**Note:** These questions will be discussed in the tutorial sessions on November 21.

**Question 1:**

The following table lists molecular weight data for a polytetrafluoroethylene. Compute:

(a) The number-average molecular weight,

(b) The weight-average molecular weight, and

(c) The degree of polymerization.

| *Molecular Weight Range (g/mol)* | $x_i$ | $w_i$ |
|---|---|---|
| 10,000–20,000 | 0.03 | 0.01 |
| 20,000–30,000 | 0.09 | 0.04 |
| 30,000–40,000 | 0.15 | 0.11 |
| 40,000–50,000 | 0.25 | 0.23 |
| 50,000–60,000 | 0.22 | 0.24 |
| 60,000–70,000 | 0.14 | 0.18 |
| 70,000–80,000 | 0.08 | 0.12 |
| 80,000–90,000 | 0.04 | 0.07 |

**Solution:**

(a) From the tabulated data, we are asked to compute $\overline{M}_n$, the number-average molecular weight. This is carried out below.

| Molecular wt Range | Mean $M_i$ | $x_i$ | $x_iM_i$ |
|---|---|---|---|
| 10,000-20,000 | 15,000 | 0.03 | 450 |
| 20,000-30,000 | 25,000 | 0.09 | 2250 |
| 30,000-40,000 | 35,000 | 0.15 | 5250 |
| 40,000-50,000 | 45,000 | 0.25 | 11,250 |
| 50,000-60,000 | 55,000 | 0.22 | 12,100 |
| 60,000-70,000 | 65,000 | 0.14 | 9100 |
| 70,000-80,000 | 75,000 | 0.08 | 6000 |
| 80,000-90,000 | 85,000 | 0.04 | 3400 |

$$\overline{M}_n = \sum x_i M_i = 49,800 \text{ g/mol}$$

(b) From the tabulated data, we are asked to compute $\overline{M}_w$, the weight-average molecular weight.

| Molecular wt. Range | Mean $M_i$ | $w_i$ | $w_i M_i$ |
|---|---|---|---|
| 10,000-20,000 | 15,000 | 0.01 | 150 |
| 20,000-30,000 | 25,000 | 0.04 | 1000 |
| 30,000-40,000 | 35,000 | 0.11 | 3850 |
| 40,000-50,000 | 45,000 | 0.23 | 10,350 |
| 50,000-60,000 | 55,000 | 0.24 | 13,200 |
| 60,000-70,000 | 65,000 | 0.18 | 11,700 |
| 70,000-80,000 | 75,000 | 0.12 | 9000 |
| 80,000-90,000 | 85,000 | 0.07 | 5950 |

$$\overline{M}_w = \sum w_i M_i = 55{,}200 \text{ g/mol}$$

(c) Now we are asked to compute the degree of polymerization, which is possible using Equation 14.6. For polytetrafluoroethylene, the repeat unit molecular weight is just

$$m = 2(A_C) + 4(A_F)$$

$$= (2)(12.01 \text{ g/mol}) + (4)(19.00 \text{ g/mol}) = 100.02 \text{ g/mol}$$

And,

$$DP = \frac{\overline{M}_n}{m} = \frac{49{,}800 \text{ g/mol}}{100.02 \text{ g/mol}} = 498$$

**Question 2:**

The density and associated percent crystallinity for two poly(tetrafluoroethylene) materials are as follows:

| ρ (g/cm$^3$) | crystallinity (%) |
|---|---|
| 2.144 | 51.3 |
| 2.215 | 74.2 |

(a) Compute the densities of totally crystalline and totally amorphous poly(tetrafluoroethylene).

(b) Determine the percent crystallinity of a specimen having a density of 2.26 g/cm$^3$.

**Solution**

(a) $C = \frac{\%\ \text{Crystallinity}}{100}$ , $C = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)}$

$$\Rightarrow \begin{cases} \rho_c(C_1\rho_{s1} - \rho_{s1}) + \rho_c\rho_a - C_1\rho_{s1}\rho_a = 0 \\ \rho_c(C_2\rho_{s2} - \rho_{s2}) + \rho_c\rho_a - C_2\rho_{s2}\rho_a = 0 \end{cases}$$

$$\begin{cases} \rho_{s1} = 2.144\ g/cm^3 \\ \rho_{s2} = 2.215\ g/cm^3 \\ C_1 = 0.513 \\ C_2 = 0.742 \end{cases}$$

$$\Rightarrow \rho_a = \frac{\rho_{s1}\rho_{s2}(C_1 - C_2)}{C_1\rho_{s1} - C_2\rho_{s2}} = \frac{2.144 \times 2.215\,(0.513 - 0.742)}{(0.513 \times 2.144) - (0.742 \times 2.215)}$$

$$\Rightarrow \rho_a = 2\ g/cm^3$$

and

$$\rho_c = \frac{\rho_{s1}\rho_{s2}(C_2 - C_1)}{\rho_{s2}(C_2 - 1) - \rho_{s1}(C_1 - 1)} = \frac{2.144 \times 2.215 \times (0.742 - 0.513)}{(2.215)(0.742 - 1) - (2.144)(0.513 - 1)}$$

$$\Rightarrow \rho_c = 2.301\ g/cm^3$$

(b) $\%\ \text{Crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$

$$= \frac{(2.301)(2.26 - 2)}{(2.26)(2.301 - 2)} \times 100 = 87.9\ \%$$

**Question 3:**

The tensile strength and number-average molecular weight for two polyethylene materials are as follows:

| Tensile Strength (MPa) | Number-Average Molecular Weight (g/mol) |
|---|---|
| 85 | 12,700 |
| 150 | 28,500 |

Estimate the number-average molecular weight that is required to give a tensile strength of 195 MPa.

**Solution**

This problem gives us the tensile strengths and associated number-average molecular weights for two polyethylene materials and then asks that we estimate the $\overline{M}_n$ that is required for a tensile strength of 195 MPa. Equation 15.3 cites the dependence of the tensile strength on $\overline{M}_n$. Thus, using the data provided in the problem statement, we may set up two simultaneous equations from which it is possible to solve for the two constants TS∞ and A. These equations are as follows:

$$85 \text{ MPa} = TS_\infty - \frac{A}{12{,}700 \text{ g/mol}}$$

$$150 \text{ MPa} = TS_\infty - \frac{A}{28{,}500 \text{ g/mol}}$$

Thus, the values of the two constants are: TS∞ = 202 MPa and A = 1.489 × 106 MPa-g/mol. Solving for $\overline{M}_n$ in Equation 15.3 and substituting TS = 195 MPa as well as the above values for TS∞ and A leads to

$$\overline{M}_n = \frac{A}{TS_\infty - TS}$$

$$= \frac{1.489 \times 10^6 \text{ MPa - g/mol}}{202 \text{ MPa} - 195 \text{ MPa}} = 213{,}000 \text{ g/mol}$$

**Question 4:**

A cylindrical metal wire 2 mm in diameter is required to carry a current of 10 A with a minimum of 0.03 V drop per 300 mm of wire. Which of the metals and alloys listed in Table 18.1 are possible candidates?

**Solution:**

Using Equations 18.3 and 18.4, let us determine the minimum conductivity required, and then select from Table 18.1, those metals that have conductivities greater than this value. Combining Equations 18.3 and 18.4, the minimum conductivity is just:

$$\sigma = \frac{1}{\rho} = \frac{Il}{VA} = \frac{Il}{V\pi\left(\frac{d}{2}\right)^2}$$

$$= \frac{(10\ \text{A})(300\ \times 10^{-3}\ \text{m})}{(0.03\ \text{V})\ (\pi)\left(\frac{2\ \times 10^{-3}\ \text{m}}{2}\right)^2} = 3.2\ \times\ 10^7\ (\Omega\text{ - m})^{-1}$$

Thus, from Table 18.1, only aluminum, gold, copper, and silver are candidates.

**Question 5:**

Germanium to which $5 \times 10^{22}$ $m^{-3}$ Sb atoms have been added is an extrinsic semiconductor at room temperature, and virtually all the Sb atoms may be thought of as being ionized (i.e., one charge carrier exists for each Sb atom). (a) Is this material n-type or p-type? (b) Calculate the electrical conductivity of this material, assuming electron and hole mobilities of 0.1 and 0.05 $m^2$/V-s, respectively.

**Solution:**

(a) This germanium material to which has been added $5 \times 10^{22}$ $m^{-3}$ Sb atoms is n-type since Sb is a donor in Ge. (Antimony is from group VA of the periodic table--Ge is from group IVA.)

(b) Since this material is *n*-type extrinsic, Equation 18.16 is valid. Furthermore, each Sb will donate a single electron, or the electron concentration is equal to the Sb concentration since all of the Sb atoms are ionized at room temperature; that is $n$=5×10$^{22}$ $m^{-3}$ and as given in the problem statement, $\mu_e$ = 0.1 $m^2$/V-s. Thus:

$$\sigma = n|e|\mu_e = (5\times10^{22}m^{-3})(1.62\times10^{-19}C)(0.1\,m^2/Vs) = 800\ (\Omega.m)^{-1}$$

**Question 6:**

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

(a) Pure copper; aluminum bronze (95 wt% Cu-5 wt% Al).

(b) Fused silica; quartz.

(c) Linear polyethylene; branched polyethylene.

(d) Random poly(styrene-butadiene) copolymer; alternating poly(styrene-butadiene) copolymer.

**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 copper will have a larger conductivity than aluminum bronze because the impurity atoms in the latter will lead to a greater degree of free electron scattering.

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

(c) The linear polyethylene will have the larger conductivity than the branched polyethylene because the former will have the higher degree of crystallinity. Linear polymers have higher degrees of crystallinity than branched polymers. Since heat transfer is accomplished 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 alternating poly(styrene-butadiene) copolymer will have a higher crystallinity than the random copolymer; alternating copolymers crystallize more easily than random ones. The influence of crystallinity on conductivity is explained in part (c).

**Question 7:**

To what temperature must a cylindrical rod of tungsten 10.000 mm in diameter and a plate of 316 stainless steel having a circular hole 9.988 mm in diameter have to be heated for the rod to just fit into the hole? Assume that the initial temperature is 25°C.

**Solution:**

This problem asks for us to determine the temperature to which a cylindrical rod of tungsten 10.000 mm in diameter must be heated in order for it of just fit into a 9.988 mm diameter circular hole in a plate of 316 stainless steel, assuming that the initial temperature is 25°C. This requires the use of Equation 19.3a, which is applied to the diameters of both the rod and hole. That is

$$\frac{d_f - d_0}{d_0} = \alpha_l (T_f - T_0)$$

Solving this expression for df yields

$$d_f = d_0 \left[ 1 + \alpha_l (T_f - T_0) \right]$$

Now all we need do is to establish expressions for df(316 stainless) and df (W), set them equal to one another, and solve for Tf. According to Table 19.1, al(316 stainless) = 16.0 × 10-6 (°C)-1 and al (W) = 4.5 × 10-6 (°C)-1. Thus

$$d_f(316 \text{ stainless}) = d_f(\text{W})$$

$$(9.988 \text{ mm}) \left[ 1 + \left\{ 16.0 \times 10^{-6} (^\circ\text{C})^{-1} \right\} (T_f - 25^\circ\text{C}) \right]$$

$$= (10.000 \text{ mm}) \left[ 1 + \left\{ 4.5 \times 10^{-6} (^\circ\text{C})^{-1} \right\} (T_f - 25^\circ\text{C}) \right]$$

Now solving for Tf gives Tf = 129.5°C