Diffusivity and Mobility Data
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DIFFUSION is the process by which molecules, atoms, ions, point defects, or other particle types migrate from a region of higher concentration to one of lower concentration. The diffusivity of an atom or diffusion coefficient is the rate at which a particle migrates through a particular material and is dependent on the temperature, composition gradient, and pressure. Diffusivity determines how quickly equilibrium is reached from a nonequilibrium state. In solid-state materials, diffusion can occur by a variety of different mechanisms. Lattice diffusion (bulk or volume diffusion) occurs as a result of individual jumps of atoms or point defects, such as vacancies, divacancies, or interstitials, within the crystal. Diffusion may also occur along the surface or along line defects, such as grain boundaries or dislocations. These mechanisms and much of the published diffusion data is for bulk diffusion processes, this article focuses primarily on the diffusivity data and modeling of lattice diffusion in solid-state materials. A list of symbols is in Table 1.

Diffusion Mechanisms

In a crystal, lattice vibrations cause atoms to oscillate around equilibrium positions with frequencies, $v_0$ (~10^12 to 10^15 Hz); however, occasionally the oscillations are large enough to allow an atom to jump to a different lattice site, resulting in diffusion of the atom. In the absence of a driving force, the energy barrier that an atom must overcome to jump to an empty site is the free energy of migration, $G_m$.

Figure 1 shows the $G_m$ as a function of atomic line, planar, and surface diffusion mechanisms are generally much faster than the lattice-diffusion-based mechanisms and, as a result, are termed high-diffusivity paths (or short-circuit diffusivity). Depending on the temperature and/ or microstructure of the material, these high-diffusivity paths or bulk diffusion may be the dominate diffusion mechanism. As a wide variety of microstructural processes are controlled by lattice diffusion mechanisms and much of the published diffusion data is for bulk diffusion processes, this article focuses primarily on the diffusivity data and modeling of lattice diffusion in solid-state materials. A list of symbols is in Table 1.
position. The jump rate, \( \omega \), for an atom to jump to a neighboring empty site is given by:

\[
\omega = v_0 \exp\left(-\frac{\Delta G_{\text{m}}}{RT}\right) \quad \text{where} \quad \Delta G_{\text{m}} = H_m - TS_m
\]  

(Eq 1)

where \( v_0 \) is the atomic vibration frequency, \( R \) is the gas constant, \( T \) is the temperature in Kelvin, and \( H_m \) and \( S_m \) are the enthalpy and entropy of migration. The jump frequency, \( \Gamma \), of an atom is then defined as the jump rate times the probability, \( p \), of the next neighboring site being vacant:

\[
\Gamma = \omega p
\]  

(Eq 2)

Two of the most common mechanisms by which atoms diffuse are interstitial diffusion and vacancy diffusion. Intersitial diffusion occurs as small interstitial atoms, which are solute atoms that are considerably smaller than the solvent atoms, jump from one interstitial site to the next-nearest unoccupied interstitial site. Thus, for a dilute interstitial alloy, the probability defined in Eq 2 is approximately equal to 1, and the diffusion rate in the absence of any driving force (concentration gradient) is:

\[
D = \left[ \frac{a^2 v_0 \exp\left(\frac{S_m}{R} - \frac{H_m}{RT}\right)}{10} \right]
\]  

(Eq 3)

where \( a \) is the nearest-neighbor atomic distance, and \( g \) is a geometric factor that depends on the lattice geometry and the type of interstitial site (i.e., octahedral or tetrahedral). This expression is commonly simplified to an Arrhenius-type equation:

\[
D = D_0 \exp\left(-\frac{\Delta Q}{RT}\right) \quad \text{where} \quad D_0 = \frac{10}{g a^2 v_0 \exp\left(\frac{S_m}{R} - \frac{H_m}{RT}\right)}
\]  

(Eq 4)

Vacancy-driven diffusion occurs when a nearest-neighbor atom (substitutional solute atom) jumps onto an unoccupied lattice site. The probability of the nearest-neighbor site being vacant, \( p \), from Eq 2, is defined by the thermal equilibrium vacancy concentration, \( c^\text{eq}_V \), which is given by:

\[
c^\text{eq}_V = \exp\left(\frac{S_V}{R} - \frac{H_V}{RT}\right)
\]  

(Eq 5)

where \( S_V \) and \( H_V \) are the formation entropy and enthalpy, respectively, of a vacancy. Thus, similar to Eq 3 for the interstitial diffusion rate, the substitutional diffusion rate in the absence of a driving force is given by:

\[
D = \left[ f a^2 v_0 \exp\left(\frac{S_m + S_v}{R} - \frac{(H_m + H_v)}{RT}\right) \right]
\]  

(Eq 6)

where \( f \) is the correlation factor that determined by the crystal structure. Like Eq 3, 6 can be written in terms of an Arrhenius relation, where:

\[
D_0 = f a^2 v_0 \exp\left(\frac{S_m + S_v}{R} - \frac{(H_m + H_v)}{RT}\right)
\]

and \( \Delta Q = H_V + H_m \). It should be noted that while these Arrhenius-type relations (Eq 4 and 6) are common. They are not universal. Grain-boundary, impurities, or other microstructural features; temperature-dependent activation parameters; and other active diffusion mechanisms may all result in deviations from an Arrhenius relation.

**Diffusion Equation**

In a steady-state one-dimensional system, the flux of particles is proportional to the concentration gradient:

\[
J_i = -D \frac{\partial c_i}{\partial z}
\]  

(Eq 7)

where \( J_i \) describes the amount of material that passes through a unit area of a plane per unit time \( t \) within a volume-fixed frame of reference (otherwise known as flux). The variable \( D_i \) is the diffusivity of component \( i \) for a given diffusion mechanism. The variable \( c_i \) is the concentration of particles \( i \) (Note: \( c_i = z x_i V_m \), where \( x_i \) is the mole fraction of component \( i \), and \( V_m \) is the molar volume of the phase), and \( z \) is the diffusion distance. Equation 7, better known as Fick’s law (Ref 1, 2), assumes there are no external forces or driving forces acting on the particles and is formally identical to Fourier’s law of heat conduction and Ohm’s law of current flow.

For a nonsteady-state one-dimensional system where the flux at each point varies with time, Fick’s law must be combined with a mass balance or continuity equation (Eq 8) to determine the time-dependent concentration, where \( t \) is the time in seconds:

\[
\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial z} \left( D_i \frac{\partial c_i}{\partial z} \right)
\]  

(Eq 8)

Equations 7 and 8 are combined to form the general diffusion equation, which is a second-order linear partial differential equation and cannot be solved analytically:

\[
\frac{\partial c_i}{\partial t} = D_i \frac{\partial}{\partial z} \left( \frac{\partial c_i}{\partial z} \right)
\]

(Eq 9)

However, if \( D_i \) is assumed to be concentration independent, the diffusion equation can be solved for a variety of initial and boundary conditions, as demonstrated by Ref 3 and 4. Two simple examples of these solutions that are commonly used experimentally are the thin-film and error-function solutions.

**The thin-film solution** assumes that a thin layer, with a thickness, \( b \), of the diffusing species \( A \) is concentrated at \( z = 0 \) of a semi-infinite sample, as seen in Fig. 2. Then, concentration profiles after time, \( t \), are given by:

\[
c(z, t) = \frac{b c_0}{\sqrt{4 \pi D t}} \exp\left(-\frac{z^2}{4 D t}\right)
\]  

(Eq 10)

where \( c_0 \) is the initial concentration of the \( A \) layer. The diffusion length, \( \lambda \), is represented by the \( \sqrt{D t} \) quantity and is a characteristic length used in solving diffusion equations. The thin-film solution is valid for applications where \( \lambda \) is much greater than the initial layer thickness. The geometry represented by the thin-film solution (Eq 10) is commonly used to measure tracer diffusion coefficients in substitutional alloys (defined in the section “Tracer Diffusivity” in this article).

**Infinite and Semi-Infinite Solutions.** Error-function solutions can be applied to semi-infinite and infinite samples. The concentration profiles in a semi-infinite solid with a constant concentration of a component at the surface, \( c_o \), are defined by the following error functions and initial and boundary conditions:

Initial conditions: \( t = 0; \ z > 0; \ c_o(z, 0) = c_o \), where \( c_o \) is the initial concentration in the solid

Boundary conditions: at all \( t > 0, \ z = 0; \ c(0, t) = c_i \)

The concentration profile for a given time is then given by:

\[
c(z, t) = \frac{c_i - c_0}{c_i - c_o} \frac{z}{2 \sqrt{D t}} \text{erf}\left(\frac{z}{2 \sqrt{D t}}\right)
\]

(Eq 11)

These types of solutions are applicable to modeling various carburization and coating problems.

For an infinite sample with a concentration profile defined by a step function, the composition profile at given time, \( t \), is:

\[
c(z, t) = \left\{ \begin{array}{ll}
\frac{c_0}{2} & \text{for} \ z = 0 \\
\frac{c_0}{2} & \text{for} \ z > 0
\end{array} \right.
\]

(Eq 12)

where the initial boundaries at \( t = 0 \) are given by:

\[
t = 0 \frac{z(0)}{c} = c_i \quad c = c_0 \quad z = 0, c = c_i
\]

and \( c_1 \) and \( c_2 \) are the compositions at either end of the infinite couple, as seen in Fig. 3. This type of solution is often used when the diffusion distances in the two materials are much smaller than the width of the samples. While analytical solutions to the diffusion equation assuming a constant diffusivity are useful in solving some practical problems, to solve most problems of interest, the composition and temperature dependence of the diffusivity must be considered, and the equation must be solved numerically.
**Diffusivity Data**

Diffusivity in a material can be evaluated in variety of different ways, including measurement of diffusion coefficients, composition profiles, and layer growth widths. Tracer, intrinsic, and chemical diffusivities can all be extracted from various types of direct and indirect diffusion experiments. Table 2 reviews some of the common direct and indirect methods to measure these diffusion coefficients. Direct experiments are based on Fick’s law (Eq 7) and the phenomenological definitions of the diffusion coefficients. Indirect experimental methods are not based on Fick’s law and require a microscopic model of the atomic jump processes to deduce a diffusion coefficient.

**Tracer Diffusivity.** Tracer diffusion is the migration of a tagged atom through a material of which it is a component. As such, the tracer diffusivity is generally measured by introducing a radioactive isotope in dilute concentration into an otherwise homogeneous material. Thus, the only driving force in the system is that of the concentration gradient of the tracer. In a homogeneous material, the mean square displacement of the tracer in the z-direction is defined by the Einstein formula for Brownian motion (random walk) as:

\[
\langle z^2 \rangle = 2D_{t}t \quad \text{where} \quad D_{t} = RTM_i
\]

(Eq 13)

where \( D_{t} \) is the tracer diffusion coefficient, \( t \) is the diffusion time, and \( M_i \) is the atomic mobility of the \( i \) atoms or the movement of atoms in response to a given force, in this case, the result of continuous random movement. (Note that for a multicomponent alloy, the mobility is a function of each component in the alloy. Further description of the calculation of the composition-dependent mobility matrix is given in the section “Disordered Phase” in this article.) The tracer diffusion coefficient is equal to the self-diffusion coefficient, \( D_{i}^s \), if diffusion takes place by uncorrelated atomic jumps; otherwise, the tracer diffusion coefficient is related to the self-diffusion coefficient by the correlation factor, \( f = D_{i}^s / fD_{i}^s \). The correlation factor is dependent on crystal structure and introduces off-diagonal terms into the \( M_i \) matrix. For the body-centered cubic (bcc) and face-centered cubic (fcc) crystal structures assuming a vacancy-diffusion mechanism, the contribution of these off-diagonal terms is small. Thus, for simplicity, these terms are not included in the present discussion; however, calculation methods are discussed by Ref 5 and 6. When a tracer impurity is measured in a homogeneous material (i.e., solute C in a pure A alloy or homogeneous AB alloy), the measured tracer diffusivity is often referred to as the impurity diffusivity.

**Chemical Diffusivity (Interdiffusion).** In contrast to tracer diffusivity measurements that only consider negligible amounts of a tracer element in an otherwise homogeneous material, interdiffusion (chemical diffusion) and intrinsic diffusion coefficient measurements are performed in nonhomogeneous materials where the diffusion flux is proportional to the gradient of the chemical potential (e.g., in the presence of a driving force). The interdiffusion coefficient, \( VD_{i}^s \), is defined in the volume-fixed frame of reference, where the sum of the fluxes equals zero, and is given by:

![Fig. 2 Schematic of (a) thin-film geometry and (b) solution. (a) A thin layer of the diffusing species (A atoms per unit area) is concentrated at z = 0. As time increases, the A atoms diffuse such that concentration becomes negligible. (b) The concentration of A atoms as a function of distance for different times, where the time increments are given as \( D_{t}t \), where \( D \) is a constant.](image)

### Table 2 Direct and indirect methods for measuring diffusion coefficients

<table>
<thead>
<tr>
<th>Method</th>
<th>( \Delta x )</th>
<th>( D_i ), ( \text{m}^2/\text{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Direct</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lath sectioning, grinding</td>
<td>0.1–1000 ( \mu \text{m} )</td>
<td>( 10^{-10} ) to ( 10^{-10} )</td>
</tr>
<tr>
<td>Microtome</td>
<td>1–10 ( \mu \text{m} )</td>
<td>( 10^{-17} ) to ( 10^{-12} )</td>
</tr>
<tr>
<td>Chemical</td>
<td>10 ( \mu \text{m} )</td>
<td>( 10^{-17} ) to ( 10^{-11} )</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>50 ( \mu \text{m} )</td>
<td>( 10^{-20} ) to ( 10^{-17} )</td>
</tr>
<tr>
<td>Sputtering</td>
<td>5–100 ( \text{nm} )</td>
<td>( 10^{-22} ) to ( 10^{-17} )</td>
</tr>
<tr>
<td>Modulated structures</td>
<td>0.5–5 ( \text{nm} )</td>
<td>( 10^{-22} ) to ( 10^{-17} )</td>
</tr>
<tr>
<td>Ion microprobe (secondary ion mass spectroscopy)</td>
<td>1–100 ( \text{nm} )</td>
<td>( 10^{-23} ) to ( 10^{-17} )</td>
</tr>
<tr>
<td>Electron microprobe</td>
<td>( \geq 2 \text{ \mu m} )</td>
<td>( 10^{-15} ) to ( 10^{-12} )</td>
</tr>
<tr>
<td>Rutherford backscattering</td>
<td>50 ( \text{nm} )</td>
<td>( 10^{-20} ) to ( 10^{-17} )</td>
</tr>
<tr>
<td>Nuclear reaction analysis</td>
<td>20–1000 ( \text{nm} )</td>
<td>( 5 \times 10^{-21} ) to ( 5 \times 10^{-16} )</td>
</tr>
<tr>
<td><strong>Indirect</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nuclear magnetic resonance</td>
<td>. . .</td>
<td>( 10^{-20} ) to ( 10^{-9} )</td>
</tr>
<tr>
<td>Neutron inelastic scattering</td>
<td>. . .</td>
<td>( 10^{-11} ) to ( 10^{-9} )</td>
</tr>
<tr>
<td>Mossbauer effect</td>
<td>. . .</td>
<td>( 10^{-15} ) to ( 10^{-11} )</td>
</tr>
<tr>
<td>Conductivity (ionic crystals)</td>
<td>. . .</td>
<td>( 10^{-17} ) to ( 10^{-10} )</td>
</tr>
<tr>
<td>Resistivity (semiconductors)</td>
<td>. . .</td>
<td>( 10^{-20} ) to ( 10^{-12} )</td>
</tr>
<tr>
<td>Elastic after-effect</td>
<td>. . .</td>
<td>( 10^{-25} ) to ( 10^{-21} )</td>
</tr>
<tr>
<td>Internal friction</td>
<td>. . .</td>
<td>( 10^{-20} ) to ( 10^{-15} )</td>
</tr>
<tr>
<td>Magnetic anisotropy</td>
<td>. . .</td>
<td>( 10^{-25} ) to ( 10^{-21} )</td>
</tr>
</tbody>
</table>

Source: Ref 5

![Fig. 3 Example of error-function solutions for an infinite couple with initial end-member compositions of \( C_0 \) and \( C_1 \). The composition profiles show the diffusion of the species with increasing time.](image)
The component $j$ is the diffusing component, and $k$ is the gradient component. The $\delta_{kj}$ is the Kronecker delta symbol and equals 1 when $i = k$ and 0 when $i \neq k$. The partial derivative of the chemical potential, $\mu$, with respect to the mole fraction, $x_c$, corresponds to the thermodynamic factor. Note that the partial derivative of the chemical potential can be easily calculated using a functional representation of the Gibbs energy, for example, an appropriate multicomponent thermodynamic database. However, the thermodynamic factor must be evaluated in the component thermodynamic database. The concentrations $x_i$ moved in the positive and negative directions. When significant molar volume ever, this commonly used method does not determine an average interdiffusion coefficient from measured concentration profiles with different terminal compositions must intersect at one common intersection point. An effort to overcome this complexity, Ref 13 derived a new analysis method that enables the determination of an average interdiffusion coefficient over a selected range of compositions. This method has been implemented in the computational software program MultiDiFlux (Ref 14). (Commercial products are referenced in this paper as examples. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology.)

\[
\sum_{i=1}^{n} V D_{ik} = 0 \quad \text{(Eq 14)}
\]

\[
\nabla D_{ik} = \sum_{j=1}^{n} (\delta_{kj} - \delta_{ik}) x_{j} M_{j} \frac{\partial \mu}{\partial x_{m}} \quad \text{(Eq 15)}
\]

The intrinsic diffusion coefficient, \(D_{ik}\), is the gradient component. The \(\partial \mu / \partial x_{m}\) when \(i = k\) and 0 when \(i \neq k\). The partial derivative of the chemical potential, \(\mu\), with respect to the mole fraction, \(x_c\), corresponds to the thermodynamic factor. Note that the partial derivative of the chemical potential can be easily calculated using a functional representation of the Gibbs energy, for example, an appropriate multicomponent thermodynamic database. However, the thermodynamic factor must be evaluated in the component thermodynamic database. The concentrations \(x_i\) moved in the positive and negative directions. When significant molar volume ever, this commonly used method does not determine an average interdiffusion coefficient from measured concentration profiles with different terminal compositions must intersect at one common intersection point. An effort to overcome this complexity, Ref 13 derived a new analysis method that enables the determination of an average interdiffusion coefficient over a selected range of compositions. This method has been implemented in the computational software program MultiDiFlux (Ref 14). (Commercial products are referenced in this paper as examples. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology.)

\[
J_k = -\sum_{i=1}^{n} D_{ik} \frac{\partial \mu}{\partial x_{i}} \quad \text{(Eq 17)}
\]

where the sum of the fluxes equals zero, can be written as:

\[
J_k = -\sum_{i=1}^{n} D_{ik} \frac{\partial \mu}{\partial x_{i}} \quad \text{(Eq 17)}
\]

Fig. 4 Example of Boltzmann-Matano calculation for a single-phase interdiffusion experiment with end-member composition of \(c_i\) and \(c_j\). The Matano plane is located at \(z_0\) and is chosen such that the two shaded areas, E and F, are equal. The diffusion coefficient at given \(c_i\) concentration is then given by Eq 18.

\[
D = \frac{V_{M}}{2l} \frac{dz}{dX} \left[ (1 - Y_i) \int_{-\infty}^{0} \frac{Y_j}{V_{M}} dz + Y_i \left( \frac{1 - Y_j}{V_{M}} \right) \right] \quad \text{where} \ Y_i = \frac{c_i - c_j}{c_j - c_i} \quad \text{(Eq 19)}
\]

where \(Y_i\) is a normalized concentration variable. This method also eliminates the need to determine a Matano interface, which is often a source of error. An example of the method is shown in Fig. 4 for a cobalt-nickel diffusion couple. As the number of elements in the diffusion couples increases, determining the interdiffusion coefficients becomes more difficult; for each interdiffusion coefficient, \(n - 1\) composition profiles with different terminal compositions must intersect at one common intersection point. In an effort to overcome this complexity, Ref 13 derived a new analysis method that enables the determination of an average interdiffusion coefficient over a selected range of compositions. This method has been implemented in the computational software program MultiDiFlux (Ref 14). (Commercial products are referenced in this paper as examples. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology.)

Intrinsic Diffusivity. The intrinsic diffusion coefficient defines the diffusion of a component relative to the lattice planes and is the product of the diffusion mobility and the thermodynamic factor in the lattice-fixed frame of reference, where the sum of the diffusion fluxes equals the vacancy flux:

\[
\sum_{i=1}^{n} J_k = -L_{\text{vacancy}} \quad \text{(Eq 20)}
\]

A net flux of atoms across any lattice plane occurs during interdiffusion as the diffusion rates of the components in a material are different. Thus, there is a shift of lattice planes relative to a fixed lattice axis, which is known as the Kirkendall effect. This shift of lattice planes is observed by placing inert markers at the initial interface of a diffusion couple (Fig. 6) (Ref 15, 16). The velocity of the inert markers equals the Kirkendall velocity. Thus, the difference between Eq 15, \(\nabla D_{ij}\), and Eq 21, \(l\, D_{ij}\), is the reference state. The \(\nabla D_{ij}\) represents the measurement of the diffusivity relative to a fixed position, while the \(l\, D_{ij}\) represents the measurement of diffusivity relative to a fixed lattice plane. This difference in the frame of reference is similar to measuring the speed of a train when the observer is standing at a fixed position on the train platform (in the volume-fixed frame of reference) versus when the observer is sitting in one of the train cars (the lattice-fixed frame of reference).

For a substitutional binary alloy, the intrinsic and tracer diffusivities are related to the interdiffusion coefficient and the Kirkendall...
velocity. For example, for a binary AB alloy, Darken (Ref 17) deduced the following approximate relations, which disregard the coupling between the fluxes of the two atoms and the vacancy flux:

$$\sqrt{D_{AB}} = z_a D_A + z_b D_B = (z_a D_A^0 + z_b D_B^0) \left( e^{\Delta \mu_{AV}} - 1 \right)$$

(Eq 22)

The Kirkendall velocity, $v_K$, is given by:

$$v_k = \left( D_A^{-1} + D_B^{-1} \right) \frac{\partial \mu_A}{\partial z}$$

(Eq 23)

For a more complete description of the relationship between the diffusivities in a "random" alloy during a vacancy-driven diffusion process, the Darken-Manning relations (Ref 18, 19) should be used.

As an example of the relationship between the diffusivities, consider the fcc diffusivities for the iron-nickel system at 1200 °C (Fig. 7). Figure 7 (a) shows the calculated thermodynamic factors, and Fig. 7(b) shows the mobilities for nickel and iron. The Darken relationship (Eq 22) is demonstrated in Fig. 7(c):

$$D_{FeNi} = D_{Fe} + D_{Ni}$$

(Eq 24)

where the intrinsic lattice diffusivities, $D_{Fe}$ and $D_{Ni}$, are calculated by multiplying the thermodynamic factor (Fig. 7a) by the mobility (Fig. 7b).

First-Principles Data. In addition to the variety of experimental methods available for measuring diffusivity, first-principles calculations may be available to help estimate difficult-to-measure or metastable diffusion coefficients. Density-functional methods can be used to calculate the self-activation diffusion energies (Ref 20). Embedded-atom potentials can be used to evaluate diffusion mechanisms and determine activation energies (Ref 21–23). Diffusion coefficients can be extracted from kinetic Monte Carlo simulations using Kub-Green expressions (Ref 24, 25).

**Modeling Multicomponent Diffusivity Data**

While much of the diffusivity data for the pure elements and many binary alloys have been measured and are available in the literature, diffusivity data for multicomponent systems are scarce and difficult to measure. Experimentally determining all the needed diffusion coefficient matrices for a multicomponent diffusion simulation is simply not practical or efficient. However, these multicomponent data are critical for correctly predicting diffusion behavior in many industrial (commercial) applications and may be strongly dependent on composition. Thus, multicomponent diffusion mobility databases are developed to predict the needed bulk diffusion coefficients.

**Disordered Phase**

**Substitutional Diffusion.** Assuming a vacancy diffusion mechanism in a crystalline phase, the mobility matrix in the lattice-fixed frame, $\mathbf{M}$, which is both composition and temperature dependent, can be written in terms of an Arrhenius-type relation similar to Eq 4 and 6:

$$k_M = \exp \left( \frac{\Delta Q_i}{R T} \right)$$

(Eq 25)

$$M_i = k_M \exp \left( \frac{\Delta Q_i^0}{R T} \right)$$

(Eq 26)

Following the work of Ref 29, the off-diagonal terms of the diffusion mobility matrix are assumed to be zero; that is, correlation effects are assumed to be negligible. $M_i$ is the mobility of component $i$ in a given phase (this is the same $M_i$ as in Eq 13, 15, and 21), $\Theta_i$ represents the effects of the atomic jump distance (squared) and the jump frequency, and $\Delta Q_i^0$ (with units of J/mol) is the diffusion-activation energy of component $i$ in a given phase. The partial molar volumes are assumed to be constant, and the composition and temperature dependence of each $\Delta Q_i^0$ are expressed in terms of a Redlich-Kister (Ref 30) polynomial (Ref 29, 31–35):

$$\Delta Q_i^0 = \sum_{p} x_p Q_i^0 + \sum_{j > p} x_j x_p \sum_{i} A_{ij}^0 (x_p - x_j)^i$$

(Eq 27)

where $Q_i^0$ and $A_{ij}^0$ are linear functions of temperature. The expansion of the composition dependence in terms of a Redlich-Kister polynomial is similar to the development of thermodynamic databases with the Calphad method (Ref 26–28). Note that for a given diffusing component, $i$, if all $Q_i^0$ are equal and $A_{ij}^0$ equals zero, then $\Delta Q_i^0$ and the corresponding $M_i$ are not concentration dependent. The composition dependence of $\Theta_i$ can also be
represented by Eq 27. If there is no ferromagnetic contribution, it is frequently assumed that \( \Theta \) depends exponentially on composition (Ref 36), and it is included in the activation energy term. With this assumption, Eq 26 can be written as:

\[
M_i = \frac{1}{RT} \exp \left( \frac{\Delta Q'_i}{RT} \right)
\]

(Eq 28)

Intercalated Diffusion. Intercalated elements can be added to the database by using a sublattice description and by assuming the partial molar volume of the intercalated element is zero (Ref 37). An example of this model is the addition of carbon to the Fe-Ni-Cr fcc phase in the diffusion assessment by Ref 38.

Magnetic Transition. For substitutional elements in bcc alloys, such as transition metals, the effect of the transition between the paramagnetic and ferromagnetic states contributes to the diffusion. The effect of magnetic ordering on diffusion can be included (Ref 39, 40), using the model of Braun and Feller-Kniepmeyer (Ref 41), which relates the change in diffusivity to the magnetic enthalpy. For interstitial elements, such as carbon or nitrogen, the effect of the magnetic transition is less well established. The magnetic transition has a strong effect on carbon diffusivity (Ref 42), which can be modeled by applying the same activation energy to both the paramagnetic and ferromagnetic states (Ref 43). However, no significant change in the nitrogen diffusivity is observed as the magnetic transition occurs.

Ordered Phases

For an ordered phase, the composition dependence of the diffusion mobilities must include the effect of chemical ordering. Based on the model by Girifalco (Ref 44), which assumes the activation energy from chemical ordering is dependent on a long-range order parameter, the effect of chemical ordering is included by dividing the activation energy into two terms (Ref 35). The first term represents the contribution from the disordered state, \( \Delta Q'_k^{\text{ord}} \), and the other term represents the contribution from the ordered state, \( \Delta Q'_k^{\text{ord}} \), which is based on a long-range order-type parameter, the site fraction of a given component \( i \):

\[
\Delta Q'_k = \Delta Q'_k^{\text{ord}} + \Delta Q'_k^{\text{dis}}
\]

(Eq 29)

where \( \Delta Q'_k^{\text{ord}} \) is defined as:

\[
\Delta Q'_k^{\text{ord}} = \sum_{i,j} \sum_{i,j} \Delta Q'_k^{\text{ord}} \left[ y'_i y'_j - x_{ij} \right]
\]

(Eq 30)

\( \Delta Q'_k^{\text{dis}} \) and \( \Delta Q'_k^{\text{ord}} \) are the contributions to the activation energy for component \( k \) as a result of the chemical ordering of the \( i \) and \( j \) atoms on the two sublattices; \( x_{ij} \) is the mole fraction of component \( i \); and \( y'_i \) and \( y'_j \) are the site fractions of component \( i \) on the given sublattices:

\[
y'_i = \frac{N_i}{N_{\text{total}}}
\]

(Eq 31)

where \( N_i \) equals the number of \( i \) atoms on the \( \alpha \) sublattice, and \( N_{\text{total}} \) equals the total number of atoms on the \( \alpha \) sublattice. This approach was developed for an AB (B2) alloy where diffusion occurs via jumps between two metal sublattices; however, the approach is also valid for A-B (Fe-Al) alloys (D03 ordering) (Ref 45), where diffusion occurs via a network of nearest-neighbor jumps and where the fcc or hexagonal close-packed crystal structure is the base for the ordered phase. This model has been successfully used to describe the Fe-Ni-Al diffusion in the B2 phase (Ref 34) and to describe the Ni-Al-Cr diffusion in the B2 and \( \gamma \) phases (Ref 46).

Stoichiometric Phases

For binary stoichiometric phases, the diffusivity is assumed to be proportional to the difference in the chemical potentials at each end of the stoichiometric phase multiplied by the mobility for the component in the phase. Tracer diffusivity data for the component in the stoichiometric phase are used to assess the diffusion mobility functions. This type of model has been applied to the diffusion of carbon in cementite (Ref 47).

Determination of Diffusion Mobility Coefficients

Similar to the Gibbs energy function coefficients used in multicomponent thermodynamic databases, the diffusion mobility parameters in Eq 26 and 30 are determined from experimental data for each system and can be evaluated using trial-and-error methods or mathematical methods that minimize the error between the calculated and experimental diffusion coefficients, as indicated in Fig. 8. The trial-and-error method is only feasible if a few different data types are available. This method becomes increasingly cumbersome as the number of components and/or number of data types increases. When this occurs, mathematical methods, such as the least-squares method of Gauss (Ref 48), the Marquardt method (Ref 49), or the Bayesian estimation method (Ref 50), are more efficient. The PARROT optimizer (Ref 51) within the DICTRA code (Ref 52, 53) allows direct optimization of diffusion mobility functions.

General Principles. The same principles guiding the assessment of thermodynamic data (Ref 28) also apply to diffusion data, with a few additional constraints. First, a thermodynamic database (or description) must be selected to calculate the needed thermodynamic factors for intrinsic and interdiffusion coefficients. In choosing a thermodynamic database, the phase models used for the thermodynamics must be the same as those used in the diffusion mobility database. For example, if a thermodynamic description uses a two-sublattice model of an fcc phase (one sublattice for the substitutional elements and a second sublattice for the interstitials), then the same two-sublattice model must be used in the diffusion mobility database. After selecting a thermodynamic database/description to use for developing the diffusion mobility database, a critical evaluation of all the available data must be performed. As the tracer diffusivity data are not dependent on the thermodynamics, these data are preferred and often weighted more heavily than other diffusivity data, which are dependent on the thermodynamic description used. The assessment process continues by optimizing the mobility parameters for each component in each phase separately and then optimizing the mobility parameters for all of the components in a given phase with all of the relevant, and appropriately weighted, diffusion data. Zero-order binary and ternary interaction parameters may be needed as needed to fit the available diffusion data. Generally, ternary and higher-order binary interactions are rarely needed to fit the experimental data, or there are insufficient experimental data to justify such terms. After all of the needed mobility parameters are optimized, the assessment is verified using diffusion data not considered during optimization, such as a comparison of calculated and measured composition profiles from diffusion-couple experiments. The assessed parameters may also be evaluated by comparing activation energies with diffusion correlations published in the literature (Ref 54) or with first-principles calculations.

Binary Assessment Example. The assessment of the nickel-tungsten diffusion mobilities in the fcc phase is described here as an example. The thermodynamic description developed by Gustafson et al. (Ref 55) is used. The fcc phase nickel-tungsten system is modeled using a two-sublattice description (nickel, tungsten; vacancies), where nickel and tungsten occupy the substitutional sublattice, and vacancies occupy the interstitial sublattice. For the nickel-tungsten system in the fcc phase, both tracer (Ref 56) (Fig. 9) and interdiffusion (Ref 57) (Fig. 10) data are available. The nickel and tungsten diffusion mobilities in the fcc phase are described as:

\[
M_i = \frac{1}{RT} \exp \left( \frac{\Delta Q'_i}{RT} \right)
\]

(Eq 32)

\[
\Delta Q'_n = x_n Q'_n^N + x_w Q'_w^N + x_n x_w A_{nw}^N
\]

\[
\Delta Q'_w = x_n Q'_n^W + x_w Q'_w^N + x_n x_w A_{nw}^W
\]

(Eq 33)

(Note that because this phase has no ferromagnetic contribution, the mobilities are expressed using Eq 28.) If a ferromagnetic contribution were present, separate composition-dependent functions for the activation energy and pre-exponential terms would be needed (Eq 26).
$Q^N_{W}$ is the self-activation energy for diffusion of nickel in pure fcc nickel; it is well established experimentally, and the mobility parameters are previously determined in the assessment work by Ref 32. Two metastable end-member self-activation energies must be determined: one for the diffusion of tungsten in pure fcc tungsten, $Q^W_{W}$, and one for nickel in pure fcc tungsten, $Q^W_{Ni}$. Because these quantities cannot be measured experimentally (fcc tungsten is not stable), they are determined during the optimization, using diffusion correlations or first principles as initial estimates. The activation energy for tungsten diffusing in fcc nickel, $Q^W_{Ni}$, is determined using the available tracer and interdiffusion data. The three activation energies are modeled using the following form, where $B$ and $C$ are constants:

$$B + RT \ln(C)$$

(Eq 34)

The binary interaction parameters, $^0 A^W_{Ni}^W$ and $^0 A^W_{Ni}^W$, are also considered in the optimization and are modeled using a constant value.

To start the assessment, the initial values for the activation energies are all set to equal the value of nickel in pure nickel: $-28,700 + 69.8^\circ C$ (Ref 32) (Table 3). The binary interaction parameters are initially set to zero. Note that with this initial set of parameters, there is no concentration dependence for the tracer diffusivities. As seen in Fig. 9(a, b), the tracer diffusivities for all three alloy compositions are equal, using the initial parameters. The first parameters optimized are activation energies for the diffusion of tungsten in pure tungsten and nickel, $Q^W_{W}$ and $Q^W_{Ni}$, using the tungsten tracer diffusivity data from Ref 56. The optimization is done by comparing the diffusivities calculated using the values defined for Eq 33 in Eq 13 and the experimental values:

$$D_{ex}(x, T) = \frac{1}{RT} \exp \left( \frac{x_0 Q^W_{W} + x_0 Q^W_{Ni} + x_0 x_0^0 A_{Ni}^W \text{ or } A_{Ni}^W}{RT} \right)$$

(Eq 35)

After these parameters are optimized, the binary interaction term, $^0 A_{Ni}^W$, is optimized, using a start value of $-5000$ J/mol. Once the tungsten mobility parameters have been optimized using tracer diffusivity data, the values for $Q^W_{Ni}$, $Q^W_{Ni}$, and $^0 A_{Ni}^W$ are then fixed, and the nickel mobility parameters ($Q^N_{Ni}$ and $^0 A_{Ni}^W$) are optimized using the nickel tracer diffusivity data. After these nickel mobility values are optimized, all of the mobility values (excluding the values for $Q^N_{Ni}$) are optimized using both the tracer diffusivity data and the interdiffusion data. Again, the optimized parameters are used to calculate the tracer and interdiffusion diffusivities given by Eq 13 and 15 and then compared to the experimental values. The optimized mobility parameters are listed in Table 3.

The comparison of the diffusivities calculated with the optimized parameters and the experimental values are shown in Fig. 9 and 10. Good agreement between the measured and calculated tracer diffusivity and interdiffusion coefficients is achieved. Other recent diffusion mobility assessment examples are given in the literature by Ref 58 to 60.

In addition to optimizing the mobility functions using various composition-dependent diffusion coefficient data, diffusion mobility functions can be optimized directly from experimental composition profiles. Both Ref 61 and 62 developed methods that combine DICTRA with an optimization tool (MatLab or Mathematica) to assess the mobility parameters from experimental composition profiles. For a given set of mobility parameters, the difference between the experimental composition and calculated composition is defined by a least-squares error function. The mobility parameters are optimized to minimize the error. This method has been successfully demonstrated for binary and ternary systems.

**Strengths and Weaknesses of Assessment Method.** The Calphad-based approach to modeling the diffusion mobilities provides an efficient representation of the composition dependence in multicomponent systems. The reduced number of parameters needed to describe diffusion in a multicomponent system occurs as a result of the assumption that the correlation factors are negligible in the lattice-fixed frame of reference, and only the diagonal terms of the mobility matrix must be evaluated. However, if the vacancy concentration is not in local equilibrium, the off-diagonal terms resulting from the correlation factors should be considered (Ref 5, 19). Using the Calphad method to describe the composition dependence of the mobility terms requires the determination of mobilities for fictive metastable end-member phases. Examples of such quantities are the mobility of tungsten in fcc tungsten and the mobility of tungsten in fcc aluminum at temperatures above the fcc aluminum melting temperature (e.g., 1300 °C). Determination of these end-member quantities may follow approaches similar to those used to determine the lattice stabilities of the metastable thermodynamic quantities of the elements (Ref 26–28). This determination of diffusion-activation energies for fictive end-member phases may appear to limit the Calphad method; however, it is these determinations that enable the extrapolation to higher-order systems where diffusion data are limited.

These optimization methods have been employed to develop several commercial
diffusion mobility databases, as well as many smaller databases for specific research applications. Table 4 lists several of the commercial and research databases available. All of these databases can be employed by a variety of diffusion codes, finite-difference codes that assume local equilibrium at each grid point (e.g., DICTRA), random walk methods (Ref 71), and phase-field codes.

**Application**

**Single-Phase Diffusion.** The most common diffusion simulation is the diffusion of one single-phase material into another at constant temperature and pressure. The results of these simulations are generally shown as composition profiles as a function of distance at a specified time. The complexity associated with an 11-component nickel-base superalloy diffusion couple is demonstrated in Fig. 11, where the interdiffusion between two single-phase γ(fcc) nickel-base superalloys (René-N4/René-N5) after 100 h at 1293 °C (Ref 72) is shown. The predictions were made using the DICTRA software in conjunction with the National Institute of Standards and Technology (NIST)-NiMob diffusion mobility database (Ref 64) and the Thermotech Ni-Data thermodynamic database (Ref 73). In addition to accurately predicting the composition profiles, the diffusion simulation also predicts the location of the maximum pore formation resulting from Kirkendall porosity. Figure 12(a) shows the predicted location of the maximum pore formation, given by the maximum of the negative derivative of the vacancy flux with respect to distance (Ref 74), and Fig. 12(b) reveals that the predicted location corresponds well to the location of Kirkendall porosity observed on the René-N4 side of the diffusion couple.
Multiphase Diffusion. The formation of an additional phase is also a common occurrence during the diffusion process between two single-phase materials. Figure 13 shows the formation of a Ni₃Al (gamma prime, γ') layer between the NiAl-B2 and fcc nickel diffusion couple after heat treating for 1000 h at 1150 °C (1423 K). The Ni-NiAl section of the nickel-aluminum phase diagram is shown in Fig. 13(a). In Fig. 13(b), both the measured and predicted composition profiles show the formation of a Ni₃Al (gamma prime) layer between the initially present NiAl-B2 and nickel layers. The dashed lines between Fig. 13(a) and (b) show how the jumps in the composition profiles relate to the phase boundaries on the phase diagram.

In addition to the complexity of multicomponent single-phase diffusion couples, industrially relevant diffusion simulations often involve complicated time-temperature schedules and the precipitation and dissolution of a variety of different phases, both as planar layers and dispersed particles. These simulations are characterized by a variety of outputs, including the position of a moving phase boundary as a function of time, phase fraction profiles, particle-size diameters during coarsening, and locations of Kirkendall porosity. These outputs are essential in optimizing heat treating cycles and solidification schedules, predicting service lifetimes, and determining weldability. Examples of the complex uses of diffusion data to predict microstructure evolution are found in other articles of this Handbook.

Appendix 1: Example of Diffusion Matrices for the Ni-0.05Al-0.10Cr fcc Composition at 1200 °C

The following is an example of the calculation of the various diffusion matrices for a ternary Ni-Al-Cr system, for a given set of diffusion mobilities and chemical potentials. The diffusion mobilities and chemical potentials are calculated using the data from Engström (Ref 33) and the SSOL4 substance database (Ref 75), respectively.

For the given Ni-0.05Al-0.10Cr (atomic fraction) composition at 1200 °C, the diffusion mobilities, in a lattice-fixed frame of reference, assuming the correlation effects are negligible, are given as:

$$
\left[ \begin{array}{c}
M_{Al} \\
M_{Cr} \\
M_{Ni}
\end{array} \right] = \left[ \begin{array}{ccc}
\frac{M_{Al}}{M_{Cr}} & \frac{M_{Al}}{M_{Ni}} & \frac{M_{Cr}}{M_{Ni}}
\end{array} \right] = \left[ \begin{array}{ccc}
Al & Cr & Ni \\
Al (0.05 - 0.23) & 0 & 0 \\
Cr (0.10 - 2.35) & 0 & 0 \\
Ni (0.05 - 1.75) & 0 & 0
\end{array} \right] \quad 10^{-10} \text{m}^2/\text{s}
$$

(Eq 1.1)

Assuming nickel is the dependent variable, the matrix of chemical potentials at 1200 °C is given by:

$$
\left[ \begin{array}{c}
\frac{\partial \mu}{\partial T} \\
\frac{\partial \mu}{\partial x}
\end{array} \right] = \left[ \begin{array}{ccc}
Al & Cr & Ni \\
+39.2 & +9.23 & +0 \\
+8.60 & +18.3 & +0 \\
-3.32 & -2.70 & +0
\end{array} \right] \quad \text{10^4 J/mol}
$$

(Eq 1.2)

The tracer diffusivities for the Ni-5Al-10Cr composition at 1200 °C are then calculated using Eq 13:
Solution of these flux equations enables the calculation of composition profiles as a function of time in a single-phase region.

REFERENCES

15. E.O. Kirkendall, Diffusion of Zinc in Alpha Brass, Trans. AIMME, Vol 147, 1942, p 104–110
17. L.S. Darken, Diffusion, Mobility and their Interrelation through Free Energy in Binary Metallic Systems, Trans. AIMME, Vol 175, 1948, p 184–201

\[ D' = \begin{bmatrix} Al & 5.20 \\ Cr & 2.87 \\ Ni & 2.14 \end{bmatrix} \times (\times 10^{-14} \text{m}^2/\text{s}) \] (Eq 1.3)

The diffusion matrix in the lattice frame of reference is the product of the mobility matrix (Eq 1.1) times the chemical potential matrix (Eq 1.2), as defined in Eq 21:

\[ \dot{1}D = (\delta_{i,j}x_i)M = \begin{bmatrix} Al & Cr & Ni \\ Al & +8.33 & +1.96 & +0 \\ Cr & +2.09 & +4.30 & +0 \\ Ni & -4.95 & -4.02 & +0 \end{bmatrix} \times 10^{-14} \text{m}^2/\text{s} \] (Eq 1.4)

The diffusion matrix in the volume-fixed frame of reference, assuming constant molar volumes, is given by Eq 15:

\[ \dot{V}D_{ij} = (\delta_{i,j} - x_i x_j) \frac{\partial V}{\partial \Omega_i} \] (Eq 1.5)

Using this matrix of interdiffusion coefficients, the flux equations for the specified composition can be written in terms of Eq 16:

\[ \dot{J}_{Al} = -\dot{V}D_{AAl} \frac{\partial [Al]}{\partial z}, \dot{V}D_{AANi} \frac{\partial [Ni]}{\partial z} \] (Eq 1.7)

\[ \dot{J}_{Ni} = -\dot{V}D_{NiAl} \frac{\partial [Al]}{\partial z}, \dot{V}D_{NiCr} \frac{\partial [Cr]}{\partial z} \] (Eq 1.8)