Chapter 6

Phase Equilibrium Principles

INTRODUCTION

Equilibrium principles play an important role in designing and predicting the performance of many mass transfer processes. In fact, several mass transfer calculations are based primarily on the application of equilibrium principles and equilibrium data. Distillation is a prime example; virtually every calculational procedure is based on vapor–liquid equilibrium data, e.g., acetone–water. Similarly, adsorption engineering applications almost always utilize vapor (gas)–solid equilibrium data, e.g., acetone–activated carbon. It is for this reason that phase equilibrium principles in general and specific equilibrium systems are reviewed in this chapter.

The term *phase*, for a pure substance, indicates a *state of matter*, i.e., solid, liquid, or gas. For mixtures, however, a more stringent connotation must be used, since a totally liquid or solid system may contain more than one phase (e.g., a mixture of oil and water). A phase is characterized by uniformity or *homogeneity*, which means that the same composition and properties must exist throughout the phase region. At most temperatures and pressures, a pure substance normally exists as a single phase. At certain temperatures and pressures, two or perhaps even three phases can coexist in equilibrium. This is shown on the phase diagram for water (see Fig. 6.1). Regarding the interpretation of this diagram, the following points should be noted:

1 The line between the gas and liquid phase regions is the *boiling point* and *dew point* line and represents equilibrium between the gas and liquid.

2 The boiling point of a liquid is the temperature at which its vapor pressure is equal to the *external* pressure. The temperature at which the vapor pressure is equal to 1 atm is the *normal* boiling point.

3 The line between the solid and gas phase regions is the *sublimation point* and *deposition point* line and represents equilibrium between the solid and gas.

4 The line between the solid and liquid phase regions is the *melting point* and *freezing point* line and represents equilibrium between the liquid and solid.
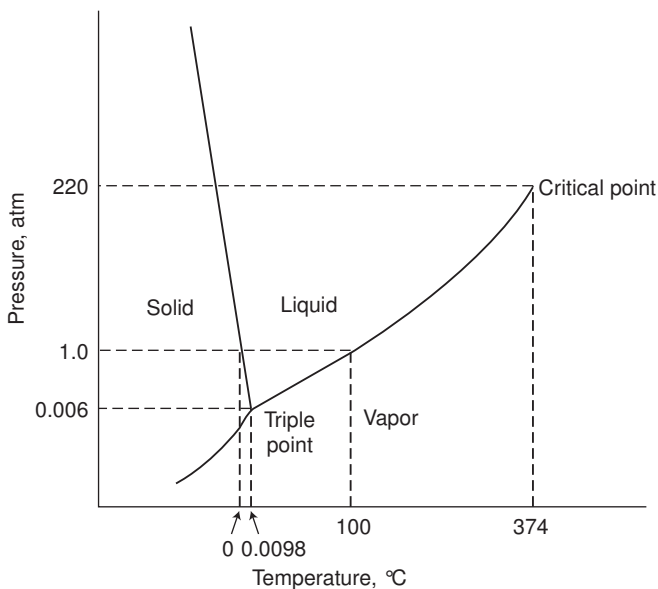
Figure 6.1   Phase diagram for water.

5 The point at which all three equilibrium lines meet (i.e., the one pressure and temperature where solid, liquid, and gas phases can all coexist) is the *triple point*.

6 The liquid–gas equilibrium line is bounded on one end by the triple point and the other end by the *critical* point. The *critical temperature* (the temperature coordinate of the critical point) is defined as the temperature above which a gas or vapor cannot be liquefied by the application of pressure alone.

The term *vapor*, strictly speaking, is used only for a *condensable* gas, i.e., a gas below its *critical* temperature, and should not be applied to a noncondensable gas. It should also be pointed out that the phase diagram for water (Fig. 6.1) differs from that of other substances in one respect—the freezing point line is *negatively* sloped; for other substances, the slope of this line is *positive*. This is a consequence of the fact that liquid water is denser than ice.

Mass transfer calculations rarely involve single (pure) components. Phase equilibria for multicomponent systems are considerably more complex, mainly because of the addition of *composition* variables. For example, in a *ternary* (three-component) system, the mole fractions of two of the components are pertinent variables along with temperature and pressure. In a single-component system, dynamic equilibrium between two phases is achieved when the rate of molecular transfer from one phase to the second equals that in the opposite direction. In multicomponent systems, the equilibrium requirement is more stringent—the rate of transfer of *each component* must be the same in both directions.

Relationships governing the equilibrium distribution of a substance between two phases, particularly gas and liquid phases, are the principal subject matter of phase-equilibrium thermodynamics. As noted above, these relationships form the basis of calculational procedures that are employed in the design and the prediction of performance of several mass transfer processes.[1]

For many, mass transfer has come to be defined as the tendency of a component in a mixture to travel from a region of high concentration to one of low concentration. For example, if an open beaker with some alcohol in it is placed in a room in which the air is relatively dry, alcohol vapor will diffuse out through the column of air in the beaker. Thus, there is mass transfer of alcohol from a location where its concentration is high (just above the liquid surface) to a place where its concentration is low (at the top of the beaker). If the gas mixture in the beaker is stagnant (void of any motion), the transfer is said to occur by molecular diffusion. If there is a bulk mixing of the layers of gas in the beaker, mass transfer is said to occur by the mechanism of either forced or natural convection, or both. These two mechanisms are analogous to the transfer of heat by conduction and convection.[2] Analogies with fluid flow are not nearly as obvious.[3]

In discussing the principles and applications of mass transfer, the presentation will primarily consider binary mixtures, although some multicomponent mixture issues are addressed. Binary mixtures serve as an excellent starting point for training and educational purposes. However, real world applications often involve more than two components.

The problem of transferring materials from one phase to another is encountered in many engineering operations. There are generally three classes of phases encountered in practice: gas, liquid, and solid. If mass transfer occurs between two phases, with one phase being treated and the other performing the treatment, a total of $(3)^2$ or nine possible combinations of operations with two phases is possible. These mini-scenarios are listed in Table 6.1.

Table 6.1   Mass Transfer Scenarios

Scenario	Phase undergoing treatment	Phase performing treatment
1	Gas	Gas
2	Gas	Liquid
3	Gas	Solid
4	Liquid	Gas
5	Liquid	Liquid
6	Liquid	Solid
7	Solid	Gas
8	Solid	Liquid
9	Solid	Solid

GIBB'S PHASE RULE

The general subject of phases and equilibrium is only one of several topics highlighted in this chapter. Equilibrium in a multiphase system is subject to certain restrictions. These restrictions can be expressed in an equation form, defined as the Phase Rule.

The state of a $P-V-T$ system is established when its temperature and pressure and the compositions of all phases are fixed. However, these variables are not all independent for equilibrium states, and fixing a limited number of them automatically establishes the others. This number of independent variables is given by Gibb's Phase Rule and is defined as the number of *degrees of freedom* of the system. This number of variables must be specified in order to fix the state of a system at equilibrium. The following nomenclature is employed in the discussion to follow:

P = number of phases

C = number of chemical components

r = number of independent chemical reactions; components minus elements

F = number of degrees of freedom

The phase-rule variables are temperature, pressure, and $C-1$ mole fractions in each phase. The number of these variables is therefore $2 + (C-1)P$. The masses of the phases are not phase-rule variables because they have no effect on the state of the system. It should also be noted that the temperature and pressure have been assumed to be uniform throughout the system for an equilibrium state.

The total number of independent equations (by componential balance) is $(P-1)C + r$. These equations are functions of temperature, pressure, and compositions; therefore, they represent relations connecting the phase-rule variables. Since F is the difference between the number of variables and the number of equations:

$$F = 2 + (C-1)P - (P-1)C - r$$
$$F = 2 - P + C - r$$

(6.1)

The variable r can be determined by subtracting the number of elements in the system from the number of components. Note that $r = 0$ in a non-reacting system.

ILLUSTRATIVE EXAMPLE 6.1

A gaseous system at equilibrium consists of CO_2, H_2, H_2O, CH_4, and C_2H_6. Determine the degrees of freedom.

SOLUTION: Determine the number of phases, P, and the number of components,

$$P = 1 \qquad C = 5$$

Determine the number of independent chemical reactions, r.

Number of elements = 3; C, H, and O

Number of components = 5

Therefore,

$$r = 5 - 3 = 2$$

Write the equation for the Gibb's Phase Rule and calculate the degrees of freedom

$$F = 2 - P + C - r \tag{6.1}$$

Substituting

$$= 2 - 1 + 5 - 2 = 4$$

Since $F = 4$, one is free to specify, e.g., T, P and two mole fractions in an equilibrium mixture of these five chemical species, provided nothing else is arbitrarily set. ∎

In mass transfer applications, the most important equilibrium phase relationship (as noted above) is that between liquid and vapor. Raoult's law and Henry's law theoretically describe liquid–vapor behavior and under certain conditions are applicable in practice. Raoult's law and Henry's law are the two equations most often used in the introductory study of phase equilibrium—specifically, within the boundaries of ideal vapor–liquid equilibrium (VLE). Both Raoult's and Henry's law help one understand the equilibrium properties of liquid mixtures. The next two sections review these laws.

Phase equilibrium examines the physical properties of various classes of mixtures, and analyzes how different components affect each other within those mixtures. There are four key classes of mixtures (see Table 6.1):

1 vapor–liquid
2 vapor–solid
3 liquid–solid
4 liquid–liquid

Topics (2) and (3) receive superficial treatment later in this chapter.

It is the authors' opinion that the two most important traditional mass transfer operations are distillation and absorption. As such, the presentation to follow will primarily address principles that directly apply to these two mass transfer processes. For example, material on Raoult's law and equilibrium relationships will be employed in Chapter 9, Distillation. Material on Henry's law and mass transfer coefficients will be directly applied to absorption processes in Chapter 10.

RAOULT'S LAW

Raoult's law states that the partial pressure of each component (p_i) in a solution is proportional to the mole fraction (x_i) of that component in the liquid mixture being studied. The "proportionality constant" is its vapor pressure (p_i'). Therefore, for component i in a mixture, Raoult's law can be expressed as:

$$p_i = p_i' x_i \tag{6.2}$$

where p_i is the partial pressure of component i in the vapor, p_i' is the vapor pressure of pure i at the same temperature, and x_i is the mole fraction of component i in the liquid. This expression may be applied to all components so that the total pressure P is given by the sum of all the partial pressures. If the gas phase is ideal, Dalton's law applies $p_i = y_i P$ and one may write

$$P = \sum_i x_i p_i' \tag{6.3}$$

Therefore, Equation (6.2) can then be written as follows:

$$y_i = x_i \left(\frac{p_i'}{P} \right) \tag{6.4}$$

where y_i is the mole fraction of component i in the vapor and P is the total system pressure. For example, the mole fraction of water vapor in air that is saturated, and in equilibrium contact with pure water ($x = 1.0$), is simply given by the ratio of the vapor pressure of water at the system temperature divided by the system pressure. While it is true that some of the air dissolves in the water (making $x_w < 1.0$), one usually neglects this to simplify calculations. These equations primarily find application in distillation, and to a lesser extent, absorption and stripping.

The basis of Raoult's law can be best understood in molecular terms by considering the rates at which molecules leave and return to the liquid. Raoult's law illustrates how the presence of a second component, say B, reduces the rate at which component A molecules leave the surface of the liquid, but it does not inhibit the rate at which they return.[4] In order to finally deduce Raoult's law, one must draw on additional experimental information about the relation between the vapor pressures and the composition of the liquid. Raoult himself obtained this data from experiments on mixtures of closely related liquids in order to develop his law.

Most mixtures obey Raoult's law to *some* extent, however small it may be. The mixtures that closely obey Raoult's law are those whose components are structurally similar—and therefore Raoult's law is most useful when dealing with these types of solutions. Mixtures that obey Raoult's law for the entire composition range are called ideal solutions. A graphical representation of this behavior can be seen in Figure 6.2.

Many solutions do deviate significantly from Raoult's law. However, the law is obeyed even in these cases for the component in excess (which, in this case, would be the *solvent*) as it approaches purity. Therefore, if the solution of solute is dilute, the properties of the solvent can be approximated using Raoult's law. Raoult's law, however, does not have universal applications. There are several aspects of this law which give it limitations. First, it assumes that the vapor is an ideal gas, which is not necessarily the case. Second, Raoult's law only applies to ideal solutions, and, in reality, there are no ideal solutions. Also, a third problem to be aware of is that Raoult's law only really works for *solutes* which do not change their nature when they dissolve (i.e., they do not ionize or associate). A correction factor which accounts for liquid-phase deviations from Raoult's law is developed later in this chapter.
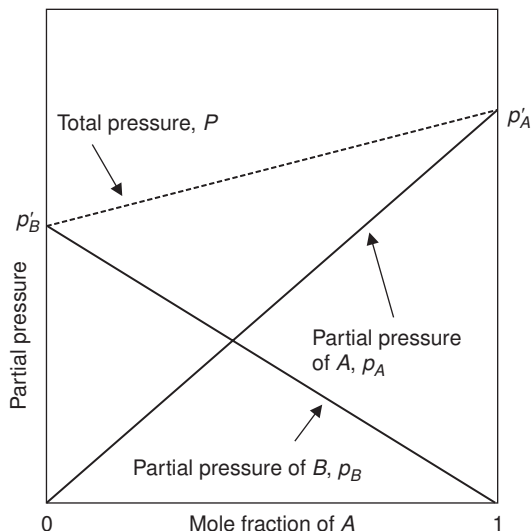
Figure 6.2   Graphical representation of the vapor pressure of an ideal binary solution, i.e., one that obeys Raoult's law for the entire composition range.

Raoult law applications require vapor pressure information. Vapor pressure data is available in the literature.[1] However, there are two equations that can be used in lieu of actual vapor pressure information—the Clapeyron equation and the Antoine equation. The Clapeyron equation is given by

$$\ln p' = A - (B/T) \tag{6.5}$$

where p' and T are the vapor pressure and temperature, respectively. The Antoine equation is given by

$$\ln p' = A - B/(T + C) \tag{6.6}$$

Table 6.2   Approximate Clapeyron Equation Coefficients*

	A	B
Acetaldehyde	18.0	3.32×10^3
Acetic anhydride	20.0	5.47×10^3
Ammonium chloride	23.0	10.0×10^3
Ammonium cyanide	22.9	11.5×10^3
Benzyl alcohol	21.9	7.14×10^3
Hydrogen peroxide	20.4	5.82×10^3
Nitrobenzene	18.8	5.87×10^3
Nitromethane	18.5	4.43×10^3
Phenol	19.8	5.96×10^3
Tetrachloroethane	17.5	4.38×10^3

*T in K, p' in mm Hg.

Table 6.3   Antoine Equation Coefficients*

	A	B	C
Acetone	14.3916	2795.82	230.00
Benzene	13.8594	2773.78	220.07
Ethanol	16.6758	3674.49	226.45
n-Heptane	13.8587	2911.32	216.64
Methanol	16.5938	3644.30	239.76
Toluene	14.0098	3103.01	219.79
Water	16.2620	3799.89	226.35

*T in °C, p' in kPa.

Note that for both equations, the units of p' and T *must* be specified for given values of A and B and/or C. Values for the Clapeyron equation coefficients—A and B—are provided in Table 6.2 for some compounds. Some Antoine equation coefficients—A, B, and C—are listed in Table 6.3. Additional values for these coefficients for both equations are available in the literature.[1,4]

ILLUSTRATIVE EXAMPLE 6.2

The Clapeyron equation coefficients for acetone have been experimentally determined to be

$$A = 15.03$$
$$B = 2817$$

with p' and T in mm Hg and K, respectively. Estimate its vapor pressure at 0°C.

SOLUTION: The Clapeyron equation is given by

$$\ln p' = A - (B/T) \tag{6.5}$$

Employ the correct units. Substituting, the vapor pressure, p', of acetone at 0°C is

$$\ln p' = 15.03 - 2817/(0 + 273)$$
$$= 4.7113$$
$$p' = 111.2 \text{ mm Hg} \qquad ■$$

ILLUSTRATIVE EXAMPLE 6.3

The Antoine coefficients for acetone are:

$$A = 14.3916$$
$$B = 2795.82$$
$$C = 230.00$$

with p' and T in the same units noted in the previous example. Use the Antoine equation to estimate the vapor pressure of acetone at 0°C.

SOLUTION: The Antoine equation is given by

$$\ln p' = A - B/(T + C) \tag{6.6}$$

Substituting, the vapor pressure of acetone at 0°C predicted by the Antoine equation is

$$\ln p' = 14.3916 - 2795.82/(0 + 230.00)$$
$$= 2.236$$
$$p' = 9.35 \text{ kPa} \qquad \blacksquare$$

The reader should note that the Clapeyron equation generally overpredicts the vapor pressure at or near ambient conditions. The Antoine equation is widely used in industry and usually provides excellent results. Also note that, contrary to statements appearing in the *Federal Register* and some *Environmental Protection Agency* (*EPA*) publications, vapor pressure is not a function of pressure.

ILLUSTRATIVE EXAMPLE 6.4

If the vapor pressure of acetone at a given temperature is 71 mm Hg, calculate the maximum vapor phase concentration in mole fraction units at 1 atm total pressure.

SOLUTION: The maximum concentration of a component in a noncondensable gas obeying Raoult's law is given by its vapor pressure p' divided by the total pressure, P. Any increase in concentration will result in the condensation of the component in question. The maximum mole fraction of acetone in air at 0°C and 1 atm is therefore:

$$y_{\text{max}} = \frac{p'}{P} \tag{6.2}$$

Substituting,

$$y_{\text{max}} = \frac{71}{760} = 0.0934 \qquad \blacksquare$$

It is important to note that vapor mixtures do not condense at one temperature as a pure vapor does. The temperature at which a vapor begins to condense as the temperature is lowered is defined as the *dew point*. It is determined by calculating the temperature at which a given vapor mixture is saturated. The *bubble point* of a liquid mixture is defined as the temperature at which it begins to vaporize. The bubble point may also be viewed as the temperature at which the last vapor condenses, while the dew point is the temperature at which the last liquid vaporizes.[1] These examples are based on a given and constant pressure, and are thus referred to as the dew point and bubble point temperatures. Calculations based on holding the temperature constant lead to the dew point and bubble point pressures.

Dew point and bubble point calculations enable one to obtain vapor–liquid equilibrium (VLE) relationships for a binary mixture; these are often provided as a *P-x, y* diagram (with the temperature constant) or a *T-x, y* diagram (with the pressure constant), or both. VLE data can be generated assuming Raoult's law applies, and there are two types of diagrams of interest: the aforementioned *P-x, y* and *T-x, y*.

Additional details and procedures for obtaining these graphs are provided in the literature[1]; algorithms are also available. The next two Illustrative Examples serve as an introduction to VLE calculations which assume that Raoult's law applies.

ILLUSTRATIVE EXAMPLE 6.5

A liquid stream contains 5 gmol % ethane (A) and 95 gmol % n-hexane (B) at 25°C. The vapor pressure of ethane at 25°C is 4150 kPa and the vapor pressure of n-hexane at 25°C is 16.1 kPa. If the pressure is such that this is a saturated liquid, what is the pressure and what is the composition of the first vapor to form?

SOLUTION: For a two component (A−B) system, Equation (6.3) reduces to

$$P = x_A p_A' + x_B p_B' \tag{6.3}$$

Substituting,

$$P = (0.05)(4150) + (0.95)(16.1)$$
$$= 222.8 \text{ kPa} = 32.3 \text{ psia}$$

From Equation (6.4),

$$y_A = x_A p_A'/P$$

Substituting,

$$y_A = (0.05)(4150)/222.8$$
$$= 0.931$$
$$y_B = 1 - 0.931$$
$$= 0.069$$

This is an example of a bubble point pressure calculation (since the temperature is fixed) for a liquid mixture. ∎

ILLUSTRATIVE EXAMPLE 6.6

The vapor pressures of carbon tetrachloride and ethyl acetate at 27°C are:

carbon tetrachloride (A) = 111 mm Hg
ethyl acetate (B) = 92 mm Hg

Calculate the composition of the liquid and vapor phases in equilibrium at this temperature and a total pressure of 100 mm Hg.

SOLUTION: Substitute into Equation (6.3) for the total pressure

$$P = p_A' x_A + p_B'(1 - x_A)$$
$$100 = 111 x_A + 92(1 - x_A)$$
$$x_A = 0.421$$

The vapor phase composition is given by

$$y_A = p'_A x_A / P \tag{6.4}$$
$$y_A = (111)(0.421)/100$$
$$y_A = 0.467$$

■

ILLUSTRATIVE EXAMPLE 6.7

Using the vapor–liquid equilibrium (VLE) data for the ethanol–water system provided in Table 6.4, generate a T-x, y diagram.

Table 6.4   Vapor–Liquid Equilibrium Data for Ethanol–Water at 1.0 atm

T (°C)	x_{ETOH}	y_{ETOH}
212	0.000	0.000
192	0.072	0.390
186	0.124	0.470
181	0.238	0.545
180	0.261	0.557
177	0.397	0.612
176	0.520	0.661
174	0.676	0.738
173	0.750	0.812
172	0.862	0.925
171	1.000	1.000

SOLUTION: The T-x, y diagram is plotted in Figure 6.3. The top curve (y vs T) represents saturated vapor and the bottom curve (x vs T) is saturated liquid.
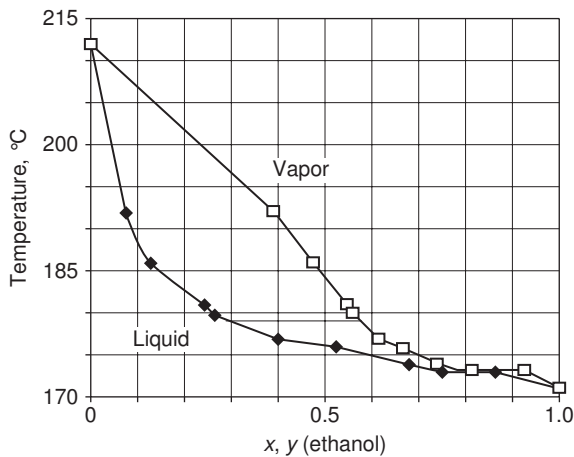

Figure 6.3   T-x, y diagram for the ethanol–water system.   ■

Finally, the reader should note that all the phase equilibrium calculations in this chapter are based on the assumption that the vapor and liquid are in *equilibrium*. The above presentation is also limited to two-component systems. An approach to multiphase (two or more coexisting liquid phases) VLE is available in the literature.[1]

ILLUSTRATIVE EXAMPLE 6.8

The following *P-x, y* data is provided in Table 6.5 for the methanol (m)–water (w) system at 40°C. Plot a *P-x, y* diagram. Also provide an *x–y* plot.

Table 6.5   *P-x, y* Data for Methanol–Water System ($T = 40°C$)

P, kPa	x_m	y_m
7.356	0.0	0.000
10.16	0.1	0.349
12.97	0.2	0.546
15.77	0.3	0.674
18.58	0.4	0.762
21.39	0.5	0.828
24.19	0.6	0.878
27.00	0.7	0.918
29.81	0.8	0.951
32.61	0.9	0.977
35.42	1.0	1.000

SOLUTION: Applicable plots are provided in Figures 6.4 and 6.5.
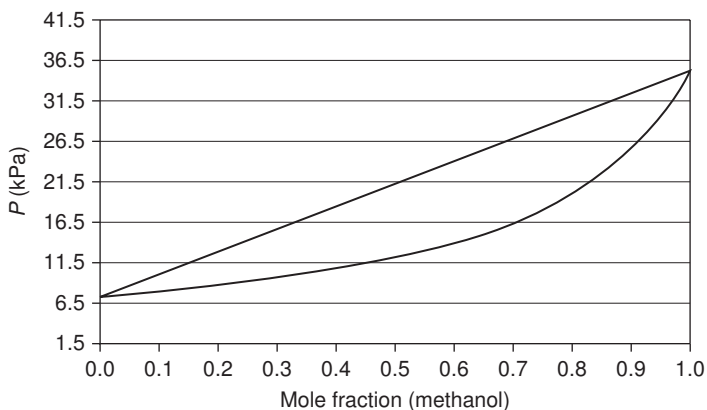

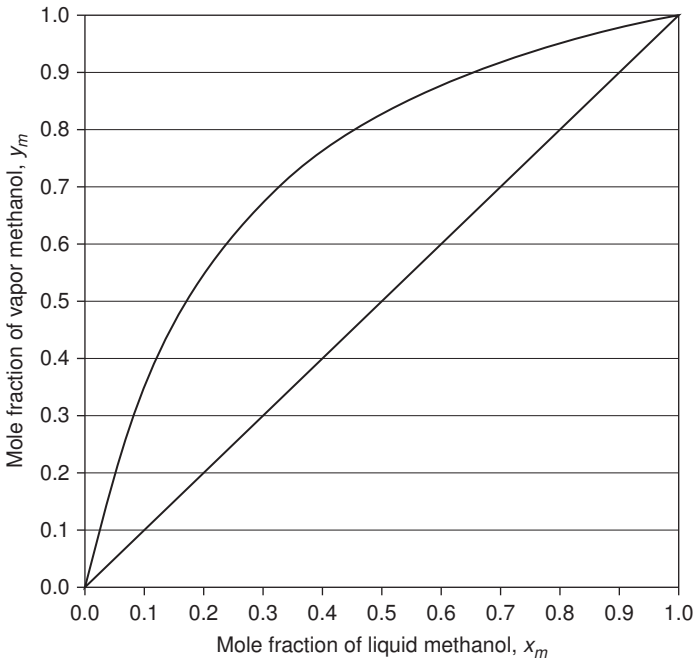**Figure 6.4**   *P-x, y* diagram for methanol–water at 40°C (Raoult's law).

Figure 6.5 $x-y$ diagram for methanol–water ($40^\circ C$).   ■

Another application of interest arises in gas absorption operations. The equilibrium of interest is that between a nonvolatile absorbing liquid (solvent) and a solute gas. The solute is ordinarily removed from its mixture in a relatively large amount of a carrier gas which does not dissolve in the absorbing liquid. Therefore, it is often possible, and frequently the case when considering the removal and/or recovery of a gaseous component by absorption, to assume that only the component in question is transferred between phases. Both the solubility of the nondiffusing (inert) gas in the liquid and the presence of vapor from the liquid in the gas phase are usually neglected. The important variables to be considered then are the pressure, temperature, and the concentrations of the component in the liquid and the gas phase. The temperature and pressure may be fixed and the concentration(s) of the component(s) in the various phases are defined from phase equilibrium relationships. An equation that may be employed to relate the equilibrium concentration of the absorbed species in the liquid phase is the aforementioned Henry's law.[5]

HENRY'S LAW

Unfortunately, relatively few mixtures follow Raoult's law. Henry's law is another empirical relationship used for representing data on many systems. Henry's law states that the partial pressure of the solute is proportional to its mole fraction, but the proportionality constant is not the vapor pressure of the pure substance (as it is

in Raoult's law). Instead, the proportionality constant is some empirical constant, denoted H_B. Therefore, for some component B of a solution, Henry's law[5] can be written as:

$$p_B = H_B x_B \qquad (6.7)$$

The value of the Henry's law constant, H_B, is found to be temperature dependent. The value generally increases with increasing temperature. As a consequence, the solubility of gases generally decreases with increasing temperature. In other words, the dissolved gases in a liquid can be driven off by heating the liquid. Mixtures which obey Henry's law are known as ideal-dilute solutions. The above equation has also been written, for component A in this instance, as

$$y_A = m_A x_A \qquad (6.8)$$

where m_A is once again an empirical constant.

In order to fully understand the concepts behind Henry's law, one can once again examine the basic physical properties of a dilute solution on a molecular level. In a dilute solution, the solvent molecules are in an environment which is not that much different from the one they experience in a pure liquid. The solute molecules, however, are in a completely different environment than that of the pure solute state. Because of this, the solvent behaves as a slightly modified pure liquid, whereas the solute behaves entirely differently from its pure state. In this case, the rate of escape of solute molecules will be proportional to their concentration in the solution, and solute will accumulate in the gas until the return rate is equal to the rate of escape. This return rate will be proportional to the partial pressure of solute with a very dilute gas. It is important to remember that if the solute and solvent are very similar in structure, the solute obeys Raoult's law. It may be rigorously proven that all non-ionic binary solutions (at relatively low pressures such that the vapor phase is ideal) obey Equation (6.7) as component "B" approaches infinite dillution. Moreover, when the dilute component (B) follows Henry's law, the other component (A) must obey Raoult's law over the same range of composition.

The results obtained from Henry's law for the mole fraction of dissolved gas is valid for the liquid layer just beneath the interface, but not necessarily the entire liquid. The latter will be the case only when thermodynamic equilibrium is established throughout the entire liquid body. There, the use of Henry's law is limited to dilute gas–liquid solutions, i.e., liquids with a small amount of gas dissolved in them. The linear relationship of Henry's law does not apply in the case when the gas is highly soluble in the liquid.

Henry's law has been found to hold experimentally for all dilute solutions in which the molecular species is the same in the solution as in the gas. One of the most conspicuous and apparent exceptions to this is the class of electrolytic solutions, or solutions in which the solute has ionized or dissociated. As in the case of Raoult's law, Henry's law in this particular case, does not hold. Several constants for Henry's law are provided in Table 6.6. However, equations are available to estimate this constant.[1]

Table 6.6 Henry's Law Constants for Gases in Water at Approximately 25°C

Gas	H, (bar)$^{-1}$
Acetylene	1350
Air	73,000
Carbon dioxide	1700
Ethane	31,000
Ethylene	11,500
Methane	42,000

ILLUSTRATIVE EXAMPLE 6.9

Explain why there is a temperature increase when a gas is "dissolved" in a liquid.

SOLUTION: Since gases usually liberate heat when they dissolve in liquids, thermodynamics reveals (as noted earlier) that an increase of temperature will result in a decrease in solubility. This is why gases may be readily removed from solution by heating.   ■

Another important factor influencing the solubility of a gas is pressure. As is to be expected from kinetic considerations, compression of the gas will tend to increase its solubility.

ILLUSTRATIVE EXAMPLE 6.10

Given Henry's law constant for and the partial pressure of H_2S, determine the maximum mole fraction of H_2S that can be dissolved in solution. Data are provided below.

  Partial pressure of $H_2S = 0.01$ atm
  Total pressure $= 1.0$ atm
  Temperature $= 60°F$
  Henry's law constant, $H_{H_2S} = 483$ atm/mole fraction (1 atm, 60°F)

SOLUTION: Write the equation describing Henry's law.

$$p_{H_2S} = H_{H_2S} x_{H_2S}$$
$$p_{H_2S} = y_{H_2S} P$$

(6.7)

Calculate the maximum mole fraction of H_2S that can be dissolved in solution

$$x_{H_2S} = p_{H_2S}/H_{H_2S}$$
$$= 0.01/483$$
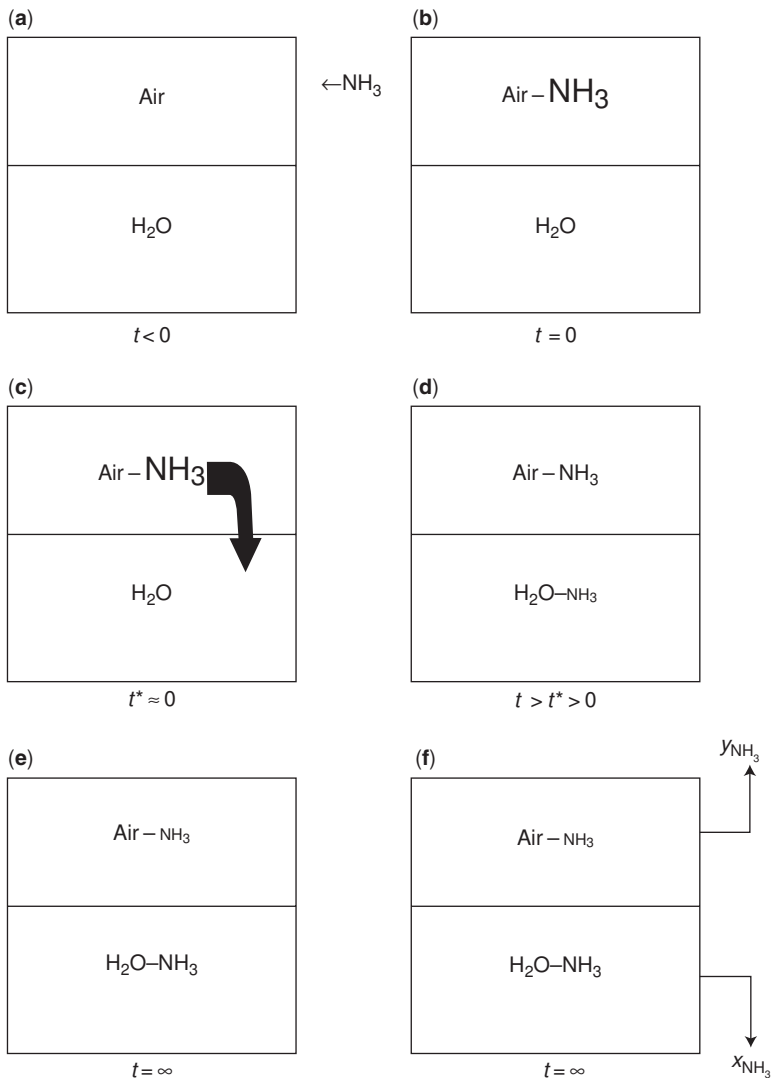$$= 2.07 \times 10^{-5}$$

■

Figure 6.6   Ammonia absorption system at T and P.

To illustrate the application of Henry's law to the aforementioned absorption process,[1] consider the air–water–ammonia system at the T and P pictured in Figure 6.6a–f. In this system, NH_3 is added to the air at time $t = 0$ (b). The NH_3 slowly proceeds to distribute itself (c, d) until "equilibrium" is reached in (e). The mole fractions in both phases are measured in (f). This data is represented as point (1) in Figure 6.7.

If the process in Figure 6.6 is repeated several times with additional quantities of NH_3, additional equilibrium points will be generated. These points appear in Figure 6.8.
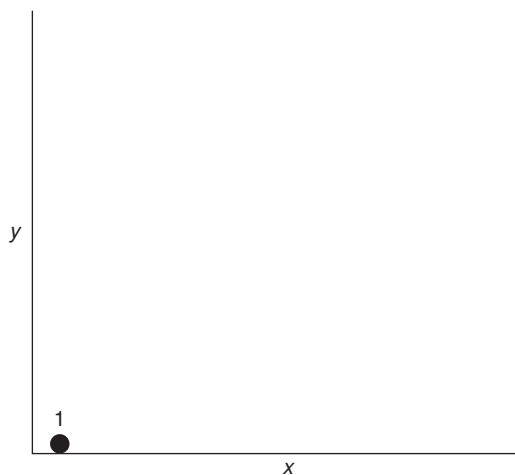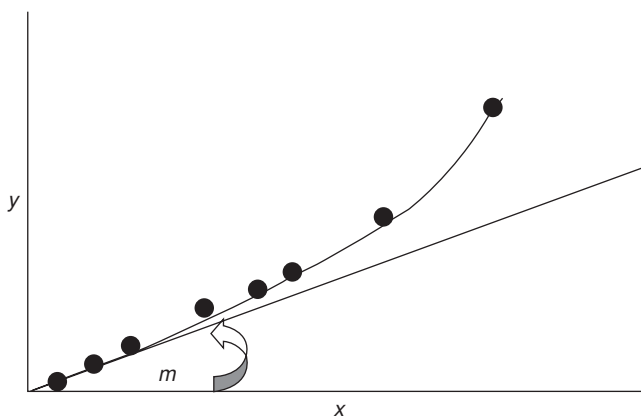
Figure 6.7 $x-y$ equilibrium point.

Figure 6.8 $x-y$ equilibrium diagram.

Although the plot in Figure 6.8 curves upwards, the data approaches a straight line of slope m at low values of x. It is this region where it is assumed that Henry's law applies. One of the coauthors[6] of this text believes that as $x \to 0$, $m \to 0$. This conclusion, and its ramifications, has received further attention in the literature.[6]

ILLUSTRATIVE EXAMPLE 6.11

Convert the ammonia–water equilibrium data given in Table 6.7 to an $x-y$ plot at 30°C and 1 atm. Evaluate Henry's law constant for this system. Over what range of liquid mole

Table 6.7   Equilibrium Data for Ammonia–Water System; 30°C, 1 atm

x, mole fraction NH$_3$ in liquid	p_{NH_3}, mm Hg
0	0
0.0126	11.5
0.0167	15.3
0.0208	19.3
0.0258	24.4
0.0309	29.6
0.0405	40.1
0.0503	51.0
0.0737	79.7
0.0960	110.0
0.1370	179.0
0.1750	260.0
0.2100	352.0
0.2410	454.0
0.2970	719.0

Table 6.8   Ammonia-Water Equilibrium (x–y) Data; 30°C, 1 atm

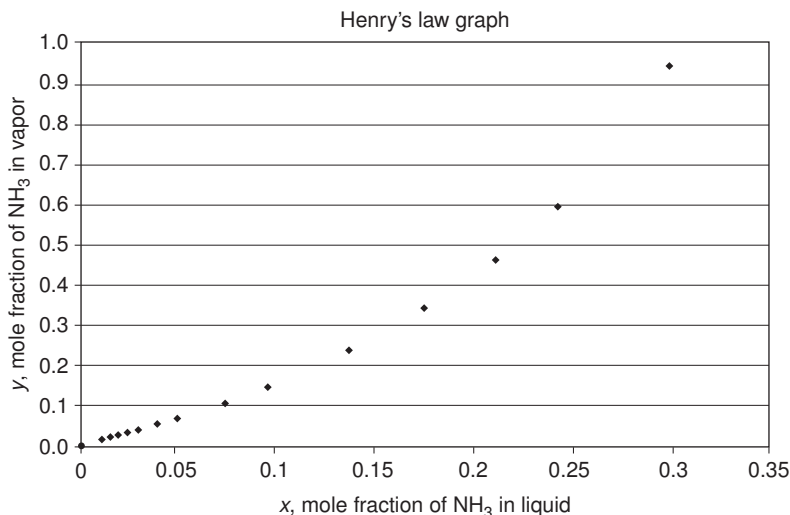| x_{NH_3}	$y_{NH_3} = \dfrac{p_{NH_3}}{P}$
0	0
0.0126	0.015
0.0167	0.0210
0.0208	0.0254
0.0258	0.0321
0.0309	0.03894
0.0405	0.05276
0.0503	0.06710
0.0737	0.10486
0.0960	0.145
0.1370	0.236
0.1750	0.342
0.2100	0.463
0.2410	0.596
0.2970	0.945

Figure 6.9   Ammonia–water equilibrium at 30°C and 1 atm.

fraction will Henry's law predict the equilibrium ammonia vapor content to within 5% of the experimental data?

SOLUTION: The partial pressure of ammonia is converted below to mole fraction in the vapor. See Table 6.8. These results are plotted in Figure 6.9.

Henry's law constant from the graph is approximately 1.485 ($= 0.141/0.095$) at $x = 0.095$ based on linear regression. Since

$$y_{actual} = 0.148$$
$$y_{calculated} = 1.485(0.095) = 0.141$$
$$\text{Percent agreement} = \left(\frac{0.141}{0.148}\right)100 = 95.27\%$$

Thus, from $x = 0$ to $x = 0.095$, Henry's law equation, $y = 1.485x$, predicts the equilibrium vapor content to within 5% of the experimental data.   ■

RAOULT'S LAW VS HENRY'S LAW[7]

A basic difference between Raoult's and Henry's laws is that Raoult's law applies to the solvent, while Henry's law applies to the solute. In ideal solutions, both the solute and the solvent obey Raoult's law. However, in ideal *dilute* solutions, the solute obeys Henry's law whereas the solvent obeys Raoult's law. In Figure 6.10, one can see the differences between Raoult's law and Henry's law in graphical form, in addition to the behavior of a real solution. It provides information on how two components
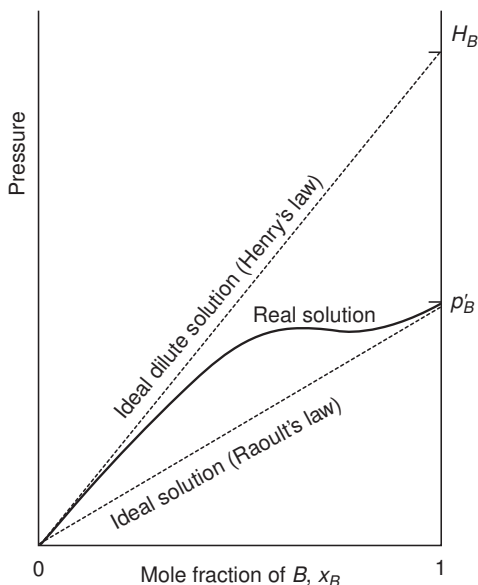
Figure 6.10   Graphical representation of the differences between Raoult's and Henry's law; component *B* represents the solute.

are distributed between the vapor and liquid phase, e.g., acetone–water, while Henry's law provides how a component, e.g., acetone will be distributed between a gas and liquid phase, e.g., air and water.

There are several other significant differences between these two laws which must be recognized. Raoult's law is much more theory-based, since it only applies to ideal situations. Henry's law, on the other hand, is more empirically based, making it a more general and practical law.

In addition to providing a link between the mole fraction of the solute and its partial pressure, Henry's law constants may also be used to calculate gas solubilities. This plays an important role in biological functions, such as the transport of gases in the bloodstream. A knowledge of Henry's law constants for gases in fats and lipids is important in discussing respiration.[4,7] For example, consider scuba diving. In this recreational activity, air is supplied at a higher pressure so as to allow the pressure within the diver's chest to match the pressure exerted by the surrounding water. This water pressure of the ocean increases at approximately 1 atm per 10 meters of depth. However, air inhaled at higher pressures makes nitrogen more soluble in fats and lipids rather than water—causing nitrogen to enter the central nervous system, bone marrow, and fat reserves of the body. The nitrogen then bubbles out of its lipid solution if the diver rises to the surface too quickly, causing a condition called decompression sickness, also known as *the bends*. This condition can be fatal. The nitrogen gas bubbles can block arteries and cause unconsciousness as they rise to the brain.

Another interesting application of Henry's law is in the treatment of carbon monoxide poisoning. In a hyperbaric oxygen chamber, oxygen is raised to an elevated

partial pressure. When an individual with carbon monoxide poisoning steps inside this chamber, there is a steep pressure gradient between the partial pressure of arterial blood's oxygen, and the partial pressure of the oxygen in freshly inhaled air. In this way, oxygen floods quickly into arterial blood, allowing a rapid re-supply of oxygen to the bloodstream.

As noted above, Henry's law and Raoult's law have several similarities and differences, and each has their restrictions. The knowledge of both of these laws is invaluable not only academically, but practically as well.

VAPOR–LIQUID EQUILIBRIUM IN NONIDEAL SOLUTIONS[1]

In the case where liquid solutions cannot be considered ideal, Raoult's law will give highly inaccurate results. For these nonideal liquid solutions, various alternatives are available. These are considered in most standard thermodynamics texts and will be treated to some extent below. One important case will be mentioned because it is frequently encountered in distillation, namely, where the liquid phase is not an ideal solution, but the pressure is low enough so that the vapor phase behaves as an ideal gas. In this case, the deviations from ideality are localized in the liquid and treatment is possible by quantitatively considering deviations from Raoult's law. These deviations are taken into account by incorporating a correction factor, γ, into Raoult's law. The purpose of γ, defined as the activity coefficient, is to account for the departure of the liquid phase from ideal solution behavior. It is introduced into Raoult's law equation (for component A) as follows:

$$y_A P = p_A = \gamma_A x_A p'_A \tag{6.9}$$

The activity coefficient is a function of liquid phase composition and temperature. Phase-equilibria problems of the above type are often effectively reduced to evaluating γ.

Vapor–liquid equilibrium calculations performed with Equation (6.9) are slightly more complex than those made with Raoult's law. The key equation then becomes

$$P = \sum p_i = \sum (y_i P) = \sum \gamma_i x_i p'_i \tag{6.10}$$

When applied to a two-component (A–B) system, Equation (6.10) becomes

$$P = y_A P + y_B P = \gamma_A x_A p'_A + \gamma_B x_B p'_B \tag{6.11}$$

so that

$$y_A P = p_A = \gamma_A x_A p'_A \tag{6.12}$$

$$y_B P = p_B = \gamma_B x_B p'_B \tag{6.13}$$

Information on methods to determine the activity coefficient(s) follows.

Theoretical developments in the molecular thermodynamics of non-ideal liquid solution behavior are often based on the concept of *local composition*. Within a liquid solution, local compositions, different from the overall mixture composition, are presumed to account for the short-range order and nonrandom molecular orientations that result from differences in molecular size and intermolecular forces. The concept was introduced by G. M. Wilson in 1964 with the publication of a model of solution behavior, since known as the Wilson equation.[8] The success of this equation in the correlations of vapor–liquid equilibrium data prompted the development of several alternative local-composition models. Perhaps the most notable of these is the NRTL (Non-Random-Two Liquid) equation of Renon and Prausnitz.[9] The application of both approaches (briefly discussed below) has received extensive treatment in the literature.[1,10]

The Wilson equation contains just two adjustable parameters for a binary system (E_{AB} and E_{BA}), and the activity coefficients are written as:

$$\ln \gamma_A = -\ln(x_A + x_B E_{AB}) + x_B \left(\frac{E_{AB}}{x_A + x_B E_{AB}} - \frac{E_{BA}}{x_B + x_A E_{BA}} \right) \qquad (6.14)$$

$$\ln \gamma_B = -\ln(x_B + x_A E_{BA}) - x_A \left(\frac{E_{AB}}{x_A + x_B E_{AB}} - \frac{E_{BA}}{x_B + x_A E_{BA}} \right) \qquad (6.15)$$

For infinite dilution, these equations become:

$$\ln \gamma_A^\infty = -\ln(E_{AB}) + 1 - E_{BA} \qquad (6.16)$$
$$\ln \gamma_B^\infty = -\ln(E_{BA}) + 1 - E_{AB} \qquad (6.17)$$

Note that γ_i^∞ is to be applied for any component i as $x_i \to 0$. Also note that the Wilson parameters, E_{AB} and E_{BA}, must always be positive numbers. The temperature dependence of the Wilson parameter is given by:

$$E_{ij} = \frac{V_j}{V_i} \exp \frac{-a_{ij}}{RT}; \quad i \neq j \qquad (6.18)$$

where V_j and V_i are the molar volumes at temperature T of pure liquids j and i, respectively, and $-a_{ij}$ is a constant independent of composition and temperature. Thus, the Wilson equation has built into it an approximate temperature dependence for the parameters. Wilson model coefficients are provided in Table 6.9 for a number of binary systems.[8,10]

The NRTL equation, containing three parameters for a binary system, is:

$$\ln \gamma_A = x_B^2 \left[\tau_{BA} \left(\frac{G_{BA}}{x_A + x_B G_{BA}} \right)^2 + \frac{G_{AB} \tau_{AB}}{(x_B + x_A G_{AB})^2} \right] \qquad (6.19)$$

$$\ln \gamma_B = x_A^2 \left[\tau_{AB} \left(\frac{G_{AB}}{x_B + x_A G_{AB}} \right)^2 + \frac{G_{BA} \tau_{BA}}{(x_A + x_B G_{BA})^2} \right] \qquad (6.20)$$

Table 6.9 Wilson Equation Parameters[8,10]

System	V_A V_B (cm^3/gmol)	Wilson equation (cal/gmol)	
		a_{AB}	a_{BA}
Acetone	74.05	291.27	1448.01
Water	18.07		
Methanol	40.73	107.38	469.55
Water	18.07		
1-Propanol	75.14	775.48	1351.90
Water	18.07		
Water	18.07	1696.98	−219.39
1,4-Dioxane	85.71		
Methanol	40.73	504.31	196.75
Acetonitrile	66.30		
Acetone	74.05	−161.88	583.11
Methanol	40.73		
Methyl acetate	79.84	−31.19	813.18
Methanol	40.73		
Methanol	40.73	1734.42	183.04
Benzene	89.41		
Ethanol	58.68	1556.45	210.52
Toluene	106.85		

The parameters G and τ can be obtained using the following equations

$$G_{AB} = \exp(-\alpha\tau_{AB}) \tag{6.21}$$
$$G_{BA} = \exp(-\alpha\tau_{BA}) \tag{6.22}$$

Furthermore,

$$\tau_{AB} = \frac{b_{AB}}{RT}$$
$$\tau_{BA} = \frac{b_{BA}}{RT} \tag{6.23}$$

where α, b_{AB}, b_{BA} are parameters specific to a particular pair of species, independent of composition and temperature. The infinite-dilution values of the activity coefficients are given by:

$$\ln \gamma_A^\infty = \tau_{BA} + \tau_{AB}\exp(-\alpha\tau_{AB}) \tag{6.24}$$
$$\ln \gamma_B^\infty = \tau_{AB} + \tau_{BA}\exp(-\alpha\tau_{BA}) \tag{6.25}$$

Tabulated values of the parameters for the NRTL model can be found in Table 6.10.[9,10]

Table 6.10   NRTL Equation Parameters[9,10]

System	NRTL equation (cal/gmol)		
	b_{AB}	b_{BA}	α
Acetone Water	631.05	1197.41	0.5343
Methanol Water	-253.88	845.21	0.2994
1-Propanol Water	500.40	1636.57	0.5081
Water 1,4-Dioxane	715.96	548.90	0.2920
Methanol Acetonitrile	343.70	314.59	0.2981
Acetone Methanol	184.70	222.64	0.3084
Methyl acetate Methanol	381.46	346.54	0.2965
Methanol Benzene	730.09	1175.41	0.4743
Ethanol Toluene	713.57	1147.86	0.5292

VAPOR–SOLID EQUILIBRIUM

This section is concerned with a discussion of vapor–solid equilibria. The relation between the amount of substance adsorbed by an adsorbent (solid) and the equilibrium partial pressure or concentration of the substance at constant temperature is called the adsorption isotherm. The adsorption isotherm is the most important and by far the most often used of the various vapor–solid equilibria data which can be measured. Note that, if the substance being adsorbed (adsorbate) is above its critical temperature, it is technically considered a "gas". Under such conditions, the term "gas–solid" equilibrium is more appropriate.

Most available data on adsorption systems are determined at equilibrium conditions. *Adsorption equilibrium* is the set of conditions at which the number of molecules arriving on the surface of the adsorbent equals the number of molecules that are leaving. An adsorbent bed is said to be "saturated with vapors" and can remove no more vapors from the exhaust stream. Equilibrium determines the maximum amount of vapor that may be adsorbed on the solid at a given set of operating conditions. Although a number of variables affect adsorption, the two most important ones in determining equilibrium for a given system are temperature and pressure.
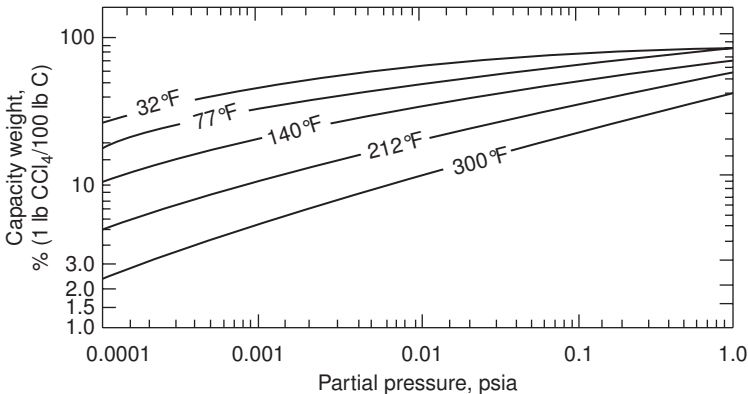
Figure 6.11   Adsorption isotherms for carbon tetrachloride on activated carbon.

Three types of equilibrium graphs and/or data are used to describe adsorption systems: isotherm at constant temperature, isobar at constant pressure, and isostere at constant amount of vapors adsorbed.

As noted above, the most common and useful adsorption equilibrium data is the adsorption *isotherm*. The isotherm is a plot of the adsorbent capacity vs the partial pressure of the adsorbate at a constant temperature. Adsorbent capacity is usually given in weight fraction (or percent) expressed as grams of adsorbate per 100 g of adsorbent. Figure 6.11 shows a typical example of an adsorption isotherm for carbon tetrachloride on activated carbon. Graphs of this type are used to estimate the size of adsorption systems.[1,6]

Attempts have been made to develop generalized equations that can predict adsorption equilibrium from physical data. This is very difficult because adsorption isotherms take many shapes depending on the forces involved. Isotherms may be concave upward, concave downward, or "S"-shaped. To date, most of the theories agree with data only for specific adsorbate-systems and are valid over limited concentration ranges.

Two additional adsorption equilibrium relationships are the aforementioned isostere and the isobar. The isostere is a plot of the *ln p* vs $1/T$ at a constant amount of vapor adsorbed. Adsorption isostere lines are usually straight for most adsorbate–adsorbent systems. The isostere is important in that the slope of the isostere (approximately) corresponds to the heat (enthalpy) of adsorption. The isobar is a plot of the amount of vapors adsorbed vs temperature at a constant partial pressure. However, in the design of most engineering systems, the adsorption isotherm is by far the most commonly used equilibrium relationship.

Several models have been proposed to describe this equilibrium phenomena. Freundlich proposed the following equation to represent the variation of the amount of adsorption per unit area or unit mass with partial pressure,

$$Y = kp^{1/n} \qquad\qquad (6.26)$$

where Y is the weight or volume of gas (or vapor) adsorbed per unit area or unit mass of adsorbent and p is the equilibrium partial pressure of the adsorbate. The k and n are empirical constants dependent on the nature of the solid and adsorbate, and on the temperature. Equation (6.26) may be rewritten as follows. Taking logarithms of both side,

$$\log Y = \log k + \left(\frac{1}{n}\right)\log p \tag{6.27}$$

If $\log Y$ is now plotted against $\log p$, a straight line should result with slope equal to $1/n$ and an ordinate intercept equal to $\log k$. Although the requirements of the equation are met satisfactorily at lower pressures, the experimental points curve away from the straight line at higher pressures, indicating that this equation does not have general applicability in reproducing adsorption of gases (or vapors) by solids.

A much better equation for isotherms was deduced by Langmuir from theoretical considerations. The final form is given in Equation (6.28).

$$Y = \frac{ap}{1 + bp} \tag{6.28}$$

Equation (6.28) may be rewritten as

$$\frac{p}{Y} = \frac{1}{a} + \left(\frac{b}{a}\right)p \tag{6.29}$$

Since a and b are constants, a plot of p/Y vs p should yield a straight line with slope equal to b/a and an ordinate intercept equal to $1/a$.

By assuming that adsorption on solid surfaces takes place with the formation of secondary, tertiary, and finally multilayers upon the primary monomolecular layer, researchers Brunauer, Emmett, and Teller[11] derived the relation

$$\frac{P}{v(p' - p)} = \frac{1}{v_m c} + \left(\frac{c - 1}{v_m c}\right)\frac{p}{p'} \tag{6.30}$$

where v is the volume, reduced to standard conditions of gas (or vapor) adsorbed at system pressure P and T; p is the partial pressure of adsorbate; T is the temperature; p' is the vapor pressure of the adsorbate at temperature T; v_m is the volume of gas (or vapor), reduced to standard conditions, adsorbed when the surface is covered with a unimolecular layer; and, c is the constant at any given temperature. The constant c is approximately given by

$$c = e^{(E_1 - E_L)/RT} \tag{6.31}$$

where E_1 is the enthalpy of adsorption of the first adsorbed layer and E_L is the enthalpy of liquefaction of the gas (or vapor).

The most useful theory from an engineering design viewpoint, in trying to predict adsorption isotherms, is the Polanyi potential theory. The Polanyi theory states that the adsorption potential is a function of the reversible isothermal work done by

the system. Polyani[12] as well as Dubinin and co-workers[13–15] showed that the adsorption isotherms of various vapors can be represented by the following equations

$$\ln(W) = \ln(W_0) - k(E/\beta)^2 \tag{6.32}$$

where

$$E = (RT)\ln(p'/p) \tag{6.33}$$

and W is the volume of condensed adsorbate per gram of carbon (m^3/g); W_0 is the active pore volume of carbon (m^3/g); k is a constant related to pore structure (cal/gmol)$^{-2}$; β is an affinity coefficient which permits comparison of the adsorption potential of the (test) adsorbate to a reference adsorbate; R is the gas constant, 1.987 cal/gmol · K; T is the absolute temperature (K); p is the equilibrium partial pressure of adsorbate; and p' is the vapor pressure of adsorbate at T.

The above equations were suggested by Dubinin for the case when the pores of the adsorbent are comparable in size to the adsorbed molecules. These can be used to determine the equilibrium adsorption isotherm of any given vapor from the adsorption isotherm of a reference vapor, provided that the value of the affinity coefficient, β, of this vapor is available. The adsorption of nonpolar and weakly polar vapors is dominated by dispersion forces. For this situation, Dubinin proposed that β be determined from the ratio of the molar volume, V, of a test solvent to that of reference solvent used to obtain the values of W_0 and k for the given carbon.

ILLUSTRATIVE EXAMPLE 6.12

The representation of adsorption data at a constant temperature that indicates the amount adsorbed vs the partial pressure of the adsorbate is called an

    1 Isobar
    2 Isostere
    3 Isotherm
    4 Isokinetic

SOLUTION: Adsorption equilibrium data at a constant temperature are referred to collectively as an *isotherm*. The correct answer is therefore (3).   ∎

ILLUSTRATIVE EXAMPLE 6.13

Determine the equilibrium capacity of an activated carbon bed during the adsorption phase for carbon tetrachloride (CCl_4) at the following operating conditions:

    Airflow rate = 12,000 cfm at 77°F
    Concentration of CCl_4 air (inlet) = 410 ppmv
    System at atmospheric pressure
    Steam regeneration at 212°F

Refer to Figure 6.11.

SOLUTION: The only pertinent data provided are the operating temperature, pressure, and CCl_4 concentration during the adsorption step. At 410 ppmv, the partial pressure is given by

$$p = (410/10^6)(14.7); \quad P = 1\,\text{atm} = 14.7\,\text{psia}$$

$$= 6.03 \times 10^{-3}\,\text{psia}$$

Referring to Figure 6.11, the equilibrium capacity at this partial pressure at a temperature of 77°F is approximately 40%, or 40 lb CCl_4/100 lb activated carbon.   ■

LIQUID–SOLID EQUILIBRIUM

The simplest system in liquid–solid equilibria is one in which the components are completely miscible in the liquid state and the solid phase consists of a pure component. These systems find application in water purification processes. The equilibrium equations and relationships presented in the vapor–solid equilibrium section generally apply to these systems as well. Details are available in the literature.[16]

ILLUSTRATIVE EXAMPLE 6.14

Adsorption processes are often used as a follow-up to chemical wastewater treatment to remove organic reaction products that cause taste, odor, color, and toxicity problems. The equilibrium relationship between adsorbents (solid materials that adsorb organic matter, e.g., activated carbon) and adsorbates (substances that are bound to the adsorbents, e.g., benzene) may be simply expressed as

$$q = Kc^n \tag{6.34}$$

where q = amount of organic matter adsorbed per amount of adsorbent, c = concentration of organic matter in water, n = experimentally determined constant, and K = equilibrium distribution constant.

   Based upon the data given in Table 6.11 that were obtained from a laboratory sorption experiment, a college student who worked for a company as an intern was asked to evaluate the K and n values for a certain type of activated carbon to be used to remove undesirable by-products formed during chemical treatment. What are the approximate values of K and n that the intern should have generated?

Table 6.11   Sorption Data Collected in Laboratory Experiments; Illustrative Example 6.14

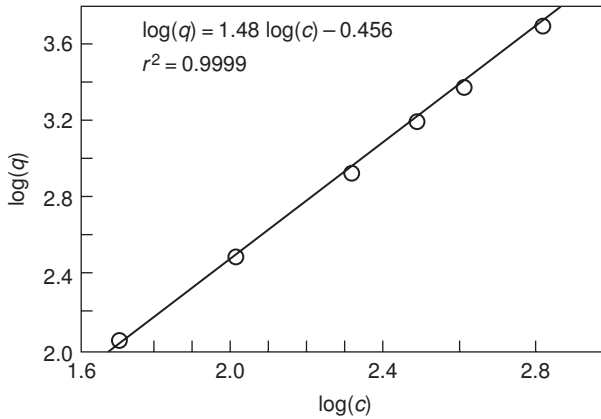| c (mg/L)	q (µg/g)
50	118
100	316
200	894
300	1640
400	2530
650	5240

Figure 6.12   Log–log plot of sorption data; Illustrative Example 6.14.

SOLUTION: The equilibrium relationship given in the problem statement can be linearized by taking the log of both sides of the equation. This yields the following equation:

$$\log(q) = \log(K) + n\log(c)$$

A plot of $\log(q)$ versus $\log(c)$ yields a straight line if this relationship can be used to represent the experimental data. The slope of this line is equal to n, while the intercept is $\log(K)$. The experimental data analyzed using the equation above are plotted in Figure 6.12 and shows that the data fit this linearized isotherm quite well.

The equation generated from a regression analysis[17] indicates that

$$n = 1.48$$
$$\log(K) = -0.456 \quad \text{or} \quad K = 0.35$$

provided the units of c and q are mg/L and µg/g, respectively.   ■

REFERENCES

1. L. THEODORE, F. RICCI, and T. VAN VLIET, "*Thermodynamics for the Practicing Engineer*," John Wiley & Sons, Hoboken, NJ, 2009.
2. L. THEODORE, "*Heat Transfer for the Practicing Engineer*," John Wiley & Sons, Hoboken, NJ, 2011 (in preparation).
3. P. ABULENCIA and L. THEODORE, "*Fluid Flow for the Practicing Engineer*," John Wiley & Sons, Hoboken, NJ, 2009.
4. P. ATKINS and J. DE PAULA, "*Atkins' Physical Chemistry*," 8th edition, W. H. Freeman and Co., San Francisco, CA, 2006.
5. W. HENRY, Publication unknown, 1803.
6. L. THEODORE, "*Air Pollution Control Equipment Calculations*," John Wiley & Sons, Hoboken, NJ, 2009.
7. A. MOHAN, adapted from homework assignment submitted to L. Theodore, 2007.
8. G. WILSON, *J. Am. Chem. Soc.*, 86, 27–130, 1964.
9. H. RENON and J. PRAUSNITZ, *AIChE J.*, **14**, 135–144, 1968.

10. J. SMITH, H. VAN NESS, and M. ABBOTT, "*Chemical Engineering Thermodynamics*," 6th edition, McGraw-Hill, New York City, NY, 2001.
11. S. BRUNAUER, P. H. EMMETT, and E. TELLER, *J. Am. Chem. Soc.*, **60**, 309, 1938.
12. K. POLANYI, *Trans. Faraday Soc.*, **28**, 316, 1932.
13. J. DUBININ, *Chem. Rev.*, **60**, 235, 1960.
14. A. KADLEC and J. DUBININ, *Coll. Int. Sci.*, **31**, 479, 1969.
15. J. DUBININ, "*Chemistry and Physics of Carbon*," Vol. 2, P. L. Walker (ed), Marcel Dekker, New York City, NY, 51, 1966.
16. D. GREEN and R. PERRY, "*Perry's Chemical Engineers' Handbook*," 8th edition, McGraw-Hill, New York City, NY, 2008.
17. S. SHAEFER and L. THEODORE, "*Probability and Statistics Applications for Environmental Science*," CRC Press/Taylor & Francis Group, Boca Raton, FL, 2007.

NOTE: Additional problems are available for all readers at www.wiley.com. Follow links for this title. These problems may be used for additional review, homework, and/or exam purposes.