Mass Transfer in Heterogeneous Catalysis

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M.I.T. PRESS
Cambridge, Massachusetts, and London, England

Set in Monotype Times Roman.
Printed and bound in the United States of America by
The Colonial Press Inc., Clinton, Massachusetts.

SBN 262 19 062 1 (hard cover)

Library of Congress catalog card number: 70–87307

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1.1 Introduction

Most of the important chemical reactions utilized in the chemical and petroleum-refining industries are catalytic and in a major fraction of these the catalyst is a solid substance. The contact process for the manufacture of sulfuric acid, which is now the predominant method, became industrially practicable at the beginning of the twentieth century. World War I saw the first commercial plants for the synthesis of ammonia. Continuous catalytic processes are employed in many large chemical plants, as in the oxidation of ethylene to form ethylene oxide, and napthalene or ortho-xylene to form phthalic anhydride. Styrene is formed by catalytic dehydrogenation of ethyl benzene, butadiene by dehydrogenation of butane or butylene, acrylonitrile by ammoxidation of natural gas. Hydrodesulfurization, cracking, hydrocracking, and reforming are carried out catalytically by the petroleum industry on a very large scale. Continuous processes frequently employ fixed or fluidized beds with reactions in the gas phase, although some hydrogenations and one variation of the Fischer-Tropsch process employ continuous fluidized beds of catalyst suspended in a liquid as a slurry. Trickle beds, in which a liquid flows down through a bed of particles in the presence of a gas phase, are coming into increasing use. The fine-chemical industry employs batch reactors with catalyst suspensions for the hydrogenation of a wide variety of organic chemicals.

Although many millions of dollars are spent each year on the development of new catalysts and new catalytic processes, the phenomena occurring on the catalyst surface are still poorly understood. The selection and manufacture of catalysts for specific purposes is largely empirical, and remains more an art than a science. The investigation of catalytic reactions and catalytic processes is complicated by the fact that diffusion as well as chemical phenomena are usually involved; the two are not easy to separate so as to identify the factors affecting each. One or the other may dominate any particular heterogeneous reaction; the relative importance of these quite different rate processes determines the proper design as well as the performance of catalytic reactors.

In the usual situation, a particle or pellet of solid catalyst is in contact with a gas or liquid in which the reactants are present. The reactants diffuse to the active surface of the catalyst, the reaction takes place, and the products diffuse back to the main body of the ambient fluid. It is usually desirable to employ porous catalysts, since such materials can be made to provide hundreds of square meters of catalytic surface in each gram of solid. If this large internal surface is to be used effectively, the reactants must diffuse first from the fluid to the outside surface of the pellet and then through minute and irregularly shaped pores to the interior.

The pores vary in cross section along their lengths; they branch and interconnect, and some are "dead end." The geometry of the pore structure of common catalysts is poorly defined, and the quantitative treatment of pore diffusion requires a partly empirical approach. Chemical potential decreases in the direction of diffusion through the porous structure, so catalyst surface in the interior of the pellet is in contact with a fluid of lower reactant concentration and higher product concentration than the external or ambient fluid. The internal surface is not as "effective" as it would be if it were all exposed to contact with the external fluid.

Measurements, as of composition and temperature, which the experimenter uses for interpretation of his data are almost invariably those of the bulk of the fluid, yet the observed course of the reaction is the sum of the events occurring throughout the catalyst, being determined by the conditions actually existing at each point on the internal surface of the catalyst. When gradients caused by diffusion are significant, a "falsification of the kinetics" occurs in the sense that the rate and selectivity of the reaction change with bulk concentration and temperature in a different manner than they would in the absence of such gradients. We shall use the term "intrinsic kinetics" to refer to the behavior of the reaction in the absence of diffusional effects and the adjective "apparent" or "effective" to refer to that which is actually observed. When the difference is significant the term "mass transfer limitation" or "diffusion limitation" is frequently used, but this phraseology is subject to misinterpretation. Diffusion causes dissipation of chemical potential, and significant effects of diffusion may be observed when the potential difference between the bulk and the reaction sites amounts to but a few percent of the over-all decrease in potential.

It is difficult to avoid this coupling of physical phenomena with chemical reaction, particularly in industrial processing, where high reaction rates are desired. The scientist or engineer engaged in research or development needs to be able to conduct chemical kinetics studies free of physical transport limitations, if possible, in order to interpret his results correctly, so he must know how to design such experiments properly, be aware of warning signs to look for in his data and have some knowledge of what he may be able to do if diffusion effects become significant. The engineer concerned with development, design, and operation of reactors needs to be aware of what changes in conversion and selectivity may occur as he changes scale or alters operating parameters. Though the interactions between diffusion and chemical reaction are evidently of considerable complexity, many situations are amenable to analysis by the theoretical relations presented in the following chapters. Sufficient experimental data now exist to confirm the value of these theories for application to many practical problems of reactor design.

The general purpose of this book is to describe the role of diffusion in heterogeneous catalysis. The remainder of this chapter is devoted to ordinary molecular or "bulk diffusion," and to diffusion in pores and includes a brief description of typical porous solid catalysts and methods for their physical characterization. Chapter 2 deals with mass transfer between ambient fluid and porous catalyst, for fixed beds, trickle beds, and for particles suspended in liquid or gas. The flow pattern and nature of the contacting is highly complex for most industrial reactors other than one involving a single-phase reactant flowing through a fixed catalyst bed, and even this system is frequently difficult to analyze quantitatively. A brief description is provided in Chapter 2 of fluidized beds, trickle beds, and slurry reactors to assist in the interpretation and prediction of diffusion effects in these systems. The design of packed-bed catalytic reactors, including consideration of radial and axial dispersion, is outside the scope of the present volume. Chapter 3 describes the theory of simultaneous diffusion and reaction in porous structures and the methods for determining the effectiveness factor of a catalyst. The treatment here is based on certain simplifying assumptions; isothermal conditions, a diffusion process following Fick's law, irreversible reaction involving a single reactant and following simple power-law kinetics. The validation of theory by experiment is then discussed. Chapter 4 presents methods of determining the effectiveness factor in more complex situations: those involving temperature gradients inside catalyst pellets, complicated intrinsic kinetic expressions, different catalyst geometries, and volume change upon reaction. Chapter 5 treats the interaction between diffusion and catalyst poisoning and the effects of diffusion on reaction selectivity and on catalyst regeneration. The general approach presented in this book also applies to uncatalyzed heterogeneous reactions such as that of carbon with carbon dioxide or with water vapor, the reduction of iron ore, and to the reaction of solids with acids. The principal differences are that the diffusion process then involves a net flow of mass and the porous character of the solid, if any, changes significantly as reaction proceeds.

1.1.1 *Reaction Regimes*

Visualize a porous solid catalyst pellet in contact with a fluid reactant and consider how the rate of the reaction will change as the temperature is increased. As pointed out by Wicke [384]*, three different catalytic reaction regimes may be observed, as shown diagrammatically on the Arrhenius-type diagram, Figure 1.1, and on Figure 1.2. At sufficiently low temperatures the rate of the reaction will be so low that the potential required to provide the diffusion flux is insignificant and intrinsic kinetics will be observed. With increased temperature, the rate of diffusion per unit potential difference increases but slowly, whereas the intrinsic rate constant increases exponentially. Thus an increasing fraction of the total available potential is required for diffusion, leaving less to drive the chemical reaction. Concentration gradients within the catalyst pores usually become significant before those in the ambient fluid. In this second regime, in which pore diffusion is significant, it will be shown that the apparent activation energy as calculated from an Arrhenius plot will be the arithmetic average of that for the intrinsic reaction and that for diffusion, providing the reaction is simple and the intrinsic kinetics can be expressed by a power-law relationship. In gas phase reactions the effect of temperature on diffusion rates is equivalent to an activation energy of the order of only 1 to 3 kcal, which is so small compared to that of most heterogeneous reactions that the observed activation energy will be little more than one-half the intrinsic value. The apparent order of the reaction will shift toward first order; for example, an intrinsic

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* Numbers in brackets are keyed to references at the end of the book.

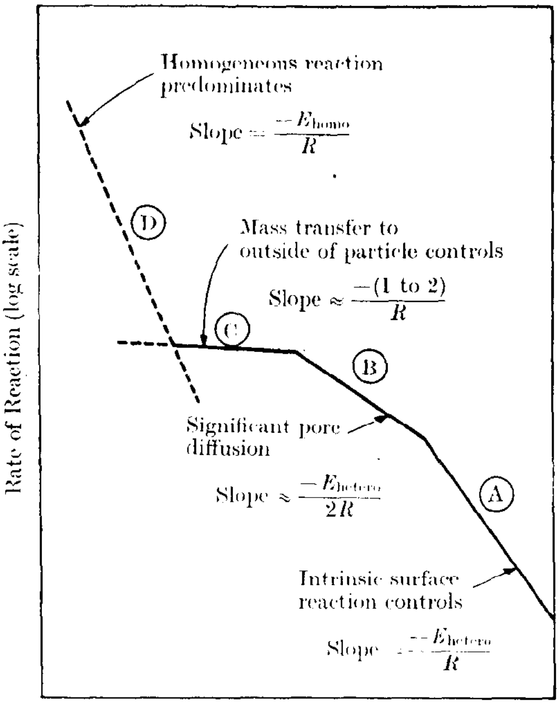
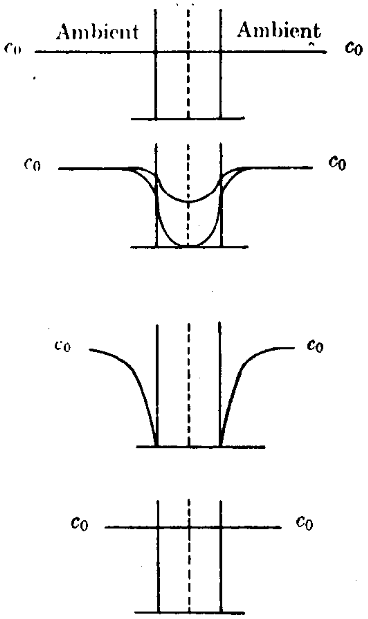


Figure 1.1. Possible kinetic regimes in a gas-phase reaction occurring on a porous solid catalyst.

second-order reaction will appear to be 3/2 order Section (3.3). Of greatest importance, in complex reactions the selectivity toward an intermediate product will almost invariably be reduced; e.g., in the reaction A → B → C, the yield of B will fall below that otherwise attainable (Section 5.2). The degree of diffusion limitation in this second regime is characterized by the "effectiveness factor" η, defined as the ratio of the observed rate of reaction to that which would occur in the absence of diffusion effects within the pores of the catalyst.

As temperature is further increased, the effectiveness factor becomes progressively smaller, and in another range the concentration difference between the bulk of the fluid and the outside of the catalyst pellet becomes significant. In this third reaction regime the concentration of reactant at the outside surface of the catalyst pellet approaches zero; the rate-limiting process is one of mass transfer from the ambient fluid, and shows the same characteristics as bulk diffusion. The apparent activation energy is then about 1 to 3 for gases, 2.5 to 4.5 in liquid hydrocarbons, and 2.0 to 2.5 in aqueous sytems. In this regime all reactions



A. Low temperature.
Very slow reaction.

B. Potential available
to cause reaction
in porous catalyst
is less than c_0.

C. Very active catalyst.
Reaction occurs at or
near outside surface.
Rate limited by mass
transfer from ambient
fluid to surface.

D. Homogeneous reaction
in ambient fluid.
Little or none in
porous catalyst.

Figure 1.2. Concentration profiles in a porous catalyst under different reaction regimes.

appear to be first order regardless of their intrinsic kinetics, since mass transfer is a first-order process. All catalysts will appear to have the same activity and selectivity, as determined by the relative rates of diffusion of reactants, intermediates, and products rather than by the intrinsic characteristics of the reaction. In this third regime the reaction rate is said to be limited by mass transfer to the catalyst surface, sometimes termed a "film-diffusion-limited" process. This terminology may be confusing. When two processes occur in series, as in regime C, the two rates must be equal under steady-state conditions. The rate-limiting process is the one that consumes the predominant portion of the chemical potential available. In regime B, diffusion through the pore structure occurs simultaneously with reaction. Although reactions in this regime are sometimes described loosely as being "limited by pore diffusion" the process is not controlled by a single step as in regime C.

If the same reaction can occur both homogeneously and catalyzed heterogeneously, the effective activation energy for the homogeneous path is almost invariably greater than that for the heterogeneous route. Since the two competing processes occur in parallel, whichever is inherently faster is the one that will be observed. Homogeneous reaction may predominate over catalytic reaction even at low temperature, depending upon the system, but we show it on the left on Figure 1.1 to emphasize that it will play an increasing role at higher temperatures and that the possibility of contributions from homogeneous reaction must be considered in analyzing the results of a seemingly "catalytic" reaction.

The above picture is somewhat simplified. It represents the intrinsic reaction rate by an Arrhenius expression, whereas more complex kinetics are frequently encountered and indeed, in a few cases, such as the catalytic hydrogenation of ethylene, the intrinsic rate may even exhibit a maximum with increase in temperature. The temperature of the gas and solid are taken to be the same, whereas with high heats of reaction significant temperature gradients between the two may occur, particularly with highly exothermic reactions. Instability effects may develop from the consequences of coupling between temperature and concentration gradients. Nevertheless, the above broad outline describes the transitions from one regime to another as temperature is changed, and has been clearly demonstrated in many experimental studies. (Figure 1.1 represents the separate regimes by intersecting straight lines and omits representation of transition regions.) The order in which the three catalytic regimes will be encountered with increased temperature will be as shown in Figure 1.1, except perhaps in a few highly complex situations. The relative location of the three lines with respect to one another depends on several factors. In the pore-diffusion regime B the rate but not the apparent activation energy will be increased by reducing the size of the catalyst particle or by altering the pore structure so as to increase the diffusivity, provided that this does not move the reaction into another regime: The line will shift upward, its slope remaining the same. With sufficiently small particles, or nonporous solids, this regime will be completely eliminated and transition will occur from intrinsic kinetics directly to regime C. Here the rate is a strong function of the linear velocity of the ambient fluid, whereas in regime B it is independent of it. The relative importance of homogeneous reaction depends upon the ratio of bulk gas volume to catalytic surface as well as the relative rate constants. Broadly useful experimental approaches to determining the regime within which one is operating are thus to observe the effects of particle size, temperature, and agitation or fluid velocity.

The transition temperatures between regimes will vary widely with different reactions and different catalysts. In the burnoff of carbonaceous deposits from a silica-alumina cracking catalyst in the form of 0.20 cm beads, the transition temperature from A to B was 460–475°C (see

Illustrative Example 4.7). The transition region would be at a higher temperature if the particles were smaller. Below this temperature, the rate per unit volume of catalyst did not change as particle size was reduced. An Arrhenius plot of data with the 0.20 cm beads shows the transition expected between regimes A and B. Various other examples of the transition between these two regimes are discussed in Chapter 3. In studies of the combustion of single carbon spheres in air, Hottel and co-workers [339] found that mass transfer to the carbon surface became controlling at temperatures above about 900°C, where, as expected, the observed rate of reaction was strongly affected by gas velocity. An Arrhenius plot showed a pronounced transition between regimes A and C. For the decomposition of nickel carbonyl to deposit metallic nickel on a heated filament, an Arrhenius plot of the rate showed the same type of transition between regimes A and C occurring at about 175°C [65]. In the decomposition of iron pentacarbonyl at 20 Torr (mm Hg) the transition temperature was about 200°C [64]. Deposition of metals by vapor decomposition or other reactions is involved in epitaxial film growth as used in semiconductor technology. In the formation of silicon metal films by reduction of silicon tetrachloride with hydrogen at 1050–1300°C variation in the patterns of deposition on substrates in different furnaces was traced to variation in the natural convection patterns which altered the local rates of this mass-transfer-controlled process. At least three studies have been reported of the dehydrogenation of cyclohexane to benzene on a platinum-on-alumina catalyst [16, 123, 170], in the range of 370–500°C, pressures of about 13 to 42 atm, and with a high ratio of hydrogen to cyclohexane to preserve catalyst activity. At the higher temperatures and pressures the reaction was controlled by mass transfer to the outside of the catalyst particles, regime C [123, 170], but under milder conditions, by diffusion inside catalyst pellets, regime B [16]. A clearly defined transition from intrinsic heterogeneous kinetics with an activation energy of 15 kcal/g-mol to homogeneous reaction with an activation energy of about 55 kcal/g-mol (regime A to regime D) has been shown to occur at about 450°C for the decomposition of hydrogen peroxide vapor at about 7.6 Torr partial pressure (760 Torr total pressure) in contact with Pyrex glass and at a surface-to-volume ratio of 1 cm^{-1} [301]. A marked drop in activation energy upon increasing the temperature of reaction, however, is not of itself proof that a mass transfer limitation is being observed, for such a change may also be brought about solely by a change in chemical mechanism. A good example is the vapor phase oxidation of benzene to maleic anhydride on a V_2O_5-MoO_3/SiO_2 catalyst as reported by

Vaidyanathan and Doraiswamy [340]. The activation energy dropped sharply from 20 kcal/g-mol at temperatures below 350°C to about 2 kcal/g-mol at higher temperatures. Studies with four different catalyst sizes showed that in this case the effect could not be attributed to diffusion limitations. As noted above, the intrinsic catalytic hydrogenation of ethylene and other olefins usually exhibits a maximum rate upon increasing the temperature and then decreases [40]; the same phenomenon has been observed in other hydrogenation reactions.

1.2 Diffusion in Gases

Ordinary molecular diffusion in gases (remote from solid or liquid surfaces) results from differences in concentration between regions of a mixture; diffusion tends to make the concentration uniform throughout.

In a stagnant *binary* gas mixture, the molal flux J (g-mol/sec·cm^2) is proportional to the concentration gradient in the direction of diffusion

$$J_1 = -D_{12}\frac{dc_1}{dx} = -D_{12}c_T\frac{dY_1}{dx}. \tag{1.1}$$

The proportionality constant D_{12} is the diffusion coefficient for gas 1 diffusing in gas 2. This is a function of the molecular properties of the two gases, and increases with increase in temperature or reduction in pressure. The value of D_{12} varies little with the mole fractions Y_1 or Y_2 of the two gases, but does vary with changes in c_T, the total molal concentration of the mixture (g-mol/cm^3). This is Fick's first law.

Motion must be related to some coordinate system. A gas of uniform composition may move as a bulk with respect to fixed coordinates (e.g., an apparatus) so that a flux of the gas can occur without diffusion. However, in many cases net molar transport relative to fixed coordinates occurs even in a stagnant gas, as in the Stefan experiment for measuring diffusivity of a vapor in which a pool of liquid is evaporated at the bottom of a vertical tube and the vapor is allowed to diffuse through a stagnant gas to the top of the tube where it is removed. It is therefore convenient to define a molar flux relative to the plane of *no net molar transport*. The symbol J will be used for this flux, and N for the flux relative to stationary coordinates.

If a binary gas mixture of uniform molal density moves at a constant velocity u_m in the x direction, then Equation 1.1 gives the diffusion flux *relative to the moving gas*:

$$J_1 = (u_1 - u_m)c_1 = -D_{12}c_T\frac{dY_1}{dx}, \tag{1.2}$$

where u_1 is the mean molecular velocity of species 1 relative to fixed coordinates resulting from both bulk motion and diffusion. The flux N_1 is $u_1 c_1$ and the total of the two fluxes (relative to the fixed coordinate system) is $N_1 + N_2$, which is equal to $u_m c_T$. From this, we have

$$N_1 = u_1 c_1 = (N_1 + N_2)Y_1 - D_{12} c_T \frac{dY_1}{dx}. \tag{1.3}$$

A more general result, including a term for the variation of c_1 with time, is

$$\frac{\partial c_1}{\partial t} + u_m \frac{\partial c_1}{\partial x} = D_{12} c_T \frac{\partial^2 Y_1}{\partial x^2} \tag{1.4}$$

or

$$\frac{\partial Y_1}{\partial t} + u_m \frac{\partial Y_1}{\partial x} = D_{12} \frac{\partial^2 Y_1}{\partial x^2}. \tag{1.5}$$

This is for diffusion and flow in the x direction only; the vector form for any direction is

$$\frac{\partial Y_1}{\partial t} + (\mathbf{u}_m \cdot \nabla)Y_1 = D_{12} \nabla^2 Y_1. \tag{1.6}$$

In cases where diffusion is accompanied by chemical reaction, the relations must be modified to allow for the formation or disappearance of the diffusing species. Let Q_1 and Q_2 represent the rate of formation of the two species (g-mol/sec·cm^3) in a binary system diffusing at constant c_T in the x direction only; then by a molar balance on a differential element,

$$\frac{\partial c_1}{\partial t} + \frac{\partial N_1}{\partial x_1} = Q_1 \tag{1.7}$$

with a similar equation relating c_2, N_2, and Q_2. Adding these equations, and noting that $c_1 + c_2 = c_T$, we obtain

$$Q_1 + Q_2 = \frac{\partial}{\partial x}(N_1 + N_2) = c_T \frac{\partial u_m}{\partial x}. \tag{1.8}$$

Equation 1.3 may be differentiated with respect to x and the derivative used to replace the second term of Equation 1.7; combination with Equation 1.8 then gives

$$\frac{\partial Y_1}{\partial t} + u_m \frac{\partial Y_1}{\partial x} = \frac{Q_1}{c_T} - \frac{Y_1}{c_T}(Q_1 + Q_2) + D_{12} \frac{\partial^2 Y_1}{\partial x^2}, \tag{1.9}$$

where u_m may be replaced by $(N_1 + N_2)/c_T$.

If one mole of species 1 disappears to form one mole of species 2 ($Q_1 = -Q_2$), the second term on the right is absent; if Q_1 and Q_2 are both zero (no reaction), Equation 1.5 results. The general relation in vector form (binary mixture, constant c_T) is

$$\frac{\partial Y_1}{\partial t} + (\boldsymbol{u}_m \cdot \nabla) Y_1 = \frac{Q_1}{c_T} - \frac{Y_1}{c_T}(Q_1 + Q_2) + D_{12}\nabla^2 Y_1. \qquad (1.10)$$

It may be noted that $c_T = P/RT$ in cases where the mixture behaves as an ideal gas.

Equation 1.3 may be integrated for application to several important cases of steady-state diffusion in nonreacting binary gas systems at constant c_T. Thus for the steady-state unidirectional diffusion of species 1 through a stagnant, or nondiffusing, layer of species 2 ($N_2 = 0$),

$$N_1 = -\frac{c_T D_{12}}{1 - Y_1}\frac{dY_1}{dx}. \qquad (1.11)$$

If the gas mixture is ideal, $c_T = P/RT$ and $p_1 + p_2 = P$;

$$\begin{aligned} N_1 &= -\frac{D_{12}P}{RTp_2}\frac{dp_1}{dx} = \frac{D_{12}P}{RTx_0}\ln\frac{(Y_2)_2}{(Y_2)_1} \\ &= \frac{D_{12}P}{RTx_0}\frac{[(p_1)_1 - (p_1)_2]}{(p_2)_M}. \qquad (1.12) \end{aligned}$$

Here x_0 is the thickness of the gas layer, and $(p_2)_M$ is the logarithmic mean of the values of p_2 at $x = 0$ and $x = x_0$, i.e.

$$\frac{(p_2)_2 - (p_2)_1}{\ln[(p_2)_2/(p_2)_1]}.$$

If the two species diffuse at constant but unequal rates, integration of Equation 1.3 gives

$$N_1 + N_2 = \frac{c_T D_{12}}{x_0}\ln\frac{[1 - (Y_1)_2]N_1 - (Y_1)_2 N_2}{[1 - (Y_1)_1]N_1 - (Y_1)_1 N_2}. \qquad (1.13)$$

If the molar diffusion fluxes are constant and equal in opposite directions ($N_1 = -N_2$),

$$N_1 = J_1 = -N_2 = \frac{c_T D_{12}}{x_0}[(Y_1)_1 - (Y_1)_2]. \qquad (1.14)$$

The equations given in the foregoing section apply only to binary gas systems at constant-mixture molar density. The limitation to constant

c_T is not often serious in common application, but many cases involving more than two components are encountered. The theory of diffusion in multicomponent mixtures is quite complex, but it has been found possible to deal with the problem in an approximate manner by employing a diffusion coefficient D_{1m} for species 1 in the mixture, related to the binary coefficients by the relation

$$D_{1m} = (1 - Y_1)\left(\sum_{j=2}^{n} \frac{Y_j}{D_{1j}}\right)^{-1}. \tag{1.15}$$

This evidently works well for the diffusion of a single component in a mixture. The analysis of the simultaneous diffusion of two or more components of a mixture is complicated [147]. Where the diffusing components are present in low concentrations, as in many catalytic hydrogenations, the substitution of D_{1m} from Equation 1.15 into equations for single-component diffusion may introduce no great error.

1.3 Diffusion Coefficients: Binary Gas Mixtures

Experimental data on D_{12} for gas systems are available in considerable number; a limited list is given in Table 1.1.

The best present method of extrapolating experimental values, or of estimating coefficients that have not been measured, is the theoretical equation based on the modern kinetic theory and the Lennard-Jones expression for intermolecular forces [147]. This is

$$D_{12} = \frac{0.001858 T^{3/2}[(M_1 + M_2)/M_1 M_2]^{1/2}}{P \sigma_{12}^2 \Omega_D}, \tag{1.16}$$

where T is the absolute temperature (°K), M_1, M_2 are the molecular weights of the two species, P is the total pressure (atm), Ω_D is the "collision integral," a function of kT/ε_{12} (see Table 1.2), ε, σ are the force constants in the Lennard-Jones potential function, and k is the Boltzmann constant.

Values of ε and σ, usually obtained from viscosity data, are available for a number of pure gases: Table 1.3 presents a selection from the values reported by Svehla [331] for over 200 compounds. Earlier sets of values are reported by Hirschfelder and co-workers [146, 147] and by Rowlinson and Townley [282]. The values of ε and σ for a species should both be taken from the same table. A larger value of ε is substantially compensated for by a smaller value of σ. Where not reported,