Thermodynamic Equilibrium Diagrams

When a gas is brought into contact with the surface of a liquid, some of the molecules of the gas striking the liquid surface will dissolve. These dissolved molecules will continue in motion in the dissolved state, some returning to the surface and re-entering the gaseous state. The dissolution of gas in the liquid will continue until the rate at which gas molecules leave the liquid is equal to the rate at which they enter. Thus a state of dynamic equilibrium is established, and no further changes will take place in the concentration of gas molecules in either the gaseous or liquid phases.

Olaf A. Hougen and Kenneth M. Watson, 1943

Stagewise calculations require the simultaneous solution of material and energy balances with equilibrium relationships. It was demonstrated in Example 1.1 that the design of a simple extraction system reduces to the solution of linear algebraic equations if (1) no energy balances are needed and (2) the equilibrium relationship is linear.

In cases involving complex equilibrium functions and/or energy balances, solutions to large sets of nonlinear simultaneous equations are required. If many stages are involved, the system of equations becomes so large that rigorous analytical solutions cannot be easily obtained by manual means, and computers are required. However, when separation problems involve only two or three components or when only approximate solutions are needed, graphical techniques provide a convenient alternative to the computer. Furthermore, graphical methods provide a lucid visual display of the stage-to-stage extent of component separation. Some of the more commonly used thermodynamic equilibrium

The first phase-equilibrium diagrams discussed are for two-component liquid-vapor systems. Next, three-component diagrams used in extraction, absorption, leaching, and ion exchange are developed. Finally, enthalpy-composition diagrams, which include energy effects, are constructed.

3.1 Homogeneous and Heterogeneous Equilibrium

If a mixture consisting of one or more components possesses uniform physical and chemical properties throughout, it is said to be a *single-phase*, *homogeneous* system. If, however, a system consists of one or more parts that have different properties and are set apart from each other by bounding surfaces, so that the phases are mechanically separable, the system is *heterogeneous*. When equilibrium exists between the distinct parts of the system, this condition is known as *heterogeneous equilibrium*.

3.2 The Phase Rule

The phase rule of J. Willard Gibbs relates the variance (degrees of freedom) \mathscr{F} for a nonchemically reactive system at heterogeneous equilibrium to the number of coexisting phases \mathscr{P} and the number of components (chemical species), C present.

$$\mathcal{F} = \mathbf{C} - \mathcal{P} + 2$$

The variance designates the number of intensive properties that must be specified to completely fix the state of the system. For the systems to be treated here only the intensive properties T, P, and concentration are considered.

For a gas having n components, C = n, so \mathcal{F} is n + 1, and the specification of the temperature, pressure, and n - 1 concentration variables completely defines the state of the system.

Figure 3.1 is a schematic one-component, three-phase equilibrium diagram. The three different phase regions are separated by lines *D-TP* (solid vapor pressure, or sublimation curve), *F-TP* (melting point curve), and *TP-C* (liquid vapor pressure or boiling-point curve). Point C is the critical point where the vapor and liquid phases become indistinguishable and *TP* is the triple point where solid, liquid, and vapor phases can coexist. There are only two in-

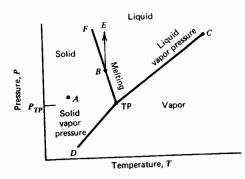


Figure 3.1. Phase equilibrium diagram.

dependent variables, T and P. Applying the phase rule, we note that, at point A, $\mathcal{P}=1$; hence $\mathcal{F}=2$. There are two independent variables, T and P, which we can change by small amounts without creating a new phase. At B, which is on the solid-liquid equilibrium line, there are two phases in equilibrium; hence $\mathcal{F}=1$. If we raise the pressure to E, the temperature, which is now a dependent variable, must be lowered if we are to continue to have two phases in equilibrium. We note that, at TP, $\mathcal{P}=3$ and $\mathcal{F}=0$. There are no independent variables, and any changes in temperature or pressure will immediately result in the disappearance of one of the phases. It is thus impossible to make an equilibrium mixture of solid, liquid, and vapor by cooling water vapor at a constant pressure other than P_{TP} , which for water is 610 Pa.

3.3 Binary Vapor-Liquid Mixtures

For vapor-liquid mixtures of component A and B, $\mathcal{F} = 2$. The two independent variables can be selected from T, P, and, since both liquid and vapor phases are present, the concentration of one of the components in the vapor y_A and in the liquid x_A . The concentrations of B, y_B , and x_B are not independent variables, since $y_A + y_B = 1$ and $x_A + x_B = 1$. If the pressure is specified, only one independent variable remains $(T, y_A, \text{ or } x_A)$.

Four isobaric (constant pressure) phase equilibrium diagrams involving the variables T, x, and y can be constructed: T-y, T-x, combined T-x-y, and x-y diagrams. Figures 3.2a and 3.2b are schematic T-x-y and x-y diagrams for a two-component vapor-liquid system. In Fig. 3.2a the temperatures $T_{\rm A}$ and $T_{\rm B}$ are the boiling points of the pure components A and B at a given pressure. The lower curve connecting T_A to T_B is the isobaric bubble-point temperature (saturated liquid) curve. The upper curve connecting T_A and T_B is the dew-point temperature (saturated vapor) curve. A "subcooled" liquid of composition x_A at

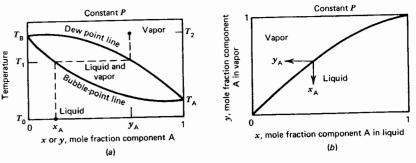


Figure 3.2. Vapor-liquid phase equilibrium. (E. J. Henley and E. M. Rosen, Material and Energy Balance Computations, John Wiley & Sons, New York, @ 1969.)

 T_o , when heated to T_1 , will produce the first bubble of equilibrium vapor of composition y_A . Conversely, a superheated vapor of composition y_A at T_2 , when cooled to T_1 , will condense, the first drop of liquid being of composition x_A . Figure 3.2a also shows that, in general, complete vaporization or condensation of a binary mixture occurs over a range of temperatures, rather than at a single temperature as with a pure substance.

It is important to note that, since $\mathcal{F} = 2$ and the pressure is fixed, the specification of only one additional thermodynamic variable completely defines a binary vapor-liquid mixture. If the composition of the liquid is x_A , both the vapor-phase composition y_A and the bubble-point temperature T_1 are uniquely fixed.

Figure 3.2b, an x-y vapor-liquid equilibrium diagram, is an alternative way of presenting some of the information in Fig. 3.2a. Here each point on the x-y equilibrium curve is at a different but undesignated temperature. Figure 3.2b is widely used in calculating equilibrium-stage requirements even though it contains less information than Fig. 3.2a.

3.4 Use of Physical Properties to Predict Phase Equilibrium Composition

Chapter 4 describes the generation of vapor-liquid and liquid-liquid equilibria data using analytical correlations based on physical properties. It will be seen that correlations based solely on properties of pure components are successful only for homologous systems when molecular size differences are small and interactions among like molecules are similar to the interactions among unlike molecules. For mixtures of liquid n-hexane and n-octane, for example, we might correctly predict that the components will be miscible, and bubble- and dewpoint temperatures will be between the boiling points of the pure components and closer to that of the component present in higher concentrations. In addition, we might predict that, to a first approximation, no heat will be released upon mixing and that the total solution volume will equal the sum of the volumes of the pure components. For such mixtures, which are termed *ideal solutions*, it is possible to predict the distribution of components between phases at equilibrium from the molecular properties of the pure components. A rigorous thermodynamic definition of ideal solutions will be given in Chapter 4.

3.5 Raoult's Law for Vapor-Liquid Equilibrium of Ideal Solutions

If two or more liquid species form an ideal liquid solution with an equilibrium vapor mixture, the partial pressure p_i of each component in the vapor is proportional to its mole fraction in the liquid x_i . The proportionality constant is the vapor pressure P_i^s of the pure species at the system temperature, and the relationship is named *Raoult's law* in honor of the French scientist who developed it.

$$p_i = P_i^s x_i \tag{3-1}$$

Furthermore, at low pressure, Dalton's law applies to the vapor phase, and

$$p_i = Py_i \tag{3-2}$$

where P is the total pressure and y_i the vapor-phase mole fraction. Combining (3-1) and (3-2), we have

$$y_i = (P_i^s/P)x_i \tag{3-3}$$

With this equation, values for the vapor pressures of the pure components suffice to establish the vapor-liquid equilibrium relationship.

Departures from Raoult's law occur for systems in which there are differing interactions between the constituents in the liquid phase. Sometimes the interaction takes the form of a strong repulsion, such as exists between hydrocarbons and water. In a liquid binary system of components A and B, if these repulsions lead to essentially complete immiscibility, the total pressure P over the two liquid phases is the sum of the vapor pressures of the individual components, and

$$P = P_A^s + P_B^s \tag{3-4}$$

Example 3.1. Vapor pressures for n-hexane, H, and n-octane, O, are given in Table 3.1.
(a) Assuming that Raoult's and Dalton's laws apply, construct T-x-y and x-y plots for this system at 101 kPa (1 atm).

Table 3.1 Vapor pressures for n-hexane and n-octane

Temperature		Vapor Pressure, kPa	
°F	°C	n-Hexane	n-Octane
155.7	68.7	101	16
175	79.4	137	23
200	93.3	197	37
225	107.2	284	58
250	121.1	400	87
258.2	125.7	456	101

Source. J. B. Maxwell, Data Book on Hydrocarbons, D. Van Nostrand and Co., Inc., New York, 1950, 32, 34.

- (b) When a liquid containing 30 mole % H is heated, what is the composition of the initial vapor formed at the bubble-point temperature?
- (c) Let the initial (differential amount) of vapor formed in (b) be condensed to its bubble point and separated from the liquid producing it. If this liquid is revaporized, what is the composition of the initial vapor formed? Show the sequential processes (b) and (c) on the x-y and T-x-y diagrams.

Solution. (a) According to Raoult's law (3-1)

$$p_{\rm H} = P_{\rm H}^{\,s} x_{\rm H}$$
 and $p_{\rm O} = P_{\rm O}^{\,s} x_{\rm O}$

By Dalton's law (3-2)

$$p_{\rm H} = P y_{\rm H}$$
 and $p_{\rm O} = P y_{\rm O}$

Also

$$p_{\rm H} + p_{\rm O} = P$$
 $x_{\rm H} + x_{\rm O} = 1$ and $y_{\rm H} + y_{\rm O} = 1$

From (3-3)

$$y_{\rm H} = \frac{P_{\rm H}^{s} x_{\rm H}}{P} \qquad y_{\rm O} = \frac{P_{\rm O}^{s} x_{\rm O}}{P}$$
 (3-5)

Combining the expressions for y_H and y_O , we have

$$x_{\rm H} = \frac{P - P_0^{\, \rm o}}{P_0^{\, \rm d} - P_0^{\, \rm o}} \tag{3-6}$$

Equations (3-5) and (3-6) permit calculation of y_H and x_H at a specified temperature. Using the vapor pressures from Table 3.1, 79.4°C, for example, we find that

$$x_{\rm H} = \frac{101 - 23}{137 - 23} = 0.684$$

$$y_{\rm H} = \frac{137}{101}(0.684) = 0.928$$

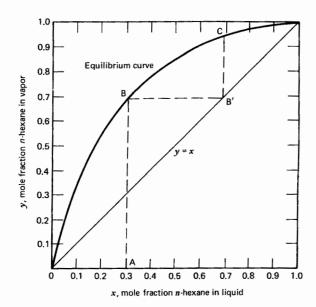


Figure 3.3. The x-y diagram for n-hexane-n-octane, at 101 kPa. (E. J. Henley and E. M. Rosen, Material and Energy Balance Computations, John Wiley & Sons, New York, © 1969.)

It should be noted that, if alternatively one assumes a value for either x_H or y_H , the result is a trial-and-error calculation since $P_i^s = P_i^s \{T\}$ and T is not easily expressed as $T = T\{P_i^s\}$. The results of the calculations are shown in Figs. 3.3 and 3.4 as solid lines. The 45° line y = x also shown in Fig. 3.3 is a useful reference line. In totally condensing a vapor, we move horizontally from the vapor-liquid equilibrium line to the y = x line, since the newly formed liquid must have the same composition as the (now condensed) vapor.

- (b) The generation of an infinitesimal amount of vapor such that x_H remains at 0.30 is shown by line \overline{AB} in Fig. 3.3 and by line \overline{AOA} in Fig. 3.4. The paths $A \rightarrow B$ and $A \rightarrow A_O$ represent isobaric heating of the liquid, $x_H = 0.3$. From Fig. 3.4 we see that boiling takes place at 210°F (98.9°C), the vapor formed (B) having the composition $y_H = 0.7$. Although Fig. 3.3 does not show temperatures, it does show a saturated liquid of $x_H = 0.3$ in equilibrium with a saturated vapor of $y_H = 0.7$ at point B.
- (c) When the vapor at B is totally condensed $(B \rightarrow B')$ and then brought to the bubble point $(B' \rightarrow C)$ the concentration of hexane in the vapor is 0.93. Thus, starting with a liquid containing only 30% hexane, one produces a vapor containing 93% hexane. However, only a differential amount of this vapor is produced. Practical techniques for producing finite amounts of pure products will be discussed in subsequent chapters.

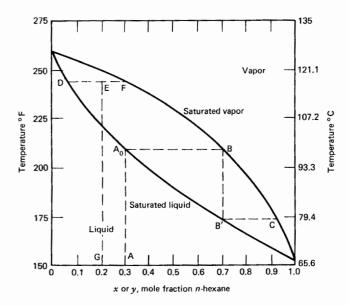


Figure 3.4. The T-x-y diagram for n-hexane-n-octane, at 101 kPa.

Example 3.2. A liquid mixture of 25 kgmoles of benzene (B), 25 kgmoles of toluene (T), and 50 kgmoles of water (W) is at equilibrium with its vapor at 50°C. Assuming that benzene and toluene follow Raoult's law, but that neither are miscible with water, calculate:

- (a) The total pressure above the mixture.
- (b) The composition of the vapor assuming that Dalton's law applies.

Solution. Vapor pressures of the three components at 50°C are

$$P_{W}^{s} = 12.3 \text{ kPa}$$
 $P_{B}^{s} = 40.0 \text{ kPa}$ $P_{T}^{s} = 11.3 \text{ kPa}$

(a) Mole fractions in the hydrocarbon liquid phase are

$$x_{\rm B} = \frac{25}{50} = 0.5$$
 $x_{\rm T} = \frac{25}{50} = 0.5$

From (3-1)

$$p_{\rm B} = (40.0)(0.5) = 20.0 \text{ kPa}$$

 $p_{\rm T} = (11.3)(0.5) = 5.65 \text{ kPa}$

The separate liquid-water phase exerts a partial pressure equal to its pure vapor pressure. Thus, $p_w = P_w^s = 12.3 \text{ kPa}$. Extending (3-4), the total pressure is

$$P = p_B + p_T + p_W = 20.0 + 5.65 + 12.3 = 37.95 \text{ kPa}$$

3.8 Azeotropic Systems

(b) From (3-2), $y_i = p_i/P$. Thus,

$$y_B = \frac{20.0}{37.95} = 0.527$$
 $y_T = \frac{5.65}{37.95} = 0.149$ $y_W = \frac{12.3}{37.95} = 0.324$

3.6 Vapor-Liquid Material Balances Using Phase Equilibrium Diagrams

Graphical solutions to material balance problems involving equilibrium relationships offer the advantages of speed and convenience. Fundamental to all graphical methods is the so-called inverse lever rule, which is derived in Example 3.3 and applied in Example 3.4.

Example 3.3. Prove that the ratio of the moles of liquid to vapor in the two-phase mixture E (at 240°F, 115.6°C) shown in Fig. 3.4 is in the ratio of the line segments FE/ED.

Solution. Letting \mathcal{M}_E , \mathcal{M}_D and \mathcal{M}_F represent the moles of total mixture, liquid, and vapor, respectively, and z_E , z_D , and y_F the corresponding mole fractions of hexane, a material balance for hexane yields

$$\mathcal{M}_E z_E = (\mathcal{M}_D + \mathcal{M}_F) z_E = \mathcal{M}_D x_D + \mathcal{M}_F y_F$$

Solving for the mole ratio of liquid L to vapor V, we have

$$\frac{\mathcal{M}_D}{\mathcal{M}_F} = \frac{L}{V} = \frac{y_F - z_E}{z_E - x_D} = \frac{\overline{FE}}{\overline{ED}}$$

Similarly

$$\frac{\mathcal{M}_D}{\mathcal{M}_E} = \frac{L}{L+V} = \frac{y_F - z_E}{y_F - z_D} = \frac{\overline{FE}}{\overline{FD}}$$

and

$$\frac{\mathcal{M}_F}{\mathcal{M}_E} = \frac{V}{L+V} = \frac{z_E - x_D}{y_F - x_D} = \frac{\overline{ED}}{\overline{FD}}$$

Example 3.4. A solution F containing 20 mole % *n*-hexane and 80 mole % *n*-octane is subject to an equilibrium vaporization at 1 atm such that 60 mole % of the liquid is vaporized. What will be the composition of the remaining liquid?

Solution. This process can be shown directly on Fig. 3.4, the T-x-y diagram for hexane-octane. We move along the path $G \rightarrow E$ until, by trial and error, we locate the isotherm \overline{DEF} such that it is divided by the x = 0.2 vertical line into two segments of such lengths that the ratio of liquid to vapor $L/V = 0.4/0.6 = \overline{FE/ED}$. The liquid remaining D has the composition x = 0.07; it is in equilibrium with a vapor y = 0.29. This method of solving the problem is essentially a graphical trial-and-error process and is equivalent to solving the hexane material balance equation

$$Fx_F = yV + xL = (1)(0.2)$$

or

$$y(0.6) + x(0.4) = 0.2$$

where y and x are related by the equilibrium curve of Fig. 3.3. We thus have two equations in two unknowns, the equilibrium relation and the material balance.

3.7 Binary Vapor-Liquid Equilibrium Curves Based on Constant Relative Volatility

For systems where the liquid phase is an ideal solution that follows Raoult's law and where the gas phase follows the ideal gas laws, it is possible to formulate relative volatilities that are functions only of temperature. For component i of a mixture, in accordance with (1-4) and (3-3)

$$K_i = \frac{y_i}{x_i} = \frac{P_i^s}{P} \tag{3-7}$$

If the mixture also contains component j, the relative volatility of i to j can be expressed as a ratio of the K-values of the two components

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{P_i^s}{P_j^s} = \frac{y_i / x_i}{y_j / x_j}$$
 (3-8)

In a two-component mixture, where $y_i = (1 - y_i)$, and $x_j = (1 - x_i)$, (3-8) becomes

$$y_i = \frac{\alpha_{ij} x_i}{1 + x_i (\alpha_{ii} - 1)}$$
 (3-9)

It is possible to generate x-y equilibrium curves such as Fig. 3.3 using (3-9) by assuming that the relative volatility is a constant independent of temperature. This is convenient for close-boiling mixtures forming ideal solutions, but can lead to erroneous results for mixtures of components with widely different boiling points because it assumes that both P_i^x and P_i^y are identical functions of T. For example, inspection of the vapor pressure data for the hexane-octane system, Table 3.1, reveals that α varies from 101/16 = 6.3 at 68.7° C to 456/101 = 4.5 at 125.7° C. Calculation of relative volatilities by more accurate methods will be considered in Chapter 4.

3.8 Azeotropic Systems

Departures from Raoult's law frequently manifest themselves in the formation of *azeotropes*, particularly for mixtures of close-boiling species of different chemical types. Azeotropes are liquid mixtures exhibiting maximum or minimum



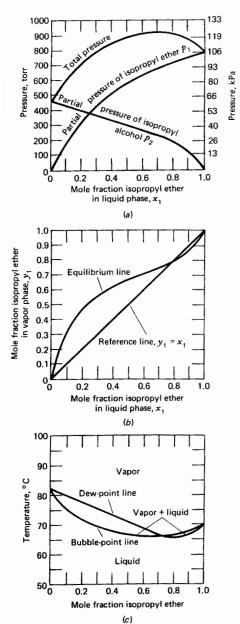


Figure 3.5. Minimum-boiling-point azeotrope, isopropyl ether-isopropyl alcohol system. (a) Partial and total pressures at 70°C. (b) Vapor-liquid equilibria at 101 kPa. (c) Phase diagram at 101 kPa. [Adapted from O. A. Hougen, K. M. Watson, and R. A. Ragatz, Chemical Process Principles, Part II, 2nd ed., John Wiley and Sons, N. Y. © (1959).]

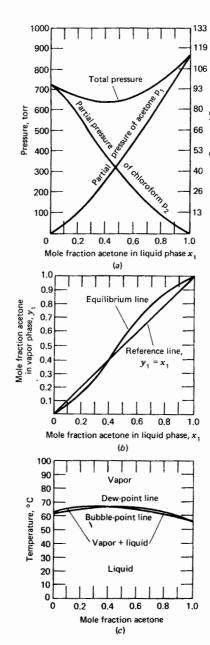
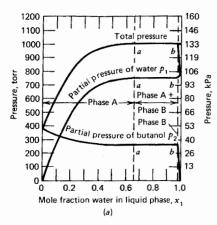
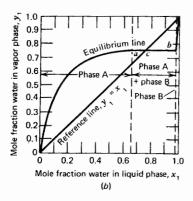




Figure 3.6. Maximum-boiling-point azeotrope, acetone-chloroform system. (a) Partial and total pressures at 60°C. (b) Vapor-liquid equilibria at 101 kPa. (c) Phase diagram at 101 kPa pressure. [Adapted from O. A. Hougen, K. M. Watson, and R. A. Ragatz, Chemical Process Principles, Part II, 2nd ed., John Wiley and Sons, N. Y. © (1959).]





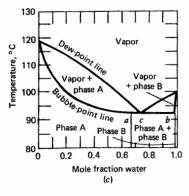


Figure 3.7. Minimum-boiling-point (two liquid phases) water-n-butanol system. (a) Partial and total pressures at 100°C. (b) Vapor-liquid equilibria at 101 kPa. (c) Phase diagram at 101 kPa pressure. [Adapted from O. A. Hougen, K. M. Watson, and R. A. Ragatz, Chemical Process Principles, Part II, 2nd ed., John Wiley and Sons, N.Y. © (1959).]

boiling points that represent, respectively, negative or positive deviations from Raoult's law. Vapor and liquid compositions are identical for azeotropes.

If only one liquid phase exists, the mixture is said to form a homogeneous azeotrope; if more than one liquid phase is present, the azeotrope is said to be heterogeneous. In accordance with the Phase Rule, at constant pressure in a two-component system the vapor can coexist with no more than two liquid phases, while in a ternary mixture up to three dense phases can coexist with the vapor.

Figures 3.5, 3.6, and 3.7 show three types of azeotropes commonly encountered in two-component mixtures.

For the *minimum-boiling* isopropyl ether-isopropyl alcohol mixture in Fig. 3.5a, the maximum total pressure is greater than the vapor pressure of either component. Thus, in distillation, the azeotropic mixture would be the overhead product. The y-x diagram in Fig. 3.5b shows that at the azeotropic mixture the liquid and vapor have the same composition. Figure 3.5c is an isobaric diagram at 101 kPa, where the azeotrope, at 78 mole % ether, boils at 66°C . In Fig. 3.5a, which displays isothermal (70°C) data, the azeotrope, at 123 kPa, is 72 mole % ether.

For the maximum-boiling azeotropic acetone-chloroform system in Fig. 3.6a, the minimum total pressure is below the vapor pressures of the pure components, and the azeotrope would concentrate in the bottoms in a distillation operation. Heterogeneous azeotropes are always minimum-boiling mixtures. The region a-b in Fig. 3.7a is a two-phase region where total and partial pressures remain constant as the relative amounts of the two phases change. The y-x diagram in Fig. 3.7b shows a horizontal line over the immiscible region and the phase diagram of Fig. 3.7c shows a minimum constant temperature.

Azeotropes limit the separation that can be achieved by ordinary distillation techniques. It is possible, in some cases, to shift the equilibrium by changing the pressure sufficiently to "break" the azeotrope, or move it away from the region where the required separation must be made. Ternary azeotropes also occur, and these offer the same barrier to complete separation as binaries.

Azeotrope formation in general, and heterogeneous azeotropes in particular, can be usefully employed to achieve difficult separations. As discussed in Chapter 1, in azeotropic distillation an *entrainer* is added (frequently near the bottom of the column) for the purpose of removing a component that will combine with the agent to form a minimum boiling azeotrope, which is then recovered as the distillate.

Figure 3.8 shows the Keyes process^{1,2,3} for making pure ethyl alcohol by heterogeneous azeotropic distillation. Water and ethyl alcohol form a binary minimum-boiling azeotrope containing 95.6% by weight alcohol and boiling at 78.15°C at 101 kPa. Thus it is impossible to obtain absolute alcohol (bp 78.40°C) by ordinary distillation. The addition of benzene to alcohol-water results in the formation of a minimum-boiling heterogeneous ternary azeotrope containing by

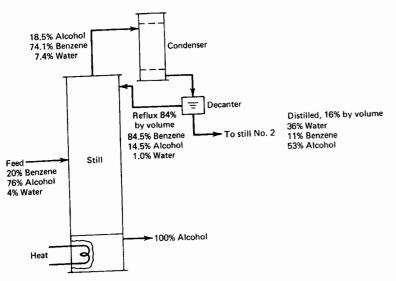


Figure 3.8. The Keyes process for absolute alcohol. All compositions weight percent.

weight, 18.5% alcohol, 74.1% benzene, and 7.4% water and boiling at 64.85°C. Upon condensation, the ternary azeotrope separates into two liquid layers: a top layer containing 14.5% alcohol, 84.5% benzene, and 1% water, and a bottoms layer of 53% alcohol, 11% benzene, and 36% water, all by weight. The benzene-rich layer is returned as reflux. The other layer is processed further by distillation for recovery and recycle of alcohol and benzene. Absolute alcohol, which has a boiling point above that of the ternary azeotrope, is removed at the bottom of the column. A graphical method for obtaining a material balance for this process is given later in this chapter as Example 3.7.

In extractive distillation, as discussed in Chapter 1, a solvent is added, usually near the top of column, for the purpose of increasing the relative volatility between the two species to be separated. The solvent is generally a relatively polar, high-boiling constituent such as phenol, aniline, or furfural, which concentrates at the bottom of the column.

3.9 Vapor-Liquid Equilibria in Complex Systems

Petroleum and coal extracts are examples of mixtures that are so complex that it is not feasible to identify the pure components. Vaporization properties of these substances are conventionally characterized by standard ASTM (American

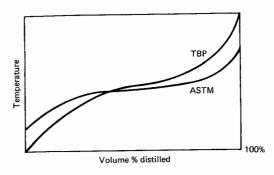


Figure 3.9. Typical distillation curve.

Society for Testing and Materials) boiling-point curves obtained by batch fractionation tests, (e.g., ASTM D86, D158, D1160). Figure 3.9 is a representative curve. Alternatively, data are obtained from more elaborate tests, including equilibrium flash vaporization (EFV), or true-boiling batch distillation (TBP) involving a large number of stages and a high reflux ratio. If either a TBP, EFV, or ASTM curve is available, the other two can be predicted.^{4,5} Techniques for processing TBP curves to characterize complex mixtures, for relating them to pseudocomponents, and for obtaining K-values to design fractionators to produce jet fuel, diesel fuel base stock, light naphtha, etc. are available.⁶

3.10 Liquid-Liquid Systems, Extraction

A convenient notation for classifying mixtures employed in liquid-liquid extraction is C/N, where C is the number of components and N the number of partially miscible pairs. Mixtures 3/1, 3/2, and 3/3 are called "Type I, Type II, and Type III" by some authors. A typical 3/1 three-component mixture with only one partially miscible pair is furfural-ethylene glycol-water, as shown in Fig. 3.10, where the partially miscible pair is furfural-water. In practice, furfural is used as a solvent to remove the solute, ethylene glycol, from water; the furfural-rich phase is called the extract, and the water-rich phase the raffinate. Nomenclature for extraction, leaching, absorption, and adsorption always poses a problem because, unlike distillation, concentrations are expressed in many different ways: mole, volume, or mass fractions; mass or mole ratios; and special "solvent-free" designations. In this chapter, we will use V to represent the extract phase and L the raffinate phase, and y and x to represent solute concentration in these phases, respectively. The use of V and L does not imply that the extract phase in extraction is conceptually analogous to the vapor phase in distillation; indeed the reverse is more correct for many purposes.