# LIQUID EXTRACTION

Liquid extraction, sometimes called solvent extraction, is the separation of the constituents of a liquid solution by contact with another insoluble liquid. If the substances constituting the original solution distribute themselves differently between the two liquid phases, a certain degree of separation will result, and this can be enhanced by use of multiple contacts or their equivalent in the manner of gas absorption and distillation.

A simple example will indicate the scope of the operation and some of its characteristics. If a solution of acetic acid in water is agitated with a liquid such as ethyl acetate, some of the acid but relatively little water will enter the ester phase. Since at equilibrium the densities of the aqueous and ester layers are different, they will settle when agitation stops and can be decanted from each other. Since now the ratio of acid to water in the ester layer is different from that in the original solution and also different from that in the residual water solution, a certain degree of separation will have occurred. This is an example of stagewise contact, and it can be carried out either in batch or in continuous fashion. The residual water can be repeatedly extracted with more ester to reduce the acid content still further, or we can arrange a countercurrent cascade of stages. Another possibility is to use some sort of countercurrent continuous-contact device, where discrete stages are not involved. The use of reflux, as in distillation, may enhance the ultimate separation still further.

In all such operations, the solution which is to be extracted is called the *feed*, and the liquid with which the feed is contacted is the *solvent*. The solvent-rich product of the operation is called the *extract*, and the residual liquid from which solute has been removed is the *raffinate*.

More complicated processes may use two solvents to separate the components of a feed. For example, a mixture of *p*- and *o*-nitrobenzoic acids can be of nearly the same molecular weight are impossible to separate by distillation because their vapor pressures are nearly the same, but they can readily be separated by extraction with any of a number of solvents, e.g., liquid sulfur dioxide, diethylene glycol, or sulfolane. (Extractive distillation is also useful for such operations, but it is merely extraction of the *vapor* phase with a solvent, whereas liquid extraction is extraction of the *liquid* phase. Frequently the same solvents are useful for both, as might be expected.) Many pharmaceutical products, e.g., penicillin, are produced in mixtures so complex that only liquid extraction is a feasible separation device.

## LIQUID EQUILIBRIA

Extraction involves the use of systems composed of at least three substances, and although for the most part the insoluble phases are chemically very different, generally all three components appear at least to some extent in both phases. The following notation scheme will be used to describe the concentrations and amounts of these ternary mixtures, for purposes of discussing both equilibria and material balances.

### Notation Scheme

1. A and B are pure, substantially insoluble liquids, and C is the distributed solute. Mixtures to be separated by extraction are composed of A and C, and B is the extracting solvent.
2. The same letter will be used to indicate the quantity of a solution or mixture and the location of the mixture on a phase diagram. Quantities are measured by mass for batch operations, mass/time for continuous operation. Thus,

   $E$ = mass/time of solution $E$, an extract, shown on a phase diagram by point $E$
   $R$ = mass/time of solution $R$, a raffinate, shown on a phase diagram by point $R$
   $B$ = mass/time of solvent B

Solvent-free (B-free) quantities are indicated by primed letters. Thus,

   $E'$ = mass B-free solution/time, shown on a phase diagram by point $E$
   $E = E'(1 + N_E)$

3. $x$ = weight fraction C in the solvent-lean (A-rich), or raffinate, liquids
   $y$ = weight fraction C in the solvent-rich (B-rich), or extract, liquids
   $x' = x/(1 - x)$ = mass C/mass non-C in the raffinate liquids
   $y' = y/(1 - y)$ = mass C/mass non-C in the extract liquids
   $X$ = weight fraction C in the raffinate liquids on a B-free basis, mass C/(mass A + mass C)

## Fields of Usefulness

Applications of liquid extraction fall into several categories: those where extraction is in direct competition with other separation methods and those where it seems uniquely qualified.

**In competition with other mass-transfer operations** Here relative costs are important. Distillation and evaporation are direct separation methods, the products of which are composed of essentially pure substances. Liquid extraction, on the other hand, produces new solutions which must in turn be separated, often by distillation or evaporation. Thus, for example, acetic acid can be separated from dilute solution with water, with difficulty by distillation or with relative ease by extraction into a suitable solvent followed by distillation of the extract. For the more dilute solutions particularly, where water must be vaporized in distillation, extraction is more economical, especially since the heat of vaporization of most organic solvents is substantially less than that of water. Extraction may also be attractive as an alternative to distillation under high vacuum at very low temperatures to avoid thermal decomposition. For example, long-chain fatty acids can be separated from vegetable oils by high-vacuum distillation but more economically by extraction with liquid propane. Tantalum and niobium can be separated by very tedious fractional crystallization of the double fluorides with potassium but with relative ease by liquid extraction of the hydrofluoric acid solutions with methyl isobutyl ketone.

**As a substitute for chemical methods** Chemical methods consume reagents and frequently lead to expensive disposal problems for chemical by-products. Liquid extraction, which incurs no chemical consumption or by-product production, can be less costly. Metal separations such as uranium-vanadium, hafnium-zirconium, and tungsten-molybdenum and the fission products of atomic-energy processes are more economical by liquid extraction. Even lower-cost metals such as copper and inorganic chemicals such as phosphoric acid, boric acid, and the like are economically purified by liquid extraction, despite the fact that the cost of solvent recovery must be included in the final reckoning.

**For separations not now possible by other methods** In distillation, where the vapor phase is created from the liquid by addition of heat, the vapor and liquid are necessarily composed of the same substances and are therefore chemically very similar. The separations produced then depend upon the vapor pressures of the substances. In liquid extraction, in contrast, the major constituents of the two phases are chemically very different, and this makes separations according to chemical type possible. For example, aromatic and paraffinic hydrocarbons

$Y$ = weight fraction C in the extract liquids on a B-free basis, mass C/(mass A + mass C)

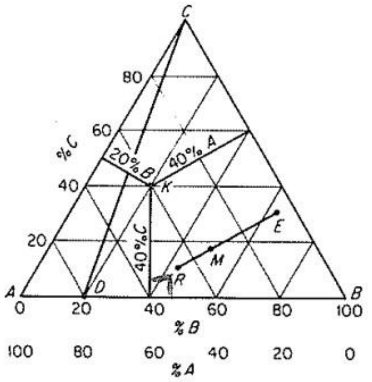
$N$ = weight fraction B on a B-free basis, mass B/(mass A + mass C)

Subscripts identify the solution or mixture to which the concentration terms refer. Stages are identified by number. Thus, $x_3$ = wt fraction C in the raffinate from stage 3, $Y_3$ = wt fraction C (B-free basis) in the extract from stage 3, etc. For other solutions identified by a letter on a phase diagram, the same letter is used as an identifying subscript. Thus, $x_M$ = wt fraction C in the mixture $M$. An asterisk specifically identifies equilibrium concentrations where the condition of equilibrium is emphasized. Thus, $y_E^*$ = wt fraction C in the equilibrium solution $E$.

4. Throughout the discussion of equilibria, material balances, and stagewise calculations, mole fractions, mole ratios, and kilomoles may be consistently substituted for weight fractions, weight ratios, and kilograms, respectively.

## Equilateral-Triangular Coordinates

These are used extensively in the chemical literature to describe graphically the concentrations in ternary systems. It is the property of an equilateral triangle that the sum of the perpendicular distances from any point within the triangle to the three sides equals the altitude of the triangle. We can therefore let the altitude represent 100 percent composition and the distances to the three sides the percentages or fractions of the three components. Refer to Fig. 10.1. Each apex of the triangle represents one of the pure components, as marked. The perpendicular distance from any point such as $K$ to the base $AB$ represents the percentage of C in the mixture at $K$, the distance to the base $AC$ the percentage of B, and that to the base $CB$ the percentage of A. Thus $x_K = 0.4$. Any point on a side of the triangle represents a binary mixture. Point $D$, for example, is a binary containing 80 percent A, 20 percent B. All points on the line $DC$ represent mixtures containing the same ratio of A to B and can be considered as



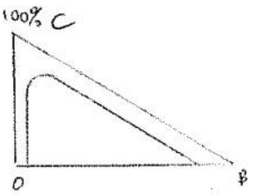


Figure 10.1 Equilateral-triangular coordinates.

mixtures originally at $D$ to which C has been added. If $R$ kg of a mixture at point $R$ is added to $E$ kg of a mixture at $E$, the new mixture is shown on the straight line $RE$ at point $M$, such that

$$\frac{R}{E} = \frac{\text{line } ME}{\text{line } RM} = \frac{x_E - x_M}{x_M - x_R} \tag{10.1}$$

inverse
lever arm
rule

Alternatively the composition corresponding to point $M$ can be computed by material balances, as will be shown later. Similarly, if a mixture at $M$ has removed from it a mixture of composition $E$, the new mixture is on the straight line $EM$ extended in the direction away from $E$ and located at $R$ so that Eq. (10.1) applies.

**Equation (10.1) is readily established. Refer to Fig. 10.2, which again shows $R$ kg of mixture at $R$ added to $E$ kg of mixture at $E$. Let $M$ represent the kilograms of new mixture as well as the composition on the figure. Line $RL$ = weight fraction C in $R = x_R$, line $MO$ = weight fraction C in $M = x_M$, and line $ET$ = weight fraction C in $E = x_E$. A total material balance,**

$$R + E = M$$

**A balance for component C,**

$$R(\text{line } RL) + E(\text{line } ET) = M(\text{line } MO)$$
$$Rx_R + Ex_E = Mx_M$$

**Eliminating $M$, we get**

$$\frac{R}{E} = \frac{\text{line } ET - \text{line } MO}{\text{line } MO - \text{line } RL} = \frac{x_E - x_M}{x_M - x_R}$$

**But line $ET$ − line $MO$ = line $EP$, and line $MO$ − line $RL$ = line $MK$ = line $PS$. Therefore**

$$\frac{R}{E} = \frac{\text{line } EP}{\text{line } PS} = \frac{\text{line } ME}{\text{line } RM}$$

The following discussion is limited to those types of systems which most frequently occur in liquid-extraction operations. For a complete consideration of the many types of systems which may be encountered, the student is referred to one of the more comprehensive texts on the phase rule [51].

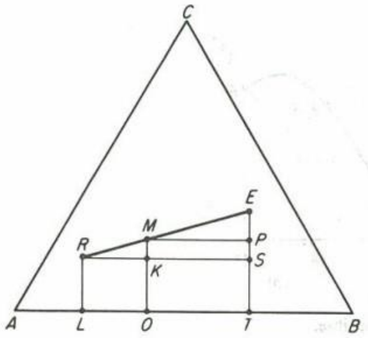


**Figure 10.2** The mixture rule.

## Systems of Three Liquids—One Pair Partially Soluble

This is the most common type of system in extraction, and typical examples are water (A)–chloroform (B)–acetone (C) and benzene (A)–water (B)–acetic acid (C). The triangular coordinates are used as *isotherms*, or diagrams at constant temperature. Refer to Fig. 10.3*a*. Liquid C dissolves completely in A and B, but A and B dissolve only to a limited extent in each other to give rise to the saturated liquid solutions at *L* (A-rich) and at *K* (B-rich). The more insoluble the liquids A and B, the nearer the apexes of the triangle will points *L* and *K* be located. A binary mixture *J*, anywhere between *L* and *K*, will separate into two insoluble liquid phases of compositions at *L* and *K*, the relative amounts of the phases depending upon the position of *J*, according to the principle of Eq. (10.1).

Curve *LRPEK* is the binodal solubility curve, indicating the change in solubility of the A- and B-rich phases upon addition of C. Any mixture outside this curve will be a homogeneous solution of one liquid phase. Any ternary mixture underneath the curve, such as *M*, will form two insoluble, saturated liquid phases of equilibrium compositions indicated by *R* (A-rich) and *E* (B-rich). The line *RE* joining these equilibrium compositions is a tie line, which must necessarily pass through point *M* representing the mixture as a whole. There are an infinite number of tie lines in the two-phase region, and only a few are shown. They are rarely parallel and usually change their slope slowly in one direction as shown. In a relatively few systems the direction of the tie-line slope changes, and one tie line will be horizontal. Such systems are said to be *solutropic*. Point *P*, the *plait point*, the last of the tie lines and the point where the A-rich and B-rich solubility curves merge, is ordinarily not at the maximum value of C on the solubility curve.

The percentage of C in solution *E* is clearly greater than that in *R*, and it is said that in this case the distribution of C favors the B-rich phase. This is

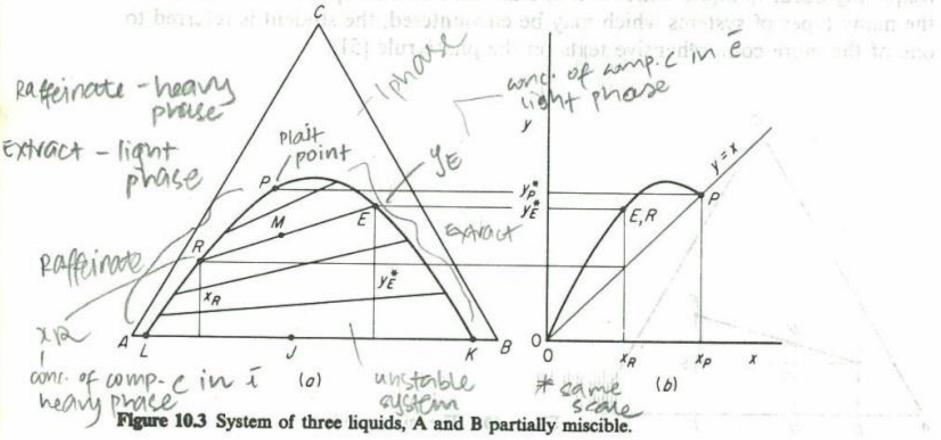


**Figure 10.3** System of three liquids, A and B partially miscible.

conveniently shown on the distribution diagram (Fig. 10.3*b*), where the point $(E, R)$ lies above the diagonal $y = x$. The ratio $y^*/x$, the *distribution coefficient*, is in this case greater than unity. The concentrations of C at the ends of the tie lines, when plotted against each other, give rise to the distribution curve shown. Should the tie lines on Fig. 10.3*a* slope in the opposite direction, with C favoring A at equilibrium, the distribution curve will lie below the diagonal. The distribution curve may be used for interpolating between tie lines when only a few have been experimentally determined. Other methods of interpolation are also available [72].

**Effect of temperature** To show the effect of temperature in detail requires a three-dimensional figure, as in Fig. 10.4*a*, where temperature is plotted vertically and the isothermal triangles are seen to be sections through the prism. For most systems of this type, the mutual solubility of A and B increases with increasing temperature, and above some temperature $t_4$, the critical solution temperature, they dissolve completely. The increased solubility at higher temperatures influences the ternary equilibria considerably, and this is best shown by projection of the isotherms onto the base triangle, as in Fig. 10.4*b*. Not only does the area of heterogeneity decrease at higher temperatures, but the slopes of the tie lines may also change. Liquid-extraction operations, which depend upon the formation of insoluble liquid phases, must be carried on at temperatures below $t_4$. Other, less common, temperature effects are also known [51, 72].

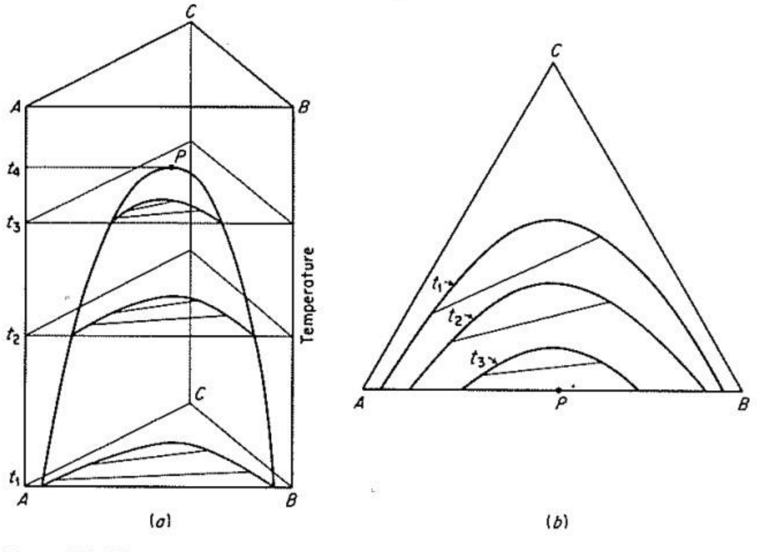


**Figure 10.4** Effect of temperature on ternary equilibria.

**Effect of pressure** Except at very high pressures, the influence of pressure on the liquid equilibrium is so small that it can generally be ignored. All the diagrams shown are therefore to be considered as having been plotted at sufficiently high pressure to maintain a completely condensed system, i.e., above the vapor pressures of the solutions. However, should the pressure be sufficiently reduced to become less than the vapor pressure of the solutions, a vapor phase will appear and the liquid equilibrium will be interrupted. Such an effect on a binary solubility curve of the type *APB* of Fig. 10.4*a* is shown in Fig. 9.8.

## Systems of Three Liquids—Two Pairs Partially Soluble

This type is exemplified by the system chlorobenzene (A)–water (B)–methyl ethyl ketone (C), where A and C are completely soluble, while the pairs A–B and B–C show only limited solubility. Refer to Fig. 10.5*a*, a typical isotherm. At the prevailing temperature, points *K* and *J* represent the mutual solubilities of A and B and points *H* and *L* those of B and C. Curves *KRH* (A-rich) and *JEL* (B-rich) are the ternary solubility curves, and mixtures outside the band between these curves form homogeneous single-phase liquid solutions. Mixtures such as *M*, inside the heterogeneous area, form two liquid phases at equilibrium at *E* and *R*, joined on the diagram by a tie line. The corresponding distribution curve is shown in Fig. 10.5*b*.

**Effect of temperature** Increased temperature usually increases the mutual solubilities and at the same time influences the slope of the tie lines. Figure 10.6 is typical of the effect that can be expected. Above the critical solution temperature of the binary B–C at $t_3$, the system is similar to the first type discussed. Other temperature effects are also possible [51, 72].

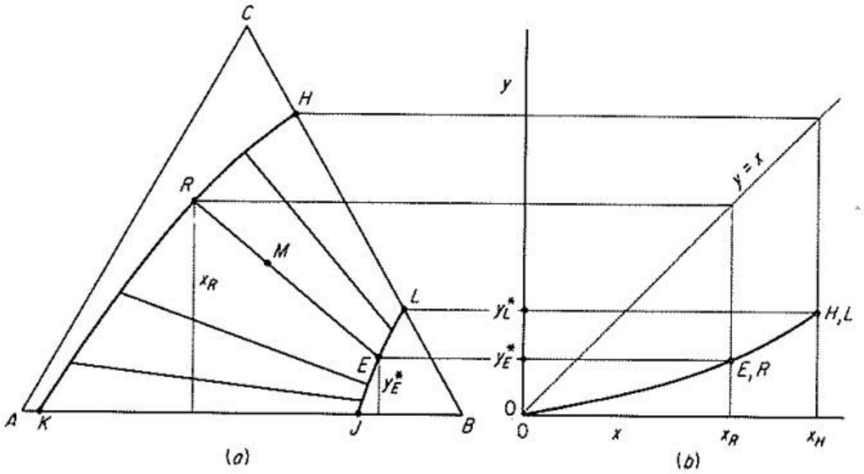


**Figure 10.5** System of three liquids, A–B and B–C partially miscible.

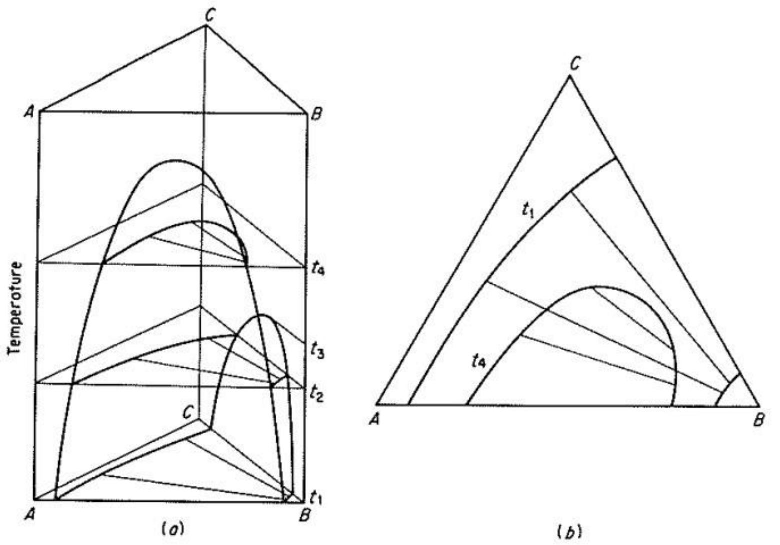


**Figure 10.6** Effect of temperature on ternary equilibria.

## Systems of Two Partially Soluble Liquids and One Solid

When the solid does not form compounds such as hydrates with the liquids, the system will frequently have the characteristics of the isotherm of Fig. 10.7, an example of which is the system naphthalene (C)–aniline (A)–isooctane (B). Solid C dissolves in liquid A to form a saturated solution at *K* and in liquid B to give the saturated solution at *L*. A and B are soluble only to the extent shown at *H*

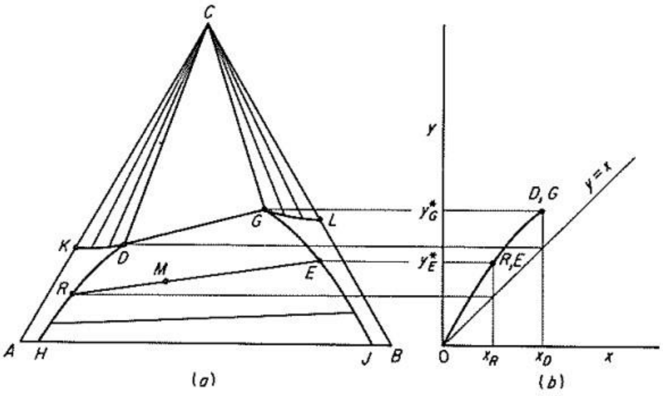


**Figure 10.7** System of two partially soluble liquids A and B and one solid C.

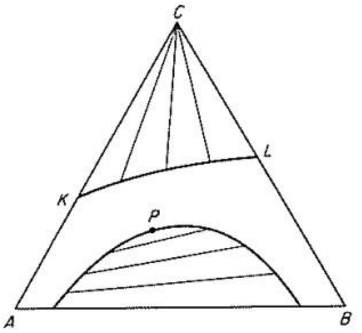


**Figure 10.8** System of two partially soluble liquids A and B and one solid C.

and $J$. Mixtures in the regions $AKDH$ and $BLGJ$ are homogeneous liquid solutions. The curves $KD$ and $GL$ show the effect of adding A and B upon the solubilities of the solid. In the region $HDGJ$ two liquid phases form: if C is added to the insoluble liquids $H$ and $J$ to give a mixture $M$, the equilibrium liquid phases will be $R$ and $E$, joined by a tie line. All mixtures in the region $CDG$ consist of three phases, solid C, and saturated liquid solutions at $D$ and $G$. Liquid-extraction operations are usually confined to the region of the two liquid phases, which is that corresponding to the distribution curve shown.

Increased temperature frequently changes these systems to the configuration shown in Fig. 10.8.

## Other Coordinates

Because the equilibrium relationship can rarely be expressed algebraically with any convenience, extraction computations must usually be made graphically on a phase diagram. The coordinate scales of equilateral triangles are necessarily

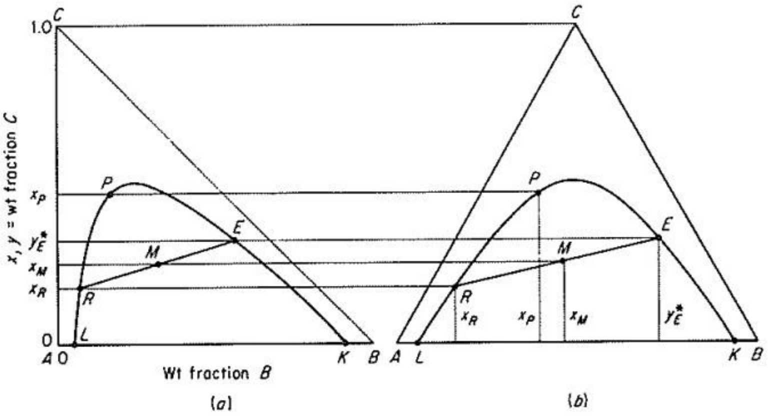
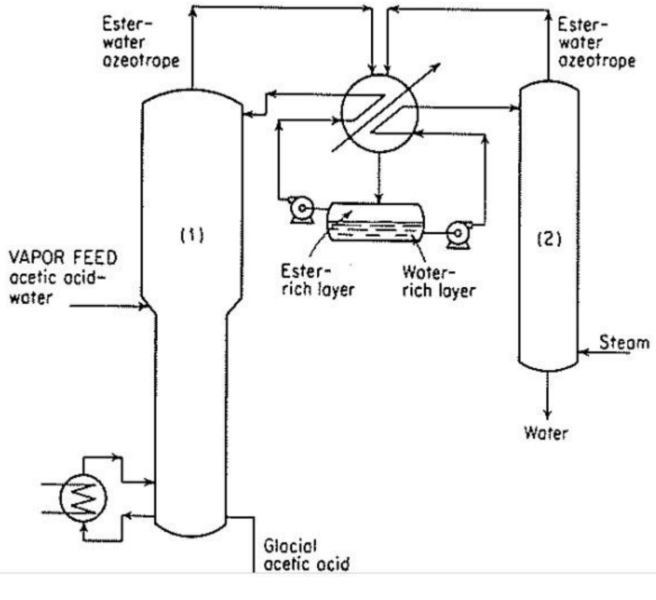


**Figure 10.9** Rectangular coordinates.

## Azeotropic Distillation

This is a special case of multicomponent distillation [23] used for separation of binary mixtures which are either difficult or impossible to separate by ordinary fractionation. If the relative volatility of a binary mixture is very low, the continuous rectification of the mixture to give nearly pure products will require high reflux ratios and correspondingly high heat requirements, as well as towers of large cross section and numbers of trays. In other cases the formation of a binary azeotrope may make it impossible to produce nearly pure products by ordinary fractionation. Under these circumstances a third component, sometimes called an *entrainer*, may be added to the binary mixture to form a new low-boiling azeotrope with one of the original constituents, whose volatility is such that it can easily be separated from the other original constituent.

As an example of such an operation, consider the flowsheet of Fig. 9.53 for the azeotropic separation of acetic acid–water solutions, using butyl acetate as entrainer [39]. Acetic acid can be separated from water by ordinary methods, but only at great expense because of the low relative volatility of the constituents despite their fairly large difference in boiling points at atmospheric pressure (nbp acetic acid = 118.1°C, nbp water = 100°C). Butyl acetate is only slightly soluble in water and consequently forms a heteroazeotrope with it (bp = 90.2°C). Therefore if at least sufficient butyl acetate is added to the top of the distillation column (1) to form the azeotrope with all the water in the binary feed, the azeotrope can readily be distilled from the high-boiling acetic acid, which leaves as a residue product. The heteroazeotrope on condensation forms two insoluble liquid layers, one nearly pure water but saturated with ester, the other nearly pure ester saturated with water. The latter is returned to the top of the column as reflux and is the source of the entrainer in the column. The former can be stripped of its small entrainer content in a second small column (2). The separation of the heteroazeotrope from acetic acid is readily done, so that relatively few trays are required in the principal tower. On the other hand, heat must be supplied, not only to vaporize the water in the overhead distillate, but to vaporize the entrainer as well. The operation can also be done batchwise, in which case sufficient entrainer is charged to the still kettle, together with the feed, to azeotrope the water. The azeotrope is then distilled overhead.



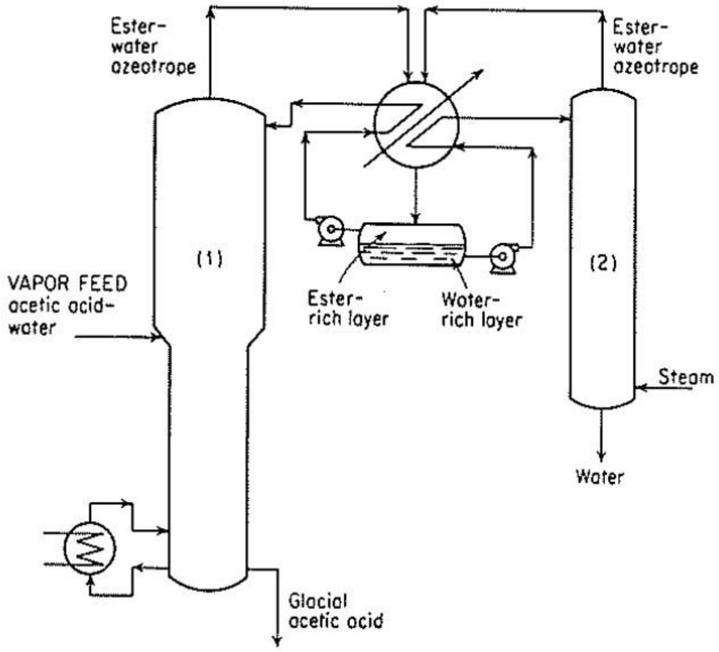


**Figure 9.53** Azeotropic distillation of acetic acid–water with butyl acetate.

Sometimes the new azeotrope which is formed contains all three constituents. The dehydration of ethanol-water mixture with benzene as added substance is an example. Dilute ethanol-water solutions can be continuously rectified to give at best mixtures containing 89.4 mole percent ethanol at atmospheric pressure, since this is the composition of the minimum-boiling azeotrope in the binary system. By introducing benzene into the top of a column fed with an ethanol-water mixture, the ternary azeotrope containing benzene (53.9 mol %), water (23.3 mol %), ethanol (22.8 mol %), boiling at 64.9°C, is readily separated from the ethanol (bp = 78.4°C), which leaves as a residue product. In this case also the azeotropic overhead product separates into two liquid layers, one rich in benzene which is returned to the top of the column as reflux, the other rich in water which is withdrawn. Since the latter contains appreciable quantities of both benzene and ethanol, it must be rectified separately. The ternary azeotrope contains nearly equal molar proportions of ethanol and water, and consequently dilute ethanol-water solutions must be given a preliminary rectification to produce substantially the alcohol-rich binary azeotrope which is used as a feed.

In still other cases the new azeotrope which is formed does not separate into two insoluble liquids, and special means for separating it, such as liquid extraction, must be provided, but this is less desirable.

It is clear that the choice of entrainer is a most important consideration. The added substance should preferably form a low-boiling azeotrope with only one of the constituents of the binary mixture it is desired to separate, preferably the