Name
Section
Rec TA

Side 1 of 3

Ch 1a, Problem Set Nine
Due Friday, Dec. 1, 2006
at 4 PM in the Drop Box

Problems one and four are designated (⚐) as "no collaboration" problems.

⚐ 1. (20 Points) Determine the oxidation number of the metal in each of the following complexes:

   a. $[PtCl_6]^{2-}$
   b. $[PtCl_4]^{2-}$
   c. $Mn(CO)_5Cl$
   d. $[Rh(SO_4)(NH_3)_5]^{1+}$

2. (40 Points, 10 Each) In lecture you learned of three different forms of packing in crystals which have a 1:1 stoichiometry, face centered cubic, body centered cubic, and the zinc blende structure. Crystals arrange into these structures based on the sizes of the cations and anions involved.

   I. Determine the packing efficiency for each of these three structures as a function of a cationic radius r_c and an anionic radius r_a. You may treat these ions as hard spheres to simplify the problem.

   II. Plot these three packing efficiencies as a function of r_c for structures involving a chloride anion. You need only plot the efficiency from $r_c = 0$ to $r_c = 3r_{chloride}$. The ionic radius of chloride may be found on page 44 of Gray.

   III. From your answers in parts a. and b., over what values of r_a would you expect chlorine to bond in a body centered cubic arrangement?

   IV. Over what values of r_a would you expect chloride to bond in a face centered cubic arrangement? Zinc blende arrangement?

3. (20 Points) Consider the following arrays of point charges. For each array calculate the Madelung constant for the central charge. Assume that all charges are equal, and that the spacing between charges is uniform and identical in both the x and y dimensions.

   a. + – + – + – + – + – + – +

   b. + – + – + – + + – + – + –

   c.

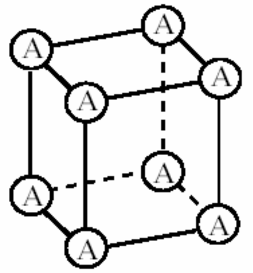
+	–	+	–	+
–	+	–	+	–
+	–	+	–	+
–	+	–	+	–
+	–	+	–	+

4. (30 Points) Using the 18-electron rule, predict *x* in the following transition metal complexes. [*Hint: Use the neutral/covalent counting method.*]

   a. $\left[\mathrm{RuCl(OH_2)_5}\right]^{x+}$
   b. $\left[\mathrm{Ru}\left(\eta^4\text{ - 2,2'–bipy}\right)_x\right]^{2+}$
   c. $\left[\mathrm{Co}\left(\eta^x - \mathrm{C_5}H_5\right)_2\right]^{1+}$
   d. $\mathrm{W}\left(\eta^x - \mathrm{C_5H_5}\right)\left(\eta^5 - \mathrm{C_5H_5}\right)\left(\mathrm{CO}\right)_2$
   e. $[\mathrm{Cr(CO)}_x(\eta^5\text{-}\mathrm{C_5H_5})]_2$

5. (50 Points) As you saw in problem one and in lecture, crystals adopt various structures according to the relative size of the cations and anions. The spaces filled are usually either octahedral or tetrahedral in geometry.

   I. (10 Points) In the picture at right, ion A is at the corners of a primitive cubic unit cell. Put in ion B such that A and B together form a face-centered cubic (fcc) crystal. What is the stoichiometry of the resultant solid (express the answer in terms of a relative stoichiometric formula: A_xB_y)?



   II. (10 Points) If ion C fills in all of the tetrahedral spaces of the fcc crystal from part (a.), what is the stoichiometry of the resultant solid (in terms of $A_xB_yC_z$)?

   III. (30 Pts, 5 Ea) Using the ionic radii given in Gray (page 44) and the table below, predict crystal packing structures for the following compounds. Show your work!

      a. MgS
      b. BaO
      c. RbF
      d. NaBr
      e. LiI
      f. KI

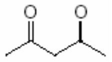
Limiting ratio of cationic radius to anionic radius	**Lattice type**
> 0.23	Zinc blende
> 0.41	Face-centered cubic (fcc or rock salt)
> 0.75	Body-centered cubic (bcc)

6. (40 Points) In lecture, coordination complexes with 18 electrons around the metal center were discussed which included CO, allyl, and cyclopentadienyl ligands. For each of the following ligands, determine the number of electrons that it donates to the metal center, assuming that the 18-electron rule is observed for all of the example complexes. [*Note: You may use either the ionic or the covalent/neutral counting method EXCEPT where the ligand is listed as an ion. In those cases, you must use the ionic counting method. Label each answer with the counting method used.*]

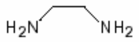
   a. cyanide (CN^-) complex: $[Fe(CN)_6]^{4-}$

   b. carbene (CH_2) complex: $Ta(CH_3)(\eta^5-C_5H_5)_2(CH_2)$

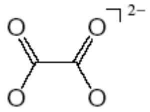
   c. acetylacetone ("acac") complex: $[Mn(CO)_2(acac)_2]^{1+}$



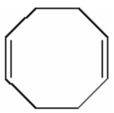
   d. ethylenediamine ("en") complex: $[Pt(en)_2Cl_2]^{2+}$



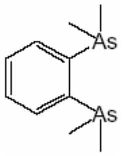
   e. oxalate ("ox") complex: $[Co(ox)_3]^{3-}$



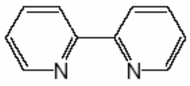
   f. cyclooctadiene ("cod") complex: $Ni(cod)_2$



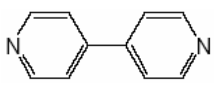
   g. o-phenylene *bis*(dimethylarsine) ("diars") complex: $Mo(CO)_4(diars)$



   h. 2,2'-bipyridine ("2,2'-bipy") complex: $Ru(2,2'-bipy)_2Cl_2$



   i. 4,4'-bipyridine ("4,4'-bipy") complex: $[Cu(4,4'-bipy)_4]^{1+}$



   j. terpyridine ("terpy") complex: $[Re(CO)_3(terpy)]^{1+}$