Available: Jan. 16, 2008   Due: Jan. 25, 2008

1.   Write an equation that can be used to define the mean S-F bond energy in SF_6.
        How is this value likely to be related in magnitude to the energy of the process?

$$SF_6 \text{ (g)} \rightarrow SF_5 \text{ (g)} + F \text{ (g)}$$

$\Delta E_{S-F} = (1/6)\Delta H_{f(SF_6)}$ **$\Delta H_{rxn} = \Delta E_{S-F} = (1/6)\Delta H_{f(SF_6)}$**

2.   What is a qualitative definition of entropy and how does it relate to the tendency
        for reactions to occur?
   What will be the signs of ΔS for the following reactions?

a.	$H_2O \text{ (l)} \rightarrow H_2O \text{ (g)}$	**$\Delta S > 0$ (entropy increase)**
b.	$P_4 \text{ (g)} + 10 F_2 \text{ (g)} \rightarrow 4 PF_5 \text{ (g)}$	**$\Delta S < 0$ (entropy decrease)**
c.	$I_2 \text{ (g)} + Cl_2 \text{ (g)} \rightarrow 2 ICl \text{ (g)}$	**$\Delta S = 0$ (entropy gained by loss of symmetry is miniscule)**
d.	$BF_3 \text{ (g)} + NH_3 \text{ (g)} \rightarrow H_3NBF_3 \text{ (g)}$	**$\Delta S < 0$ (entropy decrease)**
e.	$CO_2 \text{ (g)} \rightarrow CO_2 \text{ (s)}$	**$\Delta S < 0$ (entropy decrease)**

3.   Prepare graphs of the concentration of reactant A as a function of time if A
        disappears in a first-order fashion. Assume that $[A]_{initial} = 1$ M and $k = 1\times10^{-3}$ $M^{-1}s^{-1}$. How should the data for a first-order reaction be plotted in order to obtain a
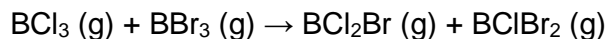   straight line?

Graph of a first order reaction:
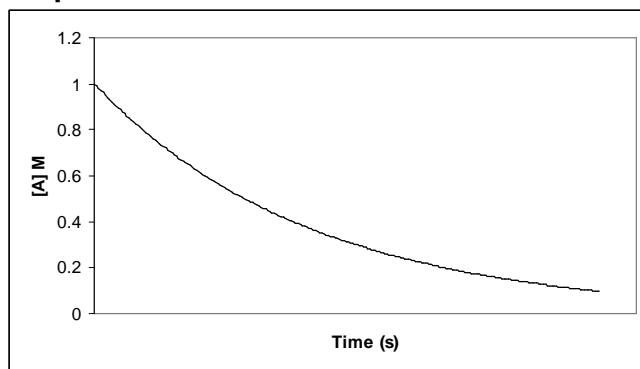

In order to plot a straight line use the natural log:
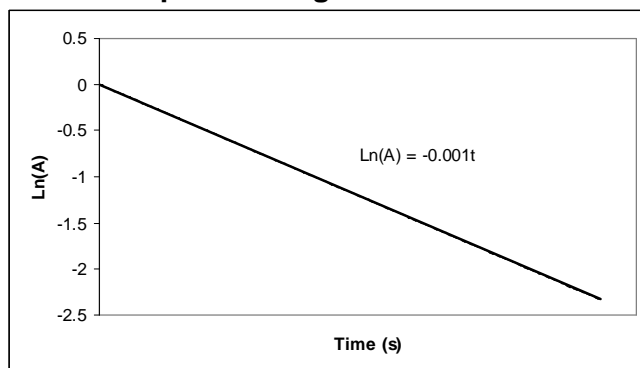
4. What do you suppose is the main thermodynamic reason why the following reaction has an equilibrium constant >1?

$$BCl_3 \text{ (g)} + BBr_3 \text{ (g)} \rightarrow BCl_2Br \text{ (g)} + BClBr_2 \text{ (g)}$$

From the equation $\Delta G = -RTlnK$ we know that if $K > 1$ (i.e. favoring products), then $\Delta G < 0$. We also know that $\Delta S = 0$ (see problem 2c). So in $\Delta G = \Delta H - T\Delta S$, $T\Delta S = 0$ and $\Delta G = \Delta H$. So if $\Delta G < 0$ then $\Delta H < 0$, or exothermic. The reaction is enthalpically driven.

5. What is the value of an equilibrium constant that has a ΔG^0 value of zero? Draw a Reaction Profile for such a system.
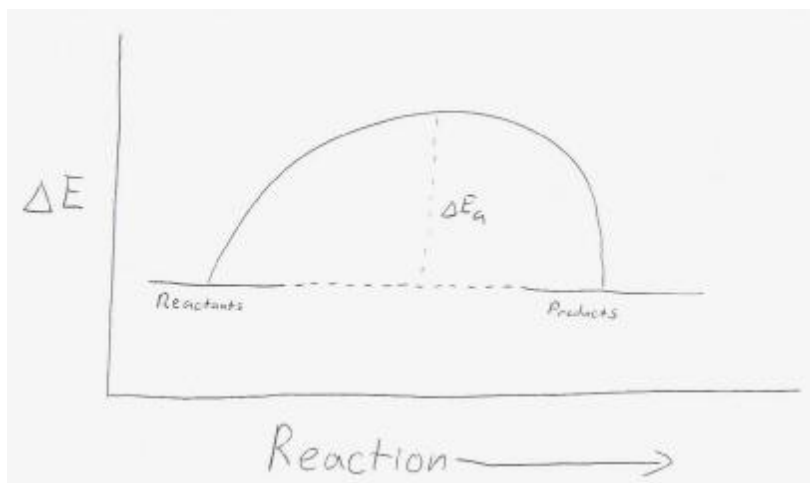
6. The conversion of diamond into graphite is a spontaneous reaction (thermodynamically favored). Why doesn't diamond eventually change into graphite?

Spontaneity is governed by thermodynamics and kinetics. If the reaction is thermodynamically favorable ($\Delta G < 0$), then it must be kinetically disfavored (slow rate, high activation energy (ΔE_a)).

7. What were the two bold postulates made by Bohr that allowed him to derive an equation for the energies of an electron in the H atom?
    What does the term Bohr radius mean?

Bohr postulated that:
1.   The electrons can orbit the nucleus of an atom in fixed orbits indefinitely.
2.   The angular momentum, radius and energy of these orbits are quantized.

Bohr radius – The smallest radius for the orbit of an electron in the Bohr model of the hydrogen atom. ($a_o = 0.529$ Å)

8. State the quantum numbers for the following orbitals:
       1s, 2s, 2p, 2d, 4d, 4f

    1s   n = 1, l = 0
    2s   n = 2, l = 0
    2p   n = 2, l = 1
    2d   n = 2, l = 2   (this orbital *cannot* exist)
    4d   n = 4, l = 2
    4f   n = 4, l = 3

9. State the Pauli Exclusion Principle in the form relevant to atomic structure. Show how it leads to the conclusion that, in a given principal shell, there can be only two s, six p, ten d, and fourteen f, electrons.

    Pauli Exclusion Principle – no 2 electrons in an atom may have the same 4 quantum number, i.e. 2 electrons in the same orbital must have opposite spins (m_s = +1/2, m_s = -1/2).

    The *s* orbital has l = 0, m_l = 0. 1 orbital with a maximum of 2 electrons.
    The *p* orbital has l = 1, m_l = 1, 0, -1. 3 orbitals with a maximum of 2 electrons per orbital or 6 electrons.
    The *d* orbital has l = 2, m_l = 2, 1, 0, -1, -2. 5 orbitals with a maximum of 2 electrons per orbital or 10 electrons.
    The *f* orbital has l = 3, m_l = 3, 2, 1, 0, -1, -2, -3. 7 orbitals with a maximum of 2 electrons per orbital or 14 electrons.

10. Why is the first ionization enthalpy of the O atom lower than that of the N atom?

    N: $[He]2s^2 2p^3$ (all p electrons are unpaired, N has a half filled subshell)
   **O: $[He]2s^2 2p^4$ (2 p electrons are paired, 2 are unpaired).**

    If oxygen were to loss 1 p electron, not only would it gain the stable half filled subshell, it would also gain the energy that it normally loses to electron repulsion between the paired electrons. This is why it does not fit the trend of ionization enthalpy increasing as you move from left to right across the periodic table.

11. Prepare dot density diagrams similar to that found of page 41 of Chapter 2 (Fig. 2-3) for:
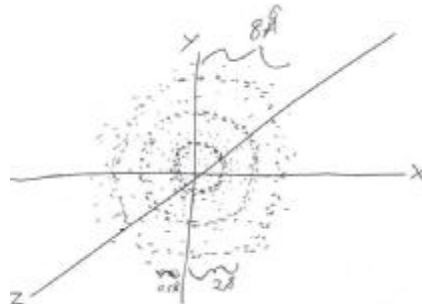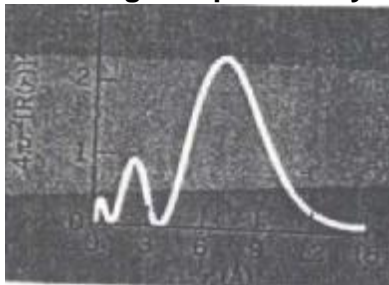
    a. $2p_x$ orbital
    b. $3s$ orbital
    c. $3d_{xy}$ orbital

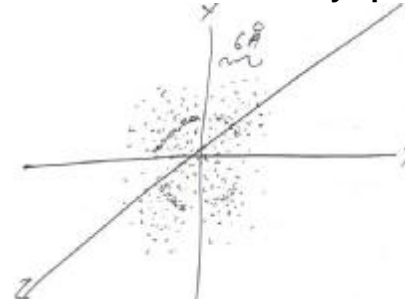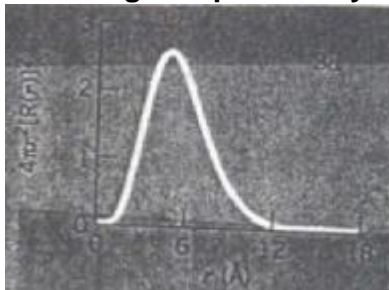Remember that one must take both the shape and function $r^2[R(r)]^2$ into consideration.

a.   (from pg 45 in Cotton) Highest probability is at 2Å, node in the yz plane.
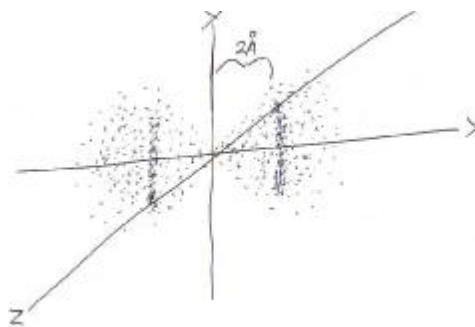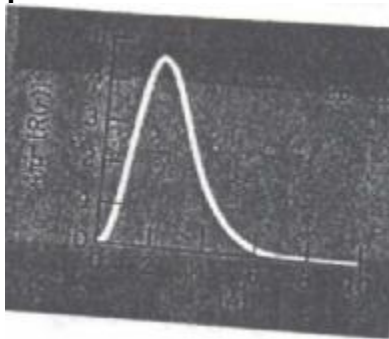
b.   Highest probability is at 8Å, with 2 radial nodes at 1Å and 5Å

c.   Highest probability is at 6Å with nodes in the xz and yz planes.

12. Arrange the following in order of increasing *second* ionization energy (i.e. put the lowest ionization energy first).

    $_{19}$K $_{56}$Ba $_{49}$In $_{52}$Te

Ba < Te < In < K

In order to make these assignments consider the valence shell of each element.

Ba: [Xe]6s^2 loses 2 electrons to become [Xe], obtaining noble gas config.

Te: $[Kr]4d^{10}5s^25p^4$ loses 2 electrons to become $[Kr]4d^{10}5s^25p^2$

In: $[Kr]4d^{10}5s^25p^1$ loses 2 electrons to become $[Kr]4d^{10}5s^1$, breaking a filled subshell

K: $[Ar]4s^1$ loses 2 electrons to become $[Ne]3s^23p^5$, breaking noble gas config.

13. In what way(s) do 3*d* and 4*d* orbitals differ?

The two largest differences between the 3*d* and 4*d* are the size of the orbital and the energy. The 4*d* orbital is both larger (farther away from the nucleus) and is higher in energy than the 3*d* orbital. (full credit)

There are various other differences between the two, 4*d* has a radial node while 3*d* does not. The two orbitals have different electron densities. The ionization energy of an electron in the two orbitals would be different. These are *some* examples of other differences. (partial credit)

14. Which member of the following pairs has the lower electron affinity?

$_8O$ or $_7N$ $_{37}Rb$ or $_{55}Cs$ $_{33}As$ or $_{32}Ge$ $_{19}K^+$ or $_{11}Na$

15. Based on their ground state electronic configurations, list what you would expect as common oxidation states for:

$_{81}Tl$ $_{82}Pb$ $_{34}Se$ $_{58}Ce$ $_{92}U$

Tl: $[Kr]4d^{10}5s^25p^1$ +1, +3

Pb: $[Xe]4f^{14}5d^{10}6s^26p^2$ +2, (maybe +4, but I don't think we'll break the full s subshell)

Se: $[Ar]3d^{10}4s^24p^4$ +1, +4, -2

Ce: $[Xe]4f^15d^16s^2$ +2, +3, +4

U: $[Rn]5f^36d^17s^2$ +2, +3, +6

Please note that these values are predicted based on the nature of the element (metal, metalloid, nonmetal) as well as the valence electron configuration. I also miss graded this problem and in accepting the following for partial credit: U^{5+}.

16. What are the different types of radii that must be considered when discussing the elements?
Tell how they are defined and how the values are determined.

Single Bond Covalent Radius – the radius of an atom that contributes to a covalent single bond. Determined from a known covalent bond for a single element, i.e. H_2. $r_{cov(H)}$ = (1/2) H-H bond.

van der Waals Radius – the radius of an atom that contributes to the nonbonded distance between two atoms whose electron clouds are in contact. Determined from the closest contact between two atoms in the solid state that are not bonded.

Ionic Radius – the radius of an ion that contributes to an ionic compound. Determined from the known distance between 2 ions and an ionic lattice. Depends on the oxidation state of the ions involved and the arrangement of the ions involved.