Final Exam: Atomic Structure, Bonding, Equilibria, and Kinetics

Chemistry 123 **Tuesday, March 11 or Saturday, March 15** **Winter Term 2003**
Final Exam **5 Pages / 5 Problems SHOW YOUR WORK!** **Instructor: R. Rossi**

"Take it easy, kid, it's only a Chem Exam." - Ham Solo

Instructions:

- The mind is like a parachute; it works much better when it is open.
- I'm running out of sympathy for people who make messy craters because they don't read the directions on the package. *For crying out loud, read these directions before you start!*
- There are a total of five problems in this exam, one on each double-sided page. Your score on this exam will be based on your answers to the questions on *one* side of *four different* problem pages. Those page sides will be those you manage to answer *most successfully*.
- Your mission is to answer at least four, and up to seven, page sides; it's up to you which sides you answer. If you do both sides of the same page, the side you do a better job on will count. YOU'LL BE HURTIN' IF YOU DON'T ANSWER ONE SIDE OF AT LEAST FOUR PROBLEMS. My advice is to go through all five problems, answering whichever side you feel better about. Then, to the extent that time permits, go back and answer the other side of the one or two problems you feel the least confident about. Don't do more than 7 sides.
- I have tried to make the front side of each page more quantitative, and the back side more qualitative, should you have a strong preference for one type of question over the other.
- Yes, significant figures do matter. Carry them through carefully in all calculations.
- You'll likely need more paper for some of your answers. Please get that from me.
- You may refer to the equations and conversion factors on the back of this sheet, your textbook, your notes [notes you or I wrote, but not copies of what someone else wrote], your returned homework and anything you have written on it, and your lab notebooks. If you have to look *everything* up, you won't finish this exam, but *do* use these references!
- With the exception of Assignment 6, you *MAY NOT USE COPIES OF MY SOLUTIONS TO ANYTHING,* including my assignment solutions and the sample exam solutions; but if you make notes and corrections on your own homework and sample exams, that's fine.
- You may use a calculator, a computer, a periodic table, a ruler, and any other tools you OK with me in advance. *You may not use references or tools other than those listed above. You may not use a calculator or computer except as a computational or writing aid.*
- You can start working on this exam when I give it to you. You must hand in your exam four hours later (you *can* have four hours, even on Saturday), if not before that time.
- SHOW YOUR WORK AND LOGIC UNLESS SPECIFIED OTHERWISE. If you don't offer a good explanation of how your answer came to be, you will get no credit!!!
- If you think there is an error in your exam, ask me about it! It's OK to ask me questions. I'm also happy to help explain a question to you if you don't understand what it's asking.

Restrictions:

- You may not get any form of help from others in answering these questions.
- ***You may not talk about the exam with anyone else*** *until after 11:30 pm on March 15.*

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

Formulas and Equations

$$E_{photon} = \frac{hc}{\lambda} \qquad c = \lambda\nu \qquad E_{photon} = h\nu$$

$$E_{Bohr\ Electron} = R_H\left(\frac{Z^2}{n^2}\right) \qquad E_{photon(Emission)} = R_H Z^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad E_{photon} = |\Delta E_{electron}|$$

$$P_{tot} = \rho g h + P_o \qquad \rho = \frac{m}{V} \qquad P_x \cdot V = \eta_x \cdot R \cdot T$$

$$q = \eta\ \tilde{C}_p\ \Delta T = \eta\ \Delta\tilde{H} \qquad P_{gas} = k\ C_{gas}\ \text{(Henry's Law)} \qquad P_{solution} = \chi_{solvent}\ P^o_{solvent}$$

$$w_{system} = -P_{opposing}\ \Delta V_{system} \qquad \Delta E_{system} = q + w \qquad H \equiv E + PV, \quad G \equiv H - TS$$

$$A = \varepsilon\ b\ C \qquad k = Ae^{\left(\frac{-\Delta G^{\ddagger}}{RT}\right)} \qquad K_{eq} = e^{\left(\frac{-\Delta G^\circ}{RT}\right)} = \text{Equilibrium constant in terms of activities}$$

$Q_\alpha = \prod_i \alpha_i^{\chi_i}$ where χ_i is the stoichiometric coefficient of species i, and is negative for reactants, positive for products

Constants and Conversion Factors

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

$$c = 2.998 \times 10^8\ \frac{m}{s} \qquad \rho_{H_2O} = 1.00\ \frac{g}{m\ell} \qquad R = 8.3145\frac{J}{mol \cdot K} = 0.08206\frac{\ell \cdot atm}{mol \cdot K}$$

$$1\ m = 10^9\ nm = 10^{10}\ \text{Å} \qquad 1\ m = 3.2808\ feet \qquad 1\ m = 100\ cm = 10^3\ mm = 10^6\ \mu m$$

$$1\ eV = 1.602 \times 10^{-19}\ Joules \qquad R_H = 13.6\ eV = 2.18 \times 10^{-18}\ J \qquad 10^{-3}\ kg = 1\ g = 10^3\ mg = 10^6\ \mu g$$

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

$$1.00000\ atm = 760.000\ Torr = 101325\ Pa \qquad 1\ mole = 6.022 \times 10^{23} \qquad 1\ m^3 = 1000\ \ell = 264.17\ gallons$$

The table at right is from Daniel C. Harris, *Quantitative Chemical Analysis*, 2^{nd} ed., New York: W. H. Freeman (1987).
A complete electromagnetic spectrum chart appears in Figure 7.2 on p. 293 of your textbook, and a detailed color spectrum can be found in Figure 20.23 on p. 994.

Common unit conversions: See Appendix 6 in your book, p. A-28

Complete electromagnetic spectrum: in your book on p. 293

Thermodynamic Data: See Appendix 4 in your book, pp. A21-A24

Table of Bond Energies: in your book on p. 373

Pauling Electronegativities: Figure 8.3, p. 354 of your book

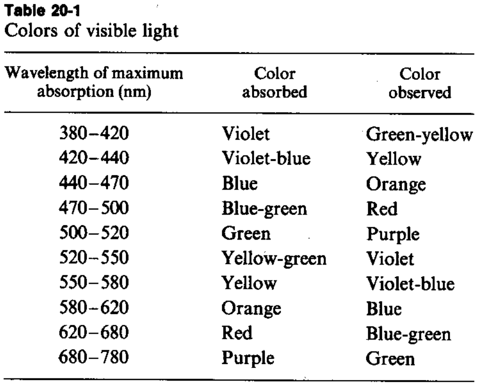


Table 20-1
Colors of visible light

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

Problem 1: Properties of Atoms

A. Calculate the wavelength of visible light that would be absorbed by a lone Li^{2+} ***ion*** in the gas phase if its electron underwent a transition from $n = 4$ to $n = 5$.

B. What color of visible light does the photon in part A correspond to?

C. The wavelength of electromagnetic radiation absorbed by a lone, neutral, Li ***atom*** in the gas phase with an electron undergoing an $n = 4$ to $n = 5$ transition is actually in the infrared portion of the spectrum. Explain why the energy required for this transition in the atom is so different from that required in the Li^{2+} ion.

If you haven't read the directions for this exam, you really ought to go back and read them now.

Walking along the banks of the Cannon River one morning, you are hit by a falling star and sucked into a vortex of immense improbability. You emerge from it a bit dazed, but still on the bank of a river that looks very much like the Cannon. You continue your walk back to campus, grab your books, and head off to chemistry class. You sit down and are greeted by this bizarre-looking periodic table:

Alternate Universe Periodic Table

Period									
1	A								
2	B						C	D	E
3	F						G	H	I
4	J	K	L	M	N	O	P	Q	R
5	S	T	U	V	W	X	Y	Z	a
6	b	c*	k	l	m	n	o	p	q
7	r	s**	aa	ab	ac	ad	ae		

*	d	e	f	g	h	i	j
**	t	u	v	w	x	y	z

D. What *one* modification of the normal rules of quantum mechanics and/or the properties of electrons would lead to a periodic table like this one?

E. Give the likely electronic configuration of element ae, the heaviest so far discovered by the inhabitants of this strange universe. [Shorthand OK!]

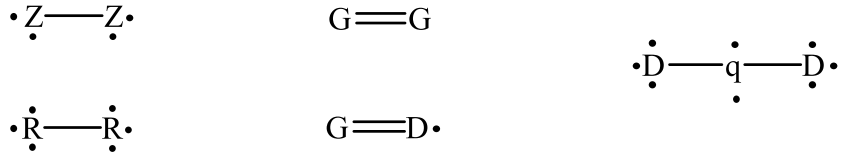
F. Consulting your chemistry textbook, you learn that in this universe the second ionization energy of element F is appreciably larger than that of element G, even though G has more protons in its nucleus. (In less technical terms, this means that it is more difficult to remove an electron from F^+ than it is to remove one from G^+.) Explain why, in terms of factors like shielding, effective nuclear charge, the number of protons in the nuclei of these ions, and their electronic configurations.

G. Explain why the H^{3+} ion is appreciably smaller than the D^- ion. (Don't do this simply by analogy to our universe; consider the same types of factors you did in answering the previous question.)

H. Below I've assembled eight simple ions and molecules, some of which are stable in this universe, and some which are not. Cross off the ones that are unstable and circle the ones that are stable. You don't need to explain your answers, but if you are unsure, don't guess: you get half credit if you just leave it alone!

Ions: S^+ G^{2-} J^-

Molecules:

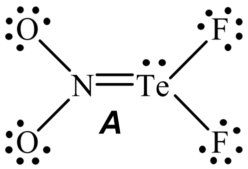


Problem 2: Properties of Molecules

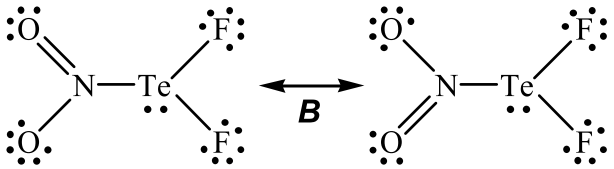
Shown below are ***six*** putative Lewis structures for the $[O_2NTeF_2]^-$ ion (three of them are ***resonant pairs***).

A. Indicate all ***non-zero*** formal charges in all of these structures by writing the formal charge in a small box next to the relevant atom, as shown in the example at right. Example $\overset{\boxed{-}}{:C}\equiv N:$

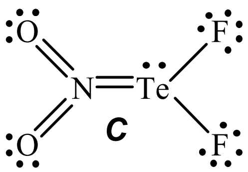
B. Three of the structures shown below are absolutely unworkable for $[O_2NTeF_2]^-$, because they violate at least one cardinal rule of Lewis structures. Cross these out, and indicate the sin for which you cast them out. *(Note: The way I'm using the term "structure," each resonant pair should be considered to be* ***one*** *structure.)*



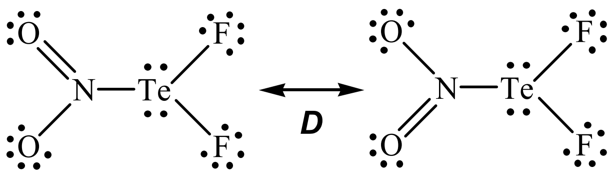
A



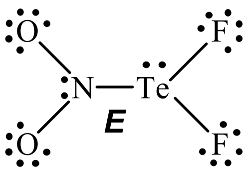
B



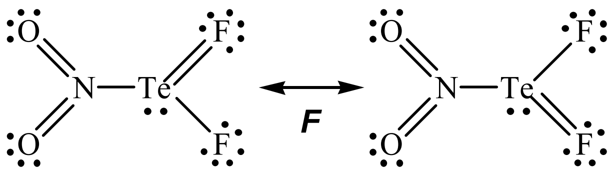
C



D



E



F

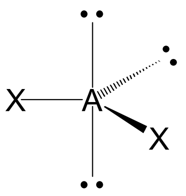
C. Rank the remaining structures from best to worst, using the letters in italics as a shorthand to refer to them.

Best ____ ____ ____ **Worst** Explain the reasoning that led to your rankings. The rankings here are not all that clear-cut, but don't worry. It's your explanation that I'm really interested in.

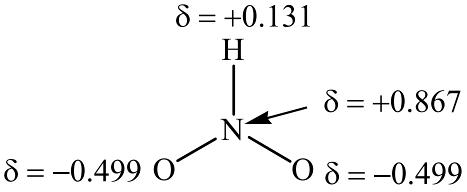
D. Draw the optimal Lewis representation of the $[O_2NTeF_2]^-$ ion. You can choose to employ one or more of the structures I've provided, and/or come up with your own, if you can come up with a good one I didn't. *(Note: The atoms in $[O_2NTeF_2]^-$* ***are connected*** *as shown in my structures: two O's to N to Te to two F's.)*

If you haven't read the directions for this exam, you really ought to go back and read them now.

E. Why is the molecular structure shown at right never observed in nature? Explain fully.

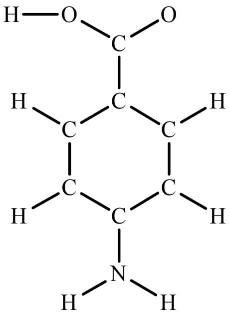


F. As best I can tell, the seemingly innocent little HNO_2 molecule whose connective skeleton I've drawn at right doesn't really exist. That doesn't bother Spartan Pro! According to Spartan, the electrostatic charges on the atoms would be as indicated in the figure at right. Draw the optimal Lewis representation of a molecule connected in this way, and use it and electronegativities to explain why each atom in this structure has the electrostatic charge that it does.



G. HNO_2 does actually exist, but its atoms are not connected as shown above. Draw the optimal Lewis representation of a plausible HNO_2 molecule. What makes it better than the structure in part F?

H. *para*-Aminobenzoic acid is also known by the trade names "Super Shade by Coppertone" and "PreSun," but it is most often referred to as PABA. It's actually a critical vitamin for bacteria, but we human-types know it as a chemical sunscreen. PABA's connective skeleton is shown at right. Given that none of the atoms carry any formal charge, draw the optimal Lewis representation of PABA. Show all the electrons.



I. Based on your answer above, is PABA capable of lying perfectly flat? If not, why not?

Problem 3: Kinetics and Equilibria

As I hinted at in question 3 on assignment 4, although H and D are chemically very similar, they are not, in fact, truly chemically identical. Here's some data on that from our old friend, the NIST Chemistry WebBook:

$$\Delta H_f^o\left[HD_{(g)}\right] = +0.32\frac{kJ}{mol} \qquad \Delta S^\circ\left[HD_{(g)}\right] = 143.80\frac{J}{mol\cdot K} \qquad \Delta S^\circ\left[D_{2(g)}\right] = 144.96\frac{J}{mol\cdot K}$$

Note: The standard state of deuterium is $D_{2(g)}$, and data for $H_{2(g)}$ appears in Appendix 4 of Zumdahl.

A. Calculate K_{eq} at 25°C for the balanced chemical reaction $H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$. Show your work.

B. The statistical analysis we applied to this system in Assignment 4 assumed that H and D are chemically identical. The result of that entropy-only analysis suggested an equilibrium distribution of something like

$$P_{H_{2(g)}} = 0.86\text{ atm} \qquad P_{D_{2(g)}} = 0.86\text{ atm} \qquad P_{HD_{(g)}} = 2.29\text{ atm}$$

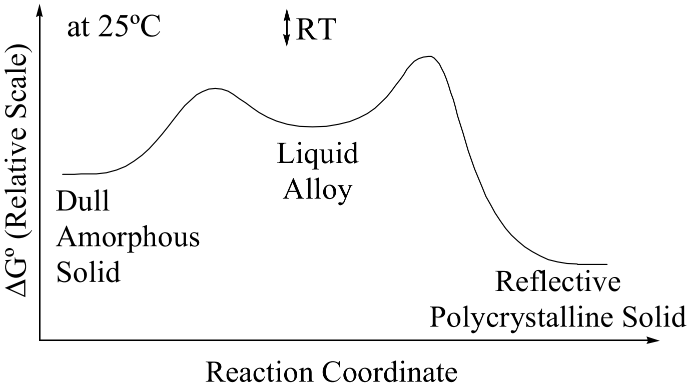
in a vessel initially charged with 4.00 atm of pure $HD_{(g)}$. When enthalpy (ΔH) is taken into account (as in part A), does it predict more or less $HD_{(g)}$ will be present at equilibrium? Justify your answer.

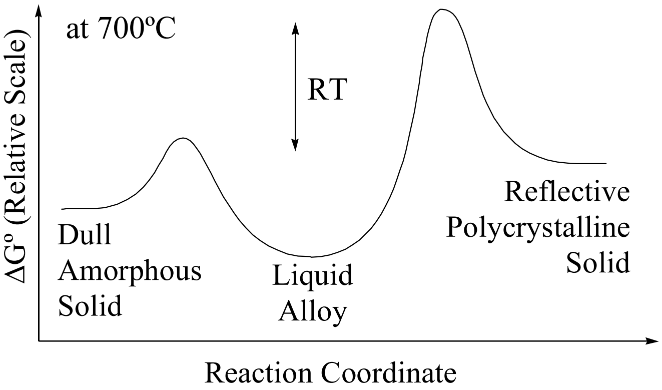
C. What can be said about the relative strength of H–D, D–D, and H–H bonds based on $\Delta H_f^o\left[HD_{(g)}\right]$? Be careful: you can certainly say *something* here, but resist the impulse to say more than you can back up!

D. Identify ***one*** thing you could do to keep as many HD molecules as possible in a magic syringe here on earth, initially filled with pure HD. You are free to mess with the syringe. Explain why your approach would work.

If you haven't read the directions for this exam, you really ought to go back and read them now.

CD-RW's (rewriteable CD's) are clear polycarbonate plastic discs covered with an alloy of silver, indium, antimony, and tellurium that melts at about 500ºC. This alloy can solidify into a polycrystalline form, which is quite reflective, or into an amorphous form, which is dull. By producing a pattern of reflective and dull spots on the disk, a sequence of zeroes and ones can be recorded: viola, binary data storage that can be read with a laser beam! Shown below are room-temperature and elevated temperature reaction coordinate diagrams showing the standard free energy of the dull and reflective solid forms, and that of the liquid alloy. A CD-RW system can make a spot reflective by warming it to 200ºC for a little while with gentle laser pulses. It can make a spot dull by hitting it with maximum laser power for a few seconds, melting it, and then cutting laser power off to that spot entirely, such that it rapidly cools.





A. Explain why heating the CD-RW thermal alloy to its melting point and then allowing it to cool quickly leads to the formation of the dull solid.

B. Explain how keeping the CD-RW alloy at 200ºC for a little while yields the reflective form.

C. Justify the claim that the transition amorphous alloy → polycrystalline alloy has a negative ΔS_{rxn} value. (There are several different answers you can provide here, you need only provide one good justification.)

D. Why would counting on a CD-RW as a very-long-term data storage medium not be a good idea?

Problem 4: Applied Science

Incomplete combustion of a hydrocarbon fuel, like methane, $CH_{4(g)}$, occurs when there isn't enough oxygen in the vicinity of a flame to produce the products of complete combustion, $CO_{2(g)}$ and $H_2O_{(\ell)}$. If there is ***almost*** enough oxygen available, the products of the incomplete combustion are $CO_{(g)}$ and $H_2O_{(\ell)}$.

A. Demonstrate numerically that less heat is released as a result of the incomplete combustion of methane at 25ºC and 1 atm than is released when the same amount of methane undergoes complete combustion. *(There are several different approaches to this: you don't have to use the one that gives the most accurate numerical result, because we are just trying to demonstrate a semi-quantitative principle here. Use whatever's easiest.)*

B. Why aren't $CO_{2(g)}$ and $H_{2(g)}$ produced instead of $CO_{(g)}$ and $H_2O_{(\ell)}$ when there is a slight shortage of oxygen?

C. My uncle Marco fixes cars for a living, and he has learned his trade by experience. That doesn't mean he doesn't know his stuff! The other day he told me that all cars emit lots of CO when they first start up, but once the catalytic converter is hot, they emit lots of CO only if they are running rich. Can you explain this?

D. You can learn a heck of a lot of science by staring at candles. When you're desparate, it can even lead you to a decent exam question. I've noticed that fat, stubby candles usually have shorter, rounder flames than the tall, thin, pointy flames on thin taper candles, even if they are made from the same wax. What's up with that?

If you haven't read the directions for this exam, you really ought to go back and read them now.

E. My friend Akif has a small greenhouse behind his home in Oklahoma, in which he has grown garden plants year-round for several years. While he likes getting fresh veggies throughout the winter, he has recently become quite homesick, and he is entertaining the idea of swapping out his vegetable garden for a desert-like cactus garden. This would entail removing the black potting soil currently on the floor of the greenhouse and replacing it with white sand reminiscent of Akif's homeland in Egypt. Although his greenhouse has no heating unit, the greenhouse effect keeps it quite warm. In fact, the temperature inside is currently on the hot side for a vegetable garden, even throughout the winter. Provided the temperature levels didn't change, the cacti Akif wants to install would do just great. Nonetheless, I've cautioned Akif that he should expect the greenhouse temperatures to be appreciably cooler after he makes the change, and warned him that he may have to invest in a heater to get the temperatures back up to their current levels. What's my logic?

F. You are sitting on the jury in the trial of Ross "Fishy" Daago, a controversial politician who was elected mayor in your city, and who, to all appearances, immediately set to work aggressively trying to clean up corruption. He is on trial for racketeering, which some in the city believe to be a trumped-up charge brought by the corrupt officials he is threatening, while others point to Fishy's criminal past with organized crime and say that despite his campaign claims, he hasn't reformed at all, let alone become a crusader against the type of crime in which he used to participate. The prosecution's case hinges on an unusual chemical found in the saliva used to lick shut an envelope of payola, and the testimony of a forensic scientist, who you can't help but swear you saw playing a scientist in a third-rate movie you saw last week. At any rate, this guy said:

> If we hadn't suspected Mr. Daago of this, we would have never have caught him. But the compound we found on the envelope seal is called trimethylamine, $N(CH_3)_3$, and it is what gives Mr. Daago his nickname. It is the cause of his chronic halitosis, which he covers up by sucking down Altoids like he owns stock in the manufacturer. Despite his efforts, this trimethylamine stuff is always present in his breath, even if covered up with breath mints. Trimethylamine is hard to identify with certainty, because it is a highly symmetric molecule and can't be seen with infrared spectroscopy. However, using mass spectroscopy, I was able to pick up its characteristic fragments and determine that the saliva of the person who licked shut this envelope contained 300 mg/ℓ of trimethylamine. Medical science knows that concentrations of this chemical above 200 mg/ℓ in the saliva indicate an abnormal condition. (These numerical quantities were written out on a chart, just as they are written here.) These results indicate that this envelope must have been licked by someone with an abnormally high level of trimethylamine in their breath.

On the stand, Mr. Daago states that he does indeed suffer chronic halitosis, in the form of a rare, recessive, genetic disorder called trimethylaminuria, and that his doctor has told him it causes his body to constantly release trimethylamine. (He also said that he does, in fact, hold stock in the maker of Altoids.) But he insisted upon his innocence, and pleaded to the jury to see through the fabricated evidence presented against him. The judge informs the jury that trimethylaminuria is such a rare disorder that prior case law requires you to view an indisputable connection between a crime and the disorder as evidence beyond a reasonable doubt. (Future lawyers: bear with me on this one.) So this case comes down to whether or not the scientist has convinced you of his competence and of the connection between the envelope and someone suffering from trimethylaminuria. Would you try to convince your fellow jurors to acquit or convict the crusading Mr. Daago? What would be your argument to them? Sorry, you'll need to answer this one on a separate page.

Problem 5: Applied Science II and Odds and Ends

Bert and Ernie (of Sesame Street fame) have recently become interested in amateur photography, and have learned just enough about how it works to become dangerous. Instead of taking their baths, they are preparing a photographic emulsion in their bathtub, by dissolving a precious bit of AgCl in hot (distilled) water to which they plan to add a packet of unflavored, uncolored Jell-O mix. Knowing that they have used up all of their AgCl, and that it has all dissolved, they have become agitated. They know they need to have crystals of solid AgCl precipitate out in their emulsion in order for it to work, and they worry they won't get them. Bert insists that as the liquid cools, some of the AgCl is bound to come back out of solution. Ernie vehemently disagrees, arguing that once the water cools, the AgCl will precipitate out even more slowly. As Bert advances toward the tub with the Jell-O packet, Ernie threatens to physically harm him with Rubber Ducky. You are sent in on a domestic violence call, and skillfully defuse the situation by explaining to them that to some extent, they are both correct. Not wanting to be called back again, you avert further potential crisis by dropping a few cubes of platinum metal coated with NaCl into the tub. (What can I say, you carry them around in your pocket. Work with me, here.) Minutes later, the telltale milky white color of solid AgCl precipitates is seen in the tub.

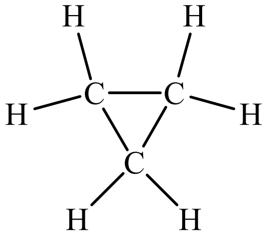
(Note: Silver appears following Si in Appendix 4, not with the A's!)

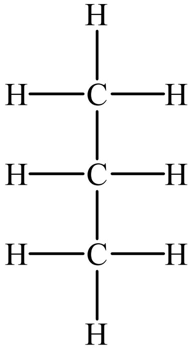
E. Explain how Bert and Ernie can both be correct in their assertions, to some extent. (You'll need a simple calculation or two to verify that Bert is right; show those calculations as part of your answer.)

F. Why did solid AgCl precipitate out after you threw your cubes into the tub? Don't jump to hasty conclusions.

If you haven't read the directions for this exam, you really ought to go back and read them now.

A. My rules for assembling Lewis structures dictate that you should avoid forming small rings of atoms. Why is that? Well, consider the molecule shown at right, $C_3H_{6(g)}$. It looks pretty good, but the fact the three carbon atoms are tied together into an equilateral triangle causes trouble! (You can see this in the thermodynamic data in Appendix Four.) Taking VSEPR and the desired geometry of the C atoms into account, explain what makes this molecule much less stable than straight-chain C_3H_8.





B. Dr. Bob (of Muppet Show fame) is researching ways to remove radioactive ^{131}I from medical patients after it is used to monitor iodine uptake in their thyroid glands. (See p. 1037 of Zumdahl.) Because iodine is an important body nutrient, he can't just suck all the iodine out of a patient after the test is complete - he has to replace it with non-radioactive iodine. He's built a model system, consisting of a beaker of water containing a small amount of solid, radioactive $Ag^{131}I$ that dissolves like this: $AgI_{(s)} \underset{H_2O_{(\ell)}}{\rightleftharpoons} Ag^+_{(aq)} + I^-_{(aq)}$. He waits until the water becomes saturated with Ag^+ and $^{131}I^-$ ions. He then adds a lot of non-radioactive $Ag^{127}I$ to the beaker, and monitors the radioactivity of the liquid solution over time. Dr. Bob finds that while the concentration of I^- ions in the solution remains constant, the radioactivity of the solution rapidly drops. How is that possible?

D. After class, Jeff asked an excellent question regarding the H_2/O_2 balloons we worked with last Friday: Which of them would eventually release the most heat into the room if I did ***not*** put a match to them? There are three potential answers to this question, one theoretical, the other two pragmatic. You can give any one of these answers and get away with it, provided you explain the rationale for your answer, and it is reasonable. You can even get bonus points if you can come up with two answers. Recall that there were four balloons:

(1) Filled with pure O_2
(2) Filled with a 1:1 volume ratio of H_2:O_2
(3) Filled with a 2:1 volume ratio of H_2:O_2
(4) Filled with pure H_2

The balloons were all the same size, that is, they had the same total volume. Explain your answer here: