

## Chapter 5

### IONIC BONDING

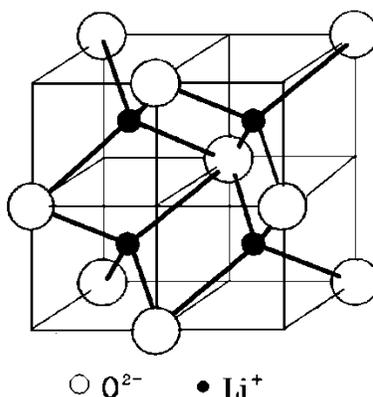
#### Exercises

- 5.1 (a) The distortion of an anion from a spherical shape.  
(b) The holes between anions in the crystal packing in which cations can fit.  
(c) The diagram used to show that many elements and compounds possess combinations of the three bonding categories: metallic, covalent, and ionic.
- 5.3 Hard and brittle crystals; high melting points; electrically conducting in liquid phase and in aqueous solution.
- 5.5 (a)  $K^+$ , because the radius will be determined by the inner orbitals ( $2s$  and  $2p$ ) while the radius of  $K$  is determined by the  $3s$  orbital.  
(b)  $Ca^{2+}$ , because the ions are isoelectronic but calcium has one more proton, and hence a higher  $Z_{\text{eff}}$  and a smaller ionic radius.  
(c)  $Rb^+$ , because again the ions are isoelectronic, with rubidium having two more protons than bromide, and hence a higher  $Z_{\text{eff}}$  and a smaller ionic radius.
- 5.7  $NaCl$ , because chloride is smaller than iodide; the charge is more concentrated (charge density is higher) and the ionic attraction will be stronger in  $NaCl$  than in  $NaI$ . The stronger the ionic attraction, the higher the temperature needed to melt the ionic lattice.
- 5.9  $Ag^+$ , because it has the lowest charge density.
- 5.11  $UCl_3$  ( $837^\circ C$ );  $UCl_4$  ( $590^\circ C$ );  $UCl_5$  ( $327^\circ C$ );  $UCl_6$  ( $179^\circ$ ). The melting points steadily decrease with increasing charge density of the uranium, resulting in increasing contribution of covalency to the bonding. In this particular series, there does not appear to be a clear divide between high (ionic) and low (covalent) melting points. The fact that uranium(V)

chloride decomposes in water and is soluble in carbon disulfide would indicate that bonding in that compound is predominantly covalent.

- 5.13  $\text{WF}_6$  ( $2^\circ\text{C}$ ) and  $\text{WO}_3$  ( $1472^\circ\text{C}$ ). The bonding in the fluoride is obviously predominantly covalent while the oxide is clearly ionic. The fluoride is more polarizable than the oxide.
- 5.15 Tin(II) chloride has a higher melting point because tin(II) has a fairly low charge density. The bonding in  $\text{SnCl}_2$  will be predominantly ionic. The high charge density of the tin(IV) ion would result in covalent bonding for  $\text{SnCl}_4$  and therefore a low melting point.
- 5.17 No, ionic compounds do not dissolve in nonpolar solvents, because the dissolving process requires the formation of ion-dipole interactions. Molecules of a nonpolar solvent do not possess dipoles.
- 5.19 Magnesium chloride, because the divalent smaller magnesium ion has a significantly higher charge density than the monovalent larger sodium ion. The magnesium ion would therefore be likely to have a “shell” of strongly attracted water molecules to diffuse the charge.
- 5.21 Lithium nitrate, because the lithium ion has a higher charge density than the sodium ion. The lithium ion would therefore be more likely to have a “shell” of water molecules to diffuse the charge.
- 5.23 The coordination number depends on the radius ratio.
- 5.25 The magnesium ion is smaller than the calcium ion. Thus, presumably, only six fluoride anions can fit around a magnesium ion, compared to eight around each calcium ion.

5.27



5.29 (a) Metallic and a lesser contribution of ionic; (b) covalent and a lesser contribution of ionic.

5.31 The choice would be metallic or covalent. With such a low melting point (and without seeing the element), the first choice would be covalent. A measurement of its high electrical conductivity (and observation of the metallic luster) would confirm it to have metallic bonding.

### Beyond the Basics

5.33 In the solid, there is shared ionic bonding with the six nearest neighbors of each ion. In the gas phase, there is direct hybrid ionic-covalent bonding between pairs of ions.

5.35 (a) Copper(II) chloride. The higher charge density copper(II) ion will result in a higher lattice energy in its chloride and therefore a higher melting point.

(b) Lead(II) chloride. The very high charge density of the lead(IV) ion will result in the compound having essentially covalent bonding and therefore a low melting point. Ionic lead(II) chloride will have a high melting point.

5.37 The diagonal length through the center of the unit cell will be  $2(r_+ + r_-)$ . Using Pythagoras's theorem, the length of the unit cell edge will be  $[2/(3)^{1/2}](r_+ + r_-) = 1.15(r_+ + r_-)$ .

5.39 The unit cell of rubidium chloride contains four pairs of ions.

$$\text{Thus mass} = \frac{4 \times 121.0 \text{ g} \cdot \text{mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 8.04 \times 10^{-22} \text{ g}$$

$$\text{Volume} = \frac{8.04 \times 10^{-22} \text{ g}}{2.76 \text{ g} \cdot \text{cm}^{-3}} = 2.91 \times 10^{-22} \text{ cm}^3 = 2.91 \times 10^8 \text{ pm}^3$$

$$\text{Length of side} = \sqrt[3]{(2.91 \times 10^8 \text{ pm}^3)} = 663 \text{ pm}$$

$$\text{Sum of ionic radii} = (663 \text{ pm})/2 = 331 \text{ pm}$$

$$\text{Thus } r(\text{Rb}^+) = 331 \text{ pm} - 167 \text{ pm} = 164 \text{ pm}$$

5.41 The unit cell of sodium hexafluoroantimonate(V) contains four pairs of ions.

$$\text{Thus mass} = \frac{4 \times 258.8 \text{ g} \cdot \text{mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 1.72 \times 10^{-21} \text{ g}$$

$$\text{Volume} = \frac{1.72 \times 10^{-21} \text{ g}}{4.37 \text{ g} \cdot \text{cm}^{-3}} = 3.94 \times 10^{-22} \text{ cm}^3 = 3.94 \times 10^8 \text{ pm}^3$$

$$\text{Length of side} = \sqrt[3]{(3.94 \times 10^8 \text{ pm}^3)} = 733 \text{ pm}$$

$$\text{Sum of ionic radii} = (733 \text{ pm})/2 = 367 \text{ pm}$$

$$\text{Thus } r(\text{SbF}_6^-) = 367 \text{ pm} - 116 \text{ pm} = 251 \text{ pm}$$

5.43 Radius ratios are 0.32 (LiAt); 0.516 (NaAt); 0.676 (KAt); 0.738 (RbAt); and 0.804 (CsAt). Thus LiAt should adopt wurtzite or sphalerite packing; NaAt and KAt, sodium chloride packing; and RbAt and CsAt, cesium chloride packing.