

HW set 3

Chapter 7

①

1. CsCl consists of two interpenetrating simple cubic lattices. Both Cs^+ and Cl^- fill cubic holes. CaF_2 consists of a face-centered Ca^{2+} lattice combined with a simple cubic lattice of F^- . The Ca^{2+} ions fill cubic holes in the F^- lattice, while the F^- ions fill T_d holes in the Ca^{2+} lattice.

2. A unit cell is the motif that, when repeated in three dimensions, gives the full structure of the ionic solid. Since only an integral number of unit cells can be used, the unit cell must contain an integral multiple of the stoichiometry of the formula.

$$\begin{aligned} \text{Na}^+ : & \quad 8 \times \frac{1}{8} = 1 \text{ corner ion} \\ & \quad 6 \times \frac{1}{2} = 3 \text{ Face ions} \\ & \quad 4 \text{ total Na}^+ \text{ ions} \end{aligned}$$

$$\begin{aligned} \text{Cl}^- : & \quad 1 \text{ center ion} \\ & \quad 12 \times \frac{1}{4} = 3 \text{ edge ions} \\ & \quad 4 \text{ total Cl}^- \text{ ions} \end{aligned}$$

The cell contains 4 NaCl formula units.

(2)

3. Formula weight of NaCl: 58.45 g/mol

$$58.45 \frac{\text{g}}{\text{mol}} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ formula units}} \times \frac{4 \text{ formula units}}{1 \text{ unit cell}} \times \frac{1 \text{ cm}^3}{2.167 \text{ g}}$$

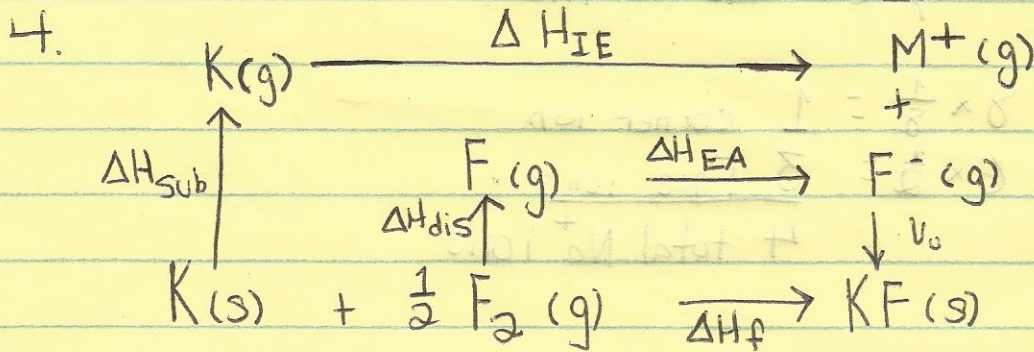
$$= 1.792 \times 10^{-22} \frac{\text{cm}^3}{\text{unit cell}} \quad (\text{Volume of unit cell})$$

$$(1.792 \times 10^{-22} \text{ cm}^3)^{1/3} = 5.638 \times 10^{-8} \text{ cm}$$

The edge of the unit cell consists $2r_+ + 2r_-$.

$$2(107 \text{ pm}) + 2(167 \text{ pm}) = 548 \text{ pm}$$

$$= 5.48 \times 10^{-8} \text{ cm}$$



$$U_0 = \frac{ANZ^+Z^-e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

Any equation you use is fine.

$$A: 1.74756$$

$$n: \text{Average for Ne and Ar} = \frac{7+9}{2} = 8$$

$$U_0 = \frac{(1.74756) (6.02 \times 10^{23}) (+1)(-1) (1.60218 \times 10^{-19} \text{ C})^2 (1 - \frac{1}{8})}{4\pi (8.85419 \times 10^{-12} \text{ C}^2 \text{ m}^{-1} \text{ J}^{-1}) (2.71 \times 10^{-10} \text{ m})}$$

$$r_0 = r_{K^+} + r_{F^-} = 138 \text{ pm} + 117 \text{ pm} = 255 \text{ pm} = 2.71 \times 10^{-10} \text{ m}$$

$$U_0 = -832.7 \text{ kJ/mol}$$

$$\Delta H_{IE} \text{ for K} = 418.8 \text{ kJ/mol}$$

$$\Delta H_{EA} \text{ for F} = -328.0 \text{ kJ/mol}$$

$$\Delta H_{dis} \text{ for F} = \frac{1}{2} (154.8 \text{ kJ/mol}) = 77.4 \text{ kJ/mol}$$

$$\Delta H_{sub} \text{ for K} = 89.62 \text{ kJ/mol}$$

$$U_0 = -832.7 \text{ kJ/mol}$$

$$\Delta H_{sub} \text{ K} = 89.62 \text{ kJ/mol}$$

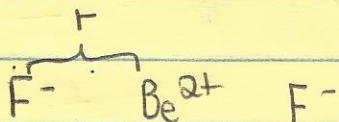
$$\Delta H_{IE} = 418.8 \text{ kJ/mol}$$

$$\Delta H_{EA} = -328.0 \text{ kJ/mol}$$

$$\Delta H_{dis} \text{ F} = 77.4 \text{ kJ/mol}$$

$$\Delta H_f = -574.18 \text{ kJ/mol}$$

5.



The coulombic energy consists of ① the attraction between Be^{2+} and its 2 neighboring F^- ions, and ② the repulsion between the two F^- ions.

$$E_c = \frac{2 Z^+ Z^- e^2}{4\pi\epsilon_0 r} - \frac{Z^+ Z^- e^2}{4\pi\epsilon_0 (2r)}$$

attraction repulsion

$$E_c = \left(2 - \frac{1}{2}\right) \frac{Z^+ Z^- e^2}{4\pi\epsilon_0 r} = \frac{3}{2} \frac{Z^+ Z^- e^2}{4\pi\epsilon_0 r}$$

∴ The Madelung constant $A = \frac{3}{2}$

6. a. The lattice energy released by the attraction of the more highly charged ions for each other more than offsets the large ionization energy and electron affinity.

b. Measure the conductivity of the ions in nonaqueous solution. (Can't do it in water because the O^{2-} is a strong base and will become OH^- . But acetonitrile or methanol might work.) The greater the conductivity of the solution, the greater the charge on the ions.

r smaller
r larger

7.	F ⁻	Cl ⁻	Br ⁻	I ⁻
Li ⁺	119 pm	167 pm	182 pm	206 pm
CN=4	60 pm	0.504 oh ✓	0.359 Tdx	0.330 Tdx
CN=6	79 pm	0.664 oh ✓	0.473 oh ✓	0.434 oh ✓
CN=8	106 pm	0.891 cubic X	0.635 oh ✓	0.582 oh ✓
Na ⁺ CN: 4	113 pm	0.950 } cubic X	0.677 } oh ✓	0.621 oh ✓
	107 pm	0.899 } should be oh	0.641 } oh ✓	0.549 oh ✓
CN=6	132 pm	0.902	0.790 cubic X	0.588 oh ✓
CN=8			0.725 oh ✓	0.519 oh ✓
K ⁺				0.641 oh ✓
CN=4	151	0.788 X cubic	0.904 } cubic X	0.830 } cubic X
CN=6	138	0.862 X cubic	0.826 } Actually oh	0.758 } Actually oh
CN=8	165	0.721 oh ✓	0.988	0.907
Rb ⁺				0.801 cubic X
CN=4				
N/A				
CN=6	166 pm	0.717 } oh ✓	0.994 } cubic X	0.912 } cubic X
CN=8	164 pm	0.726	0.982 } oh	0.901 } oh
				0.806 } cubic X
				0.796 oh



CN = 4

N/A

CN = 6

181 pm

0.657 } oh

0.923 } cubic

0.995 } cubic

0.879 } cubic

CN = 8

173 pm

0.688

0.965

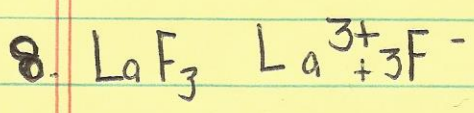
(Both cubic + Oh occur)

0.951

0.810

According to the textbook, many alkali halides share the structure of NaCl. In this lattice, the cation has a coordination number of 6, ~~and~~ filling an octahedral hole of the anion. The anion has a coordination number of 6, filling an octahedral hole of ~~the~~ the cation. The exceptions appear to be CsCl, CsBr, and CsI, which have the Cs⁺Cl⁻ lattice type. In this lattice, the cation has a coordination number of 8 and fills cubic holes of the chloride lattice. The anion has a coordination number of 8 and fills cubic holes of the sodium lattice.

∴ Using a CN of 6 for the cations except Cs in CsCl, CsBr, and CsI, the ionic compounds LiI, NaF, KF, KCl, KBr, RbCl, RbBr, and RbI violate the radius ratio rule.



$$U = \frac{120,200 \nu Z^+ Z^-}{r_0} \left(1 - \frac{34.5}{r_0}\right)$$

(kJ/mol)

ν = # of ions per molecule

$\nu = 4$

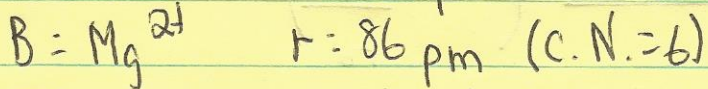
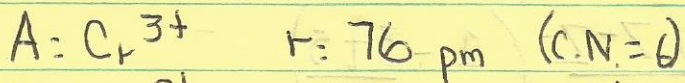
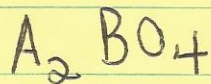
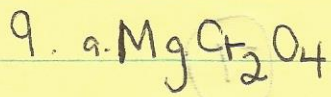
$r_{La^{3+}} = 117.0 \text{ pm (C.N. = 6)}$
 $130 \text{ pm (C.N. = 8)}$
 $r_{F^-} = 119 \text{ pm (C.N. = 6)}$
Use both

a. $r_0 = 236 \text{ pm}$

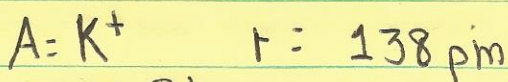
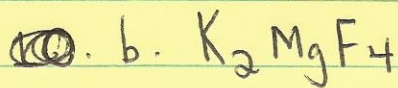
$$U = \frac{120,200(4)(+3)(-1)}{236.0} \left(1 - \frac{34.5}{236.0}\right) = -5215 \frac{\text{kJ}}{\text{mol}}$$

b. $r_0 = 249 \text{ pm}$

$$U = \frac{120,200(4)(+3)(-1)}{249} \left(1 - \frac{34.5}{249}\right) = -4990 \frac{\text{kJ}}{\text{mol}}$$



This corresponds to the spinel structure



Can predict the K_2NiF_4 structure.

10. Diamond is completely covalently bonded in all directions; it consists entirely of σ bonds, and there are no extra electrons to be delocalized.

Graphite consists of stacks of 2-dimensional sheets of C that are aromatic. The delocalization of the π electrons throughout the 2 dimensions makes a good conductor.

11. We know that the more electronegative an atom is, the more tightly it holds its orbitals and therefore the lower they are in energy. Since electronegativity

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increases $Ga < Ge < As$, we expect energy levels to decrease
 $Ga > Ge > As$.

12. CdS

$$\text{Band Gap} = 2.485 \text{ eV} \rightarrow 239.8 \text{ kJ/mol}$$

$$1 \text{ eV} = 96.5 \frac{\text{kJ}}{\text{mol}}$$

$$239.8 \frac{\text{kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ molecules}} = 3.98 \times 10^{-22} \frac{\text{kJ}}{\text{molecules}}$$

$$3.98 \times 10^{-22} \frac{\text{kJ}}{\text{mol}} \times \frac{10^3 \text{ J}}{1 \text{ kJ}} = 3.98 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \frac{\text{m}}{\text{s}})}{3.98 \times 10^{-19} \text{ J}} \times \frac{10^9 \text{ nm}}{1 \text{ m}} = 499 \text{ nm}$$

visible region

13. Infrared radiation runs from about 10^4 cm to 10^{-2} cm in wavelength.

$$E = \frac{hc}{\lambda}$$

$$E = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \frac{\text{m}}{\text{s}})}{10^{-4} \text{ cm}} \times \frac{100 \text{ cm}}{1 \text{ m}} = 2 \times 10^{-19} \text{ J}$$

\downarrow
 $2 \times 10^{-22} \text{ kJ}$

$$E = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \frac{\text{m}}{\text{s}})}{10^{-2} \text{ cm}} \times \frac{100 \text{ cm}}{1 \text{ m}} = 2 \times 10^{21} \text{ J}$$

↓
2 × 10⁻²⁴ kJ

For a mole of the compound,

$$E_1 = (2 \times 10^{-22} \text{ kJ})(6.02 \times 10^{23}) = 120 \text{ kJ/mol}$$

↳ 1.244 eV

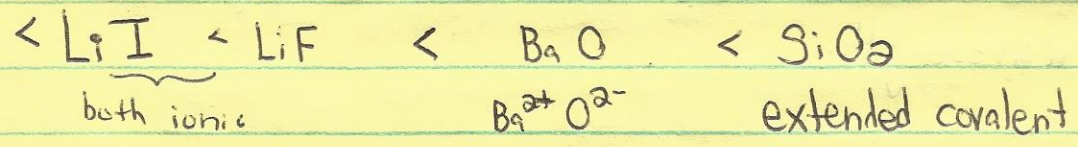
$$E_2 = (2 \times 10^{-24} \text{ kJ})(6.02 \times 10^{23}) = 1.2 \text{ kJ/mol}$$

↳ 0.0124 eV

∴ Si, Ge, α-Sn, GaSb, InAs, InSb, would work well

14. H₂ < Xe < SiCl₄ < H₂O

least polarizable, London dispersion forces	more e ⁻ than H ₂ , London dispersion forces	nonpolar, more e ⁻ than Xe. London dispersion forces	polar - (H bonds)
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F⁻ is smaller than I⁻: ionic, higher charge

∴ Lattice energy of LiF is greater

lattice

15) a. $O=O$ higher bond order

b. C-C should be stronger because the 2p orbitals are more compact and give better overlap than the 3p orbitals.

c. Xe-Xe Only London dispersion (induced dipole-induced dipole) forces are involved here, and the larger atoms (with more e^-) will be more polarizable.

d. $Mg^{2+} O^{2-}$ The coulombic attraction is greater for higher charges

e. Even though Ba^{2+} and Te^{2-} are approximately $r_{Li^+} = 79 \text{ pm}$ $r_{F^-} = 117 \text{ pm}$ twice as big as $Li^+ + F^-$; $r_{Ba^{2+}} = 149 \text{ pm}$ $r_{Te^{2-}} = 207 \text{ pm}$ their higher charge means that they will have the stronger bonding interaction.

for $BaTe$ relation to LiF :
$$E = \frac{(2Z^+)(2Z^-)e^2}{4\pi(2r)\epsilon_0} = \frac{2 \times Z^+ Z^- e^2}{\underbrace{4\pi r \epsilon_0}_{\text{energy for LiF}}}$$

f. The covalent interaction of C-C in diamond is stronger than the ionic interaction of LiF.