry magnesium turnings and 0·5 g. of resublimed iodine are placed in a 2-litre round-bottomed Pyrex flask and the latter fitted with a double surface reflux condenser : 50–75 ml. of the methyl alcohol are added through the condenser and the mixture is warmed (preferably on a water bath) until the iodine disappears. Hydrogen is usually soon vigorously evolved and it may be necessary to remove the flame from beneath the flask (or to remove the flask from the water bath). If a vigorous evolution of hydrogen does not take place, a further 0·5 g. of iodine is added and the mixture is heated until all the magnesium has been converted into the methoxide. Nine hundred ml. of the methyl alcohol are then added, and the mixture boiled for 30 minutes under reflux. The product is then distilled with exclusion of moisture, using the apparatus of Fig. *II, 47,* 2 ; the first 25 ml. of distillate are discarded.

If the small proportion of acetone present in synthetic methyl alcohol is objectionable, it may be removed when present in quantities up to one per cent. by the following procedure (Morton and Mark, 1934). A mixture of 500 ml. of the alcohol, 25 ml. of furfural, and 60 ml. of 10 per cent. sodium hydroxide solution is refluxed in a 2-litre round-bottomed flask, fitted with a double surface condenser, for 6–12 hours. A resin is formed, which carries down all the acetone present. The alcohol is then carefully fractionated through an efficient column (*e.g.*, a modified Hempel column or a Widmer column, Section **II, 17**) ; the first 5 ml. contain a trace of formaldehyde and are rejected. The recovery of methyl alcohol is about 95 per cent.

7. ***n*-Propyl alcohol.** The purest commercial *n*-propyl alcohol is dried with anhydrous potassium carbonate or with anhydrous calcium sulphate, and distilled through an efficient fractionating column. The fraction, b.p. 96·5–97·5°/760 mm., is collected. If the alcohol is required perfectly dry, it may be treated with magnesium activated with iodine (see under *5, Method 1*) ; alternatively, the ester method with *n*-propyl succinate or *n*-propyl phthalate may be used (see under *5, Method 2*).

8. ***iso*Propyl alcohol.** Two technical grades are usually marketed with *iso*propyl alcohol contents of 91 per cent. and 99 per cent. respectively. The former has a b.p. of about 80·3° and is a constant boiling point mixture with water ; it * may be refluxed with excess of freshly-burnt quicklime, distilled from the lime, and then refractionated. The latter * is dried with anhydrous calcium and distilled through a column. The fraction, b.p. 82–83°/760 mm., is collected.

9. **Higher alcohols.** These may be purified by drying with anhydrous potassium carbonate or with anhydrous calcium sulphate, and fractionated after filtration from the desiccant. Bark corks (or ground glass joints) should be used ; rubber stoppers are slightly attacked. The boiling points of the fractions to be collected are as follows :—

n-*Butyl alcohol,* b.p. 116·5–118°/760 mm.
iso-*Butyl alcohol,* b.p. 106·5–107·5°/760 mm.
sec.-*Butyl alcohol,* b.p. 99–100°/760 mm.
tert.-*Butyl alcohol,* b.p. 81·5–82·5°/760 mm., m.p. 25·5°.
n-*Amyl alcohol,* b.p. 136–137·5°/760 mm.
iso-*Amyl alcohol* (of fermentation origin), " primary *iso*amyl alcohol," b.p. 131–132°/760 mm.
iso-*Amyl alcohol* (synthetic), " primary *iso*amyl alcohol," b.p. 130–131°/760 mm.
n-*Hexyl alcohol,* b.p. 156·5–157·5°/760 mm.

If the perfectly anhydrous alcohols are required, the redistilled alcohol may be treated with the appropriate alkyl phthalate or succinate as already detailed under *Ethyl alcohol* (*5*).

10. **Mono-alkyl ethers of ethylene glycol,** $ROCH_2CH_2OH$. The mono-methyl, ethyl and *n*-butyl ethers are inexpensive and are known as *methyl cellosolve, cellosolve,* and *butyl cellosolve* respectively. They are completely miscible with water, and are excellent solvents. The commercial products are purified by drying over anhydrous potassium carbonate or anhydrous calcium sulphate, followed by fractionation after

---

* It is recommended that the *iso*propanol be tested for peroxides and, if present, removed by refluxing with solid stannous chloride (for details, see concluding paragraph of Section **VI,12**).

the removal of the desiccant. The boiling points of the pure products are :—

ethylene glycol monomethyl ether (or β-methoxyethyl alcohol), b.p. 124·5°/760 mm.
ethylene glycol monoethyl ether (or β-ethoxyethyl alcohol), b.p. 135°/760 mm.
ethylene glycol mono-*n*-butyl ether (or β-*n*-butoxyethyl alcohol), b.p. 171°/760 mm.

11. **Mono-alkyl ethers of diethylene glycol,**

$$ROCH_2CH_2OCH_2CH_2OH.$$

The mono-methyl, ethyl and *n*-butyl ethers are inexpensive commercial products and are known as *methyl carbitol*, *carbitol* and *butyl carbitol* respectively. They are all completely miscible with water and are purified as already described for the " cellosolves " (*10*). The boiling points of the pure compounds are :—

diethylene glycol monoethyl ether, b.p. 194°/760 mm.
diethylene glycol monoethyl ether, b.p. 198·5°/760 mm.
diethylene glycol mono-*n*-butyl ether, b.p. 230·5°/760 mm.

Note.

The solvents, enumerated under *10* and *11*, may contain traces of " peroxides." These can be removed either by refluxing over anhydrous stannous chloride (see concluding paragraph of Section VI, 12) or by filtration under slight pressure through a column of activated alumina.

12. **Di-alkyl ethers of ethylene glycol,** $ROCH_2CH_2OR$. The dimethyl ether, b.p. 85°/760 mm., is miscible with water, is a good solvent for organic compounds, and is an excellent inert reaction medium. The diethyl ether (*diethyl cellosolve*), b.p. 121·5°/760 mm., is partially miscible with water (21 per cent. at 20°).

The diethyl ether of diethylene glycol * (*diethyl carbitol*), b.p. 186°/760 mm., is completely miscible with water. The above three ethers may be purified by distillation from sodium.

13. **Acetone.** The analytical reagent grade contains about 1 per cent. of water and meets most requirements. Synthetic acetone of a high degree of purity (water content about 1 per cent.) is also available as a technical product.

Commercial acetone may be purified in several ways :—

(*a*) The acetone is refluxed with successive small quantities of potassium permanganate until the violet colour persists. It is then dried with anhydrous potassium carbonate or anhydrous calcium sulphate,† filtered from the desiccant, and fractionated : precautions are taken to exclude moisture.

(*b*) To 700 ml. of acetone, b.p. 56–57°, contained in a litre bottle, a solution of 3 g. of silver nitrate in 20 ml. of water is added, followed by 20 ml. of *N*-sodium hydroxide solution, and the mixture is shaken for

---

[*] Much useful information on these and other solvents will be found in the booklet *Synthetic Organic Chemicals* issued by the Carbide and Carbon Chemicals Corporation.

[†] Anhydrous calcium chloride should not be used as some chemical combination occurs.

about 10 minutes. The mixture is then filtered, dried with anhydrous calcium sulphate, and distilled.

(*c*) When only a relatively small quantity of pure dry acetone is required, it may be purified through the bisulphite compound: the latter is decomposed with sodium carbonate solution (for details, see under *Methyl ethyl ketone, 14*), dried over anhydrous calcium sulphate, and distilled.

A more convenient procedure is to make use of the addition compound with sodium iodide ($NaI,3C_3H_6O$), which decomposes on gentle heating and is particularly well adapted for the preparation of pure acetone. One hundred grams of finely powdered sodium iodide are dissolved under reflux in 440 g. of boiling commercial acetone, and the solution is cooled in a mixture of ice and salt (—8°). The crystals are filtered off, and quickly transferred to a dry distilling flask, connected to an efficient condenser and to a receiver cooled in ice. Upon gentle warming, the acetone distils rapidly. Pure acetone has b.p. 56·2°/760 mm., and is highly inflammable.

14. **Methyl ethyl ketone.** This excellent solvent has properties similar to those of acetone but it has a somewhat higher boiling point and is therefore less inflammable. A preliminary purification is effected by drying the commercial product with anhydrous potassium carbonate or anhydrous calcium sulphate, filtering from the desiccant, and fractionating through an efficient column; the fraction, b.p. 79–80°, is collected separately, and is quite satisfactory for recrystallisations. This may be further purified either through the bisulphite addition compound or through the sodium iodide addition compound. The methyl ethyl ketone b.p. 79–80°, is shaken with excess of saturated sodium bisulphite solution until reaction ceases, cooled to 0°, the bisulphite compound filtered off, washed with a little ether, and then dried in the air. The dry bisulphite compound is decomposed with a slight excess of sodium carbonate solution, and distilled in steam. The ketone is salted out from the distillate with potassium carbonate, separated, dried with anhydrous potassium carbonate (this will also remove traces of sulphur dioxide and carbon dioxide present), and, after filtration, allowed to stand for several hours over anhydrous calcium sulphate. It is then distilled. In the sodium iodide method, the ketone is saturated with sodium iodide by boiling under reflux, the solution is filtered through a hot water funnel, cooled in a freezing mixture, the white crystals (which have a m.p. of 73–74°) filtered off, and fractionally distilled through a column. Pure methyl ethyl ketone has b.p. 79·5°/760 mm.

15. **Benzene.** The analytical reagent grade benzene is satisfactory for most purposes; if required dry, it is first treated with anhydrous calcium chloride, filtered, and then placed over sodium wire (for experimental details, see under *Diethyl ether, 1*).

Commercial benzene may contain thiophene C_4H_4S, b.p. 84°, which cannot be separated by distillation or by fractional crystallisation. The *presence of thiophene may be detected* by shaking 3 ml. of benzene with a solution of 10 mg. of isatin in 10 ml. of concentrated sulphuric acid and allowing the mixture to stand for a short time: a bluish-green colouration is produced if thiophene is present. The **thiophene may be removed from benzene** by any of the following methods :—

1. *By shaking with concentrated sulphuric acid*, advantage being taken of the fact that thiophene is more readily sulphonated than benzene. The technical benzene is shaken repeatedly with about 15 per cent. of its volume of concentrated sulphuric acid in a stoppered separatory funnel * until the acid layer is colourless or very pale yellow on standing, or until the thiophene test is negative. After each shaking lasting a few minutes, the mixture is allowed to settle and the lower layer of acid is drawn off. The benzene is then shaken twice with water in order to remove most of the acid, once with 10 per cent. sodium carbonate solution, again with water, and finally dried with anhydrous calcium chloride. After filtration, the benzene is distilled through an efficient column and the fraction, b.p. 80–81°, collected. If required perfectly dry, sodium wire must be introduced into the distilled liquid (for details, see under *Diethyl ether, 1*).

2. *By treatment with mercuric acetate* ; only the thiophene reacts to form thiophene dimercuri-hydroxyacetate $HOHg.C_4H_2S.HgOOC.CH_3$, which is filtered off. One kilogram of benzene is boiled under an efficient double surface reflux condenser for several hours with a solution of mercuric acetate, prepared by dissolving 40 g. of mercuric oxide (best, freshly precipitated) in a mixture of 40 ml. of glacial acetic acid and 300 ml. of water. If the mixture is stirred mechanically, the time of boiling can be reduced to 30 minutes. The precipitate of thiophene dimercuri-hydroxyacetate is removed by filtration, the water separated, the benzene washed twice with water, dried over anhydrous calcium chloride, and fractionated as in method 1.

Upon distilling the mercury compound with concentrated hydrochloric acid, it is readily decomposed into mercuric chloride and pure thiophene.

3. *By treatment with anhydrous aluminium chloride* (Holmes and Beeman, 1934). Ordinary commercial, water-white benzene contains about 0·05 per cent. of thiophene. It is first dried with anhydrous calcium chloride. One litre of the dry crude benzene is shaken vigorously (preferably in a mechanical shaking machine) with 12 g. of anhydrous aluminium chloride for half an hour ; the temperature should preferably be 25–35°. The benzene is then decanted from the red liquid formed, washed with 10 per cent. sodium hydroxide solution (to remove soluble sulphur compounds), then with water, and finally dried over anhydrous calcium chloride. It is then distilled and the fraction, b.p. 79·5–80·5°, is collected. The latter is again vigorously shaken with 24 g. of anhydrous aluminium chloride for 30 minutes, decanted from the red liquid, washed with 10 per cent. sodium hydroxide solution, water, dried, and distilled. The resulting benzene is free from thiophene.

Pure benzene has b.p. 80°/760 mm. and m.p. 5·5°.

16. **Toluene.** Toluene, free from sulphur compounds, may be purchased. If required dry, it is treated with anhydrous calcium chloride, followed by sodium wire (see under *Benzene, 15*).

Commercial toluene contains methyl thiophenes (thiotolenes), b.p. 112–113°, which cannot be removed by distillation. It may be purified by

---

* Alternatively, the mixture may be stirred mechanically for 20–30 minutes. After three such treatments, the acid usually has only a pale colour.

shaking or stirring several times with about 10 per cent. of its volume of concentrated sulphuric acid as in the case of benzene (*15*), but, owing to the greater ease of sulphonation of toluene itself, some temperature control is necessary. The simplest procedure consists in mechanically stirring one litre of technical toluene with 100 ml. of concentrated sulphuric acid for about 30 minutes; the temperature is not allowed to rise above 30° by occasional cooling. The lower acid layer is removed, and the process is repeated twice. The subsequent working up is carried out as described under *Benzene*.

Pure toluene has b.p. 110·5°/760 mm.

17. **Petroleum ether (light petroleum).*** The fractions of refined petroleum which are commonly used have b.p. 40–60°, 60–80°, 80–100° and 100–120°. It is not advisable to employ a fraction with a wider b.p. range than 20°, because of possible loss of the more volatile portion during its use in recrystallisation, etc. and consequent different solubility relations of the higher boiling residue. For some purposes the presence of unsaturated (chiefly aromatic) hydrocarbons in petroleum ether is undesirable. Most of the unsaturated hydrocarbons may be removed by shaking two or three times with 10 per cent. of the volume of concentrated sulphuric acid (for details, see under *Benzene*, *15*); vigorous shaking is then continued with successive portions of a concentrated solution of potassium permanganate in 10 per cent. sulphuric acid until the colour of the permanganate remains unchanged. The solvent is then thoroughly washed with water, dried over anhydrous calcium chloride, and distilled. If required perfectly dry, it should be allowed to stand over sodium wire.

Petroleum ether fractions "free from aromatic hydrocarbons" are marketed, as are also "*n*-hexane" and "*n*-heptane" from petroleum.

18. **Methyl acetate.** An anhydrous product of 99 per cent. purity (b.p. 56·5–57°) is available commercially; this is comparatively cheap so that purification of inferior products is not worth while. It is appreciably soluble in water (*ca.* 24 per cent. at 20°). The pure compound has b.p. 57°/760 mm.

If it is desired to purify an inferior product, 1 litre of it is refluxed for 6 hours with 85 ml. of acetic anhydride and then distilled through a fractionating column: the liquid passing over at 56–57° is collected. The distillate is shaken with 20 g. of anhydrous potassium carbonate for 10 minutes, filtered and redistilled. The resulting methyl acetate has a purity of 99·9 %.

19. **Ethyl acetate.** Various grades of ethyl acetate are marketed. The anhydrous compound, b.p. 76–77°, is of 99 per cent. purity, is inexpensive, and is suitable for most purposes. The 95–98 per cent. grade usually contains some water, ethyl alcohol and acetic acid, and may be purified in the following manner. A mixture of 1 litre of the commercial ethyl acetate, 100 ml. of acetic anhydride and 10 drops of concentrated sulphuric acid is refluxed for 4 hours and then fractionated. The distillate is shaken with 20–30 g. of anhydrous potassium carbonate, filtered and redistilled. The final product has a purity of about 99·7 % and boils at 77°/760 mm.

---

* Sometimes termed ligroin. The author prefers to confine the term ligroin to the fractions of b.p. above 100°.

20. **Carbon disulphide.** When working with this solvent, its toxicity (it is a blood and nerve poison) and particularly its high inflammability should be borne in mind. Distillation of appreciable quantities of carbon disulphide should be carried out in a water bath at 55–65° ; it has been known to ignite from being overheated on a steam bath.

The analytical reagent grade is suitable for most purposes. The commercial substance may be purified by shaking for 3 hours with three portions of potassium permanganate solution (5 g. per litre), twice for 6 hours with mercury, and finally with a solution of mercuric sulphate (2·5 g. per litre). It is then dried over anhydrous calcium chloride, and fractionated from a water bath at 55–65°. The pure compound boils at 46·5°/760 mm.

21. **Nitrobenzene.** Nitrobenzene, of analytical reagent quality, is satisfactory for most purposes. The technical product may contain dinitrobenzene and other impurities, whilst the recovered solvent may be contaminated with aniline. Most of the impurities may be removed by steam distillation after the addition of dilute sulphuric acid ; the nitrobenzene in the distillate is separated, dried with calcium chloride and distilled. The pure substance has b.p. 210°/760 mm. and m.p. 5·7°.

Nitrobenzene is an extremely versatile solvent, and may frequently be employed for the crystallisation of compounds which do not dissolve appreciably in the common organic solvents. The vapour is somewhat poisonous, so that recrystallisations must be carried out in the fume cupboard. After the crystals have been collected, they should be washed with a volatile solvent, such as benzene, alcohol or ether, to remove the excess of nitrobenzene (compare Section **II,32**). The only disadvantage of nitrobenzene as a solvent is that it has a pronounced oxidising action at the boiling point.

22. **Pyridine.** The analytical reagent grade pyridine will satisfy most requirements. If required perfectly dry, it should be refluxed over potassium or sodium hydroxide pellets or over barium monoxide, and then distilled with careful exclusion of moisture (compare Fig. *II*, *47*, 2). It is hygroscopic, and forms a hydrate of b.p. 94·5°. Pure pyridine has b.p. 115·5°/760 mm.

Pure pyridine may be prepared from technical coal-tar pyridine in the following manner. The technical pyridine is first dried over solid sodium hydroxide, distilled through an efficient fractionating column, and the fraction, b.p. 114–116° collected. Four hundred ml. of the redistilled pyridine are added to a reagent prepared by dissolving 340 g. of anhydrous zinc chloride in a mixture of 210 ml. of concentrated hydrochloric acid and 1 litre of absolute ethyl alcohol. A crystalline precipitate of an addition compound (probable composition $2C_5H_5N,ZnCl_2,HCl$ *) separates and some heat is evolved. When cold, this is collected by suction filtration and washed with a little absolute ethyl alcohol. The yield is about 680 g. It is recrystallised from absolute ethyl alcohol to a constant m.p. (151·8°). The base is liberated by the addition of excess of concentrated

---

* There appear to be at least two zinc chloride complexes of pyridine, one of m.p. 207° and composition $2C_5H_5N,ZnCl_2$, and the other of m.p. 152° and probable composition $2C_5H_5N,ZnCl_2,HCl$. The former is slightly soluble in water and in hot ethyl alcohol : the latter passes into the former in aqueous solution, is readily soluble in hot absolute ethanol and can therefore be readily recrystallised from this solvent.

sodium hydroxide solution (*ca.* 40 %) and steam distilled until the distillate is no longer alkaline to litmus (*ca.* 1000 ml.). The steam distillate is treated with 250 g. of solid sodium hydroxide, the upper layer separated, and the aqueous layer extracted with two 250 ml. portions of ether. The combined upper layer and ether extracts are dried with anhydrous potassium carbonate, the ether removed on a water bath, and the pyridine distilled through a fractionating column. The pure pyridine is collected at 115·3°/760 mm.

23. **Methylene chloride.** The commercial substance is purified by washing with 5 per cent. sodium carbonate solution, followed by water, dried over anhydrous calcium chloride, and then fractionated. The fraction, b.p. 40–41°, is collected.

Methylene chloride is a useful substitute for diethyl ether when it is desired to employ a solvent which is heavier than water.

24. **s-Tetrachloroethane.** The technical product is warmed on the steam bath with 8 per cent. of its volume of concentrated sulphuric acid and stirred mechanically for 30 minutes. The upper layer is decanted, and the process is repeated until the sulphuric acid layer remains colourless or almost colourless. The tetrachloroethane is then separated, distilled in steam, dried with anhydrous calcium chloride or with anhydrous potassium carbonate, and distilled. The fraction, b.p. 145–147°, is collected.

Tetrachloroethane is a good solvent for many compounds which dissolve only slightly in the common solvents; it is, however, inferior in solvent power to nitrobenzene, but, on the other hand, it does not possess oxidising properties at the boiling point.

25. **Chloroform.** The commercial product contains up to 1 per cent. of ethyl alcohol, which is added as a stabiliser. The alcohol may be removed by either of the following procedures :—

(*a*) The chloroform is shaken five or six times with about half its volume of water, then dried over anhydrous calcium chloride for at least 24 hours, and distilled.

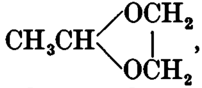
(*b*) The chloroform is shaken two or three times with a small volume (say, 5 per cent.) of concentrated sulphuric acid, thoroughly washed with water, dried over anhydrous calcium chloride or anhydrous potassium carbonate, and distilled.

Pure chloroform has b.p. 61°/760 mm. The solvent, when free from alcohol, should be kept in the dark in order to avoid the photochemical formation of phosgene. It must not be dried with sodium as an explosion may occur.

26. **Carbon tetrachloride.** The analytical reagent product is sufficiently pure for most purposes; the carbon disulphide content does not exceed 0·005 per cent. The technical product may contain up to 4 per cent. of carbon disulphide; this may be removed by the following method. One litre of commercial carbon tetrachloride is treated with potassium hydroxide (1·5 times the quantity required to combine with the carbon disulphide) dissolved in an equal weight of water and 100 ml. of rectified spirit, and the mixture is vigorously shaken for 30 minutes at 50–60°. After washing with water, the process is repeated with half the quantity of potassium hydroxide. The alcohol is then removed by shaking several times with 500 ml. of water, followed by shaking with small portions of concentrated sulphuric acid until there is no further colouration. The carbon tetrachloride is then washed with water, dried over anhydrous calcium chloride, and distilled. The pure compound boils at 76·5°/760 mm.

Carbon tetrachloride must not be dried with sodium as an explosion may result. Fire extinguishers containing this solvent (*e.g.*, " Pyrene ") cannot therefore be applied to a fire originating from sodium.

Most solvents, which are immiscible with water, may be dried by simple distillation until the distillate is clear (compare Section **II,39**) ; the residue is anhydrous. It is usually necessary to remove about 10 per cent. by distillation before the residue is completely anhydrous.

27. **Dioxan** (1 : 4-dioxan ; diethylene dioxide). The commercial substance usually contains small quantities of acetaldehyde, appreciable amounts of glycol acetal (ethylene acetal)  $CH_3CH\begin{matrix}OCH_2\\|\\OCH_2\end{matrix}$, together with some water. Upon keeping, the acetal tends to undergo hydrolysis and the liberated acetaldehyde leads to some peroxide formation. Purification may be effected by refluxing over sodium (which resinifies the acetaldehyde), followed by fractional distillation through an efficient column to remove the acetal (b.p. 82·5°). The yield by this process is low (about 30 per cent.) and better yields (up to 80 per cent.) can be obtained by decomposing the acetal with dilute acid, followed by fractionation. One litre of technical dioxan, 14 ml. of concentrated hydrochloric acid and 100 ml. of water are refluxed for 6–12 hours whilst a slow stream of nitrogen is bubbled through the solution to remove the acetaldehyde formed. The cold solution is treated with potassium hydroxide pellets with shaking until some remain undissolved, and the aqueous layer is run off ; most of the residual water is removed by keeping the dioxan over fresh potassium hydroxide pellets for 24 hours. This is followed by refluxing over excess of sodium for 6–12 hours, *i.e.*, until reaction ceases and the sodium remains bright. Finally, the diethylene dioxide is distilled from sodium ; it should be stored out of contact with air. The pure compound has b.p. 101·5°/760 mm. and m.p. 12°.

Diethylene dioxide is a very useful solvent for a variety of organic compounds ; its action is similar to that of ether but more pronounced. It is miscible with water in all proportions. Dioxan vapour is poisonous.

Note.

Dioxan develops appreciable quantities of peroxides upon exposure to air or upon keeping. These can be eliminated by refluxing over anhydrous stannous chloride (compare Section **VI,12**) or by filtration through a column of activated alumina.

28. **α-Picoline.** Commercially " pure " α-picoline may contain small amounts of pyridine, β- and γ-picolines and 2 : 6-lutidine (all of which can be largely separated by an initial fractionation) together with traces of aromatic hydrocarbons. 100 G. of the base is dissolved in 300 ml. of 1 : 1-hydrochloric acid and the solution is steam distilled until a hydrocarbon odour can no longer be detected in the distillate (*ca.* 500 ml.). The cold acid solution is treated with excess of solid sodium hydroxide (80–100 g.) portionwise with stirring and cooling. The upper layer of base is separated, the aqueous layer is extracted with three 50 ml. portions of ether, and the extracts combined with the upper layer. After drying over anhydrous potassium carbonate and removing the ether, the residual liquid is distilled through an efficient fractionating column. A fore-run of base - water azeotrope (b.p. *ca.* 90°) is followed by pure α-picoline at 129·7–130·3°/777 mm.

29. **β-Picoline.** Commercially "pure" β-picoline usually contains small amounts of γ-picoline and 2 : 6-lutidine, which have boiling points very close to it and from which it cannot be separated by fractional distillation. These impurities may be removed by reaction with phthalic anhydride and acetic anhydride, use being made of the greater reactivity of the methyl groups in the 2- and 4-positions of the pyridine ring; the condensation products are coloured. Traces of non-basic impurities (aromatic hydrocarbons, etc.) are removed by treatment of the acid solution with steam as described under *α-Picoline.* 100 G. of the dry (potassium hydroxide) base is refluxed for 10 hours with a mixture of 25 g. of phthalic anhydride and 25 g. of acetic anhydride. The dark brown reaction mixture, after cooling, is treated with a solution of 50 g. of sodium hydroxide in 150 ml. of water and steam distilled until the distillate is no longer alkaline to litmus (*ca.* 500 ml.). 50 G. of sodium hydroxide are added to the distillate in order to separate most of the base as an upper layer, the aqueous layer is extracted with three 50 ml. portions of ether, and the extracts combined with the upper layer. After drying with anhydrous potassium carbonate and removing the ether, 10 ml. of the recovered base is tested for complete removal of the impurities by refluxing with a mixture of 5 g. each of phthalic and acetic anhydrides for 10 minutes; pure β-picoline gives a pale yellow colour and the presence of impurities is revealed by the production of an intense yellow or orange colouration. If the latter occurs, the whole of the base is refluxed with the anhydride mixture for a further 5–7 hours. This second treatment usually suffices for a starting material of 90–95 % purity. The base is isolated as before and, after drying over anhydrous potassium carbonate, is carefully fractionated. Pure β-picoline is collected at 144·5°/765 mm. The recovery is about 85 per cent.

30. **γ-Picoline.** Commercially "pure" γ-picoline contains β-picoline and 2 : 6-lutidine and sometimes traces of non-basic impurities (aromatic hydrocarbons) which cannot be separated by fractionation. The non-basic impurities are removed by steam distillation of the base in dilute hydrochloric or sulphuric acid solution (for details, see under *α-Picoline*). The impure γ-picoline is converted into the zinc chloride complexes of the component bases: the 2 : 6-lutidine - $ZnCl_2$ complex is the least stable and upon steam distillation of the mixture of addition compounds suspended in water, 2 : 6-lutidine passes over first. The complete separation of the 2 : 6-lutidine may be detected by a determination of the density and the refractive index of the dry recovered base at various stages of the steam distillation. The physical properties are :—

	$d_{4°}^{20°}$	$n_D^{20°}$
γ-picoline	0·9566	1·5069
β-picoline	0·9546	1·5058
2 : 6-lutidine	0·9238	1·4977

The β-picoline in the base recovered from the residual picoline - $ZnCl_2$ complexes is separated from the γ-picoline by fractional freezing ; pure β-picoline has m.p. $-18 \cdot 2°$ and γ-picoline has m.p. $+ 3 \cdot 6°$.

250 Ml. of commercially " pure " γ-picoline are added, with stirring, to a solution of 200 g. of zinc chloride in 500 ml. of water contained in a 2-litre three-necked flask equipped with a glycerine-sealed stirrer. The flask is fitted with a steam-inlet tube and splash head ; steam is then passed into the well-stirred mixture until about 1 litre of distillate is collected. (With any particular batch of γ-picoline, the base is isolated from the steam distillate at regular intervals, dried and distilled, and the density and refractive index determined ; most of the 2 : 6-lutidine is removed when $d_{4°}^{20°}$ is about $0 \cdot 955$. The total volume of steam distillate is noted : in subsequent runs with the same batch of γ-picoline, steam distillation is stopped when this volume of distillate has been collected.) The cold residual suspension of $ZnCl_2$-complexes is treated with 100 g. of solid sodium hydroxide and the base isolated by direct ether extraction or by steam distillation (see under *a-Picoline*). After drying with anhydrous potassium carbonate and removing the ether, the last traces of water are removed as the base-water azeotrope by careful fractionation. The dry bases are separated by fractional freezing * over a period of several hours, dry nitrogen being used for stirring. When 70-80 per cent. is frozen, the liquid is poured off, the crystals melted, and the process repeated until the freezing point rises to $+ 3 \cdot 6°$. The boiling point of such a sample is $145 \cdot 4°/760$ mm.

31. **Formamide.** Commercial formamide may contain excess of formic acid. It is purified by passing ammonia gas into the mixture until a slight alkaline reaction is obtained. The ammonium formate thus formed is precipitated by the addition of acetone ; the filtrate, after drying over anhydrous magnesium sulphate, is distilled under reduced pressure. Pure formamide has b.p. 105°/11 mm.

II,48. INORGANIC REAGENTS—GASES

An account will be given in this and the two following Sections of a number of inorganic reagents which find application in organic chemistry. No attempt will be made to describe the preparation of those reagents which can be purchased at a reasonable cost. In some cases, where the purified reagents are somewhat expensive, the methods of purification from the technical products will be outlined.

1. **Hydrogen chloride.** *Method 1 (from concentrated sulphuric acid and fused ammonium chloride).* The most convenient procedure is to allow concentrated sulphuric acid to react with lumps of fused ammonium chloride in a Kipp's apparatus. The gas may be dried by passage through a wash bottle containing concentrated sulphuric acid ; the latter should be followed by an empty wash bottle or flask as a precaution against " sucking back " of the contents of the reaction vessel.

Method 2 (from concentrated sulphuric acid and concentrated hydrochloric acid). The apparatus is shown in Fig. *II, 48,* 1. The upper funnel has a capacity of 100 ml. and the lower one of 500 ml. A capillary

---

* An air bath, surrounded by a freezing mixture of ice and salt or of Dry Ice and acetone, is satisfactory.

tube, 35–40 cm. in length, is attached to the stem of the smaller funnel by means of a short length of rubber " pressure " tubing; when this capillary tube is filled with concentrated hydrochloric acid, there is sufficient hydrostatic pressure to force the hydrochloric acid into the sulphuric acid. The wash bottle contains sulphuric acid and is provided with a thistle funnel only slightly immersed in the acid to act as a safety tube. The whole apparatus is mounted on a heavy stand.

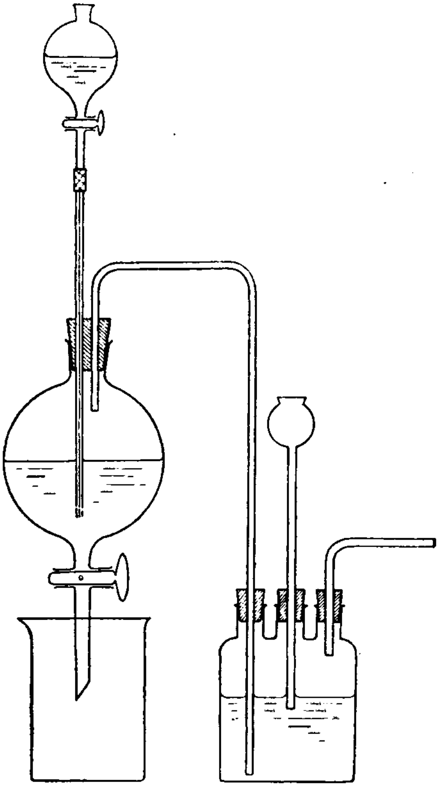


Fig. *II*, *48*, 1.

About 150 ml. of concentrated sulphuric acid is placed in the larger funnel and 100 ml. of concentrated hydrochloric acid in the smaller separatory funnel. The latter is raised until the capillary tube is above the sulphuric acid, the capillary tube is filled with concentrated hydrochloric acid, and the stopper replaced. The rate of evolution of hydrogen chloride is controlled by regulation of the supply of hydrochloric acid : this will continue until a volume of hydrochloric acid equal to that of the concentrated sulphuric acid has been used. The diluted sulphuric acid should then be removed and the apparatus recharged. The yield is 31–33 g. of hydrogen chloride per 100 ml. of concentrated hydrochloric acid. If more than an equal volume of hydrochloric acid is employed, the yield of gas decreases and continues to be formed for a time after the stopcock has been closed.

2. **Hydrogen bromide.** *Method 1 (by direct combination of hydrogen and bromine).* This gas may be readily prepared by passing a mixture of hydrogen and bromine vapour through a hot tube packed with porous porcelain chips ; excess of bromine is removed by passage through a tube containing copper turnings. The apparatus is illustrated in Fig. *II*, *48*, 2. *A* is a 125 ml. Pyrex distilling flask of which the side arm has been bent into a horizontal position. It is immersed into a 800 or 1000 ml. beaker, which acts as a water bath. The distilling flask is fitted with a two-holed rubber stopper carrying a 50 ml. dropping funnel * and a tube bent twice at right angles leading to a safety bottle *C*. The safety bottle is charged with water (or some other suitable liquid) and has an outlet tube for hydrogen in case an obstruction is formed in the apparatus ; the outlet tube must be connected to a tube leading directly to the ventilation shaft (fume cupboard). The side arm of the distilling flask is fitted by means

---

* The stopcock should preferably be lubricated with " Silicone " stopcock grease, and held in position by a rubber band.

of a rubber stopper into a Pyrex combustion tube *D*, 30–40 cm. long and 20 mm. internal diameter, filled with small pieces of porous porcelain; the other end of the tube is connected by a rubber stopper and a three-way stopcock *E* to a vertical tube *F*, 60 cm. long and 20 mm. internal diameter, packed with copper turnings held in position by glass wool plugs. The tube *D* is supported in a small gas-heated furnace, or in a suitable wide-flamed burner, or in a small metal frame and the tube is heated with one or two Bunsen burners: shields of asbestos board are fitted at distances of about 3 cm. from both ends. To operate the apparatus, the stopcock *E* is turned so that the tube *F* is disconnected and the gases pass directly into the fume chamber. The safety bottle *C* is connected to a cylinder of hydrogen provided with a fine-control reducing valve, and the tube inside the bottle is adjusted so that it is immersed in the water to a depth of about 12 cm. Bromine (not shown in the figure) is placed in the flask *A* and the water bath *B* heated to and maintained at 38°.* A slow stream of hydrogen is passed through the apparatus, and when bromine vapour completely fills the combustion tube the latter is heated to a dull red heat. The formation of hydrogen bromide will soon commence and a

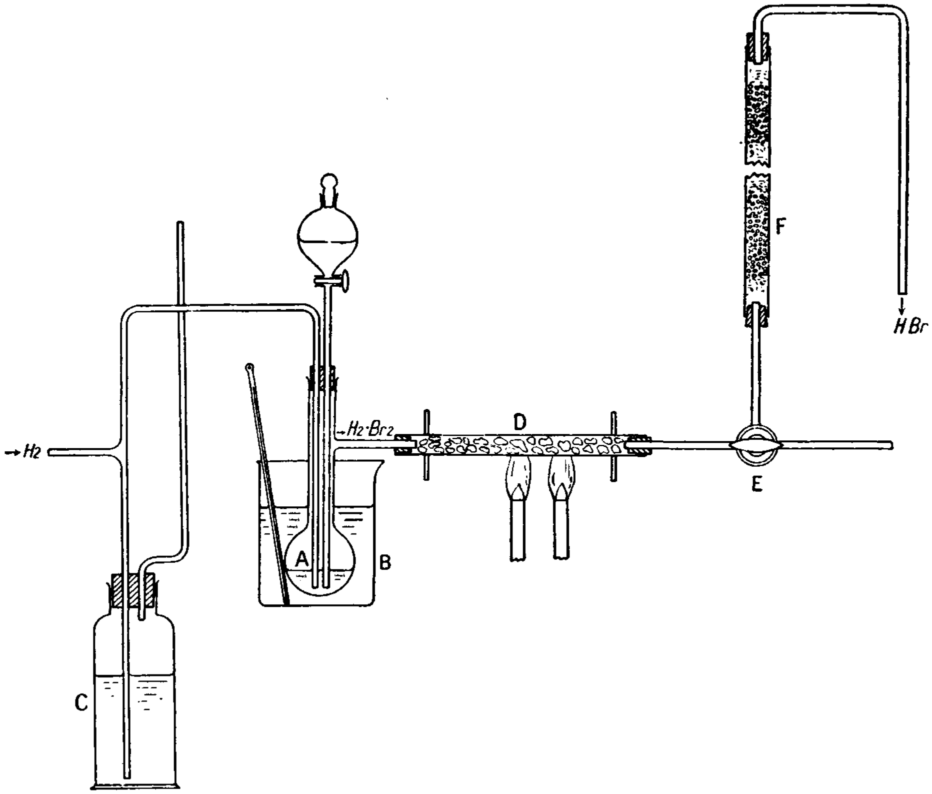


Fig. *11*, *48*, 2.

---

* The vapour pressure of the bromine should be maintained at about half an atmosphere (vapour pressures at 35° and 40° are 324 and 392 mm. respectively). If the water bath becomes too warm, it should be cooled immediately with ice, as otherwise more bromine will vapourise than can combine with the hydrogen present.

small yellow flame will be apparent in the hot part of the tube nearest *B*; the stopcock *E* is turned so that the combustion tube *D* is connected to the tube *F* containing copper turnings * in order that traces of bromine may be removed. The yield of hydrogen bromide is controlled by the rate of passage of hydrogen through the flask *A*. The apparatus will produce about 300 g. of hydrogen bromide per hour.

Traces of bromine, carried over with the gas, are removed by the copper turnings as black copper bromide; if the level of the blackened copper in tube *F* rises appreciably, excessive amounts of bromine are being carried over.

Method 2 {*by the action of bromine upon tetrahydronaphthalene* (*tetralin*)}. The reaction may be represented by the equation :

$$C_{10}H_{12} + 4Br_2 = C_{10}H_8Br_4 + 4HBr.$$

Only half of the added bromine is recovered as hydrogen bromide. It is essential that the tetralin be perfectly dry otherwise the yield is considerably reduced. The tetralin is placed in a flask fitted with a dropping funnel and a delivery tube. Dry air must be bubbled *through* the liquid for at least 30 minutes to remove water, but the time may be considerably reduced by a preliminary drying with anhydrous magnesium or calcium sulphate. The bromine is allowed to drop in at a regular rate : a steady stream of hydrogen bromide is evolved. Traces of bromine carried over with the gas may be eliminated by bubbling through dry tetralin. The yield of hydrogen bromide is 45 to 47 per cent. computed upon the weight of bromine taken.

3. **Hydrogen iodide.** This gas may be conveniently prepared by allowing a solution of two parts of iodine in one part of hydriodic acid, sp. gr. 1·7 (for preparation, see Section **II,49,***2*), to drop on to excess of red phosphorus. The evolution of hydrogen iodide takes place in the cold; when the evolution of gas slackens considerably, the mixture should be *gently* warmed.

4. **Hydrogen cyanide.** Great care must be exercised in the preparation of this gas for it is a dangerous poison; all operations must be conducted in a fume cupboard provided with an efficient draught. The apparatus used is similar to, but generally on a smaller scale than, that described for *Hydrogen chloride, Method 2*. A saturated solution of sodium cyanide (prepared by dissolving 101·5 g. of commercial sodium cyanide, about 96 per cent., in sufficient water to make 250 ml. of solution) is added 1 cm. below the surface of sulphuric acid (50 per cent. by volume) contained in a flask. Any residual hydrogen cyanide may be expelled by warming the flask on a water bath. The gas may be used directly, or may be collected in the liquid form (b.p. 26°) by passing through a glass coil, 4–5 cm. bore and 50 cm. long, surrounded by ice : a freezing mixture must not be used as this may result in solidification of the hydrogen cyanide (m.p. −15° to −14·5°) and consequent clogging of the apparatus. If the hydrogen cyanide is required anhydrous, it should be passed through three large U-tubes filled with anhydrous calcium chloride and immersed in a water bath at 30–40°.

---

* An alternative method for the complete removal of bromine consists in passing the hydrogen bromide through a solution of phenol in dry carbon tetrachloride.

5. **Boron fluoride.** This gas, b.p. —101°, is available in cylinders * and can be bubbled directly into a reaction mixture.

6. **Chlorine.** Small quantities of chlorine are readily prepared by the action of concentrated hydrochloric acid upon potassium permanganate in the apparatus shown in Fig. *II*, *48*, 3. The calculated quantity of potassium permanganate (0·367 g. $KMnO_4 \equiv 0{\cdot}412$ g. Cl_2) is placed in the distilling flask and a slight excess of concentrated hydrochloric acid in the long-stemmed funnel (1·000 g. $KMnO_4$ requires 6·2 ml. of concentrated HCl). The chlorine evolved is passed through a wash bottle containing water to remove hydrogen chloride and is then dried by means of another wash bottle charged with concentrated sulphuric acid ; it is advisable, where excessive pressure is likely to develop, to insert a safety bottle trap containing sulphuric acid (see figure). The acid is allowed to drop slowly upon the permanganate crystals : the flask should be shaken from time to time. When about half of the acid has been added, the evolution of gas commences to slacken and the distilling flask should then be warmed slightly ; after all the acid has been introduced, the mixture is boiled gently. If an absolutely quantitative yield of chlorine is required, the last traces of the gas may be expelled from the flask and wash bottles by a stream of carbon dioxide. The apparatus should be disconnected after the reaction is complete.

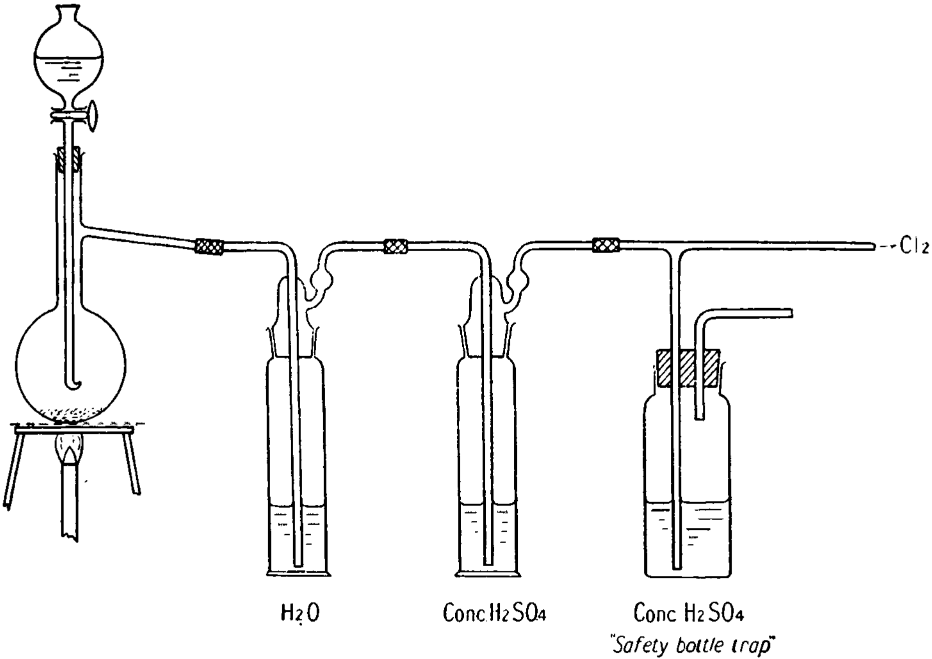


Fig. *II*, *48*, 3.

For comparatively large quantities of chlorine, a small cylinder of chlorine should be employed ; the amount of chlorine used can be determined from the loss in weight of the cylinder.

---

* For example, from Imperial Smelting Corporation. 37, Dover Street, London, W.1, or from The Matheson Company, East Rutherford, N.J., U.S.A.

7. **Ammonia.** Small quantities of ammonia may be prepared with the aid of the apparatus depicted in Fig. *II, 48,* 4. Concentrated ammonia solution (sp. gr. 0·88) is gently heated in the flask surmounted by an efficient reflux condenser. The gas is dried by passage through the tower which is loosely packed with soda lime or quicklime,* and is then passed through a safety bottle, the tubes of which are so arranged that any liquid "sucked back" from the mixture being treated with the gas will eventually be returned to the reaction vessel.

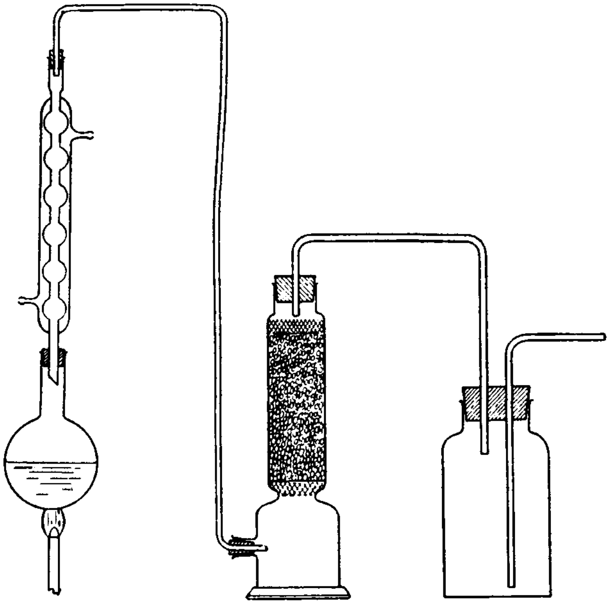


Fig. *II,* 48. 4.

Ammonia is conveniently obtained from a cylinder of the liquefied gas; the cylinder must be equipped with a reducing valve. The rate of flow of the gas may be determined by passage through a bubble counter containing a small volume of concentrated potassium hydroxide solution (12 g. of KOH in 12 ml. of water). A safety bottle should be inserted between the cylinder and the reaction vessel.

8. **Carbon dioxide.** This gas is conveniently generated from marble and dilute hydrochloric acid (1 : 1) in a Kipp's apparatus; it should be passed through a wash bottle containing water or sodium bicarbonate solution to remove acid spray and, if required dry, through two further wash bottles charged with concentrated sulphuric acid.

Large quantities of carbon dioxide may be obtained from a cylinder of the liquid gas; the gas should be dried by passing it through two wash bottles containing concentrated sulphuric acid. A little air is present in the gas.

---

* The solid in the tower may be supported on a Witt filter plate, but a plug of glass wool is satisfactory; the plug of glass wool above the solid acts as a filter for fine particles of the desiccant.

For some purposes (*e.g.*, in the Grignard reaction) solid carbon dioxide, narketed as " Dry Ice " or " Drikold," may be employed.

9. **Carbon monoxide.** This gas is readily prepared by the action of concentrated formic acid (sp. gr. 1·2; about 90 per cent.) upon concentrated sulphuric acid at 70–80°. The apparatus of Fig. *II*, *48*, 5 is recommended. The distilling flask (500 ml.) is immersed in an oil bath maintained at 70–80°, and is connected to two wash bottles containing concentrated sulphuric acid. 125 grams of concentrated sulphuric acid are placed in the distilling flask and 85 g. of the strong formic acid are slowly added from the dropping funnel; a steady stream of gas is evolved. The resulting carbon monoxide may contain traces of carbon dioxide and sulphur dioxide . these impurities may be removed, if desired, by passage of the gas through a tower filled with potassium hydroxide pellets.

Carbon monoxide is very poisonous : all operations involving its preparation and use must be carried out in an efficient fume cupboard.

10. **Sulphur dioxide.** Sulphur dioxide is available in the liquid form in heavy glass cylinders ; the gas is obtained by simply turning the metal valve.

11. **Hydrogen sulphide.** This poisonous gas is usually prepared from ferrous sulphide and dilute hydrochloric acid (1 : 3) in a Kipp's apparatus : it should be washed with water to remove acid spray. The resulting hydrogen sulphide contains hydrogen because of the presence of free iron in commercial ferrous sulphide.

Hydrogen sulphide is marketed in cylinders.*

12. **Phosgene (carbonyl chloride).** Phosgene may be purchased in steel cylinders or in the form of a solution (*ca.* 12·5 per cent. by weight) in toluene in glass ampoules. Owing to the very poisonous character of the gas (b.p. 8°), all operations with it must be conducted in a fume cupboard provided with a powerful draught, and all excess of phosgene must be absorbed in 20 per cent. sodium hydroxide solution. The preparation of the gas is rarely undertaken in the laboratory, but small quantities may be prepared by the following procedure. The apparatus (assembled in a fume chamber) consists of a flask with a short reflux condenser ; a dropping funnel and delivery tube leading to an empty wash bottle are fitted into the top of the condenser. The wash bottle is connected to a Buchner flask, which acts as a receiver. One hundred per cent. sulphuric acid, to which 2 per cent. by weight of ignited kieselguhr has been added, is placed in the flask ; carbon tetrachloride is introduced into the dropping funnel and dry toluene into the receiver. The sulphuric acid is heated to 120–130° in an oil bath and the carbon tetrachloride is allowed to drop in slowly ; the resulting phosgene is absorbed in the toluene, whilst the hydrogen chloride passes on.

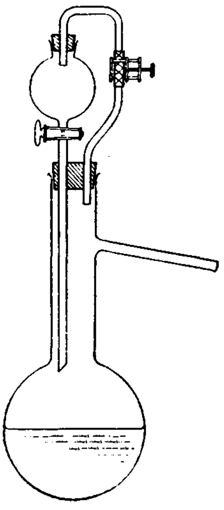


Fig. *II*, *48*, 5.

$$3CCl_4 + 2H_2SO_4 = 3COCl_2 + 4HCl + S_2O_5Cl_2.$$

---

* For example, from The Matheson Company, Inc., East Rutherford, N.J., U.S.A.

13. **Nitrogen.** Cylinders of compressed nitrogen may be purchased or hired. The gas may contain traces of oxygen which may be removed, if necessary, by passage either through an alkaline solution of pyrogallol (15 g. of pyrogallol dissolved in 100 ml. of 50 per cent. sodium hydroxide solution) or through Fieser's solution, which consists of an alkaline solution of sodium hyposulphite to which sodium anthraquinone β-sulphonate is added as a catalyst. **Fieser's solution is prepared** by dissolving 20 g. of potassium hydroxide in 100 ml. of water, and adding 2 g. of sodium anthraquinone - β-sulphonate and 15 g. of commercial sodium hyposulphite (*ca.* 85 per cent.) to the warm solution and stirring until dissolved : the blood-red solution is ready for use when it has cooled to room temperature, and will absorb about 750 ml. of oxygen. The exhaustion of this solution is indicated by the change in colour to dull-red or brown, or when a precipitate appears :

$$Na_2S_2O_4 + O_2 + H_2O = NaHSO_4 + NaHSO_3.$$

Oxygen-free nitrogen in cylinders is available commercially but is, of course, more expensive than the normal commercial compressed gas.

14. **Hydrogen.** Cylinders of compressed hydrogen may be purchased or hired. This gas is usually of electrolytic origin and is essentially pure except for traces of oxygen. Since hydrogen is chiefly employed for catalytic reductions and oxygen has, in general, no harmful effect upon the reduction, no purification is usually necessary. If, however, oxygen-free hydrogen is required, it may be removed by either of the following methods :—

(i) By passage over heated platinised asbestos.*

(ii) By passage through Fieser's solution (see under *Nitrogen, 13*), followed by a wash bottle containing concentrated sulphuric acid to which some silver sulphate has been added ; the latter will detect any hydrogen sulphide that may have formed from the decomposition of Fieser's solution.

II,49. INORGANIC REAGENTS—LIQUIDS

1. **Hydrobromic acid.** *Method 1 (from bromine and sulphur dioxide).* A mixture of 600 g. (or 188·5 ml.) of bromine, 250 ml. of water and 750 g. of crushed ice is placed in a 1·5 litre round-bottomed flask and a rapid stream of sulphur dioxide (from a siphon of the liquefied gas) is passed into the flask, care being taken that the outlet of the gas-delivery tube is below the surface of the bromine layer. The rate of flow of the gas is adjusted so that it is completely absorbed. It is advisable to cool the flask in ice and also to shake the contents from time to time. The reduction is complete when the mixture assumes a uniform yellowish-brown or yellow colour, which is unaffected by further introduction of sulphur dioxide ; excess of the latter gas should be avoided as it will be

---

* It is better to employ the special palladium catalyst which is incorporated in the "Deoxo catalytic gas purifier" (obtainable from Baker Platinum Limited, 52 High Holborn, London, W.C.1). This functions at the laboratory temperature and will remove up to 1 per cent of oxygen. The water vapour formed is carried away in the gas stream and is separated by any of the common desiccants.

evolved during the subsequent distillation. The flask is then connected with a short still head and condenser, and the mixture is distilled. The main product will pass over at 125–126°/760 mm., but the temperature may rise to 130°; the distillation is then stopped. The residue is sulphuric acid. The distillate is redistilled from a little barium bromide in order to remove traces of sulphuric acid, and the fraction, b.p. 125–126°—**constant boiling point hydrobromic acid containing 48 per cent. HBr**—collected. The yield is about 1150 g. or 90 per cent. of the theoretical.

$$Br_2 + SO_2 + 2H_2O = H_2SO_4 + 2HBr.$$

Method 2 (from potassium bromide and sulphuric acid). Potassium bromide (240 g.) is dissolved in water (400 ml.) in a litre flask, and the latter is cooled in ice or in a bath of cold water. Concentrated sulphuric acid (180 ml.) is then slowly added. Care must be taken that the temperature does not rise above 75° otherwise a little bromine may be formed. The solution is cooled to room temperature and the potassium bisulphate, which has separated, is removed by filtration through a hardened filter paper in a Buchner funnel or through a sintered glass funnel. The filtrate is distilled from a litre distilling flask, and the fraction b.p. 124–127° is collected; this contains traces of sulphate. Pure constant boiling point hydrobromic acid is obtained by redistillation from a little barium bromide. The yield is about 285 g. or 85 per cent. of the theoretical.

Method 3 (from bromine and sulphur) (1). A 1-litre three-necked flask is charged with 27 g. of flowers of sulphur and 550 ml. of water. The flask is equipped with a dropping funnel (with tip below the surface of the water), a water-sealed mechanical stirrer and an Allihn reflux condenser; ground glass joints are preferable, but used rubber stoppers are generally satisfactory. The flask is immersed in a bath of water at 60°, the mixture stirred vigorously and, when the temperature inside the flask is about 50°, 400 g. (125·5 ml.) of bromine are introduced from the dropping funnel during about 20 minutes. The temperature of the reaction mixture rises rapidly as the reaction proceeds; the flask is cooled momentarily in a bath of cold water if the condensed bromine vapour is near the top of the condenser. When all the bromine has been added, the mixture is heated on a boiling water bath for 15 minutes. The reaction product is cooled, and filtered from the residual sulphur and other solid matter through a sintered glass funnel. The filtrate is distilled and the constant b.p. hydrobromic acid collected at 125–126°/760 mm. The yield is 805 g.

Note. (1) The reaction between bromine and sulphur in the presence of water may be represented by the equation:

$$3Br_2 + S + 4H_2O = 6HBr + H_2SO_4$$

It is rather slow at moderate temperatures and the hydrobromic acid formed in the initial stages of the reaction inhibits its further progress. By carrying out the reaction at 50–70° or above in the presence of a large excess of water, the inhibition observed at lower temperatures does not occur.

Hydrobromic acid (analytical reagent grade), sp. gr. 1·46 to 1·49 (46–48 per cent. HBr) may be purchased.

2. **Hydriodic acid.** A 1·5 litre three-necked flask is charged with a mixture of 480 g. of iodine and 600 ml. of water. The central aperture is fitted with a stopper carrying an efficient mechanical stirrer leading

almost to the bottom of the flask, and the smaller apertures respectively with a lead-in tube for hydrogen sulphide extending to well below the surface of the liquid and with an exit tube attached to an inverted funnel just dipping into 5 per cent. sodium hydroxide solution. The mixture is vigorously stirred and a stream of hydrogen sulphide (either from a freshly-charged Kipp's apparatus or from a cylinder of the gas) passed in as rapidly as it can be absorbed. After several hours the liquid assumes a yellow colour (sometimes it is almost colourless) and most of the sulphur sticks together in the form of a hard lump. The sulphur is removed by filtration through a funnel plugged with glass wool (or through a sintered glass funnel), and the filtrate is boiled until the lead acetate paper test for hydrogen sulphide is negative. The solution is filtered again, if necessary. The hydriodic acid is then distilled from a 500 ml. Claisen flask, and the fraction b.p. 125·5–126·5°/760 mm. is collected. This is the **constant boiling point hydriodic acid** and contains 57 per cent. of hydrogen iodide. The yield of the constant boiling acid is 785 g. or 90 per cent. of the theoretical.

$$H_2S + I_2 \longrightarrow 2HI + S.$$

Note.

The hard lump of sulphur remaining in the flask is best removed by boiling with concentrated nitric acid in the fume cupboard.

Hydriodic acid, of analytical reagent quality, sp. gr. 1·7 (54–56 per cent HI) and sp. gr. 1·94 (64–68 per cent. HI) may be purchased.

3. **Sulphuric acid.** Ordinary concentrated acid, sp. gr. 1·84, is a constant boiling point mixture, b.p. 338°/760 mm., and contains 98 per cent. H_2SO_4. The 100 per cent. acid may be prepared by the addition of the calculated quantity of oleum * ; it is also available commercially.

Oleum is marketed in all strengths up to *ca.* 70 per cent. SO_3. From 0 to 40 per cent. free SO_3, it is a liquid ; from 40 to 60 per cent. free SO_3, it is a solid ; from 60 to 70 per cent. free SO_3, it is liquid ; above 70 per cent. free SO_3, it is a solid. The acid must be kept in ground glass stoppered, thick-walled bottles. If it is required to melt the acid, the stopper is removed, a watch glass placed on the mouth of the bottle, and the bottle placed in a layer of sand in an air bath which is warmed with a small flame. The bottle is fitted with a wash bottle attachment, and any desired quantity of acid is forced out by gentle air pressure from a hand or foot bellows (the mouth must not be used) ; this procedure is far more satisfactory than that of pouring the liquid acid from the bottle.

4. **Nitric acid.** The commercial concentrated acid, sp. gr. 1·42, is a constant boiling point mixture of maximum boiling point (120·5°/760 mm.) containing about 68 per cent. HNO_3. Colourless concentrated acid may be obtained from the coloured product (due to oxides of nitrogen or to nitrous acid) by warming to about 60° and passing in a stream of dust-free nitrogen or air ; the addition of a little urea considerably accelerates the process.

$$2HNO_2 + CO(NH_2)_2 = CO_2 + 2N_2 + 3H_2O.$$

---

* A method for determining the SO_3 content of oleum is described in the author's *Text Book of Quantitative Inorganic Analysis : Theory and Practice*, Second Edition, 1951, p. 263 (Longmans, Green and Co. Ltd.).

The so-called **fuming nitric acid,** sp. gr. 1·5 and containing about 95 per cent. HNO_3, may be purchased ; it has a yellow colour, due to the presence of oxides of nitrogen. This acid may be prepared by distilling a mixture of equal volumes of concentrated nitric acid, sp. gr. 1·42, and concentrated sulphuric acid in an all-glass apparatus, and collecting a volume of distillate slightly less than one-half of the volume of concentrated nitric acid originally used. The distillation may also be conducted in a retort, the side arm of which has been bent in the centre to act as a trap for the condensation of acid spray ; a plug of glass wool should be placed in the neck of the receiver. A colourless highly concentrated nitric acid may be obtained by the removal of the oxides of nitrogen as detailed above.

5. **Phosphoric acid.** The commercial syrupy orthophosphoric acid has a sp. gr. of 1·75 and contains about 88 per cent. of H_3PO_4. An approximately 100 per cent. acid is also marketed.

6. **Thionyl chloride.** The technical product frequently contains traces of acids and other impurities ; it is advisable to remove these before using the reagent for the preparation of acid chlorides, *etc.* " Thionyl chloride, redistilled " is satisfactory in many cases. A colourless product of high purity may be obtained by the following simple process. Commercial thionyl chloride is first fractionated, preferably in an all-glass apparatus, from quinoline in order to remove acid impurities (50 g. of thionyl chloride from 10 ml. of quinoline) ; the receiver is protected from the entrance of moisture by a drying tube, filled with cotton wool or anhydrous calcium chloride. The distillate is then refractionated as before from boiled linseed oil (50 g. of thionyl chloride from 20 ml. of linseed oil), the fraction b.p. 76–78° being collected. Pure thionyl chloride has b.p. 77°/760 mm., and must be stored in a well-fitting, glass-stoppered bottle.

7. **Sulphuryl chloride.** The technical product should be fractionated, preferably in an all-glass apparatus ; the fraction b.p. 69–70° is collected. The pure substance has b.p. 69°/760 mm.

8. **Bromine.** The commercial product may be dried (and partially purified) by shaking with an equal volume of concentrated sulphuric acid, and then separating the acid. Chlorine, if present, may be removed by fractionation in an all-glass apparatus from pure potassium bromide : the b.p. is 59°/760 mm. The analytical reagent grade is satisfactory for most purposes where pure bromine is required.

9. **Phosphorus tribromide.** Into a 500 ml. three-necked flask, provided with a mechanical stirrer (sealed with dry carbon tetrachloride), a dropping funnel and a reflux condenser, are placed 28 g. of purified red phosphorus (Section **II,50,***5*), and 200 ml. of carbon tetrachloride (dried over anhydrous calcium chloride). Dry bromine (198 g. ; 63·5 ml.) is placed in the dropping funnel and added to the vigorously stirred contents of the flask at the rate of about 3 drops per second. A little hydrogen bromide is evolved so that the preparation should be carried out in a fume cupboard. After all the bromine has been added, the mixture is refluxed for 15 minutes by immersing the flask in a water bath at 80–90°. The clear solution is then decanted through a fluted filter paper, and the carbon tetrachloride is distilled off through a short column (*e.g.*, the all-glass Dufton column, Section **II,15**) in an all-glass apparatus; the residue, upon distillation through the well-lagged column, boils at 166–169° (mainly at 168°). Upon redistillation, using an ordinary distilling flask in an all-glass apparatus, the phosphorus tribromide boils at 170–171°. The yield is 190 g.

10. **Hydrazine hydrate.** In a 750 ml. copper flask (1), fitted with a cork covered with tin foil and holding a reflux condenser, are placed 200 g. of hydrazine sulphate and 160 g. of sodium hydroxide. Seventy-five ml. of water (2) are added gradually during about 5 minutes through the condenser; the reaction becomes fairly vigorous and care should be taken that none of the vapours escape from the condenser. The mixture is refluxed for 1·5 hours. The reflux condenser is removed and arranged for downward distillation. The product is distilled by heating the flask with a free flame; strong heating is required towards the end in order to drive over the last traces of hydrazine hydrate. The distillate is a clear liquid weighing 175 g. (3), and contains 40–45 per cent. of hydrazine hydrate (4) as shown by titration with standard acid.

The 40–45 per cent. hydrazine solution may be concentrated as follows. A mixture of 150 g. (144 ml.) of the solution and 230 ml. of xylene is distilled from a 500 ml. round-bottomed flask through a well-lagged Hempel (or other efficient fractionating) column fitted into a cork covered with tin foil. All the xylene passes over with about 85 ml. of water. Upon distillation of the residue, about 50 g. of 90–95 per cent. hydrazine hydrate (5) are obtained.

Notes.

(1) Glass flasks cannot be used because of the high temperature required in the distillation.

(2) This amount of water is satisfactory; if less water is used, the yield is lowered, while more water dilutes the product without increasing the yield.

(3) The product is sometimes contaminated with silicic acid from the glass of the condenser: this may be removed by filtration. All corks should be covered with tin foil to avoid attack by the hydrazine hydrate.

(4) Hydrazine hydrate may be titrated with standard acid using methyl orange as indicator or, alternatively, against standard iodine solution with starch as indicator. In the latter case about 0·1 g., accurately weighed, of the hydrazine hydrate solution is diluted with about 100 ml. of water, 2–3 drops of starch indicator added, and immediately before titration 5 g. of sodium bicarbonate are introduced. Rapid titration with iodine gives a satisfactory end point.

$$5NH_2.NH_2,H_2O + 2I_2 \longrightarrow 4NH_2.NH_2,HI + 5H_2O + N_2$$

(5) Hydrazine hydrate of 60 per cent. and 100 per cent. are available commercially. The preparation from hydrazine sulphate is hardly worth while.

II,50. INORGANIC REAGENTS—SOLIDS

1. **Cuprous chloride.** Hydrated copper sulphate (125 g.) and sodium chloride (32·5 g.) are dissolved in water (400 ml.); boiling may be necessary. An alkaline solution of sodium sulphite (from 26·5 g. of sodium bisulphite and 17·5 g. of sodium hydroxide in 200 ml. of water) or the solution of the sodium bisulphite alone is added to the resulting hot solution during about 5 minutes with constant shaking. The solution will be decolourised or nearly so. It is then cooled to room temperature (or in an ice bath), and the supernatant liquid is decanted from the colourless cuprous chloride. The precipitate is washed twice by decantation with water containing a little dissolved sulphurous acid, the latter to prevent oxidation. For most purposes a solution of cuprous chloride is required: the moist cuprous chloride is dissolved in 200 ml. of concentrated hydrochloric acid. The solution should be used within 24 hours of its preparation as it tends to oxidise (and therefore darken) on keeping; if it is not to be used immediately, the solution is kept in a tightly stoppered bottle. If the dry solid cuprous chloride is required, the moist solid should be washed several times by decantation with dilute sulphurous acid, collected in a Buchner funnel, washed several times with small portions of glacial acetic acid, and dried in an evaporating dish (or in an air oven at 100–120°) until the odour of acetic acid has disappeared. The cuprous chloride thus obtained has a pure white colour and should be kept in a tightly stoppered bottle. The yield is almost quantitative.

$$2CuSO_4 + 2NaCl + NaHSO_3 + H_2O = 2CuCl + 3NaHSO_4.$$

2. **Cuprous bromide.** The solid salt may be prepared by dissolving 150 g. of copper sulphate crystals and 87·5 g. of sodium bromide dihydrate in 500 ml. of warm water, and then adding 38 g. of powdered sodium sulphite over a period of 5–10 minutes to the stirred solution. If the blue colour is not completely discharged, a little more sodium sulphite should be added. The mixture is then cooled, the precipitate is collected in a Buchner funnel, washed twice with water containing a little dissolved sulphurous acid, pressed with a glass stopper to remove most of the liquid, and then dried in an evaporating dish or in an air oven at 100–120°. The yield is about 80 g.

A solution of cuprous bromide may be prepared either by dissolving the solid in hot constant boiling point hydrobromic acid or by refluxing a mixture of 63 g. of crystallised copper sulphate, 20 g. of copper turnings, 154 g. of sodium bromide dihydrate, 30 g. (16·3 ml.) of concentrated sulphuric acid and 1 litre of water for 3–4 hours. If the colour of the solution has not become yellowish after this period of heating, a few grams of sodium sulphite should be added to complete the reduction.

3. **Cuprous cyanide.** *Method 1* (Barber, 1943). This is based essentially upon the reaction:

$$2CuSO_4 + 2NaCN + NaHSO_3 + H_2O = 2CuCN + 3NaHSO_4.$$

500 g. of powdered crystallised copper sulphate are placed in a 3-litre beaker or round-bottomed flask and dissolved in 1600 ml. of water at 40–50°. Solutions of 140 g. of commercial sodium bisulphite powder in 400 ml. of water (*A*) and of 140 g. of commercial potassium cyanide (96–99 per cent. KCN) in 400 ml. of water (*B*) are prepared, and filtered, if necessary, from small amounts of insoluble matter. Solutions *A* and *B* are separately warmed to 60°. The copper sulphate solution should be acidified faintly to Congo red. Solution *A* is then added with mechanical stirring during 1–2 minutes, followed immediately by solution *B*. There is a slight frothing, a little sulphur dioxide is evolved, but no appreciable amount of cyanogen or hydrogen cyanide. After about 10 minutes, the hot solution is filtered, the product washed thoroughly with boiling water,

and finally with alcohol. It is dried at 100–110° to a fine soft powder (24–36 hours). The yield is 167 g. To prepare a cuprocyanide solution of known and definite concentration, a weighed amount of the dry cuprous cyanide is dissolved in the necessary quantity (about 2 mols) of a solution of an alkali cyanide; an almost colourless solution results.

Method 2. This utilises the reaction:

$$2CuSO_4 + 4NaCN = 2CuCN + 2Na_2SO_4 + (CN)_2.$$

The disadvantages of the method are the evolution of cyanogen, thus necessitating the use of a fume cupboard, and the consequent wastage of sodium cyanide; the results, however, are quite satisfactory. A 3-litre three-necked flask is fitted with a mechanical stirrer, a separatory funnel and a gas exit tube passing to the flue of an efficient fume cupboard. A solution of 325 g. of powdered copper sulphate pentahydrate is placed in the flask and the latter surrounded by a bath heated to about 80°. A solution of 178 g. of technical sodium cyanide (96–98 per cent.) in 325 ml. of water is added from the separatory funnel during about 30 minutes to the stirred copper sulphate solution. The mixture is then boiled for 5–10 minutes in order to expel all the cyanogen gas. The cuprous cyanide, which commences to separate as a light tan powder as soon as the cyanide solution is added, is allowed to settle and the solution is decanted. The precipitate is filtered off on a Buchner or sintered glass funnel, washed with hot water (500–750 ml.), followed by alcohol (250 ml.) and ether (150 ml.). The product is dried at 105–110° for about 36 hours; if the temperature of the drying is allowed to rise appreciably, the cuprous cyanide will be gradually decomposed. The yield is 100–105 g.

Cuprous cyanide solution. The most satisfactory method is to dissolve the cuprous cyanide (1 mol) in a solution of technical sodium cyanide (2·5–2·6 mols in 600 ml. of water). If it is desired to avoid the preparation of solid cuprous cyanide, the following procedure may be adopted. Cuprous chloride, prepared from 125 g. of copper sulphate crystals as described under *1* above, is suspended in 200 ml. of water contained in a 1-litre round-bottomed flask, which is fitted with a mechanical stirrer. A solution of 65 g. of technical sodium cyanide (96–98 per cent.) in 100 ml. of water is added and the mixture is stirred. The cuprous chloride passes into solution with considerable evolution of heat. As the cuprous cyanide is usually employed in some modification of the diazo reaction, it is usual to cool the resulting solution in ice.

4. **Copper.—Copper powder.** One hundred grams of recrystallised copper sulphate are dissolved in 350 ml. of hot water in a 1-litre beaker; a mechanical stirrer is provided. After cooling to the laboratory temperature, the stirrer is set in motion and 35 g. (or more, if necessary) of high grade zinc powder are gradually added until the solution is decolourised. The precipitated copper is washed by decantation with water. Dilute hydrochloric acid (5 per cent.) is added to the precipitate in order to remove the excess of zinc, and stirring is continued until the evolution of hydrogen ceases. The copper powder is filtered, washed with water, and kept in a moist condition (as a paste) in a stoppered bottle.

Activated copper bronze. Commercial copper bronze does not always give satisfactory yields in the Ullmann reaction, but uniform results can be obtained by the following " activation process." One hundred grams of copper bronze are treated with 1 litre of a 2 per cent. solution of iodine in acetone for 5–10 minutes. This results in the production of a rather grayish colour due to the formation of copper iodide. The product is filtered off on a Buchner funnel, removed, and washed by stirring with 500 ml. of 1 : 1 solution of concentrated hydrochloric acid in acetone. The copper iodide dissolves, and the residual copper bronze is filtered and washed with acetone. It is then dried in a vacuum desiccator. The " activated " copper bronze should be used immediately after preparation.

5. **Red phosphorus.** Commercial red phosphorus is usually contaminated with small quantities of acidic products. It should be boiled for 15 minutes with distilled water, allowed to settle, decanted through a Buchner funnel, and then washed two or three times with boiling water by decantation. Finally, the phosphorus is completely transferred to the Buchner funnel and washed with hot water until the washings are neutral. It is dried at 100°, and kept in a desiccator or in a tightly stoppered bottle.

6. **Sodium.** The preparation of sodium wire is described in Section **II,47,*1*.** **Granulated sodium** (also termed **molecular sodium** and **powdered sodium**) may be prepared by either of the following methods :

Method 1. Twenty-three grams of clean sodium (most conveniently weighed under sodium-dried ether after the surface coating has been cut away with a knife) are introduced into a 750 or 1000 ml. round-bottomed Pyrex flask containing about 200 ml. of sodium-dried xylene or at least sufficient xylene to cover the sodium completely. The flask is placed on a sand bath supported on a ring burner. Two or three thicknesses of dry cloth (or a thick towel), sufficient to envelop the whole flask, are placed in a convenient position on the bench. The sand bath is heated cautiously and the " ring " of condensed vapour of the xylene is carefully watched. When the " ring " of condensed vapour has risen to within one inch from the neck of the flask,* the flame beneath the burner is extinguished, a well-fitting rubber stopper or good quality bark cork is rapidly introduced, the flask is completely wrapped in the previously prepared cloth and shaken vigorously for 30–60 seconds or until the molten sodium is converted into a fine powder. The flask is then placed on a " suberite " ring and the stopper is removed. The sodium is thus obtained in the form of small spheres, the size of which is controlled by the time and rapidity of the shaking. Any particles of sodium adhering to the sides of the flask are washed under the xylene. When the contents of the flask have cooled to room temperature, the xylene may be decanted and the sodium washed twice with 100 ml. of sodium-dried ether to remove traces of xylene ; finally the finely-divided sodium is covered with absolute ether. A bucket, half-full of dry sand, should be kept at hand in case of breakage of the flask. Not more than 25–30 g. of sodium should be powdered at one time by this procedure.

Method 2. It is convenient to prepare the powdered sodium in the flask in which the subsequent reaction is to be carried out ; this is usually a three-necked flask. Into a 1-litre three-necked flask fitted with a

---

* Beginners may prefer to fit the flask with a reflux condenser and thus considerably reduce the danger of fire.

reflux condenser (protected by a drying tube containing soda lime), a sealed stirrer (see Kyrides stirrer, Fig. *II*, 7, 10) and a dropping funnel, are placed 23 g. of clean sodium and 150–200 ml. of sodium-dried xylene. The flask is surrounded by an oil bath, which is heated until the sodium has melted. The stirrer is started and, after the sodium is suitably granulated, the oil bath is removed. When the contents of the flask have cooled to the laboratory temperature, the stirrer is stopped. The xylene may then be decanted, and the sodium washed with two 100 ml. portions of sodium-dried ether to remove traces of xylene as in *Method 1.* Large quantities of " molecular " sodium may be prepared by this method.

7. **Sodium amalgam.** The amalgam which is generally employed for reductions contains from 1 to 3 per cent. of sodium. Amalgams with a greater sodium content than 1·2 per cent. are solid at the ordinary temperature and can be powdered in a mortar; the 1·2 per cent. amalgam is semi-solid at room temperature but is completely fluid at 50°. Two methods of preparation are available.

Method 1. Nine grams of clean sodium are placed in a 500 ml. conical flask and covered with 20 ml. of dry toluene. The sodium is cautiously melted over a free flame, and the flame is extinguished. 750 g. of mercury are added from a separatory funnel in drops with occasional shaking. During the addition of the first 2–3 ml. of mercury the reaction is extremely vigorous, but subsequently the rate of addition of the mercury may be increased so that the toluene boils continuously. At the end of the reaction, the toluene is allowed to evaporate completely; if any toluene remains, the excess should be decanted. The toluene vapour remaining above the amalgam tends to protect it from the action of the air. The resulting amalgam contains about 1·2 per cent. of sodium. An amalgam of 2 per cent. strength can be prepared by this method (15·2 g. of sodium in 750 g. of mercury); if all the toluene has not evaporated completely before the end of the reaction, it should be decanted before the amalgam solidifies. If necessary, the amalgam is melted on a hot plate and then poured on to a uralite or poilite board, and then pulverised in a mortar * and transferred to a tightly stoppered bottle. The preparation must be carried out in the fume cupboard since mercury vapour is poisonous.

Method 2. The clean sodium (22·8 g.) is placed in a 500 ml. round-bottomed three-necked flask, provided with a dropping funnel (containing 750 g. of mercury) in the central aperture and inlet and outlet tubes for dry nitrogen in the two side apertures. The air is displaced by nitrogen. About 10 ml. of mercury are added and the flask is warmed gently with a free flame until the reaction commences. The flame is then removed and the reaction is maintained by the slow addition of the mercury. When about half the mercury has been introduced, the amalgam will commence to solidify; it should be kept molten by heating with occasional shaking. After the addition of all the mercury, the hot molten amalgam is poured on to a uralite or poilite board, powdered in a mortar and stored as in *Method 1.* Amalgams of 1 and 2 per cent. strength may be prepared similarly.

---

* The mortar should be provided with a tightly fitting rubber cover to protect the powdered material from oxidation in air.

8. **Sodamide.** This substance is prepared by the reaction between gaseous ammonia and molten sodium :

$$2Na + 2NH_3 = 2NaNH_2 + H_2 .$$

The apparatus consists essentially of a cast iron crucible and cover * or fusion pot in which is placed a nickel crucible or dish. The complete apparatus is illustrated in Fig. *II*, *50*, 1. The fusion pot *A* carries a combined thermometer well *T* and an inlet tube *BCD*, and a wide outlet tube *E*. The thermometer well *T* is closed at the bottom (welded) and projects 6–7 mm. below the wider inlet tube to which it is welded near the top. There is a gland or asbestos-cord packed joint at *F*, held in position by a hexagonal nut ; the nut, fixed firmly in place by means of a wrench so as to make the gas-tight joint, enables the tube *BCD* to be raised or lowered at will. The tube *B* is connected by rubber tubing (*ca.* 7 cm.) to a Kjeldahl trap *K* (to prevent mercury passing into *A*) fitted into a U-tube *G* containing just enough mercury to seal the bend (it will serve to indicate the rate of flow of the ammonia), and then to an ammonia cylinder ; *H* is a mercury safety trap to provide for the possibility of the apparatus becoming blocked by solidification of the amide due to an accidental drop of temperature. The apparatus is first completely assembled with the thermometer well in the position shown in the figure : the fusion pot is heated by means of a Fisher or equivalent burner to about 120° for 10 minutes in a slow stream of ammonia ; this will remove traces of moisture from the system. The fusion pot is then allowed to cool to 70–80°, the cover is removed and a 250 ml. nickel crucible *N* is inserted ; the tube *BCD* is raised just above the top of the nickel crucible. The crucible is charged with about 175 g. of clean sodium from which the oxide

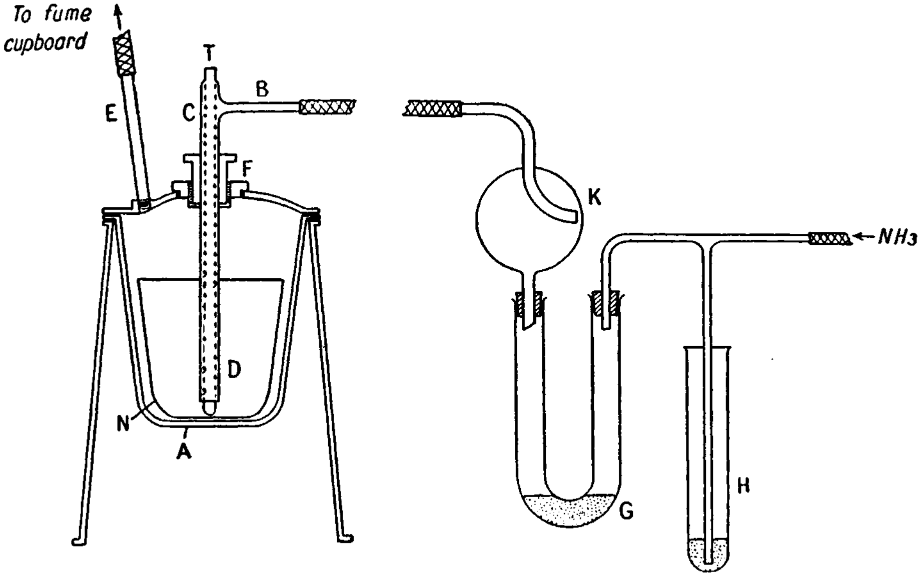


Fig. *II*, *50*, 1.

---

* A suitable cast iron crucible and cover, 1 quart capacity, is supplied by the Denver Fire Clay Company, Denver, U.S.A. It can also be made from sheet iron.

coating has been removed, the air is completely displaced by passing ammonia for 10 minutes, and the pot is heated strongly so as to melt the sodium rapidly (5–10 minutes). The inlet tube *BCD* is then pushed through the gland until it rests on the bottom of the crucible and the nut at *F* is tightened so as to make a gas-tight joint. When the temperature is about 320°, the burner is adjusted so as to maintain a temperature of 350–360°. The passage of ammonia is then adjusted so that the flow of bubbles in *G* is just too rapid to count; if the current of gas is too fast, there will be some splashing and much molten sodamide will collect in the iron pot. After 3·5–4 hours, the temperature is reduced to 320° and the cover is lifted to see whether any unreacted sodium remains; inspection is facilitated by a flash lamp, the unreacted metal being visible as a globule floating on the surface of the darker liquid.* If no unreacted sodium remains, the iron crucible is allowed to cool to 230–240° and is maintained at this temperature for 30 minutes to ensure the removal of most of any sodium hydride simultaneously formed in the reaction. The burner is now extinguished, the ammonia stream is shut off and disconnected at *B*. The nickel crucible is immediately removed from the pot with crucible tongs, and the completely molten sodamide is poured into a clean iron tray (*ca.* 14 cm. diameter and 2 cm. high). The iron tray should have been polished with emery cloth or with clean sand, and previously heated to redness to remove moisture. As soon as the sodamide has solidified sufficiently, the iron tray is transferred to a large desiccator to cool.† When cool enough to handle, the tray is inverted over a sheet of heavy clean paper, and the sodamide is removed by tapping the bottom of the pan or, if necessary, broken away from the pan. The sodamide is immediately transferred to wide-mouthed bottles and covered with dry benzene or with dry commercial heptane from petroleum, b.p. 90–100°. The product should be white or nearly white, and the yield is 275 g. It may also be preserved in an atmosphere of nitrogen or dry ammonia in a tightly sealed container.

Sodamide should never be stored in a stoppered bottle from which samples are to be removed intermittently, since dangerous mixtures may result when the substance is exposed for 2–3 days to even limited amounts of air at the ordinary temperature. As a safe practice, sodamide should be used immediately after preparation, and should not be kept longer than 12–24 hours unless it be under an inert solvent. Even small amounts of unused sodamide should be removed from the apparatus in which it was made by washing with methyl or ethyl alcohol. In all cases where a yellowish or brownish colour develops, due to the formation of oxidation

---

* An alternative method for ascertaining the end of the reaction, which does not involve the removal of the cover, is to conduct the exit gas through an empty wash bottle (to act as a trap in case of "sucking back") and then collect a sample in a test-tube over water. If an inflammable gas (hydrogen) is absent, the reaction may be considered complete. Under no circumstances should the reaction be stopped until all the sodium has completely reacted; too early arrest of the reaction may result in the product containing sodium hydride, which appears to be partially responsible for the explosive properties of the impure substance:

$$NaNH_2 + H_2 \rightleftharpoons NaH + NH_3$$

† Another procedure is to allow the sodamide to cool completely in the nickel crucible in a slow stream of ammonia, the tube *BCD* being, of course, raised well above the melt before cooling.

products, the resulting mixture may become highly explosive ; it should be destroyed by covering with benzene or toluene and slowly adding dilute ethyl alcohol with stirring.

Sodamide may be readily pulverised by grinding in a glass mortar under an inert hydrocarbon solvent (benzene, toluene, xylene, etc.).

Sodamide of high purity is available commercially.*

Small quantities of highly reactive sodamide may be prepared from liquid ammonia and sodium as required as follows. In a 500 ml. three-necked flask, having ground joints and equipped with a removable glass stopper, a mercury-sealed stirrer and a reflux condenser with soda-lime guard tube, place 300 ml. of anhydrous liquid ammonia (see Section **VI,16**). Add just sufficient sodium to the stirred liquid to produce a permanent blue colour, then 0·5 g. of powdered ferric nitrate (to catalyse the conversion of sodium into sodamide), followed by 13·8 g. of clean sodium metal (cut into small pieces) over a period of 30 minutes. When the sodium has been converted into sodamide (as indicated by the change from a blue solution to a grey suspension), evaporate the ammonia by means of a water bath, and add sufficent anhydrous ether through a dropping funnel so that the volume of the liquid remains at about 300 ml. After practically all the ammonia has evaporated, as indicated by the refluxing of the ether, stir the suspension of sodamide and heat under reflux for 5 minutes, and then cool to room temperature. A suspension of 23·4 g. of sodamide in dry ether is thus obtained. The preparation can be completed in 60–75 minutes.

9. **Anhydrous sodium acetate.** Crystallised sodium acetate, $CH_3COONa.3H_2O$, is heated in a casserole or in a shallow iron or nickel dish over a small free flame. The salt first liquefies, steam is evolved and the mass solidifies as soon as most of the water of crystallisation has been driven off. To remove the residual water, the solid is carefully heated with a larger flame, the burner being constantly moved until the solid just melts. Care must be taken that the solid is not overheated ; too strong heating will be recognised by the evolution of combustible gases and charring of the substance. The fused salt is allowed to solidify, and is removed from the vessel whilst still warm with a knife or other convenient object. It is immediately powdered and stored in a tightly stoppered bottle.

If the commercial fused sodium acetate is available, it should be melted and maintained in the fused state for several minutes in order to remove the water absorbed during storage.

10. **Anhydrous sodium sulphide.** The hydrated salt, $Na_2S.9H_2O$, is heated in a Pyrex distilling flask or retort in a stream of hydrogen or of nitrogen until water ceases to be evolved. The solid cake of anhydrous sodium sulphide is removed from the vessel with the aid of a copper wire hook or by other suitable means. No attempt should be made to fuse the sodium sulphide since at high temperatures sodium sulphide is readily oxidised to sodium sulphate.

11. **Anhydrous stannous chloride.** Crystalline stannous chloride, $SnCl_2.2H_2O$, is heated for one hour in an oil bath at 195–200°, the cooled melt is powdered, and kept in a desiccator or in a tightly stoppered bottle.

---

* For example, from May and Baker Ltd., Dagenham.

The resulting product, although satisfactory in many instances, is not entirely dependable. The following procedure (Stephen, 1930) invariably gives an excellent product. In a 400 ml. beaker are placed 102 g. (89·5 ml.) (1 mole) of redistilled acetic anhydride, and 123 g. of analytical reagent grade stannous chloride dihydrate (0·5 mol) are added whilst the liquid is stirred either manually or mechanically; dehydration is almost instantaneous. The operation should be conducted in the fume cupboard as much heat is evolved and the acetic anhydride may boil. After about one hour, the anhydrous stannous chloride is filtered off on a Buchner or sintered glass funnel, washed free from acetic acid with two 30 ml. portions of anhydrous ether, and dried overnight in a vacuum desiccator. Anhydrous stannous chloride may be kept for an indefinite period in a desiccator; it may also be stored in a tightly stoppered bottle.

The anhydrous compound is not appreciably hygroscopic, is readily soluble in acetone and amyl alcohol, and insoluble in benzene, toluene, xylene and chloroform; it is also readily soluble in absolute methyl or ethyl alcohol, but a trace of water causes immediate hydrolysis with the formation of an opalescent precipitate.

12. **Aluminium amalgam.** One hundred grams of thin aluminium foil (0·05 mm. thickness) in strips about 15 cm. long and 2·5 cm. wide, loosely folded, are placed in a 3-litre flask and covered with a 10 per cent. solution of sodium hydroxide; the flask is warmed on a water bath until a vigorous evolution of hydrogen has taken place for several minutes (*CAUTION!*). The foil is then thoroughly washed with water and with rectified spirit, the latter operation producing an exceptionally clean surface for amalgamation. Sufficient of a 2 per cent. solution of mercuric chloride is added to cover the aluminium completely and is allowed to act for about 2 minutes; it is then poured off, and the amalgam is washed with water, with rectified spirit, and finally with moist ether. The amalgam is covered with about 1·5 litres of moist ether and is ready for immediate use. If another solvent, *e.g.*, methyl or ethyl acetate, is to be employed in the reduction with moist aluminium amalgam, the ether is, of course, replaced by this solvent.

13. **Amalgamated zinc** (for Clemmensen reduction). *Method 1.* Two hundred grams of zinc wool are placed in a 2-litre three-necked flask and covered with a 10–15 per cent. solution of sodium hydroxide. The flask is gently warmed on a water bath until hydrogen is vigorously evolved (*CAUTION!*); the sodium hydroxide solution is then immediately poured off (it may be necessary to dilute with water first in order to moderate the vigour of the reaction), and the zinc is washed repeatedly with distilled water until most, if not all, of the sodium hydroxide has been removed. The zinc is then covered with a 1 per cent. solution of mercuric chloride and allowed to stand for 30–60 minutes with occasional shaking. The mercuric chloride solution is then poured off, and the amalgamated zinc is washed twice with distilled water. The amalgamated zinc is then covered with 500 ml. of concentrated hydrochloric acid and 100 ml. of water. The compound to be reduced, about 0·3–0·4 mole, is then added, and the reaction is allowed to proceed whilst a current of hydrogen chloride gas is passed through the liquid.

Method 2 (Martin, 1942). A mixture of 200 g. of zinc wool, 15 g. of mercuric chloride, 10 ml. of concentrated hydrochloric acid and 250 ml. of water is stirred or shaken for 5 minutes. The aqueous solution is decanted, and the amalgamated zinc is covered with 150 ml. of water and 200 ml. of concentrated hydrochloric acid. The material to be reduced, usually about 0·3–0·4 mole, is then added immediately, and the reaction is commenced.

14. **Lead dioxide.** A convenient method of preparation is to oxidise a plumbous salt in an alkaline medium with a hypochlorite solution :

$$2Pb(C_2H_3O_2)_2 + 4NaOH + Ca(OCl)_2 = 2PbO_2 + 4NaC_2H_3O_2 + CaCl_2 + 2H_2O.$$

A solution of 20 g. of sodium hydroxide in 180 ml. of water is added slowly and with constant stirring to a solution of 40 g. of lead acetate in 100 ml. of water. 28 G. of bleaching powder are shaken up with 400 ml. of water, and the filtered solution is added with constant stirring to the alkaline solution of lead acetate. The mixture is heated slowly to the boiling point and then boiled for a few minutes. A small portion is filtered off and tested for completeness of the oxidation by adding a few drops of hypochlorite solution ; if oxidation is incomplete, a further 20 ml. of filtered bleaching powder solution is added and the solution boiled again. The process is repeated until all the plumbous salt is oxidised. The precipitate is allowed to settle and washed five times by decantation. It is then vigorously stirred with 100 ml. of 6N nitric acid to remove any calcium plumbate or plumbous hydroxide, and again washed with water by decantation. Finally it is filtered off on a Buchner funnel and dried. The yield is nearly quantitative.

15. **Lead tetracetate.** Red lead is warmed with acetic acid in the presence of sufficient acetic anhydride to combine with the water formed :

$$Pb_3O_4 + 8HC_2H_3O_2 = Pb(C_2H_3O_2)_4 + 2Pb(C_2H_3O_2)_2 + 4H_2O.$$

The filtrate, which contains lead acetate, may be treated with chlorine :

$$2Pb(C_2H_3O_2)_2 + Cl_2 = Pb(C_2H_3O_2)_4 + PbCl_2,$$

and the resulting lead tetracetate separated from the accompanying lead chloride by recrystallisation from glacial acetic acid.

A mixture of 550 g. of glacial acetic acid and 185 g. of acetic anhydride is placed in a 1-litre three-necked flask provided with a thermometer and a mercury-sealed stirrer. The liquid is vigorously stirred, heated to 55–60°, and 300 g. of dry red lead powder are added in portions of 15–20 g. A fresh addition is made only after the colour due to the preceding portion has largely disappeared. The temperature should not be allowed to rise above 65°. Towards the end it may be necessary to warm the flask cautiously to about 80° in order to complete the reaction. At the end of the reaction, the thick and somewhat dark solution is cooled, and the precipitated lead tetracetate is filtered off (the mother liquor, *M*, is put aside) and washed with glacial acetic acid. The crude product, without being dried, is dissolved in hot glacial acetic acid containing a little acetic anhydride, the solution treated with a little decolourising carbon, filtered through a hot water funnel, and cooled. The colourless crystalline product is filtered off and dried in a vacuum desiccator over potassium hydroxide pellets. The yield is about 150 g.

A further 100 g. of lead tetracetate may be obtained from the mother liquor (*M*) by returning it to the original flask, heating to about 75° with stirring, and passing a stream of dry chlorine into it. When the reaction is complete, a few grams of decolourising carbon are added, the mixture is maintained at 75° for a few minutes, and the hot suspension is filtered with suction through a preheated Buchner funnel. The residue, consisting largely of lead chloride, is washed with hot glacial acetic acid. The filtrate, on cooling, deposits lead tetracetate in colourless needles; it is collected and dried as described above. Although contaminated with a little ($<$ 5 per cent.) lead chloride, the resulting lead tetracetate is satisfactory for most purposes; if required perfectly pure, it should be recrystallised.

16. **Selenium dioxide.** The compound is conveniently prepared by the oxidation of selenium with nitric acid, followed by dehydration of the selenious acid thus formed by cautious heating:

$$Se + 4HNO_3 = H_2SeO_3 + 4NO_2 + H_2O;$$
$$H_2SeO_3 = SeO_2 + H_2O.$$

The preparation must be conducted in a fume cupboard provided with a good draught, since selenium compounds are poisonous. One hundred grams (70·5 ml.) of concentrated nitric acid are heated in a 1-litre Pyrex beaker on a hot plate, and 50 g. of powdered selenium are cautiously added in portions of about 5 g. The frothing should be allowed to subside after each addition before more selenium is introduced into the acid. The dissolution of the selenium can be accelerated by mechanical stirring with a glass stirrer; this will break the foam produced. When all the selenium has dissolved (if this is not the case, a little more nitric acid should be added), the solution is transferred to a large evaporating dish or casserole and heated on a hot plate at a temperature not exceeding 200° until the selenious acid is completely dehydrated and the residue appears dry. The resulting crude selenium dioxide must be purified.* Either of the following procedures may be used.

(i) The crude selenium dioxide is treated with sufficient water to dissolve it, and, after filtering from any insoluble matter, 10 ml. of concentrated hydrochloric acid are added. A slow stream of sulphur dioxide is passed into the solution until heat is no longer evolved (2–5 hours); the reaction is complete when the red precipitate settles to the bottom in a coherent mass. Upon standing for a few hours or, better, on boiling for a short time, the red selenium passes into a pasty grey form, which eventually becomes brittle. The precipitated selenium is filtered off, ground in a mortar, washed free from acid, dried, and finally heated over a Bunsen burner. The cold mass is then dissolved in nitric acid and evaporated as before. To make certain that all the nitric acid has been completely removed, the residue is dissolved in 70–80 ml. of water and evaporated again. White selenium dioxide is obtained in about 90 per cent. yield.

---

* In view of the small difference in cost between selenium and selenium dioxide, the preparation of any quantity of the latter from selenium is hardly worth while. It is better to purify commercial selenium dioxide.

(ii) The crude selenium dioxide is placed in a large porcelain or silica crucible, which is supported in a hole made in a stout asbestos board. Two nested funnels are inverted over the crucible, the larger funnel having a plug of glass wool in the neck. The crucible is heated with a small flame until sublimation is complete (about 25 minutes). When the crucible has cooled, the resublimed selenium dioxide (in long needle-like crystals) is removed and stored in a tightly stoppered bottle. The yield is about 63 g.

Note.

Extreme care should be taken when working with selenium dioxide because of its poisonous properties.

17. **Silver nitrite.** Warm concentrated solutions of silver nitrate (containing 48 g. of $AgNO_3$) and potassium nitrite (containing 30 g. of KNO_2) are mixed, and the mixture is allowed to cool. The silver nitrite which separates is filtered off and washed with water. It may be recrystallised from water at 70°, and is dried either in a vacuum desiccator or in an air oven at about 40° ; the yield is about 90 per cent. Silver nitrite should be stored in an tightly-stoppered amber bottle.

18. **Zinc cyanide.** Solutions of the reactants are prepared by dissolving 100 g. of technical sodium cyanide (97–98 per cent. NaCN) in 125 ml. of water and 150 g. of anhydrous zinc chloride in the minimum volume of 50 per cent. alcohol (1). The sodium cyanide solution is added rapidly, with agitation, to the zinc chloride solution. The precipitated zinc cyanide is filtered off at the pump, drained well, washed with alcohol and then with ether. It is dried in a desiccator or in an air bath at 50°, and preserved in a tightly stoppered bottle. The yield is almost quantitative and the zinc cyanide has a purity of 95–98 per cent. (2). It has been stated that highly purified zinc cyanide does not react in the Adams' modification of the Gattermann reaction (compare Section IV,121). The product, prepared by the above method is, however, highly satisfactory. Commercial zinc cyanide may also be used.

Notes.

(1) The only important precaution in this preparation is to ensure an excess of zinc chloride over sodium cyanide. If the latter is in excess, the zinc cyanide generally precipitates as a sticky mass, which is difficult to filter and unsatisfactory for the preparation of hydroxy-aldehydes.

(2) The cyanide content may be determined by titration with standard silver nitrate solution.*

II,51. CALCULATION OF YIELDS

The theoretical yield in an organic reaction is the amount which would be obtained under ideal conditions if the reaction had proceeded to completion, *i.e.*, if the starting materials were entirely converted into the desired product and there was no loss in isolation and purification. The yield (sometimes called the actual yield) is the amount of pure product which is actually isolated in the experiment. The percentage yield is

---

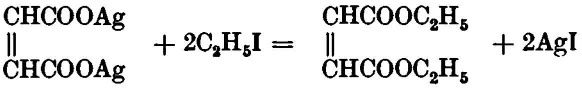
* For a convenient method, see Vogel, *Text Book of Quantitative Inorganic Analysis: Theory and Practice*, Second Edition, 1951, p. 263 (Longmans, Green and Co. Ltd.).

computed from the ratio between the weight of the pure product obtained and the weight calculated, *i.e.*,

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

In the calculation of yields, the term mol is usually employed. A mol (or mole or gram molecule) is equal to the molecular weight in grams. Hence the number of mols is equal to the weight of the substance in grams divided by the molecular weight.

Let us suppose it is desired to calculate the theoretical yield of ethyl maleate when 33 g. of silver maleate, suspended in dry ether, are treated with the calculated quantity of ethyl iodide (31·2 g.).



$$\begin{array}{cccc} \text{CHCOOAg} & & \text{CHCOOC}_2\text{H}_5 & \\ \| & +\,2\text{C}_2\text{H}_5\text{I} = & \| & +\,2\text{AgI} \\ \text{CHCOOAg} & & \text{CHCOOC}_2\text{H}_5 & \\ 1 \text{ mol} & 2 \text{ mols} & 1 \text{ mol} & 2 \text{ mols} \\ 330 \text{ g.} & 312 \text{ g.} & 172 \text{ g.} & 470 \text{ g.} \end{array}$$

From the equation representing the chemical reaction involved, it is evident that 330 g. of silver maleate will theoretically react with 312 g. of ethyl iodide in ethereal solution to produce 172 g. of ethyl maleate. It follows, therefore, that 33 g. (0·1 mol) of silver maleate will react with 31·2 g. (0·2 mol) of ethyl iodide to give a theoretical yield of 17·2 g. (0·1 mol) of ethyl maleate. In practice, the actual yield found for these quantities is of the order of 16·0 g.; the percentage yield is therefore (16·0/17·2) × 100 = 93 per cent.

After a little experience in the organic chemistry laboratory, the student will soon find that the yields frequently do not approach the theoretical values. This may be due to one or more of the following causes :—

(i) The reaction may not proceed to completion because the reverse reaction may occur under the given conditions and a state of equilibrium is established.

(ii) A portion of some of the reactants may be consumed in some alternative reaction ("side reaction"), which leads to products other than those desired ; or, one or some of the components may be lost, *e.g.*, by volatilisation (because of its low boiling point or it may be carried away by gases evolved in the reaction) in spite of most careful manipulation.

(iii) Some of the desired product may be lost by further chemical change before it can be isolated.

(iv) Mechanical losses incident upon separating and purifying the product.

(v) The purity of some of the reagents may be uncertain, *e.g.*, they may contain varying amounts of water in their commercial forms.

In order to obtain an improved yield of the desired product, an excess over the proportion required by the chemical equation of one (or more) of the reactants is often used. In a given preparation, the selection of the reagent to be employed in excess will depend upon a number of factors; these include its relative cost and ease of removal after the reaction, and its influence upon reducing the extent of "side reactions." Some examples follow, and these will incidentally illustrate the method of calculation of the percentage yield in such cases.

Two reactants. In the preparation of *n*-hexane, 61·5 g. of *n*-propyl bromide were treated with 23 g. of sodium and 18·0 g. of *n*-hexane were ultimately isolated.

$2C_3H_7{}^{\alpha}Br$	+	$2Na$	$\longrightarrow$	C_6H_{14}	+	$2NaBr$
2 gram mols		2 gram atoms		1 gram mol		
246 g.		46 g.	yield	86 g.		(*Theory*)
61·5 g.		23 g.	yielded	18 g.		(*Practice*)

It is evident from the equation that the sodium is used in excess. Actually 61·5 g. of *n*-propyl bromide is 0·5 gram mol; this will react with 0·5 gram atom or 11·5 g. of sodium, so that 100 per cent. excess was actually employed. The theoretical yield of *n*-hexane will be 0·25 gram mol or 21·5 g., since 2 mols of *n*-propyl bromide give 1 mol of *n*-hexane. The actual yield was 18 g., hence the percentage yield is (18/21·5) × 100 = 84 per cent.

n-Butyl acetate was prepared by refluxing a mixture of 37 g. of *n*-butyl alcohol, 90 g. of glacial acetic acid and 2 g. of concentrated sulphuric acid, pouring into excess of water, washing the upper layer with saturated sodium bicarbonate solution, drying and distilling; the yield of ester was 54 g. Here the sulphuric acid acts as a catalyst and therefore does not appear in the equation.

$C_4H_9{}^{\alpha}OH$	+	CH_3COOH	$\longrightarrow$	$CH_3COOC_4H_9{}^{\alpha}$	+	H_2O
1 mol		1 mol		1 mol		1 mol
74 g.		60 g.		116 g.		18 g. (*Theory*)
37 g.		90 g.		54 g.		(*Practice*)

The reactants are in the proportion of 37/74 = 0·5 mol to 90/60 = 1·5 mol, and it is therefore clear that the acetic acid is present in 200 per cent. excess. The theoretical yield must therefore be computed on the basis of the weight of *n*-butyl alcohol employed, and will be 0·5 mol or 58 g. The percentage yield is accordingly (54/58) × 100 = 93 per cent.

Three reactants. Ethyl iodide may be prepared by the interaction between iodine, ethyl alcohol and red phosphorus. The quantities employed and the yield obtained in a particular experiment are given below the equation.

P	+	$5C_2H_5OH$	+	$5I$	$\longrightarrow$	$5C_2H_5I$	+	H_3PO_4	+	H_2O
1 gram atom		5 gram mols		5 gram atoms		5 gram mols				
31 g.		230 g.		635 g.		780 g.		(*Theory*)		
4·14 g.		27·5 g.		63·5 g.		73 g.		(*Practice*)		
0·133 g. atoms		0·598 g. mols		0·500 g. atoms				(*Practice*)		

To decide which component should be employed for the calculation of the yield of ethyl iodide, the weights of the reactants are first divided by the appropriate atomic or molecular weight in order to obtain the number of gram atoms or gram mols actually used. The equation shows that the alcohol and iodine react in the ratio of 5 : 5 or 1 : 1. Inspection of the results clearly shows that the alcohol is present in about 20 per cent. excess, and on this basis 33 per cent. excess of phosphorus is employed. The yield is accordingly calculated from the weight of iodine (which, incidentally, is the most expensive component). The theoretical yield from 0·500 gram atom of iodine is 0·500 gram mol of ethyl iodide (since 5 gram atoms of iodine give 5 gram mols of ethyl iodide) or 78 g. The percentage yield is (73/78) × 100 = 94 per cent.

II,52. GENERAL INSTRUCTIONS FOR WORK IN THE LABORATORY

Before commencing any preparation in the laboratory, the student must carefully study the complete details of the experiment as well as the underlying theory. Not only should he have a clear idea of what is to be done and how he proposes to do it, but at all times he should be ready to give an intelligent reply to questions as to what he is doing and why he is doing it. The exercise may then be said to be truly scientific and not of the cookery book - recipe type. The student will soon realise that quite a number of experiments require somewhat prolonged periods of heating, refluxing or standing during which the whole of his attention is not required. A keen worker will make use of this time, *e.g.*, in writing up reports, planning other experiments, and cleaning and drying apparatus.

The results of all experiments must be recorded in a stiff-covered note-book (a loose-leaf note-book is not admissible) at the time the observations are made. If the experiment calls for records of weights, volumes, or other numerical results, these must be entered directly into the note-book and not on scraps of paper ; the latter are liable to be lost and their use tends to develop untidy and slack habits on the part of the student. When the experiment is complete, the student should calculate the yield and then submit the laboratory note-book and the product, suitably labelled (including the melting or boiling point range and the weight), to the demonstrator or instructor. It is a good plan to submit at the same time a short summary of the results (name of preparation, yield, m.p. or b.p. range, etc.) on a sheet of paper to the demonstrator ; the sheet will be retained for record purposes. If the work is approved, the student is permitted to proceed with the next experiment in the course.

Students are generally permitted to retain small specimens of their preparations : the main bulk, unless it is required for a succeeding preparation, must be returned to the chemical store. Solids may be kept in small specimen tubes and appropriately labelled (name of compound, m.p., details concerning method of purification, and date) ; if the compound exhibits signs of being deliquescent or hygroscopic, or otherwise affected by contact with air, the cork should be " waxed over " by painting it completely with molten paraffin wax. Liquids may be sealed off in specially prepared tubes. A short length of moderately thick-walled glass tubing is cleaned by immersion in a narrow cylinder containing " chromic acid cleaning mixture " (compare Section **II,2**), thoroughly washed with distilled water, followed by a little acetone, and is then dried by passing a current of warm air through it. One end is then sealed off in the blowpipe flame as in Fig. *II*, *52*, 1, *a* ; students may find it easier to blow a small bulb at the end *A*, thus ensuring uniform thickness of the glass wall. A constriction *B*, about 15–20 mm. long, is then made by carefully rotating the tube in a small blowpipe flame; it is important that the wall of the tubing remains uniformly thick at this point. Some liquid is introduced into the portion *BC* (by means of a clean drawn-out tube or a dropper, if necessary), the end *C* attached to a water pump through a calcium chloride or cotton wool guard tube, and the inclined tube is partially exhausted. Upon removing the pump connexion at *C*, the liquid will flow into the lower part of the tube. This process is repeated until a sufficient quantity of the liquid has entered *AB*. The tube is then quickly sealed off at *B* with a minute flame. Large quantities of low boiling point liquids or liquids which are affected by the air may be stored in special glass ampoules (Fig. *II*, *52*, 1, *b*), which can be purchased; such ampoules may be conveniently filled by introducing a drawn-out test-tube into the neck. When filled with liquid, they are sealed off in the manner described above.

A good indication of the student's technique will be apparent from the appearance of the working bench. The top of the bench should always be kept clean and dry; this can easily be done if a wet and a dry rag are kept at hand. Apparatus not immediately required should be kept as far as possible in a cupboard beneath the bench; if it must be placed on the bench, it should be arranged in a neat and orderly manner. All apparatus should be washed immediately after use and placed in a position to drain: at the first opportunity, the apparatus should be dried. It must be emphasised that as a general rule a deposit of dirt or tar is more easily removed when it is freshly formed; a suitable cleaning agent can usually be found while one still remembers the nature of the material or the circumstances attending its formation. It is hardly necessary to add that solid waste and filter papers must not be thrown into the sink, and that all operations requiring the handling of unpleasant and noxious materials should be carried out in the fume cupboard (" hood ").

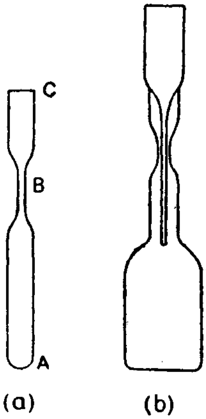


Fig. *II*, *52*, 1.

II,53. SAFETY PRECAUTIONS

The operations of practical organic chemistry are attended by certain dangers, the chief of which is that from fire since many of the liquid chemicals and the solvents are highly inflammable substances. Highly volatile liquids, such as diethyl ether, carbon disulphide, acetone and benzene, should never be handled in the vicinity of a free flame (compare full discussion in Section **II,14**); the vapours can " flow " along the top of a bench (particularly if assisted by a draught of air), become ignited by a flame at some distance and strike back to ignite the parent liquid. A common mistake by beginners is to heat an inflammable liquid in an open vessel over a free flame. The correct, and the only permissible, procedure is to heat the liquid in a vessel provided with a reflux condenser on a water or steam bath or upon an approved electric hot plate or by immersion in a bath of hot water with the burner extinguished. Volatile solvents must be removed by distillation and not by evaporation. Recovered solvents should be poured into the special bottles provided for them in the laboratory; they should not be poured down the sink nor into the waste boxes.

If a fire should occur, all flames in the vicinity should be extinguished and all inflammable materials removed. A small fire may be smothered with a wet towel or by throwing sand upon it. For a large fire, the laboratory fire extinguisher (CO_2, etc.) should be used. The well-known " Pyrene " fire extinguisher, containing carbon tetrachloride, should not be employed in the confined space of the laboratory since the highly poisonous phosgene may be formed; furthermore, an explosion may occur if it comes into contact with sodium. If the clothing of a fellow student should catch fire, he (she) should be wrapped in the special fireproof blanket or, if this is not available, in a heavy coat; he (she) should not be allowed to run about and fan the flames.

Other sources of hazard arise from the handling of such chemicals as concentrated acids, alkalis, metallic sodium and bromine, and in working with such extremely poisonous substances as sodium and potassium cyanides. The special precautions to be observed will be indicated, where necessary, in the experiments in which the substances are employed, and will also be supplied by the demonstrator. The exercise of obvious precautions and cautious handling will in most cases reduce the danger to almost negligible proportions. Thus, if concentrated sulphuric acid should be accidentally spilled, it should be immediately washed with a liberal quantity of water or of a solution of a *mild* alkali.

Finally, the student should familiarise himself with the contents of the Section in the Appendix upon *Laboratory Accidents*, with the position of the fire extinguisher. buckets of sand, first aid cabinet, and the fireproof blanket.

APPARATUS WITH INTERCHANGEABLE GROUND GLASS JOINTS

II,54. INTERCHANGEABLE GROUND GLASS JOINTS

The commercial development of glass manipulation, coupled with the use of glasses of low expansion coefficient, has made available truly interchangeable ground glass joints at moderate cost. These, fitted to apparatus of standard and special types marketed by various firms,* have made possible a new outlook on the assembly of apparatus required for practical organic chemistry and, indeed, of many other branches of practical chemistry. It is believed that if the merits of ground glass joint apparatus, as well as the actual apparatus available, were more widely known, glassware with interchangeable ground joints would find

---

* For example from: Quickfit and Quartz Ltd.; Loughborough Glass Co. Ltd.; A. Gallenkamp and Co. Ltd.; Jencons (Scientific) Ltd.; James J. Jobling and Co. Ltd.; Scientific Glass Apparatus Co. Inc.; Corning Glass Works. For precise details concerning joint size and specialised apparatus, the reader should consult the latest catalogues of the various manufacturers: the most comprehensive catalogues are those of Quickfit and Quartz and of Scientific Glass Apparatus Co.

a place in every laboratory, even for the most simple operations, such as distillation and refluxing. The advantages include :—

1. No corks or rubber stoppers are, in general, required. Contamination or discolouration due to these is therefore avoided. Occasionally, a small rubber stopper may be employed, *e.g.*, for the insertion of a thermometer, but, should the very small surface of rubber thus exposed to the action of the organic vapours be undesirable, a thermometer with a ground glass cone can be used.
2. The selection, boring, and fitting of corks is largely eliminated, thus resulting in a considerable saving of time.
3. Corrosive liquids and solids (acids, acid chlorides, *etc.*) are easily manipulated, and no impurities are introduced into the product from the apparatus.
4. Apparatus may be rapidly assembled. As all joints of the same size are interchangeable, a broken part can be rapidly replaced with every confidence that it will fit well.
5. By employing a number of comparatively simple units, most of the common operations of organic chemistry may be carried out.
6. Wider passages are provided for vapours and the comparatively narrow tubes, which are usually fitted through holes bored in cork or rubber stoppers, are absent; this considerably diminishes danger in violent reactions and also tends to give better results in distillation under reduced pressure as well as diminishing the hazard of " choking."

The interchangeability of joints is ensured by the use of a standard taper of 1 in 10 on the diameter (*i.e.*, a cone of semi-angle 2° 51′ 45″) and limited tolerances on the cone semi-angles and the dimensions of the joints. The specifications for joints in Great Britain and the U.S.A. differ. It will accordingly be necessary to treat each separately.

The interchangeable conical ground joints in Great Britain conform to the specification of the British Standards Institution, B.S.S. No. 572 of 1950.* It should be noted that the term " cone " is used for the part which is inserted and the term " socket " for the part into which the " cone " is inserted. The Series *A* (full length) has been discarded in the 1950 specification since it is considered that Series *B* is generally more useful in the construction of common laboratory apparatus. Nevertheless, details of the Series *A* (conforming to the now obsolete B.S.S. No. 572 of 1934) are included in Table **II**, 54.1, largely for comparison with the U.S. specification. The joints of all the Series have the same diameter at the larger end, but have different lengths of engagement. There are some small variations in length from the 1934 specification but the diameter at the larger end is unchanged for all joints; hence cones or sockets complying with the B.S.S. 1950 specifications may be used interchangeably with those of the B.S.S. 1934 specification having the same letter and number.

An alternative method for naming the size of the joint, which is sometimes used by manufacturers, consists in assigning a number to the joint diameter at the wide end, thus :—

Joint size	7	10	12	14	16	19	24	29	34	40	45	50	55
Joint number	00	0	12	1	16	2	3	4	5	6	7	8	9

---

* Obtainable from the British Standards Institution, British Standards House, 2 Park St., London, W. 1.

Table II, 54.1. Dimensions of British Standard Interchangeable Ground Glass Joints

Size Number of Joint	External Diameter of Smaller End of Cone (mm.)	Internal Diameter of Socket (mm.)	Length of Ground Zone (mm.)	Size Number of Joint	External Diameter of Smaller End of Cone (mm.)	Internal Diameter of Larger End of Socket (mm.)	Length of Ground Zone (mm.)
Series A				*Series B*			
A.5	3·0	5·0	20	B.5	3·5	5·0	15
A.7	5·0	7·5	25	B.7	5·7	7·5	18
A.10	7·0	10·0	30	B.10	7·8	10·0	22
A.12	9·25	12·5	32·5	B.12	10·1	12·5	24
A.14	11·0	14·5	35	B.14	12·0	14·5	25
A.16	12·5	16·0	35	B.16	13·4	16·0	26
A.19	15·0	18·8	38	B.19	16·0	18·8	28
A.24	20·0	24·0	40	B.24	21·0	24·0	30
A.29	25·0	29·2	42	B.29	26·0	29·2	32
A.34	30·0	34·5	45	B.34	31·1	34·5	34
A.40	35·0	40·0	50	B.40	36·4	40·0	36
A.45	40·0	45·0	50	B.45	41·2	45·0	38
A.50	45·0	50·0	50	B.50	46·0	50·0	40
A.55	50·0	55·0	50	B.55	50·8	55·0	42
A.60	55·0	60·0	50	B.60	55·6	60·0	44
Series C				*Series D*			
C.5	4·2	5·0	8	D.19	18·0	18·8	8
C.7	6·4	7·5	11	D.24	23·1	24·0	9
C.10	8·7	10·0	13	D.29	28·2	29·2	10
C.12	10·9	12·5	16	D.34	33·4	34·5	11
C.14	12·8	14·5	17	D.40	38·9	40·0	11
C.16	14·3	16·0	17	D.45	43·8	45·0	12
C.19	16·9	18·8	19	D.50	48·8	50·0	12
C.21	19·5	21·5	20				
C.24	22·0	24·0	20				
C.26	24·4	26·5	21				
C.29	27·0	29·2	22				
C.32	29·7	32·0	23				
C.34	32·1	34·5	24				

Table II, 54.2. Dimensions of U.S.A. Standard Interchangeable Ground Glass Joints

Standard Joint Size Number	Approximate Diameter at Small End (mm.)	Computed Diameter at Large End of Ground Zone (mm.)	Approximate Length of Ground Zone (mm.)
Full length Joints			
5/20	3	5·0	20
7/25	5	7·5	25
10/30	7	10·0	30
12/30	9	12·0	30
14/35	11	14·5	35
19/38	15	18·8	38
24/40	20	24·0	40
29/42	25	29·2	42
34/45	30	34·5	45
40/50	35	40·0	50
45/50	40	45·0	50
50/50	45	50·0	50
55/50	50	55·0	50
60/50	55	60·0	50
71/60	65	70·0	60
Medium length Joints			
5/12	3·8	5·0	12
7/15	6·0	7·5	15
10/18	8·2	10·0	18
12/18	10·2	12·0	18
14/20	12·5	14·5	20
19/22	16·6	18·8	22
24/25	21·5	24·0	25
29/26	26·6	29·2	26
34/28	31·7	34·5	28
40/35	36·5	40·0	35
Short length Joints			
10/10	9·0	10·0	10
12/10	11·0	12·0	10
14/10	13·5	14·5	10
19/10	17·8	18·8	10
24/12	22·8	24·0	12
29/12	28·0	29·2	12
34/12	33·3	34·5	12
40/12	38·8	40·0	12
45/12	43·8	45·0	12
50/12	48·8	50·0	12
55/12	53·8	55·0	12
60/12	58·8	60·0	12
71/15	69·5	71·0	15

The series letter should also be specified : thus *B*2 refers to *B*19. This system must now be regarded as obsolete.

In the U.S.A., interchangeable ground glass joints conform to the specifications of the Bureau of Standards (" Interchangeable Ground Glass Joints, Stopcocks and Stoppers," Commercial Standard CS21-39).* The taper is 1 in 10, *i.e.*, 1 ± 0·06 mm. per cm. length on the diameter and is represented by the symbol $. There are three sizes of joints, *viz.*, full length, medium length, and short length. The size of joint is designated by two figures, the first indicating the *approximate* diameter (in mm.) of the larger end (*i.e.*, to the nearest whole number) and the second giving the length of the ground surface. Thus $ 19/38 refers to a ground surface 18·8 mm. in diameter and 38 mm. in length. The various sizes of joints are collected in Table **II**, 54.2.

II,55. TYPES OF GROUND GLASS JOINTS

All ground glass joints should be constructed of a high resistance glass, such as Pyrex. The most common form is shown in Fig. *II*, *55*, 1, and this is the type largely encountered in practice. Fig. *II*, *55*, 2 is similar but has reinforcing glass bands about the female joint ; it is claimed that these add greatly to the mechanical strength of the walls.

Fig. *II*, *55*, 1.

Fig. *II*, *55*, 2.

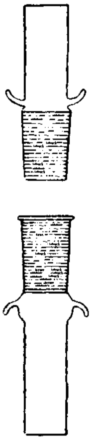


Fig. *II*, *55*, 3.

Fig. *II*, *55*, 4.

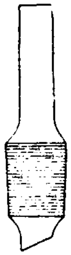


Fig. *II*, *55*, 5.

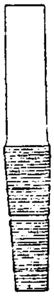


Fig. *II*, *55*, 6.

Fig. *II*, *55*, 3 depicts a ground joint with glass hooks, to which light springs may be attached. Figs. *II*, *55*, 4 and *II*, *55*, 5 are drip cones for condensers and the like ; the latter is generally employed for joints larger than 29 mm. in diameter, the orifice being reduced to about 18 mm. Fig. *II*, *55*, 6 is a double-cone joint in which two cones, *e.g.*, *B*19 and *B*24, are made like a single joint ; this is valuable as it saves the use of an adapter.

---

* Obtainable from Superintendent of Documents, Washington, D.C.

The spherical joint or semi-ball joint or ball and socket joint is illustrated in Fig. *II*, *55*, 7, which includes one type of special clamp for holding the two halves of the joint together. This connexion cannot freeze or stick (as conical ground joints sometimes do) and it introduces a degree of flexibility into the apparatus in which it is used. The area of contact between the ground surfaces is relatively small so that the joints are not intended to provide for considerable angular deflection. The main application is in conjunction with conical joints rather than as a substitute for them. The conical-spherical adapters shown in Fig. *II*, *55*, 8 provide a means of inserting a spherical joint whilst retaining the standard conical joint principle. Some sizes of spherical joints (semi-ball connections) are collected in Tables II, 55.1 and **II**, 55.2.

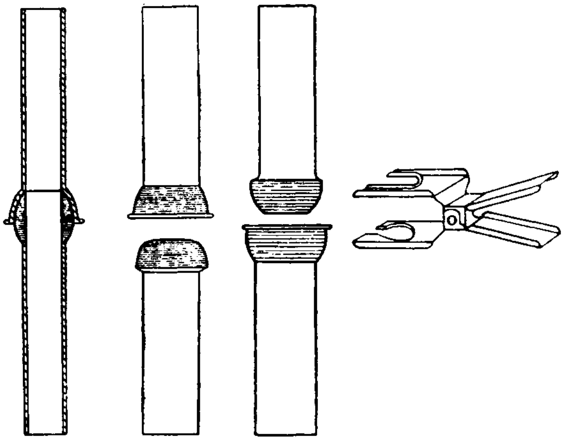


Fig. *II*, *55*, 7.

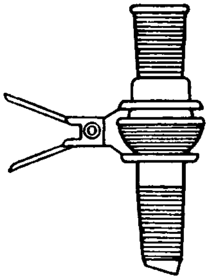


Fig. *II*, *55*, 8.

TABLE II, 55.1. DIMENSIONS OF SPHERICAL JOINTS *

SIZE DESIGNATION	NOMINAL DIAMETER OF GROUND HEMISPHERE	NOMINAL DIAMETER AT UPPER END OF GROUND ZONE	NOMINAL BORE
2/12	1/2″	12 mm.	2 mm.
5/12	1/2″	12 mm.	5 mm.
9/18	3/4″	18 mm.	9 mm.
15/28	1 1/8″	28 mm.	15 mm.
20/35	1 3/8″	35 mm.	20 mm.
25/40	1 1/2″	40 mm.	25 mm.
35/40	2″	50 mm.	35 mm.

* These dimensions were supplied by Quickfit and Quartz Ltd.

TABLE II, 55.2. DIMENSIONS OF SEMI-BALL CONNECTIONS *

SEMI-BALL SIZE	BALL DIAMETER mm.	TUBE, BORE mm.	SEMI-BALL SIZE	BALL DIAMETER mm.	TUBE, BORE mm.
12/2	12	2	28/12	28	12
12/3	12	3	28/15	28	15
12/5	12	5	35/20	35	20
18/7	18	7	35/25	35	25
18/9	18	9	40/25	40	25
28/11	28	11	50/30	50	30

For most operations of practical organic chemistry, the joint illustrated in Fig. *II*, *55*, 1 is quite satisfactory, but the simple modifications already described are used where necessary. Experiments in Great Britain have shown that the *B* Series of connections, which have the same top diameter as the obsolete *A* Series (B.S.S. No. 572 of 1934 : see Table **II**, 54.1) or the current U.S. " full-length joints " but a shorter length of engagement, are the most convenient for general use. The *B* Series will accordingly be used in the description of most of the apparatus in the succeeding Sections. There is no practical difficulty in interchanging *A* and *B* joints ; the lengths of engagement may differ, but this will affect only the appearance of the apparatus and not its utility.

II,56. APPARATUS WITH INTERCHANGEABLE GROUND GLASS JOINTS SUITABLE FOR GENERAL USE IN PREPARATIVE ORGANIC CHEMISTRY

Flasks. Round-bottomed, flat-bottomed, conical (Erlenmeyer) and bolt-head flasks up to a capacity of 2–3 litres are generally fitted with a *B*24 socket ; † those from 5 to 100 ml. are available with a *B*14 or *B*19 (from 25 ml.) socket. Round- and flat-bottomed flasks exceeding 1 litre in capacity are supplied with *B*34 necks. Whilst all sizes of sockets can be obtained from the manufacturers, it is usually convenient to limit the socket sizes to a small number (say, *B*14, *B*19, *B*24 and *B*34), thus permitting interchangeability with the minimum number of adapters.

Stoppers. Those fitted with *B*14, *B*19, and *B*24 cones are useful sizes. Stoppers with flat heads are to be preferred, since they may be stood on end when not in use, thus avoiding contamination of the ground surface. An additional refinement is the provision of a finger grip as in Fig. *II*, *56*, 1.

Reduction adapters. These may be employed to connect condensers, still-heads, etc. to flasks, extraction apparatus and the like. Numerous combinations (Fig. *II*, *56*, 2) are, of course, possible, but the commonest sizes are : socket *B*14 to cone *B*19 or *B*24 ; socket *B*19 to cone *B*24, *B*29

---

* These dimensions were taken from U.S.A. sources ; cf. Scientific Glass Apparatus Catalogue, J—52 of 1952.

† Reference will be made to current practice in Great Britain : the corresponding sizes of joints and sockets available in the U.S.A. will be found in, for example, the catalogues of the Scientific Glass Apparatus Co. Inc. and of the Corning Glass Works.

or *B*34 ; socket *B*24 to cone *B*29 or *B*34 ; socket *B*29 to cone *B*34. Fig. *II*, *56*, 3 represents the Bushing type of adapter, which is much shorter than the above and permits of more compact assemblies. It must be emphasised, however, that in a well-designed assembly of apparatus, the number of adapters should be reduced a minimum and, best of all, completely eliminated.

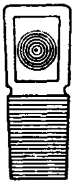


Fig. *II*, *56*, 1.

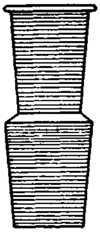


Fig. *II*, *56*, 2.

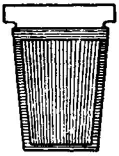


Fig. *II*, *56*, 3.

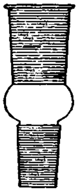


Fig. *II*, *56*, 4.

Expansion adapters (Fig. *II*, *56*, 4). Common sizes are socket *B*19, cone *B*14 ; socket *B*24, cone *B*19 ; socket *B*29, cone *B*19 or *B*24 ; socket *B*34, cone *B*19, *B*24 or *B*29.

Distillation heads (or still heads). Fig. *II*, *56*, 5 is a *bend* (" knee tube "), which is frequently employed for distillation. Convenient sizes are : bottom cone *B*19, *B*24, *B*29 or *B*34 ; side cone *B*19 or *B*24.

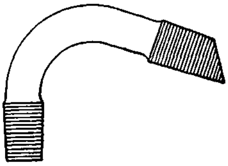


Fig. *II*, *56*, 5.

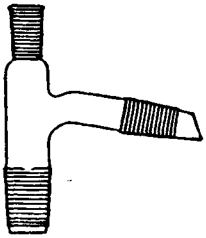


Fig. *II*, *56*, 6.

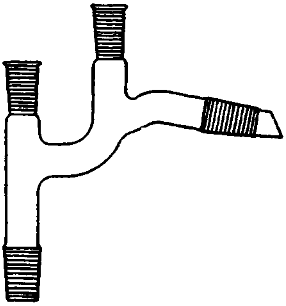


Fig. *II*, *56*, 7.

Fig. *II*, *56*, 6 is a *simple distillation head* ; when this is fitted into a flask with a ground glass socket, the assembly is virtually a distillation flask. The bottom cone is usually *B*19, *B*24 or *B*29 ; the side cone is generally *B*19 but may be *B*24 ; the thermometer socket is *B*14. For many purposes, a thermometer is fitted into a one-hole rubber stopper of correct taper and then inserted into the *B*14 socket ; the area of rubber which is exposed to the action of the organic vapour is relatively so small that the amount of contamination thus introduced is negligible. If, however, all rubber stoppers must be absent because of the highly corrosive character of the vapour, a thermometer with a *B*14 cone is employed. It is important to have the thermometer of the same glass as the distillation head, otherwise difficulties may arise owing to the different expansion coefficients of the two kinds of glass.

Fig. *II*, *56*, 7 is a *Claisen distillation head.* The lower cone is usually *B*19 or *B*24 and the side cone is generally *B*19 (sometimes *B*24) ; the sockets are *B*14. A modification is illustrated in Fig. *II*, *56*, 8 ; here the left-hand socket is replaced by a narrow opening for the insertion of a capillary for use in reduced pressure distillation, etc.

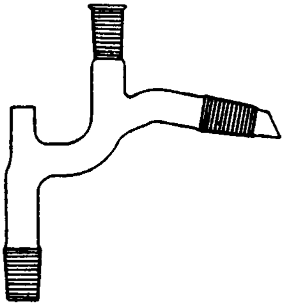


Fig. *II*, *56*, 8.

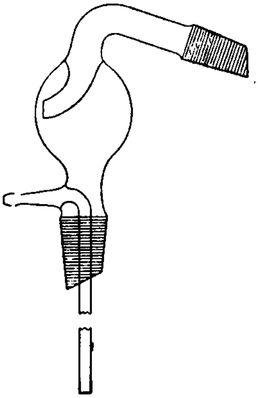
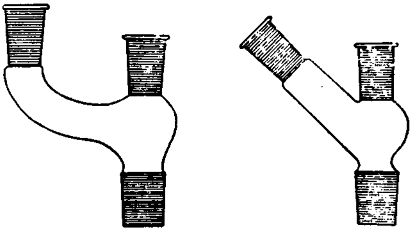


Fig. *II*, *56*, 9.

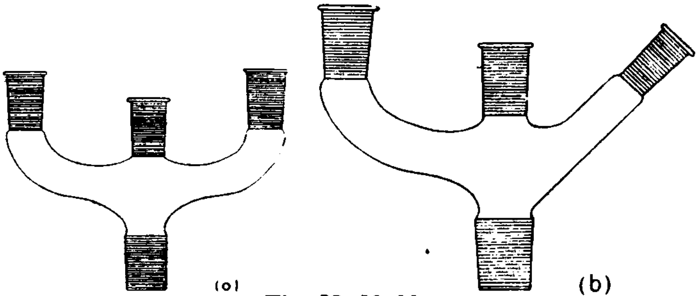
Fig. *II*, *56*, 9 depicts a *splash head* with a pear-shaped bulb and vertical delivery tube ; this is useful for steam distillation. The bottom cone is *B*24, *B*29 or *B*34 and the side cone is *B*19 or *B*24.



(a) (b)

Fig. *II*, *56*, 10.

Multiple adapters The *double neck adapter* (Fig. *II*, *56*, 10) provides as its name implies, two entries into a flask. The sizes of cones which are generally used are *B*19, *B*24, *B*29 and *B*34 ; the sockets are *B*19 or *B*24.



(a) (b)

Fig. *II*, *56*, 11.

Two forms of *triple neck adapters* are shown in Fig. *II*, *56*, 11. The sizes of cones and sockets are similar to those for the double neck adapter. These adapters convert an ordinary flask into what is virtually a three-necked flask.

The "*swan neck adapter*" of Fig. *II*, *56*, 12 is useful for "vacuum" distillations as it permits the use of a capillary tube (held in position by a short length of heavy-walled rubber tubing) not sealed to a ground joint. It may also be used for insertion of a thermometer or a gas-inlet tube in the narrow neck and a reflux condenser into the ground joint: this device virtually converts a three-necked into a four-necked flask. Common sizes are cone *B*19, *B*24, *B*29, or *B*34; socket *B*19, *B*24 or *B*29.

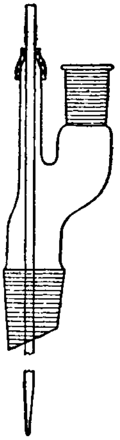
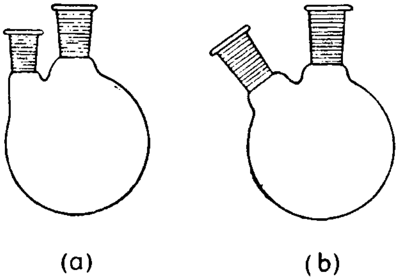


Fig. *II*, *56*, 12.

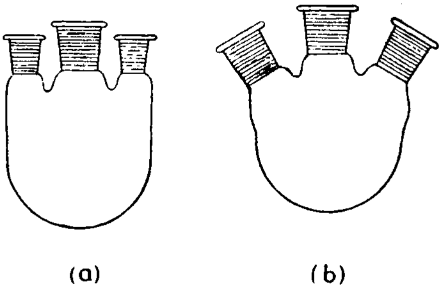
Multi-necked flasks. Various types of multi-necked flasks are illustrated in Figs. *II*, *56*, 13–15. The centre socket is usually the largest (*B*24 or *B*34) and the side sockets are generally smaller. The side tube in Fig. *II*, *56*, 15, *a* may be employed for a capillary tube in "vacuum" distillation; *b*, *c* and *d* are different types of thermometer "wells".

Condensers. Several types of condensers are widely used. Fig. *II*, *56*, 16 is an improved form of Liebig's condenser, sometimes termed a *West* condenser: it has an inner tube with very thin walls and the space between it and the heavy-walled outer tube is small, consequently there is a rapid heat transfer to the fast-flowing cooling water leading to greater efficiency. The length of the jacket is usually 15–35 cm. and it is fitted with a *B*14, *B*19 or *B*24 cone and socket.



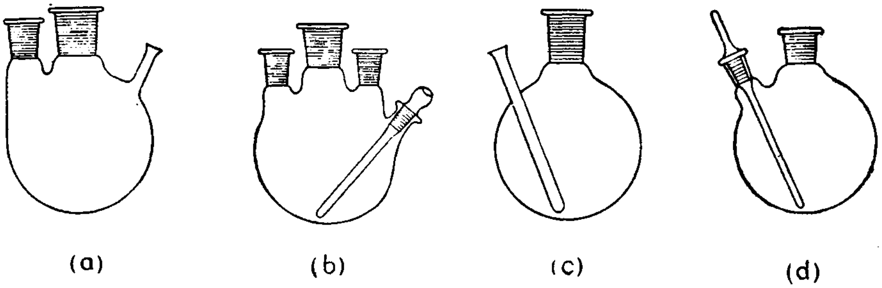
(a) (b)

Fig. *II*, *56*, 13.



(a) (b)

Fig. *II*, *56*, 14.



(a) (b) (c) (d)

Fig. *II*, *56*, 15.

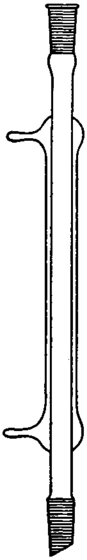


Fig. *II*, *56*, 16.

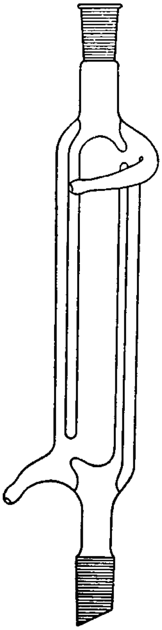


Fig. *II*, *56*, 17.

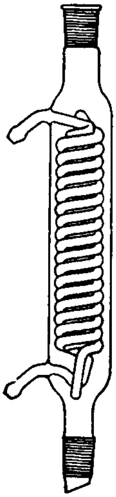


Fig. *II*, *56*, 18.

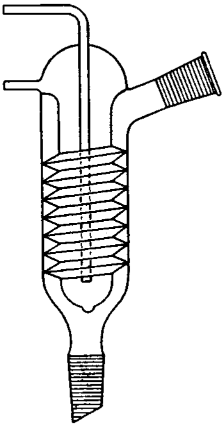


Fig. *II*, *56*, 19.

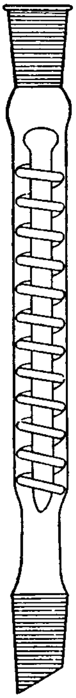


Fig. *II*, *56*, 20.

Fig. *II*, *56*, 21.

Fig. *II*, *56*, 17 (Davies types) and Fig. *II*, *56*, 18 (double coil type) are examples of efficient double surface condensers. Fig. *II*, *56*, 19 depicts a " screw " type of condenser (Friedrich pattern) ; the jacket is usually 10, 15 or 25 cm. long and the cone and sockets are *B*19 or *B*24 : this highly efficient condenser is employed for both reflux and for downward distillation.

Fractionating columns. The *Dufton all-glass column* (Fig. *II*, *56*, 20) is a satisfactory fractionating column for general use. The glass spiral must be carefully ground to fit the outer tube in order to prevent appreciable leakage of vapour past the spiral. The length of the spiral is usually 15, 20 or 30 cm., the internal diameter of the tube is 15–20 mm., and the distance between the turns of the spiral is 9–13 mm. ; the cone and socket are *B*19 or *B*24.

Fig. *II*, *56*, 22.

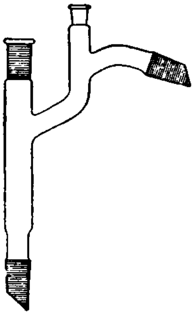


Fig. *II*, *56*, 23.

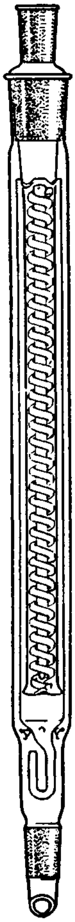


Fig. *II*, *56*, 24.

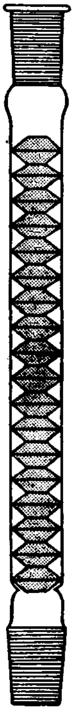


Fig. *II*, *56*, 25.

The *Vigreux column* (Fig. *II*, *56*, 21) is of simple construction but is only moderately efficient. The length is 20–60 cm., the internal diameter of the tube is about 20 mm., and the cone and socket are *B*24 (or *B*19 or *B*29).

A plain tube, similar to Fig. *II*, *56*, 21 but without the indentations, 15–25 mm. internal diameter and 25–75 cm. long, charged with a suitable packing, is essentially a *Hempel column.* The packing may be ⅛″ or ¼″ hollow glass rings, ⅛″ Raschig rings or $\frac{3}{16}$″ porcelain rings ; the packing is supported upon a cone-shaped tantalum wire spiral (wound so as to fit easily into the column), or on a small glass funnel (of diameter slightly less than that of the column) provided with three glass "feet" which rest upon a slight constriction at the base of the tube (compare Fig. *II*, *24*, 5), or on a perforated glass disc inside the tube, or (most simply) on a few large rings introduced at the lower end.

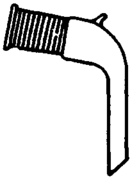


Fig. *II*, *56*, 26.

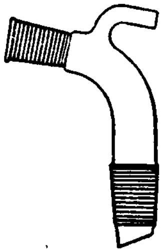


Fig. *II*, *56*, 27.

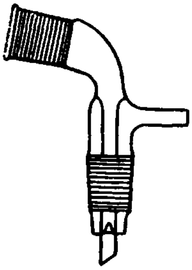


Fig. *II*, *56*, 28.

The efficiency of all the above columns (and also those described below) is increased by lagging with asbestos cloth. The best results are obtained by surrounding each column with two glass jackets and heating the inner jacket electrically to a temperature within 5–10° of the fraction being collected. The heating of the inner jacket can be effected *either* by first attaching thin asbestos strips along its length and then winding nichrome tape of suitable size and current-carrying capacity around the asbestos strips *or* by winding ½″ insulated heating tape directly round the tube (compare Fig. *II*, *17*, 2); the heat input may be controlled by a variable transformer.

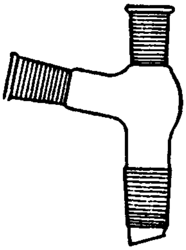


Fig. *II*, *56*, 29.

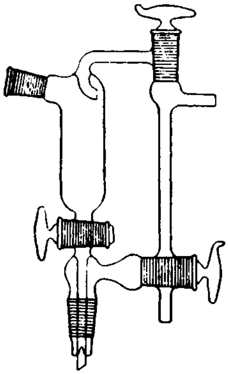


Fig. *II*, *56*, 30.

Improved results are also secured by the use of a short reflux condenser ("cold finger"), Fig. *II*, *56*, 22, inserted into the top of the column head; the simplest type is shown in Fig. *II*, *56*, 23. The condenser permits control of the reflux ratio by adjusting the rate of flow of water through it.

The *Widmer column* (Fig. *II*, *56*, 24) is a comparatively inexpensive fractionating column of high efficiency. It embodies a closely-fitting glass spiral (compare Fig. *II*, *56*, 20) but the vapour traverses the length of the column three times; a hot vapour jacket thus surrounds the spiral. The example illustrated in the Figure is of the detachable type, all glass parts being removable, thus facilitating cleaning. The cone and socket are *B*24 (or *B*19 or *B*29).

The *Stedman-type column** is shown in Fig. *II*, *56*, 25. The characteristic features are: (i) the use of a fine stainless steel wire cloth formed into conical discs, and (ii) an accurately fitting Pyrex glass jacket, produced by shrinking Pyrex glass on mandrels to the required inside dimensions. Modifications incorporating a silvered vacuum jacket and an electrically-heated jacket are marketed. This column is said to possess high efficiency but is expensive. It is generally employed in conjunction with a total-condensation variable take-off still head.

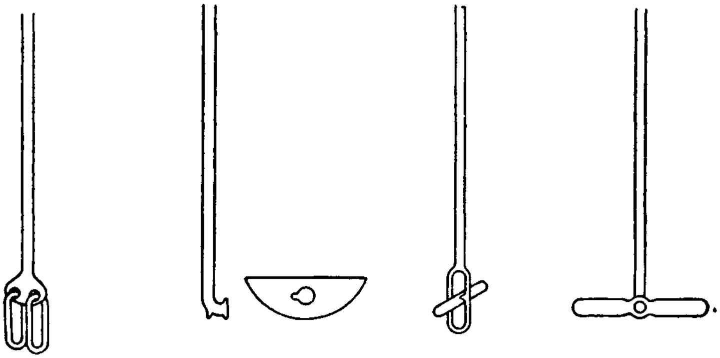

(*a*) (*b*) (*c*) (*d*)

Fig. *II*, *56*, 31.

Receiver adapters or connectors. Various forms of receiver adapters are shown in Figs. *II*, *56*, 26–29. The simplest form, Fig. *II*, *56*, 26, carries a glass hook for securing it to the condenser by means of a rubber band from the side tube to the hook; an improved form, incorporating two ground glass joints is shown in Fig. *II*, 56, 27. A useful adapter is illustrated in Fig. *II*, *56*, 28; when employed at atmospheric pressure, a drying tube may be attached to the side tube, if desired; in a distillation under reduced pressure, the side tube is connected to the pump. Fig. *II*, *56*, 29 depicts a receiver adapter with an additional socket connection.

Vacuum receivers. The conventional type of receiver, such as the Perkin triangle (Fig. *II*, *20*, 1) or the Kon receiver (Fig. *II*, *20*, 2), is available with *B*14, *B*19 or *B*24 sockets and *B*14, *B*19 or *B*24 cones. A modified Perkin triangle of increased strength and compactness is illustrated in Fig. *II*, *56*, 30.

Glass stirrers. Numerous varieties of stirrers are marketed. The four types depicted in Fig. *II*, *56*, 31 are reasonably efficient and possess the advantage of passing through narrow-necked flasks or sockets (*B*14 or

---

* Supplied by the Scientific Glass Apparatus Co.

larger). They may be fitted into a vessel by either of the devices shown in Fig. *II*, *56*, 32 and Fig. *II*, *56*, 33. The former is provided with a *B*14 or *B*19 socket and a *B*19 cone; the side tube serves for the admission of inert or other gases during the stirring operation. A subsidiary glass sleeve (smaller diagram, enlarged) must be used if a gas-tight seal is required. A short length (say, 1 cm.) of rubber tubing is slipped over the centre of the glass tube and this is fitted into the *B*14 or *B*19 socket; another short length of rubber tubing is inserted over the end of the glass bearing (as in the Figure) and the stirrer shaft is passed through the rubber tube. A little glycerine is employed as the lubricant at the rubber to glass contact surfaces. The extended stem on the cone is not a bearing, but merely serves to prevent shaft " whip " at high speeds, particularly in large flasks. Fig. *II*, *56*, 33 is a standard form of mercury-sealed stirrer and carries a *B*14, *B*19, *B*24 or *B*29 cone; a modification, with a side tube for a reflux condenser, etc., is shown in Fig. *II*, *56*, 34. A precision-ground stirrer, which eliminates the necessity of a mercury or rubber seal, is illustrated in Fig. *II*, *56*, 35; the long length of ground bearing reduces " whipping " and vibration to a minimum. The water cooling jacket, which surrounds the precision-ground tubes, helps to retain the lubricant at a constant temperature; it also acts as a " cold finger " to condense vapours back into the flask and prevent them from attacking the seal. This stirrer may be fitted with a Teflon blade (see Fig. *II*, *17*, 5).

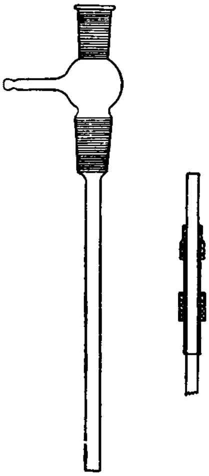


Fig. *II*, *56*, 32.

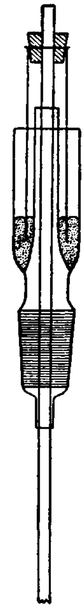


Fig. *II*, *56*, 33.

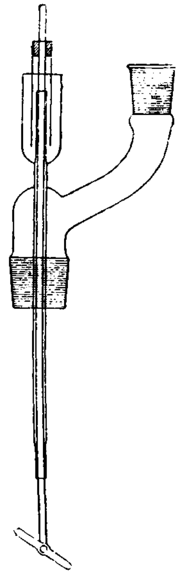


Fig. *II*, *56*, 34.

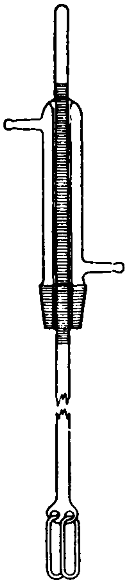


Fig. *II*, *56*, 35.

Motor stirring units are described in Section **II,7**.

Separatory funnels. For many operations the globular form (compare Fig. *II*, *1*, 5, *c*) with *B*14, *B*19 or *B*24 cone on the stem and *B*14 or *B*19 socket for the stopper, is convenient. For some purposes, *e.g.*, when used on a three-necked flask or with a multiple adapter, the cylindrical form (compare Fig. *II*, *1*, 5, *e*) is to be preferred ; this is similarly provided with a cone on the stem and a ground socket. The insertion of a dripping tip (compare Fig. *II*, *1*, 5, *f*) immediately below the stopcock is a valuable refinement. Fig. *II*, *56*, 36 represents a cylindrical funnel with pressure

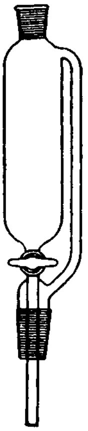


Fig. *II*, *56*, 36.

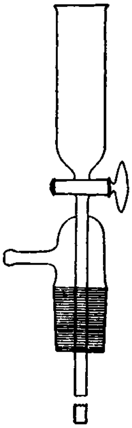


Fig. *II*, *56*, 37.

equalising tube ; this is useful for reactions which are conducted in an atmosphere of inert gas (see Fig. *II*, *7*, 13). An open dropping funnel with side tube is shown in Fig. *II*, *56*, 37.

II,57. ELECTRIC HEATING MANTLES

For successful fractional distillation, slow and even heating of the bath surrounding the flask is essential. This may be achieved by suitably designed electrically-heated air baths or by the use of oil baths provided

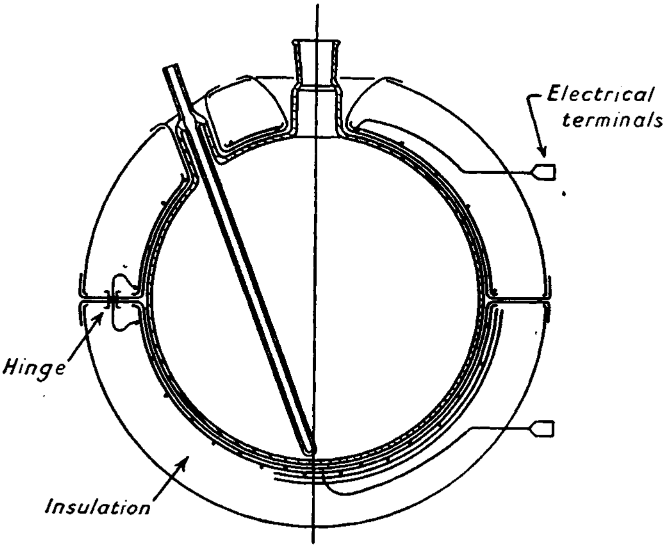


Fig. *II*, *57*, 1.

with internal electric heating ; the power input is controlled by a resistance or variable transformer.

An electric heating mantle may also be used : temperatures up to about 400° C. are readily attained, it can be employed with highly inflammable liquids and bumping is largely eliminated. The construction of a typical electric heating mantle* will be apparent from Fig. *II*, *57*, 1, in which it surrounds a single neck flask with a thermometer or sight well. The heating element (nichrome or equivalent resistance wire) is embedded in layers of glass fabric near the exposed surface and is further covered by layers of glass wool insulation. The two hemispherical halves are held together by a " Zip " fastener or by glass fibre cords. The temperature lag is small since the heating elements are very close to the flask wall. A built-in thermo-couple is available in certain types so that the internal temperature can be read with a suitable pyrometer ; a small thermostat may also be embedded in the heating elements to prevent overheating. Special supports (cradles) for the heating mantles are marketed.

In a modification, illustrated in Fig. *II*, *57*, 2, the heating mantle is contained in a hemispherical or cylindrical aluminium housing, thus providing additional rigidity. The electric heating mantle is used in conjunction with a variable transformer (*e.g.*, Variac or Powerstat). " Heating tops " or " upper covers ", with openings for one, two or three-necked flasks, for these half mantles are marketed; they are provided with an independent heating control. " Multi-size " heating mantles are available commercially ; these enable one heating mantle to be used for a variety of sizes of round-bottomed flasks.

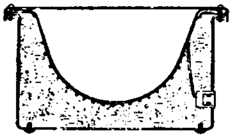


Fig. *II*, *57* 2.

Electric heating mantles are also marketed for :—

(i) Griffin-form beakers.
(ii) Conical flasks.
(iii) Glass funnels (60° type).
(iv) Buchner funnels.
(v) Fractionating columns ; these may be provided with thermocouples near each end.

II,58. APPARATUS FOR THE CONTINUOUS EXTRACTION OF SOLIDS OR LIQUIDS BY SOLVENTS

Solids by solvents. The various forms of Soxhlet apparatus illustrated in Section **II,44** can be purchased with ground glass joints. A simplified form, in which the fragile side tubes are absent, is shown in Fig. *II*, *58*, 1. The material to be extracted, if of granular form, may rest upon a sintered glass disc or upon a removable " septum " (Fig. *II*, *58*, 1, *a*) or if this is impracticable because of the disintegration of the material by the solvent or because of its physical characteristics, the substance to be extracted may be placed in a paper or alundum thimble or in a sintered glass crucible or thimble. The action is continuous; extraction is effected by the boiling or nearly boiling solvent

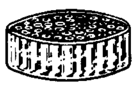


Fig. *II*, *58*, 1, *a*.

---

* Manufactured by (i) Glas-Col Apparatus Company, (ii) Electrothermal Engineering Ltd., and (iii) by Isopad Ltd.

and is thus more rapid than with the common form of Soxhlet apparatus (Fig. *II*, *44*, 4), which is intermittent in its action. Another simple form of extractor, incorporating, a sintered plate sealed into the body, is illustrated in Fig. *II*, *58*, 2.

Liquids by liquids. The apparatus represented by Fig. *II*, *58*, 3 is employed for the extraction of aqueous solutions by solvents lighter than water, such as ether or benzene. The solvent distilled from the flask (attached to the lower end) and condensed by the reflux condenser (fitted to the upper end) passes through the funnel down a narrow tube, partially open at the lower end, into the aqueous solution, then rises to the surface and returns to the flask, having during its passage extracted some portion of the dissolved material from it. To improve the efficiency of the process, devices are introduced which have as their object the more intimate contact of the solvent with the solution chiefly by reducing the size of the drops issuing from the bottom of the tube through which the extraction solvent passes into the liquid to be extracted. These include :—

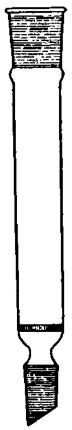


Fig. *II*, *58*, 1.

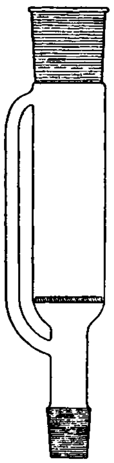


Fig. *II*, *58*, 2.

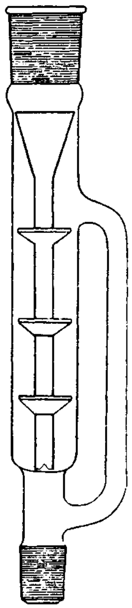


Fig. *II*, *58*, 3.

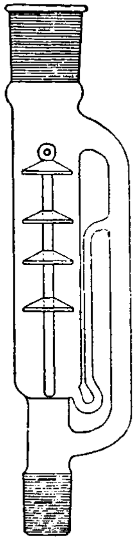


Fig. *II*, *58*, 4.

(*a*) Perforation of the tube with a number of fine holes.

(*b*) The tube is left open, but is " gashed " slightly so that it rests on the bottom of the vessel ; the solvent passes through the small apertures formed by the " gashes."

(*c*) The " solvent tube " is provided with a number of " fins " which reach nearly to the walls of the containing vessel (as in Fig. *II*, *58*, 3) ; sometimes a glass " spiral " surrounds the tube.

(*d*) A sintered glass distributor is fitted to the end of the " solvent tube."

The apparatus for the extraction of aqueous solutions by solvents heavier than water (*e.g.*, chloroform or carbon tetrachloride) is shown in Fig. *II*, *58*, 4. The solvent falling from the reflux condenser descends through the aqueous solution into a solvent layer below; a series of baffles breaks the solvent into drops. In another form of the apparatus, the solvent falling from the reflux condenser is collected in a short funnel at the lower end of which a sintered glass plate is sealed; this results in fine drops falling through the aqueous solution. A constant level of solvent is maintained by an overflow into the vapour tube.

Modifications of the liquid-liquid extraction apparatus (compare Figs. *II*, *44*, 1 and *II*, *44*, 3), which are available in capacities up to 2–5 litres, are shown in Figs. *II*, *58*, 5 and *II*, *58*, 6; the former is for extraction with solvents of the ether type (lighter than water) and the latter for solvents such as carbon tetrachloride (heavier than water).

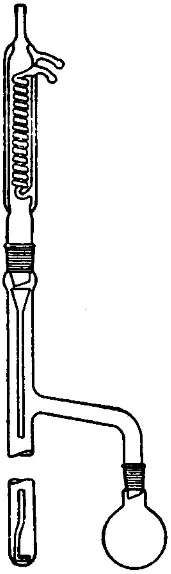


Fig. *II*, *58*, 5.

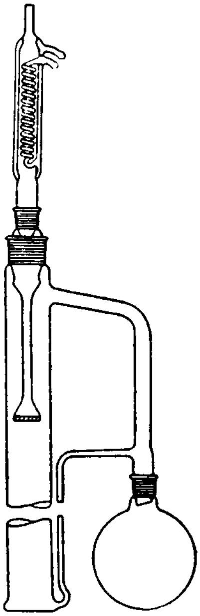


Fig. *II*, *58*, 6.

Attention is directed to the great advantage of continuous extraction over manual shaking in a separatory funnel for liquids or for solutions which tend to froth or which lead to emulsification; comparatively little difficulty is experienced in the continuous extraction process.

Extraction of steam distillates by solvents. The apparatus, depicted in Fig. *II*, *58*, 7, may be employed for the continuous extraction of substances *which are volatile in steam* from their aqueous solutions or suspensions. Solvents of the ether type (*i.e.*, lighter than water) or of the carbon tetrachloride type (*i.e.*, heavier than water) may be used. A reflux condenser is inserted in the *B*19 socket, whilst flasks of suitable capacity are fitted into the lower *B*24 cone and the upper *B*19 cone respectively. For extraction with ether, the flask attached to the upper *B*19 cone contains the ether whilst the aqueous solution is placed in the flask fitted to the lower *B*24 cone: the positions of the flasks are reversed for extractions with carbon tetrachloride. The contents of both flasks are boiled, and a rapid stream of water is passed through the reflux condenser which is inserted in the ground socket. The two liquids pass down

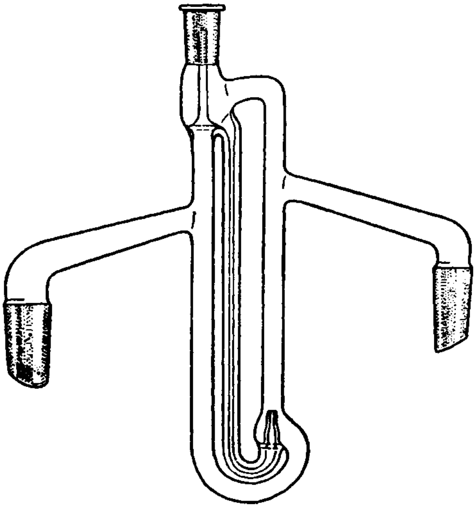


Fig. *II*, *58*, 7.

the central capillary portion in small pellets or " sausages," and finally separate and return automatically to their respective flasks. The conditions of the cycle of operations in the apparatus are such as to promote very intimate contact between the two liquids.

II,59. LUBRICATION OF GROUND GLASS JOINTS

Great care must be taken to keep all ground surfaces free from grit and dust. For work at atmospheric pressure, no lubricant should be required; it is advisable, however, in order to reduce the danger of " sticking " to apply a slight smear around the upper part of each ground joint of vaseline (if permissible), a rubber grease, Apiezon grease *L* or *M*, or Silicone stopcock grease.

When salt solutions or alkaline substances may come into contact with ground glass surfaces, light lubrication of the surfaces is essential. When greasing stopcocks, only the outer parts of the plug should be lightly smeared with lubricant; in those cases where the lubricant is not harmful, the whole of the plug may be given a very thin smear of the grease but particular care must be taken to avoid the entrance of the lubricant into the bore of the plug.

Lubrication of all ground glass surfaces is essential for distillations under reduced pressure. Suitable lubricants are Apiezon grease *L*, *M* or *N* and Silicone stopcock grease; also Alkathene (a polyethylene plastic), which is especially suitable for high temperatures.

" Sticking " of ground glass joints. Provided adequate care is exercised to use only joints which fit well and the ground surfaces are suitably lubricated, " sticking " will rarely occur. If, however, a ground joint should " seize up " or " freeze," the following suggestions may be found useful :

(i) Set the joint in a vertical position and apply a layer of glycerine to the upper surface. The glycerine will slowly penetrate into the joint, thus permitting the separation of the ground surfaces.

(ii) If procedure (i) is unsuccessful, direct a stream of hot water on the outer surface of the joint for a few seconds and gently draw the members apart ; gentle tapping on the edge of a wooden bench is sometimes helpful.

(iii) Introduce the joint into a small luminous Bunsen flame for a *few* seconds, and then gently draw the ground surfaces apart. If the glass is of Pyrex (or of any other heat-resisting variety), there is very little danger of a crack resulting from this process. The object of the heating is to cause the glass of the socket to expand before any appreciable change has occurred in the inner cone.

II,60. TYPICAL ASSEMBLIES

It is hoped that the account of the interchangeable ground glass joint apparatus already given will serve as an introduction to the subject. For the numerous applications of such apparatus, the reader is referred to the catalogues of the manufacturers listed in Section **II,54**. Most of the simple operations in practical organic chemistry may be carried out with a set of apparatus which can be purchased for a comparatively small sum (£5–£10) ; this should dispel the erroneous impression, which appears to be prevalent in several quarters, that the cost of apparatus with interchangeable ground glass joints is prohibitive for general work in preparative organic chemistry.

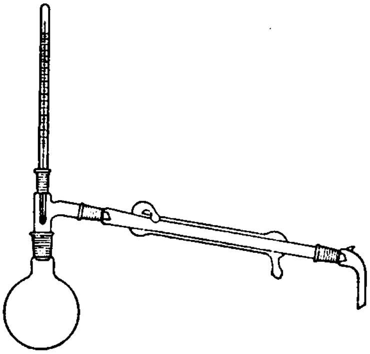


Fig. *II, 60*, 1.

Some typical assemblies are collected in the following diagrams. In all cases where thermometers with ground glass joints are shown, they may be replaced by rubber stoppers, as fully detailed in the description of Fig. *II, 56*, 6.

Simple distillation. The assembly shown in Fig. *II, 60*, 1 is of general utility ; for very volatile liquids the Liebig's condenser may be replaced by a double surface condenser.

Fractional distillation. Fig. *II, 60*, 2 illustrates a set-up for fractional distillation with a Hempel-type column and " cold finger," the latter to give manual control of the reflux ratio. Any other fractionating column, *e.g.*, an all-glass Dufton or a Widmer column may, of course, be used.

A set-up for **distillation under reduced pressure** is shown in Fig. *II*, *60*, 3; it is generally more convenient to use a Kon receiver or a Perkin triangle (Fig. *II*, *56*, 31). The vessel at the side, connected to the assembly by rubber " pressure " tubing, may be immersed in a Dry Ice - acetone bath and serves as a trap for volatile materials.

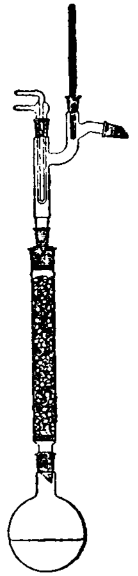


Fig. *II*, *60*, 2.

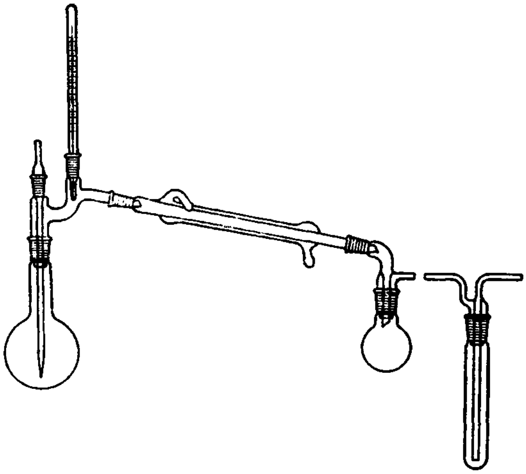


Fig. *II*, *60*, 3

Removal of an inflammable solvent. This operation (" flash distillation ") is conveniently conducted in the apparatus of Fig. *II*, *60*, 4; the receiver may be attached as in Fig. *II*, *60*, 3.

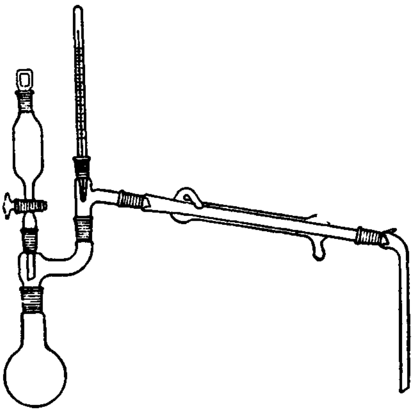


Fig. *II*, *60*, 4.

Refluxing of a mixture. The assembly is shown in Fig. *II*, *60*, 5; the Liebig's condenser may be replaced by a double surface condenser.

Reactions under reflux with stirring. One assembly is depicted in Fig. *II*, *60*, 6 ; a three-necked flask may be substituted for the flask and adapter.

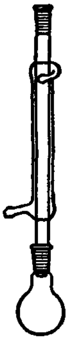


Fig. *II*, *60*, 5.

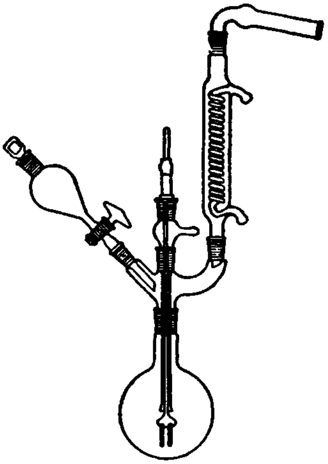


Fig. *II*, *60*, 6.

Steam distillation. A convenient set-up is shown in Fig. *II*, *60*, 7. An equivalent result may be obtained by the use of a two- or three-necked flask.

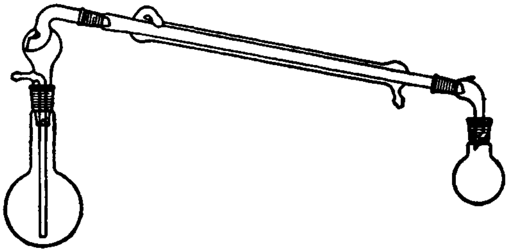


Fig. *II*, *60*, 7.