10.2 (a) This problem first asks that we rewrite the expression for the total free energy change for nucleation (analogous to Equation 10.1) for the case of a cubic nucleus of edge length \(a\). The volume of such a cubic radius is \(a^3\), whereas the total surface area is \(6a^2\) (since there are six faces each of which has an area of \(a^2\)).

Thus, the expression for \(\Delta G\) is as follows:

\[
\Delta G = a^3 \Delta G_v + 6a^2 \gamma
\]

Differentiation of this expression with respect to \(a\) is as

\[
\frac{d}{da} \Delta G = \frac{d}{da} (a^3 \Delta G_v) + \frac{d}{da} (6a^2 \gamma)
\]

\[
= 3a^2 \Delta G_v + 12a \gamma
\]

If we set this expression equal to zero as

\[
3a^2 \Delta G_v + 12a \gamma = 0
\]

and then solve for \(a\) (= \(a^*\)), we have

\[
a^* = -\frac{4\gamma}{\Delta G_v}
\]

Substitution of this expression for \(a\) in the above expression for \(\Delta G\) yields an equation for \(\Delta G^*\) as

\[
\Delta G^* = (a^*)^3 \Delta G_v + 6(a^*)^2 \gamma
\]

\[
= \left(-\frac{4\gamma}{\Delta G_v}\right)^3 \Delta G_v + 6\gamma \left(-\frac{4\gamma}{\Delta G_v}\right)^2
\]

\[
= \frac{32\gamma^3}{(\Delta G_v)^2}
\]
(b) \( \Delta G_v \) for a cube—i.e., \( \left( \frac{\gamma^3}{3(\Delta G_v)^2} \right) \)—is greater than for a sphere—i.e., \( \left( \frac{16\pi}{3}\frac{\gamma^3}{(\Delta G_v)^2} \right) \) = \\
(16.8) \left[ \frac{\gamma^3}{(\Delta G_v)^2} \right] \). The reason for this is that surface-to-volume ratio of a cube is greater than for a sphere.
10.3 This problem states that ice homogeneously nucleates at \(-40^\circ\text{C}\), and that we are to calculate the critical radius given the latent heat of fusion \((-3.1 \times 10^8 \text{ J/m}^3)\) and the surface free energy \((25 \times 10^{-3} \text{ J/m}^2)\). Solution to this problem requires the utilization of Equation 10.6 as

\[
\begin{align*}
    r^* &= \left( -\frac{2\gamma T_m}{\Delta H_f} \right) \left( \frac{1}{T_m - T} \right) \\
    &= \left( -\frac{(2)(25 \times 10^{-3} \text{ J/m}^2)(273 \text{ K})}{-3.1 \times 10^8 \text{ J/m}^3} \right) \left( \frac{1}{40 \text{ K}} \right) \\
    &= 1.10 \times 10^{-9} \text{ m} = 1.10 \text{ nm}
\end{align*}
\]
10.4 (a) This portion of the problem asks that we compute $r^*$ and $\Delta G^*$ for the homogeneous nucleation of the solidification of Ni. First of all, Equation 10.6 is used to compute the critical radius. The melting temperature for nickel, found inside the front cover is 1455°C; also values of $\Delta H_f$ ($-2.53 \times 10^9$ J/m$^3$) and $\gamma$ (0.255 J/m$^2$) are given in the problem statement, and the supercooling value found in Table 10.1 is 319°C (or 319 K). Thus, from Equation 10.6 we have

$$r^* = \left(\frac{2\gamma T_m}{\Delta H_f}\right) \left(\frac{1}{T_m - T}\right)$$

$$= -\frac{(2)(0.255 \text{ J/m}^2)(1455 + 273 K)}{-2.53 \times 10^9 \text{ J/m}^3} \left(\frac{1}{319 \text{ K}}\right)$$

$$= 1.09 \times 10^{-9} \text{ m} = 1.09 \text{ nm}$$

For computation of the activation free energy, Equation 10.7 is employed. Thus

$$\Delta G^* = \frac{16\pi \gamma^2 r^3}{3 \Delta H_f^2 (T_m - T)^2}$$

$$= \frac{(16)(\pi)(0.255 \text{ J/m}^2)^3 (1455 + 273 K)^2}{(3)(-2.53 \times 10^9 \text{ J/m}^3)^2} \left(\frac{1}{(319 \text{ K})^2}\right)$$

$$= 1.27 \times 10^{-18} \text{ J}$$

(b) In order to compute the number of atoms in a nucleus of critical size (assuming a spherical nucleus of radius $r^*$), it is first necessary to determine the number of unit cells, which we then multiply by the number of atoms per unit cell. The number of unit cells found in this critical nucleus is just the ratio of critical nucleus and unit cell volumes. Inasmuch as nickel has the FCC crystal structure, its unit cell volume is just $a^3$ where $a$ is the unit cell length (i.e., the lattice parameter); this value is 0.360 nm, as cited in the problem statement. Therefore, the number of unit cells found in a radius of critical size is just

$$\# \text{ unit cells/particle} = \frac{4\pi r^3}{3a^3}$$

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\[
\frac{4}{3} \pi (1.09 \text{ nm})^3 \quad \text{(0.360 nm)}^3 = 116 \text{ unit cells}
\]

Inasmuch as 4 atoms are associated with each FCC unit cell, the total number of atoms per critical nucleus is just

\[(116 \text{ unit cells/critical nucleus})(4 \text{ atoms/unit cell}) = 464 \text{ atoms/critical nucleus}\]
10.5 (a) For this part of the problem we are asked to calculate the critical radius for the solidification of nickel (per Problem 10.4), for 200 K and 300 K degrees of supercooking, and assuming that there are $10^6$ nuclei per meter cubed for homogeneous nucleation. In order to calculate the critical radii, we replace the $T_m - T$ term in Equation 10.6 by the degree of supercooling (denoted as $\Delta T$) cited in the problem.

For 200 K supercooling,

$$r_{200}^* = \left( -\frac{2\gamma T_m}{\Delta H_f} \right) \frac{1}{\Delta T} = \frac{-2(0.255 \text{ J/m}^2)(1455 + 273 \text{ K})}{-2.53 \times 10^9 \text{ J/m}^3} \left( \frac{1}{200 \text{ K}} \right)$$

$$= 1.74 \times 10^{-9} \text{ m} = 1.74 \text{ nm}$$

For 300 K supercooling,

$$r_{300}^* = \frac{-2(0.255 \text{ J/m}^2)(1455 + 273 \text{ K})}{-2.53 \times 10^9 \text{ J/m}^3} \left( \frac{1}{300 \text{ K}} \right)$$

$$= 1.16 \times 10^{-9} \text{ m} = 1.16 \text{ nm}$$

In order to compute the number of stable nuclei that exist at 200 K and 300 K degrees of supercooling, it is necessary to use Equation 10.8. However, we must first determine the value of $K_1$ in Equation 10.8, which in turn requires that we calculate $\Delta G^*$ at the homogeneous nucleation temperature using Equation 10.7; this was done in Problem 10.4, and yielded a value of $\Delta G^* = 1.27 \times 10^{-18} \text{ J}$. Now for the computation of $K_1$, using the value of $n^*$ for at the homogenous nucleation temperature ($10^6$ nuclei/m$^3$):

$$K_1 = \exp \left( \frac{-\Delta G^*}{kT} \right) = \exp \left( \frac{-1.27 \times 10^{-18} \text{ J}}{1.38 \times 10^{-23} \text{ J/atom-K}(1455 \text{ K} - 319 \text{ K})} \right)$$

$$= 1.52 \times 10^{41} \text{ nuclei/m}^3$$
Now for 200 K supercooling, it is first necessary to recalculate the value $\Delta G^*$ of using Equation 10.7, where, again, the $T_m - T$ term is replaced by the number of degrees of supercooling, denoted as $\Delta T$, which in this case is 200 K. Thus

$$
\Delta G^*_{200} = \left( \frac{16 \pi \gamma^3 T_m^2}{3 \Delta H_f^2} \right) \frac{1}{(\Delta T)^2}
$$

$$
= \left[ \frac{16(\pi)(0.255 \text{ J/m}^2)^3 (1455 + 273 \text{ K})^2}{(3)(-2.53 \times 10^9 \text{ J/m}^3)^2} \right] \left[ \frac{1}{(200 \text{ K})^2} \right]
$$

$$
= 3.24 \times 10^{-18} \text{ J}
$$

And, from Equation 10.8, the value of $n^*$ is

$$
n^*_{200} = K_1 \exp \left( -\frac{\Delta G^*_{200}}{kT} \right)
$$

$$
= (1.52 \times 10^{41} \text{ nuclei/m}^3) \exp \left[ -\frac{3.24 \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/atom-K})(1455 \text{ K} - 200 \text{ K})} \right]
$$

$$
= 8.60 \times 10^{-41} \text{ stable nuclei}
$$

Now, for 300 K supercooling the value of $\Delta G^*$ is equal to

$$
\Delta G^*_{300} = \left[ \frac{16(\pi)(0.255 \text{ J/m}^2)^3 (1455 + 273 \text{ K})^2}{(3)(-2.53 \times 10^9 \text{ J/m}^3)^2} \right] \left[ \frac{1}{(300 \text{ K})^2} \right]
$$

$$
= 1.44 \times 10^{-18} \text{ J}
$$

from which we compute the number of stable nuclei at 300 K of supercooling as

$$
n^*_{300} = K_1 \exp \left( -\frac{\Delta G^*_{300}}{kT} \right)
$$
\[ n^* = \left( 1.52 \times 10^{41} \text{ nuclei/m}^3 \right) \exp \left( \frac{1.44 \times 10^{-18} \text{ J}}{\left( 1.38 \times 10^{-23} \text{ J/atom-K} \right) \left( 1455 \text{ K} - 300 \text{ K} \right)} \right) \]

= 88 stable nuclei

(b) Relative to critical radius, \( r^* \) for 300 K supercooling is slightly smaller than for 200 K (1.16 nm versus 1.74 nm). [From Problem 10.4, the value of \( r^* \) at the homogeneous nucleation temperature (319 K) was 1.09 nm.] More significant, however, are the values of \( n^* \) at these two degrees of supercooling, which are dramatically different—8.60 \( \times 10^{-41} \) stable nuclei at \( \Delta T = 200 \text{ K} \), versus 88 stable nuclei at \( \Delta T = 300 \text{ K} \)!
10.6 This problem calls for us to compute the length of time required for a reaction to go to 90% completion. It first becomes necessary to solve for the parameter \( k \) in Equation 10.17. It is first necessary to manipulate this equation such that \( k \) is the dependent variable. We first rearrange Equation 10.17 as

\[
\exp(-kt^n) = 1 - y
\]

and then take natural logarithms of both sides:

\[
-kt^n = \ln(1 - y)
\]

Now solving for \( k \) gives

\[
k = -\frac{\ln (1 - y)}{t^n}
\]

And, from the problem statement, for \( y = 0.25 \) when \( t = 125 \) s and given that \( n = 1.5 \), the value of \( k \) is equal to

\[
k = -\frac{\ln (1 - 0.25)}{(125 \text{ s})^{1.5}} = 2.06 \times 10^{-4}
\]

We now want to manipulate Equation 10.17 such that \( t \) is the dependent variable. The above equation may be written in the form:

\[
t^n = -\frac{\ln (1 - y)}{k}
\]

And solving this expression for \( t \) leads to

\[
t = \left[ -\frac{\ln (1 - y)}{k} \right]^{1/n}
\]

Now, using this equation and the value of \( k \) determined above, the time to 90% transformation completion is equal to

\[
t = \left[ -\frac{\ln (1 - 0.90)}{2.06 \times 10^{-4}} \right]^{1/1.5} = 500 \text{ s}
\]
10.8 This problem gives us the value of \( y \) (0.30) at some time \( t \) (100 min), and also the value of \( n \) (5.0) for the recrystallization of an alloy at some temperature, and then asks that we determine the rate of recrystallization at this same temperature. It is first necessary to calculate the value of \( k \). We first rearrange Equation 10.17 as

\[
\exp(-kt^n) = 1 - y
\]

and then take natural logarithms of both sides:

\[
-k t^n = \ln(1 - y)
\]

Now solving for \( k \) gives

\[
k = -\frac{\ln(1 - y)}{t^n}
\]

which, using the values cited above for \( y \), \( n \), and \( t \) yields

\[
k = -\frac{\ln(1 - 0.30)}{100 \text{ min}^5} = 3.57 \times 10^{-11}
\]

At this point we want to compute \( t_{0.5} \), the value of \( t \) for \( y = 0.5 \), which means that it is necessary to establish a form of Equation 10.17 in which \( t \) is the dependent variable. From one of the above equations

\[
t^n = -\frac{\ln(1 - y)}{k}
\]

And solving this expression for \( t \) leads to

\[
t = \left[-\frac{\ln(1 - y)}{k}\right]^{1/n}
\]

For \( t_{0.5} \), this equation takes the form

\[
t_{0.5} = \left[-\frac{\ln(1 - 0.5)}{k}\right]^{1/n}
\]
and incorporation of the value of $k$ determined above, as well as the value of $n$ cited in the problem statement (5.0), then $t_{0.5}$ is equal to

$$t_{0.5} = \left[ \frac{-\ln (1 - 0.5)}{3.57 \times 10^{-11}} \right]^{1/5} = 114.2 \text{ min}$$

Therefore, from Equation 10.18, the rate is just

$$\text{rate} = \frac{1}{t_{0.5}} = \frac{1}{114.2 \text{ min}} = 8.76 \times 10^{-3} \text{ (min)}^{-1}$$