7   LIQUIDS AND SOLUTIONS

In this chapter, you will learn about the liquid state, one of the three states of matter. The strength of interaction between the particles in a liquid is intermediate between that in a gas and that in a solid state.

The most interesting aspect among the physical properties of a liquid is the mutual conversion to the gas and to the liquid, namely, vaporization/evaporation and condensation between gas and liquid. This is related to the widely used chemical process of distillation, one of the most important and useful methods for purifying liquids. In addition, you will learn the phase rule as an extension of gas/liquid interconversion.

In the latter half of this chapter, you will learn about liquids with two or more ingredients, namely, solutions. Because solutions are often used in the laboratory, it is very important and practical to understand solutions. The density and vapor pressure of a solution are particularly important properties.

7.1   Characteristics of liquid

Gases are liquefied by cooling under an appropriate pressure. As the temperature lowers, the kinetic energy of the gas molecules decreases; and it will become comparable to the intermolecular attraction. Finally the intermolecular distances diminish to the point where the gas becomes liquid.

Liquids have a constant volume at constant temperature but do not have a constant shape. In this regard, a liquid is like a gas. However, as far as the intermolecular distance is concerned, there is a large difference between liquids and gases. 1.0 g of liquid water has a volume of *ca*. 1 cm^3, but water vapor occupies a volume of 1.69 x 10^3 cm^3 at 373 K and 1 atm. You can estimate the intermolecular distances for the two cases, and by comparing that data, you will realize the difference between liquids and gases.

Sample exercise 7.1 Comparison of intermolecular distances

Using the data given above, determine the ratio of intermolecular distances of liquid water and water vapor.
Solution
The space occupied by water vapor may be treated as a cube. The length of the edge for the water vapor is $\sqrt[3]{1.69 \times 10^3}$ = 11.9 cm. Thus the ratio of intermolecular distances is 11.9:1.

You have learned that the kinetic molecular theory assumes that the intermolecular interaction in the gaseous state is negligibly small. In the case of the liquid phase, the situation is not so simple because each molecule is surrounded by many other molecules and hence collisions may take place. The first interesting observation of the molecular motion of liquids was that by Brown regarding the curious movement of pollen floating on the surface of water. The origin of the Brownian motion is the collision between pollen and tiny molecules of water and it was interpreted as follows: since the magnitude and direction that each collision exerts on the pollen varies, pollen particles move randomly.

It is possible to treat the motion of liquid particles using a simple mechanical model as in the case of gas particles. However, the effect of colliding molecules or that of nearby molecules is so large that it is not easy to treat the liquid quantitatively. In high school chemistry, only a rather vague explanation was given for liquid motion, saying that the liquid state is intermediate between the gaseous state and the solid state. Furthermore, it was explained that such entities as the kinetic energy or the intermolecular distances of liquid particles are also intermediate between the gaseous and solid states. Similarly the regularity of the relative positions of the particles was also considered intermediate. That is the reason that there is not much quantitative description in high school chemistry textbooks (Fig. 7.1).

This textbook also will avoid a microscopic treatment of liquids, and the various properties of

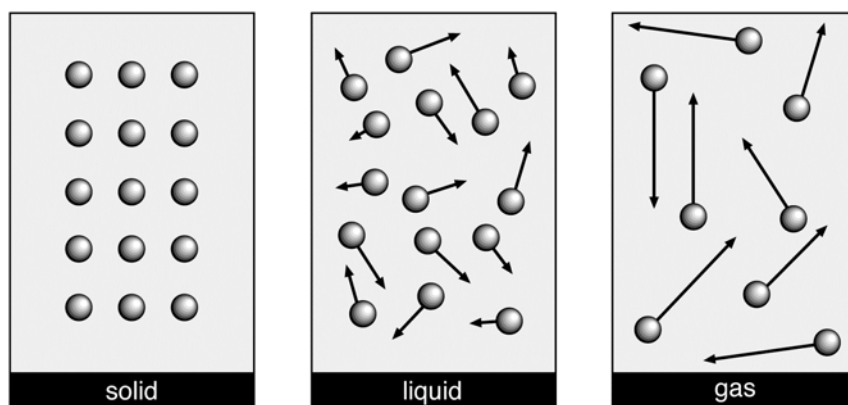liquids will only be treated from the macroscopic viewpoint.

Figure 7.1 Schematic representation of the movement of molecules in solids, liquids and gases.
As the temperature increases, the velocity of molecular motion, and hence the
kinetic energy of the molecules will become relatively larger than the intermolecular attraction.

Gas volumes can be compressed whereas the extent to which liquid volumes can be compressed is rather small since the intermolecular distances are much shorter. In solids, each molecule tends to occupy a fixed position. When the arrangement of molecules in the solid state is regular, it is called a **crystal**. When pressure is applied to a crystal, the extent of solid compression is smaller than that for liquids. When the solid melts, its volume increases by 10% in most cases. This corresponds to the difference in the packing of molecules in the liquid and solid states. Comparatively speaking, liquids are closer to solids than to gases.

Gaseous particles diffuse because they move rapidly. Liquid molecules move more slowly. Particles in a solid never diffuse because the intermolecular attraction is so strong that the molecular kinetic energy cannot overcome it.

7.2 Properties of liquids

(a) Vapor pressure
As is the case with a gas, the molecular kinetic energy of liquid molecules is not uniform but varies. There is regularity in this variety, and the distribution of kinetic energy is governed by **Boltzmann's distribution law**. This law states that the most abundant particles are those with the average kinetic energy, and the number of particles decreases regularly as the deviation of their kinetic energy from the average value becomes larger.

Some of the molecules that have a kinetic energy larger than the average values can break free from the intermolecular attraction and vaporize. If the liquid is contained in a vessel without a lid, it gradually evaporates (**evaporation**), and finally disappears. If the vessel has a lid and the liquid is confined, the molecules lose their energy by collision, *etc.*, and the kinetic energy of some of the molecules becomes so low that these are attracted by the intermolecular attraction at the surface of the liquid, and enter the liquid. This is **condensation** of vapor in the macroscopic description. Finally the number of molecules evaporating from the surface of a liquid and the number of vapor molecules returning to the liquid will become equal, attaining a dynamic equilibrium. This state is called the **vapor-liquid equilibrium** (Fig. 7.2).

The pressure of the gas, that is, the vapor pressure of the liquid when the vapor-liquid equilibrium is attained, is determined only by the temperature. Neither the quantity of liquid nor the volume above the liquid has any effect so long as liquid is present. In other words, the pressure of the vapor of the liquid in a vessel is determined by the given liquid and the given temperature.
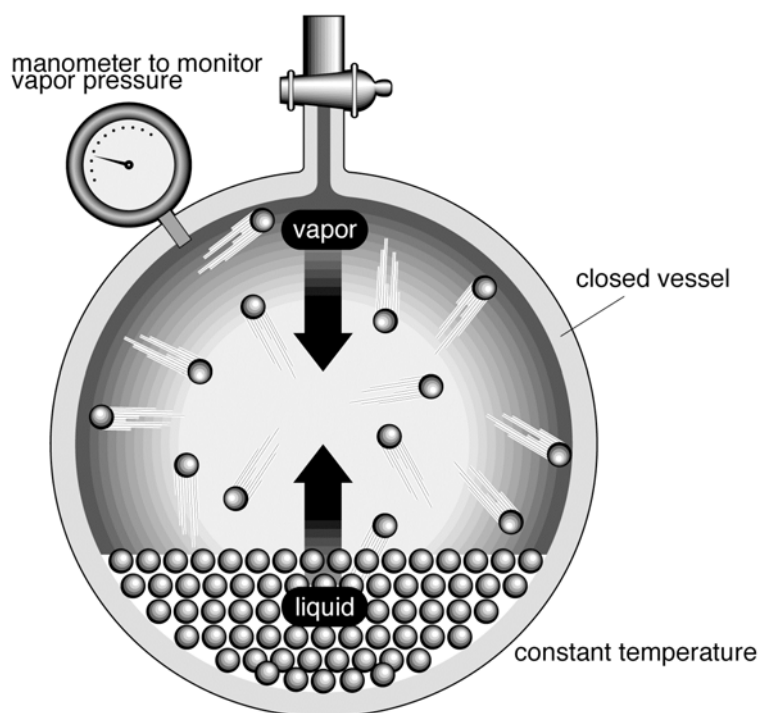
Figure 7.2 A schematic drawing of vapor-liquid equilibrium
The state where the number of molecules evaporating from the surface of the liquid,
and the number of vapor molecules returning into the liquid is equal.

The vapor pressure of the liquid increases as the temperature rises. The pattern of the increase is characteristic of the given liquid. As the temperature rises, the ratio of molecules that possess sufficient energy to overcome the intermolecular interaction will increase (Fig. 7.3).
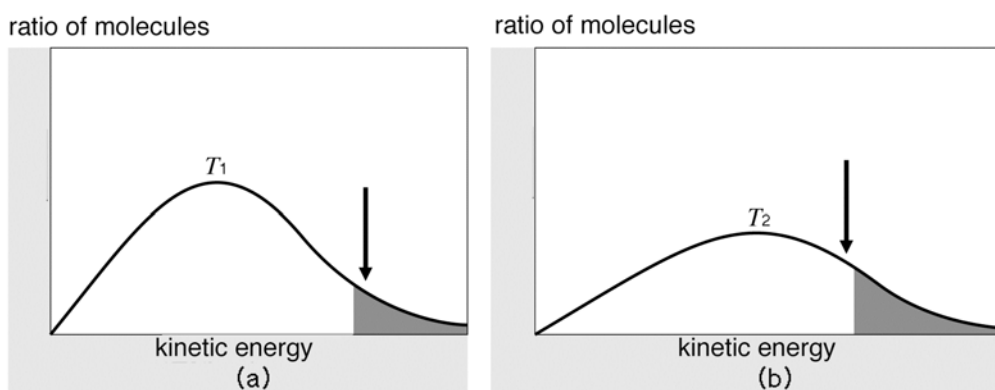

Figure 7.3 The temperature and the kinetic energy of molecules ($T_1 < T_2$)
The kinetic energy of molecules depends on the temperature. In fact the velocity of molecules at a given temperature is not uniform; its divergence is governed by Boltzmann's distribution law. The shaded areas in the figures correspond to the molecules that have sufficient kinetic energy to escape from the surface of the liquid.

The vapor pressure increases as the temperature rises. Figure 7.4 show the relation between temperature and vapor pressure for various liquids.

(b) Boiling points
The vapor pressure of a liquid increases as the temperature rises and bubbles form in the liquid. The pressure of the gas inside the bubble is equal to the sum of the atmospheric pressure and the

hydrostatic pressure due to the height of liquid above the bubble. The state where bubbles are vigorously generated is called **boiling**, and the temperature at which boiling takes place is called the **boiling point**. The boiling point when the atmospheric pressure is 1 atm is called the **normal boiling point** (Fig. 7.4). The boiling point will change depending on the atmospheric pressure. If the atmospheric pressure is higher than 1 atm, the boiling point is higher than the normal boiling point while if the atmospheric pressure is lower than 1 atm, the boiling point is lower than the normal boiling point.
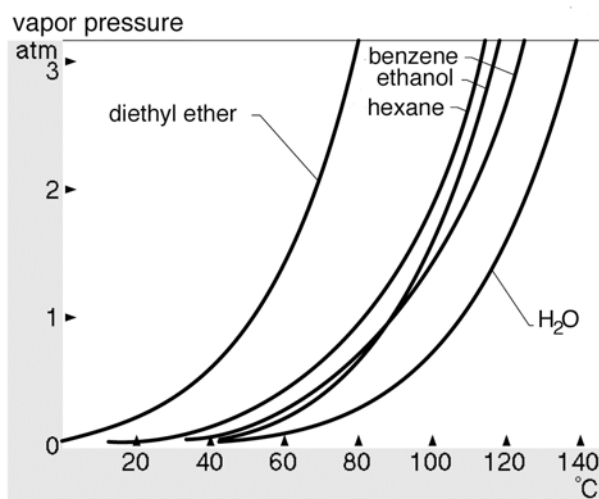

Figure 7.4 The relation between the temperature and the vapor pressure of some liquids
Draw a line parallel to the abscissa at 1 atm. The intersection of this line with each curve corresponds to the normal boiling point.

The boiling point and its change with pressure is characteristic for each compound. Hence the boiling point is one of the means for identifying substances. Identification of substances is now carried out mostly with the aid of spectroscopic methods, but boiling point data are required for reports on new liquids.

Boiling points are determined by molecular weight and the polarity of molecules. Among molecules with the same kind of polar functional groups, the larger the molecular weight, the higher is the boiling point. A good example of this is the homologue of hydrocarbons (Table 7.1). On the other hand, even if the molecular weight is small, molecules with a large polarity will experience strong intermolecular forces that make their boiling points higher. A good example of this is the large difference between boiling points among a group of organic compounds that have much the same molecular weight but different functional groups (Table 7.1). The high boiling point of water is another good example (Ch. 3.4, Ch. 7.3).

Table 7.1 Boiling points of some organic compounds

compound	b.p. (°C)	compound	b.p. (°C)
pentane C_5H_{12}	36.11	butanol C_4H_9OH	108
hexane C_6H_{14}	68.74	diethyl ether $C_2H_5OC_2H_5$	34.5
octane C_8H_{18}	125.7	methyl propyl ether $CH_3OC_3H_7$	39

The energy required converting liquids into gases at S.T.P.[a] (0°C, 1 atm) is called the **heat of vaporization**. When gases condense into liquids, the same amount of heat is released. This is called the **heat of condensation**.

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[a] S.T.P. = standard temperature and pressure.

Table 7.2 Boiling points and heats of vaporization of some liquids

substance	boiling point (°C)	heat of vaporization (J mol^{-1})
H_2	-252.8	904
CS_2	46.4	26780
$CHCl_3$	61	29500
CCl_4	77	36600
C_2H_5OH	78	38570
C_6H_6	80	30760
H_2O	100	46670
CH_3COOH	118	24390

There are some substances that tend to decompose gradually upon heating. Some such substances are difficult to vaporize, although they are liquids at room temperature, because they decompose before reaching the boiling point. Hence, not all substances have normal boiling points.

The process of vaporizing liquids and condensing their vapors in another vessel by cooling is called **distillation**. This is the method most frequently used to purify a liquid. The origin of the techniques of distillation can be traced back to the age of alchemy. A liquid mixture can be separated into its component liquids using the difference in their boiling points. This technique is called **fractional distillation** (Ch. 12.3).

Coffee Break: Vacuum

It is not easy to generate and hold a vacuum. The simplest device to generate a vacuum is the water aspirator, which can be found in any laboratory including laboratories of primary, middle and high schools. The best vacuum obtained by the aspirator is the vapor pressure of water at that temperature. A more sophisticated device is the oil rotatory pump that can generate a vacuum of 5 x 10^{-1} Torr.

With the aid of the powerful oil diffusion pump or the mercury diffusion pump, a vacuum of 10^{-3} Torr or better can be obtained. It is not easy to hold a vacuum. Without proper and careful maintenance of the vacuum line, you cannot obtain the vacuum that should be attainable with that apparatus.

When distilling substances that tend to decompose before reaching their boiling point, the distillation may possibly be done in a sealed system under a vacuum. The boiling point will be lowered depending on the degree of the vacuum attained. This technique is called **vacuum distillation**.

(c) Freezing point

As the temperature of liquids decreases, the average kinetic energy of the molecules also decreases, and hence the vapor pressure as well. When the temperature descends to a certain temperature, the intermolecular attraction will become dominant, and the random translational motion of the molecules slows down. As a consequence, the viscosity of the liquid will become larger and larger. At this stage, sometimes molecules will adopt a distinct regular geometric arrangement that corresponds to the state of crystalline solid. At constant pressure, the change will take place at constant temperature. The temperature of this solidification at 1 atm is called the **freezing point**. Generally the freezing point is equal to the melting point, the temperature at which substances change from the solid state to the liquid state.

7.3 Phase equilibrium and phase diagram

So far our treatment of the mutual change between the three states of matter has focused on the

liquid state. In other words, attention has been paid to the change between the liquid state and the solid state, and between the liquid state and the gaseous state. For discussing the critical state of substances, it is more appropriate to treat the three states simultaneously rather than to treat two out of three states.
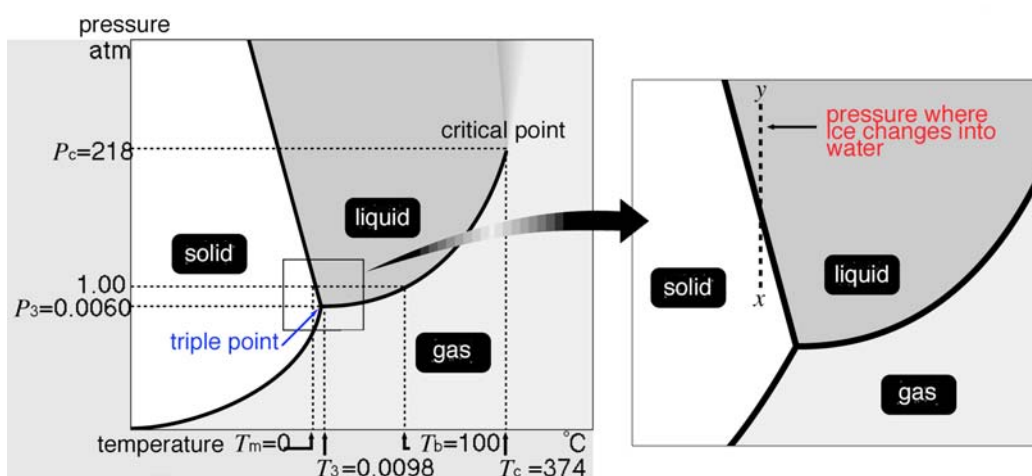

Figure 7.5 Phase diagram of water.
T_m is the normal boiling point of water, T_3 and P_3 are triple point,
T_b normal boiling point, T_c critical temperature, P_c is critical pressure.

The **phase diagram** is a convenient way to present the state of a substance as a function of the temperature and the pressure. As a typical example, the phase diagram of water is shown in Fig. 7.5. In the phase diagram, it is assumed that the substance in question is completely isolated and there is no incoming or outgoing of other substances to or from the system.

Your understanding of the phase diagram will be greatly aided by knowing Gibbs phase rule, a relationship derived by the American mathematician-physicist Josiah Willard Gibbs (1839-1903) in 1876. His rule established that for any state of equilibrium among phases in a closed system, the number of independent variables--called the degrees of freedom F--was equal to the number of components C plus 2 minus the number of phases P. F = C + 2 - P.

Thus, within the single phase areas of the diagram, the number of independent variables is 2--temperature and pressure; when two phases are in equilibrium--as indicated by the lines demarking the boundaries between two phases--only one variable is independent--either temperature or pressure; and at the triple point where three phases are present--no variable is independent.

From the phase diagram, you can confirm what you already know, and furthermore, you can learn what you do not yet know. For instance, the negative slope of the solid-liquid phase boundary has important implications as stated within the right-hand diagram, namely, that when additional pressure is applied to ice it melts and forms water. According to Le Chateliers' principle, when a system at equilibrium is subjected to more pressure, the equilibrium shifts in a direction that nullifies that change. That means that water will have a smaller volume, a higher density, than ice; and we all have experienced that ice floats in water.

On the other hand, water confined in a vessel at a pressure of 0.0060 atm exists as a liquid at low temperature, while at a temperature of 0.0098°C, the three states of water coexist. This point is called the **triple point** of water. There are no other points where the three states of water can coexist.

In addition, the critical point (for water, 218 atm, 374°C), which you have already learned, is also indicated in the phase diagram. When the liquid changes into the gas phase at the critical point, an intermediate state, a state between the liquid phase and the gas phase, emerges. In the phase diagram the state above the critical point is not defined.

7.4 Solutions

So far, the liquid of a one-component system, namely, a pure liquid, has been discussed. In the liquid phase, a two- or multi-component system, that is, a **solution**, is also very important. A solution consists of a liquid which can dissolve substances (the **solvent**) and substances soluble in it (the **solute**). Solvents are not necessarily a liquid, but can be a solid or a gas if it can dissolve substances. Such a system is called a **disperse system**. For a disperse system, the substance corresponding to the solvent is called a **dispersion** (**disperse) medium**, while the substance corresponding to the solute is called the **dispersoid**.

For both solutions and disperse systems, solutes may be solids, liquids or gases. Even when the solute is a liquid, there is no difficulty in distinguishing the role of the solvent and the solute if the quantity of the solute is smaller than that of the solvent. However, when the quantity of two entities is not very different, it is difficult to decide which is the solvent and which the solute. In such a case you can just call these component 1or component 2, *etc*.

(a) Concentration

The concentration of a solution is defined by one of the following expressions.

The expressions of concentration

(1) mass percent (%) =
   (mass of the solute/ mass of the solution) x 100
(2) molarity (molar concentration) (mol dm^{-3}) =
   (moles of solute)/(liters of solution)
(3) molality (mol kg^{-1}) =
   (moles of solute)/(kg of solvent)

Sample Exercise 7.2

Calculate the quantity of silver nitrate $AgNO_3$ necessary to prepare 0.500 dm^3 of 0.150 mol dm^{-3} solution, assuming the molar mass of $AgNO_3$ is 170 g mol^{-1}.

Solution

If the amount of required silver nitrate is x g,
x = [170 (g mol^{-1}) x 0.500 (dm^3) x 0.150 (mol dm^{-3})]/[1 (dm^3) x 1 (dm^3)] $\therefore$ x = 12.8 (mg)

Coffee break: Ice and pressure

The right-side drawing of Fig.7.5 is an expansion of the phase diagram at 0°C, 1 atm. When pressure is applied at this point, the ice (or snow) state moves vertically to reach the point y. Here water is in the liquid phase.

The pleasures of ice-skating are due to the negative slope of the ice-water phase line. The pressure exerted by the blades due to the skater's weight melts the ice and reduces the friction between blade and ice.

(b) Vapor pressure

The vapor pressure of a liquid is one of its important properties. The vapor pressure of solutions is also important and is useful for characterizing the solution. In the case of a binary system, when the components are similar in molecular size and polarity, *e.g*., benzene and toluene, the vapor pressure of the solution can be inferred from the vapor pressures of the components. It is due to the fact that the property is additive. When a solution of component A and component B (the molar fraction of each component is x_A and x_B, respectively; Ch. 6.1(e)) is in equilibrium with the gas phase, the vapor pressure of each component (the partial pressure in the gas phase) is proportional to its molar fraction in the solution. That is, the vapor pressure of component A, p_A, is

given as below:

$$p_A = p_A^0\, x_A$$

where p_A^0 is the vapor pressure of the pure liquid A at the same temperature. A similar relation holds for the vapor pressure of B, p_B.

The relation discovered by the French chemist Francois Marie Raoult (1830-1901) is called **Raoult's law**. For a solution in which Raoult's law is valid, the interaction between individual molecules of the two components is equal to the interaction between molecules of each component. Such solutions are called **ideal solutions**. Fig. 7.6 shows the vapor pressure of an ideal solution as a function of the concentration of the solute. The total pressure of the mixed gas is the sum of p_A and p_B, according to Raoult's law.
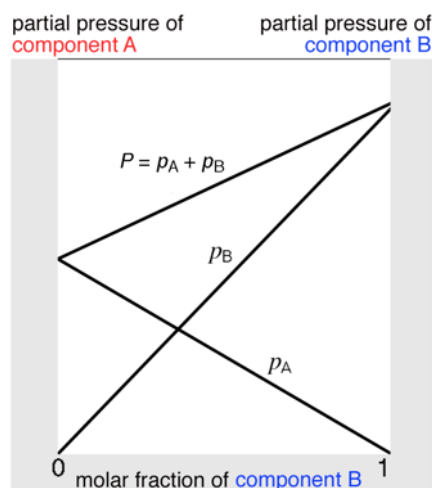

Figure 7.6 The total and partial pressures of an ideal solution

Sample exercise 7.3

The vapor pressures of liquids A and B are 15 Torr and 40 Torr, respectively, at 25°C. Determine the vapor pressure of an ideal solution composed of 1 mol of A and 5 mol of B.

Solution

$$p_A = p_A^0\, x_A = 15 \times (1/6) = 2.5 \text{ Torr}$$
$$p_B = p_B^0\, x_B = 40 \times (5/6) = 33.3 \text{ Torr}$$
$$P = p_A + p_B = 35.8 \text{ Torr}$$

(c) Ideal and real solutions

As the behavior of real gases differs from that of ideal gases, the behavior of real solution differs from that of ideal solutions, in other words, differs from Raoult's law. Fig. 7.7(a) shows the vapor pressure curve of a binary system composed of two liquids with considerably different polarities, acetone Me_2CO and carbon disulfide CS_2. In this case, a positive deviation from Raoult's law (larger vapor pressure) occurs. Fig. 7.7(b) shows the vapor pressure curve of a binary system composed of acetone and chloroform $CHCl_3$. In this case, a negative deviation from Raoult's law (smaller vapor pressure) occurs. The broken lines correspond to the behavior of an ideal solution. The behavior of a solution approaches the ideal as the molar fraction of a component becomes close to 0 or 1. As the deviation of the molar fraction from 0 or 1 increases, the deviation from the ideal becomes larger, and the vapor pressure curve will reach a maximum or a minimum.
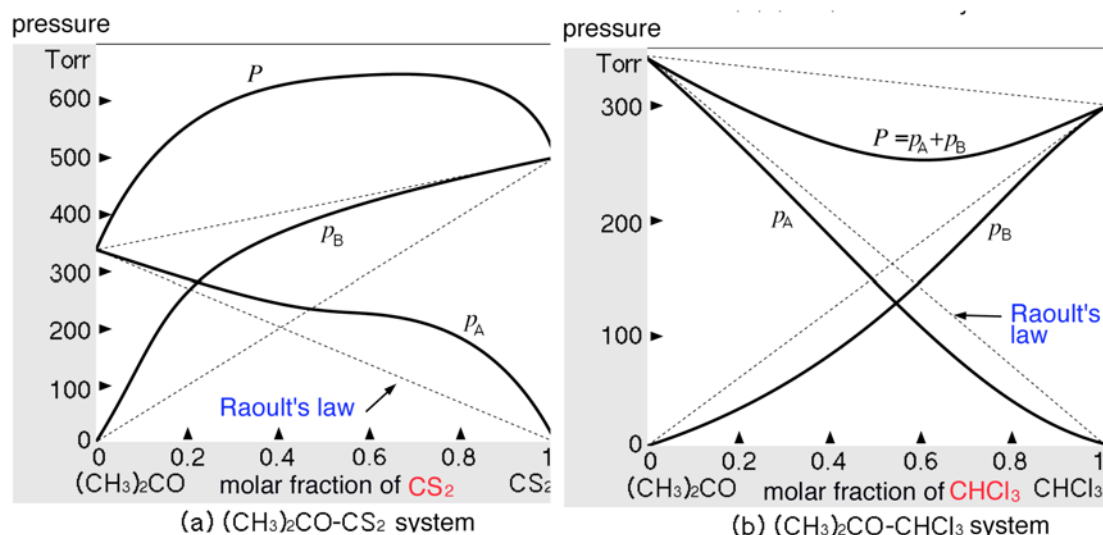
Figure 7.7 The total and partial pressure of a real solution (25°C)

The cause of deviation from ideal behavior is largely due to the magnitude of intermolecular interaction. When mixing component A and component B causes absorption of heat from the surroundings (endothermic), the intermolecular interaction between the two components is smaller than that of each component, and a positive deviation from Raoult's law will result. On the contrary, when mixing causes the discharge of heat to the surroundings (exothermic), a negative deviation from Raoult's law will result.

When a hydrogen bond is formed between component A and component B, the tendency of one component to escape from the other (*i.e.*, evaporate) is weakened, and a negative deviation from Raoult's law will be observed. In conclusion, the cause of the deviation from Raoult's law is much the same as the cause of deviation of gases from the ideal.

(d) Elevation of boiling point and depression of freezing point

When compared at constant temperature, the vapor pressure of a solution is lower than that of the pure liquid. Hence, the boiling point of a solution, that is, the temperature where the gas phase of the solvent reaches 1 atm, is necessarily higher than that of the pure liquid. This phenomenon is called the **elevation of boiling point** of the solution.

By applying Raoult's law to an ideal solution, you can obtain the following relation

$$p_A = p_A{}^0 x_A = p_A{}^0 [n_A/(n_A + n_B)]$$
$$(p_A{}^0 - p_A)/ p_A{}^0 = 1 - x_A = x_B$$

where x_A and x_B are molar fractions, and n_A and n_B are the moles of each component. The equation indicates that, for an ideal solution in which a nonvolatile solute is dissolved, the depression of the vapor pressure is proportional to the molar fraction of the solute.

For a dilute solution where $n_A + n_B$ is nearly equal to n_A, the mole n_B and mass molar concentration m_B are correlated by the following expression.

$$x_B = n_B/(n_A + n_B) \cong n_B/n_A = n_B/(1/M_A) = M_A m_B$$

where M_A is the molar mass of the solvent A. For a dilute ideal solution, the depression of the vapor pressure is proportional to m_B, the mass molar concentration of solute B.

The difference between the boiling points of solution and that of the solvent is called the **elevation of boiling point**, ΔT_f. For dilute solutions, the elevation of boiling point is proportional to

the mass molar concentration of the solute m_B.

$$\Delta T_b = K_b \, m_B$$

where the proportionality constant K_b is a characteristic value for each solvent and called **molar elevation of boiling point**.

A similar relation is valid when an ideal dilute solution is cooled to freezing. The freezing point of a solution is lower than that of the pure solvent. The difference between the freezing point of solution and that of the solvent is called the **depression of freezing point**, ΔT_f. For dilute solutions, the depression of freezing point is proportional to the mass molar concentration of the solute m_B

$$\Delta T_f = K_f \, m_B$$

where the proportionality constant K_b is a characteristic value for each solvent and called **molar depression of freezing point**.

Table 7.3 Molar elevation of boiling points and molar depression of freezing points

solvent	b.p. (°C)	K_b	solvent	m.p. (°C)	K_f
CS_2	46	2.40	H_2O	0	1.86
acetone	55.9	1.69	benzene	5.1	5.07
benzene	79.8	2.54	acetic acid	16.3	3.9
H_2O	100	0.51	camphor	180	40

In Table 7.3 some representative values of the molar elevation of boiling points and the molar depression of freezing points are given. It is possible to determine the molar mass (molecular weight) of the solute whose value is not yet known, using these values and the relations. Recently molecular weight is more conveniently determined with the aid of the mass spectrometer. Before the use of the mass spectrometer became routine, the molecular weight was generally determined by either the elevation of boiling point or the depression of freezing point. For both methods, a certain degree of error was unavoidable, and great skill was required to obtain accurate results.

Sample exercise 7.4 Molecular weight determination by the freezing point depression method.

An aqueous solution consisting of 100 g of H_2O and 5.12 g of a substance A (whose molecular weight is not known) froze at –0.280°C. Using the data in Table 7.3, determine the molar mass of A.

Solution

The molar mass of A is M. By use of the molar depression of freezing point, M can be determined as below.

$$0.280 = K_f \times (m/M) \times (1/W) = 1.86 \times (5.12/M) \times (1/0.11) \therefore M = 340 \text{ g mol}^{-1}.$$

(e) Osmotic pressure

A porous membrane through which the solvent can pass but the solvent cannot is called a **semipermeable membrane**. When two kinds of solutions are separated by a semipermeable membrane, the solvent moves from the low concentration side to the high concentration side through the membrane. This phenomenon is called **osmosis**. The cell membrane is a typical semipermeable membrane. Artificial semipermeable membranes are also available.

When a solution and the pure solvent are separated by a semipermeable membrane, it is necessary to apply a substantial pressure in order for the solvent to move from the solution to the pure solvent. This pressure is called the **osmotic pressure**. The osmotic pressure of a solution composed of 22.4 dm^3 of the solvent and 1 mol of the solute at 0°C is 1.1 x 10^5 N m^{-2}.

The relation between the concentration of the solvent and the osmotic pressure is given by

van't Hoff's law.

$$\pi V = nRT$$

where π is the osmotic pressure, V the volume, T the absolute temperature, n the quantity of substance (mol) and R the gas constant. You can see the formal similarity between this equation and the equation of state of gases. As is the case with the equation of state of gases, it is possible to determine the molecular weight of the solute from the above equation.

Sample exercise 7.5 van't Hoff's law
   The osmotic pressure of a solution of 60.0 g substance A in 1.00 dm^3 of water was 4.31 x 10^5 N m^{-2}. Determine the molecular weight of the substance A.
Solution
   Using the equation $\pi V = nRT$
      4.31 x 10^5 (N m^{-2}) x 1.00 x 10^{-3} (m^3)
      = [60.0 (g) x 8.314 (J mol^{-1} K^{-1}) x 298 (K)]/M (g mol^{-1})
      $\therefore M = 345$ (g mol^{-1})

(f) Viscosity
   Large intermolecular attraction in a liquid results in a high viscosity. The **coefficient of viscosity** is defined as the liquid's resistance to flow. A gas also has some viscosity, but its magnitude is negligibly small. In certain cases it has a significant role for, *e.g.*, airplanes.

Viscosity

(1)   The viscosity of a liquid with large and irregular-shaped particles is higher than that of one with small and regular-shaped particles.
(2)   The higher the temperature of a liquid, the lower its viscosity.

   These two points can be explained in terms of kinetic theory. The collision between spherical or nearly spherical particles is an elastic or a nearly elastic collision. However, the collision between irregularly shaped particles tends to be inelastic. In an inelastic collision, a part of the translational energy is converted to vibrational energy, and consequently the particles will become difficult to move, and will tend to coagulate. The effect of temperature is similar with that for gases.
   The coefficient of viscosity is also called simply 'viscosity' and is expressed by N s m^{-2} in SI. When a sphere of radius a moves in a liquid whose viscosity is h with the velocity U, the resistance D against the sphere is given as below.

$$D = 6\pi haU$$

This relation (**Stokes' law**) was discovered by the British physicist George Gabriel Stokes (1819-1903).

Coffee Break: Supercritical fluid

   Generally speaking, no matter how large a pressure is applied, gases will not liquefy at the critical temperature or above it. However, if the temperature of the gases approaches its critical temperature at high pressure, a state is attained where the gas has the properties and density close to the liquid. Materials in such a state are called **supercritical fluids**. The supercritical fluid has a much stronger dissolving power compared with that of the pure liquid state of the same substance. Furthermore, it can dissolve and separate solutes much more quickly. For this reason, extraction and separation with the aid of supercritical fluids will give results different from those with the

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conventional solvents.

In 1978, carbon dioxide in a supercritical state was successfully employed to remove caffeine from coffee. Since then, extraction with supercritical fluids has been widely employed in the field of food and pharmaceutical industries.

It is expected that a reaction in a supercritical fluid will proceed in a different manner compared with the reaction in a conventional solvent. Catalytic reactions in supercritical fluids have attracted attention. The efficiency of the catalyst is expected to be more than ten times as high as that in normal reactions. It was proposed that the concentration of the solute could be kept higher than in the normal liquid.

(g) Surface tension

Surface tension is also a physical property that relates to the intermolecular attraction in liquids and is defined as the resistance of a liquid to an increase in its surface area. Originally surface tension was defined at the interface between liquid and gas phases. However, a similar tension is in action at the interface between, *e.g.*, liquid and liquid, or between solid and gas phases. Such tensions are called in general **interfacial tensions**. The intermolecular attraction in the two phases and the interfacial tension at the interface between the two kinds of particles is reduced as the temperature is lowered. It also depends on the chemical structure of the substances involved.

A molecule in a liquid is subject to attraction by surrounding molecules, uniformly in all directions. However, molecules at the surface are affected only by the molecules inside and hence the surface area tends to be reduced. This is the origin of surface tension. Drops of human sweat and droplets of mercury are the result of surface tension.

Liquid ascending in a capillary, the **capillary phenomenon**, is a well-known phenomenon of surface tension. The larger the attraction between the liquid and the capillary, the more the liquid will wet the wall of the capillary. When the gravity of the ascended liquid and the attraction between the liquid and the wall of the capillary become balanced, the ascending will cease. The surface tension γ is expressed by the following equation.

$$\gamma = rhdg/2$$

where h is the height of the ascended of the liquid, r is the radius of the capillary and g is the gravitational acceleration. Thus, the surface tension can be determined by experiment.

Exercise

7.1 Comparison of boiling points
Align the following compounds in the order of increasing boiling point.
C_2H_6, NH_3, F_2
7.1 Answer
$NH_3 < C_2H_6 < F_2$

7.2 Phase diagram
Fig. 7.8 is a phase diagram of a certain substance. Indicate the phase in which the substance exists in areas A, B, C and H and the phases present at points D, E, F and G and indicate which lettered point identifies the triple point, normal boiling point, normal melting point, and the critical point.
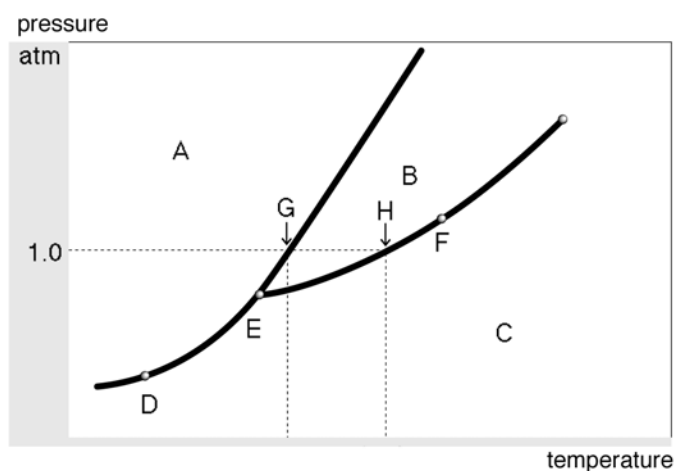
Figure 7.8 The phase diagram of a compound

7.2 Answers

A: solid, B: liquid, C: vapor (gas), D: solid + vapor, E: solid + liquid +vapor, F: liquid + vapor, G: liquid + vapor, H: vapor, triple point: E: critical point: G: normal freezing point: the point where the solid phase - liquid phase curve corresponds to 1 atm, H: normal boiling point: the point where the liquid phase - gas phase curve corresponds to 1 atm.

7.3 Concentration of a solution

The density of dilute sulfuric acid (mass percent is 12.00%) is 1.078 g cm^{-3} (25°C). Convert this concentration into the molar concentration, mass molar concentration and molar fraction.

7.3 Answer

The amount of H_2SO_4 in 100 g of dilute sulfuric acid is 12.00/98.08 = 0.1223 mol, and the amount of substance of H_2O in 100 g of dilute sulfuric acid is 88.00/18.0 = 4.889 mol. Hence the molar fraction of H_2SO_4 is 0.1223/(4.889+0.122) = 0.0244.

Since 88.00 g of H_2O dissolves 0.1223 mol of H_2SO_4, the moles of H_2SO_4 dissolved in 1 kg of H_2O, that is, molar concentration,

0.1223 mol x (1000 g kg^{-1})/(88.00 g) = 1.390 mol kg^{-1}

The amount of substance of H_2SO_4 dissolved in 1 dm^3 of the dilute sulfuric acid (*i.e.,* the molar concentration) is

0.1223 mol x (1078 g dm^{-3})/(100 g) = 1.318 mol dm^{-3}

7.4 Raoult's law

Glycerin is a nonvolatile liquid. A solution composed of 164 g of glycerin and 338 cm^3 of H_2O (density 0.992 g cm^3) was kept at 39.8°C. At this temperature, the vapor pressure of pure water is 54.74 Torr. Calculate the vapor pressure in Torr of this solution.

7.4 Answer

The amount of material of glycerin is 1.78 mol and that of H_2O is 18.63 mol.
p = 54.74 x (18.63/(18.63+1.78)) = 54.74 x 0.913 =50.00 (Torr)

7.5 Elevation of boiling point

When 0.358 g of sulfur was dissolved into 21.5 g of carbon disulfide CS_2, its boiling point rose by 0.151 K. Suggest the structure of sulfur in this solution.

7.5 Answer

M_S = (2.40 K kg mol^{-1})(0.358/1000 kg)/(0.151 K)(21.5/1000 kg) = 0.264 kg mol^{-1}.

Since 32 x 8 = 256 $\cong$ 264, sulfur dissolves as S_8.

7.6 Osmotic pressure

The osmotic pressure of an aqueous solution (100 cm^3) containing 0.36 g of a polymer is 3.26 x 10^2 Pa at 23°C.

(1) Determine the molecular weight of this polymer.

(2) Would it be practical to determine the molecular weight of this polymer by the freezing point depression method or the boiling point elevation method?

7.6 Answer

(1) M = [(8.31 J mol^{-1} K^{-1}) x (296 K) x (3.6 kg m^{-3})]/(3.26 x 10^2 Pa) = 2.7 kg mol^{-1} = 2.7 x 10^4 g mol^{-1}. M = 2.7 x 10^4.

(2) The elevation of boiling point would be 0.693 x 10^{-4} K, and the depression of freezing point would be 2.48 x 10^4 K. Such a small change of the temperature is difficult to determine accurately. Thus, neither method can be employed to determine the molecular weight of the polymer.

7.7 Surface tension

Which of these two substances, hexane C_6H_{14} or water H_2O, has a higher surface tension?

7.7 Answer

H_2O. The high surface tension of water is well known.