

## Chemistry for Earth Sciences

### Practical 2: Electronic Structures, Ions and Ionic Bonding (WORKED SOLUTIONS)

#### 1. Kinetic Energy is

$$2000 \text{ Volts} \times 1.60 \times 10^{-19} \text{ C} \times 1 \text{ Joule}/(\text{Volt-C}) = 3.2 \times 10^{-16} \text{ Joules}$$

$$\text{Since } E_{\text{kin}} = mv^2/2 \text{ then}$$

$$v = (2 E_{\text{kin}}/m)^{1/2} = ((2 * 3.2 \times 10^{-16} \text{ Joules})/(9.11 \times 10^{-31} \text{ kg}))^{1/2}$$
$$= 2.65 \times 10^7 \text{ m/s}$$

$$\text{momentum } p = m*v = 2.4 \times 10^{-23} \text{ kgm/s}$$

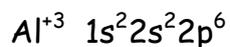
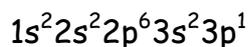
Using deBroglies relation, wavelength is  $h/p$  or

$$6.634 \times 10^{-34} \text{ (Joule-sec)}/p \text{ (kg m/s)} = 2.75 \times 10^{-11} \text{ m}$$

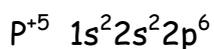
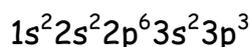
Using Bragg's law for  $n\lambda = 2d \sin(30^\circ)$  we find that  $d = 0.28 \text{ \AA}$  for  $n = 1$ .

2. Work out the electronic configuration (in the form  $1s^2 2s^2 2p^6 \dots$ ) for the following atoms and predict the most likely stable ions. Recall that the number of electronic in the neutral atom will be the same is the atom's atomic number (number of protons).

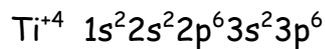
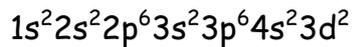
a) Al (atomic number 13)



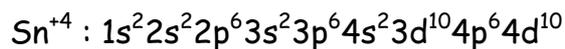
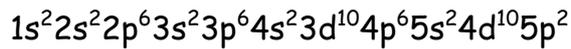
b) P (atomic number 15)



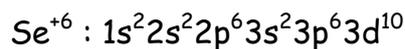
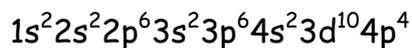
c) Ti (atomic number 22)



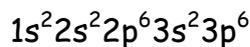
c) Sn (atomic number 50)



d) Se (atomic number 34)



e) Ar (atomic number 18)



No stable ions expected as it already has a closed-shell configuration.

3. Sulfur can lose 6 electrons to adopt a close shell configuration  $1s^2 2s^2 2p^6$  and a +6 oxidation state (as in the  $SO_4^{2-}$  ion) why won't oxygen lose 6 electrons to get the closed shell configuration  $1s^2$ ?

Oxygen is too electronegative. Actually, in the presence of fluorine, we can form strange compounds with oxygen in a positive oxidation state. However this is of no geochemical consequence.

4. Carbon can gain 4 electrons to get a closed shell configuration  $1s^2 2s^2 2p^6$  and a -4 oxidation state (as in methane  $CH_4$ ). Why won't silicon do the same thing?

Silicon is not electronegative enough to stabilize a -4 oxidation state.

5. Rank the following elements in terms of their electronegativity: Si, C, O, Cl, Mg, S and Ca. What pair of atoms should form the most ionic bonds? Which should form the most covalent?

$O \gg Cl > S > C > Si > Mg = Ca$ ; The most ionic bonds will be between oxygen and Ca or Mg. The most covalent bonds will be between any adjacent pair (e.g. O-Cl or C-S). Si, Mg and Ca always exist as cations under geochemical conditions and so could not form bonds with each other owing to the strong repulsion between like-charged ions. Under artificially reducing conditions, if you formed compounds between the neutral atoms such as MgCa, the bonds would be metallic (extremely covalent) since the electronegativity difference between atoms such as Mg and Ca is so low.

6. In olivine,  $(Mg,Fe)_2SiO_4$ ,  $Fe^{+2}$  is in octahedral coordination with oxygen. Using the attached table of Ionic Radii, predict which ions that might substitute for  $Fe^{+2}$  in olivine.

Solution:  $Ni^{+2}$ ,  $Co^{+2}$

7. Which cations might substitute for  $Fe^{+3}$  in hematite ( $Fe_2O_3$ )?

$V^{+3}$ ,  $Al^{+3}$ ,  $Cr^{+3}$ ,  $Ti^{+3}$ ,  $Ni^{+2}$

8. Using Paulings' first rule: predict the coordination number of Ca in  $CaF_2$ . Using Paulings second rule, predict the coordination number of F in  $CaF_2$ . The mineral has cubic symmetry. Can you draw what the structure must be?

Solution: CN of Ca = 8, CN of F is 4

9. Using Pauling's first and second rules, predict the structures of CaO, SrO and BaO.

Solution: All have the NaCl structure with both cations and anions in 6-fold coordination.

10. Using Pauling's first and second rules, predict the structures of crystalline ZnS (sphalerite) and PbS (galena). Note, just use the radius of  $S^{-2}$  in 6-fold coordination without assuming it necessarily has sixfold coordination. In fact, ZnS has a structure with Zn in tetrahedral coordination with S while PbS has a structure with octahedral coordination.

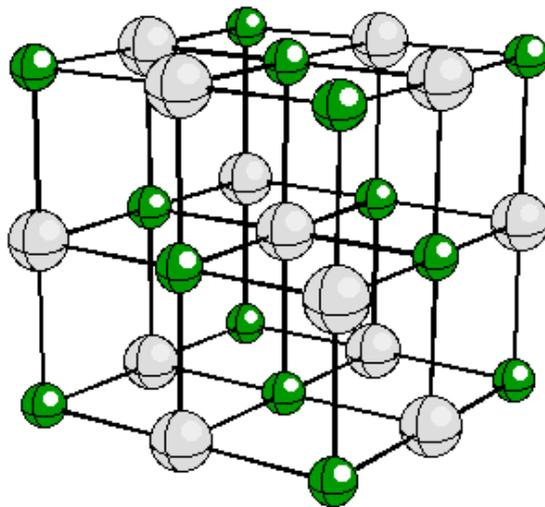
Solution:

For PbS, we are at the borderline: Radius ratio Pb/S =  $1.33/1.70 = 0.78$  implying borderline between 6 and 8-fold coordination of Pb by S. Using Pauling's 2<sup>nd</sup> rule, if Pb is in 6 fold then sulfur would be in 6-fold. If Pb is in 8-fold, then S is in 8-fold.

For ZnS, using Zn(VI) we get a radius ratio of  $0.88/1.7 = 0.51$ ; using Zn(IV) and S(VI) we get  $0.74/1.7 = 0.43$ , also suggesting octahedral coordination.

Hence, the ionic model doesn't work quite so well!

11. In MgO (solid), the O<sup>-2</sup> anions are in a close-packed array. The structure consists of a **unit cell** which is repeated in 3 dimensions. In each unit cell (as shown below), there are 4 formula (MgO) units (convince yourself of this..).



The atomic masses of Mg and O are 24.3 and 16.0 g/mole, respectively. Using the ionic radii of Mg<sup>+2</sup> (VI) and O<sup>-2</sup> (VI), predict the density (in g/cm<sup>3</sup>) of MgO. The experimental density is 3.58 g/cm<sup>3</sup>.

$$\text{Lattice constant} = 2 (R_{\text{Mg}} + R_{\text{O}}) = 2(0.86 \text{ \AA} + 1.26 \text{ \AA}) = 4.24 \text{ \AA}$$

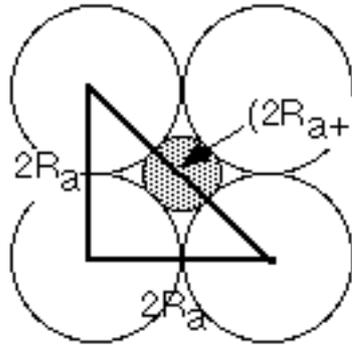
$$\text{Volume of unit cell} = (4.24 \text{ \AA})^3$$

$$\text{Density} = 12 \text{ F.U.} / (4.24 \text{ \AA})^3 \times 40.3 \text{ g/mole FU} \times 1 \text{ mole} / 6.023 \times 10^{23} \text{ F.U.}$$

$$\times (1 \text{ \AA})^3 / (10^{-8} \text{ cm})^3$$

12. Solution:

**6-Fold coordination (one plane)**



$$(2R_a)^2 + (2R_a)^2 =$$

$$(2R_a + 2R_b)^2$$

$$(1 + R_b/R_a)^2 = 2$$

$$R_b/R_a = 0.414$$

13. a) Calcium sulfide has a formula mass of = 72.14 g/mole and a density of 2.59 g/cm<sup>3</sup>. It has the cubic NaCl structure (like MgO); the length of the unit cell is 2 times the Ca-S bond length and there are 4 formula units per unit cell. Work out the Ca-S bond length. If the ionic radius of Ca<sup>+2</sup> is 1.14 Å, what is the ionic radius of S<sup>-2</sup> in CaS?

Solution:

72.13 g/mole × 1cm<sup>3</sup>/2.59g × 1mole/6.023×10<sup>23</sup> F.U. × 4 FU/unit cell

$$\times (10^8 \text{ \AA})^3/\text{cm}^3 = 185.0 \text{ \AA}^3/\text{unit cell}$$

Volume = (2 R<sub>Ca-S</sub>)<sup>3</sup> so R<sub>Ca-S</sub> = 2.85Å and R(S<sup>-2</sup>) = 1.71 Å (in good agreement with Shannon's ionic radius for S<sup>-2</sup>).

b) Galena, PbS has the same structure as CaS and the dimension of the unit cell cube is 5.936Å. If the ionic radius of S<sup>-2</sup>, is 1.70, what is the ionic radius of Pb<sup>+2</sup> in Galena? How does it compare with Shannon's (1976) value?

Ionic radius of Pb in PbS is smaller than Shannon's value (or Ionic radius of S<sup>-2</sup> in PbS is smaller than that of S<sup>-2</sup> in CaS)