CHEMISTRY 362
Descriptive Inorganic Chemistry
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Exam 3
April 24, 2015

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

Signature: ____________________________________________

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ANSWER KEY EXAM 3

20pt1. A. A blast furnace produces the conditions required to reduce iron oxides with carbon. A schematic diagram of such a blast furnace, depicting various reactions with their temperature profile, is shown below. Classify these reactions as acid-base or redox reactions. For redox reactions:

i) Indicate the change in oxidation number.
ii) Indicate the oxidant and the reductant.
iii) One of the redox reactions is either a comproportionation or a disproportionation reaction. Label that reaction with appropriate reaction type.

\[
\text{Reaction 1: } \text{Redox}\quad \text{Oxidant}\quad \text{Reductant} \quad 4 \quad \text{pts}
\]

\[
\text{Reaction 2: } \text{acid/base}\quad \text{Lux-Flood} \quad 1 \quad \text{pts}
\]

\[
\text{Reaction 3: } \text{Redox}\quad Fe^{III} \rightarrow Fe^{II} \quad C^{II} \rightarrow C^{IV} \quad 2 \quad \text{pts}
\]

\[
\text{Reaction 4: } \text{Redox; Comproportionation} \quad C^0 \rightarrow C^{II} \quad C^{IV} \rightarrow C^{II} \quad 4 \quad \text{pts}
\]

\[
\text{Reaction 5: } \text{Redox} \quad Fe^{II} \rightarrow Fe^{0} \quad C^{II} \rightarrow C^{IV} \quad 2 \quad \text{pts}
\]

\[
\text{Reaction 6: } \text{acid-base} \quad 1 \quad \text{pts}
\]

---

B. Identify the redox half reactions relating to the lithium (disposable) battery. Give the oxidation state changes. What is the oxidant? What is the reductant?

\[
\text{Li}^0 + \text{MnO}_2 \rightarrow \text{LiMnO}_2
\]

Anode reaction: \[
\text{Li}^0 \rightarrow \text{Li}^+ + e^-
\]

Cathode reaction: \[
\text{MnO}_2 + e^- \rightarrow \text{MnO}_2^-
\]

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MnO\textsubscript{2} = \text{oxidant}; Li\textsuperscript{0} = \text{reductant}

---

C. Redox half reactions are important to the discharge and recharging processes of the lithium ion battery. Give oxidation states of the cobalt in the following reactions:

i) Overdischarge: \[
\text{Li}^+ + e^- + \text{LiCoO}_2 \rightarrow \text{Li}_2\text{O} + \text{CoO (ppt)}
\]

ii) Overcharge (by 5.2 V): \[
\text{LiCoO}_2 \rightarrow \text{Li}^+ + \text{CoO}_2 + e^-
\]

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II. Redox Questions

1. The Latimer diagram expressing the interconversions of ferric (Fe³⁺), ferrous (Fe²⁺), and iron(0) is given below.

(a) Give a balanced equation for the possible disproportionation of Fe²⁺ to Fe³⁺ and Fe⁰

\[ \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} \rightarrow \text{Fe}^{0} \]

\[ 2\text{Fe}^{2+} \rightarrow \text{Fe}^{0} + 2\text{Fe}^{2+} \]

\[ 3\text{Fe}^{2+} \rightarrow \text{Fe}^{2+} + 2\text{Fe}^{2+} \]

\[ \text{Fe}^{3+} + \text{e}^{-} \rightarrow \text{Fe}^{2+} \]

\[ \text{Fe}^{3+} \rightarrow 2\text{Fe}^{2+} + \text{Fe}^{0} \]

\[ x^2 \text{Fe}^{2+} + 2\text{e}^{-} \rightarrow \text{Fe}^{0} \]

\[ 0.44 \text{V} \]

\[ -0.771 \text{V} \]

\[ -1.211 \text{V} \]

(b) Calculate \( E^0 \) for \( \Delta G^0 \) for the reaction. Is the reaction "spontaneous" as written? \( \underline{No} \)

\[ E^0 = -1.211 \text{ V} \]

\[ \Delta G^0 = -nFE^0 = -2(23 \text{ kcal})(-1.211 \text{ V}) = 55.7 \text{ kcal} \]

2. Give balanced chemical equations for the following redox reactions or processes. Give all oxidation state changes.

(a) The reaction of Na⁰ and liquid ammonia ultimately releases \( \text{H}_2 \); however, a deep blue intermediate (or metastable product) precedes the final product.

\[ \text{Na}^{0} + \text{NH}_3(\ell) \rightarrow \text{Na} \left( \text{NH}_3 \right)_n^+ + \text{e}^- \left( \text{H}_3\text{N} \right)_m^- \]

\[ 2\text{Na}^{0} + 2\text{NH}_3 \rightarrow 2\text{NaNH}_2 + \text{H}_2 \uparrow \text{ blue} \]

(b) The discharging process of a lead/acid battery

\[ \text{Pb (s)} + \text{PbO}_2 + \frac{2\text{H}_2\text{SO}_4}{\text{2H}^+} \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O (l)} \]

(c) Sulfur compounds in volcanos:

\[ 2\text{H}_2\text{S (g)} + \text{SO}_2 (g) \rightarrow 3\text{S}^0 + 2\text{H}_2\text{O} \]

\[ \text{ox} \]

\[ \text{red} \]

(d) The reaction of nitrogen dioxide and water (the redox reaction that accounts for \( \text{NO}_2 \) being an acid anhydride)

\[ \text{NO}_2^4^- + \text{H}_2\text{O (l)} \rightarrow \text{H}_3\text{NO}_3 + \text{H}^+ \text{NO}_2^- \]

(e) The disproportionation of hydrogen peroxide

\[ 2\text{H}_2\text{O}_2 \rightarrow \underline{O^2_2} + 2\text{H}_2\text{O}^{2-} \]
III. Zen and the process of dissolving of HCl in benzene. Think of yourself as an HCl molecule being taken up in a sea of benzene. Complete the paragraph using words in the following list:

(Note: some descriptive words may be used more than once)

a) Dipole moment  
b) Covalent  
c) gas  
d) liquid  
e) ion-induced dipole  
f) polar  
g) dipole-induced dipole  
h) electronegativity  
i) non-polar  
j) London  
k) $1/r^4$  
l) ionization  
m) instantaneous dipole-induced  
n) $1/r^5$

Hydrogen chloride exists as a **gas** at room temperature that is soluble in the **non-polar liquid** benzene. Hydrogen chloride is a **polar, covalent** molecule with a substantial **dipole moment** because of the great difference in electronegativity between hydrogen and chlorine. The intermolecular forces that exist within pure benzene and must be disrupted in order to take up HCl are of the **London** or **instantaneous dipole-induced dipole** type. These forces have a distance dependence of $1/r^6$. As HCl dissolves into benzene, new intermolecular forces between the **polar** HCl and the **non-polar** benzene molecules are of the **dipole-induced dipole** type. A small amount of HCl ionizes and produces **ion-induced dipole** interactions with the benzene, with a distance dependence of $1/r^4$. 
IV. Acids and Bases and the Solvent System Definition

1. Give equations that describe the autoionization of water, ammonia, and BrF₃.

   \[ 2 \text{H}_2\text{O} (l) \rightleftharpoons \underline{\text{H}_3\text{O}^+} + \underline{\text{OH}^-} \]

   \[ 2 \text{NH}_3 (l) \rightleftharpoons \underline{\text{NH}_4^+} + \underline{\text{NH}_2^-} \]

   \[ 2 \text{BrF}_3 (l) \rightleftharpoons \underline{\text{BrF}_2^+} + \underline{\text{BrF}_4} \]

2. Ammonium chloride, NH₄Cl, dissolves in liquid ammonia. Is NH₄Cl an acid or a base in NH₃ (l)? Explain.
   
   It is an acid. It increases the \( [\text{NH}_4^+] \).

3. Give the Lewis structure of BrF₃ and use VSEPR to predict its geometrical structure. What is its principal rotation axis and to what symmetry point group does it belong?

![Lewis structure of BrF₃]

4. Antimony pentafluoride dissolves in bromine trifluoride according to the following equation:

   \[ \text{SbF}_5 (s) + \text{BrF}_3 (l) \rightarrow \text{BrF}_2^+ + \text{SbF}_6^- \]

   Give Lewis structures and VSEPR predicted geometries of SbF₅, SbF₆⁻, and BrF₂⁺. Is SbF₅ (s) an acid or a base when dissolved in BrF₃?

![Lewis structure of SbF₅ and BrF₃]

5. Bonus: A product of the autoionization of HF (l), HF₂⁻ may be described as containing the strongest known hydrogen bond. Formulate a M.O. energy level diagram that accounts for the hydrogen bond within it.

![M.O. energy level diagram of HF₂⁻]
V. Chemical Equations and Acid Base Chemistry

1. Give balanced chemical equations that account for the following observations.

   a) When sodium oxide, \( Na_2O \), dissolves in water, a basic solution results.
      \[ Na_2O + H_2O \rightarrow 2NaOH \]

   b) When ammonia, a gas at room temperature, is dissolved in water, a basic solution results.
      \[ NH_3 + H_2O \rightarrow NH_4OH \]

   c) When sodium acetate, \( Na^+CH_3CO_2^- \) or \( Na^+OAc^- \), dissolves in water, a basic solution results.
      \[ NaOAc + H_2O \rightarrow NaOH + AcOH \]

   d) When gaseous \( SO_3 \) dissolves in water, an acidic solution results.
      \[ SO_3 + H_2O \rightarrow H_2SO_4 \]

   e) \( H_3BO_3 \) can partially neutralize a solution containing the strong base, \( NaOH \).
      \[ B(OH)_3 + NaOH \leftrightarrow Na^+ B(OH)_4^- \]

   f) When \( AlCl_3 \) dissolves in water, an acidic solution occurs.
      \[ AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl \]

   g) Two phosphorous oxides dissolve in water to give two different acids. Give the structures of \( P_4O_6 \) and \( P_4O_{10} \) and the structures of their aquated forms.
      \[ P_4O_6: \]
      \[ P_4O_{10}: \]
      \[ + H_2O \rightarrow \] 

   h) Zinc oxide is amphoteric and reacts with base (\( OH^- \)) as well as acid (\( H_3O^+ \)).
      Acid: \( ZnO + H_3O^+(aq) \rightarrow Zn(H_2O)_2^{2+} \)
      Base: \( ZnO + OH^-(aq) \rightarrow Zn(OH)_4^{2-} \)
VI. Rank the following according to their acid strength (Pauling’s rules might be helpful)

\[ \text{H}_3\text{PO}_4 \quad \text{H}_3\text{BO}_3 \quad \text{HClO}_4 \quad \text{H}_2\text{SO}_4 \]
\[ \text{H}_2\text{BO}_3 < \text{H}_3\text{PO}_4 < \text{H}_2\text{SO}_4 < \text{HClO}_4 \]
Weakest \( \rightarrow \) strongest

3. Rank the following according to acid strength (Pauling’s rules might be helpful)

\[ \text{H}_3\text{PO}_4 \quad \text{H}_2\text{PO}_4^- \quad \text{HPO}_4^- \quad \text{HNO}_3 \]
\[ \text{HPO}_4^- < \text{H}_2\text{PO}_4^- < \text{H}_3\text{PO}_4 < \text{HNO}_3 \]
Weakest \( \rightarrow \) strongest

4. Arrange the oxides \( \text{Al}_2\text{O}_3 \), \( \text{B}_2\text{O}_3 \), \( \text{BaO} \), \( \text{CO}_2 \), \( \text{Cl}_2\text{O}_7 \), \( \text{SO}_3 \) in order from the most acidic through amphoteric to the most basic.

\[ \text{Cl}_2\text{O}_7 < \text{SO}_3 < \text{CO}_2 < \text{B}_2\text{O}_3 < \text{Al}_2\text{O}_3 < \text{BaO} \]
Most acidic \( \rightarrow \) amphoteric \( \rightarrow \) most basic

5. Rank the following in terms of Lewis acidity

\[ \text{BBR}_3 \quad \text{BCl}_3 \quad \text{BI}_3 \quad \text{BF}_3 \]
\[ \text{BF}_3 < \text{BCl}_3 < \text{BBR}_3 < \text{BI}_3 \quad \text{or} \quad \text{or} \]
Weakest \( \rightarrow \) strongest

6. Circle the member of the following pairs that is the stronger acid:

A) \( \text{Fe(OH}_2\text{)}_3^{3+} \) or \( \text{[Fe(OH}_2\text{)}_6]^{2+} \)  
B) \( \text{B(OH)}_3 \) or \( \text{Al(OH)}_3 \)
C) \( \text{SiF}_4 \) or \( \text{SiBr}_4 \)  
D) \( \text{HNO}_2 \) or \( \text{HNO}_3 \)

7. Rank the following pure materials in terms of H-bond strength:

\[ \text{H}_2\text{O} \quad \text{H}_2\text{S} \quad \text{HF} \quad \text{CHCl}_3 \quad \text{C}_6\text{H}_6 \quad \text{(benzene)} \]

\[ \text{HF} > \text{H}_2\text{O} \quad > \text{H}_2\text{S} \quad > \text{CHCl}_3 \quad > \text{C}_6\text{H}_6 \]

\[ ? \]
V. Circle the answer that best matches the list of descriptions below:

1. The orbital containing the lone pair of electrons in :PH₃ (∠H–P–H = 93°):
   \[
   s \quad p \quad d \quad \text{sp}^2 \quad \text{sp}^3
   \]

2. The orbital containing the lone pair of electrons in :NH₃ (∠H–N–H = 107°):
   \[
   s \quad p \quad d \quad \text{sp}^2 \quad \text{sp}^3
   \]

3. The orbital containing the lone pair of electrons in :N(C₆H₁₁)₃ (∠C–N–C = 115°):
   \[
   s \quad p \quad d \quad \text{sp}^2 \quad \text{sp}^3
   \]

4. The low lying orbital with no electrons (the LUMO) in BCl₃:
   \[
   s \quad p \quad d \quad \text{sp}^2 \quad \text{sp}^3
   \]

5. The best base for accepting a proton:
   \[
   \text{NH}_3 \quad \text{NH}_2\text{Et} \quad \text{NEt}_2\text{H} \quad \text{NEt}_3
   \]

6. The best Lewis base towards the BMe₃ Lewis acid
   \[
   \text{NF}_3 \quad \text{NH}_3 \quad \text{NEt}_3 \quad \text{NMeH}_2
   \]

7. The Lewis base most likely to have “back strain”
   \[
   \text{NF}_3 \quad \text{NH}_3 \quad \text{NEt}_3 \quad \text{N(iPr)}_3
   \]

8. Not a description of Lewis base steric effects:
   \[
   \text{front strain} \quad \text{back strain} \quad \text{cone angle} \quad \text{soft}
   \]

9. The equilibrium that is NOT shifted towards the right (the products):
   a. \[
   \text{CH}_3\text{HgF} \quad + \quad \text{HI} \quad \rightleftharpoons \quad \text{CH}_3\text{Hgl} \quad + \quad \text{HF}
   \]
   b. \[
   \text{Co(NH}_3)_5(\text{NCS})_3^- \quad \rightleftharpoons \quad \text{Co(NH}_3)_5(\text{SCN})_3^-\]
   c. \[
   \text{BF}_3\text{H}^- \quad + \quad \text{BH}_3\text{F}^- \quad \rightleftharpoons \quad \text{BH}_4^- \quad + \quad \text{BF}_4^-\]

10. The characteristic properties of 1) Containing d and f electrons; 2) low oxidation state; 3) containing polarizable atoms or groups; 4) low ionization potentials --- belong to
   a) Hard acids; b) Hard bases; c) soft acids; d) soft bases