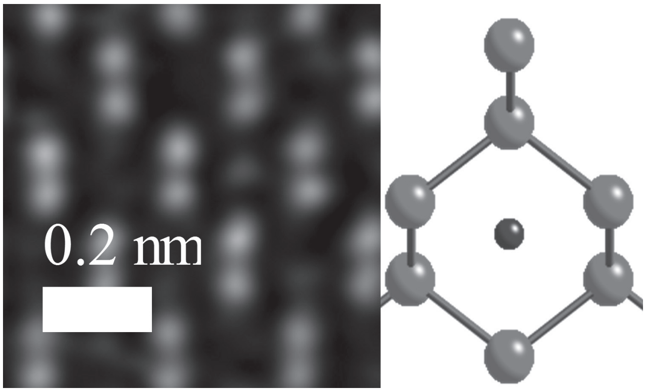
CHAPTER 5

Diffusion



Atomic diffusion as introduced in this chapter involves individual atoms moving through crystal structures. In the high-resolution transmission electron micrograph on the left, we see a subtle image of one such atom in an interstitial position. The schematic illustration on the right shows this Ni atom to be in a silicon crystal as observed along the [110] *direction, the same orientation shown in the Chapter Opening micrograph in Chapter 3. (Courtesy of Klaus van Benthem and Andrew Thron, University of California, Davis.)*

5.1 Thermally Activated Processes

A large number of processes in materials science and engineering share a common feature—the process rate rises exponentially with temperature. The diffusivity of elements in metal alloys, the rate of creep deformation in structural

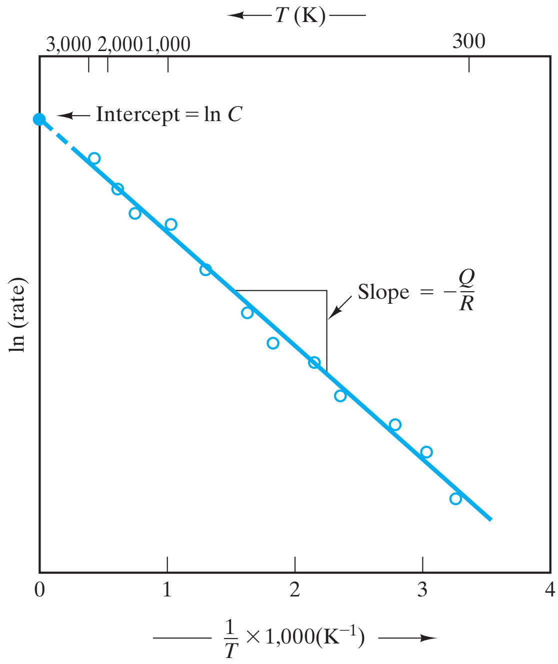


FIGURE 5.1 *Typical Arrhenius plot of data compared with Equation 5.2. The slope equals* $-Q/R$*, and the intercept* (at $1/T = 0$) *is ln C.*

materials, and the electrical conductivity of semiconductors are a few examples that will be covered in this book. The general equation that describes these various processes is of the form

$$\text{rate} = Ce^{-Q/RT}, \tag{5.1}$$

where C is a **preexponential constant** (independent of temperature), Q is the **activation energy**, R is the universal gas constant, and T is the absolute temperature. It should be noted that the universal gas constant is as important for the solid state as it is for the gaseous state. The term *gas constant* derives from its role in the perfect gas law ($pV = nRT$) and related gas-phase equations. In fact, R is a fundamental constant that appears frequently in this book devoted to the solid state.

Equation 5.1 is generally referred to as the **Arrhenius* equation**. Taking the logarithm of each side of Equation 5.1 gives

$$\ln(\text{rate}) = \ln C - \frac{Q}{R}\frac{1}{T}. \tag{5.2}$$

By making a semilog plot of ln (rate) versus the reciprocal of absolute temperature ($1/T$), one obtains a straight-line plot of rate data (Figure 5.1). The slope of the resulting **Arrhenius plot** is $-Q/R$. Extrapolation of the Arrhenius plot to $1/T = 0$ (or $T = \infty$) gives an intercept equal to ln C.

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*Svante August Arrhenius (1859–1927), Swedish chemist, made numerous contributions to physical chemistry, including the experimental demonstration of Equation 5.1 for chemical reaction rates.

The experimental result of Figure 5.1 is a very powerful one. Knowing the magnitudes of process rate at any two temperatures allows the rate at a third temperature (in the linear-plot range) to be determined. Similarly, knowledge of a process rate at any temperature and of the activation energy, Q, allows the rate at any other temperature to be determined. A common use of the Arrhenius plot is to obtain a value of Q from measurement of the slope of the plot. This value of activation energy can indicate the mechanism of the process. In summary, Equation 5.2 contains two constants. Therefore, only two experimental observations are required to determine them.

To appreciate why rate data show the characteristic behavior of Figure 5.1, we must explore the concept of the activation energy, Q. As used in Equation 5.1, Q has units of energy per mole. It is possible to rewrite this equation by dividing both Q and R by Avogadro's number (N_{AV}), giving

$$\text{rate} = Ce^{-q/kT}, \tag{5.3}$$

where $q\ (= Q/N_{\mathrm{AV}})$ is the activation energy per atomic scale unit (e.g., atom, electron, and ion) and $k\ (= R/N_{\mathrm{AV}})$ is Boltzmann's* constant ($13.8 \times 10^{-24} J/K$). Equation 5.3 provides for an interesting comparison with the high-energy end of the **Maxwell–Boltzmann† distribution** of molecular energies in gases,

$$P \propto e^{-\Delta E/kT}, \tag{5.4}$$

where P is the probability of finding a molecule at an energy ΔE greater than the average energy characteristic of a particular temperature, T. Herein lies the clue to the nature of the activation energy. It is the energy barrier that must be overcome by **thermal activation**. Although Equation 5.4 was originally developed for gases, it applies to solids as well. As temperature increases, a larger number of atoms (or any other species involved in a given process, such as electrons or ions) is available to overcome a given energy barrier, q. Figure 5.2 shows a *process path* in which a single atom overcomes an energy barrier, q. Figure 5.3 shows a simple mechanical model of activation energy in which a box is moved from one position to another by going through an increase in potential energy, ΔE, analogous to the q in Figure 5.2.

In the many processes described in the text where an Arrhenius equation applies, particular values of activation energy will be found to be characteristic of process mechanisms. In each case, it is useful to remember that various possible mechanisms may be occurring simultaneously within the material, and each mechanism has a characteristic activation energy. The fact that one activation energy is representative of the experimental data means simply that a single mechanism is dominant. If the process involves several sequential steps,

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*Ludwig Edward Boltzmann (1844–1906), Austrian physicist, is associated with many major scientific achievements of the 19th century (prior to the development of modern physics). The constant that bears his name plays a central role in the statistical statement of the second law of thermodynamics. Some ideas are difficult to put aside. His second law equation is carved on his tombstone.

†James Clerk Maxwell (1831–1879), Scottish mathematician and physicist, was an unusually brilliant and productive individual. His equations of electromagnetism are among the most elegant in all of science. He developed the kinetic theory of gases (including Equation 5.4) independently of his contemporary, Ludwig Edward Boltzmann.

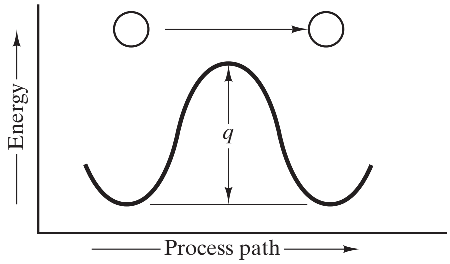

FIGURE 5.2 *Process path showing how an atom must overcome an activation energy, q, to move from one stable position to a similar adjacent position.*

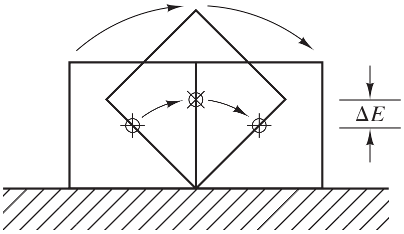

FIGURE 5.3 *Simple mechanical analog of the process path of Figure 5.2. The box must overcome an increase in potential energy, ΔE, in order to move from one stable position to another.*

the slowest step will be the **rate-limiting step**. The activation energy of the rate-limiting step, then, will be the activation energy for the overall process.

EXAMPLE 5.1

The rate at which a metal alloy oxidizes in an oxygen-containing atmosphere is a typical example of the practical utility of the Arrhenius equation (Equation 5.1). For example, the rate of oxidation of a magnesium alloy is represented by a rate constant, k. The value of k at 300°C is 1.05×10^{-8} kg/(m$^4 \cdot$ s). At 400°C, the value of k rises to 2.95×10^{-4} kg/(m$^4 \cdot$ s). Calculate the activation energy, Q, for this oxidation process (in units of kJ/mol).

SOLUTION

For this specific case, Equation 5.1 has the form

$$k = Ce^{-Q/RT}.$$

Taking the ratio of rate constants at 300°C (= 573 K) and 400°C (= 673 K), we conveniently cancel out the unknown preexponential constant, C, and obtain

$$\frac{2.95 \times 10^{-4}\,\text{kg}/[\text{m}^4 \cdot \text{s}]}{1.05 \times 10^{-8}\,\text{kg}/[\text{m}^4 \cdot \text{s}]} = \frac{e^{-Q/(8.314\,\text{J}/[\text{mol}\cdot\text{K}])(673\,\text{K})}}{e^{-Q/(8.314\,\text{J}/[\text{mol}\cdot\text{K}])(573\,\text{K})}}$$

or

$$2.81 \times 10^4 = e^{\{-Q/(8\,314\,\text{J}/[\text{mol}\cdot\text{K}])\}\{1/(673\,\text{K})-1/(573\,\text{K})\}},$$

giving

$$Q = 328 \times 10^3\,\text{J/mol} = 328\,\text{kJ/mol}.$$