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Lecturer (Zainab Hassan)
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INTRODUCTION

Many reactions and processes that are important in the treatment of materials rely on the transfer of mass either within a specific solid (ordinarily on a microscopic level) or from a liquid, a gas, or another solid phase. This is necessarily accomplished by diffusion, the phenomenon of material transport by atomic motion.

The phenomenon of diffusion may be demonstrated with the use of a diffusion couple, which is formed by joining bars of two different metals together so that there is intimate contact between the two faces this is illustrated for copper and nickel in Figure 5.1, which includes schematic representations of atom positions and composition across the interface. This couple is heated for an extended period at an elevated temperature (but below the melting temperature of both metals) and cooled to room temperature. Chemical analysis will reveal a condition similar to that represented in Figure 5.2—namely, pure copper and nickel at the two extremities of the couple, separated by an alloyed region. Concentrations of both metals vary with position as shown in Figure 5.2c. This result indicates that copper atoms have migrated or diffused into the nickel, and that nickel has diffused into copper. This process, whereby atoms of one metal diffuse into another, is termed interdiffusion, or impurity diffusion.

Interdiffusion may be discerned from a macroscopic perspective by changes in concentration that occur over time, as in the example for the Cu–Ni diffusion couple. There is a net drift or transport of atoms from high- to low-concentration regions.

Diffusion also occurs for pure metals, but all atoms exchanging positions are of the same type; this is termed self-diffusion. Of course, self-diffusion is not normally subject to observation by noting compositional changes.

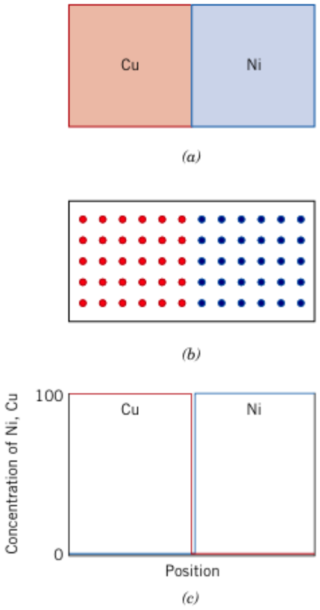


Figure 5.1 (*a*) A copper–nickel diffusion couple before a high-temperature heat treatment. (*b*) Schematic representations of Cu (red circles) and Ni (blue circles) atom locations within the diffusion couple. (*c*) Concentrations of copper and nickel as a function of position across the couple.

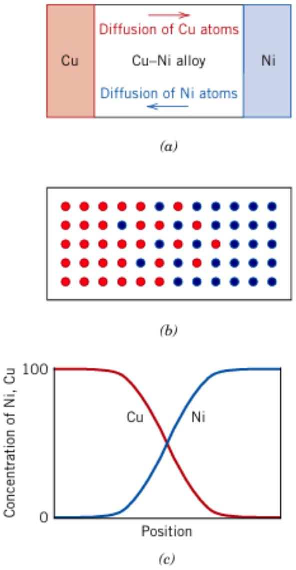


Figure 5.2 (*a*) A copper–nickel diffusion couple after a high-temperature heat treatment, showing the alloyed diffusion zone. (*b*) Schematic representations of Cu (red circles) and Ni (blue circles) atom locations within the couple. (*c*) Concentrations of copper and nickel as a function of position across the couple.

DIFFUSION MECHANISMS

From an atomic perspective, diffusion is just the stepwise migration of atoms from lattice site to lattice site. In fact, the atoms in solid materials are in constant motion, rapidly changing positions. For an atom to make such a move, two conditions must be met: (1) there must be an empty adjacent site, and (2) the atom must have sufficient energy to break bonds with its neighbor atoms and then cause some lattice distortion during the displacement. This energy is vibrational in nature (Section 4.8).

At a specific temperature some small fraction of the total number of atoms is capable of diffusive motion, by virtue of the magnitudes of their vibrational energies. This fraction increases with rising temperature.

Several different models for this atomic motion have been proposed; of these possibilities, two dominate for metallic diffusion.

1. Vacancy Diffusion

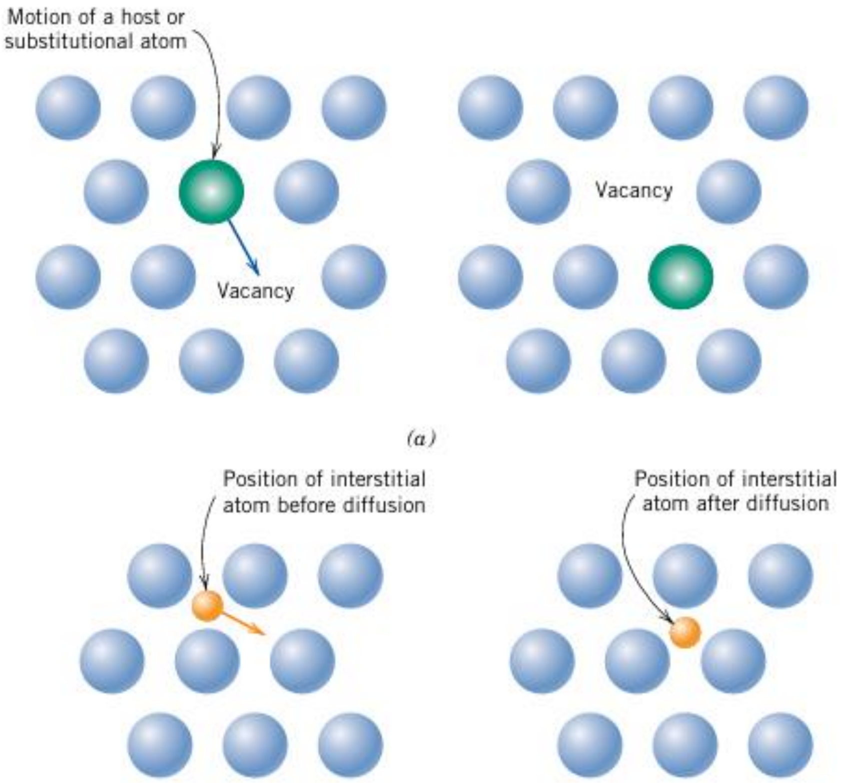
Vacancy diffusion occurs when an atom moves from its normal position in the crystal structure into a nearby vacant site—a spot where another atom is missing.

As the atom moves, it leaves behind a new vacancy, and this process continues, making it look as if the vacancies are moving through the material. This type of diffusion is common for substitutional atoms (atoms that replace host atoms in the lattice). It requires energy, because atoms must break bonds with their neighbors to move into the vacancy. Also, it becomes faster at higher temperatures, since the number of vacancies increases with temperature. Example: Diffusion of nickel atoms in copper.

2. Interstitial Diffusion

Interstitial diffusion happens when small atoms move through the interstitial sites the small spaces between the larger host atoms in the crystal.This process does not require vacancies, and because the moving atoms are small, it occurs much faster than vacancy diffusion. Typical interstitial atoms are hydrogen (H), carbon (C), and nitrogen (N). They can move easily through the lattice without displacing the larger host atoms. Example: Diffusion of carbon in iron (C in Fe), which is important in steel production.

Figure 5.3 Schematic representations of (*a*) vacancy diffusion and (*b*) interstitial diffusion.



STEADY-STATE DIFFUSION

Steady-state diffusion happens when particles such as atoms, ions, or molecules move through a material at a constant rate over time, meaning the concentration of these particles at any point does not change with time. In this state, the system is balanced the number of atoms entering a region is equal to the number leaving it and the concentration gradient (the difference in concentration across the material) remains constant. When diffusion first starts, the concentration of atoms changes with time, which is called non–steady-state diffusion. However, after some time, if the boundary conditions stay the same (for example, fixed concentrations at the surfaces), the system reaches steady state. At that point, diffusion continues, but the amount of material passing through each layer per second remains constant, resulting in a steady and unchanging diffusion pattern.

$$J = -D\frac{dC}{dx} \tag{5.3}$$

The constant of proportionality D is called the **diffusion coefficient,** which is expressed in square meters per second. The negative sign in this expression indicates that the direction of diffusion is down the concentration gradient, from a high to a low concentration. Equation 5.3 is sometimes called **Fick's first law.**

Sometimes the term **driving force** is used in the context of what compels a reaction to occur. For diffusion reactions, several such forces are possible; but when diffusion is according to Equation 5.3, the concentration gradient is the driving force.

EXAMPLE PROBLEM 5.1

Diffusion Flux Computation

A plate of iron is exposed to a carburizing (carbon-rich) atmosphere on one side and a decarburizing (carbon-deficient) atmosphere on the other side at 700°C (1300°F). If a condition of steady state is achieved, calculate the diffusion flux of carbon through the plate if the concentrations of carbon at positions of 5 and 10 mm (5×10^{-3} and 10^{-2} m) beneath the carburizing surface are 1.2 and 0.8 kg/m^3, respectively. Assume a diffusion coefficient of 3×10^{-11} m^2/s at this temperature.

Solution

Fick's first law, Equation 5.3, is utilized to determine the diffusion flux. Substitution of the values above into this expression yields

$$J = -D\frac{C_A - C_B}{x_A - x_B} = -(3 \times 10^{-11}\ \mathrm{m^2/s})\frac{(1.2 - 0.8)\ \mathrm{kg/m^3}}{(5 \times 10^{-3} - 10^{-2})\ \mathrm{m}}$$

$$= 2.4 \times 10^{-9}\ \mathrm{kg/m^2 \cdot s}$$

NONSTEADY-STATE DIFFUSION

Nonsteady-state diffusion, also called unsteady-state diffusion, occurs when the concentration of diffusing particles and the rate of diffusion change with time. At the beginning of diffusion, particles move from regions of high concentration to low concentration, causing the concentrations at different points in the material to continuously change. As diffusion proceeds, the concentration gradient may decrease and the diffusion rate may vary, meaning the system is not in equilibrium and has not yet reached a constant diffusion rate, unlike steady-state diffusion where conditions remain constant over time.

$$\frac{\partial C}{\partial t} = \frac{\partial}{x}\left(D\frac{\partial C}{\partial x}\right) \tag{5.4a}$$

known as **Fick's second law,** is used. If the diffusion coefficient is independent of composition (which should be verified for each particular diffusion situation), Equation 5.4a simplifies to

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{5.4b}$$

FACTORS THAT INFLUENCE DIFFUSION

Diffusing Species

The magnitude of the diffusion coefficient D is indicative of the rate at which atoms diffuse. Coefficients, both self- and interdiffusion, for several metallic systems are listed in Table 5.2. The diffusing species as well as the host material influence the diffusion coefficient. For example, there is a significant difference in magnitude between self-diffusion and carbon interdiffusion in α iron at 500°C, the D value being greater for the carbon interdiffusion (3.0×10^{-21} vs. 2.4×10^{-12} m^2/s). This comparison also provides a contrast between rates of diffusion via vacancy and interstitial modes as discussed earlier. Self-diffusion occurs by a vacancy mechanism, whereas carbon diffusion in iron is interstitial.

Temperature

Temperature has a most profound influence on the coefficients and diffusion rates. For example, for the self-diffusion of Fe in α-Fe, the diffusion coefficient increases approximately six orders of magnitude (from 3.0×10^{-21} to 1.8×10^{-15} m^2/s) in rising temperature from 500°C to 900°C (Table 5.2). The temperature dependence of

the diffusion coefficients is

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right) \tag{5.8}$$

where

D_0 = a temperature-independent preexponential (m^2/s)
Q_d = the **activation energy** for diffusion (J/mol or eV/atom)
R = the gas constant, 8.31 J/mol·K or 8.62×10^{-5} eV/atom·K
T = absolute temperature (K)

Equation Summary

Equation Number	*Equation*	*Solving for*	*Page Number*
5.1a	$J = \frac{M}{At}$	Diffusion flux	126
5.3	$J = -D\frac{dC}{dx}$	Fick's first law—diffusion flux for steady-state diffusion	127
5.4b	$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$	Fick's second law—for nonsteady-state diffusion	128
5.5	$\frac{C_x - C_0}{C_s - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$	Solution to Fick's second law—for constant surface composition	129
5.8	$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$	Temperature dependence of diffusion coefficient	133