

## *Multicomponent Diffusion*

Throughout this book, we have routinely assumed that diffusion takes place in binary systems. We have described these systems as containing a solute and a solvent, although such specific labels are arbitrary. We often have further assumed that the solute is present at low concentration, so that the solutions are always dilute. Such dilute systems can be analyzed much more easily than concentrated ones.

In addition to these binary systems, other diffusion processes include the transport of many solutes. One group of these processes occurs in the human body. Simultaneous diffusion of oxygen, sugars, and proteins takes place in the blood. Mass transfer of bile salts, fats, and amino acids occurs in the small intestine. Sodium and potassium ions cross many cell membranes by means of active transport. All these physiological processes involve simultaneous diffusion of many solutes.

This chapter describes diffusion for these and other multicomponent systems. The formalism of multicomponent diffusion, however, is of limited value. The more elaborate flux equations and the slick methods used to solve them are often unnecessary for an accurate description. There are two reasons for this. First, multicomponent effects are minor in dilute solutions, and most solutions are dilute. For example, the diffusion of sugars in blood is accurately described with the binary form of Fick's law. Second, some multicomponent effects are often more lucid if described without the cumbersome equations splattered through this chapter. For example, the diffusion of oxygen and carbon dioxide in blood is better described by considering explicitly the chemical reactions with hemoglobin.

Nonetheless, some concentrated systems are best described using multicomponent diffusion equations. Examples of these systems, which commonly involve unusual chemical interactions, are listed in Table 7.0-1. They are best described using the equations derived in Section 7.1. These equations can be rationalized using the theory of irreversible thermodynamics, a synopsis of which is given Section 7.2. In most cases, the solution to multicomponent diffusion problems is automatically available if the binary solution is available; the reasons for this are given in Section 7.3. Some values of ternary diffusion coefficients are given in Section 7.4 as an indication of the magnitude of the effects involved. Finally, tracer diffusion is detailed as an example of ternary diffusion in Section 7.5.

### **7.1 Flux Equations for Multicomponent Diffusion**

Binary diffusion is often most simply described by Fick's law relative to the volume average velocity  $\mathbf{v}^0$ :

$$-\mathbf{j}_i = c_i(\mathbf{v}^0 - \mathbf{v}_i) = D\nabla c_i \quad (7.1-1)$$

Table 7.0-1 Systems with large multicomponent effects

Type of System	Examples
Solutes of very different sizes	Hydrogen–methane–argon Polystyrene–cyclohexane–toluene
Solutes in highly nonideal solutions	Mannitol–sucrose–water Acetic acid–chloroform–water
Concentrated electrolytes	Sodium sulfate–sulfuric acid–water Hydrogen chloride–polyacrylic acid–water
Concentrated alloys	Zinc–cadmium–silver Chromium–nickel–cobalt

In many cases, multicomponent diffusion is described by generalizing this equation to an  $n$ -component system:

$$-\mathbf{j}_i = c_i(\mathbf{v}^0 - \mathbf{v}_i) = \sum_{j=1}^{n-1} D_{ij} \nabla c_j \quad (7.1-2)$$

in which the  $D_{ij}$  are multicomponent diffusion coefficients. The relation between these coefficients and the binary values is not known except for the dilute-gas limit, given for ternary diffusion in Table 7.1-1. In general, the diffusion coefficients are not symmetric ( $D_{ij} \neq D_{ji}$ ). The diagonal terms (the  $D_{ii}$ ) are called the “main term” diffusion coefficients, because they are commonly large and similar in magnitude to the binary values. The off-diagonal terms (the  $D_{ij, i \neq j}$ ), called the “cross-term” diffusion coefficients, are often ten percent or less of the main terms. Each cross term gives a measure of the flux of one solute that is engendered by the concentration gradient of a second solute.

For an  $n$ -component system, this equation contains  $(n-1)^2$  diffusion coefficients. This implies that one component must be arbitrarily designated as the solvent  $n$ . Because of the Onsager reciprocal relations discussed in Section 7.2, the coefficients are not all independent but instead are subject to certain restraints:

$$\sum_{j=1}^{n-1} \sum_{l=1}^{n-1} \left( \frac{\partial \mu_l}{\partial c_i} \right)_{c_k \neq i, n} \alpha_{lj} D_{jk} = \sum_{j=1}^{n-1} \sum_{l=1}^{n-1} \left( \frac{\partial \mu_l}{\partial c_k} \right)_{c_i \neq k, n} \alpha_{lj} D_{ji} \quad (7.1-3)$$

where

$$\alpha_{lj} = \left( \delta_{lj} + \frac{c_j \bar{V}_l}{c_n \bar{V}_n} \right) \quad (7.1-4)$$

where  $\bar{V}_i$  is either a partial molar or partial specific volume, depending on whether the concentration is in moles per volume or mass per volume. These restraints reduce the number of diffusion coefficients required to describe diffusion to  $(\frac{1}{2})[n(n-1)]$  for an  $n$ -component system. However, because application of these restraints requires detailed thermodynamic information that is rarely available, the restraints are frequently impossible to apply, and by default the system is treated as having  $(n-1)^2$  independent diffusion coefficients.

Equation 7.1-2 is the most useful form of the multicomponent flux equations. Because of an excess of theoretical zeal, many who work in this area have nurtured a glut of alternatives. These zealots most commonly use different driving forces or reference

Table 7.1-1 *Ternary diffusion coefficients: known functions of binary values for ideal gases*


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$D_{11} = \left[ \frac{\frac{y_1}{\mathcal{D}_{12}} + \frac{y_2 + y_3}{\mathcal{D}_{23}}}{\frac{y_1}{\mathcal{D}_{12}\mathcal{D}_{13}} + \frac{y_2}{\mathcal{D}_{12}\mathcal{D}_{23}} + \frac{y_3}{\mathcal{D}_{13}\mathcal{D}_{23}}} \right]$
$D_{12} = \left[ \frac{y_1 \left( \frac{1}{\mathcal{D}_{12}} - \frac{1}{\mathcal{D}_{13}} \right)}{\frac{y_1}{\mathcal{D}_{12}\mathcal{D}_{13}} + \frac{y_2}{\mathcal{D}_{12}\mathcal{D}_{23}} + \frac{y_3}{\mathcal{D}_{13}\mathcal{D}_{23}}} \right]$
$D_{21} = \left[ \frac{y_2 \left( \frac{1}{\mathcal{D}_{12}} - \frac{1}{\mathcal{D}_{23}} \right)}{\frac{y_1}{\mathcal{D}_{12}\mathcal{D}_{13}} + \frac{y_2}{\mathcal{D}_{12}\mathcal{D}_{23}} + \frac{y_3}{\mathcal{D}_{13}\mathcal{D}_{23}}} \right]$
$D_{22} = \left[ \frac{\frac{y_1 + y_3}{\mathcal{D}_{13}} + \frac{y_2}{\mathcal{D}_{12}}}{\frac{y_1}{\mathcal{D}_{12}\mathcal{D}_{13}} + \frac{y_2}{\mathcal{D}_{12}\mathcal{D}_{23}} + \frac{y_3}{\mathcal{D}_{13}\mathcal{D}_{23}}} \right]$

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velocities. Unfortunately, most of their answers are of limited value. The exception is for some metal alloys.

The best alternative to Eq. 7.1-2 is the Maxwell–Stefan equation for dilute gases:

$$\nabla y_i = \sum_{j=1}^{n-1} \frac{y_i y_j}{\mathcal{D}_{ij}} (\mathbf{v}_j - \mathbf{v}_i) \quad (7.1-5)$$

This equation has two major advantages over Eq. 7.1-2. First, these diffusion coefficients are the binary values found from binary experiments or calculated from the Chapman–Enskog theory given in Section 5.1. Second, the Stefan–Maxwell equations do not require designating one species as solvent, which is sometimes an inconvenience when using Eq. 7.1-2.

These advantages can be compromised for multicomponent liquid mixtures. There, the nonideal solutions require a somewhat different form

$$\frac{\nabla \mu_i}{RT} = \sum_{j=1}^{n-1} \frac{x_j}{\mathcal{D}'_{ij}} (\mathbf{v}_j - \mathbf{v}_i) \quad (7.1-6)$$

For an ideal solution in which

$$\mu_i = \mu_i^\circ + RT \ln x_i \quad (7.1-7)$$

this reduces to the ideal gas form. The new  $\mathcal{D}'_{ij}$  are a new set of diffusion coefficients often believed to be more closely related to the binary form. This belief seems to me to rest more

on faith than on data. Still, some researchers believe that this Maxwell–Stefan formulation is superior to Equation 7.1-2 because it does not require designating a solvent.

At the same time, the Maxwell–Stefan form has a serious disadvantage. It is difficult to combine with mass balances without designating one of the species as a solvent. Moreover, in many cases we benefit from identifying transport in one direction as occurring by diffusion and in the other direction as dominated by convection. When I use the Maxwell–Stefan form, I can lose this physical insight. Thus in practice, the advantage of this form is often lost. As a result, I feel Eq. 7.1-2 remains the most useful form of flux equation. We next examine the origins of these equations more carefully using irreversible thermodynamics.

## 7.2 Irreversible Thermodynamics

The multicomponent flux equations given in Eq. 7.1-2 are empirical generalizations of Fick’s law that define a set of multicomponent diffusion coefficients. Because such definitions are initially intimidating, many have felt the urge to rationalize the origin of these equations and buttress this rationale with “more fundamental principles.” This emotional need is often met with derivations based on irreversible thermodynamics.

Because the derivation of irreversible thermodynamics is straightforward, it seems on initial reading to be extremely valuable. After all those years of laboring under the restraint of equilibrium, the treatment of departures from equilibrium seems like a new freedom. Eventually one realizes that although irreversible thermodynamics does give the proper form of the flux equations and clarifies the number of truly independent coefficients, this information is of little value because it is already known from experiment. Irreversible thermodynamics tells us nothing about the nature and magnitude of the coefficients in the multicomponent equations, nor the resulting size and nature of the multicomponent effects. These are the topics in which we are interested. As a result, irreversible thermodynamics has enjoyed an overoptimistic vogue, first in chemical physics, next in engineering, and then in biophysics. Subsequently, it has been deemphasized as its limitations have become recognized. Because irreversible thermodynamics is of limited utility in describing multicomponent diffusion, only the barest outline will be given here.

### 7.2.1 The Entropy Production Equation

Three basic postulates are involved in the derivation of Eq. 7.1-2 (Fitts, 1962). The first postulate states that thermodynamic variables such as entropy, chemical potential, and temperature can in fact be correctly defined in a *differential volume* of a system that is not at equilibrium. This is an excellent approximation, except for systems that are very far from equilibrium, such as explosions. In the simple derivation given here, we assume a system of constant density, temperature, and pressure, with no net flow or chemical reaction. More complete equations without these assumptions are derived elsewhere (e.g., Haase, 1969).

The mass balance for each species in this type of system is given by

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{n}_i = -\nabla \cdot \mathbf{j}_i \quad (7.2-1)$$

In this continuity equation, we use the fact that at no net flow and constant density,  $n_i$  equals  $j_i$ , the flux relative to the volume or mass average velocity. We also imply that the concentration is expressed in mass per unit volume. The left-hand side of this equation represents solute accumulation, and the right-hand side represents the solute diffusing in minus that diffusing out. The energy equation is similar:

$$\rho \frac{\partial \hat{H}}{\partial t} = -\nabla \cdot \mathbf{q} - \nabla \cdot \sum_{i=1}^n \bar{H}_i \mathbf{j}_i \quad (7.2-2)$$

where  $\mathbf{q}$  is the conductive heat flux, and  $\bar{H}_i$  is the partial specific enthalpy. The left-hand side of this relation is the accumulation, the first term on the right-hand side is the energy conducted in minus that conducted out, and the second term is the energy diffusing in minus that diffusing out. Because we are assuming an isothermal system,  $\mathbf{q}$  is presumably zero; we include it here so that the equation will look more familiar.

By parallel arguments, we can write a similar equation for entropy:

$$\rho \frac{\partial \hat{S}}{\partial t} = -\nabla \cdot \mathbf{J}_s + \sigma \quad (7.2-3)$$

By analogy, the term on the left must be the entropy accumulation. The first term on the right includes  $\mathbf{J}_s$ , which is entropy in minus entropy out by both convection and diffusion. The second term on the right,  $\sigma$ , gives the entropy produced in the process. This entropy production, which must be positive, is the quantitative measure of irreversibility in the system and represents a novel contribution of irreversible thermodynamics.

To find the entropy production, we first recognize that in this isothermal system,

$$d\hat{G} = d\hat{H} - Td\hat{S} = \frac{1}{\rho} \sum_{i=1}^n \mu_i dc_i \quad (7.2-4)$$

in which  $\mu_i$  is the partial Gibbs free energy per unit mass, not the usual form of chemical potential; and  $\rho$  is the total mass density. This equation suggests that

$$\rho T \frac{\partial \hat{S}}{\partial t} = \rho \frac{\partial \hat{H}}{\partial t} - \sum_{i=1}^n \mu_i \frac{\partial c_i}{\partial t} \quad (7.2-5)$$

Combining with Eqs. 7.2-1 and 7.2-2

$$\rho T \frac{\partial \hat{S}}{\partial t} = -\nabla \cdot \mathbf{q} - \nabla \cdot \sum_{i=1}^n \bar{H}_i \mathbf{j}_i - \sum_{i=1}^n \mu_i (\nabla \cdot \mathbf{j}_i) \quad (7.2-6)$$

However,

$$\mu_i (\nabla \cdot \mathbf{j}_i) = \nabla \cdot (\bar{H}_i - T\bar{S}_i) \mathbf{j}_i - (\mathbf{j}_i \cdot \nabla \mu_i) \quad (7.2-7)$$

Combining Eqs. 7.2-6 and 7.2-7,

$$\rho \frac{\partial \hat{S}}{\partial t} = -\nabla \cdot \left[ \frac{\mathbf{q}}{T} + \sum_{i=1}^n \bar{S}_i \mathbf{j}_i \right] - \frac{1}{T} \sum_{i=1}^n \mathbf{j}_i \cdot \nabla \mu_i \quad (7.2-8)$$

By comparison with the entropy balance, Eq. 7.2-3, we see that the entropy flux is

$$\mathbf{J}_s = \frac{\mathbf{q}}{T} + \sum_{i=1}^n \hat{S}_i \mathbf{j}_i \quad (7.2-9)$$

The first and second terms on the right-hand side are the entropy flux by conduction and by diffusion, respectively.

The entropy production can also be found by comparing Eqs. 7.2-3 and 7.2-8:

$$\sigma = -\frac{1}{T} \sum_{i=1}^n \mathbf{j}_i \cdot \nabla \mu_i \quad (7.2-10)$$

The terms in this equation have units of energy per volume per time per temperature. Not all the fluxes and gradients in Eq. 7.2-1 are independent, because

$$\sum_{i=1}^n \mathbf{j}_i = 0 \quad (7.2-11)$$

and, because the pressure and temperature are constant,

$$\sum_{i=1}^n c_i \nabla \mu_i = 0 \quad (7.2-12)$$

Using these restraints, we can rewrite Eq. 7.2-10 in terms of  $n - 1$  fluxes and gradients relative to any reference velocity. In particular, for the mass average velocity, we can show that

$$\sigma = -\frac{1}{T} \sum_{i=1}^{n-1} \mathbf{j}_i \cdot \mathbf{X}_i \quad (7.2-13)$$

with the more general driving forces  $\mathbf{X}_i$  given by

$$\mathbf{X}_i = \sum_{j=1}^{n-1} \left( \delta_{ij} + \frac{c_j}{c_n} \right) \nabla \mu_j \quad (7.2-14)$$

Strictly speaking, Eqs. 7.3-13 and 7.3-14 apply only to the mass average reference velocity and  $\mathbf{j}_i$  should be the flux relative to this velocity. Other reference velocities can also be used with other general forces. For example, for the volume average velocity, we may show that

$$\sigma = -\frac{1}{T} \sum_{i=1}^{n-1} \mathbf{j}_i \cdot \mathbf{X}_i^0 \quad (7.2-15)$$

where  $\mathbf{j}_i$  is now relative to the volume average velocity, where

$$\mathbf{X}_i^0 = \sum_{j=1}^{n-1} \alpha_{ij} \nabla \mu_j \quad (7.2-16)$$

and where the  $\alpha_{ij}$  are given by Eq. 7.1-4. Eq. 7.2-15 is identical with Eq. 7.2-13 for a system of constant density, when the partial specific volumes all equal the reciprocal

of the density, and volume and mass fractions are identical. We will use the volume average velocity and the associated fluxes and forces in the remainder of this chapter because these forms are those commonly used for fluids.

### 7.2.2 The Linear Laws

The second postulate in the derivation of irreversible thermodynamics is that a linear relation exists between the forces and fluxes in Eq. 7.2-15

$$-\mathbf{j}_i = \sum_{j=1}^{n-1} L_{ij} \mathbf{X}_j^0, \quad (7.2-17)$$

where the  $L_{ij}$  have the mind-bending name of “Onsager phenomenological coefficients.” These  $L_{ij}$  are strong functions of concentration, especially in dilute solution, where they approach zero as  $c_i \rightarrow 0$ . The linear law can be derived mathematically by use of a Taylor series in which all but the first terms are neglected, but because I am unsure when this neglect is justified, I prefer to regard the linear relation as a postulate.

### 7.2.3 The Onsager Relations

The third and final postulate is that the  $L_{ij}$  are symmetric, that is,

$$L_{ij} = L_{ji} \quad (7.2-18)$$

These symmetry conditions, called the Onsager reciprocal relations (Onsager, 1931), can be derived by means of perturbation theory if “microscopic reversibility” is valid. The physical significance of microscopic reversibility is best visualized for a binary collision in which two molecules start in some initial positions, collide, and wind up in some new positions. If the velocities of these molecules are reversed and if microscopic reversibility is valid, the two molecules will move backward, retracing their paths through the collision to regain their original initial positions, just like a movie running backward. Those unfamiliar with the temperament of molecules running backward may be mollified by recalling that the symmetry suggested by Eq. 7.2-18 has been verified experimentally. Thus we can accept Eq. 7.2-18 as a theoretical result or as an experimentally verified postulate.

### 7.2.4 The Flux Equations

Using these three postulates, we can easily complete the derivation of the multicomponent flux equations from irreversible thermodynamics. We first rewrite Eq. 7.2-17 in terms of concentration gradients. Because the  $\bar{V}_i$  are partial extensive quantities,

$$\sum_{i=1}^n \bar{V}_i \nabla c_i = 0 \quad (7.2-19)$$

Those less well versed in thermodynamics can get the same result by assuming that the partial molar volumes are constant. As a result, only  $n - 1$  concentration gradients are independent:

$$\nabla \mu_i = \sum_{j=1}^{n-1} \left( \frac{\partial \mu_i}{\partial c_j} \right)_{c_{k \neq j, n}} \nabla c_j \quad (7.2-20)$$

Note that the concentrations that are held constant in this differentiation differ from those that are commonly held constant in partial differentiation. If we combine Eqs. 7.2-16, 7.2-17, and 7.2-20, we obtain

$$-j_i = \sum_{j=1}^{n-1} D_{ij} \nabla c_j \quad (7.2-21)$$

where

$$D_{ij} = \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} L_{ik} \alpha_{kl} \left( \frac{\partial \mu_l}{\partial c_j} \right)_{c_{m \neq j, n}} \quad (7.2-22)$$

where the  $\alpha_{kl}$  are those given by Eq. 7.1-4. Thus, by starting our argument with conservation equations plus an equation for entropy production, we have derived multicomponent diffusion equations using only three postulates.

We still know nothing from this theory about the diffusion coefficients  $D_{ij}$ ; we must evaluate these from experiment. Finding these coefficients commonly requires solving the flux equations with the techniques developed in the next section.

### 7.3 Solving the Multicomponent Flux Equations

In general, solving the multicomponent diffusion problems is not necessary if the analogous binary problem has already been solved (Toor, 1964; Stewart and Prober, 1964). We can mathematically convert the multicomponent problem into a binary problem, look up the binary solution, and then convert this solution back into the multicomponent one. In other words, multicomponent problems usually can be solved using a cookbook approach; little additional work is needed. Some use this cookbook to convert fairly comprehensible binary problems into multicomponent goulash that is harder to understand than necessary.

In this section, we first give the results for ternary diffusion and then for the general approach. By starting with the ternary results, we hope to help those who need to solve simple problems. They should not have to dig through the matrix algebra unless they decide to do so.

#### 7.3.1 The Ternary Solutions

A binary diffusion problem has a solution that can be written as

$$\Delta c_1 = \Delta c_{10} F(D) \quad (7.3-1)$$



In this,  $\Delta c_1$  is a concentration difference that generally varies with position and time,  $\Delta c_{10}$  is some reference concentration difference containing initial and boundary conditions, and  $F(D)$  is the explicit function of position and time. For example, for the diaphragm cell, the binary solution is (see Example 2.2-4)

$$(c_{1B} - c_{1A}) = (c_{1B}^0 - c_{1A}^0)e^{-\beta Dt} \quad (7.3-2)$$

where  $c_{1i}^0$  and  $c_{1i}$  are the concentrations in the diaphragm-cell compartment  $i$  at times zero and  $t$ , respectively,  $\beta$  is the cell calibration constant, and  $D$  is the diffusion coefficient. By comparison of Eqs. 7.3-1 and 7.3-2, we see that  $\Delta c_1$  is  $c_{1B} - c_{1A}$ ,  $\Delta c_{10}$  is  $c_{1B}^0 - c_{1A}^0$ , and  $F(D)$  is  $e^{-\beta Dt}$ .

Every binary diffusion problem has an analogous ternary diffusion problem that is described by similar differential equations and similar initial and boundary conditions. The differential equations differ only in the form of Fick's law that is used. The conditions are also parallel. For example, in a binary problem the solute concentration may be fixed at a particular boundary, so in the corresponding ternary problem, solute concentrations will also be fixed at the corresponding boundary. When this is true, the ternary diffusion problems have the solutions

$$\Delta c_1 = P_{11}F(\sigma_1) + P_{12}F(\sigma_2) \quad (7.3-3)$$

and

$$\Delta c_2 = P_{21}F(\sigma_1) + P_{22}F(\sigma_2) \quad (7.3-4)$$

in which the concentration differences  $\Delta c_1$  and  $\Delta c_{10}$  are the dependent and independent values in the binary problem,  $F(D)$  is again the solution to the binary problem, and the values of  $\sigma_i$  and  $P_{ij}$  are given in Table 7.3-1 (Cussler, 1976). The  $\sigma_i$  are the eigenvalues (with relative weighting factors  $\rho$ ) of the diffusion-coefficient matrix and hence are a type of pseudobinary diffusion coefficient.

The calculation of the ternary diffusion profile is now routine. For example, the result for solute 1 in the diaphragm cell will be

$$\begin{aligned} c_{1B} - c_{1A} = & \frac{(D_{11} - \sigma_2)(c_{1B}^0 - c_{1A}^0) + D_{12}(c_{2B}^0 - c_{2A}^0)}{\sigma_1 - \sigma_2} e^{-\sigma_1 t} \\ & + \frac{(D_{11} - \sigma_1)(c_{1B}^0 - c_{1A}^0) + D_{12}(c_{2B}^0 - c_{2A}^0)}{\sigma_2 - \sigma_1} e^{-\sigma_2 t} \end{aligned} \quad (7.3-5)$$

The results for the second solute can be found from Eq. 7.3-4 or by rotating the indices in Eq. 7.3-5.

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**Example 7.3-1: Fluxes for ternary free diffusion** Find the fluxes and the concentration profiles in a dilute ternary free-diffusion experiment. In such an experiment, one ternary solution is suddenly brought into contact with a different composition of the same ternary solution. Find the flux and the concentrations versus position and time at small times.

Table 7.3-1 Factors for solution of ternary diffusion problems

*Eigenvalues*

$$\sigma_1 = \frac{1}{2}[D_{11} + D_{22} + \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}]$$

$$\sigma_2 = \frac{1}{2}[D_{11} + D_{22} - \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}]$$

*Weighting factors*

$$P_{11} = \left( \frac{D_{11} - \sigma_2}{\sigma_1 - \sigma_2} \right) \Delta c_{10} + \left( \frac{D_{12}}{\sigma_1 - \sigma_2} \right) \Delta c_{20}$$

$$P_{12} = \left( \frac{D_{11} - \sigma_1}{\sigma_2 - \sigma_1} \right) \Delta c_{10} + \left( \frac{D_{12}}{\sigma_2 - \sigma_1} \right) \Delta c_{20}$$

$$P_{21} = \left( \frac{D_{21}}{\sigma_1 - \sigma_2} \right) \Delta c_{10} + \left( \frac{D_{22} - \sigma_2}{\sigma_1 - \sigma_2} \right) \Delta c_{20}$$

$$P_{22} = \left( \frac{D_{21}}{\sigma_2 - \sigma_1} \right) \Delta c_{10} + \left( \frac{D_{22} - \sigma_1}{\sigma_2 - \sigma_1} \right) \Delta c_{20}$$

*Note:* For further definitions, see Eqs. 7.1-2, 7.3-1, 7.3-3, and 7.3-4.

**Solution** When the two solutions come in contact for only a short time, they are effectively infinitely thick. The binary solution of this problem is (see Eq. 2.3-15)

$$\frac{c_1 - c_{10}}{c_{1\infty} - c_{10}} = \operatorname{erf} \frac{z}{\sqrt{4Dt}}$$

in which  $c_{10}$  and  $c_{1\infty}$  are the concentrations where the solutions are contacted (at  $z = 0$ ) and far into one solution (at  $z = \infty$ ), respectively,  $z$  and  $t$  are the position and time, and  $D$  is the binary diffusion coefficient. By comparison with Eq. 7.3-1, we see that  $\Delta c_1$  is  $c_1 - c_{10}$ ,  $\Delta c_{10}$  is  $c_{1\infty} - c_{10}$  and  $F(D)$  equals the error function of  $z/\sqrt{4Dt}$ . As a result the concentration profile for solute 1 will be

$$\begin{aligned} c_1 - c_{10} = & \left[ \frac{(D_{11} - \sigma_2)(c_{1\infty} - c_{10}) + D_{12}(c_{2\infty} - c_{20})}{\sigma_1 - \sigma_2} \right] \operatorname{erf} \frac{z}{\sqrt{4\sigma_1 t}} \\ & + \left[ \frac{(D_{11} - \sigma_1)(c_{1\infty} - c_{10}) + D_{12}(c_{2\infty} - c_{20})}{\sigma_2 - \sigma_1} \right] \operatorname{erf} \frac{z}{\sqrt{4\sigma_2 t}} \end{aligned}$$

The close similarity between this result and that for the diaphragm cell is obvious.

The fluxes can be found in the same manner as the concentration profile. Because the solutions are dilute, there is negligible convection induced by diffusion, so

$$-n_1 \doteq -j_1 = D_{11} \frac{\partial c_1}{\partial z} + D_{12} \frac{\partial c_2}{\partial z}$$

Combining this with Eqs. 2.3-17, 7.3-3, and 7.3-4,

$$-j_1 = (D_{11}P_{11} + D_{12}P_{21}) \frac{e^{-z^2/4\sigma_1 t}}{\sqrt{\pi\sigma_1 t}} \\ + (D_{11}P_{12} + D_{12}P_{22}) \frac{e^{-z^2/4\sigma_2 t}}{\sqrt{\pi\sigma_2 t}}$$

where again the  $P_{ij}$  are given in Table 7.3-1. These results are complex algebraically but straightforward conceptually.

### 7.3.2 The General Solution

We now turn from the detail of ternary diffusion to the more general solution of the multicomponent problems. The general solution of these equations is most easily presented in terms of linear algebra, a notation that is not used elsewhere in this book. In this presentation, we consider the species concentrations as a vector of  $\underline{c}$  and the multicomponent diffusion coefficients as a matrix  $\underline{\underline{D}}$ .

In matrix notation, the multicomponent flux equations are

$$-\underline{j} = \underline{\underline{D}} \cdot \nabla \underline{c} \quad (7.3-6)$$

The continuity equations for this case are

$$\frac{\partial \underline{c}}{\partial t} + (\nabla \cdot v^0 \underline{c}) = -\nabla \cdot \underline{j} \quad (7.3-7)$$

These are subject to the initial and boundary conditions

$$\Delta \underline{c}(x, y, z, t = 0) = \Delta \underline{c}_0 \quad (7.3-8)$$

$$\Delta \underline{c}(B, t) = 0 \quad (7.3-9)$$

$$\frac{\partial \underline{c}}{\partial z}(b, t) = 0 \quad (7.3-10)$$

where  $B$  and  $b$  represent two boundaries of the system. Note that the boundary conditions on all concentrations must have the same functional form. This is a serious restriction only for the case of simultaneous diffusion and chemical reaction.

We now assume that there exists a nonsingular matrix  $\underline{\underline{t}}$  that can diagonalize  $\underline{\underline{D}}$ :

$$\underline{\underline{t}}^{-1} \cdot \underline{\underline{D}} \cdot \underline{\underline{t}} = \underline{\underline{\sigma}} = \begin{bmatrix} \sigma_1 & 0 & 0 & \dots \\ 0 & \sigma_2 & 0 & \dots \\ 0 & 0 & \sigma_3 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \quad (7.3-11)$$

where  $\underline{\underline{t}}^{-1}$  is the inverse of  $\underline{\underline{t}}$  and  $\underline{\underline{\sigma}}$  is the diagonal matrix of the eigenvalues of the diffusion coefficient matrix  $\underline{\underline{D}}$ . The assumption that  $\underline{\underline{D}}$  can be put into diagonal form is not necessary for a general mathematical solution, but because this assumption is

valid for all cases encountered in practice, it is used here. For the case of ternary diffusion,

$$\underline{\underline{t}} = \begin{bmatrix} t_{11} & t_{12} \\ t_{21} & t_{22} \end{bmatrix} = \frac{\begin{bmatrix} 1 & \frac{D_{12}}{D_{22} - \sigma_1} \\ \frac{D_{22} - \sigma_2}{D_{12}} & 1 \end{bmatrix}}{\left[1 - \left(\frac{\sigma_2 - D_{22}}{\sigma_1 - D_{22}}\right)\right]} = \frac{\begin{bmatrix} 1 & \frac{D_{11} - \sigma_1}{D_{21}} \\ \frac{D_{21}}{D_{11} - \sigma_2} & 1 \end{bmatrix}}{\left[1 - \left(\frac{\sigma_1 - D_{11}}{\sigma_2 - D_{11}}\right)\right]} \quad (7.3-12)$$

Correspondingly,

$$\underline{\underline{t}}^{-1} = \begin{bmatrix} t_{11}^{-1} & t_{12}^{-1} \\ t_{21}^{-1} & t_{22}^{-1} \end{bmatrix} = \frac{\begin{bmatrix} 1 & \frac{D_{12}}{\sigma_1 - D_{22}} \\ \frac{\sigma_2 - D_{22}}{D_{12}} & 1 \end{bmatrix}}{\det(\underline{\underline{t}})} = \frac{\begin{bmatrix} 1 & \frac{\sigma_1 - D_{11}}{D_{21}} \\ \frac{D_{21}}{\sigma_2 - D_{11}} & 1 \end{bmatrix}}{\det(\underline{\underline{t}})} \quad (7.3-13)$$

where

$$\det(\underline{\underline{t}}) = \frac{\sigma_1 - \sigma_2}{\sigma_1 - D_{22}} = \frac{\sigma_2 - \sigma_1}{\sigma_2 - D_{11}} \quad (7.3-14)$$

Remember that the product of  $\underline{\underline{t}}$  and its inverse  $\underline{\underline{t}}^{-1}$  is the unit matrix.

We now use this new matrix  $\underline{\underline{t}}$  to define a new combined concentration  $\underline{\Psi}$

$$\underline{\underline{c}} = \underline{\underline{t}} \cdot \underline{\Psi} \quad (7.3-15)$$

We combine Eqs. 7.3-6, 7.3-7, and 7.3-15 and premultiply the equation by  $\underline{\underline{t}}^{-1}$  to obtain

$$\frac{\partial \underline{\Psi}}{\partial t} + \nabla \cdot \mathbf{v}^0 \underline{\Psi} = \underline{\underline{\sigma}} \cdot \nabla^2 \underline{\Psi} \quad (7.3-16)$$

which represents a set of scalar equations

$$\frac{\partial \Psi_i}{\partial t} + \nabla \cdot \mathbf{v}^0 \Psi_i = \sigma_i \cdot \nabla^2 \Psi_i \quad (7.3-17)$$

In this operation, we have made the assumption that  $\underline{\underline{D}}$  and hence both  $\underline{\underline{t}}$  and  $\underline{\underline{\sigma}}$  are not functions of composition.

The initial and boundary conditions can also be written in terms of the new combined concentration  $\underline{\Psi}$ :

$$\Delta \underline{\Psi}(x, y, z, 0) = \Delta \underline{\Psi}_0 = \underline{\underline{t}}^{-1} \cdot \Delta \underline{c}_0 \quad (7.3-18)$$

$$\Delta \underline{\Psi}(B, t) = 0 \quad (7.3-19)$$

$$\frac{\partial \underline{\Psi}}{\partial z}(b, t) = 0 \quad (7.3-20)$$

Thus a set of coupled differential equations has been separated into uncoupled equations written in terms of the new concentration  $\underline{\Psi}$ .

Equations 7.3-16 through 7.3-20 have exactly the same form as the associate *binary* diffusion problem:

$$\frac{\partial c_1}{\partial t} + \nabla \cdot \mathbf{v}^0 c_1 = D \nabla^2 c_1 \quad (7.3-21)$$

which has the same initial and boundary conditions for each species as those given in Eqs. 7.3-8 through 7.3-10. If this binary problem has the solution

$$\Delta c_1 = F(D) \Delta c_{10} \quad (7.3-22)$$

then Eqs. 7.3-17 through 7.3-20 must have the solution

$$\Delta \Psi_i = F(\sigma_i) \Delta \Psi_{i0} \quad (7.3-23)$$

where the eigenvalue  $\sigma_i$  is substituted everywhere that the binary diffusion coefficient occurs in the binary solution. If we rewrite our solution in terms of the actual concentrations, we find that

$$\Delta \underline{c} = \underline{t} \cdot \underline{F}(\underline{\sigma}) \cdot \underline{t}^{-1} \cdot \Delta \underline{c}_0 \quad (7.3-24)$$

Thus we know the concentration profiles in the multicomponent system in terms of its binary analogue. The results for the ternary case are given in Eqs. 7.3-3 and 7.3-4.

Many find this derivation difficult to grasp, even after they apparently understand every step. Their trouble usually stems from a mathematical, not physical, problem. They do not see why the derivation is more than a trick, a slick invention. The reason is that Eq. 7.3-17 and its associated conditions are shown to be mathematically the same as the binary solution. If we change the symbol  $\Psi_i$  to  $c_1$ , Eq. 7.3-17 and Eq. 7.3-21 are exactly the same. The physical circumstances in the multicomponent problem may be more elaborate, but the identity of the differential equations signals that the mathematical solutions are identical.

**Example 7.3-2: Steady-state multicomponent diffusion across a thin film** In steady-state binary diffusion, we found that the solute's concentration varied linearly across a thin film. Will solute concentrations vary linearly in the multicomponent case? What will the flux be?

**Solution** By comparison with Eq. 2.2-9, we see that

$$(c_1 - c_{10}) = \left(\frac{z}{l}\right)(c_{1l} - c_{10})$$

By comparing this with Eq. 7.3-22, we see that  $F(D)$  equals  $(z/l)$ . From Eq. 7.3-24, for the multicomponent case,

$$\Delta \underline{c} = \left(\underline{t} \cdot \frac{z}{l} \underline{\delta} \cdot \underline{t}^{-1}\right) \cdot \Delta \underline{c}_0 = \left(\frac{z}{l}\right) \Delta \underline{c}_0$$

Thus the concentration profile of each solute remains linear. The flux is

$$\begin{aligned} -\underline{j} &= \underline{D} \cdot \nabla \underline{c} \\ &= \underline{D} \cdot \frac{\Delta \underline{c}_0}{l} \end{aligned}$$

or

$$j_i = \sum_{j=1}^{n-1} \frac{D_{ij}}{l} (c_{j0} - c_{jl})$$

Note that a solute’s flux can be in the opposite direction to that expected if other gradients exist in the system.

7.4 Ternary Diffusion Coefficients

In this section, we report a variety of values for ternary diffusion coefficients. These coefficients support the generalizations given at the beginning of this chapter that multicomponent effects were significant when the system was concentrated and contained interacting species. These interactions can originate from chemical reactions, from electrostatic coupling, or from major differences in molecular weights.

Typical diffusion coefficients for gases are shown in Table 7.4-1. These values are not experimental, but are calculated from the Chapman–Enskog theory (see Section 5.1) and from Table 7.1-1. The first two rows in the table show how the values of  $D_{12}$  and  $D_{21}$  are larger as the solution becomes concentrated. The second and third rows refer to the same solution but with a different species chosen as the solute. The difference in the diffusion coefficients illustrates why ternary diffusion coefficients can be difficult to interpret. The final three rows are other characteristic situations.

Table 7.4-1 Ternary diffusion coefficients in gases at 25°C

System	$D_{11}$	$D_{12}$	$D_{21}$	$D_{22}$
Hydrogen ( $x_1 = 0.05$ )				
Methane ( $x_2 = 0.05$ )	0.78	−0.00	0.03	0.22
Argon ( $x_3 = 0.90$ )				
Hydrogen ( $x_1 = 0.2$ )				
Methane ( $x_2 = 0.2$ )	0.76	−0.01	0.12	0.25
Argon ( $x_3 = 0.6$ )				
Argon ( $x_1 = 0.6$ )				
Methane ( $x_2 = 0.2$ )	0.64	−0.39	−0.12	0.37
Hydrogen ( $x_3 = 0.2$ )				
Carbon dioxide ( $x_1 = 0.2$ )				
Oxygen ( $x_2 = 0.2$ )	0.15	−0.00	−0.01	0.19
Nitrogen ( $x_3 = 0.6$ )				
Hydrogen ( $x_1 = 0.2$ )				
Ethylene ( $x_2 = 0.2$ )	0.56	0.00	0.11	0.13
Ethane ( $x_3 = 0.6$ )				
Benzene ( $x_1 = 0.2$ )				
Cyclohexane ( $x_2 = 0.2$ )	0.028	0.000	0.001	0.026
Hexane ( $x_3 = 0.6$ )				

Note: All coefficients have units of square centimeters per second and are calculated from the equations in Table 7.1-1.

Ternary diffusion coefficients in liquids and solids cannot be found from binary values, but only from experiments. When experiments are not available, which is usually the case, one can make estimates by assuming that the Onsager phenomenological coefficients are a diagonal matrix; that is,

$$L_{ij}, i \neq j = 0 \quad (7.4-1)$$

In addition, we can assume that the main-term coefficients are related to the binary values given by

$$L_{ii} = \left( \frac{D_i c_i}{RT} \right) \quad (7.4-2)$$

where  $D_i$  is the coefficient of species  $i$  in the solvent. These assumptions can be combined with Eq. 7.1-4 and Eq. 7.2-20 to give

$$D_{ij} = \left( \frac{D_i c_i}{RT} \right) \sum_{l=1}^{n-1} \left( \delta_{il} + \frac{c_l \bar{V}_i}{c_n \bar{V}_n} \right) \left( \frac{\partial \mu_l}{\partial c_j} \right)_{c_{k \neq j, n}} \quad (7.4-3)$$

This is equivalent to saying that ternary effects result from activity coefficients. I routinely use this equation for making initial estimates.

Experimental values of ternary diffusion coefficients characteristic of liquids are shown in Table 7.4-2. In cases like KCl–NaCl–water, KCl–sucrose–water, and toluene–chlorobenzene–bromobenzene, the cross-term diffusion coefficients are small, less than ten percent of the main diffusion coefficients. In these cases, we can safely treat the diffusion as a binary process.

The cross-term diffusion coefficients are much more significant for interacting solutes. In cases like HBr–KBr–water and  $\text{H}_2\text{SO}_4$ – $\text{Na}_2\text{SO}_4$ –water, this interaction is ionic; in other cases, it may involve hydrogen-bond formation. Cross-term diffusion coefficients and the resulting ternary effects should be especially large in partially miscible systems, where few measurements have been made.

The ternary diffusion coefficients in metals shown in Table 7.4-3 have the largest cross-term values. As a result, the flux of one component in an alloy can be against its concentration gradient, from low concentration into higher concentration. These effects are especially interesting when they are superimposed on the elaborate phase diagrams characteristic of alloys because they can lead to local phase separations that dramatically alter the material's properties. As in gases and liquids, the methods of estimating ternary diffusion coefficients are risky. One must either rely on relations like Eq. 7.4-3 or undertake the difficult experiments involved. As a result, many avoid ternary diffusion even when they suspect it is important.

## 7.5 Tracer Diffusion

Imagine we want to study the diffusion of steroids like progesterone through human blood. The amounts of these steroids will be very small, making direct chemical analysis difficult. As a result, we synthesize steroids that contain carbon 14 as

Table 7.4-2 Ternary diffusion coefficients in liquids at 25 °C<sup>a</sup>

System	$D_{11}$	$D_{12}$	$D_{21}$	$D_{22}$
1.5-M KCl (1)				
1.5-M NaCl (2)	1.80	0.33	0.10	1.39
H <sub>2</sub> O (3) <sup>b</sup>				
0.10-M HBr (1)				
0.25-M KBr (2)	5.75	0.05	-2.20	1.85
H <sub>2</sub> O (3) <sup>c</sup>				
1-M H <sub>2</sub> SO <sub>4</sub> (1)				
1-M Na <sub>2</sub> SO <sub>4</sub> (2)	2.61	-0.04	-0.51	0.91
H <sub>2</sub> O (3) <sup>d</sup>				
0.06 g/cm <sup>3</sup> KCl (1)				
0.03 g/cm <sup>3</sup> sucrose (2)	1.78	0.02	0.07	0.50
H <sub>2</sub> O (3) <sup>e</sup>				
2-M urea (1)				
O-M <sup>14</sup> C-tagged urea (2)	1.24	0.01	0.00	1.23
H <sub>2</sub> O (3) <sup>f</sup>				
32 mol% hexadecane (1)				
35 mol% dodecane (2)	1.03	0.23	0.27	0.97
33 mol% hexane (3) <sup>g</sup>				
25 mol% toluene (1)				
50 mol% chlorobenzene (2)	1.85	-0.06	-0.05	1.80
25 mol% bromobenzene (3) <sup>h</sup>				
0.326 g/cm <sup>3</sup> benzene (1)				
0.265 g/cm <sup>3</sup> propanol (2)	1.64	0.78	0.17	1.33
Carbon tetrachloride (3) <sup>i</sup>				
5 wt% cyclohexane (1)				
5 wt% polystyrene (2)	2.03	-0.09	-0.02	0.09
90 wt% toluene (3) <sup>j</sup>				

Notes: <sup>a</sup>All values  $\times 10^{-5}$  square centimeters per second. <sup>b</sup>P. J. Dunlop, *J. Phys. Chem.*, **63**, 612 (1959). <sup>c</sup>A. Reojin, *J. Phys. Chem.*, **76**, 3419 (1972). <sup>d</sup>R. P. Wendt, *J. Phys. Chem.*, **66**, 1279 (1962). <sup>e</sup>E. L. Cussler and P. J. Dunlop, *J. Phys. Chem.*, **70**, 1880 (1966). <sup>f</sup>J. G. Albright and R. Mills, *J. Phys. Chem.*, **69**, 3120 (1966). <sup>g</sup>T. K. Kett and D. K. Anderson, *J. Phys. Chem.*, **73**, 1268 (1969). <sup>h</sup>J. K. Burchard and H. L. Toor, *J. Phys. Chem.*, **66**, 2015 (1962). <sup>i</sup>R. A. Graff and T. B. Drew, *IEC Fund.*, **7**, 490 (1968) (data at 200 °C). <sup>j</sup>E. L. Cussler and E. N. Lightfoot, *J. Phys. Chem.*, **69**, 1135 (1965).

a radioactive label. We then measure the steroid concentration, and calculate diffusion coefficients from these concentration measurements.

This measurement of tracer diffusion in dilute solution is a good strategy. Such a use of radioactive tracers provides a near-unique opportunity for a specific chemical analysis in highly dilute solution. Such analysis is especially important in biological systems, where complex chemistry may compromise analysis. Moreover, in dilute solution, the diffusion coefficients found with radioactive tracers are almost always indistinguishable from those measured in other ways. Exceptions occur in those systems in which the solute moves by a jump mechanism like that for protons (see Fig. 6.1.-1) or in which the solute's molecular weight is significantly altered by the isotopic mass.



Table 7.4-3 Ternary interdiffusion coefficients in solids<sup>a</sup>

Ternary system 1-2-3	Composition (mol%) and structure at temperature studied	Temperature (°C)	$D_{11}^3$	$D_{12}^3$	$D_{21}^3$	$D_{22}^3$
C-Si-Fe <sup>b</sup>	0.46C-1.97Si-97.57Fe (FCC)	1,050	$4.8 \times 10^{-7}$	$0.3 \times 10^{-7}$	$\approx 0$	$2.3 \times 10^{-9}$
Al-Ni-Fe	47Al-18Ni-35Fe (BCC) <sup>c</sup>	1,004	$4.4 \times 10^{-11}$	$-0.2 \times 10^{-11}$	$0.3 \times 10^{-11}$	$1.6 \times 10^{-11}$
	43Al-8.5Ni-48.5Fe (BCC) <sup>c</sup>	1,004	$16.4 \times 10^{-11}$	$-5.9 \times 10^{-11}$	$0.3 \times 10^{-11}$	$2.5 \times 10^{-11}$
	8Al-44.5Ni-48.5Fe (BCC) <sup>d</sup>	1,000	$23.3 \times 10^{-12}$	$-9.2 \times 10^{-12}$	$-9.9 \times 10^{-12}$	$16.4 \times 10^{-12}$
	9.5Cr-20.4Ni-70Co	1,300	$0.6 \times 10^{-9}$	$-0.13 \times 10^{-11}$	$-0.12 \times 10^{-10}$	$0.23 \times 10^{-9}$
Cr-Ni-Co <sup>e</sup>	8.8Cr-40Ni-51Co		$1.09 \times 10^{-9}$	$-0.6 \times 10^{-11}$	$-2.6 \times 10^{-10}$	$0.47 \times 10^{-9}$
	9.2Cr-79Ni-11.8Co (FCC)		$1.25 \times 10^{-9}$	$-2.5 \times 10^{-11}$	$-5.1 \times 10^{-10}$	$0.74 \times 10^{-9}$
	13.1Zn-3.5Cd-83.4Ag	600	$1.2 \times 10^{-10}$	$1.3 \times 10^{-10}$	$0.13 \times 10^{-10}$	$1.2 \times 10^{-10}$
Zn-Cd-Ag <sup>f</sup>	18.1Zn-4.4Cd-77.5Ag		$3.3 \times 10^{-10}$	$2.4 \times 10^{-10}$	$0.6 \times 10^{-10}$	$2.1 \times 10^{-10}$
	16.4Zn-8.5Cd-75.1Ag (FCC)		$4.4 \times 10^{-10}$	$4.5 \times 10^{-10}$	$1.4 \times 10^{-10}$	$5.5 \times 10^{-10}$
	10.3Zn-1.8Mn-87.9Cu (FCC)	850	$1.82 \times 10^{-9}$	$0.11 \times 10^{-9}$	$-0.02 \times 10^{-9}$	$1.46 \times 10^{-9}$
Zn-Mn-Cu <sup>g</sup>	19Zn-43Ni-38Cu (FCC)	775	$5.1 \times 10^{-11}$	$-0.8 \times 10^{-11}$	$-1.7 \times 10^{-11}$	$1.2 \times 10^{-11}$
V-Zr-Ti <sup>i</sup>	9V-9Zr-82Ti	800	$2.3 \times 10^{-10}$	$0.1 \times 10^{-10}$	$1.0 \times 10^{-10}$	$4.4 \times 10^{-10}$
	17.5V-19.5Zr-63Ti		$2.9 \times 10^{-10}$	$1.5 \times 10^{-10}$	$0.7 \times 10^{-10}$	$1.8 \times 10^{-10}$
	37.5V-7.5Zr-55Ti		$0.16 \times 10^{-10}$	$0.18 \times 10^{-10}$	$0.1 \times 10^{-10}$	$0.23 \times 10^{-10}$
	5.0V-77.5Zr-17.5Ti (FCC)		$12.4 \times 10^{-10}$	$2.6 \times 10^{-10}$	$-0.8 \times 10^{-10}$	$2.8 \times 10^{-10}$
Cu-Ag-Au <sup>j</sup>	13.1Cu-34.0Ag-52.9Au	725	$1.0 \times 10^{-10}$	$0.1 \times 10^{-10}$	$1.7 \times 10^{-10}$	$1.3 \times 10^{-10}$
	60.3Cu-12.9Ag-26.8Au (FCC)		$2.3 \times 10^{-10}$	$1.1 \times 10^{-10}$	$1.8 \times 10^{-10}$	$3.1 \times 10^{-10}$
Co-Ni-Fe <sup>k</sup>	10.3Co-31.4Ni-58.3Fe	1,315	$4 \times 10^{-10}$	$0.9 \times 10^{-10}$	$3 \times 10^{-10}$	$7.1 \times 10^{-10}$
	35.5Co-35.4Ni-29.1Fe		$6.5 \times 10^{-10}$	$2.7 \times 10^{-10}$	$3.2 \times 10^{-10}$	$7.3 \times 10^{-10}$
	31.1Co-65.6Ni-3.3Fe (FCC)		$6.1 \times 10^{-10}$	$0.2 \times 10^{-10}$	$4.0 \times 10^{-10}$	$8.8 \times 10^{-10}$

Note: <sup>a</sup>All diffusion coefficients are in square centimeters per second and are based on a solvent-fixed reference frame. <sup>b</sup>J. Kirkaldy, *Can. J. Phys.*, **35**, 435 (1957). <sup>c</sup>T. D. Moyer and M. A. Dayananda, *Met. Trans.*, **7A**, 1035 (1976). <sup>d</sup>G. H. Cheng and M. A. Dayananda, *Met. Trans.*, **10A**, 1415 (1979). <sup>e</sup>G. Guy and V. Leroy, *The Electron Microprobe*, eds. McKinley, T.D., Heinrich, K.F.J., and Wittky, D.B., New York: John Wiley and Sons (1966). <sup>f</sup>P. T. Carlson, M. A. Dayananda, and R. E. Grace, *Met. Trans.*, **3**, 819 (1972). <sup>g</sup>M. A. Dayananda and R. E. Grace, *Trans. Met. Soc. AMIE*, **233**, 1287 (1965). <sup>h</sup>R. D. Sisson, Jr. and M. A. Dayananda, *Met. Trans.*, **8A**, 1849 (1977). <sup>i</sup>A. Brunsch and S. Steel, *Zeit. Metallkunde*, **65**, 765 (1974). <sup>j</sup>T. O. Ziebold and R. E. Ogilvie, *Trans. Met. Soc. AMIE*, **239**, 942 (1967). <sup>k</sup>A. Vignes and J. P. Sabatier, *Trans. Met. Soc. AMIE*, **245**, 1795 (1969).

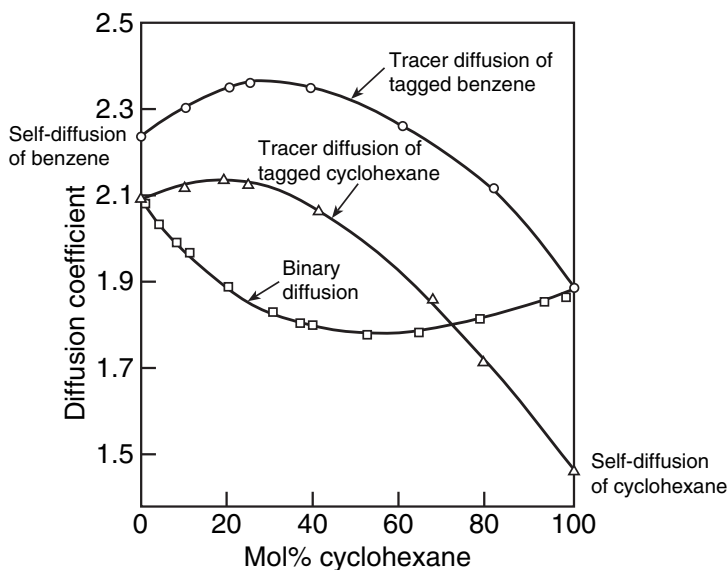


Fig. 7.5-1. Binary and tracer diffusion at 25 °C. The tracer diffusion coefficient equals the binary coefficient only in certain special cases. All coefficients are  $\times 10^{-5}$  square centimeters per second. [From Mills (1965), with permission.]

In concentrated solution, tracer diffusion is a much more complex process which may not provide coefficients identical with those in the binary system. This is illustrated by the data in Fig. 7.5-1. In this figure, we see that the diffusion coefficients using different radioactive isotopes can differ from each other and from the binary diffusion coefficient. On reflection, we realize that this is not surprising; the diffusion of radioactively tagged benzene in untagged benzene is obviously a different process than the diffusion of tagged cyclohexane in benzene.

Explaining these differences requires more careful definitions (Albright and Mills, 1965). *Binary diffusion* occurs with two chemically distinct species. In contrast, *intradiffusion* occurs with three distinguishable species. One of these species is chemically different. The other two species are very similar, for they have the same chemical formula, the same boiling point, the same viscosity, and so forth. They differ only in their isotopic composition or their asymmetrical structure. Nonetheless, this means that intradiffusion involves three species.

There are two important special cases of intradiffusion. The first, *tracer diffusion*, is the limit when the concentration of one similar species is small. This is the usual situation when one uses radioactive isotopes, for high concentrations of radioactive material are expensive, risky, and unnecessary. The second special case, *self-diffusion*, occurs when the system contains a radioactively tagged solute in an untagged but otherwise chemically identical solvent. This system may also contain traces of other solutes and so still may have more than two components. These different definitions are identified in Fig. 7.5-1.

The best available description of these various forms of diffusion is supplied by the multicomponent equations developed earlier in this chapter. Indeed, tracer diffusion is a simple example by which you can test your understanding of these ideas. To begin this

description, we define the tracer as species 1, the identical unlabeled compound as species 2, and the different species as the solvent 3. The flux equations for this system are then

$$-j_1 = D_{11} \nabla c_1 \quad (7.5-1)$$

$$-j_2 = D_{21} \nabla c_1 + D_{22} \nabla c_2 \quad (7.5-2)$$

The coefficient  $D_{12}$  is zero because the tracer concentration  $c_1$  is always near zero. When  $c_1$  and  $c_2$  are both very small,  $D_{11}$  is the tracer diffusion coefficient of species 1 in species 3. When  $c_3$  is very small,  $D_{11}$  is the self-diffusion coefficient of species 1 in species 2. We will imitate the literature and relabel the coefficient  $D_{11}$  as  $D^*$ , a reminder that it is often radioactively tagged.

We can also reach conclusions about the coefficients  $D_{22}$  and  $D_{21}$ . Since species 1 is always present at vanishingly small concentrations,  $D_{22}$  must be the binary diffusion coefficient  $D$  of species 2 in solvent 3. This has other implications. The total flux of species 1 and 2 must be the sum of the fluxes above

$$\begin{aligned} -(j_1 + j_2) &= (D_{11} + D_{21}) \nabla c_1 + D_{22} \nabla c_2 \\ &= (D^* + D_{21}) \nabla c_1 + D \nabla c_2 \end{aligned} \quad (7.5-3)$$

But now imagine that our radiation detector is broken, so we can't measure  $c_1$ ; we can only measure  $(c_1 + c_2)$ . We can still measure the binary diffusion coefficient  $D$  using the relation

$$-(j_1 + j_2) = D \nabla (c_1 + c_2) \quad (7.5-4)$$

By comparing Eqs. 7.5-3 and 7.5-4, we see that

$$D_{21} = D - D^* \quad (7.5-5)$$

Thus in this special case of ternary diffusion, the four diffusion coefficients can be written in terms of two: the tracer and the binary. This reduction to two coefficients is a consequence of the chemical identity of the solutes 1 and 2.

The physical reasons why the tracer and the binary coefficients are different can most easily be seen for the case of a dilute gas mixture of a tagged solute 1, an untagged solute 2, and a solvent 3. Diffusion in this system is described in terms of solute-solvent collisions and solute-solute collisions. Solute-solvent collisions are characterized by collision diameters  $\sigma_{13}$  and  $\varepsilon_{13}$ . Solute-solute collisions are described by  $\sigma_{12}$  and  $\varepsilon_{12}$ . With these diameters and energies, the binary diffusion coefficient can be shown from Table 7.1-1 to be a function only of solute-solvent collisions:

$$D_{22} = D = D(\sigma_{23}, \sigma_{23}) = D(\sigma_{13}, \sigma_{13}) \quad (7.5-6)$$

On the other hand, the intradiffusion coefficient  $D^*$  is seen from this table to be a weighted harmonic average of solute-solvent and solute-solute collisions:

$$D_{11} = D^* = \frac{1}{\frac{y_3}{D(\sigma_{23}, \sigma_{23})} + \frac{y_1 + y_2}{D(\sigma_{12}, \sigma_{12})}} \quad (7.5-7)$$

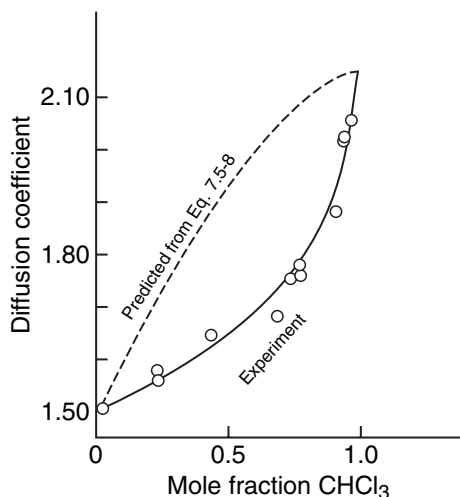


Fig. 7.5-2. Binary diffusion predicted from tracer diffusion. In general, binary diffusion cannot be predicted from tracer diffusion and activity data using empirical relations like Eq. 7.5-8. The data, for chloroform–carbon tetrachloride at 25 °C, are square centimeters per second. [From Kelly, Wirth, and Anderson (1971), with permission.]

Note that when  $(y_1 + y_2)$  is nonzero,  $D^*$  is not equal to  $D$ . In the limit of infinite dilution, both  $y_1$  and  $y_2$  approach zero, and  $D^*$  equals  $D$ .

Many investigators have tried to discover empirical connections between binary diffusion and intradiffusion. The most common is the assertion that

$$D = D^* \left( 1 + \frac{\partial \ln \gamma_1}{\partial \ln c_1} \right) \quad (7.5-8)$$

in which  $D$  is the binary diffusion coefficient,  $D^*$  is the intradiffusion coefficient measured with a radioactive tracer, and the quantity in parentheses is the increasingly familiar activity correction for diffusion. This empirical assertion is often buttressed by theoretical arguments, especially those based on the irreversible thermodynamics described in Section 7.2. Equation 7.5-8 does not always work experimentally, as shown by the results in Fig. 7.5-2.

Why Eq. 7.5-8 sometimes fails is illustrated by the case of dilute gases. Binary diffusion involves only solute–solvent interactions. Intradiffusion and tracer diffusion are the result not only of solute–solvent interactions but also of solute–solute interactions. Thus  $D^*$  contains different information than  $D$ , information characteristic of dynamic collisions as well as equilibrium activities. This difference means in general that  $D^*$  cannot be found only from  $D$  and activity coefficients.

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**Example 7.5-1: Tracer and binary diffusion of hydrogen and benzene** Find the tracer diffusion coefficient of  $^{14}\text{C}$ -tagged benzene in gas mixtures of hydrogen and benzene. At 25 °C, the binary diffusion coefficient is  $0.40 \text{ cm}^2/\text{sec}$ , and the self-diffusion coefficient of benzene is  $0.03 \text{ cm}^2/\text{sec}$ .

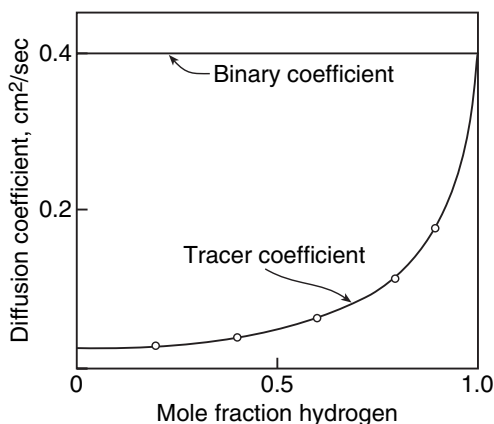


Fig. 7.5-3. Binary versus tracer diffusion of hydrogen gas and benzene vapor. The benzene is the species tagged with radioactivity. The differences between the binary and tracer values are unusually large in this case.

**Solution** To be consistent with the preceding development, let species 1, 2, and 3 be radioactively tagged benzene, untagged benzene, and hydrogen, respectively. Then, from Eq. 7.5-6, we see that the binary coefficient is

$$D = 0.40 \text{ cm}^2/\text{sec}$$

This coefficient is independent of concentration. The tracer diffusion coefficient is found from Eq. 7.5-7

$$D^* = \frac{1}{\frac{y_3}{0.40} + \frac{1-y_3}{0.03}}$$

This result is shown versus hydrogen concentration in Fig. 7.5-3. In this case, the binary and tracer values differ by an unusually large amount, a consequence of the exceptional mobility of hydrogen.

## 7.6 Conclusions

Diffusion frequently occurs in multicomponent systems. When these systems are dilute, the diffusion of each solute can be treated with a binary form of Fick's law. In concentrated solutions, the fluxes and concentration profiles deviate significantly from binary expectations only in exceptional cases. These exceptions include mixed gases containing hydrogen, mixed weak electrolytes, partially miscible species, and some alloys.

When multicomponent diffusion is significant, it is best described with a generalized form of Fick's law containing  $(n - 1)^2$  diffusion coefficients in an  $n$ -component system. This form of diffusion equation can be rationalized using irreversible thermodynamics. Concentration profiles in these multicomponent cases can be directly inferred from the binary results. However, multicomponent diffusion coefficients are difficult to estimate, and experimental values are fragmentary. As a result, you should make very sure that you need the more complicated theory before you attempt to use it.

### Questions for Discussion

1. In what multicomponent mixture can diffusion be accurately described with the binary form of Fick's law?
2. When are multicomponent diffusion coefficients different from the binary values?
3. What is a cross-term diffusion coefficient?
4. When can diffusion in one phase go from low concentration to higher concentration?
5. What is an advantage and a disadvantage of the Fick's law form of ternary diffusion equations (Eq. 7.1-2)?
6. What is an advantage and a disadvantage of the Maxwell-Stefan form of ternary diffusion equations (Eq. 7.1-5)?
7. What are the Onsager reciprocal relations?
8. Will multicomponent effects be greatest in gases, liquids, or solids?
9. How can you find a ternary concentration profile if you know the solution of an analogous binary one?
10. When will tracer diffusion equal binary diffusion?
11. Imagine a system of equimolar amounts of hydrogen and ethylene containing a trace of tritium. The diffusion coefficient of tritium would not equal the diffusion coefficient of hydrogen. Explain why without using equations.
12. Diffusion of two gases in a porous medium can be treated as ternary diffusion, where the third species is the porous medium itself. Write and simplify equations for this case.

### Problems

1. Imagine a thin membrane separating two large volumes of aqueous solution. The membrane is 0.014 cm thick and has a void fraction of 0.32. One solution contains 2-M  $\text{H}_2\text{SO}_4$  and the other 2-M  $\text{Na}_2\text{SO}_4$ . As a result, there is no gradient of sulfate across the membrane. Ternary diffusion coefficients for this system are given in Table 7.4-2. What is the sulfate flux? *Answer:*  $5.6 \cdot 10^{-7} \text{ mol/cm}^2 \text{ sec}$ .
2. A solution of 12 mol% hexadecane (1), 55 mol% dodecane (2), and 33 mol% hexane (3) is diffusing at 25 °C in a diaphragm cell into a solution of 52 mol% hexadecane (1), 15 mol% dodecane (2), and 33 mol% hexane (3). The cell constant of the cell is  $3.62 \text{ cm}^{-2}$ , and the ternary diffusion coefficients are

$$\begin{aligned} D_{11} &= 1.03, & D_{12} &= 0.23, \\ D_{21} &= 0.27, & D_{22} &= 0.97 \end{aligned}$$

all times  $10^{-5} \text{ cm}^2/\text{sec}$ . Plot the concentration differences  $\Delta c_1$  and  $\Delta c_2$  versus time.

3. In a two-bulb capillary diffusion apparatus like that in Fig. 3.1-2, one bulb contains 75%  $\text{H}_2$  and 25%  $\text{C}_6\text{H}_6$ , and the other contains 65%  $\text{H}_2$ , 34.9%  $\text{C}_6\text{H}_6$ , and 0.1% radioactively tagged  $\text{C}_6\text{H}_6$ . The system is at 0 °C. We can measure diffusion in one of two ways. First, we can measure the concentration change of all the benzene using a gas chromatograph. Second, we can measure the concentration difference of the radioactive isotopes. How different are these results? To answer this problem, let 1 be

tracer, 2 be untagged benzene, and 3 be hydrogen solvent. (a) Find the ternary diffusion coefficients assuming that the radioactive concentration is much less than the nonradioactive. (b) Using the binary solution, write out the ternary one. (c) Combine parts (a) and (b) to find  $\Delta c_1$  and  $\Delta c_2$  versus  $\beta t$ , where  $\beta$  is the cell constant of this apparatus.

4. An iron bar containing 0.86 mol% carbon is joined with a bar containing 3.94 mol% silicon. The two bars are then heated to 1,050 °C for 13 days; under these conditions, there is only one equilibrium phase, FCC austenite. Calculate the carbon concentration profile under these conditions using the values in Table 7.4-3. Remember that these coefficients are relative to the *solvent average* velocity.
5. In practical work, air is often treated as if it is a pure species. This problem tests the accuracy of this assumption for diffusion. Imagine a large slab of an isotropic porous solid centered at  $z=0$ . To the left, at  $z < 0$ , the solid's pores initially contain pure hydrogen; to the right, at  $z > 0$ , they initially contain pure air. If air were really a single component, then the mole fraction of hydrogen  $y_1$  would vary as follows (see Section 2.3, assuming that the total molar concentration  $c$  is a constant.):

$$y_1 = \frac{1}{2} \left( 1 - \operatorname{erf} \frac{z}{\sqrt{4Dt}} \right)$$

Because air is really a mixture, the exact solution involves ternary diffusion coefficients that can be calculated from Table 7.1-1. Calculate the ternary concentration profile and compare it with the binary one (S. Gehrke).

6. You are using the diaphragm cell to study diffusion in the ternary system sucrose(1)–KCl(2)–water(3). Instead of measuring the concentration differences of each species in these experiments, you find it convenient to measure the overall density and refractive-index differences, defined as

$$\Delta \rho = H_1 \Delta \rho_1 + H_2 \Delta \rho_2$$

$$\Delta n = R_1 \Delta \rho_1 + R_2 \Delta \rho_2$$

In separate experiments, you find  $H_1 = 0.379$ ,  $H_2 = 0.602$ ,  $R_1 = 0.1414$ , and  $R_2 = 0.1255$ . You find the calibration constant of the cell to be  $0.462 \text{ cm}^{-2}$ . Other relevant data are in the following table: [E. L. Cussler and P. J. Dunlop, *J. Phys. Chem.*, **70**, 1880 (1966)]:

	Exp. 20	Exp. 26	Exp. 24	Exp. 22
$\Delta \rho^{10}$	0.0000	0.00277	0.01111	0.01500
$\Delta \rho^{20}$	0.0150	0.01250	0.00313	0.00000
$\Delta n^0$	86.33	89.88	89.96	97.21
$\Delta \rho^0$	0.00904	0.00856	0.00609	0.00569
$\Delta n$	28.24	33.56	46.34	55.38
$\Delta \rho$	0.00293	0.00299	0.00279	0.00315
$10^{-5} \beta t$	0.627	0.620	0.9526	1.0598

Use these data to calculate the four ternary diffusion coefficients, and compare them with the following values found with the Gouy interferometer:  $D_{11} = 0.497$ ,  $D_{12} = 0.021$ ,

$D_{21} = 0.069$ ,  $D_{22} = 1.775$  (all times  $10^{-5} \text{ cm}^2/\text{sec}$ ). Answer:  $D_{11} = 0.498$ ,  $D_{12} = 0.022$ ,  $D_{21} = 0.071$ ,  $D_{22} = 1.776$  (all times  $10^{-5} \text{ cm}^2/\text{sec}$ ).

7. Ternary diffusion effects are expected to be common in the molten silicates that occur in the center of the Earth. In a study of one such melt, Spera and Trial [*Science* **259**, 204 (1993)] report for 40 mol% CaO (1)–20 mol%  $\text{Al}_2\text{O}_3$ –40 mol%  $\text{SiO}_2$  at 1500 K that

$$D_{11} = (10.0 \pm 0.10) \cdot 10^{-7} \text{ cm}^2/\text{sec}; \quad D_{12} = (-2.8 \pm 0.8) \cdot 10^{-7} \text{ cm}^2/\text{sec};$$

$$D_{21} = (-4.2 \pm 0.8) \cdot 10^{-7} \text{ cm}^2/\text{sec}; \quad D_{22} = (7.3 \pm 0.4) \cdot 10^{-7} \text{ cm}^2/\text{sec};$$

Large coefficients like these provide a good chance to check the Onsager reciprocal relations (cf. Eq. 7.2-18):

$$L_{12} = L_{21}$$

This is equivalent to

$$D_{11}\alpha_{12} + D_{21}\alpha_{22} = D_{12}\alpha_{11} + D_{22}\alpha_{21}$$

These authors also estimate that

$$\alpha_{11} = 8.15 \cdot 10^6 \text{ J/kg}; \quad \alpha_{12} = 4.25 \cdot 10^6 \text{ J/kg};$$

$$\alpha_{21} = 4.25 \cdot 10^6 \text{ J/kg}; \quad \alpha_{22} = 4.00 \cdot 10^6 \text{ J/kg};$$

Do the Onsager relations hold?

## Further Reading

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