Exam 1: Colligative Properties, Thermochemistry, and Quantum Mechanics

Chemistry 123 | **WEDNESDAY, May 15, 2002** | **Spring 2002**
First Exam | **5 Pages / 5 Problems** | **SHOW YOUR WORK!** | **Instructor: R. Rossi**

Don't Panic!

Instructions:

- **Aaaaah! Stop Panicking!!!**
- **There are a total of five problems in this exam, one on each page.**
- **Your grade will be based on the *four best* problems you hand in. It would be wise for you to start with the problem with which you are most comfortable and can do relatively quickly, and work your way up to the problems you find harder or you expect will take you more time. Each problem is worth 25% of your exam score.**
- **At the end of the class period you may pick *one* problem to take home with you and continue working on. You have until 6:00pm on Thursday, May 16th to complete the problem you take home. If I don't get the problem back from you by that time, your grade will be based on the four problems you hand in at the end of class.**
- **Please hand in your take-home problem to me personally, or slide it under my office door if I am not around. If you bring your take-home problem to lab I will have you go down to my office and slide it under my door, so that I do not risk losing it.**
- **You may refer to the equations and conversion factors on the back of this sheet, your textbook, your notes [notes you or I wrote, but not copies of what someone else wrote], your returned homework and anything you have written on it, and your lab notebook. If you have to look everything up, you won't finish this exam.**
- **You *MAY NOT USE COPIES OF MY HOMEWORK SOLUTIONS*, but if you make notes on your own homework, that's fine. Make sure you understand the mistakes you made on the homework! The same holds true of mistakes made in doing the labs!**
- **You may use a calculator, a computer, a periodic table, and anything else you OK with me in advance. You may not use references other than those listed above.**
- **You can start working on this exam at 11:10 am. You must give me back four of your problems when I ask you for them at 12:20 pm, if not before that time. Even if you can't finish four problems in class, I need four of them back. Only keep one.**
- **SHOW YOUR WORK AND LOGIC UNLESS SPECIFIED OTHERWISE. If you don't offer a good explanation of how your answer came to be, you will get no credit!!!**
- **If you think there is an error in your exam, ask me about it! It's OK to ask me questions.**

Restrictions:

- **You may not get any form of help from others on the questions you solve in class.**
- **You may talk with others about the problem you take home, subject to the following limitations: 1) You may not write down or otherwise record anything during or immediately after such conversations. 2) You may not bring up the numbers or other specifics involved in your problem. The spirit of these rules is that you may get help with general concepts, but you can't have someone else do your thinking for you. Please obey the spirit of this rule, not just the "letter of the law."**

Exam 1 Equation Sheet (You can add information to this sheet if you like.)

Formulas and Equations

$\Delta T_f = -K_f\, m_{\text{solute particles}}$

$\Delta T_b = K_b\, m_{\text{solute particles}}$

$m = \text{molality} = \dfrac{\text{moles of solute}}{\text{kilogram of solvent}}$

$\Pi = i\ \text{MRT}$

$\rho = \dfrac{m}{V}$

$P_{tot} = \rho g h + P_o$

$\Delta E_{photon} = \dfrac{hc}{\lambda}$

$c = \lambda\nu$

$E = h\nu$

$E_{photon(Emission)} = R_H Z^2 \left(\dfrac{1}{n_f^2} - \dfrac{1}{n_i^2}\right)$

$PV = \eta RT$

$P_i V = \eta_i RT$

$q = \eta\ \tilde{C}_p\ \Delta T = \eta\ \Delta\tilde{H}$

$w_{system} = -P_{opposing}\, \Delta V_{system}$

$\Delta U_{system} = q + w$

$H \equiv U + PV$

$A = \varepsilon\, b\, C$

$\Delta G = \Delta H - T\Delta S$

Constants and Conversion Factors

$g = 9.8067\ \dfrac{m}{s^2}$

$h = 6.626 \times 10^{-34}\ J\cdot s = 4.136 \times 10^{-15}\ eV\cdot s$

$273.15\ K = 0^{o}C$

$c = 2.998 \times 10^{8}\ \dfrac{m}{s}$

$\rho_{H_2O} = 1.00\ \dfrac{g}{m\ell}$

$R = 8.3145 \dfrac{J}{mol\cdot K} = 0.08206 \dfrac{\ell\cdot atm}{mol\cdot K}$

$1\ m = 10^{9}\ nm = 10^{10}$ Å

$1\ m = 3.2808$ feet

$1\ m = 100\ cm = 10^{3}\ mm = 10^{6}\ \mu m$

$1\ eV = 1.602 \times 10^{-19}$ Joules

$R_H = 13.6\ eV = 2.18 \times 10^{-18}\ J$

$10^{-3}\ kg = 1\ g = 10^{+3}\ mg = 10^{-6}\ \mu m$

$1\ \text{Newton} \equiv 1\ \dfrac{kg\cdot m}{s^2}$

$1\ \text{Joule} \equiv 1\ \dfrac{kg\cdot m^2}{s^2}$

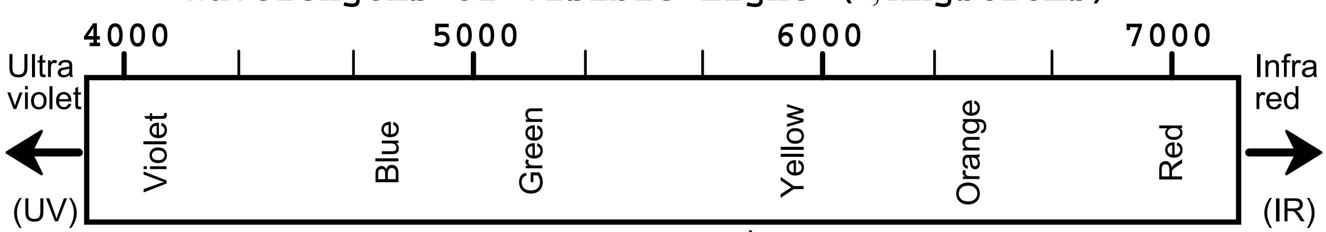
$1\ \text{Pascal} \equiv 1\ \dfrac{kg}{m\cdot s^2}$

1.00000 atm = 760.000 Torr = 101325 Pa

$1\ \text{mole} = 6.022 \times 10^{23}$

$1\ m^3 = 1000\ \ell = 264.17$ gallons

Wavelengths of Visible Light (λ, Angstroms)



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

Complete electromagnetic spectrum: in your book on page 272.

Tables of Bond Energies: in your book on pages 380 and 382. Be careful to use the correct one!

Problem 1: Colligative Properties, Solutions, and Applied Chemistry

In January, the Kiersaw-Barton family flies south for a warm Florida vacation. They completely turn off the heat off in their house when they leave. That seems like a smart energy-saving measure to them, and it's what they always did when they lived in New Mexico…Alas! They now live in Northfield, and they are likely to learn a painful climatological lesson. With the heat completely off, the temperature in their home begins to plummet…and before long, their water pipes will get cold enough that they will be at risk of freezing. If that happens, their pipes will burst and their home may well flood. Not a pretty picture! Will freezing point depression save them from this terrible fate?!? Let's find out.

The Northfield tap water coming into the home is rich in minerals, as specified in the table below. The family has a water softener in the basement, and it completely softens all the water that circulates through the rest of the house. The house is at about the same temperature at all points inside, being well-insulated.

a. Chemically, what does the water softener do to the water? Specifically, what ion concentrations would change (see table below) as the water went through the softener? [Say what you can, admit what you're unsure of.]

b. Is the water upstream or downstream of the water softener at the greatest risk of freezing? Why?

c. At what temperature will unsoftened Northfield tap water freeze, assuming the ions listed in the table below are the only ones warranting consideration?

Principal Ions Present in (unsoftened) Northfield Tap Water	
Ion Identity	Ion Concentration (moles/kg of water)
Chloride, Cl^-	0.071
Sodium, Na^+	0.033
Calcium, Ca^{2+}	0.009
Magnesium, Mg^{2+}	0.008
Sulfate, SO_4^{2-}	0.004
Iron(III), Fe^{3+}	0.002

Mercury is the closest planet to the sun, and it has essentially no atmosphere. The temperature at Mercury's equator varies wildly, from –183 ºC shortly before dawn to +407 ºC around noon. The position of the sun in the Mercurian sky has an immense and immediate effect on its surface temperature. In contrast, the temperature on the surface of Venus is a reasonably stable 460 ºC. The rising and setting of the sun has almost no impact on the Vesuvian surface temperature. Venus has a dense, thick atmosphere, composed primarily of carbon dioxide streaked with dense clouds of sulfuric acid. Explain as clearly as you can how the surface temperature of Venus can be both higher than that ever seen on the surface of Mercury (despite the fact Venus is much farther from the Sun) and stable to such an extent that the rising and setting of the sun has very little effect on it.

Briefly explain **one** of the following phenomena (your choice):

1. If you put a tray of ice cubes in a normal, working freezer, closed the door, and then walked away, not opening the fridge again for a year, what would you find when you did open the door again? Why?
2. Why is it easier to broadcast AM radio to listeners on the streets of downtown Chicago than it is to broadcast FM radio to the same audience?
3. Why do plain old cucumbers become infested with mold and bacteria much more readily than do pickles?

Problem 2: Thermochemistry

Consider the following two reactions between hydrogen gas and a halogen:

i) $H_{2(g)} + F_{2(g)} \rightarrow 2HF_{(g)}$

ii) $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$

a. Calculate the $\Delta H^{o}_{reaction}$ value for (i) and (ii), with an eye toward getting as accurate a value as possible.

b. In terms of the strength of the bonds involved, explain why one of these reactions is far more exothermic (capable of giving off more heat per mole) than the other. A more complete analysis of the relevant factors will fetch a higher score than will a less complete one [that is, there is more than one comparison to make between (i) and (ii) that contributes to a full understanding of why the ΔH values are what they are].

c. By whatever means you prefer, balance and calculate ΔHº for the following reaction of sucrose at 25ºC:

$CO_{2(g)} + H_2O_{(\ell)} \rightarrow C_{12}H_{22}O_{11(s)} + O_{2(g)}$ [Sucrose is a sugar, and is listed at the end of Appendix 2]

I gave my cousin Vinnie a nifty magic syringe for his birthday. Bad idea. Of course, Vinnie's idea of putting this rare gift to good use is using it as a party gag. He fills the magic syringe with hairspray and air, then ignites the mixture with various people sitting on top of it. Needless to say, most of them go flying, to a chorus of giggles from the partygoers. Well, Vinnie went a little too far at his last party. He invited Don Pesante to sit on the syringe. Don Pesante is not only the local heavy, someone no sane person would mess with, but he is also incredibly heavy in the literal sense of the word. Don Pesante was so heavy, in fact, that Vinnie's little device didn't manage to shoot the Don anywhere. (Probably to the benefit of Vinnie's health.) With Don Pesante on board, the syringe just stayed compressed down to a super-small volume: its volume did not change.

Infatuated as he was with the magic syringe party gag, Vinnie actually went to great lengths to make the gag a reproducible hoot. He developed a process that allowed him to put the same amount of air and hairspray into the syringe each time he used it, and he even studied it quantitatively. He found that with nobody seated on the syringe, but compressed to a very small initial volume, it would expand against the pressure of the atmosphere to do some work, and also release some heat. If allowed to cool to room temperature and re-compressed to the initial volume, the net work done by the syringe would be 160 kJ and on net 465 kJ worth of heat were released.

a. How much heat was released by the syringe with Don Pesante sitting on it, once it had cooled back to room temperature? Remember, the volume of the syringe stays effectively constant. Explain your work!

b. Vinnie has learned that if, after a fun-filled launch, he simply sprays more hairspray into the syringe and then tries to set it off again, nothing much happens. Why is that?

c. Vinnie tried this same trick with my grandfather's magic syringe, back in the 60's. It didn't work, because back then the hairspray wouldn't burn. This is because the propellant used in aerosol cans has changed markedly between the 1960's and today; today light, flammable hydrocarbons like propane are used, whereas back in the 60's they used CFC's. Briefly, what prompted this change in propellant chemistry?

Problem 3: Quantum Mechanics and the Properties of Atoms

This morning you wake up feeling a little strange but can not immediately figure out why. While taking your Chem 123 exam, it dawns on you…that "dream" you had about Dr. Who (he's a hip BBC television science fiction character, in case you don't know) dragging you off into the fourth dimension *wasn't* a dream. You really have become a fourth-dimensional being, and can now travel backwards and forwards in time as easily as you can jump up and down or step right and left. Life is good. But this has led to a rather strange complication in your elemental structure. We know that the rules governing quantum numbers change somewhat with the dimensionality of the system. In the fourth dimension, the periodic table looks somewhat different. The rules governing the allowed values for quantum numbers are as follows:

(i) the principal and angular quantum numbers (n and ℓ) still follow the same rules as in 3-dimensional space

(ii) m_ℓ now ranges from -2ℓ to 2ℓ; but zero is no longer allowed! For the p orbitals, this means that the basis set of degenerate orbitals consists of four possibilities: a p-orbital aligned with the x axis, one aligned with the y axis, one with the z axis, and last but not least, one aligned with the time axis. There is a corresponding increase in the number of degenerate orbitals allowed for higher values of ℓ.

(iii) the only allowed value for m_s is 0; electrons no longer have spin, so each orbital can only hold one electron!

(iv) however, electrons still fill atomic orbitals in the order same order as they do in our universe

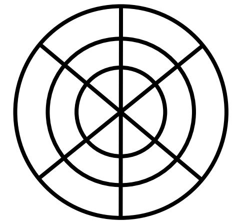
The periodic table in this alternate dimension has only one element in the first row, the first noble gas. The second row is also short, having only five elements; it contains the second noble gas, which has an atomic number of 6. The new periodic table reflects the modified electronic configurations that atoms are allowed to have in 4-dimensional space. Please answer the following questions:

a. Only one electron can be held in each s orbital in this alternate universe. How many electrons can be held in each degenerate set of orbitals having ℓ = 1, 2, and 3 (the p, d, and f orbitals)? Show the work that leads you to the answers you provide; you need not explain in detail.

b. Draw the valence orbital diagram of the noble gas atom at the end of the third row of this alternate universe's periodic table. (You need not explain your logic on this one.)

c. Give the atomic number of the noble gas atom at the end of the fourth row of this alternate universe's periodic table. Explain your logic.

By putting small black particles on an oscillating kettledrum head, it is possible to determine the location of the nodes in the drumhead's wavefunction. What $n\ell$ combination (e.g., 2s, 4d, 6f, stuff like that) would correspond to the pattern of black particles on a kettledrum that looks like the one at right? Note that the outermost circle is the edge of the drumhead, and thus not a node. If you want partial credit, explain!



He^+ is, whaddayaknow, a one-electron system! Thus its electronic structure is well-described by the Bohr model. What kind of radiation (and if it is visible, what color) is emitted when an electron in the He^+ $n = 6$ state relaxes into the $n = 4$ state? If you haven't been paying attention in class, you don't want to do this problem…your book says very little about how to apply the Bohr model to anything other than hydrogen!

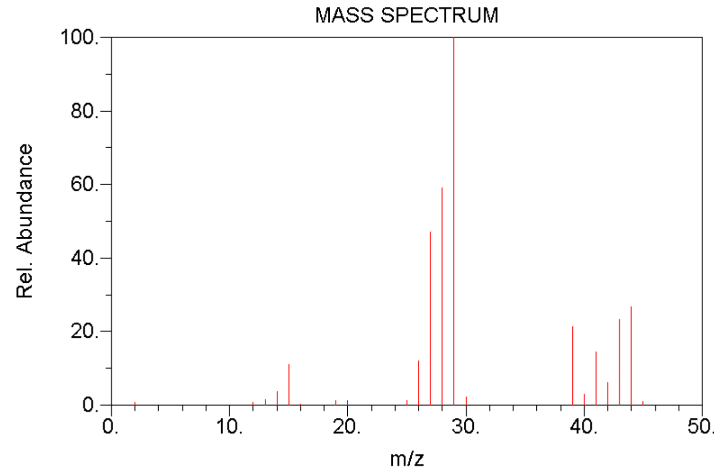
What is the electronic configuration of the Ti^{4+} ion? (You may just write it out, or you may use a box diagram.)

Would you expect the Ti^{4+} ion to be larger or smaller than the Ca^{2+} ion? Explain your answer.

Problem 4: Stuff From Lab

Here's an excerpt from my cousin Vinnie's lab notebook. It's pretty sad, really. Vinnie never was the sharpest knife in the drawer. I invited Vinnie over to my lab to try his hand at the Mystery Gases experiment, and this is what he came up with: some of his raw data, calculations, and conclusion. You'll find many things are wrong. Your mission, if you choose to accept it, is as follows:

a. Identify and explain three technical (rather than grammatical) mistakes in Vinnie's lab notebook
b. Correctly identify Vinnie's unknown gas, explaining the logic behind your identification



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Possible Mystery Gas Identities	
Name and Chemical Formula	Molar Mass (g/mol)
propane (C_3H_8)	44.096_{52}
nitrous oxide (N_2O)	44.0128
carbon dioxide (CO_2)	44.009_8

Vinnie's Awesome Lab Book (by Vinnie)

⇑ mass spectrum of mystery gas

So, like, beautiful, I'm here with Rob-o and we're gonna figure out this gas, see?

~Later, in the running account~

Mass of evacuated bulb = 57.32_{35} g

Mass of bulb filled with O_2 @ room T + P = 57.95_{43} g

Mass of bulb filled with mystery gas @ room T+P = 58.19_{10} g

~Later, in the calculations~

Mass of O_2 in bulb = 57.95_{43} g − 57.32_{35} g = 0.6308 g O_2

Mass of mystery gas in bulb = ~~58.19_{10} − 57.95_{43}~~

58.19_{10} g − 57.32_{35} g = 0.8675 g mystery gas

Since the number of moles of ideal gas in da bulb will not change as long as the T + P are constant,

$$n_{O_2} = n_{mystery} \qquad \frac{\text{mass of } O_2}{\text{MW of } O_2} = \frac{\text{mass of mystery}}{\text{MW of mystery}}$$

$$\text{MW of mystery} = \frac{\text{mass of mystery}}{\text{mass of } O_2} \times \text{MW of } O_2$$

$$= \frac{0.8675\text{ g}}{0.6308\text{ g}}(32.00\text{ g/mol})$$

$$= 44.00_8 \text{ g/mol}$$

Which means da mystery gas has gotta be CO_2.
See Rob-O, I don't need no stinkin' mass spec! Hah!

~Later, in the error analysis~

So, like, if I <u>had</u> let any air into the bulb with the mystery gas, then my MW value woulda been too big, 'cuz there'd'a been extra stuff in the bulb, see? Oh, did I mention that I didn't actually run the mass spec? That was Rob-O. I was havin' a smoke.

Exam 1 **Chemistry 123 Spring 2002**

My second cousin Billy-Bob Rossi came back up to visit me for another chemistry barbecue! We went into the lab and calibrated a fancy constant-pressure calorimeter, like the ones we used in lab but a bit more accurate. Then we took a crack at determining the identity of an "unknown" fuel that Julie mixed up for us. Julie told us that the mystery fuel has a formula weight of 60.05 g/mol, and consists of only carbon, hydrogen, and two oxygen atoms. [We noticed it smelled horribly of vinegar, by the way.] Using this information, determine the chemical formula of our mystery fuel. Clearly explain what you are doing, don't just spit out an answer!

B.B. and I got a heat capacity of $3.2 \pm 0.9\ kJ \cdot K^{-1}$ for our calorimeter. Following the same procedure you did in lab, but with our unknown, we got an initial lamp mass of 159.34 g and a final mass of 154.21 g. Our calorimeter started out at 23.8 ºC and topped out at 45.2 ºC. We calculated $\Delta H_{combustion}$ for our unknown fuel, as follows: [Uncertainties are as implied by significant figures unless given explicitly.]

$$\Delta\tilde{H}^{o}_{combustion} = \frac{q_{released}}{moles_{burned}} = \frac{C_P \Delta T}{\left(\frac{\Delta mass_{fuel}}{MW_{fuel}}\right)} = \frac{\left(3._{2}\,\frac{kJ}{K}\right)(45.2-23.8)C^{\circ}}{\left(\frac{159.34\ g\ -\ 154.21\ g}{60.05\ g/mol}\right)} = 8_{01.6}\,\frac{kJ}{mol}$$

Do a worst case error analysis on our result and, based on that, identify which fuels from the list of possibilities below can be eliminated from consideration because they do not fall within the range of "possible" ΔH^{o}_{c} values consistent with our calorimetry result. Assume our calorimeter is as reliable as our C_p value suggests it is, so that the worst case error gives a good upper bound on the uncertainty in ΔH^{o}_{c}.

Fuel Name	$\Delta H^{o}_{combustion}$ (kJ/mol)
Formic Acid	-255
Methanol	-726
Acetic Acid	-875
Acetaldehyde	-1166
Ethanol	-1368

Problem 5: Did You Understand the Homework?

My girlfriend Alex has recently arrived in Northfield, having driven up here from Atlanta. Atlanta is a warm place, so much so that we jokingly refer to it as 'Hotlanta.' On the day she left Hotlanta, Alex checked the pressure in her tires and found it to be right on target, at 32 psig. Her car had been sitting in the shade, but the air temperature was a whopping 90.ºF ($32._2$ºC) in Hotlanta that day. It's a few weeks later, and time for her to check her tire pressure again. This time it's on a mild morning in Northfield, with the temperature at 61ºF ($16._1$ºC). Her tire pressure gauge tells her the gauge pressure in the tires is 28 psig. What percentage of the air originally present in her tires leaked out in the three weeks between her measurements? Assume atmospheric pressure to be constant at 1.0 atm, and the volume of the tires to be constant. Please watch significant digits!

Handy data: $R = 0.0820578\ \ell\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ 101325 Pa = 760.00 torr = 14.696 psi = 1.0000 atm 0°C = 273.15 K

CFC's (chlorofluorocarbons) cause much of the trouble they do because while they are chemically very stable, they contain relatively weak C–Cl bonds that can be easily broken by photolysis (interaction with light). This happens when they make it into the upper atmosphere, and because the C–Cl bonds in them are the weak link, a lot of atomic Cl is released into the stratosphere. Atomic chlorine catalyzes (hastens) the decomposition of ozone, and its presence in the upper atmosphere is thought to be directly responsible for the phenomenon of ozone depletion we are currently experiencing.

Using data from your book, calculate the wavelength of a photon capable of breaking a typical C–Cl bond. What kind of radiation does this correspond to?

Consider the seemingly simple reaction $NaBr_{(s)} + KCl_{(s)} \rightarrow NaCl_{(s)} + KBr_{(s)}$

a. Is this reaction favored by entropy?
b. Is this reaction favored by enthalpy?
c. Is this reaction spontaneous at 25ºC and 1.0 atm?
d. Will heating this reaction encourage it to proceed from left to right, as written?