HW 10 & 11
CHEM 362

Available: April 21, 2008 Due: April 28, 2008

Chapter 14

1. The electronic structure of C in its ground state is $1s^2\ 2s^2\ 2p^2$. Why does carbon typically form four single bonds and not two?

   One of the valence electrons in carbon is promoted from the 2s orbital to one of the 2p orbitals. The four unpaired valence electrons now occupy all 4 valence orbitals (the 2s and the 3 2p orbitals). When bonding, the 2s and the 3 2p orbitals mix, yielding 4 sp^3 hybrid orbitals. Each hybrid orbital can form a favorable overlap with the orbitals of the adjacent atom. The reason for this behavior is that the hybrid orbitals have better overlap when bonding (as compared to the unhybridized orbitals on the carbon atom) and this improved overlap provides more energy than that spent in promoting the electron and hybridizing the orbitals in the first place. Thus it is more favorable for the carbon to hybridize and form 4 single bonds than to only form 2 single bonds (with the 2 electrons in its p subshell) and leave the $2s^2$ electrons as a lone pair.

2. What is meant by catenation? Why does silicon have much less tendency to catenate than carbon? Could the same be said of nitrogen?

   Catenation is the ability of an element to bond with itself to form chains or rings. Silicon does not undergo catenation because the strength of the Si-Si bond is less than that of the Si-O bond (which is very favorable to form), meaning Si would rather form oxides than catenate. Nitrogen should be able to undergo catenation, but the stability of the triply bonded diatomic N_2 precludes the stability of higher catenation.

3. List ways in which CO can be made.

   CO can be produced by burning hydrocarbons in an atmosphere deficient in oxygen. It is also prepared industrially along with hydrogen gas in the process of steam reformation from methane and water.

4. List ways in which CO_2 can be made.

   CO_2 is produced in the following ways. The total combustion of hydrocarbons (given enough oxygen) produces water and CO_2. The heating of carbonates, such as $CaCO_3$, gives metal oxides and CO_2. Reactions of acids and solutions of carbonates gives water and CO_2.

5. On which side is the equilibrium favored? L or R?

   $$CO_{2(aq)} + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

   The left side is favored. In solution, the majority of the dissolved CO_2 exists as hydrates with only a small portion of the molecules reacting to form carbonic acid.

6. Why does $CaCO_3$ dissolve, to some extent, to form CO_2 saturated water? Write balanced equations for the reactions involved. (see the book)

$CaCO_3$ is fairly insoluble but when $CaCO_3$ dissolves in water, some of the carbonate anions react with water to form bicarbonate anion and carbonic acid, which in turn can decompose to reform water and CO_2. As was mentioned in the previous problem, CO_2 is favored over carbonic acid in aqueous solutions, so the equilibrium is shifted to the CO_2 side of the reaction. Thus the process continues to saturation.

$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$
$HCO_3^- + H_2O \rightarrow OH^- + H_2CO_2$
$H_2CO_3 \rightarrow H_2O + CO_2$

7. How does HCN act in the body? Why are KCN water solutions alkaline?

HCN is a highly poisonous gas that irreversibly binds to the mitochondrial heme copper, preventing oxygen transport within the mitochondria which stops respiration.

Solutions of KCN are slightly basic because the CN^- anion is partially hydrolyzed forming HCN and OH^-. $CN^- + H_2O \rightarrow HCN + OH^-$

8. The C-C bond length in graphite is 1.42 Å. How does this compare with the C-C bond length in: (see the book)

a. diamond **1.54 Å**
b. ethylene **1.33 Å**
c. benzene **1.39 Å**

What do you expect the bond order is in graphite?

I would expect the bond order of graphite to be most similar to that of benzene given the similar bond distances in these 2 compounds.

In graphite, each carbon atom is sp^2 hybridized and exits in a sheet of hexagons (each C atom is bonded to 3 others). This means that each carbon atom forms 3 σ bonds with its 3 neighbors and then shares a π bond across all 3. So the overall bond order is 4 bonds / 3 atoms = 1.33.

9. Explain the roles of CO and CO_2 in the environment. Be as complete as possible in your response.

CO is a poisonous gas often formed by incomplete combustion of hydrocarbons that acts in the body by bonding to the heme iron in hemoglobin more favorably than O_2. This action cuts off O_2 causing death. A source of CO in the environment is automobile exhaust.

CO_2 is formed by complete combustion of hydrocarbons. CO_2 is a critical part of the natural carbon cycle wherein plants and phytoplankton take up CO_2 and convert it to sugars by photosynthesis yielding oxygen as a byproduct. CO_2 is also a naturally occurring greenhouse gas and aids in maintaining the temperature on the Earth. Recently, the amount of CO_2 in the atmosphere has been increasing (mainly from the production of CO_2 by vehicles and industry) and is a cause of global warming. There is also some evidence that the increased CO_2 levels may help to increase plant growth.

Chapter 16

1. Complete and balance the following reactions:
   a. $H_2O_2 + 2NO_2 \rightarrow \mathbf{2HNO_3}$
   b. $\mathbf{6}Li + N_2 \rightarrow \mathbf{6Li_3N}$
   c. $O_3 + \mathbf{2}NO_2 \rightarrow \mathbf{N_2O_5 + O_2}$
   d. $\mathbf{2}HI + \mathbf{2}HNO_2 \rightarrow \mathbf{I_2 + 2NO + 2H_2O}$
   e. $C + NO_2 \rightarrow \mathbf{CO_2 + ½\, N_2}$
   f. $\mathbf{2}Cu + NO_2 \rightarrow \mathbf{Cu_2O + NO}$

2. Write balanced equations for the different preparations of nitric oxide.

   $\mathbf{8HNO_3 + 3Cu \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO}$
   $\mathbf{2NaNO_2 + 2NaI + 4H_2SO_4 \rightarrow I_2 + 4H_2SO_4 + 2H_2O + 2NO}$
   $\mathbf{2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO}$
   $\mathbf{3KNO_2 + KNO_3 + Cr_2O_3 \rightarrow 2K_2CrO_4 + 4NO}$

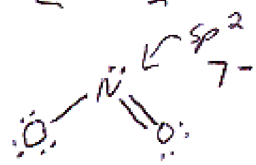
3. How can NO_2 and NO_3 be bonded to transition metals? (this was covered a long time ago but is still important)

   NO_2 can bind to transition metals through either the N atom or one of the oxygen atoms. The molecules themselves can also bind in a monodentate, chelating or bridging arrangement.

4. Draw the Lewis structure and explain the geometry and hybridization at each atom in

NO_2^-, NO_3^-, NO_2^+, NO, N_2, N_3^-, FNO, N_2O

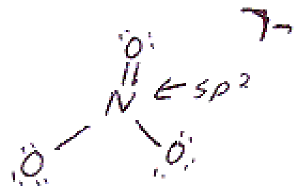
$[NO_2]^-$



bent

(in resonance)

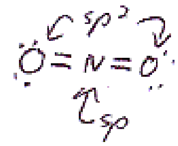
$[NO_3]^-$



trigonal planar

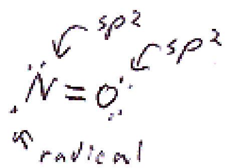
(in resonance)

$[NO_2]^+$



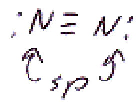
linear

NO



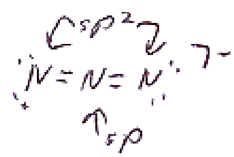
linear

N_2



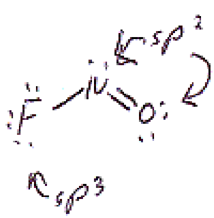
linear

N_3^-



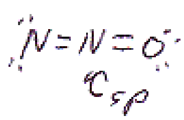
linear

FNO



bent

N_2O



linear

(in resonance)

5. Use MO theory to compare the bonding in CO, N_2, CN^- and NO^+. Why does N_2 form complexes with metals much less than CO? (this is review but is being re-emphasized in this section)

All these species have a bond order of three a similar ordering in the molecular orbitals ($1\sigma^2\, 2\sigma^2\, 1\pi^4\, 3\sigma^2$). The major difference between them is the relative positions of the molecular orbitals (in terms of energy). Both CO and N_2 have a MO arrangement of $1\sigma^2\, 2\sigma^2\, 1\pi^4\, 3\sigma^2$ but N_2 is less likely to bind to metal complexes because the lone pair that engages in σ bonding to the metal is lower in energy than that in CO.

6. Why does N_2 form a diatomic molecule unlike Phosphorus and other elements in Group VB(15)?

N_2 forms while P_2 does not because nitrogen atoms are small enough for the close approach needed to engage in pπ-pπ overlap allowing for the formation of multiple bonds. The phosphorus atom, which is much larger, experiences a much higher amount of internuclear repulsion at those distances than nitrogen does, so it can not form multiple bonds.

7. Give the principal products of the reactions:
   a. $O_2 + NH_3 \rightarrow$ (uncatalyzed)
      $4O_2 + 3NH_3 \rightarrow 2N_2 + 6H_2O$
   b. Disproportionation of NO
      $3NO \rightarrow N_2O + NO_2$
   c. Oxidation of NO_2 by ozone
      $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$
   d. Reduction of NO_2 by excess hydrogen
      $NO_2 + 2H_2 \rightarrow \frac{1}{2} N_2 + 2H_2O$
   e. The Haber process for ammonia
      $N_2 + 3H_2 \rightarrow 2NH_3$
   f. Dimerization of NO_2
      $2NO_2 \rightarrow N_2O_4$

8. Outline the synthesis of HNO_3 staring from the elements.

$N_2 + O_2 \rightarrow 2NO$
$2NO + O_2 \rightarrow 2NO_2$
$2NO_2 + H_2O_2 \rightarrow 2HNO_3$

9. What is the role of NO_x gases in the environment? Be as complete as possible in your response.

NO_x gases often result from man made sources and can react with water in the atmosphere to produce nitric acid, one of the causes of acid rain.

Chapter 18

1. What is the difference between oxygenation and oxidation?

Oxygenation means the ligation of an intact O_2 molecule. No reaction to break the O_2 molecule occurs in this process. Oxidation is generally the loss of an electron(s) from a chemical species. It can also refer to a chemical process whereby a species forms a compound with oxygen, and undergoes an increase in oxidation state (O_2 is reduced).

2. Describe the interaction with water of acidic, basic and neutral oxides. Give two examples of each type.

Basic oxides are ionic oxide, superoxide or peroxide compounds that yield hydroxide, and hence, basic solutions when added to water.

ex: $Na_2O_2 + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_2O_2$

$BaO + H_2O \rightarrow Mg^{2+} + 2OH^-$

Acidic oxides are covalent oxides that, when dissolved in water, react to yield acidic solutions.

ex: $N_2O_5 + H_2O \rightarrow 2H^+ + 2NO_3^-$

$CO_2 + H_2O \rightarrow H_2CO_3$

Neutral oxides are generally insoluble in acidic or basic solutions, or when they are soluble, they undergo redox chemistry instead of acid/base type reactions.

ex: $MnO_2 + 4HCl \rightarrow Mn^{2+} + 2Cl^- + Cl_2 + 2H_2O$

3. Give the electronic configuration of the oxygen *atom*.

$1s^22s^22p^4$

4. Explain why the oxygen atom is paramagnetic.

Elemental oxygen is not atomic, but diatomic. The dioxygen molecule is paramagnetic because in the Aufbau filling the HOMO level is a π orbital, which is actually 2 orbitals, containing 2 electrons. Hund's Rule places one electron in each of the 2 orbitals (they are unpaired) which renders the molecule paramagnetic.

If you consider atomic oxygen, the valence shell is $2s^22p^4$ and there are 2 unpaired electrons in the p sub-shell so the atom, if it could be isolated, would be paramagnetic as well.

5. Describe and compare the geometries of the oxygen atoms in the following pairs of molecules:

a. O_2 and O_3

O_2 is linear with a bond order of 2 and a O-O distance of 1.21 Å. O_3 is bent with and O-O-O angle of 117º and a O-O bond length is 1.28 Å. This distance is longer than the double bond in O_2 but shorter than a single bond indicating the presence of a shared double bond between the 3 oxygen atoms in O_3.

b. CH_3OH and H_2O

Both molecules are bent with respect to the oxygen atom which has 2 single bonds in both molecules (sp^3 hybridized). The main difference is the larger extent of hydrogen bonding that the water molecule can perform.

c. O_2 and O_2^{2-}

Both are linear. O_2^- (superoxide) has a bond length of 1.33 Å while O_2^{2-} (peroxide) has a bond length of 1.49 Å. This reflects the additional electrons in the π^* orbital (HOMO) of the two molecules relative to that of O_2.

d. CO_2 and SO_3

CO_2 is a linear molecule with 2 double bonds. The O is sp^2 hybridized. SO_3 is a trigonal planar molecule with the three oxygen atoms in resonance.