fractionated by distillation into groups of compounds of roughly equal molecular size. These groups are then further subdivided by type of compound by selective adsorption, azeotropic distillation, or distillation at reduced pressure. Final purification then is achieved by fractional crystallization or by high-efficiency distillation.

Simple distillation will serve only as a convenient means for the separation of petroleum into broad fractions roughly according to molecular weight, since, in general, the volatility of a compound is inversely proportional to its molecular weight and boiling point. These fractions are usually referred to as the gas, gasoline, kerosene, gas-oil, and lubricating-oil fractions. Although the properties of each fraction are rather distinct, it must be kept in mind that the general properties are simply the average of what might be extremely diverse values for the individual hydrocarbons in each fraction. For, as the molecular weight of organic materials increases, the number of possible compounds of similar volatility increases greatly and separations by fractional distillation become very difficult, if not impossible. The paraffin octane, for example, has 15 isomers, all of which may be present in a given sample. Added to this is the complication that compounds of different molecular type can have almost the same volatility and boiling points. For example, the six-carbon hydrocarbons benzene and cyclohexane boil at 80.1 and 80.8°, respectively.

Although a complete separation by fractional distillation often is impossible in such cases, it is possible to separate further the narrow-boiling fractions containing different molecular types by extractive or azeotropic distillation or by distillation at reduced pressure.

Azeotropic Distillation. In azeotropic distillation a solvent is added to the close-boiling mixture which will form a constant-boiling mixture or azeotrope with one or more of the components of the mixture. An azeotrope boils or distills without a change in composition and in general has a boiling point which is higher or lower than that of any of its pure constituents. Thus, the shift in the boiling point of a substance when it forms an azeotrope is often large enough to effect a further separation of close-boiling materials.

The two basic requirements for an azeotropic distillation are that the added component reduce the partial pressure of one of the original components more than the other and that it be easily removed from the distillate. Consider the separation of a close-boiling binary mixture AB. The addition to the still of a third component C capable of forming an azeotrope with A will yield a distillate containing A and C in a fixed ratio as long as both A and C are present. The quantitative removal of A is therefore dependent on the addition of an excess of C. By a careful selection of the entrainer solvent the entrainer and component B can then

be resolved by distillation. (b)The maximum boiling-point depression (most azeotropes exhibit a minimum boiling point) is obtained when the boiling points of the two pure solvents forming the azeotrope are the same, but practical considerations require that the boiling point of the entrainer be sufficiently different from the close-boiling mixture that the excess entrainer can then be separated from the residue in the still by a fractional distillation. With an entrainer which boils within 30° of the material to be separated, a 5° lowering of the boiling point of the azeotrope is not uncommon. Thus, the azeotrope AC can be distilled off, leaving a mixture of B and C which can be resolved by fractional distillation.

The separation of an azeotrope from a nonazeotrope or from another azeotrope can be calculated by the conventional methods by simply treating the azeotrope as a pure component. In many instances, though, the separations are appreciably better than the calculations indicate they should be.

Two noteworthy cases of azeotropic distillation familiar to the analytical chemist are the preparation of constant-boiling hydrochloric acid and anhydrous ethyl alcohol. The preparation of anhydrous alcohol will illustrate the method well.

At atmospheric pressure water and ethyl alcohol form a constant-boiling mixture (bp 78.15°C) which is 95 per cent alcohol. Since water is a major component in the commercial preparation of alcohol, pure alcohol cannot be recovered by a simple fractional distillation. If, however, benzene is added to the alcohol-water azeotrope, a new lower-boiling (65°C) ternary azeotrope is formed among benzene, water, and alcohol (74 per cent benzene, 18.5 per cent alcohol, 7.5 per cent water). Distillation of the ternary azeotrope accomplishes the quantitative removal of water from the system but leaves the alcohol contaminated with benzene. The benzene and alcohol in turn form an azeotrope (67.6 per cent benzene and 32.4 per cent alcohol, bp 68.3°C) which distills over, leaving anhydrous ethyl alcohol which can be collected at 78.5°C.

In petroleum analyses, a given entrainer may form azeotropes with each type of hydrocarbon in a given boiling range or be somewhat specific in its action. For example, paraffins, naphthenes, olefins, and aromatics boiling in the range 100 to 110°C form minimum-boiling azeotropes with methanol whereas paraffins, olefins, and naphthenes (but not toluene) form an azeotrope with methyl ethyl ketone. Thus, the judicious selection of entrainer liquids (azeotrope formers) can facilitate the separation of complex mixtures. Tables of known azeotropes can be consulted for practical purposes.[22,23]

Specifically, acetic acid can be used to separate ethyl benzene from vinyl benzene (styrene), and butyl acetate is good for the dehydration of acetic acid.

Another logical development in the application of fractional distillation is the modification of the volatilities of sample components by the addition of certain solvents (extractive distillation) and by distillation at reduced pressures.

Extractive Distillation. Extractive distillation is a technique used to separate close-boiling ideal and nonideal mixtures, including azeotropes. It involves the addition of a relatively nonvolatile liquid to the sample mixture which enhances the relative volatility of the components to be separated. The added component acts as a preferential solvent for one of the components, thus lowering the vapor pressure of the dissolved material and raising the relative volatility of the two-component mixture to be separated. In effect, a nonideal system is deliberately created to enhance the separability of the two substances. This is a little-used technique in the laboratory but one quite versatile for industrial distillations. The following examples will indicate the effectiveness of the method.

Benedict and Rubin[24] resolved a mixture of paraffins and toluene by extractive distillation using phenol as the solvent. Without the phenol, the relative volatilities of the components were unity and no separation was possible. With phenol, the relative volatility increased to 3.7, giving a boiling-point difference of about 80°C for the two fractions collected.

Dicks and Carlson[25] using a single column were able to increase the column efficiency for the separation of *n*-heptane and methylcyclohexane from 13.1 theoretical plates to an effective 51.9 plates by changing from a normal fractional-distillation technique to an extractive distillation using aniline as the solvent. By the same method, using aniline as solvent, a constant-boiling mixture of cyclohexane and benzene (47 mole per cent cyclohexane) can be broken so as to give a pure cyclohexane distillate.

Distillation under Reduced Pressure. The chief advantage to distillation under reduced pressure is that the boiling point is usually lowered considerably. As a consequence, it is a widely used technique for the separation of compounds which would change chemically or distill too slowly at the temperature needed for a normal atmospheric-pressure distillation. It is significant also that the ratio of the vapor pressure of two substances (i.e., the relative volatility of two substances) should increase as the boiling temperature decreases. As a result, separations frequently are more effective when performed at reduced pressures.

2.8. Fractional Distillation of Inorganics. The elements which are generally recognized as being volatile under normal conditions and those which form compounds that can be volatilized from aqueous solution are outlined in Fig. 2.13. The form in which these elements are volatilized from aqueous solution is listed below.