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SKU: 9780135650127-SOLUTIONS

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) $N_{Mg\ atoms} = 6.64 \times 10^{10}\ \text{atoms Cu} \times \dfrac{(1.74\ \text{g/cm}^3)\text{Mg}}{(8.93\ \text{g/cm}^3)\text{Cu}}$

$$\times \frac{63.55\ \text{g Cu}/N_{AV}\ \text{atoms Cu}}{24.31\ \text{g Mg}/N_{AV}\ \text{atoms Mg}}$$

$$= \underline{\underline{3.38 \times 10^{10}\ \text{atoms Mg}}}$$

(b) $N_{Pb\ atoms} = 6.64 \times 10^{10}\ \text{atoms Cu} \times \dfrac{(11.34\ \text{g/cm}^3)\text{Pb}}{(8.93\ \text{g/cm}^3)\text{Cu}}$

$$\times \frac{63.55\ \text{g Cu}/N_{AV}\ \text{atoms Cu}}{207.2\ \text{g Cu}/N_{AV}\ \text{atoms Pb}}$$

$$= \underline{\underline{2.59 \times 10^{10}\ \text{atoms Pb}}}$$

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 × 100 mm × 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) $\text{edge} = \left(\dfrac{63.55\ \text{g/mol}}{8.93\ \text{g/cm}^3}\right)^{1/3} \times 10\ \text{mm/cm} = \underline{\underline{19.23\ \text{mm}}}$

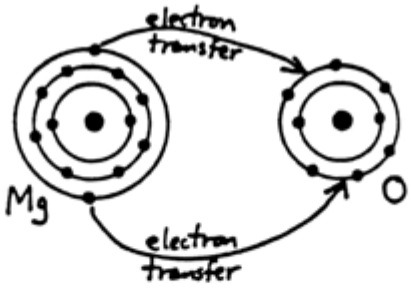
(b) $\text{edge} = \left(\dfrac{207.2\ \text{g/mol}}{11.34\ \text{g/cm}^3}\right)^{1/3} \times 10\ \text{mm/cm} = \underline{\underline{26.34\ \text{mm}}}$

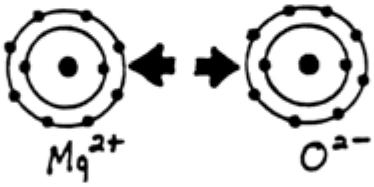
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Section 2.2 – The Ionic Bond

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)





(b) $Mg: 1s^2 2s^2 2p^6 3s^2$ $\quad O: 1s^2 2s^2 2p^4$

$Mg^{2+}: 1s^2 2s^2 2p^6$ $\quad O^{2-}: 1s^2 2s^2 2p^6$

(c) Ne and Ne

PP 2.5 **(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,

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

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

Then,

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

$$F_c = -\frac{(9\times10^9\,V\cdot m/C)(+2)(0.16\times10^{-19}\,C)(-2)(0.16\times10^{-19}\,C)}{(0.210\times10^{-9}\,m)^2}$$

$$= 20.9\times10^{-9}\,N$$

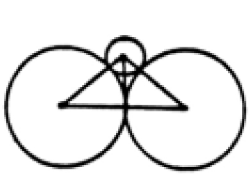
(b) $F_R = -F_c = -20.9\times10^{-9}\,N$

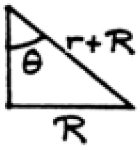
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PP 2.6 Calculate the minimum radius ratio for a coordination number of **(a)** 4 and **(b)** 6. (See Example 2.7.)

PP 2.6

(a)





$\theta = \frac{109.5°}{2}$ (see Figure 2.19)

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

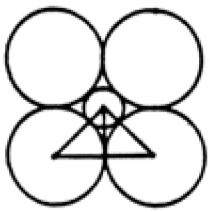
$0.8166\,r + 0.8166\,R = R$

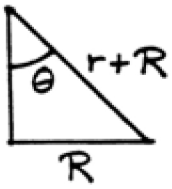
$0.1834\,R = 0.8166\,r$

giving, finally

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

(b)





$\theta = 45°$

$\sin 45° = \frac{R}{r+R}$

$0.707\,r + 0.707\,R = R$

giving, finally

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

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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,

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

For FeO,

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

CN = 6

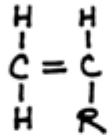
For NiO,

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

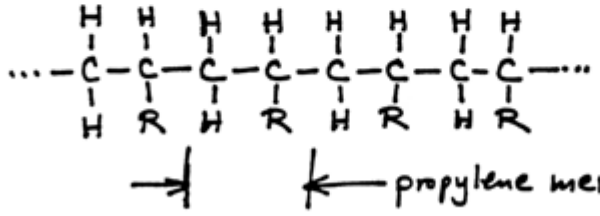
Section 2.3 – The Covalent Bond

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



polypropylene molecule

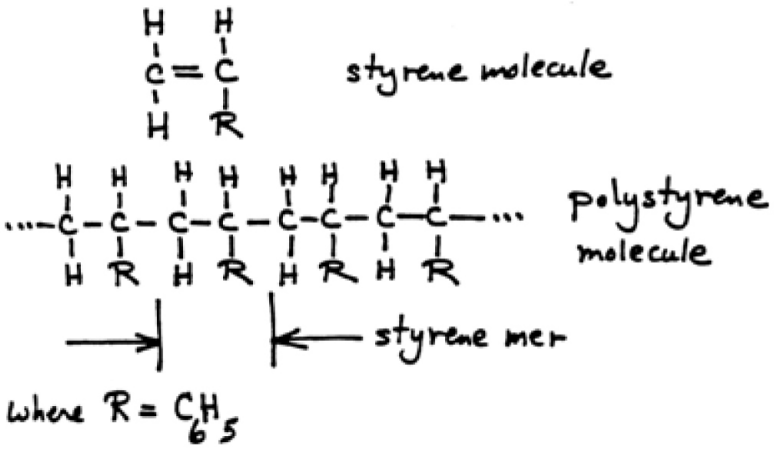
propylene mer

where $R = CH_3$

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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



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:

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

(b) Again,

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

PP 2.11 The length of an average polyethylene molecule in a commercial clear plastic wrap is 0.2 μm. What is the average degree of polymerization (n) for this material? (See Example 2.11.)

PP 2.11

As illustrated in Example 2.11,

$$L = 2nl$$

or

$$n = \frac{L}{2l}$$

$$= \frac{0.2\times10^{-6}\,m}{2\times0.126\times10^{-9}\,m} = \underline{\underline{794}}$$

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.

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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.

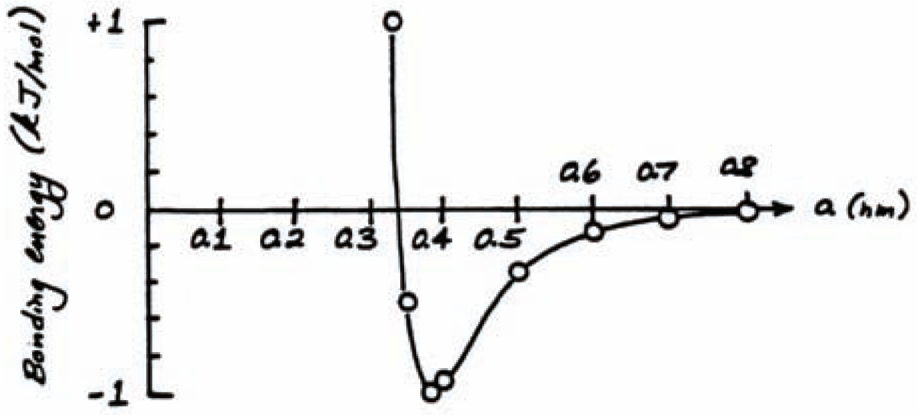
PP 2.13

From Example 2.13:

$$E_{bonding} = \left[-\frac{(10.37\times10^{-78}\ J\cdot m^6)}{a^6} + \frac{(16.16\times10^{-135}\ J\cdot m^{12})}{a^{12}} \right] \times 0.6023\times10^{24}\ mol^{-1}$$

For the given range of a:

a	$E_{bonding}$
0.33×10^{-9} m	+0.999 kJ/mol
0.35 × "	− 0.517 "
0.382 × "	−0.999 " (from Example 2.13)
0.4 × "	−0.945 "
0.5 × "	−0.360 "
0.6 × "	−0.129 "
0.7 × "	−0.052 "
0.8 × "	−0.024 "



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).

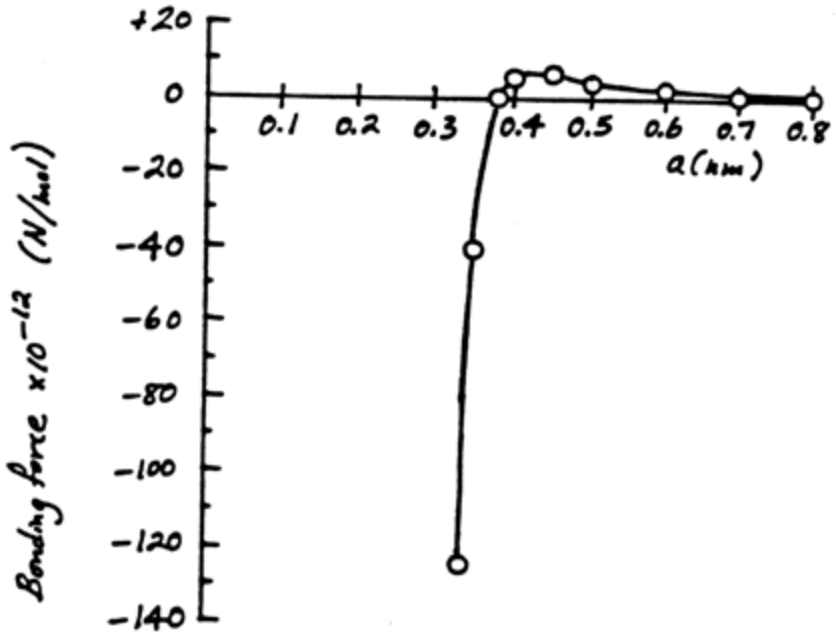
PP 2.14

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

$$F_{bonding} = \left[\frac{6(10.37\times10^{-78}\ J\cdot m^6)}{a^7} - \frac{12(16.16\times10^{-135}\ J\cdot m^{12})}{a^{13}}\right] \times 0.6023\times10^{24}\ mol^{-1}$$

For the given range of a:

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



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Instructor's Solution Manual

J.F. Shackelford, *Introduction to Materials Science for Engineers*, 9th Edition

Chapter 2 End of Chapter Problems

Section 2.1 • Atomic Structure

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

$$N_{atoms} = \rho V \left(\frac{N_{AV}}{at.\ wt.}\right) = 19.28\times10^{6}\ g\ Au/m^3 \times 100\times10^{-3}\ m \times \pi \left(\frac{1.5\times10^{-3}\ m}{2}\right)^2 \times \left(\frac{0.6023\times10^{24}\ atoms}{196.97\ g\ Au}\right)$$

$$= \underline{\underline{10.4\times10^{21}\ atoms}}$$

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 ft^2 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 $N_{atoms} = \rho V \left(\frac{N_{Av}}{\text{at. wt.}}\right) = 2.70 \times 10^6 \text{ g Al/m}^3 \times 12.7 \times 10^{-6} \text{ m}$
$\times 304 \times 10^{-3} \text{ m} \times 22.8 \text{ m} \times \left(\frac{0.6023 \times 10^{24} \text{ atoms}}{26.98 \text{ g Al}}\right)$
$= \underline{\underline{5.31 \times 10^{24} \text{ atoms}}}$

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

$m_{SiO_2} = 2.20 \times 10^6 \text{ g/m}^3 \times 1.5 \times 10^{-13} \text{ m}^3 = 3.30 \times 10^{-7} \text{ g}$

1 mol SiO_2 has $(28.09 + 2[16.00])$ g = 60.09 g for

N_{Av} atoms Si and $2N_{Av}$ atoms O

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

$= \underline{\underline{3.31 \times 10^{15} \text{ atoms}}}$

$N_{O\,atoms} = 2 \times N_{Si\,atoms} = \underline{\underline{6.62 \times 10^{15} \text{ atoms}}}$

2.4 A box of clear plastic wrap for household use is polyethylene, $-(C_2H_4)_n$ 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 μm) thick, calculate the number of carbon atoms and the number of hydrogen atoms in this roll.

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2.4

$V = 12.7\,\mu m \times 304\,mm \times 30.5\,m = 12.7\times10^{-6}\,m \times 0.304\,m \times 30.5\,m$
$= 1.18\times10^{-4}\,m^3$

$m_{C_2H_4} = 0.910\times10^{6}\,g/m^3 \times 1.18\times10^{-4}\,m^3 = 107\,g$

1 mol C_2H_4 has $(2[12.01]+4[1.008])\,g = 28.05\,g$ for $2N_{AV}$ atoms C and $4N_{AV}$ atoms H

$\therefore N_{C\,atoms} = \frac{107\,g}{28.05\,g} \times 2 \times 0.6023\times10^{24}\,atoms$

$= \underline{\underline{4.60\times10^{24}\,atoms}}$

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

$= \underline{\underline{9.20\times10^{24}\,atoms}}$

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 μm and a length of 25 μm. (The density of Al_2O_3 is 3.97 Mg/m^3.)

2.5

$V = \pi\left(\frac{1\,\mu m}{2}\right)^2 \times 25\,\mu m = \pi\left(0.5\times10^{-6}\,m\right)^2 \times 25\times10^{-6}\,m$

$= 19.6\times10^{-18}\,m^3$

$m_{Al_2O_3} = 3.97\times10^{6}\,g/m^3 \times 19.6\times10^{-18}\,m^3 = 7.79\times10^{-11}\,g$

1 mol Al_2O_3 has $(2[26.98]+3[16.00])\,g = 101.96\,g$ for $2N_{AV}$ atoms Al and $3N_{AV}$ atoms O

$\therefore N_{Al\,atoms} = 7.80\times10^{-11}\,g \times \frac{2\,(0.6023\times10^{24}\,atoms)}{101.96\,g}$

$= \underline{\underline{0.921\times10^{12}\,atoms}}$

$N_{O\,atoms} = 3/2 \times N_{Al\,atoms}$

$= 3/2\,(1.11\times10^{12}\,atoms) = \underline{\underline{1.38\times10^{12}\,atoms}}$

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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 μm in diameter?

2.6

For 1 mm section of fiber:

$$V = \pi \left(\frac{10\,\mu m}{2}\right)^2 \times 1\,mm = \pi (5\times10^{-6}\,m)^2 \times 1\times10^{-3}\,m$$

$$= 7.85\times10^{-14}\,m^3$$

$$m_{SiO_2} = 2.20\times10^{6}\,g/m^3 \times 7.85\times10^{-14}\,m^3 = 1.73\times10^{-7}\,g$$

1 mol SiO_2 has $(28.09 + 2[16.00])\,g = 60.09\,g$

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

$$\therefore N_{Si\ atoms} = \frac{1.73\times10^{-7}\,g}{60.09\,g} \times 0.6023\times10^{24}\ atoms = \underline{\underline{1.73\times10^{15}\ atoms}}$$

$$N_{O\ atoms} = 2\times N_{Si\ atoms} = \underline{\underline{3.46\times10^{15}\ atoms}}$$

2.7 Thirty 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?

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2.7

(a) $Mg + \frac{1}{2}O_2 \rightarrow MgO$

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

or $\frac{30\text{g Mg}}{24.31\text{ g/g-atom}} = 1.234$ g-atom Mg will be

oxidized by $\frac{1.234}{2}$ mol. $O_2 = 0.617$ mol. O_2

$\therefore$ no. molecules $O_2 = 0.617\text{ mol} \times 0.6023\times10^{24}$ molec./mol.

$= 3.72\times10^{23}$ molec.

$= \underline{0.372\times10^{24}\text{ molec.}}$

(b) no. moles $= 0.372\times10^{24}\text{ molec} \times 1\text{ mol}/0.6023\times10^{24}\text{ molec.}$

$= \underline{0.617\text{ mol } O_2}$

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

2.8

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

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:

72.5 % ^{63}Cu and 27.5 % Cu^{65}

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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:

$$n_{neutrons} = \text{atomic weight} - \text{atomic number}$$
$$= 63.55 - 29.00 = 34.55$$

$$\therefore \text{mass}_{neutrons} = \frac{34.55}{63.55} \times 2.60\,g$$
$$= \underline{\underline{1.41\,g}}$$

(b) For an "average" copper atom,

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

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

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

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

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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 1*s* electron from a ^{12}C atom. (See Figure 2.3.)

2.10

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

Then, $\lambda_{max} = \dfrac{hc}{E}$

$$= \frac{(0.6626\times10^{-33}\,J\cdot s)(0.2998\times10^{9}\,m/s)}{(283.9\,eV)(1\,J/6.242\times10^{18}\,eV)}$$

$$= 4.37\times10^{-9}\,m \times 1\,nm/10^{-9}\,m$$

$$= \underline{\underline{4.37\,nm}}$$

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 What is the difference between a *gram-atom* and a *mole*?

2.11

The *gram-atom* is Avogadro's number of atoms of a given element. The *mole* is the corresponding term for a compound. For example, a mole of NaCl contains Avogadro's number of Na atoms and Avogadro's number of Cl atoms.

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2.12 What is the common feature of the electronic configuration of the group IVA elements in the periodic table?

2.12

All have two *s*-shell electrons and two *p*-shell electrons associated with their 4+ valence.

One might also note that, as one goes to higher atomic numbers, the shell numbers increase:

Element	Atomic Number	Outer Shell Electrons
C	6	2*s* and 2*p*
Si	14	3*s* and 3*p*
Ge	32	4*s* and 4*p*
Sn	50	5*s* and 5*p*
Pb	82	6*s* and 6*p*

Finally, one can also note that sp^3 hybridization corresponds to the uniform (tetrahedral) bonding configuration of elements such as C and Si.

Section 2.2 • The Ionic Bond

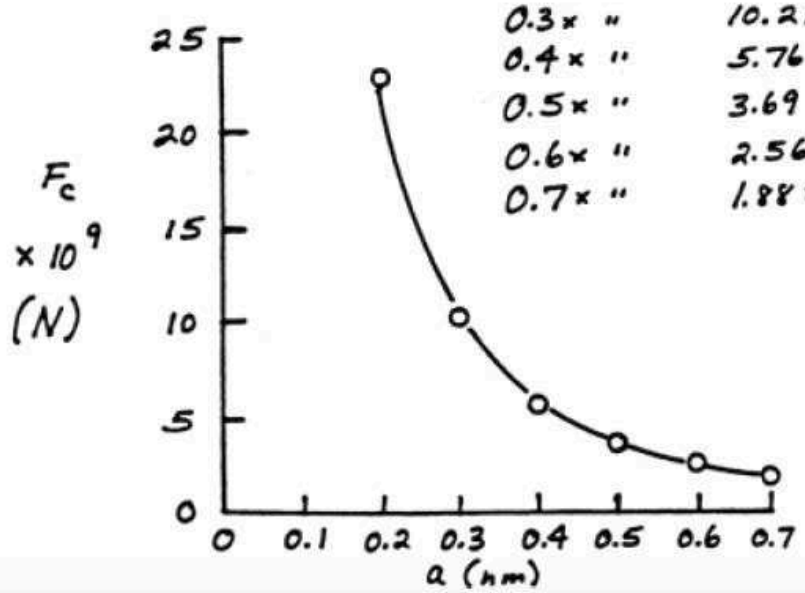
2.13 Make an accurate plot of F_c versus a (comparable to that shown in Figure 2.6) for a Mg^{2+}–O^{2-} pair. Consider the range of a from 0.2 to 0.7 nm.

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2.13

$$F_c = -\frac{(9\times10^9\ V\cdot m/C)(+2)(0.16\times10^{-19}\ C)(-2)(0.16\times10^{-19}\ C)}{a^2}$$

a	F_c
0.2×10^{-9} m	23.0×10^{-9} N
0.3× "	10.2× "
0.4× "	5.76× "
0.5× "	3.69× "
0.6× "	2.56× "
0.7× "	1.88× "



2.14 Describe the *electron transfer* involved in making an Mg^{2+}–O^{2-} ionic bond.

2.14

The two electrons in the outer (3*s*) shell of magnesium are transferred to the outer (2*p*) shell of oxygen.

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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.

2.15

$$F_c = -\frac{A_o(Z_1 e)(Z_2 e)}{a^2}$$

$$= -\frac{(9\times10^9\ V\cdot m/C)(+1)(0.16\times10^{-18}C)(+1)(0.16\times10^{-18}C)}{(2)(0.278\times10^{-9}\ m)^2}$$

$$= \underline{\underline{-1.49\times10^{-9}\ N}}$$

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,

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

Then,

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

$$F_c = -\frac{(9\times10^9\ V\cdot m/C)(+2)(0.16\times10^{-18}C)(-2)(0.16\times10^{-18}C)}{(0.238\times10^{-9}\ m)^2}$$

$$= \underline{\underline{16.3\times10^{-9}\ N}}$$

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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,

$$a = \sqrt{2}\, a_o$$

Using the calculation for Problem 2.16,

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

Then,

$$F_c = -\frac{(9\times10^9\ V\cdot m/C)(+2)^2(0.16\times10^{-18}\ C)^2}{(0.337\times10^{-9}\ m)^2}$$

$$= \underline{\underline{-8.13\times10^{-9}\ N}}$$

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,

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

And,

$$F_c = -\frac{(9\times10^9\ V\cdot m/C)(-2)^2(0.16\times10^{-18}\ C)^2}{(0.337\times10^{-9}\ m)^2}$$

$$= \underline{\underline{-8.13\times10^{-9}\ N}}$$

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2.19 What is the relationship between *bonding force* and *bonding energy*?

2.19

The *bonding force* is the derivative of *bonding energy*. The *bonding force* is zero when the *bonding energy* is a minimum.

2.20 Why is the radius of a positively charged cation smaller than the radius of its corresponding neutral atom?

2.20

The loss of an electron (or electrons) in forming the cation means that the positively charged protons in the nucleus are attracting a smaller number of electrons more tightly.

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.

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

$$r/R = \frac{0.039\,nm}{0.132\,nm} = 0.295,$$ well within the range for 4-fold coordination.

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

$$r/R = \frac{0.057\,nm}{0.132\,nm} = 0.432,$$ 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 Why is the radius of a negatively charged anion larger than the radius of its corresponding neutral atom?

2.22

The gain of an electron (or electrons) in forming the anion means that the positively charged protons in the nucleus are attracting a larger number of electrons less tightly.

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?

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2.23 Using the data from Appendix 2,

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

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 $Be^{2+} - F^-$, Appendix 2 gives:

$$r/R = 0.054\,nm / 0.133\,nm = 0.406$$, 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.

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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,

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

Then;

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

$$F_c = -\frac{(9\times10^9\,V\cdot m/C)(+2)(0.16\times10^{-18}\,C)(-2)(0.16\times10^{-18}\,C)}{(0.204\times10^{-9}\,m)^2}$$

$$= \underline{\underline{22.1\times10^{-9}\,N}}$$

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-}.

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2.26 From Appendix 2,

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

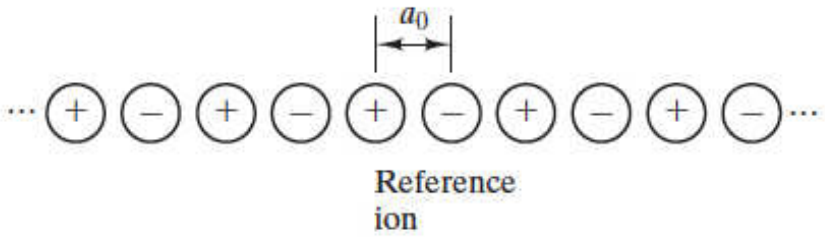
Then,

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

$$F_c = -\frac{(9\times10^9\ V\cdot m/C)(+1)(0.16\times10^{-19}\ C)(-2)(0.16\times10^{-19}\ C)}{(0.228\times10^{-9}\ m)^2}$$

$$= \underline{\underline{8.86\times10^{-9}\ N}}$$

•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.

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2.27

(a) For the "crystal,"

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

$$= -\frac{2K}{a_o^2}\left(+1 - \frac{1}{4} + \frac{1}{9} - \frac{1}{16} + \cdots\right)$$

For an adjacent ion pair,

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

Or $F = F_c\, 2\left(1 - \frac{1}{4} + \frac{1}{9} - \frac{1}{16} + \cdots\right)$

$= A F_c$ where $A = 2\left(1 - \frac{1}{4} + \frac{1}{9} - \frac{1}{16} + \cdots\right)$

(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

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

giving:

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

2.28 What is meant by the ionic bond being *nondirectional*?

2.28

The positively charged cation will attract the negatively charged anions equally in all directions, and vice versa.

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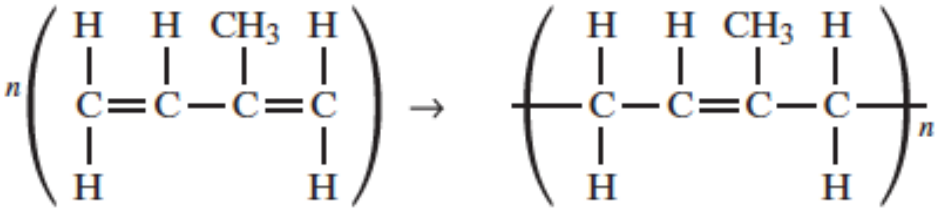
Section 2.3 • The Covalent Bond

2.29 What is meant by the covalent bond being *directional*?

2.29

The cooperative sharing of the bonding electrons is concentrated along a line between adjacent nuclei.

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):

1 C=C → 2 C–C

giving a reaction energy of:

(740 – 680) kJ/mol = 60 kJ/mol

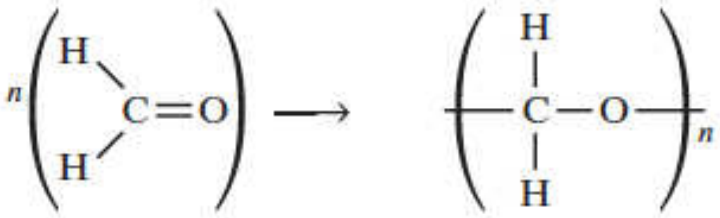
2.31 Distinguish the role played by *valence electrons* in covalent bonding in contrast to ionic bonding.

2.31

The valence electrons in covalent bonding are involved in the highly directional sharing between two adjacent nuclei. In ionic bonding, the valence electrons are transferred from one atom to another, leaving behind a positively charged cation and creating a negatively charged anion.

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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 C=O → 2 C-O

giving a reaction energy of:

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

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:

1 C=O + 2 C-H → 2 C-C + 2 O-H

giving a reaction energy of:

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

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

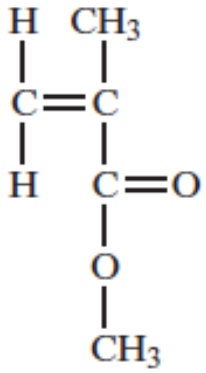
2.34

Using the data of Appendix 1, we obtain

$$\text{mol. wt.} \left\{C_2H_4\right\}_{n=500} = 500[2(12.01) + 4(1.008)] \text{ amu}$$

$$= \underline{\underline{14{,}030 \text{ amu}}}$$

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 $n = 600$.

2.35

Using the chemical formula and the data of Appendix 1, we obtain

$$\text{mol. wt.} \left\{C_5H_8O_2\right\}_{n=500}$$

$$= 600[5(12.01) + 8(1.008) + 2(16.00)] \text{ amu}$$

$$= \underline{\underline{60{,}068 \text{ amu}}}$$

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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. = $200\,[5(12.01)+8(1.008)+2(16.00)]$ amu to $700\,[\ "\ +\ "\ +\ "\ ]$ amu

= 20,020 amu to 70,080 amu

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

1 mol $C_5H_8O_2$ 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:

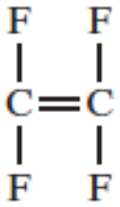
$(740-680)$ kJ/mol = 60 kJ/mol

Then, the total reaction energy the implant cement is:

$$E_{reaction} = \frac{60\ kJ}{mol.\ bonds} \times \frac{1\ mol.\ bonds}{100.1\ g} \times 20g = 12.0\ kJ$$

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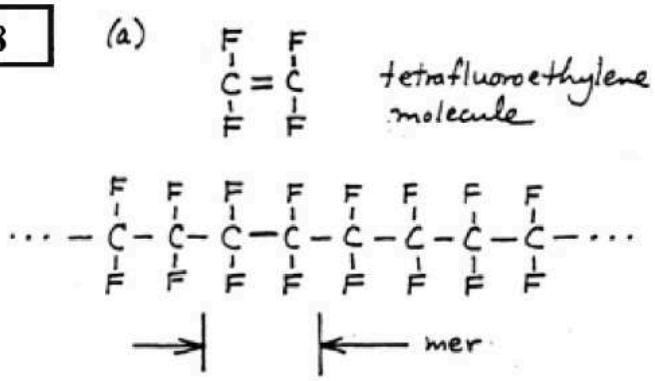
2.38 The monomer for the common fluoroplastic, polytetrafluoroethylene, is



(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)



(b) Reaction energy = (740 − 680) kJ/mol
= 60 kJ/mol

(c) Using the data of Appendix 1,

mol. wt. = 500[2(12.01) + 4(19.00)] amu

= 50,010 amu

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2.39 Distinguish the role played by *valence electrons* in metallic bonding in contrast to ionic and covalent bonding.

2.39

Like covalent bonding, the valence electrons in metallic bonding are shared among adjacent atoms. Similar to ionic bonding, the valence electrons are shared in a nondirectional manner.

2.40 How is the silica tetrahedron shown in Figure 2.17 consistent with both ionic *and* covalent bonding?

2.40

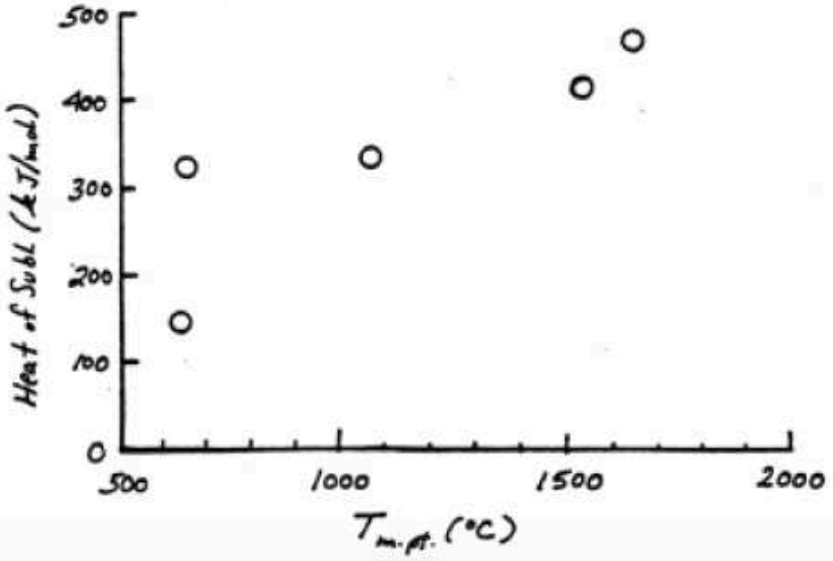
For ionic bonding, the radius ratio of Si^{4+} to O^{2-} (0.039 nm/0.132 nm = 0.295) falls within the range associated with 4-fold coordination ($0.225 < r/R < 0.414$). For covalent bonding, silicon (element 14) exhibits sp^3 hybridization, consistent with the 4-fold bonding characteristic of group IVA elements.

Section 2.4 • The Metallic Bond

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	$T_{m.pt.}$ (°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



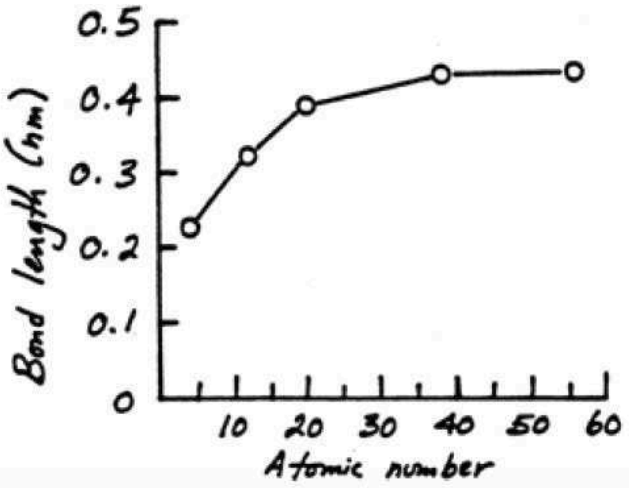
Comment: There is clearly a positive correlation between these two indicators of bond strength. However, the nature of the two processes (sublimation and melting) are sufficiently different to prevent a more precise relationship.

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

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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

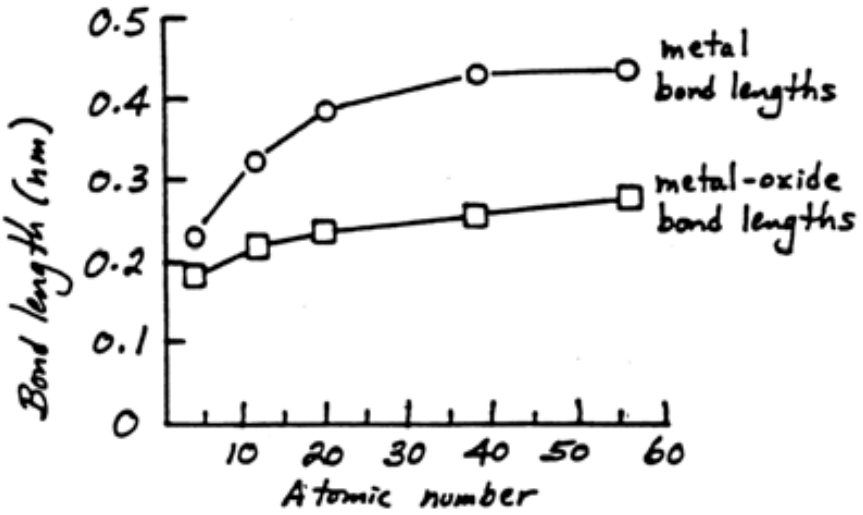


2.43 Superimpose on the plot generated for Problem 2.42 the metal-oxide bond lengths for the same range of elements.

2.43 Using Figure 2.2 and Appendix 2 gives us:

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

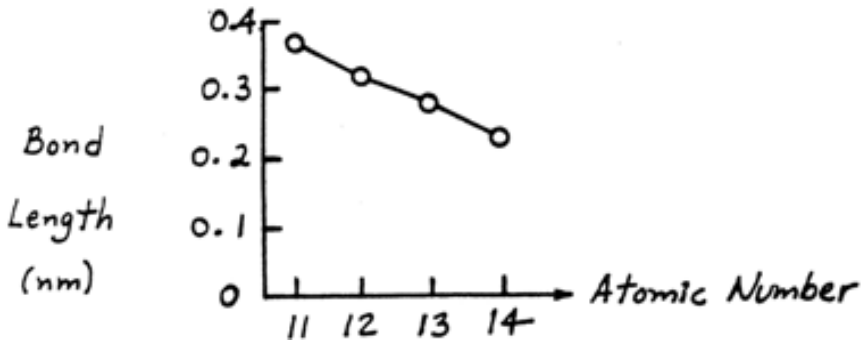


2.44 To explore another trend within the periodic table, plot the bond length of the metals in the row Na to Si as a function of atomic numbers. (For this purpose, Si is treated as a semimetal.)

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

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2.45 Discuss the role played by the valence electrons of metallic bonding in the electrical conductivity of metals.

2.45

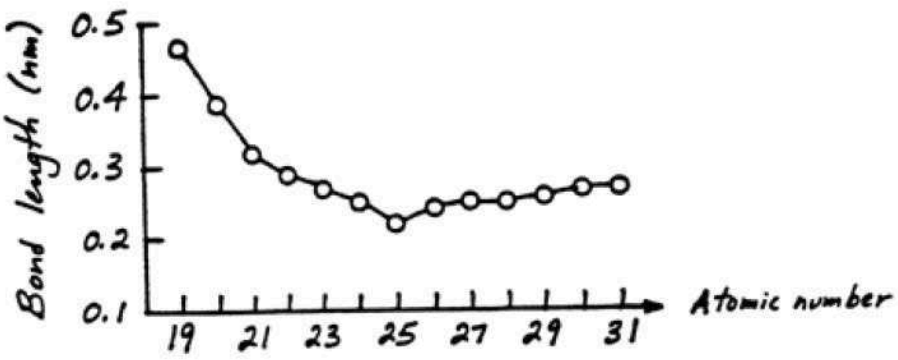
The delocalized valence electrons correspond to an electron "gas." This mobile electron gas is the basis of the typically high electrical conductivity of metals.

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	0.231nm	0.462nm
Ca	20	0.197nm	0.394nm
Sc	21	0.160nm	0.320nm
Ti	22	0.147nm	0.294nm
V	23	0.132nm	0.264nm
Cr	24	0.125nm	0.250nm
Mn	25	0.112nm	0.224nm
Fe	26	0.124nm	0.248nm
Co	27	0.125nm	0.250nm
Ni	28	0.125nm	0.250nm
Cu	29	0.128nm	0.256nm
Zn	30	0.133nm	0.266nm
Ga	31	0.135nm	0.270nm

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2.47 Why is the bond length for metal oxides generally smaller than the bond length of the corresponding pure metal?

2.47

The ionic radius of a metal cation is smaller than the corresponding neutral metal atom's radius due to the force of attraction of the positively charged nucleus to the smaller number of electrons in the cation.

•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 next. For the simple example of NaCl,

$$\begin{array}{ccc} \text{Na (solid)} + \frac{1}{2}\text{Cl}_2\text{ (g)} & \longrightarrow & \text{Na (g)} + \text{Cl (g)} \\ \Big\downarrow \Delta H_f^\circ & & \Big\downarrow \quad \Big\downarrow \\ \text{NaCl (solid)} & \longleftarrow & \text{Na}^+\text{ (g)} + \text{Cl}^-\text{ (g)} \end{array}$$

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; and heat of formation, ΔH_f°, of NaCl = −411 kJ/mol.)

2.48 Note that $\Delta H_f^\circ = \Delta E_{subl,Na} + \frac{1}{2}\Delta E_{dissoc,Cl_2} + \Delta E_{ion,Na} + \Delta E_{ion,Cl} + \Delta E_{ionic\ bonding,NaCl}$

or, $\Delta E_{ionic\ bonding,NaCl} = \Delta H_f^\circ - \Delta E_{subl,Na} - \frac{1}{2}\Delta E_{dissoc,Cl_2} - \Delta E_{ion,Na} - \Delta E_{ion,Cl}$

$= \left(-411 - 100 - \frac{243}{2} - 496 + 361\right)\text{kJ/mol}$

$= \underline{\underline{-768\ \text{kJ/mol}}}$

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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 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 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.)

2.49

$$pV = nRT \quad \text{or} \quad n = \frac{pV}{RT} = \frac{(1\,\text{atm})(9\times10^{3}\times10^{-9}\,\text{m}^3)}{(8.314\,\text{J/K})(273\,\text{K})}\,\text{mol N}_2$$

$$\times \frac{1\,\text{N/m}^2}{9.869\times10^{-6}\,\text{atm}} \times 0.6023\times10^{24}\,\frac{\text{molec.}}{\text{mol}}$$

$$= 2.42\times10^{20}\ \text{molec. N}_2$$

$$\text{Area covered} = 0.162\times10^{-18}\,\frac{\text{m}^2}{\text{molec.}} \times 2.42\times10^{20}\ \text{molec.}$$

$$= 39.2\ \text{m}^2\ (\text{per } 100\,\text{g Cu})$$

$$\text{or, } S = \frac{39.2\,\text{m}^2}{100\,\text{g}} \times \frac{1000\,\text{g}}{\text{kg}} = \underline{\underline{392\,\text{m}^2/\text{kg}}}$$

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2.50 What is the difference between an *induced* dipole and a *permanent* dipole?

2.50

An *induced* dipole is a distortion of the charge distribution in an atom due to the influence of an adjacent atom. A *permanent* dipole is the result of asymmetrical charge distributions in a molecule.

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

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

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/(m$^3 \cdot$ atm) at 25°C, calculate the solubility at 250°C.

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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

$$S_{200°C} = S_{25°C}\, e^{-\frac{\Delta H_s}{R}\left(\frac{1}{523\,K} - \frac{1}{298\,K}\right)}$$

$$= (5.51\times10^{23}\ \text{atoms}/(\text{m}^3\cdot\text{atm}))$$
$$\times e^{-\frac{(-3{,}960\ \text{J/mol})}{(8.314\ \text{J/mol}\cdot\text{K})}(-1.44\times10^{-3}\ \text{K}^{-1})}$$

$$= \underline{\underline{2.77\times10^{23}\ \text{atoms}/(\text{m}^3\cdot\text{atm})}}$$

2.52 What role does secondary bonding play in our common observation that water expands upon freezing?

2.52

Upon freezing, the water molecules become aligned. The resulting open structure of the frozen state is less dense than the random packing of H_2O molecules in the liquid state.

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