

## Chapter 5

### IONIC BONDING

#### Exercises

- 5.2 (a) The electrostatic attraction between an ion and a polar molecule.  
(b) The ratio of the cation radius over the anion radius.  
(c) The arrangement in which one ion is surrounded by eight nearest neighbors of opposite charge.
- 5.4 Magnesium chloride, because there is a much higher electronegativity difference between the two atoms than in the case of sulfur dichloride.
- 5.6 (a)  $\text{Br}^-$ . The two ions are isoelectronic, but bromide has one more proton; hence a higher  $Z_{\text{eff}}$  and a smaller ionic radius.  
(b)  $\text{S}^{2-}$ . With more “layers” of electrons, the ion will be larger even though there are more protons in the nucleus.
- 5.8  $\text{NaCl}$ ; because sodium is smaller than potassium, the charge is more concentrated (charge density is higher) and the ionic attraction will be stronger in  $\text{NaCl}$  than  $\text{KCl}$ . The stronger the ionic attraction, the higher the temperature needed to melt the ionic lattice.
- 5.10  $\text{I}^-$ . Because the iodide ion is much larger than the fluoride ion (and thus iodide has the lower charge density), the iodide ion can be more readily polarized.
- 5.12 Manganese(II) oxide (m.p.  $1650^\circ\text{C}$ ); manganese(III) oxide (d.  $1080^\circ\text{C}$ ); manganese(IV) oxide (d.  $535^\circ\text{C}$ ); manganese(VII) oxide (m.p.  $6^\circ\text{C}$ ). The shift between bonding types seems to occur above the +4 oxidation state.
- 5.14 The free  $\text{Ti}^{4+}$  would have too high a charge density to exist in aqueous solution, thus it likely to be present as the hexaaquatitanium(IV) ion,  $[\text{Ti}(\text{OH}_2)_6]^{4+}(\text{aq})$ .

- 5.16 Copper(II) chloride, because the copper(II) ion has a non-noble gas electron configuration, which according to Fajans' third rule is more likely to result in covalent bonding and hence in a lower melting point. An alternative explanation is that the copper(II) ion has a lower electronegativity than magnesium and thus is more likely to form covalent bonds.
- 5.18 The ionic attractions between the dipositive calcium cation and the dipositive carbonate anion are stronger than the ion-dipole attractions that would be formed between each ion and the solvent water molecules.
- 5.20 The hydrate formula is likely to be  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ . Most dipositive and tripositive ions attract six water molecules, while one water molecule is usually associated with the sulfate ion. The formula of the salt is more accurately written as  $[\text{Ni}(\text{OH}_2)_6]^{2+}[\text{SO}_4 \cdot \text{H}_2\text{O}]^{2-}$ .
- 5.22 Ions are assumed to be charged, incompressible, nonpolarizable spheres. Ions try to surround themselves with as many ions of the opposite charge as possible and as closely as possible.
- The cation-to-anion ratio must reflect the chemical composition of the compound.
- 5.24 In general, the anions are much larger than the cations; hence it is more appropriate to consider the lattice as an array of anions with the smaller cations fitting the interstices.
- 5.26 (a) Fluorite structure; (b) sodium chloride structure; (c) zinc sulfide structure.
- 5.28 Sodium ion. Low-charge anions are stabilized by large, low charge density cations.
- 5.30 (a) Covalent and metallic; (b) metallic and ionic; (c) covalent and a lesser contribution of ionic.

## Beyond the Basics

5.32 It is certainly generally true that metals have a long liquid range, often in excess of 1000°C. Among the shorter are the Group 12 elements; for example, the liquid range of mercury is only 396°C. A long liquid range cannot be used as the sole criterion for metallic bonding, as several nonmetallic elements—those having network covalent bonding—have very long liquid ranges as well. For example, silicon has a liquid range of about 1267°.

5.34 Melting points for ionic compounds depend upon the lattice energy. Sodium fluoride will have the higher lattice energy because the fluoride ion is smaller (higher charge density) than the chloride ion in sodium chloride. Thus sodium fluoride will have the higher melting point.

For the carbon compounds, these are small-molecule covalent in their bonding. The melting point will depend upon the strength of their intermolecular forces—in this case, dispersion forces. It is the number of electrons that provides the most important effect in this case. Because carbon tetrafluoride has 42 electrons while carbon tetrachloride has 74, the latter will have the higher melting point.

5.36 The face length will be  $2(r_+ + r_-)$ .

5.38 The unit cell of cesium chloride contains only one pair of ions. Thus:

$$\text{Mass} = \frac{168.4 \text{ g} \cdot \text{mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 2.80 \times 10^{-22} \text{ g}$$

$$\text{Volume} = \frac{2.80 \times 10^{-22} \text{ g}}{3.97 \text{ g} \cdot \text{cm}^{-3}} = 7.05 \times 10^{-23} \text{ cm}^3 = 7.05 \times 10^7 \text{ pm}^3$$

$$\text{Length of side} = \sqrt[3]{(7.05 \times 10^7 \text{ pm}^3)} = 413 \text{ pm}$$

$$\begin{aligned} \text{Using the result from 5.37, the sum of ionic radii} &= (413 \text{ pm})/1.15 \\ &= 359 \text{ pm} \end{aligned}$$

$$\text{Thus } r(\text{Cs}^+) = 359 \text{ pm} - 181 \text{ pm} = 178 \text{ pm}.$$

5.40 Using the result from 5.37, the sum of ionic radii =  $(366 \text{ pm})/1.15$   
= 318 pm

Thus  $r(\text{NH}_4^+) = 318 \text{ pm} - 167 \text{ pm} = 151 \text{ pm}$ .

5.42  $\text{NaWO}_3$ .