Exam 2: Bonding, Equilibria, and Kinetics

Chemistry 123 | **Friday, June 7 12:00 noon – 2:00 pm** | **Spring Term 2002**
Final Exam | **5 Pages / 4 Problems SHOW YOUR WORK!** | **Instructor: R. Rossi**

Don't Panic!

Instructions:

- **Aaaaah! Stop Panicking!!!**
- **There are a total of four problems in this exam. You *must answer the first one*, plus your choice of two of the last three.**
- **50% of your exam score will be based on the first problem. The remainder will be based on the *two best* problems you hand in of the last three, at 25% each. It would be wise for you to start with problem one, then proceed to the problem with which you are most comfortable and can do relatively quickly. Work your way up to the problems you find harder or you expect will take you more time.**
- **You may refer to the equations and conversion factors on the back of this sheet, your textbook, your notes [notes you wrote, but not copies of what someone else wrote], your returned homework and anything you have written on it, and your lab notebook. If you have to look everything up, you won't finish this exam.**
- **You *MAY NOT USE COPIES OF MY HOMEWORK SOLUTIONS*, but if you make notes on your own homework, that's fine. Make sure you understand the mistakes you made on the homework! The same holds true of mistakes made in doing the labs!**
- **You may use a calculator, a computer, a periodic table, and anything else you OK with me in advance. You may not use references other than those listed above.**
- **You can start working on this exam at noon. You must give me back all four of your problems when I ask you for them at 2:00 pm, if not before that time. Even if you can't finish all four problems, I need all four of them back.**
- **Please write your name clearly on the front of each page, in the blank at the top.**
- **SHOW YOUR WORK AND LOGIC UNLESS SPECIFIED OTHERWISE. If you don't offer a good explanation of how your answer came to be, you will get no credit!!!**
- **If you think there is an error in the exam, or you aren't sure that you understand what a questions is asking for, ask me about it! It's OK to ask me questions.**

Restrictions:

- **You may not get any form of help from others in working this exam.**

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

Formulas and Equations

$PV = \eta RT$ $c = \lambda\nu$ $E = h\nu$

$\Delta T_f = -K_f\, m_{\text{solute particles}}$ $\Delta T_b = K_b\, m_{\text{solute particles}}$ $\pi = i\, MRT$

$\Delta E = \frac{hc}{\lambda}$ $\lambda = \frac{h}{mv}$ $m = \text{molality} = \frac{\text{moles of solute}}{\text{kilogram of solvent}}$

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

$\Delta G = -RT\ln(K_{eq})$ $\Delta G = \Delta H - T\Delta S$ $k = Ae^{\frac{-E_a}{RT}}$

Constants and Conversion Factors

$g = 9.8067\ \frac{m}{s^2}$ $h = 6.626 \times 10^{-34}\ J\cdot s = 4.136 \times 10^{-15}\ eV\cdot s$ $273.15\ K = 0^{o}C$

$c = 2.998\times10^{8}\ \frac{m}{s}$ $\rho_{H_2O} = 1.00\ \frac{g}{m\ell}$ $R = 8.3145\frac{J}{mol\cdot K} = 0.08206\frac{\ell\cdot atm}{mol\cdot K}$

$10^{-10}\ m = 10^{-1}\ nm = 1\ Å$ $1\ m = 3.2808\ feet$ $1\ m = 100\ cm = 10^{3}\ mm = 10^{6}\ \mu m$

$1\ eV = 1.602 \times 10^{-19}\ Joules$ $1\ mole = 6.022 \times 10^{23}$ $10^{-3}\ kg = 1\ g = 10^{3}\ mg = 10^{6}\ \mu g$

1.00000 atm = 760.000 Torr = 101325 Pa $1\ m^3 = 1000\ \ell = 264.17\ gallons$

$1\ Newton \equiv 1\ \frac{kg\cdot m}{s^2}$ $1\ Joule \equiv 1\ \frac{kg\cdot m^2}{s^2}$ $1\ Pascal \equiv 1\ \frac{kg}{m\cdot s^2}$

Table 20-1
Colors of visible light

Wavelength of maximum absorption (nm)	Color absorbed	Color observed
380–420	Violet	Green-yellow
420–440	Violet-blue	Yellow
440–470	Blue	Orange
470–500	Blue-green	Red
500–520	Green	Purple
520–550	Yellow-green	Violet
550–580	Yellow	Violet-blue
580–620	Orange	Blue
620–680	Red	Blue-green
680–780	Purple	Green

From Daniel C. Harris, *Quantitative Chemical Analysis*, 2nd ed., New York: W. H. Freeman (1987). See also the color wheel on p. 947 of Jones/Atkins. A complete spectrum chart appears on p. 272 of Jones/Atkins.

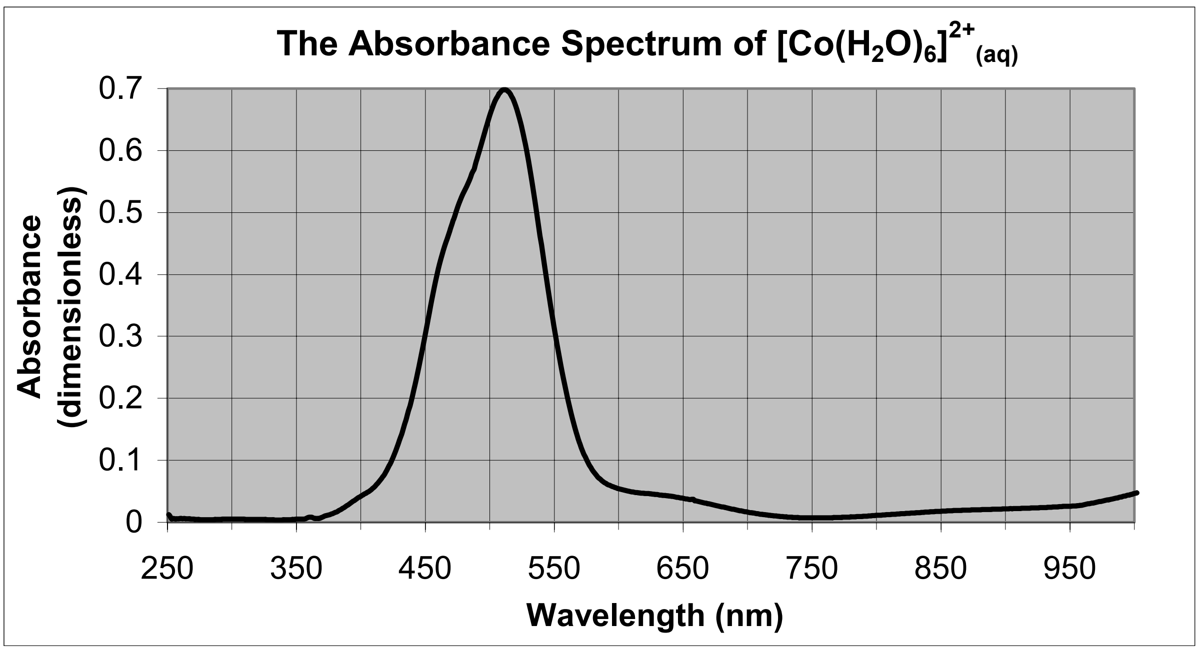
Problem 1: Synthesis and Analysis of a Transition Metal Complex (REQUIRED: You must answer this question.)

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:

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

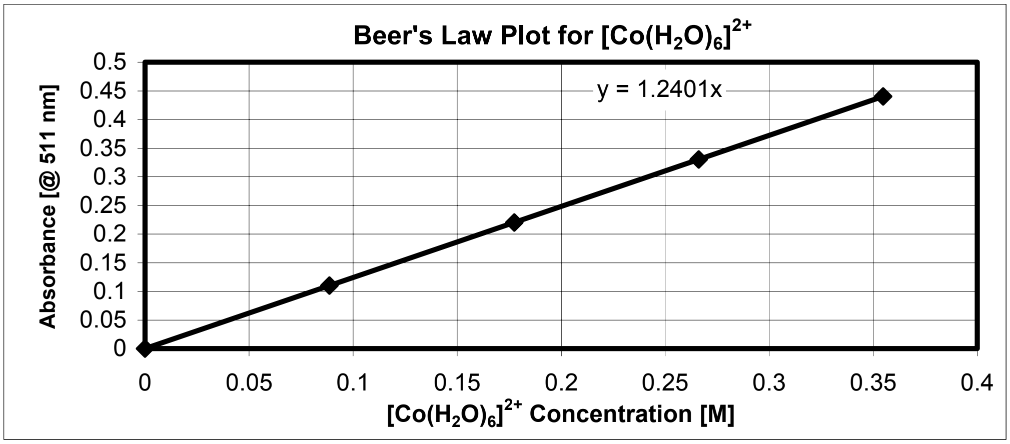
You dissolve some of these crystals in dilute nitric acid and measure their absorbance spectrum in a properly blanked spectrometer. This is what you get:



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

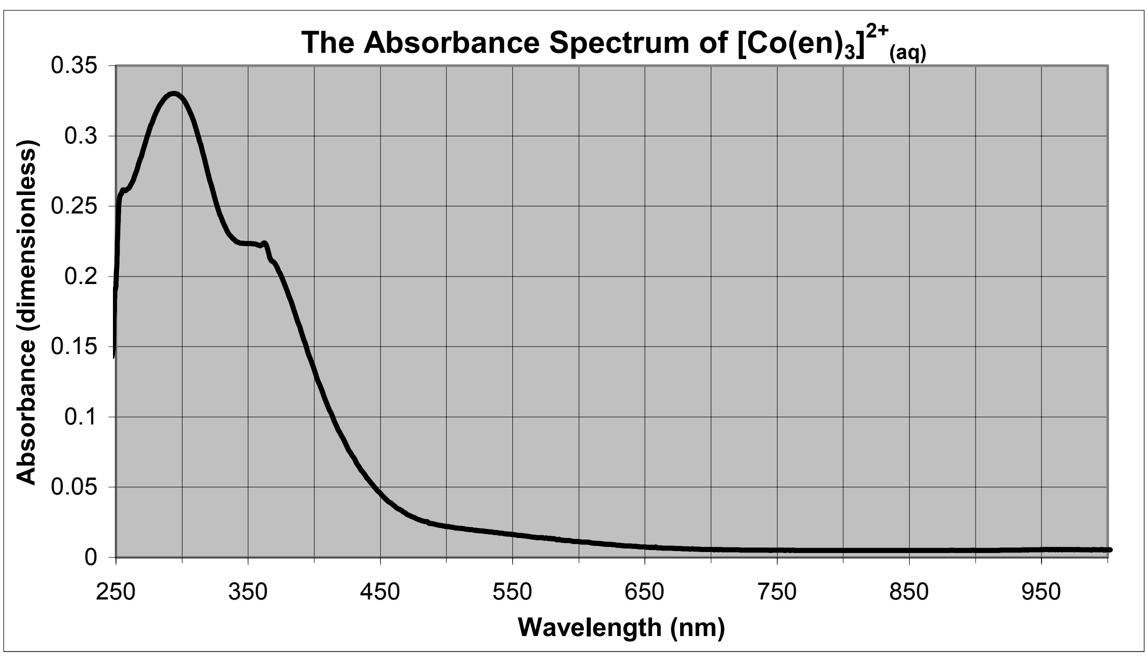
Problem 1, continued…

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?

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.

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.)

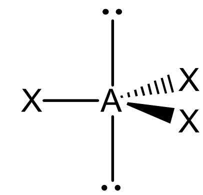
Problem 1, continued…

- 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.

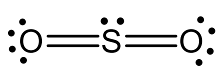
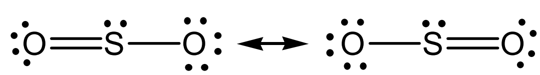
f. Based on the results obtained above, what do you expect would happen to x, y, and the % yield if you let your product dry for an additional two weeks, and then repeated the product analysis? Why? (Would each of these values go up, down, or stay the same, and why?)

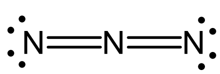
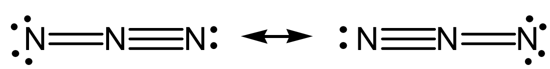
Problem 2: Bonding and Molecular Shape



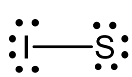
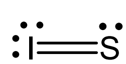
A. Why is the molecular structure shown at right never observed in nature?

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 

b. N_3^-  or 

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

c. IS^-  or 

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.

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. *(Please err on the side of drawing many plausible structures, and cross off the ones you think really stink.)*

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*

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.***

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:

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

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

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:

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

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

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.***

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!)

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?

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?

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."

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."