Chemistry 123 **DUE FRIDAY, February 7 @ 6:30 p.m.** **Winter Term 2003**
Assignment #4 **4 Pages / 6 Problems** **SHOW YOUR WORK!** **Instructor: R. Rossi**

Your Name: ______________________________

At what time and on what day was this handed in? ______________________________

---

1. Ima Bingedrinker, tired of paying what she considers to be draconian alcohol taxes to the state, has decided to ferment her own liquor. Having a breadth of interests with regard to the impurities present in her alcohol, she decides to set up two different stills. In each still, the same fermentation reaction takes place:

$$C_6H_{12}O_{6(aq)} \rightarrow 2C_2H_5OH_{(aq)} + 2CO_{2(g)} \qquad \Delta H^o_{rxn} = -67\ kJ\cdot mol^{-1}$$

The standard enthalpy change associated with this reaction (ΔH^o_{rxn}) is -67 kJ per mole of glucose ($C_6H_{12}O_6$) that ferments at a constant temperature and pressure of 25ºC and 1.0 atm. Ima doesn't really know what she is doing, but she's determined. The first thing on Ima's wish list of inebriants is bourbon whiskey. The still she's trying to use for this (let's call it "Still A") is essentially a huge (30 gallon) garbage bag with 5 gallons of malted corn mash in it, "burped" before sealing so that all the air is removed and only the liquid remains inside. As the corn ferments, the CO_2 produced causes the bag to expand, but never to the point where the bag is actually full. Thus the reaction takes place at constant pressure, expanding against the atmosphere's pressure of 1.0 atm. [Ima doesn't realize that whiskey is a distilled liquor…] Ima hopes to make beer in her other still ("Still B"), and so she's designed it to keep the CO_2 produced in the above reaction under high pressure. Still B is actually a stolen commercial (5 gallon) pony keg which Ima has filled to the brim with yeasty barley extract and tightly sealed. The fermentation reaction will take place in this fixed volume, and all the CO_2 released in the reaction will be forced to remain in the fermenting liquid, because it has nowhere else to go. By the time Ima's beer is ready the pressure should be very high. Ima hopes this will allow her to tap into Still B just like it was a store-bought keg. (Ima doesn't know how kegs work, either…)

   a. Is the fermentation reaction shown above exothermic or endothermic?
   b. Suppose the corn mash in Still A initially contains 200. g of glucose. How much heat will be released into or extracted from Ima's basement by this glucose fermenting according to the reaction above?
   c. How much work will Still A do against the atmosphere as it expands? (Assume a temperature of 25ºC in Ima's basement, and a constant atmospheric pressure of 1.0 atm.)
   d. Say Still B also initially contains 200. g of glucose. Suppose (as isn't unlikely) the pressure in Still B rises to a point where the keg explodes. "Beer" goes flying everywhere. When all is said and done all that's left behind is a pool of flat alcoholic liquid of effectively the same volume and composition as what is sitting in Still A. Once this liquid reaches room temperature, the internal energy change associated with the entire process will be the same as that experienced by Still A. Is the total heat released into Ima's basement as a net result of the events in Still B more than, less than, or the same as the amount of heat released as a result of the process that took place in Still A? Why?

Units: $R = 0.08206\ \ell\cdot atm\cdot mol^{-1}\cdot K^{-1}$ $MW_{C_6H_{12}O_6} = 180.156\ g\cdot mol^{-1}$ 1 mol of ideal gas occupies 24.45 ℓ at 25ºC and 1 atm
$1\ m^3 = 1000\ \ell$ 1.000 atmosphere (atm) = 760.00 torr = 101325 Pascals (Pa) $1\ Pa \equiv 1\ kg\cdot m^{-1}\cdot s^{-2}$ $1\ J \equiv 1\ kg\cdot m^2\cdot s^{-2}$

Hints: Fermentation doesn't give off light or any other form of radiation, so it is safe to assume that the only work done in these scenarios is PV work. Assume that the reaction vessels stay in thermal equilibrium with Ima's 25ºC basement during the entire fermentation process, if you think that is important at any point along the way. You smarties who know about heat capacities should assume they are the same for the contents of the two stills. After all, the mashes are both mostly water.

I fear Ima's going to be disappointed. Among other things, she's going to get some methanol (CH_3OH) as a side product of her fermentations, which will cause her to go blind: at least temporarily. Temporary or even permanent loss of eyesight is a price commonly paid by those who try to make their own booze without asking enough questions or reading enough books.

2. Based on the thermodynamic data given in Appendix 4 of Zumdahl, determine which of the following reactions are spontaneous at 25ºC and 1 atm. Show your work.

    a. $C_{(s),\ \text{diamond}} \rightarrow C_{(s),\ \text{graphite}}$
    [The conversion of diamond into graphite: understand that thermodynamics gives no indication of how *fast* a reaction will occur – that is the dominion of kinetics, which we will learn about near the end of the term.]

    b. $Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$
    [The reduction of iron oxide to form iron metal, used in the process of refining taconite ore to produce steel.]

    c. $N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$
    [Ammonia, a major agricultural fertilizer and chemical precursor, is produced commercially using this reaction.]

    d. $6\ CO_{2(g)} + 6\ H_2O_{(\ell)} \rightarrow C_6H_{12}O_{6(s)} + 6\ O_{2(g)}$
    [This is the net result of photosynthesis, the reaction in which plants generate glucose, a simple sugar.]

3. Deuterium(D) is an *isotope* of hydrogen(H), with one neutron in its nucleus (in addition to the one proton normally found in a hydrogen atom). The extra neutron in the deuterium nucleus has almost no chemical effect. H and D are chemically identical, or nearly so. As a result, at least for the purposes of this problem, we can consider H–H, H–D, and D–D bonds to all be of equal strength, and the H_2, HD, and D_2 molecules all of equal stability. At room temperature the energy difference between one of these "isotopic variants" and another is negligibly small, and so they exist in proportions that are dominantly determined by the effects of entropy, which favors the most probable distribution amongst the possible arrangements.

    a. A small, ultra-high vacuum chamber is completely evacuated, then charged with isotopically distinct hydrogen and deuterium gases. Specifically, 1 H_2 molecule and 1 D_2 molecule were put into to the chamber. Because of the chemical similarity of H and D, there is no appreciable enthalpic reason for a reaction to occur between H_2 and D_2. However, entropy causes the following reaction to occur:

    $$H_{2(g)} + D_{2(g)} \rightarrow 2\ HD_{(g)}$$

    At room temperature, the extent to which this reaction occurs may be assumed to be determined solely by entropic considerations. For a system containing 2 H atoms and 2 D atoms, each atom bonded to one other (so that there are a total of two molecules in the chamber):

    1) List or diagram all the possible microstates for this system (there are 3 possible microstates)
    2) Identify the most probable arrangement of atoms for this system (there are 2 possible arrangements)
    3) Determine the relative probability of each arrangement. Unless you are a whiz at statistics, I recommend doing this experimentally – not because the statistics are hard here, but because part (b) is a killer unless you know the following method! Get (or make) four playing cards, say two aces and two deuces. Deal the four cards into two pairs: this is one possible arrangement. Pick the cards back up, shuffle, and deal them into two pairs again. Do this twenty times and keep track of the results: do you end up with mixed pairs (A2 and A2) more often than with two pairs (AA and 22)? How much more often, i.e., in what fraction of your twenty trials did you get mixed pairs?

    b. Consider what would happen if the same chamber were charged up with a total of 4 H and 4 D atoms. Here the number of microstates is huge! But using playing cards you can still figure out the most likely arrangement without having to do lots of painful statistics. What is the most likely of arrangement of 4 H and 4 D atoms in a system like this, subject to the requirement that the atoms are always found in pairs? Does the chemical reaction listed in part (a) go to completion in this system? (That is, do you expect to find 4 HD in the vacuum chamber?) (Better do 40 trials here.)

4. In class we have been learning about a variety of ways in which we make use of the electromagnetic radiation emitted when certain atoms or molecules undergo specific electronic transitions. One of the key things you will want to develop this week is a firm grasp on how energy and wavelength are related in electromagnetic radiation. To that end, here are a few simple, but illustrative, calculations we'd like you to do. Use the figure at the bottom of the page, or Figure 7.2 on page 293 of Zumdahl, to help you:

   a. KRLX (“Carleton’s Best Radio Station!”) broadcasts over the FM radio waves at a frequency(ν) of 88.1 MHz. What is the wavelength(λ) of these radio signals? Please give your answer in meters. Pretty big, huh? (FM radio waves basically act as particles [hitting and bouncing off things] when they interact with objects larger than this, and like waves [diffracting around things] when they interact with smaller objects.)

   b. KRLX also occasionally broadcasts on the AM band at a frequency(ν) of 680 kHz. Calculate the wavelength(λ) of these radio waves, again in meters please. (The differences between FM and AM radio are due in part to this difference in wavelength, and in part to the fact FM radio uses Frequency Modulation to carry information, while AM uses Amplitude Modulation. Hopefully if you're interested you'll learn all about this in physics class, if you haven't already! Or you can ask me to explain.)

   c. Although it wouldn't generally be too bright an idea to carry out a flame test on the toxic metal mercury (Hg), some bozo must have done it because Oxtoby and Nachtrieb say (p. 524, Problem 16) that it emits strongly at a wavelength of 454 nm. What would the color of this flame be? (You don't have to get out your Pantone™ color-matching kit, just give the approximate color.) Mercury is a cumulative brain toxin that leads to insanity. Bahahahaha! Er, sorry. The liquid itself is not readily absorbed into the body, but some vapor is always present wherever there is liquid mercury...and the vapor is readily and nearly permanently absorbed into your body…specifically, your brain. The guys who made felt top hats used to soften them with metallic mercury: and their constant contact with the vapor led to the expression "mad as a hatter."

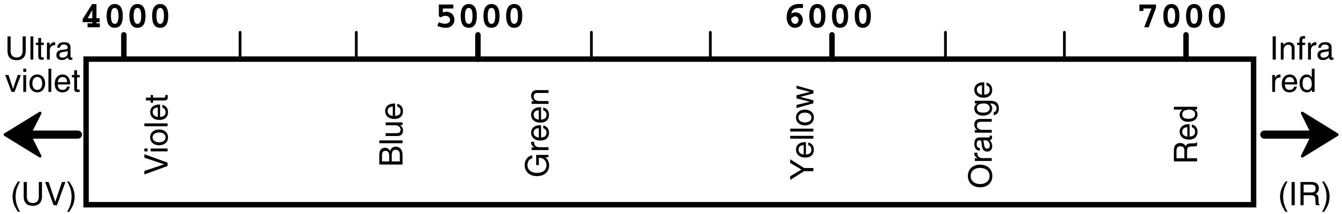
   d. Also from Oxtoby and Nachtrieb (Problem 18): "Potassium atoms in a flame emit light as they undergo transitions from one energy level to another that is 4.9×10^{-19} Joules lower in energy." Determine the wavelength (in nm) and the color of this light.

   e. The coating on the walls of a fluorescent light tube primarily converts 2540 Å ultraviolet light to 6125 Å visible light, by absorbing and then emitting again. However, conservation of energy requires that it also do something with the remainder of the energy it absorbed from the UV photon! How many eV (electron volts) of energy are left over after one absorption and emission event? (Since this is more than enough energy to emit another visible photon, ideally the coating would emit a second photon. Unfortunately, the design of a phosphor capable of this is currently beyond predictive inorganic chemistry. The energy is probably lost as heat. Despite this, fluorescent lighting produces far more visible light per Joule than incandescent lighting does.)

Handy Equations: $E_{\text{Photon}} = -\Delta E_{\text{electron}}$ $E_{\text{Photon}} = h\nu = h \cdot c \cdot \lambda^{-1}$ $\lambda \cdot \nu = c$

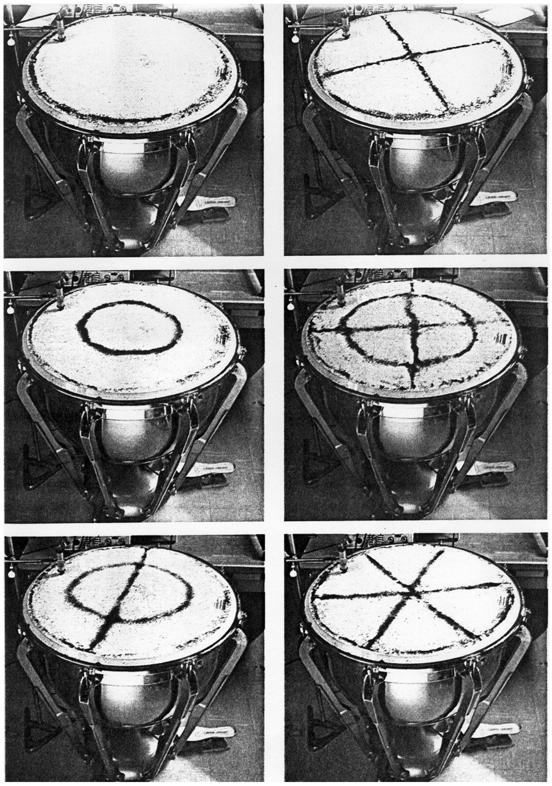
Helpful data: $c = 2.998 \times 10^{8}\ \text{m} \cdot \text{s}^{-1}$ $h = 6.626 \times 10^{-34}\ \text{J} \cdot \text{s}$ $1\ \text{Hz} = 1\ \text{s}^{-1}$ $10^{10}\ \text{Å} = 10^{9}\ \text{nm} = 10^{2}\ \text{cm} = 1\ \text{m}$
$R_H = 13.6\ \text{eV} = 2.18 \times 10^{-18}\ \text{J} = 3.29 \times 10^{15}\ \text{Hz} = 1.10 \times 10^{5}\ \text{cm}^{-1} = 1.10 \times 10^{7}\ \text{m}^{-1}$ $1\text{eV} = 1.602 \times 10^{-19}$ Joules

5. Does a photon of violet light with a wavelength of 420 nm have enough energy to break a typical C–C bond? Explain how you arrive at your answer.

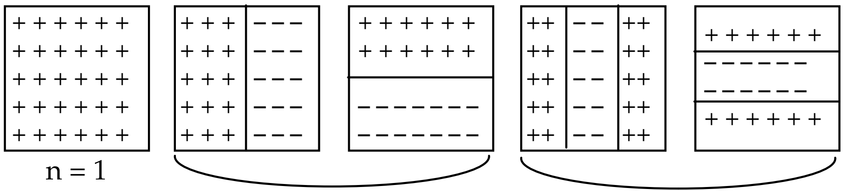

Wavelength of Visible Light (λ, in Ångstroms)

After D.C. Harris, Quantitative Chemical Analysis, 2nd Ed., New York: Freeman & Co. (1987).

6. The six pictures at right [from "The Physics of Kettledrums" by Thomas D. Rossing in *Scientific American*, November 1982, p. 173] show the surface of a kettle drum with a fine black powder sprinkled on it. In each picture, the drum head is being oscillated at a different frequency by the small device in the upper left-hand corner. As the surface of the drum oscillates, the powder is thrown around; it collects at the nodes, where there is a minimum of vibration. Thus the dark lines are a visible indication of the locations of the nodes in this two-dimensional system with circular symmetry. Although this system is not perfectly analogous to a spherically symmetric atom (most of the drum's energies are mixed up), it is possible to apply an analysis similar to that used for three dimensional atoms to obtain some meaningful insights. *You will probably find this problem challenging. Please start on it early.*



   a. I don't want to ask you for fancy artwork, so let me introduce a simple way of depicting two-dimensional standing waves (wavefunctions) in two dimensions. To demonstrate how this works, below I have pictured the square box wavefunctions we talked about in class using a simplified, schematic top-view method:



n = 1
Zero nodes

n = 2 ; One node in each
Degenerate Set

n = 3 ; Two nodes in each
Degenerate Set

   Your first challenge is to draw diagrams analogous to those above for the circularly symmetric drum system, corresponding to the six kettledrum photographs shown above. Your diagrams will be circles, not squares, and the nodes will fall where the black lines appear in each drum picture.

   b. This two-dimensional system has two types of nodes: circular nodes and linear nodes. These are analogous to radial and angular nodes in three dimensions. Hopefully after a bit of thought you'll see that you can apply the three-dimensional orbital nomenclature that we have learned to this simpler system. Once you see how this works, identify each of the wavefunctions you depicted in part (a) with a name of the form $n\ell$, like 4d or 6g, with the principal quantum number first and a letter corresponding to the angular quantum number second.

   c. Your answers to part (b) should indicate to you that four of the expected wavefunctions (from the group $n \leq 4$) are "missing" from the drumhead pictures. Identify these four wavefunctions and draw a simplified + / – diagram for each (like those at the top of this page), depicting what they look like.

   d. Which of the diagrams you drew for part (a) corresponds to the lowest energy state? (Give the $n\ell$ name if you figured it out.) Briefly justify your answer.

   e. If r is defined as the radial distance from the center of the drum head, sketch a qualitative plot of what $\Psi(r)$ would look like for the lowest energy state you specified in (d). Remember that r must be greater than zero. Your plot should have r on the horizontal axis and $\Psi(r)$ on the vertical axis. [Don't put numbers on the axes, and ignore the time dependence of Ψ; show its maximum amplitude. $\Psi(r)$ is the displacement of the drumhead above or below its rest position, as a function of the distance from the center of the drum (r).]

   f. Make a similar $\Psi(r)$ vs. r sketch for the 2s state. Don't worry about the relative amplitudes, exact node location, or the absolute sign; but get the sign **change** and the basic shape right!