1
Introduction

1.1
The Beginnings of Mass Transfer

Separation technology using phase equilibria was perhaps first used by the Greek alchemists of Alexandria [7]. However, modern development of the technology from the viewpoint of rates of mass transfer had to wait until the early 20th century, when W. K. Lewis and W. G. Whitman [4] applied their famous *two-film theory* to gas absorption in 1924. They assumed that there exist two thin fluid films on both sides of an interface, in which the concentration distribution varies sharply and through which transfer of the material takes place by diffusion, and they proposed the important concept of the *mass transfer coefficient* in analogy to the coefficient of heat transfer. Subsequent studies of mass transfer were directed towards experimental approaches to obtaining mass transfer coefficients and delineating empirical correlations thereof. In 1935, R. Higbie [3] applied the transient diffusion model to the absorption of gases by bubbles and proposed a theoretical equation for the prediction of mass transfer coefficients. Although this model represented a milestone in the early days of the studies of mass transfer, its significance was unfortunately not well understood among practical engineers and its application to practical problems was quite limited because it could not deal with mass transfer in flow systems. In 1937, T. K. Sherwood [5] published a well-known textbook on mass transfer, "*Absorption and Extraction*", and demonstrated a systematic approach to the problem.

In 1960, R. B. Bird, W. E. Stewart, and E. N. Lightfoot published a groundbreaking textbook, "*Transport Phenomena*" [1], in which they proposed a new approach to momentum, heat, and mass transfer based on a common understanding that the transport phenomena of these quantities in fluid media are governed by similar fundamental laws and that they should be treated from a common viewpoint in a similar way. In a few decades, this new concept has developed into one of the new fields of engineering science and the title of the book has even become a name of the new engineering science. Nowadays, studies of heat and mass transfer tend to be directed towards a more systematic and theoretical understanding of the phenomena, as opposed to the empirical and case-by-case approach of earlier studies. Many textbooks have since been published in

Mass Transfer. From Fundamentals to Modern Industrial Applications. Koichi Asano

ISBN: 3-527-31460-1

the field of transport phenomena. Studies of mass transfer are now recognized as a branch of transport phenomena. Although this approach has led to remarkable successes in many fields of practical application, especially in the field of heat transfer, too much emphasis has been placed on systematic interpretation of the phenomena and on the similarity between heat and mass transfer, with consequently too little emphasis on practical applications. As a result, some practically important aspects of mass transfer have inevitably been neglected and because of this comparatively less success has been achieved in this field. The only exceptional case is the textbook, "*Mass Transfer*", by T. K. Sherwood, R. L. Pigford, and C. R. Wilke, which was published in 1975, but more than 30 years have elapsed since then.

1.2 Characteristics of Mass Transfer

Modern transport phenomena are based on the fundamental assumption that momentum, heat, and mass transfer are similar in nature. However, as far as mass transfer is concerned, there are some specific issues that need to be addressed before any real approach to actual problems can be made. Some of these are summarized in the following.

Phase Equilibria: Figure 1.1 shows the temporal variation in the concentration of a dissolved gas *A* in a liquid contained in a closed vessel upon contact with the gas at constant pressure and temperature. The rate of increase of the concentration in the liquid is very rapid immediately after exposure to the gas, but it soon becomes gradual and the concentration finally approaches a certain limiting value, which remains constant as long as the pressure and the temperature of the system remain unchanged. This stable state is known as phase equilibrium (saturated solubility of gas *A*), and the conditions of the phase equilibrium depend solely on the thermodynamic nature of the system. This indicates that the phase equilibrium determines an upper limit for mass transfer, whereas no such limitation exists for heat transfer.

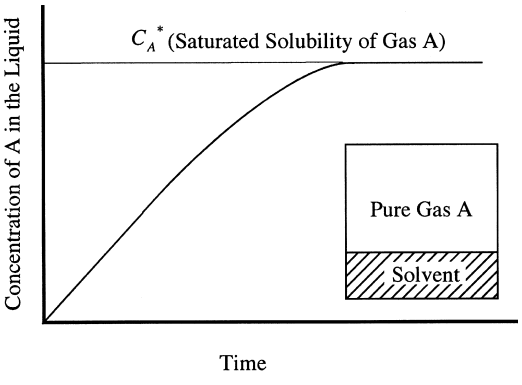

Fig. 1.1 Absorption of a gas by a liquid and solubility of gases in liquids.

Mixture: In momentum and heat transfer, we are mostly concerned with systems consisting of pure fluids, but in mass transfer our main targets are mixed systems of fluids; the simplest case is a binary system, and in most cases we have to deal with ternary or multi-component systems. Consequently, various definitions of concentrations have been used in a case-by-case manner, which can lead to serious confusion in describing rates of mass transfer.

Convective mass flux: Mass transfer can be defined as the transfer of material through an interface between the two phases, whereas diffusion can be defined in terms of the relative motion of molecules from the center of mass of a mixture, moving at the local velocity of the fluid. This means that mass fluxes are not identical to diffusional fluxes at the interface, as is usually assumed in primitive mass transfer models. Rather, mass fluxes are accompanied by convective mass fluxes, as will be discussed in detail in later sections, and can be expressed as the sum of the diffusional fluxes at the interface and the convective mass fluxes. In this respect, mass transfer is completely different from heat transfer, which is not associated with such accompanying fluxes. The existence of convective mass fluxes is a characteristic feature of mass transfer and this needs careful consideration when dealing with mass transfer problems.

High mass flux effect: Convective mass fluxes can also have a significant effect on the velocity and concentration distributions near the interface if the order of magnitude of the flux becomes considerable. This is known as the high mass flux effect.

Effect of latent heat: Mass transfer is a phenomenon involving the transfer of material from one phase to another, and the transfer of material is always accompanied by the energy transfer associated with the phase change, that is, the latent heat. This means that energy transfer is always accompanied by mass transfer, which will affect the interface conditions. In this respect, mass transfer is interrelated with heat transfer through the boundary conditions at the interface. Except for gas absorption in a very low concentration range, the effect is usually quite considerable and we cannot neglect the effect of latent heat.

1.3 Three Fundamental Laws of Transport Phenomena

1.3.1 Newton's Law of Viscosity

Figure 1.2 shows a flow of fluid between two parallel plates, where the upper plate moves at a constant velocity, U [m s^{-1}], and the lower one is at rest. In a steady state, a linear velocity profile is established, as shown in the figure, due to the effect of the viscosity of the fluid. Because of this frictional drag caused by the viscosity of the fluid, a drag force, R_f [N], will act on the surface of the plate. The following empirical equation is known for the fluid friction:

$$\tau = \tau_w = R_f/A \tag{1.1}$$

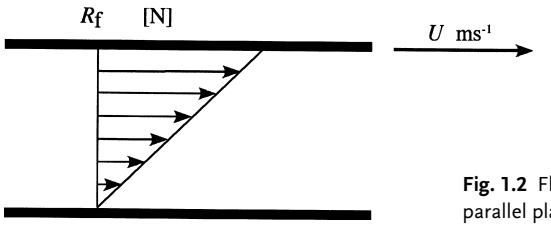

Fig. 1.2 Flow of a viscous fluid between two parallel plates.

$$\tau = -\mu \frac{du}{dy} \tag{1.2}$$

where A is the surface area of the plate [m^2], y is the distance from the wall [m], τ is the shear stress in the fluid [Pa], $\tau_w (\equiv R_f/A)$ is the shear stress at the wall [Pa], and μ is the *viscosity* [Pa s], which is one of the important physical properties of the fluid. Equation (1.2) is usually known as *Newton's law of viscosity*. Fluids are classified into two groups: *Newtonian fluids*, which obey Newton's law of viscosity, and *non-Newtonian fluids*, which do not obey Newton's law. Common fluids such as air, water, and oils generally behave as Newtonian fluids, whereas polymer solutions usually behave as non-Newtonian fluids.

1.3.2
Fourier's Law of Heat Conduction

Figure 1.3 shows the temperature distribution in a solid plate of surface area A [m^2] and thickness δ [m], where the temperature of one surface is kept at T_1 [K] and that of the other at T_2 [K] ($T_1 > T_2$). Heat will be transferred from the hot to the cold surface and this phenomenon is known as the *conduction of heat*. In a steady state, a linear temperature profile is established in the solid and the rate of heat transfer, Q [W], is observed to be proportional to the temperature difference between the two surfaces ($T_1 - T_2$) and the surface area of the plate, A [m^2], and inversely proportional to the thickness of the plate, δ [m]:

$$Q \propto A \frac{(T_1 - T_2)}{\delta} \tag{1.3}$$

The above expression reduces to the following familiar empirical equation as the thickness of the plate approaches an infinitesimally small value:

$$q = \frac{Q}{A} = -\kappa \frac{dT}{dy} \tag{1.4}$$

where $q (\equiv Q/A)$ is the heat flux [W m^{-2}], T is the temperature [K], y [m] is the distance in the direction of heat conduction, and κ is a physical property of the fluid

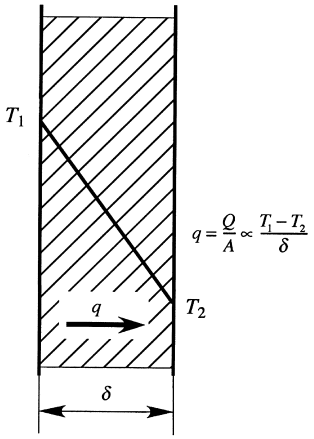

Fig. 1.3 Conduction of heat through a solid wall.

known as the *thermal conductivity* [W m^{-1} K^{-1}]. Equation (1.4) is referred to as *Fourier's law of heat conduction*.

1.3.3 Fick's Law of Diffusion

If we place a small amount of a volatile liquid in the bottom of a test tube and let it be in contact with a dry air stream, as shown in Fig. 1.4, a linear concentration profile is established in the test tube at steady state, and steady evaporation of the liquid will take place. This phenomenon, whereby a transfer of material is caused by a non-uniform distribution of concentration, is called *diffusion*. The following empirical law is known for the rate of diffusion:

$$J_A = -cD\frac{dx_A}{dy} \tag{1.5}$$

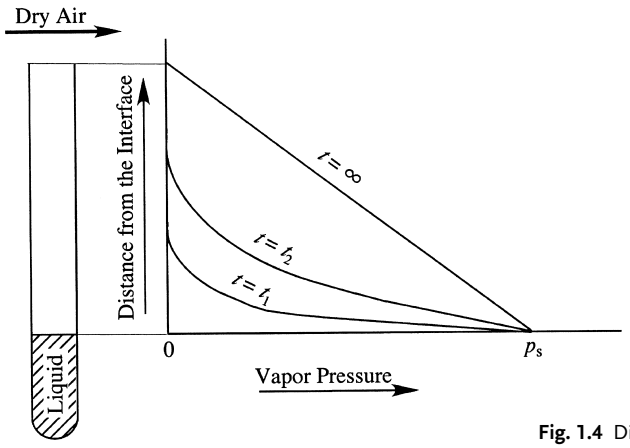

Fig. 1.4 Diffusion of vapor in a gas.

where c is the molar density [kmol m^{-3}], D is the diffusivity [m^{-2} s^{-1}], J_A is the rate of diffusion of component $\boldsymbol{A}$ per unit area of the surface (diffusional flux) [kmol m^{-2} s^{-1}], and y is the distance in the direction of diffusion [m]. Equation (1.5) was first reported by A. Fick [2] in 1855 following observation of the dissolution of salt in water and so is referred to as *Fick's law of diffusion*.

1.4 Summary of Phase Equilibria in Gas-Liquid Systems

The fact that the upper limit of a mass transfer is restricted by the relevant phase equilibrium and that the rate of mass transfer also depends on the phase equilibrium means that we have to be familiar with the phase equilibrium of the system before we can deal with mass transfer problems. Here, we briefly summarize some of the important quantitative relationships of the phase equilibria commonly encountered in gas-liquid systems. More detailed discussions of these topics can be found in standard textbooks on chemical engineering thermodynamics.

Solubility of gases in liquids: The solubility of a gas in a liquid usually increases with increasing pressure and decreases with increasing temperature. For sparingly soluble gases, the well-known Henry's law applies:

$$p_i = Hx_i \tag{1.6}$$

where H is the Henry constant [MPa], p_i is the partial pressure of component $\boldsymbol{i}$ [MPa], and x_i is the mole fraction of dissolved gas in the liquid in equilibrium with the gas.

Vapor pressures of pure liquids: The vapor pressure of a pure liquid is a function only of temperature and can be approximated by *Antoine's equation* over a wide range of temperatures:

$$\log p^* = A - \frac{B}{T + C} \tag{1.7}$$

where p^* is the saturated vapor pressure of the liquid [Pa], T [K] is the temperature, and A, B, and C are so-called Antoine's constants.

Vapor pressures of solutions: The vapor pressure of a component i in a solution consisting of members of the same chemical series, such as a mixture of homologous paraffin hydrocarbons, is expressed by the following equation:

$$p_i = p_i^* x_i \tag{1.8}$$

This equation is referred to as *Raoult's law*. The solubility of the vapor of a hydrocarbon in an oil is usually described by *Raoult's law*.

Solutions can be classified into two groups, *ideal solutions*, which obey Raoult's law, and *non-ideal solutions*, which do not obey Raoult's law. Most actual solutions

behave as non-ideal solutions. The vapor pressure of a component ***i*** in a non-ideal solution can be expressed in a similar way as for an ideal solution through the use of an *activity coefficient*:

$$p_i = p_i^* \gamma_i x_i \tag{1.9}$$

where p_i is the vapor pressure of component ***i*** [Pa], p_i^* is the vapor pressure of the pure component ***i*** [Pa], x_i is the mole fraction of component ***i*** in the liquid [–], and γ_i is the activity coefficient of component ***i*** [–].

The estimation of activity coefficients is one of the important subjects of chemical engineering thermodynamics. Readers interested in this subject may refer to the appropriate standard textbooks.

References

1 R. B. Bird, W. E. Stewart, and E. N. Lightfoot, "*Transport Phenomena*", Wiley, (1960).

2 A. Fick, "Ueber Diffusion", *Annalen der Physik und Chemie*, **94**, 59–86 (1855).

3 R. Higbie, "The Rate of Absorption of a Pure Gas into a Still Liquid during Short Periods of Exposure", *Transactions of the American Institute of Chemical Engineers*, **31**, 365–389 (1935).

4 W. K. Lewis and W. G. Whitman, "Principles of Absorption", *Industrial and Engineering Chemistry*, **16**, [12], 1215–1220 (1924).

5 T. K. Sherwood, "*Absorption and Extraction*", McGraw-Hill (1937).

6 T. K. Sherwood, R. L. Pigford, and C. R. Wilke, "*Mass Transfer*", McGraw-Hill (1975).

7 A. J. V. Underwood, "The Historical Development of Distilling Plant", *Transactions of Institutions of Chemical Engineers*, **13**, 34–62 (1935).