

Section 2.1 – Atomic Structure

PP 2.1

Calculate the number of atoms contained in a cylinder 1 μm in diameter by 1 μm deep of (a) magnesium and (b) lead. (See Example 2.1.)

PP 2.1 (a) $N_{\text{Mg atoms}} = 6.64 \times 10^{10} \text{ atoms Cu} \times \frac{(1.74 \text{ g/cm}^3) \text{ Mg}}{(8.93 \text{ g/cm}^3) \text{ Cu}}$
 $\times \frac{63.55 \text{ g Cu} / N_{\text{Av atoms Cu}}}{24.31 \text{ g Mg} / N_{\text{Av atoms Mg}}}$
 $= \underline{\underline{3.38 \times 10^{10} \text{ atoms Mg}}}$

(b) $N_{\text{Pb atoms}} = 6.64 \times 10^{10} \text{ atoms Cu} \times \frac{(11.34 \text{ g/cm}^3) \text{ Pb}}{(8.93 \text{ g/cm}^3) \text{ Cu}}$
 $\times \frac{63.55 \text{ g Cu} / N_{\text{Av atoms Cu}}}{207.2 \text{ g Pb} / N_{\text{Av atoms Pb}}}$
 $= \underline{\underline{2.59 \times 10^{10} \text{ atoms Pb}}}$

PP 2.2

Using the density of MgO calculated in Example 2.2, calculate the mass of an MgO refractory (temperature-resistant) brick with dimensions: 50 mm \times 100 mm \times 200 mm.

PP 2.2 $m = \rho V = (3.60 \text{ g/cm}^3)(10^{-3} \text{ cm}^3/\text{mm}^3)$
 $\times (50)(100)(200) \text{ mm}^3$
 $= 3.60 \times 10^3 \text{ g} = \underline{\underline{3.60 \text{ kg}}}$

PP 2.3

Calculate the dimensions of (a) a cube containing 1 mol of copper and (b) a cube containing 1 mol of lead. (See Example 2.3.)

PP 2.3 (a) $\text{edge} = \left(\frac{63.55 \text{ g/mol}}{8.93 \text{ g/cm}^3} \right)^{1/3} \times 10 \text{ mm/cm} = \underline{\underline{19.23 \text{ mm}}}$

(b) $\text{edge} = \left(\frac{207.2 \text{ g/mol}}{11.34 \text{ g/cm}^3} \right)^{1/3} \times 10 \text{ mm/cm} = \underline{\underline{26.34 \text{ mm}}}$

- 2.1. A gold O-ring is used to form a gastight seal in a high-vacuum chamber. The ring is formed from a 80-mm length of 1.5-mm-diameter wire. Calculate the number of gold atoms in the O-ring.

$$\begin{aligned}
 \boxed{2.1} \quad N_{\text{atoms}} &= \rho V \left(\frac{N_{\text{Av}}}{\text{at. wt.}} \right) = 19.28 \times 10^6 \text{ g Au/m}^3 \times 80 \times 10^{-3} \text{ m} \\
 &\quad \times \pi \left(\frac{1.5 \times 10^{-3} \text{ m}}{2} \right)^2 \\
 &\quad \times \left(\frac{0.6023 \times 10^{24} \text{ atoms}}{196.97 \text{ g Au}} \right) \\
 &= \underline{\underline{8.33 \times 10^{21} \text{ atoms}}}
 \end{aligned}$$

- 2.2 Common aluminum foil for household use is nearly pure aluminum. A box of this product at a local supermarket is advertised as giving 75 ft² of material (in a roll 304 mm wide by 22.8 m long). If the foil is 0.5 mil (12.7 μm) thick, calculate the number of atoms of aluminum in the roll.

$$\begin{aligned}
 \boxed{2.2} \quad N_{\text{atoms}} &= \rho V \left(\frac{N_{\text{Av}}}{\text{at. wt.}} \right) = 2.70 \times 10^6 \text{ g Al/m}^3 \times 12.7 \times 10^{-6} \text{ m} \\
 &\quad \times 304 \times 10^{-3} \text{ m} \times 22.8 \text{ m} \times \left(\frac{0.6023 \times 10^{24} \text{ atoms}}{26.98 \text{ g Al}} \right) \\
 &= \underline{\underline{5.31 \times 10^{24} \text{ atoms}}}
 \end{aligned}$$

- 2.3. In a metal-oxide-semiconductor (MOS) device, a thin layer of SiO₂ (density = 2.20 Mg/m³) is grown on a single crystal chip of silicon. How many Si atoms and how many O atoms are present per square millimeter of the oxide layer? Assume that the layer thickness is 100 nm.

$$\begin{aligned}
 \boxed{2.3} \quad V &= 100 \text{ nm} \times 1 \text{ mm}^2 = 10^2 \times 10^{-9} \text{ m} \times (10^{-3} \text{ m})^2 = 1 \times 10^{-13} \text{ m}^3 \\
 m_{\text{SiO}_2} &= 2.20 \times 10^6 \text{ g/m}^3 \times 1 \times 10^{-13} \text{ m}^3 = 2.20 \times 10^{-7} \text{ g} \\
 1 \text{ mol SiO}_2 &\text{ has } (28.09 + 2[16.00]) \text{ g} = 60.09 \text{ g per} \\
 &N_{\text{Av}} \text{ atoms Si and } 2 N_{\text{Av}} \text{ atoms O} \\
 \therefore N_{\text{Si atoms}} &= \frac{2.20 \times 10^{-7} \text{ g}}{60.09 \text{ g}} \times 0.6023 \times 10^{24} \text{ atoms} \\
 &= \underline{\underline{2.21 \times 10^{15} \text{ atoms}}} \\
 N_{\text{O atoms}} &= 2 \times N_{\text{Si atoms}} = \underline{\underline{4.41 \times 10^{15} \text{ atoms}}}
 \end{aligned}$$

- 2.4 A box of clear plastic wrap for household use is polyethylene, $\text{-(C}_2\text{H}_4\text{)}_n$, with density = 0.910 Mg/m^3 . A box of this product contains 100 ft^2 of material (in a roll 304 mm wide by 30.5 m long). If the wrap is 0.5 mil ($12.7 \mu\text{m}$) thick, calculate the number of carbon atoms and the number of hydrogen atoms in this roll.

2.4

$$V = 12.7 \mu\text{m} \times 304 \text{ mm} \times 30.5 \text{ m} = 12.7 \times 10^{-6} \text{ m} \times 0.304 \text{ m} \times 30.5 \text{ m} \\ = 1.18 \times 10^{-4} \text{ m}^3$$

$$m_{\text{C}_2\text{H}_4} = 0.910 \times 10^6 \text{ g/m}^3 \times 1.18 \times 10^{-4} \text{ m}^3 = 107 \text{ g}$$

$$1 \text{ mol C}_2\text{H}_4 \text{ has } (2[12.01] + 4[1.008]) \text{ g} = 28.05 \text{ g for}$$

$$2 N_{\text{AV}} \text{ atoms C and } 4 N_{\text{AV}} \text{ atoms H}$$

$$\therefore N_{\text{C atoms}} = \frac{107 \text{ g}}{28.05 \text{ g}} \times 2 \times 0.6023 \times 10^{24} \text{ atoms} \\ = \underline{\underline{4.60 \times 10^{24} \text{ atoms}}}$$

$$N_{\text{H atoms}} = 2 \times N_{\text{C atoms}}$$

$$= \underline{\underline{9.20 \times 10^{24} \text{ atoms}}}$$

- 2.5. An Al_2O_3 whisker is a small single crystal used to reinforce metal-matrix composites. Given a cylindrical shape, calculate the number of Al atoms and the number of O atoms in a whisker with a diameter of $1 \mu\text{m}$ and a length of $30 \mu\text{m}$. (The density of Al_2O_3 is 3.97 Mg/m^3 .)

2.5

$$V = \pi \left(\frac{1 \mu\text{m}}{2} \right)^2 \times 30 \mu\text{m} = \pi (0.5 \times 10^{-6} \text{ m})^2 \times 30 \times 10^{-6} \text{ m} \\ = 23.6 \times 10^{-18} \text{ m}^3$$

$$m_{\text{Al}_2\text{O}_3} = 3.97 \times 10^6 \text{ g/m}^3 \times 23.6 \times 10^{-18} \text{ m}^3 = 9.35 \times 10^{-11} \text{ g}$$

$$1 \text{ mol Al}_2\text{O}_3 \text{ has } (2[26.98] + 3[16.00]) \text{ g} = 101.96 \text{ g}$$

$$\text{for } 2 N_{\text{AV}} \text{ atoms Al and } 3 N_{\text{AV}} \text{ atoms O}$$

$$\therefore N_{\text{Al atoms}} = \frac{9.35 \times 10^{-11} \text{ g}}{101.96 \text{ g}} \times 2 (0.6023 \times 10^{24} \text{ atoms}) \\ = \underline{\underline{1.11 \times 10^{12} \text{ atoms}}}$$

$$N_{\text{O atoms}} = \frac{3}{2} \times N_{\text{Al atoms}}$$

$$= \frac{3}{2} (1.11 \times 10^{12} \text{ atoms}) = \underline{\underline{1.66 \times 10^{12} \text{ atoms}}}$$

- 2.6 An optical fiber for telecommunication is made of SiO_2 glass (density = 2.20 Mg/m^3). How many Si atoms and how many O atoms are present per millimeter of length of a fiber $10 \mu\text{m}$ in diameter?

2.6

For 1 mm section of fiber:

$$V = \pi \left(\frac{10 \mu\text{m}}{2} \right)^2 \times 1 \text{ mm} = \pi (5 \times 10^{-6} \text{ m})^2 \times 1 \times 10^{-3} \text{ m}$$

$$= 7.85 \times 10^{-14} \text{ m}^3$$

$$m_{\text{SiO}_2} = 2.20 \times 10^6 \text{ g/m}^3 \times 7.85 \times 10^{-14} \text{ m}^3 = 1.73 \times 10^{-7} \text{ g}$$

$$1 \text{ mol SiO}_2 \text{ has } (28.09 + 2[16.00]) \text{ g} = 60.09 \text{ g}$$

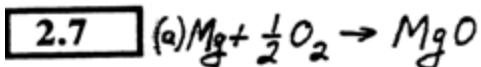
for N_{AV} atoms Si and $2 N_{\text{AV}}$ atoms O

$$\therefore N_{\text{Si atoms}} = \frac{1.73 \times 10^{-7} \text{ g}}{60.09 \text{ g}} \times 0.6023 \times 10^{24} \text{ atoms} = \underline{\underline{1.73 \times 10^{15} \text{ atoms}}}$$

$$N_{\text{O atoms}} = 2 \times N_{\text{Si atoms}} = \underline{\underline{3.46 \times 10^{15} \text{ atoms}}}$$

- 2.7. Twenty-five grams of magnesium filings are to be oxidized in a laboratory demonstration. (a) How many O_2 molecules would be consumed in this demonstration? (b) How many moles of O_2 does this represent?

2.7



i.e., 1 gm-atom Mg is oxidized by 0.5 mol O_2

$$\text{or } \frac{25 \text{ g Mg}}{24.31 \text{ g/g-atom}} = 1.028 \text{ g-atom Mg will be}$$

$$\text{oxidized by } \frac{1.028}{2} \text{ mol. O}_2 = 0.514 \text{ mol. O}_2$$

$$\therefore \text{no. molecules O}_2 = 0.514 \text{ mol} \times 0.6023 \times 10^{24} \text{ molec./mol.}$$

$$= 3.10 \times 10^{23} \text{ molec.}$$

$$= \underline{\underline{0.310 \times 10^{24} \text{ molec.}}}$$

$$(b) \text{no. moles} = 0.310 \times 10^{24} \text{ molec} \times 1 \text{ mol} / 0.6023 \times 10^{24} \text{ molec.}$$

$$= \underline{\underline{0.514 \text{ mol O}_2}}$$

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- 2.8 Naturally occurring copper has an atomic weight of 63.55. Its principal isotopes are Cu^{63} and Cu^{65} . What is the abundance (in atomic percent) of each isotope?

2.8

$$x \text{ Cu}^{63} + y \text{ Cu}^{65} = \text{Cu}^{63.55}$$

or

$$63x + 65y = 63.55$$

or

$$63x + 65(1-x) = 63.55$$

or

$$65 - 2x = 63.55$$

or

$$2x = 65.00 - 63.55$$

or

$$x = 0.725$$

and

$$y = 1 - x = 0.275$$

giving:

$$\underline{\underline{72.5\% \text{ Cu}^{63} \text{ and } 27.5\% \text{ Cu}^{65}}}$$

- 2.9 A copper penny has a mass of 2.60 g. Assuming pure copper, how much of this mass is contributed by (a) the neutrons in the copper nuclei? and (b) electrons?

2.9

(a) Compared to neutrons and protons, the mass of an electron is negligible. The mass of neutrons can be determined from the average number of neutrons in an isotope:

$$\begin{aligned} n_{\text{neutrons}} &= \text{atomic weight} - \text{atomic number} \\ &= 63.55 - 29.00 = 34.55 \end{aligned}$$

$$\begin{aligned} \therefore \text{mass}_{\text{neutrons}} &= \frac{34.55}{63.55} \times 2.60 \text{ g} \\ &= \underline{\underline{1.41 \text{ g}}} \end{aligned}$$

(b) For an "average" copper atom,

$$\begin{aligned} \text{mass}_{\text{electrons}} &= (\text{atomic number})(m_{e^-}) \\ &= 29 \times 0.911 \times 10^{-27} \text{ g} \\ &= 2.64 \times 10^{-26} \text{ g} \end{aligned}$$

$$\begin{aligned} \text{mass}_{\text{atom}} &= (\text{atomic weight})(\text{amu}) \\ &= 63.55 \times 1.661 \times 10^{-24} \text{ g} \\ &= 1.056 \times 10^{-22} \text{ g} \end{aligned}$$

$$\begin{aligned} \therefore \text{wt. fraction electrons} &= \frac{2.64 \times 10^{-26} \text{ g}}{1.056 \times 10^{-22} \text{ g}} \\ &= 2.50 \times 10^{-4} \end{aligned}$$

$$\begin{aligned} \therefore \text{mass}_{\text{electrons}} &= 2.50 \times 10^{-4} \times 2.60 \text{ g} \\ &= \underline{\underline{6.50 \times 10^{-4} \text{ g}}} \end{aligned}$$

2.10. The orbital electrons of an atom can be ejected by exposure to a beam of electromagnetic radiation. Specifically, an electron can be ejected by a photon with energy greater than or equal to the electron's binding energy. Given that the photon energy (E) is equal to hc/λ , where h is Planck's constant, c the speed of light, and λ the wavelength, calculate the maximum wavelength of radiation (corresponding to the minimum energy) necessary to eject a 1s electron from a C^{12} atom. (See Figure 2.3.)

2.10

From Figure 2.3, $|E| = 283.9 \text{ eV}$.

Then, $\lambda_{\text{max}} = \frac{hc}{E}$

$$\begin{aligned} &= \frac{(0.6626 \times 10^{-33} \text{ J}\cdot\text{s})(0.2998 \times 10^9 \text{ m/s})}{(283.9 \text{ eV})(1 \text{ J}/6.242 \times 10^{18} \text{ eV})} \\ &= 4.37 \times 10^{-9} \text{ m} \times 1 \text{ nm}/10^{-9} \text{ m} \\ &= \underline{\underline{4.37 \text{ nm}}} \end{aligned}$$

Note: We use the magnitude of the electron binding energy rather than the arbitrary negative sign convention to provide a physically meaningful positive wavelength.

- 2.11 Once the 1s electron is ejected from a ^{12}C atom, as described in Problem 2.10, there is a tendency for one of the $2(sp^3)$ electrons to drop into the 1s level. The result is the emission of a photon with an energy precisely equal to the energy change associated with the electron transition. Calculate the wavelength of the photon that would be emitted from a ^{12}C atom. (You will note various examples of this concept throughout the text in relation to the chemical analysis of engineering materials.)

2.11

From Figure 2.3 and again using the magnitude of the energies involved,

$$|\Delta E| = |-283.9 - (-6.5)| \text{ eV} \\ = 277.4 \text{ eV}$$

or

$$\lambda = \frac{hc}{\Delta E} \\ = \frac{(0.6626 \times 10^{-33} \text{ J}\cdot\text{s})(0.2998 \times 10^9 \text{ m/s})}{(277.4 \text{ eV})(1 \text{ J}/6.242 \times 10^{18} \text{ eV})} \\ = 4.47 \times 10^{-9} \text{ m} \times 1 \text{ nm}/10^{-9} \text{ m} \\ = \underline{\underline{4.47 \text{ nm}}}$$

- 2.12 The mechanism for producing a photon of specific energy is outlined in Problem 2.11. The magnitude of photon energy increases with the atomic number of the atom from which emission occurs. (This is due to the stronger binding forces between the negative electrons and the positive nucleus as the numbers of protons and electrons increase with atomic number.) As noted in Problem 2.10, $E = hc/\lambda$, which means that a higher-energy photon will have a shorter wavelength. Verify that higher atomic number materials will emit higher-energy, shorter-wavelength photons by calculating E and λ for emission from iron (atomic number 26 compared to 6 for carbon), given that the energy levels for the first two electron orbitals in iron are at -7.112 eV and -708 eV .

2.12

$$|\Delta E| = |-7.112 - (-708)| \text{ eV} = 6404 \text{ eV}$$

$$\text{or } \lambda = \frac{hc}{\Delta E} = \frac{(0.6626 \times 10^{-33} \text{ J}\cdot\text{s})(0.2998 \times 10^9 \text{ m/s})}{(6404 \text{ eV})(1 \text{ J}/6.242 \times 10^{18} \text{ eV})} \\ = 1.94 \times 10^{-10} \text{ m} \times 1 \text{ nm}/10^{-9} \text{ m} = \underline{\underline{0.194 \text{ nm}}}$$

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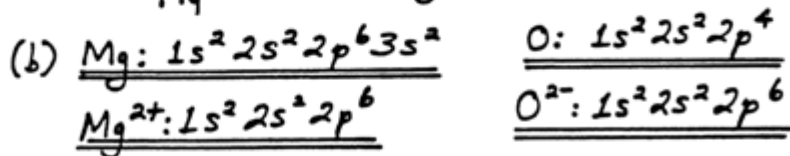
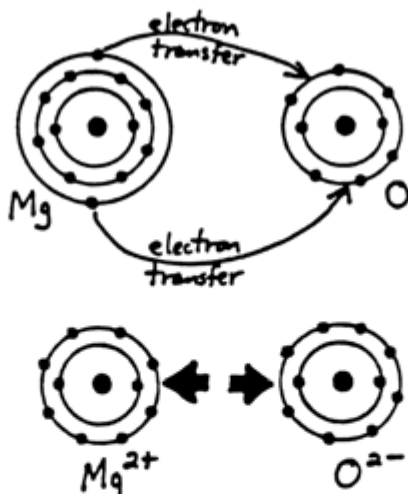
Section 2.2 – The Ionic Bond

PP 2.4

(a) Make a sketch similar to Figure 2.4, illustrating Mg and O atoms and ions in MgO. (b) Compare the electronic configurations for the atoms and ions illustrated in part (a). (c) Show which noble gas atoms have electronic configurations equivalent to those illustrated in part (a). (See Example 2.4.)

PP 2.4

(a)



(c) Ne and Ne

PP 2.5

(a) Using the ionic radii data in Appendix 2, calculate the coulombic force of attraction between the $\text{Mg}^{2+}-\text{O}^{2-}$ ion pair. (b) What is the repulsive force in this case? (See Examples 2.5 and 2.6.)

PP 2.5

(a) From Appendix 2,

$$r_{\text{Mg}^{2+}} = 0.078 \text{ nm}$$

$$r_{\text{O}^{2-}} = 0.132 \text{ nm}$$

Then,

$$r_0 = r_{\text{Mg}^{2+}} + r_{\text{O}^{2-}} = 0.078 \text{ nm} + 0.132 \text{ nm} = 0.210 \text{ nm}$$

$$F_c = - \frac{(9 \times 10^9 \text{ V}\cdot\text{m}/\text{C})(+2)(0.16 \times 10^{-18} \text{ C})(-2)(0.16 \times 10^{-18} \text{ C})}{(0.210 \times 10^{-9} \text{ m})^2}$$

$$= \underline{20.9 \times 10^{-9} \text{ N}}$$

(b) $F_R = -F_c = \underline{-20.9 \times 10^{-9} \text{ N}}$

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PP 2.6

Calculate the minimum radius ratio for a coordination number of
(a) 4 and (b) 6. (See Example 2.7.)

PP 2.6

(a)



$$\theta = \frac{109.5^\circ}{2} \quad (\text{see Figure 2-19})$$

$$\sin\left(\frac{109.5^\circ}{2}\right) = \frac{R}{r+R}$$

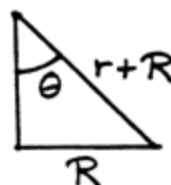
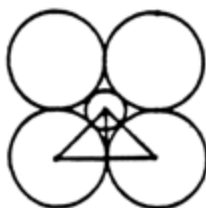
$$0.8166 r + 0.8166 R = R$$

$$0.1834 R = 0.8166 r$$

giving, finally

$$\underline{\underline{\frac{r}{R} = 0.225}}$$

(b)



$$\theta = 45^\circ$$

$$\sin 45^\circ = \frac{R}{r+R}$$

$$0.707 r + 0.707 R = R$$

giving, finally

$$\underline{\underline{\frac{r}{R} = 0.414}}$$

PP 2.7

In the next chapter we shall see that MgO, CaO, FeO, and NiO all share the NaCl crystal structure. As a result, in each case the metal ions will have the same coordination number (6). The case of MgO and CaO is treated in Example 2.8. Use the radius ratio calculation to see if it estimates the CN = 6 for FeO and NiO.

PP 2.7

From Appendix 2,

$$r_{\text{Fe}^{2+}} = 0.087 \text{ nm}, r_{\text{Ni}^{2+}} = 0.078 \text{ nm}, r_{\text{O}^{2-}} = 0.132 \text{ nm}$$

For FeO,

$$\frac{r}{R} = \frac{0.087 \text{ nm}}{0.132 \text{ nm}} = 0.66 \text{ for which Table 2.1 gives}$$

$$\underline{\underline{\text{CN} = 6}}$$

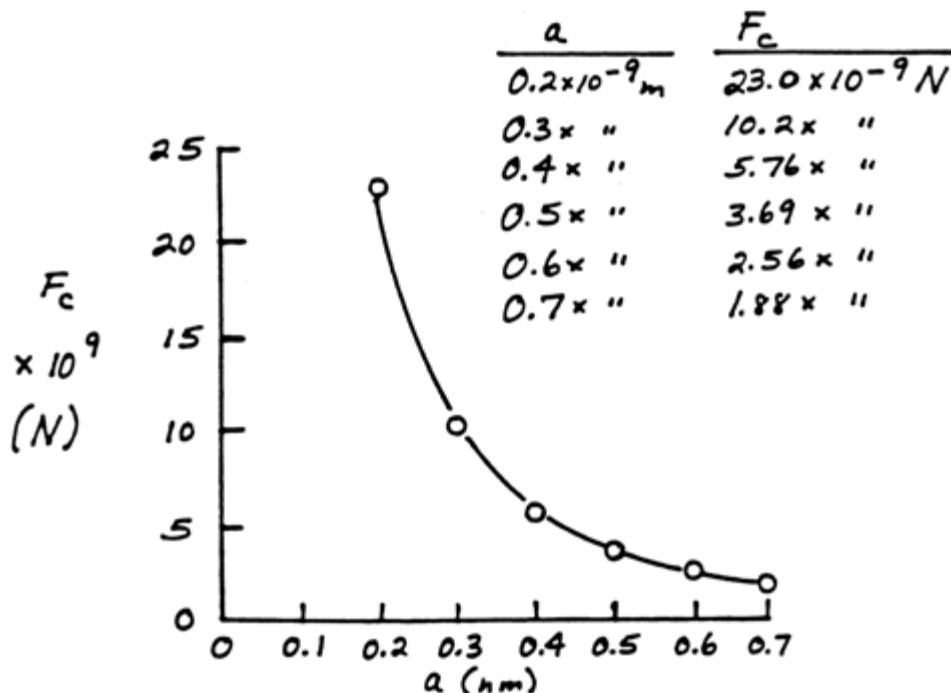
For NiO,

$$\frac{r}{R} = \frac{0.078 \text{ nm}}{0.132 \text{ nm}} = 0.59 \text{ giving } \underline{\underline{\text{CN} = 6}}$$

2.13 Make an accurate plot of F_c versus a (comparable to Figure 2.6) for an $\text{Mg}^{2+} - \text{O}^{2-}$ pair. Consider the range of a from 0.2 to 0.7 nm.

2.13

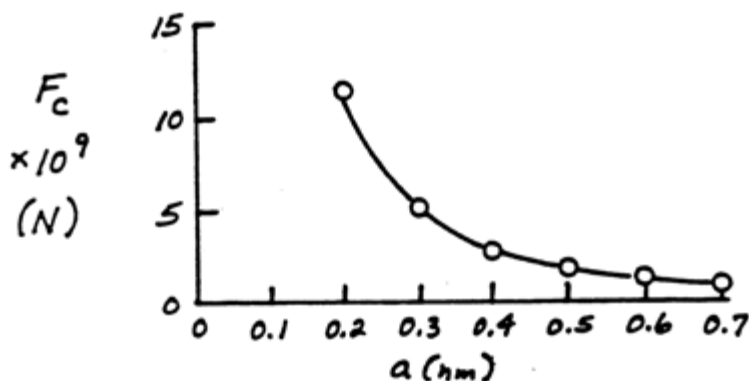
$$F_c = - \frac{(9 \times 10^9 \text{ V}\cdot\text{m}/\text{C})(+2)(0.16 \times 10^{-18} \text{ C})(-2)(0.16 \times 10^{-18} \text{ C})}{a^2}$$



2.14 Make an accurate plot of F_c versus a for a $\text{Na}^+ - \text{O}^{2-}$ pair.

$$\boxed{2.14} \quad F_c = - \frac{(9 \times 10^9 \text{ V}\cdot\text{m}/\text{C})(+1)(0.16 \times 10^{-18} \text{ C})(-2)(0.16 \times 10^{-18} \text{ C})}{a^2}$$

a	F_c
$0.2 \times 10^{-9} \text{ m}$	$11.5 \times 10^{-9} \text{ N}$
$0.3 \times "$	$5.12 \times "$
$0.4 \times "$	$2.88 \times "$
$0.5 \times "$	$1.84 \times "$
$0.6 \times "$	$1.28 \times "$
$0.7 \times "$	$0.940 \times "$



2.15 So far, we have concentrated on the coulombic force of attraction between ions. But like ions repel each other. A nearest-neighbor pair of Na^+ ions in Figure 2.5 are separated by a distance of $\sqrt{2}a_0$, where a_0 is defined in Figure 2.7. Calculate the coulombic force of *repulsion* between such a pair of like ions.

$$\begin{aligned} \boxed{2.15} \quad F_c &= - \frac{k_e (Z_1 e)(Z_2 e)}{a^2} \\ &= - \frac{(9 \times 10^9 \text{ V}\cdot\text{m}/\text{C})(+1)(0.16 \times 10^{-18} \text{ C})(+1)(0.16 \times 10^{-18} \text{ C})}{(2)(0.278 \times 10^{-9} \text{ m})^2} \\ &= \underline{\underline{-1.49 \times 10^{-9} \text{ N}}} \end{aligned}$$

2.16 Calculate the coulombic force of attraction between Ca^{2+} and O^{2-} in CaO , which has the NaCl -type structure.

2.16

From Appendix 2,

$$r_{\text{Ca}^{2+}} = 0.106 \text{ nm} \quad \& \quad r_{\text{O}^{2-}} = 0.132 \text{ nm}$$

Then,

$$a_0 = r_{\text{Ca}^{2+}} + r_{\text{O}^{2-}} = 0.106 \text{ nm} + 0.132 \text{ nm} = 0.238 \text{ nm}$$

$$\begin{aligned} F_c &= - \frac{(9 \times 10^9 \text{ V}\cdot\text{m}/\text{C})(+2)(0.16 \times 10^{-18} \text{ C})(-2)(0.16 \times 10^{-18} \text{ C})}{(0.238 \times 10^{-9} \text{ m})^2} \\ &= \underline{\underline{16.3 \times 10^{-9} \text{ N}}} \end{aligned}$$

2.17 Calculate the coulombic force of repulsion between nearest-neighbor Ca^{2+} ions in CaO . (Note Problems 2.15 and 2.16.)

2.17

As noted in Problem 2.15,

$$a = \sqrt{2} a_0$$

Using the calculation for Problem 2.16,

$$a = \sqrt{2} (0.238 \text{ nm}) = 0.337 \text{ nm}$$

Then,

$$\begin{aligned} F_c &= - \frac{(9 \times 10^9 \text{ V}\cdot\text{m}/\text{C})(+2)(0.16 \times 10^{-18} \text{ C})^2}{(0.337 \times 10^{-9} \text{ m})^2} \\ &= \underline{\underline{-8.13 \times 10^{-9} \text{ N}}} \end{aligned}$$

2.18 Calculate the coulombic force of repulsion between nearest-neighbor O^{2-} ions in CaO. (Note Problems 2.15, 2.16, and 2.17.)

2.18

As in Problem 2.17,

$$a = \sqrt{2} a_0 = \sqrt{2} (0.238 \text{ nm}) = 0.337 \text{ nm}$$

And,

$$F_c = - \frac{(9 \times 10^9 \text{ V}\cdot\text{m/C})(-2)^2 (0.16 \times 10^{-18} \text{ C})^2}{(0.337 \times 10^{-9} \text{ m})^2}$$

$$= \underline{\underline{-8.13 \times 10^{-9} \text{ N}}}$$

2.19 Calculate the coulombic force of repulsion between nearest-neighbor Ni^{2+} ions in NiO, which has the NaCl-type structure. (Note Problem 2.17.)

2.19

$$a = \sqrt{2} a_0 = \sqrt{2} (r_{Ni^{2+}} + r_{O^{2-}})$$

From Appendix 2,

$$a = \sqrt{2} (0.078 \text{ nm} + 0.132 \text{ nm}) = 0.297 \text{ nm}$$

Then,

$$F_c = - \frac{(9 \times 10^9 \text{ V}\cdot\text{m/C})(+2)^2 (0.16 \times 10^{-18} \text{ C})^2}{(0.297 \times 10^{-9} \text{ m})^2} = \underline{\underline{-10.4 \times 10^{-9} \text{ N}}}$$

2.20 Calculate the coulombic force of repulsion between nearest-neighbor O^{2-} ions in NiO. (Note Problems 2.18 and 2.19.)

2.20

As in Problem 2.19,

$$a = \sqrt{2} (0.078 \text{ nm} + 0.132 \text{ nm}) = 0.297 \text{ nm}$$

and,

$$F_c = - \frac{(9 \times 10^9 \text{ V}\cdot\text{m/C})(-2)^2 (0.16 \times 10^{-18} \text{ C})^2}{(0.297 \times 10^{-9} \text{ m})^2} = \underline{\underline{-10.4 \times 10^{-9} \text{ N}}}$$

2.21 SiO_2 is known as a "glass former" because of the tendency of SiO_4^{4-} tetrahedra (Figure 2.17) to link together in a noncrystalline network. Al_2O_3 is known as an intermediate glass former due to the ability of Al^{3+} to substitute for Si^{4+} in the glass network, although Al_2O_3 does not by itself tend to be noncrystalline. Discuss the substitution of Al^{3+} for Si^{4+} in terms of the radius ratio.

2.21

As discussed in Section 2.3, the radius ratio for $\text{Si}^{4+} - \text{O}^{2-}$ is:

$$r/R = \frac{0.039 \text{ nm}}{0.132 \text{ nm}} = 0.295, \text{ well within}$$

the range for 4-fold coordination.

For $\text{Al}^{3+} - \text{O}^{2-}$, data in Appendix 2 gives:

$$r/R = \frac{0.057 \text{ nm}}{0.132 \text{ nm}} = 0.432, \text{ just above}$$

the range for 4-fold coordination indicating that the role of Al_2O_3 as an intermediate glass former is reasonably consistent with this simple ionic calculation.

2.22 Repeat Problem 2.21 for TiO_2 , which like Al_2O_3 , is an intermediate glass former.

2.22

For $\text{Ti}^{4+} - \text{O}^{2-}$, Appendix 2 gives:

$$r/R = 0.064 \text{ nm} / 0.132 \text{ nm} = 0.485$$

As with Al^{3+} , Ti^{4+} gives a value just above the range for 4-fold coordination consistent with its intermediate role.

- 2.23 The coloration of glass by certain ions is often sensitive to the coordination of the cation by oxygen ions. For example, Co^{2+} gives a blue-purple color when in the fourfold coordination characteristic of the silica network (see Problem 2.21) and gives a pink color when in a sixfold coordination. Which color from Co^{2+} is predicted by the radius ratio?

2.23 Using the data from Appendix 2,

$$\frac{r_{\text{Co}^{2+}}}{r_{\text{O}^{2-}}} = \frac{0.082 \text{ nm}}{0.132 \text{ nm}} = 0.621$$

which is in the range for 6-fold coordination in Table 2.1. Therefore, a pink color is indicated.

Note: The rich blue-purple color known as "cobalt blue" associated with 4-fold coordination of Co^{2+} is, then, determined by more than simple ionic considerations.

- 2.24 One of the first nonoxide materials to be produced as a glass was BeF_2 . As such, it was found to be similar to SiO_2 in many ways. Calculate the radius ratio for Be^{2+} and F^- and comment.

2.24 For $\text{Be}^{2+} - \text{F}^-$, Appendix 2 gives:

$$r/R = 0.054 \text{ nm} / 0.133 \text{ nm} = 0.406, \text{ which is}$$

in the range for 4-fold coordination. As a result, tetrahedrally-coordinated Be^{2+} leads to network formation similar to the case for Si^{4+} in SiO_2 .

- 2.25. A common feature in high-temperature ceramic superconductors is a Cu-O sheet that serves as a superconducting plane. Calculate the coulombic force of attraction between a Cu^{2+} and an O^{2-} within one of these sheets.

2.25 From Appendix 2,

$$r_{\text{Cu}^{2+}} = 0.072 \text{ nm} \text{ \& } r_{\text{O}^{2-}} = 0.132 \text{ nm}$$

Then,

$$a_0 = r_{\text{Cu}^{2+}} + r_{\text{O}^{2-}} = 0.072 \text{ nm} + 0.132 \text{ nm} = 0.204 \text{ nm}$$

$$\begin{aligned} F_c &= - \frac{(9 \times 10^9 \text{ V}\cdot\text{m}/\text{C})(+2)(0.16 \times 10^{-18} \text{ C})(-2)(0.16 \times 10^{-18} \text{ C})}{(0.204 \times 10^{-9} \text{ m})^2} \\ &= \underline{\underline{22.1 \times 10^{-9} \text{ N}}} \end{aligned}$$

- 2.26 In contrast to the calculation for the superconducting Cu-O sheets discussed in Problem 2.25, calculate the coulombic force of attraction between a Cu^+ and an O^{2-}

2.26 From Appendix 2,

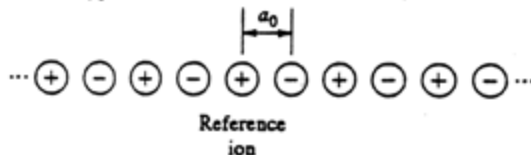
$$r_{\text{Cu}^+} = 0.096 \text{ nm} \text{ \& } r_{\text{O}^{2-}} = 0.132 \text{ nm}$$

Then,

$$a_0 = r_{\text{Cu}^+} + r_{\text{O}^{2-}} = 0.096 \text{ nm} + 0.132 \text{ nm} = 0.228 \text{ nm}$$

$$\begin{aligned} F_c &= - \frac{(9 \times 10^9 \text{ V}\cdot\text{m}/\text{C})(+1)(0.16 \times 10^{-18} \text{ C})(-2)(0.16 \times 10^{-18} \text{ C})}{(0.228 \times 10^{-9} \text{ m})^2} \\ &= \underline{\underline{8.86 \times 10^{-9} \text{ N}}} \end{aligned}$$

- 2.27 For an ionic crystal, such as NaCl, the net coulombic bonding force is a simple multiple of the force of attraction between an adjacent ion pair. To demonstrate this, consider the hypothetical, one-dimensional "crystal" shown:



- (a) Show that the net coulombic force of attraction between the reference ion and all other ions in the crystal is

$$F = AF_c$$

where F_c is the force of attraction between an adjacent ion pair (see Equation 2.1) and A is a series expansion.

- (b) Determine the value of A .

2.27 (a) For the "crystal,"

$$\begin{aligned} F_{c,net} = F &= -K \left(\frac{2}{a_0^2} - \frac{2}{(2a_0)^2} + \frac{2}{(3a_0)^2} - \frac{2}{(4a_0)^2} + \dots \right) \\ &= -\frac{2K}{a_0^2} \left(+1 - \frac{1}{4} + \frac{1}{9} - \frac{1}{16} + \dots \right) \end{aligned}$$

For an adjacent ion pair,

$$F_c = -\frac{K}{a_0^2} \quad (\text{Of course, } K \text{ for the adjacent pair is negative in sign.})$$

$$\begin{aligned} \text{Or } F &= F_c 2 \left(1 - \frac{1}{4} + \frac{1}{9} - \frac{1}{16} + \dots \right) \\ &= A F_c \quad \text{where } A = 2 \left(1 - \frac{1}{4} + \frac{1}{9} - \frac{1}{16} + \dots \right) \end{aligned}$$

- (b) One can evaluate A by carrying out the series a sufficiently large number of terms until the net value converges.

One can also note that

$$1 - \frac{1}{2^2} + \frac{1}{3^2} - \frac{1}{4^2} + \dots = \frac{\pi^2}{12}$$

giving:

$$A = \frac{2\pi^2}{12} = \underline{\underline{1.645}}$$

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2.28 In Problem 2.27, a value for A was calculated for the simple one-dimensional case. For the three-dimensional NaCl structure, A has been calculated to be 1.748. Calculate the net coulombic force of attraction, F , for this case.

2.28

$$F = A F_C$$

From Example 2.5,

$$F_C = 2.98 \times 10^{-9} \text{ N}$$

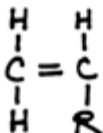
$$\therefore F = (1.748)(2.98 \times 10^{-9} \text{ N}) = \underline{\underline{5.21 \times 10^{-9} \text{ N}}}$$

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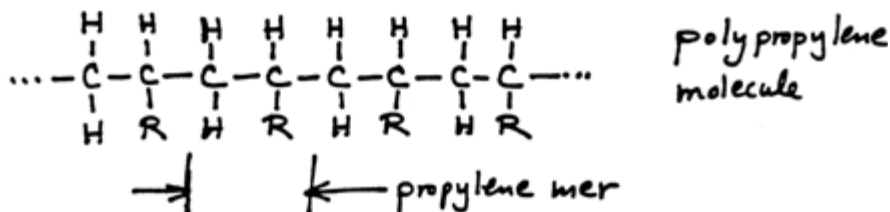
Section 2.3 – The Covalent Bond

PP 2.8 In Figure 2-14 we see the polymerization of polyethylene $(-C_2H_4-)_n$ illustrated. Example 2.9 illustrates polymerization for poly(vinyl chloride) $(-C_2H_3Cl-)_n$. Make a similar sketch to illustrate the polymerization of polypropylene $(-C_2H_3R-)_n$, where R is a CH_3 group.

PP 2.8



propylene molecule

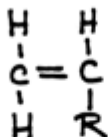


where $R = CH_3$

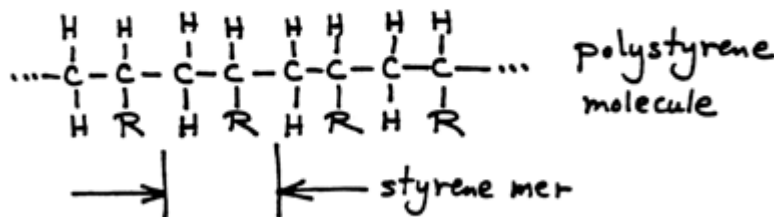
PP 2.9

Use a sketch to illustrate the polymerization of polystyrene $(-C_2H_3R-)_n$, where R is a benzene group, C_6H_5 .

PP 2.9



styrene molecule



where $R = C_6H_5$

PP 2.10

Calculate the reaction energy for polymerization of (a) propylene (see Practice Problem 2.8) and (b) styrene (see Practice Problem 2.9).

PP 2.10

(a) The backbone reaction is the same. Therefore, the calculation is the same:

$$(740 - 680) \text{ kJ/mol} = \underline{\underline{60 \text{ kJ/mol}}}$$

(b) Again,

$$(740 - 680) \text{ kJ/mol} = \underline{\underline{60 \text{ kJ/mol}}}$$

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PP 2.11

The length of an average polyethylene molecule in a commercial clear plastic wrap is $0.2 \mu\text{m}$. What is the average degree of polymerization (n) for this material? (See Example 2.11.)

PP 2.11

As illustrated in Example 2.11,

$$L = 2n\ell$$

or
$$n = \frac{L}{2\ell}$$

$$= \frac{0.2 \times 10^{-6} \text{ m}}{2 \times 0.126 \times 10^{-9} \text{ m}} = \underline{\underline{794}}$$

2.29 Calculate the total reaction energy for polymerization required to produce the roll of clear plastic wrap described in Problem 2.4.

2.29

From Problem 2.4, we obtain:

4.60×10^{24} C atoms in the sheet of polyethylene.

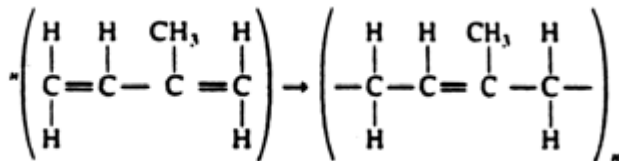
From Example 2.10, we note there is a

reaction energy of 60 kJ/mol (of double bonds).

Then, the total reaction energy for the polymer wrap is:

$$\begin{aligned} E_{\text{reaction}} &= \frac{60 \text{ kJ}}{\text{mol bonds}} \times 4.60 \times 10^{24} \text{ atoms C} \\ &\times \frac{1 \text{ mol C atoms}}{0.6023 \times 10^{24} \text{ atoms C}} \times \frac{1 \text{ bond}}{2 \text{ atoms}} \\ &= \underline{\underline{229 \text{ kJ}}} \end{aligned}$$

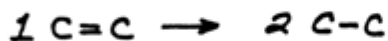
2.30 Natural rubber is polyisoprene. The polymerization reaction can be illustrated as



Calculate the reaction energy (per mole) for polymerization.

2.30

Although this reaction appears more complex, the net effect is (as in Example 2.10):

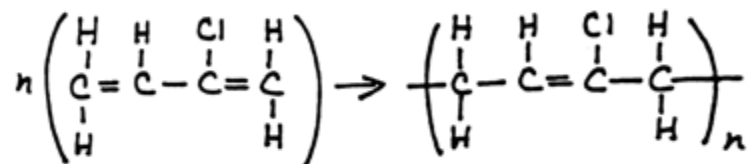


giving a reaction energy of:

$$(740 - 680) \text{ kJ/mol} = \underline{\underline{60 \text{ kJ/mol}}}$$

2.31 Neoprene is a synthetic rubber, polychloroprene, with a chemical structure similar to natural rubber (see Problem 2.30) except that it contains a Cl atom in place of the CH_3 group of the isoprene molecule. (a) Sketch the polymerization reaction for neoprene, and (b) calculate the reaction energy (per mole) for this polymerization. (c) Calculate the total energy released during the polymerization of 1 kg of chloroprene.

2.31 (a) Similar to the reaction in Problem 2.30:



(b) Again (as in Example 2.10), the net reaction is: $1 \text{ C}=\text{C} \rightarrow 2 \text{ C}-\text{C}$ giving a reaction energy of:

$$(740 - 680) \text{ kJ/mol} = \underline{\underline{60 \text{ kJ/mol}}}$$

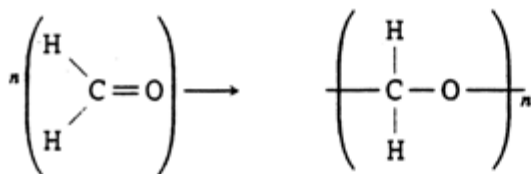
(c) The mer molecular weight is:

$$(4 \times 12.01 + 5 \times 1.008 + 35.45) \text{ g} = 88.53 \text{ g}$$

As there is one bond reaction [as shown in part (b)] for each mer, we can write:

$$\begin{aligned} \text{energy released} &= 1 \text{ kg} \times \frac{1 \text{ mol}}{88.53 \text{ g}} \times \frac{1000 \text{ g}}{\text{kg}} \\ &\times 60 \text{ kJ/mol} = \underline{\underline{678 \text{ kJ}}} \end{aligned}$$

2.32 Acetal polymers, which are widely used for engineering applications, can be represented by the following reaction, the polymerization of formaldehyde:



Calculate the reaction energy for this polymerization.

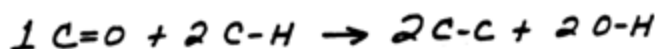
2.32 In this case, the net reaction is: $1 \text{ C}=\text{O} \rightarrow 2 \text{ C}-\text{O}$ giving a reaction energy of:

$$2(360 \text{ kJ/mol}) - 535 \text{ kJ/mol} = \underline{\underline{185 \text{ kJ/mol}}}$$

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- 2.33. The first step in the formation of phenolformaldehyde, a common phenolic polymer, is shown in Figure 12.6. Calculate the net reaction energy (per mole) for this step in the overall polymerization reaction.

2.33 In this case, the net reaction is:



giving a reaction energy of:

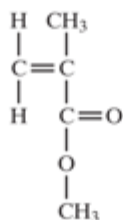
$$\begin{aligned} & 2(370 \text{ kJ/mol}) + 2(500 \text{ kJ/mol}) \\ & - 2(435 \text{ kJ/mol}) - 1(535 \text{ kJ/mol}) = \underline{\underline{335 \text{ kJ/mol}}} \end{aligned}$$

- 2.34 Calculate the molecular weight of a polyethylene molecule with $n = 500$.

2.34 Using the data of Appendix 1, we obtain

$$\begin{aligned} \text{mol. wt. } (\text{C}_2\text{H}_4)_{n=500} &= 500[2(12.01) + 4(1.008)] \text{ amu} \\ &= \underline{\underline{14,030 \text{ amu}}} \end{aligned}$$

- 2.35. The monomer upon which a common acrylic polymer, polymethyl methacrylate, is based is



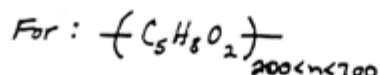
Calculate the molecular weight of a polymethyl methacrylate molecule with $n = 500$.

2.35 Using the chemical formula given by Table 13.1 and the data of Appendix 1, we obtain

$$\begin{aligned} \text{mol. wt. } (\text{C}_5\text{H}_8\text{O}_2)_{n=500} &= 500[5(12.01) + 8(1.008) + 2(16.00)] \text{ amu} \\ &= \underline{\underline{50,060 \text{ amu}}} \end{aligned}$$

- 2.36 Bone "cement" used by orthopedic surgeons to set artificial hip implants in place is methyl methacrylate polymerized during the surgery. The resulting polymer has a relatively wide range of molecular weights. Calculate the resulting range of molecular weights if $200 < n < 700$.

2.36



$$\begin{aligned} \text{mol. wt.} &= 200 [5(12.01) + 8(1.008) + 2(16.00)] \text{ amu to} \\ &\quad 700 [\quad " \quad + \quad " \quad + \quad " \quad] \text{ amu} \\ &= \underline{\underline{20,020 \text{ amu to } 70,080 \text{ amu}}} \end{aligned}$$

- 2.37. Orthopedic surgeons notice a substantial amount of heat evolution from polymethyl methacrylate bone cement during surgery. Calculate the reaction energy if a surgeon uses 15 g of polymethyl methacrylate to set a given hip implant.

2.37

Note that 1 mol of polymethyl methacrylate contains 1 mol of C=C double bonds.

$$1 \text{ mol } \text{C}_5\text{H}_8\text{O}_2 \text{ has } [5(12.01) + 8(1.008) + 2(16.00)] \text{ g} = 100.1 \text{ g}$$

As calculated numerous times in this section, the reaction energy for $1 \text{ C}=\text{C} \rightarrow 2 \text{ C}-\text{C}$ is:

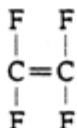
$$(740 - 680) \text{ kJ/mol} = 60 \text{ kJ/mol}$$

Then, the total reaction energy the implant cement is:

$$E_{\text{reaction}} = \frac{60 \text{ kJ}}{\text{mol. bonds}} \times \frac{1 \text{ mol. bonds}}{100.1 \text{ g}} \times 15 \text{ g} = \underline{\underline{8.99 \text{ kJ}}}$$

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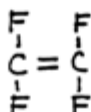
2.38 The monomer for the common fluoroplastic, polytetrafluoroethylene, is



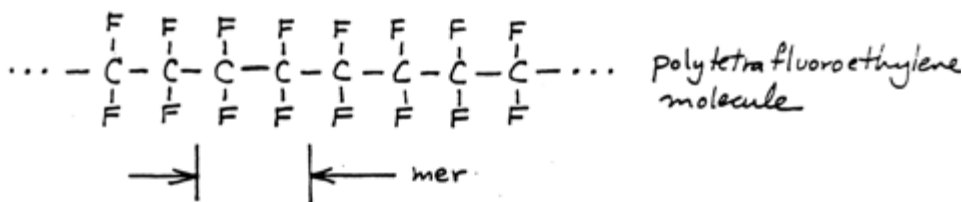
- (a) Sketch the polymerization of polytetrafluoroethylene.
 (b) Calculate the reaction energy (per mole) for this polymerization. (c) Calculate the molecular weight of a molecule with $n = 500$.

2.38

(a)



tetrafluoroethylene
molecule

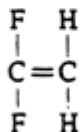


(b) Reaction energy = $(740 - 680) \text{ kJ/mol}$
 $= \underline{\underline{60 \text{ kJ/mol}}}$

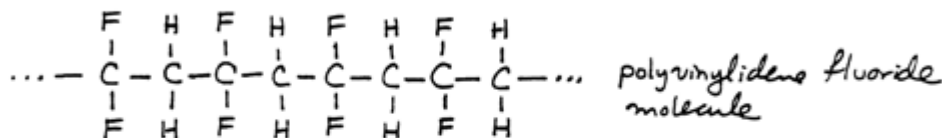
(c) Using the data of Appendix 1,

$$\begin{aligned} \text{mol. wt.} &= 500 [2(12.01) + 4(19.00)] \text{ amu} \\ &= \underline{\underline{50,010 \text{ amu}}} \end{aligned}$$

2.39 Repeat Problem 2.38 for polyvinylidene fluoride, an ingredient in various commercial fluoroplastics, having the monomer:



2.39

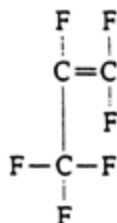


(b) Reaction energy = $(740 - 680) \text{ kJ/mol}$
 $= \underline{\underline{60 \text{ kJ/mol}}}$

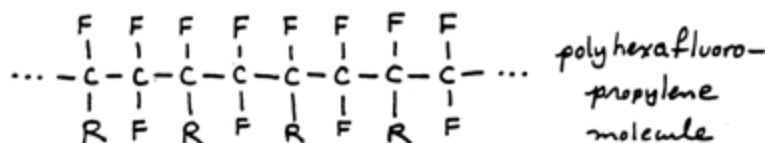
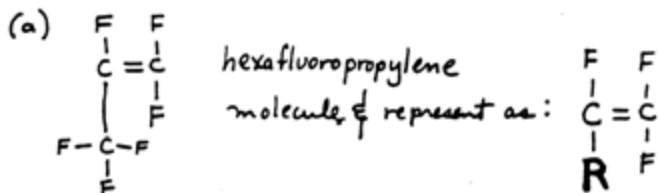
(c) Using the data of Appendix 1,

mol. wt. = $500 [2(12.01) + 2(1.008) + 2(19.00)] \text{ amu}$
 $= \underline{\underline{32,020 \text{ amu}}}$

2.40 Repeat Problem 2.38 for polyhexafluoropropylene, an ingredient in various commercial fluoroplastics, having the monomer:



2.40



(b) Reaction energy = $(740 - 680) \text{ kJ/mol} = \underline{\underline{60 \text{ kJ/mol}}}$

(c) Using Appendix 1,

mol. wt. = $500 [3(12.01) + 6(19.00)] \text{ amu} = \underline{\underline{75,020 \text{ amu}}}$

Section 2.4 – The Metallic Bond

PP 2.12

Discuss the low coordination number (= 4) for the diamond cubic structure found for some elemental solids, such as silicon. (See Example 2.12.)

PP 2.12

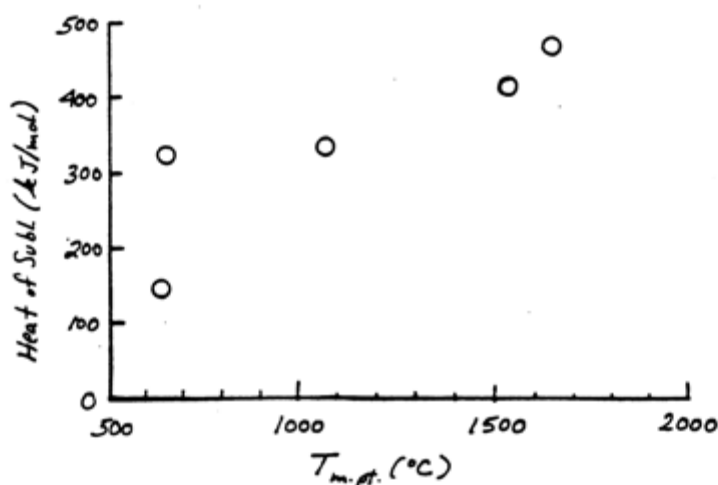
A greater degree of covalency in the Si-Si bond provides even stronger directionality and lower coordination number.

2.41 In Table 2.3, the heat of sublimation was used to indicate the magnitude of the energy of the metallic bond. A significant range of energy values is indicated by the data. The melting point data in Appendix 1 are another, more indirect indication of bond strength. Plot heat of sublimation versus melting point for the five metals of Table 2.3 and comment on the correlation.

2.41

Using Table 2.3 and Appendix 1, we obtain:

Atomic No.	Metal	$T_{m.pt.} (^{\circ}C)$	Heat of Subl. (kJ/mol)
12	Mg	649	148
13	Al	660	326
22	Ti	1660	473
26	Fe	1535	416
29	Cu	1083	338



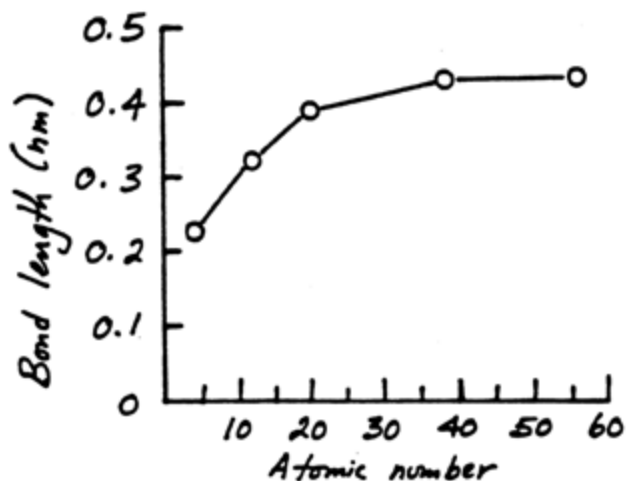
Comment: There is clearly a positive correlation between these two indicators of bond strength. However, the nature of the two processes (sublimation and melting) are sufficiently different to prevent a more precise relationship.

2.42 In order to explore a trend within the periodic table, plot the bond length of the group IIA metals (Be to Ba) as a function of atomic number. (Refer to Appendix 2 for necessary data.)

2.42

Using Figure 2.2 (the periodic table) with Appendix 2 we obtain:

IIA element	Atomic number	Atomic radius (r)	Bond length (= 2r)
Be	4	0.114 nm	0.228 nm
Mg	12	0.160 nm	0.320 nm
Ca	20	0.197 nm	0.394 nm
Sr	38	0.215 nm	0.430 nm
Ba	56	0.217 nm	0.434 nm

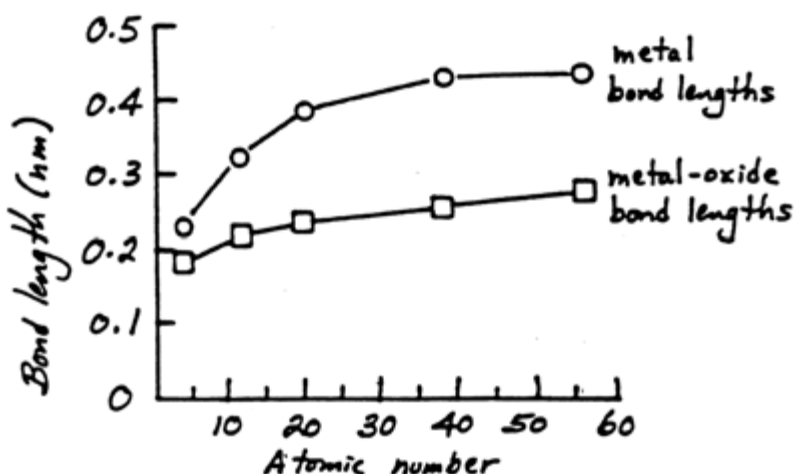


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2.43 Superimpose on the plot generated for Problem 2.42 the metal-oxide bond lengths for the same range of elements.

2.43 Using Figure 2.2 and Appendix 2 gives us:

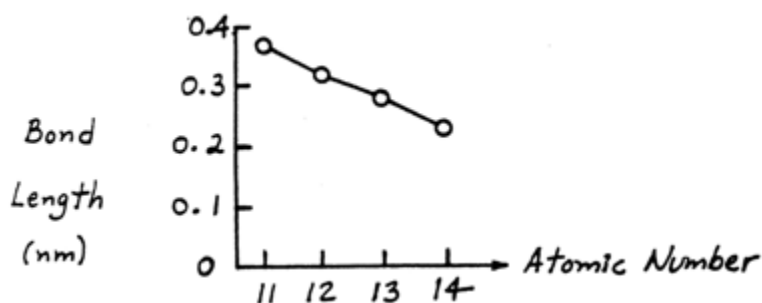
<u>IIA element</u>	<u>Atomic number</u>	<u>Ionic radius + $r_{O^{2-}}$ (0.132 nm) = Bond length</u>	<u>Bond length</u>
Be	4	0.054 nm	0.186 nm
Mg	12	0.078 nm	0.210 nm
Ca	20	0.106 nm	0.238 nm
Sr	38	0.127 nm	0.259 nm
Ba	56	0.143 nm	0.275 nm



2.44 To explore another trend within the periodic table, plot the bond length of the metals in the row Na to Si as a function of atomic numbers. (For this purpose, Si is treated as a semimetal.)

2.44 Using Figure 2.2 and Appendix 2 gives us:

Element	Atomic Number	Atomic Radius (r)	Bond Length (=2r)
Na	11	0.186 nm	0.372 nm
Mg	12	0.160 nm	0.320 nm
Al	13	0.143 nm	0.286 nm
Si	14	0.117 nm	0.234 nm

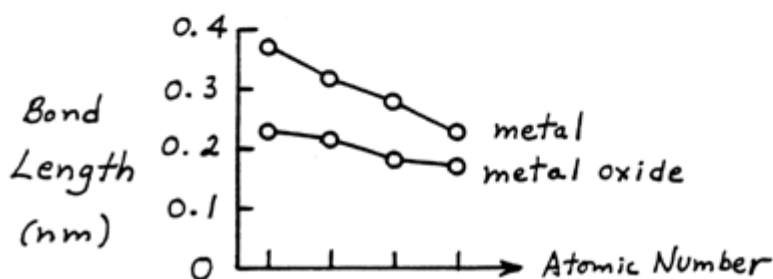


2.45 Superimpose on the plot generated for Problem 2.44 the metal-oxide bond lengths for the same range of elements.

2.45 Using Figure 2.2 and Appendix 2 gives:

Element	At. No.	Ionic Radius* + $r_{O^{2-}}$ (=0.132 nm) = Bond Length
Na	11	0.098 nm + 0.132 nm = 0.230 nm
Mg	12	0.078 nm + 0.132 nm = 0.210 nm
Al	13	0.057 nm + 0.132 nm = 0.189 nm
Si	14	0.039 nm + 0.132 nm = 0.171 nm

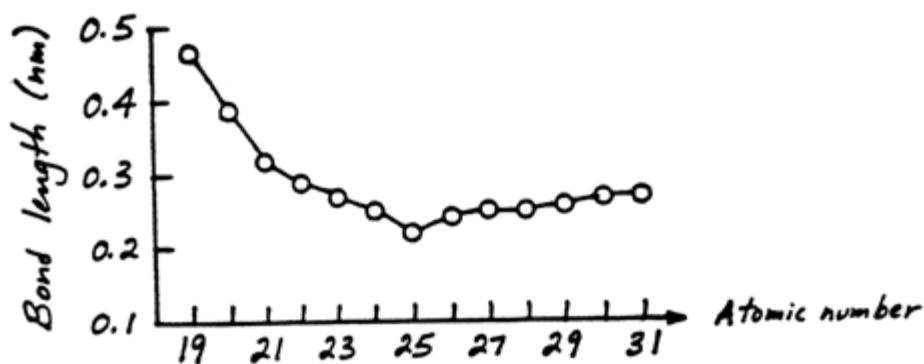
* using the most common valence, as noted on inside, back cover



2.46 Plot the bond length of the metals in the long row of metallic elements (K to Ga).

2.46 Using Figure 2.2 and Appendix 2 gives us:

Element	Atomic number	Atomic radius (r)	Bond length ($=2r$)
K	19	0.231 nm	0.462 nm
Ca	20	0.197 nm	0.394 nm
Sc	21	0.160 nm	0.320 nm
Ti	22	0.147 nm	0.294 nm
V	23	0.132 nm	0.264 nm
Cr	24	0.125 nm	0.250 nm
Mn	25	0.112 nm	0.224 nm
Fe	26	0.124 nm	0.248 nm
Co	27	0.125 nm	0.250 nm
Ni	28	0.125 nm	0.250 nm
Cu	29	0.128 nm	0.256 nm
Zn	30	0.133 nm	0.266 nm
Ga	31	0.135 nm	0.270 nm

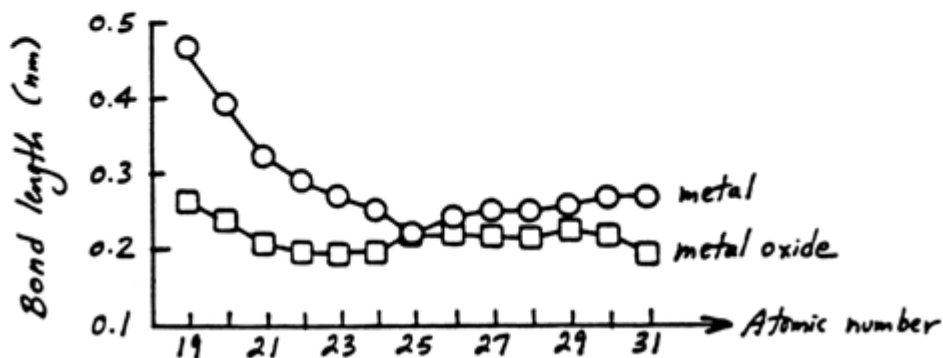


2.47 Superimpose on the plot generated for Problem 2.46 the metal-oxide bond lengths for the same range of elements.

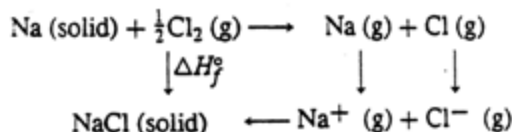
2.47 Using Figure 2.2 and Appendix 2 gives:

Element	At. No.	Ionic radius* + $r_{O^{2-}} = (0.132 \text{ nm})$	Bond length
K	19	0.133 nm	0.265 nm
Ca	20	0.106 nm	0.238 nm
Sc	21	0.083 nm	0.215 nm
Ti	22	0.064 nm	0.196 nm
V	23	0.061 nm	0.193 nm
Cr	24	0.064 nm	0.196 nm
Mn	25	0.091 nm	0.223 nm
Fe	26	0.087 nm	0.219 nm
Co	27	0.082 nm	0.214 nm
Ni	28	0.078 nm	0.210 nm
Cu	29	0.096 nm	0.228 nm
Zn	30	0.083 nm	0.215 nm
Ga	31	0.062 nm	0.194 nm

* using the most common valence, as noted on inside, back cover



- 2.48 The heat of sublimation of a metal, introduced in Table 2.3, is related to the ionic bonding energy of a metallic compound discussed in Section 2.2. Specifically, these and related reaction energies are summarized in the Born-Haber cycle, illustrated below. For the simple example of NaCl



Given the heat of sublimation to be 100 kJ/mol for sodium, calculate the ionic bonding energy of sodium chloride. (Additional data: ionization energies for sodium and chlorine = 496 kJ/mol and -361 kJ/mol, respectively; dissociation energy for diatomic chlorine gas = 243 kJ/mol; heat of formation, ΔH_f° , of NaCl = -411 kJ/mol.)

2.48

Note that $\Delta H_f^\circ = \Delta E_{\text{subl, Na}} + \frac{1}{2} \Delta E_{\text{dissoc, Cl}_2} + \Delta E_{\text{ion, Na}} + \Delta E_{\text{ion, Cl}} + \Delta E_{\text{ionic bonding, NaCl}}$

$$\begin{aligned}
 \text{or, } \Delta E_{\text{ionic bonding, NaCl}} &= \Delta H_f^\circ - \Delta E_{\text{subl, Na}} - \frac{1}{2} \Delta E_{\text{dissoc, Cl}_2} \\
 &\quad - \Delta E_{\text{ion, Na}} - \Delta E_{\text{ion, Cl}} \\
 &= (-411 - 100 - \frac{243}{2} - 496 + 361) \text{ kJ/mol} \\
 &= \underline{\underline{-768 \text{ kJ/mol}}}
 \end{aligned}$$

Section 2.5 – The Secondary, or van der Waals, Bond

PP 2.13

The bond energy and bond length for argon are calculated (assuming a "6-12" potential) in Example 2.13. Plot E as a function of a over the range 0.33 to 0.80 nm.

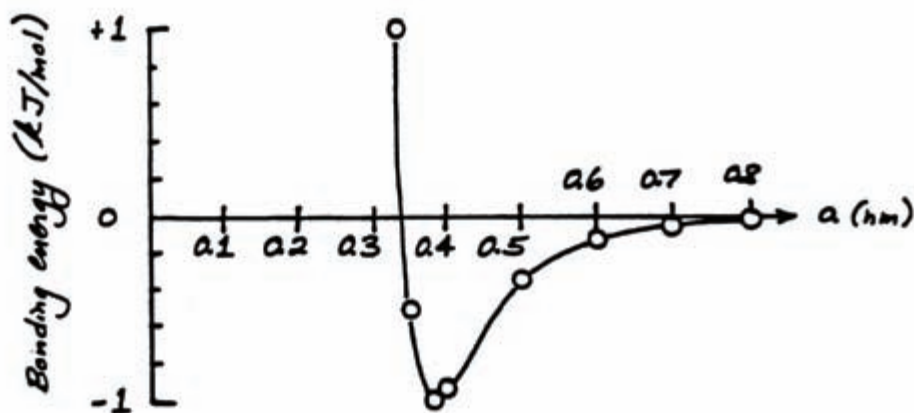
PP 2.13

From Example 2.13:

$$E_{\text{bonding}} = \left[-\frac{(10.37 \times 10^{-78} \text{ J} \cdot \text{m}^6)}{a^6} + \frac{(16.16 \times 10^{-135} \text{ J} \cdot \text{m}^{12})}{a^{12}} \right] \times 0.6023 \times 10^{24} \text{ mol}^{-1}$$

For the given range of a :

a	E_{bonding}
$0.33 \times 10^{-9} \text{ m}$	$+0.999 \text{ kJ/mol}$
$0.35 \times "$	$-0.517 "$
$0.382 \times "$	$-0.999 "$ (from Example 2.5-1)
$0.4 \times "$	$-0.945 "$
$0.5 \times "$	$-0.360 "$
$0.6 \times "$	$-0.129 "$
$0.7 \times "$	$-0.052 "$
$0.8 \times "$	$-0.024 "$



PP 2.14

Using the information from Example 2.13, plot the vander Waals bonding force curve for argon, that is, F versus a over the same range covered in Practice Problem 2.13.

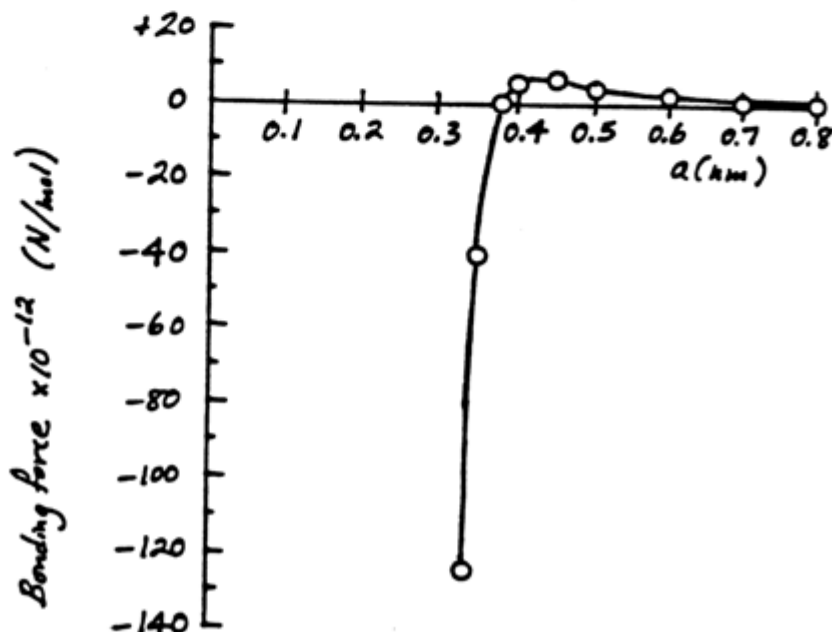
PP 2.14

$$F = \frac{dE}{da} = \frac{6K_A}{a^7} - \frac{12K_R}{a^{13}}$$

$$F_{\text{bonding}} = \left[\frac{6(10.37 \times 10^{-78} \text{ J} \cdot \text{m}^6)}{a^7} - \frac{12(16.16 \times 10^{-135} \text{ J} \cdot \text{m}^{12})}{a^{13}} \right] \times 0.6023 \times 10^{24} \text{ mol}^{-1}$$

For the given range of a :

a	F_{bonding}
$0.33 \times 10^{-9} \text{ m}$	$-124 \times 10^{12} \text{ N/mol}$
$0.35 \times "$	$-40.5 \times "$
$0.382 \times "$	0
$0.4 \times "$	$+5.47 \times "$
$0.45 \times "$	$+6.26 \times "$
$0.5 \times "$	$+3.84 \times "$
$0.6 \times "$	$+1.25 \times "$
$0.7 \times "$	$+0.44 \times "$
$0.8 \times "$	$+0.18 \times "$



- 2.49 The secondary bonding of gas molecules to a solid surface is a common mechanism for measuring the surface area of porous materials. By lowering the temperature of a solid well below room temperature, a measured volume of the gas will condense to form a monolayer coating of molecules on the porous surface. For a 100 g sample of fused copper catalyst, a volume of $9 \times 10^3 \text{ mm}^3$ of nitrogen (measured at standard temperature and pressure, 0°C and 1 atm) is required to form a monolayer upon condensation. Calculate the surface area of the catalyst in units of m^2/kg . (Take the area covered by a nitrogen molecule as 0.162 nm^2 and recall that, for an ideal gas, $pV = nRT$ where n is the number of moles of the gas.)

$$\begin{aligned}
 \boxed{2.49} \quad pV &= nRT \text{ or } n = \frac{pV}{RT} = \frac{(1 \text{ atm})(9 \times 10^3 \times 10^{-9} \text{ m}^3)}{(8.314 \text{ J/K})(273 \text{ K})} \text{ mol } N_2 \\
 &\quad \times \frac{1 \text{ N/m}^2}{9.869 \times 10^{-6} \text{ atm}} \times 0.6023 \times 10^{24} \frac{\text{molec.}}{\text{mol}} \\
 &= 2.42 \times 10^{20} \text{ molec. } N_2 \\
 \text{Area covered} &= 0.162 \times 10^{-18} \frac{\text{m}^2}{\text{molec.}} \times 2.42 \times 10^{20} \text{ molec.} \\
 &= 39.2 \text{ m}^2 \text{ (per 100 g Cu)} \\
 \text{or, } S &= \frac{39.2 \text{ m}^2}{100 \text{ g}} \times \frac{1000 \text{ g}}{\text{kg}} = \underline{\underline{392 \text{ m}^2/\text{kg}}}
 \end{aligned}$$

- 2.50. Repeat Problem 2.49 for a highly porous silica gel that has a volume of $1.16 \times 10^7 \text{ mm}^3$ of N_2 gas (at STP or Standard Temperature and Pressure) condensed to form a monolayer.

$$\begin{aligned}
 \boxed{2.50} \quad &\text{In this case,} \\
 n &= \frac{pV}{RT} = \frac{(1 \text{ atm})(1.16 \times 10^7 \times 10^{-9} \text{ m}^3)(1 \text{ N/m}^2)(0.6023 \times 10^{24} \text{ molec./mol})}{(8.314 \text{ J/K})(273 \text{ K})(9.869 \times 10^{-6} \text{ atm})} \\
 &= 3.12 \times 10^{23} \text{ molec. } N_2 \\
 \text{Area covered} &= 0.162 \times 10^{-18} \frac{\text{m}^2}{\text{molec.}} \times 3.12 \times 10^{23} \text{ molec.} \\
 &= 5.05 \times 10^4 \text{ m}^2 \text{ (per 100 g silica gel)} \\
 \text{or, } S &= \frac{5.05 \times 10^4 \text{ m}^2}{100 \text{ g}} \times \frac{1000 \text{ g}}{\text{kg}} = \underline{\underline{5.05 \times 10^5 \text{ m}^2/\text{kg}}}
 \end{aligned}$$

- 2.51. Small-diameter noble gas atoms, such as helium, can dissolve in the relatively open network structure of silicate glasses. (See Figure 1.8b for a schematic of glass structure.) The secondary bonding of helium in vitreous silica is represented by a heat of solution, ΔH_s , of -3.96 kJ/mol. The relationship between solubility, S , and the heat of solution is

$$S = S_0 e^{-\Delta H_s / (RT)}$$

where S_0 is a constant, R is the gas constant, and T is the absolute temperature (in K). If the solubility of helium in vitreous silica is 5.51×10^{23} atoms/(m³ · atm) at 25°C, calculate the solubility at 200°C.

2.51

Using the given expression for solubility, we have

$$\frac{S_{200^\circ\text{C}}}{S_{25^\circ\text{C}}} = \frac{S_0 e^{-\Delta H_s / R(200+273)\text{K}}}{S_0 e^{-\Delta H_s / R(25+273)\text{K}}}$$

or

$$\begin{aligned} S_{200^\circ\text{C}} &= S_{25^\circ\text{C}} e^{-\frac{\Delta H_s}{R} \left(\frac{1}{473\text{K}} - \frac{1}{298\text{K}} \right)} \\ &= (5.51 \times 10^{23} \text{ atoms/(m}^3 \cdot \text{atm)}) \\ &\quad \times e^{-\frac{(-3,960 \text{ J/mol})}{(8.314 \text{ J/(mol} \cdot \text{K)})} (-1.24 \times 10^{-3} \text{ K}^{-1})} \\ &= \underline{\underline{3.05 \times 10^{23} \text{ atoms/(m}^3 \cdot \text{atm)}}} \end{aligned}$$

- 2.52. Due to its larger atomic diameter, neon has a higher heat of solution in vitreous silica than helium. If the heat of solution of neon in vitreous silica is -6.70 kJ/mol and the solubility at 25°C is 9.07×10^{23} atoms/(m³ · atm), calculate the solubility at 200°C. (See Problem 2.51.)

2.52

Using the solubility expression from Problem 2.51,

$$\frac{S_{200^\circ\text{C}}}{S_{25^\circ\text{C}}} = \frac{S_0 e^{-\Delta H_s / R(200+273)\text{K}}}{S_0 e^{-\Delta H_s / R(25+273)\text{K}}}$$

or

$$\begin{aligned} S_{200^\circ\text{C}} &= S_{25^\circ\text{C}} e^{-\frac{\Delta H_s}{R} \left(\frac{1}{473\text{K}} - \frac{1}{298\text{K}} \right)} \\ &= (9.07 \times 10^{23} \text{ atoms/(m}^3 \cdot \text{atm)}) \\ &\quad \times e^{-\frac{(-6,700 \text{ J/mol})}{(8.314 \text{ J/(mol} \cdot \text{K)})} (-1.24 \times 10^{-3} \text{ K}^{-1})} \\ &= \underline{\underline{3.33 \times 10^{23} \text{ atoms/(m}^3 \cdot \text{atm)}}} \end{aligned}$$