# Section 3 Solutions from Shriver and Atkins

3.3 Lattice layers directly on top of each other will form cubic (not close-packed) structures, therefore ABBA and ABCCB are not valid. All the rest are.

3.4 $XA_2$

3.5 $K_3C_{60}$

3.7 The mass of 2 sodiums (the number of Na in a bcc unit cell) is:

$2*(23\ g\ mol^{-1}) / (6.022x10^{23}\ mol^{-1}) = 7.64x10^{-23}\ g = 7.64x10^{-26}\ kg$

Therefore the volume of the unit cell is:

$V = 7.64x10^{-26}\ kg / 970\ kg\ m^{-3} = 7.87x10^{-29}\ m^3$

Therefore the length of a side is the cubed root = $4.29x10^{-10}$ m (or 4.29 Å)

3.8 8 corner Au = 1 total Au atom
6 facial Cu = 3 total Cu atoms

Therefore, this face-centred cubic alloy is $Cu_3Au$, which is, presumably, 6 carat?? (1/4 of 24)

3.10 (a) Rock salt has coordination number 6,6; CsCl has coordination 8,8.
(b) This is actually unanswerable, because we cannot tell how far apart the $Cl^-$ are forced by the inclusion of the $Rb^+$ in the bcc structure. However, the book is probably assuming the bcc structure will give the larger apparent radius.

3.11 $Cs^+$ has nearest neighbours directly out through the faces, 6 faces on a cube = 6 next-nearest neighbours.

3.13 See Table 3.6 (you do not have to memorize this).

| | |
|---|---|
| (a) ratio = 86/140 = 0.61 | fcc with octahedral holes filled |
| (b) ratio = 196/220 = 0.89 | probably bcc |
| (c) ratio = 45/140 = 0.32 | fcc with tetrahedral holes filled |
| (d) ratio = 62/146 = 0.42 | borderline? fcc with oct or tet holes filled |

3.16 MgO is 2+/2-, therefore $\Delta H_L° = 4*786 = 3140$ kJ/mol
AlN is 3+/3-, therefore $\Delta H_L° = 9*786 = 7070$ kJ/mol

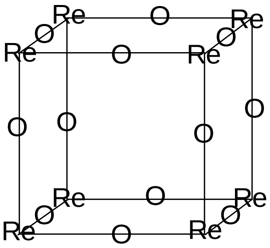
3.17 (a) (using 140 pm for $O^{2-}$) $\Delta H_L° = 10500$ kJ/mol
(b) (using 138 for $K^+$) $\Delta H_L° = 1960$ kJ/mol
(c) (using 76 for Li+) $\Delta H_L° = 690$ kJ/mol

3.18 The greater the difference in size, the greater the solubility. Therefore, looking up the ionic radii gives:
$MgSO_4 > SrSO_4$
$NaBF_4 > NaF$

3.19 charge is most important, so one set is 1+/1- (LiF, RbCl, CsI), another is 2+/2- (CaO, NiO), and AlN will be the strongest with 3+/3-
after that, sum of the radii are important (smaller radii = stronger lattice)
Therefore, overall order should be something like:
CsI < RbCl < LiF < CaO < NiO < AlN

3.20 Any cation with a size similar to $CO_3^{2-}$ (185 pm) should do, *e.g.*, $Ba^{2+}$

3.p5



This has 6,2 coordination. Putting a cation in the middle generates a perovskite structure.

3.p9 Across the face of an fcc structure, there are 4 ionic radii of the anion. Therefore, if the Se2- are in contact, then

$(4r)^2 = 545^2 + 545^2$

therefore, $r(Se^{2-}) = 193$ pm

Along an edge is two anion + two cation radii in the rock salt structure. Therefore,

$545 = 2r(Mg^{2+}) + 2r(Se^{2-}) = 2r(Mg^{2+}) + 2(193)$

solving for $r(Mg^{2+}) = 80$ pm

Similarly, $r(Ca^{2+}) = 103$ pm

$r(Sr^{2+}) = 119$ pm

$r(Ba^{2+}) = 138$ pm

3.p12 This structure is fcc (cubic close-packed) $Ca^{2+}$ with $CO_3^{2-}$ in the octahedral holes.

3.p16 Using the same argument from exercise 3.19, NaCl < MgO < AlN

3.p18 $Li^+$ is a "harder" sphere than $Ag^+$, so the compound LiCl is more ionic than AgCl. By the same argument, $BeCl_2$ would be more ionic than $PtCl_2$, for example.

9.4 The question requires knowing the enthalpies of the various steps in the process of creating $NaCl_2$ from Na (*s*) and $Cl_2$ (*g*). Ionization energies are from Resource Section 2, see Table 9.1 for atomization energies. The only value that needs to be estimated is the lattice enthalpy $\Delta H_L$, which should be somewhere from -2000 to -3000 kJ/mol (see similar $MX_2$ salts in Table 3.7). To get $\Delta H_f$ we need to get the following: $Na(s) + Cl_2(g) \rightarrow NaCl_2(s)$

| | | | |
|---|---|---|---|
| Therefore, | $Cl_2(g) \rightarrow 2\,Cl^\bullet(g)$ | $\Delta H_{dissociation}$ | = 242 kJ/mol |
| | $2\,Cl^\bullet(g) + 2\,e^- \rightarrow 2\,Cl^-(g)$ | $-\Delta H_{IE}$ | = -698 kJ/mol |
| | $Na(s) \rightarrow Na(g)$ | $\Delta H_{sublimation}$ | = 109 kJ/mol |
| | $Na(g) \rightarrow Na^+(g) + e^-$ | $\Delta H_{IE}$ | = 496 kJ/mol |
| | $Na^+(g) \rightarrow Na^{2+}(g) + e^-$ | $\Delta H_{IE(2)}$ | = 4562 kJ/mol |
| | $Na^{2+}(g) + 2\,Cl^-(g) \rightarrow NaCl_2(s)$ | $\Delta H_L$ | = approx. -2500 kJ/mol |
| | $Na(s) + Cl_2(g) \rightarrow NaCl_2(s)$ | $\Delta H_f$ = | approx. +2200 kJ/mol |

The largest positive number that dominates all the other values is the second ionization energy of sodium ($Na^+ \rightarrow Na^{2+}$), which is why $NaCl_2$ does not form.

11.6 Another size comparison – the difference in size between $Li^+$ and $X^-$ is greater for $I^-$, therefore LiI is more soluble. $Cs^+$ is a very large cation, so its salt with a small $X^-$, namely CsF, would be the most soluble.

11.8 NaCl is Figure 3.30 (6,6 coordination) and CsCl is Figure 3.32 (8.8 coordination)
The "hole" in CsCl is larger, so it is adopted more often by compounds where the size of the cation and anion are very close in size. The NaCl structure implies that the $Na^+$ is significantly smaller than the $Cl^-$ in order to fit into the smaller octahedral holes.