Capítulo tomado del libro clásico Fenómenos de Transporte **“Transport Phenomena”** de R. Byron, Warren E. Stewart y Edwin N. Lighfoot, publicado en el año 1960 en N. York por John Wiley and Sons Inc.

FICK'S LAW OF DIFFUSION

§16.2 FICK'S LAW OF DIFFUSION

In Eq. 1.1-2 the viscosity μ is defined as the proportionality factor between momentum flux and velocity gradient (Newton's law of viscosity). In Eq. 8.1-6 the thermal conductivity *k* is defined as the proportionality factor between heat flux and temperature gradient (Fourier's law of heat conduction).

TABLE 16.2-1

EQUIVALENT FORMS OF FICK'S FIRST LAW OF BINARY DIFFUSION

Flux	Gradient	Form of Fick's First Law	
n_A	$\nabla \omega_A$	$n_A - \omega_A(n_A + n_B) = -\rho \mathscr{D}_{AB} \nabla \omega_A$	(*A*)
N_A	∇x_A	$N_A - x_A(N_A + N_B) = -c \mathscr{D}_{AB} \nabla x_A$	(*B*)
j_A	$\nabla \omega_A$	$j_A = -\rho \mathscr{D}_{AB} \nabla \omega_A$	(*C*)
$J_A^\star$	∇x_A	$J_A^\star = -c \mathscr{D}_{AB} \nabla x_A$	(*D*)
j_A	∇x_A	$j_A = -\left(\frac{c^2}{\rho}\right) M_A M_B \mathscr{D}_{AB} \nabla x_A$	(*E*)
$J_A^\star$	$\nabla \omega_A$	$J_A^\star = -\left(\frac{\rho^2}{c M_A M_B}\right) \mathscr{D}_{AB} \nabla \omega_A$	(*F*)
$c(v_A - v_B)$	∇x_A	$c(v_A - v_B) = -\frac{c \mathscr{D}_{AB}}{x_A x_B} \nabla x_A$	(*G*)

Now we define the mass diffusivity $D_{AB} = D_{BA}$ in a binary system in an analogous fashion:

$$J_A^\star = -c \mathscr{D}_{AB} \nabla x_A \qquad (16.2\text{–}1)$$

This is *Fick's first law of diffusion,*[1] written in terms of the molar diffusion flux J_A^*. This equation states that species *A* diffuses (moves relative to the mixture) in the direction of decreasing mole fraction of *A,* just as heat flows by conduction in the direction of decreasing temperature.

A number of other mathematically equivalent statements of Fick's first law have appeared in the literature, and some of them are summarized in Table I6.2-1 for reference only. The diffusivity D_{AB} is *identical* in all these equations. Of special importance in the following chapters is the form of Fick's first law in terms of N_A the molar flux relative to stationary coordinates:

$$N_A = x_A(N_A + N_B) - c \mathscr{D}_{AB} \nabla x_A \qquad (16.2\text{–}2)$$

[1] Temperature gradients, pressure gradients, and external forces also contribute to the diffusion flux, although their effects are usually minor. More complete expressions for the diffusion flux are given in §18.4.

This equation shows that the diffusion flux N_A relative to stationary coordinates is the *resultant* of two *vector* quantities: the vector $x_A(N_A + N_B)$, the unit area being fixed in space. We shall relate the molar flux to the concentration gradient (see Eq. 16.2-2) by

$$\underbrace{N_{Az}}_{\text{flux with respect to fixed axes}} = \underbrace{-c\mathscr{D}_{AB}\frac{\partial x_A}{\partial z}}_{\text{flux resulting from diffusion}} + \underbrace{x_A(N_{Az} + N_{Bz})}_{\text{flux resulting from total molar bulk flow}} \tag{17.0-1}$$

for two-component systems. Keep in mind that N_{AZ}, is the z-component of the vector N_A. Before Eq. 17.0-1 can be used, we shall have to eliminate N_{BZ}. This can be done only if something is known beforehand about the ratio N_{BZ}/N_{AZ}, In each of the problems discussed in this chapter we begin by specifying this ratio on physical grounds.

In this chapter we study diffusion in both *nonreacting* and *reacting* systems. When chemical reactions occur, we distinguish between two types: *homogeneous,* in which the chemical change occurs in the entire volume of the fluid, and *heterogeneous,* in which the chemical change takes place only in a restricted region in the system, such as at the surface of a catalyst. Not only is the physical picture different for homogeneous and heterogeneous reactions, but there is also a difference in the way in which the two reactions are described. The rate of production by a homogeneous reaction appears in a source term in the differential equation obtained from the shell mass balance, just as the thermal source term appears in the shell energy balance. The rate of production by a heterogeneous reaction, on the other hand, appears not in the differential equation but rather in the boundary condition al! the surface on which the reaction occurs.

In order to set up problems involving chemical reactions, some information has to be available about the rate at which the various chemical species appear or disappear by reaction. This brings us then to the subject of *chemical kinetics,* that branch of physical chemistry that deals with the mechanisms of chemical reactions and the rates at which they occur[1]. In this chapter we assume that the mechanisms of the reactions are known and that the reaction rates are describable by means of simple functions of the concentrations of the reacting species. Mention needs to be made at this point of the notation to be used for the chemical rate constants. For homogeneous reactions, the volume rate of production of species *A* may be given by an expression of the form

$$R_A = k_n''' c_A{}^n \tag{17.0-2}$$

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[1] For an introduction to chemical kinetics, see F. Daniels and R. A. Alberty, *Physical Chemistry,* Wiley, New York (1955), Ch. 13. A more mathematical discussion is given by E. A. Moelwyn-Hughes, *Physical Chemistry,* Pergamon Press, New York (I957).

in which R_A [=] moles cm^{-3} sec^{-1} and c_A [=] moles cm^{-3}. The index *n* indicates the "order" of the reaction,[2] for a first-order reaction, k'''_1 [=] sec^{-1}

For heterogeneous reactions, the rate of reaction at the catalytic surface may be specified by a relation of' the form

$$N_{Az}\big|_{\text{surface}} = k_n'' c_A^{\,n}\big|_{\text{surface}} \qquad (17.0\text{-}3)$$

in which N_{AZ}, [=] moles cm^{-2} sec^{-1} and c_A [=] moles cm^{-3}. Here k_1''' [=] cm sec^{-1}. Note that ´´´ indicates a rate constant related to a volume source and ´´ indicates a rate constant related to a surface source.

We begin in §17.1 with a statement of the shell mass balance and the kinds of boundary conditions that may arise in solving diffusion problems. In §17.2 a discussion of diffusion in a stagnant film is given, this topic being necessary to the understanding of the film theories of the diffusional operations in chemical engineering. Then, in §§17.3 and 17.4, we give some elementary examples of diffusion with chemical reaction-both homogeneous and heterogeneous; it is hoped that these examples will illustrate the role that diffusion plays in chemical kinetics and the important fact that there is generally a difference between the rate of the chemical reaction and the rate of the combined diffusion-reaction process. In §17.5 we turn our attention to the subject of forced-convection mass transfer-that is, diffusion superimposed on a flow field; we could also have included for the sake of completeness. a section on free-convection mass transfer, which would have paralleled the discussion on free-convection heat transfer in Chapter 9. Finally, in the last section, §17.6, we discuss diffusion in porous catalysts.

§17. 1 SHELL MASS BALANCES: BOUNDARY CONDITIONS

The diffusion problems in this chapter are solved by making mass balances for a specific chemical species over a thin shell of solid or fluid, ttaving

$$\begin{Bmatrix}\text{rate of}\\ \text{mass of}\\ A \text{ in}\end{Bmatrix} - \begin{Bmatrix}\text{rate of}\\ \text{mass of}\\ A \text{ out}\end{Bmatrix} + \begin{Bmatrix}\text{rate of production}\\ \text{of mass of } A \text{ by}\\ \text{homogeneous chemical}\\ \text{reaction}\end{Bmatrix} = 0 \quad (17.1\text{-}1)$$

selected an appropriate system, the law of conservation of mass is written in the form

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[2] Not all rate expressions are of the simple form of Eq. 17.0-2. The reaction rate may depend in a more complex way on the concentrations of all species present. Similar remarks hold for Eq. 17.0-3

The conservation statement may, of course, also be expressed in terms of moles. The chemical species *A* may enter or leave the system by means of diffusion and by virtue of the over-all motion of the fluid. Also species *A* may be produced or destroyed by homogeneous chemical reactions.

After a balance is made on a shell of finite thickness, according to Eq. 17.1-1, we then let the dimensions of the system become infinitesimally small. As a result of this process, a differential equation is generated, the solution of which gives the distribution of species *A* in the system.

When the differential equation has been integrated, constants of integration appear, which have to be evaluated by use of boundary conditions.

The boundary conditions used are very similar to those used in energy transfer. (See §9.1.)

a. The concentration at a surface can be specified; for example, $x_A = X_{A0}$.

b. The mass flux at a surface can be specified (if the ratio N_A/N_B is known, this is tantamount to giving the concentration gradient); for example, $N_A=N_{A0}$.

c. If diffusion is occurring in a solid, it may happen that at the solid surface substance A is lost to a surrounding fluid stream according to the relation

$$N_{A0} = k_c(c_{A0} - c_{Af}) \qquad (17.1\text{–}2)$$

in which N_{A0} is the mass flux at the surface, c_{A0} is the surface concentration, c_{Af} is the concentration in the fluid stream, and the proportionality constant k_c, is a "mass-transfer coefficient"; the methods of correlating rnass-transfer coefficients are discussed in Chapter 21. Equation 17.1-2 is analogous to "Newton's law of cooling" defined in Eq. 9.1-2.

d. The rate of chemical reaction at the surface can be specified. For example, if substance *A* disappears at a surface by a first-order chemical reaction, $N_{A0} = k_1''c_A$; that is, the rate of disappearance at a surface is proportional to the surface concentration, the proportionality constant k_1'' being a first-order chemical rate constant.

In the following sections we shall see how these various boundary conditions are used.

§17.2 DIFFUSION THROUGH A STAGNANT GAS FILM

Consider the diffusion system shown in Fig. 17.2-1. Liquid *A* is evaporating into gas *B,* and we imagine that there is some device which maintains the liquid level at $z = z_1$. Right at the liquid-gas interface the gas-phase concentration of *A,* expressed as mole fraction, is x_{A1}.

This is taken to be the gas-phase concentration of *A* corresponding to equilibrium[1] with the liquid at the interface; that is x_{A1} is the vapor pressure of *A* divided by the total pressure, $p_A^{(vap)}/p$, provided that *A* and *B* form an ideal gas mixture. We further assume that the solubility of *B* in liquid *A* is negligible.

At the top of the tube (at $z = z_2$) a stream of gas mixture *A*-*B* of concentration x_{A2} flows past slowly; thereby the mole fraction of *A* at the top of the column is maintained at x_{A2}. The entire system is presumed to be held at constant temperature and pressure. Gases *A* and *B* are assumed to be ideal.

When this evaporating system attains a steady state, there is a net motion of *A* away from the evaporating surface and the vapor *B* is stationary.

Hence we can use the expression for N_{AZ}, given in Eq. 17.0-1 with N_{Bz} = 0. Solving for N_{Az},, we get

$$N_{Az} = -\frac{c\mathscr{D}_{AB}}{1 - x_A}\frac{dx_A}{dz} \qquad (17.2\text{–}1)$$

A mass balance over an incremental column height Δz (see Fig. 17.2-1) states that at steady state

$$SN_{Az}\big|_z - SN_{Az}\big|_{z+\Delta z} = 0 \qquad (17.2\text{–}2)$$

in which S is the cross-sectional area of the column. Division by *S* Δz and taking the lift, it as Δz approaches zero gives

$$-\frac{dN_{Az}}{dz} = 0 \qquad (17.2\text{–}3)$$

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[1] The assumption of equilibrium at the interface has been subjected to experimental test by L. N. Tung and H. G. Drickamer, J. *Chem, Phys.,* 20, 6-12 (1952), and by R. E. Emmert and R. L. Pigford, *Chem. Eng. Prog.,* 50, 87-93 (1954). A kinetic theory approach was made by R. W. Schrage, *A Theoretical Study of Interphase Mass Transfer,* Columbia University Press, New York (1953). These studies seem to indicate that only at very high mass-transfer rates is there a significant departure from equilibrium at the interface.

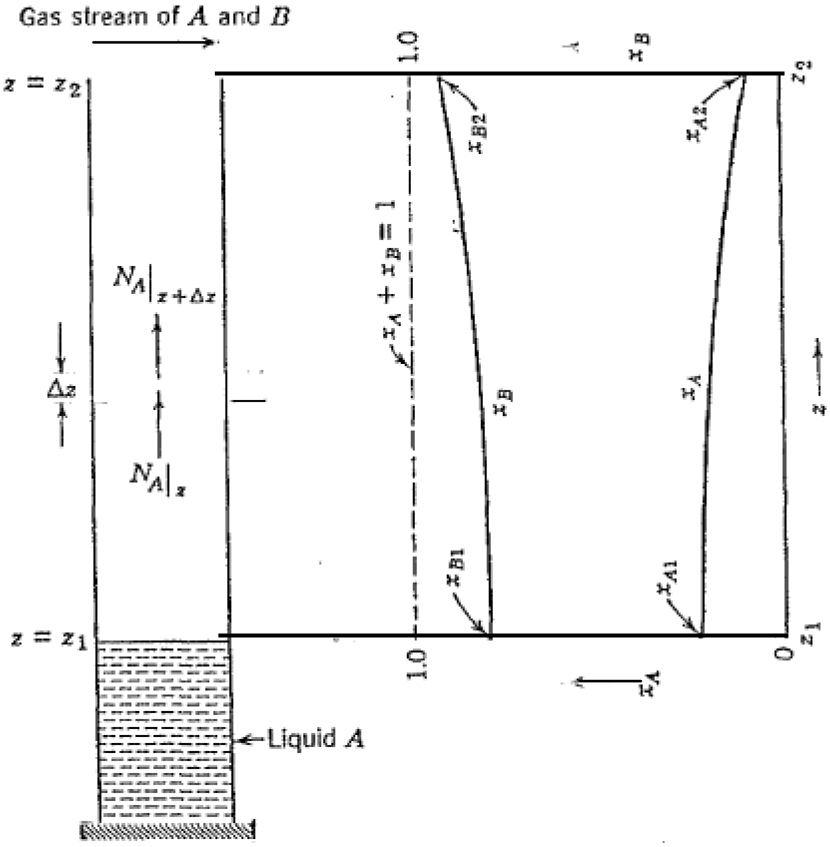

Fig. 17.2-1. Diffusion of A through B in steady state with B not in motion. Graph shows how concentration profile for B is distorted because of diffusion of A.

Substitution of Eq. 17.2-1 into Eq. 17.2-3 gives

$$\frac{d}{dz}\left(\frac{c\mathscr{D}_{AB}}{1-x_A}\frac{dx_A}{dz}\right)=0 \qquad (17.2\text{-}4)$$

For ideal-gas mixtures at constant temperature and pressure, *c* is a constant, and D_{AB} is very nearly independent of concentration, Hence D_{AB} can be taken outside the derivative to get

$$\frac{d}{dz}\left(\frac{1}{1-x_A}\frac{dx_A}{dz}\right)=0 \qquad (17.2\text{-}5)$$

This is a second-order equation for the concentration profile expressed as mole fraction of *A*. Integration with respect to z gives

$$\frac{1}{1-x_A}\frac{dx_A}{dz}=C_1 \qquad (17.2\text{-}6)$$

A second integration then gives

$$-\ln(1-x_A)=C_1z+C_2 \qquad (17.2\text{-}7)$$

The two constants of integration may be determined by the use of the boundary conditions

B.C. 1: at $z=z_1, \quad x_A=x_{A1}$ (17.2-8)

B.C. 2: at $z=z_2, \quad x_A=x_{A2}$ (17.2-9)

When the constants so obtained[2] are substituted into Eq. 17.2-7, the following expressions for the concentration profiles are obtained:

$$\boxed{\left(\frac{1-x_A}{1-x_{A1}}\right)=\left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{\frac{z-z_1}{z_2-z_1}}} \qquad (17.2\text{-}10)$$

or

$$\boxed{\left(\frac{x_B}{x_{B1}}\right)=\left(\frac{x_{B2}}{x_{B1}}\right)^{\frac{z-z_1}{z_2-z_1}}} \qquad (17.2\text{-}11)$$

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[2] The constants are

$$C_1=\frac{\ln x_{B1}-\ln x_{B2}}{z_2-z_1}=\frac{\ln(x_{B1}/x_{B2})}{z_2-z_1}\,; \qquad C_2=\frac{z_1\ln x_{B2}-z_2\ln x_{B1}}{z_2-z_1}$$

To get Eq. 17.2-10, first rewrite C_2 thus:

$$C_2 = \frac{z_1 \ln x_{B2} - (z_2 - z_1) \ln x_{B1} - z_1 \ln x_{B1}}{z_2 - z_1} = -\frac{z_1}{z_2 - z_1} \ln \frac{x_{B1}}{x_{B2}} - \ln x_{B1}$$

These concentration distributions are depicted in Fig. 17.2-1. An examination of these curves shows that the slope dx_A/dz is not constant with respect to z, although the molar flux N_{Az} is.

Although the concentration profiles are helpful in picturing the diffusion process, in engineering calculations it is usually the average concentration or the mass flux at some surface that is of interest. For example, the average concentration of *B* in the region between $z = z_1$ and $z = z_2$ is

$$\frac{x_{B,\mathrm{avg}}}{x_{B1}} = \frac{\int_{z_1}^{z_2} (x_B/x_{B1})\, dz}{\int_{z_1}^{z_2} dz} = \frac{\int_0^1 (x_{B2}/x_{B1})^{\zeta}\, d\zeta}{\int_0^1 d\zeta} = \left.\frac{(x_{B2}/x_{B1})^{\zeta}}{\ln (x_{B2}/x_{B1})}\right|_0^1 \qquad (17.2\text{–}12)$$

whence

$$x_{B,\mathrm{avg}} = \frac{x_{B2} - x_{B1}}{\ln (x_{B2}/x_{B1})} \qquad (17.2\text{–}13)$$

That is, the average value of x_B is the logarithmic mean of the terminal values, (x_B)ln. In the foregoing S is a reduced length $(z - z_1)/(z_2 - z_1)$.

The rate of mass transfer at the liquid-gas interface--that is, the rate of evaporation--is obtained by using Eq. 17.2-1:

$$N_{Az}\big|_{z=z_1} = -\frac{c\mathscr{D}_{AB}}{1 - x_{A1}} \left.\frac{dx_A}{dz}\right|_{z=z_1} = +\frac{c\mathscr{D}_{AB}}{x_{B1}} \left.\frac{dx_B}{dz}\right|_{z=z_1} = \frac{c\mathscr{D}_{AB}}{(z_2 - z_1)} \ln \left(\frac{x_{B2}}{x_{B1}}\right) \qquad (17.2\text{–}14)$$

Equations 17.2-13 and 17.2-14 may be combined to give an alternative expression for the mass-transfer rate:

$$N_{Az}\big|_{z=z_1} = \frac{c\mathscr{D}_{AB}}{(z_2 - z_1)(x_B)_{\ln}}(x_{A1} - x_{A2}) \qquad (17.2\text{–}15)$$

This expression shows how the rate of mass transfer is related to a characteristic concentration driving force x_{A1}-x_{A2}. Equations 17.2-14 and 15 may also be expressed in terms of total pressure and partial pressures:

$$N_{Az}\big|_{z=z_1} = \frac{(p\mathscr{D}_{AB}/RT)}{(z_2 - z_1)}\ln\frac{p_{B2}}{p_{B1}} = \frac{(p\mathscr{D}_{AB}/RT)}{(z_2 - z_1)(p_B)_{\ln}}(p_{A1} - p_{A2}) \qquad (17.2\text{–}15a)$$

in which $(p_B)_{\ln}$ is the logarithmic mean of p_{B1} and p_{B2} defined analogously to $(x_B)\ln$ in Eq. 17.2-15.

The results of this section have been used for experimental determination of gas diffusivities.[3] Furthermore, these results find use in the "film theories"

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[3] See, for example, C. Y. Lee and C. R. Wilke, *Ind. Eng. Chem., 46,* 2381-2387 (1954); T. K. Sherwood and R. L. Pigford, *Absorption and Extraction,* McGraw-Hill (1952).