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PART II

Diffusion Coefficients
CHAPTER 5

Values of Diffusion Coefficients

Until now, we have treated the diffusion coefficient as a proportionality constant, the unknown parameter appearing in Fick's law. We have found mass fluxes and concentration profiles in a broad spectrum of situations using this law. Our answers have always contained the diffusion coefficient as an adjustable parameter.

Now we want to calculate values of the flux and the concentration profile. For this, we need to know the diffusion coefficients in these particular situations. We must depend largely on experimental measurements of these coefficients, because no universal theory permits their accurate a-priori calculation. Unfortunately, the experimental measurements are unusually difficult to make, and the quality of the results is variable. Accordingly, we must be able to evaluate how good these measurements are.

Before we begin, we should list the guidelines that tend to stick in everyone's mind. Diffusion coefficients in gases, which can be estimated theoretically, are about 0.1 cm²/sec. Diffusion coefficients in liquids, which cannot be as reliably estimated, cluster around 10⁻⁵ cm²/sec. Diffusion coefficients in solids are slower still, 10⁻¹⁰ cm²/sec, and they vary strongly with temperature. Diffusion coefficients in polymers and glasses lie between liquid and solid values, say about 10⁻⁸ cm²/sec, and these values can be strong functions of solute concentration.

The accuracy and origins of these guidelines are explored in this chapter. Gases, liquids, solids, and polymers are discussed in Sections 5.1 through 5.4, respectively. In these sections we give a selection of typical values, as well as one common method of estimating these values. After we sketch the sources of these estimations, we explore other concerns, like the pressure dependence of diffusion in gases or the concentration variations of diffusion in liquids. Section 5.5 summarizes Brownian motion, showing how random walks are related to diffusion. Section 5.6 discusses the common experimental methods of measuring diffusion coefficients.

5.1 Diffusion Coefficients in Gases

Diffusion coefficients in gases are illustrated by the values in Table 5.1. At one atmosphere and near room temperature, these values lie between 0.1 and 1 cm²/sec. Indeed, given the variation of the chemistry, the values vary remarkably little. To a first approximation, the coefficients are inversely proportional to pressure, so doubling the pressure cuts the diffusion coefficient in half. They vary with the 1.5 to 1.8 power of the temperature, so an increase of 300 K triples the coefficients. They vary in a more complicated fashion with factors like molecular weight.

The physical significance of diffusion coefficients of this size is best illustrated by remembering unsteady-state diffusion problems like the semi-infinite slab discussed in Chapter 2. In these problems, the key experimental variable is \( z^2/4Dt \). When this variable
<table>
<thead>
<tr>
<th>Gas pair</th>
<th>Temperature (K)</th>
<th>Diffusion coefficient (cm$^2$/sec)</th>
</tr>
</thead>
<tbody>
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<td>298.2</td>
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</tbody>
</table>

(Continued)
equals unity, the diffusion process has proceeded significantly. In other words, where \( z^2 = 4D t \), the diffusion has penetrated a distance \( z \) in the time \( t \).

In gases, this penetration distance is much larger than in other phases. For example, the diffusion coefficient of water vapor diffusing in air is about 0.3 cm\(^2\)/sec. In 1 second, the diffusion will penetrate 0.5 cm; in 1 minute, 4 cm; and in 1 hour, 30 cm.

### 5.1.1 Gaseous Diffusion Coefficients From the Chapman-Enskog Theory

The most common method for theoretical estimation of gaseous diffusion is that developed independently by Chapman and by Enskog (Chapman and Cowling, 1970). This theory, accurate to an average of about eight percent, leads to the equation

\[
D = \frac{1.86 \cdot 10^{-3} T^{3/2}(1/\hat{M}_1 + 1/\hat{M}_2)^{1/2}}{\rho \sigma_{12}^2 \Omega}
\] (5.1-1)

in which \( D \) is the diffusion coefficient measured in cm\(^2\)/sec, \( T \) is the absolute temperature in Kelvin, \( \rho \) is the pressure in atmospheres, and the \( \hat{M}_i \) are the molecular weights.
The quantities $\sigma_{12}$ and $\Omega$ are molecular properties characteristic of the detailed theory. The collision diameter $\sigma_{12}$, given in angstroms, is the arithmetic average of the two species present:

$$\sigma_{12} = \frac{1}{2} (\sigma_1 + \sigma_2)$$  \hspace{1cm} (5.1-2)

Values of $\sigma_1$ and $\sigma_2$ are listed in Table 5.1-2. The dimensionless quantity $\Omega$ is more complex, but usually of order one. Its detailed calculation depends on an integration of the interaction between the two species. This interaction is most frequently described by the Lennard–Jones 12-6 potential. The resulting integral varies with the temperature and the energy of interaction. This energy $\varepsilon_{12}$ is a geometric average of contributions from the two species:

$$\varepsilon_{12} = \sqrt{\varepsilon_{1} \varepsilon_{2}}$$  \hspace{1cm} (5.1-3)

Values of the $\varepsilon_{12}/k_B$ are also given in Table 5.1-2. Once $\varepsilon_{12}$ is known, $\Omega$ can be found as a function of $k_B T/\varepsilon_{12}$ using the values in Table 5.1-3. The calculation of the diffusion coefficients now becomes straightforward if the $\sigma_i$ and the $\varepsilon_i$ are known.

### 5.1.2 The Nature of Kinetic Theories

The results of the Chapman–Enskog theory are based on detailed analyses of molecular motion in dilute gases. These analyses depend on the assumption that molecular interactions involve collisions between only two molecules at a time (Fig. 5.1-1). Such interactions are much simpler than the lattice interactions in solids or the less regular and still more complex interactions in liquids.

The nature of theories of this type is best illustrated for a gas of rigid spheres of very small molecular dimensions (Cunningham and Williams, 1980). For such a theory, the diffusion flux has the following form:

$$n_1 = -\frac{1}{3} \bar{v} \frac{dc_1}{dz} + c_1 v^0$$  \hspace{1cm} (5.1-4)

The second term on the right represents convection and the first indicates diffusion. The diffusion term has three parts: $\bar{v}$, the average molecular velocity; $l$, the mean free path of the molecules; and $dc_1/dz$, the concentration gradient. This term makes physical sense: the flux will certainly increase if either the velocity of the molecules or the average distance they travel increases.

If we compare Eq. 5.1-4 with Fick's law, we find

$$D = \frac{1}{3} \bar{v} l$$  \hspace{1cm} (5.1-5)

Both the average velocity $\bar{v}$ and the mean free path $l$ of the rigid spheres can be calculated. The average velocity is

$$\bar{v} = \sqrt{\frac{2 k_B T}{m}}$$  \hspace{1cm} (5.1-6)
5.1 / Diffusion Coefficients in Gases

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \sigma(\text{Å}) )</th>
<th>( \epsilon_{12}/k_B(\text{K}) )</th>
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*Note: Data from Hirschfelder et al. (1954).*
Table 5.1-3 *The collision integral* $\Omega$

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<th>$k_B T/e_{12}$</th>
<th>$\Omega$</th>
<th>$k_B T/e_{12}$</th>
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Source: Data from Hirschfelder et al. (1954).

in which $m$ is the molecular mass. The mean free path $l$ is

$$l = \frac{k_B T}{p \left( \frac{4}{3} \sigma^2 \right)} \quad (5.1-7)$$

in which $\sigma$ is the diameter of the spheres, and $p/k_B T$ is the concentration of molecules per volume. Combining, we find

![Molecular motion in a dilute gas.](image)

**Fig. 5.1-1.** Molecular motion in a dilute gas. In a gas, molecular collisions occur at low density, and so may be treated as bimolecular. This simplicity facilitates development of good kinetic theories for diffusion.

$$D = \left( \frac{4\sqrt{2}}{3\pi} \right) \frac{(k_B T)^{3/2}}{m^{1/2} p \sigma^2} \quad (5.1-8)$$

When we compare this result with Eq. 5.1-1, we see that the rigid-sphere theory predicts essentially the same dependence on temperature, pressure, molecular weight, and molecular size. The Chapman–Enskog theory is an improvement over the simple theory because the details of the collisions are explicitly included.
5.1.3 Gaseous Diffusion Coefficients From Empirical Correlations

Predictions from the Chapman–Enskog kinetic theory tend to be limited in two ways. First, the theory requires estimates of $\sigma_{12}$ and $\epsilon_{12}$; such estimates are not available for all gases. Second, the theory assumes nonpolar gases, and this excludes compounds like water and ammonia. These interactions depend on replacing the Lennard–Jones potential used to characterize the collision with more exact potentials. Such replacement is often complex.

Instead, many authors have developed empirical relations. One effective example (Fuller, Schettler, and Giddings, 1966) is

$$D = 10^{-3} \frac{T^{4.75} (1/\dot{M}_1 + 1/\dot{M}_2)^{1/2}}{p \left[ (\sum_i V_{i1})^{1/3} + (\sum_i V_{i2})^{1/3} \right]^2}$$  \hspace{1cm} (5.1-9)

in which $T$ is in Kelvin, $p$ is in atmospheres, and the $V_{ij}$ are the volumes of parts of the molecule $j$, tabulated in Table 5.1-4. This correlation is about as successful as Eq. 5.1-1. To me, the impressive feature is the similarity between the two equations: the pressure and molecular-weight dependence are unchanged. The temperature dependence is not much different when we remember that $\Omega$ is a function of temperature. The term for diffusion volumes here parallels the term in $\sigma^2$. It is not surprising that the two equations have similar success.

5.1.4 Gas Diffusion at High Pressure

The equations given earlier in this chapter allow prediction of diffusion coefficients in dilute gases to within an average of eight percent. These predictions, which are about twice as accurate as those for liquids, are often hailed as a final answer. However,

<table>
<thead>
<tr>
<th>Atomic and structural diffusion-volume increments $V_{ij}$</th>
<th>Diffusion volumes for simple molecules $\Sigma V_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H$_2$</td>
</tr>
<tr>
<td>H</td>
<td>He</td>
</tr>
<tr>
<td>O</td>
<td>N$_2$</td>
</tr>
<tr>
<td>(N)</td>
<td>O$_2$</td>
</tr>
<tr>
<td>(Cl)</td>
<td>Air</td>
</tr>
<tr>
<td>(S)</td>
<td>Ar</td>
</tr>
<tr>
<td>Aromatic ring</td>
<td>Kr</td>
</tr>
<tr>
<td>Heterocyclic ring</td>
<td>CO</td>
</tr>
<tr>
<td></td>
<td>CO$_2$</td>
</tr>
<tr>
<td></td>
<td>N$_2$O</td>
</tr>
<tr>
<td></td>
<td>NH$_3$</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
</tr>
<tr>
<td></td>
<td>(Cl)$_2$</td>
</tr>
<tr>
<td></td>
<td>(SO$_2$)</td>
</tr>
</tbody>
</table>

*Note: Parentheses indicate that the value is uncertain.*

*Source: Adapted from Fuller, Schettler, and Giddings (1966).*
I have the nagging suspicion that their success is promulgated by those who have worked hard on these methods or who have become intimidated by the intellectual edifice erected by Maxwell, Enskog, and others. In fact, although these equations agree with experiment at low pressures, they are much less successful at high pressures. At higher pressures, few binary data are available; for self-diffusion, a sensible empirical suggestion is

\[ pD = p_0 D_0 \]  

(5.1-10)

in which the subscript 0 indicates values at low pressure at the same temperature. The inverse relation between diffusion and pressure, consistent with Eq. 5.1-1, is a good guideline.

Some more elaborate theories have attempted to correlate the product \( pD \) with the reduced pressure and temperature, that is, with the pressure and temperature relative to values at the critical point. Such a correlation, implicitly based on the theory of corresponding states, can be applied to transport phenomena by assuming that thermodynamic variables can be defined in nonequilibrium situations. We will make such an assumption in the irreversible thermodynamics arguments in Section 7.2. In the current case, however, this effort at correlation suggests significant corrections only when the reduced temperature is less than 1.4. Under these circumstances, Fick’s law breaks down because diffusion occurs not as single solute molecules but as a cluster of solute molecules, as described in Section 6.3. In the face of this complexity, I would use Equation 5.1-10 with confidence when the temperature divided by the critical temperature is above 1.4 and make experiments at lower temperatures.

Some other aspects of gaseous diffusion remain unexplored. For example, diffusion of molecules of very different sizes, like hydrogen and high molecular weight \( n \)-alkanes, has not been sufficiently studied. Concentration-dependent diffusion in gases, although a common phenomenon, has been largely ignored. These aspects deserve careful inspection.

---

**Example 5.1-1: Estimating diffusion with the Chapman–Enskog theory**  
Calculate the diffusion coefficient of argon in hydrogen at 1 atmosphere and 175 °C. The experimental value is 1.76 cm²/sec.

**Solution**  
We first need to find \( \sigma_{12} \) and \( \varepsilon_{12} \). From the values in Table 5.1-2,

\[
\sigma_{12} = \frac{1}{2} (\sigma_1 + \sigma_2) \\
= \frac{1}{2} (3.54 + 2.83) = 3.18 \text{Å}
\]

and

\[
\frac{\varepsilon_{12}}{k_B T} = \sqrt{\left(\varepsilon_1/k_B\right)\left(\varepsilon_2/k_B\right)/T} \\
= \sqrt{124(38.0)/448} = 0.166
\]
From Table 5.1-3, we find that $\Omega$ is 0.81. Thus, from Eq. 5.1-1,

$$D = \frac{1.86 \cdot 10^{-3} T^{3/2}(1/N_1 + 1/N_2)^{1/2}}{p \sigma_{12}^2 \Omega}$$

$$= \frac{1.86 \cdot 10^{-3} (448)^{3/2}(1/39.9 + 1/2.02)^{1/2}}{(1)(3.18)^2(0.81)} = 1.55 \text{ cm}^2/\text{sec}$$

The theoretical prediction is about ten percent below the experimental observation.

---

**Example 5.1-2: Comparing two estimates of gas diffusion** Use the Chapman–Enskog theory and the empirical correlation in Equation 5.1-9 to estimate the diffusion of hydrogen in nitrogen at 21 °C and 2 atmospheres. The experimental value is 0.38 cm$^2$/sec.

**Solution** For the Chapman–Enskog theory, the key parameters are

$$\sigma_{12} = \frac{1}{2} (\sigma_{H_2} + \sigma_{N_2}) = \frac{1}{2} (2.92 + 3.68) = 3.30 \text{ Å}$$

and

$$\frac{\epsilon_{12}}{k_B T} = \frac{\sqrt{\epsilon_{H_2}/k_B} (\epsilon_{N_2}/k_B)}{T} = \frac{\sqrt{38.0}(91.5)}{294} = 0.201$$

This second value allows interpolation from Table 5.1-3:

$$\Omega = 0.842$$

Combining these results with Eq. 5.1-1 gives

$$D = \frac{1.86 \cdot 10^{-3} T^{3/2}(1/N_{H_2} + 1/N_{N_2})^{1/2}}{p \sigma_{12}^2 \Omega}$$

$$= \frac{1.86 \cdot 10^{-3} (294)^{3/2}(1/2.02 + 1/28.0)^{1/2}}{(2)(3.30)^2(0.842)} = 0.37 \text{ cm}^2/\text{sec}$$

The value is about three percent low, a very solid estimate.

For the Fuller correlation, the appropriate volumes are found from Table 5.1-4. The results can then be combined with Eq. 5.1-9:

$$D = \frac{10^{-3} T^{1.75}(1/N_{H_2} + 1/N_{N_2})^{1/2}}{p \left[ (V_{H_2})^{1/3} + (V_{N_2})^{1/3} \right]^2}$$

$$= \frac{10^{-3} (294)^{1.75}(1/2.02 + 1/28.0)^{1/2}}{2 \left[ (7.07)^{1/3} + (17.9)^{1/3} \right]^2} = 0.37 \text{ cm}^2/\text{sec}$$

Again, the error is about three percent.
Example 5.1-3: Diffusion in supercritical carbon dioxide  Carbon dioxide, above its critical point, may become an important industrial solvent because it is cheap, nontoxic, and nonexplosive. Estimate the diffusion of iodine in carbon dioxide at 0°C and 33 atmospheres. The diffusion coefficient measured under these conditions is $7 \cdot 10^{-4}$ cm$^2$/sec.

Solution  The binary diffusion coefficient at 0°C and 1 atmosphere can be found from Eq. 5.1-1:

$$D_0 = 0.043 \text{ cm}^2/\text{sec}$$

From Eq. 5.1-10,

$$D = 0.43 \text{ cm}^2/\text{sec} \left( \frac{1 \text{ atm}}{33 \text{ atm}} \right)$$

$$= 13 \cdot 10^{-4} \text{ cm}^2/\text{sec}$$

This is as accurate as we have any right to expect, especially because the critical point for carbon dioxide is close, at 30°C and 72 atmospheres.

5.2 Diffusion Coefficients in Liquids

Diffusion coefficients in liquids are exemplified by the values given in Tables 5.2-1 and 5.2-2. Most of these values fall close to $10^{-5}$ cm$^2$/sec. This is true for common organic solvents, mercury, and even molten iron. Exceptions occur for high molecular-weight solutes like albumin and polystyrene, where diffusion can be 100 times slower. Actually, the range of these values is remarkably small. At 25°C, almost none are faster than $10 \cdot 10^{-5}$ cm$^2$/sec, and those significantly below $10^{-5}$ cm$^2$/sec are macromolecules, like hemoglobin. The reasons for this narrow range is that the viscosity of simple liquids like water and hexane varies little, and that diffusion coefficients are only a weak function of solute size.

Diffusion coefficients in liquids are about ten thousand times slower than those in dilute gases. To see what this means, we again calculate the penetration distance $\sqrt{4Dt}$, which was the distance we found central to unsteady diffusion. As an example, consider benzene diffusing into cyclohexane with a diffusion coefficient of about $2 \cdot 10^{-5}$ cm$^2$/sec. At time zero, we bring the benzene and cyclohexane into contact. After 1 second, the diffusion has penetrated 0.004 cm, compared with 0.3 cm for gases; after 1 minute, the penetration is 0.03 cm, compared with 4 cm; after 1 hour, it is 0.3 cm, compared with 30 cm.

The sloth characteristic liquid diffusion means that diffusion often limits the overall rate of processes occurring in liquids. In chemistry, diffusion limits the rate of acid–base reactions; in physiology, diffusion limits the rate of digestion; in metallurgy, diffusion can control the rate of surface corrosion; in the chemical industry, diffusion is responsible for the rates of liquid–liquid extractions. Diffusion in liquids is important because it is slow.

5.2.1 Liquid Diffusion Coefficients From the Stokes–Einstein Equation

The most common basis for estimating diffusion coefficients in liquids is the Stokes–Einstein equation. Coefficients calculated from this equation are accurate to
Table 5.2-1  Diffusion coefficients at infinite dilution in water at 25°C

<table>
<thead>
<tr>
<th>Solute</th>
<th>$D (10^{-5} \text{ cm}^2/\text{sec})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>1.21</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.16</td>
</tr>
<tr>
<td>Ammonia</td>
<td>1.64</td>
</tr>
<tr>
<td>Argon</td>
<td>2.00</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.02</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>1.00</td>
</tr>
<tr>
<td>Bromine</td>
<td>1.18</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>1.92</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>2.03</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1.25</td>
</tr>
<tr>
<td>Ethane</td>
<td>1.20</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.84</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1.87</td>
</tr>
<tr>
<td>Glycine</td>
<td>1.06</td>
</tr>
<tr>
<td>Helium</td>
<td>6.28</td>
</tr>
<tr>
<td>Hemoglobin</td>
<td>0.069</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.50</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>1.41</td>
</tr>
<tr>
<td>Methane</td>
<td>1.49</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.84</td>
</tr>
<tr>
<td>$n$-Butanol</td>
<td>0.77</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.88</td>
</tr>
<tr>
<td>Oxygen</td>
<td>2.10</td>
</tr>
<tr>
<td>Ovalbumin</td>
<td>0.078</td>
</tr>
<tr>
<td>Propane</td>
<td>0.97</td>
</tr>
<tr>
<td>Sucrose</td>
<td>$(0.5228 - 0.265c_1)^a$</td>
</tr>
<tr>
<td>Urea</td>
<td>$(1.380 - 0.0782c_1 + 0.00464c_1^2)^a$</td>
</tr>
<tr>
<td>Urease</td>
<td>0.035</td>
</tr>
<tr>
<td>Valine</td>
<td>0.83</td>
</tr>
</tbody>
</table>

*Note: Known to very high accuracy, and so often used for calibration; $c_1$ is in moles per liter. Source: Data from Cussler (1976) and Poling et al. (2001).*

only about twenty percent (Poling et al., 2001). Nonetheless, this equation remains the standard against which alternative correlations are judged.

The Stokes–Einstein equation is

$$D = \frac{k_B T}{f} = \frac{k_B T}{6\pi\eta R_0}$$  \hspace{1cm} (5.2-1)

where $f$ is the friction coefficient of the solute, $k_B$ is Boltzmann’s constant, $\eta$ is the solvent viscosity, and $R_0$ is the solute radius. The temperature variation suggested by this equation is apparently correct, but it is much smaller than effects of solvent viscosity and solute radius. A discussion of these larger effects follows.

The diffusion coefficient varies inversely with viscosity when the ratio of solute to solvent radius exceeds five. This behavior is reassuring because the Stokes–Einstein equation is derived by assuming a rigid solute sphere diffusing in a continuum of solvent. Thus, for a large solute in a small solvent, Eq. 5.2-1 seems correct.
For an oblate ellipsoid with \(a \ll b\), it is
\[
D_{\text{rot}} = \frac{3}{32\eta b^5} k_B T
\]  
(5.2-6)

These results are sometimes used to infer the shape of proteins in solution.

### 5.2.2 Deriving the Stokes–Einstein Equation

To predict diffusion in liquids, we do not account for molecular motion as in the theories used for gases. Instead, we idealize our system as a single rigid solute sphere moving slowly through a continuum of solvent (Fig. 5.2-1). We expect that the net velocity of this sphere will be proportional to the force acting on it:

\[
\text{force} = f v_1
\]  
(5.2-4)

where \(f\) is defined as the friction coefficient. Because the sphere moves slowly, this friction coefficient can be found from Stokes' law (first published in 1850) to be \(6\pi\mu R_0\). The force was taken by Einstein to be the negative of the chemical potential gradient (Einstein, 1905). Thus Eq. 5.2-4 can be rewritten:

\[
- \nabla \mu_1 = (6\pi\mu R_0) v_1
\]  
(5.2-5)

The chemical potential gradient, defined per molecule (not per mole), is often described as a “virtual force,” a thermodynamic parallel to mechanical or electrostatic forces.

When the solution is dilute, we can assume that it is ideal:

\[
\mu_1 = \mu_1^0 + k_B T \ln x_1 = \mu_1^0 + k_B T \ln \frac{c_1}{c_1 + c_2} = \mu_1^0 + k_B T \ln c_1 - k_B T \ln c_2
\]  
(5.2-6)

In this result, we recognize that solvent concentration \(c_2\) far exceeds solute concentration \(c_1\), so \(c_2\) is approximately constant. The gradient is then

\[
\nabla \mu_1 = \frac{k_B T}{c_1} \nabla c_1
\]  
(5.2-7)

Combining this with Eq. 5.2-5, we find

\[
\hat{j}_1 = \hat{n}_1 = c_1 v_1 = -\frac{k_B T}{6\pi\mu R_0} c_1
\]  
(5.2-8)

Comparison with Fick’s law produces the Stokes–Einstein equation, Eq. 5.2-1.

The interesting assumption in this analysis is the way in which the velocity or flux is assumed to vary with the chemical potential gradient. This type of assumption is made frequently in studies of diffusion. It is central to the development of irreversible thermodynamics, and so it is at the core of the theories of multicomponent diffusion described in Chapter 7. Interestingly, it is known experimentally to be wrong in the highly nonideal solutions near critical points (see Section 6.3).
5.2 / Diffusion Coefficients in Liquids

(a) Actual situation

(b) Stokes–Einstein model

Fig. 5.2-1. Molecular motion in a liquid. In contrast with a gas, molecular motion in a liquid takes place at high density (a). Diffusion is complex, involving many interactions and vacancies. The available kinetic theories are good, but complex. To avoid this, many use the simple model of a solute sphere in a solvent continuum (b).

Because the Stokes–Einstein equation is limited to cases in which the solute is larger than the solvent, many investigators have developed correlations for cases in which solute and solvent are similar in size. The impressive aspect of these efforts is their similarity to the Stokes–Einstein equation. Almost all show the same temperature and viscosity dependence. All authors claim marginally better accuracy, but for such increased complexity that their results are rarely used. The exception is the Wilke–Chang correlation (1955), which predicts

\[
D = \frac{7.4 \cdot 10^{-8} \left( \phi M_2 \right)^{1/2}}{\mu V_1^{0.6}} T
\]

where \( D \) is the diffusion coefficient of solute “1,” in \( \text{cm}^2/\text{sec} \); \( M_2 \) is the molecular weight of solvent “2,” in daltons; \( T \) is the temperature, in K; \( \mu \) is the viscosity, in centipoises; and \( V_1 \) is the molar volume of the solute, in \( \text{cm}^3/\text{mol} \). The empirical parameter \( \phi \) is 1 for most organic solvents, 1.5 for alcohols, and 2.6 for water. This result is widely used for fast estimates.

At this point, the common conclusion is to bemoan the accuracy of the predictions in liquids and to praise the accuracy of those in gases. In fact, the predictions in liquids are only twice as inaccurate as those in gases, even though the complexity of solute–solvent interactions in liquids is much greater. As a result, I do not share the frequent despair about these estimates, but feel that care and good judgment can lead to success.

5.2.3 Diffusion in Concentrated Solutions

The Stokes–Einstein equation and its empirical extensions are limited to infinitely dilute solutions. In fact, the diffusion coefficient in liquids varies with solute concentration, frequently by several hundred percent and sometimes with a maximum
and minimum. We need a means of estimating these variations. Such estimations usually involve two steps. First, we assume that Eq. 5.2-4 can be written

\[-v_t = \frac{1}{f} \nabla \mu_t = \frac{D_0}{RT} \nabla \mu_t\]  

(5.2-10)

where \(D_0\) is a new transport coefficient. For a nonideal solution,

\[\mu_t = \mu_t^0 + k_B T \ln c_1 \gamma_t\]  

(5.2-11)

where \(\gamma_t\) is an activity coefficient. Combining these two equations, we find

\[n_t \hat{=} j_t \hat{=} c_1 v_t = -\left[ D_0 \left( 1 + \frac{\partial\ln \gamma_t}{\partial \ln c_1} \right) \right] \nabla c_t\]  

(5.2-12)

The quantity in brackets is the diffusion coefficient. This first step is a restatement of the idea that the velocity of diffusion varies with the gradient of chemical potential.

The second step consists of empirical estimates of the quantity \(D_0\). These estimates are based on diffusion coefficients in dilute solutions. One of the most frequently cited estimates, used by Darken (1948), Hartley and Crank (1949), and others, is the arithmetic average:

\[D_0 = x_1 D_0(x_1 = 1) + x_2 D_0(x_2 = 1)\]  

(5.2-13)

Another estimate, suggested by Vignes (1966) is the geometric average:

\[D_0 = \left[D_0(x_1 = 1)\right]^x_1 \left[D_0(x_2 = 1)\right]^{x_2}\]  

(5.2-14)

The geometric average seems more successful than the arithmetic one.

I am not convinced that these efforts to correct diffusion coefficients with activity coefficients are correct. I agree that some form of correction is indicated, and I admit that much of the correction must be empirical. However, I have found that the corrections suggested by Eq. 5.2-12 are usually too big. For example, if \(D\) drops with increasing concentration \(c_t\), then the \(D_0\) inferred from this equation tends to rise with increasing \(c_t\). In the same sense, if \(D\) rises with increasing \(c_t\), then \(D_0\) drops over the same concentration range. Moreover, these corrections are wrong near the spinodal phase boundary, as detailed in Section 6.3. Thus I always treat these corrections with caution.

**Example 5.2-1: Oxygen diffusion in water** Estimate the diffusion at 25°C for oxygen dissolved in water using the Stokes–Einstein equation and the Wilke–Chang correlation. Compare your results with the experimental value of \(1.8 \cdot 10^{-5} \text{ cm}^2/\text{sec}\).

**Solution** For the Stokes–Einstein equation, the chief problem is to estimate the radius of the oxygen molecule. If we assume that this is half the collision diameter in the gas, then from Table 5.1-2,

\[R_0 = \frac{1}{2} \sigma_t = 1.73 \cdot 10^{-8} \text{ cm}\]

When we insert this into the Stokes–Einstein equation,

\[D = \frac{k_B T}{6\pi \mu R_0} = \frac{(1.38 \cdot 10^{-16} \text{ g cm}^2/\text{sec}^2 \text{ K})298 \text{ K}}{6\pi(0.01 \text{ g/cm sec})1.73 \cdot 10^{-8} \text{ cm}} = 1.3 \cdot 10^{-5} \text{ cm}^2/\text{sec}\]
This value is thirty percent low. Replacing \(6\pi\) with \(4\pi\) gives a more accurate result; replacing \(6\pi\) with \(2\) gives too high a value. The Wilke–Chang correlation is somewhat better:

\[
D = \frac{7.4 \cdot 10^{-8} (\phi \tilde{M}_{\text{H}_2\text{O}})^{1/2} T}{\mu_{\text{H}_2\text{O}} V_{\text{O}_2}^{0.6}} = \frac{7.4 \cdot 10^{-8} \left[ \frac{2.6 \left( 18 \text{ cm}^3/\text{mol} \right)}{1 \text{ cp} \left( 25 \text{ cm}^3/\text{mol} \right)^{0.6}} \right]^{1/2}}{298 \text{ K}} = 2.2 \cdot 10^{-5} \text{ cm}^2/\text{sec}
\]

This is twenty percent high.

**Example 5.2-2: Estimating molecular size from diffusion**  Fibrinogen has a diffusion coefficient of about \(2.0 \cdot 10^{-7} \text{ cm}^2/\text{sec}\) at \(37^\circ\text{C}\). It is believed to be rod-shaped, about thirty times longer than it is wide. How large is the molecule?

**Solution**  Because the molecule is rod-shaped, it can be approximated as a prolate ellipsoid. Thus, from Eq. 5.2-2,

\[
D = \frac{k_B T}{6\pi \mu a} \left[ \frac{[1 - (b/a)^2]^{1/2}}{\ln \left( \frac{a}{b} + \left( \frac{a^2}{b^2} - 1 \right)^{1/2} \right)} \right]
\]

\[
2.0 \cdot 10^{-7} \text{ cm}^2/\text{sec} = \frac{(1.38 \cdot 10^{-16} \text{ g cm}^2/\text{sec}^2 \text{ K})(310 \text{ K})}{6\pi(0.00695 \text{ g/cm sec})a \left[ \frac{[1 - (1/30)^2]^{1/2}}{\ln[30 + (30^3 - 1)^{1/2}]} \right]}
\]

Solving, we find that \(a\) equals 67 nm and \(b\) equals 2.2 nm. If fibrinogen were a sphere, its radius would be about 16 nm.

**Example 5.2-3: Diffusion in an acetone–water mixture**  Estimate the diffusion coefficient in a 50-mole\% mixture of acetone (1) and water (2). This solution is highly nonideal, so that \(\partial \ln \gamma_1/\partial \ln c_1\) equals \(-0.69\). In pure acetone, the diffusion coefficient is \(1.26 \cdot 10^{-5} \text{ cm}^2/\text{sec}\); in pure water, it is \(4.68 \cdot 10^{-5} \text{ cm}^2/\text{sec}\). The experimental value in the mixture is \(0.79 \cdot 10^{-5} \text{ cm}^2/\text{sec}\), less than both limits.

**Solution**  We first must estimate \(D_0\). Because Eq. 5.2-14 is most often successful, we use it here:

\[
D_0 = \left[ D_0(x_1 = 1) \right]^{x_1} \left[ D_0(x_2 = 1) \right]^{x_2} = (1.26 \cdot 10^{-5} \text{ cm}^2/\text{sec})^{0.5} (4.86 \cdot 10^{-5} \text{ cm}^2/\text{sec})^{0.5} = 2.43 \cdot 10^{-5} \text{ cm}^2/\text{sec}
\]
From Eq. 5.2-13,

\[ D = D_0 \left( 1 + \frac{\partial \ln \gamma_i}{\partial \ln c_1} \right) \]

\[ = 2.43 \cdot 10^{-5} \text{ cm}^2/\text{sec} (1 - 0.69) \]

\[ = 0.75 \cdot 10^{-5} \text{ cm}^2/\text{sec} \]

The agreement with the experimental value is unusually good.

### 5.3 Diffusion in Solids

Diffusion in solids is beyond the scope of this book. However, I want to give the briefest synopsis to provide a comparison with gases and liquids. Diffusion in solids is described by the same form of Fick's law as gases or liquids. The diffusion coefficients, however, are much, much smaller, as shown by the values in Table 5.3-1. These values do increase quickly with temperature. The exception is hydrogen. In metals, diatomic hydrogen first dissociates to form atomic hydrogen, which then loses its electron to the electron cloud within the metals. Thus in this case, "hydrogen diffusion" refers to the motion of naked protons, whose small size gives them an unusually large mobility.

The small value for diffusion coefficients in solids has two important consequences. First, the values are so small that almost all significant transport occurs through flaws and gaps in the solid, especially along grain boundaries. This is especially true for metals and crystals. Second, transport in solids almost always approaches the limit of a semi-infinite solid, rather than diffusion across a thin film. Again, hydrogen is the exception because it is so fast. For example, diffusion of hydrogen across thin membranes of palladium is sometimes suggested as a route to purify hydrogen.

The estimation of diffusion coefficients in solids is not accurate. In almost every case, one must use experimental results. Methods for rough estimates based on the theory for face-centered-cubic (FCC) metals are the standard by which other theories are judged.

| Table 5.3-1 Diffusion coefficients at 25°C in some characteristic solids |
|-----------------------------|----|----------------|
| Solid                      | Solute | \( D \) (cm\(^2\)/sec) |
| Iron (\( \alpha \) Fe; BCC) | Fe    | \( 3 \cdot 10^{-48} \) |
|                            | C     | \( 6 \cdot 10^{-21} \) |
|                            | \( \text{H}_2 \) | \( 2 \cdot 10^{-9} \) |
| Iron (\( \alpha \) Fe; FCC) | Fe    | \( 8 \cdot 10^{-55} \) |
|                            | C     | \( 3 \cdot 10^{-31} \) |
| Copper                     | Cu    | \( 8 \cdot 10^{-42} \) |
|                            | Zn    | \( 2 \cdot 10^{-38} \) |
| \( \text{SiO}_2 \)         | \( \text{H}_2 \) | \( 6 \cdot 10^{-13} \) |
|                            | He    | \( 4 \cdot 10^{-10} \) |

*Note: In most cases, these values are extrapolated from values at higher temperatures.*
just as the Stokes–Einstein equation is the standard for liquids. The diffusion coefficient in this case is

$$D = R_0^2 N \omega$$  \hspace{1cm} (5.3-1)

in which \(R_0\) is the spacing between atoms; \(N\) is the fraction of sites vacant in the crystal; and \(\omega\) is the jump frequency, the number of jumps per time from one position to the next. Values for \(R_0\) are guessed from crystallographic data, and the fraction \(N\) is commonly estimated from the Gibbs free energy of mixing. The frequency \(\omega\) is estimated by reaction-rate theories for the concentration of activated complexes, atoms midway between adjacent sites. The results of these estimations are commonly expressed as

$$D = D_0 e^{-\Delta H/RT}$$  \hspace{1cm} (5.3-2)

where \(D_0\) and \(\Delta H\) are estimated empirically. Values of \(\Delta H\) are large, often above 100 kJ/mol, so that diffusion increases much more with temperature than for gases or for liquids.

**Example 5.3-1: Diffusion of carbon in iron**  
Experiments show that the diffusion of carbon in body-centered cubic (BCC) iron is \(2.4 \cdot 10^{-8} \text{ cm}^2/\text{sec}\) at \(500^\circ\text{C}\), but \(1.7 \cdot 10^{-6} \text{ cm}^2/\text{sec}\) at \(900^\circ\text{C}\). Find an equation which allows estimating carbon diffusion at other temperatures.

**Solution**  
The form of this relation is that of Equation 5.3-2

$$D = D_0 e^{-\Delta H/RT}$$

Inserting the values for \(D\) and \(T\), we find

$$D = \left[6.2 \cdot 10^{-3} \text{ cm}^2/\text{sec}\right] e^{-\left(80 \text{ kJ/mol}\right)/RT}$$

The values for \(D_0\) and for \(\Delta H\) are slightly smaller than those commonly observed.

### 5.4 Diffusion in Polymers

Diffusion coefficients in high polymers are closer to those for liquids than to those for solids. This is true even for crystalline polymers, where the coefficients reflect transport around, not through, the small crystals. Typical values for synthetic high polymers are shown in Fig. 5.4-1. The values of these coefficients vary strongly with concentration. Naturally occurring polymers like proteins are not included in Fig. 5.4-1 because these species are best handled with the dilute-solution arguments in Section 5.2.

The results in Fig. 5.4-1 show that very different limits exist. The first of these limits occurs in dilute solution, where a polymer molecule is imagined as a solute sphere moving through a continuum of solvent. The second limit is in highly concentrated solution, where small solvent molecules squeeze through gaps in the polymer matrix.
The third, not illustrated in Fig. 5.4-1, involves mixtures of two polymers. Each limit is discussed briefly below.

### 5.4.1 Polymer Solutes in Dilute Solution

A polymer molecule dissolved in a low-molecular-weight solvent is imagined as a necklace of spherical beads connected by a string that has no resistance to flow. The necklace is floating in a neutrally buoyant solvent continuum. If the solution is very dilute, the polymer molecules are greatly separated, so that they do not interact with each other, but only with the solvent. In some cases, the solvent will expand the polymer necklace in the solution; such a solvent is referred to as “good.” In other cases the solvent and polymer will not strongly interact, and the polymer necklace will shrink into a small, introspective blob; such a solvent is called “poor.”

Between these two extremes, the polymer and solvent can interact just enough so that the segments of the polymer necklace will be randomly distributed. This limit of a “random coil” of polymer is conventionally chosen as the “ideal” polymer solution, and a solvent showing these characteristics is called a \( \theta \) solvent. Under these conditions, the diffusion of the polymer can be calculated as a correction to the Stokes–Einstein equation:

\[
D = \frac{k_B T}{6 \pi \mu R_e}
\]  

(5.4-1)
where \( R_e \) is the equivalent radius of the polymer. This radius is calculated to be

\[
R_e = 0.676 (R^2)^{1/2}
\]

(5.4-2)

in which \((R^2)^{1/2}\) is the root-mean-square radius of gyration, the common measure of the size of the polymer molecule in solution. This root-mean-square radius can be measured in a variety of ways; one common method is by light scattering. Equations 5.4-1 and 5.4-2 are confirmed by experiment. The measured ratio of equivalent radius to root-mean-square radius is 0.68, which is very close to the 0.676 suggested theoretically.

In good solvents and poor solvents, the diffusion coefficient still is estimated from the Stokes–Einstein equation, but the relation between the equivalent radius \( R_e \) and the root-mean-square radius \((R^2)^{1/2}\) seems less well known. Moreover, in good solvents, the diffusion coefficient can increase sharply with polymer concentration. This increase, which occurs in the face of rapidly increasing viscosity, is apparently the result of a highly nonideal solution. The increase is often estimated using parallels to Eq. 5.2-12. The accuracy of these estimates is uncertain.

### 5.4.2 Low Molecular Weight Solutes in a Polymer Solvent

The second limiting case of polymer diffusion occurs when a small dilute solute diffuses in a concentrated polymer solvent. Some examples are given on the right-hand side of Fig. 5.4-1. In addition to its scientific interest, this case has considerable practical value. It is important in devolatilization, that is, the removal of solvent and unreacted monomer from commercial polymers. This is especially important for polymers with consumer applications like food wrapping, because the volatile species may not be benign. Diffusion in this second case is also central to drying many solvent-based coatings. There, rapid solvent evaporation from the surface of the coating can produce a concentrated polymer skin. Slower diffusion through this skin then limits the coating's drying.

This case of diffusion in polymers is described by ideas drawn from both diffusion in liquids and diffusion in solids. The theoretical development takes place in two steps. First, the binary diffusion coefficient \( D \) is corrected for the nonideal solution

\[
D = D_0 \left( 1 + \frac{\partial \ln \gamma_1}{\partial \ln \phi_1} \right)
\]

(5.4-3)

where \( D_0 \) is a new, "improved" coefficient; \(\gamma_1\) is the activity coefficient of the small solute; and \(\phi_1\) is its volume fraction, the appropriate concentration variable to describe concentrations in a polymer solution. We should remember that the activity correction in parentheses has not often been critically examined. As stated above, it is often an over-correction when it is used to describe diffusion in conventional liquids.

We now turn to predicting the corrected coefficient \(D_0\). We expect that this coefficient must include consideration of the solute's activation energy, which must be sufficient to overcome any attractive forces that constrain it near neighbouring polymer segments. We expect that this coefficient must vary with any space or "free volume" between the polymer chains. Only a fraction of this free volume will be accessible to the solute as a result of thermal fluctuations; it is this fraction which permits the diffusion.
While the details of these free-volume arguments are beyond the scope of this book, we can appreciate the arguments involved by looking at the form of the final prediction

$$D_0 = D_0 e^{E_e / RT} \exp\left[-\frac{(\omega_1 V_{10} + \omega_2 V_{20})}{(\omega_1 K_1 + \omega_2 K_2)}\right]$$

(5.4-4)

where $D_0$ is a constant preexponential factor, $E_e$ is the solute–polymer attractive energy, and the second exponential is the effect of free volume. More specifically, the $\omega_i$ are mass fractions, the $V_i$ are specific critical free volumes, and the $K_i$ are additional free volume parameters. These last parameters are strong functions of temperature. Equation 5.4-4 is successful in correlating experimental data, especially above the polymer's glass transition temperature.

One curious effect, called “non-Fickian diffusion” or “type II transport,” sometimes occurs in the dissolution of high polymers by a good solvent. In these cases, diffusion may not follow Fick's law. For example, the speed with which the solvent penetrates into a thick polymer slab may not be proportional to the square root of time, which is the behavior expected from Fick's law (see Section 2.3).

This effect is believed to result from configurational changes in the polymer. As the solvent penetrates, the polymer molecules relax from their greatly hindered configuration as a partially crystalline solid into the more randomly coiled shape characteristic of a polymer dissolved in dilute solution. When this relaxation process is slower than the diffusion process, the dissolution is controlled by the relaxation kinetics, not by Fick's law. Although the process does not involve any phase boundaries, it is similar to a slow interfacial chemical reaction followed by fast diffusion. Again, it is common only in the case of fast dissolution in good solvent.

**5.4.3 A Polymer Solute in a Polymer Solvent**

In the third limiting case of polymer diffusion, both the solute and the solvent are polymers. This case has practical importance in adhesion, in material failure, and in polymer fabrication. In the simplest terms, this case includes why glue sticks.

Efforts to explain this case of polymer diffusion begin with a model, developed by Rouse, which represents the polymer chain as a linear series of beads connected by springs. The diffusion coefficient derived from this model is

$$D(\text{Rouse}) = \frac{k_B T}{N \zeta}$$

(5.4-5)

where $N$ is the degree of polymerization and $\zeta$ is a friction coefficient characteristic of the interaction of a bead with its surroundings. Because $N$ is proportional to the molecular weight, this Rouse diffusion coefficient is proportional to the inverse of the polymer's molecular weight. In contrast, if the polymer were an untangled random coil, $D$ would depend on the inverse square root of the molecular weight; if the polymer really condensed into one small sphere, $D$ would vary with $M^{-1/3}$. The Rouse prediction is not verified experimentally except for polymers of low molecular weight. We need a better model.
The better model, called reptation, imagines the polymer chain confined within a curved tube (deGennes, 1979). Within this tube, the Rouse model governs the chain dynamics, but the polymer diffusion is governed by the time required to escape from the tube. Because motion in the tube is one-dimensional, this escape time $\tau$ is given by

$$L^2 = 2D(\text{Rouse})\tau$$  \hspace{1cm} (5.4-6)

where $L$ is the tube length, proportional to the polymer’s molecular weight. The macromolecular diffusion coefficient $D$, in the three dimensions, can be found from

$$\langle R^2 \rangle = 6D\tau$$  \hspace{1cm} (5.4-7)

where $\langle R^2 \rangle$ is again the root-mean-square radius of gyration, proportional to the square root of the molecular weight. Combining Eqs. 5.4-5 to 5.4-7, we find

$$D = \left( \frac{k_BT}{3\sqrt{\zeta}} \right) \frac{\langle R^2 \rangle}{NL^2} \propto \hat{M}^{-2}$$  \hspace{1cm} (5.4-8)

This result frequently comes close to predicting the molecular weight dependence of this case of polymer–polymer diffusion.

5.5 Brownian Motion

The diffusion coefficients listed above are easy to accept as experimentally valuable parameters, but they are harder to understand as a consequence of molecular motion. These coefficients are most often experimental values. In some cases, they are estimated from theories which imply models for the system involved. For gases, this is the model of gas molecules colliding in space. For liquids, they most often imply a solute sphere in a solvent soup. For solids, these estimates are based on a crystal lattice. In every case, the diffusion coefficients are not very directly related to random molecular motions.

In this short section, we want to reexamine these coefficients in terms of molecular motions. Such random “Brownian” motions were first observed in pollen grains by Robert Brown in June of 1827. He concluded that these motions “arose neither from currents in the fluid nor from gradual evaporation but from the particles [themselves].” In our terms, diffusion comes from random molecular motions. Such random motions are now widely studied, not only in physical science but in areas like fluctuations of exchange rates of currencies.

In this section, we describe these random motions in terms of probability theory, and so connect diffusion to this broader topic. Because we want a simple, easily understood connection, we consider only the simplest case of one-dimensional motion. This simplest case depends on three rules:

1. Each particle moves either to the right or the left every $\tau$ seconds with a velocity $v$.
2. The probability of moving right and that of moving left is 0.5. Moreover, the particles do not remember their earlier steps.
3. Each particle moves independently of the others. This is again our old friend, the assumption of dilute solution.

The rules may be relaxed in many ways, but we are interested here only in this simplest limit.

These three rules have two consequences. First, the average position of a particle does not change. To demonstrate this, we consider a system of \( N \) independent particles. We then consider \( z_i(n) \), the position of the \( i \)th particle after \( n \) steps. This particle must have arrived from a position either \( \delta \) larger or \( \delta \) smaller, i.e.,

\[
z_i(n) = z_i(n - 1) \pm \delta
\]  
(5.5-1)

Because these steps are random, the mean displacement of these particles after \( n \) steps is thus

\[
\langle z(n) \rangle = \frac{1}{N} \sum_{i=1}^{N} z(n) \\
= \frac{1}{N} \sum_{i=1}^{N} [z(n - 1) \pm \delta] \\
= \frac{1}{N} \sum_{i=1}^{N} [z(n - 1)] \\
= \langle z(n - 1) \rangle
\]  
(5.5-2)

The average position of the particles doesn’t move. For example, if all the particles start at zero, their average position stays at zero.

The second consequence of the three rules given above is the estimation of how much the particles spread out. This can be described as the root mean square of the particle position \( \langle z^2(n) \rangle^{1/2} \). To find this quantity, we note from Equation 5.5-1 that

\[
z_i^2(n) = z_i^2(n - 1) \pm 2\delta z_i(n - 1) + \delta^2
\]  
(5.5-3)

As before, we average this over all the \( N \) particles to find

\[
\langle z^2(n) \rangle = \frac{1}{N} \sum_{i=1}^{N} z_i^2(n) \\
= \langle z^2(n - 1) \rangle + \delta^2
\]  
(5.5-4)

Now imagine we have zero steps, so

\[
\langle z^2(0) \rangle = 0
\]  
(5.5-5)

For one step

\[
\langle z^2(1) \rangle = \delta^2
\]  
(5.5-6)

For two steps,

\[
\langle z^2(2) \rangle = \langle z^2(1) \rangle + \delta^2 \\
= 2\delta^2
\]  
(5.5-7)
For $n$ steps

$$\langle z^2(n) \rangle = n\delta^2$$  \hspace{1cm} (5.5-8)

As we allow more and more steps, the particle spread becomes more and more.

We want to connect this result with the diffusion coefficients used elsewhere in this book. To do so, we return to the example of the one-dimensional decay of a pulse, given in Equation 2.4-14 as

$$c_1 = \frac{M/A}{\sqrt{4\pi Dt}} e^{-z^2/4Dt}$$  \hspace{1cm} (5.5-9)

For such a pulse, the standard deviation $\sigma$ is defined as

$$\sigma^2 = 2Dt$$  \hspace{1cm} (5.5-10)

But this standard deviation is exactly the same as the mean square of the particle position $\langle z^2(n) \rangle$. Moreover, the time $t$ for the peak to spread is just $\langle n\tau \rangle$. Thus

$$\langle z^2(n) \rangle = \left(\frac{1}{\tau}\right)\sigma^2 = 2Dt$$  \hspace{1cm} (5.5-11)

and

$$D = \frac{\langle z^2(n) \rangle}{2\tau}$$  \hspace{1cm} (5.5-12)

The diffusion coefficient is the mean square particle displacement divided by twice the time for movement $\tau$. Another way to write this result recognizes that the mean square distance per time is just the size of a step $\delta$ times the time-averaged velocity $\bar{v}$:

$$D = \frac{\langle z^2(n) \rangle}{2\tau} = \frac{\delta\bar{v}}{2}$$  \hspace{1cm} (5.5-13)

This form is sometimes easier to apply than the previous equation. Like that previous equation, it is written for one-dimensional diffusion.

These results can be extended in many ways. If the result for one dimension is extended to diffusion in two dimensions

$$D = \frac{\langle z^2(n) \rangle}{4\tau}$$  \hspace{1cm} (5.5-14)

For three dimensions, the result is

$$D = \frac{\langle z^2(n) \rangle}{6\tau}$$  \hspace{1cm} (5.5-15)

More importantly, the small steps need not be by molecular diffusion but may also be from turbulent velocity fluctuations. In that case, the diffusion coefficient will be replaced by the dispersion coefficient as defined in Chapter 4. Alternatively, we can consider random motions under some sort of external force so that the probability of moving in one direction is different than that for movement in the opposite direction.
While in these cases, this type of calculation will give only rough estimates, the calculation is so easy that it may still be very useful.

**Example 5.5-1: Self-diffusion in water** Estimate the diffusion at 25°C of a trace of tritium-labeled water in regular water. Water molecules are about 0.26 nm in diameter, separated by 0.30 nm.

**Solution** The distance of a step will be $0.30 - 0.26 = 0.04$ nm.

The velocity is given by

$$
\frac{1}{2} m v^2 = k_B T
$$

$$
\frac{1}{2} \left( \frac{20 \text{g}}{6 \cdot 10^{33}} \right) v^2 = \left( 1.38 \cdot 10^{-16} \frac{\text{g cm}^2}{\text{sec K}} \right) 298 K
$$

$$
v = 5 \cdot 10^4 \text{ cm/sec}
$$

Thus from Eqs. 5.5-13 and 5.5-15

$$
D = \frac{0.04 \cdot 10^{-7} \text{ cm} \left( 5 \cdot 10^4 \text{ cm/sec} \right)}{6}
$$

$$
= 3 \cdot 10^{-5} \text{ cm}^2/\text{sec}
$$

This is close to the experimentally observed value.

**Example 5.5-2: Random walks in a flake-filled film** We are studying random motions in a composite of aligned impermeable flakes like those shown in Figure 5.5-1(a). When random motions like these are averaged over many trajectories, we get the mean square displacement as a function of the total distance traveled, as shown in Figure 5.5-1(b). If the distance occurs in steps of a unit distance per second, what diffusion coefficient is inferred from these data?

**Solution** The key to this calculation is $\sigma^2$, the slope of the data in Figure 5.5-1(b), which is 0.014. The mean square displacement $\sigma^2$ varies linearly with the distance traveled, which in this case is numerically equal to the time in seconds. For example, from Equation 5.5-10, we get,

$$
D = \frac{\sigma^2}{2t} = \frac{0.014}{2(150)} = 4.7 \cdot 10^{-5}
$$

Note this is for diffusion vertically, detouring around the plates. Diffusion in the horizontal direction would give a different distance, and a different diffusion coefficient.

### 5.6 Measurement of Diffusion Coefficients

In this section, we want to discuss the most convenient ways in which diffusion coefficients can be measured. This section is the counterpoint to the previous ones.
Fig. 5.5-1. Random walk in a flake-filled film. A typical path through the aligned flakes is shown in (a). The distance traveled perpendicular to the flakes is shown vs. the total distance travelled, which is proportional to time $t$.

Whereas the focus has been on using past experience to guide predictions, this section replaces the hope of prediction with the necessity of accurate measurements.

Measuring diffusion coefficients is reputed to be difficult. For example, Tyrell (1961) stated that “this is not an easy field of study in any sense. It took eighty years from the time when Thomas Graham worked on diffusion before precise data on diffusion coefficients began to be collected.” This suggests that measurements of diffusion are a Holy Grail requiring noble knights who dedicate their lives to the quest.
In fact, although measurements are rarely routine, diffusion coefficients usually can be determined to within about five- or ten-percent accuracy without excessive effort. Because such accuracy is sufficient for most situations, we should always consider measuring the coefficients we need. The reputed difficulty of diffusion measurements stems from inherent masochists, like me, who make many of the experiments. We are never satisfied. When we attain coefficients accurate to 10%, we want 2%; when we achieve 2%, we want 0.5%.

If we have decided that measurements are essential, we must decide how to make them. There are many methods available, all described in glowing terms by their proponents. An exhaustive description of these methods could fill this book.

Instead of such an oppressive list, we shall consider only those methods of measuring diffusion that are reasonably accurate, that are easy to use, or that have some special advantage. I have tried below to state concisely the advantages and disadvantages of each method. I want to give the flavor of the laboratories themselves, and not just the polished publications that result.

The most useful methods of studying diffusion are shown in Table 5.6-1. The first three on this list are used most frequently. These three methods give accuracies sufficient for most practical purposes. They and the other methods will be described in greater detail in the following paragraphs.

### 5.6.1 Diaphragm Cell

The Stokes diaphragm cell is probably the best tool to start research on diffusion in gases or liquids or across membranes. It is inexpensive to build, rugged enough to use in an undergraduate lab, and yet capable of accuracies as high as 0.2%.

Diaphragm cells consist of two compartments separated either by a glass frit [Fig. 5.6-1(a)] or by a porous membrane [Fig. 5.6-1(b)] (Stokes et al., 1950). The two compartments are most commonly stirred at about 60 rpm with a magnet rotating around the cell. Initially, the two compartments are filled with solutions of different concentrations. When the experiment is complete, the two compartments are emptied and the two solution concentrations are measured. The diffusion coefficient \( D \) is then calculated from the equation

\[
D = \frac{1}{\beta t} \ln \left[ \frac{(c_1, \text{bottom} - c_1, \text{top})_{\text{initial}}}{(c_1, \text{bottom} - c_1, \text{top})_{\text{at time}}} \right]
\]  

(5.6-1)

in which \( \beta \) (in cm \(^2\)) is a diaphragm-cell constant, \( t \) is the time, and \( c_1 \) is the solute concentration under the various conditions given. The detailed derivation of this equation is given in Example 2.2-4.

Four points about the diaphragm cell deserve emphasis. First, calculation of the diffusion coefficients requires accurate knowledge of the concentration differences, not the concentrations themselves. This means that very accurate chemical analyses may be required. For example, imagine we are measuring the diffusion of anthracene in hot decalin. Using gas chromatography, we measure the anthracene concentration as \( 5.1 \pm 0.1\% \) in the top solution and \( 6.1 \pm 0.1\% \) in the bottom solution. The concentration difference is then \( 1.0 \pm 0.2\% \), an error of twenty percent, even though our chemical
### Table 5.6-1 Characteristics of the best methods of measuring diffusion coefficients

<table>
<thead>
<tr>
<th>Nature of diffusion</th>
<th>Apparatus expense</th>
<th>Apparatus construction</th>
<th>Concentrations difference required</th>
<th>Method of obtaining data</th>
<th>Overall value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>The three best methods</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diaphragm cell</td>
<td>Pseudosteady state</td>
<td>Small</td>
<td>Easy</td>
<td>Concentration at known time; requires chemical analysis</td>
<td>Excellent; simple equipment outweighs occasionally erratic results</td>
</tr>
<tr>
<td>Infinite couple</td>
<td>Unsteady in an infinite slab</td>
<td>Small</td>
<td>Easy</td>
<td>Large</td>
<td>Concentration vs. position at known time; requires chemical analysis</td>
</tr>
<tr>
<td>Particle uptake</td>
<td>Unsteady into particles</td>
<td>Small</td>
<td>Easy</td>
<td>Large</td>
<td>Requires accurate chemical analysis</td>
</tr>
<tr>
<td><strong>Three more expensive but important methods</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taylor dispersion</td>
<td>Decay of a pulse</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Average</td>
<td>Refractive index vs. time at known position</td>
</tr>
<tr>
<td>Nuclear magnetic resonance</td>
<td>Decay of a pulse</td>
<td>Large</td>
<td>Difficult</td>
<td>None</td>
<td>Change in nuclear spin</td>
</tr>
<tr>
<td>Dynamic light scattering</td>
<td>Decay of a pulse</td>
<td>Large</td>
<td>Difficult</td>
<td>None</td>
<td>Doppler shift in scattered light</td>
</tr>
<tr>
<td><strong>Other interesting methods</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gouy interferometer</td>
<td>Unsteady in an infinite cell</td>
<td>Large</td>
<td>Moderate</td>
<td>Small</td>
<td>Refractive-index gradient vs. position and time is photographed</td>
</tr>
</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>Experiments</th>
<th>Exceptional Analysis</th>
<th>Exceptional Reduction</th>
<th>Small Convection</th>
<th>Moderate</th>
<th>Large</th>
<th>Exceptional Analysis</th>
<th>Exceptional Reduction</th>
<th>Small Convection</th>
<th>Moderate</th>
<th>Large</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reviewing authors' suggestions using many factors. Quantity of liquid in the cell.</td>
<td>Large</td>
<td>Moderate</td>
<td>Small</td>
<td>Easy</td>
<td>Large</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Performing a chemical analysis of the liquid.</td>
<td>Large</td>
<td>Moderate</td>
<td>Small</td>
<td>Easy</td>
<td>Large</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measuring the concentration of reactants and products.</td>
<td>Average</td>
<td>Easy</td>
<td>Small</td>
<td>Easy</td>
<td>Large</td>
<td></td>
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</tr>
<tr>
<td>Measuring the concentration of reactants and products.</td>
<td>Small</td>
<td>Difficult</td>
<td>Large</td>
<td>Difficult</td>
<td>Small</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Overall Value</th>
<th>Method of Obtaining Data</th>
<th>Method of Applicating Concentrations</th>
<th>Convection Applicability</th>
<th>Application of Diffusion Applicability</th>
<th>Nature of Diffusion</th>
</tr>
</thead>
</table>

Table 5.9-1 (Contd.)
analyses are accurate to two percent. As a result, we might do better to use a differential refractometer to try to determine the concentration difference directly.

The second point about the diaphragm cell is the calibration constant $\beta$. This quantity is

$$\beta = \frac{A}{l} \left( \frac{1}{V_{\text{top}}} + \frac{1}{V_{\text{bottom}}} \right)$$

(5.6-2)

in which $A$ is the area available for diffusion, $l$ is the effective thickness of the diaphragm, and $V_{\text{top}}$ and $V_{\text{bottom}}$ are the volumes of the two cell compartments. We should note that $A$ is the total area open for diffusion and so is not a strong function of the pore size in the diaphragm. As a rule, small pores are preferred. Large pores may give a slightly larger area, but they often allow accidental mixing caused by flow through the diaphragm. Because $A$ and $l$ are, as a rule, not exactly known, $\beta$ must be found by experiment. In liquids, this calibration is commonly made with KCl–water or urea–water. Sucrose–water is less reliable because the solution often becomes contaminated by microorganisms. In gases, calibration depends on the method chosen to measure concentration.

The time required for diaphragm-cell measurements is determined by the value of $\beta$ and hence by the nature of the diaphragm. For accurate work, the diaphragm should be a glass frit, and the experiments may take several days; for routine laboratory work, the diaphragm can be a piece of filter paper, and the experiments may take as little as a few hours. For studies of membrane transport, a piece of membrane can be used in place of the filter paper. For studies in gases, the entire diaphragm can be replaced by a long, thin capillary tube, like the apparatus in Fig. 3.1-2.

The third point is that diffusion should always take place vertically. In other words, the diaphragm should lie in the horizontal plane. If the diaphragm is vertical, free convection can be generated, leading to spurious results. Interestingly, if the diaphragm
is horizontal, then placing the more dense solution in the upper compartment may be
done without fear of free convection. Many investigators routinely do this, feeling that
they get superior results. At the same time, most investigators have done away with the
elaborate initial diffusion period suggested in early experiments. This period is signif-
cant only when the diaphragm volume is about one-sixth of the compartment volumes
(Mills et al., 1968).

The final point about this method is its occasional unreliability. Every good experi-
mentalist subjectively judges the quality of his experiments as he goes along. Most can correctly
estimate an experiment's success even without detailed analysis. With the diaphragm cell,
however, I have never been able to guess. Experiments I expect to be erratic often are, but
experiments that I think are correct sometimes give answers that are in error by an order of
magnitude. One of my students minimized such unpleasant surprises by carefully wrapping
his cells in a particular brand of plastic bag purchased from a particular store in Cleveland,
Ohio. For him, this worked. I have never found a similar trick.

### 5.6.2 Infinite Couple

This experimental geometry, which is limited to solids, consists of two solid bars
of differing compositions, as shown in Fig. 5.6-2. To start an experiment, the two bars
are joined together and quickly raised to the temperature at which the experiment is to be
made. After a known time, the bars are quenched, and the composition is measured as
a function of position. In the past, this analysis was made by grinding off small amounts
of bar and determining the composition by a series of wet chemical tests; now, the
analysis is made more easily and quickly by an electron microprobe.

Because diffusion in solids is a slow process, the compositions at the ends of the solid
bars away from the interface do not change with time. As a result, the concentration
profile is that derived in Section 2.3:

$$
\frac{c_1 - \bar{c}_1}{c_{1\infty} - \bar{c}_1} = \text{erf} \left( \frac{z}{\sqrt{4Dt}} \right)
$$

in which $c_{1\infty}$ is the concentration at that end of the bar where $z = \infty$ and $\bar{c}_1 [= (c_{1\infty} + c_{1=\infty})/2]$ is the average concentration in the bars. The measured concentration
profile is fit numerically to find the diffusion coefficient.

It must be remembered that diffusion in solids can be more complex than these
paragraphs suggest. Some of this complexity stems from the different mechanisms by
which diffusion in solids can occur. More subtle complexities arise from factors like
residual stress in metal or the reference velocity on which diffusion is based. Such com-
plexities dictate caution.

The infinite couple is a good method to measure diffusion in solids, but it is tedious. A
faster though less accurate method is simply to drop some solid particles into a liquid
solution and to measure the solution concentration $c_1$ as a function of time. At small
times, the solute flux out of the solution and into the particles is given by

$$
n_1 = j_1 = -\sqrt{\frac{D}{\pi t}} H c_{10}
$$

(5.6-4)
where $c_{10}$ is the initial concentration in the solution (cf. Equation 2.3-18). From a mass balance on the solution,

$$V \frac{dc_1}{dt} = -An_1 = -A \sqrt{\frac{D}{\pi t}} H c_{10}$$  \hspace{1cm} (5.6-5)

where $V$ is the total volume of solution, $A$ is the total area of particles, and $H$ is the partition coefficient between the solution and the solid particles. This mass balance is subject to the initial condition that

$$t = 0, \quad c_1 = c_{10}$$  \hspace{1cm} (5.6-6)

Integrating, we find that

$$\frac{c_1}{c_{10}} = 1 - \left\{ \left( \frac{A}{V} \right) \sqrt{\frac{4D}{\pi H c_{10}}} \right\} \sqrt{t}$$  \hspace{1cm} (5.6-7)

Thus a plot of $(c_1/c_{10})$ vs. the square root of time has a slope which is proportional to the diffusion coefficient $D$.

I have given this example to illustrate the mathematical approximations which are usually successful in making experimental measurements. In this case, three of these approximations are especially obvious

1. The particles are taken as semi-infinite slabs, so that the flux is accurately described by Equation 5.6-3. This is true only if the time for the experiments is much less than (particle size)$^2/D$.

2. The concentration $c_{10}$ doesn’t change during the experiment so that the flux remains that given by Equation 5.6-3. This assumption seems especially foolish because our experiment depends on measuring changes in $c_1$. 
3. The solution is well mixed so its concentration \( c_1 \) has the same value throughout the liquid, even right up to the solid particles. This is often true even if the liquid is not mixed because the diffusion coefficient in the liquid is so much greater than that in the solid.

Each of these three assumptions is serious and initially not obvious. If any one of these is not accurate, our calculations of diffusion using this method may be seriously in error.

However, in my experience the use of Eq. 5.6-7 does give accurate values of the diffusion coefficient. Thus the three assumptions above must be reasonably accurate, and the chief limitation of the experiment is accurately measuring the concentration \( c_1 \). This accuracy is essential because we are basing our calculation on a concentration difference \((c_{10} - c_1)\), a small difference between large numbers. This fact is the key for this experiment, as it was for the diaphragm cell.

In my experience, most novices measuring diffusion do not concentrate on this experimental measurement but rather on improving the mathematics behind Equation 5.6-7. These novices assume a finite slab and solve the diffusion equations for that case, getting results like those in Section 3.5. They include the variation of solution concentration with time, performing an analysis like that in Example 3.5-3. These novices are then dismayed that their results are poorly reproducible, and they conclude that their mathematics is incorrect. It often isn't; it is unnecessary. The novices need instead to focus on their measurement of concentration.

The reason that so many novices make mistakes like this is that in their training, they practice harder and harder mathematics. They rarely practice better and better experimental accuracy. Thus this example has a moral: Please, when you start making measurements, use the simplest analysis possible until you are sure from experiment that it is inadequate.

### 5.6.3 Taylor Dispersion

We now turn to more complex and more expensive methods, which can also be easier to run or which give more accurate results. The first of these is Taylor dispersion, illustrated schematically in Fig. 5.6-3 (Ouano, 1972). This method, which is valuable for both gases and liquids, employs a long tube filled with solvent that slowly moves in laminar flow. A sharp pulse of solute is injected near one end of the tube. When this pulse comes out the other end, its shape is measured with a differential refractometer. Except for the refractometer, which can be purchased off the shelf, the apparatus is inexpensive and moderately easy to build. This apparatus can be used routinely by those with little training. It can be operated relatively easily at high temperature and pressure. It has the potential to give results accurate to better than one percent.

The concentration profile found in this apparatus is that for the decay of a pulse (see Section 4.2):

\[
c_1 = \frac{M}{\pi R^2} \exp \left( \frac{-(z - vt)^2}{4Et} \right) \frac{1}{\sqrt{4\pi Et}}
\]

(5.6-8)
where $M$ is the total solute injected, $R$ is the tube radius, $v^0$ is the average velocity of the flowing solvent, and $E$ is a dispersion coefficient given by

$$E = \frac{(v^0 R)^2}{48 D} \quad (5.6-9)$$

Because the refractive index varies linearly with the concentration, knowledge of the refractive-index profile can be used to find the concentration profile and the diffusion coefficient.

The fascinating aspect of this apparatus is the way in which the diffusion coefficient appears. Equation 5.6-8 has the same mathematical form as Eq. 2.4-14, but the dispersion coefficient $E$ replaces the diffusion coefficient. So far, as good. However, $E$ varies inversely with $D$, as explained in Section 4.4. Consequently, a widely spread pulse means a large $E$ and a small $D$. A very sharp pulse indicates small dispersion and hence fast diffusion.

### 5.6.4 Spin Echo Nuclear Magnetic Resonance

The next two methods, spin echo nuclear magnetic resonance and dynamic light scattering, represent the adoption of expensive, complex equipment built to obtain molecular information to the new task of measuring diffusion. Because neither method tries only to measure diffusion coefficients, the accuracy is modest. Neither method requires an initial concentration difference, a major convenience in highly viscous
systems. The real attraction of each system is the promise that existing equipment can be reapplied to the new objective of measuring diffusion.

Diffusion coefficients can be measured with nuclear magnetic resonance to an accuracy of around five percent. To do so, we first place a homogeneous sample in a large magnetic field. This external field aligns the magnetic moments of the atomic nuclei in the solute of interest. When the magnetic field is slightly perturbed, the atomic moments process, which can induce in an adjacent coil a small voltage of amplitude $A$ oscillating with time:

$$A = A_0 \sin(t/\tau)$$  \hspace{0.5cm} (5.6-10)

The period of this oscillation $\tau$ is normally the focus of interest, for it gives information about the local chemical environment.

Our interest is not in the period $\tau$ but in the amplitude $A_0$. To study this amplitude, we apply a second perturbation in the magnetic field. This second “pulsed gradient” is applied not in time, but in space. It is applied first in one direction and then – after a short time $\tau'$ – in the opposite direction. If the solute molecules were fixed in space, the two perturbations in space would produce no change in the amplitude $A_0$. However, these molecules aren’t fixed but are moving by Brownian motion, so the amplitude $A_0$ is reduced.

We can measure this amplitude reduction as a function of the time $\tau'$ between the gradient pulses. The slope of this variation is a direct measure of the Brownian motion and hence of the diffusion coefficient. Thus if we make measurements on a solute of known diffusion coefficient and a solute of unknown diffusion coefficient, we can find the unknown as

$$\frac{D'(\text{unknown})}{D'(\text{known})} = \frac{\partial A_0 / \partial \tau'}{\partial A_0 / \partial \tau'}(\text{known})$$  \hspace{0.5cm} (5.6-11)

Strictly speaking, such a measurement is not of the binary diffusion coefficient $D$ but of the tracer diffusion coefficient $D'$ (cf. Section 7.5). In dilute solution, these have the same value.

5.6.5 Dynamic Light Scattering

Like nuclear magnetic resonance, dynamic light scattering uses expensive equipment for a relatively easy measurement of the diffusion coefficient. Like nuclear magnetic resonance, the measurement requires no initial concentration difference, and so is especially suited to viscous solutions. Unlike nuclear magnetic resonance, the measurement is of the binary coefficient, not the tracer diffusion coefficient.

Dynamic light scattering depends on measuring the autocorrelation function of scattered light as a function of scattering angle and time. To understand the method, we must first consider what happens to a wave of light traveling through the solution which we are studying. The wave will move in a constant direction until it strikes an inhomogeneity. Then part of the wave may be scattered by a changed impedance, that is, by an altered resistance to its motion that is proportional to the refractive index of the solution. How the light is scattered depends on how the inhomogeneities in the
solution are organized. If the solution contains a completely random array of inhomogeneities, then the scattering will be the same in all directions. However, if the solution contains a perfectly ordered array of inhomogeneities, then the scattering will exist only at particular angles, called Bragg diffraction angles. At these angles, scattering results from constructive interference when scatterers are exactly an integral number of wavelengths apart. At all other angles, scattering produces destructive interference.

For the important case of concentrated polymer solutions, the scattering results from a solution that is between a random array and an ordered array. Each monomer unit can be considered a point scatterer; while the polymer molecules are randomly distributed in the solution, monomer units are not because they are part of polymer chains. However, the polymer molecules do move relative to each other because of Brownian motion. Hence any apparent order in the solution will decay with time.

This decay of order is measured as an autocorrelation function by the dynamic light scattering apparatus. Such a function gives the correlation between the solution's order at some arbitrary time zero and at some second time \( t \). When \( t \) is near zero, the autocorrelation function is near one: The order hasn't changed much. When \( t \) becomes large the autocorrelation function is near zero: Any apparent order has vanished, replaced by a new apparent structure. In many cases, this decay can be described as a first-order exponential:

\[
\langle A(0)A(t) \rangle \propto e^{-q^2Dt} \quad (5.6-12)
\]

where \( \langle A(0)A(t) \rangle \) is the autocorrelation function, \( D \) is the binary diffusion coefficient, \( t \) is the time, and \( q \) is the "scattering vector":

\[
q = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right) \quad (5.6-13)
\]

where \( \lambda \) is the wavelength of the scattered light and \( \theta \) is the scattering angle.

Thus measurements of the autocorrelation function versus time allow calculation of the diffusion coefficient \( D \). In practice, the range of diffusion coefficients that we can measure is determined by the scattering vector \( q \), which has dimensions of reciprocal length. Roughly speaking, \( q^{-1} \) is a measure of the distance over which the measurement is being made. For visible light with a wavelength of 500 nanometers, we sample a distance of around 100 nm; for neutrons with a wavelength of 1 nanometer, we sample distances around 3 nm. Still, the important point is that the dynamic light scattering method provides a measurement of binary diffusion especially suitable for polymer solutions.

### 5.6.6 Some Very Accurate Methods

So far, we have discussed three easy methods and three more highly instrumented methods for measuring diffusion coefficients. Each of these six methods can give results accurate to a few percent, a suitable goal for most research. If higher accuracy is needed, we should turn to the interferometers shown in Fig. 5.6-4. These instruments depend on measuring an unsteady-state refractive index profile in a transparent system,
and so they are most useful for liquids. Their high accuracy is purchased at a great cost of both equipment and effort.

The interferometers differ optically. The Gouy interferometer, shown schematically in Fig. 5.6-4(a), is the more highly developed, accurate to better than 0.1%. It is relatively simple to build and easy to align. If one already has a method for measuring the interference fringes, this instrument is not particularly expensive. The Gouy method has been so highly developed that the extremely specialized jargon used in its operation may discourage newcomers. In fact, the experiments are simple to do; the hardest step is to understand the theory well enough to write the appropriate computer program. Average results with this instrument are at least equivalent to the best results obtained with any other device.

The Gouy interferometer measures the refractive-index gradient between two solutions that are diffusing into each other. The basic apparatus for measuring the gradient uses the lenses L to send parallel light rays from a light source LS through a diffusion cell C. If this cell contains a refractive-index profile, then light passing through the center of the cell will be deflected to produce an interference pattern of black horizontal lines, as shown at the right in Fig. 5.6-4(a). The amount of this deflection is proportional to the refractive-index gradient, a function of cell position and time.

The Mach–Zehnder and Rayleigh interferometers are solid alternatives to the Gouy interferometer. Although they are difficult to construct and adjust, they give information that is simpler to interpret. In the Mach–Zehnder apparatus, shown in Fig. 5.6-4(c),
collimated light is split by the first half-silvered mirror \( M' \). Half the light passes through each of the twin cells \( C \) and is recombined by the second half-silvered mirror \( M'' \). In the Rayleigh apparatus, these mirrors are replaced by a cylindrical lens, shown in Fig. 5.6-4(b).

Both instruments measure refractive index versus cell position. If both cells contain homogeneous solutions, the interference fringes are sets of parallel vertical lines; if one cell contains a refractive-index gradient caused by diffusion, the interference fringes look like those shown at the right of Figs. 5.6-4(b) and (c). For both interferometers, these fringes can be used to calculate the diffusion coefficient.

5.6.7 Other Methods

The remaining common methods for measuring diffusion are listed in Table 5.6-1 roughly in order of their value. None of these methods is commonly superior to those described above, although each may be useful in specific cases.

The capillary method is most suitable for measurements with radioactive tracers. It uses a small diffusion cell made of precision-bore capillary tubing, perhaps 3 cm long and 0.05 cm in diameter. One end of this cell is sealed shut. After the cell is filled with a solution of known concentration, it is dropped into a large, stirred, thermostated solvent bath. At the end of the experiment, the cell is removed and the solute concentration within the cell is measured. The diffusion coefficient \( D \) can then be found from the equation

\[
\frac{\bar{c}_1}{\bar{c}_{10}} = \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp \left(-\frac{\pi^2}{4}(2n-1)^2(Dt/4l^2)\right) \tag{5.6-14}
\]

in which \( \bar{c}_{10} \) and \( \bar{c}_1 \) are the average concentrations in the cell at times zero and \( t \), respectively, and \( l \) is the length of the cell.

Four characteristics of this method deserve mention. First, with careful technique it is accurate to better than 0.3\%. The caveat is "careful technique"; it is unusually easy to fool yourself with this equipment, obtaining reproducible inaccurate results. Second, the small size of the diffusion cell dictates careful chemical analysis of very small volumes of solution. In practice, this suggests using either radioactive tracers or some other microanalytical method. Third, the power series in Eq. 5.6-14 converges rapidly. If you use reasonably long experiments, you can base your analysis on the first term in the series. Finally, for radioactive tracers this method may give an intradiffusion coefficient, not a binary coefficient (cf. Section 7.5).

The spinning-disc method depends on a solid or liquid disc of solute slowly rotating in a solvent volume (see Fig. 3.4-3). The solute concentrations in the solvent are analyzed versus time. If the disc's dissolution is diffusion-controlled, these concentrations allow calculation of the diffusion coefficient from Example 3.4-3 (Levich, 1962). If the disc's dissolution is not diffusion-controlled, we must choose another method.

The wedge interferometer is cheap and cute, a simple alternative to the expensive interferometers described earlier. It consists of two microscope slides separated at one edge with a coverslip. To start an experiment, one places drops of two different solutions
next to each other on one slide. One then places the other slide and coverslip so that the
drops are in contact in a wedge-shaped channel. When this wedge is put in a microscope,
interference fringes indicate the concentration profile. Measuring the change of fringe
position versus time allows calculation of the diffusion coefficient simply, cheaply, and
approximately. Moreover, because only drops of solution are needed, one needs only
very small amounts of solute.

The last entry in Table 5.6-1 refers to steady-state methods. These methods are like
the diaphragm cell, but they replace the two well-stirred compartments with two flowing
solutions. In principle such a replacement gives a true steady state, simplifying the
analysis. In practice, the methods are a nightmare. The two solutions must flow at
exactly the same rate, so expensive pumps and valves are needed. The experiments
can consume huge amounts of solution. My advice is to choose a complex analysis
and a simple unsteady experiment.

5.7 A Final Perspective

The characteristics of diffusion coefficients described in this chapter are sum-
marized in Table 5.7-1. In general, diffusion coefficients in gases and in liquids can often
be accurately estimated, but coefficients in solids and in polymers cannot. In gases,
estimates based on the Chapman–Enskog kinetic theory are accurate to around ten
percent. In liquids, estimates are based on the Stokes–Einstein equation or its empirical
parallels. These estimates, accurate to around twenty percent, can be supplemented by
a good supply of experimental data. In solids and polymers, theories allow coefficients to
be correlated but rarely predicted.

These common generalizations help to solve only the routine problems with which we
are faced. Many problems remain. For example, we may want to know the rate at which
hydrochloric acid diffuses into oil-bearing sandstone. We may need to estimate the
drying speed of lacquer. We may seek the rate of flavor release from lemon pie filling.
All these examples depend on diffusion; none can be accurately estimated with the
common generalizations.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Typical value cm²/sec</th>
<th>Variations with</th>
<th>Remarks</th>
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<tr>
<td></td>
<td></td>
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<td>Pressure</td>
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<td>$T^{3/2}$</td>
<td>$p^{-1}$</td>
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<tr>
<td>Polymers</td>
<td>$10^{-8}$</td>
<td>Large</td>
<td>Small</td>
</tr>
</tbody>
</table>

*Note: These heuristics summarize the more detailed discussions in this chapter.*
In some cases, diffusion coefficients can be adequately estimated by more carefully considering the chemistry. Specific cases, discussed in the next chapter, include electrolytes and critical points. However, in most nonroutine problems the detailed chemistry is not known and experiments are essential. The primer on experiments given in this chapter should be your initiation.

Questions for Discussion

1. What are typical values of diffusion coefficients in gases, liquids, and solids?
2. If the diffusion of hydrogen in nitrogen gas is 0.78 cm²/sec at 1 bar, what will it be at 50 bars?
3. Describe an experiment to measure the diffusion of oxygen in nitrogen. List any equipment needed.
4. Diffusion in liquids commonly assumes a rigid sphere in a continuum. When would this model be most accurate? When could it fail?
5. How would the diffusion coefficient of a protein vary with its molecular weight?
6. Describe an experiment to measure the diffusion of glucose in water. List any equipment needed.
7. What are the limits of the diffusion of an ellipsoid as the ratio of axes \( a/b \) becomes very large?
8. Diffusion varies with viscosity to the \((\pm 1)\) power in gases but to the \((-1)\) power in liquids. Why?
9. Why does hydrogen diffuse so much faster in metals than other solutes do?
10. Diffusion in metals often varies strongly with temperature in metals with an activation energy \( \Delta H \) around 100 kJ/mol. What are the corresponding activation energies in gases and in liquids?

Problems

1. Estimate the diffusion coefficient of carbon dioxide in air at 740 mm Hg and 37°C. How does this compare with the experimental value of 0.177 cm²/sec? Answer: about 4% low.

2. As part of a course on diffusion, you are to measure the diffusion coefficient of ammonia in 25°C air, using the two-bulb capillary apparatus shown in Fig. 3.1-2. In your apparatus, the bulbs have volumes of about 17 cm³, and the capillary is 2.6 cm long and 0.083 cm in diameter. You are told that you should make your measurements when the concentration difference is about half the initial value. (a) Use the Chapman–Enskog theory to estimate how long you should run your experiment. Answer: 3.6 hrs (b) Why are you told to make your measurement near this particular concentration difference?

3. Estimate the diffusion coefficient at 25°C of traces of ethanol in water and of traces of water in ethanol. Compare your estimates with the experimental values of \( 0.84 \cdot 10^{-5} \) cm²/sec and \( 1.24 \cdot 10^{-5} \) cm²/sec, respectively.

4. Tobacco mosaic virus has been shown by electron microscopy to be shaped like a cylinder 150 Å in diameter and 3,000 Å long. Its molecular weight is about 40 million, and its partial specific volume is 0.73 cm³/g. Estimate the diffusion coefficient of this
material and compare with the experimental value at 25 °C of \(3 \cdot 10^{-8} \, \text{cm}^2/\text{sec}\). \textit{Answer:} \(2.7 \cdot 10^{-8} \, \text{cm}^2/\text{sec}\).

5. Estimate the diffusion coefficient of lactic acid under each of the following conditions: (a) in air at room temperature and pressure; (b) in milk in the refrigerator; (c) through the wall of a plastic milk bottle.

6. In an experiment to determine the diffusion coefficient of urea in water at 25 °C with the diaphragm cell, you find that a density difference of 0.01503 g/cm³ decays to 0.01090 g/cm³ after a time of 16 hrs and 23 min. The cell’s calibration constant is 0.397 cm⁻². If the density of these solutions varies linearly with concentration, what is the diffusion coefficient? Compare your answer with the value of \(1.373 \cdot 10^{-5} \, \text{cm}^2/\text{sec}\) obtained with the Gouy interferometer. \textit{Answer:} \(1.37 \cdot 10^{-5} \, \text{cm}^2/\text{sec}\).

7. The concentration profile of \(\text{Ni}_2\text{SiO}_4\) diffusing into \(\text{Mg}_2\text{SiO}_4\) is given below [M. Morioka, \textit{Geochim Cosmochim Acta}, \textbf{45}, 1573 (1981)]. These data were found after 20 hrs using an infinite couple at 1,350 °C. Calculate the diffusion coefficient in this system. \textit{Answer:} \(1.2 \cdot 10^{-11} \, \text{cm}^2/\text{sec}\).

8. The ionic diffusion coefficient \(D\) or, more exactly, the ionic conductivity \(\lambda\) can frequently be described by the equation

\[
\lambda = \frac{a_0}{T} \exp\left(\frac{-E}{RT}\right)
\]

For \(\beta\)-alumina, the following values are obtained:

[G. C. Farrington and J. L. Briant, \textit{Science}, \textbf{204}, 1371 (1979)]. (a) Calculate the ionic conductivity at 25 °C for each of these ions. (b) Show that these conductivities can be as large as that in 1-M KCl, in which the diffusion coefficient is \(2.0 \cdot 10^{-5} \, \text{cm}^2/\text{sec}\). (c) Because we usually expect transport in solids to be much slower than transport in
liquids, we recognize that β-alumina is an exceptional material. Discuss the factors that might cause this effect.

9. Jeng-Ping Yao and D. N. Bennion [J. Phys. Chem., 75, 3586 (1971)] measured the electrolytic conductance of aqueous solutions of tetra-n-amylammonium thiocyanate at 55 °C. The data are most easily presented graphically (see below). Note that this salt is a liquid at this temperature and is completely miscible with water; so the measurements go all the way from mass transfer at infinite dilution through to mass transfer in the molten salt. As detailed in Section 6.1, specific conductance is approximately equivalent to the diffusion coefficient times the ionic concentration. Use your knowledge of diffusion to suggest how the data at high salt concentration might be conveniently correlated.

10. Diffusion in molten silicate deep within the earth is central to many of the chemical processes that take place there. However, the diffusion coefficients in such magma seem to vary widely. For example, for cesium ion dissolved in obsidian at 2 kilobars pressure,

\[ D = 8 \cdot 10^{-2} \exp^{-49.9 \text{kcal}/RT} \text{cm}^2/\text{sec} \]

For cesium ion dissolved in obsidian containing 6 wt% water,

\[ D = 7 \cdot 10^{-5} \exp^{-19.52 \text{kcal}/RT} \text{cm}^2/\text{sec} \]

[E. B. Watson, Science, 205, 1259 (1979)]. (a) How much does the diffusion coefficient at 800 °C differ in the dry and the water-saturated samples? (b) The reason for this difference is not known. Assume that the water causes thin pores to form, and diffusion in the pores is that in bulk water. What is the pore area per obsidian area?

Further Reading


Diffusion of Interacting Species

In this chapter, we turn to systems in which there are significant interactions between diffusing molecules. These interactions can strongly affect the apparent diffusion coefficients. In some cases, these effects produce unusual averages of the diffusion coefficients of different solutes; in others, they suggest a strong dependence of diffusion on concentration; in still others, they result in diffusion that is thousands of times slower than expected.

The discussion of these interactions involves a somewhat different strategy than that used earlier in this book. In Chapters 1–3, we treated the diffusion coefficient as an empirical parameter, an unknown constant that kept popping up in a variety of mathematical models. In more recent chapters, we have focused on the values of these coefficients measured experimentally. In the simplest cases, these values can be estimated from kinetic theory or from solute size; in more complicated cases, these values require experiments. In all these cases, the goal is to use our past experience to estimate the diffusion coefficients from which diffusion fluxes and the like can be calculated.

In this chapter, we consider the chemical interactions affecting diffusion much more explicity, rather than hiding them as part of the empirically measured diffusion coefficient. The interactions affecting diffusion are conveniently organized into three groups. As a first group, we consider in Section 6.1 solute–solute interactions, particularly in strong electrolytes. We want to discover how sodium chloride diffusion is an average of the diffusion of sodium ions and of chloride ions. In Section 6.2, we turn to the transport of associating solutes like weak electrolytes and dyes. We want to know how the total diffusion of acetic acid varies from dilute solutions, where it is almost completely ionized, to concentrated solutions, where it is almost completely unionized.

The second group of interactions affecting diffusion involves solute–solvent interactions. In Section 6.3, we explore the extremely large solute–solvent interactions which occur near the spinodal limit, where phase separation is incipient. Diffusion in these regions leads to the phenomenon of spinodal decomposition, which is also discussed in Section 6.3.

In the last section of this chapter, we summarize diffusion affected by solute–boundary interactions, which is the third important group of interactions. Solute–boundary interactions occur in porous solids with fluid-filled pores. They include such diverse phenomena as Knudsen diffusion, capillary condensation, and molecular sieving. Because these phenomena promise high selectivity for separations, they are an active area for research. They and the other interactions illustrate the chemical factors that can be hidden in the diffusion coefficients which are determined by experiment.

6.1 Strong Electrolytes

Every high school chemistry student knows that when sodium chloride is dissolved in water, it is ionized. Sodium chloride in water does not diffuse as a single
molecule; instead, the sodium ions and chloride ions move separately through the solution. The movement of the ions means that a 0.1-M sodium chloride solution passes an electric current one million times more easily than water does. The large ion size relative to electrons means that such a solution passes current ten thousand times less easily than a metal does.

The diffusion of sodium chloride can be accurately described by a single diffusion coefficient. Somehow this does not seem surprising, because we always refer to sodium chloride as if it were a single solute and ignore the knowledge that it ionizes. We get away with this selective ignorance because the sodium and chloride ions diffuse at the same rate. If they did not do so, we could easily separate anions from cations.

Values of ionic diffusion coefficients are given in Table 6.1-1. These data, which are hidden in the literature of electrochemistry, are obtained by a variety of experimental methods, including tracer diffusion determinations. The table shows that different ions have different diffusion coefficients. The proton and the hydroxyl ion are unusually fast; big fat organic ions like tetrabutylammonium and tetraphenylborate are slow. Somewhat surprisingly, a potassium ion diffuses faster than a lithium ion does. This suggests that in aqueous solution, a potassium ion is smaller than a lithium ion. These sizes are unexpected from crystallographic measurements on the solid state that show the potassium ion is larger. The sizes in solution occur because the potassium ion is less strongly hydrated than the lithium, as discussed in Section 6.2-4.

The anomalously high value for protons merits discussion. This high value is inconsistent with the ion's size, which would suggest a more normal value. The reason for this behavior is that proton transport occurs by a different "Grotthus" mechanism. In this mechanism, shown schematically in Fig. 6.1-1, a proton does not move through water as an intact entity. Instead, it reacts with a water molecule, forcing a proton off the other side. This newly generated molecule reacts again to produce a third proton; this third proton continues the chain reaction. This transport may also involve proton tunnelling.

Another interesting result in Table 6.1-1 is that the sodium ion diffuses more slowly than the chloride ion. In other words, the sodium ion does not have the same diffusion

<table>
<thead>
<tr>
<th>Cation</th>
<th>Anion</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>OH⁻</td>
<td>9.31</td>
</tr>
<tr>
<td>Li⁺</td>
<td>F⁻</td>
<td>1.03</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Cl⁻</td>
<td>1.33</td>
</tr>
<tr>
<td>K⁺</td>
<td>Br⁻</td>
<td>1.96</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>I⁻</td>
<td>2.07</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>NO₃⁻</td>
<td>2.06</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>CH₃COO⁻</td>
<td>1.65</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>CH₃CH₂COO⁻</td>
<td>1.96</td>
</tr>
<tr>
<td>N(C₆H₅)₄⁺</td>
<td>B(C₆H₅)₄⁻</td>
<td>0.52</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>SO₄²⁻</td>
<td>0.79</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>CO₃⁻</td>
<td>0.71</td>
</tr>
<tr>
<td>La³⁻</td>
<td>Fe(CN)₆³⁻</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Note: Values at infinite dilution in 10⁻⁵ cm²/sec. Calculated from data of Robinson and Stokes (1960).
coefficient as the chloride ion. However, because sodium chloride diffuses with only one coefficient, the ionic diffusion coefficients must somehow be combined to give an average value. We shall now calculate this average, first for a simple 1-1 electrolyte like sodium chloride and then for more complicated electrolytes. With these results as a basis, we shall then briefly discuss electrical conductance.

6.1.1 Basic Arguments

Imagine a large, fat grandfather taking a small rambunctious girl for a walk. The rate at which the two travel will be largely determined by the grandfather. He will move slowly, even ponderously, toward their goal. The girl may run back and forth, taking many more steps and so covering more distance, but her progress will be dominated by her elder.

In the same way, the diffusion of a large, fat cation and a small, quick anion will be dominated by the slower ion. The diffusion will proceed as does the walk, and the smaller ion may move around more. However, the two ions are tied together electrostatically, and so their overall progress will be the same and will tend to be dominated by the slower ion (Fig. 6.1-2).

To examine this analogy more exactly, we must first write a flux equation for ion diffusion. In this effort, we consider only dilute solutions, like those in Chapter 2, and so ignore problems like the complicated reference velocities of Chapter 3. The obvious choice of a flux equation is the simplest form of Fick’s law, which for a sodium ion will be

$$-j_{Na} = D_{Na} \nabla c_{Na}$$  \hspace{1cm} \text{(6.1-1)}

However, we quickly realize that this choice is inadequate, for it suggests that an electric field will not affect diffusion.

To include this electric field, we return to the argument used to derive the Stokes–Einstein equation in Section 5.2: that the ion velocity is proportional to the sum of all the forces acting on the ion. In symbolic terms, this is

$$v_i = -u_i (\nabla \mu_i + z_i F \nabla \psi)$$  \hspace{1cm} \text{(6.1-2)}
where \( u_i \) is the ion mobility, \( z_i \) is the ionic charge (equal to +1 for Na\(^+\)), \( F \) is Faraday’s constant, and \( \psi \) is the electrostatic potential.

Each of these terms deserves discussion. First, the mobility \( u_i \) is a physical property of the ion, a phenomenological coefficient that must be measured by experiment. This mobility is often taken to be \( 1/6\pi\mu R_0 \), which, we recall, is a feature of the Stokes–Einstein equation. In fact, the use of this value simply restates our ignorance of mobility in terms of an effective ion radius, \( R_0 \).

Because the mobility is almost equivalent to the diffusion coefficient, it is something of a cultural artifact. It is included here because many papers dealing with electrolyte transport report their results in terms of mobilities, not in terms of diffusion coefficients. Faraday’s constant is even more of a cultural artifact: it is a unit conversion factor explicitly included whenever this equation is written. The apparent supposition is that no one can properly use electrostatic units without a warning.

The charge and potential in Eq. 6.1-2 make explicit the electrical effects connecting the ions. Including the charge seems sensible; note that if the ion has a negative charge, the direction of the electrical effect is reversed. The potential also looks sensible. It has two distinct parts. One part includes the effect of any potential applied to the system, for example, by electrodes attached to a battery. A second part is the potential generated by the different diffusion rates of diffusion ions. For example, for sodium chloride, the potential includes the electrostatic interaction of the quicker chloride ions and the more sluggish sodium ions. It is thus the route by which we average ion diffusion coefficients.

To rewrite Eq. 6.1-2 as a flux relation, we take advantage of the fact that we are working in dilute solution and so assume that the solution is ideal:

\[
\mathbf{v}_i = \frac{RT}{c_i} \nabla c_i
\]

(6.1-3)

When this result is combined with Eq. 6.1-2, we get

\[
- \mathbf{v}_i = \frac{[u_i RT]}{c_i} \left( \nabla c_i + c_i z_i \frac{F \nabla \psi}{RT} \right)
\]

(6.1-4)
which is equivalent to the flux equation
\begin{equation}
-j_i = -c_i v_i \\
= [RTu_i] \left( \nabla c_i + c_i z_i \frac{F \nabla \psi}{RT} \right) \\
= [D_i] \left( \nabla c_i + c_i z_i \frac{F \nabla \psi}{RT} \right)
\end{equation}
(6.1-5)

These relations, sometimes called the Nernst–Planck equations (Bard and Faulkner, 2000), could be written down directly as a definition for \( D_i \). If this were done, then the restriction to dilute solutions in Eq. 6.1-3 and the implicit neglect of a reference velocity in the first line of Eq. 6.1-5 would be hidden in the final flux equation, lumped into the experimental coefficient \( D_i \). I find the derivation a sensible, reassuring rationalization, even though I know that it is arbitrary.

### 6.1.2 1-1 Electrolytes

We now want to describe the ion fluxes of a single strong 1-1 electrolyte. Such an electrolyte ionizes completely, producing equal numbers of cations and anions. Although the concentrations of anions and cations may vary through the solutions, the concentrations and the concentration gradients of these species are equal everywhere because of electroneutrality:
\begin{equation}
c_1 = c_2 \\
\nabla c_1 = \nabla c_2
\end{equation}
(6.1-6)

where 1 and 2 refer to cation and anion, respectively. Like the ion concentrations, the ion fluxes are also related.
\begin{equation}
-j_1 - j_2 = i/|z|
\end{equation}
(6.1-7)

where \(|z|\) is the magnitude of the ionic charge and \( i \) is the current density in appropriate units. This current density is defined as positive when it goes from positive to negative.

To find the electrolyte flux, we first return to the basic flux equation for each ion:
\begin{equation}
-j_1 = D_1 (\nabla c_1 + |z| c_1 F \nabla \psi /RT)
\end{equation}
(6.1-8)
\begin{equation}
-j_2 = D_2 (\nabla c_2 - |z| c_2 F \nabla \psi /RT)
\end{equation}
(6.1-9)

These equations can be combined with Eq. 6.1-7 to find the current:
\begin{equation}
|z|i = D_2 \nabla c_2 - D_1 \nabla c_1 - (D_1 c_1 + D_2 c_2) |z| F \nabla \psi /RT
\end{equation}
(6.1-10)

But this equation now allows \( \nabla \psi \) to be removed from the flux equations:
\begin{equation}
-j_1 = \frac{2D_1 D_2}{D_1 + D_2} \nabla c_1 - \frac{D_1}{D_1 + D_2} (i/|z|)
\end{equation}
(6.1-11)

where we have used the fact that \( c_1 = c_2 \) to simplify the final expression. A similar equation for the anion flux \( j_2 \) can be derived.
Two important limits of the flux $j_i$ exist. First, when there is no current,

$$j_1 = j_2 = -D \nabla c_1 = -\left[\frac{2}{1/D_1 + 1/D_2}\right] \nabla c_1$$  \hfill (6.1-12)

The quantity in brackets is the average diffusion coefficient of the electrolyte. Because it is a harmonic average of the diffusion coefficients of the individual ions, it is dominated by the slower ion. However, there is only one diffusion coefficient for the two diffusing ions because the ions are electrostatically coupled.

The second interesting limit of Eq. 6.1-11 occurs when the solution is well mixed, so that no gradients of anion and cation exist. In this case,

$$j_1 = [t_1](|z|\bar{v}) = -\left[\frac{D_1}{D_1 + D_2}\right] (\bar{v}/|z|)$$  \hfill (6.1-13)

$$j_2 = [t_2](-|z|\bar{v}) = -\left[\frac{D_2}{D_1 + D_2}\right] (\bar{v}/|z|)$$  \hfill (6.1-14)

where the $t_i$, equal to the quantities in brackets, are the transference numbers, that is, the fractions of current transported by specific ions. Unlike the diffusion coefficient, these transference numbers are arithmetic averages of the ion diffusion coefficients. As a result, the transference numbers and the current in solution are both dominated by the faster ion.

**Example 6.1-1: Diffusion of hydrogen chloride**  What is the diffusion coefficient at 25 °C for a very dilute solution of HCl in water? What is the transference number for the proton under these conditions?

**Solution**  From the data in Table 6.1-1, the ionic diffusion coefficients are $9.31 \cdot 10^{-5}$ cm$^2$/sec for H$^+$ and $2.03 \cdot 10^{-5}$ cm$^2$/sec for Cl$^-$. The electrolyte diffusion coefficient is given by Eq. 6.1-12:

$$D_{\text{HCl}} = \left[\frac{2}{1/D_{\text{H}^+} + 1/D_{\text{Cl}^-}}\right] = 3.3 \cdot 10^{-5} \text{ cm}^2/\text{sec}$$

The slow ion dominates. The result is only 1.5 times greater than the chloride’s diffusion coefficient, but it is 3.5 times less than the proton’s diffusion coefficient.

The transference number, $t_{\text{H}^+}$, can be found in a straightforward manner from Eq. 6.1-13:

$$t_{\text{H}^+} = \frac{D_{\text{H}^+}}{D_{\text{H}^+} + D_{\text{Cl}^-}} = 0.82$$

The faster protons carry eighty-two percent of the current.

### 6.1.3 Non-1-1 Electrolytes

We now turn from the simple 1-1 electrolytes to more complicated electrolytes. Mathematical description of non-1-1 electrolytes is parallel to that developed earlier but more complex algebraically. The basic flux equation is the same as Eq. 6.1-5:

$$-j_i = D_i(\nabla c_i + c_i z_i \mathcal{F} \nabla \psi /RT)$$  \hfill (6.1-15)
The constraints on concentration and flux at zero current are
\[ z_1 c_1 + z_2 c_2 = 0 \] (6.1-16)
and
\[ z_1 j_1 + z_2 j_2 = 0 \] (6.1-17)

When the electrostatic potential is eliminated, the diffusion equation for ion 1 becomes
\[ -j_1 = D \nabla c_1 = \frac{D_1 D_2 (z_1^2 c_1 + z_2^2 c_2)}{D_1 z_1^2 c_1 + D_2 z_2^2 c_2} \nabla c_1 \] (6.1-18)

where the quantity in brackets is \( D \), the diffusion coefficient of the electrolyte.

This equation can be somewhat misleading because of the unequal charge. For example, imagine that we are interested in the diffusion of very dilute solutions of calcium chloride. If the calcium is ion 1, then its flux will be half the flux of chloride. When only one electrolyte is present, we may wish to rewrite this equation in terms of the total electrolyte flux \( j_T \) and the total electrolyte concentration \( c_T \), defined as
\[ j_T = j_1 / |z_2| = j_2 / |z_1| \] (6.1-19)
\[ c_T = c_1 / |z_2| = c_2 / |z_1| \] (6.1-20)

The diffusion equation for a single non-1-1 electrolyte now becomes
\[ -j_T = D \nabla c_T = \frac{|z_1| + |z_2|}{|z_2|/D_1 + |z_1|/D_2} \nabla c_T \] (6.1-21)

where the quantity in brackets is again the diffusion coefficient of the non-1-1 electrolyte.

This diffusion forms a curious contrast with the special case of a 1-1 electrolyte described by Eq. 6.1-12. Both equations involve a type of harmonic average of the ionic diffusion coefficients. Thus we might expect that both cases are more strongly influenced by the slower ion. However, if this slower ion has a much larger charge than the faster ion, the faster ion may come to dominate the diffusion, because the harmonic average is weighted by the ion charge. The effect of this weighting can be more clearly shown by examples.

---

**Example 6.1-2: Diffusion of lanthanum chloride**  What is the diffusion coefficient of 0.001-M lanthanum chloride?

**Solution**  From Table 6.1-1, the diffusion coefficients of \( \text{La}^{3+} \) and \( \text{Cl}^- \) are \( 0.62 \times 10^{-5} \text{cm}^2/\text{sec} \) and \( 2.03 \times 10^{-5} \text{cm}^2/\text{sec} \), respectively. In water, the average coefficient can be found either from Eq. 6.1-18 or from Eq. 6.1-21. From Eq. 6.1-21, taking \( \text{La}^{3+} \) as ion 1 and chloride as ion 2, we get
\[
D = \frac{|z_1| + |z_2|}{|z_1|/D_2 + |z_2|/D_1} \\
= \left[ \frac{|3| + |1|}{|3|/2.03 \times 10^{-5} + |1|/0.62 \times 10^{-5}} \right] \text{cm}^2/\text{sec} \\
= 1.29 \times 10^{-5} \text{cm}^2/\text{sec}
\]
From Eq. 6.1-18, because \( c_1 = 0.001 \text{ M} \) and \( c_2 = 0.003 \text{ M} \), we can find the same result.

---

**Example 6.1-3: Diffusion of lanthanum chloride in excess sodium chloride** How will the result of the previous example be changed if the lanthanum chloride diffuses through 1 M NaCl?

**Solution** Answering this question requires the assumption that there are no ternary diffusion effects in this system. These effects may arise because the diffusion of sodium ion couples with the diffusion of chloride ion, which in turn affects the diffusion of \( \text{La}^{3+} \). However, these effects vanish for any solute present in high dilution, as \( \text{LaCl}_3 \) is in this case (see Section 7.4).

Because of the added sodium chloride we cannot use Eq. 6.1-21, which is valid only for a single non-1-1 electrolyte. We can use Eq. 6.1-18. If we again label lanthanum as ion 1 and chloride as ion 2, we recognize that \( c_1 \) equals 0.001 M, but \( c_2 \) is about 1 M. These unequal concentrations mean that Eq. 6.1-18 becomes

\[
-j_1 = \frac{D_1 D_2 (z_2^2 c_2)}{D_1 z_1^2 c_1 + D_2 z_2^2 c_2} \nabla c_1
\]

\[
= D_1 \nabla c_1
\]

In other words, the diffusion of the lanthanum chloride is \( 0.62 \cdot 10^{-5} \text{cm}^2/\text{sec} \), which is the same as the solitary ion. Thus the diffusion of dilute \( \text{LaCl}_3 \) in concentrated NaCl is dominated by the diffusion of the uncommon ion, \( \text{La}^{3+} \).

---

### 6.1.4 Diffusion versus Conductance

Although diffusion is a very common process, diffusion coefficients can be difficult to measure. This is true for most of the systems discussed in this book, including solutions of electrolytes. However, for electrolyte solutions, the electrical resistance and its reciprocal, the electrical conductivity, are very easy to measure. Nothing in my experimental experience is as satisfying as a conductance experiment: I get fantastically accurate results with embarrassingly little effort. Because diffusion and conductance give similar information about the system, it is worth comparing the two processes in some detail.

The conductance of a single electrolyte in solution is most easily measured in cells like those shown in Fig. 6.1-3. The electrical resistance of the stirred solution is measured with a rapidly oscillating AC field of fixed maximum voltage, so that the solution remains homogeneous throughout the experiment. The resistance is inversely proportional to the current through the cell, but the current, in turn, is proportional to the ion fluxes:

\[
(\text{resistance})^{-1} = K_{\text{cell}} i = K_{\text{cell}} (z_1 j_1 + z_2 j_2)
\]

(6.1-22)

The proportionality constant \( K_{\text{cell}} \) in this relation is a function of the electrode area, the electrode separation, and the cell shape. It is found by calibration of the cell, most commonly with a potassium chloride solution.
The ion fluxes in the cell are described by equations analogous to those used for ion diffusion. First, we assume that the ion flux is proportional to the ion concentration:

\[ j_i = c_i v_i \]  

(6.1-23)

We also assume that the ion velocity is proportional to the electrical force acting on the ion:

\[ v_i = -u_i z_i \mathcal{F} \nabla \psi \]  

(6.1-24)

where, as in Eq. 6.1-2, \( u_i \) is the ion mobility and \( \psi \) is the electrostatic potential acting on the ions. Because in this case the solution is homogeneous, the concentration gradient is zero. The only flux comes from the electrostatic potential applied by the electrodes.

We now can combine Eqs. 6.1-22 through 6.1-24 to find an expression for the resistance in terms of the ion mobilities:

\[ (\text{resistance})^{-1} = K_{\text{cell}} (z_1^2 c_1 u_1 + z_2^2 c_2 u_2) \mathcal{F} \nabla \psi \]  

(6.1-25)

The ion concentrations are related to the total concentration \( c_T \) by

\[ c_T = \frac{c_1}{|z_1|} + \frac{c_2}{|z_2|} \]  

(6.1-26)

Equations 6.1-25 and 6.1-26 can now be combined and simplified to define the most convenient measure of conductivity, the equivalent conductance:

\[ \Lambda = |z_1| u_1 + |z_2| u_2 \]

\[ = \{(\text{resistance})|K_{\text{cell}} \mathcal{F} \nabla \psi|z_1 z_2/c_T^{-1}\} \]  

(6.1-27)

The quantity \( \Lambda \) is most frequently reported in studies of conductance. It can be measured by determining each of the quantities in the braces. Because the gradient is fixed, the entire quantity in brackets can be treated as a cell constant.

The equivalent conductance \( \Lambda \) can be extremely accurately measured, often to accuracies of 0.01%. It is known to vary slightly with concentration, as shown in Fig. 6.1-4. This variation follows the equation

\[ \Lambda = \Lambda_0 - S \sqrt{c_T} + E c_T \ln c_T + J c_T^{3/2} \]  

(6.1-28)