

DISTILLATION

Distillation is a method of separating the components of a solution which depends upon the distribution of the substances between a gas and a liquid phase, applied to cases where all components are present in both phases. Instead of introducing a new substance into the mixture in order to provide the second phase, as is done in gas absorption or desorption, the new phase is created from the original solution by vaporization or condensation.

In order to make clear the distinction between distillation and the other operations, let us cite a few specific examples. In the separation of a solution of common salt and water, the water can be completely vaporized from the solution without removal of salt since the latter is for all practical purposes quite nonvolatile at the prevailing conditions. This is the operation of evaporation. Distillation, on the other hand, is concerned with the separation of solutions where all the components are appreciably volatile. In this category, consider the separation of the components of a liquid solution of ammonia and water. By contacting the ammonia-water solution with air, which is essentially insoluble in the liquid, the ammonia can be stripped or desorbed by processes which were discussed in Chap. 8, but the ammonia is then mixed with water vapor and air and is not obtained in pure form. On the other hand, by application of heat, we can partially vaporize the solution and thereby create a gas phase consisting of nothing but water and ammonia. And since the gas will be richer in ammonia than the residual liquid, a certain amount of separation will have resulted. By appropriate manipulation of the phases or by repeated vaporizations and condensations it is then ordinarily possible to make as complete a separation as may be desired, recovering both components of the mixture in as pure a state as we wish.

The advantages of such a separation method are clear. In distillation the new phase differs from the original by its heat content, but heat is readily added or removed, although of course the cost of doing this must inevitably be considered. Absorption or desorption operations, on the other hand, which depend upon the introduction of a foreign substance, provide us with a new solution which in turn may have to be separated by one of the diffusional operations unless it happens that the new solution is useful directly.

There are in turn certain limitations to distillation as a separation process. In absorption or similar operations, where it has been agreed to introduce a foreign substance to provide a new phase for distribution purposes, we can ordinarily choose from a great variety of solvents in order to provide the greatest possible separation effect. For example, since water is ineffectual in absorbing hydrocarbon gases from a gas mixture, we choose instead a hydrocarbon oil which provides a high solubility. But in distillation there is no such choice. The gas which can be created from a liquid by application of heat inevitably consists only of the components constituting the liquid. Since the gas is therefore chemically very similar to the liquid, the change in composition resulting from the distribution of the components between the two phases is ordinarily not very great. Indeed, in some cases the change in composition is so small that the process becomes impractical; it may even happen that there is no change in composition whatsoever.

Nevertheless the direct separation, which is ordinarily possible by distillation, into pure products requiring no further processing has made this perhaps the most important of all the mass-transfer operations.

VAPOR-LIQUID EQUILIBRIA

The successful application of distillation methods depends greatly upon an understanding of the equilibria existing between the vapor and liquid phases of the mixtures encountered. A brief review of these is therefore essential. The emphasis here will be on binary mixtures.

Pressure-Temperature-Concentration Phase Diagram

Let us first consider binary mixtures which we shall term *ordinary*; by this is meant that the liquid components dissolve in all proportions to form homogeneous solutions which are not necessarily ideal and that no complications of maximum or minimum boiling points occur. We shall consider component A of the binary mixture A-B as the more volatile, i.e., the vapor pressure of pure A at any temperature is higher than the vapor pressure of pure B. The vapor-liquid equilibrium for each pure substance of the mixture is of course its vapor-pressure-temperature relationship, as indicated in Fig. 7.1. For binary mixtures an additional variable, concentration, must likewise be considered. Mole fractions are the most convenient concentration terms to use, and throughout this discus-

sion x will be the mole fraction of the more volatile substance A in the liquid and y^* the corresponding equilibrium mole fraction of A in the vapor.

Complete graphical representation of the equilibria requires a three-dimensional diagram [29, 47], as in Fig. 9.1. The curve marked p_A is the vapor-pressure curve of A, lying entirely in the nearest composition plane at $x = 1.0$. The curve extends from its critical point C_A to its triple point T_A , but the complications of the solid phase which do not enter into distillation operations will not be considered. Similarly curve p_B is the vapor pressure of pure B, in the far plane at $x = 0$. The liquid and vapor regions at compositions between $x = 0$ and 1.0 are separated by a double surface which extends smoothly from p_A to p_B . The shape of this double surface is most readily studied by considering sections at constant pressure and constant temperature, examples of which are shown in the figure.

Constant-Pressure Equilibria

Consider first a typical section at constant pressure (Fig. 9.2a). The intersection of the double surface of Fig. 9.1 with the constant-pressure plane produces a looped curve without maxima or minima extending from the boiling point of pure B to that of pure A at the pressure in question. The upper curve provides the temperature-vapor composition (t - y^*) relationship, the lower that of the temperature-liquid composition (t - x). Liquid and vapor mixtures at equilibrium are at the same temperature and pressure throughout, so that horizontal *tie lines*

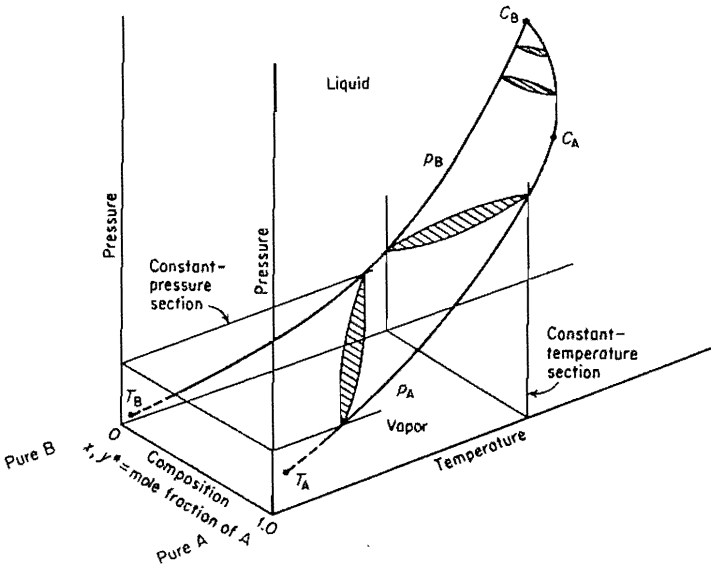


Figure 9.1 Binary vapor-liquid equilibria.

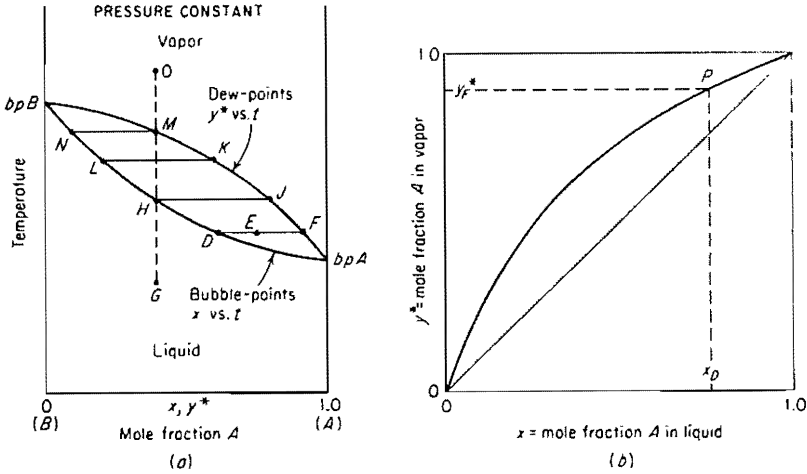


Figure 9.2 Constant-pressure vapor-liquid equilibria.

such as line DF join equilibrium mixtures at D and F . There are an infinite number of such tie lines for this diagram. A mixture on the lower curve, as at point D , is a saturated liquid; a mixture on the upper curve, as at F , is a saturated vapor. A mixture at E is a two-phase mixture, consisting of a liquid phase of composition at D and a vapor phase of composition at F in such proportions that the average composition of the entire mixture is represented by E . The relative amounts of the equilibrium phases are related to the segments of the tie line,

$$\frac{\text{Moles of } D}{\text{Moles of } F} = \frac{\text{line } EF}{\text{line } DE} \quad (9.1)$$

Consider a solution at G in a closed container which can be kept at constant pressure by moving a piston. The solution is entirely liquid. If it is heated, the first bubble of vapor forms at H and has the composition at J , richer in the more volatile substance, and hence the lower curve is called the *bubble-point-temperature curve*. As more of the mixture is vaporized, more of the vapor forms at the expense of the liquid, giving rise, for example, to liquid L and its equilibrium vapor K , although the composition of the entire mass is still the original as at G . The last drop of liquid vaporizes at M and has the composition at N . Superheating the mixture follows the path MO . The mixture has vaporized over a temperature range from H to M , unlike the single vaporization temperature of a pure substance. Thus, the term *boiling point* for a solution ordinarily has no meaning since vaporization occurs over a temperature range, i.e., from the bubble point to the dew point. If the mixture at O is cooled, all the phenomena reappear in reverse order. Condensation, for example, starts at M , whence the upper curve is termed the dew-point curve, and continues to H .

If a solution like that at H is boiled in an open vessel, on the other hand, with the vapors escaping into the atmosphere, since the vapor is richer in the more volatile substance, the liquid residue must therefore become leaner. The temperature and composition of the saturated residual liquid therefore move along the lower curve toward N as the distillation proceeds.

The vapor-liquid equilibrium compositions can also be shown on a distribution diagram (x vs. y^*) as in Fig. 9.2*b*. Point P on the diagram represents the tie line DF , for example. Since the vapor is richer in the more volatile substance, the curve lies above the 45° diagonal line, which has been drawn in for comparison.

Relative Volatility

The greater the distance between the equilibrium curve and the diagonal of Fig. 9.2*b*, the greater the difference in liquid and vapor compositions and the easier the separation by distillation. One numerical measure of this is called the *separation factor* or, particularly in the case of distillation, the *relative volatility* α . This is the ratio of the concentration ratio of A and B in one phase to that in the other and is a measure of the separability,

$$\alpha = \frac{y^*/(1-y^*)}{x/(1-x)} = \frac{y^*(1-x)}{x(1-y^*)} \quad (9.2)$$

The value of α will ordinarily change as x varies from 0 to 1.0. If $y^* = x$ (except at $x = 0$ or 1), $\alpha = 1.0$ and no separation is possible. The larger the value of α above unity, the greater the degree of separability.

Increased Pressures

At higher pressures the sections at constant pressure will of course intersect the double surface of Fig. 9.1 at increased temperatures. The intersections can be projected onto a single plane, as in Fig. 9.3*a*. It should be noted that not only do the looped curves occur at higher temperatures, but they also usually become narrower. This is readily seen from the corresponding distribution curves of Fig. 9.3*b*. The relative volatilities and hence the separability therefore usually become less at higher pressures. As the critical pressure of one component is exceeded, there is no longer a distinction between vapor and liquid for that component, and for mixtures the looped curves are therefore shorter, as at pressures above p_{13} , the critical pressure for A in the figure. Distillation separations can be made only in the region where a looped curve exists.

For particular systems, the critical pressure of the less volatile substance may be reached before that of the more volatile, and it is also possible that the double surface of Fig. 9.1 will extend at intermediate compositions to a small extent beyond the critical pressures of either substance.

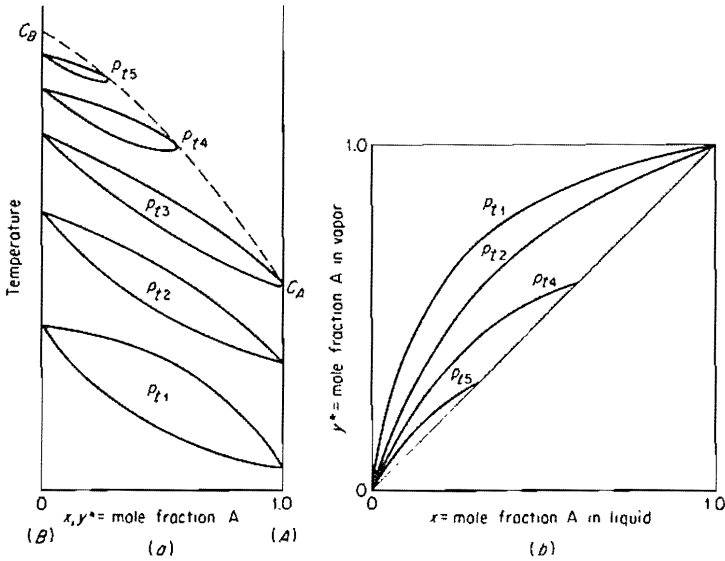


Figure 9.3 Vapor-liquid equilibria at increased pressures.

Constant-Temperature Equilibria

A typical constant-temperature section of the three-dimensional phase diagram is shown in Fig. 9.4. The intersection of the constant-temperature plane with the double surface of Fig. 9.1 provides the two curves which extend without maxima or minima from the vapor pressure of pure B to that of pure A. As before, there are an infinite number of horizontal tie lines, such as TV , which join an

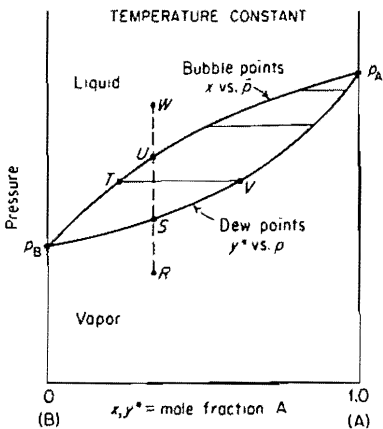


Figure 9.4 Constant-temperature vapor-liquid equilibria.

equilibrium vapor as at V to its corresponding liquid at T . A solution in a closed container at W is entirely a liquid, and if the pressure is reduced at constant temperature, the first bubble of vapor forms at U , complete vaporization occurs at S , and further reduction in pressure results in a superheated vapor as at R .

Vapor-liquid equilibrium data, except in the special situations of ideal and regular solutions, must be determined experimentally. Descriptions of experimental methods [18], extensive bibliographies [67], and lists of data [7, 22] are available.

Ideal Solutions—Raoult's Law

Before studying the characteristics of mixtures which deviate markedly from those just described, let us consider the equilibria for the limiting case of mixtures whose vapors and liquids are ideal. The nature of ideal solutions and the types of mixtures which approach ideality were discussed in Chap. 8.

For an ideal solution, the equilibrium partial pressure \bar{p}^* of a constituent at a fixed temperature equals the product of its vapor pressure p when pure at this temperature and its mole fraction in the liquid. This is Raoult's law.

$$\bar{p}_A^* = p_A x \quad \bar{p}_B^* = p_B(1 - x) \quad (9.3)$$

If the vapor phase is also ideal,

$$p_i = \bar{p}_A^* + \bar{p}_B^* = p_A x + p_B(1 - x) \quad (9.4)$$

and the total as well as the partial pressures are linear in x at a fixed temperature. These relationships are shown graphically in Fig. 9.5. The equilibrium vapor composition can then be computed at this temperature. For example, the value of y^* at point D on the figure equals the ratio of the

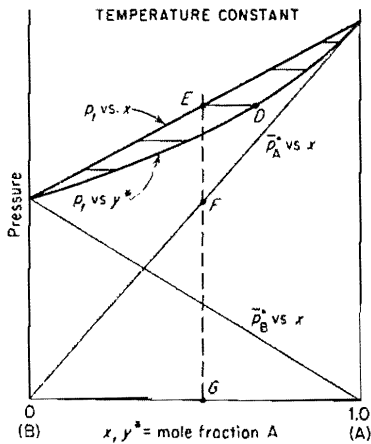


Figure 9.5 Ideal solutions.

distances FG to EG ,

$$y^* = \frac{\bar{p}_A^*}{p_i} = \frac{p_A x}{p_i} \quad (9.5)$$

$$1 - y^* = \frac{\bar{p}_B^*}{p_i} = \frac{p_B(1-x)}{p_i} \quad (9.6)$$

The relative volatility α is, by substitution in Eq. (9.2),

$$\alpha = \frac{p_A}{p_B} \quad (9.7)$$

For ideal solutions, it is then possible to compute the entire vapor-liquid equilibria from the vapor pressures of the pure substances. For pressures too high to apply the ideal-gas law, fugacities are used instead of pressures [29, 42]. It is also possible to compute the equilibria for the special class of solutions known as *regular* [21]. For all other mixtures, however, it is necessary to obtain the data experimentally.

Illustration 9.1 Compute the vapor-liquid equilibria at constant pressure of 1 std atm for mixtures of *n*-heptane with *n*-octane, which may be expected to form ideal solutions.

SOLUTION The boiling points at 1 std atm of the substances are *n*-heptane (A), 98.4°C and *n*-octane (B), 125.6°C. Computations are therefore made between these temperatures. For example, at 110°C, $p_A = 1050$ mmHg, $p_B = 484$ mmHg, $p_i = 760$ mmHg. Eq. (9.4):

$$x = \frac{p_i - p_B}{p_A - p_B} = \frac{760 - 484}{1050 - 484} = 0.487 \text{ mole fraction heptane in liquid}$$

Eq. (9.5):

$$y^* = \frac{p_A x}{p_i} = \frac{1050(0.487)}{760} = 0.674 \text{ mole fraction heptane in vapor}$$

Eq. (9.7):

$$\alpha = \frac{p_A}{p_B} = \frac{1050}{484} = 2.17$$

In similar fashion, the data of the following table can be computed:

$t, ^\circ\text{C}$	p_A, mmHg	p_B, mmHg	x	y^*	α
98.4	760	333	1.0	1.0	2.28
105	940	417	0.655	0.810	2.25
110	1050	484	0.487	0.674	2.17
115	1200	561	0.312	0.492	2.14
120	1350	650	0.1571	0.279	2.08
125.6	1540	760	0	0	2.02

Curves of the type of Fig. 9.2 can now be plotted. Note that although the vapor pressures of the pure substances vary considerably with temperature, α for ideal solutions does not. In this case, an average of the computed α 's is 2.16, and substituting this in Eq. (9.2), rearranged,

$$y^* = \frac{\alpha x}{1 + x(\alpha - 1)} = \frac{2.16x}{1 + 1.16x}$$

provides an expression which for many purposes is a satisfactory empirical relation between y^* and x for this system at 1 atm.

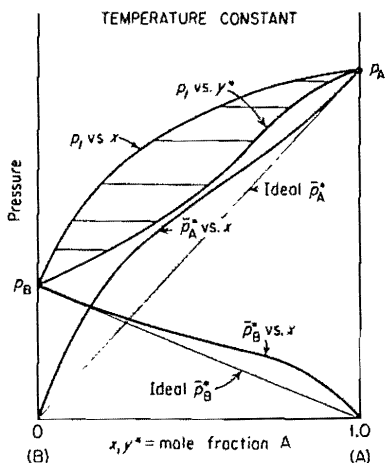


Figure 9.6 Positive deviations from ideality.

Positive Deviations from Ideality

A mixture whose total pressure is greater than that computed for ideality [Eq. (9.4)] is said to show positive deviations from Raoult's law. Most mixtures fall into this category. In these cases the partial pressures of each component are larger than the ideal, as shown in Fig. 9.6.† It should be noted that as the concentration for each component approaches unity mole fraction, the partial pressures for that substance approach ideality tangentially. Raoult's law, in other words, is nearly applicable to the substance present in very large concentrations. This is the case for all substances except where association within the vapor or electrolytic dissociation within the liquid occurs.

The distribution diagram (x vs. y^*) for systems of this type appears much the same as that of Fig. 9.2*b*.

Minimum-boiling mixtures—azeotropes When the positive deviations from ideality are sufficiently large and the vapor pressures of the two components are not too far apart, the total-pressure curves at constant temperature may rise through a maximum at some concentration, as in Fig. 9.7*a*. Such a mixture is said to form an *azeotrope*, or *constant-boiling mixture*. The significance of this is more readily seen by study of the constant-pressure section (Fig. 9.7*b* or *c*). The liquid- and vapor-composition curves are tangent at point *L*, the point of

† The ratio of the actual equilibrium partial pressure of a component \bar{p}^* to the ideal value px is the activity coefficient referred to the pure substance: $\gamma = \bar{p}^*/px$. Since γ is greater than unity in these cases and $\log \gamma$ is therefore positive, the deviations are termed positive deviations from ideality. A very extensive science of the treatment of nonideal solutions through activity coefficients has been developed by which, from a very small number of data, all the vapor-liquid equilibria of a system can be predicted [42].

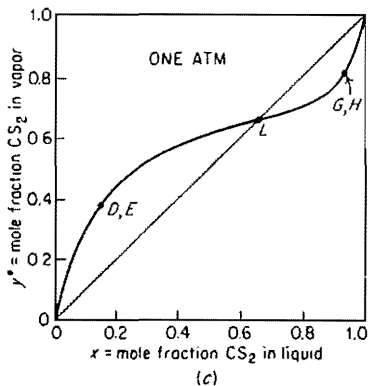
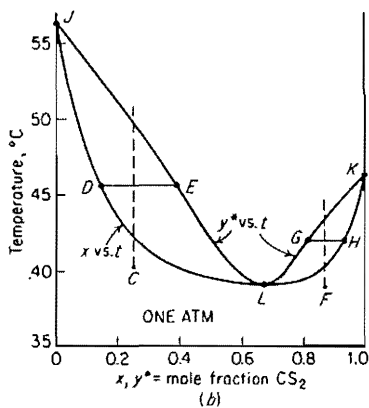
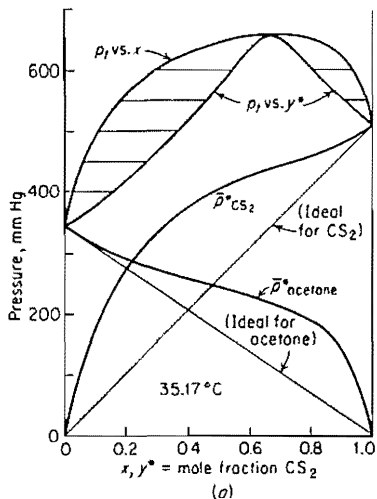


Figure 9.7 Minimum-boiling azeotropism in the system carbon disulfide-acetone: (a) at constant temperature; (b) and (c) at constant pressure.

azeotropism at this pressure, which represents the minimum-boiling temperature for this system. For all mixtures of composition less than L , such as those at C , the equilibrium vapor (E) is richer in the more volatile component than the liquid (D). For all mixtures richer than L , however, such as at F , the equilibrium vapor (G) is less rich in the more volatile substance than the liquid (H). A mixture of composition L gives rise to a vapor of composition identical with the liquid, and it consequently boils at constant temperature and without change in composition. If solutions either at D or H are boiled in an open vessel with continuous escape of the vapors, the temperature and composition of the residual liquids in each case move along the lower curve away from point L (toward K for a liquid at H , and toward J for one at D).

Solutions like these cannot be completely separated by ordinary distillation methods at this pressure, since at the azeotropic composition $y^* = x$ and $\alpha = 1.0$.† The azeotropic composition as well as its boiling point changes with pressure. In some cases, changing the pressure may eliminate azeotropism from the system.

Azeotropic mixtures of this sort are very common, and thousands have been recorded [25]. One of the most important is the ethanol-water azeotrope which at 1 atm occurs at 89.4 mole percent ethanol and 78.2°C. Azeotropism disappears in this system at pressures below 70 mmHg.

Partial liquid miscibility Some substances exhibit such large positive deviations from ideality that they do not dissolve completely in the liquid state, e.g., isobutanol-water (Fig. 9.8). The curves through points C and E represent the solubility limits of the constituents at relatively low temperatures. Mixtures of composition and temperature represented by points within the central area, such as point D , form two liquid phases at equilibrium at C and E , and line CE is a liquid tie line. Mixtures in the regions on either side of the solubility limits such as at F are homogeneous liquids. The solubility ordinarily increases with increased temperature, and the central area consequently decreases in width. If the pressure were high enough for vaporization not to occur, the liquid-solubility curves would continue along the broken extensions as shown. At the prevailing pressure, however, vaporization occurs before this can happen, giving rise to the branched vapor-liquid equilibrium curves. For homogeneous liquids such as that at F , the vapor-liquid equilibrium phenomena are normal, and such a mixture boils initially at H to give the first bubble of vapor of composition J . The same is true of any solution richer than M , except that here the vapor is leaner in the more volatile component. Any two-phase liquid mixture within the composition range from K to M will boil at the temperature of the line KM , and all these give rise to the same vapor of composition L . A liquid mixture of average composition L , which produces a vapor of the same composition, is sometimes called a

† For compositions to the right of L (Fig. 9.7) α as usually computed is less than unity, and the reciprocal of α is then ordinarily used.

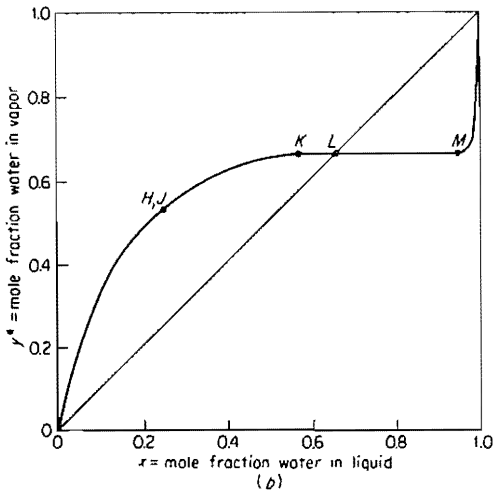
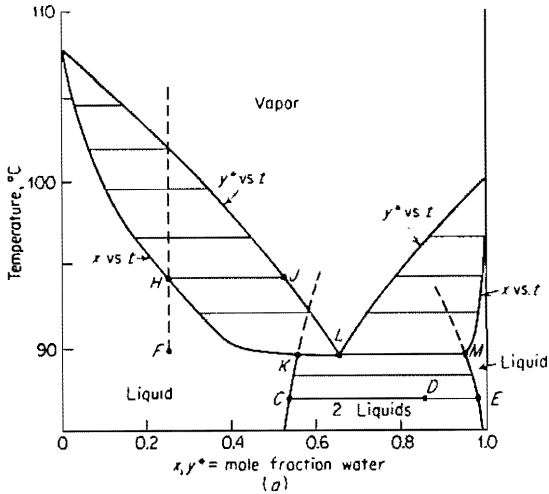


Figure 9.8 Isobutanol-water at 1 std atm.

heteroazeotrope. The corresponding distribution diagram with the tie line HJ , solubility limits at the bubble point K and M , and the azeotropic point L is shown in Fig. 9.8b.

In relatively few instances the azeotropic composition lies outside the limits of solubility, as in the systems methyl ethyl ketone–water and phenol–water. In others, especially when the components have a very large difference in their boiling points, no azeotrope can form, as for ammonia–toluene and carbon dioxide–water.

Insoluble liquids; steam distillation The mutual solubility of some liquids is so small that they can be considered substantially insoluble: points *K* and *M* (Fig. 9.8) are then for all practical purposes on the vertical axes of these diagrams. This is the case for a mixture such as a hydrocarbon and water, for example. If the liquids are completely insoluble, the vapor pressure of either component cannot be influenced by the presence of the other and each exerts its true vapor pressure at the prevailing temperature. When the sum of the separate vapor pressures equals the total pressure, the mixture boils, and the vapor composition is readily computed, assuming the applicability of the simple gas law,

$$p_A + p_B = p_t \quad (9.8)$$

$$y^* = \frac{p_A}{p_t} \quad (9.9)$$

So long as two liquid phases are present, the mixture will boil at the same temperature and produce a vapor of constant composition.

Illustration 9.2 A mixture containing 50 g water and 50 g ethylaniline, which can be assumed to be essentially insoluble, is boiled at standard atmospheric pressure. Describe the phenomena that occur.

SOLUTION Since the liquids are insoluble, each exerts its own vapor pressure, and when the sum of these equals 760 mmHg, the mixture boils.

<i>t</i> , °C	<i>p</i> _A (water), mmHg	<i>p</i> _B (ethylaniline), mmHg	<i>p</i> _t = <i>p</i> _A + <i>p</i> _B , mmHg
38.5	51.1	1	52.1
64.4	199.7	5	205
80.6	363.9	10	374
96.0	657.6	20	678
99.15	737.2	22.8	760
113.2	1225	40	1265
204		760	

The mixture boils at 99.15°C.

$$y^* = \frac{p_A}{p_t} = \frac{737.2}{760} = 0.97 \text{ mole fraction water}$$

$$1 - y^* = \frac{p_B}{p_t} = \frac{22.8}{760} = 0.03 \text{ mole fraction ethylaniline}$$

The original mixture contained 50/18.02 = 2.78 g mol water and 50/121.1 = 0.412 g mol ethylaniline. The mixture will continue to boil at 99.15°C, with an equilibrium vapor of the indicated composition, until all the water has evaporated together with 2.78(0.03/0.97) = 0.086 g mol of the ethylaniline. The temperature will then rise to 204°C, and the equilibrium vapor will be pure ethylaniline.

Note that by this method of distillation with steam, so long as liquid water is present, the high-boiling organic liquid can be made to vaporize at a temperature much lower than its normal boiling point without the necessity of a

vacuum-pump equipment operating at 22.8 mmHg. If boiled at 204°C, this compound will undergo considerable decomposition. However, the heat requirements of the steam-distillation process are great since such a large amount of water must be evaporated simultaneously. Alternatives would be (1) to operate at a different total pressure in the presence of liquid water where the ratio of the vapor pressures of the substances may be more favorable and (2) to sparge superheated steam (or other insoluble gas) through the mixture in the absence of liquid water and to vaporize the ethylaniline by allowing it to saturate the steam.

Negative Deviations from Ideality

When the total pressure of a system at equilibrium is less than the ideal value, the system is said to deviate negatively from Raoult's law. Such a situation is shown in Fig. 9.9 at constant temperature. Note that in this case, as with positive deviations, where neither vapor association nor liquid dissociation occurs, the partial pressures of the constituents of the solution approach ideality as their concentrations approach 100 percent. The constant-pressure diagram for such a case has the same general appearance as the diagrams shown in Fig. 9.2.

Maximum-boiling mixtures—azeotropes When the difference in vapor pressures of the components is not too great and in addition the negative deviations are large, the curve for total pressure against composition may pass through a minimum, as in Fig. 9.10a. This condition gives rise to a maximum in the boiling temperatures, as at point *L* (Fig. 9.10b), and a condition of azeotropism. The equilibrium vapor is leaner in the more volatile substance for liquids whose *x* is less than the azeotropic composition and greater if *x* is larger. Solutions on either side of the azeotrope, if boiled in an open vessel with escape of the vapor, will ultimately leave a residual liquid of the azeotropic composition in the vessel.

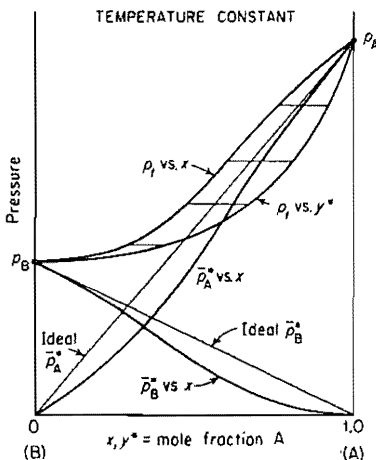


Figure 9.9 Negative deviations from ideality.

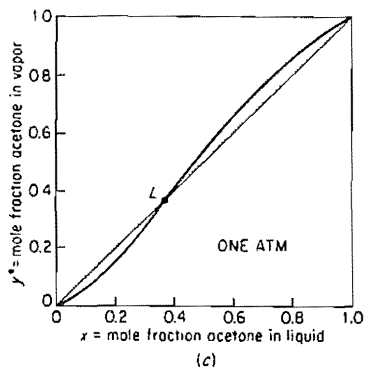
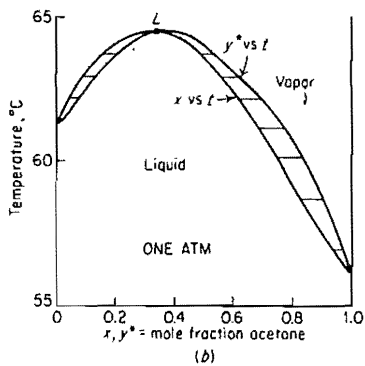
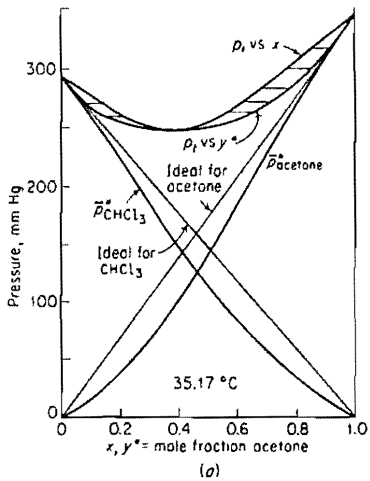


Figure 9.10 Maximum-boiling azeotropism in the system acetone-chloroform: (a) at constant temperature; (b) and (c) at constant pressure.

Maximum-boiling azeotropes are less common than the minimum type. One which is very well known is that of hydrochloric acid–water (11.1 mole percent HCl, 110°C, at 1 std atm), which can be prepared simply by boiling a solution of any strength of the acid in an open vessel. This is one method of standardizing hydrochloric acid.

Enthalpy-Concentration Diagrams

Binary vapor-liquid equilibria can also be plotted on coordinates of enthalpy vs. concentration at constant pressure. Liquid-solution enthalpies include both sensible heat and the heat of mixing the components

$$H_L = C_L(t_L - t_0)M_{av} + \Delta H_S \quad (9.10)$$

where C_L is the heat capacity of the solution, energy/(mol) (degree), and ΔH_S is the heat of solution at t_0 and the prevailing concentration referred to the pure liquid components, energy/mol solution. For saturated liquids, t_L is the bubble point corresponding to the liquid concentration at the prevailing pressure. Heat-of-solution data vary in form, and some adjustment of the units of tabulated data may be necessary. If heat is evolved on mixing, ΔH_S will be negative, and for ideal solutions it is zero. For ideal solutions, the heat capacity is the weighted average of those for the pure components.

For present purposes, saturated-vapor enthalpies can be calculated adequately by assuming that the unmixed liquids are heated separately as liquids to the gas temperature t_G (the dew point), each vaporized at this temperature, and the vapors mixed

$$H_G = y[C_{L,A}M_A(t_G - t_0) + \lambda_A M_A] + (1 - y)[C_{L,B}M_B(t_G - t_0) + \lambda_B M_B] \quad (9.11)$$

where λ_A and λ_B are latent heats of vaporization of pure substances at t_G in energy per mole and $C_{L,A}$ and $C_{L,B}$ are heat capacities of pure liquids, energy/(mole)(degree).

In the upper part of Fig. 9.11, which represents a typical binary mixture, the enthalpies of saturated vapors at their dew points have been plotted vs. y and those of the saturated liquids at their bubble points vs. x . The vertical distances between the two curves at $x = 0$ and 1 represent, respectively, the molar latent heats of B and A. The heat required for complete vaporization of solution C is $H_D - H_C$ energy/mole solution. Equilibrium liquids and vapors may be joined by tie lines, of which line EF is typical. The relation between this equilibrium phase diagram and the xy plot is shown in the lower part of Fig. 9.11. Here the point G represents the tie line EF , located on the lower plot in the manner shown. Other tie lines, when projected to the xy plot, produce the complete equilibrium-distribution curve.

Characteristics of the H_{xy} and xy diagrams [46] Let point M on Fig. 9.11 represent M mol of a mixture of enthalpy H_M and concentration z_M , and

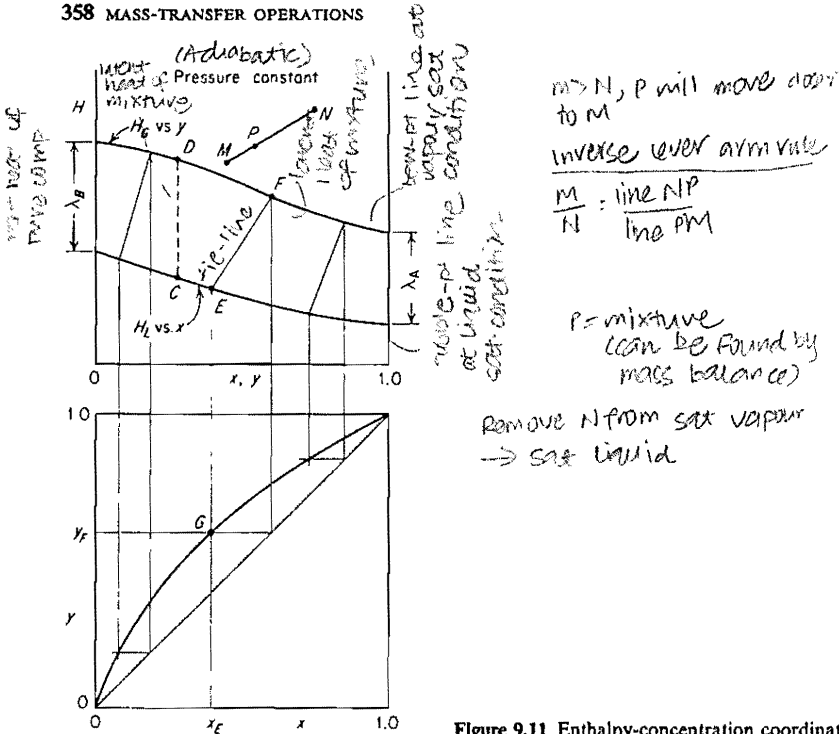


Figure 9.11 Enthalpy-concentration coordinates.

similarly N is N mol of a mixture of properties H_N, z_N . Adiabatic mixing of M and N will produce P mol of a mixture of enthalpy H_P and concentration z_P . A total material balance is

$$M + N = P \tag{9.12}$$

and a balance for component A is

$$Mz_M + Nz_N = Pz_P \tag{9.13}$$

An enthalpy balance is

$$MH_M + NH_N = PH_P \tag{9.14}$$

Elimination of P between Eqs. (9.12) and (9.13) and between (9.12) and (9.14) yields

$$\frac{M}{N} = \frac{z_N - z_P}{z_P - z_M} = \frac{H_N - H_P}{H_P - H_M} \tag{9.15}$$

This is the equation of a straight line on the enthalpy-concentration plot, passing through points (H_M, z_M) , (H_N, z_N) , and (H_P, z_P) . Point P is therefore on the straight line MN , located so that $M/N = \text{line NP}/\text{line PM}$. Similarly if mixture N were removed adiabatically from mixture P , the mixture M would result.

Consider now mixture $C(H_C, z_C)$ in Fig. 9.12. It will be useful to describe such a mixture in terms of saturated vapors and liquids, since distillation is

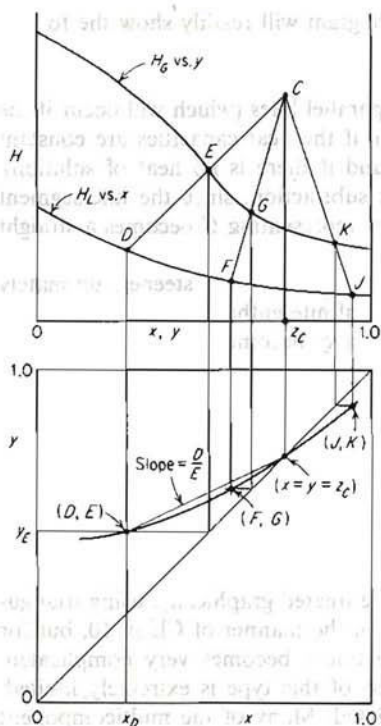


Figure 9.12 Relation between the diagrams.

mostly concerned with such mixtures. C can be considered the result of adiabatically removing saturated liquid D from saturated vapor E (DE is not a tie line), and x_D and y_E can be located on the lower diagram as shown. But C can equally well be considered as having been produced by adiabatically subtracting F from G , or J from K , or indeed by such a combination of saturated liquids and vapors given by any line from C which intersects the saturated-enthalpy curves. These, when projected to the lower diagram, form the curve shown there. Thus any point C on the Hxy diagram can be represented by the difference between saturated vapors and liquids and in turn also by a curve on the xy plot. For the combination $E-D = C$, a material balance shows

$$\frac{D}{E} = \frac{z_C - y_E}{z_C - x_D} = \frac{\text{line } CE}{\text{line } CD} \quad (9.16)$$

This is the equation on the xy diagram of the chord of slope D/E drawn between point (y_E, x_D) and $y = x = z_C$ on the 45° line. Similarly, the ratios F/G and J/K would be shown by the slopes of chords drawn from these points to $y = x = z_C$.

Consideration of the geometry of the diagram will readily show the following:

1. If the $H_G y$ and $H_L x$ curves are straight parallel lines (which will occur if the molar latent heats of A and B are equal, if the heat capacities are constant over the prevailing temperature range, and if there is no heat of solution), then $D/E = F/G = J/K$ for adiabatic subtraction, since the line-segment ratios are then equal, and the curve on xy representing C becomes a straight line.
2. If point C is moved upward, the curve on xy becomes steeper, ultimately coinciding with the 45° line when C is at infinite enthalpy.
3. If point C is on the $H_G y$ curve, the curve on xy becomes a horizontal straight line; if C is on the $H_L x$ curve, the curve on xy becomes a vertical straight line.

These concepts will be useful in understanding the applications of these diagrams.

Multicomponent Systems

Nonideal systems of three components can be treated graphically, using triangular coordinates to express the compositions in the manner of Chap. 10, but for more than three components graphical treatment becomes very complicated. Actually our knowledge of nonideal systems of this type is extremely limited, and relatively few data have been accumulated. Many of the multicomponent systems of industrial importance can be considered nearly ideal in the liquid phase for all practical purposes. This is particularly true for hydrocarbon mixtures of the same homologous series, e.g., those of the paraffin series or the lower-boiling aromatic hydrocarbons.[†] In such cases Raoult's law, or its equivalent in terms of fugacities, can be applied and the equilibria calculated from the properties of the pure components. But it is generally unsafe to predict detailed behavior of a multicomponent system from consideration of the pure components alone, or even from a knowledge of the simple binary systems that may be formed from the components. For example, three-component systems sometimes form ternary azeotropes whose equilibrium vapor and liquid have identical compositions. But the fact that one, two, or three binary azeotropes exist between the components does not make the formation of a ternary azeotrope certain, and a ternary azeotrope need not necessarily coincide with the composition of minimum or maximum bubble-point temperature for the system at constant pressure. The complexities of the systems make the digital computer helpful in dealing with the data [44].

[†] Hydrocarbons of different molecular structure, however, frequently form such nonideal solutions that azeotropism occurs, for example, in the binary systems hexane–methyl cyclopentane, hexane–benzene, and benzene–cyclohexane.

For multicomponent systems particularly, it is customary to describe the equilibrium data by means of the distribution coefficient m^\dagger . For component J,

$$m_J = \frac{y_J^*}{x_J} \quad (9.17)$$

where in general m_J depends upon the temperature, pressure, and composition of the mixture. The relative volatility α_{IJ} of component I with respect to J is

$$\alpha_{IJ} = \frac{y_I^*/x_I}{y_J^*/x_J} = \frac{m_I}{m_J} \quad (9.18)$$

For *ideal* solutions at moderate pressure, m_J is independent of composition and depends only upon the temperature (as this affects vapor pressure) and the total pressure:

$$K_i = \frac{p_i}{x_i} \quad m_J = \frac{p_J}{p_i} \quad (9.19)$$

and $\alpha_{ij} = \frac{K_i}{K_j}$ $\alpha_{IJ} = \frac{p_i}{p_j} \quad (9.20)$

Bubble point For the bubble-point vapor,

$$\sum y_i^* = 1.0 \quad (9.21)$$

or $m_A x_A + m_B x_B + m_C x_C + \dots = 1.0 \quad (9.22)$

With component J as a reference component,

$$\frac{m_A x_A}{m_J} + \frac{m_B x_B}{m_J} + \frac{m_C x_C}{m_J} + \dots = \frac{1.0}{m_J} \quad (9.23)$$

or $\alpha_{AJ} x_A + \alpha_{BJ} x_B + \alpha_{CJ} x_C + \dots = \frac{1}{m_J} \quad (9.24)$

The equilibrium bubble-point vapor composition is given by

$$y_i = \frac{\alpha_{i,J} x_i}{\sum \alpha_{i,J} x_i} \quad (9.25)$$

The liquid composition and total pressure having been fixed, the calculation of the temperature is made by trial to satisfy Eq. (9.24). Convergence is rapid since α 's vary only slowly with changing temperature (see Illustration 9.3).

Dew point For the dew-point liquid,

$$\sum x_i^* = 1.0 \quad (9.26)$$

$$\frac{y_A}{m_A} + \frac{y_B}{m_B} + \frac{y_C}{m_C} + \dots = 1.0 \quad (9.27)$$

\dagger K rather than m is generally used to denote the distribution coefficient, but here we shall use K for the overall mass-transfer coefficient.

With component J as a reference component,

$$\frac{m_J y_A}{m_A} + \frac{m_J y_B}{m_B} + \frac{m_J y_C}{m_C} + \dots = m_J \tag{9.28}$$

$$\frac{y_A}{\alpha_{AJ}} + \frac{y_B}{\alpha_{BJ}} + \frac{y_C}{\alpha_{CJ}} + \dots = \sum \frac{y_i}{\alpha_{i,J}} = m_J \tag{9.29}$$

The dew-point liquid composition is given by

$$x_i = \frac{y_i / \alpha_{i,J}}{\sum (y_i / \alpha_{i,J})} \tag{9.30}$$

Illustration 9.3 demonstrates the method of computation.

Illustration 9.3 A solution of hydrocarbons at a total pressure 350 kN/m² (50.8 lb_f/in²) has the analysis n-C₃H₈ = 5.0, n-C₄H₁₀ = 30.0, n-C₅H₁₂ = 40.0, n-C₆H₁₄ = 25.0 mol%. Compute the bubble point and the dew point.

SOLUTION Values of *m* will be taken from the DePriester nomograph [*Chem. Eng. Prog. Symp. Ser.*, 49(7), 1 (1953)]; also "Chemical Engineers' Handbook," 5th ed., fig. 13-6*b*), which assumes ideal liquid solutions.

Bubble point Column 1 lists the mole-fraction compositions. As a first estimate of the bubble point, 60°C is chosen, and column 2 lists the corresponding *m*'s at 60°C, 350 kN/m². The reference component is chosen to be the pentane, and column 3 lists the relative volatilities (α_{C₃, C₃} = 4.70/0.62 = 7.58, etc.). Σα_{*i*, C₃} *x_i* = 1.702 (column 4), whence [Eq. (9.23)] *m*_{C₃} = 1/1.702 = 0.588. The corresponding temperature, from the nomograph, is 56.8°C (135°F). The calculations are repeated for this temperature in columns 5 to 7. *m*_{C₃} = 1/1.707 = 0.586, corresponding to *t* = 56.7°C, which checks the 56.8°C assumed. This is the bubble point, and the corresponding bubble-point vapor composition is given in column 8 (0.391/1.707 = 0.229, etc.).

	<i>x_i</i>	<i>m_i</i> , 60°C	α _{<i>i</i>, C₃}	α _{<i>i</i>, C₃} <i>x_i</i>	<i>m_i</i> , 56.8°C	α _{<i>i</i>, C₃}	α _{<i>i</i>, C₃} <i>x_i</i>	<i>y_i</i>
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
n-C ₃	0.05	4.70	7.58	0.379	4.60	7.82	0.391	0.229
n-C ₄	0.30	1.70	2.74	0.822	1.60	2.72	0.816	0.478
n-C ₅	0.40	0.62	1.00	0.400	0.588	1.00	0.400	0.234
n-C ₆	0.25	0.25	0.403	0.1008	0.235	0.40	0.100	0.0586
				1.702			1.707	1.000

	<i>y_i</i>	<i>m_i</i> , 80°C	α _{<i>i</i>, C₃}	<i>y_i</i> /α _{<i>i</i>, C₃}	<i>m_i</i> , 83.7°C	α _{<i>i</i>, C₃}	<i>y_i</i> /α _{<i>i</i>, C₃}	<i>x_i</i>
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
n-C ₃	0.05	6.30	6.56	0.00762	6.60	6.11	0.00818	0.0074
n-C ₄	0.30	2.50	2.60	0.1154	2.70	2.50	0.120	0.1088
n-C ₅	0.40	0.96	1.00	0.400	1.08	1.00	0.400	0.3626
n-C ₆	0.25	0.43	0.448	0.558	0.47	0.435	0.575	0.5213
				1.081			1.103	1.000