CHEMISTRY 362
Descriptive Inorganic Chemistry

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Examination II  March 25, 2015

<table>
<thead>
<tr>
<th>Question</th>
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<tr>
<td>I</td>
<td>16</td>
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<td>III</td>
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<td>IV</td>
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<td>V</td>
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<td></td>
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<tr>
<td>Bonus</td>
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<tr>
<td><strong>Total</strong></td>
<td><strong>105</strong></td>
<td></td>
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</tbody>
</table>

Useful Formulae:

\[ 2\sqrt{S (S + 1)} \]
\[ 2S + 1_L \]

<table>
<thead>
<tr>
<th>radius ratio</th>
<th>predicted coordination number of cations</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.15</td>
<td>( \Rightarrow ) 2</td>
</tr>
<tr>
<td>0.15 – 0.22</td>
<td>( \Rightarrow ) 3</td>
</tr>
<tr>
<td>0.22 – 0.41</td>
<td>( \Rightarrow ) 4</td>
</tr>
<tr>
<td>0.41 – 0.73</td>
<td>( \Rightarrow ) 6</td>
</tr>
<tr>
<td>&gt; 0.73</td>
<td>( \Rightarrow ) 8</td>
</tr>
</tbody>
</table>

An Aggie does not lie, cheat or steal or tolerate those who do.

Signature: __________________________________________

Print Name: __________________________________________
I. a) The solid phase of elemental sodium is described as sodium atoms packed in a body-centered cubic arrangement. Making use of cube a below, place atoms in or on it, to illustrate the unit cell for elemental sodium. How many atoms are in the unit cell of the bcc, and what is the coordination number of sodium (i.e., how many nearest neighbors does Na have?)

\[ \text{CN of Na} = 8 \] \hspace{1cm} \text{BCC (a)}

\[ \text{CN of Po} = 6 \] \hspace{1cm} \text{sc (b)}

b) Polonium crystallizes in a simple cubic unit cell. Use cube (b) above and illustrate-- how many atoms are in the unit cell of the simple cubic and what is the coordination number of Po in the unit cell? Which is more space efficient, simple cubic or body centered cubic?

\text{BCC is more space efficient.}

c) Use the third cube, (c), to illustrate the cesium chloride unit cell. Draw a second unit cell, attached to the right face of the cube. With this drawing, identify the nearest neighbors of Cs\(^+\) and the 2\(^{nd}\) nearest neighbors.

Nearest neighbours of Cs\(^+\) \(\Rightarrow\) 8 Cs\(^-\) ions

2\(^{nd}\) nearest neighbours of Cs\(^+\) \(\Rightarrow\) 6 Cs\(^+\) ions

d) Sodium’s neighbor in the periodic table, magnesium, adopts a hexagonal close-packed structure. The density of one of these metals is 1.74 g/cc and that of the other is 0.97 g/cc. Which is which? Give a reason for your choice.

The atoms per unit cell of Mg (in HCP structure) = \( (12 \times \frac{1}{6}) + (2 \times \frac{1}{2}) + 3 = 6 \)

And has a packing fraction of 78%.

While atoms species in BCC structure has \((8 \times \frac{1}{8}) + 1 = 2\) atoms per unit cell

With a packing fraction of 68%. Hence Mg should have a higher density of 1.74 g/cc compared to Na having 0.97 g/cc.

e) In contrast to magnesium whose solid structure is hcp, copper adopts a cubic close-packed structure. Their properties of ductility, electrical and thermal conductivities are quite different. How do they differ? Give the reason(s) why.

Cubic close packed structures have four sets of two parallel planes. These planes can slide over each other which provides the characteristic features (physical) like ductility, electrical and thermal conductivity.
II. Ionic Salts

1. Consider the equation at right. Define the symbols as requested and describe by a concise descriptive sentence.

\[ U_L = \frac{N_0 A z^+_z e^2}{4 \pi \varepsilon_0 r_0} \left( 1 - \frac{1}{n} \right) \]

\( \Delta U_L \) : lattice energy; standard molar enthalpy change accompanying the formation of gaseous ions from solid

A Madelung constant: represents repulsion between ions at short range

r_o distance between the centers of neighboring cations & anions also represents the "scale" of the unit cell

N_o Avogadro's constant

2. What is the significance of the 1/n term in the equation? Born exponent: determined by measuring the compressibility of solid.

3. The melting point of NaF is 993°C and that of MgO is 2800°C. What factor or factors in the above equation will most likely account for the difference? (Hint: Assume both crystallize in the rock salt structure.) For NaF \( |z^+_z + 2^-| = 1 \) while for MgO \( |2^+ + 2^-| = 4 \) i.e. the charge of the cations & anions are responsible for the difference.

4. Use the following thermodynamic data to create a Born-Haber Cycle. Label each process and calculate the lattice energy of MgBr_2 (s).

<table>
<thead>
<tr>
<th>Step:</th>
<th>( \Delta H^0 ) kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sublimation of Mg (s)</td>
<td>+148</td>
</tr>
<tr>
<td>Ionization of Mg^{0} (g) to Mg^{2+} (g)</td>
<td>+2187</td>
</tr>
<tr>
<td>Vaporization of Br_2 (l)</td>
<td>+31</td>
</tr>
<tr>
<td>Dissociation of Br_2 (g)</td>
<td>+193</td>
</tr>
<tr>
<td>Electron gain (affinity) by Br^{0} (g)</td>
<td>-331</td>
</tr>
<tr>
<td>Formation of MgBr_2 (s)</td>
<td>-524</td>
</tr>
</tbody>
</table>

\[ \Delta H_f = \left[ \Delta H_{sub} + \left( \frac{1}{2} \right) \Delta H_{nep} \right]_{Mg} + \left[ \Delta H_{nep} \right]_{Br} + \Delta H_{BDE} + 2 \Delta E \]

\[ \Delta H_f = 1897 + LE \]

\[ \Delta H_f = 1897 + LE \]

\[ LE = -524 - 1897 = -2421 \text{ kJ/mol} \]
III. **More Solid structures; Needed ionic radii data:**

\[ \text{O}^{2-} = 1.25 \text{ Å}; \text{Mg}^{2+} = 0.86 \text{ Å}; \]
\[ \text{Al}^{3+} = 0.53 \text{ Å}; \text{Fe}^{2+} = 0.77 \text{ Å}; \text{Fe}^{3+} \text{ (high spin)} = 0.78 \text{ Å} \]

The mineral magnetite, Fe₃O₄, is naturally occurring (found sometimes along the beach—black stuff). As its name suggests, magnetism is associated with this ore. The oxidation states of the iron are 2⁺ and 3⁺, and its structure is related to that of spinel, MgAl₂O₄. (Recall that in spinel the oxides are in a ccp lattice with certain cations fitted into octahedral holes and the other cations into the Td holes.)

1. Use the graphic at right of two layers of a close packing array of spheres (in ionic salts the spheres are typically the larger anions) to identify an octahedral "hole" and a tetrahedral "hole". Point to each by an arrow and label.

2. Given the ionic radii above, which ion Mg²⁺ or Al³⁺ is expected from radius ratio predictions to fit into which hole?

\[ \frac{\text{y}_{\text{Mg}^{2+}}}{\text{y}_{\text{O}^{2-}}} = 0.688 \Rightarrow \text{oh hole}. \]
\[ \frac{\text{y}_{\text{Al}^{3+}}}{\text{y}_{\text{O}^{2-}}} = 0.424 \Rightarrow \text{td hole}. \]

\[ \text{Although, it just exceeds 0.41 (as the limiting ratio for Td "} \]

\[ \text{hole" it should be in the Td hole"} \]

3. Magnetite is said to be an "inverse" spinel. What might that mean? Why might that happen?

Spinel: A²⁺B³⁺⁴ O²⁻ are normal spinels with larger cations filling up oh holes, and smaller cations going for td holes.

In inverse spinels the larger cations swap sites in Td holes and smaller cations go for oh holes. In Fe₃O₄ which is Fe²⁺(Fe³⁺)₂O₄ the \[ \text{Fe}^{3+} \text{ (high spin)} \]

\[ \text{y}_{\text{Fe}^{2+}} (0.77 \text{ Å}) \text{. Hence Fe}²⁺ \text{ goes for Td hole, } \text{ & Fe}^{3+} \text{ fills oh hole.} \]

4. Give the electronic configurations of Fe²⁺ and Fe³⁺. What is the spin only magnetic moment of a single high spin (all d-electrons unpaired) Fe³⁺ ion within this mineral? What is its Term Symbol?

\[ \text{Fe}^{2+} = [\text{Ar}] 3dⁿ, \quad 3d ≪ \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \text{, } \sum m_l = l = 0 \Rightarrow S \]
\[ \text{Fe}^{3+} = [\text{Ar}] 3dⁿ = [\text{Ar}] 3d ² \text{, } 2m_s = s = \frac{5}{2} \text{, } 2s + 1 = 6 \]

\[ \mu_{\text{Spin onal}} = 2\sqrt{s(s+1)} = 8.92 \text{ B.M.} \]

\[ \lambda \text{, Fe}^{3+} \]
IV. Semi-conductors and other solids

1. a) Which of the graphics given below describe the “bands” of delocalized molecular orbitals of n-type semi-conductors and the p-type semi-conductors? Place your answer on the appropriate line below the graphic.

2. a) In the following list, circle the element that is an intrinsic semi-conductor. b) From the same list of components, formulate examples of an extrinsic semi-conductor comprised of a major material and a dopant for the n-type and p-type semi-conductors. Place your answer in the appropriate line below.
   
   Note, not all of the following components can be used:

   C  Al  Si  Li  P

   Type:  p-type  n-type
   Example:  Al into Si (extrinsic semi-conductor)  P into Si (extrinsic semi-conductor)

3. Which of the pure elements in the list above is (are) a molecular solid?  Phosphorus, Carbon.

4. All of the elements in the above list react with oxygen to form oxides. Give the formulae of these oxides. Identify which oxide is a gas, which is (are) a molecular solid(s) at room temperature, which has a cage structure, and which is (are) an ionic solid(s).

   \[ \begin{align*}
   C^0 + O_2 & \rightarrow \text{CO}_2(g) \\
   2C + O_2 & \rightarrow 2\text{CO}_2(g) \\
   \text{Si}^0 + O_2 & \rightarrow \text{SiO}_2(s) \\
   4\text{Li}^0 + 3O_2 & \rightarrow 2\text{Li}_2\text{O}_3(s) \\
   P^0 + 5O_2 & \rightarrow \text{P}_4\text{O}_{10}(s) \\
   P^0 + 3O_2 & \rightarrow \text{P}_4\text{O}_{6}(s)
   \end{align*} \]

   gas  CO, CO\_2  cage structure  P\_4O\_10, P\_4O\_6  ionic solid  Al\_2O\_3, Li\_2O  molecular solid  \( \text{[SiO}_2\text{]}_n \)
V. Review from last exam.
1. Give the electronic configurations (KK $\sigma_{2s}^2 \ldots$) of NO, NO$^+$, and NO$^-$. 

A) What is the bond order and what is the ground state term symbol for each?

$$
\begin{align*}
\text{NO} & \quad \text{KK } \sigma_{2s}^2 \quad \Omega_{2s}^2 \quad \sigma_{2p_x}^2 \quad \pi_{2p_y}^1 \quad \pi_{2p_z}^1 \\
\text{NO}^+ & \quad \text{KK } \sigma_{2s}^2 \quad \Omega_{2s}^2 \quad \sigma_{2p_z}^2 \quad \pi_{2p_y}^4 \quad \pi_{2p_x}^4 \\
\text{NO}^- & \quad \text{KK } \sigma_{2s}^2 \quad \Omega_{2s}^2 \quad \sigma_{2p_z}^2 \quad \pi_{2p_y}^4 \quad \pi_{2p_x}^5 \\
\end{align*}
$$

$$
\begin{align*}
\text{Bond Order} & = \frac{1}{2} \sum (\text{Occupied Orbitals}) \\
\text{Term Symbol} & = \frac{1}{2} \sum (\text{Energy Levels})
\end{align*}
$$

B) Which has the shortest N-O distance? \text{NO}$^+$

C) Which is isoelectronic with N$_2$? \text{NO}$^+$

D) Which is isoelectronic with O$_2$? \text{NO}$^-$

2. Diborane, B$_2$H$_6$, and ethane, C$_2$H$_6$ (eclipsed configuration), have the same formula but quite different structures.

A) Give the Lewis structure and geometrical structure of each; on your drawings of the structures, identify at least three symmetry elements in each, and assign each to their respective symmetry point groups.

B) Describe the connection of the two monomeric units in terms of orbital overlap that make up the bonds. Which is the electron deficient molecule?
Bonus: With respect to the compound $B_2H_6$, answer the following questions.

a) Sketch the orbital overlap that accounts for one localized $B - H_{\text{terminal}}$ bond.

$$\psi^{\text{bonding/bridged}} = H_{1S} + (B_{\text{sp}^3} + B_{\text{sp}^3})$$

b) Sketch the SALC that is the HOMO of diborane:

$$\psi^{\text{bonding/bridged}} = H_{1S} + (B_{\text{sp}^3} + B_{\text{sp}^3})$$

(c) Give and sketch the orbital combination that accounts for the anti-bonding orbital in the bridge bond of diborane.

$$\psi^{\text{bridged}} = H_{1S} - (B_{\text{sp}^3} + B_{\text{sp}^3})$$

d) Give and sketch the SALC that is the non-bonding orbital of the bridge in diborane: $\psi^{\text{non-bonding}} = ?$

$$\left( B_{\text{sp}^3} - B_{\text{sp}^3} \right)$$

e) Give a MO energy level diagram for the bridge bonding of diborane. Label the levels and assign electrons. What is the bond order of this delocalized bridge bond?

\[ \text{bond order} = \frac{2}{3} = 0.67 \]