chloric acid is passed

2.9. Molecular Distillation.

1) In conventional distillation processes, distillation occurs at a well-defined temperature, namely, at the boiling point of the material being distilled, and continues with the ebullition of the liquid. A dynamic equilibrium exists between the vapor phase and liquid phase, causing a large proportion of the evaporated molecules to return to the liquid phase. Use is made of this equilibrium tendency in establishing a fractional-distillation process with improved separating powers.

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2) In contrast to conventional distillation, a distillation in high vacuum (less than 0.001 mm of mercury) does not commence at any well-defined temperature but occurs at any temperature as long as there is a thermal gradient between the evaporator and condenser. 3) In distillations in high vacuum the mean free path of molecules of the distillate is relatively long (5.09 cm for air at 25°C and 0.001 mm of mercury) compared with that at atmospheric pressure (6.7×10^{-6} cm). Consequently, the distilling vapor molecules pass directly from the vaporizing surface to the condensing surface with very few vapor molecules ever returning to the distilland if the distance between evaporator and condenser surfaces is less than the mean free path of the vapor molecules. No equilibrium exists between the vapor and liquid phases. Ideal distillation conditions are attained when the rate of evaporation is equal to the rate of condensation.

Distillation in high vacuum goes under several names, the more common of which are *molecular distillation* and *evaporative distillation*. The former seems preferable here.

4) Strictly speaking, a *molecular still* can be defined as any still in which the distance between the evaporating surface and the condenser surface is less than the mean free path of the vapor molecules. 5) A simple form of the apparatus (Fig. 2.14) is that in which a cooled condensing surface is supported a few centimeters (or millimeters) above a thin, heated layer of liquid and the whole is enclosed in a highly evacuated chamber. Since the mean free path of large molecules is appreciably less than that for air,

the distance between the condenser and evaporator surface is usually reduced to several millimeters and the temperature of the condenser is kept quite low to reduce the rebound of vapor molecules from the condenser surface. Liquid air and dry-ice–acetone mixtures are common condenser coolants.

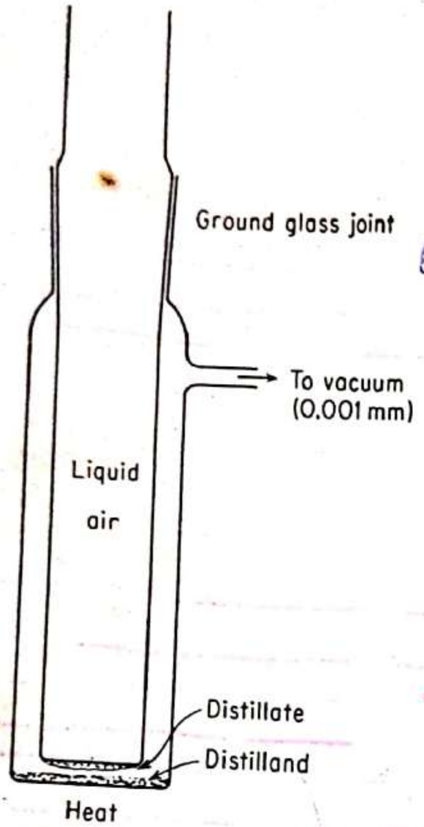

FIG. 2.14. Basic features of simple molecular still. The distance between distilland and condensing surface is limited to several millimeters.

Whereas Fig. 2.14 represents an apparatus particularly well suited for the distillation (sublimation) of solids, the still depicted in Fig. 2.15 is better suited for the distillation and collection of high-boiling liquids where it is necessary or desirable to collect the distillate in successive fractions.

6) For apparatus of the type described above the rate of distillation is determined by the rate at which the liquid surface can produce vapor. According to Langmuir the theoretical rate of distillation (and condensation under ideal conditions) is given by the expression

$$Q = \frac{P}{(2\pi MRT)^{1/2}} \tag{2.19}$$

where Q = moles of substance evaporating per second per square centimeter of liquid surface

M = molecular weight of the distilling substance

R = molar gas constant

P = vapor pressure of the distilling substance, dynes per sq cm measured at absolute temperature T

In practice, lower values for Q are obtained than predicted because of the rebound of some vapor molecules from the condenser surface and molecular collisions. To take these factors into account the general equation is usually written as

$$Q = \frac{\alpha P}{(2\pi MRT)^{1/2}} \tag{2.20}$$

where α is an efficiency factor. A simplified form of the equation useful to the chemist is

$$W = \boxed{\frac{0.0583P}{(M/T)^{1/2}}} = \frac{0.0583PT^{1/2}}{M^{1/2}} \tag{2.21}$$

where W is the distilling rate in grams per second per square centimeter of liquid surface and P is the vapor pressure in millimeters of mercury. The constant 0.0583 is the resultant of combining the molar gas constant and various conversion factors.

7) It is apparent from the general equation that the rate of evaporation at any given temperature is a function of the ratio of P/M and that the relative quantities of different sample constituents distilling are given by the ratios

$$\frac{P_1}{M_1^{1/2}} \qquad \frac{P_2}{M_2^{1/2}} \qquad \cdots \qquad \frac{P_n}{M_n^{1/2}}$$

where P is the partial pressure of the constituent. By contrast, in conventional distillation the relative quantities of each constituent distilling over are proportional to their partial pressures; that is, the effect of the molecular mass is not involved.

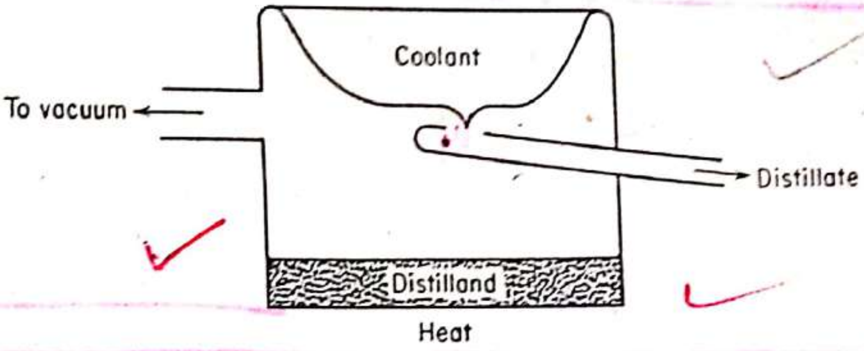

FIG. 2.15. Schematic of a simple molecular still suitable for fractional distillation through control of distillation temperature.

b) The simplest separation to achieve by molecular distillation is the distillation of the desired substance from a residue of higher molecular weight. Owing to the temperature dependence of the rate of distillation, a fractionation of substances with different molecular weights can be effected by holding the temperature constant until the more volatile constituent is removed. Then the temperature is raised sufficiently to give a practical distillation rate for the less volatile substance, etc.

The degree of separation effected by molecular distillation is comparable to that produced by a simple batch distillation and is greatest when components differ in boiling point by 50° or more. Where fractionation is not complete in a single distillation, a greater degree of separation can be attained by redistillation of the distillate, the operation being repeated as many times as necessary to give the desired purity.

a Since the fractionating power of the molecular still is restricted to the preferential evaporation of the most volatile constituents from the surface layer of the liquid, it is imperative that the surface layer be continually replenished. Any condition which leads to the removal of a volatile constituent more rapidly than that component can diffuse to the surface of the distilland reduces the efficiency of the distillation. "Flowing film" stills and others that continually replenish the distilland surface are well described in the literature by Perry.[38]

Several other devices have been proposed for increasing the fractionating efficiency of a molecular still. One[39] interposes a semipermeable barrier between the evaporator and condenser to retard the least-volatile molecules while allowing the more volatile molecules to reach the condenser. Another method[40] provides for multiple redistillations, and still another[41] for countercurrent reflux.

10 The great advantage of molecular distillation is that the "boiling point" of high-molecular-weight, high-boiling substances is greatly reduced (in some cases as much as 200 to 300°), making it possible to distill these substances without the thermal decomposition attendant upon their distillation at higher temperatures and atmospheric pressure. Molecular distillation is particularly adapted to the purification of a substance which is difficult or impossible to distill at ordinary pressures. Frequently, it is the only satisfactory method for the isolation of heat-labile substances and polymers.

Numerous references to the fractionation of fats and oils, fatty acids, esters of fatty acids, monoglycerides, phthalate esters, polymeric substances, sterols, tall oil, uranium chlorides, vitamins A and E, whale oil, etc., can be found in the work by Rose and Rose.[42]