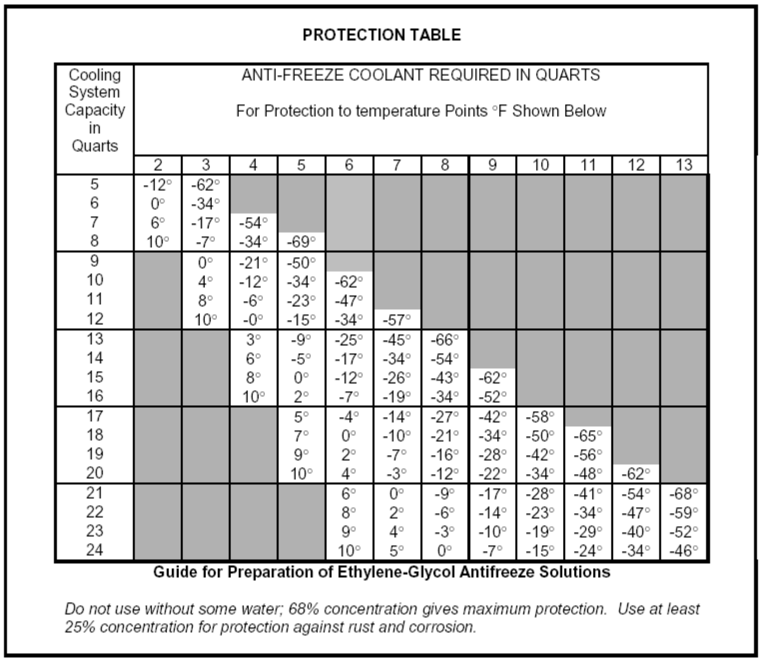
Exam 1 **Your Name: The Keymaster** **Chemistry 123 Fall 2002**

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.

You can avoid dealing with a lot of unit hassle by noting that the freezing point depends only on the (water:ethylene glycol) ratio, just as we would expect for a colligative property. (Thus 2 quarts in 6 protects to the same temperature as 3 in 9, or 4 in 12.) Say I want to check the entry for 5 quarts of antifreeze in a system with a capacity of 10 quarts: I can get the same number much more easily by considering a 2 liter system containing one liter of antifreeze. Assuming that the volume change associated with mixing is negligible, that would be a mixture of one liter of ethylene glycol and one liter of water. Since we don't know K_f for ethylene glycol, we will treat water as our solvent, although with such concentrated solutions the decision is really quite arbitrary.

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$$\underline{1}\ \ell\ \mathrm{H_2O}_{(\ell)}\left(\frac{\underline{1000}\ \mathrm{m}\ell}{\underline{1}\ \ell}\right)\left(\frac{1.0\ \mathrm{g\ H_2O}}{\underline{1}\ \mathrm{m}\ell\ \mathrm{H_2O}}\right)\left(\frac{\underline{1}\ \mathrm{kg}}{\underline{1000}\ \mathrm{g}}\right)=1.0\ \mathrm{kg\ \ of\ \ water\ (the\ solvent)}$$

$$\underline{1}\ \ell\ \mathrm{C_2H_6O_2}_{(\ell)}\left(\frac{\underline{1000}\ \mathrm{m}\ell}{\underline{1}\ \ell}\right)\left(\frac{1.1_2\ \mathrm{g\ C_2H_6O_2}}{\underline{1}\ \mathrm{m}\ell\ \mathrm{C_2H_6O_2}}\right)\left(\frac{\underline{1}\ \mathrm{mol\ C_2H_6O_2}}{62.07\ \mathrm{g\ C_2H_6O_2}}\right)=18._{044}\ \mathrm{mol\ C_2H_6O_2\ \ (the\ solute)}$$

We've learned that the freezing point of a solution is depressed from that of the pure solvent, according to the formula $\Delta T_f = -K_f m_{solute\ particles}$ where K_f is a constant that depends on the solvent and m_{solute} is the molality of solute particles.

Table 11.5 on p. 537 of Zumdahl tells us that water has a K_f value of 1.86 Cº·kg/mol

The problem tells us that ethylene glycol is a non-dissociating solute, so that 1 mol of it produces 1 mol of solute particles. So,

$$\Delta T_f = -K_f m_{solute\ particles} = -\left(1.86\frac{\mathrm{C^\circ\ kg}}{\mathrm{mol}}\right)\left(\frac{18._{044}\ \ \mathrm{mol\ solute}}{1.0\ \mathrm{kg\ solvent}}\right) = -33._{56}\,\mathrm{C^\circ}$$

Golly, that's actually pretty substantial! Since the normal freezing point of water is 0.0 Cº, this mixture would freeze at $-33._{56}$ºC, or $^\circ\mathrm{F} = \frac{9}{5}(^\circ\mathrm{C}) + 32 = \frac{9}{5}(-33.56) + 32 = -28._{41}{}^\circ\mathrm{F}$, which is in reasonable (though not super) agreement with the tabulated value of -34ºF.

For a 1:4 mixture, I get +16ºF, while the table claims +10ºF. For a 12:20 mixture, I get $-58._6$ºF to the table's -62ºF. While the agreement isn't perfect, we really shouldn't expect it to be, since some of these solutions are so rich in ethylene glycol that it's iffy to call the water the solvent. I honestly don't know why the table is systematically low, though; there may be some dissociation going on.

Why does the table claim that 68% ethylene glycol gives the maximum protection? Think about that for a second…if you fill your radiator with *pure* antifreeze, it will freeze at -13ºC, or +8.6 ºF. That's not good at all! You really need a mixture of two miscible fluids in there to get the freezing point down to Minnesota-proof levels. The maximum protection occurs at a ratio roughly weighted by the freezing points of the two pure components. (This ratio is also weighted by *i* in the case of ionic solutes.)

Note that adding "antifreeze" also elevates the boiling point of stuff in your radiator, helping to prevent your radiator from boiling over in hot weather. Pure ethylene glycol normally boils at 197.6ºC, though, so for optimum boilover protection you would want to use more than 68% ethylene glycol…and in perennially hot places people often do, sometimes just because they boil off their water.

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.

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Modern snack chip bags are sealed systems, and are actually filled with nitrogen at the factory to keep the chips fresh and to help keep them from getting crushed into dust. (That's not critical to the problem, I just though you might find it interesting; what is critical is that they contain a fixed amount of gas.) Since I keep the temperature in my car pretty constant, and the bags are full of gas but the bags can't really expand, we have a fixed amount of gas at essentially constant temperature and volume. That means that the *absolute* pressure of the gas in the bags remains roughly constant, which you may not have needed any convincing about, but if you did, there it was. If the pressure outside the bag is equal to that inside the bag, the bag just sits there. If the pressure outside is higher than that inside, the bag crumples up. If the pressure inside the bag is higher than that outside, the bag swells up bigger (or at least it tries to). The difference between the pressure outside the bag (the atmospheric pressure) and that inside the bag is the *gauge* pressure. So in other words, the condition of the bag, normal, "flat," or "fat," depends on the gauge pressure. The pressure inside the bag stays reasonably constant, but as I drive up into the mountains, the atmospheric pressure steadily drops. (We learned this in Problem 4 on Assignment 3.) As a result the gauge pressure gets ever larger, causing the bag first to puff up like the Sta-Puff marshmallow man, stretching and shuffling as it pushes other things around and the plastic strains under the pressure, and then to finally pop when a seam on the bag gives way and the gas trapped inside escapes.

For you mathematical types, $P_{gauge} = P_{absolute} - P_{atmosphere}$ = constant – (decreasing) = an increasing quantity ⇒ a swelling bag!

This actually happened to my girlfriend and I! Thankfully, we were able to figure out what happened so it didn't freak us out!

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?

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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!)

a. Carbonated beverages are fizzy because they contain dissolved carbon dioxide, CO_2. Like most gases, the solubility of CO_2 decreases with increasing temperature. When the cold pop hits the warm glass, the pop in contact with the glass heats up and the solubility of CO_2 drops rapidly. CO_2 bubbles out of solution until the concentration drops to match the new solubility. In the meantime, the glass cools down, and the solubility of CO_2 near the glass walls rises again. Once the glass is in thermal equilibrium with the drink, the fizzing subsides. This takes far less time with an insulated plastic glass than with a heavy metal or glass one.

b. The paper the college started using in about the middle of the term contains a lot more fluorescent dye than the stuff we used to use! In light with a substantial ultraviolet component, (this includes fluorescent light and sunlight, and to a lesser extent light from incandescent bulbs of the non-halogen variety,) this dye absorbs UV light and emits blue light, making the paper appear "whiter than white," reflecting more visible light than actually hits it!

c. When we talk about the efficiency of an electric light source, we are referring to the number of visible photons it can produce per joule of electrical energy it consumes. Incandescent bulbs give off electromagnetic radiation as a result of their being very hot, it's a phenomenon called blackbody radiation. They emit every type of photon imaginable, though most of the photons fall in the infrared part of the spectrum for typical incandescent bulb the filament temperatures; less than 12% of the photons are in the visible part of the spectrum, and thus useful for reading a book or finding one's way in the dark. In contrast, the Hg plasma in a fluorescent light tube emits almost exclusively those photons corresponding to common electronic transitions in mercury atoms: primarily visible blue and (invisible) UV photons. Because fluorescent tubes are coated with a fluorescent dye that absorbs the UV photons and emits visible photons (their color chosen to balance out the blue photons and make the light coming from the fluorescent tube appear white), almost all the radiation from a fluorescent tube ends up being in the visible portion of the spectrum, and they are very efficient at turning electricity into visible light.

Problem 2: Science Officer's Log, Stardate 47329.4

Atmospheric Constituent	$\%_{\text{mol}}$ 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

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.

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?

$$\tilde{m}_{\text{gas mixture}} = \frac{\text{total mass of all components}}{\text{total moles of components}} = \frac{\text{total mass of 1 mole of gas}}{\text{1 mole of gas}} = \frac{\sum \text{mass of each component}}{\text{1 mol}} = \frac{\sum_i \chi_i \tilde{m}_i}{\text{mol}}$$

$$\begin{aligned}\tilde{m}_{\text{gas mixture}} &= (39.6\%)(\tilde{m}_{Ar}) + (35.3\%)(2\cdot\tilde{m}_N) + (21.2\%)(2\cdot\tilde{m}_O) + (3.2\%)(2\cdot\tilde{m}_F) + (0.65\%)(2\cdot\tilde{m}_{Cl}) \\ &\quad + (0.04\%)(2\cdot\tilde{m}_{Br}) + (0.005\%)(\tilde{m}_{Ne}) + (0.005\%)(\tilde{m}_{Kr}) \\ &= (0.396)(39.95) + (0.353)(2\cdot 14.01) + (0.212)(2\cdot 16.00) + (0.032)(2\cdot 19.00) + (0.0065)(2\cdot 35.45) \\ &\quad + (0.0004)(2\cdot 79.90) + (0.00005)(20.18) + (0.00005)(83.80) \\ &= 15.8_{202} + 9.89_{106} + 6.78_{4} + 1.2_{16} + 0.46_{085} + 0.06_{392} + 0.00_{1009} + 0.00_{419} \quad \text{(The last 3 terms are negligible)} \\ &= 34.2_4 \ \frac{\text{grams}}{\text{mol}} \quad \left(\begin{array}{l}\text{Note that significant figures mattered here; because the first term in the sum was} \\ \pm\ 0.1 \text{ g/mol, the sum as a whole couldn't be known any more precisely than that.}\end{array}\right)\end{aligned}$$

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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.)

Gasoline is actually a mixture of lots of different things, and we have no way of knowing exactly what…but we are told that 14.7 g of earth air contains exactly the right amount of oxygen to completely combust one gram of the gas in the Captain's tank. So this question is most easily worked out by recasting it to ask if 14.7 g of Zorton's air contains more or less oxygen than does 14.7 g of earth's air.

Table 5.4 in Zumdahl tells us that one mole of (dry) earth air contains 0.20948 moles of O_2, and the information given above tells us that the mass of this mole of air should be 28.9 grams. Thus earth air contains approximately

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$$\frac{0.20948 \text{ moles of } O_2}{28.9 \text{ grams of earth air}} = 0.00725 \frac{\text{moles of } O_2}{\text{gram of earth air}}$$

We know from the sensors and our work in part A that one mole of Zorton air contains 0.212 moles of O_2, and has a mass of 34.2_4 g.

$$\frac{0.212 \text{ moles of } O_2}{34.2_4 \text{ grams of Zorton air}} = 0.00619 \frac{\text{moles of } O_2}{\text{gram of earth air}}$$

This tells us that 14.7 g of earth air contains a bit more oxygen than does 14.7 g of Zortonian air; so if the engine sucks in Zorton's air at the rate appropriate for earth air, it will be running a little short of O_2, which means it will be running rich. (But it'll still run.)

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?

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The "dry ice" melted into liquid CO_2! That's only possible under certain combinations of temperature and pressure above 5.1 atmospheres and -56.6ºC, but those are exactly the conditions prevalent in the valley where the away team is waiting.

(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!

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In two words: Zorton has no Greenhouse Effect! Notice that all of the gases in Zorton's atmosphere are either monatomic or homonuclear diatomics. As a result, none of them can interact with infrared radiation to any appreciable extent. Some of them are lightly colored in the visible portion of the spectrum (Cl_2 and Br_2, in particular, which are likely to fall as rain and freeze as ice on Zorton), but this is an atmosphere completely transparent to the infrared portion of the spectrum. That has two important consequences: First, all the infrared radiation spit out by Alpha Chromi (the bulk of its radiation, given its temperature) comes right through the atmosphere and warms things up exposed to sunlight. This makes things very toasty when not in the shade. But the other effect of the atmosphere's transparency to IR radiation is that the IR radiation constantly emitted by its surface escapes right back out into the void rather than being reflected back to the surface by the greenhouse effect. Areas not exposed to sunlight don't get to feel any of the warmth of the illuminated portions of the planet, and cool off quickly to truly unlivable, sub-Minnesota temperatures.

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

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It'll be a liquid! Contrary to the behavior of most substances, water is actually less dense as a solid than it is as a liquid. As a result, the line dividing the solid from the liquid on the phase diagram has a negative slope (dP/dT is negative, see Figure 10.47). This in turn means that as you increase the pressure, the freezing point of water actually drops. On Zorton, where the surface pressure is well above one atmosphere, water will not freeze until it gets appreciably colder than 0°C. It's also possible to arrive at the same conclusion by remembering that in our discussion about ice skating, we learned that a significant part of what makes ice skating possible is that the melting point of the ice immediately under your skate, where the pressure is higher, is much warmer than it would be otherwise.

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.

There are a slew of acceptable answers here - this is, after all, a real-life question. But the ones directly relating to what we've learned about in class are as follows:

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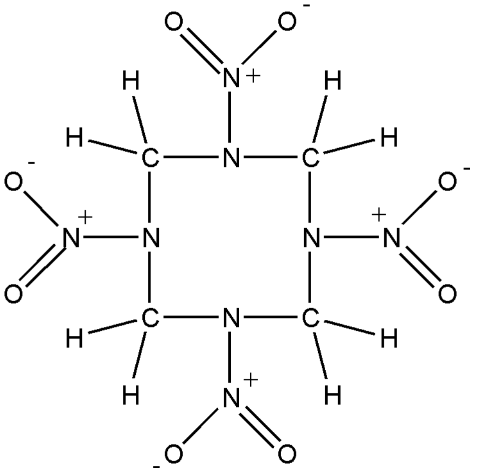
1. The Captain's engine is likely to knock like crazy! Here on Zorton the pressure is much higher than it would be anywhere you could reasonably drive a car on earth. As a result, a really really high octane rating would be needed to prevent knock. The Captain's car is old enough that it doesn't have a knock sensor, so not only would it have no power, but she might do some serious damage to her precious SS 396 engine!
2. (4ea) While it is possible the Captain's radiator is filled with coolant that could avoid freezing at -50°C (-58°F), it's very unlikely that it wouldn't boil over after even a short time operating at an ambient air temperature of +50°C (+122°F). That's as hot as it gets at high noon in the dead of summer in Death Valley or Baker, California, or in the Dallol Depression in Ethiopia.
3. Unless the captain thought to check and adjust her tire pressure, she'd be riding on some very flat tires! Even in the sun, where the temperature would raise the pressure inside the tires, the absolute pressure inside the tires wouldn't even get close to the 11.7 atm pressure outside them, leading to a negative gauge pressure! If the Captain did try to pump up her tires, they might be able to take the required absolute pressure, because it is really the gauge pressure that determines how much strain they are under. But with the huge temperature variations prevalent on Zorton, she could easily end up with flat tires again, or worse, blowing the tires right off the rims!

A few other likely problems that we didn't explicitly talk about in class: If the oil in her crankcase wasn't frozen into molasses at -50°C, preventing her from turning over her engine with the battery weakened by the cold, then it would be too thin to survive any length of time operating at +50°C and would boil right out of the engine block. I think the 66 Chevelle also had gas shocks in the suspension system, and on Zorton they would arrive and forever stay completely bottomed out.

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)



$$\rightarrow\ N_{2(g)} + H_2O_{(g)} + CO_{(g)} \qquad \Delta H^\circ = \Delta H^\circ_{\text{detonation}}\,[\text{HMX}]$$

HMX is $C_4H_8O_8N_8$, and when it detonates it doesn't have time to react with anything but itself (That is part and parcel of the definition of detonation).

$$\begin{array}{ccccccc} \cancel{C}_4\cancel{H}_8\cancel{O}_8\cancel{N}_8 & \rightarrow & \cancel{N}_2 & + & \cancel{H}_2\cancel{O} & + & \cancel{C}\cancel{O} \\ & & \cancel{N}_2 & & \cancel{H}_2\cancel{O} & & \cancel{C}\cancel{O} \\ & & \cancel{N}_2 & & \cancel{H}_2\cancel{O} & & \cancel{C}\cancel{O} \\ & & \cancel{N}_2 & & \cancel{H}_2\cancel{O} & & \cancel{C}\cancel{O} \end{array}$$

2pts

So the balanced reaction for the detonation of HMX is: $C_4H_8O_8N_8 \rightarrow 4\,N_2 + 4\,H_2O + 4\,CO$

To calculate ΔH°_{rxn} for this reaction using bond energies, we have to break all the bonds in HMX, putting energy into the system and making ΔH° more positive, and then combine all the atoms thus released to form the products, forming new bonds which release energy and make ΔH° more negative. We should expect a net negative ΔH° for any decent explosive!

Bonds Broken	ΔH (kJ/mol)	Bonds Formed	Net ΔH (kJ/mol)
4 N=O	+4 (607)		242_8
4 N–O	+4 (201)		804
4 N–N	+4 (160)		64_0
8 C–N	+8 (305)		244_0
8 C–H	+8 (413)		330_4
	-4 (941)	4 N≡N	-376_4
	-8 (467)	8 O–H	-373_6
	-4 (1072)	4 C≡O	-4288
	-217_2		-217_2

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Note that Zumdahl is pretty darn sloppy about sig figs in his average bond enthalpy table, and he probably means 160. instead of 160 and 200. instead of 200 when he puts those numbers with trailing zeroes into the table. Still, we'll treat the table as if it was put together by a careful scientist, and take him at implied face value on the precision of his values. Because Zumdahl wasn't careful about it, I didn't take any points off for significant figure errors arising from plausible interpretations of his data; but it was still possible to make sig fig errors on this problem, particularly in adding up the component ΔH values!

∴ The heat of detonation for HMX, as calculated from bond enthalpies, is -2170 kJ per mole of HMX, or -217_2 kJ per mole of 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 $\Delta H^\circ_{\text{detonation}} = -\ 1040$ kJ per mole of TNT; Nitroglycerine is $C_3H_5O_9N_3$ and has $\Delta H^\circ_{\text{detonation}} = -\ 1415$ kJ per mole of nitroglycerine; the molar mass of HMX is 296.184 g/mol.]

As outlined in our book, the "punch" of an explosive actually depends on the volume of gas generated from a given amount of the explosive (occupying a much smaller volume) upon detonation. This, in turn, depends on both the number of moles of gas released by the detonation, and the temperature to which the gas is heated by the energy released in the detonation reaction. The former is readily determined from the balanced detonation reaction, while the latter is adequately estimated from $\Delta H^\circ_{\text{detonation}}$. For HMX, we know from our work above that one mole detonates to form 12 moles of gas, with a ΔH° of about -2170 kJ/mol. In contrast, the book tells us that TNT detonates to yield 20 moles of gas per 2 moles of TNT, or 10 moles of gas per mole of TNT, while nitroglycerine explodes into 29 moles of gas per 4 moles of nitroglycerine, or 7.25 moles of gas per mole of nitroglycerine. To determine the "punch" of these explosives on a per gram basis, we simply need to divide all these ratios and ΔH values by the molar mass of each:

$$\text{HMX}: \frac{12\text{ moles of gas}}{1\text{ mol HMX}}\left(\frac{1\text{ mol HMX}}{296.184\text{ g/mol}}\right) = 0.0405153_{55}\,\frac{\text{moles of gas}}{\text{g of HMX}} \qquad -217_2\,\frac{\text{kJ}}{\text{mol HMX}}\left(\frac{1\text{ mol HMX}}{296.184\text{ g/mol}}\right) = -7.33_{33}\,\frac{\text{kJ}}{\text{g of HMX}}$$

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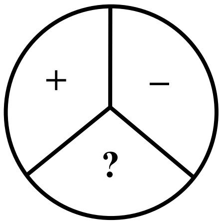
$$\text{TNT}: \frac{10\text{ moles of gas}}{1\text{ mol TNT}}\left(\frac{1\text{ mol TNT}}{227.13\text{ g/mol}}\right) = 0.044027_{65}\,\frac{\text{moles of gas}}{\text{g of TNT}} \qquad -1040\,\frac{\text{kJ}}{\text{mol TNT}}\left(\frac{1\text{ mol TNT}}{227.13\text{ g/mol}}\right) = -4.57_{89}\,\frac{\text{kJ}}{\text{g of TNT}}$$

$$\text{Nitroglycerine}: \frac{7.25\text{ moles of gas}}{1\text{ mol nitrogly.}}\left(\frac{1\text{ mol nitrogly.}}{227.09\text{ g/mol}}\right) = 0.031925_{67}\,\frac{\text{moles of gas}}{\text{g of nitrogly.}} \qquad -1415\,\frac{\text{kJ}}{\text{mol}}\left(\frac{1\text{ mol nitrogly.}}{227.09\text{ g/mol}}\right) = -6.231\,\frac{\text{kJ}}{\text{g nitrogly.}}$$

I made a tactical error in writing this problem, so it's not clear whether TNT or HMX is more powerful. I graded accordingly. =(

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!) 5



The wavefunction (Ψ) must change sign every time it crosses a node. With this pattern, that is not possible. If the top two regions are positive and negative, respectively, the last region must be positive if crossing into it from the negative region, but negative if crossing into it from the positive region; both can't be satisfied simultaneously.

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?

Solid candle wax does not react with oxygen quickly enough to carry on a self-sustaining combustion reaction. (Even liquid candle wax can not, as such, participate in a self-sustaining combustion reaction in normal air.) However, when warmed sufficiently, candle wax will first melt and then vaporize into a very flammable gas. That gas *is* capable of carrying out a self-sustaining combustion reaction in normal air, and what's more, the heat it gives off is sufficient to keep the wax in and near the wick of a candle in the liquid state, and to cause it to vaporize quickly enough to provide enough new fuel for the fire to keep it going. (That is, unless it is *really* cold, or there's a stiff breeze blowing the heat away and cooling the wick!) This is far more explanation than you needed to provide, but it should clarify for you why you need to hold a match to a candle for a little while before the candle will stay lit. At any rate, the other key to answering this question is understanding that when a burning candle is snuffed out (that is, deprived of oxygen), it remains hot and continues to release highly flammable vapor into the air above the wick until it cools back down. If any source of flame, even a small spark, is brought into that mixture of air and flammable vapor, a self-sustaining combustion reaction will ensue, and the candle will re-light as the flammable gas burns back down to the wick and begins again the self-sustaining vaporization process there.

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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.)

3 It takes energy to break bonds, while energy is released when you form new bonds. In this case we are forming new H–H bonds, and thus we expect energy to be released, some of it as heat. That means the reaction should be exothermic, and thus its ΔH value should be negative.

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

3 This is actually a very tricky question, but I didn't expect anyone to catch the subtlety it entails. The answer one gets by considering it at face value is correct, but technically the justification has to be a bit more involved than what most of you wrote. We established above that the reaction is exothermic, and that's true no matter under what conditions we carry out the reaction. But, technically, $q = \Delta H$ *only* under constant opposing pressure…and if this bulb doesn't break, the pressure inside it will actually rise quickly (as the temperature of the gas will rise), then eventually become less than it was at the outset as the products cool; it's not a constant pressure situation. So just saying that it releases heat because ΔH is negative misses some of the argument. In a true constant pressure situation, i.e., if the reaction took place in a magic syringe, the net work done by the system might be either positive or negative, depending on the external pressure and the initial conditions of the system. If the bulb doesn't break, then the volume of the system is constant and *no* work is done by the system: all the energy released when the bonds are formed will be released as 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.

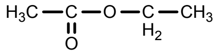
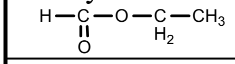
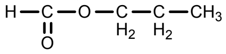
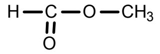
Next, we performed an analogous ~~procedure~~ procedure with our unknown fuel. We selected unknown 37, which the label indicates has a molar mass of 74.08 g/mol, and which the lab manual tells us contains two oxygens as part of a $\left(\underset{\overset{\|}{O}}{C}-O-C\right)$ group. It is a clear, 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 = $m_i = 124.6_7$ g

Final calorimeter temperature = $T_f = 46._5$°C

Final mass of unknown 37 = $m_f = 122.9_8$ g

Name and Structure of Fuel	$\Delta\tilde{H}^{o}_{combustion}$ o (kJ/mol)
Ethyl Acetate  $H_3C-\underset{\overset{\|}{O}}{C}-O-\underset{H_2}{C}-CH_3$	2238.1
Ethyl Formate  $H-\underset{\overset{\|}{O}}{C}-O-\underset{H_2}{C}-CH_3$	1639.5
Propyl Formate  $H-\underset{\overset{\|}{O}}{C}-O-\underset{H_2}{C}-\underset{H_2}{C}-CH_3$	2217
Methyl Formate  $H-\underset{\overset{\|}{O}}{C}-O-CH_3$	972.6

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

I intentionally gave you too little information to determine C_p for the calorimeter, because just as in the real lab, the easy way to do this was based on the molar mass and the given structural information. Knowing that the molecule has a molar mass of 74.08 g/mol and that it contains two oxygen atoms, we can quickly ascertain that the mass of carbon + hydrogen in it must be

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$$74.08\frac{g}{mol}-2\left(16.00\frac{g}{mol}\right)\text{for two oxygen atoms}=42.08\frac{g}{mol}\,C+H\;\Rightarrow\;1,\,2,\text{ or }3\text{ C, most likely }3$$

$$42.08\frac{g}{mol}C+H-3\left(12.01\frac{g}{mol}\right)\text{for three oxygen atoms}=6.05\frac{\text{g of H}}{mol}\left(\frac{\text{1 mol H atoms}}{\text{1.008 g of H}}\right)=6.00\text{ H atoms}\;\Rightarrow\;C_3H_8O_2$$

With the right formulas in the boxes, the only fuel that matches this molar mass is ethyl formate. One could also add up the mass of each of the four possibilities, but that's a lot more work.

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?

$$\text{Mass of fuel burned}=(124.6_7\text{ g}-122.9_8\text{ g})=1.6_9\text{ g of }C_3H_8O_2\left(\frac{1\text{ mol }C_3H_8O_2}{74.08\text{ g }C_3H_8O_2}\right)=0.022_{813}\text{ mol }C_3H_8O_2\text{ burned}$$

If the fuel combusts completely under constant pressure conditions (in the atmosphere), the heat released will be

$$q=\eta\,\Delta\tilde{H}^{\circ}=0.022_{813}\text{ mol}\left(-1639.5\frac{kJ}{mol}\right)=-37._{4022}\text{ kJ}\quad\text{(Heat released by complete combustion of fuel)}$$

We're going to want to compare this to the amount of heat absorbed by the water in the calorimeter:

$$q_{H_2O}=m_{H_2O}\left(\tilde{C}_{p,H_2O}\right)\Delta T=(200.\text{ g})\left(4.18\frac{J}{g\ C^{\circ}}\right)\left(46._5\,C^{\circ}-24._3\,C^{\circ}\right)=836\frac{J}{C^{\circ}}\left(22._2\,C^{\circ}\right)=18_{559}\,J\left(\frac{1\text{ kJ}}{1000\text{ J}}\right)=18._{559}\text{ kJ}$$

The fraction of the heat released by combustion of the fuel in the water of the calorimeter is therefore

$$\frac{18._{559}\text{ kJ}}{37._{402}\text{ kJ}}\times100\%=49._{62}\%$$

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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.

My father's math could be sniped at, in that the heat capacity of beer may not, in fact, be equal to that of water; but the difference will be small. It does, in fact, require about 11000 calories to heat up liquid beer from 5ºC to 37ºC, and that does in fact happen in the short time between when you chug back a beer and when it begins to be digested in your stomach. If you chug back a can of cold water, that's the whole story, in fact: a can of cold water really does have "negative calories." But beer also contains carbohydrates, which are carbon compounds that your body can combine with oxygen to release energy. Put another way, a typical can of beer contains on the order of 100-150 Calories. (Note the capital letter "C") That doesn't sound like much compared against the 11360 calories outlined above, but food labels actually give their values in *kilo*calories (hence the capital C), so we're talking 100000 "positive" calories in a can of light beer, more than enough to offset the 11000 "negative" calories lost to heating up the beer. Before you go kicking back cold water to try to lose weight, keep in mind that 11000 negative calories means that you need to drink an entire can of cold water to offset 11 Calories of food energy…that's roughly a can of cold water for every three peanuts you eat.

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C. The specific heats of combustion ($\Delta\hat{H}^{o}_{\text{combustion}}$) 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 ($\Delta\tilde{H}^{o}_{\text{combustion}}$). Explain, as best you can, the reason(s) for the observed trend.

Fuel Name and Formula	$\Delta\hat{H}^{o}_{\text{combustion}}$ (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

Each of these alcohols contain some amount of carbon connected to H or other C atoms, and one C–O–H group. You can think of the former as unburned wood, while the latter is analogous to partly burned wood: it has made part of the journey from weak C–C and C–H bonds to the stronger C=O and O–H bonds present in the products of combustion, CO_2 and H_2O. As a result, the C–O–H group doesn't release as much heat when combusted as does the hydrocarbon (C and H) portion of the molecule. So these molecules all have a "partly burned" end, connected to a segment of unburned wood of varying length. As you make the unburned end longer, the size and mass of the molecule goes up, but the density of the molecular material you are adding, and the amount of heat it gives off per gram of it you burn, is pretty much the same. So as the "log" gets longer and longer, the fact that the end of it is partly burned matters less and less, and the specific heat of combustion approaches the value of plain hydrocarbons. (The specific heat of combustion of $C_{20}H_{42}$ is 11.3 kcal/gram, while that of $C_{20}H_{42}O$ is 10.5 kcal/gram; the reason a difference persists is that the alcohol can hydrogen bond, so it takes appreciably more energy to pull apart the molecules of the alcohol's condensed phase than it does to pull apart the molecules of the simple hydrocarbon, which does not exhibit hydrogen bonding.) This is why the specific heat of combustion of these alcohols starts out low (initially more than half of the mass of the "log" is partly burned wood) and rises gradually to an asymptote (the value one would get for a sample of completely unburned wood, regardless of its size). To put this in terms of another concept we've learned about, the heat of combustion per CH_2 group in a hydrocarbon and the mass of a CH_2 group are both intensive properties, while the heat of combustion for a given collection of molecules and the mass of that collection of molecules are both extensive functions. If you keep adding the same unit to a molecule (in this case, CH_2) then the ratio of the two extensive functions for a homologous series will be an intensive variable whose value approaches a constant value representative of the ratio of the two extensive quantities described above.

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