2.5. Apparatus. Laboratory distillation is probably the most convenient tool available to the chemist for the separation of mixtures of liquids because of the ease with which it is possible to obtain a large number of theoretical plates in a single column. Thus, relatively difficult separations can be carried out quickly in fairly simple apparatus.

Figure 2.8 illustrates a simple distillation unit which consists of a distilling flask, thermometer, water-cooled condenser, and receiving flask. Keep in mind that such a unit has very little resolving power, since the enrichment of the distillate with the more volatile component is probably no greater than that achieved with one theoretical plate.

The introduction of a rectifying or fractionating column in the simple equipment is illustrated in Fig. 2.9. Since the actual separation of components is effected in the column, this discussion will be centered about the several basic column designs usually employed in laboratory equipment.

There are, in general, two types of columns encountered—the film and the plate. The film column can be exemplified in varying degrees of complexity starting with a vertical open tube and progressing through

various modifications of the shape and length of path in which the ascending vapor and descending liquid are kept in intimate contact. The plate column consists of a tube containing a series of equally spaced horizontal plates which impede the downward flow of the reflux. Liquid collects on the upper surface of each plate until it reaches a predetermined overflow level. In such a column there are definite increments in the

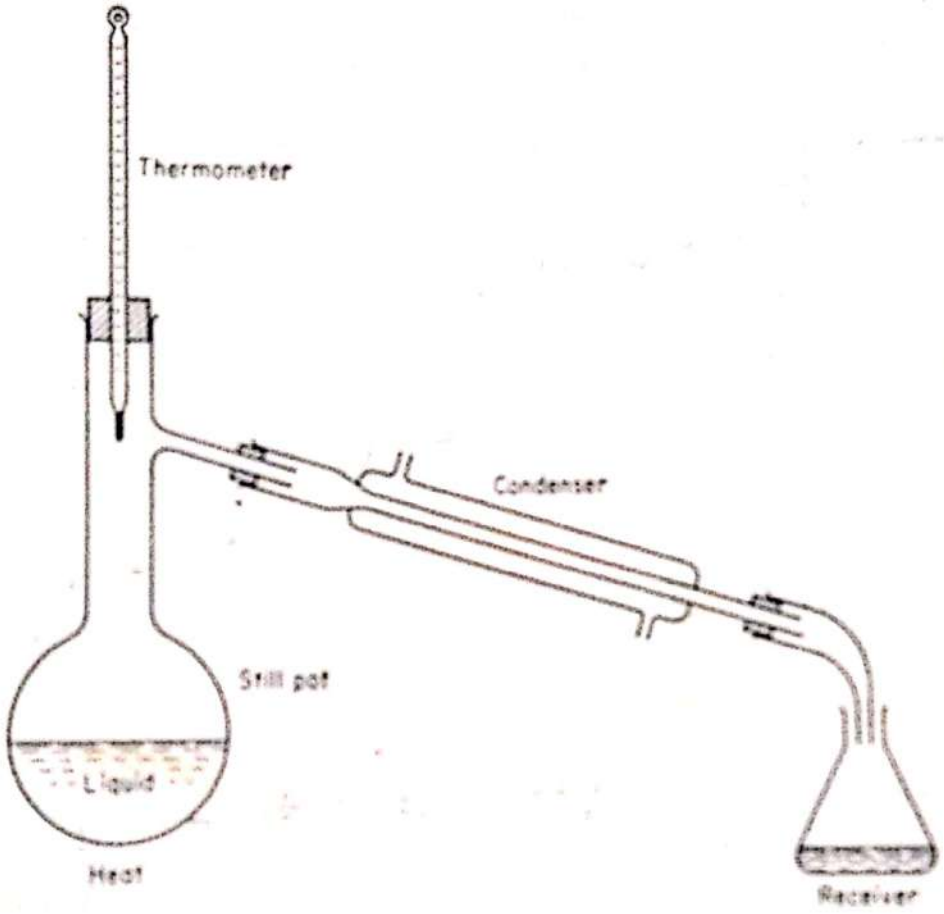

FIG. 2.8. Apparatus suitable for a simple distillation.

composition of liquid from plate to plate. Advantages and disadvantages are associated with the use of both types of columns.

One of the simplest film columns is the Vigreux illustrated in Fig. 2.10. It is made up from a cylindrical glass tube with indentations projecting inside it according to a definite pattern. The indentations occur in sets of three or four around the circumference of the tube. Alternate sets of indentations are pointed downward at a 45° angle with the other sets horizontal. Each set of indentations is rotated slightly with respect to the set above it to give a somewhat spiral arrangement of the drip points. Columns 1 m in length may have up to about 12 theoretical plates. The holdup is quite small, and there is a very low pressure drop through the column.

The spiral columns illustrated in Fig. 2.11 provide vapor and liquid paths considerably longer than they would be in an empty-tube column of the same length. The spiral column in various modifications is still very popular.

The most widely used film column is the *packed column*, which consists of a vertical tube filled with a porous packing which breaks up the direct

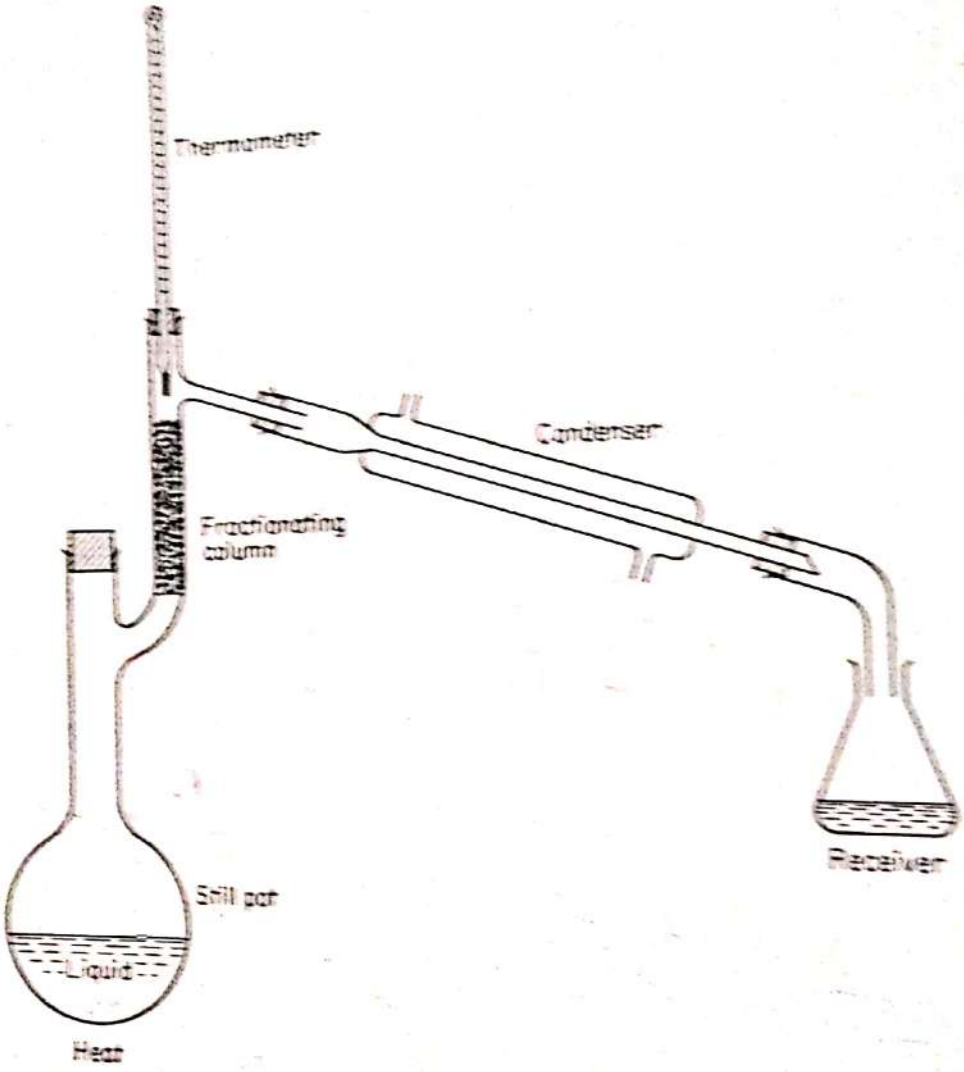

FIG. 2.9. Basic laboratory equipment for fractional distillation.

path through the tube and provides a large liquid surface for contact between the vapor and reflux.

Packing material for laboratory columns should be of small dimensions (generally 2 to 8 mm) and must be readily wetted by the liquid and inert to the liquids and vapors. Most packings are glass, porcelain, or metal. For general use the columns are packed with hollow open-end cylinders (Raschig rings) of approximately equal height and diameter, hollow open-end cylinders with a central partition (Lessing rings) to increase the surface area, Berl saddles, helices, or beads. The promiscuous arrange-

ment of the various packings in a column provides a rather tortuous path through the column which assures intimate contact between ascending vapors and reflux. At the same time the packing is porous enough that little pressure is built up between the top and bottom of the column.

Because of the large contact surfaces provided by packed columns, the columns are usually quite efficient, having as many as 20 to 40 theoretical

FIG. 2.10. Vigreux column.

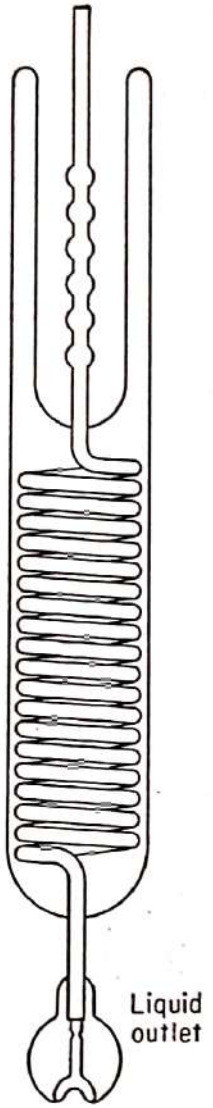

FIG. 2.11. Simple spiral column.

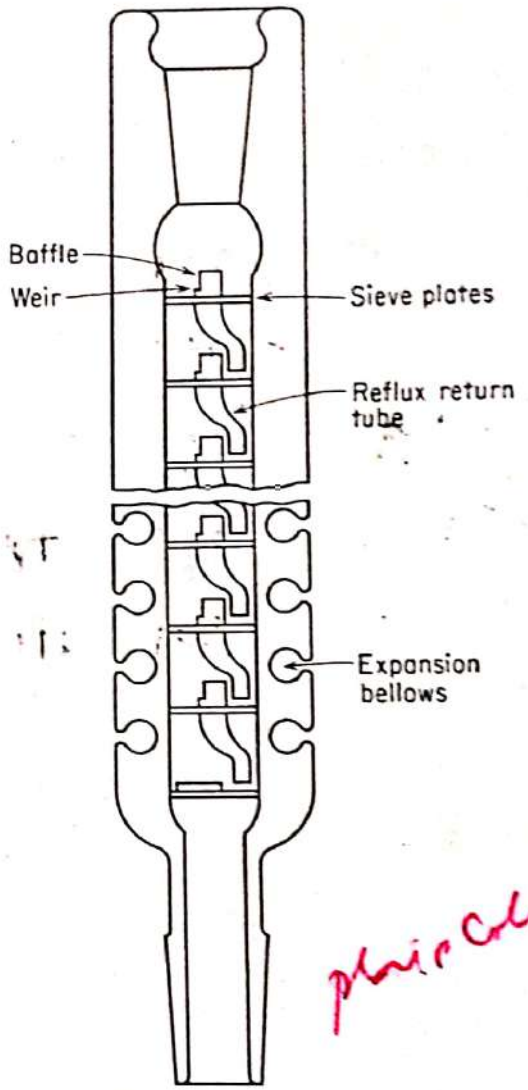

FIG. 2.12. Oldershaw sieve-plate column.

plates per meter of column length. Compared with a Vigreux column of the same size, packed columns have a higher separating power, a larger holdup, and a much larger pressure drop in the column.

The Oldershaw[15] sieve-plate column shown in Fig. 2.12 is an example of a well-designed plate column. A column 1 m in length containing 30 sieve plates can possess as many as 15 to 18 theoretical plates, giving a fairly high resolving power. Operating conditions with such a column are highly reproducible, but the holdup per theoretical plate is greater than that for a theoretical plate in a packed column.

Since the effectiveness of a column depends upon the height as well as upon the packing or internal construction of the column, the efficiency is frequently expressed in terms of the height equivalent of a theoretical plate (HETP) for direct comparisons.

In the final selection of fractionating equipment for laboratory use a compromise must be found which combines high separating power per unit length of column (a low HETP) and high capacity with low holdup. If the absolute quantity of material to be separated is small, there is, of course, a definite limit on the holdup that can be tolerated. The holdup must not be of the same order of magnitude as the material to be resolved, and preferably it should be less than 10 per cent of the amount of material to be separated.

There is not much point in trying to use apparatus with more than 40 or 50 theoretical plates for normal laboratory work because of the unusually long time required for the column to come to equilibrium and the difficulty of operating such columns efficiently.

The Podbielniak automatic distillation apparatus[16] removes much of the tedium associated with the fractional-distillation process by automatically recording the boiling point as a function of the volume of distillate over a temperature range from 190 to 300°C. It is excellent for the efficient separation of all but the closest boiling components.

For more detailed information on packing materials, column designs (including spinning band columns), column evaluation, and the very necessary auxiliary equipment which complements the column, the interested reader is referred to the selected bibliography at the end of this chapter.

2.6. General Applications. Fractional distillation is used for a number of purposes in the laboratory, the most important of which are qualitative and quantitative analysis, the preparation of pure compounds, and the fractionation of complex mixtures into pure substances or classes of substances. Since the purely determinative applications of fractional distillation are far less important now than before the emergence of gas chromatography as an analytical tool, the discussion will be directed along the lines of utilizing distillation as a general separation technique of wide applicability, especially when sizable quantities of material must be handled. The distillation of a pure substance is of no interest because a separation of components is not involved.

Fractional distillation is widely used for the analysis and fractionation of complex mixtures of hydrocarbons, fluorocarbons, petroleum products, etc. It is a particularly powerful tool used with great success when coupled with other separation methods such as adsorption and partition chromatography, solvent extraction, crystallization, azeotropic distillation, and extractive distillation. One must recognize, though, that

only through a knowledge of the limitations of fractional distillation and the other techniques can judicious combinations of these techniques be made which will result in the successful fractionation of mixtures. Specific examples of separations achieved with fractional distillation are given in the following section to illustrate the resolving power of the process when used alone and in conjunction with other methods. The illustrations employed in Sec. 2.7 will be confined to organic systems, since almost all the literature on fractional distillation pertains to the separation of organics.

It is interesting to note, though, how extensively fractional distillation has been used to fractionate inorganic materials. The general subject of the separation of isotopes falls outside the realm of this study, but it is worthwhile to mention that isotopic separations by distillation of hydrogen, helium, oxygen, carbon, boron, and lithium as elements or compounds are of much interest.[17] Recently, distillation methods for the purification of arsenic, titanium, tellurium, niobium, hafnium, zirconium, yttrium, and scandium have been devised which utilize either the elements or their halides.[18] In addition, many inorganics, including the metals and pseudometals, form compounds which can be volatilized from aqueous solutions and which are useful in the isolation and purification of the parent element[19,20] It is this last group of elements that has commanded the greatest attention of analytical chemists.

Section 2.8 is devoted to a discussion of the isolation of inorganic substances from aqueous solutions by volatilization techniques. Only those separations which can be effected in a simple still or volatilization chamber will be mentioned, since these are the only ones which have been widely accepted by the analyst. In general, less sophisticated equipment is employed for inorganic separations than for organic separations because the difference in volatility of similar inorganic species is usually rather great. It is not customary to use a highly efficient column for inorganic separations, but it is feasible.

2.7. Fractional Distillation of Organics. A classic example of the successful fractionation of complex mixtures by distillation is the work dealing with the composition of petroleum sponsored by the American Petroleum Institute and done at the National Bureau of Standards.[21] This work is a remarkably fine example of what can be done with fractional distillation, but what is probably more important, it illustrates what a combination of fractional distillation and other separation techniques can accomplish.

Over 80 hydrocarbons have been separated from one petroleum by a combination of distillation, selective adsorption, extraction, and crystallization. The scheme utilized can be described as one in which the original petroleum (a mixture of paraffins, cycloparaffins, and aromatics) is first