Exam 1 **Your Name:** Señor Key **Chemistry 123 Spring 2002**

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.]

Water softeners replace cations (+ ions) with sodium ions, so the Ca^{2+}, Mg^{2+}, and Fe^{3+} concentrations would go down (to nearly zero) and the Na^+ concentration would go way up.

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

The water upstream of the softener (the hard water) would be at the greatest risk of freezing, because the softener puts in two Na^+ (two particles) for each +2 ion it takes out, 3 Na^+ for each +3 ion it removes. So it increases the concentration of particles in the water, and lowers the freezing point.

c. At what temperature will unsoftened Northfield tap water freeze, assuming the ions listed in the table below are the only ones warranting consideration? $K_f = 1.86\ K\cdot kg/mol$ for H_2O ← Table 12.8 in textbook.

$$\Delta T_f = -K_f m_{particles} = -\left(1.86 \frac{K\cdot kg}{mol}\right)(\text{total molality of particles})$$

$$= -\left(1.86 \frac{K\cdot kg}{mol}\right)(0.071+0.033+0.009+0.008+0.004+0.002)\frac{mol}{kg}$$

$$= -\left(1.86 \frac{K\cdot kg}{mol}\right)\left(0.127 \frac{mol}{kg}\right)$$

$$= -0.236\ K \text{ (yes, 3 sig figs!)}$$

The tap water would freeze at −0.236°C; probably won't save the house! !!

Just for your info: After going through the water softener, $m_{particles}$ would be $0.071 + 0.033 + 2(0.009) + 2(0.008) + 0.004 + 3(0.002)\ \frac{moles}{kg}$, or 0.148 mol/kg, such that the freezing point of the softened water should be −0.275 °C, just a wee bit colder.

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 °C shortly before dawn to +407 °C 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 °C. 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.

CO_2 is a greenhouse gas, and so Venus experiences an incredibly powerful greenhouse effect. The thick layer of CO_2 around it acts like a blanket, preventing the rapid transfer of IR (infrared) radiation between outer space and the Venusian surface. This keeps the temperature pretty stable. Because CO_2 is transparent to visible light, a lot of radiation from the sun passes through the atmosphere, is absorbed by the surface, and is effectively turned into heat energy by dark things on the surface. This heat can't easily escape, which is why Venus is so hot. mercury, having no atmosphere, easily exchanges heat with outer space: so it is hot when and only when it is being heated.

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?

1. You would find the ice tray empty, and frost on the freezer coils! Over so long a time, all the water molecules would sublime into the gas phase and re-freeze preferentially onto the coldest surface in the freezer. The colder their location, the lower their likelihood of entering into the gas phase + roaming again.

2. AM radio waves are longer, and can diffract around (pass through) big obstacles, like buildings. FM radio waves have shorter wavelengths and are reflected by buildings.

3. Bacteria + mold cells are dehydrated by the salinity of the pickle juice - they litterally shrivel up and die because the salty water sucks all the water out of them by osmosis.

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

$\Delta H^\circ_{rxn} = \Sigma \Delta H^\circ_f$ [products] $- \Sigma \Delta H^\circ_f$ [reactants], but all of our reactants in both cases are elements in their standard states, & thus have ΔH°_f values of zero. Soooo...

i) $\Delta H^\circ_{rxn} = 2\Delta H^\circ_f[HF_{(g)}] = 2(-271.1 \text{ kJ/mol}) = -542.2 \text{ kJ/mol}$

ii) $\Delta H^\circ_{rxn} = 2\Delta H^\circ_f[HCl_{(g)}] = 2(-92.31 \text{ kJ/mol}) = -184.6_2 \text{ kJ/mol}$

Note: you could also get an accurate value from bond strengths, as these are all diatomics.

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].

From Table 9.2

Bond Strength of

$F_2 = 158$ kJ/mol

$Cl_2 = 242$ kJ/mol

HF = 565 kJ/mol

HCl = 431 kJ/mol

There are two relevant factors:

- In (i) we are breaking a relatively weak F-F bond rather than the stronger Cl-Cl bond in (ii). That means less energy input to start rxn (i).
- In (i) we are forming a relatively strong H-F bond compared against the weaker H-Cl bond in (ii). The stronger the bond formed, the more heat released.

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

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

CO_2 H_2O $11O_2$
CO_2 H_2O
CO_2 H_2O
CO_2 H_2O
CO_2 H_2O
CO_2 H_2O
CO_2 H_2O
CO_2 H_2O
CO_2 H_2O
CO_2 H_2O
CO_2 H_2O
H_2O

Balanced: $12CO_{2(g)} + 11H_2O_{(\ell)} \rightarrow C_{12}H_{22}O_{11(s)} + 12O_{2(g)}$

The easy way to get the ΔH is to realize that this is the reverse of the combustion reaction, and that $\Delta H^\circ_{combustion}$ [sucrose] is given in Appendix 2 as -5645 kJ/mol.

So $\Delta H^\circ_{reaction} = +5645$ kJ/mol

(Calculation using ΔH_f's and Hess' Law yields +5644.25 kJ/mol.)

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 trick. 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, it would expand against the pressure of the atmosphere to do 160 kJ worth of work and release 465 kJ worth of heat. ~~If~~ once allowed to cool, ~~he would see water condensed in the magic syringe.~~ and compressed back down to the starting volume.

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

With the question modified, the initial and final states in Vinnie's test run and the Don Pesante experience match up, and we can count on any Δ(state function) to be the same in both cases. In the test run, the system gave up energy as both heat and work, so

$$\Delta U = q + w = -465\,\text{kJ} + (-160\,\text{kJ}) = -625\,\text{kJ}$$

U being a state function, we expect ΔU to be the same with Don Pesante on board. But since $dw = P_{opp}\,dV$ and dV is zero, the system can do no work and now all the energy will be released as heat. We can expect a $q = \Delta U - w = -625\,\text{kJ} - 0 = -625\,\text{kJ}$ bun-roasting for Don Pesante!

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? Most or all of the O_2 in the syringe is used up, and unless he flushes the burnt gasses out of it (like I did with the ethanol cannon) and fills it with fresh air, the hairspray won't be able to burn.

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?

See problem 5!

Well, OK. Basically, CFC's were found to reduce the amount of O_3 in the stratosphere, and thereby increase the amount of UV radiation getting to the earth's surface. To avoid this problem, the Montreal Protocol mandated a phase-out of CFC's, starting with non-critical uses like aerosol propellants.

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.

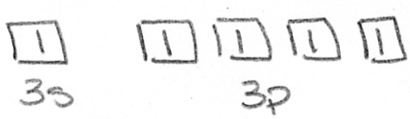
$\ell=1$ $m_\ell = -2, -1, +1, ~~0~~ +2$ $m_s = 0$ ⇒ 4e⁻ can be held in the p's

$\ell=2$ $m_\ell = -4, -3, -2, -1, 1, 2, 3, 4$ $m_s = 0$ ⇒ 8e⁻ can be held in the d's

$\ell=3$ $m_\ell = -6, -5, -4, -3, -2, -1, +1, +2, +3, +4, +5, +6$ $m_s = 0$

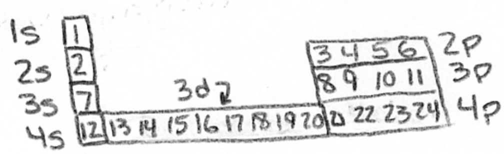
⇒ 12e⁻ can be held in the f's

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.

Here's the funkyverse periodic table:



The electronic configuration will be

$1s^1 2s^1 2p^4 3s^1 3p^4 4s^1 3d^8 4p^4$,

for a total of 24e⁻, indicating 24 protons in the nucleus and thus an atomic # of 24.

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!

This oscillation has three linear and two circular nodes, for a total of 5. n is one more than the total number of nodes, so $n=6$. ℓ is the number of linear nodes, 3 in this case, and f is the shorthand for $\ell=3$. **6f**

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!

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

Z is the nuclear charge, +2 for He^{+}. $n_f = 4$ and $n_i = 6$, $R_H = 2.18\times10^{-18}$ J

$$= (2.18\times10^{-18}\,J)(+2)^2\left(\frac{1}{4^2} - \frac{1}{6^2}\right) = 3.02_{78}\times10^{-19}\,J$$

$$E_{photon} = \frac{hc}{\lambda} \quad \text{so} \quad \lambda = \frac{hc}{E_{ph}} = \frac{(6.626\times10^{-34}\,J\cdot s)(2.998\times10^{8}\,\frac{m}{s})}{3.02_{78}\times10^{-19}\,J}$$

$$= 6.56_{,}\times10^{-7}\,m\cdot\left(\frac{10^{10}\,Å}{1\,m}\right)$$

$$= 656_{,}\,Å$$

which, according to the spectrum on the equation page, corresponds to visible light that's essentially orange in color.

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

$1s^2 2s^2 2p^6 3s^2 3p^6$ or [Ar] or [Ar] □ (4s) □□□□□ (3d) □□□ (4p)

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

I'd expect it to be smaller, personally. Ti^{4+} and Ca^{2+} both have $18e^-$: they are isoelectronic with Argon. (They have the same number of fans, seated in the same parts of the concert venue.) Difference is, Ti^{4+} has more protons in its nucleus than does Ca^{2+}, so it draws its electrons in a little closer, resulting in a smaller ionic radius. (It's a slightly better band, so the fans crowd in a bit closer to the stage!)

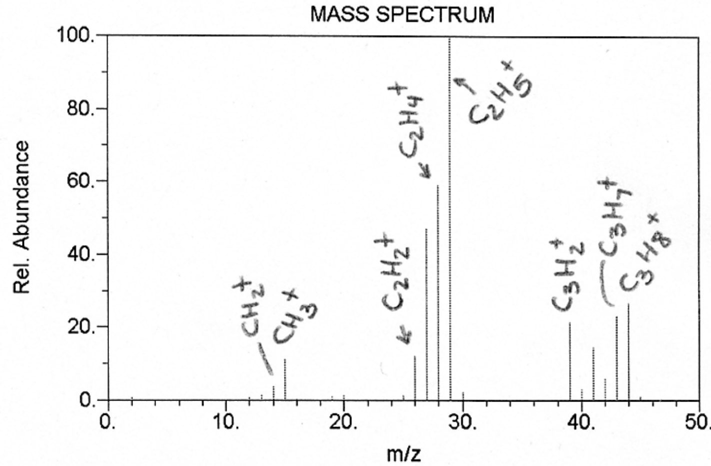
Problem 4: Stuff From Lab

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

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



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

⇑ mass spectrum of mystery gas

Vinnie's Awesome Lab Book (by Vinnie)

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,

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

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

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

$= 44.00_8$ g/mol ← Should be $44.00\bar{8}$ 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 ⑤ Even with his sig fig error, Vinnie's result doesn't rule out N_2O!

So, like, if I had 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.

a)

① Sig fig error! Each mass contributing to the difference is ±.01 g, there's no way the difference itself could be accurate to the nearest 0.0001 g!

② Errors should never be scribbled out like this!

③ This claim is untrue! Air has an average molar mass of 29.3 g/mol, so air contamination would move the measured molar mass toward this value, i.e. lower, in this case. Air contamination would not change the total moles of gas in the bulb!

④ A comment like this belongs with the data it is relevant to - either in the running account or on the mass spectrum.

b) Vinnie's unknown is almost certainly propane. His MW result really can't descriminate between the three listed possibilities, but there's no way N_2O or CO_2 can loose fragments of mass 1, which his unknown certainly did in the mass spec. 29 = C_2H_5, which comes from splitting off CH_3, mass 15.

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!

60.05 g/mol	C+H+O
− 32.00 g/mol	for 2 O atoms
28.05 g/mol	C+H
− 24.02 g/mol	for 2 C atoms
4.03 g/mol	H → implies 4H

Looks like $C_2H_4O_2$

We start with the total molar mass, then subtract off the mass associated with the two O atoms we know are there. That leaves 28.05 g/mol of C and H. So we could have 1 or 2 C's, but experience has taught us to guess high. 2 C's leave us with 4.03 g/mol worth of H, or $4.03 \frac{\text{g H}}{\text{mol fuel}}\left(\frac{\text{mol of H}}{1.0079\text{ g H}}\right) = 3.99_8 \frac{\text{mol H}}{\text{mol fuel}}$. Altogether, that implies $C_2H_4O_2$.

B.B. and I got a heat capacity of 3.2 ± 0.9 kJ·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 °C and topped out at 45.2 °C. We calculated $\Delta H_{combustion}$ for our unknown fuel, as follows: [Uncertainties are as implied by significant figures unless given explicitly.]

$$\Delta\tilde{H}^o_{combustion} = \frac{q_{released}}{moles_{burned}} = \frac{-C_P\Delta T}{\left(\frac{\Delta mass_{fuel}}{MW_{fuel}}\right)} = \frac{-\left(3._2\frac{kJ}{K}\right)(45.2-23.8)C^o}{\left(\frac{159.34\text{ g} - 154.21\text{ g}}{60.05\text{ g/mol}}\right)} = -8_{01.6}\frac{kJ}{mol}$$

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

~~These should really have been ⊕~~ ↑

$$\max = \frac{(3.2+0.9)(45.3-23.7)}{\left[\frac{(159.33-154.22)}{60.06}\right]} = 1041$$

$$\min = \frac{(3.2-0.9)(45.1-23.9)}{\left[\frac{(159.35-154.20)}{60.04}\right]} = 568$$

$$\text{max error} = \frac{\max-\min}{2} = \frac{1041-568}{2} = 236$$

So our result is actually −800 ± 200 kJ/mol, which could include methanol or acetic acid, but which excludes all the other possibilities in the table.

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.°F ($32._2$°C) 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 61°F ($16._1$°C). 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 ℓ·atm·mol^{-1}·K^{-1} 101325 Pa = 760.00 torr = 14.696 psi = 1.0000 atm   0°C = 273.15 K

We can safely treat the air in her tires as an ideal gas. We have no guarantee that the moles of air don't change, in this case, but we are told that we may assume the volume is constant. In that case, $PV = nRT \Rightarrow \frac{V}{R} = \frac{nT}{P}$

$\frac{V}{R}$ = a constant $= \frac{n_1 T_1}{P_1} = \frac{n_2 T_2}{P_2}$ $\frac{n_2}{n_1} = \frac{T_1 P_2}{P_1 T_2}$ = % of original air still present in tires

T_1 = Hotlanta tire temperature = $32._2$°C = $305._{35}$ K

P_1 = Hotlanta tire pressure = 32 psig $\frac{1.0000 \text{ atm}}{14.696 \text{ psi}}$ = 2.1_{774} atm$_g$

→ need an absolute pressure, so add atmospheric pressure

$P_1 = 2.1_{774}$ atm$_g$ + 1.0 atm = 3.1_{774} atm$_a$

T_2 = Northfield tire temperature = $16._1$°C = $289._{25}$ K

P_2 = Northfield tire pressure = 28 psig $\frac{1.0000 \text{ atm}}{14.696 \text{ psi}}$ = 1.9_{053} atm$_g$

= 1.9_{053} atm$_g$ + 1.0 atm = 2.9_{053} atm$_a$

$$\frac{n_2}{n_1} = \frac{T_1 P_2}{P_1 T_2} = \frac{(305._{35}\text{K})(2.9_{053}\text{ atm}_a)}{(3.1_{774}\text{ atm}_a)(289._{25}\text{K})} = 0.96_{52} \times 100\% = 96._{52}\%$$

$96._{52}$% of the original air is still in the tire, which means that 100% − $96._{52}$% = $3._{48}$% of the original air has leaked out. That's about normal!

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 maximum wavelength of a photon capable of breaking a C–Cl bond. What kind of radiation does this correspond to?

Table 9.3 in my book tells me that the average C-Cl bond requires $338 \frac{kJ}{mol}\left(\frac{1000 J}{1 kJ}\right)\left(\frac{1 mol}{6.022\times10^{23}}\right) = 5.61_{275}\times10^{-19}$ J to break.

To get that from a photon, the photon must have

$$E_{photon} = \frac{hc}{\lambda} = 5.61_{275}\times10^{-19} J \qquad \lambda = \frac{hc}{5.61_{275}\times10^{-19} J}$$

$$\lambda = \frac{(6.626\times10^{-34} J\cdot s)(2.998\times10^{8} m/s)}{5.61_{275}\times10^{-19} J} = 3.53_{92}\times10^{-7} m \left(\frac{10^{10} Å}{1 m}\right)$$

= 3540 Å, which is in the ultraviolet, according to the chart on the equations page. Shorter photons have more energy and could potentially also break C-Cl bonds.

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

a. Is this reaction spontaneous at 25°C and 1.0 atm?

b. Is this reaction favored by entropy?

c. Is this reaction favored by enthalpy?

d. Will heating this reaction encourage it to proceed from left to right, as written?

From Appendix 2

	ΔH°_f (kJ/mol)	S° (J/mol·K)	
$NaBr_{(s)}$	-361.06	+86.82	reactants ↑
$KCl_{(s)}$	-436.75	+82.59	
$NaCl_{(s)}$	-411.15	+72.13	↓ products
$KBr_{(s)}$	-393.80	+95.90	

$\Delta H^\circ_{rxn} = \Delta H^\circ_f$[products] − ΔH°_f[reactants]

= −411.15 − 393.80 − [−361.06 + −436.75] kJ/mol

= −804.95 − [−797.81] kJ/mol

= −7.14 kJ/mol favored by enthalpy

$\Delta S^\circ_{rxn} = S^\circ$[products] − S°[reactants] = 72.13 + 95.90 − [82.59 + 86.82] $\frac{J}{mol K}$

= −1.38 J/mol K disfavored by entropy

$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn} = -7.14 \frac{kJ}{mol} - (298.15 K)(-1.38 J/mol K)\left(\frac{kJ}{1000 J}\right)$

= −7.14 kJ/mol − −.411$_{45}$ kJ/mol

= −6.72 kJ/mol spontaneous @ 25°C

d) As T↑, ΔG° will become more positive, or *less* spontaneous, so heating actually pushes the reaction more toward the products!