Unit IIIb Homework Set

General Chemistry I

(includes oxidation number problems from previous homework assignments)

Oxidation Numbers

1. (***Unit II***) Earlier in semester we considered the Earth-saving chemistry of selenium, including some of the compounds listed below, and we introduced the selenate ion, SeO_4^{2-}.

   A. For each of the compounds shown, assign the oxidation numbers and write them in the spaces provided.

   SeO_2 Se _____ O _____

   K_2Se K _____ Se _____

   H_2Se H _____ Se _____

   H_2SeO_4 Se _____

   H_2SeO_3 Se _____

   B. In part A, the last compound is formed from the first compound according to the following chemical equation:

   $$SeO_2 + H_2O \rightarrow H_2SeO_3$$

   Is the above reaction a redox reaction? Explain your reasoning.

2. (***Unit II***) Appendicitis is caused by inflammation of the appendix...

   B. The gases used in this procedure have advantages and disadvantages relative to each other. For example, N_2O gas has a mild analgesic effect. On the other hand...

   During prolonged laparoscopic procedure N_2O should not be a preferred gas for pneumoperitoneum because it supports combustion better than air.

   Consider this reaction with methane.

   $$4N_2O(g) + CH_4(g) \longrightarrow 4N_2(g) + 2H_2O(g) + CO_2(g)$$

   2. Assign oxidation numbers for all of the atoms in this reaction. Write the oxidation numbers in parentheses above the formula.

   $$\underset{\backslash\ /}{\_\_\_}\ \underset{\backslash\ /}{\_\_\_}\ \underset{\backslash\ /}{\_\_\_}\ \underset{\backslash\ /}{\_\_\_}\qquad \underset{|}{\_\_\_}\ \underset{\backslash\ /}{\_\_\_}\ \underset{\backslash\ /}{\_\_\_}\ \underset{\backslash\ /}{\_\_\_}\ \underset{\backslash\ /}{\_\_\_}$$
   $$4N_2O(g) + CH_4(g) \longrightarrow 4N_2(g) + 2H_2O(g) + CO_2(g)$$

   Which element is oxidized? Which is reduced?

3. (***Unit II***) The proper assignments of oxidation numbers (ON) are necessary for recognizing and balancing redox reactions (e.g. questions IV and V on page 3), but they are also useful for understanding other aspects of chemical reactivity. For example, I mentioned in class that oxidation numbers allow one to deduce the relative strength of analogous acids.

   A. Assign the requested oxidation numbers for the following pairs of acids:

   1. HNO_2 HNO_3

      ON of N _____ ON of N _____

2. H_2SO_4 H_2SO_3

   ON of S _____ ON of S _____

3. $HClO_4$ $HClO_2$

   ON of Cl _____ ON of Cl _____

B. Circle the stronger acid in each of the above pairs.

C. What is the general relationship between oxidation number and acid strength?

D. On October 12, 2008, an oleum spill at a chemical plant in western Pennsylvania forced about 2,500 residents to evaluate. Oleum – also known as fuming sulfuric acid, $H_2SO_4 \cdot xSO_3$ – is especially dangerous because the sulfur trioxide escapes as a gas and reacts with moisture in the air to form sulfuric acid according to the reaction $SO_3(g) + H_2O(g) \rightarrow H_2SO_4(g)$.

   Is this a redox reaction? Explain your reasoning.

4. (***Unit II***) Titration with an aqueous solution of potassium dichromate is a useful procedure for determining the amount of iodide in solution. The *unbalanced* chemical equation for this reaction is given below. Assign the oxidation number of the atoms indicated below (all atoms except H and O).

$$K_2Cr_2O_7(aq) + HI(aq) \rightarrow CrI_3(aq) + I_2(s) + KI(aq) + H_2O(l)$$

   Identify the oxidizing agent and the reducing agent in the above reaction.

   oxidizing agent _____ reducing agent _____

4. (***Unit II***) Several years ago an undergraduate working in my lab needed acetylene gas, HCCH(g), for an experiment. Normally acetylene is purchased in a tank like other gases, but in the published experiment he was trying to repeat, the researchers generated acetylene by adding calcium carbide to a large volume of water and collecting the acetylene gas, according to this reaction

$$CaC_2(s) + H_2O(l) \rightarrow HCCH(g) + CaO(s)$$

A. Is this a redox reaction? Explain your reasoning.

5. (***Unit II***) We carried out the thermite reaction...

C. Write the oxidation numbers in the spaces provided.

$$2Al(s) + 3H_2O(s) \rightarrow Al_2O_3(s) + 3H_2(g)$$

9. (***Unit IIIa***) Yttrium is also a useful starting material for making other yttrium compounds...

D. Circle the one that is larger?

   1. O F 2. O^{2-} F^- 3. Cl F

E. Why would picking the larger between oxygen and chlorine be more difficult?

ATOMS: Electronic Structure and Properties

1. (***Fall 2008***) Consider the following gas phase reaction: $F_2(g) + I_2(g) \rightarrow 2FI(g)$

   A. You will note from the data provided that the bond energy for FI(g) is greater than the bond energies of either $F_2(g)$ or $I_2(g)$.

      1. Speculate on why the bond enthalpy of FI(g) is greater than the bond enthalpies of either $F_2(g)$ or $I_2(g)$.

      2. Based on the bond energies, do you expect the above reaction to be endothermic or exothermic? Explain your reasoning.

   B. Now use bond energies to estimate $\Delta H°$ for the above reaction.

      Does your answer agree with your prediction in I.A.1 above? _____

   C. Fluorine and iodine form a number of other compounds, including IF_3 and IF_5. In the space below, draw dot structures for these molecules and sketch the expected shape of the molecule.

IF_3	IF_5
dot structure	dot structure
~~IF_3~~	~~IF_5~~
~~molecular shape~~	~~molecular shape~~

2. (***Fall 2015***) Draw dot structures as instructed below, and answer any associated questions. Be sure to show all non-zero formal charges.

   A. Draw the best dot structure you can for OF_2.

   B. Draw the best dot structure you can for HNNH, where the atoms are connected as written.

   C. Draw the best dot structure you can for the hypothetical molecule NCOF which contains all of the nonmetal elements from the second row of the periodic table, except neon.

      Which bond in NCOF do you expect to be the strongest? _____

      Why?

   D. Draw two dot structures for SeO_2.

best dot structure you can that obeys the octet rule	best dot structure you can that exceeds the octet rule to minimize formal charge

Would the molecular geometries corresponding to the two dot structures you drew above be the same or different? _____

Explain why or why not.

3. (***Fall 2012***) Write the best dot structure you can and assign all non-zero formal charges for the following molecules/ions. Draw a box around the structure you consider to be the best (i.e. the one you want graded).

OBrF (Br is the central atom) PF_4^-

4. (***Fall 2012***) I really botched the question on the last exam involving the partial oxidation of hydrocarbons as a route to make hydrogen gas. Let's see if I can get it right this time. We'll keep things simple by considering the partial oxidation of ethane as shown in the following reaction:

$$C_2H_6(g) + O_2(g) \rightarrow 2CO(g) + 3H_2(g)$$

And I do not want to leave out any important reactions and $\Delta H°$ values, so instead of using Hess's law, let's use the bond enthalpy data provided on the last page of the info sheet.

A. First, write dot structures for C_2H_6, O_2, CO, and H_2. You will need these dot structures for parts B and C.

C_2H_6	O_2	CO	H_2

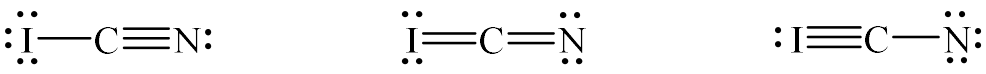
~~B. Now calculate $\Delta H°$ for the partial oxidation of ethane.~~

C. Was ethane really oxidized in this reaction? Assign oxidation numbers

$$C_2H_6(g) + O_2(g) \rightarrow 2CO(g) + 3H_2(g)$$

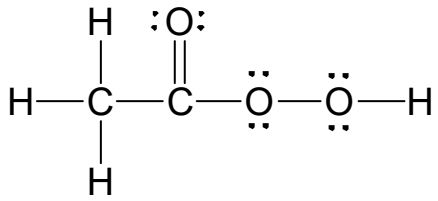
Was C_2H_6 oxidized? _____ If so, did oxidation occur at C or H or both?

5. Resonance structure for the molecule ICN are given below. Assign nonzero formal charges for these dot structures.



Which dot structure is the best resonance structure for ICN?

6. (***Fall 2009***) Assign the oxidation numbers for all of the carbon and oxygen atoms in the following organic reagent:



7. (***Fall 2009***) The previous question allowed you to demonstrate your ability to write dot structures and use them to deduce geometries and hybridization. The next two examples, drawn from the recent literature, are a bit more interesting, but the fundamental tools used to describe the electronic structure and physical geometry are the same.

   A. Hydrazine borane, $NH_2NH_2BH_3$, has been proposed as a material for storing hydrogen (*J. Am. Chem. Soc.* **2009**, *131*, 7444-7446). In combination with lithium hydroxide, hydrogen gas is released according to the reaction

$$NH_2NH_2BH_3(s) + LiH(s) \rightarrow LiN_2H_3BH_3(s) + H_2(g)$$

   Write a dot structure for $NH_2NH_2BH_3$
   and assign all nonzero formal charges.

   B. When $NH_2NH_2BH_3$ reacts to form $NH_2NHBH_3^-$, why is the hydrogen ion lost from the middle nitrogen instead of the outer nitrogen?

8. (***Fall 2009***) DOT STRUCTURES

   1. Write the best dot structure you can and assign all non-zero formal charges for each of the following molecules/ions. Draw a box around the structure you consider to be the best (i.e. the one you want graded).
   2. ~~Sketch the molecular geometry, using wedges for bonds coming out of the paper and dashed lines for bonds going into the plane of the paper. You only need to show the lone pairs on the central atom. Use arrows to show any expected distortions from the idealized geometry.~~
   3. ~~Give a descriptive name for the molecular geometry (atoms only): bent, T-shaped, see-saw, trigonal pyramidal, trigonal planar, trigonal bipyramidal, square planar, square pyramidal, tetrahedral, octahedral.~~
   4. ~~Give the hybridization about the central atom.~~

   A. OBrF (Br is the central atom)

      1. dot structure

   B. NO_3^-

      1. dot structure

   C. PF_4^-

      1. dot structure

9. (***Fall 2009***) Xenon forms bonds with oxygen and fluorine, but compounds containing Xe-N bonds are rare (*J. Am. Chem. Soc.* **2009**, *131*, 7272-7286). The cation $F_3S{\equiv}NXeF^+$ was investigated and found to rearrange to form $F_4S{=}NXe^+$. In both ions the atoms are connected as S–N–Xe, and the multiplicity of the bonding between sulfur and nitrogen is indicated in the formulas.

   A. Write a good dot structure for $F_3S{\equiv}NXeF^+$ ~~and give the molecular geometry and hybridization of the sulfur, nitrogen, and xenon atoms.~~

   ~~sulfur: molecular geometry _____ hybridization _____~~

   ~~nitrogen: molecular geometry _____ hybridization _____~~

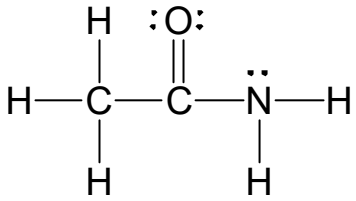
   ~~xenon: molecular geometry _____ hybridization _____~~

   B. Write a good dot structure for $F_4S{=}NXe^+$ ~~and give the molecular geometry and hybridization of the sulfur and nitrogen atoms.~~

   ~~sulfur: molecular geometry _____ hybridization _____~~

   ~~nitrogen: molecular geometry _____ hybridization _____~~

10. (***Fall 2009***) A dot structure for methyl amide is shown on the right.



    Draw a resonance structure for this dot structure.

    Which structure do you think is the better resonance structure: the one given above, or the one you drew? Why?