Thermally Activated Processes, Phase Diagrams, and Phase Transitions

W6.1 Concentration Profiles Resulting from Diffusion

The following physical situations are often important in experimental measurements of the diffusion coefficient D and also in processes in which impurities are intentionally introduced into materials (e.g., the diffusion of dopants such as P and B into Si). The first case involves the presence of a thin layer of material on a solid surface, the second involves bringing two "thick" samples of different materials into intimate contact with each other, and the third corresponds to modifying the composition profile near the surface of a solid by maintaining a source of atoms with constant activity at the surface. In all three cases the one-dimensional form of Fick's second law, Eq. (6.8) in the textbook,[†] is solved to obtain a prediction for the concentration profiles that result after diffusion has been allowed to occur.

1. Consider a thin layer of A atoms of thickness d and with N_A atoms per unit area, deposited on the surface of a second material B. When the diffusion coefficient D_A of A atoms in B is assumed to be independent of concentration, and hence of x, the concentration profile of A atoms in B for long diffusion times, such that the diffusion length $\sqrt{D_A t} \gg d$, will be given by

$$C_A(x \geq 0, t) = \frac{N_A}{\sqrt{\pi D_A t}} \exp\left(-\frac{x^2}{4 D_A t}\right). \qquad \text{(W6.1)}$$

The resulting *Gaussian* profiles for the normalized concentration $C_A(x, t)/N_A$ are shown in Fig. W6.1 for several values of the diffusion length $2\sqrt{D_A t}$ on both linear and logarithmic scales. Note that the normalized surface concentration $C_A(x = 0, t)/N_A = 1/\sqrt{\pi D_A t}$ decreases with increasing time, due to the finite source of A atoms available at the surface.

2. Consider two thick solids composed of A and B atoms that are in intimate contact with each other. The source of A atoms diffusing into B is now essentially unlimited, so that the concentration of A atoms at the interface, $C_A(0, t)$, can be assumed to be constant, C_{Ao}. Other boundary conditions are $C_A(\infty, t) = 0$ and

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[†] The material on this home page is supplemental to *The Physics and Chemistry of Materials* by Joel I. Gersten and Frederick W. Smith. Cross-references to material herein are prefixed by a "W"; cross-references to material in the textbook appear without the "W."
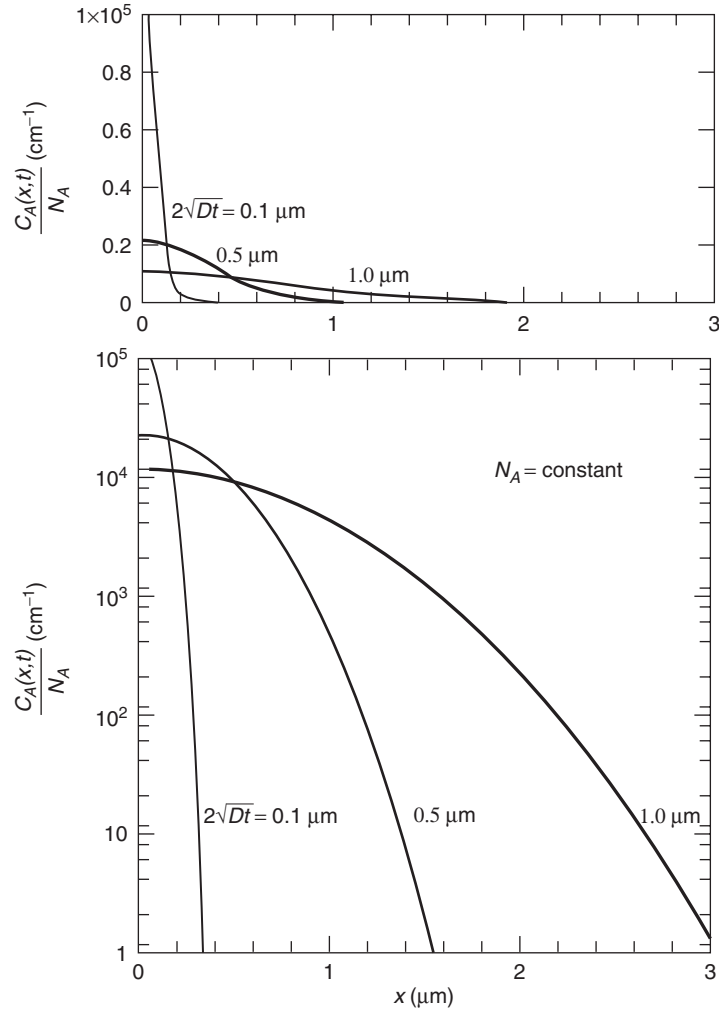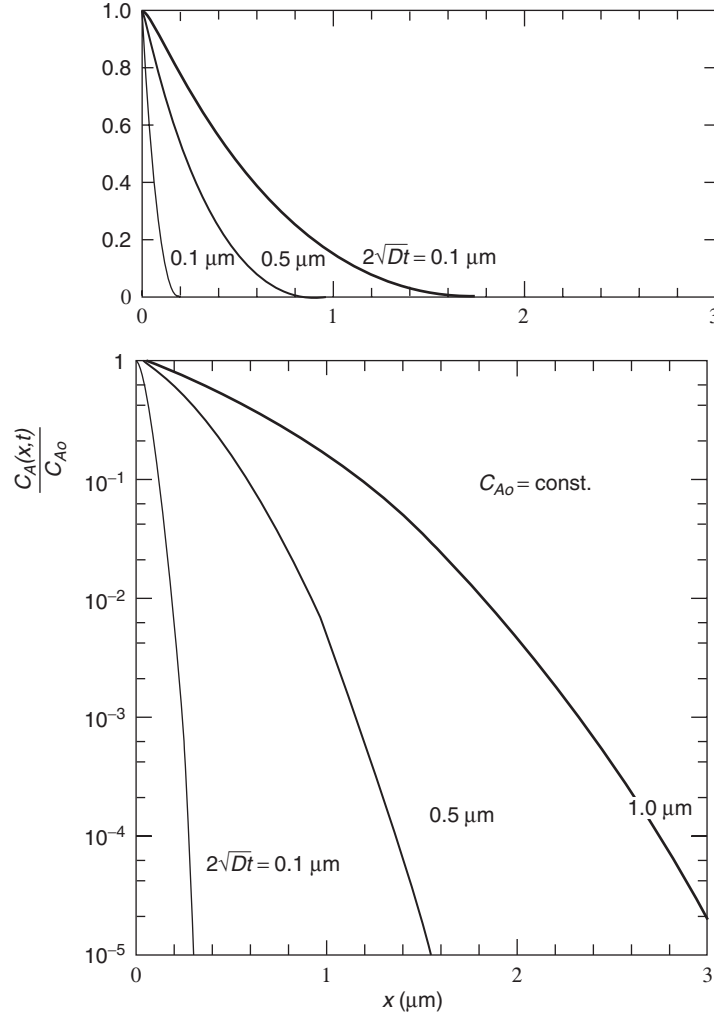
Figure W6.1. Normalized Gaussian concentration profiles originating from a thin layer of atoms on the surface of a solid at $x = 0$ for several values of $2\sqrt{D_A t}$ on both linear and logarithmic scales. (From A. S. Grove, *Physics and Technology of Semiconductor Devices*, copyright 1967 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

$C_A(x, 0) = 0$. After interdiffusion is allowed to occur, the concentration profile of A atoms in B is given by

$$C_A(x, t) = C_{Ao} \left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{D_A t}} \right) \right] = C_{Ao} \, \mathrm{erfc}\left(\frac{x}{2\sqrt{D_A t}} \right). \qquad \text{(W6.2)}$$

Here the chemical diffusion coefficient D_A is again assumed to be independent of x. The function $\mathrm{erf}(x)$, called the *error function*, is one of the most important functions in diffusion theory and $\mathrm{erfc}(x) = 1 - \mathrm{erf}(x)$ is the *complementary*
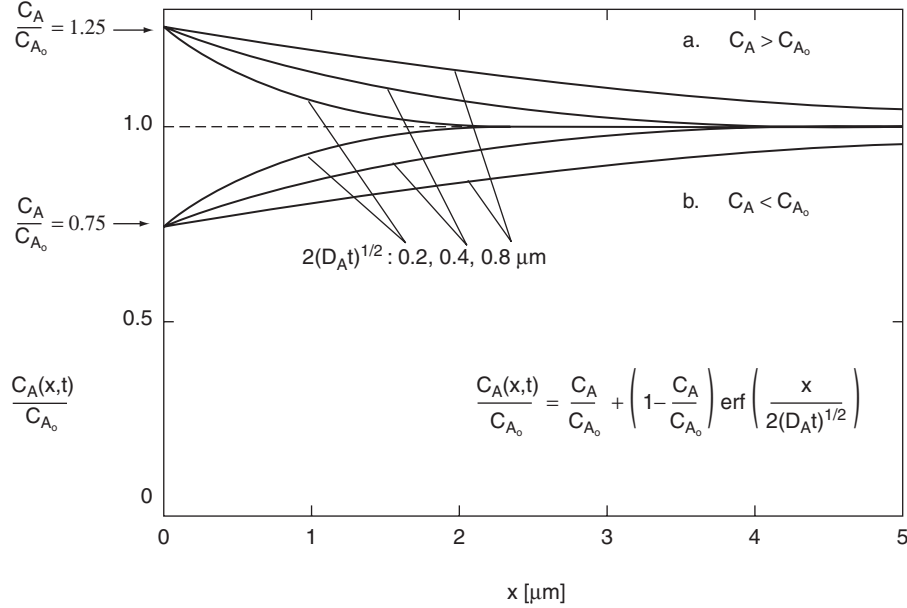
Figure W6.2. Normalized concentration profiles originating from an essentially unlimited source of atoms for several values of the diffusion length $\sqrt{D_A t}$ on both linear and logarithmic scales. (From A. S. Grove, *Physics and Technology of Semiconductor Devices*, copyright 1967 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

error function.[†] The resulting normalized concentration profiles $C_A(x, t)/C_{Ao}$ are shown in Fig. W6.2 for several values of $\sqrt{D_A t}$ on both linear and logarithmic scales.

3. Another important situation corresponds to modifying the concentration profile near the surface of a solid by maintaining a constant concentration C_A of A atoms at the surface of an initially homogeneous solid of composition C_{Ao}. This can be accomplished, for example, by exposing the solid to a source of A atoms

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[†] $\mathrm{erf}(x) = (2/\sqrt{\pi}) \int_0^x e^{-a^2}\, da$, with $\mathrm{erf}(0) = 0$ and $\mathrm{erf}(\infty) = 1$.

Figure W6.3. Normalized concentration profiles in a solid obtained when its surface is exposed to a source of atoms in the vapor phase with constant activity for several values of the diffusion length $2\sqrt{D_A t}$ using only a linear scale. Here C_A is the constant concentration at the surface and C_{Ao} is the initial concentration in the solid. Data used to generate these plots: for B diffusing into Si at $T \approx 1025°C$, $D_A = 10^{-2}$ μm²/h, and $t = 1, 4, 16$ h.

in the vapor phase with constant activity. The net diffusion of A atoms either into the solid ($C_A > C_{Ao}$) or out of the solid ($C_A < C_{Ao}$) is then allowed to take place. If the solid has a thickness $d \gg \sqrt{D_A t}$, the resulting concentration profile of A atoms is given by

$$\frac{C_A(x, t) - C_A}{C_{Ao} - C_A} = \text{erf}\left(\frac{x}{2\sqrt{D_A t}}\right). \tag{W6.3}$$

These normalized concentration profiles are shown in Fig. W6.3 for several values of $2\sqrt{D_A t}$ using only a linear scale but for $C_A > C_{Ao}$ and $C_A < C_{Ao}$. When $C_{Ao} = 0$ this result is identical to that given in Eq. (W6.2). Note that $C_A = 0$ for desorption of A atoms into a vacuum.

W6.2   Examples of Diffusion Studies

Self-Diffusion in Cu. Experimental results for the self-diffusion coefficient $D(T)$ of Cu are presented in Fig. W6.4 together with data on the fractional vacancy concentration $n_v(T)$, also shown in Fig. 4.23. As discussed in Section 4.7, Schottky defects (i.e., simple vacancies) are identified as the dominant intrinsic defect in FCC metals such as Cu and are responsible for the self-diffusion process. As a result, the following
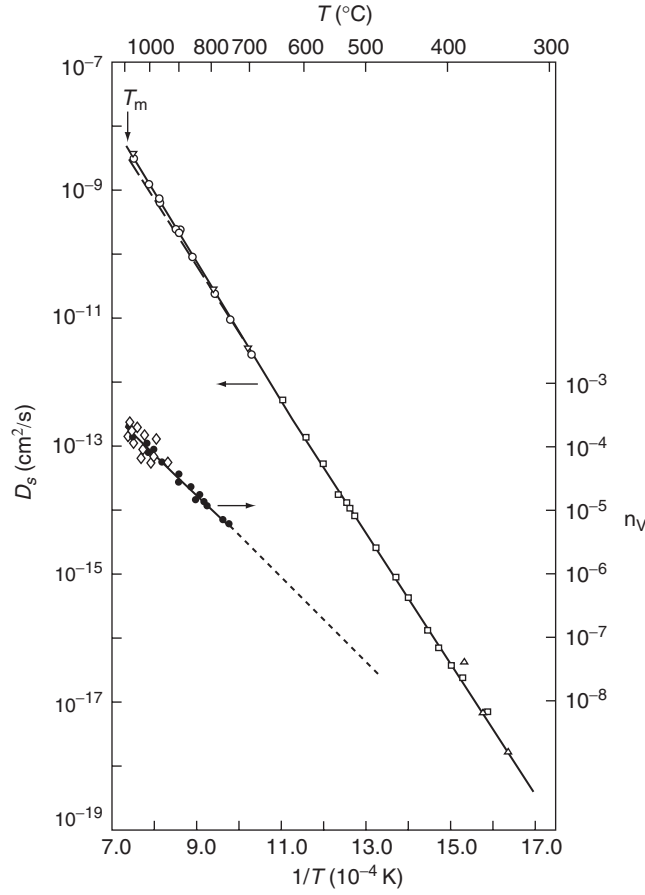
Figure W6.4. Experimental results for the self-diffusion coefficient $D(T)$ of Cu along with data on the vacancy concentration $n_v(T)$. [from A. S. Berger et al., *J. Phys. F: Met Phys.*, **9**, 1023 (1979). Reprinted by permission of the Institute of Physics.]

expressions from the textbook, Eqs. (6.14), (6.18), and (6.19),

$$D(T) = D_{\mathrm{o}} \exp\left(-\frac{E_a}{k_B T}\right),$$

$$D_{\mathrm{o}} = f a^2 \frac{\omega_D}{2\pi} \exp\left(\frac{\Delta S_f + S_m}{k_B}\right),$$

$$E_a = \Delta H_f + H_m,$$

can be used to analyze these data, except just below T_m, where there appears to be some upward curvature in $D(T)$, possibly due to a contribution from divacancies. Self-diffusion data such as these are often obtained using the *tracer method*, in which the motion of radioactive isotopes of the host crystal atoms are "traced" using radiochemical analysis.

The activation energy for self-diffusion in Cu is found from the data presented in Fig. W6.4 to be $E_a = 2.07$ eV. From this result and the value of $\Delta H_f = 1.28$ eV for vacancy formation in Cu presented in Section 4.7, it follows that the enthalpy of migration of vacancies in Cu is given by

$$H_m = E_a - \Delta H_f = 2.07 - 1.28 = 0.79 \text{ eV}. \tag{W6.4}$$

This value of H_m is typical for the noble metals. The prefactor D_o for self-diffusion in Cu obtained from Fig. W6.4 is 10^{-5} m^2/s. It is difficult to obtain a more precise value for D_o due to the lengthy extrapolation involved.

An interesting correlation exists between measured values of E_a for self-diffusion in metals and their melting temperatures T_m. The observed empirical relationship is given, to within about $\pm 10\%$, by

$$E_a(\text{eV}) \approx \frac{T_m(\text{K})}{700}. \tag{W6.5}$$

This correlation results from the fact that both T_m and E_a are determined by the strength of the bonding of atoms in the solid. Typical values of D_o for self-diffusion in metals are in the range 10^{-5} to 10^{-4} m^2/s, and typical diffusion coefficients $D(T_m)$ at the melting temperature are on the order of 10^{-12} m^2/s.

An important diffusion-related phenomenon occurring in Si-based electronic devices is the *electromigration* of Al and Cu ions in the metal lines connecting various elements and levels within the planar structure. The diffusion of the metal ions in this case is driven by the electrical current in the interconnect lines, the mechanism being the transfer of momentum from the electrons to the ions. In this respect Cu has an advantage over Al due to its higher atomic mass. The higher resistances and voids created in the metal lines due to electromigration can lead to the failure of the device. Electromigration is described in more detail in Chapter 12.

Self-Diffusion and Impurity Diffusion in Si. Experimental results for self-diffusion and for the diffusion of several substitutional and interstitial impurities in Si are summarized in Fig. W6.5. Concentration profiles and diffusion coefficients for dopant impurities in semiconductors are typically measured using electrical techniques (e.g., the measurement of capacitance–voltage characteristics of *p-n* junctions). Self-diffusion in Si remains an area of active research, with the question of whether the diffusion is via vacancies or interstitials still under discussion. Recent calculations[†] have indicated that only the self-interstitial diffusion mechanism can explain the magnitude of the observed self-diffusion of Si that occurs with an activation energy E_a in the range 4.5 to 5 eV and a prefactor $D_o \approx 0.01$ to 0.1 m^2/s. This value of D_o is much higher than the values typically observed for diffusion in metals. The dominance of the self-interstitial, corresponding to a "dumbbell" configuration of two Si atoms occupying a single lattice site, has been attributed to its predicted lower enthalpy of formation, $\Delta H_f = 3.3$ eV, compared with a predicted value of $\Delta H_f = 4.1$ eV for the vacancy.

[†] P. E. Bloechl et al., *Phys. Rev. Lett.*, **70**, 2435 (1993).
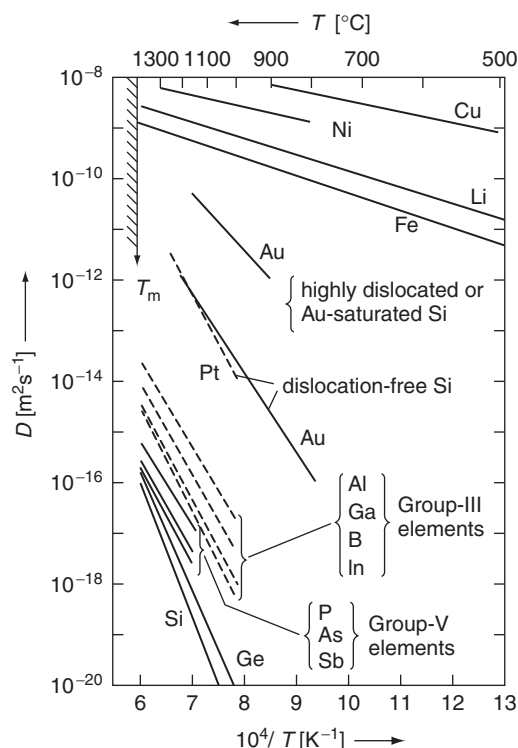
Figure W6.5. Experimental results for self-diffusion and for the diffusion of several substitutional and interstitial impurities in Si. (From W. Frank, *Defect and Diffusion Forum* 75, 121 (1991). Reprinted by permission of Scitec Publications.)

The diffusion of substitutional dopant impurities in Si is mediated by self-interstitials and vacancies and is an essential part of the processing of Si-based devices. It can be seen from Fig. W6.5 that the group III and V elements all diffuse faster in Si than does Si itself, with values of E_a in the range 3.4 to 3.6 eV for acceptors and 3.9 to 4.2 eV for donors. Donors and acceptors diffuse much slower, however, than the metal impurities shown, which have values of E_a in the range 0.4 to 0.8 eV and which diffuse via the direct interstitial mechanism. These observations are consistent with the group III and V elements entering the Si lattice substitutionally, thus participating in the covalent bonding, while the metal atoms enter interstitial sites. The rapid diffusion of unwanted metallic impurities in Si also plays an important role in their removal or trapping near dislocations or other extended defects in the process known as *gettering*.

A recent study has found that in Si near $T = 800°C$, the acceptor ion B^- diffuses via an interstitial mechanism, while the donor ion Sb^+ diffuses via a vacancy mechanism.[†] This is consistent with a net negative charge for vacancies in Si, which therefore attract donor ions such as Sb^+ and repel acceptor ions such as B^-. In addition, the larger atomic size of group V donors makes them less likely to diffuse through the interstitial sites in Si compared to smaller group III acceptors such as B^-.

[†] H.-J. Grossman et al., *Appl. Phys. Lett.*, **71**, 3862 (1997).

W6.3   Examples of Vaporization Studies

Typical experimental methods employed for the determination of the vaporization flux $J_{vap}(T)$ or, equivalently, of the equilibrium vapor pressure $P_{eq}(T)$ involve direct measurement of the weight loss of the crystal and the detection of the evaporated species via mass spectrometry.

The equilibrium vapor pressures $P_{eq}(T)$ for Fe and Si presented in Fig. W6.6 are the recommended values from a critical review[†] of the data for the thermodynamic properties of Fe and Si. It can be seen that vaporization is indeed thermally activated for Fe and Si. From these data the enthalpies and entropies of vaporization, defined in terms of $\Delta_r G^o$ by

$$\Delta_r G^o = \Delta H_{vap} - T\Delta S_{vap}, \tag{W6.6}$$

can be determined. The enthalpy of vaporization $\Delta H_{vap} = H(\text{vapor}) - H(\text{solid})$ is simply equal to the standard enthalpy of formation $\Delta_f H°$ of the vapor [i.e., Fe(g) or Si(g)] since the solid is in its standard state, where $\Delta_f H°$ is defined to be zero. Values of ΔH_{vap} and ΔS_{vap} at $T = 298.15$ K for Fe and Si are presented in Table W6.1 along with the melting temperature T_m and the equilibrium vapor pressure at T_m. Note that, as expected, $\Delta H_{vap} = 4.66$ eV/atom for Si is quite close to 2E(Si–Si), where $E(\text{Si–Si}) = 2.34$ eV is the Si–Si covalent bond energy (see the discussion of bond
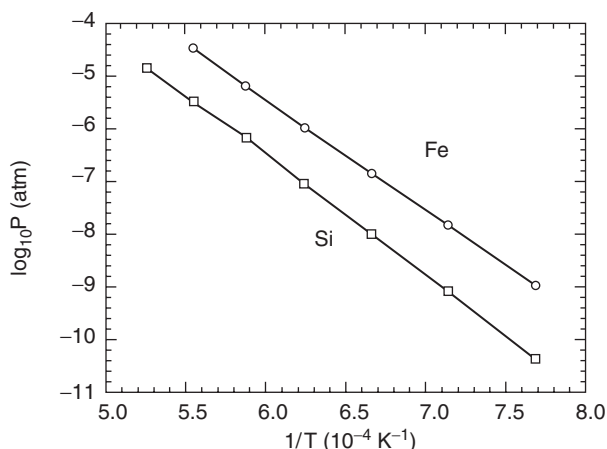
Figure W6.6. Equilibrium vapor pressures $P_{eq}(T)$ of Fe and Si. [Data from P. D. Desai, *J. Phys. Chem. Ref. Data*, **15**, 967 (1986).]

TABLE W6.1   Vaporization Results for Fe and Si

	$\Delta H_{vap}(298.15$ K) (kJ/mol; eV/atom)	$\Delta S_{vap}(298.15$ K) (J/mol·K)	T_m (K)	$P_{eq}(T_m)$ (atm)
Fe	$415.5 \pm 1.3;\ 4.31 \pm 0.01$	180.49	1811	3.58×10^{-5}
Si	$450 \pm 4;\ 4.66 \pm 0.04$	167.98	1687	5.41×10^{-7}

Source: Data from P. D. Desai, *J. Phys. Chem. Ref. Data*, **15**, 967 (1986).

[†] P. D. Desai, *J. Phys. Chem. Ref. Data*, **15**, 967 (1986).

energies in Chapter 2). Mass spectrometry has shown that the Si_2 dimer and Si_3 trimer represent about 0.4% and 0.1%, respectively, of the equilibrium vapor of Si at T_m.

When determining the vapor pressure of Si, care must be taken to ensure that the vaporization of Si atoms occurs from a clean surface. The presence of carbon atoms on the Si surface can retard vaporization due to the formation of the high-melting-point compound SiC. The presence of oxygen atoms, on the other hand, can lead to greatly enhanced vaporization rates due to the formation of the volatile molecule SiO.

W6.4   Gibbs Phase Rule

In a binary eutectic alloy such as Pb–Sn there are three separate phases whose compositions can be varied. In addition, the temperature and pressure of the alloy can be varied. There would thus appear to be five quantities or *degrees of freedom* that can be controlled independently (i.e., x_l, x_α, x_β, T, and P). In practice, however, these degrees of freedom are not all independent, as illustrated by the *Gibbs phase rule*.

Consider a system of C components, labeled $c = 1, 2, \ldots, C$, with P possible phases, labeled $p = 1, 2, \ldots, P$. Let μ_{cp} be the chemical potential for component c in phase p. At thermal equilibrium the system has a common pressure and temperature, and the chemical potential for each component is the same in every phase. Thus

$$\mu_{11} = \mu_{12} = \cdots \mu_{1P}$$

$$\mu_{21} = \mu_{22} = \cdots \mu_{2P}$$

$$\vdots \tag{W6.7}$$

$$\mu_{C1} = \mu_{C2} = \cdots \mu_{CP},$$

for a total of $C(P - 1)$ independent equations.

Let x_{cp} denote the mole fraction of component c in phase p. There are C times P compositional variables, x_{cp}, and for each phase there is the constraint that

$$\sum_{c=1}^{P} x_{cp} = 1, \qquad p = 1, 2, \ldots, P. \tag{W6.8}$$

There are thus a total of $(C - 1)P$ independent mole fractions. Including the pressure and temperature, the number of independent variables is $(C - 1)P + 2$. The number of degrees of freedom F (sometimes called the *variance*) is the difference between the number of independent variables and the number of equations relating them to each other, that is,

$$F = (C - 1)P + 2 - C(P - 1) = C - P + 2, \tag{W6.9}$$

which proves the Gibbs phase rule.

PROBLEMS

W6.1 Show that the total number of atoms diffusing either into or out of the surface of a solid of area A in time t is given by $\Delta N_A(t) = 2(C_A - C_{Ao})A\sqrt{Dt/\pi}$ when

the concentration profile $C_A(x, t)$ in the solid is given by Eq. (W6.3). Note that $\int_0^\infty \text{erfc}(x)\, dx = 1/\sqrt{\pi}$.

W6.2 Using the fact that the average distance of diffusion of an atom in a solid in time t is given approximately by $L = \sqrt{\langle X^2 \rangle} \approx \sqrt{Dt}$, calculate the average time $\langle t \rangle$ it takes for a Cu atom (see Fig. W6.4) to "diffuse" one NN distance at $T = 1000$ K. On average, what is the order of magnitude of the number of oscillations that a Cu atom undergoes during this time?