Chapter 6

Transformations

The chapter on surfaces began with the statement, ''Everything has to end somewhere.'' With respect to transformations, we can also observe that ''Everything has to start somewhere.'' The dynamics of phase transformations, especially their initiation, influence many of the changes in the properties of solids that take place during their manufacture.

Phase transformations may be divided into two broad categories: diffusional and displacive (nondiffusional). The former requires movement of atoms by a diffusional process, that is, a process in which atoms move individually, driven by chemical potential gradients. Displacive transformation, on the other hand, involves cooperative movement of atoms in a shearing action during phase transformation. The most striking and commercially important example is the martensite reaction in steel, which accounts for its ability to be hardened. Examples are also to be found in ceramic materials. Good discussions of displacive transformations are to be found in especially the metallurgical literature (Refs. 1 and 2).

Diffusional transformations may be subdivided into two categories: spinodal transformations and those that proceed by nucleation of a new phase, followed by its growth.

6.1 TYPES OF DIFFUSIONAL TRANSFORMATIONS

Gibbs, more than 100 years ago, when considering the transformation of supersaturated solutions in binary systems, observed that there could be two types of transformations: those that are initially small in degree, but large in extent, and those that are initially small in extent, but large in degree. The former are spinodal transformations. To explore the basis for this observation, consider the phase diagram in Figure 6.1, and the corresponding curve for Gibbs free energy versus composition at a temperature of about 800 K in Figure 6.2. The points of inflection in Figure 6.2 where the second derivative of the Gibbs free energy–composition curve is zero, separate the region of positive from negative second derivatives and are called spinodal points. If a solution is cooled rapidly from above the miscibility gap to 800 K, its transformation behavior as it decomposes into α and β phases depends on the overall composition of the material relative to these spinodal points. If the overall composition is inside (between) the spinodal points, the transformation may proceed incrementally over a large region, without the nucleation of a new phase. Outside the spinodal points, nucleation of a new phase is required.

To explain this difference, let us follow, in Figure 6.2, the trajectory of Gibbs free energy during transformations in the two regions: the one with positive second derivative (concave up, point A) and the one with negative second derivative (concave down, point B). In the concave down region, inside the spinodal curve, the decomposition may begin without an initial increase in Gibbs free energy. As the material decomposes into two others, the combined Gibbs free energies of the two resulting phases is always below the Gibbs free energy of the original solution. There is no energy barrier to be overcome. This is the reaction that Gibbs referred to as small in degree, but large in extent. The reaction can take place over a wide region, but the changes in composition are continuous and small.

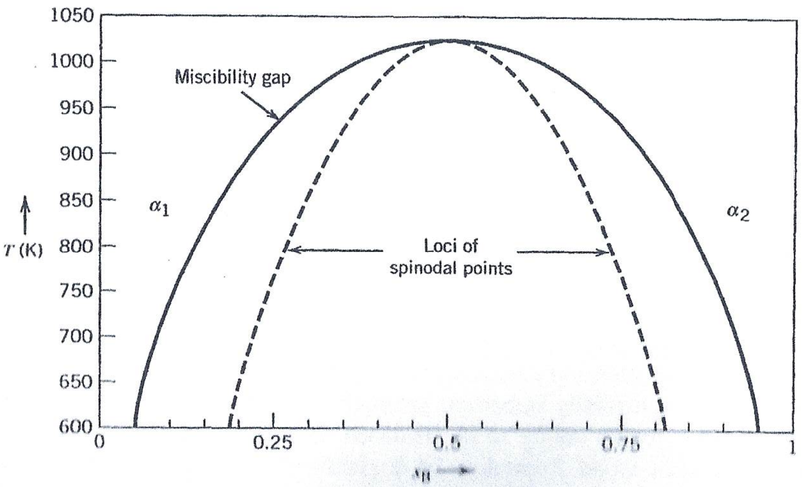


Figure 6.1 Phase diagram showing the miscibility gap and the loci of the spinodal points.

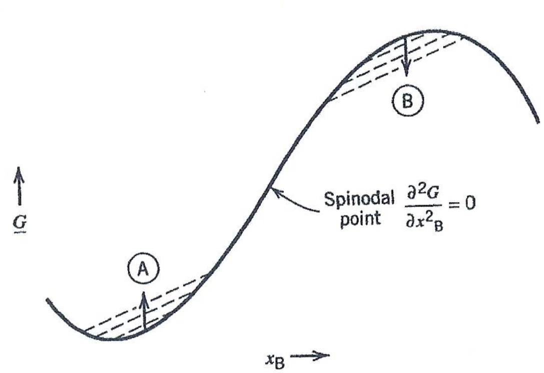


Figure 6.2 Illustration of different paths for changes in $\underline{G}$ on different sides of spinodal point.

In the region of positive second derivative (point A), the overall Gibbs free energy of the material must be increased before transformation to a lower free energy state can occur. The sum of the Gibbs free energies of the transformed material is initially higher than the Gibbs free energy of the solution. As the reaction proceeds, the sum of the two will eventually be less than that of the solution, but there is an energy barrier to be overcome in the overall process. These reactions proceed by the process of nucleation and growth, and are, in Gibbs's terms, small in extent, but large in degree.

The difference in transformation kinetics between the two can be visualized nicely using a mechanical analogue (Ref. 3). Consider the rectangular block in Figure 6.3. The stable equilibrium of the block is on its side, portrayed at the right. The position on the left, on its end, is labeled "metastable" because a certain amount of work is

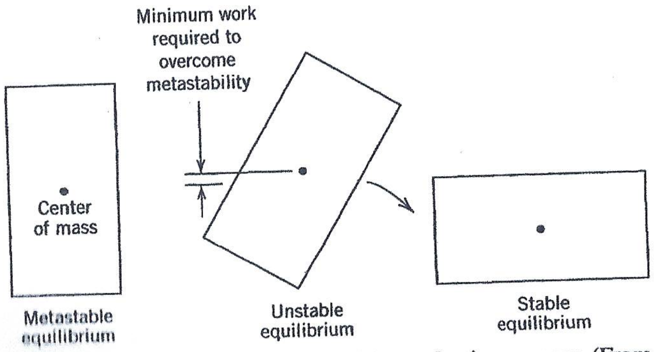


Figure 6.3 Mechanical analogue of the nucleation process. (From Ref. 3.)

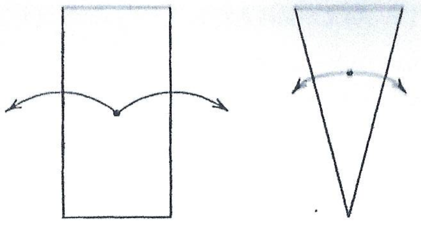


Figure 6.4 Illustration of the difference between metastable equilibrium and unstable equilibrium. (From Ref. 3.)

first required to lift its center of gravity as the block falls to its stable equilibrium position.

Consider, now, the difference between the rectangular block and the triangular block in Figure 6.4. The triangular block, balanced on its tip, represents unstable equilibrium because any slight perturbation from the vertical position will cause the block to fall to its stable position (on its side) without the addition of any work to start the process. The energy path followed by the rectangular block is analogous to transformations characterized by nucleation. The energy path followed by the triangular block is analogous to spinodal transformations. Nucleation is discussed first in this chapter. Section 6.8 deals with spinodal transformation.

6.2 HOMOGENEOUS NUCLEATION

To begin the discussion of phase changes of the second kind (nonspinodal), consider the Gibbs free energy changes during the solidification of a pure material. At temperatures below a material's melting point (T_m), the driving force for solidification is the difference in Gibbs free energy (ΔG) between the liquid and the solid. If we assume that the heat capacities of the liquid and solid are equal, then the molar enthalpy and molar entropy of solidification will each remain constant as a function of temperature, and $\Delta \underline{G}$ can be calculated as follows:

$$\text{liquid} \rightarrow \text{solid}$$

$$\Delta \underline{G} = \Delta \underline{H} - T\,\Delta \underline{S}$$

Note that $\Delta \underline{H} = -L$, where L is the latent heat of fusion.

$$\Delta \underline{G} = -L + T\frac{L}{T_m}$$

$$\Delta \underline{G} = \frac{L}{T_m}(T - T_m) \tag{6.1}$$

When a spherical particle of solid of radius r is formed, the change in Gibbs free energy is the volume of the particle multiplied by the volumetric Gibbs free energy change, $\Delta \underline{G}_v$.

$$\Delta G_{vol} = \tfrac{4}{3}\pi r^3 \Delta \underline{G}_v$$

where $\Delta \underline{G}_v$ is the Gibbs free energy change per unit volume,

$$\Delta \underline{G}_v = \frac{1}{\underline{V}}\frac{L}{T_m}(T - T_m) \tag{6.2}$$

$$\Delta G_{vol} = \frac{4}{3}\pi r^3 \frac{1}{\underline{V}}\frac{L}{T_m}(T - T_m) \tag{6.3}$$

But when the particle of radius r is formed, there is another energy term to be considered, the surface energy. The surface energy of the particle is

$$\Delta G_s = 4\pi r^2 \gamma \tag{6.4}$$

where $\gamma = \gamma_{s-l}$, the surface energy between solid and liquid.

The sum of the two energy terms is:

$$\Delta G_r = 4\pi r^2 \gamma + \tfrac{4}{3}\pi r^3 \Delta \underline{G}_v \tag{6.5}$$

The first of these terms involves the increase in energy required to form a new surface. The second term is negative and represents the decrease in Gibbs free energy upon solidification. Because the first is a function of the second power of the radius, and the second a function of the third power of the radius, the sum of the two increases, goes through a maximum, and then decreases (Figure 6.5). The radius at which the Gibbs free energy curve is at a maximum is called the critical radius r^*, for a nucleus of solid in liquid. The driving force of the Gibbs free energy will tend to cause a particle with a smaller radius than r^* to decrease in size. This is a particle of subcritical size for nucleation. A viable nucleus is one with radius greater than or equal to r^*. The critical Gibbs free energy corresponding to the radius r^* is ΔG^*. In terms of physical parameters, these terms can be shown to be:

$$r^* \quad \text{when} \quad \left(\frac{\partial \Delta G_r}{\partial r}\right)_T = 0 = 8\pi r \gamma + 4\pi r^2 \Delta \underline{G}_v \tag{6.6}$$

$$r^* = -\frac{2\gamma}{\Delta \underline{G}_v} \tag{6.7}$$

$$\Delta G^* = \frac{16}{3}\frac{\pi \gamma^3}{\Delta \underline{G}_v^2} \tag{6.8}$$

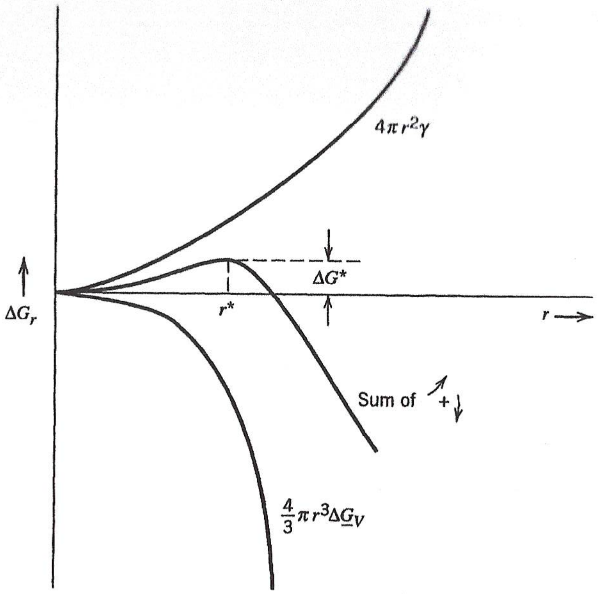


Figure 6.5 Gibbs free energy of nuclei as a function of radius.

6.3 SIZE DISTRIBUTION OF NUCLEI

One may well ask why nucleation takes place at all. How does a nucleus of size greater than r^* form at any time? Based on the principles discussed in Chapter 2 (Statistical Thermodynamics), we can calculate the probability that a particle of radius r will exist at a given temperature, and that probability will be greater than zero. Let the particle with radius r have a Gibbs free energy of formation ΔG_r, calculated according to Eq. 6.5. Consider now the entropy of mixing of these particles (numbering n_r) with atoms of the liquid (i.e., particles having atomic radius: numbering n_0). To minimize the Gibbs free energy of the combination of the two:

$$\Delta S_{\text{mix}} = k \ln \frac{(n_0 + n_r)!}{n_0! n_r!} \qquad (6.9)$$

$$\Delta G = n_r \Delta G_r - kT[(n_0 + n_r)\ln(n_0 + n_r) - n_0 \ln n_0 - n_r \ln n_r]$$

At the equilibrium value of n_r, $(\partial \Delta G_r/\partial n_r)_T = 0$ and

$$\Delta G_r + kT\left(\ln\left[\frac{n_r}{n_0 + n_r}\right]\right) = 0$$

Noting that $n_0 >> n_r$,

$$\frac{n_r}{n_0} = \exp\left(-\frac{\Delta G_r}{kT}\right) \qquad (6.10)$$

One could, based on Eq. 6.10, calculate the concentration of solid nuclei of radius r in a liquid at its melting point. In this case, the value of $\Delta \underline{G}_v$ is zero because the two phases, liquid and solid, are in equilibrium. Only the surface energy term of the equation comes into play. As an example, let us calculate the distribution of nuclei in nickel at its melting point, 1725 K.

For nickel: $T_m = 1725$ K

$$\frac{L}{T_m} = 10 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\gamma = 0.25 \text{ J/m}^{-2}$$

$$\underline{V} = 7 \text{ cm}^3\text{/mol}$$

$$n_0 = \frac{N_A}{\underline{V}} = 8.6 \times 10^{22} \text{ cm}^{-3}$$

From Eq. 6.5:

$$\Delta G_r = 4\pi r^2\gamma + \tfrac{4}{3}\pi r^3 \Delta \underline{G}_v$$

At the melting point, T_m, $\Delta \underline{G}_v = 0$ (see Eq. 6.2)

Thus:

$$\Delta G_r = 4\pi r^2\gamma$$

As an example, let us calculate the concentration of clusters of radius 7 Å at the melting point:

$$\Delta G_r = 4\pi(7 \times 10^{-10})^2(0.25) = 1.54 \times 10^{-18} \text{ J}$$

$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

$$n_r = 8.6 \times 10^{22} \exp\left[-\frac{1.5 \times 10^{-18}}{(1.38 \times 10^{-23})(1725)}\right]$$

$$n_r = 7.3 \times 10^{-6} \text{ clusters/cm}^3$$

By repeating the calculation for a series of cluster radii, we obtain the results in Table 6.1.

Table 6.1 Calculated Concentration of Solid Clusters in Liquid Nickel at the Melting Temperature as a Function of Cluster Size

r(Å)	n_r(clusters/cm^3)
5	4×10^9
6	2×10^2
7	7.3×10^{-6}
8	1.8×10^{-14}
10	4.4×10^{-35}

The results of the calculations in Table 6.1 show that the concentration of solid nuclei depends very strongly on cluster radius. This strong dependence enables us to speak of a "maximum" cluster radius at a given temperature (see Figure 6.6). Based on Eqs. 6.10 and 6.5, there is no true maximum cluster radius at a specified temperature. For every cluster size, there is a calculated concentration level. But a consideration of Table 6.1 should convince us that when concentrations of nuclei fall below one per cubic centimeter, we enter a size regime in which concentrations fall very rapidly as a function of cluster radius. We may, for our purposes, pick a reasonable concentration of nuclei, say one per cubic centimeter, and specify the cluster radius that exists at that concentration to be the maximum size. At the melting point of nickel, that calculated maximum radius would be about 6.3 Å.

6.4 SUPERCOOLING

Based on Eqs. 6.7, 6.8, and 6.10, we should be able to calculate the temperature at which a liquid will start to solidify through the process of homogeneous nucleation. As an example, let us calculate the probability of finding nuclei of critical size in pure nickel that has been supercooled 10 K below its melting point. Using the physical properties of nickel from Section 6.3, we express the critical radius for such a nucleus as follows:

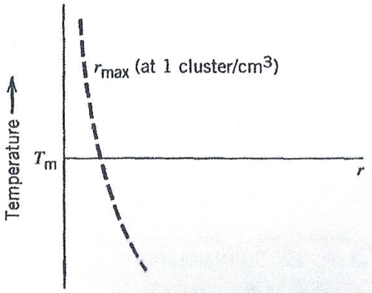


Figure 6.6 Maximum cluster radius r_{max} as a function of temperature.

$$r^* = -\frac{2\gamma}{\frac{L}{T_m}\frac{1}{\underline{V}}(T - T_m)} = -\frac{(2)(0.25)}{10\left(\frac{1}{7 \times 10^{-6}}\right)(-10)}$$

$$r^* = 350 \text{ Å}$$

The Gibbs free energy of this nucleus is:

$$\Delta G^* = \frac{16}{3}\frac{\pi\gamma^3}{\left[\frac{L}{T_m}\frac{1}{\underline{V}}(T_m - T)\right]^2}$$

$$\Delta G^* = 1.3 \times 10^{-15} \text{ J}$$

Based on Eq. 6.10, the concentration of such nuclei is

$$n_r = n_0 \exp\left[-\frac{\Delta G^*}{kT}\right] = 8.6 \times 10^{22} \exp\left[-\frac{1.3 \times 10^{-15}}{(1.38 \times 10^{-23})(1715)}\right]$$

$$n_r = (8.6 \times 10^{22})(10^{-24{,}000})$$

$$n_r \approx 10^{-24{,}000} \text{ cm}^{-3}$$

We may thus safely conclude that homogeneous nucleation does not take place in nickel at 10 K below its melting point, because the concentration of nuclei of the critical size is so low.

Using the same equations, we may calculate the maximum cluster size in liquid nickel as a function of temperature (Figure 6.6), noting that by "maximum" we mean the cluster size that is present in a concentration of at least one per cubic centimeter. The critical radius of nuclei as a function of temperature may be

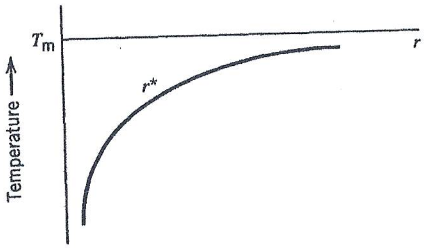


Figure 6.7 Critical radius r^* as a function of temperature.

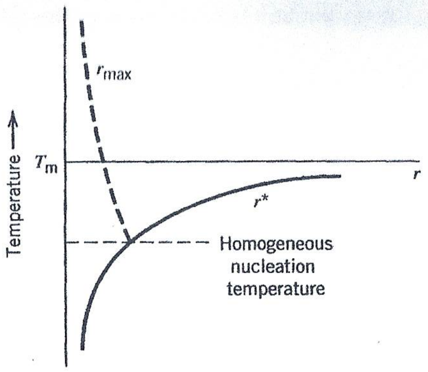


Figure 6.8 Superposition of Figures 6.6 and 6.7.

calculated from Eq. 6.7. The results are shown schematically in Figure 6.7. Figure 6.8 is a superposition of Figures 6.6 and 6.7. The intersection of the critical radius curve of Figure 6.7 with the maximum radius curve of Figure 6.6 should be at the temperature of homogeneous nucleation. We can calculate this temperature for pure nickel by repeating the calculation above for various degrees of supercooling. The results of such a calculation are presented in Table 6.2.

Based on Table 6.2, homogeneous nucleation should take place at about 340–350 K of supercooling. In fact, the maximum degree of supercooling for nickel is 319 K, observed in an experiment on the solidification of very fine droplets of liquid nickel.

6.5 HETEROGENEOUS NUCLEATION

Although it is possible to achieve supercooling levels exceeding 300 K in nickel, substantial supercooling of this magnitude takes place only under very carefully controlled experimental conditions. Under practical solidification conditions, supercooling of only a few degrees is observed because nuclei of the solid can be formed on surfaces that catalyze solidification, such as inclusions in the material being solidified, the walls of the container in which it is being held, or the surfaces of the casting molds. To catalyze solidification, the nucleus of solid must wet the catalyst to some extent. A nucleus catalyzed on a surface is shown schematically in Figure 6.9.

Table 6.2 Critical Radius and Concentration of Nucleii of Critical Radius as a Function of Temperature for Nickel[a]

$T - T_m$	r^* (Å)	ΔG (J)	n_r^* (cm^{-3})
10	350	1.3×10^{-15}	$10^{-24,000}$
100	35	1.3×10^{-17}	10^{-253}
300	11.7	1.45×10^{-18}	7×10^{-10}
325	10.7	1.24×10^{-18}	1.4×10^{-5}
340	10.3	1.12×10^{-18}	2.8×10^{-3}
400	9.0	8.2×10^{-19}	3700

[a] Actually: $T - T_m$ is observed for Ni at approximately 319 K.

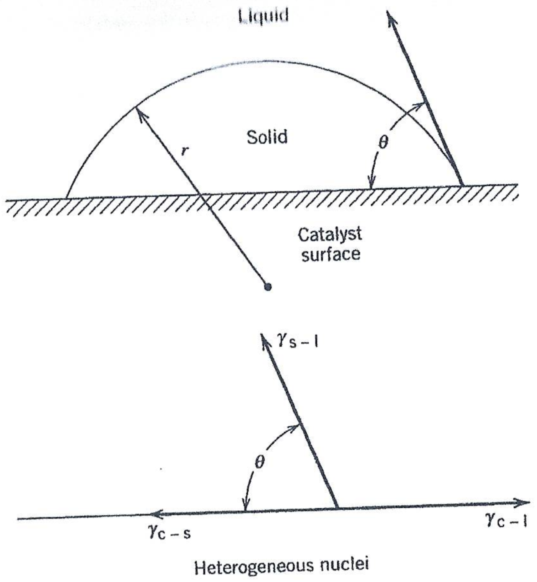


Figure 6.9 Catalysis of a nucleus on a surface.

The analysis of the energies involved in heterogeneous nucleation follows the same method as the one used for homogeneous nucleation in Section 6.2. In the case of a heterogeneous nucleus in the form of a spherical cap (Figure 6.9), the surface energy term involves the surface energy between the solid nucleus and the liquid, and the change in surface energy of the catalyst surface as it is coated by the nucleus. The surface energy term is derived as follows:

$$\text{solid–liquid surface} = 2\pi r^2(1 - \cos\theta) \tag{6.11}$$

$$\text{catalyst–solid surface} = \pi r^2(1 - \cos^2\theta) \tag{6.12}$$

where r is the radius of curvature of the nucleus. Then we write

$$\Delta G_{\text{surface}} = 2\pi r^2(1 - \cos\theta)\gamma_{s-l} + \pi r^2(1 - \cos^2\theta)(\gamma_{c-s} - \gamma_{c-l}) \tag{6.13}$$

where γ_{s-l} = solid–liquid interfacial energy
γ_{c-s} = solid–catalyst interfacial energy
γ_{c-l} = liquid–catalyst interfacial energy

The terms involving the interactions between the catalyst surface and the liquid and the solid can be expressed in terms of the solid–liquid interfacial energy by noting the relationships among them (Section 4.10):

$$\gamma_{c-l} = \gamma_{c-s} + \gamma_{s-l}(\cos\theta)$$

The volumetric Gibbs free energy change is the product of the volume of the cap and $\Delta\underline{G}_v$, the specific Gibbs free energy change. That volume, in terms of its radius of curvature and contact angle, is:

$$V = \frac{4}{3}\pi r^3 \left\{\frac{(2+\cos\theta)(1-\cos\theta)^2}{4}\right\} \qquad (6.14)$$

or

$$\Delta G_{\text{volumetric}} = \tfrac{4}{3}\pi r^3 \Delta\underline{G}_v f(\theta) \qquad (6.15)$$

where

$$f(\theta) = \left\{\frac{(2+\cos\theta)(1-\cos\theta)^2}{4}\right\} \qquad (6.16)$$

Following the method of Section 6.2 yields the following conclusion:

$$r^* = -\frac{2\gamma_{s-l}}{\Delta\underline{G}_v} \quad \text{and} \quad \Delta G^* = \frac{16}{3}\frac{\pi\gamma_{s-l}^3}{\Delta\underline{G}_v^2} f(\theta) \qquad (6.17)$$

It is particularly important to note that the critical radius of curvature, r^*, does not change when the nucleation becomes heterogeneous. The critical Gibbs free energy, ΔG^*, however, is strongly influenced by the wetting that occurs at the surface of the material that catalyzes the nucleation. A lower value of ΔG^* means a lower activation energy to be overcome in nucleation; that is, nucleation takes place more easily. The magnitude of the effect can be appreciated by considering values of $f(\theta)$, shown in Table 6.3. It can be shown that $f(\theta)$ is the ratio of the volume of the heterogeneous nucleus (the cap) to the volume of the sphere with the same radius of curvature.

Table 6.3 Values of $f(\theta)$ in Eq. 6.17, Indicating the Extent to Which the Activation Energy Is Reduced by Wetting of the Nucleus

θ	$f(\theta)$
90°	0.50
60°	0.16
30°	1.3×10^{-2}
10°	7.0×10^{-4}

Figure 6.10, a graph of ΔG as a function of radius of curvature of the nucleus, shows the effect of wetting on the critical Gibbs free energy to be overcome for the nucleus to form.

The critical Gibbs free energy for nucleation depends on the nucleus volume. This can be demonstrated by considering a nucleus having the shape of spherical cap with radius of curvature r. The Gibbs free energy of the nucleus depends on the interfacial energy and the volumetric Gibbs free energy change as follows:

$$\Delta G_r = \alpha r^2\gamma + \beta r^3 \Delta\underline{G}_v \qquad (6.18)$$

The parameters α and β are determined by the particular geometry of the nucleus. The surface energy term, γ, is an average surface energy for the nucleus determined according to the geometrical factors.

The volume of the nucleus is βr^3. To determine r^*,

$$\left(\frac{\partial \Delta G_r}{\partial r}\right)_T = 0$$

$$2\alpha\gamma r^* + 3\beta r^{*2}\Delta\underline{G}_v = 0$$

$$r^* = -\frac{2\alpha}{3\beta\Delta\underline{G}_v}\gamma \quad \text{or} \quad \alpha = -\frac{3\beta\Delta\underline{G}_v}{2\gamma} r^* \qquad (6.19)$$

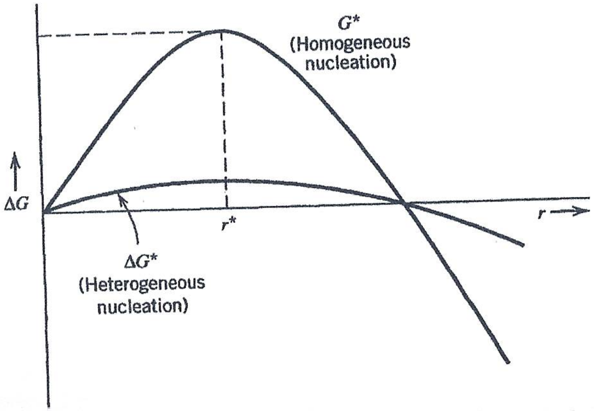


Figure 6.10 Plot of ΔG versus r for homogeneous nucleation and an example of heterogeneous nucleation.

Substituting in Eq. 6.18, we have

$$\Delta G_r^* = -\frac{3\beta\Delta\underline{G}_v r^*}{2}(r^*)^2 + \Delta\underline{G}_v\beta(r^*)^3$$

$$\Delta G_r^* = -\tfrac{1}{2}\beta(r^*)^3\Delta\underline{G}_v$$

$$\Delta G_r^* = -\tfrac{1}{2}V^*\Delta\underline{G}_v \tag{6.20}$$

where V^* is the volume of the critical nucleus.

From this analysis, it is apparent that any factors that reduce the volume of the nucleus reduce the critical Gibbs free energy of formation of that nucleus, making nucleation more probable.

6.6 RATE OF NUCLEATION

The rate of nucleation in a transformation is determined by the concentration of nuclei of the critical size and the rate at which they are "activated" through the addition of atoms or molecules to their surfaces. This may be expressed as follows:

$$\dot{N} = \nu n_s n^* \tag{6.21}$$

where n^* = concentration of critical nuclei
n_s = number of atoms or molecules on the nucleus surface
ν = collision frequency of molecules with nuclei

In the case of the formation of nuclei from a vapor (ideal gas), the collision frequency is given by the Langmuir equation (Section 2.12). The rate of nucleation is then:

$$\dot{N} = \frac{\alpha_c P}{(2\pi mkT)^{1/2}} A^* n_0 \exp\left(-\frac{\Delta G^*}{kT}\right) \tag{6.22}$$

where A^* is the area of the critical nucleus.

In the case of transformation in condensed phases, the collision frequency at the nucleus interface may be expressed as follows:

$$\nu = \nu_0 \exp\left(-\frac{\Delta G_M}{kT}\right) \tag{6.23}$$

where ν_0 is the jump frequency of the molecules or atoms at the surface of the nucleus and ΔG_M is the activation energy for the movement to the nucleus.

The nucleation rate would have the form:

$$N = \nu_0 n_s n_0 \exp\left(-\frac{\Delta G^*}{kT}\right)\exp\left(-\frac{\Delta G_M}{kT}\right) \tag{6.24}$$

The first exponential term in Eq. 6.24 increases as the temperature decreases below the equilibrium temperature for the reaction. To use solidification as an example,

$$\Delta G^* = \frac{16}{3}\frac{\pi\gamma^3}{\left[\frac{L}{T_m}\frac{1}{\underline{V}}(T - T_m)\right]^2} \tag{6.25}$$

At the melting temperature, T_m, ΔG^* is infinite and $\exp(-\Delta G^*/kT)$ is zero. As the temperature drops, the value of this exponential term increases.[1] The value of the second exponential term, $\exp(-\Delta G_M/kT)$, decreases as the temperature decreases, assuming that the activation energy term, ΔG_M, remains constant. The product of the two goes through a maximum as the temperature drops farther below the equilibrium temperature. This is illustrated in Figure 6.11. Because the nucleation rate passes through a maximum, we have the possibility of cooling a material rapidly enough to suppress the transformation altogether. This would be accomplished by passing through the temperature of the maximum nucleation rate before the equilibrium phase nucleates.

---

[1] It is interesting to note that the term $\exp(-\Delta G^*/kT)$ does not increase monatonically as temperature decreases below the equilibrium temperature. It can be shown to have a maximum as follows:

$$\frac{\Delta G^*}{kT} = \frac{16}{3}\frac{\pi\gamma^3}{(L^2/T^2)(1/\underline{V}^2)k}\left(\frac{1}{T}\right)\left(\frac{1}{T - T_m}\right)^2 = K\left(\frac{1}{T}\right)\left(\frac{1}{T - T_m}\right)^2$$

Maximum at

$$\frac{d[\exp(-\Delta G_m/kT)]}{dT} = 0$$

$$\exp\left[-K\left(\frac{1}{T}\right)\left(\frac{1}{T - T_m}\right)^2\right]\left[\frac{2}{T}\left(\frac{1}{T - T_m}\right)^3 - \left(\frac{1}{T - T_m}\right)\left(\frac{1}{T^2}\right)\right] = 0$$

$$T = \frac{T_m}{3} \text{ at maximum}$$

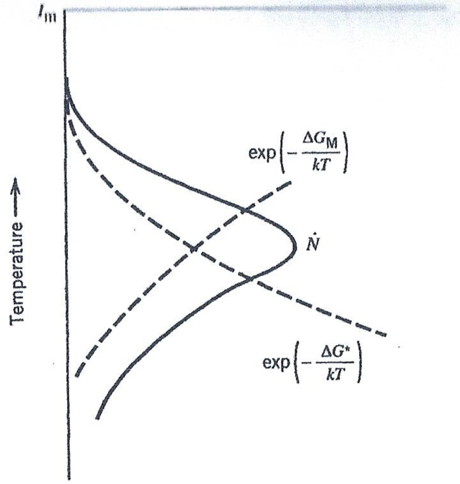


Figure 6.11 Nucleation rate $\dot{N}$ as a function of temperature.

6.7 GROWTH OF TRANSFORMED PHASE

The rate of growth of a transformation product is determined by the driving force for the transformation and the frequency with which molecules successfully make the transition from the reactant phase to the product phase. To use solidification as an example, the *driving force* is the negative of the ΔG of solidification:

$$-\Delta \underline{G} = \frac{L}{T_m}(T_m - T) \tag{6.26}$$

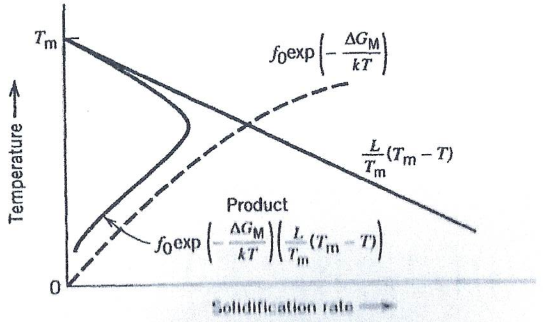


Figure 6.12 Solidification rate as a function of temperature.

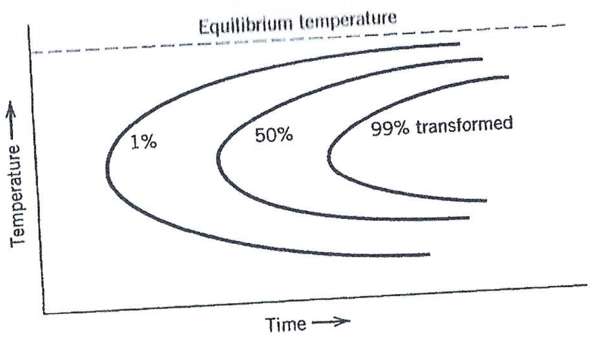


Figure 6.13 A TTT diagram.

The jump frequency across the liquid–solid interface has a temperature dependence of the form:

$$f = f_0 \exp\left(-\frac{\Delta G_M}{kT}\right) \tag{6.27}$$

where ΔG is the activation energy for movement across the liquid–solid interface. The product of the two is:

$$\text{solidification rate} = f_0 \exp\left(-\frac{\Delta G_M}{kT}\right)\left(\frac{L}{T_M}\right)(T_m - T) \tag{6.28}$$

As the temperature decreases, the driving force increases but the jump frequency decreases. These two opposing dependencies can produce a maximum in the rate of growth as a function of temperature, as illustrated in Figure 6.12.

The temperature dependencies of both nucleation of a new phase and its rate of growth result in a strong temperature dependence of transformation rate. Results of transformation studies are often presented in the form of diagrams in which the time required to transform a specific amount of the material is plotted against the temperature of transformation. A schematic example is shown in Figure 6.13. These curves are often referred to as time–temperature–transformation (TTT) curves, or "C" curves because their shape is in the form of the letter C.

The TTT curve of a transformation indicates that it may be possible to cool a material rapidly enough to slide past the nose of the curve, that is, to avoid the transformation and to arrive at a temperature where the transformation rate is very slow. This accounts for the existence of nonequilibrium structures, such as silicate glasses, and amorphous metals.

6.8 SPINODAL TRANSFORMATIONS

Two different types of diffusive transformations were discussed in Section 6.1—spinodal and those that are initiated by nucleation. The difference between the two was shown in graphical form in Figures 6.2–6.4. Nucleation was discussed in Section 6.2. Now we discuss the principles of decomposition of homogeneous solutions by the spinodal mechanism.

Recognize at the outset that we are discussing the decomposition of a supersaturated solution into its equilibrium phases. The solution became supersaturated, presumably, by being cooled into a temperature–composition region inside a miscibility gap. In the binary system we are considering, the solution will eventually decompose into a mixture of two phases.

Consider, first, the change of Gibbs free energy of the homogeneous, supersaturated solution as it undergoes composition fluctuations. For the purpose of our analysis, let the solution of overall composition c_o undergo local fluctuations of $\pm\delta c$; that is, it will split up into two regions of composition $c_o + \delta c$ and $c_o - \delta c$. We can expand the Gibbs free energy of the solution as a function of composition around the composition c_o by a Taylor series:

$$G_{c_o+\delta} = G_{c_o} + (\pm\delta c)G'_{c_o} + \tfrac{1}{2}(\pm\delta c)^2 G''_{c_o}$$

where

$$G'_{c_o} = \left(\frac{\partial G}{\partial c}\right)_{c_o} \qquad \text{and} \qquad G''_{c_o} = \left(\frac{\partial G^2}{\partial^2 c}\right)_{c_o}$$

The change in Gibbs free energy accompanying the composition fluctuation is:

$$\Delta G = G_{c_o \pm \delta_c} - G_{c_o}$$

$$\Delta G = \tfrac{1}{2}[(\delta c)G'_{c_o} + \tfrac{1}{2}(\delta c)^2 G''_{c_o}] + \tfrac{1}{2}[(-\delta c]G'_{c_o} + \tfrac{1}{2}(-\delta c)^2 G''_{c_o}]$$

$$\Delta G = \tfrac{1}{2}(\delta c)^2 G''_{c_o} \qquad \textbf{(6.29)}$$

If the second derivative of G with respect to composition is positive, then ΔG accompanying the fluctuation is positive, and the fluctuation will tend to collapse. This tells us that the solution is in a *metastable*, but not *unstable*, state. The decomposition of such a solution requires that nuclei of a new phase be formed as discussed in Section 6.2.

If, however, the second derivative of G with respect to composition is negative, then the ΔG accompanying the fluctuation is negative, and the fluctuations will tend to intensify. The solution is unstable. This is the spinodal decomposition case. The differences in composition profiles during the development of a new phase from the supersaturated solution are shown schematically in Figure 6.14 (Ref. 3) for the two cases.

As we have so far developed the basis for spinodal decomposition, we could conclude that there is no size limit or dimensional scale that characterizes the new phase. This is not the case, however. A wavelength or characteristic dimension is observed in spinodal decompositions. The explanation for this phenomenon lies in the observation that the Gibbs free energy of an atom in a *concentration gradient* is not the same as the Gibbs free energy of that atom in a solution of *uniform* composition (Ref. 4). Hillert showed this to be the case using a regular solution model. A rigorous derivation of the relationship (Ref. 5) yields, for a one-dimensional case:

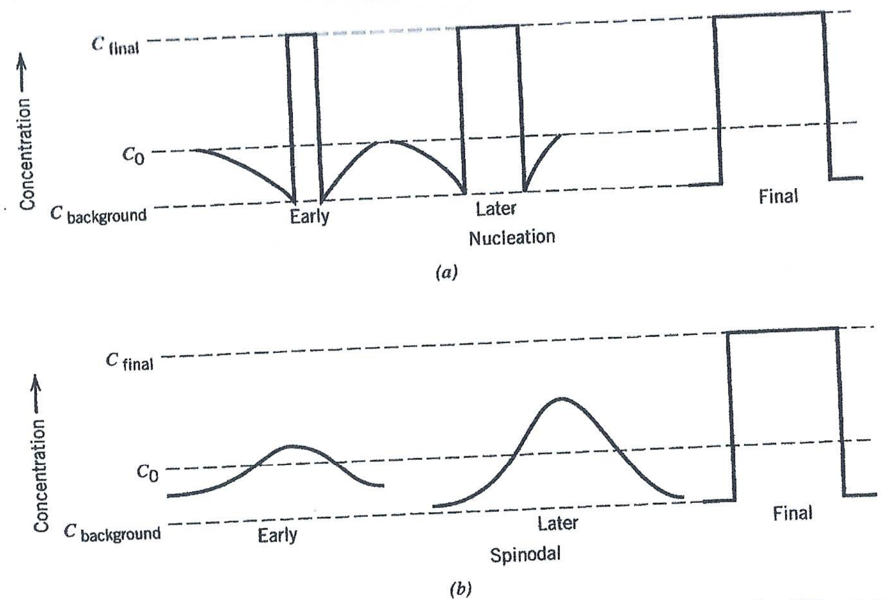


Figure 6.14 Schematic evolution of concentration profiles to illustrate the difference between the spinodal mechanism (*b*) and nucleation and growth (*a*).

$$G = N_V \int_V \left[\underline{G}_c + \kappa\left(\frac{dc}{dx}\right)^2\right] dV \qquad \textbf{(6.30)}$$

where N_V = number of atoms per unit volume
$\underline{G}(c)$ = Gibbs free energy (per atom) of a homogeneous solution of composition c
dc/dx = concentration gradient
κ = a constant that is positive when two phases tend to separate

Equation 6.30 tells us that the Gibbs free energy of a volume V of solution in a concentration gradient has two parts: the Gibbs free energy the volume would have if it existed as a part of a homogeneous solution of uniform composition, and another part that depends on the concentration gradient at that point. This last term is called the *gradient energy*. The concept of "gradient energy" is not intuitively obvious. Its plausibility can be demonstrated by comparing the energy associated with the bond energy of an atom with its nearest neighbors in a uniform solution, and in a concentration gradient. An example of such a calculation is presented in Appendix 6A.

If we expand $\underline{G}(c)$ in Eq. 6.30 in a Taylor series, and note that the odd terms will vanish in an isotropic medium, then the equation becomes:

$$\Delta G = N_V \int_V \left[\frac{1}{2} G''_{c_o} (\delta c)^2 + \kappa \left(\frac{dc}{dx} \right)^2 \right] dV \tag{6.31}$$

where G''_{c_o} is the second derivative of G with respect to concentration at C_o.

In Eq. 6.31, the value of G''_{c_o} is inherently negative inside the spinodal curve. The decomposition as a spinodal can proceed only if the overall ΔG is negative, that is, if[a]:

$$\frac{1}{2} \left| G''_{c_o} \right| (\delta c)^2 > \kappa \left(\frac{dc}{dx} \right)^2 \tag{6.32}$$

Based on Eq. 6.32, there is a minimum magnitude of fluctuation, δc, below which it is unstable. One solution of Eq. 6.31 has the form of a wave. Consider a composition fluctuation of size δc in the x direction expressed as a wave:

$$c - c_o = \delta c = A \cos \beta x \tag{6.33}$$

where $\beta = 2\pi/\lambda$.

By substituting in Eq. 6.33 in Eq. 6.31, and noting that $\int_0^{\pi} \sin^2 ax\, dx = \int_0^{\pi} \cos^2 ax\, dx = \pi/2$,

$$\frac{\Delta G}{V} = \frac{\pi A^2}{A} [G''_{c_o} + 2\kappa\beta^2] \tag{6.34}$$

Within the spinodal region the term G''_{c_o} is negative. The homogeneous solution of interest becomes unstable; that is, it will decompose as a spinodal, when $\Delta G < 0$. The critical value of β, β_c, at which $\Delta G = 0$ is:

$$\beta_c = \left[-\frac{1}{2\kappa} G''_{c_o} \right]^{1/2} \tag{6.35}$$

At values of β greater than β_c ($\lambda < \lambda_c$), the spinodal decomposition will not proceed. The critical wavelength, λ_c is

$$\lambda_c = \left[\frac{-8\pi^2\kappa}{G''_{c_o}} \right]^{1/2} \tag{6.36}$$

At values of λ less than λ_c, spinodal fluctuations will decay. The solution can still decompose to its equilibrium state, but not by the spinodal mechanism.

We can extend the treatment above to a consideration of the kinetics of the spinodal transformation (Refs. 3 and 5). The amplitude of a sinusoidal fluctuation can be expressed as follows:

$$A(\beta, t) = A(\beta, 0) \exp[R(\beta)t] \tag{6.37}$$

The amplification factor, $R(\beta)t$, is:

$$R(\beta)t = -\frac{B\beta^2}{N_V} [G''_{c_o} + 2\kappa\beta^2] \tag{6.38}$$

where B is the mobility, $A(\beta, t)$ is the amplitude of the fluctuation with wavelength β at time t, and $A(\beta, 0)$ is the initial amplitude at $t = 0$.

Based on Eq. 6.38, when $|G''_{c_o}| > 2\kappa\beta^2$, $R(\beta)$ is positive. Remember that G''_{c_o} is

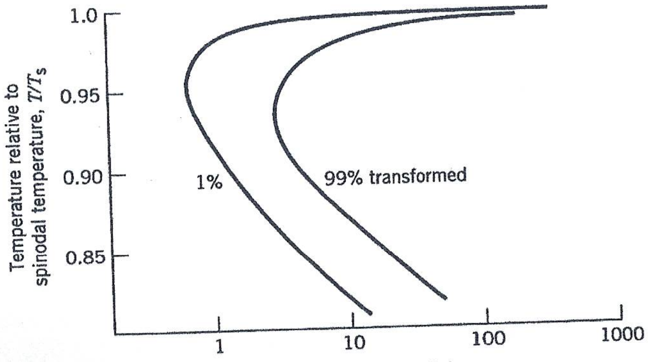


Figure 6.15 Schematic time–temperature–transformation diagram for spinodal decomposition. (From Ref. 7.)

---

[a] There can be other terms in the equation, such as the one representing elastic energy, if region of composition fluctuation is crystallographically coherent with the lattice of the solution but has different dimensions. This is discussed in Ref. 5. The conclusions reached relative to the existence of a minimum length of the new phase do not depend on this coherency energy, although it is important.

negative in the spinodal region. If the opposite is true ($|G''_{\mathrm{c}}| < 2\kappa\beta^2$), $R(\beta)$ will be negative, and the fluctuation will decay with time.

The amplification factor, $R(\beta)$, varies with wave number β and shows a maximum value, β_m when $\lambda = \sqrt{2}\lambda_c$, where λ_c is the critical wavelength (Eq. 6.36). The extent of a spinodal transformation can be expressed as a TTT diagram (or C curve) as in the case of nucleation and growth (Figure 6.13). A representative sample of such a curve is shown in Figure 6.15(7).

Spinodal transformations are observed in metallic, ceramic (Refs. 3 and 4), and polymer systems (Ref. 8).

REFERENCES

1. Porter, D. A., and Easterling, K. E., *Phase Transformations in Metals and Alloys,* second edition, Chapman and Hall, *London,* 1992.
2. Massalski, T. B., *Phase Transformations,* pp 433–483, American Society for Metals, 1968.
3. Cahn, J. W., *Trans. A.I.M.E., 242,* 166 (1968).
4. Hillert, M., *Acta Met., 9,* 525 (1961).
5. Cahn, J. W., and Hilliard, J. E., *J. Chem. Phys., 28,* 258 (1958).
6. Kingery, W. D., Bowen, H. K., and Uhlmann, D. R., *Introduction to Ceramics,* second edition. Wiley, New York, 1976.
7. Huston, E. L., Cahn, J. W., and Hilliard, J. E., *Acta Met., 14,* 1053 (1966).
8. "Structure and Properties of Polymers," *Materials Science and Technology,* Vol. 12, VCH Publishers, *Weinheim,* Germany, 1993.

APPENDIX 6A

Gradient Energy in a Regular Solution

Equation 6.30 indicates the Gibbs free energy of an atom in a *concentration gradient* is not the same as the Gibbs free energy of that atom in a solution of *uniform* composition. According to the equation, a gradient energy term, proportional to *dc/dx* must be added to the Gibbs free energy term for the atom in a uniform solution.

$$G = N_V \int_V \left[\underline{G}_c + \kappa \left(\frac{dc}{dx} \right)^2 \right] dV \qquad \textbf{(6.30)}$$

where $\underline{G}(c)$ is the Gibbs free energy (per atom) of a homogeneous solution of composition c, and dc/dx is the concentration gradient.

The purpose of this calculation is to demonstrate that a gradient energy term will arise when a regular solution model of atomic interactions (nearest neighbor) is used to describe the energy of an atom in a concentration gradient. Only the energy term of the regular solution model is needed.

In a regular solution, the energy of an atom in a uniform binary solution of composition c with coordination number Z is $\omega c(1 - c)$, where ω is $Z(E_{AB} - \frac{1}{2}(E_{AA} + E_{BB}))$. For convenience, let us write this as $Zc(1 - c)\Delta E$, where ΔE is $[E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})]$.

Let us consider an atom in a close-packed plane in a close-packed structure. Its overall coordination number is 12. In the close-packed plane there are six nearest neighbors, and there are three nearest neighbors in each of the neighboring planes. The energy of this atom will be the sum of its interaction with the 12 nearest neighbors, six in its plane and three each in the neighboring planes.

If the atom exists on a plane where the concentration is c_o, the next plane (to its right) will have a concentration of $c_o + (dc/dx)\Delta x$, where Δx is the interplanar spacing and dc/dx is the concentration gradient. The plane to the left will have a concentration of $c_o - (dc/dx)\,\Delta x$. For the purpose of this calculation, let $\Delta c = (dc/dx)\Delta x$. The energy of the atom in the concentration gradient is:

$$\begin{aligned} E &= 6[c(1 - c)\Delta E] + 3[(c + \Delta c)(1 - (c + \Delta c))]\Delta E \\ &\quad + 3[(c - \Delta c)(1 - (c - \Delta c))]\Delta E \\ E &= 6[c(1 - c)\Delta E] + 6[c(1 - c) + (\Delta c)^2]\Delta E \\ E &= 12[c(1 - c)\Delta E] + 6(\Delta c)^2\Delta E \\ E &= 12[c(1 - c)\Delta E] + 6\left(\frac{dc}{dx}\right)^2 (\Delta x)^2\Delta E \end{aligned}$$

This first term in the energy equation, $12c(1 - c)\Delta E$, is the energy the atom would have if it were in a uniform solution of composition c. The second term, $6(dc/dx)^2(\Delta x)^2\Delta E$, is the gradient energy term.

PROBLEMS

6.1 For pure, liquid copper at its melting point, what is the Gibbs free energy of formation of a spherical crystalline cluster of solid (a nucleus of solid) of radius 5, 7, 10Å?

Estimate the concentration of such nuclei (r = 5, 7, 10 Å).

For copper:

Melting temperature = 1083°C
γ_{s-l} = 200 ergs/cm^2
Heat of fusion = 3120 cal/mol
Assume that the molar volume is 7.0 cm^3/mol for both solid and liquid.

6.2 In experiments on homogeneous nucleation, it has been found that solidification of many pure metals can be suppressed to a temperature where $\Delta G^*/kT$, the exponential term in the nucleation equation, reaches a value of about 30. Assuming that copper is such a metal, estimate the value of the liquid–solid interfacial energy using the following data.

DATA

Melting point = 1356 K
Entropy of fusion = 2.29 cal/(mol·K)
Specific volume = 7 cm^3/mol
Maximum observed supercooling is 236 K

6.3 What is the radius of the critical-sized nucleus of solid copper at 236 K below the melting point using the information in Problem 6.2?

6.4 The temperature at which nuclei of solid water (ice) form homogeneously from undercooled water is −40°C.

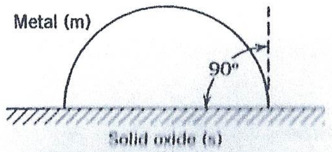
(a) What is the critical radius of the solid water nuclei at this temperature?
(b) Why do ponds freeze when the temperature is just a few degrees below the equilibrium freezing point (0°C)?

DATA

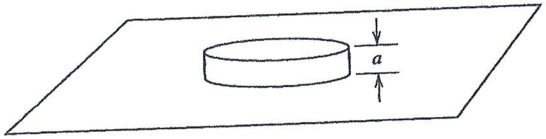
Interfacial energy between solid and liquid water is 25 ergs/cm^2.
Latent heat of fusion of ice is 335 J/g.
Density of ice is 0.92 g/cm^3.

6.5 A metal (m) being deposited on a solid oxide surface (s) from the vapor (v) condenses as spherical caps. The contact angle θ is 90°, as indicated in the accompanying diagram.

(a) What is the relationship between the surface energy of the solid surface (γ_{sv}) and the interfacial energy between the metal and the surface (γ_{sm})?
(b) Derive an equation for the critical radius size of a nucleus of the metal as a function of the surface energy of the metal (γ_{mv}) and the volumetric change of Gibbs free energy ($\Delta \underline{G}_v$).
(c) Derive an equation for the Gibbs free energy of the critical nucleus as a function of the surface energy of the metal (γ_{mv}) and the change of Gibbs free energy per unit volume ($\Delta \underline{G}_v$).



6.6 Cylindrical particles of a metal are being grown on the flat surface of the same metal. The height of the particles is constant (a). (This could represent the growth of a new layer of atoms.) Derive an equation for the critical radius of the particles and for the critical free energy change necessary for the nucleation of the particles in terms of the solid–vapor interfacial energy, the entropy of sublimation, and the specific volume of the metal.



Chapter 7

Reaction Kinetics

The principles discussed in the preceding chapters can now be combined to study the rates of change in various chemical and physical systems. This is the study of reaction kinetics. In this chapter, we consider reactions of three different types: homogeneous reactions in fluids, solid state reactions, and heterogeneous reactions.

In homogeneous reactions, the reactants and products exist in the same phase—for example, two gases reacting to form a third gas. In heterogeneous reactions, the reactants and products exist in different phases. An example is the reaction between gaseous oxygen and solid aluminum to form solid aluminum oxide. Solid state reactions, as the words imply, are reactions in which the reactants and products are in the solid state. The kinetics in solid state reactions differ from the other two classes because of the relatively low mobility of the reactants and the products. An example of this type of transformation is the recrystallization of a cold-worked piece of metal to form relatively strain-free grains. Another is the growth of crystallites in an amorphous polymer, or a glass.

Before studying the individual reaction types, we will review the terminology used in the study of chemical reaction kinetics.

7.1 RATE OF REACTION

Consider the following reaction in which "a" moles of material A react with "b" moles of B to form "c" moles of C and "d" moles of D.

$$aA + bB = cC + dD \tag{7.1}$$

The number of moles of C at any time after the reaction has begun (n_c) can be expressed as follows:

$$n_C = n_C^\circ + c\xi \tag{7.2}$$

where ξ is the extent of the reaction.

In general form, Eqs. 7.1 and 7.2 are written as Eqs. 7.3a and 7.3b:

$$0 = \sum_i \nu_i A_i \tag{7.3a}$$

$$n_i = n_i^\circ + \nu_i \xi \tag{7.3b}$$

where ν_i represents stoichiometric coefficients (negative for reactants, positive for products).

Take as an example the following situation:

3A	+	B	=	C	+	2D	
1		1		0		0	Before reaction (n_i°)
$1 - 3\xi$		$1 - \xi$		ξ		2ξ	After reaction (ξ)

The rate of reaction R is defined as the rate of change of ξ with time.

$$R = \frac{d\xi}{dt} \tag{7.4}$$

The rate of change of the number of moles of species i can be written as follows:

$$\frac{dn_i}{dt} = \nu_i \frac{d\xi}{dt} \tag{7.5}$$

If species involved in a chemical reaction are contained in a volume (which is assumed to be constant), Eq. 7.5 can be written in terms of concentrations:

$$C_i = \frac{n_i}{V}$$

$$\frac{1}{V}\frac{d\xi}{dt} = \frac{1}{\nu_i}\frac{dC_i}{dt} \tag{7.6}$$

7.2 ORDER OF REACTIONS

When reaction rates are determined experimentally, it is often found that the expression for the rate or the extent of reaction can be expressed in the following way[1]:

$$\frac{1}{V}\frac{d\xi}{dt} = kC_A^\alpha C_B^\beta \quad \text{or} \quad k[A]^\alpha[B]^\beta \tag{7.7}$$

The exponents of the concentrations, α and β, are called the orders of the reaction. In this case the reaction would be called "of order α" with respect to A, "of order β" with respect to B, or "of order α plus β" overall.

As an example, consider the dissociation of hydrogen iodide into hydrogen and iodine:

$$2HI \rightarrow H_2 + I_2$$

For this reaction it has been found experimentally that

$$-\frac{d[HI]}{dt} = k[HI]^2$$

Because of this relationship, this decomposition is a second-order reaction. It is important to note that the order of a reaction is not necessarily related to the stoichiometric coefficients (a, b, c, d). For example, the reaction of ozone to form oxygen can be written as follows:

$$2O_3 \rightarrow 3O_2$$

If the reaction were an elementary bimolecular reaction, it would be expected to be second order with relation to ozone as follows:

$$-\frac{d[O_3]}{dt} = k\,[O_3]^2$$

Actually, measurements have shown that

$$-\frac{d[O_3]}{dt} = k\,\frac{[O_3]^2}{[O_2]}$$

---

[1] The square bracket notation for concentration—for example, [C] for the concentration of C—will be used interchangeably with the symbol C_C.

This suggests a much more complex reaction path for the formation of oxygen from ozone. One explanation might entail the assumption that ozone breaks down into oxygen and monatomic oxygen in the following reaction:

$$\mathrm{O_3} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{O_2} + \mathrm{O}$$

Further assume that this monatomic oxygen reacts with ozone to form two diatomic oxygen molecules.

$$\mathrm{O} + \mathrm{O_3} \xrightarrow[k_2]{} 2\mathrm{O_2}$$

If the first reaction proceeds rapidly so that equilibrium is achieved, then the equilibrium constant for the reaction will be:

$$[\mathrm{O}] = K\frac{[\mathrm{O_3}]}{[\mathrm{O_2}]}$$

where $K = \dfrac{k_1}{k_{-1}}$ (see section 7.3)

And for the second reaction we will have

$$-\frac{d[\mathrm{O_3}]}{dt} = k_2[\mathrm{O}][\mathrm{O_3}]$$

Then the overall reaction rate can be expressed as follows:

$$-\frac{d[\mathrm{O_3}]}{dt} = k_2[\mathrm{O}][\mathrm{O_3}] = k_2K\frac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]}$$

This is one explanation for the form of the experimentally determined rate of the reaction.

The important point made by the example above is that the order of reaction is not necessarily related to the stoichiometric coefficients.

The order of a reaction with respect to a particular component can be determined from experimental data. The data needed are the concentrations of that component as a function of time in the reaction of interest. As an example, consider the reaction of A and B to form another compound. The rate of reaction is expressed by Eq. 7.7:

$$\frac{1}{V}\frac{d\xi}{dt} = k[A]^{\alpha}[B]^{\beta}$$

Our task is to determine α, the order of the reaction with respect to A, from data. Let us assume that the data are reliable and accurate enough to determine the slope of the plot of $[A]$ versus time, $d[A]/dt$. From Eq. 7.6,

$$\frac{1}{V}\frac{d\xi}{dt} = -\frac{d[A]}{dt} = k[A]^{\alpha}[B]^{\beta} \tag{7.8}$$

Taking the logarithm of both sides of eq. 7.8,

$$\ln\left(-\frac{d[A]}{dt}\right) = \ln k + \beta \ln [B] + \alpha \ln [A]$$

Assuming that $[B]$, the concentration of B, does not change appreciably during the reaction, the slope of the graph of the logarithm of $(-d[A]/dt)$ versus the logarithm of $[A]$ is α, the order of the reaction with respect to A.

7.3 EQUILIBRIUM CONSTANTS: RELATION TO REACTION RATE CONSTANTS

Consider the reaction of a molecule dissociating to form two ions:

$$\mathrm{MX} \rightarrow \mathrm{M^+} + \mathrm{X^-} \tag{7.8}$$

The equilibrium constant for this reaction (considering all the species to be present as ideal solutions) would be, in terms of concentrations:

$$K = \frac{[\mathrm{M^+}][\mathrm{X^-}]}{[\mathrm{MX}]} \tag{7.9}$$

If we think of this reaction in kinetic terms, we can define a reaction rate constant in the forward and reverse directions (f^+ and f^-). Assuming first-order kinetics, the rate of change of the concentration of the molecule MX is

$$\mathrm{MX} \underset{f^-}{\overset{f^+}{\rightleftarrows}} \mathrm{M^+} + \mathrm{X^-} \tag{7.10}$$

$$\frac{d[\mathrm{MX}]}{dt} = -f^+[\mathrm{MX}] + f^-[\mathrm{M^+}][\mathrm{X^-}] \tag{7.11}$$

At equilibrium, the rate of change of the concentration of this salt will be zero; hence,

$$\frac{d[\mathrm{MX}]}{dt} = 0 \tag{7.12}$$

$$f^+[\mathrm{MX}] = f^-[\mathrm{M}^+][\mathrm{X}^-] \tag{7.13}$$

$$\frac{[\mathrm{M}^+][\mathrm{X}^-]}{[\mathrm{MX}]} = \frac{f^+}{f^-}$$

which implies

$$\frac{f^+}{f^-} = K_{\mathrm{equilibrium}} \tag{7.14}$$

The ratio of the forward and reverse reaction rates is the equilibrium constant. Thus we can conclude that chemical equilibrium is not necessarily a static situation. Rather, we can view it as a balance between forward and reverse reaction rates so that the concentration of the various species remains constant, but the form of the individual chemical reactants and products may change with time. In the solid state, for example, we have the formation and annihilation of Schottky defects. Schottky defects may, through time, be formed and destroyed at various sites in the crystal. But at equilibrium, the product of the concentrations of vacancies on the anion and cation sites is constant, $[V'_{\mathrm{M}}] \times [V^{\bullet}_{\mathrm{X}}] = K$. At equilibrium, the rate of formation of the defects must equal their rate of annihilation.

7.4 FIRST-ORDER REACTIONS

An example of a first-order reaction is the decomposition of material A into a product (or products). As a simplification, let us first treat a case in which only the forward reaction (from the reactant to the product) is important. This means that the reverse rate, f^-, is negligible in comparison with the forward rate, f^+. Said another way, the equilibrium constant is large; that is, the reaction strongly favors the product or products. Because the reaction is first order, reaction rate and concentrations are related as follows:

$$\mathrm{A} = \text{products}$$

from

$$\frac{1}{V}\frac{d\xi}{dt} = \frac{1}{\nu_i}\frac{dC_i}{dt} \quad \text{with} \quad \nu_{\mathrm{A}} = -1$$

$$\frac{1}{V}\frac{d\xi}{dt} = -\frac{d[\mathrm{A}]}{dt}$$

If the reaction is first order:

$$\frac{1}{V}\frac{d\xi}{dt} = k[\mathrm{A}] \tag{7.15}$$

Thus, the simple differential equation relating concentration and time is

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}] \tag{7.16}$$

Assuming that the concentration of material A at time zero is $[\mathrm{A}_0]$, the integrated form of the equation can be derived as follows:

$$\int_{[\mathrm{A}_0]}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = -k\int_0^t dt$$

$$\ln\frac{[\mathrm{A}]}{[\mathrm{A}_0]} = -kt$$

$$[\mathrm{A}] = [\mathrm{A}_0]\exp(-kt) \tag{7.17}$$

A good example of this kind of reaction is the decay of a radioactive species. In this case the relationship between the number of moles of the radioactive species present at any time (N) and the amount originally present at time zero (N_0) is:

$$N = N_0\exp(-\lambda t) \tag{7.18}$$

where λ is called the decay constant.

By taking the natural logarithm of both sides of Eq. 7.18, we can see that a graph of the natural log of the number of moles of the species present at any time versus time will be a straight line with the slope negative λ.

$$\ln N = \ln N_0 - \lambda t$$

In the case of radioactive species, this decay constant is often expressed in terms of the half-life of the species (τ), the time in which the concentration is reduced to half the original concentration. In this case $N/N_0 = \frac{1}{2}$; thus:

$$\frac{N}{N_0} = \frac{1}{2} = \exp(-\lambda\tau)$$

$$2 = \exp(\lambda\tau) \qquad \text{or} \qquad \lambda = \frac{\ln 2}{\tau}$$

Substituting in Eq. 7.18:

$$N = N_0 2^{-t/\tau} \quad \text{or} \quad N = N_0\left(\frac{1}{2}\right)^{t/\tau} \tag{7.19}$$

An application of Eq. 7.19 is in the carbon dating of archaeological samples. Carbon-14 is a radioactive isotope of carbon with a half-life of 5760 years. Cosmic radiation in the upper atmosphere synthesizes carbon-14, which balances the loss due to radioactive decay. Living matter exchanges carbon with the atmosphere and maintains a level of carbon-14 that produces 15.3 disintegrations per minute per gram of carbon contained. Dead organisms no longer exchange carbon with atmospheric CO_2, and the amount of carbon-14 in dead material decreases with time as a result of radioactive decay. As an example, let us calculate the age of an archaeological sample that undergoes 10 disintegrations per minute per gram of carbon in the sample. Because we are dealing with a first-order reaction, the rate of disintegration is proportional to the amount of carbon-14 present. Hence:

$$\frac{N}{N_0} = \frac{10}{15.3} = 0.65$$

From Eq. 7.18,

$$\ln\frac{N}{N_0} = -\lambda t = \ln 0.65 = -0.43$$

From the definition of the half-life,

$$\lambda = \ln\frac{2}{\tau} = \ln\frac{2}{5760} = 1.23 \times 10^{-4}\ \text{year}^{-1}$$

$\frac{\ln 2}{\tau}$

Hence, the age of the sample is about

$$t = \frac{0.43}{1.23 \times 10^{-4}} = 3530\ \text{years},$$

better stated as 3500 years, considering the accuracy possible in these measurements.

7.5 FIRST-ORDER REACTIONS WITH FORWARD AND REVERSE RATES

Section 7.4 dealt with the type of first-order reaction, such as radioactive decay, in which the forward rate dominates. It is hard to imagine that process of radioactive decay reversing itself spontaneously.

In this section we consider a first-order reaction in which both the forward and reverse reactions must be considered. We will demonstrate that the rate of a reaction (the reaction rate constant) depends on the driving force (the decrease in Gibbs free energy) when the driving force is small compared to RT, as in the case of nucleation or diffusion. The reaction rate will be independent of the magnitude of the driving force when the driving force is large compared to RT, as in radioactive decay or oxidation reactions with large values of ΔG.

Consider the reaction below.

$$\mathrm{A} \underset{f^-}{\overset{f^+}{\rightleftarrows}} \mathrm{B} \tag{7.20}$$

If we assume first-order kinetics for both the forward and reverse reactions, then:

$$-\frac{d[\mathrm{A}]}{dt} = -[\dot{\mathrm{A}}] = f^+[\mathrm{A}] - f^-[\mathrm{B}] \tag{7.21}$$

At equilibrium, the rate of change of the concentration of A, $[\dot{\mathrm{A}}]$, is zero, hence:

$$\frac{f^+}{f^-} = \frac{[\mathrm{B}]_e}{[\mathrm{A}]_e} = K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{\mu_B^\circ - \mu_A^\circ}{RT}\right)$$

where $[\mathrm{A}]_e$ is the equilibrium concentration of A.

Substituting in Eq. 7.21 yields

$$-[\dot{\mathrm{A}}] = f^+\left([\mathrm{A}] - \frac{[\mathrm{A}]_e}{[\mathrm{B}]_e}[\mathrm{B}]\right)$$

$$-[\dot{\mathrm{A}}] = f^+\left(1 - \frac{[\mathrm{A}]_e}{[\mathrm{B}]_e}\frac{[\mathrm{B}]}{[\mathrm{A}]}\right)[\mathrm{A}] \tag{7.22a}$$

If we want to use the simple form of the kinetic equation derived in Section 7.4 (Eq. 7.17), we can substitute as follows:

$$f = f^+\left(1 + \frac{[\mathrm{A}]_e}{[\mathrm{B}]_e}\frac{[\mathrm{B}]}{[\mathrm{A}]}\right) \tag{7.22b}$$

To put this expression in terms of the Gibbs free energy, or chemical potential change involved in the reaction, we can make the following substitutions:

$$\mu_A = \mu_A^\circ + RT\ln a_A$$

Assuming ideal solutions,

$$a_A = x_A \qquad \text{and} \qquad x_A = \frac{N_A}{N_A + N_B}$$

The concentration of A, [A] = N_A/V, where N_A is the number of moles of A and V is the volume. Thus:

$$\mu_A = \mu_A^\circ + RT \ln\left\{[A]\left(\frac{V}{N_A + N_B}\right)\right\}$$

The term $V/(N_A + N_B)$ is the molar volume, $\underline{V}$. Setting the molar volumes of A and B each equal to the overall molar volume,

$$\mu_A = \mu_A^\circ + RT_{\ln}\{[A]\underline{V}\}$$

or

$$[A] = \frac{1}{\underline{V}} \exp\left(\frac{\mu_A - \mu_A^\circ}{RT}\right)$$

The same is true for component B.

Then:

$$\frac{[B]}{[A]} = \exp\left(\frac{\mu_B - \mu_A}{RT}\right) \exp\left(\frac{\mu_A^\circ - \mu_B^\circ}{RT}\right) = \exp\left(\frac{\mu_B - \mu_A}{RT}\right) \exp\left(-\frac{\Delta G^\circ}{RT}\right)$$

But,

$$\frac{[B]_e}{[A]_e} = K = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$$

Hence,

$$\frac{[B]}{[A]} = \exp\left(\frac{\mu_B - \mu_A}{RT}\right) \frac{[B]_e}{[A]_e}$$

Substituting in Eq. 7.22b, we have

$$-[\dot{A}] = f^+ \left\{1 - \exp\left(\frac{\mu_B - \mu_A}{RT}\right)\right\} [A]$$

Thus the first-order rate constant is

$$f = f^+ \left\{1 - \exp\left(\frac{\mu_B - \mu_A}{RT}\right)\right\} \tag{7.23}$$

This expression is sometimes written in terms of the driving force for the reaction ΔG_r, or $\mu_A - \mu_B$, which is the negative of the ΔG of reaction as normally written.

$$f = f^+ \left\{1 - \exp\left(-\frac{\Delta G_r}{RT}\right)\right\} \tag{7.24}$$

When the driving force for the reaction is large (i.e., ΔG is large as compared to RT), the exponential term in Eq. 7.24 becomes negligible compared to 1 and the overall reaction rate is simply the forward rate as in Section 7.4.

$$f = f^+ \left\{1 - \exp\left(-\frac{\Delta G_r}{RT}\right)\right\} = f^+ \tag{7.25a}$$

One such case has already been discussed, that of radioactive decay. Another illustration is the oxidation of silicon to form silicon dioxide. At 900°C (1173 K), the ΔG° for the reaction is about $-700{,}000$ J/mol. The term $\Delta G^\circ/RT$ is about 72, and $\exp(-\Delta G^\circ/RT)$ is about 6×10^{-32}. Thus the frequency of the reverse reaction is negligible, and the overall reaction rate is simply equal to the forward reaction rate.

By contrast, when ΔG_r is small compared to RT, Eq. 7.24 becomes (noting that $\exp x = 1 - x$ when x is small):

$$f = f^+ \left\{1 - 1 + \frac{\Delta G_r}{RT}\right\}$$

$$f = f^+ \left\{\frac{\Delta G_r}{RT}\right\} \tag{7.25b}$$

In many condensed state reactions ΔG_r is indeed small compared to RT. Grain growth in a solid is one example. In a solid with an average grain size of 0.1 mm, there is about 300 cm^2 of grain boundary per cubic centimeter of material. The driving force for grain growth is the reduction of total interfacial energy. Assuming a specific interfacial energy of about 300 ergs/cm^2 gives a total grain boundary energy of the order of 10^5 ergs per cubic centimeter of material, or about 0.1 J per mole of material, assuming a molar volume of about 10 cm^3/mol. The term $\Delta G_r/RT$ at a temperature of about 900 K is about 3×10^{-5}, a value small compared to 1. This means that the reaction rate for grain growth takes the form of Eq. 7.25b. The reaction rate depends on the magnitude of the driving force in the case at hand. There is no universal rate that characterizes grain growth in a particular material. The recrystallization of cold-worked material is another example. The degree of cold work (or amount of energy stored in the lattice distortion) will influence the reaction rate as the material recrystallizes to form stress-free grains.

As another example, consider the process of diffusion as a reaction. In this case, we think of the reaction as the jump of atoms from one lattice position to another, a movement through a distance λ. The velocity of the atom is

$$v = f\lambda \tag{7.26a}$$

where f is the "reaction rate."

The flux of diffusing atoms is

$$J = vC = f\lambda C \tag{7.26b}$$

where C is the concentration of the diffusing species. Expressing the reaction rate according to Eq. 7.25b because the term $\Delta G_r/RT$ is small, we write

$$f = f^+\left\{\frac{\Delta G_r}{RT}\right\}$$

Substituting for the chemical potential and assuming ideal solutions:

$$\Delta G_r = -\left(\frac{\partial\mu}{\partial x}\right)_T \Delta x = -\left(\frac{\partial\mu}{\partial x}\right)_T \lambda = -\left(\frac{\partial(RT\ln C)}{\partial x}\right)_T \lambda$$

At constant T,

$$\frac{\Delta G_r}{RT} = -\frac{dC}{dx}\left(\frac{1}{C}\right)\lambda \quad \text{or} \quad f = -f^+\lambda\frac{1}{C}\frac{dC}{dx}$$

$$J = f\lambda C = -f^+\lambda^2\frac{dC}{dx}$$

Thus the reaction rate approach yields a relationship that is parallel to Fick's first law, where the diffusion coefficient D is

$$D = f^+\lambda^2 \tag{7.27}$$

7.6 HIGHER ORDER REACTIONS

The mathematical representation of the kinetics of higher order reactions is a straightforward exercise in calculus. For a second-order reaction of the form

$$2\text{A} = \text{products} \tag{7.28}$$

the differential equation relating concentration and time is:

$$-\frac{d[\text{A}]}{dt} = k[\text{A}]^2 \tag{7.29a}$$

In integrated form this yields:

$$\frac{1}{[\text{A}]} - \frac{1}{[\text{A}_0]} = kt \tag{7.29b}$$

Consider a second-order reaction involving reactants A and B:

$$\text{A} + \text{B} = \text{products}$$

The reaction rate equation is:

$$\frac{d[\text{A}]}{dt} = -k[\text{A}][\text{B}] \tag{7.30}$$

The integrated form of the Eq. 7.30 depends on the relationship of the initial concentrations of A and B, $[\text{A}_0]$ and $[\text{B}_0]$. If $[\text{A}_0] = [\text{B}_0]$, then:

$$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}_0]} + kt \quad \text{or} \quad \frac{1}{[\text{B}]} = \frac{1}{[\text{B}_0]} + kt \tag{7.31}$$

If the initial concentrations of A and B, $[\text{A}_0]$ and $[\text{B}_0]$, are different, then:

$$\ln\left(\frac{[\text{A}]}{[\text{A}_0]}\right) - \ln\left(\frac{[\text{B}]}{[\text{B}_0]}\right) = -k([\text{B}_0] - [\text{A}_0])t \tag{7.32a}$$

An interesting special case arises when one of the reactants, B for example, is present in very much larger concentration than A. During the reaction, the concentration of B will not change much, i.e., $[\text{B}] = [\text{B}_0]$ or $[\text{B}]/[\text{B}_0] = 1$. Eq. 7.32a then becomes:

$$\ln\frac{[\text{A}]}{[\text{A}_0]} = -(k[\text{B}_0])t \tag{7.32b}$$

The reaction, thus, becomes essentially first-order with respect to A. The rate constant is $k[\text{B}_0]$. (See text following Eq. 7.8.)

For third-order reactions of the kind:

$$3\text{A} = \text{products} \tag{7.33}$$

The corresponding equations are:

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^3 \qquad (7.34a)$$

$$\frac{1}{[\mathrm{A}]^2} - \frac{1}{[\mathrm{A}_0]^2} = kt \qquad (7.34b)$$

7.6 REACTIONS IN SERIES

In this section we consider a situation in which two reactions may take place in series. Material A reacts (or decomposes) into material B, which in turn forms material C. Diagrammatically this can be shown as

$$\begin{tikzcd}
\mathrm{A} \arrow[r, "f_1"] \arrow[rr, bend left, "f"] & \mathrm{B} \arrow[r, "f_2"] & \mathrm{C}
\end{tikzcd}$$

$[\mathrm{A}_0]$	0	0	Initial concentrations
$[\mathrm{A}]$	$[\mathrm{B}]$	$[\mathrm{C}]$	Concentration during reaction

Through the mathematical manipulations to be shown, we will illustrate that the overall rate of reaction A to C will be governed by the relative rates of reaction f_1 and f_2. The slower of the two will control the overall reaction.

For simplicity, assume that the reactions are all first order, and that at zero time the concentration of A is $[\mathrm{A}_0]$ and the concentrations of B and C are zero. The differential equations that govern the concentrations of the various species are as follows:

$$-\frac{d[\mathrm{A}]}{dt} = f_1[\mathrm{A}] \qquad (7.35a)$$

$$-\frac{d[\mathrm{B}]}{dt} = -f_1[\mathrm{A}] + f_2[\mathrm{B}] \qquad (7.36a)$$

$$\frac{d[\mathrm{C}]}{dt} = f_2[\mathrm{B}] \qquad (7.37a)$$

The integrated forms of these equations are:

$$[\mathrm{A}] = [\mathrm{A}_0]\exp(-f_1t) \qquad (7.35b)$$

$$[\mathrm{B}] = \frac{f_1}{f_2 - f_1}[\mathrm{A}_0]\exp(-f_2t)[\exp(f_2 - f_1) - 1] \qquad (7.36b)$$

$$[\mathrm{C}] = [\mathrm{A}_0]\left[1 - \frac{f_2}{f_2 - f_1}\exp(-f_1t) + \frac{f_1}{f_2 - f_1}\exp(-f_2t)\right] \qquad (7.37b)$$

In the first case, consider the situation in which the reaction rate for A to B (f_1 is very much slower than f_2, the reaction between B and C. In this case the concentration of material C becomes:

$$[\mathrm{C}] = [\mathrm{A}_0][1 - \exp(-f_1t)] \quad \text{or} \quad \frac{d[\mathrm{C}]}{dt} = f_1([\mathrm{A}_0] - [\mathrm{C}]) \qquad (7.38$$

This illustrates that reaction from A to C is controlled by the reaction rate constan f_1, the reaction from A to B.

In the second case, assume that the reaction rate constant from B to C (f_2) i slower than the one from A to B (f_1).

$$[\mathrm{C}] = [\mathrm{A}_0][1 - \exp(-f_2t)] \quad \text{or} \quad \frac{d[\mathrm{C}]}{dt} = f_2([\mathrm{A}_0] - [\mathrm{C}]) \qquad (7.39$$

The foregoing is an example of what is often called the *bottleneck principle*. Thi implies that in a series of reactions, the overall rate of reaction is controlled by th bottleneck rate, that is, the slowest rate in the series.

7.8 TEMPERATURE DEPENDENCE OF REACTION RATE

One of the factors that can be used to control the rate of a reaction is the temperatur at which the reaction takes place. Usually higher temperatures mean faster reactio rates.

The seminal work on the subject was that of Arrhenius in the latter part of th nineteenth century. He observed that the rate of change of the equilibrium constan for a reaction with temperature could be expressed as follows:

$$\frac{d(\ln Ka)}{dT} = \frac{\Delta H}{RT^2} \qquad (7.40)$$

But, as we have shown, the equilibrium constant can really be thought of as th ratio of two reaction rate constants, the forward and the reverse reaction rates ($K = f^+/f^-$). It was thus a reasonable assumption that these individual reaction rate should follow the same basic mathematical form:

$$\frac{d(\ln f^+)}{dT} = \frac{E^*}{RT^2} \quad \text{or} \quad d(\ln f^+) = -\frac{E^*}{R}\,d\left(\frac{1}{T}\right)$$

where E^* is called an activation energy. Integrating the equation yields:

$$\ln f^+ = A\exp\left(-\frac{E^*}{RT}\right) \qquad (7.41$$

205

From Eq. 7.41 it is apparent that a graph of the natural logarithm of the reaction rate constant as a function of inverse absolute temperature should be a straight line with a negative slope of the activation energy (E) divided by R, the universal gas constant. The preexponential factor A is sometimes called the frequency factor.

One way of looking at this is to consider a chemical potential barrier between the reactant A and its decomposition products (Figure 7.1). We can think of a pseudo-equilibrium between the material A and A*, where A* is an activated complex on the path between A and its decomposition products.

The equilibrium constant relating the concentration of this activated complex to the concentration of the reactant is:

$$K = \frac{[A^*]}{[A]} = \exp\left(-\frac{\Delta G^*}{RT}\right) \qquad (7.42a)$$

where ΔG* is the Gibbs free energy of formation of this activated complex from the reactant A.

The forward reaction rate is determined by the concentration of the activated species, [A*], and the decomposition frequency, f°.

$$f^+ = [A^*]f^\circ$$

This yields an equation of the form:

$$f^+ = f^\circ \exp\left(-\frac{\Delta G^*}{RT}\right) = f^\circ \exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \qquad (7.42b)$$

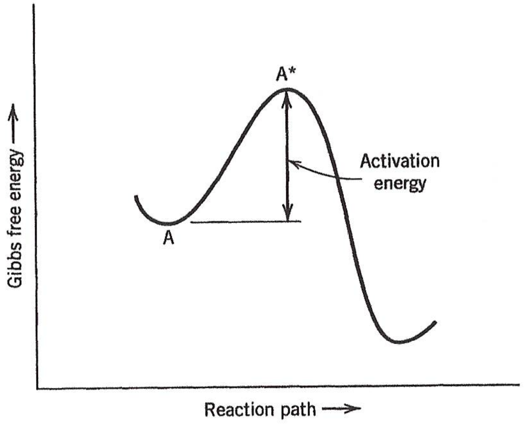


Figure 7.1 Schematic diagram of activation energy along reaction path.

The decomposition rate of the activated complex is governed by its vibratio pattern. By a consideration of the energy required to disintegrate the complex it ca be shown that the decomposition frequency, f°, is kT/h, where h is the Planck constant and k is the Boltzmann constant. Based on this approach, the reaction rat constant, f^+, is:

$$f^+ = \exp\left(\frac{\Delta S^*}{R}\right)\frac{kT}{h}\exp\left(-\frac{\Delta H^*}{RT}\right) \qquad \text{(7.42c}$$

The rate constant, using the activation energy approach, is then dependent o temperature as follows[2]:

$$f^+ \propto T\exp\left(-\frac{\Delta H^*}{RT}\right) \quad \text{or} \quad T\exp\left(-\frac{E^*}{RT}\right) \qquad \text{(7.42d}$$

One may also derive the temperature dependence of the reaction rate constant i gas reactions by postulating that molecules that undergo a collision with energ greater than a specified level, E^*, will react. Consider a reaction in which two molecules of A form another compound. The collision rate of two molecules of A pe unit volume, N_{AA}/t, is:

$$\frac{N_{AA}}{t} = \sigma_A^2\left(\frac{4\pi kT}{M_A}\right)^{1/2}[A]^2 \qquad \text{(7.43a}$$

where σ_A is the diameter of the molecule, and M_A is the mass of the A molecule.

In terms of temperature, this equation is of the form:

$$\frac{N_{AA}}{t} \propto T^{1/2}[A]^2 \qquad \text{(7.43b}$$

If we postulate that only collisions with energy greater than E^* will result in reaction, then the reaction rate constant will be of the form:

$$f^+ \propto T^{1/2}\exp\left(-\frac{E^*}{RT}\right) \qquad \text{(7.43}$$

We thus have three forms of the temperature dependence of the reaction rat constant, f^+. We can express f^+ as:

$$f^+ \propto T^m\exp\left(-\frac{E^*}{RT}\right) \qquad \text{(7.44}$$

---

[2] The terms ΔH^* and E^* will be used interchangeably in this section.

The value of the factor m can be between zero and one. Taking the logarithm of Eq. 7.44a and differentiating with respect to temperature:

$$\ln f^{+} = \mathrm{m} \ln T - \frac{E^{*}}{RT} \tag{7.44b}$$

$$\frac{d \ln f^{+}}{dT} = \frac{\mathrm{m}}{T} + \frac{E^{*}}{RT^{2}} = \frac{\mathrm{m}RT + E^{*}}{RT^{2}} \tag{7.44c}$$

If we note that mRT is usually much less than E^*, it becomes apparent that the temperature dependence of the reaction rate constant can well be approximated by the Arrhenius form of Eq. 7.41.

7.9 HETEROGENEOUS REACTIONS

Most studies concerned with chemical reaction rates deal with homogeneous chemical reactions, that is, reactions occurring within a single fluid phase. However, many of the reactions of interest to materials scientists and engineers are heterogeneous; that is, reactants are initially present in different phases and therefore have to react at a phase boundary. These heterogeneous reactions take place by way of a series of consecutive steps. Consider the simple reaction of a gas dissolving in a metal—for example, hydrogen dissolving in aluminum (Figure 7.2a). The overall reaction (Figure 7.2b) may be written as follows:

$$H_2 \text{ (gas)} = 2\underline{H} \text{ (in solution)}$$

This expression represents the stoichiometry of the equilibrium involved. It does not, however, express the mechanism of the reaction, which consists of a series of consecutive steps.

1. The transport of hydrogen molecules by diffusion (or convection) in the gas phase to the gas–metal phase boundary.
2. The adsorption of hydrogen molecules on the surface of the aluminum.
3. The decomposition of the adsorbed molecules into adsorbed hydrogen atoms.
4. The solution of adsorbed hydrogen atoms into the aluminum at the gas–metal phase boundary.
5. The transport of the dissolved hydrogen atoms away from the phase boundary.

In principle, all these steps can be regarded as limiting the rate of the overall reactions. They act as resistances in series. In practice, however, it is usually one step that is slow enough (the bottleneck) to effectively determine the overall rate of reaction. (This was illustrated in Section 7.7.) In the example cited, possible rate-limiting steps include the transport of hydrogen to the gas–metal interface or away from the interface into the metal, and the surface reaction itself.

Because each of these consecutive reactions has its own activation energy, hence its own temperature dependence, the rate-limiting reaction may vary as the temperature is varied, or as other physical parameters are varied.

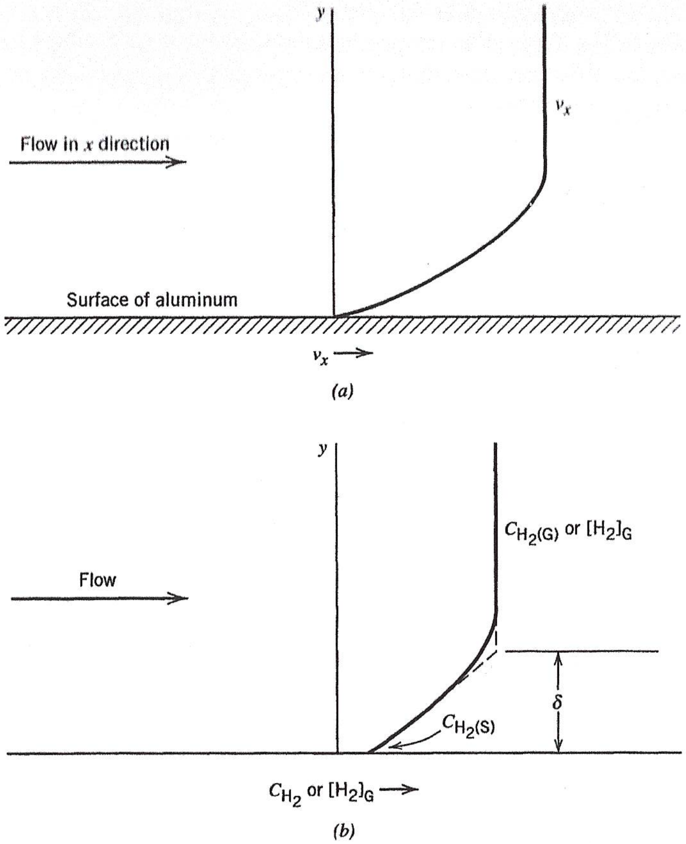


Figure 7.2 (*a*) Velocity of flowing gas as a function of distance from the surface. (*b*) Concentration of hydrogen as a function of distance from the surface.

As an example, consider the situation of diffusion to the gas–metal interfa Assume, for the time being, that the hydrogen is contained in a carrier gas such argon. The diffusion of hydrogen to the surface may well be controlled by the d fusion of the hydrogen through a boundary layer (Figure 7.2) which is in turn depe dent on the flow rate of the gases over the metallic surface as follows:

$$J_{H_2} = -D_{H_2} \frac{d[H_2]}{dx}$$

$$J_{H_2} = -D_{H_2} \left\{ \frac{[H_2]_S - [H_2]_G}{\delta} \right\} \qquad h = \frac{D}{\delta}$$

$$J_{H_2} = -\frac{D_{H_2}}{\delta} \{[H_2]_S - [H_2]_G\} \qquad (7.4$$

$$= -h\{[H_2]_S - [H_2]_S\}$$

In this case the temperature dependence of the reaction rate would not be of the Arrhenius form (Eq. 7.41). The temperature dependence is determined by the rate-limiting step, the diffusion through the boundary layer. In that case the rate depends on $T^{3/2}$, as discussed in Chapter 2 (Section 2.14).

The oxidation of silicon by an oxygen-containing gas provides an interesting example (Ref. 1). Figure 7.3 illustrates the oxygen concentration and chemical potentials after some silicon dioxide has been formed. The rates of oxygen movement or consumption in the three phases present are:

$$F_1 = h(\mu_G - \mu_S) \qquad \text{[in gas]}$$

$$F_2 = D\frac{\mu_S - \mu_I}{x} \qquad \text{[oxide]}$$

$$F_3 = k\mu_I \qquad \text{[at metal-oxide interface]}$$

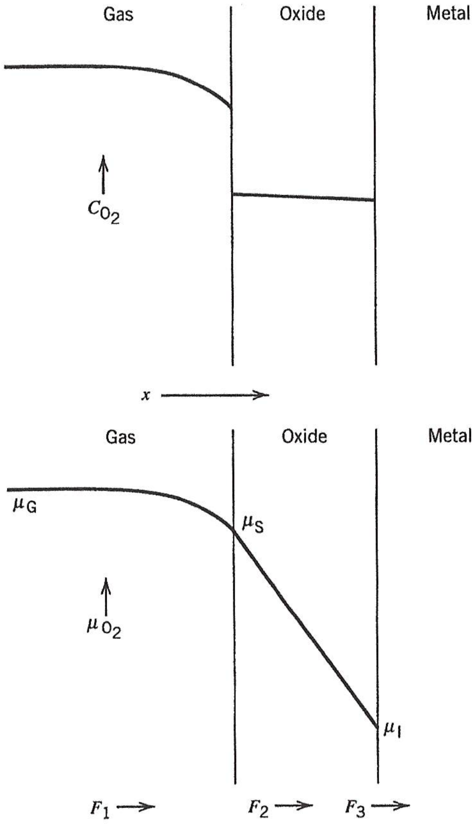


Figure 7.3 Concentration of oxygen (C_{O_2}) and chemical potential of oxygen (μ_{O_2}) in the oxidation of silicon metal.

At steady state, $F_1 = F_2 = F_3$. We have established that the slowest step will limit the rate of reaction. In this case, it is known that F_1 is fast compared to F_2 and F_3. This simplifies the situation, as shown in Figure 7.4.

Because $F_2 = F_3$,

$$\frac{D(\mu_S - \mu_I)}{x} = k\mu_I$$

and $\mu_s = \mu_G$, and μ_I is

$$\mu_I = \frac{D\mu_G}{kx + D} = \frac{\mu_G}{kx/D + 1}$$

An expression for F_2 is then:

$$F_2 = D\frac{(\mu_G - \mu_I)}{x} = \frac{D}{x}\left[\mu_G - \frac{\mu_G}{1 + kx/D}\right]$$

$$F_2 = \frac{Dk\mu_G}{D + kx}$$

But F_2 is the rate of growth of the silicon dioxide layer

$$F_2 = \frac{dx}{dt}N$$

where N is a constant related to the volume change from silicon to silicon dioxide.

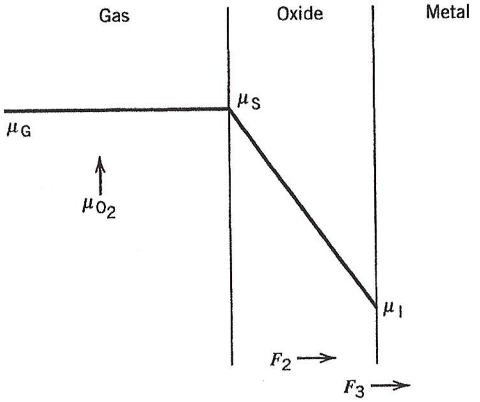


Figure 7.4 The chemical potential of oxygen in the oxidation of silicon metal with very fast diffusion in the gas phase relative to transport in the oxide or reaction at the oxide–metal interface.

Then,

$$\frac{dx}{dt} = \frac{F_2}{N} = \frac{Dk\mu_G}{N(D + kx)}$$

$$(D + kx)dx = \frac{Dk\mu_G}{N}\,dt$$

Integrating, we have

$$\int_0^x (D + kx)\,dx = \frac{Dk\mu_G}{N}\int_0^t dt$$

$$Dx + \frac{k}{2}x^2 = \frac{Dk\mu_G}{N}\,t$$

$$x^2 + \frac{2D}{k}x - \frac{2D\mu_G}{N}t = 0$$

This equation is of the form:

$$x^2 + Bx - Ct = 0$$

where $B = 2D/k$ and $C = \dfrac{2D\mu_G}{N}$

$$x = \frac{-B + (B^2 + 4Ct)^{1/2}}{2}$$

$$x = \frac{B}{2}\left[\left(1 + \frac{t}{B^2/4C}\right)^{1/2} - 1\right]$$

Now consider two cases. In case I, $t \ll B^2/4C$. Then, $(1 + \varepsilon)^{1/2} = 1 + \varepsilon/2$

$$x = \frac{C}{B}t = \frac{k\mu_G}{N}t$$

and the thickness x is linear with time; that is, the reaction rate is constant.

In case II, where $t \gg B^2/4C$,

$$x = \frac{B}{2}\left[\frac{t}{B^2/4C}\right]^{1/2} = (Ct)^{1/2}$$

$$x^2 = Ct = \frac{2D\mu_G}{N}t$$

The thickness x is parabolic with time; that is, it is a function of the square root of time. This is illustrated in Figure 7.5.

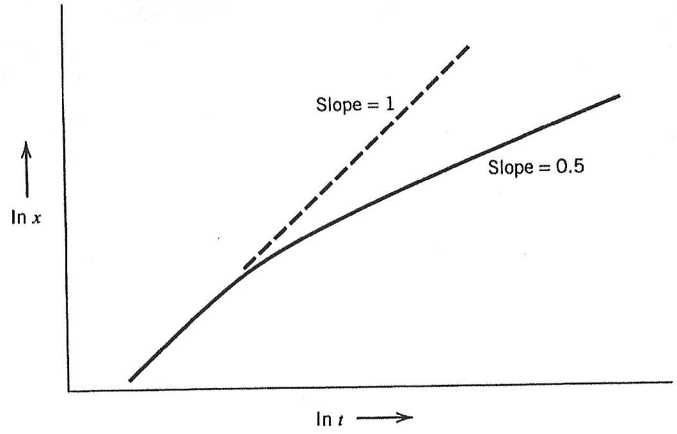


Figure 7.5 Thickness of oxide (x) versus time for the oxidation of silicon metal.

In the preceding example, the rate-limiting step changed during the course of reaction, and the rate changed accordingly.

7.10 SOLID STATE TRANSFORMATION KINETICS

Many of the reactions of interest to materials scientists involve transformation the solid state, reactions such as recrystallization of a cold-worked material, precipitation of a crystalline polymer from an amorphous phase, or simply the gro of an equilibrium phase from a nonequilibrium structure, the driving force for wh is brought about by cooling from one temperature to another. Consider the ini phase to be α and the resulting phase to be β; the reaction is thus written:

$$\alpha \rightarrow \beta$$

The total volume of the sample is the sum of the volumes of α and β:

$$V = V^{\alpha} + V^{\beta} \quad (7.$$

The fraction transformed is simply:

$$F = \frac{V^{\beta}}{V} \quad (7.$$

Assume that the process of transforming α to β is controlled by nucleation growth, that is, the nucleation of phase β within α and then the rate of growth o

Consider that:

$\dot{N}$ = nucleation rate per unit volume

$\dot{G}$ = growth rate in one direction = dr/dt (assuming spherical form of β)

Referring to Figure 7.6, consider the time line from zero to a time, t. We will consider another measure of time (τ), which starts when a nucleus is formed. The number of nuclei formed in the differential time $d\tau$ is equal to

$$\dot{N}V^{\alpha}d\tau$$

Assuming that the particles nucleated in this time $d\tau$ grow as spheres, the radius of the particles formed during $d\tau$, after they have grown to time t, is:

$$\int_0^r dr = \int_\tau^t \dot{G}\,d\tau$$

$$r = \dot{G}(t - \tau) \tag{7.48}$$

The volume of the particle nucleated during $d\tau$ at time t is:

$$dV^{\beta} = \tfrac{4}{3}\pi\dot{G}^3(t - \tau)^3(\dot{N}V^{\alpha})d\tau$$

$$dV^{\beta} = \tfrac{4}{3}\pi\dot{G}^3\dot{N}(V - V^{\beta})(t - \tau)^3 d\tau \tag{7.49}$$

Early in the transformation, when V^{β} is small, V^{β} can be considered negligible with respect to V. In this case, the fraction transformed may be calculated as follows:

$$\int_0^{V^{\beta}} dV^{\beta} = \int_0^t \tfrac{4}{3}\pi\dot{G}^3\dot{N}V(t - \tau)^3 d\tau$$

$$V^{\beta} = V\frac{\pi}{3}\dot{G}^3\dot{N}t^4$$

$$F = \frac{V^{\beta}}{V} = \frac{\pi}{3}\dot{G}^3\dot{N}t^4 \tag{7.50}$$

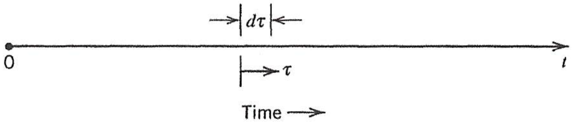


Figure 7.6 Definitions of t and τ for derivation of solid state transformation equations.

To treat the regime beyond the early transformation, we adopt what is cal *extended volume concept.* In this case we separate the nucleation and growt from geometrical considerations such as impingement. The extended volum is the volume that would have been formed if the entire volume had particip nucleation and growth, even that portion transformed (V^{β}). In this case,

$$dV_e^{\beta} = V\tfrac{4}{3}\pi\dot{G}^3\dot{N}(t - \tau)^3 d\tau$$

$$V_e^{\beta} = \tfrac{4}{3}\pi V\int_0^t \dot{G}^3\dot{N}(t - \tau)^3 d\tau$$

But the total volume is equal to the sum of the volumes of α and β:

$$V = V^{\alpha} + V^{\beta}$$

$$\frac{V^{\alpha}}{V} = 1 - \frac{V^{\beta}}{V} = 1 - F$$

where $F = V^{\beta}/V$.

The amount of β formed, dV^{β}, is the fraction of α times dV_e^{β}

$$dV^{\beta} = \left(1 - \frac{V^{\beta}}{V}\right)dV_e^{\beta}$$

Integrating Eq. 7.52,

$$V_e^{\beta} = -V\ln\left(1 - \frac{V^{\beta}}{V}\right) = -V\ln(1 - F)$$

Combining Eqs. 7.53 and 7.51 yields:

$$-\ln(1 - F) = \tfrac{4}{3}\pi\int_0^t \dot{G}^3\dot{N}(t - \tau)^3 d\tau$$

If $\dot{G}$ and $\dot{N}$ are constant,

$$-\ln(1 - F) = \tfrac{4}{3}\pi\dot{G}^3\dot{N}\int_0^t (t - \tau)^3 d\tau = \frac{\pi}{3}\dot{G}^3\dot{N}t^4$$

$$F = 1 - \exp\left(-\frac{\pi}{3}\dot{G}^3\dot{N}t^4\right)$$

The resulting equation relating the fraction transformed to nucleation rate, rate, and time is called the *Johnson–Mehl* equation.

A similar treatment of the subject is given by Avrami. In general he expresses the fraction transformed as

$$F = 1 - \exp(-kt^n) \tag{7.55}$$

where n is called "the Avrami n."

The variation of n from 4 (in the Johnson–Mehl equation) can occur for a number of reasons. In some solid state reactions, the nucleation rate is a decaying function of time. In that case the Avrami n would be 4 early in the reaction, but decreasing to 3 as the nucleation decreases as a function of time, and the transformation is governed strictly by the growth rate. In general, for three-dimensional solids, the Avrami n is between 3 and 4.

In the case of growth of a phase in two dimensions such as in a sheet or a film, the Avrami n is between 2 and 3. In the case of wire, a one-dimensional solid, the Avrami n is between 1 and 2.

To determine the value of the Avrami n from Eq. 7.55, the following mathematical manipulation is performed:

$$F = 1 - \exp(-kt^n)$$

$$1 - F = \exp(-kt^n)$$

$$\ln(1 - F) = -kt^n$$

$$\ln \ln(1 - F) = \ln k - n \ln t$$

Thus the Avrami n is the slope of the plot of the logarithm of the logarithm of $(1 - F)$ versus the negative of the logarithm of t.

REFERENCES

1. Ohring, M., *The Material Science of Thin Films,* Academic Press, San Diego, CA, 1992, Section 8.7.

PROBLEMS

7.1 In a diffusion experiment, radioactive copper (^{64}Cu) is plated on one end of a sample and then "diffused" by heating in a furnace for a specified period of time. The concentration of copper-64 as a function of distance is determined by taking thin slices of the sample and counting the rate of isotope decay in them.

The last slice is analyzed 4 hours after the first. What correction factor must be applied to the last reading to make it comparable to the first?

The half-life of ^{64}Cu is 12.8 hours.

7.2 How many disintegrations occur per minute in a sample containing 1 gram ^{235}U? The half-life of ^{235}U is 7.04×10^8 years.

7.3 The decay rate of the isotope carbon-14 (^{14}C) is often used to establish the d on which carbon-containing matter died. In the upper atmosphere, cosmic ra ation synthesizes ^{14}C. This process balances the loss of ^{14}C through radioacti decay. Living matter, which exchanges carbon with atmospheric carbon dio ide and maintains its ^{14}C level, produces 15.3 disintegrations per minute p gram of carbon it contains. Dead organisms no longer exchange carbon wi the atmosphere, and the ^{14}C content decreases with time because of radioacti decay.

A 0.5 g sample of a plant from an excavation shows 3.5 disintegrations p minute from its ^{14}C. How long ago did the plant die?

7.4 A well-known generalization (rule of thumb) concerning biochemical reactio near room temperature (300 K) is that their rates double for every 10 K rise temperature.

- **(a)** What is the activation energy for the reactions implied by this rule?
- **(b)** In an experiment on one of these reactions conducted near room temp ature, the rate constant (k) is to be determined to an accuracy of ±1 How accurately must the temperature be controlled to achieve at least t level of accuracy in k? State answer in ± degrees kelvin.

7.5 The following statement appears on the side of a milk carton:

The contents will spoil in 8 days if stored at 5°C.
The contents will spoil in 12 hours if stored at 30°C.

If the mechanism and definition of spoilage remain constant in this te perature range, how long will the milk remain unspoiled at 20°C?

7.6 An amorphous polymer fiber is being treated to form polymer crystals. Y may assume that the fiber is thin enough to be treated as a one-dimensio solid.

- **(a)** Write an equation for the functional relationship between the fraction the amorphous polymer that has crystallized (F) and time (t). Assume t the nucleation of crystals is homogeneous and that the rate of nucleati is constant. Assume also that the rate of crystal growth is constant.
- **(b)** After 1 hour of the treatment, 10% of the polymer fiber is crystalline. H long will it take for 50% of the fiber to become crystalline?
- **(c)** Will your answer to part a be changed if the nucleation is *heterogeneo* and all the nuclei become active at the beginning of the transformati ($t = 0$)? If so, how?

7.7 For simple decomposition reactions (i.e., those with no reverse reaction) "half-life" concept yields a convenient equation for the amount of react remaining as a function of time:

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^{t/\tau}$$