

6.29 This probably results in a Schottky-type defect, since a second silver ion must be vacant somewhere else in the lattice to retain electrical neutrality.

CHAPTER 7

7.2 Such a nucleus would have no pion binding force.

7.3 For ${}^4_2\text{He}$ and ${}^{40}_{20}\text{Ca}$, $n/p = 1.00$; for ${}^{56}_{26}\text{Fe}$, $n/p = 1.15$; for ${}^{118}_{50}\text{Sn}$, $n/p = 1.36$; and for ${}^{208}_{82}\text{Pb}$, $n/p = 1.54$. The neutron/proton ratio increases with increasing nuclear size. This can be rationalized as a "dilution" effect - extra neutrons are needed to counterbalance the proton-proton repulsions.

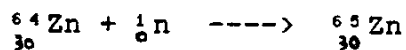
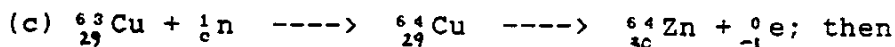
7.4 The n/p ratios are 0.75, 0.83, and 1.33 for ${}^7_4\text{Be}$, ${}^{11}_6\text{C}$, and ${}^{14}_6\text{C}$, respectively. The first two have fewer neutrons than protons, and are positron emitters. The ratio for ${}^{14}_6\text{C}$ is too large for such a small nucleus, so it is a beta emitter.

7.5 The expected mass for two protons, two neutrons, and two electrons is 4.03300 amu. Therefore, $\Delta m = 0.03040$ amu per atom, or 3.040×10^{-5} kg/mol. Then $\Delta E = \Delta mc^2 = 2.736 \times 10^{12}$ J/mol, 2.736×10^9 kJ/mol, or 2.835×10^7 eV.

7.6 (a) ${}^{60}_{28}\text{Ni}$; (b) ${}^3_1\text{H}$, ${}^{39}_{19}\text{K}$, and ${}^{52}_{24}\text{Cr}$.

7.7 ${}^{209}_{83}\text{Bi}$, since it has a magic number of neutrons (126) and a reasonable n/p ratio (1.52).

7.8 (a) ${}^{16}_8\text{O} + {}^{16}_8\text{O} \rightarrow {}^{32}_{16}\text{S}$



7.9 (a) The preferred oxidation state of chlorine is -1, and most chloride salts are soluble. (b) Positive nickel is reduced by metallic iron. The free metal was alloyed with Fe during the formation of the earth and drawn into the core. (c) Silver's oxidation to Ag^+ is much less favored than the oxidation of metallic calcium to Ca^{2+} . Hence silver occurs in deposits of the free metal, while calcium is found in Ca^{2+} salts such as CaCO_3 . (d) Phosphorus forms exceptionally strong bonds to oxygen. In the phosphate ion the P-O interactions are stabilized by partial π bonding, and are not subject to adjacent atom lone pair repulsions. PO_4^{3-} is therefore found in a variety of naturally-occurring salts.

7.10 (a) lithophile; (b) chalcophile; (c) chalcophile; (d) siderophile.

7.11 The unit cell edge length is $2r$, so the total volume is $(2r)^3 = 8r^3$. There is one spherical atom per unit cell, so the occupied volume is $\frac{4}{3}\pi r^3$. Then the percent occupancy is $100\%(\frac{4}{3}\pi r^3)/8r^3 = 52\%$.

7.12 In the bcc lattice atoms are in contact along the body diagonal, which is $\sqrt{3}$ times the edge length. Hence the edge length is $4r/\sqrt{3}$, and the total volume is $(4r/\sqrt{3})^3 = 12.317r^3$. Since there are two atoms per unit cell, the occupied volume

is $2^{4/3} \pi r^3 = 8.378r^3$. The percent occupancy is therefore $100\%(8.378/12.317) = 68\%$.

7.13 The mass of a unit cell (4 molecules) is 8.064 amu or 1.339×10^{-23} g. The unit cell volume is $(5.338 \times 10^{-8} \text{ cm})^3 = 1.521 \times 10^{-22} \text{ cm}^3$. The density is then $1.339 \times 10^{-23} \text{ g}/1.521 \times 10^{-22} \text{ cm}^3 = 0.088 \text{ g/cm}^3$.

7.14 For a ccp (fcc) lattice, the face diagonal is $\sqrt{2} \cdot l = 4r$. Therefore, $r = \sqrt{2}l/4 = 239 \text{ pm}$.

7.15 (a) The unit cell mass is $2(51.996)/6.022 \times 10^{23} = 1.727 \times 10^{-22} \text{ g}$; the unit cell volume is $(288.4 \times 10^{-10})^3 = 2.399 \times 10^{-23} \text{ cm}^3$. The density is therefore 7.199 g/cm^3 .

(b) The body diagonal is $4r = \sqrt{3} \cdot l$. Then $r = \sqrt{3}l/4 = 125 \text{ pm}$. Table 7.6 gives 129 pm. (Values in that table are for 12-coordination.)

7.16 The values are 27.53 eV for Be, 22.68 eV for Mg, and 17.98 eV for Ca. As these energies increase, the electron delocalization per mole of atoms decreases. This lowers both the melting temperature and the electrical conductivity.

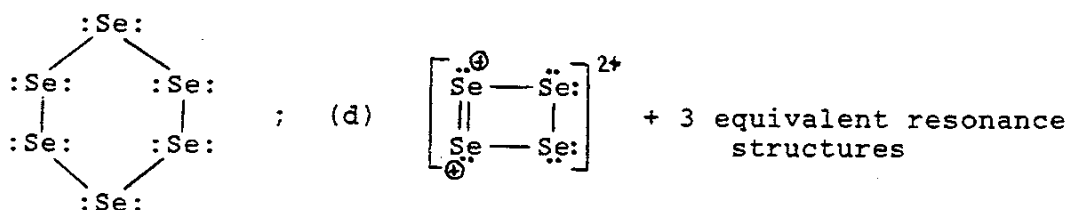
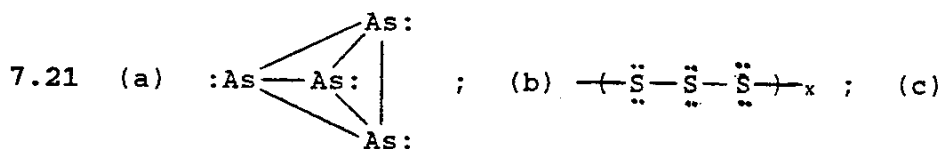
7.17 (a) Calcium and strontium delocalize two electrons per atom, while rubidium delocalizes only one; hence rubidium is the lowest-melting of the three. Between Ca and Sr, the smaller size of calcium yields a greater metallic lattice energy and therefore a higher melting temperature. (b) This is due to the different numbers of delocalized electrons per atom - see (a). (c) This can be rationalized as a size

effect - see (a).

7.18 The overlap of the s and p bonding bands is akin to s - p orbital mixing. (Recall that hybridization is the mixing of two or more orbitals of the same atom - see Chapter 3.)

7.19 As temperature increases, more and more electrons occupy antibonding orbitals (according to the Boltzmann distribution). Those electrons are free to migrate throughout the lattice, enhancing the electrical conductivity.

7.20 Each icosahedral edge defines a nearest-neighbor interaction. Since there are 30 edges and 36 shared electrons, it can be argued that the average bond order is $(36/2)/30 = 0.60$.



7.22 Both S_2 and S_3 require an S - S π bond (assuming an ozone-like structure for S_3). Since S - S π bonding is disfavored compared to S - S σ bonding, these species are unstable toward decomposition to σ -only networks.

7.23 The lattice is cubic, with atoms occupying the corner and face-centered positions and all of the tetrahedral holes

(c.f. Figure 6.10(b) with carbon replacing both Zn^{2+} and S^{2-}). The face diagonal is $\sqrt{2} \cdot (356.7) = 504.4$ pm. A right triangle can be constructed having one leg equal to $504.4/4$ and a hypotenuse of $2r$. Then since the C-C-C bond angles are 109.5° , $\sin(109.5^\circ/2) = 0.8166 = 504.4/4(2r)$; $r = 77.2$ pm.

CHAPTER 8

8.1 (a) $1.66 D \times \frac{20.82 Z \cdot \text{unit} \cdot \text{pm}}{1 D} = 34.6 Z\text{-unit} \cdot \text{pm}$; (b)

$|Z| = 34.6/97.1 = 0.36$; the bond is predicted to be about 36% ionic. (c) $E = 1.389 \times 10^5 (0.36)^2 / 97.1 \approx 180$ kJ/mol.

8.2 The answer depends on the distance chosen. A reasonable estimate for the ionic radius of K^+ plus the van der Waals radius of fluorine is 300 pm. Insertion into equation (8.3) then gives $E = -1.389 \times 10^5 (18 Z\text{-unit} \cdot \text{pm}) (+1) / (300)^2$, or about -28 kJ/mol.

8.3 The lattice energy of $MgCl_2$ is more than twice that of $NaCl$ (because of charge and size effects), which mitigates against dissolution.

8.5 The more exothermic dissolution of $NaOH$ reflects the large hydration energy of OH^- compared to Cl^- , primarily because of strong hydrogen bonding.

8.6 (a) The sizes of Li^+ and F^- are more similar than those of Li^+ and Br^- ; hence according to Fajans' competition principle, $LiBr$ should be the more soluble salt. (b) Cs^+ and Br^- are more similar in size than are Cs^+ and F^- , so CsF is