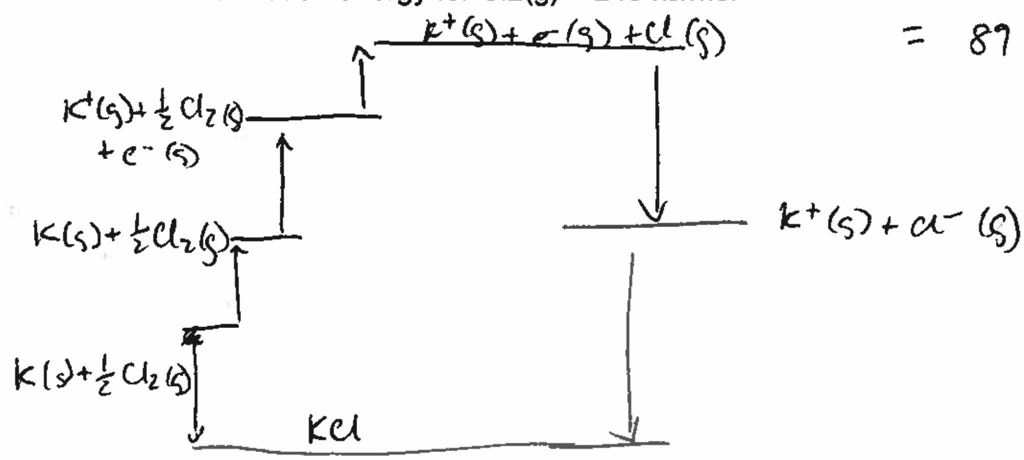
CHEM 362 – Fall 2019
Prof K .R. Dunbar
TA: Ellen Song

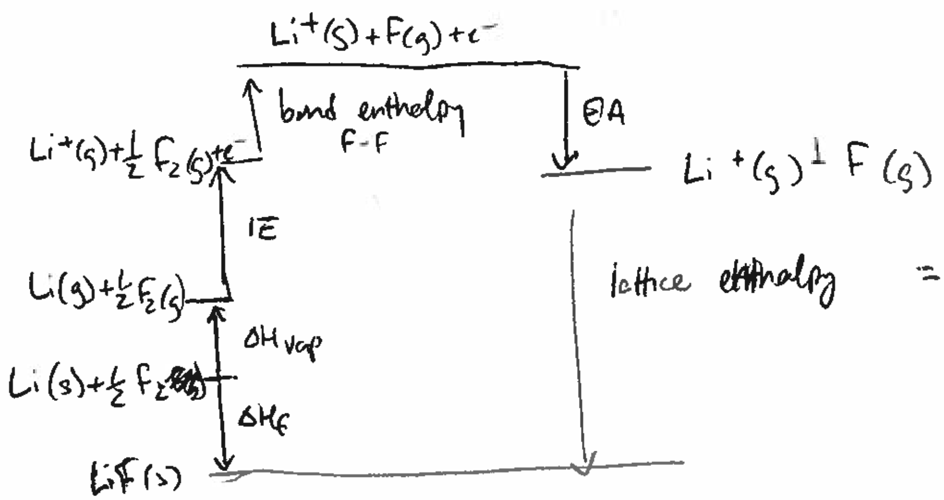
PLTL Worksheet #4:
Ionic Bonding

1. *Born Haber Cycle*
   a. Write out balanced chemical equations for each step in the Born-Haber cycle for KCl(s). Use the following information to calculate the heat of sublimation for potassium:
      Heat of formation for KCl(s) = -437 kJ/mol
      Electron affinity for Cl = -349 kJ/mol
      Ionization energy for K = 418 kJ/mol
      Lattice energy for KCl = 717 kJ/mol
      Heat of formation for Cl(g) = 122 kJ/mol
      Bond dissociation energy for Cl2(g) = 243 kJ/mol

heat of sublimation = 89 kJ/mol



   b. Write out balanced chemical equations for each step in the Born-Haber cycle for LiF(s). Calculate the lattice enthalpy for lithium fluoride, given the following information:
      Enthalpy of sublimation for solid lithium = 161 kJ/mol
      First ionization energy for lithium = 520 kJ/mol
      F-F bond dissocation energy = 154 kJ/mol
      Enthalpy of formation for F(g) = 77 kJ/mol
      Electron affinity for fluorine = -328 kJ/mol
      Enthalpy of formation for solid lithium fluoride = -617 kJ/mol



lattice enthalpy = -1047 kJ/mol

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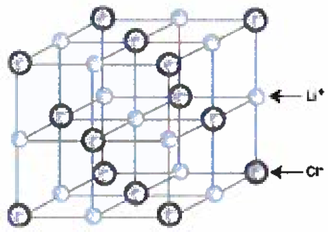
2. *Types of Ionic Solids*
    a. Study the unit cell drawings for the following compounds. For each, determine the empirical formula (by considering the contributions of corner, edge, face or internal atoms), unit cell type, and coordination number about each atom.

i. Rock salt (NaCl) type



Cl → 4 face + 8 corner

$= 4 \times \frac{1}{2} + 8 \times \frac{1}{8}$

$= 4$

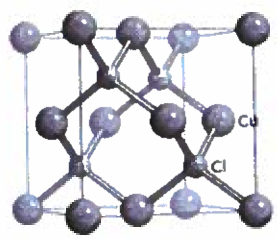
Li → 1 center + 12 edge

$= 1 + 12 \times \frac{1}{4} = 4$

CN=6

LiCl

ii. Zinc Blende (or sphalerite)



Cl → 4 center / internal

$= 4$

Cu → 8 corners + 6 faces

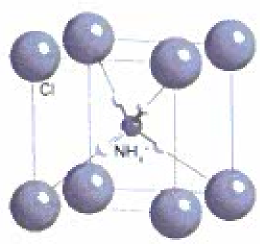
$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2}$

$= 4$

CN=4

CuCl

iii. CsCl structure

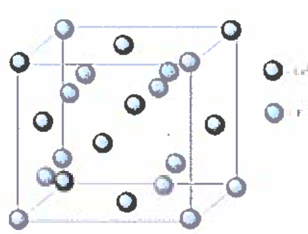


NH_4^+ → 1 center = 1

Cl → 8 × corner = $8 \times \frac{1}{8} = 1$

NH_4Cl

iv. Fluorite



Ca → 8 corners + 6 faces

$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2}$

$= 4$

CN=8

F → 8 internal

$= 8$

CaF_2

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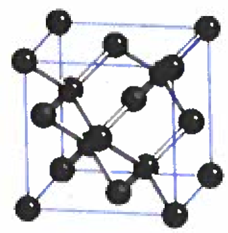
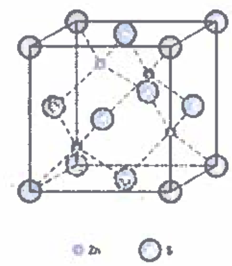
b. The unit cell of diamond is shown on the left, and the unit cell of zinc blende is shown on the right. Calculate the number of carbon atoms in the unit cell of diamond. Show how you arrive at the answer. Calculate the number of zinc and sulfur ions in the unit cell of zinc blende. Show how you arrive at your answer.



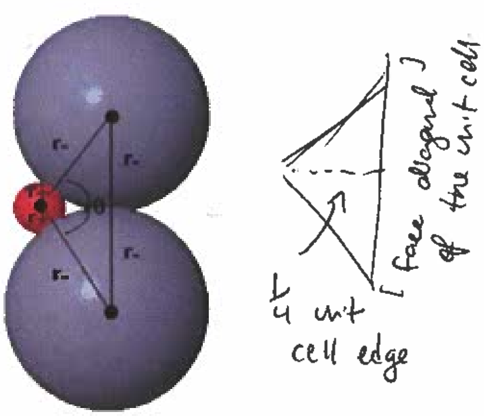


8 in each. (see 2 a. ii) for breakdown)

This is challenging. Skip if you don't have time / use your discretion for the students in the room

3. *Radius Ratios*

a. Derive the limiting ratio for 4-coordination.
Hint:



$r^- = \frac{1}{4} a\sqrt{2}$

$\frac{r^-}{\sqrt{2}} = \frac{1}{4} a$

$r^- + r^+ = \sqrt{\left(\frac{r^-}{\sqrt{2}}\right)^2 + (r^-)^2}$

$\frac{r^+}{r^-} = \frac{\sqrt{6}}{2} - 1 = 0.225$

b. From radius ratios, what is the expected crystal form (or structure type) of the alkali metal chlorides?

The Pauling ionic radii of the alkali metals are

Li+ = 0.60 Å,
Na+ = 0.95 Å;
K+ = 1.33 Å; and
Rb+ = 1.48 Å.

The ionic radius of the chloride anion, Cl− , is 1.67Å.

$\frac{r^+}{r^-}$

LiCl : $\frac{0.60}{1.67} = 0.359$ → ZnS type

NaCl: $\frac{0.95}{1.67} = 0.569$ → NaCl rock salt type

KCl : $\frac{1.33}{1.67} = 0.796$ → CsCl type structure

RbCl : $\frac{1.48}{1.67} = 0.886$ → CsCl type structure

4. *Packing*
   a. Of the closest-packed structures, cubic, body centered cubic and face centered cubic, rank them in terms of %volume.
   b. Can you derive the %volume for each of these?

a. cubic < body centered cubic < face centered cubic

52% 68% 74%

↳ Dr Dunbar pulled the math in her notes from a 2017 Youtube video called "Unit Cell - Simple Cubic, Body Centered Cubic, Face centered cubic crystal lattice structures"