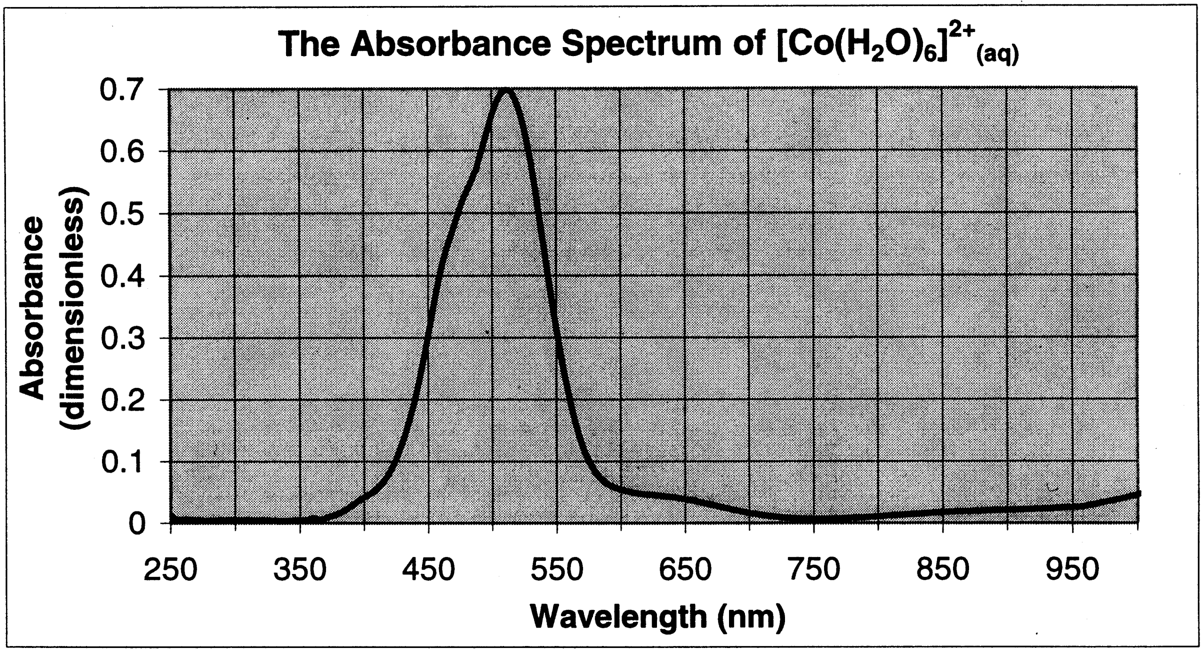
Problem 1: Synthesis and Analysis of a Transition Metal Complex (REQUIRED: You must answer this question.)

Thinking the glowing pickle demo was nifty, and not really so stinky, you buy a jar of pickles and attempt to reproduce it. When it actually comes time to throw the switch, though, your common sense gets the better of you and you opt not to risk your life at the hands of a roommate enraged by burnt pickle odor, if not outright electrocution. Instead, you eat a few pickles and go to bed. There must be something to that urban legend about pickles causing strange dreams though, because you find yourself reliving the nickel complex lab you had so much fun with, but with a different metal.

The metal in question is cobalt, and you are given cobalt (II) chloride hexahydrate crystals to work with. According to the label, the formula weight of this stuff is 237.9 g/mol, and it has a structure that you can think of as $[Co(H_2O)_6]Cl_2$. It dissolves in water as follows:

$$[Co(H_2O)_6]Cl_2 \rightarrow [Co(H_2O)_6]^{2+}{}_{(aq)} + 2\,Cl^-{}_{(aq)}$$

You dissolve some of these crystals in dilute nitric acid and measure their absorbance spectrum in a properly blanked spectrometer. This is what you get:

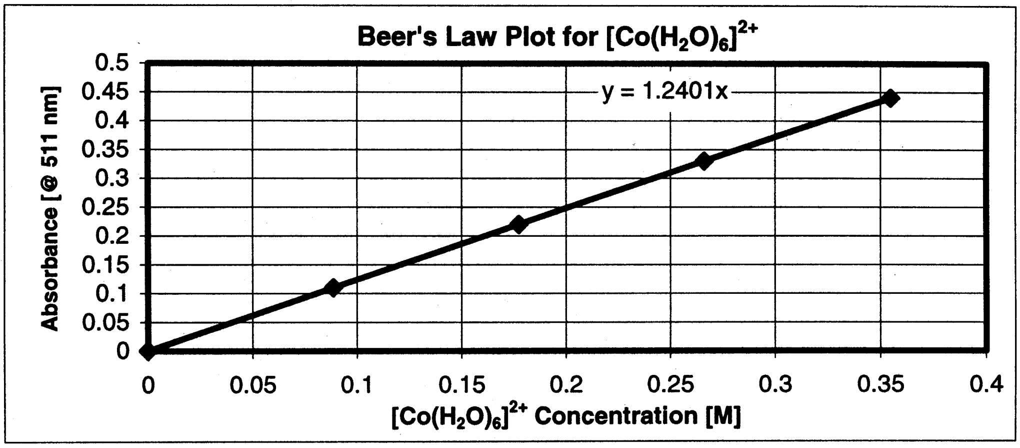


a. What color (approximately) did the solution appear to your eyes?. Explain your logic.

This solution absorbs photons of ~520nm, which are green. When our eyes are exposed to "white" light missing a particular color, they perceive the complement of that color, which Table 20-1 on the equation sheet says is purple, and which Figure 21.41 in Jones+Atkins says is red. (In actuality, the solution was a pink to light purple color.)

Problem 1, continued...

With a little diligent work and a 1.00 cm pathlength cuvette, you prepared a Beer's Law plot for this complex at 511 nm, its wavelength of maximum absorbance. It looked like this:

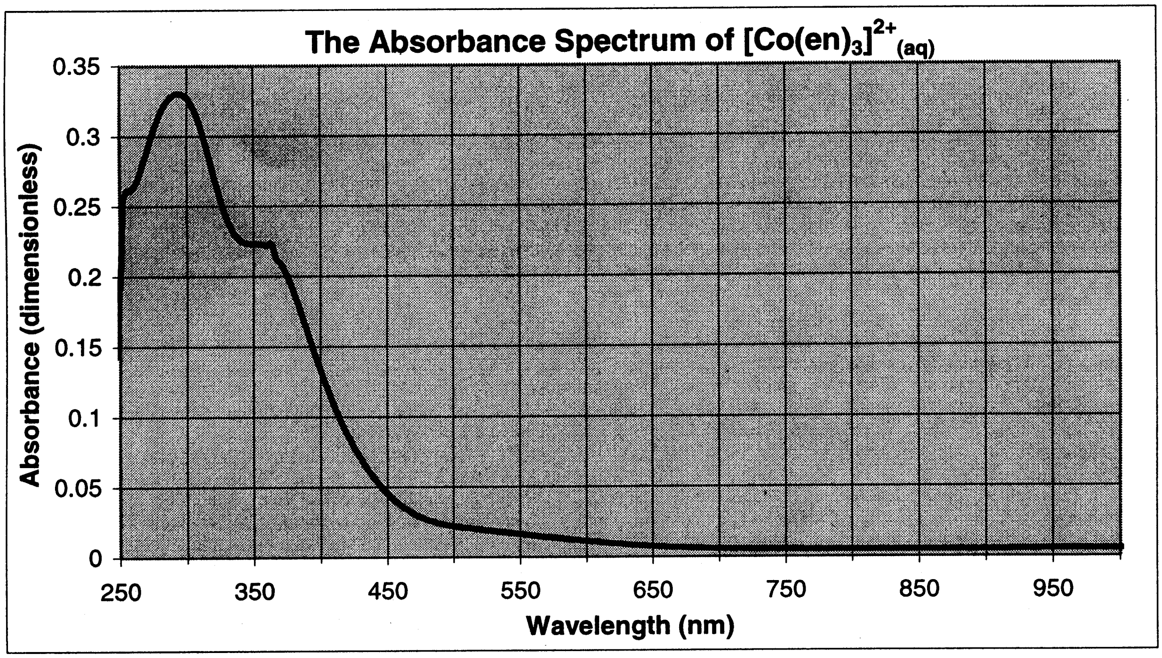


b. What is the molar absorbtivity of the $[Co(H_2O)_6]^{2+}$ ion, according to this Beer's Law plot?

$A = \varepsilon bC$ $\quad \varepsilon = \frac{A}{C}\frac{1}{b} = \text{slope} \cdot \frac{1}{b} = \frac{1.2401\ M^{-1}}{1.00\text{cm}} = 1.24\ M^{-1}\ \text{cm}^{-1}$

Units and significant figures matter here! The units of the slope are $\frac{\text{rise}}{\text{run}} [=] \frac{\text{absorbance}}{\text{concentration}} [=] \frac{\text{dimensionless}}{M} [=] M^{-1}$

You add several drops (enough to fully displace all the aquo groups from the Co, and then some) of 2.0 M en solution to the cuvette and notice that it changes color markedly. The absorbance spectrum now looks like this:



c. What color does the $[Co(en)_3]^{2+}$ complex ion appear to the human eye? Explain your logic.

Our eyes don't respond to λ's shorter than ~380 nm, so we white light missing a few violet (380-430nm) photons. Our eyes perceive this as a faint green-yellow to yellow tint. (In actuality, the stuff was more of an amber, straw-like color. Our eyes barely notice the missing violet photons compared with the missing blues; our eyes are not very sensitive to violet photons!)

Problem 1, continued...

Following a process essentially analogous to that you used in the Ni lab, you synthesize and dry a sample of solid $[Co(en)_2(H_2O)_2]Cl_2$. You then analyze it to determine its composition, using an acid titration to determine the en content and UV/Visible spectroscopy to determine the Co content. The data you obtain is as follows:

- It took an average of 128 mℓ of 0.100 M HCl per gram of product to pull off and neutralize all the en
- An average absorbance value of 0.2511 at 511 nm was obtained for a solution prepared from 0.5937 g of product dissolved in nitric acid to make a total solution volume of 10.00 ± .03 mℓ in a volumetric flask.

d. Calculate the values of x and y indicated by the data above, where the product is $[Co(en)_x(H_2O)_y]Cl_2$.

(You may need to use the blank page at the back of your exam for extra space.)

$$\frac{128\ \cancel{\text{m}\ell\ \text{titrant}}}{1\ \text{g product}} \times \frac{0.100\ \text{mol}\ \cancel{\text{HCl}}}{1000\ \cancel{\text{m}\ell\ \text{titrant}}} \times \frac{1\ \text{en}}{2\ \cancel{\text{HCl}}} = 0.00640\ \frac{\text{mol en}}{\text{g product}}$$

$$0.2511\ \text{absorbance} \times \frac{1\ \text{M}\ [Co(H_2O)_6]^{2+}}{1.2401\ \text{absorbance}} = 0.2024_{84}\ \text{M}\ [Co(H_2O)_6]^{2+}$$

This was the concentration of $[Co(H_2O)_6]^{2+}$ in a solution of 0.5937 g of product dissolved into a total solution volume of 10.0 mℓ. The total amount of Co in that 0.5937g was therefore:

$$0.2024_{84}\ \cancel{\text{M}\ [Co(H_2O)_6]^{2+}} \times \frac{1\ \frac{\text{mol Co atoms}}{\cancel{\ell}\ \text{of solution}}}{1\ \cancel{\text{M}\ [Co(H_2O)_6]^{2+}}} \times 10.0\ \cancel{\text{m}\ell\ \text{solution}} \times \frac{1\ \cancel{\ell}}{1000\ \cancel{\text{m}\ell}}$$

$$= 0.00202_{484}\ \text{mol Co atoms in } 0.5937\text{g product}$$

So we found $\frac{0.00202_{484}\ \text{mol Co}}{0.5937\text{g product}} = 0.00341_{05}\ \frac{\text{mol Co}}{\text{g product}}$

$$x = \frac{\text{moles en}}{\cancel{\text{mole product}}} \times \frac{\cancel{1\ \text{mol product}}}{1\ \text{mol Co}} = \frac{\left(\frac{\text{mol en}}{\text{g product}}\right)}{\left(\frac{\text{mol Co}}{\text{g product}}\right)} = \frac{0.00640\ \frac{\text{mol en}}{\text{g product}}}{0.00341_{05}\ \frac{\text{mol Co}}{\text{g product}}} = 1.87_{65}\ \frac{\text{en}}{\text{Co}}$$

$$FW = \frac{\text{g product}}{\text{mol Co}} = \left(\frac{\text{mol Co}}{\text{g product}}\right)^{-1} = \left(0.00341\ \frac{\text{mol Co}}{\text{g product}}\right)^{-1} = 293._2\ \frac{\text{g product}}{\text{mol Co}}$$

$$FW = m_{Co} + x\,m_{en} + y\,m_{H_2O} + 2m_{Cl^-}$$ (round off x to a realistic value of 2)

$$293._2\ \text{g/mol} = 58.93\ \text{g/mol} + 2(60.10\ \text{g/mol}) + y(18.02\ \text{g/mol}) + 2(35.45\ \text{g/mol})$$

$$y = \frac{43.18\ \text{g/mol}}{18.02\ \text{g/mol}} = 2.3_{96} \Rightarrow \text{likely value is } 2$$

x = 2, y = 2 is a viable combination. It is important to replace x = 1.88 with x = 2 in calculating y, because we are trying to make a best estimate of the composition of a single product, and there must be a whole number of en's on a given Co. (y comes out to be 2.8 if x = 1.88 is used.)

Problem 1, continued...

- You began the synthesis with 2.382 g of $[Co(H_2O)_6]Cl_2$ and added 10.0 mℓ of 2.00 M en.
- You ended up with 2.93 g of the product, which you know should be $[Co(en)_2(H_2O)_2]Cl_2$

e. Determine the percent yield of this experiment. Do this very correctly, including significant figures.

① What's the limiting reagent? We need 2en per mol of Co.

$FW([Co(H_2O)_6]Cl_2) = FW(x=0, y=6) = 58.93 + 0 + 6(18.02) + 2(35.45) = 237.95\ g/mol$

We start with $2.382g\ [Co(H_2O)_6]Cl_2 \times \frac{1\ mol\ Co}{237.95\ g} = 0.01001\ mol\ Co$

and $10.0 m\ell \times 2.00 \frac{mol\ en}{\ell} \times \frac{1\ell}{1000\ m\ell} = 0.0200\ mol\ en \rightarrow$ can react with 0.0100 mol Co

en is our limiting reagent → it might be as low as 0.0199 mol

FW of theoretical product $= FW([Co(en)_2(H_2O)_2]Cl_2) = FW(x=2, y=2) = 286.07\ g/mol$

Theoretical yield $= 0.0100\ mol\ [Co(en)_2(H_2O)_2]Cl_2 \times \frac{286.07g}{mol} = 2.86_{07}\ g$

$\%\ yield = \frac{actual\ yield}{theoretical\ yield} \times 100\% = \frac{2.93g}{2.86_{07}\ g} \times 100\% = 102.4\%$

It is important to use the theoretical formula weight in this calculation, not the one calculated in part d).

f. Based on the results obtained above, what do you expect would happen to x, y, and the % yield if you let your product dry for an additional two weeks, and then repeated the product analysis? Why? (Would each of these values go up, down, or stay the same, and why?)

It looks like our product was still wet, so every sample we took was actually product + a little water. We assumed it was all product, though, so our mass was artificially large in all cases. With that in mind, let's think this through:

If our product had contained $1\%_{wt}$ water two weeks ago, and was now dry

$\frac{mol\ en}{1g\ product}$ would become $\frac{mol\ en}{0.99g\ product}$ $\frac{mol\ Co}{1g\ product}$ would become $\frac{mol\ Co}{0.99\ g\ product}$

$x = \frac{mol\ en}{mol\ Co} = \frac{\left(\frac{mol\ en}{0.99\ g\ product}\right)}{\left(\frac{mol\ Co}{0.99\ g\ product}\right)}$ would not change, $FW = \frac{0.99\ g\ product}{mol\ Co}$ would drop

Since y is calculated by difference from x & FW, a smaller FW would mean a smaller value of y at the same x. We'd find 2.93 - 0.293 g = 2.64g of product, but still think it to be the same stuff, with the same theoretical FW, so our % yield would go down.

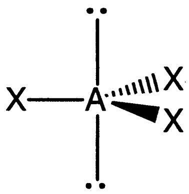
x ⇒ stay the same

y ⇒ go down

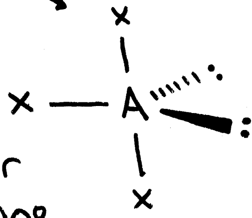
% yield ⇒ go down

Problem 2: Bonding and Molecular Shape

A. Why is the molecular structure shown at right never observed in nature?



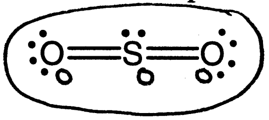
The lone pairs have a total of 3 "neighbors" each, at 90°. They can reduce this to 2 "neighbors" each by moving to equatorial positions, as shown at right. →



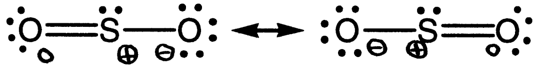
At 120° to each other, the two lone pairs are still far enough apart that they hardly notice one another. Since 90° lone-pair to bonding-pair interactions are appreciably stronger than are 90° bonding-pair to bonding pair interactions, they are what we focus on in thinking about this molecular shape.
(90° LP-LP interactions would be far worse, but neither of these options has any.)

B. Identify which potential Lewis dot structure(s) are the more favorable of the two options presented. Circle the better structure in each pair, and briefly explain why it is better.

a. SO_2

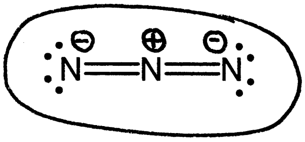


or

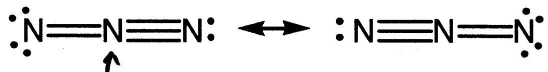


Less total formal charge

b. N_3^-



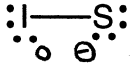
or



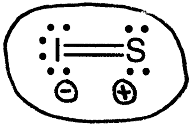
hypervalent N!
Impossible!

(The following structures can actually resonate with each other, but which of them is the better structure?)

c. IS^-

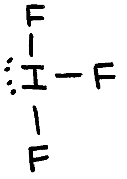


or



Better formal charge distribution (I is more electronegative than S, Figure 8.21.)

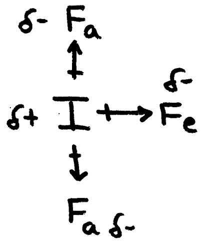
C. Does the IF_3 molecule have a net dipole moment? Justify your answer based on VSEPR and electronegativity data, but don't worry about explaining in detail how you arrive at its shape.



AX_3E_2 – trigonal bipyramidal frame, lone pairs go equatorial (see A.), so molecule is T-shaped.

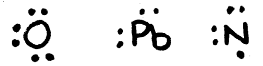
I–F bond is quite polar, because according to Figure 8.21, F=4.0, I=2.7 => different electronegativities.

The bond dipoles look like this:



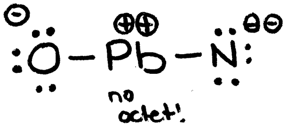
The two to the Fa's cancel each other, but that of the Fe remains; so the molecule is polar, with a net dipole

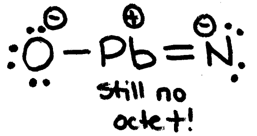
D. Draw the Lewis structure, or set of resonance structures, that best represent(s) the bonding in the $OPbN^-$ ion. If you draw more than one, circle the best one. Clearly indicate any and all non-zero formal charges. You need not explain what you are doing, but explaining will help you garner partial credit if you make a mistake.

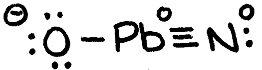


+ $1e^-$ Electronegativities: O=3.4, N=3.0, Pb=2.3

=> Pb is the most electronegative, put it in the middle.

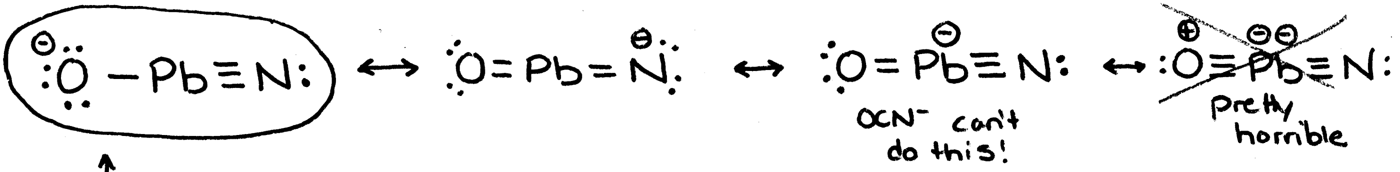






very nice! O is most electronegative!

Can this very nifty structure resonate? Yep, even more than OCN⁻!



This one is the best, because O is the most electronegative of these elements

This one isn't great, but it's good enough to warrant including

Final Exam **Your name:** Good Guy / Good Gal **Chemistry 123 Spring 2002**

Problem 3: Dr. Evil Must Be Stopped!

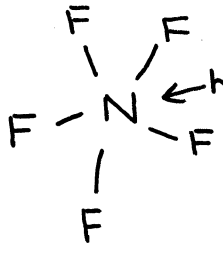
A. The nefarious Dr. Evil is trying (once again) to destroy the world. Trapped in his secret hideout, with the deshaggilizer aimed at your sensitive parts, you know your only hope is to engage him in intellectual banter so as to distract him from killing you and proceeding with his sinister plans. You note that he is staring at a table of boiling points for a series of liquids. He has highlighted two entries and is clearly puzzled by them. Perhaps if you could explain why those two entries buck the trend that is otherwise apparent, he might be interested enough to talk with you. ***Why are the boiling points of the two entries in italics so much higher than one might expect based solely on their mass?***

Chemical Formula	Normal Boiling Point (K)	Formula Mass (g/mol)
CH_3CH_2H	185	30.07
$CH_3CH_2CH_3$	231	44.10
CH_3CH_2F	236	48.06
CH_3CH_2Cl	289	64.51
$CH_3CH_2NH_2$	*309*	*45.08*
CH_3CH_2Br	311	108.97
CH_3CH_2I	346	155.97
CH_3CH_2OH	*350.*	*46.07*

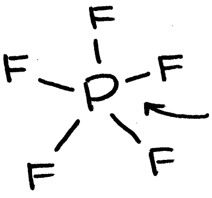
These two entries (an alcohol and an amine) are capable of hydrogen bonding! The N-H and O-H bonds are both quite polar X-H bonds, so these molecules can hydrogen bond to each other, and that makes them much happier in the liquid phase than the others. C-F and C-Cl bonds are quite polar, too, but they can't hydrogen bond - their dipole-dipole interactions are weaker because they can't get their dipoles as close together. F is small, but it's still a giant compared to H! (See Figure 9.24)

B. Seduced by your intellect, Dr. Evil decides to hold off on killing you and instead attempts to pick your brain. It seems part of his latest plan for world domination entails the preparation of NF_5, which he figures should be readily made since he's made PF_5 several times. Yet he has failed in every attempt to make NF_5. Deciding that you need to learn more of his plans, you opt to move further into his confidence by ***explaining, with Lewis structures, why PF_5 is relatively stable while NF_5 is essentially impossible to prepare.***

Since F can only form one single bond, the structure of XF_5 must have X as the central atom, and have all the F's singly-bonded to the X. Phosphorus can handle 5 single bonds, it can be hypervalent; but not so with nitrogen.



hypervalent N, no go!



hypervalent P, no problem!

C. Frustrated to learn that his current plan for world domination has been foiled by the fickle rules of chemistry, Dr. Evil tips back a few beers while sifting through his file drawer. He eventually extracts a folder and starts mumbling something about "Plan 544B." It becomes clear that this plan involves creating a bomb using ammonium nitrate, NH_4NO_3, a common fertilizer. As the governments of the world have become wise to ammonium nitrate's potential as a bomb material, trade in it is now closely watched, and Dr. Evil has decided he will have to buy precursor materials and synthesize the ammonium nitrate himself. He's gotten his hands on some ammonia (NH_3) and some nitric acid (HNO_3), and he plans to simply combine them as follows:

$$NH_{3(g)} + HNO_{3(\ell)} \rightarrow NH_4NO_{3(s)} \qquad \Delta H^\circ_{rxn} = -145.35 \text{ kJ/mol}$$

(kinetically quite fast at room temperature) $\Delta S^\circ_{rxn} = -196.97 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

He turns to you for advice on how to maximize his yield of ammonium nitrate, and you realize that your chance has come. Ammonia (NH_3) is capable of paralyzing one's lung muscles, and a good whiff of it will knock out Dr. Evil long enough for you to save the world. Better yet, laughing gas (nitrous oxide, N_2O) is readily produced from ammonium nitrate via the following reaction:

$$NH_4NO_{3(s)} \rightarrow 2H_2O_{(\ell)} + N_2O_{(g)} \qquad \Delta H^\circ_{rxn} = +124.05 \text{ kJ/mol}$$

(kinetically quite slow at room temperature) $\Delta S^\circ_{rxn} = +208.59 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

It has become very clear to you that when he took his chemistry classes, Dr. Evil was so busy thinking evil thoughts he didn't pay any attention, so you can tell him to do whatever you like and he'll up and do it. ***What would you tell Dr. Evil to do in order to make it very likely that he ends up with a lot of NH_3 and/or N_2O in his reaction vessel, and thus becomes incapacitated when he goes to collect his bomb making material? Explain which incapacitating gas(es) you are hoping to have him encounter, and why he'll end up getting a significant amount of it/them. Note that there are several correct answers to this problem.***

The surest way to save the day is also the simplest, a theme we've encountered before! If you have Dr. Evil use a large excess of NH_3 and a small amount of HNO_3, he's guaranteed a facefull of ammonia. Stoichiometry saves the day! But there are also a multitude of kinetic and thermodynamic solutions. Generally they require thought along both fronts. For example, while lowering the system pressure encourages the formation of N_2O, the decomposition process is quite slow at room temperature and without heating you would be unlikely to get much N_2O unless you told Dr. Evil to wait a long time. Similarly, just heating a sealed vessel would increase the rate of the second reaction, but at high enough temperatures would push it toward the reactant due to both entropy and pressure effects. There are too many viable, correct answers to list them all, but here are a few:

At low pressure you would also have very little of each gas, reactant or product!

① Mix ingredients, then warm gently or wait a long time with the reaction in a constant pressure (rather than constant volume) vessel.

② Keep the ingredients very cold, so that the kinetics of the first reaction are slowed. Have Dr. Evil open the vessel "early."

③ Carry out the reaction at 1 atm, with ingredients above 738K, so the first reaction isn't spontaneous.

Final Exam **Your name:** Sugar Daddy / Momma **Chemistry 123 Spring 2002**

Problem 4: Equilibria and Phase Diagrams

A. On Monday, you prepared a saturated solution of sucrose (table sugar) in water by pouring a bunch of powdered sugar into a jar of distilled water. You kept adding sugar until you simply could not dissolve any more of it in the water, and then you added 50.0 extra grams of sugar, which settled at the bottom in a fine cloud of powdered sugar. (Just like snow! Ooops, some of you will be angry at me for mentioning that.) You put a lid on the jar and set it on your desk. At this point the system was in perfect equilibrium, maintained at a constant temperature by the remarkably good thermal control system in your dorm. (Just pretend, OK?) It stayed in thermodynamic equilibrium (at exactly the same temperature) all week.

When Friday night rolled around and you had a chance to look at it again, you found that the jar was filled with about twenty large sugar crystals (rock candy), and that the powdered sugar grains were all gone.

a. What should the total mass of the large sugar crystals be, assuming that none of the water evaporated and that the temperature stayed exactly the same? (Circle ONE choice, please. You need not explain.)

i) Significantly less than 50.0 grams

[✓ ii)] Very close to 50.0 grams

iii) Substantially more than 50.0 grams

iv) I can't answer this question without knowing: ____________________

(Fill in the blank at right if your choose this option, or you're guaranteed to get it wrong!)

Why? ① T is unchanged, so $K_c = K_{eq} = K_{sp}$ is the same
② $Sugar_{(s)} \rightleftharpoons Sugar_{(aq)}$ has $K_{blah} = [Sugar_{(aq)}]$
③ Sugar does not evaporate or react w/ H_2O, so the only way the amount of solid sugar could change was if $[sugar_{(aq)}]$ changed, and it is fixed.

b. The saturated sugar solution was in equilibrium with solid sugar during the entire week. How could the sugar possibly have re-formed itself into larger crystals?

Equilibrium is a dynamic phenomenon! Even if $Sugar_{(s)} \rightleftharpoons Sugar_{(aq)}$ is in equilibrium, sugar molecules are constantly leaving the solid to go into solution, and dissolved sugar molecules are constantly re-attaching themselves to the solid. Because sugar molecules are more easily dissolved from the corners and edges of a sugar crystal than from the center of a face, crystals grow progressively larger with time spent at equilibrium.

c. The large sugar crystals are a more ordered state than the small grains, so the crystal growth process is entropically unfavorable; ΔS for the crystallization process is negative. What can you say about the sign of ΔH for crystal growth? Is it **positive**, [✓ **negative**], or **zero**? Why? $Sugar_{(s,powder)} \rightarrow Sugar_{(s,crystal)}$

We have learned that sugar will spontaneously form larger crystals from a powder, so ΔG must be negative for that transformation. Since ΔS is negative for that change, entropy doesn't favor it; so it can only be spontaneous if enthalpy does, which means a negative ΔH. More mathematically, $\Delta G = \Delta H - T\Delta S$ and we know ΔG is $\ominus$ while ΔS is negative. Since T is absolute, it can never be negative, and the $-T\Delta S$ term will make ΔG more positive. Thus ΔG can only be negative if ΔH is negative (and larger in magnitude than TΔS, to boot!).

B. While giving a campus tour, you are shocked to discover Dr. Smartypants, web-surfing know-it-all and major weenie, in your tour group. What's more, he is now Professor Smartypants, of South Park College. Seems they'll give anyone a professorship these days. You proceed with the tour only to find that mid-way through, Professor Smartypants tries to sabotage it by talking up his own institution, at Carleton's expense! "Parents, I don't know why you would send your kids here. I surf the Carleton websites, I know what goes on here! I shudder for America's future! Why, even the education is second-rate. For example…" You decide that the only way to defend Carleton's honor is to debunk the chemical mythology he's spewing. ***For each claim made by Professor Smartypants, explain the error in his logic and correct him. He's partly wrong in every case, but there is a grain of truth in what he's saying as well. Correct him carefully!!!***

"At South Park, students never have to study, they just surf the web and get smart by osmosis. Here at Carleton they work the students like dogs, and they don't emerge any smarter! We also have a great sports program to round out our sedentary learning approach. For example, we offer ice skating!"

a. "Did you know that it is possible to ice skate because high pressure encourages ice to melt? Ice is less dense than liquid water, so by Le Châtelier's Principle, the equilibrium

$$H_2O_{(s)} \rightleftharpoons H_2O_{(\ell)}$$

is forced to the right by high pressures. You can also see this on the phase diagram for water, Figure 10.45 in Jones and Atkins.*Next term I'm going to set up a dry ice (solid CO_2) skating rink, because it will be so darn cool to float on a layer of CO_2 gas instead of slipping on liquid. It'll be even better skating."

Smartypants speaks true until the *, but ice skating on CO_2 wouldn't work. First off, if you apply more pressure to CO_2 at constant temperature, it will tend to solidify, not sublime. The phase diagram for CO_2 (10.47) and the fact that solid CO_2 is denser than CO_2 gas both make this clear, in light of Smartypants' own (correct) arguments. The other problem is that even at −78°C, the normal sublimation point of CO_2, you could only keep a CO_2 rink intact w/ 1 atm of CO_2 on top of it. Kenny and the other South Park College kids would either be asphyxiated, or freeze, or both!

b. "Ya know what else? Figure 10.48 shows that solid sulfur can exist in two different allotropic forms, just as solid carbon can exist as either diamond or graphite (see phase diagram in problem 10.70). Because the monoclinic allotrope of sulfur is favored at higher temperatures, I know that*enthalpy favors it over the rhombic form. Also, because the rhombic allotrope becomes the stable one at very high pressures, I know it is the denser of the two."

$$S_{(s,\text{rhombic})} \rightleftharpoons S_{(s,\text{monoclinic})} + \text{heat}$$

makes no sense in light of the phase diagram! The reaction shifts to the <u>right</u> at <u>higher</u> temperatures, so heat must appear on the left. The rhombic → monoclinic transition occurs only because entropy favors it, and entropy becomes more important at high temperatures. This is also clear from Appendix 2A:

$$\Delta H^\circ = \Delta H^\circ_f[\text{monoclinic}] - \Delta H^\circ_f[\text{rhombic}] = +0.33\ \text{kJ/mol} - 0 = +0.33\ \text{kJ/mol}$$

$$\Delta S^\circ = S^\circ[\text{monoclinic}] - S^\circ[\text{rhombic}] = (32.6 - 31.8)\ \text{J/mol·K} = +0.8\ \text{J/mol K}$$

Enthalpy disfavors this reaction, entropy favors it, so it only becomes spontaneous at higher temperatures. Smarty's right about rhombic being the denser of the two forms…that's why ΔS° is ⊕!