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Part A

Overview

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Chapter 1

Introduction to mass transport mechanisms

O world invisible, we view thee,
O world intangible, we touch thee,
O world unknowable, we know thee.
Francis Thompson, *The Kingdom of God*

The transport of matter within materials can occur either by diffusion or by convective flow. Diffusion can occur in both solids and fluids while convective flow is found only in fluids. This chapter provides a brief overview of these processes. It also offers a summary of the mechanisms involved, for diffusion in solids, liquids and gases. While these are presented in a highly simplified fashion they do offer sufficient insight to enable many mass transport problems of practical interest to be solved.

1.1 Mass transport processes

When a drop of dye is added to a beaker of still water the highly concentrated dye spreads throughout the liquid until a uniform pale colour results. There are two processes which can contribute to this. The first is called *diffusion*. This process is driven by differences in the concentration of a substance (in this case the molecules that make up the dye) from one region to another. Diffusion occurs until the concentration becomes uniform, *i.e.* the concentration gradient goes to zero everywhere. The same process happens in the solid state when two soluble substances are mixed together. In this case, however, the process is

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usually much slower and equilibrium may not be reached in sensible periods of time, especially at low temperatures.

A second process can also contribute to this mixing, at least in fluids (*i.e.* gases and liquids). This involves the bulk motion of the fluid, commonly called *convection*. Convection can carry concentrated packets of the dye into the far reaches of the beaker, thus enhancing the diffusion process. For example, you know intuitively that if you stir the water after adding the dye, the dye will mix much more quickly. Stirring, which induces convection in the liquid, forces regions of high and low dye concentration to mix together, thus reducing the concentration gradients.

1.2 Statement of Fick's First Law

While diffusion can occur in all three *states* (gases, liquids and solids), the mechanisms involved in each at the atomic or molecular scale are likely to be quite different. In a gas, for example, individual molecules are well separated and the rate of diffusion can be understood in terms of the kinetic theory of gases. At the other extreme, we now know that solid-state diffusion is due to the movement of point defects such as vacancies and interstitial atoms within crystalline solids. At the macroscopic scale however, the phenomenon of diffusion is similar whatever state of matter we consider. In fact, this phenomenon was well known and its kinetics could be predicted with reasonable accuracy long before the atomistic mechanisms were properly understood. We can therefore study the process of diffusion without considering these mechanisms in detail, and indeed for most of this book we will largely ignore them. This is not to say that understanding diffusion mechanisms is not important. There are a range of important phenomena which cannot be understood otherwise, and we will return to this important topic later on. But, for the most part, we will consider a range of engineering problems involving diffusion for which a phenomenological understanding of the diffusion process is sufficient.

What do I mean by a 'phenomenological' understanding? This is simply another way of saying that we will use empirical relationships which describe the 'phenomenon' of diffusion as the basis for solving problems. The fundamental relationship in this case is due to Adolf Fick and was first developed by him in 1855. Fick surmised, on the basis of experiment and intuition, that diffusion occurs in solids in response to a concentration gradient. The process was thought to be analogous to that of heat transfer which had been analyzed by Fourier some years previously. Suppose we consider a binary mixture of two materials, say B dissolved in A. Wherever a concentration gradient exists (as illustrated in Fig. 1.1) Fick suggested that diffusion should occur in order to reduce the gradient. This produces a 'flux', defined as the rate of flow per unit of

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cross-sectional area.[¶] Once the concentration gradient is removed then the flux should be zero. The simplest possible equation that relates a flux to the concentration gradient which drives it, and that meets these conditions, is

$$J_B = -D_B \frac{\partial C_B}{\partial y}. \tag{1.1}$$

Here, J_B is the flux of solute B in the A–B solution, while C_B is the concentration of this solute. The ∂ symbol represents a partial derivative. The equation is clearly written for a concentration gradient in one dimension only, along the y-axis (as illustrated in Fig. 1.1). The minus sign is required since the flux drives solute 'down' a concentration gradient. Finally, we have introduced a proportionality constant D_B which we call the 'diffusion coefficient'. This equation is generally referred to as *Fick's First Law*.

Of course we can always write an equation of this sort but it is not very useful unless D_B is independent of position y, or least approximately so. This really means that D_B should be independent of the solute concentration. As we will see, while this is not universally the case it is usually so to an adequate level of approximation, enabling many problems to be solved using this simple governing equation.

Before proceeding we should investigate the units of the various parameters in Fick's First Law. We generally use units of moles per unit volume (*e.g.* mol/m^3) for concentration, although concentration can also be represented in terms of mass per unit volume (*e.g.* kg/m^3). The flux has units of matter (either in moles or mass) per unit of cross-sectional area per unit time (*i.e.* mol/m^2 s or kg/m^2 s).

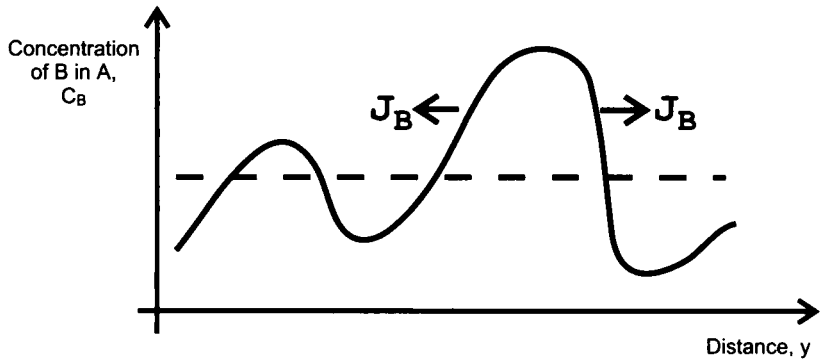


Figure 1.1 A schematic illustration of the diffusive response to a concentration gradient.

[¶] The rate of matter flow will depend on the width of the path through which diffusion occurs, *i.e.* for a given concentration gradient we expect twice as much flow if the piece has an area of 2 cm^2 than if it had an area of only 1 cm^2. (This is the same as saying that for cars travelling at 100 km/h and spaced 100 m apart the rate of cars passing a given point is twice as high on a four-lane road than on a two-lane road). By normalizing flow rates by the cross-sectional area of the path to define the 'flux' we remove this dependence from consideration.

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The units of the diffusion coefficient can then be deduced. They are, in SI units, given as m^2/s. You should note that whichever unit of concentration you choose (*i.e.* based on either mass or moles) the units of flux you use must be consistent.

1.3 Mechanisms of diffusion

While many diffusion problems can indeed be solved without a detailed understanding of the mechanisms involved, it is useful to develop some physical picture of the process involved at the outset. We will discuss this here only in general terms. We want merely to develop a conceptual picture of a solid, liquid or gas and the way in which atoms are able to move around within them.

In the *condensed* states (*i.e.* solids and liquids), diffusion is known to occur due to a random process in which atoms or molecules are able to exchange positions with neighbours due to random thermal fluctuations. Therefore diffusion belongs to a class of basic physical processes we refer to as *thermally activated processes*. Like all such processes the kinetics are temperature dependent, and obey an Arrhenius equation of the form

$$\text{rate} \sim \exp\left(-\frac{Q}{RT}\right), \tag{1.2}$$

where T is the absolute temperature and R is the universal gas constant (8.314 J/mol K). The parameter Q is the activation energy for the process, having units of energy per mole and is related to the thermal energy (or, to be more precise, the enthalpy) needed for an atom or molecule to overcome the barrier between one stable position and another. This equation leads to a substantial temperature dependence. For example, with an activation energy of 200 kJ/mol, typical for many diffusion processes in solids, the rate increases by almost a factor of 15 following a 100 deg K increase in temperature from 900 to 1000 K. Moreover, at room temperature a similar 100 deg K temperature increase would increase the rate by over nine orders of magnitude. Therefore, processes that proceed at a reasonable rate at high temperature do not seem to occur at all if we cool things down. Examples of this are readily seen around us. Consider a plate-glass window. This has the same structure at 800 °C and room temperature. However at the high temperature it flows readily and can be easily shaped. At room temperature it holds its shape without any visible change for years. This is because the viscous flow of a glass is a thermally activated process.

Example 1.1: Effect of temperature on diffusion in liquids

In a typical liquid the activation energy for diffusion is 10 kJ/mol. Estimate by how much the diffusion coefficient is increased on raising the temperature from T_1 to T_2, say 20 to 120 °C.

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According to eq. (1.2) we can write the ratio of diffusion rates at the two temperatures as

$$\frac{\text{rate}_{T_2}}{\text{rate}_{T_1}} = \exp\left[\frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right].$$

By substitution into this equation we find that the ratio is

$$\frac{\text{rate}_{T_2}}{\text{rate}_{T_1}} = \exp\left[\frac{10{,}000}{8.314}\left(\frac{1}{293} - \frac{1}{393}\right)\right]$$

which is equal to 2.84. In other words the small activation energy found in liquids leads to a much weaker temperature dependence than that for solid-state diffusion.

1.4 Diffusion in solids

In crystalline solids diffusion occurs by the movement of *point defects*. There are several different types of point defects, but we will be primarily interested in just two – vacancies and interstitial atoms. A vacancy is simply an unoccupied lattice site, as shown in Fig. 1.2.

These defects are created by thermal fluctuations within a lattice and any crystal has an equilibrium vacancy concentration X_v^o which increases with temperature according to an Arrhenius relationship of the form

$$X_v^o = \exp\left(-\frac{\Delta G_v^f}{kT}\right), \tag{1.3}$$

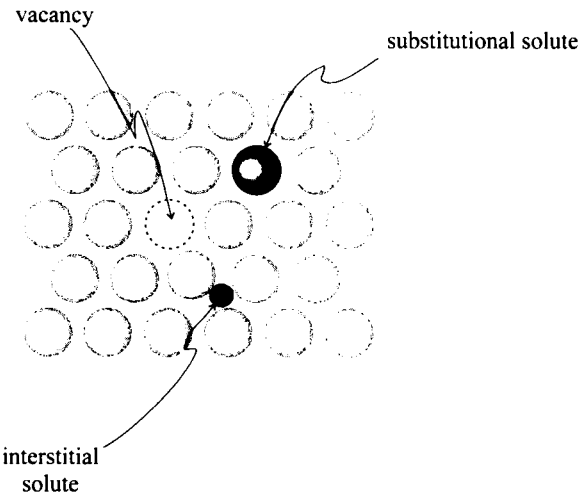


Figure 1.2 A schematic illustration of a vacant site in a crystalline solid, called a 'vacancy', and solute atoms located at both interstitial and substitutional sites.

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where ΔG_v^f is the free energy of formation of a vacancy, and k is Boltzmann's constant.• These vacant lattice sites play a major role in diffusion, as we will see.

Example 1.2: Vacancy concentration in a typical metal

The free energy of vacancy formation in aluminum is 0.76 eV per vacancy. Estimate the vacancy concentration in this material just below the melting temperature (660 °C).

Free energies for atomic processes are often listed in units of electron volts (eV). The conversion to SI units is: 1 eV per atom = 96.5 kJ/mol. Therefore the free energy of vacancy formation is 73.3 kJ/mol. We now substitute this into eq. (1.3) to find the equilibrium vacancy concentration at 660 °C = 933 K. The answer is 7.9×10^{-5}. This is a typical value for a metal near its melting point, *i.e.* $X_v^o \approx 10^{-4}$.

Foreign or solute atoms can enter a crystal either by occupying the same lattice sites as the host atom (in which case we refer to the site as 'substitutional') or else they can occupy sites between those occupied by the host atoms (in which case we refer to the site as 'interstitial'). Both cases are illustrated in Fig. 1.2.

1.4.1 Interstitial diffusion

We start with the diffusion of interstitial atoms since this is the simplest to understand. Solute atoms which are much smaller than the host enter the lattice interstitially (see Fig. 1.2). The solubility of such atoms is, however, usually rather limited. Therefore almost all interstitial atoms are well-separated from one another. From a diffusional viewpoint this means that all of the neighbouring interstitial sites around a particular solute atom are usually vacant. These sites are therefore available for the solute atom to jump to. However, in order for an atom to jump to one of these sites from its current position it must squeeze through the narrow channel that separates stable sites. This requires thermal energy, also referred to as vibrational energy. The change of free energy of an atom with position is illustrated schematically in Fig. 1.3. The activation barrier, which an atom (or ion) must overcome to move from one stable position to another, has a height ΔG_i^m, where the subscript and superscript refer to 'interstitial' and 'migration' respectively. Whether a given interstitial atom has sufficient vibrational energy to overcome this barrier is determined by Boltzmann statistics which describe how the thermal energy of a large assemblage of atoms is distributed. While the average energy of the atoms is proportional to kT, at any given instant some atoms

• Note that the universal gas constant R, and Boltzmann's constant k, are related by Avogadro's number N_0, such that $R = k \cdot N_0$. We can use these interchangeably in an Arrhenius relationship, providing that we adjust the activation energy, *i.e.* with k the energy per atom is required while with R the energy per mole is used.

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will have higher than average energy while others have less. The probability that any given atom has an excess thermal energy greater than ΔG_i^m is given by

$$p = \exp\left(-\frac{\Delta G_i^m}{kT}\right). \tag{1.4}$$

Because of the exponential dependence, this probability increases steeply with temperature, which explains why the rates of diffusion-controlled processes are highly temperature sensitive. Atoms vibrate back and forth within each site with a characteristic frequency ν. This is known as the Debye frequency and, from the theory of harmonic oscillators, it can be shown to be proportional to (atomic mass)$^{-1/2}$, and of order $10^{12}\,s^{-1}$. The frequency Γ, with which an interstitial atom jumps from its current position to an adjacent site, is just the product of the vibration frequency ν and the probability of making a successful jump p. Thus

$$\Gamma = \nu p \tag{1.5}$$

Now in order to relate this to the process of diffusion we need to think about how these atomic jumps, multiplied many times over, affect an initially non-uniform distribution of solute atoms. Let us consider a simple one-dimensional problem as illustrated in Fig. 1.4. Two adjacent lattice planes are separated by a distance a, the lattice spacing. We will call these two planes 1 and 2. There are n_1 solute atoms in plane 1 and n_2 in plane 2. Atoms in plane 1 can jump either right or left. We will assume that they do so with equal likelihood. Therefore they have a jump frequency $\frac{1}{2}\Gamma$ in each direction. Thus the number of solute atoms jumping from plane 1 to plane 2 in a time interval δt is $\frac{1}{2}\Gamma \cdot n_1 \cdot \delta t$, while the number of solute atoms jumping from plane 2 to plane 1 in a time interval δt is $\frac{1}{2}\Gamma \cdot n_2 \cdot \delta t$. The difference between these two

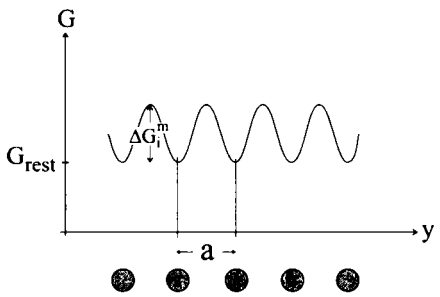


Figure 1.3 When small atoms enter a crystal, they occupy positions between the lattice atoms, called interstitial sites. The free energy of an atom depends on its position. The points of lowest energy are the equilibrium, or rest, positions with energy G_{rest}. In order to move between these positions, atoms must overcome an energy barrier. For interstitial atoms, this barrier has height ΔG_i^m.

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values produces a net flow of solute. If we divide the net flow by the cross-sectional area of the plane A and by the time interval δt, this becomes a net flux

$$J = \frac{1}{2}\frac{\Gamma}{A}(n_1 - n_2).$$

The concentration C of solute within each plane is given by $n/(Aa)$. Therefore the flux can be written as

$$J = \tfrac{1}{2}\Gamma a(C_1 - C_2). \tag{1.6}$$

We now want to convert the difference in the concentration of solute atoms in each plane to a concentration gradient

$$J = -\tfrac{1}{2}\Gamma a^2 \frac{\partial C}{\partial y}.$$

This is, of course, just Fick's First Law with the diffusion coefficient now given by $D = \frac{1}{2}\Gamma \cdot a^2$. Note that this equation does not depend on the mechanism by which diffusion occurs. It is therefore a general result. We have therefore shown that the empirical equation first developed by Fick also has a sound basis in theory.

It is important to recognize that this model treats diffusion as a purely random process. The individual atoms have no sense of the concentration gradient, *i.e.* they do not feel any force driving them towards regions of lower concentration.

Before proceeding we should generalize this result to three dimensions. This is done simply by replacing the $\frac{1}{2}$ term by a more general geometric parameter g, which represents the larger range of possible directions in which an atom can jump. Generally, $g \approx 1/6$. Thus

$$J = -g\Gamma a^2 \frac{\partial C}{\partial y}. \tag{1.7}$$

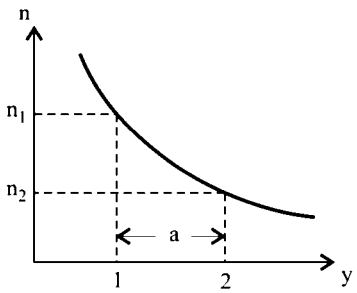


Figure 1.4 A schematic illustration of a concentration profile. The difference in jump rate from plane 1 to plane 2, as compared with the rate from plane 2 to plane 1, results in a net flux.

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The mechanism by which diffusion occurs affects the result through the jump frequency term. For the interstitial case we substitute eqs. (1.4) and (1.5) into eq. (1.7). Therefore the interstitial diffusion coefficient is given by

$$D_i = g\Gamma_i \cdot a^2 = g\nu a^2 \exp\left(-\frac{\Delta G_i^m}{kT}\right) \tag{1.8}$$

where the subscript 'i' is used throughout to indicate that these terms refer specifically to the interstitial mechanism of diffusion. We can determine the temperature dependence of the diffusion coefficient more precisely by separating the free energy into two terms for the enthalpy and entropy, such that $\Delta G_i^m = \Delta H_i^m - T \cdot \Delta S_i^m$. By substituting this into eq. (1.8) we get

$$D_i = g\nu a^2 \exp\left(\frac{\Delta S_i^m}{k}\right) \exp\left(-\frac{\Delta H_i^m}{kT}\right) = D_{0i} \exp\left(-\frac{Q_i}{kT}\right). \tag{1.9}$$

Here all of the temperature-independent terms are combined into a single parameter D_{0i}, while the enthalpy has been rewritten as an activation energy Q_i. These two parameters are all that is required to characterize the diffusion coefficient and they are found tabulated in many compilations of diffusion data, such as that given in Appendix B.

1.4.2 Vacancy diffusion

When large atoms• enter a lattice they do so 'substitutionally', *i.e.* they use the same lattice positions as the host atoms. It is difficult for these solute atoms, and for the host atoms themselves, to diffuse through the lattice. In a perfect lattice, with every site occupied by a host or substitutional atom, there would be no sites to which atoms could jump. However as we have already discussed, each lattice contains a certain fraction of vacant sites, *i.e.* vacancies. Whenever an atom is sitting next to a vacancy it can move into that unoccupied site. Otherwise it is immobilized. We therefore have to take this into account in calculating the jump frequency of host atoms and substitutional solutes. We will start by considering the diffusion of vacancies themselves.

The concentration of vacancies in crystalline solids varies considerably with temperature. However, vacancies are always present in dilute concentrations. (For example, as we noted in Example 1.2, the vacancy concentration in a face-centred-cubic metal at its melting point is about 10^{-4} and decreases rapidly as the temperature drops). Therefore, vacancies are inevitably surrounded by occupied lattice sites. Just as interstitial atoms must overcome an activation barrier in order to jump between adjacent sites, so must vacancies. Thus the probability that a vacancy has sufficient energy ΔG_v^m to move

• In this case 'large' means atoms whose radii are comparable with or larger than that of the host atoms.

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