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Introduction to Materials Science for Engineers

Instructors Solution Manual Eighth Edition

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Section 2.1 – Atomic Structure

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

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 $50 \text{ mm} \times 100 \text{ mm} \times 200 \text{ mm}$.

PP 2.2
$$m = \rho V = (3.60 g/cm^3)(10^{-3} cm^3/mm^3)$$

 $\times (50)(200) mm^3$
 $= 3.60 \times 10^3 g = 3.60 kg$

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) edge =
$$\left(\frac{63.55 \text{ g/mol}}{8.93 \text{ g/cm}^3}\right)^{1/3} \times 10 \text{ mm/cm} = \frac{19.23 \text{ mm}}{11.34 \text{ g/cm}^3}$$

$$\times 10 \text{ mm/cm} = \frac{19.23 \text{ mm}}{26.34 \text{ mm}}$$

2.1 A gold O-ring is used to form a gastight seal in a high-vacuum chamber. The ring is formed from a 100-mm length of 1.5-mm-diameter wire. Calculate the number of gold atoms in the O-ring.

2.1
$$N_{atoma} = \rho V \left(\frac{N_{AV}}{at. \ \omega t.} \right) = 19.28 \times 10^{6} g Au_{m3}^{2} \times 100 \times 10^{-3} \text{m}$$

$$\times 77 \left(\frac{1.5 \times 10^{-3} \text{m}}{2} \right)^{2}$$

$$\times \left(\frac{0.6023 \times 10^{24} \text{atoma}}{196.97 g Au} \right)$$

$$= 10.4 \times 10^{21} \text{ atoms}$$

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.

2.2
$$N_{atoms} = \rho V \left(\frac{N_{av}}{at \ wt} \right) = 2.70 \times 10^6 g \ Al/m^3 \times 12.7 \times 10^{-6} m$$

$$\times 304 \times 10^{-3} m \times 22.8 m \times \left(\frac{0.6023 \times 10^{-24} atoms}{26.98 g \ Al} \right)$$

$$= 5.3/ \times 10^{-24} atoms$$

2.3 In a metal-oxide-semiconductor (MOS) device, a thin layer of SiO_2 (density = 2.20 Mg/m^3) 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 150 nm.

2.3
$$V = 150 \text{ nm} \times 1 \text{ mm}^2 = 1.5 \times 10^{-9} \text{m} \times (10^{-3} \text{m})^2 = 1.5 \times 10^{-13} \text{m}^3$$

$$m_{S,O_2} = 2.20 \times 10^{6} \text{g/m}^3 \times 1.5 \times 10^{-13} \text{m}^3 = 3.30 \times 10^{-7} \text{g}$$

$$1 \text{ mol } S:O_2 \text{ has } (28.09 + 2[16.00]) \text{g} = 60.09 \text{ g} \text{ for}$$

$$N_{AV} \text{ atoms } S: \text{ and } 2N_{AV} \text{ atoms } 0$$

$$\therefore N_{S:\text{ atoms}} = \frac{3.30 \times 10^{-7} \text{g}}{60.09 \text{ g}} \times 0.6023 \times 10^{24} \text{ atoms}$$

$$= \frac{3.31 \times 10^{15} \text{ atoms}}{60.09 \text{ g}} = \frac{6.62 \times 10^{$$

2.4 A box of clear plastic wrap for household use is polyethylene, \(\lambda \) C₂H₄ \(\rangle \)_n, with density = 0.910 Mg/m³. A box of this product contains 100 ft² of material (in a roll 304 mm wide by 30.5 m long). If the wrap is 0.5 mil (12.7 μm) thick, calculate the number of carbon atoms and the number of hydrogen atoms in this roll.

2.4
$$V = 12.7 \mu m \times 304 mm \times 30.5 m = 12.7 \times 10^{-6} m \times 0.304 m \times 30.5 m$$

$$= 1.18 \times 10^{-4} m^{3}$$

$$m_{C_{8}H_{4}} = 0.910 \times 10^{6} g/m^{3} \times 1.18 \times 10^{-4} m^{3} = 107 g$$

$$1 \text{ mol } C_{2}H_{4} \text{ hac } \left(2[12.01] + 4[1.008]\right) g = 28.05 g \text{ for}$$

$$2 N_{8V} \text{ atoma } C \text{ and } 4 N_{8V} \text{ atoma } H$$

$$\therefore N_{Catoma} = \frac{1079}{28.05 g} \times 2 \times 0.6023 \times 10^{24} \text{ atoma}$$

$$= 4.60 \times 10^{24} \text{ atoma}$$

$$N_{H atoma} = 2 \times N_{C atoma}$$

$$= 9.20 \times 10^{24} \text{ atoma}$$

$$= 9.20 \times 10^{24} \text{ atoma}$$

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 μ m and a length of 25 μ m. (The density of Al_2O_3 is 3.97 Mg/m³.)

2.5
$$V = \pi \left(\frac{1 \mu m}{2}\right)^{2} \times 25 \mu m = \pi \left(0.5 \times 10^{-6} m\right)^{2} \times 25 \times 10^{-6} m$$

$$= 19.6 \times 10^{-18} m^{3}$$

$$m_{A|20_{3}} = 3.97 \times 10^{6} g / m^{3} \times 19.6 \times 10^{-18} m^{3} = 7.79 \times 10^{-11} g$$

$$1 mol A|_{20_{3}} \text{ here } \left(2[26.98] + 3[16.00]\right) g = 101.96 g$$

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$$1 mol A|_{20_{3}} \text{ here } \left(2[26.98]$$

2.6 An optical fiber for telecommunication is made of SiO₂ glass (density = 2.20 Mg/m³). How many Si atoms and how many O atoms are present per millimeter of length of a fiber 10 μm in diameter?

2.6 For 1 mm section of fiben:

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

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

$$m_{S:0_{2}} = 2.20 \times 10^{6} \text{ g/m}^{3} \times 7.85 \times 10^{-14} \text{ m}^{3} = 1.73 \times 10^{-7} \text{ g}$$

$$1 \text{ mol } S:0_{2} \text{ has } (28.09 + 2[16.00]) \text{ g} = 60.09 \text{ g}$$

$$\text{for } N_{AV} \text{ atoms } Si \text{ and } 2 N_{AV} \text{ atoms } 0$$

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

$$N_{O} \text{ atoms } = 2 \times N_{S}; \text{ atoms } = \frac{3.46 \times 10^{15} \text{ atoms}}{2.40 \times 10^{15} \text{ atoms}}$$

2.7 Thirty grams of magnesium filings are to be oxidized in a laboratory demonstration. **(a)** How many O₂ molecules would be consumed in this demonstration? **(b)** How many moles of O₂ does this represent?

- **2.8** Naturally occurring copper has an atomic weight of 63.55. Its principal isotopes are ⁶³Cu and ⁶⁵Cu. What is the abundance (in atomic percent) of each isotope?
- 2.8 $x^{63}Cu + y^{65} = Cu^{63} \le 0$ or 63x + 65y = 63.55or 63x + 65(1-x) = 63.55or 65 2x = 63.55or 2x = 65.00 63.55or x = 0.725and y = 1 x = 0.275

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?

72.5 % 63 Cu and 27.5 % Cu65

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

neutrone = atomic weight - atomic number

= 63.55 - 29.00 = 34.55

: mass noutrone = \frac{34.55}{63.55} \times 2.60 g

= \frac{1.41 g}{4}

(b) For an "average" copper atom,

$$mass_{electrona} = (atomic number)(m_{e-})$$
 $= 29 \times 0.911 \times 10^{-27}g$
 $= 2.64 \times 10^{-26}g$
 $mass_{atom} = (atomic weight)(amu)$
 $= 63.55 \times 1.661 \times 10^{-24}g$
 $= 1.056 \times 10^{-22}g$
 $\therefore wt. fraction_{electrona} = \frac{2.64 \times 10^{-26}g}{1.056 \times 10^{-22}g}$
 $= 2.50 \times 10^{-4}g$
 $\therefore mass_{electrona} = 2.50 \times 10^{-4}g$
 $= 6.50 \times 10^{-4}g$

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 12 C atom. (See Figure 2.3.)

Then,
$$\lambda = \frac{hc}{E}$$

$$= \frac{(0.6626 \times 10^{-33} J.s)(0.2998 \times 10^{9} m/s)}{(283.9 eV)(1J/6.242 \times 10^{42} eV)}$$

$$= 4.37 \times 10^{-9} m \times 1 m / 10^{-9} m$$

$$= 4.37 m m$$

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 ¹²C atom, as described in Problem 2.10, there is a tendency for one of the 2(sp³) 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 ¹²C 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, $|\Delta E| = |-283.9 - (-6.5)|eV$ = 277.4 eVor 2 = hc

 $\lambda = \frac{hc}{AE}$ $= \frac{(0.6626 \times 10^{-33} J.s)(0.2998 \times 10^{9} m/s)}{(277.4 eV)(1J/6.242 \times 10^{18} eV)}$ $= 4.47 \times 10^{-9} m \times 1 mm/10^{-9} m$ = 4.47 nm

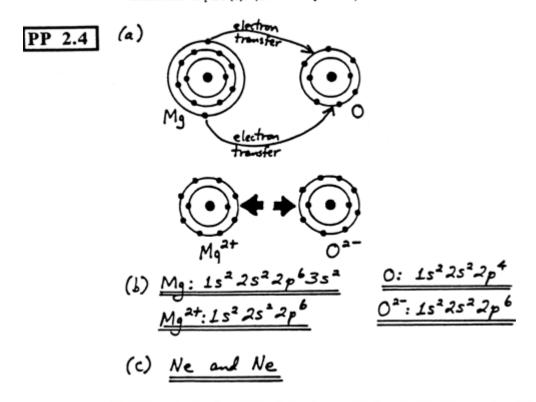
2.12 The mechanism for producing a photon of specific energy is outlined in Problem 2.11. The magnitude of photon energy increases with the atomic number of the atom from which emission occurs. (This is due to the stronger binding forces between the negative electrons and the positive nucleus as the 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 -7,112eV and -708eV.

2.12
$$|\Delta E| = |-7,112 - (-708)| eV = 6404 eV$$

or $\lambda = \frac{hc}{\Delta E} = \frac{(0.6626 \times 10^{-33} \text{ J. s})(0.2998 \times 0^{9} \text{ m/s})}{(6404 eV)(1\text{ J/6242} \times 10^{18} eV)}$
 $= 1.94 \times 10^{-10} \text{ m} \times 1 \text{ nm} / 10^{-9} \text{m} = \underline{0.194 \text{ nm}}$

Section 2.2 - The Ionic Bond

(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.)



(a) Using the ionic radii data in Appendix 2, calculate the coulombic force of attraction between the $Mg^{2+} - O^{2-}$ 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,

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

$$r_{0^{2-}} = 0.132 \, \text{nm}$$

Then,
$$q_0 = r_{Mg^{2+}} + r_{0^{2-}} = 0.078 \, \text{nm} + 0.132 \, \text{nm} = 0.210 \, \text{nm}$$

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

$$= \frac{20.9 \times 10^{-9} \, \text{N}}{(0.210 \times 10^{-9} \, \text{N})^2}$$
(b) $F_R = -F_c = \frac{-20.9 \times 10^{-9} \, \text{N}}{(0.210 \times 10^{-9} \, \text{N})^2}$

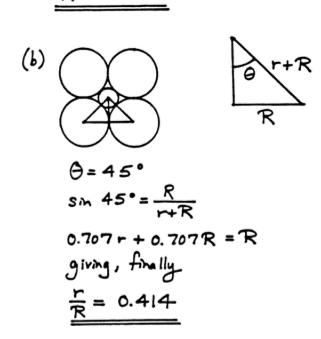
PP 2.6 Calculate the minimum radius ratio for a coordination number of (a) 4 and (b) 6. (See Example 2.7.)

PP 2.6

(a) $\theta = \frac{109.5^{\circ}}{2}$ (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 $\frac{r}{r} = 0.225$



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,

$$r_{\text{Fe}}^{24} = 0.087 \, \text{nm}$$
, $r_{\text{Ni}}^{24} = 0.078 \, \text{nm}$, $r_{\text{O}}^{2} = 0.132 \, \text{nm}$

For FeO,

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

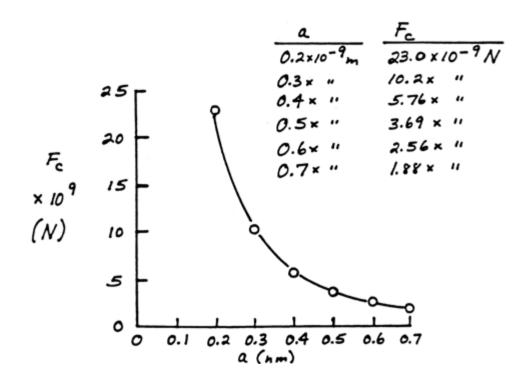
 $\frac{CN = 6}{R}$

For NiO,

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

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

2.13
$$F_{c} = -\frac{(9 \times 10^{9} \text{ V·m/c})(+2)(0.16 \times 10^{-18} \text{c})(-2)(0.16 \times 10^{-18} \text{c})}{a^{2}}$$



2.14 Make an accurate plot of F_c versus a for a Na⁺-O²⁻ pair.

2.14
$$F_{c} = -\frac{(9 \times 10^{9} \text{ V.m/c})(+1)(0.16 \times 10^{-18} \text{ C})(-2)(0.16 \times 10^{-18} \text{ C})}{a^{2}}$$

$$\frac{a}{0.2 \times 10^{-9} \text{ m}} \frac{F_{c}}{11.5 \times 10^{-9} \text{ N}}$$

$$0.3 \times \text{ "} \qquad 5.12 \times \text{ "}$$

$$0.4 \times \text{ "} \qquad 2.88 \times \text{ "}$$

$$0.5 \times \text{ "} \qquad 1.84 \times \text{ "}$$

$$0.6 \times \text{ "} \qquad 1.28 \times \text{ "}$$

$$0.7 \times \text{ "} \qquad 0.940 \times \text{ "}$$

$$F_{c} \times 10^{9} \text{ (N)}$$

$$5 \times 10^{9} \text{ (N)}$$

$$6 \times 10^{10} \text{ (N)}$$

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 √2a₀, where a₀ is defined in Figure 2.7. Calculate the coulombic force of repulsion between such a pair of like ions.

2.15
$$F_{c} = -\frac{R_{o}(Z_{18})(Z_{28})}{\alpha^{2}}$$

$$= -\frac{(9 \times 10^{9} \text{ V·m/c})(+1)(0.16 \times 10^{-18} \text{ c})(+1)(0.16 \times 10^{-18} \text{ c})}{(2)(0.278 \times 10^{-9} \text{ m})^{2}}$$

$$= -1.49 \times 10^{-9} \text{ N}$$

2.16 Calculate the coulombic force of attraction between Ca²⁺ and O²⁻ in CaO, which has the NaCl-type structure.

2.16 From Appendix 2,

$$r_{Cat} = 0.106 \text{ nm} \quad \text{f} \quad r_{0a} = 0.132 \text{ nm}$$

Then,

 $a_{i} = r_{Ca} + r_{0a} = 0.106 \text{ nm} + 0.132 \text{ nm} = 0.238 \text{ nm}$
 $F_{C} = -\frac{(9 \times 10^{9} \text{ V.m/c})(+2)(0.16 \times 10^{-18}\text{ c})}{(0.238 \times 10^{-9}\text{ m})^{2}}$
 $= \frac{16.3 \times 10^{-9} \text{ N}}{10.16 \times 10^{-18} \text{ c}}$

2.17 Calculate the coulombic force of repulsion between nearest-neighbor Ca²⁺ 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,
$$F_c = -\frac{(9 \times 10^9 \, \text{V·m/c})(+2)(0.16 \times 10^{-18} \, \text{c})^2}{(0.337 \times 10^{-9} \, \text{m})^2}$$

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

2.18 Calculate the coulombic force of repulsion between nearest-neighbor O²⁻ ions in CaO. (Note Problems 2.15, 2.16, and 2.17.)

2.18 As in Problem 2.17,
$$\alpha = \sqrt{2} \, \alpha_{\circ} = \sqrt{2} \, (0.238 \, \text{nm}) = 0.337 \, \text{nm}$$
And,
$$F_{c} = -\frac{(9 \times 10^{9} \, \text{V·m/c})(-2)^{2} (0.16 \times 10^{-18} \, \text{C})^{2}}{(0.337 \times 10^{-9} \, \text{m})^{2}}$$

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

2.19 Calculate the coulombic force of repulsion between nearest-neighbor Ni²⁺ ions in NiO, which has the NaCltype structure. (Note Problem 2.17.)

2.19
$$a = \sqrt{2} \ a_0 = \sqrt{2} \left(r_{Ni}^{2+} + r_{02-} \right)$$
From Appendix 2,
$$a = \sqrt{2} \left(0.078 \text{ nm} + 0.132 \text{ nm} \right) = 0.297 \text{ nm}$$
Then,
$$F_c = -\frac{\left(9 \times 10^9 \text{ V·m/c} \right) \left(+2 \right)^2 \left(0.16 \times 10^{-18} \text{ C} \right)^2}{\left(0.297 \times 10^{-9} \text{ m} \right)^2} = -10.4 \times 10^{-9} \text{ N}$$

2.20 Calculate the coulombic force of repulsion between nearest-neighbor O²⁻ ions in NiO. (Note Problems 2.18 and 2.19.)

2.20 As m Problem 2.19,

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

and,
 $F_{c} = -\frac{(9 \times 10^{9} \text{ V.m/c})(-2)^{2} (0.16 \times 10^{-18} \text{ C})^{2}}{(0.297 \times 10^{-9} \text{ m})^{2}} = -10.4 \times 10^{-9} \text{ N}$

- 2.21 SiO₂ is known as a "glass former" because of the tendency of SiO₄⁴— tetrahedra (Figure 2.17) to link together in a noncrystalline network. Al₂O₃ is known as an intermediate glass former due to the ability of Al³⁺ to substitute for Si⁴⁺ in the glass network, although Al₂O₃ does not by itself tend to be noncrystalline. Discuss the substitution of Al³⁺ for Si⁴⁺ in terms of the radius ratio.
- 2.21 As discussed in Section 2.3, the radius ratio for $Si^{4+} O^{2-}$ is: $\frac{r}{R} = \frac{0.039 \, \text{nm}}{0.132 \, \text{nm}} = 0.295, \text{ well within}$ the range for 4-fold coordination.

 For $A1^{3+} O^{2-}$, data in Appendix 2 gives: $\frac{r}{R} = \frac{0.057 \, \text{nm}}{0.132 \, \text{nm}} = 0.432, \text{ just above}$ the range for 4-fold coordination indicating that the role of $A1_{0}$ as an intermediate glass former is reasonably consistent with this simple ionic calculation.
- 2.22 Repeat Problem 2.21 for TiO₂, which like Al₂O₃, is an intermediate glass former.
 - 2.22 For $T_i^{4+} 0^{2-}$, Appendix 2 gives: $\frac{7}{8} = \frac{0.064 \text{ nm}}{0.132 \text{ nm}} = 0.485$

As with A13+, Ti4+ 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, Co²⁺ 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 Co²⁺ is predicted by the radius ratio?
 - 2.23 Using the data from Appendix 2, $\frac{r_{02+}}{r_{02-}} = \frac{0.082 \, \text{nm}}{0.132 \, \text{nm}} = 0.621$ 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 (0^{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 BeF₂. As such, it was found to be similar to SiO₂ in many ways. Calculate the radius ratio for Be²⁺ and F⁻ and comment.
- 2.24 For Be 2+ F-, Appendix 2 gives: $\frac{7}{R} = 0.054 \, \text{nm} / 0.133 \, \text{nm} = 0.406, \text{ which is}$ in the range for 4-fold coordination. As a

 result, tetra hedrally-coordinated Be 2+ leads
 to network formation similar to the case for

 S:4+ in SiO2.

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 Cu²⁺ and an O²⁻ within one of these sheets.

2.25 From Appendix 2,

$$\Gamma_{Cu2+} = 0.072 \, \text{nm} \quad \xi \, \Gamma_{O2-} = 0.132 \, \text{nm}$$

Then;

$$Q_0 = \Gamma_{Cu2+} + \Gamma_{O2-} = 0.072 \, \text{nm} + 0.132 \, \text{nm} = 0.204 \, \text{nm}$$

$$F_C = -\frac{(9 \times 10^9 \, \text{V.m/c})(+2 \times 0.16 \times 10^{-18} \, \text{c}) \times (-2) \times (0.16 \times 10^{-18} \, \text{c})}{(0.204 \times 10^{-9} \, \text{m})^2}$$

$$= \frac{22.1 \times 10^{-9} \, \text{N}}{2}$$

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^{2+} and an O^{2-} .

 $= 8.86 \times 10^{-9} N$

2.26 From Appendix 2,

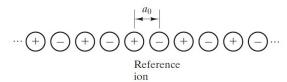
$$r_{Cut} = 0.096 \text{ nm} \quad \xi^{l} \quad r_{O2-} = 0.132 \text{ nm}$$

Then,

$$q_{o} = r_{Cut} + r_{O2-} = 0.096 \text{ nm} + 0.132 \text{ nm} = 0.228 \text{ nm}$$

$$F_{C} = -\frac{(9 \times 10^{9} \text{ V.m/c})(+1)(0.16 \times 10^{-18} \text{ C})(-2)(0.16 \times 10^{-18} \text{ C})}{(0.238 \times 10^{-9} \text{ m})^{2}}$$

•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 concept, 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,"
$$F_{c,net} = F = -K \left(\frac{2}{a_0^2} - \frac{2}{(2a_0)^2} + \frac{2}{(3a_0)^2} - \frac{2}{(4a_0)^2} + \cdots \right)$$

$$= -\frac{2K}{a_0^2} \left(+1 - \frac{1}{4} + \frac{1}{4} - \frac{1}{16} + \cdots \right)$$

For an adjacent ion pair, $F_c = -\frac{K}{a_0 z} \qquad (of course, K for the adjacent pair is negative in sign.)$

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

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,

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

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

Section 2.3 – The Covalent Bond

In Figure 2-14 we see the polymerization of polyethylene PP 2.8 ←C₂H₄→ a illustrated. Example 2.9 illustrates polymerization for poly(vinyl chloride) $(-C_2H_3Cl)$. Make a similar sketch to illustrate the polymerization of polypropylene $(-C_2H_3R)$ where R is a CH3 group.

PP 2.8

i = i propylene molecule

Use a sketch to illustrate the polymerization of polystyrene PP 2.9 $(-C_2H_3R)$, where R is a benzene group, C_6H_5 .

PP 2.9

c= c styrene molecule

Where R = CH =

Calculate the reaction energy for polymerization of (a) propylene (see Practice Problem 2.8) and (b) styrene (see Practice Prob-PP 2.10 lem 2.9).

PP 2.10

(a) The bulkbone reaction is the same. Therefore, the Calculation in the same:

The length of an average polyethylene molecule in a commercial clear plastic wrap is 0.2 μ 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,
$$L = 2n l$$
or
$$n = \frac{L}{2l}$$

$$= \frac{0.2 \times 10^{-6} \text{m}}{2 \times 0.126 \times 10^{-9} \text{m}} = \frac{794}{100}$$

- 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 × 10²⁴ C atoma in the sheet of polyethylene.

 From Example 2.10, we note there is a

 Neaction energy of 60 & J/mol (of double bonds).

 Then, the total neaction energy for the polymen wrap is:

 Erection = \frac{60 & J}{\text{mol bonds}} \times \frac{4.60 \times 10^{24}}{\text{atoma}} \text{c}

 \times \frac{1 \text{mol C atoma}}{0.6023 \times 10^{24} \text{atoma}} \times \frac{1}{2} \text{ atoma}

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

$$\begin{pmatrix}
H & H & CH_3 & H \\
C & = C & -C & = C \\
H & H & CH_3 & H
\end{pmatrix}
\rightarrow
\begin{pmatrix}
H & H & CH_3 & H \\
-C & -C & = C & -C \\
H & H & CH_3 & H
\end{pmatrix}$$

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):

1 C=C -> 2 C-C

giving a reaction energy of:

(740-680) L J/mol = 60 L J/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 CH₃ 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:

$$n\begin{pmatrix} H & H & CI & H \\ C & C & C & C & C \\ I & I & I & I \end{pmatrix} \rightarrow \begin{pmatrix} H & H & CI & H \\ I & I & CI & I \\ I & I & I & I \end{pmatrix}_{N}$$

- (b) Again (as in Example 2.10), the net reaction is: 1 C=C -> 2 C-C giving a reaction energy of:

 (740-680) & J/mol = 60 & J/mol
- (c) The mer molecular weight is: $(4 \times 12.01 + 5 \times 1.008 + 35.45) g = 88.53 g$ As there is one bond reaction [as shown in part (b)] for each men, we can write:

 energy released = $1 \text{ kg} \times \frac{1 \text{ mol}}{88.53 g} \times \frac{1000 \text{ g}}{\text{kg}}$ $\times 60 \text{ kJ/md} = 678 \text{ kJ}$
- 2.32 Acetal polymers, which are widely used for engineering applications, can be represented by the following reaction, the polymerization of formaldehyde:

$$\begin{pmatrix}
H \\
C = 0
\end{pmatrix}
\longrightarrow
\begin{pmatrix}
H \\
C \\
H
\end{pmatrix}$$

Calculate the reaction energy for this polymerization.

2.32 In this case, the net reaction is: 1 C=0 -> 2 C-0 giving a reaction energy of:

2 (360 & J/mol) - 535 & J/mol = 185 & J/mol

- **2.33** The first step in the formation of phenolformal-dehyde, 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:

 1 C=0 + 2 C-H -> 2 C-C + 2 0-H

 giving a reaction energy of:

 2(370 & J/mol) + 2(500 & J/mol)

 2(435 & J/mol) 1(535 & J/mol) = 335 & J/mol
 - **2.34** Calculate the molecular weight of a polyethylene molecule with n = 500.
- 2.34 Using the data of Appendix 1, we obtain mol. wt. $+ C_2 H_4 \rightarrow_{n=500} = 500 [2(12.01) + 4(1.008)]$ amu = 14,030 amu
 - **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 = 600.

Using the chemical formula and the data of Appendix 1, we obtain $mol. \ \omega t \cdot \left(C_5 H_8 O_2 \right)_{n=500}$ $= 500 \left[5(12.01) + 8(1.008) + 2(16.00) \right] emu$ = 50,060 emu

- **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. (Note Problem 2.35.)
- 2.36 For: $(C_5H_8O_2)$ 200<n<700

 mol. wt. = 200 [5(12.01) + 8(1.008) + 2(16.00)] ama to 700 [" + " + "] ama

 = 20,020 ama to 70,080 ama

- **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 20 g of polymethyl methacrylate to set a given hip implant. (Note Problems 2.35 and 2.36.)
- 2.37 Note that I mol of polymethyl methacylate contains

 1 mol of C=C double bonds.

 1 mol (s Hg O2 has [5(12.01) + 8(1.008) + 2(16.00)] g = 100.1 g

 As calculated numerous times in this section, the reaction energy for 1 C=C -> 2 C-C is:

 (740-680) & J/mol = 60 & J/mol

 Then, the total reaction energy the implent cement is:

 Ereaction = \frac{60 & J}{mol. bonds} \times \frac{1}{100.1 g} \times \frac{20g}{100.1 g} = \frac{12.0 & J}{100.1 g}

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.

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

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

Section 2.4 - The Metallic Bond

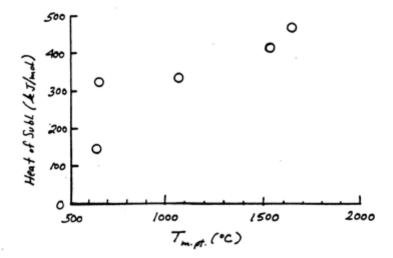
PP 2.12 Discuss the low coordination number (= 4) for the diamond cubic structure found for some elemental solids, such as silicon. (See Example 2.12.)

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	Tm.pt. (°C)	Heat of Subl. (AJ/mol)
12	Mg	649.	148
13	AΤ	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

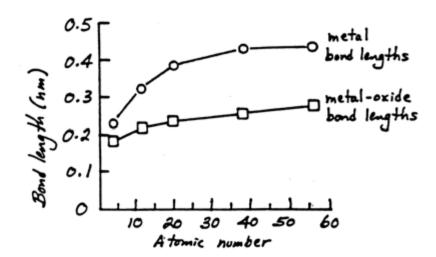
we obtain: IIA element	Ataic number	Atomic radius (r)	Bond laugth (=2r)
Be	4	0.114 Am	0.228 nm
Mg	12	0.160 nm	0.320 nm
Ca	20	0.197 mm	0.394 nm
Sr	38	0.215 nm	0.430 Am
Ba	56	0.217 nm	0.434 nm
0.5 (wy) Homal 0.2 0.2 0.1 10 20 30 40 50 60			

Atomic number

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:

IIA element	Homic number	Inic radius + Toa- la	5.132 m) = Bond length
8e	4	0.054 AM	0.186 nm
Mg	12	0.078 Am	0. 210 n
Ca	20	0.106 nm	0.238 Am
Sr	38	0.127am	0.259 Am
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.)

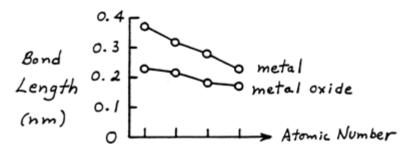
2.45 Superimpose on the plot generated for Problem 2.44 the metal—oxide bond lengths for the same range of elements.

12

2.45 Using Figure 2.2 and Appendix 2 gives:

Element	At. No.	Ionic Radius	+ 102-(=0.132 nm) = Bond Lengt
Na	11	0.098 Am	0.230 nz
Ma	12	0.078 hm	0.210 nr
AI	13	0.057 nm	0.189 nm
Si	14	0 0 39 nm	0.17/ ni

* 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 Usin	Figure 2.2	and Appendix 2	girca us:
Element	Atomic number	Atomic radius (r)	Bond langth (=2r)
K	19	0.23/nm	0.462nm
Ca	20	0.197nm	0.394nm
Sc	21	0.160 nm	0.320 nm
T_i	22	0.147 mm	0.294 nm
V	23	0.132 nm	0.264nm
Cr	24	0. /25 nm	0.250hm
Mn	25	0.112 nm	0.224 nm
Fe	26	0.124 nm	0.248 hm
C.	27	0.125 nm	0.250 nm
Nī	28	0.125 mm	0.250 hm
Cu	29	0.128 hm	0.256 hm
Zn	30	0.133 nm	0.266 Am
Ga	31	0.135 Am	0.270 mm
Bond length (mm) 800 0.7	9 21 23 22	00000 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Atomic number

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 Fig.	are 2.2 and A	opendix 2 gres:
Element	At. No.	Ionic radius + roz	= (0.132 mm) = Bond length
K Co Stive on F Co Nice of Garage	19 21 22 23 4 25 25 28 28 30 31	0.133 hm 0.166 hm 0.083 nm 0.064 nm 0.064 nm 0.091 hm 0.087 nm 0.082 nm 0.082 nm 0.096 nm 0.096 nm 0.062 nm	0.265 nm 0.238 nm 0.215 nm 0.196 nm 0.196 nm 0.223 nm 0.219 nm 0.214 nm 0.216 nm 0.228 nm 0.228 nm 0.225 nm
length (nm)		Common valence, es	noted on inside, beck cover
80nd 0.	, [Metal oxide

 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

Na (solid) +
$$\frac{1}{2}$$
Cl₂ (g) \longrightarrow Na (g) + Cl (g)

$$\downarrow \triangle H_f^o \qquad \qquad \downarrow \qquad \downarrow$$

NaCl (solid) \leftarrow Na⁺ (g) + Cl⁻ (g)

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, $\Delta H_{\rm p}^{o}$, of NaCl = -411 kJ/mol.)

2.48 Note that
$$\Delta H_1^* = \Delta E_{Subl}$$
, $Na + \frac{1}{2} \Delta E_{dissoc}$, Cl_2
+ ΔE_{Ion} , $Na + \Delta E_{Ion}$, Cl
+ ΔE_{Ionic} bonding, $Na Cl$

or,
$$\Delta E_{ionic}$$
 bonding, $NaCI = \Delta H_f^o - \Delta E_{subl}$, $Na - \frac{1}{2} \Delta E_{dissec}$, CI_2

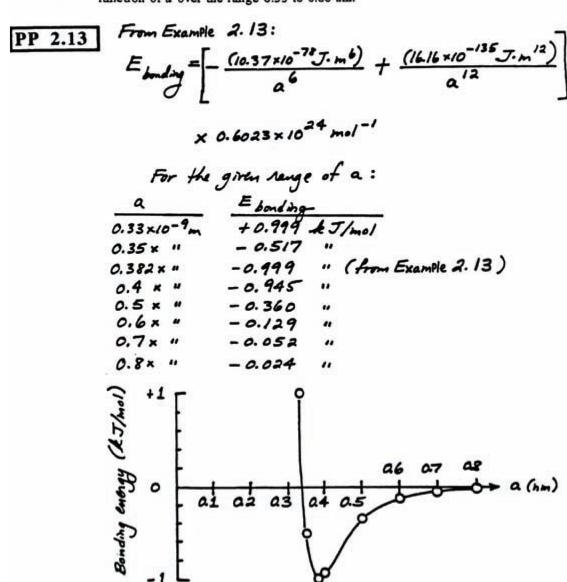
$$-\Delta E_{ion}Na - \Delta E_{ion}$$
, CI

$$= (-411 - 100 - \frac{243}{2} - 496 + 361) kJ/meI$$

$$= -768 k J/meI$$

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 2.14

Using the information from Example 2.13, plot the van der Waals bonding force curve for argon (i.e., *F* versus *a* over the same range covered in Practice Problem 2.13).

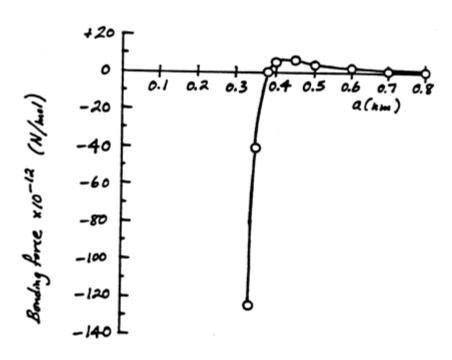
$$F = \frac{dE}{da} = \frac{6K_A}{a^7} - \frac{12K_R}{a^{13}}$$

$$F_{binding} = \left[\frac{6(10.37 \times 10^{-78} \text{ J·m}^6)}{a^7} - \frac{12(16.16 \times 10^{-135} \text{ J·m}^{12})}{a^{13}} \right]$$

$$\times 0.6023 \times 10^{24} \text{ mol}^{-1}$$

For the given range of a:

_ a	Flooding
0.33×10-9 m	-124 x 1012 N/mol
0.35 × "	-40.5 × "
0.382 × "	0
0.4 × "	+5.47× "
0.45× "	+6.26 × -
0.5 × "	+3.84 × "
0.6 × "	+1.25 × "
0.7 × *	+ 0.44 × "
0.8 × "	+ 0.18 x "



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 9×10^3 mm³ 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 m²/kg. (Take the area covered by a nitrogen molecule as 0.162 nm² and recall that, for an ideal gas, pV = nRT where n is the number of moles of the gas.)

2.49
$$pV = nRT$$
 or $n = \frac{pV}{RT} = \frac{(latm)(9 \times 10^{3} \times 10^{-9}m^{3})}{(8.314J/K)(273K)} mol N_{2}$

$$\times \frac{lN/m^{2}}{9.869 \times 10^{-6}atm} \times 0.6023 \times 10^{24} \frac{molec.}{mol}$$

$$= 2.42 \times 10^{20} \text{ molec. } N_{2}$$
Area correct = $0.162 \times 10^{-18} \frac{m^{2}}{molec} \times 2.42 \times 10^{20} \frac{molec.}{molec}$

$$= 39.2 m^{2} (per 1009 Cu)$$
or, $S = \frac{39.2 m^{2}}{1009} \times \frac{10009}{kg} = \frac{39.2 m^{2}/kg}{kg}$

2.50. Repeat Problem 2.49 for a highly porous silica gel that has a volume of 1.16×10⁷ mm³ of N₂ gas (at STP or Standard Temperature and Pressure) condensed to form a monolayer.

2.50 In this case,

$$n = \frac{pV}{RT} = \frac{(latin)(1.16 \times 10^{7} \times 10^{-9} \cdot 3)(lN/m^{2})(0.6023 \times 10^{24} \text{ mobs./mol})}{(P.314 J/R)(275 K)(9.869 \times 10^{-48} \text{ tur.})}$$

$$= 3.12 \times 10^{23} \text{ molec. } N_{2}$$
Area cornel = 0.16 \(2 \times 10^{-18} \text{ m}^{2} \times \) 3.12 \times 10^{23} \text{ molec.}
$$= 5.05 \times 10^{4} \text{ m}^{2} \left(\text{per 100g silica gel} \right)$$
or, $S = \frac{5.05 \times 10^{4} \text{ m}^{2}}{1009} \times \frac{1000 \text{ g}}{\text{log}} = \frac{5.05 \times 10^{5} \text{ m}^{2}/\text{log}}{\text{log}}$

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 250°C.

2.51 Using the given expression for solubility, we have
$$\frac{S_{200°C}}{S_{25°C}} = \frac{S_0 e^{-\Delta H_S/R(250+273)K}}{S_0 e^{-\Delta H_S/R(25+273)K}}$$
or
$$S_{200°C} = S_{25°C} e^{-\Delta \frac{1}{8}} \left(\frac{1}{523K} - \frac{1}{298K} \right)$$

$$= (5.5/\times10^{23} atoma (m^3 atm))$$

$$\times e^{-\frac{(-3,960 J/mol)}{(8.314 J/knol·K)}} (-1.44 \times 10^{-3} K^{-1})$$

$$= 2.77 \times 10^{23} atoma/(m^3 atm)$$

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 $-6.70 \, \text{kJ/mol}$ and the solubility at 25°C is $9.07 \times 10^{23} \, \text{atoms/(m}^3 \cdot \text{atm})$, calculate the solubility at 250°C. (See Problem 2.51.)

2.52 Using the solubility expression from Problem 2.51,
$$\frac{S_{200^{\circ}C}}{S_{25^{\circ}C}} = \frac{S_{o} e^{-\Delta H_{S}/R(250+273)K}}{S_{o} e^{-\Delta H_{S}/R(25+273)K}}$$
or
$$S_{200^{\circ}C} = S_{25^{\circ}C} e^{-\frac{\Delta H_{S}}{R}(\frac{1}{523K} - \frac{1}{298K})}$$

$$= (9.07 \times 10^{23} \text{ atoms } / (m^{3} \cdot \text{atm}))$$

$$\times e^{-\frac{(-6,700 \text{ J/mol})}{(8\cdot314 \text{ J/(mol\cdot K)})}} (-1.44 \times 10^{-3} \text{ K}^{-1})$$

$$= \frac{2.83 \times 10^{23} \text{ atoms } / (m^{3} \cdot \text{atm})}{(m^{3} \cdot \text{atm})}$$