Part I
Introduction

Diffusion in Nanoporous Materials. Jörg Kärger, Douglas M. Ruthven, and Doros N. Theodorou.

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Elementary Principles of Diffusion

The tendency of matter to migrate in such a way as to eliminate spatial variations in composition, thereby approaching a uniform equilibrium state, is well known. Such behavior, which is a universal property of matter at all temperatures above absolute zero, is called diffusion and is simply a manifestation of the tendency towards maximum entropy or maximum randomness. The rate at which diffusion occurs varies widely, from a time scale of seconds for gases to millennia for crystalline solids at ordinary temperatures. The practical significance therefore depends on the time scale of interest in any particular situation.

Diffusion in gases, liquids, and solids has been widely studied for more than a century [1–3]. In this book we are concerned with the specific problem of diffusion in porous solids. Such materials find widespread application as catalysts or adsorbents, which is a subject of considerable practical importance in the petroleum and chemical process industries and have recently attracted even more attention due to their potential as functional materials with a broad range of applications ranging from optical sensing to drug delivery [4]. To achieve the necessary surface area required for high capacity and activity, such materials generally have very fine pores. Transport through these pores occurs mainly by diffusion and often affects or even controls the overall rate of the process. A detailed understanding of the complexities of diffusional behavior in porous media is therefore essential for the development, design, and optimization of catalytic and adsorption processes and for technological exploitation of porous materials in general. Moreover, systematic diffusion studies in such systems lead to a better understanding of such fundamental questions as the interaction between molecules and solid surfaces [5] and the behavior of molecular systems of reduced dimensionality [6–8].

One class of microporous materials that is of special interest from both practical and theoretical points of view is the zeolites, where this term is used in its broad sense to include both microporous crystalline aluminosilicates and their structural analogs such as the titanosilicates and aluminophosphates. These materials form the basis of many practical adsorbents and catalysts. They combine the advantages of high specific area and uniform micropore size and, as a result, they offer unique properties such as size selective adsorption that can be exploited to achieve

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practically useful separations and to improve the efficiency of catalytic processes. The regularity of the pore structure, which is determined by the crystal structure rather than by the mode of preparation or pretreatment, offers the important advantage that it is possible, in such systems, to investigate the effect of pore size on the transport properties. In more conventional adsorbents, which have a very much wider distribution of pore size, such effects are more difficult to isolate. In the earlier chapters of this book diffusion in nanoporous solids is treated from a general perspective, but the later chapters focus on zeolitic adsorbents; because of their practical importance, these materials have been studied in much greater detail than amorphous materials.

Since the first edition of this book was published [9], an important new class of nanoporous materials based on metal–organic frameworks (MOFs) has been discovered and studied in considerable detail. Although their composition is quite different, MOFs are structurally similar to the zeolites and show many similarities in their diffusional behavior. Some of the recent studies of these materials are reviewed in Chapter 19.

1.1
Fundamental Definitions

1.1.1
Transfer of Matter by Diffusion

The quantitative study of diffusion dates from the early work of two pioneers, Thomas Graham and Adolf Fick (for a detailed historical review, see, for example, Reference [10]), during the period 1850–1855. Graham's initial experiments, which led to Graham's law of diffusion, involved measuring the rate of interdiffusion of two gases, at constant pressure, through a porous plug [11, 12]. He concluded that:

> *The diffusion or spontaneous inter-mixture of two gases in contact is, in the case of each gas, inversely proportional to the density of the gas.*

In later experiments with salt solutions he, in effect, verified the proportionality between the diffusive flux and the concentration gradient, although the results were not reported in precisely those terms. He also established the very large difference in the orders of magnitude of gas and liquid diffusion rates.

Fick's contribution was to recognize that Graham's observations could be understood if the diffusion of matter obeys a law of the same general form as Fourier's law of heat conduction, an analogy that remains useful to this day. On this basis he formulated what is now generally known as Fick's first law of diffusion, which is in fact no more than a definition of the "diffusivity" (D):

$$J = -D\frac{\partial c}{\partial z} \tag{1.1}$$

or, more generally:

$$\boldsymbol{J} = -D\,\mathrm{grad}\,c$$

He showed that for diffusion in a parallel-sided duct with a constant diffusivity, this leads to the conservation equation:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} \tag{1.2}$$

or:

$$\frac{\partial c}{\partial t} = D\,\mathrm{div}(\mathrm{grad}\,c)$$

which is commonly known as Fick's second law of diffusion. He then proceeded to verify these conclusions by a series of ingenious experiments involving the measurement of concentration profiles, under quasi-steady state conditions, in conical and cylindrical vessels in which uniform concentrations were maintained at the ends [10, 13, 14].

These experiments were carried out with dilute solutions in which the diffusivity is substantially independent of composition. The definition of Eq. (1.1) makes no such assumption and is equally valid when the diffusivity varies with concentration. The additional assumption that the diffusivity does not depend on concentration is, however, introduced in the derivation of Eq. (1.2). The more general form of the conservation equation, allowing for concentration dependence of the diffusivity, is:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left[D(c)\frac{\partial c}{\partial z}\right] \tag{1.3}$$

or:

$$\frac{\partial c}{\partial t} = \mathrm{div}\,[D(c)\,\mathrm{grad}\,c]$$

which reverts to Eq. (1.2) when D is constant.

In an isothermal binary system, Eq. (1.1) may also be written, equivalently, in terms of the gradient of mole fraction or (for gases) the partial pressure:

$$J = -D\frac{\partial c}{\partial z} = -cD\frac{\partial y_{\mathrm{A}}}{\partial z} = -\frac{D}{RT}\frac{\partial P_{\mathrm{A}}}{\partial z} \tag{1.4}$$

but these formulations are no longer equivalent in a non-isothermal system. Momentum transfer arguments lead to the conclusion that for diffusion in a gas mixture the gradient of partial pressure should be regarded as the fundamental "driving force," since that formulation remains valid even under non-isothermal conditions. A more detailed discussion of this point has been given by Haynes [15]. However, in this book problems of diffusion under non-isothermal conditions are not addressed in any substantial way and so the equivalence of Eq. (1.4) can generally be assumed.

The mathematical theory of diffusion, which has been elaborated in detail by Crank [16], depends on obtaining solutions to Eq. (1.1) [or Eqs. (1.2) and (1.3)] for the appropriate initial and boundary conditions. A number of such solutions are summarized in Chapter 6 for some of the situations commonly encountered in the measurement of diffusivities. In this chapter we present only the solution for one simple case that is useful for elaboration of the analogy between diffusion and a “random walk.”

1.1.2
Random Walk

In the late 1820s, that is, about 20 years before the experiments of Graham and Fick, the Scottish botanist Robert Brown gave a detailed description of another phenomenon that turned out to be closely related to diffusion [10, 17]. On observing a suspension of pollen grains with the aid of the then new achromatic microscope he noticed that the individual particles undergo a sequence of rapid and apparently random movements. Today we know this behavior results from the continuously changing interaction between small particles and the molecules of the surrounding fluid. Although this microdynamic explanation was only suggested much later [18] this phenomenon is generally referred to as Brownian motion. The close relationship between Brownian motion and diffusion was first elaborated by Einstein [19] and, eventually, turned out to be nothing less than the ultimate proof of nature’s atomic structure [10]. An experimentally accessible quantity that describes Brownian motion is the time dependence of the concentration distribution of the Brownian particles (diffusants) that were initially located within a given element of space. To apply Fick’s equations [Eqs. (1.1) and (1.2)] to this process the particles initially within this space element must be considered to be distinguishable from the other particles, that is, they must be regarded as “labeled.” The concentration distribution of these labeled particles will obey Eq. (1.2), which, in this situation, holds exactly since the total concentration of particles (and therefore their mobility or diffusivity) remains constant throughout the region under consideration.

It is easy to show by differentiation that for a constant diffusivity system:

$$c = \frac{A}{\sqrt{t}} \mathrm{e}^{-z^2/4Dt} \tag{1.5}$$

(in which A is an arbitrary constant) is a general solution of Eq. (1.2). The total quantity of diffusing substance (M), assuming a parallel-sided container of unit cross-sectional area and infinite length in the z direction, is given by:

$$M = \int_{-\infty}^{+\infty} c \, \mathrm{d}z \tag{1.6}$$

and, on writing $\xi^2 = z^2/4Dt$, we see that:

$$M = 2A\sqrt{D} \int_{-\infty}^{+\infty} \mathrm{e}^{-\xi 2} \, \mathrm{d}\xi = 2A\sqrt{\pi D} \tag{1.7}$$

Substitution in Eq. (1.5) shows that if this quantity of solute is initially confined to the plane at $z = 0$, the distribution of solute at all later times will be given by:

$$\frac{c}{M} = \frac{\mathrm{e}^{-z^2/4Dt}}{\sqrt{4\pi Dt}} \tag{1.8}$$

The corresponding solution for isotropic diffusion from a point source in three-dimensional space may be derived in a similar way:

$$\frac{c}{M} = \frac{\mathrm{e}^{-r^2/4Dt}}{(4\pi Dt)^{3/2}} \tag{1.9}$$

where $\boldsymbol{r}$ represents the position vector from the origin. Equations (1.8) and (1.9) thus give the probability of finding, at position $\boldsymbol{r}$, a particle (or molecule) that was located at the origin at time zero. This quantity is termed the "propagator" and, as it is a Gaussian function, it is completely defined by the mean square half-width or the "mean square displacement" of the diffusants, which may be found directly from Eqs. (1.8) or (1.9) by integration:

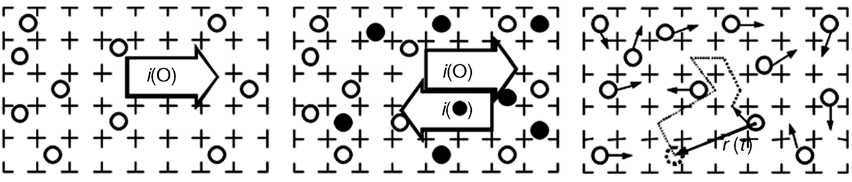
$$\begin{aligned} \langle z^2(t)\rangle &= \int_{-\infty}^{+\infty} z^2 \frac{\mathrm{e}^{-z^2/4Dt}}{\sqrt{4\pi Dt}} \mathrm{d}z = 2Dt \\ \langle r^2(t)\rangle &= \int \boldsymbol{r}^2 \frac{\mathrm{e}^{-r^2/4Dt}}{(4\pi Dt)^{3/2}} \mathrm{d}z = 6Dt \end{aligned} \tag{1.10}$$

These equations are generally known as Einstein's relations [19] and provide a direct correlation between the diffusivity, as defined by Fick's first equation, and the time dependence of the mean square displacement, which is the most easily observable quantitative feature of Brownian motion.

Chapter 2 explores the equivalence between a "random walk" and diffusion in greater detail. Starting from the assumption that the random walkers may step with equal probability in any direction, it is shown that the distribution and mean square displacement for a large number of random walkers, released from the origin at time zero, are given by Eqs. (1.8–1.10). From the perspective of the random walk one may therefore elect to consider Eq. (1.10) as defining the diffusivity and, provided the diffusivity is independent of concentration, this definition is exactly equivalent to the Fickian definition based on Eq. (1.1).

1.1.3
Transport Diffusion and Self-Diffusion

Two different diffusion phenomena may be distinguished: mass transfer (or transport diffusion) resulting from a concentration gradient (Figure 1.1a) and Brownian molecular motion (self-diffusion), which may be followed either by tagging a certain fraction of the diffusants (Figure 1.1b) or by following the trajectories of a large number of individual diffusants and determining their mean square displacement



(a) (b) (c)

Figure 1.1 Microscopic situation during the measurement of transport diffusion (a) and self-diffusion by following the flux of labeled molecules (○) counterbalanced by that of the unlabeled molecules (●, b) or by recording the displacement of the individual molecules (c).

(Figure 1.1c). Because of the difference in the microphysical situations represented by Figures 1.1a–c the diffusivities in these two situations are not necessarily the same.

Following general convention we call the diffusivity corresponding to the situation represented by Figure 1.1a (in which there is a concentration gradient rather than merely a gradient in the fraction of marked molecules) the transport diffusivity (D), since this coefficient is related directly to the macroscopic transport of matter. Completely synonymously, the terms collective or chemical diffusion are sometimes also used [3].

The quantity describing the rate of Brownian migration under conditions of macroscopic equilibrium (Figure 1.1b and c) is referred to as the tracer or self-diffusivity ($\mathfrak{D}$). A formal definition of the self-diffusivity may be given in two ways based on either Eqs. (1.1) or (1.10):

$$J^* = -\mathfrak{D}\left.\frac{\partial c^*}{\partial z}\right|_{c=\mathrm{const}} \tag{1.11}$$

or:

$$\left\langle r^2(t)\right\rangle = 6\mathfrak{D}t \tag{1.12}$$

but, as noted above, these definitions are in fact equivalent. Note that the self-diffusivity may vary with the total concentration, but it does not vary with the fraction of marked molecules.

Although both diffusion and self-diffusion occur by essentially the same microdynamic mechanism, namely, the irregular (thermal) motion of the molecules, the coefficients of transport diffusion and self-diffusion are generally not the same. Their relationship is discussed briefly in Section 1.2.3 and in greater detail in Section 3.3.3 as well as in Chapters 2 and 4 on the basis of various model assumptions for molecular propagation.

Mass transfer phenomena following Eqs. (1.11) and (1.12) are referred to as normal diffusion. It is shown in Section 2.1.2 that this describes the common situation in porous materials. Anomalous diffusion [7, 8, 20] leads to a deviation from the linear interdependence between the mean square displacement and the observation time as predicted by Eq. (1.12), which may formally be taken account of by considering the self-diffusivity as a parameter that depends on either the observation time in Eq. (1.12) or on the system size in Eq. (1.11) [21]. Such deviations, however, necessitate a highly correlated motion with a long "memory" of the diffusants, which occurs under only very exceptional conditions such as in single-file systems (Chapter 5). Anomalous diffusion is generally therefore of no technological relevance for mass transfer in nanoporous materials.

1.1.4
Frames of Reference

The situation shown in Figure 1.1a is only physically reasonable in a microporous solid where the framework of the solid permits the existence of an overall gradient of concentration under isothermal and isobaric conditions. Furthermore, in such systems the solid framework provides a convenient and unambiguous frame of reference with respect to which the diffusive flux may be measured. In the more general case of diffusion in a fluid phase the frame of reference must be specified to complete the definition of the diffusivity according to Eq. (1.1). For the interdiffusion of two components A and B we may write:

$$J_\mathrm{A} = -D_\mathrm{A}\frac{\partial c_\mathrm{A}}{\partial z}, \quad J_\mathrm{B} = -D_\mathrm{B}\frac{\partial c_\mathrm{B}}{\partial z} \tag{1.13}$$

If the partial molar volumes of A and B are different ($V_\mathrm{A} \neq V_\mathrm{B}$), the interdiffusion of the two species will lead to a net (convective) flow relative to a fixed coordinate system. The total volumetric flux is given by:

$$J_\mathrm{V} = V_\mathrm{A} D_\mathrm{A}\frac{\partial c_\mathrm{A}}{\partial z} + V_\mathrm{B} D_\mathrm{B}\frac{\partial c_\mathrm{B}}{\partial z} \tag{1.14}$$

and the plane across which there is no net transfer of volume is given by $J_\mathrm{V} = 0$. If there is no volume change on mixing:

$$V_\mathrm{A} c_\mathrm{A} + V_\mathrm{B} c_\mathrm{B} = \text{constant} \tag{1.15}$$

$$V_\mathrm{A}\frac{\partial c_\mathrm{A}}{\partial z} + V_\mathrm{B}\frac{\partial c_\mathrm{B}}{\partial z} = 0 \tag{1.16}$$

For both Eqs. (1.14) and (1.16) to be satisfied with $J_\mathrm{V} = 0$ and V_A and V_B finite, it follows that $D_\mathrm{A} = D_\mathrm{B}$. The interdiffusion process is therefore described by a single diffusivity provided that the fluxes, and therefore the diffusivity, are defined relative to the plane of no net volumetric flow. The same result can be shown to hold even when there is a volume change on mixing, provided that the fluxes are defined relative to the plane of no net mass flow. In general the interdiffusion of two components can always be described by a single diffusivity but the frame of reference required to achieve this simplification depends on the nature of the system.

To understand the definition of the diffusivity for an adsorbed phase we must first consider the more general case of diffusion in a convective flow. The diffusive flux (relative to the plane of no net molal flow) is conventionally denoted by ***J*** and the total flux, relative to a fixed frame of reference, by ***N***. For a binary system (A, B) we have:

$$N_A = J_A + y_A N = J_A + y_A(N_A + N_B) \tag{1.17}$$

If component B is stationary ($N_B = 0$) then:

$$J_A = N_A(1 - y_A) \tag{1.18}$$

which thus defines the relationship between the fluxes N_A and J_A. Diffusion of a mobile species within a porous solid may be regarded as a special case of binary diffusion in which one component (the solid) is immobile. The flux, and therefore the diffusivity, is normally defined with respect to the fixed coordinates of the solid rather than with respect to the plane of no net molal flux. There is no convective flow, so:

$$N_A = J'_A = \frac{J_A}{1 - y_A} = -D'_A \frac{\partial c_A}{\partial z}; \quad D'_A = \frac{D_A}{(1 - y_A)} \tag{1.19}$$

but J'_A and D'_A are now defined in the fixed frame of reference. In discussing diffusion in an adsorbed phase the distinction between J' and J and between D' and D is generally not explicit. The symbols J and D are commonly applied to fluxes in both fluid and adsorbed phases but it is important to understand that their meanings are not identical. This is especially important when applying results derived for diffusion in a homogeneous fluid to diffusion in a porous adsorbent.

1.1.5
Diffusion in Anisotropic Media

Extension of the unidimensional diffusion equations to diffusion in two or three dimensions [e.g., Eqs. (1.2), (1.3) or (1.8) and (1.9)] follows in a straightforward manner for an isotropic system in which the diffusivity in any direction is the same. In most macroporous adsorbents, randomness of the pore structure ensures that the diffusional properties should be at least approximately isotropic. For intracrystalline diffusion the situation is more complicated. When the crystal structure is cubic, intracrystalline diffusion should be isotropic since the micropore structure must then be identical in all three principal directions. However, when the crystal symmetry is anything other than cubic, the pore geometry will generally be different in the different principal directions, so anisotropic diffusion is to be expected. Perhaps the most important practical example is diffusion in ZSM-5/silicalite, which is discussed in Chapter 18.

In an isotropic medium the direction of the diffusive flux at any point is always perpendicular to the surface of constant concentration through that point, but this is not true in a nonisotropic system. This means that, for a nonisotropic system, Eq. (1.1) must be replaced by:

$$\begin{aligned}
-J_x &= D_{xx}\frac{\partial c}{\partial x} + D_{xy}\frac{\partial c}{\partial y} + D_{xz}\frac{\partial c}{\partial z} \\
-J_y &= D_{yx}\frac{\partial c}{\partial x} + D_{yy}\frac{\partial c}{\partial y} + D_{yz}\frac{\partial c}{\partial z} \\
-J_z &= D_{zx}\frac{\partial c}{\partial x} + D_{zy}\frac{\partial c}{\partial y} + D_{zz}\frac{\partial c}{\partial z}
\end{aligned} \tag{1.20}$$

In this notation the coefficients D_{ij} (with $i, j = x, y$, z) represent the contribution to the flux in the i direction from a concentration gradient in the j direction. The set:

$$\begin{bmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{bmatrix}$$

is commonly called the diffusion tensor.

The equivalent of Eq. (1.2) for a (constant diffusivity) non-isotropic system is:

$$\begin{aligned}
\frac{\partial c}{\partial t} &= D_{xx}\frac{\partial^2 c}{\partial x^2} + D_{yy}\frac{\partial^2 c}{\partial y^2} + D_{zz}\frac{\partial^2 c}{\partial z^2} + (D_{yz} + D_{zy})\frac{\partial^2 c}{\partial y\,\partial z} \\
&\quad + (D_{zx} + D_{xz})\frac{\partial^2 c}{\partial z\,\partial x} + (D_{xy} + D_{yx})\frac{\partial^2 c}{\partial x\,\partial y} = 0
\end{aligned} \tag{1.21}$$

but it may be shown that a transformation to the rectangular coordinates ξ, η, ζ can always be found, which reduces this to the form:

$$\frac{\partial c}{\partial t} = D_1\frac{\partial^2 c}{\partial \xi^2} + D_2\frac{\partial^2 c}{\partial \eta^2} + D_3\frac{\partial^2 c}{\partial \zeta^2} \tag{1.22}$$

If we make the further substitutions:

$$\xi_1 = \xi\sqrt{D/D_1}, \quad \eta_1 = \eta\sqrt{D/D_2}, \quad \zeta_1 = \zeta s\sqrt{D/D_3}$$

in which D may be arbitrarily chosen, Eq. (1.22) reduces to:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial \xi_1^2} + \frac{\partial^2 c}{\partial \eta_1^2} + \frac{\partial^2 c}{\partial \zeta_1^2}\right) \tag{1.23}$$

which is formally identical with the diffusion equation for an isotropic system. In this way many of the problems of diffusion in nonisotropic systems can be reduced to the corresponding isotropic diffusion problems. Whether this is possible in any given situation depends on the boundary conditions, but where these are simple (e.g., step change in concentration at $t = 0$) this reduction is usually possible. The practical consequence of this is that in such cases one may expect the diffusional behavior to be similar to an isotropic system so that measurable features such as the transient uptake curves will be of the same form. However, the apparent diffusivity derived by matching such curves to the isotropic solution will be a complex average of D_1, D_2, and D_3, the diffusivities in the three principal directions ξ, η, and ζ. It is in general not possible to extract the individual values of D_1, D_2, and D_3 with satisfactory accuracy, although given the values of the principal coefficients (e.g., from an a priori prediction) it would be possible to proceed in the reverse direction and calculate the value of the apparent diffusivity.

1.2
Driving Force for Diffusion

1.2.1
Gradient of Chemical Potential

Fick's first law [Eq. (1.1)] and the equivalent definition of the diffusivity according to Eq. (1.10) both carry the implication that the driving force for diffusion is the gradient of concentration. However, since diffusion is simply the macroscopic manifestation of the tendency to approach equilibrium, it is clear that the true driving force must be the gradient of chemical potential (μ). This seems to have been explicitly recognized first by Einstein [22]. If the diffusive flux is considered as a flow driven by the gradient of chemical potential and opposed by frictional forces, the steady-state energy balance for a differential element is simply:

$$fu_\mathrm{A} = -\frac{\mathrm{d}\mu_\mathrm{A}}{\mathrm{d}z} \tag{1.24}$$

where u_A is the flow velocity of component A and f is a friction coefficient. The flux (J_A) is given by $u_\mathrm{A}c_\mathrm{A}$. To relate the chemical potential to the concentration we may consider the equilibrium vapor phase in which, neglecting deviations from the ideal gas law, the activity may be identified with the partial pressure:

$$\mu_\mathrm{A} = \mu_\mathrm{A}^0 + RT\ln p_\mathrm{A} \tag{1.25}$$

The expression for the flux may then be written:

$$J_\mathrm{A} = u_\mathrm{A}c_\mathrm{A} = -\frac{RT}{f}\frac{\mathrm{d}\ln p_\mathrm{A}}{\mathrm{d}\ln c_\mathrm{A}}\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}z} \tag{1.26}$$

Comparison with Eq. (1.1) shows that the transport diffusivity is given by:

$$D_\mathrm{A} = \frac{RT}{f}\frac{\mathrm{d}\ln p_\mathrm{A}}{\mathrm{d}\ln c_\mathrm{A}} = D_0\frac{\mathrm{d}\ln p_\mathrm{A}}{\mathrm{d}\ln c_\mathrm{A}} \tag{1.27}$$

where $\mathrm{d}\ln p_\mathrm{A}/\mathrm{d}\ln c_\mathrm{A}$ represents simply the gradient of the equilibrium isotherm in logarithmic coordinates. This term [the "thermodynamic (correction) factor"] may vary substantially with concentration and, in general, approaches a constant value of 1 only at low concentrations within the Henry's law region.

The principle of the chemical potential driving force is also implicit in the Stefan–Maxwell formulation [23, 24] (presented in Section 3.3) which, for a binary system, may be written in the form:

$$-\frac{\partial}{\partial z}\left(\frac{\mu_A}{RT}\right)=\frac{y_B}{Đ_{AB}}(u_A-u_B) \tag{1.28}$$

where y_B denotes the mole fraction of component B, $Đ_{AB}$ is the Stefan–Maxwell diffusivity, and u_A, u_B are the diffusive velocities. For an isothermal system with no net flux, Eq. (1.28) reduces to:

$$J_A=-Đ_{AB}\frac{\mathrm{d}\ln p_A}{\mathrm{d}\ln c_A}\cdot\frac{\mathrm{d}c_A}{\mathrm{d}z} \tag{1.29}$$

which is equivalent to Eq. (1.26).

An alternative and equivalent form may be obtained by introducing the activity coefficient γ_A (defined by $f_A \approx p_A = \gamma_A c_A$ where f_A is the fugacity):

$$J_A=-Đ_{AB}\left(\frac{\partial\ln\gamma_A}{\partial\ln c_A}+1\right)\frac{\mathrm{d}c_A}{\mathrm{d}z} \tag{1.30}$$

This form of expression was applied by Darken [25] in his study of interdiffusion in binary metal alloys. The use of "thermodynamically corrected" diffusion coefficients is therefore sometimes attributed to Darken. However, it is apparent from the preceding discussion that the idea actually predates Darken's work by many years and is probably more correctly attributed to Maxwell and Stefan or Einstein.

The same formulation can obviously be used to represent diffusion of a single component (A) in a porous adsorbent (B). In this situation $u_B = 0$ and $Đ_{AB}$ is the diffusivity for component A relative to the fixed coordinates of the pore system. Furthermore, in a microporous adsorbent there is no clear distinction between molecules on the surface and molecules in the "gas" phase in the central region of the pore. It is therefore convenient to consider only the total "intracrystalline" concentration (q). Assuming an ideal vapor phase, the transport equation is then written in the form:

$$J=-D\frac{\mathrm{d}q}{\mathrm{d}z},\quad D=D_0\frac{\mathrm{d}\ln p}{\mathrm{d}\ln q} \tag{1.31}$$

D_0, defined in this way, is generally referred to as the "corrected diffusivity" and $\mathrm{d}\ln p/\mathrm{d}\ln q$ ($\equiv \Gamma$) as the "thermodynamic factor." Comparison with Eq. (1.29) shows that, under the specified conditions, D_0 is identical to the Stefan–Maxwell diffusivity $Đ_{AB}$.

If the system is thermodynamically ideal ($p \propto q$) $\mathrm{d}\ln p/\mathrm{d}\ln q \rightarrow 1.0$ and the Fickian and corrected diffusivities become identical. However, in the more general case of a thermodynamically nonideal system, the Fickian transport diffusivity is seen to be the product of a mobility coefficient (D_0) and the thermodynamic correction factor $\mathrm{d}\ln p/\mathrm{d}\ln q$, which arises from nonlinearity of the relationship between activity and concentration. Thermodynamic ideality is generally approached only in dilute systems (gases, dilute liquid or solid solutions) and, under these conditions, one may also expect negligible interaction between the diffusing molecules, leading to a diffusivity that is independent of concentration. Since diffusion is commonly first encountered under these near ideal conditions, the idea that the diffusivity should be constant and that departures from such behavior are in some sense abnormal, has become widely accepted. In fact, except in dilute systems, the Fickian diffusivity is generally found to be concentration dependent. Equation (1.31) shows that this concentration dependence may arise from the concentration dependence of either D_0 or $\mathrm{d}\ln p/\mathrm{d}\ln q$.

In liquid-phase systems both these effects are often of comparable magnitude [26] and one may therefore argue that there is little practical advantage to be gained from using the corrected diffusivity (D_0) rather than the Fickian transport diffusivity (D). The situation is different in adsorption systems. In the saturation region the equilibrium isotherm becomes almost horizontal so that $\mathrm{d}\ln p/\mathrm{d}\ln q \rightarrow \infty$ whereas in the low-concentration (Henry's law) region $\mathrm{d}\ln p/\mathrm{d}\ln q \rightarrow 1.0$. The concentration dependence of this factor and, as a result, the concentration dependence of the Fickian diffusivity is therefore generally much more pronounced than the concentration dependence of the corrected diffusivity. Indeed, for many systems the corrected diffusivity has been found experimentally to be almost independent of concentration. Correlation of transport data for adsorption systems in terms of the corrected diffusivity is therefore to be preferred for practical reasons since it generally provides a simpler description.

In addition to these practical considerations there is a strong theoretical argument in favor of using corrected diffusivities. According to Eq. (1.31), and as will become clearer from the statistical mechanical considerations presented in Section 8.1.3, the transport diffusivity is seen to be a hybrid quantity, being the product of a mobility coefficient and a factor related to the driving force. In attempting to understand transport behavior at the molecular level it is clearly desirable to separate these two effects. Two systems with the same transport diffusivity may, as a result of large differences in the correction factor, have very different molecular mobilities. In any fundamental analysis the "corrected" diffusivity is therefore clearly the more useful quantity.

Beyond the Henry's law region the simple Langmuir model is often used to represent the behavior of adsorption systems in an approximate way. For a single adsorbed component:

$$\theta = \frac{q}{q_\mathrm{s}} = \frac{bp}{1+bp}; \qquad \frac{\mathrm{d}\ln p}{\mathrm{d}\ln q} = \frac{1}{1-q/q_\mathrm{s}} = \frac{1}{1-\theta} \tag{1.32}$$

where θ is referred to as the fractional loading and b is the adsorption equilibrium constant (per site). This expression has the correct asymptotic behavior ($p \rightarrow 0$, $q \rightarrow Kp$ where $K = bq_\mathrm{s}$ and $p \rightarrow \infty$, $q \rightarrow q_\mathrm{s}$) and, although it provides an accurate representation of the isotherms for only a few systems, it provides a useful approximate representation for many systems. The extension to a binary system is:

$$\theta_A = \frac{q_A}{q_{As}} = \frac{b_A p_A}{1 + b_A p_A + b_B p_B} \tag{1.33}$$

The partial derivatives required for the analysis of diffusion in a binary system (Section 3.3.2) follow directly:

$$\frac{\partial \ln p_A}{\partial \ln q_A} = \frac{1-\theta_B}{1-\theta_A-\theta_B}; \quad \frac{\partial \ln p_A}{\partial \ln q_B} = \frac{\theta_A}{1-\theta_A-\theta_B} \tag{1.34}$$

1.2.2
Experimental Evidence

Direct experimental proof that the driving force for diffusive transport is the gradient of chemical potential, rather than the gradient of concentration, is provided by the experiments of Haase and Siry [27, 28] who studied diffusion in binary liquid mixtures near the consolute point. At the consolute point the chemical potential, and therefore the partial pressures, are independent of composition so that, according to Eq. (1.29), the transport diffusivity should be zero. The consolute point for the system *n*-hexane–nitrobenzene occurs at 20 °C at a mole fraction 0.422 of nitrobenzene. The system shows complete miscibility above this temperature but splits into two separate phases at lower temperatures. The opposite behavior is shown by the system water–triethylamine, for which the consolute temperature occurs at 18 °C at a mole fraction of triethylamine of 0.087. The mixture is completely miscible at lower temperatures but separates into two phases at higher temperature. Figure 1.2 shows the results of diffusion measurements. In both systems the Fickian diffusivity approaches zero as the consolute temperature is approached, as required by Eq. (1.29). The behavior of the water–triethylamine system is especially noteworthy since the diffusivity actually decreases with increasing temperature as the upper consolute point (18 °C) is approached. Such behavior, which follows naturally from the assumption that chemical potential is the driving force, cannot be easily accounted for in terms of a strictly Fickian model.

Despite the compelling evidence provided by Haase and Siry's experiments, the contrary view has been expressed that diffusive transport is a stochastic process for which the true driving force must be the gradient of concentration [29]. This argument is based on the random walk model with the implicit assumption that molecular propagation is a purely random process that occurs with equal a-priori probability in any direction. In fact when the relationship between activity and concentration is nonlinear, the propagation probabilities in the presence of a chemical potential gradient are not the same in all directions. To reconcile the random walk argument with the implications of Eq. (1.31) requires only the additional assumption that the a-priori jump probability varies in proportion to the local gradient of chemical potential.

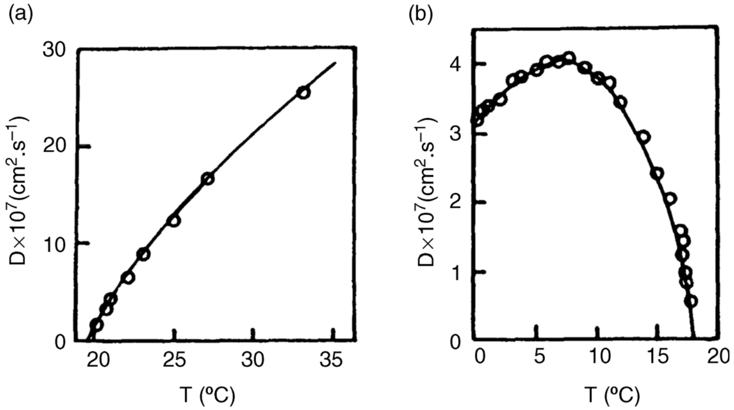


Figure 1.2 Variation of Fickian diffusivity with temperature for liquid mixtures of the critical composition, close to the consolute point: (a) *n*-hexane–nitrobenzene, mole fraction of nitrobenzene = 0.422, consolute temperature = 20 °C; (b) water–triethylamine, mole fraction triethylamine = 0.087, consolute temperature = 18 °C. Reprinted from Turner [28], with permission.

1.2.3
Relationship between Transport and Self-diffusivities

A first approximation to the relationship between the self- and transport diffusivities may be obtained by considering Eq. (1.26). In a mixture of two identical species, distinguishable only by their labeling (Figure 1.1b), the relation between p_A and c_A is clearly linear, and so the self-diffusivity is given simply by $\mathfrak{D} = RT/f$. The expression for transport diffusivity [Eq. (1.27)] may therefore be written in the form:

$$D = \mathfrak{D}\frac{\mathrm{d}\ln p}{\mathrm{d}\ln q} \tag{1.35}$$

implying the self-diffusivity can be equated with the corrected transport diffusivity ($\mathfrak{D} = D_0$). In conformity with this equation it has been shown experimentally that in a dilute binary liquid solution the mutual or transport diffusivity approaches the self-diffusivity of the solute [30, 31]. It has therefore been generally assumed that in an adsorption system the transport and self-diffusivities should coincide in the low concentration limit where the nonlinearity correction vanishes and encounters between diffusing molecules occur only infrequently. Satisfactory agreement between transport and self-diffusivities has indeed been demonstrated experimentally for several adsorption systems. However, the argument leading to Eq. (1.35) contains the hidden assumption that the "friction coefficient" is the same for both self-diffusion (where there is no concentration gradient) and for transport diffusion (where there is a concentration gradient). Such an assumption is only valid if the adsorbent can be regarded as an inert framework that is not affected in any significant way by the presence of the sorbate.

A series of informative examples of systems following Eq. (1.35) are given in Section 19.3.1. They include cases where the thermodynamic factor yields values both larger and smaller than 1, thus giving rise to self-diffusivities both smaller (the usual case for nanoporous host–guest systems) and larger than the transport diffusivities. Note in particular Figure 19.12, which illustrates the correlation of the thermodynamic factor with the shape of the adsorption isotherm.

1.3
Diffusional Resistances in Nanoporous Media

Nowadays materials with pore diameters in the range 1–100 nm (10–1000 Å) are commonly referred to as "nanoporous" but, according to the IUPAC classification [32], pores are classified in three different categories based on their diameter:

$$\text{micropores} \quad d < 20\,\text{Å}; \quad \text{mesopores} \quad 20\,\text{Å} < d < 500\,\text{Å}; \quad \text{macropores}\ 500\,\text{Å} < d$$

This division, although somewhat arbitrary, is based on the difference in the types of forces that control adsorption behavior in the different size ranges. In the micropore range, surface forces are dominant and an adsorbed molecule never escapes from the force field of the surface even when at the center of the pore. In mesopores, capillary forces become important, while the macropores actually contribute very little to the adsorption capacity, although of course they play an important role in the transport properties. This classification is appropriate where small gaseous sorbates are considered, but for larger molecules the micropore regime may be shifted to substantially large pore sizes.

1.3.1
Internal Diffusional Resistances

Different mechanisms of diffusion control the transport in different regions of porosity. Diffusion in micropores is dominated by interactions between the diffusing molecule and the pore wall. Steric effects are important and diffusion is an activated process, proceeding by a sequence of jumps between regions of relatively low potential energy (sites). Since the diffusing molecules never escape from the force field of the pore walls it is logical to consider the fluid within the pore as a single "adsorbed" phase. Diffusion within this regime is known variously as "configurational" diffusion, "intra-crystalline" diffusion, or simply "micropore" diffusion but these terms are essentially synonymous.

Within the macropore range the role of the surface is relatively minor. Diffusion occurs mainly by the bulk or molecular diffusion mechanism, since collisions between diffusing molecules occur more frequently than collisions between a diffusing molecule and the pore wall, although of course this depends on the pressure. Within the mesopore range Knudsen diffusion is generally more important but there may also be significant contributions from surface diffusion and capillarity effects. Chapter 4 gives a more detailed discussion.

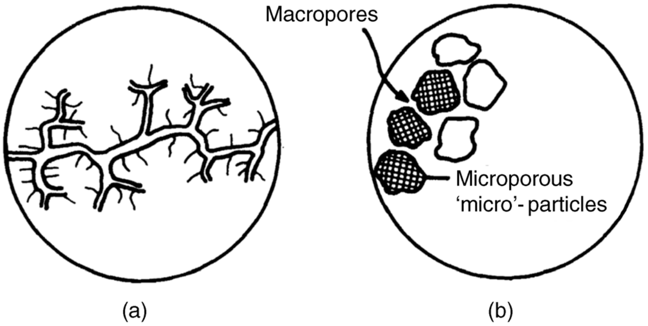


Figure 1.3 Two common types of microporous adsorbent: (a) homogeneous particle with a wide range of pore size distribution and (b) composite pellet formed from microporous microparticles giving rise to a well-defined bimodal distribution of pore size.

Uptake rate measurements with sufficiently large zeolite crystals can generally be interpreted according to a simple single (micropore) diffusion resistance model but with small commercial crystals the situation is not so straightforward. The assemblage of crystals in the measuring device can act like a macroporous adsorbent since the diffusion rate may be significantly affected, indeed controlled, by transport within the intercrystalline space. To interpret kinetic data in these circumstances it may be necessary to use a more complicated model including both "micropore" and "macropore" diffusional resistances.

The situation is even more complicated in commercial pelleted adsorbents. Two common types are shown schematically in Figure 1.3. In materials such as silica or alumina (Figure 1.3a) there is generally a wide distribution of pore size with no clear distinction between micropores and meso/macropores. In such adsorbents it is experimentally possible to measure only an average diffusivity and the relative contribution from pores of different size is difficult to assess. The situation is somewhat simpler in many zeolite and carbon molecular sieve adsorbents since these materials generally consist of small microporous particles (of zeolite or carbon sieve) aggregated together, often with the aid of a binder, to form a macroporous pellet of convenient size (Figure 1.3b). In such adsorbents there is a well-defined bimodal distribution of pore size so that the distinction between the micropores and the meso/macropores is clear.

Depending on the particular system and the conditions, either macropore or micropore diffusion resistances may control the transport behavior or both resistances may be significant. In the former case a simple single-resistance diffusion model is generally adequate to interpret the kinetic behavior but in the latter case a more complex dual resistance model that takes account of both micropore and macropore diffusion may be needed. Some of these more complex situations are discussed in Chapter 6. In any particular case the nature of the controlling regime may generally be established by varying experimental conditions such as the particle size.

1.3.2
Surface Resistance

Mass transfer through the surface of a zeolite crystal (or other nanoporous adsorbent particle) can be impeded by various mechanisms, including the collapse of the genuine pore structure close to the particle boundary and/or the deposition of strongly adsorbed species on the external surface of the particle. This may result in either total blockage of a fraction of the pore mouths or pore-mouth narrowing as well as the possibility that the surface may be covered by a layer of dramatically reduced permeability for the guest species under consideration. In all these cases the flux though the particle boundary can be represented by a surface rate coefficient (k_s) defined by:

$$J = k_s(q^* - q) \tag{1.36}$$

where $(q^* - q)$ represents the difference between the equilibrium concentration of the adsorbed phase and the actual boundary concentration within the particle. If the surface resistance is brought about by a homogeneous layer of thickness δ with dramatically reduced diffusivity D_s, the surface rate coefficient is easily seen to be given by $k_s = R_s D_s/\delta$, with R_s denoting the ratio of the guest solubilities in the surface layer and in the genuine particle pore space.

1.3.3
External Resistance to Mass Transfer

In addition to any surface resistance and the internal diffusional resistances discussed above, whenever there is more than one component present in the fluid phase, there is a possibility of external resistance to mass transfer. This arises because, regardless of the hydrodynamic conditions, the surface of an adsorbent or catalyst particle will always be surrounded by a laminar boundary layer through which transport can occur only by molecular diffusion. Whether or not the diffusional resistance of this external fluid "film" is significant depends on the thickness of the boundary layer, which in turn depends on the hydrodynamic conditions. In general, for porous particles, this external resistance to mass transfer is smaller than the internal pore diffusional resistance but it may still be large enough to have a significant effect.

External resistance is generally correlated in terms of a mass transfer coefficient (k_f), defined in the usual manner according to a linearized rate expression of similar form to that used to represent surface resistance [Eq. (1.36)]:

$$J = k_f(c - c_s^*) \tag{1.37}$$

in which c is the sorbate concentration in the (well-mixed) bulk phase and c^* is the fluid phase concentration that would be at equilibrium with the adsorbed phase concentration at the particle surface. The capacity of the fluid film is small compared with that of the adsorbent particle and so there is very little accumulation of sorbate within the film. This implies a constant flux and a linear concentration gradient through the film. The time required to approach the steady state profile in the film will be small so that, even in a transient situation, in which the adsorbed phase concentration changes with time, the profile through the film will be of the same form, although the slope will decrease as equilibrium is approached and the rate of mass transfer declines. This is shown schematically in Figure 1.4.

The concentration gradient through the film is given by $(c - c^*)/\delta$ where δ is the film thickness and, comparing Eqs. (1.1) and (1.36), it is evident that $k_f = D/\delta$. However, since δ is generally unknown and can be expected to vary with the hydrodynamic conditions, this formulation offers no real advantage over a direct correlation in terms of the mass transfer coefficient. It is mainly for this reason that external fluid film resistance is generally correlated in terms of a mass transfer coefficient while internal resistances are correlated in terms of a diffusivity. For an isolated spherical adsorbent particle in a stagnant fluid it may be easily shown (by analogy with heat conduction) that:

$$k_f \approx 2D/d; \quad \mathrm{Sh} = k_f d/D \approx 2 \tag{1.38}$$

Under flow conditions the Sherwood number (Sh) may be much greater than 2.0. The relevant dimensionless parameters that characterize the hydrodynamics are the

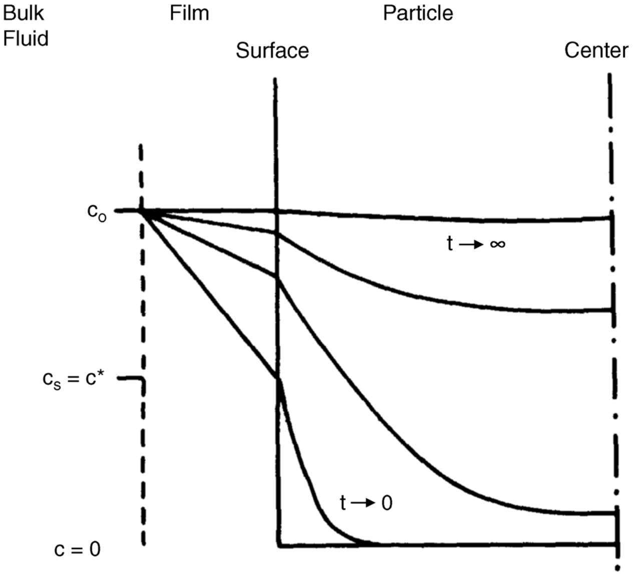


Figure 1.4 Schematic diagram showing the form of concentration profile for an initially sorbate-free particle exposed at time zero to a steady external fluid phase concentration or sorbate under conditions of combined external fluid film and internal diffusion control.

Schmidt number ($\mathrm{Sc} \equiv \eta/\varrho D$) and the Reynolds number ($\mathrm{Re} \equiv \varrho \varepsilon v d/\eta$). Correlations of the form:

$$\mathrm{Sh} = f(\mathrm{Re},\ \mathrm{Sc}) \tag{1.39}$$

have been presented for various well-defined fluid–solid contacting patterns. For example, for flow through a packed bed [33, 34]:

$$\mathrm{Sh} = 2.0 + 1.1\ \mathrm{Re}^{2/3}\mathrm{Sc}^{-0.3} \tag{1.40}$$

This correlation has been shown to be valid for both gases and liquids over a wide range of flow conditions.

1.4
Experimental Methods

There are three distinct but related aspects to the study of diffusion: the investigation of the elementary process at the molecular level, the study of tracer or self-diffusion, and the measurement of transport diffusion. The first two involve measurements under equilibrium conditions while the third type of study necessarily requires measurements under non-equilibrium conditions. A wide variety of different experimental techniques have been applied to all three classes of measurement; a short summary is given in Table 1.1, in which the various techniques are classified according to the scale of the measurement. Some of these methods are discussed in detail in Part Four (Chapters 10–14).

The study of the elementary steps of diffusion requires measurement of the movement of individual molecules and this can be accomplished only by spectroscopic methods. Nuclear magnetic resonance (NMR) and neutron scattering have been successfully applied. NMR phenomena are governed by the interaction of the magnetic dipole (or for nuclei with spin $I > \frac{1}{2}$, the electric quadrupole) moments of the nuclei with their surroundings. Information can therefore be obtained concerning the spatial arrangement of individual molecules and the rate at which the positions and orientations of the molecules are changing. In scattering experiments with neutrons, molecular motion may be traced over distances of a few Ångströms up to the nanometer range. Such distances are, however, short compared with the length scales required for the study of the overall diffusion process.

Diffusion in the strict sense can be studied only over distances substantially greater than the dimensions of the diffusing molecules. Such measurements fall into two broad classes: self-diffusion measurements that are made by following the movement of labeled molecules under equilibrium conditions and transport diffusion measurements that are made by measuring the flux of molecules under a known gradient of concentration. The “microscopic” equilibrium techniques (incoherent QENS and PFG NMR) measure self-diffusion directly by determining the mean square molecular displacement in a known time interval. The “macroscopic” techniques generally measure transport diffusion at the length scale of the individual

Table 1.1 Classification of experimental methods for measuring intracrystalline diffusion in nanoporous solids. After References [35, 36].

Non-equilibrium		Equilibrium
Transient	**Stationary**	
Macroscopic		
Sorption/desorption Frequency response (FR) Zero length column (ZLC) IR-FR Positron emission profiling (PEP) Temporal product analysis (TAP) IR spectroscopy	Membrane permeation Effectiveness factor in chemical reactions	Tracer sorption/desorption Tracer ZLC (zero length column)
Mesoscopic		
IR microscopy (IRM)	Single-crystal-permeation	Tracer IR microscopy
Microscopic		
Interference microscopy (IFM) IR micro-imaging (IRM)		Tracer IR micro-imaging Pulsed field gradient NMR (PFG NMR) Quasi-elastic neutron scattering (QENS)

crystal by following either adsorption/desorption kinetics, under transient conditions, or flow through a zeolite membrane, generally under steady-state conditions. Such techniques can be adapted to measure self-diffusion by using an isotopically labeled tracer. Single-crystal FTIR and single crystal permeance measurements can be regarded as intermediate (mesoscopic) techniques since measurements are made on an individual crystal. Recently, microscopic measurement of transport diffusion has also become possible. In coherent QENS, the relevant information is extracted from density fluctuations analogous to the situation in light scattering. In interference microscopy (IFM) this information is acquired by monitoring the evolution of intracrystalline concentration profiles.

In recent years it has become clear that the length scale at which intracrystalline diffusion measurements are made can be important since the effect of structural defects becomes increasingly important when the measurement scale spans many unit cells. As a result, the diffusivity values derived from macroscopic measurements may be much smaller than those from microscopic measurements which approximate more closely the behavior for an ideal zeolite crystal. Uniquely among the techniques considered, PFG NMR offers the possibility of varying the length scale from sub-micron to several microns (or even mm under favorable conditions), thus allowing a direct quantitative assessment of the impact of structural defects. NMR

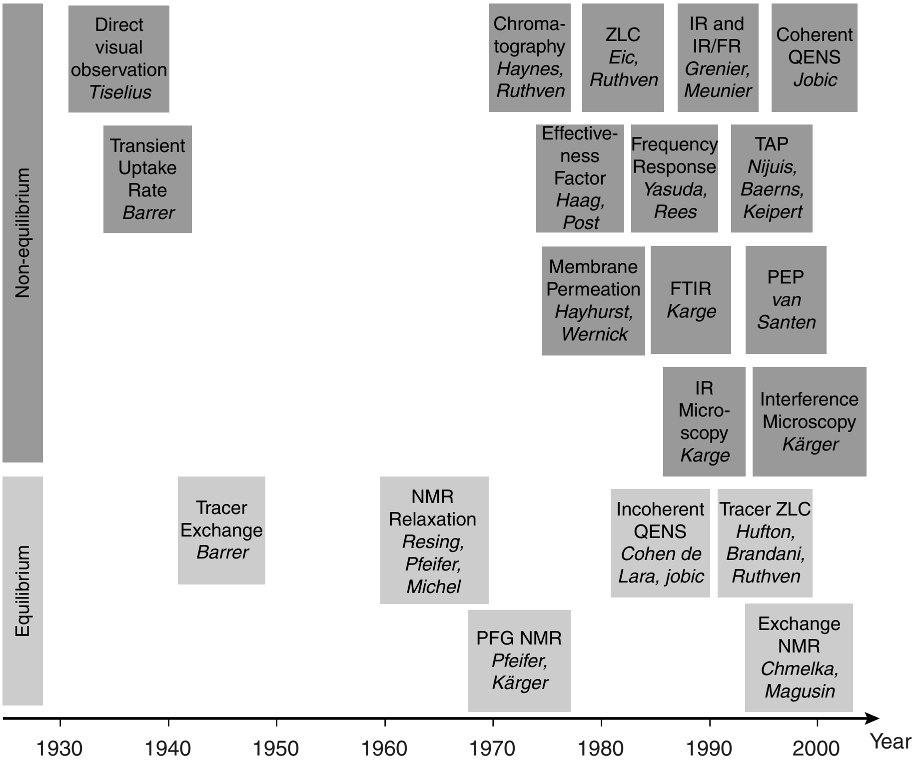


Figure 1.5 Measurement of zeolitic diffusion: historical development [37].

methods are also applicable to the measurement of long-range (intercrystalline or macropore) diffusion in an adsorbent particle. NMR labeling may also be applied to tracer diffusion measurements, thus providing essentially the same information that can be obtained from measurements with isotopically labeled molecules.

Figure 1.5 depicts the historical development of the study of intracrystalline diffusion and shows how the stimulus provided by the earliest PFG NMR measurements led to the introduction of a large spectrum of new experimental techniques.

With the impressive increase of computer power, over the last few decades molecular modeling and computer simulation have become powerful tools that complement the direct measurement of diffusion. The unique option to "play" with system parameters that, in reality, are invariable provides insights into the diffusion mechanisms that are often inaccessible from "real" experiments. With the widespread availability of very fast computers this approach, which is discussed in Part Three (Chapters 7–9), has become increasingly popular. In assessing results derived from molecular simulations it is, however, important not to lose sight of the limitations of this approach. Our knowledge of repulsive forces remains rudimentary and, for hindered diffusion, the impact of such forces is often dominant. As a result minor errors in the assumed force field can lead to very large errors in the predicted diffusivities, especially for diffusion in small pores. Direct experimental validation therefore remains critically important.

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