Final Exam Key *Note: Pagination differs from that of the original exam* **Chemistry 123 Winter 2003**

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 $n = 5$.

We don't know how to get quantitative values for the energies of anything except one-electron systems…but hey, what do you know! Lithium has three protons, and usually three electrons. Take two of those electrons away to make a 2+ ion, and you have only one electron left…so Li^{2+} is a one-electron system, amenable to analysis with the Bohr model. It has Z = 3, because lithium has three protons in its nucleus, and we are interested in the energy difference between the $n = 4$ and the $n = 5$ states:

$$E_{\text{Bohr Electron}} = R_H\left(\frac{Z^2}{n^2}\right)$$

$$E_{\text{photon}} = \left|\Delta E_{\text{electron}}\right| = \left|E_{\text{final}} - E_{\text{initial}}\right| = \left|E_{\text{electron},\, n=5} - E_{\text{electron},\, n=4}\right| = \left|R_H Z^2\left(\frac{1}{\underline{5}^2} - \frac{1}{\underline{4}^2}\right)\right|$$

$$= \left(2.18\times10^{-18}\,\text{J}\right)\left(\underline{3}^2\right)\left|\frac{1}{\underline{25}} - \frac{1}{\underline{16}}\right| = 4.41_{45}\times10^{-19}\,\text{Joules}$$

$$E_{\text{photon}} = \frac{hc}{\lambda} \quad\Rightarrow\quad \lambda = \frac{hc}{E_{\text{photon}}} = \frac{\left(6.626\times10^{-34}\,\text{J}\cdot\text{s}\right)\left(2.998\times10^{8}\,\frac{\text{m}}{\text{s}}\right)}{4.41_{45}\times10^{-19}\,\text{Joules}}\left(\frac{10^9\,\text{nm}}{\text{m}}\right) = 449._{99}\ \text{nm} = 450.\ \text{nm}$$

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

Color being a rather subjective thing, anything in the vicinity of blue will be an acceptable answer here. According to the table on the equation sheet, 450. nm falls smack in the middle of the blue portion of the spectrum, and, to my eyes, Zumdahl's two figures agree on this one. A solution of this ion (if it could exist in solution) would appear orange if there were a lot of electrons undergoing $n = 4$ to $n = 5$ transitions, but that's not what this question is asking! The photon that gets absorbed is blue.

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.

The fact that the photon associated with this transition in a Li atom is in the infrared portion of the spectrum tells us that it involves a much smaller amount of energy than does the same transition taking place in a Li^{2+} ion. The difference has to do with the fact that a Li atom has three electrons, two of which will most likely be in orbitals with $n < 4$, and thus effectively "between" the electron undergoing the 4 → 5 transition and the three positive charges in the nucleus. As a result, the *effective nuclear charge* seen by an electron in the $n = 4$ orbital (or in the $n = 5$ orbital, for that matter) is less than three. If we replace Z^2 in our calculation above with a smaller value $(Z_{\text{eff}})^2$, the energy we calculate will be appreciably less. This, in turn, implies a longer wavelength for the photon required to cause the transition to occur. The obstruction of some portion of the nuclear charge by (some of) the other electrons is referred to as shielding. Shielding is never perfect, but assuming that it is gives us a rough estimate of its effect. If there are two electrons in the $n = 1$ orbital, an electron in the $n = 4$ orbital would see an effective nuclear charge of about (3 – 2 =) one. This value of Z_{eff} would cause the energy for the 4 → 5 transition to be 1/9th of the value calculated above, which would in turn result in a photon wavelength nine times larger than the 450. nm calculated above, or about 4050 nm, which is way into the infrared. The actual effect isn't that pronounced, but the reasoning behind the actual shift is completely analogous.

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 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?

If electrons did not have spin, and their quantum states were completely described by the quantum numbers n, ℓ, and m_ℓ, we would end up with a periodic table just like this one. One electron can sit in each s orbital, three in each set of p orbitals, five in each set of d orbitals, and seven in each set of f orbitals: in each case, half the number allowed in our universe. Assuming all the other aspects relating the quantum mechanical behavior of atoms to the periodic table remain unchanged, we get the periodic table at right, with half as many elements in each orbital group as in our universe. The filling order remains the same, as do the relative properties of the elements as one moves across the table. The noble gases are in the rightmost column.

E. Give the likely electronic configuration of element ae, the heaviest so far discovered in this strange universe.

This could be done in either shorthand or longhand, the latter is more work but allows you to check that your answer makes sense. ae = $1s^1 2s^1 2p^3 3s^1 3p^3 4s^1 3d^5 4p^3 5s^1 4d^5 5p^3 6s^1 4f^7 5d^5 6p^3 7s^1 5f^7 6d^5 7p^1$ (57 electrons total, which is right because ae is element 57!) or, realizing that q is the preceding noble gas, we can use the following shorthand: ae = $[q]7s^1 5f^7 6p^5 7p^1$

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.

Let's start by writing out the electronic configurations of these two ions: $F^+ = 1s^1 2s^1 2p^3$ $G^+ = 1s^1 2s^1 2p^3 3s^1$ We'll also want to note that F has an atomic number of 6, and thus six protons in its nucleus, while G has an atomic number of 7, and seven protons in its nucleus. This is a rather extreme case, and is actually most clearly explained exclusively in terms of screening and effective nuclear charge. To whit: if I want to remove an electron from F^+, I'll have to pull off a 2p electron, which sees an effective nuclear charge of roughly (6 – 2 =) 4 positive charges. (The 1s and 2s electrons block 2p's view of the nucleus; to some extent the 2p electrons block each other's views as well, but not much.) If I want to pull an electron off of G^+, there's a 3s electron that sees roughly only (7 – 5 =) 2 positive charges, and is thus much easier to pull off. (The 1s, 2s, and 2p electrons do a very good job of obstructing its view of the nucleus!) So it's hardly surprising that it is easier to ionize G^+ than it is to ionize F^+. In fact, the difference is even more pronounced, because the 3s electron I want to pull off of G^+ not only sees less nuclear charge than does the 2p electron in F^+, it is also appreciably farther away from the nucleus. (It is sitting another row back!)

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.)

We are again well-served by starting with the electronic configurations of these two ions: H^{3+}: $1s^1 2s^1 2p^3$ D^-: $1s^1 2s^1 2p^3$ Well, what do you know…they are isoelectronic! So the only factor that can differentiate them is their nuclei, and they are certainly different in that regard! The H^{3+} ion has 8 protons in its nucleus, while the D^- ion has only 4. So the H^{3+} ion pulls in its entourage of 5 electrons much more tightly and closely than does D^-, and thus H^{3+} is appreciably smaller.

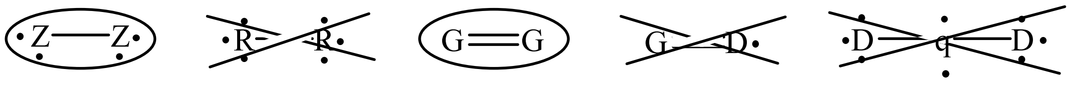
H. Below I've assembled eight simple ions and molecules, some of which are stable in this universe, and some which are not. Cross off the ones that are unstable and circle the ones that are stable. You don't need to explain your answers, but if you are unsure, don't guess: you get half credit if you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

Answering this question requires adjusting the rules of Lewis structures for this strange universe. The questions above help lead you to the key modification, namely, that atoms before H or so follow a "four electron rule," and electrons do not pair up, they just exist as single entities, because they do not have spin and can not share an orbital. Electrons still strive to resemble the ideal gases in the far right column of the periodic table. Thus S^+ is probably stable, since it shares the electronic configuration of the noble gas element R. Similarly, G^{2-} is likely to be stable, as it shares its electronic configuration with the noble gas I. On the other hand, J^- shares the electronic configuration of K, the first transition metal, which is not a particularly envious position to be in. Still, J is analogous to K or Ca in our universe, and both of those elements have (very slightly) favorable electron affinities, so J^- might exist. In short, J^- wasn't a great ion to put into this question, and I accepted either a thumbs up or thumbs down answer with respect to it.

Ions: [✓ S^+] [✓ G^{2-}] ~~J^-~~ (J^- is correct either crossed out or circled)

Things are a bit more cut and dried with the molecules. Z_2 does indeed exist; it gives each Z atom a claim to the 4 valence electrons it wants, gives each a formal charge of zero, and doesn't break any rules. G_2 is also a good egg, with each atom having zero formal charge and a claim to a "full quartet," and again, no rules being broken. Not so for R_2! R is a noble gas, and it isn't going to bond with anything except under extreme duress. R_2 gives each R claim to 5 e^-, which is plausible in that R has access to d orbitals and might be hypervalent if it bonds, but it won't do so for the benefit of another R, which will also end up hypervalent! GD, as drawn, has no formal charges, but it gives D claim to five electrons, which *is* problematic because D has no reasonable access to d orbitals and can not be hypervalent. (It's the analog to N, O, or F in our universe – in any case, a no-go.) The last little monster, qD_2, is tricky. q is a noble gas, so at first blush this seems like a non-starter. But D is analogous to fluorine, likely to be the most electronegative element known, and so this might be something like XeF_2, which does indeed exist even though Xe is a noble gas. But wait! The formal charges on the D's here are each minus one, while the q has a formal charge of zero. That would make this a 2- ion…which may or may not be problematic. What is a death knell is that each of the D's has a claim to 5 electrons, and we are again faced with hypervalent D, a big no-no. So we can rule this manifestation of qD_2 right out. I had intended this to be a XeF_2 analog, and circled it when I wrote my key, so the "Rob screwed up the key" rule comes into play here: you get cut some slack! You got 2 free points. This is good, because this problem was pretty hard and stumped quite a few of you.

Molecules:



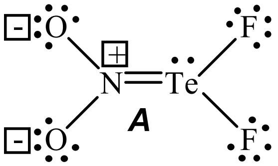
Problem 2: Properties of Molecules

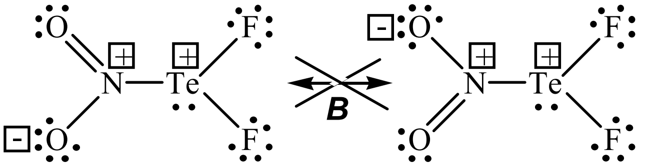
Shown below are ***six*** putative Lewis structures for the $[O_2NTeF_2]^-$ ion (three of them are ***resonant pairs***).

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

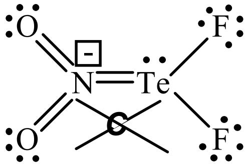
This wasn't too difficult, but in my effort to write the key I managed to forget a matched pair of + formal charges in structure B, so we whip out the "Rob screwed up the key" rule again. You got -0 if you made the same number of mistakes I did, and more generally, you got +½ vs. whatever you would have gotten otherwise. Don't you love it when I flub it?!?

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.)*

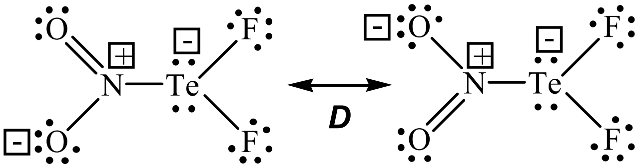


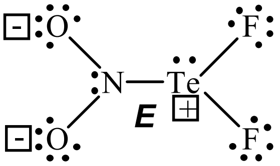


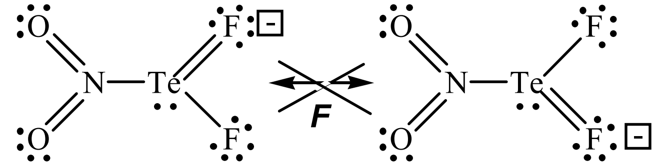
This is a +1 ion, not a -1 ion! The formal charge adds to +1.



Contains hypervalent N







Contains both hypervalent N and F, making it very non-Scottish.

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

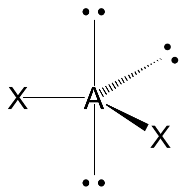
Best E > A > D Worst Explain the reasoning that led to your rankings. The rankings here are not all that clear-cut, but don't worry. It's your explanation that I'm really interested in.

You could get away with just about any ordering here, provided you were consistent into part D and you gave a plausible explanation for your ranking. A strict reading of my rules would suggest that structure E is the best, since it adheres best to rule 6. The electronegativities of the atoms involved are as follows: Te = 2.1; N = 3.0; O = 3.5; and F = 4.0. We'd like to put the negative formal charge(s) on F, but as we can see in structure F, that would make it hypervalent, which violates rule 4. So the next best place to put any negative formal charge is on O, with Te the best resting place for any positive formal charges. Since all three options are identical in the eyes of rule 5, in that they all have a total formal charge of 3, rule 6 causes us to favor E over A because Te is less electronegative than N (by a good margin…I originally had Se in place of Te, which made things even murkier.) A is still appreciably better than D, which put a negative formal charge on Te, the least electronegative element. Sounds like a closed case, but recall that rule 9 is particularly important for ions, to the extent that it delocalizes the excess charge. That sounds a big horn in favor of structure D, which at least manages to split up one formal negative charge between two O atoms, and to make rule 8 happy by arranging the formal charges in a favorable (-)(+)(-) sandwich. On this scale, A is a distant second, and E, with two negative formal charges far away from the positive charge and no resonance, would be the worst. A and D both have more bonding than E, which favors them in light of rule 7. So when you add that all up, it's really something of a toss-up as to who's the best. It depends on whether you feel a preponderance of the later rules overrides the clear edict of rule 6.

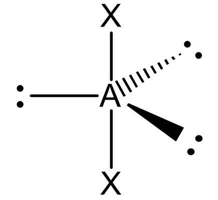
D. Draw the optimal Lewis representation of the $[O_2NTeF_2]^-$ ion. You can choose to employ one or more of the structures I've provided, and/or come up with your own, if you can come up with a good one I didn't. *(Note: The atoms in* $[O_2NTeF_2]^-$ ***are connected*** *as shown in my structures: two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

It's darn tempting to create a structure that has a total formal charge of only one…but to the best of my knowledge, it can't be done without breaking a major rule. Failing in that effort, one might be tempted to resonate together some mix of my structures E, A, and D. But careful inspection (which it seems most of you thought to do!) reveals that the steric number of either N or Te changes between each of these, and so you are forced to pick just one. That should be the one you considered best when answering the previous question; in my case I would list structure E, and only structure E, as my answer to this question.

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

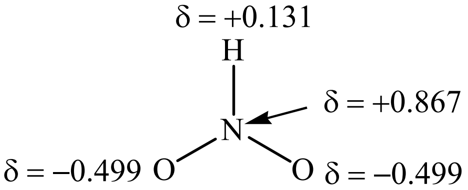


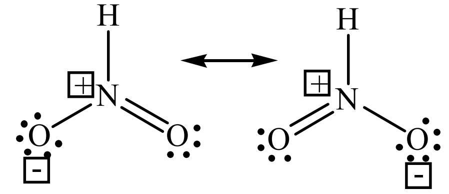
The problem with this structure is that the lone pairs are much more crowded than they have to be. According to VSEPR, by moving them all to equatorial positions, the same molecule can be obtained, with far less "steric hindrance." Recall that the practical mythology which is VSEPR teaches us that lone pairs are "fat," and take up more space than does a bonding pair of electrons. As such, we want to try to minimize the number of <120º interactions they have with other electron pairs, particularly with other "fat" lone pairs.



As things currently stand, in this structure, the lone pairs experience a total of 4 90º lone-pair to lone-pair interactions, and a total of 8 90º interactions of all types. By moving them to the locations shown in the lower diagram, and shifting the bonded X atoms to axial locations (so that the resulting molecule is linear,) we cut that down to no 90º lone-pair to lone-pair interactions, and only 6 total 90º interactions, all lone-pair to bonding pair. That's a pretty marked improvement, at essentially no cost to the molecule; so (at least according to our pal VSEPR) we should always find AX_2 molecules with three lone pairs to be linear. It's reassuring to learn that, for example, XeF_2 is indeed linear, so this "works" at least some of the time!

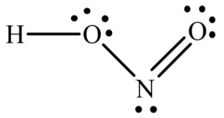
F. As best I can tell, the seemingly innocent little HNO_2 molecule whose connective skeleton I've drawn at right doesn't really exist. That doesn't bother Spartan Pro! According to Spartan, the electrostatic charges on the atoms would be as indicated in the figure at right. Draw the optimal Lewis representation 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.





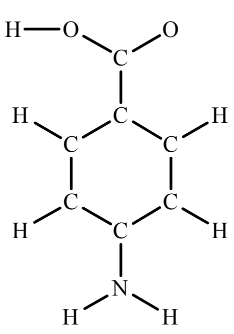
The optimal Lewis representation of this HNO_2 structure would be the resonant pair shown at right. It's not super, because it has a total formal charge of two, and we'd rather have a total of zero for this neutral molecule, but with this connectivity there's no other way to get every atom a full valence shell. Realizing that the actual structure will be the weighted average of these two resonance structures, and that the weighting will be 50/50, because the two structures are identical by symmetry, we expect a formal charge of -½ on each of the oxygen atoms, a formal charge of +1 on the nitrogen, and a formal charge of zero on the hydrogen. This is actually pretty darn close to what's actually observed, save for a slight positive charge on H, and the charge on N being less than +1 by about the same amount. That makes perfect sense in light of the electronegativity difference between N and H, namely, that N is more electronegative than H and is likely to drain some electron density away from it, effectively transferring some of its positive "pain" to the hapless hydrogen atom by hogging the electron pair that the two of them are sharing.

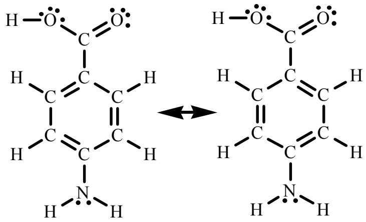
G. HNO_2 does actually exist, but its atoms are not connected as shown above. Draw the optimal Lewis representation of a plausible HNO_2 molecule. What makes it better than the structure in part F?



In the HNO_2 structure shown at left, the total formal charge is zero, and the relatively weak N–H bond (391 kJ/mol) is also replaced by a stronger O–H bond (467 kJ/mol). On both counts, that makes it an appreciable improvement over the structure shown above, and thus it's not surprising that this is the form in which HNO_2 is actually found in nature. That H atom readily pops off, to form a H^+ ion and a NO_2^- ion, so HNO_2 is in fact a pretty powerful acid; it's called nitrous acid.

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.





In order to get to a reasonable structure, we have to add the missing electrons to the skeletal structure. It turns out that calls for adding several double bonds, which can resonate, as well as lone pairs on the oxygens and the nitrogen. PABA contains a benzene ring, which means resonance! Not much though, because the H on one of the oxygens breaks up what would be a heck of a lot more resonance without that H atom on there, in the $PABA^-$ ion. Notice that these two resonance structures are going to be equal contributors, and that none of the atoms in the structure have any formal charges.

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

Nope, PABA is going to have a bump on it where the NH_2 group is! That nitrogen has a steric number of four, and thus it's going to have a trigonal pyramidal molecular geometry. The rest of the molecule has the potential to sit flat, though: (the carbon up on top has a steric number of three, and thus a trigonal planar molecular geometry, as do every one of the carbons in the ring.)

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:

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

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 25ºC for the balanced chemical reaction $H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$. Show your work.

Well, golly, I miffed this one at the exam *writing* stage. See those ΔSº[blah]'s up there? Well, they don't exist. Sº[blah]'s sure do, and that's what I wanted them to be. We can also talk about what ΔS^o_f [blah] would be for various things, but if $D_{2(g)}$ is the standard state of deuterium, then $\Delta S^o_f\,[D_{2(g)}]$ darn well better be zero, because it is ΔSº for the reaction $D_{2(g)} \rightarrow D_{2(g)}$. Unfortunately, despite that, a lot of you treated the ΔSº values I provided as if they were ΔS^o_f values. Well, I did screw up, so I let you off the hook on that. If you correctly treated ΔSº as Sº, you got a chunky two bonus points. I'm only going to work this out treating S the right way, but you got credit on subsequent parts as long as your answers there were consistent with whatever you did up here. Here's how this was supposed to unfold: I intentionally provided you with ΔH and ΔS data, but no ΔG data, for HD and D_2. That forced you to go through ΔG = ΔH – TΔS in order to obtain ΔGº, on your way to K_{eq}. That still left you a lot of latitude. The first approach is to calculate $\Delta G^o_f\,[HD_{(g)}]$, and use ΔG^o_f values to determine ΔG^o_{rxn} for $H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$. To do that correctly, we need to realize that the formation reaction for $HD_{(g)}$ would be ½ $H_{2(g)}$ + ½ $D_{2(g)} \rightleftharpoons HD_{(g)}$, which looks pretty familiar, eh? Realizing that $D_{2(g)}$ is the standard state for deuterium, and that $\Delta H^o_f\,[D_{2(g)}]$ is therefore zero, and looking up data on $H_{2(g)}$ in Appendix Four, we can then determine $\Delta H^o_f\,[HD_{(g)}]$ and $\Delta S^o_f\,[HD_{(g)}]$ for this reaction, as follows:

$$\Delta H^o_{rxn} = \sum_i \chi_i \Delta H^o_f[i] = \left(-\tfrac{1}{2}\Delta H^o_f[H_{2(g)}]\right) + \left(-\tfrac{1}{2}\Delta H^o_f[D_{2(g)}]\right) + \left(+1\cdot\Delta H^o_f[HD_{(g)}]\right)$$

$$= \left(-\tfrac{1}{2}\left[0\frac{kJ}{mol}\right]\right) + \left(-\tfrac{1}{2}\left[0\frac{kJ}{mol}\right]\right) + \left(+1\cdot\left[0.32\frac{kJ}{mol}\right]\right) = +0.32\frac{kJ}{mol}$$

$$\Delta S^o_{rxn} = \sum_i \chi_i S^\circ[i] = \left(-\tfrac{1}{2}S^\circ[H_{2(g)}]\right) + \left(-\tfrac{1}{2}S^\circ[D_{2(g)}]\right) + \left(+1\cdot S^\circ[HD_{(g)}]\right)$$

$$= \left(-\tfrac{1}{2}\left[131\frac{J}{mol\cdot K}\right]\right) + \left(-\tfrac{1}{2}\left[144.96\frac{J}{mol\cdot K}\right]\right) + \left(+1\cdot\left[143.80\frac{J}{mol\cdot K}\right]\right)$$

$$= -65.5\frac{J}{mol\cdot K} - 72.480\frac{J}{mol\cdot K} + 143.80\frac{J}{mol\cdot K} = +5.8_2\frac{J}{mol\cdot K}$$

This allows us to calculate ΔG^o_{rxn} for the formation of $HD_{(g)}$, and thus $\Delta G^o_f\,[HD_{(g)}]$, from the definition of free energy and the realization that the temperature of interest is 25ºC, which must be converted to Kelvins: T (K) = 25ºC + 273.15 = $298._{15}$ K

$$\Delta G = \Delta H - T\Delta S \quad \Rightarrow \quad \Delta G^o_f[HD_{(g)}] = \Delta H^o_f[HD_{(g)}] - T\left(\Delta S^o_f[HD_{(g)}]\right)$$

$$\Delta G^o_f[HD_{(g)}] = +0.32\frac{kJ}{mol}\left(\frac{1000\ J}{kJ}\right) - 298._{15}K\left(+5.8_2\frac{J}{mol\cdot K}\right)$$

$$= 32_0\frac{J}{mol} - 173_5\frac{J}{mol} = -141_5\frac{J}{mol}$$

We can now determine ΔG^o_{rxn} for the reaction of interest, $H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$, either by realizing this is just twice the formation reaction we just worked with, or by applying the usual state function calculation process, like so:

$$\Delta G^o_{rxn} = \sum_i \chi_i \Delta G^o_f[i] = \left(-1\cdot\Delta G^o_f[H_{2(g)}]\right) + \left(-1\cdot\Delta G^o_f[D_{2(g)}]\right) + \left(+2\cdot\Delta G^o_f[HD_{(g)}]\right)$$

$$= \left(-\left[0\frac{J}{mol}\right]\right) + \left(-\left[0\frac{J}{mol}\right]\right) + \left(+2\cdot\left[-141_5\frac{J}{mol}\right]\right) = -283_0\frac{J}{mol}$$

This allows us to calculate the desired value, K_{eq}:

$$K_{eq} = e^{\left(\frac{-\Delta G^o_{rxn}}{RT}\right)} = e^{\left(\frac{-\left[-283_0\frac{J}{mol}\right]}{\left[8.3145\frac{J}{mol\cdot K}\right]\left[298._{15}K\right]}\right)} = e^{\left(1.14_{18}\right)} = 3.13_{24}$$

Problem 3A, continued...

The other approach to accomplishing this objective is calculating ΔH^o_{rxn} and ΔS^o_{rxn} for the reaction $H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$ directly, and then using those quantities to determine ΔG^o_{rxn} for the same, bypassing the formation reaction for $HD_{(g)}$. The result is identical, but for a reduction in the significant figures in the final result. Because significant figures did count in this problem, I'll work out the result using this alternate approach as well, for purposes of comparison. So, for $H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$,

$$\Delta H^o_{rxn} = \sum_i \chi_i \Delta H^o_f[i] = \left(-1\cdot\Delta H^o_f[H_{2(g)}]\right) + \left(-1\cdot\Delta H^o_f[D_{2(g)}]\right) + \left(+2\cdot\Delta H^o_f[HD_{(g)}]\right)$$

$$= \left(-1\left[0\frac{kJ}{mol}\right]\right) + \left(-1\left[0\frac{kJ}{mol}\right]\right) + \left(+2\cdot\left[0.32\frac{kJ}{mol}\right]\right) = +0.64\frac{kJ}{mol}$$

$$\Delta S^o_{rxn} = \sum_i \chi_i S^\circ[i] = \left(-1\cdot S^\circ[H_{2(g)}]\right) + \left(-1\cdot S^\circ[D_{2(g)}]\right) + \left(+2\cdot S^\circ[HD_{(g)}]\right)$$

$$= \left(-1\left[131\frac{J}{mol\cdot K}\right]\right) + \left(-1\left[144.96\frac{J}{mol\cdot K}\right]\right) + \left(+2\cdot\left[143.80\frac{J}{mol\cdot K}\right]\right)$$

$$= -131\frac{J}{mol\cdot K} - 144.96\frac{J}{mol\cdot K} + 287.60\frac{J}{mol\cdot K} = +11._{64}\frac{J}{mol\cdot K}$$

$$\Delta G = \Delta H - T\Delta S \quad \Rightarrow \quad \Delta G^o_{rxn} = \Delta H^o_{rxn} - T\left(\Delta S^o_{rxn}\right)$$

$$\Delta G^o_{rxn} = +0.64\frac{kJ}{mol}\left(\frac{1000\ J}{kJ}\right) - 298._{15}K\left(+11._{64}\frac{J}{mol\cdot K}\right) = 64_0\frac{J}{mol} - 34_{70}\frac{J}{mol} = -28_{30}\frac{J}{mol}$$

$$K_{eq} = e^{\left(\frac{-\Delta G^o_{rxn}}{RT}\right)} = e^{\left(\frac{-\left[-28_{30}\frac{J}{mol}\right]}{\left[8.3145\frac{J}{mol\cdot K}\right]\left[298._{15}K\right]}\right)} = e^{(1.1_{418})} = 3.1_{324}$$

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.

You can answer this part either numerically or logically. Logically, the argument would be that ΔH was assumed to be zero for this reaction, and that in actuality it is slightly positive. The result will be that the reaction is somewhat less favored than predicted, and thus that slightly less $HD_{(g)}$ will exist at equilibrium than an analysis of entropy alone would lead us to expect.

More quantitatively, we can calculate Q_α for the concentrations specified here, and compare it to the calculated value of K_{eq} from part A. Recalling that the reaction in question is $H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$, and that the activity of a gaseous component is the numerical value of its partial pressure, measured in atmospheres, we find that the values given above yield a Q_α value of

$$Q_\alpha = \prod_i (\alpha_i)^{\chi_i} = \left(\alpha_{H_{2(g)}}\right)^{-1}\left(\alpha_{D_{2(g)}}\right)^{-1}\left(\alpha_{HD_{(g)}}\right)^2 = \frac{\left(\alpha_{HD_{(g)}}\right)^2}{\alpha_{H_{2(g)}}\alpha_{D_{2(g)}}} = \frac{\left(\frac{P_{HD}}{atm}\right)^2}{\left(\frac{P_{H_2}}{atm}\right)\left(\frac{P_{D_2}}{atm}\right)} = \frac{P^2_{HD}}{P_{H_2}P_{D_2}} = \frac{(2.29\text{ atm})^2}{(0.86\text{ atm})(0.86\text{ atm})} = 7.09$$

This is larger than the K_{eq} calculated in part A, which took ΔH into account, and in order to attain equilibrium, we would have to reduce the partial pressure of HD and increase the partial pressure of H_2 and D_2. Thus the statistical estimate predicts more HD than does the complete thermodynamic treatment, and when enthalpy (ΔH) is taken into account the prediction is that less $HD_{(g)}$ will be present at equilibrium.

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!

In the reaction we considered above, we broke one H–H bond and one D–D bond, and formed two H–D bonds. (Alternately, we broke ½ H–H bond and ½ D–D bond, and formed one H–D bond, but the implication is the same!) Because ΔH is positive, we know that it took more energy to break the bonds than we got back when we formed the new bond(s). Most of you got that, but it was common for you to then assert that H–D bonds are weaker than H–H *and* D–D bonds. That's not actually true! In fact, according to the NIST WebBook, the bond energy for H–H is $2\cdot\Delta H_f^o\left[H_{(g)}\right] = 2\cdot(218.00\text{ kJ/mol}) = 436.00\text{ kJ/mol}$, while that for D–D is $2\,\Delta H_f^o\left[D_{(g)}\right] = 2\cdot(221.72\text{ kJ/mol}) = 443.44\text{ kJ/mol}$. From the data given in this problem, this allows us to determine that the bond energy of an H–D bond is $\dfrac{+436.00\frac{\text{kJ}}{\text{mol}}+443.44\frac{\text{kJ}}{\text{mol}}-0.64\frac{\text{kJ}}{\text{mol}}}{2}=439.40\frac{\text{kJ}}{\text{mol}}$. That puts it nearly mid-way between the two, and importantly, an H–D bond is actually appreciably stronger than is an H–H bond! *All* that we know from the given information in this problem is that it takes more energy to break an H–H and a D–D bond than it does to break two H–D bonds.

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.

There are (as in so many other parts of this problem!) two good approaches to this, and the class divided between them about equally. One approach is based on kinetics, and the idea that if reactions are kept from progressing, you'll keep what you started with. The other approach centers on thermodynamics, and works to make HD as thermodynamically comfortable as possible.

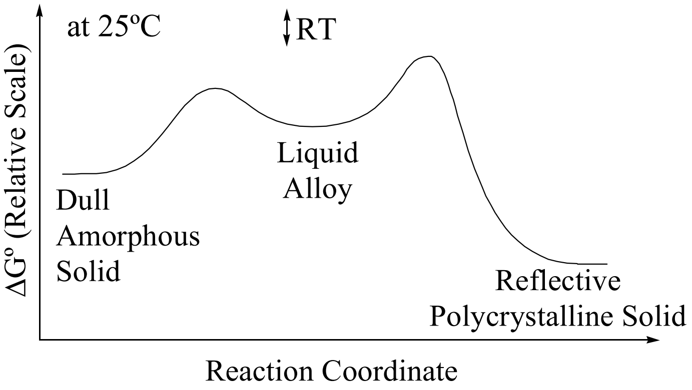
Kinetically, any reaction will occur more slowly as the temperature is lowered. Because we are starting with a sample of pure HD, if we chill our syringe to a very low temperature, we will slow down the reaction $2HD_{(g)} \rightarrow H_{2(g)} + D_{2(g)}$. In fact, if we get it cold enough and apply enough pressure to it, the HD should even liquefy, then solidify, making the transformation almost stop.

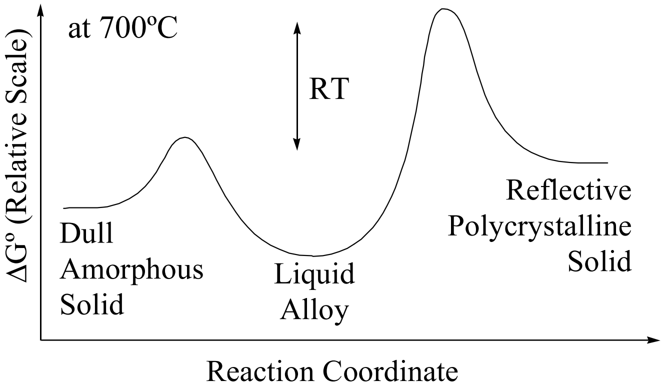
Thermodynamically, we know the reaction $H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$ is endothermic. Thus, by Le Châtelier's principle, adding heat to the reaction (warming it up) will shift the thermodynamic equilibrium point toward the product, HD. At very high temperatures, the entropically favored HD will be found at higher concentrations, while the reactants favored by enthalpy (D_2 in particular, as we learned in part C) will be found at lower concentrations. Thus a very warm syringe will come to equilibrium very quickly, but will contain mostly HD even when it does get to equilibrium. [Technical note: As the temperature gets higher and higher, the equilibrium composition will actually asymptotically approach that predicted by entropy, and we'll end up with a composition very similar to that calculated statistically, as given in part B. That's (2.29 / [2.29 + 0.86 + 0.86] =) 57% HD, which really isn't all that much, really. But over the long haul, that's the most you'll be able to keep in the syringe, no matter what you do to it. The only way you can do better than that is to employ kinetics to keep the purer HD around longer, delaying the inevitable.]

The one way that a lot of people flubbed this problem was in arguing that by exerting pressure on the syringe, Q_α could be made to change in favor of HD. If you look carefully at the Q_α expression in part B, or at the balanced reaction, you'll see that the total system pressure does not change as the reaction proceeds, and that increasing or decreasing the total pressure will not change Q_α. The reaction consumes two moles of gas for every two moles of gas that it produces, and so, assuming that the reactants and products are about equally condensable, jumping up and down on, tugging at, or pushing on an isothermal syringe will not shift the equilibrium in either direction. The reaction is pressure-independent as long as nothing warms up or condenses.

Explanatory header for problem on subsequent page:

CD-RW's (re-writeable 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.

At 700ºC, the alloy will quickly adopt the thermodynamically favored liquid state. When it cools below 500ºC, it will solidify, at first forming the kinetically favored product, the dull amorphous solid. If it is cooled quickly to well below the melting point, very little of the thermodynamically favored, reflective, polycrystalline material will have a chance to form. That's because the transition state energy for the amorphous solid is appreciably less than that for the polycrystalline solid, so it will form more quickly from the freezing solid than will the polycrystalline form, and at room temperature, the average kinetic energy of the alloy components is far less than what they need in order to overcome the kinetic barrier separating them from the polycrystalline form.

In terms of the marble analogy, marbles in the liquid well can roll over to the dull well much more easily than they can overcome the barrier between the liquid and the reflective well. Once the marbles roll into the dull well and the temperature drops to near 25ºC, very very few of them will be able to overcome the energy barriers that separate them from the polycrystalline solid, and only a scant few of them will do so per unit time (though those are even less likely to come back than they were to make the trip in the first place!).

Even without the given diagrams, it would make sense that the disordered, amorphous form would be obtained if the liquid were cooled quickly, such that its components did not have a chance to arrange themselves into the regular array of the polycrystalline form; and as we learned with diamond, condensed phases can stay in non-thermodynamically favored forms for very long periods of time. Entire chunks of the solid have to change their atomic arrangement, one atom alone can't (re-)crystallize!

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

At 200ºC, the reflective polycrystalline form is still clearly thermodynamically favored, if a little less so than at room temperature. Much more importantly, however, the average kinetic energy of the alloy components, given by the quantity RT, will become substantially larger (T goes from about 300 K to about 475 K, an increase of 58%), vastly increasing the rate at which the amorphous solid crystallizes into the reflective form. This also increases the rate at which the crystalline alloy returns to the amorphous state, but the net flow will favor formation of the reflective form until the vast majority of the alloy is crystalline.

This gentle warming to obtain the thermodynamically favored crystalline form is called annealing, and is used with lots of alloys.

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.)

A negative ΔS value means that the probability of the product is less than that of the reactant…and if you think about whapping down a bit of liquid alloy onto a table, it seems pretty darn clear that you won't end up with a regular, ordered arrangement of the atoms as often as you end up with a random one. Yup, the entropy of the amorphous alloy is appreciably greater than that of the polycrystalline form, and so ΔS for the reaction above is pretty definitively negative. But say you didn't want to trust your intuitive understanding of entropy? Well, looking at the reaction coordinate diagrams above also provides an answer to this question. We can see that the relative free energy of the three phases changes with temperature, and specifically, that the reaction we are interested in, amorphous → polycrystalline, goes from non-spontaneous to spontaneous as the temperature goes up. Knowing that ΔS and ΔH are weak functions of temperature, and that $\Delta G^o = \Delta H - T\Delta S^o$, we expect that ΔG^o is changing sign primarily because T is increasing. Given the change is becoming *more* spontaneous with increasing temperature, ΔS^o for the transformation must be positive so that as T gets larger, the quantity $-T\Delta S^o$ becomes more negative, and so does ΔG^o.

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

As the reaction coordinate diagram clearly indicates, at 25ºC the transition amorphous → polycrystalline is spontaneous. That means that over a long enough time, the amorphous spots on the disc (the zeroes) would transform themselves into polycrystalline regions (into ones), and the data stored on the CD-RW would be lost. No more Emenem or Britney or manuscript for your novel! (How quickly does this actually happen? I don't know…you can bet it's slow. I'm sure the effort to slow this process was part of what led to the use of a funky four-component alloy: four components are harder to organize into a crystal than are three or two.)

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.)*

The easiest and most intuitive way to think about this is in terms of bond energies, so I'll start with that. In choosing to produce CO rather than CO_2, we are choosing to make one C≡O bond, rather than two C=O bonds. But we also get away with breaking ½ less O=O bonds to get the oxygen in the first place. According to Table 8.4, forming a C≡O bond releases 1072 kJ/mol, while forming two C=O bonds releases 2·(799 kJ/mol) = 1598 kJ/mol, a difference of 526 kJ/mol in favor of CO_2. Breaking ½ of an O=O bond requires ½·(495 kJ/mol) = $247._5$ kJ/mol, not enough to make up the difference. Thus, incomplete combustion of a given quantity of C atoms (from any source) releases less heat at constant pressure than does complete combustion of the same material. Since very few of you adopted this approach, I'll also detail a rigorous thermodynamic analysis. Recalling that ΔH is the heat released when a chemical reaction is carried out at constant pressure, we can compare ΔH_{rxn} for comparable chemical reactions, one describing the complete combustion of $CH_{4(g)}$, and the other its incomplete combustion. We'll want them to consume the same quantity of $CH_{4(g)}$, though the latter will clearly require a little less oxygen:

$$\text{Complete combustion: } CH_{4(g)} + 2\,O_{2(g)} \rightarrow CO_{2(g)} + 2\,H_2O_{(\ell)}$$
$$\text{Incomplete combustion: } CH_{4(g)} + {}^{3}\!/_{2}\,O_{2(g)} \rightarrow CO_{(g)} + 2\,H_2O_{(\ell)}$$

While we could compute and compare ΔH^o_{rxn} for each of these (and a lot of you did), a shorter path is to look at the difference of these two reactions, namely $\tfrac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} - CO_{(g)}$, or more properly, $\tfrac{1}{2}O_{2(g)} + CO_{(g)} \rightarrow CO_{2(g)}$. Its ΔH^o_{rxn} is

$$\Delta H^o_{rxn} = \sum_i \chi_i \Delta H^o_f[i] = \left(-\tfrac{1}{2}\cdot\Delta H^o_f[O_{2(g)}]\right) + \left(-1\cdot\Delta H^o_f[CO_{(g)}]\right) + \left(+1\cdot\Delta H^o_f[CO_{2(g)}]\right)$$
$$= \left(-\tfrac{1}{2}\left[0\frac{kJ}{mol}\right]\right) + \left(-1\left[-110.5\frac{kJ}{mol}\right]\right) + \left(+1\cdot\left[-393.5\frac{kJ}{mol}\right]\right) = -283.0\frac{kJ}{mol}$$

Since this reaction has a negative ΔH, and ΔH is a state function, and this reaction is (complete – incomplete), complete combustion must have a more negative ΔH_{rxn} than does incomplete combustion, and thus it releases more heat. (283 kJ/mol more, in fact, which agrees pretty well with what we figured out above based on bond energies!)

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?

First, let me say that this has nothing to do with electronegativity! Electronegative and electropositive elements alike are neutral when isolated, so they don't "call out to each other" through the ether; and very strong bonds can certainly form in molecules composed of atoms of equal electronegativity! N≡N is a great example of this.

Most of you answered this based on ΔH comparisons, which was OK as long as you didn't go to far in your claims about the implications of your result. ΔH in and of itself doesn't decide what's going to happen, especially at high temperatures. The best answer to this question would really involve kinetics, but we really don't have the information needed to discuss that. Given that flames are quite hot, and thus rapidly approach thermodynamic equilibrium, we can get a reasonable explanation from an analysis of relative ΔGº values. As in part A, we could calculate ΔGº for a pair of comparable reactions, but a thought experiment applied to the difference of those two reactions is again the easier way! Let's suppose that we did form $CO_{2(g)}$ and $H_{2(g)}$…would this spontaneously turn into $CO_{(g)}$ and $H_2O_{(g)}$? I asked you to consider this based on $H_2O_{(\ell)}$, which really wasn't very realistic. Using $H_2O_{(g)}$ would make for a much fairer comparison, because at the flame temperatures where the outcome is decided, water will definitely be a gas. (However, that also makes the problem a good deal trickier, as you're about to see.) Let's consider the reaction

$$CO_{2(g)} + H_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)} \qquad \text{which has}$$

$$\Delta H^o_{rxn} = \sum_i \chi_i \Delta H^o_f[i] = \left(-1\cdot\Delta H^o_f[CO_{2(g)}]\right) + \left(-1\cdot\Delta H^o_f[H_{2(g)}]\right) + \left(+1\cdot\Delta H^o_f[CO_{(g)}]\right) + \left(+1\cdot\Delta H^o_f[H_2O_{(g)}]\right)$$
$$= \left(-1\left[-393.5\frac{kJ}{mol}\right]\right) + \left(-1\left[0\frac{kJ}{mol}\right]\right) + \left(+1\cdot\left[-110.5\frac{kJ}{mol}\right]\right) + \left(+1\cdot\left[-242\frac{kJ}{mol}\right]\right) = +41\frac{kJ}{mol}$$

and

$$\Delta S^o_{rxn} = \sum_i \chi_i S^\circ[i] = \left(-1\cdot S^\circ[CO_{2(g)}]\right) + \left(-1\cdot S^\circ[H_{2(g)}]\right) + \left(+1\cdot S^\circ[CO_{(g)}]\right) + \left(+1\cdot S^\circ[H_2O_{(g)}]\right)$$
$$= \left(-1\left[214\frac{J}{mol\cdot K}\right]\right) + \left(-1\left[131\frac{J}{mol\cdot K}\right]\right) + \left(+1\cdot\left[198\frac{J}{mol\cdot K}\right]\right) + \left(+1\cdot\left[189\frac{J}{mol\cdot K}\right]\right) = +42\frac{J}{mol\cdot K}$$

Problem 4B, continued...

At room temperature, this reaction actually is **not** spontaneous:

$$\Delta G^o_{rxn} = \Delta H^o_{rxn} - T\left(\Delta S^o_{rxn}\right) = +41\frac{kJ}{mol}\left(\frac{1000\ J}{kJ}\right) - 300\ K\left(+42\frac{J}{mol\cdot K}\right) = 41000\frac{J}{mol} - 12_{600}\frac{J}{mol} = +28_{400}\frac{J}{mol}$$

But as mentioned above, flames are hot! Air-fed methane flames run in the 1800ºC range, well above the temperature (which I'll call T_{eq}) at which $CO_{(g)} + H_2O_{(g)}$ becomes favored over $CO_{2(g)} + H_{2(g)}$:

$$0 = \Delta G^o_{rxn} = \Delta H^o_{rxn} - T_{eq}\left(\Delta S^o_{rxn}\right) \quad \Rightarrow \quad \Delta H^o_{rxn} = T_{eq}\left(\Delta S^o_{rxn}\right) \quad \Rightarrow \quad T_{eq} = \frac{\Delta H^o_{rxn}}{\Delta S^o_{rxn}} = \frac{+41\frac{kJ}{mol}\left(\frac{1000\ J}{kJ}\right)}{42\frac{J}{mol\cdot K}} = 97_6\ K$$

At temperatures above 980 K, $CO_{(g)} + H_2O_{(g)}$ will be favored over $CO_{2(g)} + H_{2(g)}$, and the scales will only tip more in favor of $CO_{(g)} + H_2O_{(g)}$ as the flame gets hotter. That said, it was surprising to me how close a call it actually turns out to be!

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?

When cold, all cars will emit some CO, because the exhaust gases don't get hot enough to reach equilibrium, even if they contain enough oxygen to turn all of the carbon into carbon dioxide. Even in the presence of a catalyst (which is what a catalytic converter contains), there is an activation energy barrier, and reactions in the exhaust gases will not have time to come to equilibrium in the short time they spend inside a cold catalytic converter. Once the engine and the exhaust system warm up, all reactions will move toward equilibrium far more quickly, catalyzed or not; provided there is excess oxygen present (the engine is running lean), nearly all the CO in the engine exhaust will be converted to CO_2 by the time it exits the catalytic converter. But if the engine is running rich, that means that oxygen is the limiting reagent, and there simply isn't enough oxygen available to put two oxygens onto every carbon atom! Even if the exhaust gas gets all the way to equilibrium, some CO will remain in it.

D. You can learn a heck of a lot of science by staring at candles. When you're desperate, 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?

The main reason is that with the thin candle, fresh air can be rapidly pulled into the flame from below, while with the stubby candle, air is blocked from approaching the flame anywhere but from the sides. In both cases the air is warmed in the flame, and it rises. The stubby candle is pretty hard up for oxygen, so the flame expands outward further, looking for more oxygen to react with. The thin candle, on the other hand, has oxygen constantly flowing into it from below, and the flame doesn't expand outward as far looking for it. Instead, it heats the air around the flame that's not actually involved in the combustion reaction, which rises and increases the upward convection around the skinny candle's flame, making it even taller. Concisely, upwards convection is appreciably more pronounced around the skinny candle, so it is tall and pointed. Convection can't be established as well around the stubby candle flame because the candle itself is in the way, and the flame looks more like one in microgravity.

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?

There are two factors at work here, one more obvious than the other. The first is the change in the color of the material lining the floor of the greenhouse. While the black soil currently in place is a very effective absorber of visible light, the white sand that Akif plans to replace it with is not. The process of visible light being absorbed and effectively converted into infrared light is critical to the greenhouse effect, and the white sand just isn't going to do that nearly as well as the black soil does, leading the temperature inside the greenhouse to drop. The other factor is the makeup of the atmosphere actually inside the greenhouse! While the glass or plastic walls of the greenhouse itself are usually chosen for their ability to absorb infrared radiation, greenhouse gases, like CO_2 and H_2O, present in the air inside the greenhouse, also help. Cacti are bizarre in that most of them take in the CO_2 they need for photosynthesis at night (an adaptation to limit their water loss via their stoma during the day) and they release very

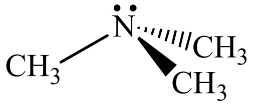
Problem 4E solution, continued...

little water into the air around them during the day. This means that CO_2 is removed from the greenhouse air when it is most needed to keep the greenhouse warm (at night), and that the concentration of water vapor inside the greenhouse air is also much lower. Thus the greenhouse is less effective at keeping infrared radiation trapped inside it (esp. at night), and it will be cooler.

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.



There are two critical mistakes made by our supposed "expert" on the witness stand. The first is the rather bold claim that trimethylamine is a symmetric molecule, and thus invisible to infrared spectroscopy. Lots of highly symmetric molecules, such as CH_4 and CO_2, have asymmetric vibrational modes that make them *very* visible to infrared spectroscopy, and since trimethylamine is composed of three atoms of differing electronegativity, the same would most likely be true for it. Even if that weren't true, trimethylamine isn't really very symmetric, either! Doing a Lewis structure analysis on it and applying VSEPR, we find that the nitrogen has a lone pair, and a steric number of four. As a result, the molecule itself has an appreciable dipole moment, and there's no way in heck that it won't light up like a Christmas tree for an infrared spectrometer. Ok, suppose we didn't catch that, or our fellow jurors didn't understand it…well, the other issue you could and should raise with them would be one of significant figures. If we thought our scientist was competent, then his figure of 200 mg/ℓ actually means 200 ± 100 mg/ℓ, or anything between 100 and 300 mg/ℓ. Similarly, his 300 mg/ℓ figure is actually anything between 200 and 400 mg/ℓ. So the envelope might in fact have only 200 mg/ℓ trimethylamine on it, which would be entirely compatible with the envelope having been licked by an individual who does not suffer from trimethylaminuria, and the case against Mr. Daago evaporates. He certainly isn't guilty beyond a reasonable doubt!

Note: Some of you took umbrage at the idea that mass spectroscopy could be used to unambiguously identify and quantify a specific chemical. It may not always be the *best* tool for such a job, but quantitative GCMS is routinely relied upon in criminal cases, particularly with drugs, and it could certainly provide a concentration estimate with one significant figure, like that cited by our expert. The *pattern* of fragments appearing the mass spectrometer would be pretty hard to confuse with other molecules, and certainly with likely problem-children like amino acids and the nitrogen and carbon in the air. Recall that bonds are broken, but new ones do not have a chance to form, when accelerated electrons ionize molecules in a mass spectrometer!

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!)

A. 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.)

Bert's thinking thermodynamics, while Ernie is thinking kinetics! Ernie is correct to some extent, in that the rate of any chemical change will drop with temperature. Since he and Bert are waiting for a chemical change to take place, a decreasing temperature will make it occur more slowly than it would otherwise. Put another way, the rate at which Ag^+ and Cl^- ions are combining to form solid AgCl *will* go down as the temperature drops. Bert's even "more right," though, because at this high temperature, not only is the rate at which Ag^+ and Cl^- ions combine to form solid AgCl quite high, so is the rate at which solid AgCl dissolves to form Ag^+ and Cl^- ions! Before you arrived on the scene, solid AgCl was dissolving just as quickly as it formed (and it could have dissolved even faster than that), and the system wasn't at equilibrium. Bert's thinking is that as the temperature drops, the solubility of AgCl will drop to the point that the solid doesn't dissolve as quickly as it forms, and some solid AgCl will build up. That's a good guess, because the solubility of most solids in water does drop with temperature. But that's not true of *all* solids, so we had better check! How do we do that? Well, we want to know if $K_{eq} = [Ag^+][Cl^-]\ M^{-2}$ will decrease as the temperature drops:

$$Q_\alpha = \frac{\alpha_{Ag^+_{(aq)}}\alpha_{Cl^-_{(aq)}}}{\alpha_{AgCl_{(s)}}} = \frac{\left(\frac{[Ag^+]}{M}\right)\left(\frac{[Cl^-]}{M}\right)}{1} = [Ag^+][Cl^-]\ M^{-2} \underset{\text{at equilibrium}}{=} K_{eq} = e^{\left(\frac{-\Delta G^\circ}{RT}\right)} = e^{\left(\frac{\Delta H+T\Delta S}{RT}\right)} = e^{\left(\frac{-\Delta H}{RT}+\frac{T\Delta S}{RT}\right)} = e^{\left(\frac{-\Delta H}{RT}\right)}e^{\left(\frac{\Delta S}{R}\right)}$$

The second term in the final expression above does not change appreciably with temperature, but the first one does. It will lead to a smaller K_{eq} value at lower temperatures if and only if ΔH is positive. This is just what Le Châtelier's principle would lead us to expect: if the reaction is endothermic, cooling it off will make it less favorable. Is $AgCl_{(s)} \rightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$ endothermic?

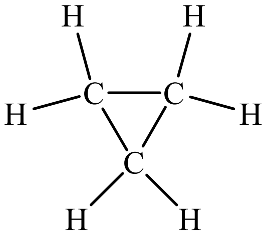
$$\Delta H^o_{rxn} = \sum_i \chi_i \Delta H^o_f[i] = \left(-1\cdot\Delta H^o_f[AgCl_{(s)}]\right) + \left(+1\cdot\Delta H^o_f[Ag^+_{(aq)}]\right) + \left(+1\cdot\Delta H^o_f[Cl^-_{(aq)}]\right)$$

$$= \left(-1\left[-127\frac{kJ}{mol}\right]\right) + \left(+1\left[+105\frac{kJ}{mol}\right]\right) + \left(+1\cdot\left[-167\frac{kJ}{mol}\right]\right) = +65\frac{kJ}{mol}$$

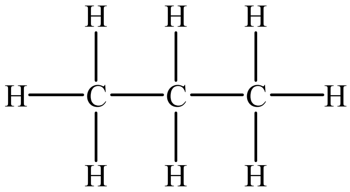
Yup, guess it is. So Bert's correct in asserting that the solubility of AgCl will drop as the temperature does.

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

This was all about the NaCl coating, actually. Platinum is a common catalyst, but it's unlikely to catalyze the precipitation of AgCl. Pt may well bind Cl, but there's no bond that needs to break before solid AgCl can form, so it doesn't help lower an activation energy barrier. Even if it did, the solid AgCl whose formation it helped catalyze would form on the surface of the platinum cubes, and inhibit further catalysis. The addition of a catalyst also wouldn't shift the equilibrium position in any way, so only to the extent that Ernie's claim was relevant, and to the extent that the water cooled down to the point where AgCl would want to precipitate out, could a catalyst have any impact whatsoever. On the other hand, the NaCl coating on the cubes was very soluble, and when it dissolved it released Cl^- ions into the solution, increasing $[Cl^-]$. If that caused the product ($[Ag^+][Cl^-]\ M^2$) to exceed K_{eq}, (which is very likely, because AgCl is not very soluble: see Table 15.4) then solid AgCl would immediately start precipitating out of the solution. What's more, the dissolution of NaCl is slightly endothermic (ΔH_{rxn} = +3 kJ/mol), so its dissolution would also help to cool off the tub to the point where the AgCl solubility dropped below the amount present in the tub.



C. 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.



The three carbon-carbon bond angles in C_3H_6 have to add up to 180º; there's no way around it. If they all suffer equally, and form an equilateral triangle, the C–C–C bond angles will all be 60º. That's far less than the carbon atoms' steric number of four suggests they want! They'd like to have all of their electron pairs separated by the ideal tetrahedral angle of 109.5º, so, forced to adopt a 60º angle they would experience a lot of what we old hacks refer to as "angle strain," or in this particular context, "ring strain." Even though I've drawn 90º bond angles in C_3H_8, those atoms and bonds are free to twist about into a zigzag, so that every bond angle is the ideal 109.5º, and there's no angle strain to contend with at all. Cyclic C_3H_6 does actually exist, but it has a great tendency to pop open, and it isn't very stable. It's a lot harder to make than $H_2C{=}CH{-}CH_3$, which doesn't suffer any angle strain.

D. 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?

While the system remains at equilibrium the whole time, and the concentration of Ag^+ and I^- ions in solution remains constant, equilibrium is not the same as stasis! Solid AgI is constantly dissolving to release Ag^+ and I^- ions, and Ag^+ and I^- ions are constantly combining to form solid AgI. By adding a large amount of solid AgI containing non-radioactive iodine, the rate at which radioactive I^- ions become part of some solid AgI remains about the same, but the vast majority of the I^- ions that dissolve to replace them are not radioactive. Since solubility is almost blind to isotopic influences, over time the radioactive iodine ions will randomly distribute themselves between the solid and solution phases. If they make up 5% of the total I atoms in the beaker, they will make up 5% of the I^- ions in solution and 5% of the I in the solid AgI. So as long as the amount of non-radioactive I added by Doctor Bob was appreciably more than the amount of radioactive I initially present, the concentration of radioactive I^- floating about in solution will go down markedly as the radioactive iodine is incorporated into the solid AgI and replaced by non-radioactive iodine in the solution phase.

E. 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:

Let's start by writing out and balancing the reaction we are considering here: $2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(\ell)}$
The theoretical answer to this question assumes that nothing leaks out of the balloon. In that case, balloon 3 can allow one mole of reaction to take place, whereas balloon 2 can only provide enough hydrogen for ½ mole of reaction, and balloons 1 and 4 are missing one reactant and will not release any heat at all. Theoretically, balloon 3 will definitely release the most heat into the room, though it will certainly take its sweet time! Pragmatically, as we discussed in class, H_2 is a very small molecule, and it will leak out of the balloon pretty quickly. If that H_2 reacts to form H_2O before it leaves the room, then balloon 4 would release the most heat, because it contains the most fuel, just as when we put a flame to it. If the H_2 that leaks out generally escapes from the room before it has a chance to react, then all bets are off and you could get away with saying that none of them would release much heat; or, alternately, that balloon 2, which would do the best job of keeping some H_2 in contact with O_2 for an extended period of time, would release the largest amount of heat, though it would most likely be miniscule. Note: Because O_2 is a relatively bulky molecule, it isn't going to diffuse through the balloon's polymeric skin nearly as quickly as does H_2.