

19.3 The constant A in Equation 19.2 is $12\pi^4 R / 5\theta_D^3$, where R is the gas constant and θ_D is the Debye temperature (K). Estimate θ_D for aluminum, given that the specific heat is 4.60 J/kg-K at 15 K.

Solution

For aluminum, we want to compute the Debye temperature, θ_D , given the expression for A in Equation 19.2 and the heat capacity at 15 K. First of all, let us determine the magnitude of A using the following rearranged form of Equation 19.2:

$$A = \frac{C_v}{T^3} \quad (19.2a)$$

Inasmuch as the specific heat is given in the problem statement, and heat capacity is required in the above expression, it is necessary to convert c_v to C_v , which is possible using the following equation:

$$C_v = c_v A' \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right)$$

Here we use A' to represent the atomic weight (so as not to confuse this parameter with the A in Equation 9.2). Making the above substitution into Equation 19.2a above yields the following expression for A :

$$A = \left[\frac{c_v A' \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right)}{T^3} \right]$$

We now compute the value of A using the following values for parameters in this equation:

$T = 15 \text{ K}$ (given in problem statement)

$c_v = 4.60 \text{ J/kg-K}$ (given in problem statement)

$A' = 26.98 \text{ g/mol}$ (from inside the front book cover)

Therefore, the A is determined as follows:

$$A = \left[\frac{c_v A' \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right)}{T^3} \right]$$

$$= \left[\frac{(4.60 \text{ J/kg-K})(26.98 \text{ g/mol}) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right)}{(15 \text{ K})^3} \right]$$

$$= 3.68 \times 10^{-5} \text{ J/mol-K}^4$$

The problem statement cites the following expression for A :

$$A = \frac{12\pi^4 R}{5\theta_D^3}$$

From this equation we solve for the Debye temperature, θ_D , as requested as follows:

$$\theta_D = \left(\frac{12\pi^4 R}{5A} \right)^{1/3}$$

$$= \left[\frac{(12)(\pi)^4 (8.31 \text{ J/mol-K})}{(5)(3.68 \times 10^{-5} \text{ J/mol-K}^4)} \right]^{1/3} = 375 \text{ K}$$

19.6 When a metal is heated, its density decreases. There are two sources that give rise to this decrease of ρ : (1) the thermal expansion of the solid and (2) the formation of vacancies (Section 4.2). Consider a specimen of gold at room temperature (20°C) that has a density of 19.320 g/cm³.

(a) Determine its density upon heating to 800°C when only thermal expansion is considered.

(b) Repeat the calculation when the introduction of vacancies is taken into account. Assume that the energy of vacancy formation is 0.98 eV/atom and that the volume coefficient of thermal expansion, α_v is equal to $3\alpha_l$.

Solution

(a) In this portion of the problem we are asked to determine the density of gold at 800°C when only thermal expansion is considered. Let us use as the basis for this determination 1 cm³ of gold at 20°C that has a mass of 19.320 g. If it is assumed that the mass of gold (19.320 g) remains constant upon heating, then the density at 800°C is just this mass divided by the 800°C volume; this volume will be greater than 1 cm³, as a result of thermal expansion. Let us compute the volume of this specimen of gold when it is heated to 800°C. A volume expansion expression is given in Equation 19.4—viz.,

$$\frac{\Delta V}{V_0} = \alpha_v \Delta T$$

or, rearranging leads to

$$\Delta V = V_0 \alpha_v \Delta T \quad (19.4a)$$

But since

$$\Delta V = V_f - V_0$$

in which V_f and V_0 represent the final and initial volumes, respectively, we can rewrite Equation 19.4a as follows:

$$V_f - V_0 = V_0 \alpha_v \Delta T$$

From this expression we want to solve for the final volume V_f at 800°C; therefore, we may rewrite the above equation as follows:

$$V_f = V_0 \alpha_v \Delta T + V_0 = V_0 (1 + \alpha_v \Delta T)$$

Also, $\alpha_v = 3\alpha_l$, as noted in the problem statement, which, when substituted into the above equation leads to the following:

$$V_f = V_0 (1 + 3\alpha_l \Delta T) \quad (19.4b)$$

The value of α_l for gold given in Table 19.1 is $14.2 \times 10^{-6} (\text{°C})^{-1}$. Therefore, the volume of this specimen of Au at 800°C (V_f), using Equation 19.4b, is determined as follows:

$$\begin{aligned} V_f &= V_0 (1 + 3\alpha_l \Delta T) \\ &= (1 \text{ cm}^3) \left\{ 1 + (3) \left[14.2 \times 10^{-6} (\text{°C})^{-1} \right] (800\text{°C} - 20\text{°C}) \right\} \\ &= 1.03323 \text{ cm}^3 \end{aligned}$$

(Note: In this computation we have taken room temperature to be 20°C.) Thus, the 800°C density is just the 19.320 g mass divided by this new volume—i.e.,

$$\rho = \frac{19.320 \text{ g}}{1.03323 \text{ cm}^3} = 18.699 \text{ g/cm}^3$$

(b) Now we are asked to compute the density at 800°C taking into consideration the creation of vacancies which will further lower the density. To begin, this determination requires that we calculate the number of vacancies using Equation 4.1. But it first becomes necessary to compute the number of Au atoms per cubic centimeter (N_{Au}) at 800°C using Equation 4.2. Thus,

$$N_{\text{Au}} = \frac{N_A \rho_{\text{Au}}}{A_{\text{Au}}}$$

And since the atomic weight of gold (A_{Au}) is 196.97 g/mol, then

$$\begin{aligned} N_{\text{Au}} &= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(18.699 \text{ g/cm}^3)}{196.97 \text{ g/mol}} \\ &= 5.717 \times 10^{22} \text{ atoms/cm}^3 \end{aligned}$$

Now, from Equation 4.1, the total number of vacancies per centimeter cubed, N_v , is computed as follows:

$$\begin{aligned} N_v &= N_{\text{Au}} \exp \left(-\frac{Q_v}{kT} \right) \\ &= (5.717 \times 10^{22} \text{ atoms/cm}^3) \exp \left[-\frac{0.98 \text{ eV/atom}}{(8.62 \times 10^{-5} \text{ eV/K})(800 + 273 \text{ K})} \right] \\ &= 1.431 \times 10^{18} \text{ vacancies/cm}^3 \end{aligned}$$

We now want to determine the number of vacancies per unit cell, which is possible if the unit cell volume is multiplied by N_v . The unit cell volume (V_C) may be calculated using Equation 3.8 taking $n = 4$ inasmuch as Au has the FCC crystal structure. Thus, from a rearranged form of Equation 3.8 we compute the value of V_C as follows:

$$\begin{aligned} V_C &= \frac{nA_{\text{Au}}}{\rho_{\text{Au}} N_A} \\ &= \frac{(4 \text{ atoms/unit cell})(196.97 \text{ g/mol})}{(18.699 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})} \\ &= 6.997 \times 10^{-23} \text{ cm}^3/\text{unit cell} \end{aligned}$$

Now, the number of vacancies per unit cell, n_v , is equal to

$$\begin{aligned} n_v &= N_v V_C \\ &= (1.431 \times 10^{18} \text{ vacancies/cm}^3)(6.997 \times 10^{-23} \text{ cm}^3/\text{unit cell}) \\ &= 0.0001001 \text{ vacancies/unit cell} \end{aligned}$$

What this means is that instead of there being 4.0000 atoms per unit cell, there are only $4.0000 - 0.0001001 = 3.9998999$ atoms per unit cell. And, finally, the density may be computed using Equation 3.8 taking $n = 3.9998999$; thus

$$\begin{aligned} \rho_{\text{Au}} &= \frac{nA_{\text{Au}}}{V_C N_A} \\ &= \frac{(3.9998999 \text{ atoms/unit cell})(196.97 \text{ g/mol})}{(6.997 \times 10^{-23} \text{ cm}^3/\text{unit cell})(6.022 \times 10^{23} \text{ atoms/mol})} \\ &= 18.698 \text{ g/cm}^3 \end{aligned}$$

Thus, the influence of the vacancies is almost insignificant—their presence reduces the density by only 0.001 g/cm^3 (from 18.699 g/cm^3 to 18.698 g/cm^3).

19.10 For each of the following pairs of materials, decide which has the larger thermal conductivity. Justify your choices.

- (a) Pure silver; sterling silver (92.5 wt% Ag–7.5 wt% Cu)
- (b) Fused silica; polycrystalline silica
- (c) Linear and syndiotactic poly(vinyl chloride) ($DP = 1000$); linear and syndiotactic polystyrene ($DP = 1000$)
- (d) Atactic polypropylene ($\bar{M}_w = 10^6$ g/mol); isotactic polypropylene ($\bar{M}_w = 10^5$ g/mol)

Solution

This question asks for us to decide, for each of several pairs of materials, which has the larger thermal conductivity and why.

(a) Pure silver will have a larger conductivity than sterling silver because the impurity atoms in the latter will lead to a greater degree of free electron scattering.

(b) Polycrystalline silica will have a larger conductivity than fused silica because fused silica is noncrystalline and lattice vibrations are more effectively scattered in noncrystalline materials.

(c) The poly(vinyl chloride) will have the larger conductivity than the polystyrene because the former will have the higher degree of crystallinity. Both polymers are syndiotactic and have the same degree of polymerization. However, with regard to side-group bulkiness, the PVC is more likely to crystallize. Since heat transfer is by molecular chain vibrations, and the coordination of these vibrations increases with percent crystallinity, the higher the crystallinity, the greater the thermal conductivity.

(d) The isotactic polypropylene will have a larger thermal conductivity than the atactic polypropylene because isotactic polymers have higher degrees of crystallinity. The influence of crystallinity on conductivity is explained in part (c).

19.12 (a) Briefly explain why thermal stresses may be introduced into a structure by rapid heating or cooling.

(b) For cooling, what is the nature of the surface stresses?

(c) For heating, what is the nature of the surface stresses?

Answer

(a) Thermal stresses may be introduced into a structure by rapid heating or cooling because temperature gradients are established across the cross section due to more rapid temperature changes at the surface than within the interior; thus, the surface will expand or contract at a different rate than the interior and since this surface expansion or contraction will be restrained by the interior, stresses will be introduced.

(b) For cooling, the surface stresses will be tensile in nature since the interior contracts to a lesser degree than the cooler surface.

(c) For heating, the surface stresses will be compressive in nature since the interior expands to a lesser degree than the hotter surface.

