

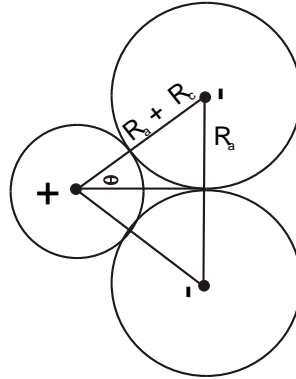
**PRINCIPLES OF GEOCHEMISTRY**  
**GEOL 423**  
**FALL 2009**  
**PROBLEM SET 4 – ANSWER KEY**

Problem 1:

- a)  $\chi_I - \chi_{Li} = 2.5 - 1.0 = 1.5$ ; 43% ionic, 57% covalent.
- b)  $\chi_{Cl} - \chi_{Ni} = 3.0 - 1.8 = 1.2$ ; 30% ionic, 70% covalent.
- c)  $\chi_{Cl} - \chi_{Ag} = 3.0 - 1.9 = 1.1$ ; 26% ionic, 74% covalent.
- d)  $\chi_{Cl} - \chi_{Ga} = 3.0 - 1.6 = 1.4$ ; 39% ionic, 61% covalent.
- e)  $\chi_C - \chi_{Si} = 2.5 - 1.8 = 0.7$ ; 12% ionic, 88% covalent.

Problem 2:

We only need to draw the three ions involved here.



$$\theta = 109.5/2 = 54.75^\circ$$

$$\sin \theta = r_a / (r_a + r_c)$$

$$\sin 54.75^\circ = r_a / (r_a + r_c)$$

$$0.8166 = r_a / (r_a + r_c)$$

$$0.8166r_a + 0.8166r_c = r_a$$

$$0.8166r_c = 0.1834r_a$$

$$r_c / r_a = 0.225$$

Problem 3:

We need to use the radius ratio rule. Consider the data in the following table:

CN	6	8
$Sr^{2+}$	1.21 Å	1.33 Å
$Ca^{2+}$	1.08 Å	1.20 Å
$O^{2-}$	1.32 Å	1.34 Å

We can calculate the following radius ratios.

CN	6	8
Sr <sup>2+</sup> /O <sup>2-</sup>	0.92	0.99
Ca <sup>2+</sup> /O <sup>2-</sup>	0.82	0.90

The critical radius ratio for CN = 8 is 0.732, so these data suggest that both Sr<sup>2+</sup> and Ca<sup>2+</sup> favor eight coordination with O<sup>2-</sup>. However, because Sr<sup>2+</sup> is larger, it should prefer to go into aragonite, where the cation site is larger than that in calcite.

Problem 4:

We must use Goldschmidt's Rules to determine the answer.

Rule 1 –  $r_{\text{Sr}^{2+}}$  (CN 8) = 1.33 Å;  $r_{\text{Cd}^{2+}}$  (CN 8) = 1.15 Å. The radii are 13.5% different, which is within 15%.

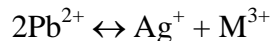
Rule 2 – Sr<sup>2+</sup> and Cd<sup>2+</sup> are both divalent (same charge).

Rule 3 – Ionic potentials are 1.50 and 1.74 for Sr<sup>2+</sup> and Cd<sup>2+</sup>, respectively. So Cd<sup>2+</sup> is preferred (but remember that this rule does not dictate whether substitution will occur, only which ion will be preferred if substitution can occur by rules 1 and 2!).

Rule 4 -  $\chi_{\text{Cd}} = 1.7$  and  $\chi_{\text{Sr}} = 1.0$ . The electronegativity difference may be too great to permit extensive substitution.

Problem 5:

We must have a trivalent (+3) ion to balance charge in a coupled substitution:



We are also told that this ion is chalcophile, so we should be looking for a metal on the right side of the periodic table, one with a relatively high electronegativity.

$$r_{\text{Pb}^{2+}} \text{ (CN 6)} = 1.26 \text{ \AA}; \chi_{\text{Pb}} = 1.8$$

The only really good possibility is Bi<sup>3+</sup>

$$r_{\text{Bi}^{3+}} \text{ (CN 6)} = 1.10 \text{ \AA} \text{ (12.7\% difference in ionic radii)}; \chi_{\text{Bi}} = 1.9.$$

Problem 6:

The following are the preferred solutions, but others may be possible:

- $r_{\text{Rb}^{+}} = 1.57 \text{ \AA}; \chi_{\text{Rb}} = 0.8$  should substitute for K<sup>+</sup>:  $r_{\text{K}^{+}} = 1.46 \text{ \AA}; \chi_{\text{K}} = 0.8$ .
- $r_{\text{Sr}^{2+}} = 1.21 \text{ \AA}; \chi_{\text{Sr}} = 1.0$  should substitute for Ca<sup>2+</sup>:  $r_{\text{Ca}^{2+}} = 1.08 \text{ \AA}; \chi_{\text{Ca}} = 1.0$ .
- $r_{\text{Ga}^{3+}} = 0.70 \text{ \AA}; \chi_{\text{Ga}} = 1.6$  should substitute for Al<sup>3+</sup>:  $r_{\text{Al}^{3+}} = 0.61 \text{ \AA}; \chi_{\text{Al}} = 1.5$  (Fe<sup>3+</sup> is also acceptable).
- $r_{\text{Sc}^{3+}} = 0.83 \text{ \AA}; \chi_{\text{Sc}} = 1.3$  should substitute for Fe<sup>3+</sup>:  $r_{\text{Fe}^{3+}} = 0.63\text{-}0.73 \text{ \AA}; \chi_{\text{Fe}} = 1.8$  (Mg<sup>2+</sup> and Al<sup>3+</sup> are also acceptable).

- e)  $r_{\text{Li}^+} = 0.82 \text{ \AA}$ ;  $\chi_{\text{Li}} = 1.0$  should substitute for  $\text{Mg}^{2+}$  provided the appropriate coupled substitution occurs:  $r_{\text{Mg}^{2+}} = 0.80 \text{ \AA}$ ;  $\chi_{\text{Mg}} = 1.2$ .
- f)  $r_{\text{Ba}^{2+}} = 1.44 \text{ \AA}$ ;  $\chi_{\text{Ba}} = 0.9$  should substitute for  $\text{K}^+$ :  $r_{\text{K}^+} = 1.46 \text{ \AA}$ ;  $\chi_{\text{K}} = 0.8$ .
- g)  $r_{\text{Ge}^{4+}} = 0.62 \text{ \AA}$ ;  $\chi_{\text{Ge}} = 1.8$  should substitute for  $\text{Si}^{4+}$ :  $r_{\text{Si}^{4+}} = 0.48 \text{ \AA}$ ;  $\chi_{\text{Si}} = 1.8$  ( $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  are also possible).
- h)  $r_{\text{REE}^{3+}} = 1.13\text{-}0.94 \text{ \AA}$ ;  $\chi_{\text{REE}} = 1.1\text{-}1.2$  should substitute for  $\text{Ca}^{2+}$ :  $r_{\text{Ca}^{2+}} = 1.08 \text{ \AA}$ ;  $\chi_{\text{Ca}} = 1.0$ .
- i)  $r_{\text{Se}^{6+}} = 0.42 \text{ \AA}$ ;  $\chi_{\text{Se}} = 2.4$  should substitute for  $\text{S}^{6+}$ :  $r_{\text{S}^{6+}} = 0.30 \text{ \AA}$ ;  $\chi_{\text{S}} = 2.5$ .
- j)  $r_{\text{Ni}^{2+}} = 0.77 \text{ \AA}$ ;  $\chi_{\text{Ni}} = 1.8$  should substitute for  $\text{Mg}^{2+}$ :  $r_{\text{Mg}^{2+}} = 0.80 \text{ \AA}$ ;  $\chi_{\text{Mg}} = 1.2$  or  $\text{Fe}^{2+}$ :  $r_{\text{Fe}^{2+}} = 0.69\text{-}0.86 \text{ \AA}$ ;  $\chi_{\text{Fe}} = 1.8$ .
- k)  $r_{\text{Tl}^+} = 1.58 \text{ \AA}$ ;  $\chi_{\text{Tl}} = 1.8$  may substitute for  $\text{K}^+$ :  $r_{\text{K}^+} = 1.46 \text{ \AA}$ ;  $\chi_{\text{K}} = 0.8$ , although rule #4 may limit substitution (in fact, this substitution actually occurs in nature).

#### Problem 7:

We need to calculate the bonds strengths. The Mg-O bond strength is  $2/4 = 1/2$  and the Cr-O bond strength is  $3/6 = 1/2$ .

The sum of the bond strengths reaching oxygen is then:  $1 \times 1/2 + 3 \times 1/2 = 2$ , which is equal to the absolute value of the charge on oxygen, -2. So Pauling's 2<sup>nd</sup> rule is obeyed.