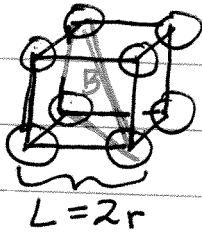


Ch. 7 Homework: #3, 4a, 5, 6, 12, 18, 26(including energy equation); plus 3 additional problems from handout provided

3. Here, you are asked to determine the size of the (cubic) hole in the body center of the primitive cubic unit cell, expressing it in terms of the radius of the atoms,  $r$ .

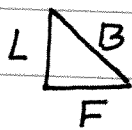


Atoms touch along the edges in this unit cell, so that  $L = 2r$ . Atoms do not touch along the body diagonal.

\*  $B = 2r + x$  where  $x$  is the diameter of the gap (hole) in the body center.

Our goal, therefore is to express  $x$  in terms of  $r$  and then find the radius of the sphere that fills  $x$  (which will be equal to  $\frac{x}{2}$ ).

Using trigonometry and the red triangle above:

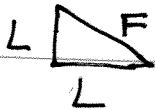


$$L = 2r$$

$F = \text{face diagonal} = \sqrt{2}L$  - See below \*

$B = \text{body diagonal} = 2r + x$

\* [ Using a second triangle on a face of the cell: ]



$$F^2 = 2L^2$$

$$F = \sqrt{2}L$$

$$L^2 + F^2 = B^2 \rightarrow L^2 + (\sqrt{2}L)^2 = B^2 \quad \frac{x}{2} = \text{sphere radius}$$

$$3L^2 = B^2$$

$$\sqrt{3}L = B$$

$$\sqrt{3}(2r) = 2r + x$$

$$3.4641r = 2r + x$$

$$1.464 = x$$

$$\frac{x}{2} = \frac{1.464}{2}$$

$$\boxed{\text{sphere radius} = 0.732r}$$

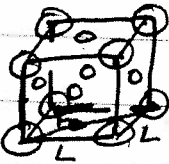
Fig. 2

4.

In each part of this problem, you were to compare the volume occupied by atoms to the total volume of a unit cell.

a)

fcc atoms per unit cell =  $8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 4$



$$V_{\text{atoms}} = 4V_{\text{sphere}} = 4\left(\frac{4}{3}\pi r^3\right)$$

$$V_{\text{total}} = L^3$$

To express % of occupied volume, express  $L$  in terms of  $r$  (so that  $r$ 's can cancel):

Face diag.  $F = 4r$  - because atoms touch along this length.

$$L^2 + L^2 = F^2$$

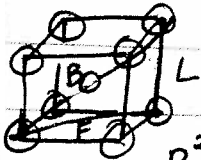
$$F^2 = 2L^2 \quad F = \sqrt{2}L = 4r$$

$$L = \frac{4r}{\sqrt{2}}$$

$$\begin{aligned} \% \text{ occupied} &= \frac{V_{\text{atoms}}}{V_{\text{total}}} \times 100\% \\ &= \frac{4\left(\frac{4}{3}\pi r^3\right)}{\left(\frac{4r}{\sqrt{2}}\right)^3} = \frac{4\left(\frac{4}{3}\pi r^3\right)}{\frac{64r^3}{2\sqrt{2}}} = \frac{16.755}{22.627} \times 100\% \\ &= \underline{\underline{74.0\%}} \end{aligned}$$

\*\*Problem 4b NOT assigned\*\*

b) bcc  $8\left(\frac{1}{8}\right) + 1 = 2$  atoms per unit cell



$$V_{\text{atoms}} = 2\left(\frac{4}{3}\pi r^3\right); \quad V_{\text{total}} = L^3$$

Relating  $L$  to  $r$ :

$$B^2 = L^2 + F^2; \quad F^2 = 2L^2 \rightarrow B^2 = 3L^2$$

$$B = \sqrt{3}L = 4r \rightarrow L = \frac{4r}{\sqrt{3}}$$

$$\begin{aligned} \% \text{ occupied} &= \frac{\frac{8}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{8.3776}{12.3168} \times 100\% \\ &= \underline{\underline{68.0\%}} \end{aligned}$$

Pg. 3

5. NaCl, CsCl and CaF<sub>2</sub> unit cells are shown (left → right)

NaCl: Anions:  $8(\frac{1}{8}) + 6(\frac{1}{2}) = 4$ ; Cations:  $12(\frac{1}{4}) + 1 = 4$   
4 NaCl formula units per unit cell.

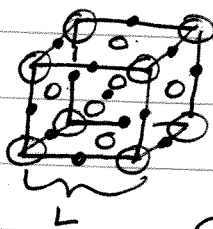
CsCl: Cl<sup>-</sup>:  $8(\frac{1}{8}) = 1$  Cs<sup>+</sup>:  $1(1) = 1$

1 CsCl formula unit per unit cell

CaF<sub>2</sub>: F<sup>-</sup>:  $8(\frac{1}{8}) + 6(\frac{1}{2}) + 12(\frac{1}{4}) + 1(1) = 8$

Ca<sup>2+</sup>:  $4(1) = 4$  → 4 CaF<sub>2</sub> formula units

6.



Ions touch along cell edges:  $L = 2r_+ + 2r_-$   
Solve for L and compare to sum of tabulated radii (from App. B-1).

$$\text{density} = \frac{m_{\text{cell}}}{V_{\text{cell}}} \quad m_{\text{cell}} = 4 \text{ LiBr formula units} \\ = 4(86.845 \text{ amu}) \left( \frac{1.66054 \times 10^{-24} \text{ g}}{1 \text{ amu}} \right)$$

$$m_{\text{cell}} = 5.768 \times 10^{-22} \text{ g}$$

Use density provided to solve for V<sub>cell</sub> and L:

$$V_{\text{cell}} = \frac{m_{\text{cell}}}{\text{density}} = \frac{5.768 \times 10^{-22} \text{ g}}{3.464 \text{ g/cm}^3} = 1.6651 \times 10^{-22} \text{ cm}^3$$

$$L = \sqrt[3]{V} = 5.5015 \times 10^{-8} \text{ cm} \left( \frac{1 \times 10^{10} \text{ pm}}{1 \text{ cm}} \right) = \underline{550.15 \text{ pm}}$$

Interionic distance =  $r_{\text{Li}^+} + r_{\text{Br}^-}$

$$L = 2r_+ + 2r_- \therefore \text{Interionic distance} = \frac{L}{2}$$

$$\frac{L}{2} = \underline{275.1 \text{ pm}}$$

Comparing to radii in App. B-1:

$$\text{Li}^+ (6\text{-coord.}) = 90 \text{ pm} \quad \text{Br}^- (6\text{-coord.}) = 182 \text{ pm}$$

$$r_{\text{Li}^+} + r_{\text{Br}^-} = \underline{272 \text{ pm}} \quad \text{(estimate is within 1.1\% of experimental value above.)}$$

12.

a) When a neutral atom forms an anion or cation, its # of protons is unchanged. When  $e^-$  are added (for an anion), the attractive force between the nucleus and the outermost  $e^-$  decreases, and radius increases. When  $e^-$  are removed (for a cation), this attractive force increases, causing a decrease in radius.

b)  $O^{2-}$  and  $F^-$  are isoelectronic with  $10 e^-$ .  $F^-$  has more protons in the nucleus (i.e., 9, vs. 8 for  $O^{2-}$ ), causing a stronger force of attraction and a smaller radius.

18.

In order to use a Born-Haber cycle to determine  $\Delta H_f^\circ$ , we must first estimate the lattice enthalpy, using the Born-Mayer equation:

$$\Delta H_{\text{lattice}} \approx \Delta U_{\text{lattice}} = \frac{NMZ_+Z_-e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{\rho}{r_0}\right) \quad \begin{array}{l} M = 1.74756 \text{ (NaCl struct.)} \\ r_0 = r_{K^+} + r_{Br^-} \\ = 152 + 182 = 334 \text{ pm} \\ = 3.34 \times 10^{-10} \text{ m} \end{array}$$

$$\Delta U = \frac{(6.022 \times 10^{23} \text{ mol}^{-1})(1.74756)(+1)(-1)(1.602 \times 10^{-19} \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1})(3.34 \times 10^{-10} \text{ m})} \left(1 - \frac{30 \text{ pm}}{334 \text{ pm}}\right)$$

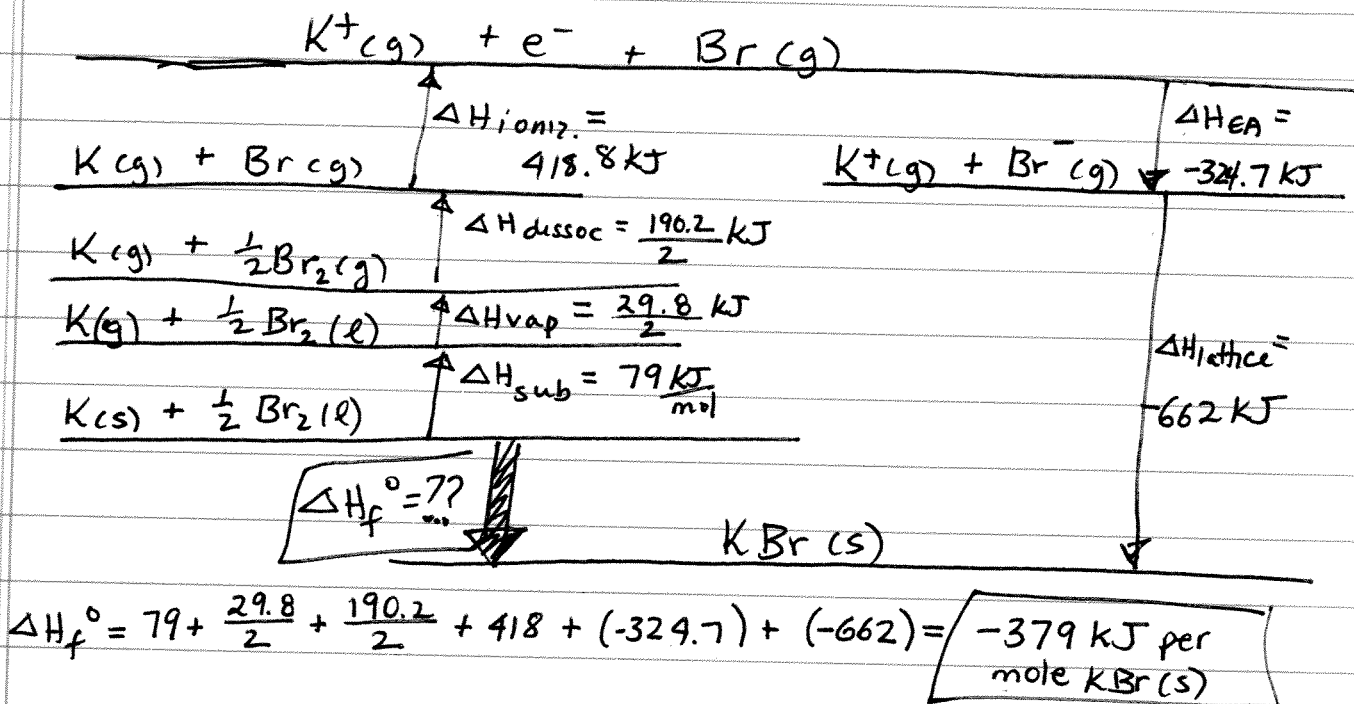
$$\Delta U = (-7.268 \times 10^5 \text{ J/mol})(0.91018)$$

$$\Delta U = -6.6152 \times 10^5 \text{ J/mol} = \boxed{-662 \text{ kJ/mol} \approx \Delta H_{\text{lattice}}}$$

Now, we can use a Born-Haber cycle to determine the standard enthalpy of formation ( $\Delta H_f^\circ$ ) for 1 mole of  $KBr(s)$  from its elements:



Note: The  $\Delta H_{\text{vap}}(\text{Br}_2)$  and  $\Delta H_{\text{dissoc}}(\text{Br}_2)$  given in the problem are for 1 mole  $\text{Br}_2$ . Since we only have  $\frac{1}{2}$  mole  $\text{Br}_2$  (to form 1 mole  $\text{KBr}$ ), these values must be divided by 2.



26.

The smallest dots will emit the highest energy photons; the largest dots will have the lowest energy emissions. This results from quantum confinement: when particles reach nanoscale dimensions (i.e., a few nm in diameter), they behave like single molecules. Energy levels can be predicted by the particle-in-a-box model (where the electron is the particle and the quantum dot serves as the box). Energy is proportional to  $1/L^2$ , where  $L$  is the length of the box. As  $L$  (or quantum dot size) increases, energy levels get closer together and emission shifts to lower energies (longer wavelengths).

In one dimension,

$$E_n = (n^2 h^2) / (8mL^2)$$

1)

$$a) X: 1 + 8\left(\frac{1}{8}\right) = 2$$

$$\text{Formula} = MX$$

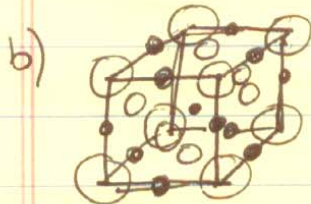
$$b) M: 2(1) = 2$$

2 MX formula units  
per unit cell

c) CN = 6 for both ions

2)

$$a) r_+/r_- = 89/126 = 0.706 \rightarrow \text{NaCl structure predicted}$$



c)

MnO likely does adopt the NaCl structure, because it likely has significant ionic character, as is the case for most compounds of  $2+$  cations.

d)

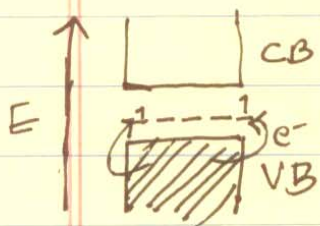
Ions touch along unit cell edges

$$L = 2r_{\text{Mn}^{2+}} + 2r_{\text{O}^{2-}} = 2(89 + 126 \text{ pm})$$

$$L = 2(215) = \boxed{430 \text{ pm}}$$

3)

Ge doped with Ga  $\rightarrow$  element with fewer valence  $e^-$   
 $\Rightarrow$  p-type doping



P-type doping introduces empty dopant orbitals in the band gap, just above the filled VB.  $e^-$  from the VB can occupy these orbitals, creating mobile holes in the valence band. This increase in charge carriers increases  $\sigma$ . [Note: there are NOT increased #'s of  $e^-$  in the conduction band.]