

**HW 6 & 7  
CHEM 362  
Answer Key**

Available: March 31, 2008

Due: April 14, 2008

**Chapter 8**

1. Why is white phosphorus much more chemically reactive than black phosphorus?

**White phosphorus is more reactive than black phosphorus because the tetrahedral geometry leads to more strain in the angles ( $P-P-P = 60^\circ$ ) than in black phosphorus which exhibits normal angles ( $90^\circ$ - $100^\circ$ ).**

2. Why are Cu, Ag, and Au considered as transition metals?

**Cu, Ag and Au are  $d^{10}$  elements (full d shell) and their compounds, for example Cu(II),  $d^9$ , can have partially filled d orbitals. Most importantly, their chemical and physical properties are more like transition elements than main group elements.**

3. Why is dinitrogen normally unreactive?

**Dinitrogen is unreactive due to the strength of the N-N triple bond and because the lone pairs on the nitrogen atoms are in very low energy bonding orbitals which renders them inaccessible for donation and chemistry in most cases.**

4. Why is there a discontinuity between the ionization energy of N and O?

**In general, the first ionization energy increases as you move across the periodic table. But as you move from N to O, the energy decreases. This discontinuity between the first ionization energies of N and O can be explained by the valence electron configurations of the two elements. O ( $2s^2 2p^4$ ) has 1 set of paired electrons in its p orbitals while N ( $2s^2 2p^3$ ) has none. Oxygen will more readily lose a p electron in order to alleviate the  $e^-e^-$  repulsion.**

5. What are Lewis Acids and Lewis bases? Give two examples of each.

**Lewis bases donate electron pairs into empty orbitals on Lewis acids. Examples of Lewis bases are  $NH_3$  and  $H_2O$  while examples of Lewis acids are  $AlCl_3$  and  $Mg^{2+}$ .**

6. Why is there no silicon analog of graphite?

**Silicon does not form  $p\pi-p\pi$  interactions like carbon does. In order to have graphite, the Si would have to be  $sp^2$  hybridized instead of  $sp^3$  (in other words, it would form three  $\sigma$  bonds and one  $\pi$  bond and silicon, unlike carbon, doesn't gain any energy by doing this). In general,  $\pi$ -bonding in the second short row is not favored due to larger sizes of atoms and the fact that, in order to achieve good  $\pi$ -overlap, the atoms would have to be close enough together to cause electron-electron repulsions between the atoms.**

7. What are the principal properties and structural types of metals?

**Metals exhibit high reflectivities, high electrical conductivities, high thermal conductivities, strength and ductility. They form body centered cubic, cubic closest packing and hexagonal closest packing structures.**

8. Use MO theory to explain the bonding in  $N_2$ ,  $O_2$  and  $F_2$ . Why is  $O_2$  paramagnetic?

$N_2$  adopts a  $\sigma_1^2 \sigma_2^{*2} \pi_1^4 \sigma_3^2$  configuration in the MO diagram, giving a BO = 3.

$O_2$  adopts a  $\sigma_1^2 \sigma_2^{*2} \sigma_3^2 \pi_1^4 \pi_2^{*2}$  configuration in the MO diagram, giving a BO = 2.

$F_2$  adopts a  $\sigma_1^2 \sigma_2^{*2} \sigma_3^2 \pi_1^4 \pi_2^{*4}$  configuration in the MO diagram, giving a BO = 1.

**In all cases, the MO diagram correctly predicts the bonding between the molecules,  $N_2$  has a triple bond,  $O_2$  has a double bond and  $F_2$  has a single bond.**

**The two electrons in the two degenerate antibonding  $\pi$  orbitals on  $O_2$  are not spin paired resulting in paramagnetism.**

9. Why is  $CH_2$  unstable while  $PbCl_2$  is stable?

**The stability arises from a combination of oxidation state of the central atom and M-X bond strength. If you consider the reaction  $MX_2 + X_2 \rightarrow MX_4$ , the principle factor in determining the outcome of the reaction is the strength of the M-X bond. For  $CH_2 + H_2 \rightarrow CH_4$  the C-H bond is very strong and the reaction is favored.  $PbCl_2 + Cl_2 \rightarrow PbCl_4$  on the other hand is not favored due to a weaker Pb-Cl bond. The bonding of the two Cl atoms does not outweigh the cost of going from  $Pb^{II} \rightarrow Pb^{IV}$ .**

10. Why are the chemical consequences of partially filled  $d$  orbitals so much more pronounced than the consequences of partially filled  $f$  orbitals.

**There are two reasons. The first is that d-orbitals are more diffuse than f orbitals (due to angular part of the wavefunction- i.e. shape) allowing for better orbital overlap between the metal and the ligand. Secondly the f orbitals are very penetrating and are contracted due to nuclear charge not being shielded very well) hence d-orbitals are more energetically accessible to ligands as the f orbitals are buried underneath the outer d and s orbitals.**

11. Why are there 14 other elements between La and Hf?

**There are seven f orbitals total which allows for 14 additional elements (Note: elements are technically defined by the number of protons, but in the neutral case the number of protons and number of electrons are equal). La is  $[Xe]5d^1 6s^2$  and then if one adds 14 electrons to the seven 4f orbitals you get to Lu which is  $[Xe]4f^{14} 5d^1 6s^2$ .**

12. What is the lanthanide contraction? What effect does it have on the third row of the transition metals in the d block?

**The lanthanide contraction is the name given to the trend in the 4f elements to shrink a great deal due to a huge increase in the effective nuclear charge as one adds subsequent electrons to the same shell. This occurs because f orbitals are not very good at shielding the s and d orbitals above them. The shielding effect exerted by the inner electrons decreases in order  $s > p > d > f$ . Usually, as a particular subshell is filled in a period, atomic radii decreases. This effect is particularly pronounced in the case of lanthanides, as their 4f subshells are being filled across the period and they are less and less able to shield the outer (5th and 6th) shell electrons. Thus the shielding effect is less able to counter the decrease in radius caused by increasing nuclear charge. The result is that the second and third rows of the d-block transition metals have nearly the same atomic sizes.**

### Chapter 9

13. Finish and balance the following equations.
- $\text{KH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{KOC}_2\text{H}_5 + \text{H}_2$
  - $2\text{UH}_3 + 4\text{H}_2\text{O} \rightarrow 2\text{UO}_2 + 7\text{H}_2$
  - $\text{KH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{KOC}_2\text{H}_5 + \text{H}_2$
  - $\text{CaH}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2\text{H}_2$
  - $\text{B}_2\text{H}_6 + 2\text{NaH} \rightarrow 2\text{NaBH}_4$
14. Explain the trend of the boiling points of the hydrogen halides.  
 $\text{HF} (20^\circ\text{C}) > \text{HCl} (-85^\circ\text{C}) < \text{HBr} (-67^\circ\text{C}) < \text{HI} (-36^\circ\text{C})$

**In general, the higher the molecular weight of a compound, the higher the boiling point. (This should make sense as larger molecules require more energy to become gases). The exception is HF. HF forms extensive hydrogen bonding networks in the liquid state. These hydrogen bonds “stabilize” the liquid state accounting for the comparatively higher boiling point.**

15. Suggest a way to prepare HD.

**There may be more than one correct answer:**



16. Which H bond would you expect to be stronger and why?  
 $\text{S-H} \cdots \text{O}$  or  $\text{O-H} \cdots \text{S}$

**In the case of  $\text{O-H} \cdots \text{S}$ , the O-H bond is very polar given a significant partial positive charge to the H atom allowing it to H-bond to the electron rich S atom. S-H bonds are much less polar meaning that the O atom, while electron rich, would not be able to form a very strong hydrogen bond due to the low partial positive charge on the H atom.**

17. Give an explanation of the structural role of water in each of the following compounds and give an example of each type.
- A hydrated compound  
**A compound containing discrete water molecules bound to some other molecule via hydrogen bonding and/or cation-oxygen bonds.**  
**ex:  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$**
  - A hydrous compound  
**Similar to a hydrated compound. Unlike hydrated compounds which contain distinct, known amounts of water, hydrous compounds are much more general and are represented by  $n\text{H}_2\text{O}$  because the numbers of waters are undetermined or can vary. ex:  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$**
  - A gas hydrate  
**A clathrate formed around a small molecule of a gaseous substance.**  
**ex:  $\text{Cl}_2 \cdot 7.3\text{H}_2\text{O}$**
  - A liquid hydrate  
**A clathrate formed around a molecule of a liquid substance.**  
**ex:  $\text{CHCl}_3 \cdot x\text{H}_2\text{O}$**
  - A salt hydrate  
**A hydrogen bonded network of water molecules containing anions and cations. i.e. a crystalline salt with high water content.**  
**ex:  $[(\text{C}_4\text{H}_9)\text{N}][\text{C}_6\text{H}_5\text{CO}_2] \cdot 39.5 \text{H}_2\text{O}$**
18. When a H bond is symbolized as X-H-----Y, what do the solid and dashes lines mean? Which distance is shorter?

**The solid line indicates the shorter (and stronger) polar covalent bond and the dashed line indicates the longer (weaker) hydrogen bond.**

19. Define and cite examples of the different types of hydrogen-containing compounds that are discussed in this chapter, listing the distinguishing electronic, structural, and reactivity characteristics of each class.

**Water – very stable, forms extensive hydrogen bonding networks in the liquid and solid phase. Ice is less dense than water because of H bonding. Water is capable of interactions with charged or partially charged species. Water is reactive towards certain metals and metal hydrides.**

**Hydrates/Clathrates – Hydrogen bonding networks built around “guest” molecules of varying types (see problem 17). Water can be easily removed upon heating, but, under some conditions, this can cause a reaction of the original compound.**  
**i.e.  $\text{ScCl}_3 \cdot 6\text{H}_2\text{O} \rightarrow \text{ScOCl} + 2\text{HCl} + 5\text{H}_2\text{O}$ .**

**Hydrides – The hydrogen atoms in a molecule are negatively charged. There are several distinct types of hydrides. Covalent hydrides are hydrides of non-transition elements and can be neutral, weakly basic, weakly acidic, amphoteric or strongly acidic depending on the molecule. These tend to form with the main group elements. Saline hydrides contain the alkali and alkaline earth elements and are very ionic in character with a negative charge entirely on the hydrogen atom. These are very reactive (especially towards water and other related compounds). The final category is transition metal hydrides. These hydrides are diverse and exhibit a number of structures. Simple M-H bonding can occur stoichiometrically and non-stoichiometrically. Transition metals can also bond to  $\text{H}_2$  as a ligand.**

20. What are the three methods for producing hydrogen gas? Describe *one* of them.

**Electrolysis of Water:**  $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$  (electrochemical reaction)

**Electrolysis of Brine:**  $2\text{Na}^+ + 2\text{Cl}^- + 2\text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{OH}^- + \text{H}_2 + \text{Cl}_2$   
(electrochemical reaction)

**Steam Reformation of Hydrocarbons:**  $\text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O} \rightarrow n\text{CO} + (2n+1)\text{H}_2$

**Water-Gas Shift Reaction:**  $n\text{CO} + n\text{H}_2\text{O} \rightarrow n\text{CO}_2 + n\text{H}_2$   
(catalytic reactions at high temperature)

21. Write out representative reactions for the 7 reaction types of hydrogen gas as discussed in class.

**Preparation of HBr:**  $\text{H}_2 + \text{Br}_2 \xrightarrow[350\text{ }^\circ\text{C}]{\text{catalyst}} 2\text{HBr}_{(g)}$

**Haber-Bosch Process:**  $\text{N}_2 + 3\text{H}_2 \xrightarrow[\text{pressure}]{\text{Fe catalyst}} 2\text{NH}_3$

**Formation of Hydrides:**  $\text{H}_2 + 2\text{Li} \xrightarrow{700\text{ }^\circ\text{C}} 2\text{Li}^+\text{H}^-$

**Isolation of Pure Metals from Ores:**  $\text{Cu}_2\text{S} + 2\text{O}_2 \rightarrow 2\text{CuO} + \text{SO}_2$

**Hydrogenation Reactions:**  $\text{R-HC=CHR} + \text{H}_2 \rightarrow \text{RCH}_2\text{-CH}_2\text{R}$

**CO + H<sub>2</sub> Synthesis Reactions:**  $\text{CO} + 2\text{H}_2 \xrightarrow[400\text{ }^\circ\text{C}]{\text{Cu, Zn catalyst}} \text{CH}_3\text{OH}$

**Fischer-Tropsch Synthesis:**  $\text{CO} + \text{H}_2 \xrightarrow{\text{catalyst}} \text{Mixture of hydrocarbons}$

22. What is the difference between a proton, atomic hydrogen and hydride?

**The charge is the significant difference. A proton is  $\text{H}^+$ , atomic hydrogen  $\text{H}$  (exists as molecular hydrogen  $\text{H}_2$ , as atomic hydrogen doesn't exist in nature). Hydride is  $\text{H}^-$ .**

23. Water has several interesting properties that are needed for life as we know it. Three of these were discussed in class. List them and *briefly* mention why each is needed for life.

**Very high boiling point** – if not for this, water would be a gas at room temperature (life on earth would be impossible, our bodies need *liquid* water, nature needs liquid water to penetrate the soil, we need oceans etc.,

**Very low density of the solid form (ice)** – if not the case there would be no aquatic life as lakes would freeze from the bottom up as instead of freezing from the top down.

**Hydrogen bonding** – this forms the “glue” that holds proteins and DNA together, without it we would quite literally “fall apart” J .

24. What are clathrates?

**Hydrogen bound water cages in which molecules are trapped.**