Exam 1: Colligative Properties, Thermochemistry, and Quantum Mechanics

Chemistry 123 | **WEDNESDAY, October 30, 2002** | **Fall 2002**
First Exam | **4 Pages / 4 Problems** | **SHOW YOUR WORK!** | **Instructor: R. Rossi**

Don't Panic!

Instructions:

- **Aaaaah! Stop Panicking!!!**
- **There are a total of four problems comprising this exam, one on each double-sided page.**
- **I have tried to make the front side of each page more quantitative, and the back side more qualitative, should you have a strong preference for one type of problem over the other.**
- **You need to answer the questions on *one* side of at least three of the pages, and it's your choice which side that is. It's also up to you which three of the pages you answer now.**
- **You get to choose how you want to deal with the last problem, but there are two distinct possibilities. You can choose to answer just one side of it, and hand it in now. Your other choice is to make that problem a take-home question; but then you must answer *both* sides of the page. If you don't remember to complete it and hand it in, you'll be hurtin'.**
- **If you decide to take one problem home, you have until 6:00pm on Thursday, May 16th to complete it and return it to my office. If I don't get the problem back from you by that time, your exam grade will be based on the three problems you handed in at the end of class.**
- **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 notebooks. If you have to look *everything* up, you won't finish this exam, but *do* use these references!**
- **You *MAY NOT USE COPIES OF MY HOMEWORK SOLUTIONS*, but if you make notes and corrections 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, a ruler, and anything else you OK with me in advance. *You may not use references or tools other than those listed above.***
- **You can start working on this exam at 9:50 am. You must hand in the non-take-home portion of your exam when I ask you for it at 11:00 am, if not before that time.**
- **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

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

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

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

$\Pi = i\,MRT$

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

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

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

$c = \lambda \nu$

$E_{photon} = |\Delta E_{electron}|$

$E_{\text{Bohr Electron}} = R_H \left(\dfrac{Z^2}{n^2} \right)$

$PV = \eta RT$

$P_i V = \eta_i RT$

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

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

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

$H \equiv E + PV$

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

$G \equiv H - TS$

Constants and Conversion Factors

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

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

273.15 K = 0ºC

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

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

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

1 m = 10^9 nm = 10^{10} Å

1 m = 3.2808 feet

1 m = 100 cm = 10^3 mm = 10^6 μm

1 eV = 1.602×10^{-19} Joules

R_H = 13.6 eV = 2.18×10^{-18} J

10^{-3} kg = 1 g = 10^3 mg = 10^6 μg

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

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

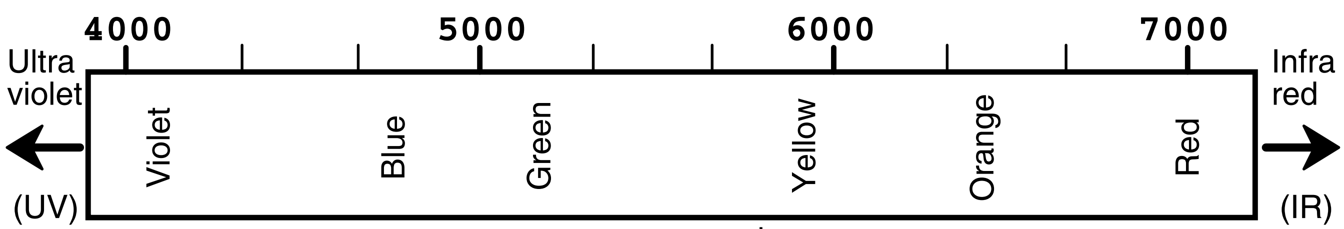
$1 \text{ Pascal} \equiv 1 \ \dfrac{kg}{m \cdot s^2}$

1.00000 atm = 760.000 Torr = 101325 Pa

1 mole = 6.022×10^{23}

1 m^3 = 1000 ℓ = 264.17 gallons

Wavelength of Visible Light (λ, in Ångstroms)



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

Common unit convesions: See Appendix 6 in your book, page A-28
Complete electromagnetic spectrum: in your book on page 293
Tables of Thermodynamic Data: See Appendix 4 in your book, pages A21-A24
Table of Bond Energies: in your book on page 373

Problem 1: Applied Chemistry

A. The U.S. Army Field Manual entitled "Operations and Maintenance of Ordnance Materiel in Cold Weather" includes instructions for keeping vehicle radiators from freezing in cold weather. It provides the handy table at right, which is not unlike that you would find on the back of a bottle of commercial antifreeze. It indicates down to what temperature a mixture of water and ethylene glycol will resist freezing. Your job is to determine to what extent any *one* of these entries agrees with the stuff we have learned in class about freezing point depression. You'll need to use data from your book, and possibly some of the following information:

PROTECTION TABLE

Cooling System Capacity in Quarts	ANTI-FREEZE COOLANT REQUIRED IN QUARTS For Protection to temperature Points °F Shown Below											
	2	3	4	5	6	7	8	9	10	11	12	13
5	-12°	-62°										
6	0°	-34°										
7	6°	-17°	-54°									
8	10°	-7°	-34°	-69°								
9		0°	-21°	-50°								
10		4°	-12°	-34°	-62°							
11		8°	-6°	-23°	-47°							
12		10°	-0°	-15°	-34°	-57°						
13			3°	-9°	-25°	-45°	-66°					
14			6°	-5°	-17°	-34°	-54°					
15			8°	0°	-12°	-26°	-43°	-62°				
16			10°	2°	-7°	-19°	-34°	-52°				
17				5°	-4°	-14°	-27°	-42°	-58°			
18				7°	0°	-10°	-21°	-34°	-50°	-65°		
19				9°	2°	-7°	-16°	-28°	-42°	-56°		
20				10°	4°	-3°	-12°	-22°	-34°	-48°	-62°	
21					6°	0°	-9°	-17°	-28°	-41°	-54°	-68°
22					8°	2°	-6°	-14°	-23°	-34°	-47°	-59°
23					9°	4°	-3°	-10°	-19°	-29°	-40°	-52°
24					10°	5°	0°	-7°	-15°	-24°	-34°	-46°

Guide for Preparation of Ethylene-Glycol Antifreeze Solutions

Do not use without some water; 68% concentration gives maximum protection. Use at least 25% concentration for protection against rust and corrosion.

Table 2-2. Antifreeze mixing guide

1. Ethylene Glycol is $C_2H_6O_2$ and has a molar mass of 62.07 g/mol. It is a covalently bonded molecule, rather than a salt, so it does not dissociate in water, just as camphor didn't dissociate in problem 2 of assignment 2.
2. The density of water may be assumed to be 1.0 g/mℓ, that of ethylene glycol is 1.1_2 g/mℓ
3. The normal freezing point of pure ethylene glycol is -13ºC; that of pure water is 0.0ºC.
4. Unit conversions essential to working this problem appear in Appendix 6 on page A28 in Zumdahl.

B. You and a friend have decided to go on a camping trip out west. You load up your car with the essentials here in Minnesota, including two yummy bags of chips in the back seat. As you drive into Wyoming and begin a serious ascent into the Bighorn Mountains, you periodically hear strange shuffling and stretching sounds from behind you. At first you think a squirrel may have gotten into your car at your last stop, but no squirrel is to be found. Puzzled, you continue driving up into the mountains, with more stretching and shuffling noises coming from behind you. Finally, there is a loud pop from behind you, which really gets your attention. But you can't track down where it came from. A bit shaken but not knowing what else to do, you continue up the mountains, only the be jarred by another loud pop shortly thereafter. Really worried, you go through the back seat carefully, only to discover that both chip bags have broken open, literally popped like an over-inflated tire. Why did this happen? Be explicit in your explanation, but not quantitative. This is a qualitative question.

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

a. Cold carbonated beverages poured into a warm glass fizz rapidly at first, then the fizzing subsides, even though there is plenty of carbon dioxide still dissolved in the liquid. Why?

b. Some of the paper I handed out later in the term is markedly brighter than that I handed out earlier in the term. What's up with that?

c. Incandescent light bulbs are appreciably less efficient than are fluorescent bulbs. Why? (Be sure to clearly state what "efficiency" means in this context! Incandescent bulbs are no less efficient at turning electricity into electromagnetic radiation than are fluorescent bulbs!)

Problem 2: Science Officer's Log, Stardate 47329.4

You are serving as the science officer aboard the Starfleet vessel Trovaré. Arriving in orbit around the planet Zorton in the Alpha Chromi star system, your sensors inform you that the composition of the atmosphere is as shown in the table at right. The away team is headed for a valley on the surface, where the atmospheric pressure is 11.7 atm and the temperature is -50ºC; they'll obviously need their environmental protection suits!

The eccentric captain is having her '66 Chevelle (a classic automobile) beamed down to the surface with her, so she can drive it out of the valley and across the plateau to a cave she wants to explore. Sensors indicate that as soon as she comes out of the valley and into the sun, the temperature will jump to a whopping 50ºC *above* zero.

Atmospheric Constituent	$\%_{mol}$ in atmosphere
Argon, Ar	39.6
Nitrogen, N_2	35.3
Oxygen, O_2	21.2
Fluorine, F_2	3.2
Chlorine, Cl_2	0.65
Bromine, Br_2	0.04
Neon, Ne	0.00_5
Krypton, Kr	0.00_5

Note: The correct molar mass of the earth's air is 28.9 g/mol (dry or wet it's the same to this many sig figs), and the composition of earth's atmosphere appears on p. 225 of Zumdahl in Table 5.4.

A. What is the average molar mass of Zorton's atmosphere, within the ability of your instruments to measure it?

B. Will the Captain's engine be running rich or lean, if it has a massflow air sensor calibrated to work on earth? (It pulls in 14.7 grams of air per gram of gasoline, and that's stoichiometrically dead-on for earth.)

C. The rest of the away team brought Berduskan lemonade down to the surface to drink while awaiting the captain's return. (They know better than to go with her, lest they be the "sixth crew member," the one that always dies.) They packed the stuff in dry ice on board the ship. They radio you in a panic from the surface, reporting something bizarre has happened to their dry ice. Having consulted the phase diagram for CO_2 (p. 500 in Zumdahl) even before they called, you are unfazed, and in fact anticipating this event. What happened?

(You'll want to read the scenario on the other side of this page before answering this question.)

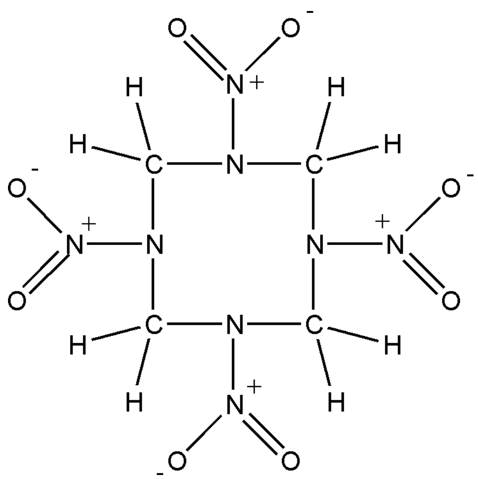
D. Alpha Chromi is very similar to our Sun, and Zorton is actually a little closer to its star than the Earth is to the Sun. So why is it so hot on Zorton's surface in view of Alpha Chromi, but so darn cold as soon as you move into the shade? You'll want to give an explanatory answer, but two words are capable of really summing it up!

E. If you have a bucket of water at 0ºC on the surface of Zorton, will it be a liquid, or frozen solid as ice? Why?

F. Besides running rich or lean, identify at least two serious problems that could impact the operation of the Captain's car and explain why or how they are likely to come about.

Problem 3: Quantum Mechanics and Chemical Reactions

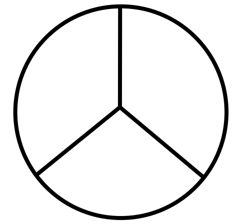
A. The high explosive HMX ($C_4H_8O_8N_8$) is purported to detonate according to the unbalanced reaction shown below. Use bond energies to estimate the enthalpy of detonation for HMX. (Bond Energy Table on p. 373)



$\rightarrow$ $N_{2(g)}$ + $H_2O_{(g)}$ + $CO_{(g)}$ $\Delta H^o = \Delta H^o_{detonation}$ [HMX]

B. Two other high explosives, TNT and nitroglycerine, are discussed on p. 922 of Zumdahl. **Gram for gram**, which high explosive packs the most punch: HMX, TNT, or nitroglycerine? Explain the basis for your answer.
[TNT is $C_7H_5O_6N_3$ and has $\Delta H^o_{detonation} = -$ 1040 kJ per mole of TNT; Nitroglycerine is $C_3H_5O_9N_3$ and has $\Delta H^o_{detonation} = -$ 1415 kJ per mole of nitroglycerine; the molar mass of HMX is 296.184 g/mol.]

C. 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. Why could you never see a pattern of black particles on a kettledrum that looks like the one at right? (Hint: Think about what has to happen when you cross a node!)



D. If a match is held an inch above a candle wick, the candle will not light. But if it is held above the candle in the very same spot shortly after the candle has been snuffed out, the candle *will* re-light. Why the difference?

E. Cleaning out your dorm room one day, you happen upon a remarkable artifact of an advanced civilization: it is a glass bulb in a time stasis field, containing $H_{(g)}$, that is, individual hydrogen atoms. You know that if you deactivate the stasis field, the H atoms will combine to form H_2, molecular hydrogen.

a. Is ΔH for this transformation positive or negative? (You need not explain your logic here.)

b. Assuming it doesn't break, does a vessel undergoing this reaction release or absorb heat?

Problem 4: Stuff From Lab

A. Below you'll find an excerpt from the lab book of a pretty good chemist who carried out the calorimetry lab in pretty much the same way you did. Next to their lab book entry appears a table of possible fuels.

Next, we performed an analogous ~~proceedure~~ procedure with our unknown fuel. We selected unknown 37, which the label indicates has a molar mass of 74.08 g/mol, and which the lab manual tells us contains two oxygens as part of a (C(=O)–O–C) group. It is a clear, clean-burning, non-viscous liquid with a fruity odor. With 200. ml of water in our erlenmeyer flask, we carried out the same process as we did with the ethanol, and obtained the following numbers:

Initial calorimeter temperature = T_i = 24.3 °C

Initial mass of unknown 37 = m_i = 124.67 g

Final calorimeter temperature = T_f = 46.5 °C

Final mass of unknown 37 = m_f = 122.98 g

Name and Structure of Fuel	$\Delta\tilde{H}^o_{combustion}$ (kJ/mol)
Ethyl Acetate $H_3C-C(=O)-O-CH_2-CH_3$	-2238.1
Ethyl Formate $H-C(=O)-O-CH_2-CH_3$	-1639.5
Propyl Formate $H-C(=O)-O-CH_2-CH_2-CH_3$	-2217
Methyl Formate $H-C(=O)-O-CH_3$	-972.6

a. What is the identity of the unknown fuel, given that it is one of those in the table? Explain your logic.

b. Assuming it underwent complete combustion, what fraction of the heat released by the combustion of the unknown was trapped in the water of the calorimeter?

B. My Father is a technically inclined fellow, but enjoys yanking my chain. I recall a few years ago he declared with conviction that "Beer has negative calories! The more beer you drink, the more calories you burn!" When questioned, he explained that a typical 355 mℓ can of beer arrives in your hands at about 5ºC, and your body has to warm it up to 37ºC. That requires your body provide 11360 calories of heat energy to the beer!

Unfortunately for you beer drinkers out there, my Dad's argument isn't the whole story. Why do you in fact gain weight when you chug back beer? Identify at least one important flaw in my Father's argument.

C. The specific heats of combustion ($\Delta\hat{H}^{o}_{combustion}$) for a *homologous (closely related)* series of alcohols appear in the table at right. Note that the trend is far less pronounced than when one looks at *molar* heat of combustion data ($\Delta\tilde{H}^{o}_{combustion}$). Explain, as best you can, the reason(s) for the observed trend.

Fuel Name and Formula	$\Delta\hat{H}^{o}_{combustion}$ (kcal/gram)
Methanol [CH_3OH]	5.34
Ethanol [CH_3CH_2OH]	7.11
1-Propanol [$CH_3CH_2CH_2OH$]	8.00
1-Butanol [$CH_3CH_2CH_2CH_2OH$]	8.61
1-Pentanol [$CH_3CH_2CH_2CH_2CH_2OH$]	9.03
1-Dodecanol [$CH_3(CH_2)_{10}CH_2OH$]	10.2