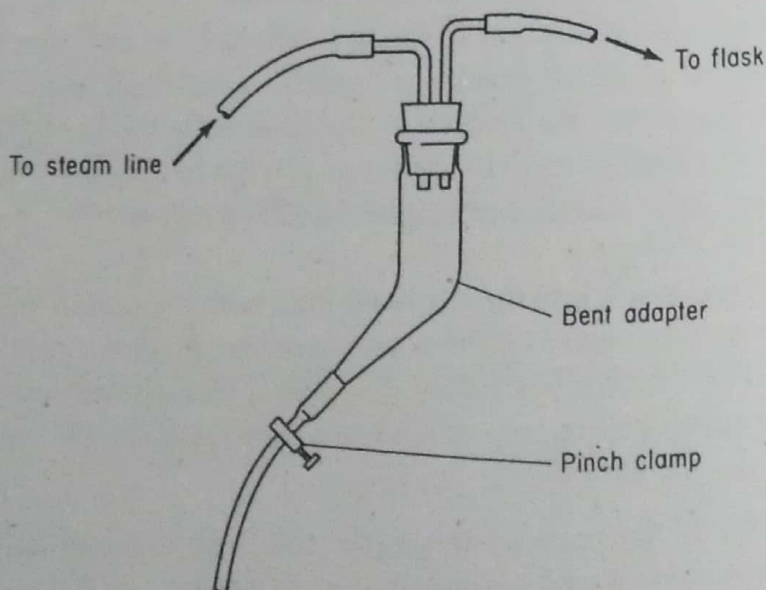


**FIGURE 21.27**  
External steam generator  
equipped with boiling chips  
and a safety tube.

**CAUTION** Steam will cause severe burns. Handle with care!

**DANGER** If the substance crystallizes in the condenser, it will close the tube. Steam pressure could build up when the tube closes and cause an explosion. *Use care! Drain the condenser of cooling water. The crystals will melt and pass into the distillate. When the tube is clear, slowly pass the cooling water through the condenser.*

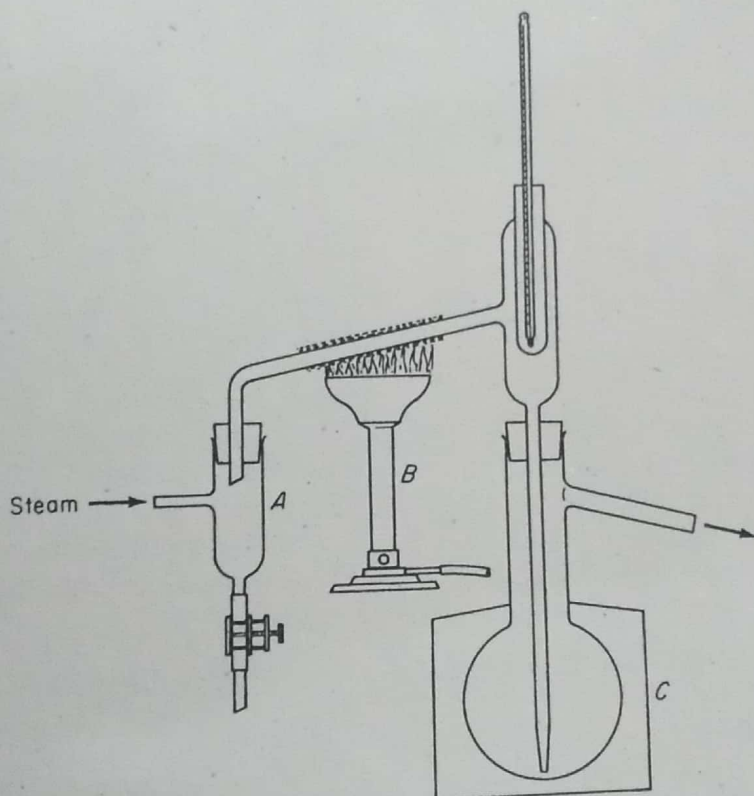
4. Always disconnect the steam-inlet tube from the flask.



**FIGURE 21.28**  
Water trap.

## Steam Distillation with Superheated Steam

The use of superheated steam can increase the proportion of the low-vapor-pressure component in the distillate, and, at the same time, reduce the amount of steam condensate in the distilling flask. The distilling flask is surrounded by a heating bath (refer to Chap. 10, "Heating and Cooling") which is heated to the same temperature as the superheated steam; this minimizes any cooling of the steam which could occur before it enters the flask. (See Fig. 21.29.)



**FIGURE 21.29**

Distillation apparatus for use with superheated steam.

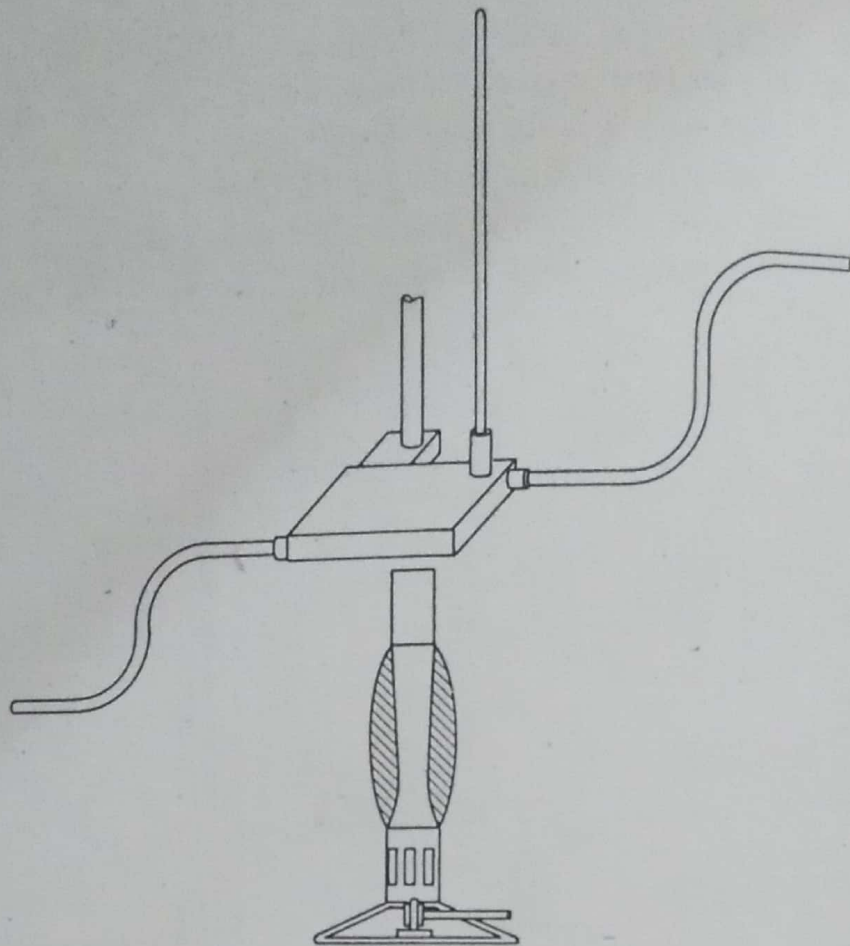
A commercially available metal superheater, heated by a Meker burner, is shown in Fig. 21.30.

## REFLUXING

The reflux procedure allows you to heat a reaction mixture for an extended period of time without loss of solvent. The condenser, which is fixed in a vertical position directly above the heated flask, condenses all vapors to liquid. Because none of the vapors escape, the volume of liquid remains constant.

Reflux procedures are carried out in neutral, acid, or basic solution, depending upon the reaction.

Typical operations include hydrolysis-saponification of acid amides, esters, fats, nitriles, substituted amides, and sulfonamides. Hydrolysis-saponification is used to



**FIGURE 21.30**  
Commercially available metal  
superheater, heated with a  
Meker burner.

split organic molecules (which were made by combination of two or more compounds) into the original compounds.

Experimental setups are shown in Figs. 21.31 to 21.34.

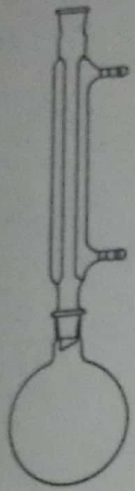
### *Procedure*

1. The water inlet to the condenser is the lower one. The water outlet to the condenser is the upper one.
2. Fill the heating flask no more than half full; add a few boiling stones.
3. Turn on the cooling water.
4. Heat to reflux for the desired period of time.

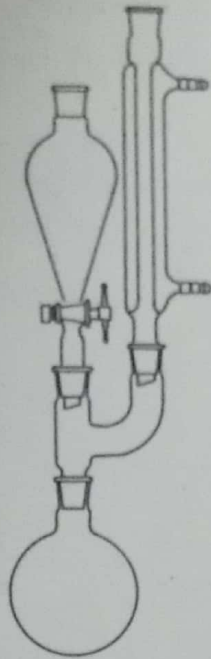
### **MOLECULAR STILLS**

Many organic substances cannot be distilled by any of the ordinary distilling methods because (1) they are extremely viscous, and any condensed vapors would plug up the distilling column, side arm, or condenser; (2) their vapors are extremely susceptible to condensation.

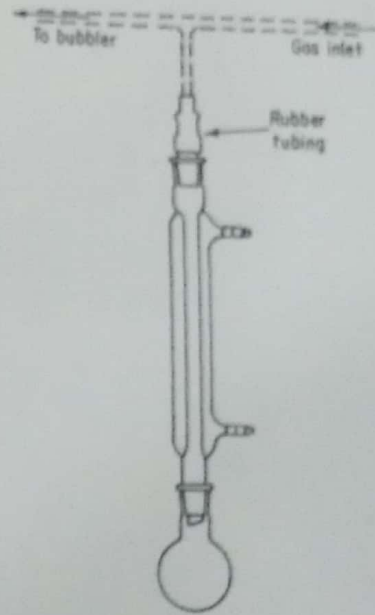
To distill high-molecular-weight substances (molecular weights around 1300 for hydrocarbons and around 5000 for silicones and halocarbons) molecular stills are used. Molecular distillations differ from other distillations because:



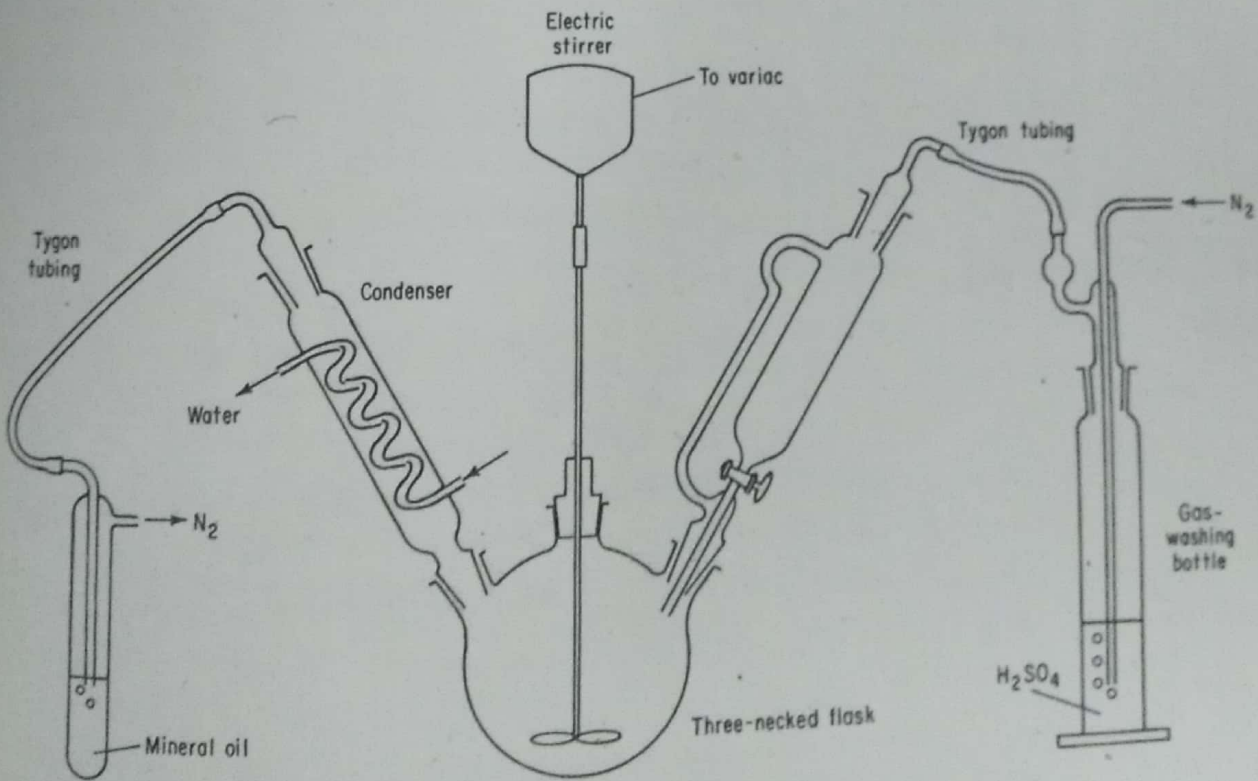
**FIGURE 21.31**  
Simple reflux condenser.



**FIGURE 21.32**  
Addition tube and reflux condenser for use with high-boiling liquids.

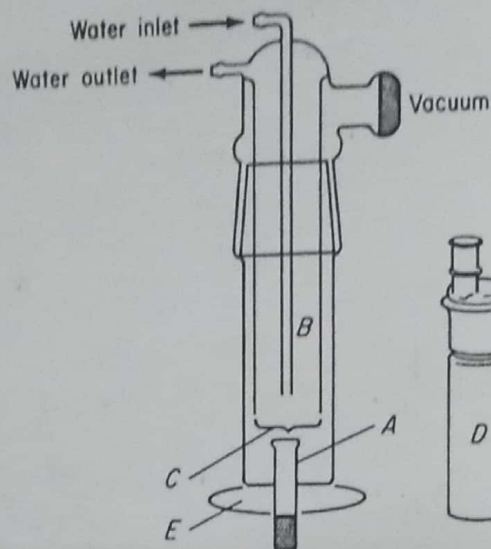


**FIGURE 21.33**  
Apparatus for refluxing in an inert atmosphere.



**FIGURE 21.34**  
Apparatus with mechanical stirrer for reflux reaction in an inert atmosphere.

1. All condensed vapor flows to the distillate receiver or collector.
2. Very low pressure (high vacuum) in the system favors vaporized molecules reaching the condensing surface without collision with other molecules to condense prematurely.
3. There is a very short distance between the surface of the evaporating liquid and the condenser surface. (See Fig. 21.35.)



**FIGURE 21.35**  
Simple molecular still made of glass. A, sample to be distilled; B, cold-finger condenser; C, tip of condenser to guide condensate into D; D, distillate collector; E, source of heat.

Laboratory models include a rotating still. Materials are fed at slightly above their melting point into the rotating still. They are distributed evenly and thinly over the heated evaporating surface. The sample distills, requiring a very short time, and its vapors condense to run into the collector. The degree of vacuum is controlled to collect the distillate effectively at the condenser, and the pressure can be as low as  $1 \mu\text{m Hg}$ .

## EVAPORATION OF LIQUIDS

### Small Volumes

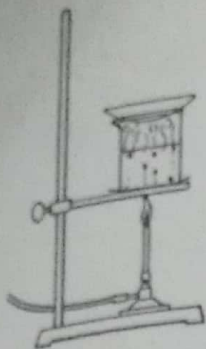
Evaporation of solvents is necessary at times to concentrate solutions and to obtain crystallization of solutes.

#### Method 1

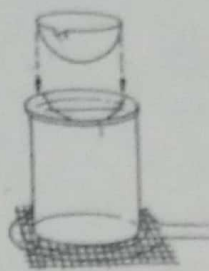
1. Pour the small volume of solution into the watch glass placed over a beaker of water (Fig. 21.36). (Refer to Chap. 10, "Heating and Cooling.")
2. Boil the water. The heat transfer through the steam formed evaporates the solvent of the solution.

#### Method 2

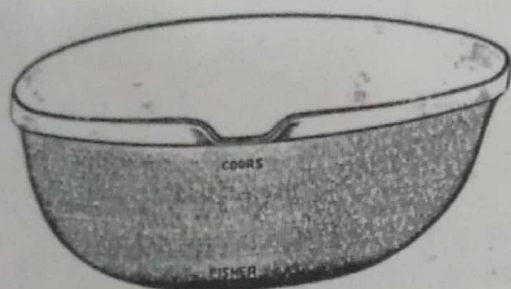
Use an evaporating dish instead of a watch glass (Fig. 21.37). Evaporating dishes come in various sizes and are made of various materials (Fig. 21.38). Use the appropriate one.



**FIGURE 21.36**  
Evaporation over a water bath.



**FIGURE 21.37**  
Alternate procedure using evaporating dish instead of watch glass.



(a)

(b)

(c)

**FIGURE 21.38**  
Evaporating dishes: (a) porcelain with heavy rim, (b) nickel, (c) crystallizing dish to hold or contain solutions from which solids are expected to crystallize.

## Direct Heating of Evaporating Dishes

You can speed up the evaporation of water by directly heating the evaporating dish with a Bunsen burner, diffusing the heat with a wire gauze.

When the volume is very low, transfer the evaporating dish to the top of a beaker of boiling water. The steam acts as the heating agent. (See Fig. 21.38.)

## Transferring Residues from Watch Glasses or Evaporating Dishes

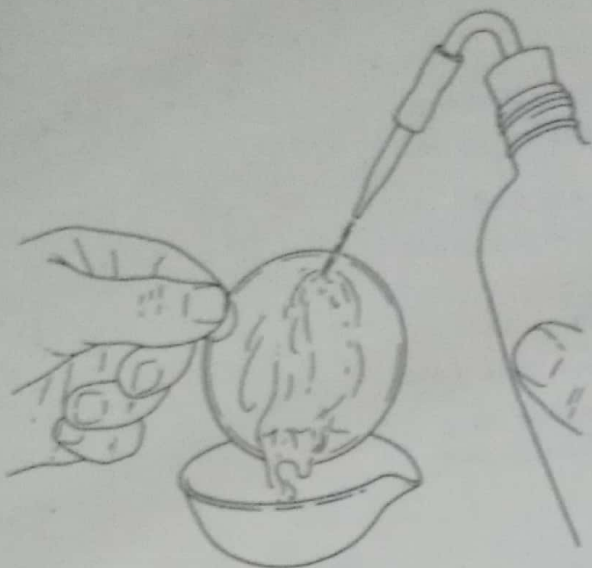
When the water has been evaporated to the desired volume or the desired concentration, the material can be transferred to an appropriate container, such as a smaller evaporating dish, by rinsing with distilled water. The watch glass or evaporating dish is rinsed with a wash bottle, using a back-and-forth motion (Fig. 21.39).

## Large Volumes

Concentrate solutions by boiling off the desired volume of solvent. Refer to the sections on heating flammable liquids and heating organic liquids in Chap. 10, "Heating and Cooling."

### Method 1

1. Pour the solution that is to be concentrated by boiling off solvent into a suitably sized beaker that is covered by a watch glass resting on glass hooks (Fig. 21.40).
2. Heat the solution to evaporate the solvent.



**FIGURE 21.39**  
Watch glass is rinsed with a wash bottle using a back-and-forth motion.



**FIGURE 21.40**  
Arrangement for the evaporation of liquids.

## Method 2

When you need to concentrate a solution by evaporating the solvent, you can accelerate the process by directing a stream of air (or nitrogen gas, for easily oxidized substance) gently toward the surface of the liquid. This stream of gas will remove the vapors that are in equilibrium with the solution.

**CAUTION** If toxic or flammable solvent vapors should be involved, conduct the evaporation in a hood.

Compressed air sometimes contains oil and water droplets. Filter the air by passing it through a cotton-filled tube and a tube filled with a drying agent, such as anhydrous calcium chloride.

## Evaporation Under Reduced Pressure

Solvents can be evaporated more quickly by evaporating them at reduced pressure and gently heating (Fig. 21.41). Refer to Fig. 21.42 for trap bottle.

### Procedure

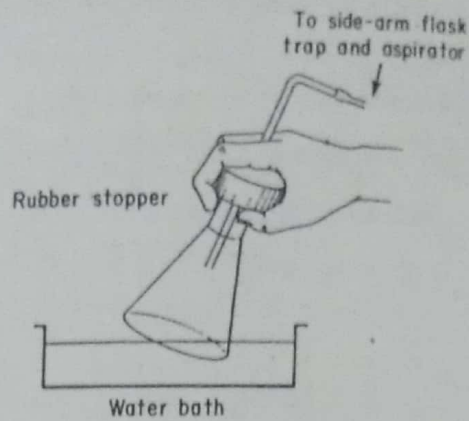
1. Place the solution to be concentrated in a round-bottomed flask or suction flask.

**CAUTION** Do not use Erlenmeyer flasks having volumes larger than 125 mL. There is a danger of implosion and collapse.

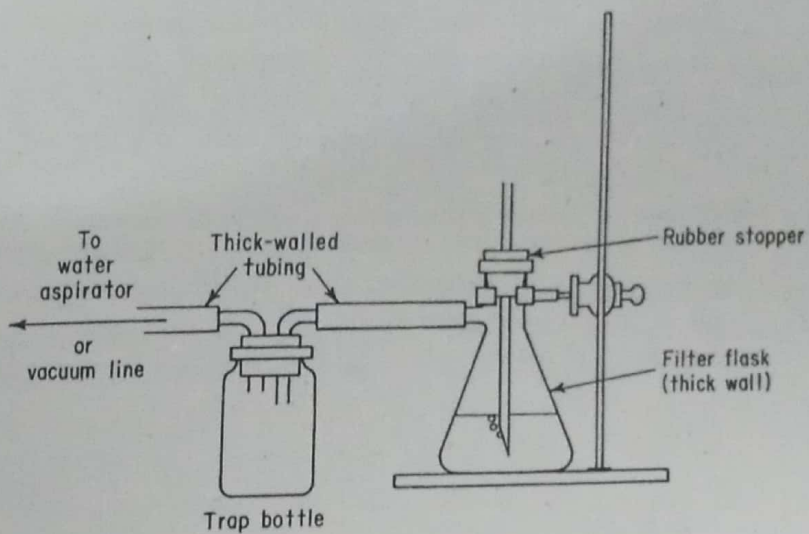
2. Connect with rubber tubing to a safety trap which in turn is connected to a water aspirator.

3. Apply vacuum by turning on water.

4. *Swirl* the flask to expose large areas of the liquid and speed evaporation.



**FIGURE 21.41**  
Evaporation of solvent under reduced pressure at elevated temperature.



**FIGURE 21.42**  
Evaporation of solvent under reduced pressure at room temperature.

**NOTE** *Swirling* technique helps suppress bumping.

5. The flask cools as the solvent evaporates.
6. Heat the flask by immersing in a warm-water bath.

## Evaporation Under Vacuum

### Water Aspirator

1. Place liquid in a flask (fitted with a capillary air-inlet tube, Fig. 21.42) that is connected to a water aspirator with tubing.
2. Turn on the water aspirator to apply vacuum; adjust the capillary in the flask.
3. Gently apply heat with a warm-water bath.
4. When evaporation is completed, disconnect the tubing from the water aspirator *before* turning off the water.



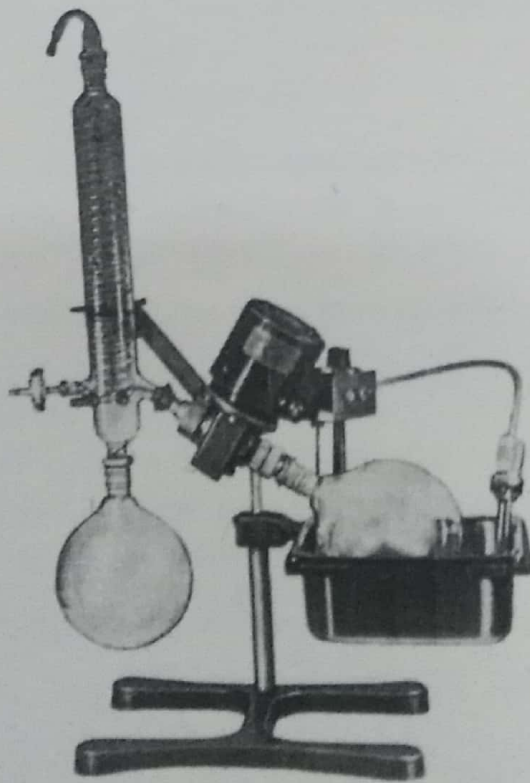
## Mechanical Vacuum Pump

1. Place liquid in a flask (fitted with a capillary air-inlet tube) connected to a dry-ice trap by tubing.
2. Connect the outlet of the trap to a vacuum pump.
3. Turn on vacuum pump; adjust capillary on flask to a fine-air-bubble stream.
4. Gently apply heat with a warm-water bath.
5. Disconnect the tubing, connecting the flask to the vapor trap *before* turning off the vacuum pump.

## ROTARY EVAPORATOR

Rotary evaporators (Fig. 21.43) provide a very rapid means to evaporate solvents and concentrate solutions. The flask rotates while the system is under vacuum (see section on the water aspirator in Chap. 5, "Pressure and Vacuum") providing a very large surface area for evaporation. The walls of the flask are constantly rewetted as the flask rotates, minimizing superheating and bumping. Heat is supplied to the flask by steam bath, oil bath, heating mantle, or other heat source to meet the need.

Rotary evaporators can be used for evaporation and vacuum drying of powders and solids, and for low-temperature distillation of heat-sensitive substances. Substances can be degassed and distilled under inert atmospheres. The rotating flask ensures good mixing and good heat transfer from the heating bath.



**FIGURE 21.43**  
Rotary evaporator.

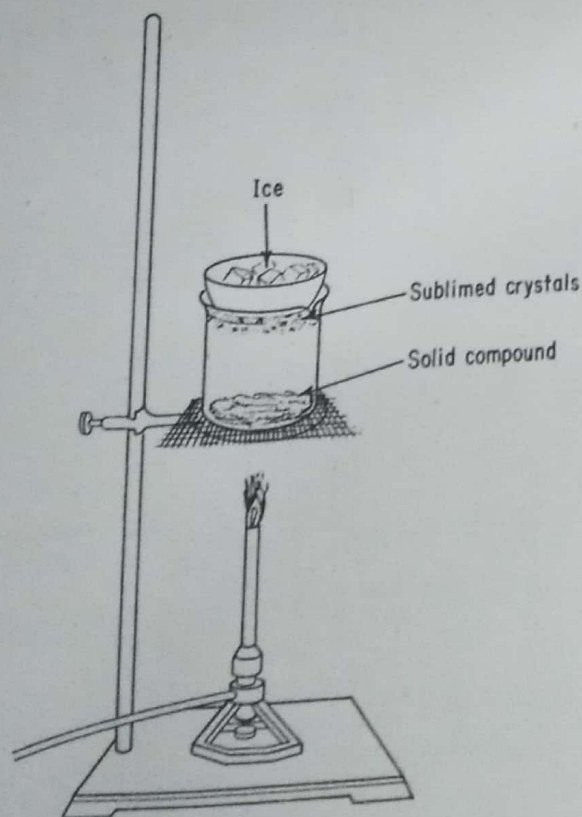
## SUBLIMATION

The vapor pressure of solids increases as the temperature increases, and because of this some solids can go from the solid to the vapor state without passing through the liquid state. This phenomenon is called *sublimation*, and the vapor can be resolidified by reducing its temperature. The process can be used for purifying solids if the impurities in the solids have a much lower vapor pressure than that of the desired compound.

The advantages of sublimation as a purification method are:

1. No solvent is used.
2. It is a faster method of purification than crystallization.
3. More volatile impurities can be removed from the desired substance by subliming them off.
4. Substances that contain occluded molecules of solvation can sublime to form the nonsolvated product, losing the water or other solvent during the sublimation process.
5. Nonvolatile or less volatile solids can be separated from the more volatile ones.

The disadvantage of sublimation as a purification method is that the process is not as selective as crystallization because the vapor pressures of the sublimable solids may be very close together.



**FIGURE 21.44**  
Simple laboratory setup for  
sublimation.

## Atmospheric and Vacuum Sublimation

A sublimation point is a point at which the vapor pressure of a solid equals the applied pressure: it is a constant property like a melting point or a boiling point. Many liquids evaporate at temperatures below their boiling points, and some solids sublime (evaporate) below their melting points. If a substance sublimates below its melting point at atmospheric pressure, its melting point must be determined under pressure, in a sealed capillary tube.

Many solids do not develop enough vapor pressure at 760 mmHg (atmospheric pressure) to sublime, but they do develop enough vapor pressure to sublime at reduced pressure. For this reason, most sublimation equipment is constructed with fittings making it adaptable for vacuum connections. Furthermore, the use of vacuum is advantageous because the lower temperatures required reduce thermal decomposition.

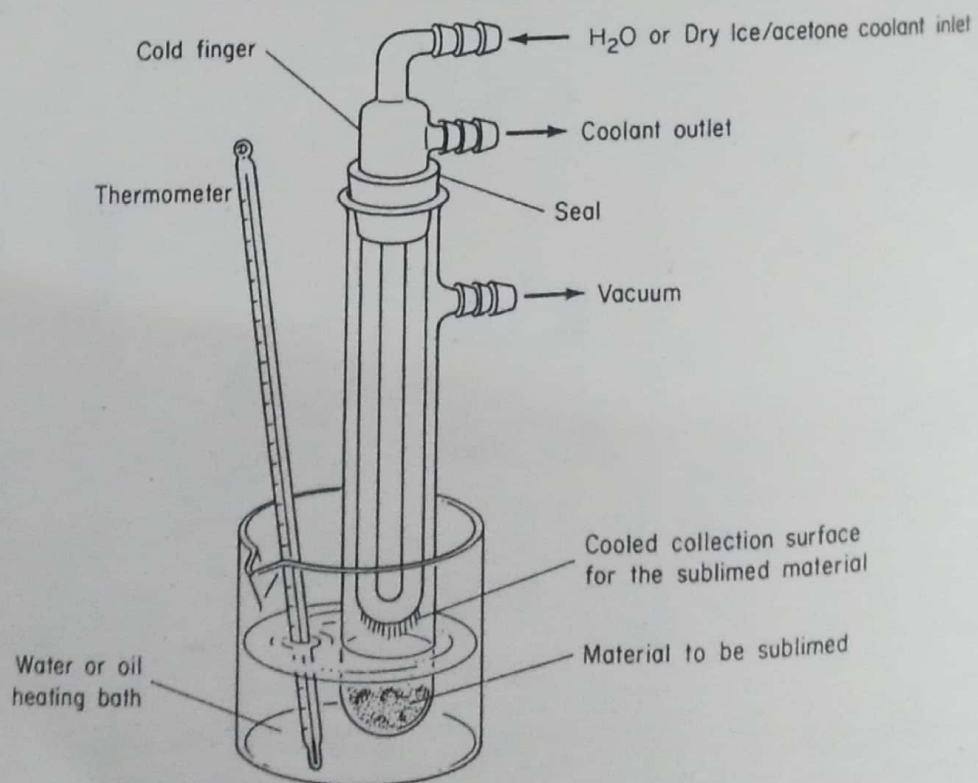
## Methods of Sublimation

### Simple Laboratory Procedure at Atmospheric Pressure

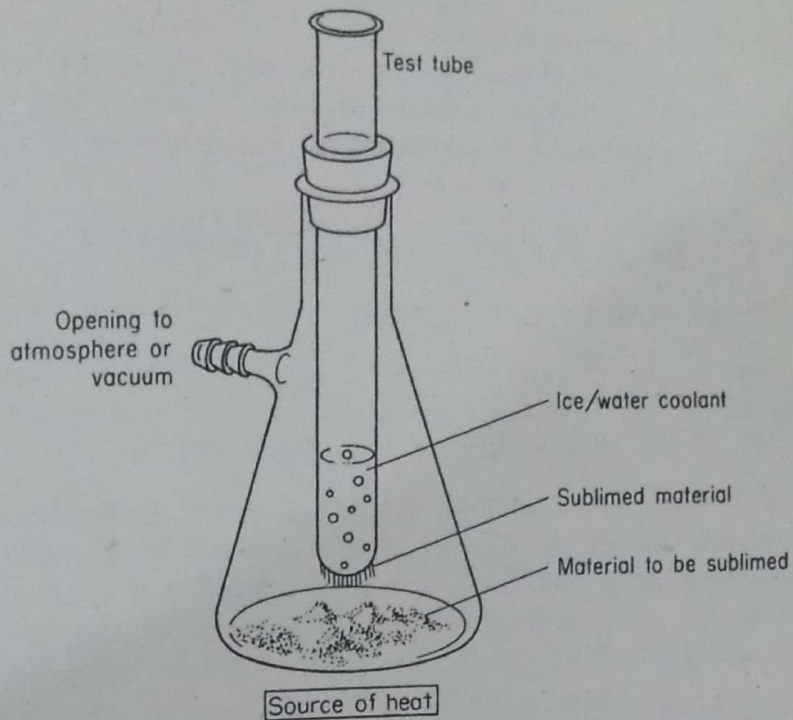
Gently heat the sublimable compound in a container that has a loosely fitting cover that is chilled with cold water or ice (Fig. 21.44).

### Methods Useful at Atmospheric or Reduced Pressure

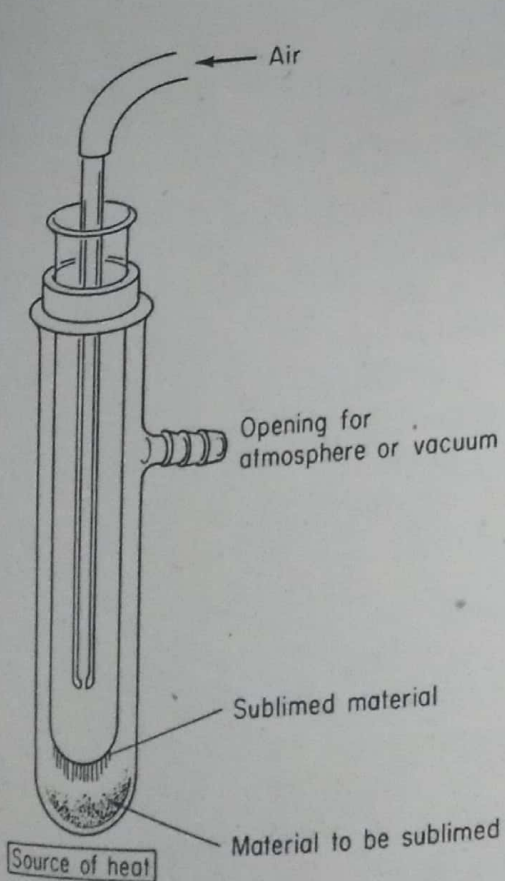
The sublimation equipment illustrated in Figs. 21.45 to 21.48 can be easily constructed in the laboratory and can be used for sublimation procedures at normal atmospheric pressure or at reduced pressure.



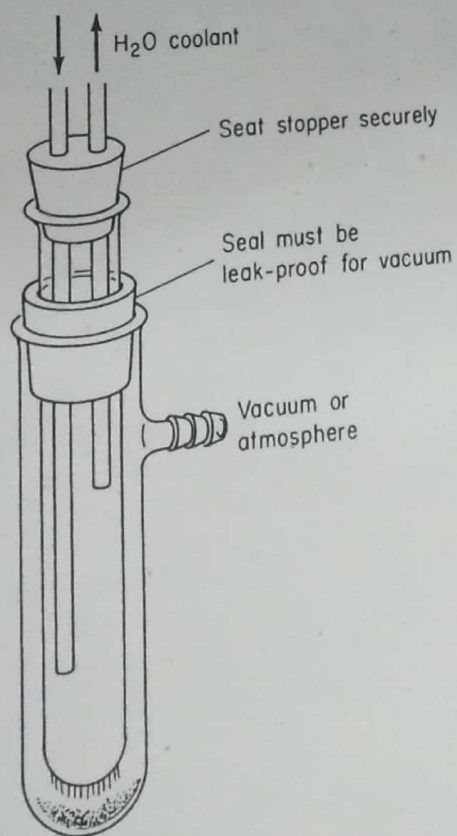
**FIGURE 21.45**  
Cold-finger sublimation apparatus.



**FIGURE 21.46**  
Test-tube/filter-flask setup  
for sublimation.



**FIGURE 21.47**  
Air-cooled test-tube/filter-flask setup.



**FIGURE 21.48**  
Test-tube/filter-flask setup with continuous  
water coolant.