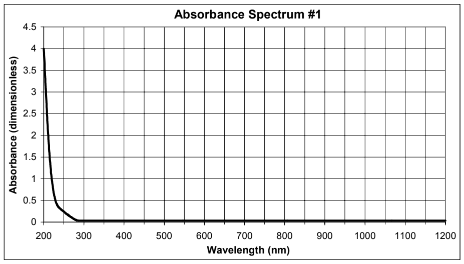
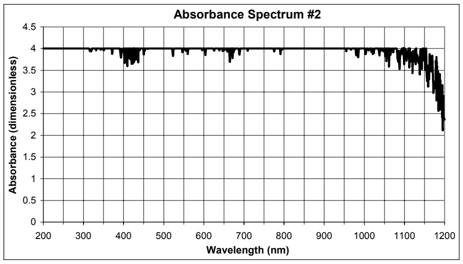
Problem 1: Properties of Atoms, Intermolecular Forces, and Condensed Phases

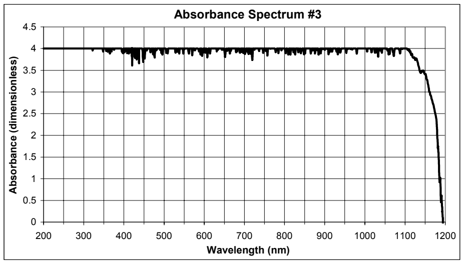
A. Shown below are the UV/Vis spectra of three familiar solids, as if taken with our lab spectrophotometers:



Diamond



Alumin(i)um

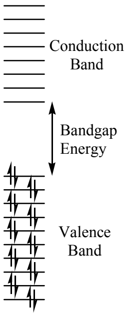


Silicon

Match up these spectra with the correct solid, given that each corresponds to a different one of the following:

- Diamond (a network solid insulator with a 5.5 eV bandbap)
- Silicon (a network solid semiconductor with a 1.1 eV bandgap)
- Alumin(i)um (a metal)

You need not explain your work, but if you do you can garner partial credit. The information in parentheses can be quantitatively helpful, but isn't truly needed in arriving at the correct answer to this question.



You can determine which spectrum belongs to which solid without doing any math, but a little math sure helps confirm things! Recall that the bandgap of a solid indicates the separation between the top of the highest-energy full (valence) band and the bottom of the lowest-energy empty (conduction) band, as shown in the little diagram at right. At low temperatures, a solid can absorb essentially all photons with energies larger than that of the bandgap, but effectively none with energies smaller than the bandgap. So in the case of diamond, that means that all photons with energies greater than 5.5 eV can be absorbed, while photons with lower energies can pass right through a diamond. Let's figure out what kind of radiation a 5.5 eV photon corresponds to, shall we? We know that $E_{\text{photon}} = hc/\lambda$, and the equation page even gives us h and c in handy units, so let's determine λ for a 5.5 eV photon:

$$E_{\text{photon}} = \frac{hc}{\lambda} \quad \Rightarrow \quad \lambda = \frac{hc}{E_{\text{photon}}} = \frac{\left(4.136\times10^{-15}\,\text{eV}\cdot\text{s}\right)\left(2.998\times10^{8}\,\text{m}\cdot\text{s}^{-1}\right)}{5.5\ \text{eV}} = 2.2_{545}\times10^{-7}\left(\frac{10^{9}\ \text{nm}}{\underline{1}\ \text{m}}\right) = 22_{5}\ \text{nm}$$

Consulting the complete electromagnetic spectrum in Figure 7.2, we see this falls into the ultraviolet portion of the spectrum. Thus a diamond absorbs UV light, but allows visible light to pass through it: as a result it appears clear to the human eye. Of the three absorbance spectra above, two absorb visible light very strongly while the last has an absorbance near zero throughout the visible spectrum. It's the latter, spectrum #1, that corresponds to the diamond. In fact, whaddayaknow…the absorbance rises sharply right around 225 nm. We can carry out essentially the same calculation for silicon, which has a much smaller bandgap of 1.1 eV:

$$\lambda = \frac{hc}{E_{\text{photon}}} = \frac{\left(4.136\times10^{-15}\,\text{eV}\cdot\text{s}\right)\left(2.998\times10^{8}\,\text{m}\cdot\text{s}^{-1}\right)}{1.1\ \text{eV}} = 1.1_{27}\times10^{-6}\left(\frac{10^{9}\ \text{nm}}{\underline{1}\ \text{m}}\right) = 11_{27}\ \text{nm}$$

So silicon can absorb photons with energies greater than 1.1 eV, and thus wavelengths shorter than 11_{27} nm. 11_{27} nm falls into the infrared portion of the electromagnetic spectrum, so silicon can absorb essentially all colors of visible light, and we expect it to appear dark, if not black, to our eyes. It might (does, actually) appear shiny, because the photons it absorbs might be very quickly re-emitted rather than converted into other forms of energy. The absorption spectrum of silicon is the one on the right, #3, because the material in that spectrum is absorbing (or scattering) all the photons hitting it except those with the longest wavelengths; in fact, the break between absorbing and transmitting occurs right around 1100 nm. That leaves the center spectrum, #2, and alumin(i)um. Aluminum is a metal, and metals have no energy range devoid of allowed states between the filled and empty states. As a result, they can absorb (or most often, scatter, which means absorb and then quickly re-emit) essentially any kind of photon. Keeping in mind that our spectrophotometers shoot photons through the sample toward a detector, and that if those photons never make it they are considered to have been absorbed, we expect a mirror-like object (like a shiny metal) to show complete absorbance of all wavelengths. That's what we see in the center spectrum, with a slight caveat: the absorbance drops slightly as we move into the infrared portion of the spectrum. This is not actually because aluminum can not absorb these photons. I blanked the spectrometer on air, and then measured the aluminum. The aluminum absorbed (actually reflected, for the most part) all the photons coming out of the light source; but it also *emitted* photons into the detector. What we are seeing in the infrared portion of spectrum #2 is the blackbody emission of the aluminum! I blanked the spectrometer on air, which emits blackbody radiation, but not much because it contains relatively little matter per unit volume. When I put the aluminum in there, it being at about 300K, it emitted blackbody radiation, most strongly in the infrared portion of the spectrum. It being dense, containing a lot of matter per unit volume, it emitted more blackbody radiation than was blanked out by the spectrometer when it was looking at air. So we see the edge of the blackbody emission spectrum of the aluminum as a slight drop in absorbance in the infrared. We would see the same thing for any opaque condensed phase at 300 K that was placed in the beam path of the spectrometer.

Note: In order to save paper, the pagination of the key does not match that of the exam.

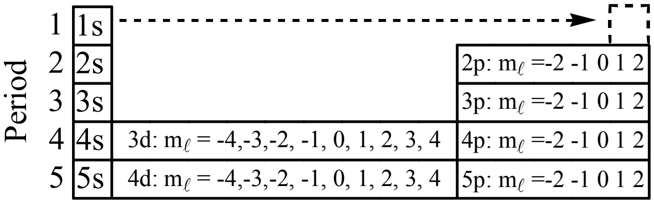
B. One Monday morning you wake up feeling a little strange, but can not figure out why. Sitting in class, you suddenly realize that while some things are vaguely familiar, certain key rules governing the properties of matter have changed! Somehow you are in a parallel universe! Looking at the periodic table, it looks very different. In this universe there are different rules governing the allowed values for quantum numbers:

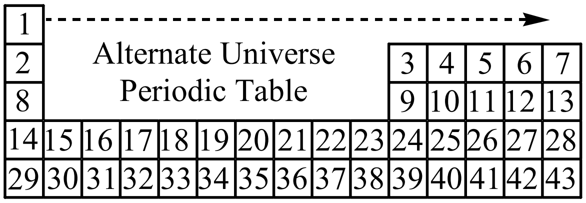
- The principal and angular momentum quantum numbers (n and ℓ) follow the same rules as in our universe.
- The magnetic quantum number m_ℓ now ranges from -2ℓ to $+2\ell$; there's more degeneracy for each $n\ell$ orbital.
- The only allowed value for m_s is 0;electrons no longer have spin, so each orbital can only hold one electron!
- However, electrons still fill atomic orbitals in the order same order as they do in our universe.

The periodic table in this alternate universe has only one element in the first row, the first ideal gas. The second row is also short, consisting of only six elements; it contains the second noble gas, which has an atomic number of 7. The novel periodic table reflects the modified electronic configurations that electrons in atoms are allowed to have in this universe. Please answer the following questions:

a. Prepare a sketch of the **first 5 rows** of this universe's periodic table, akin to ours as shown in Figure 7.26 on p. 323 of Zumdahl. (You don't need to come up with new "Group" labels, but do label everything else.) Briefly explain your logic if you want to be eligible for partial credit, but don't go into great detail.

This should have been a cakewalk if you worked through the sample exam. This wasn't *exactly* the same scenario, but it was darn close. The difference was that here m_ℓ is allowed to take on a value of zero, and so the p orbitals consist of five possibilities, $m_\ell = -2, -1, 0, 1,$ and 2. (Recall that "p" indicates that $\ell = 1$, and we know that m_ℓ can range from -2ℓ to $+2\ell$ in this universe.) Thus the p block of the periodic table is 5 elements wide, and by similar logic, the d block is nine elements wide. The resulting periodic table is shown above. You didn't have to include the m_ℓ values, I just put them in there to help you understand where things came from. Note that there in this universe there is even more ambiguity about where to put element 1 than there is in ours about where to put elements 1 and 2 in our periodic table: but that's not the point of this question. The numbered version of the periodic table would look like that at right; I've included it here because it helps in the explanation of part (b).





b. Explain why, in this universe, element 28 might have about the same atomic radius as does element 9.

As we can see in the numbered periodic table above, element 28 comes at the end of the fourth row, while element 9 comes rather early in the third row. We might consider these elements roughly analogous to our Kr and P…and what do you know, Figure 7.35 does indeed indicate that those two atoms have about the same radius, though it doesn't explain why. That's our job! Well, there are basically two counteracting forces determining how far from the nucleus the valence electrons of an atom spend the bulk of their time. The first is the nuclear charge: for electrons in a *given* orbital, say the 3p orbital, the greater the positive charge in the nucleus the more tightly they are pulled in toward the nucleus and the smaller the atomic radius. Thus the atomic radius would be expected to decrease in this universe as we go across period 3 from element 9 to element 13. The other factor is the difference in the basic size of orbitals as a function of principal quantum number. For a given effective nuclear charge, the radius of a 4p orbital is appreciably larger than that of a 3p orbital, which is in turn appreciably larger than a 2p. So we would expect a general increase in atomic radius as we go down a column of the periodic table, and thus an increase in radius if we drop from element 13 down to element 28, just below it. This increase in radius could readily offset the increase caused by moving across the period above, and so we can reasonably rationalize elements 9 and 28 having similar radii.

C. This term we compared the atomic emission spectrum of low-pressure hydrogen gas against that of low-pressure deuterium gas (deuterium is a heavier isotope of hydrogen, with a neutron in the nucleus), and found them to be exactly the same. Why do H and D have identical electronic emission spectra?

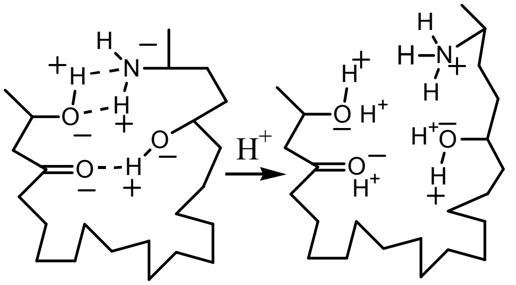
They are both one-electron atoms with one proton in their nuclei. Thus their electronic structure is well-described by the Bohr model, with Z = 1. The Bohr model doesn't care how many neutrons are in the nucleus, it specifies that the electronic structure of an atom depends only on Z and *n*. There's an even better answer, and that is that the electronic structure of any isotopes of the same element will be identical. The mass of a nucleus depends on the number of neutrons that it contains, but gravity isn't what keeps the electrons "in orbit" around the nucleus: in fact, gravitational forces between nuclear particles are infinitesimally weak compared with electrostatic forces. So while the number of protons in the nucleus and the number and quantum state of the electrons in an atom all have a significant impact on that atom's electronic structure, neutrons are moot.

D. Explain in detail why the Bohr model can not be used to predict the electronic structure of the Li^+ ion.

Li^+ is a two-electron ion. Li itself has an atomic number of three, and thus normally has three electrons. Take one of those away to make a +1 ion, and you're left with two. Two is one too many for the Bohr model: it only works on one-electron atoms! Why's that, you ask? Well, the Bohr model doesn't take into account the effects of *screening*: it assumes any electron in any orbital sees the same positive charge, namely the whole of the nuclear charge. Although the two electrons in Li^+ are both in the 1s orbital, and barely screen each other, they do screen electrons in the orbitals with higher *n* values: and it is the energy of precisely those orbitals that we need to calculate in order to arrive at "electronic structure" of the Li^+ ion. A side note: while the two electrons in the 1s orbital of the Li^+ atom don't screen each other very much, they **do** do so a little bit. Some of the time one of the electrons in the 1s orbital will be between the nucleus and the other electron: remember that *orbitals are not orbits*! To the extent that happens, both electrons in the Li^+ 1s orbital see less nuclear charge than does the one electron in a Li^{2+} ion, and their energy is slightly higher (less negative) than that of the single 1s electron in the one-electron Li^{2+} ion.

E. Proteins are long molecular chains essential to life here on earth. A large part of their utility stems from their ability to "fold" into pre-programmed shapes as a result of their chemical composition: they hydrogen bond to themselves, and work to maximize other forms of intermolecular attraction, by twisting back on themselves to touch themselves in as many appropriate places as possible. (Get your mind out of the gutter!) All proteins undergo a process called "denaturation" when they are heated: they unfold from their natural, programmed shape into a random, floppy chain. (This is what happens when you cook a protein.) It turns out that you can accomplish denaturation in many other ways as well, including adding them to water containing a lot of acid, base, or surfactant. Choose any one of these four means of denaturation and explain how it acts to break up the intermolecular forces (especially the strong ones) and thereby "unfold" a protein.

Proteins are programmed to fold a certain way when in a given environment by the strategic placement of amino acids along their length, some of which are polar and some of which are non-polar. In an aqueous environment, the nonpolar amino acids tend to associate with each other, while the polar ones happily associate with water molecules – just like the ends of a micelle-formed from surfactant, but with all the bits of the micelle composing parts of the *same* molecule! Certain folded shapes are stabilized over others, and the folded protein really cemented together, by the formation of strong hydrogen bonds between pairs of amino acids capable of hydrogen bonding having complementary structures that "fit together nicely." At any rate, the bottom line is that you have a bunch of intermolecular forces holding a folded protein in its proper shape. Anything that significantly disrupts those intermolecular forces will denature the protein. So let's start with heating – that is, increasing the temperature of – a protein as a means of denaturing it. We have learned that increased temperature means increased random atomic motion: so imagine a protein stuck to itself, with a few loose strands here and there. As you heat the protein, it starts to wiggle and vibrate, and the loose ends start to flop around. As the temperature rises further the atoms that are held together by the weakest forces, the London dispersion forces, will be wiggling around so much that their kinetic energy exceeds the binding energy available and they are no longer stuck together. (We've reached the melting point of, say, hexane, but the protein hasn't yet unfolded because it is held together by stronger forces). As the temperature rises further still, the random breaking of hydrogen bonds, rare at lower temperatures, becomes more frequent because more and more often a given pair of atoms randomly end up with enough energy directed in the right directions to pull the hydrogen bond apart. When these bonds re-form less frequently than they break, the structure of the protein begins to unravel and it unfolds into a randomly oriented chain. Basically, heat can unfold a protein by causing the atoms in it to wiggle with such vigor that the weak intermolecular forces are no longer able to keep them in place – it's the same driving force that causes heating to melt a molecular solid. In contrast, the other three methods all work by replacing intermolecular forces between two separate parts of the protein with intermolecular forces between parts of the protein and other molecules, which are free to move independently. The diagram at right is a rather simplistic and exaggerated picture of what happens to a protein in the presence of a lot of acid, but I think it makes the point. Hydrogen bonds between parts of the folded protein are replaced with hydrogen bonds between H^+ and those same parts (the acid actually protonates the NH_2 group, in this picture). The protons (H^+) allow polar, hydrogen-bonding parts of the protein to move away from other similar parts without giving up hydrogen bonding, thereby weakening the motivation for the protein to stay folded up. Adding a surfactant is even more effective: in addition to covering up the polar, hydrogen-bonding parts of the protein with non-polar groups, they coat the nonpolar parts of the protein and make them happy to play with water. The net effect can often be described as turning the protein "inside out" and greatly reducing, if not blocking, the protein's ability to hydrogen bond to itself and hold any given shape for an extended period of time.



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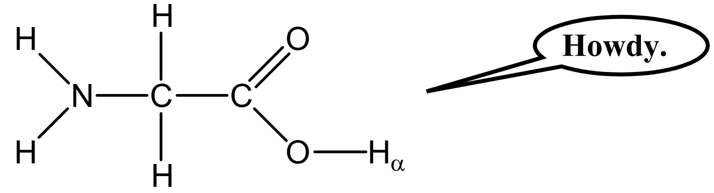
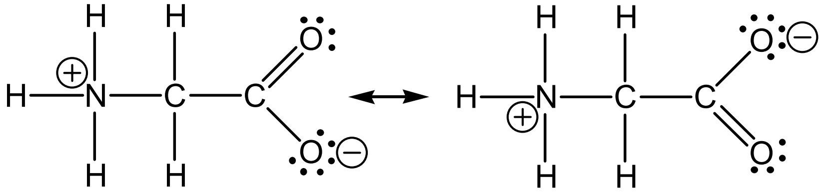
Problem 2: Properties of Molecules

A. Amino acids are the "links" that make up molecular chains called proteins, essential to life here on earth. There are lots of different amino acids, but they each have a good deal in common, and we can learn a lot about them by getting to know the simplest amino acid of them all, glycine. Hey glycine, c'mon out here!



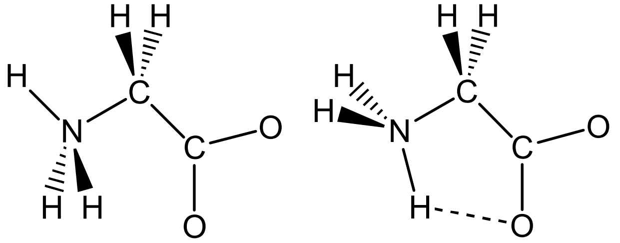
a) Amino acids are actually ***amphoteric***, which means that they can act as both acids and bases. In fact, under typical biological conditions, the H_α proton on glycine (and most amino acids) moves to the N atom, leaving its home on the O atom. The resulting molecular ion has both a positive and a negative end, and is called a "***zwitterion***." Draw the complete Lewis structure of the resulting $(H_3N)(CH_2)(CO_2)$ zwitterion.



Don't forget resonance!

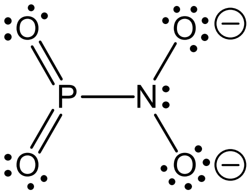
b) Clearly draw the three-dimensional shape of the glycine zwitterion, as predicted by VSEPR.

The steric numbers of the central atoms N, C, and C are, from left to right, 4, 4, and 3. Drawing as many of the atoms as we can in the plane of the page, we get a VSEPR structure for the zwitterion that looks like the one immediately at right. The N and the central C are tetrahedral centers, while the C on the end is trigonal planar. Actually, in order to hydrogen bond with itself, the zwitterion might adopt the shape at far right…or not. Water can probably hydrogen bond better to both parts of the zwitterion than the zwitterion can hydrogen bond to itself – which is why water encourages the formation of the zwitterion. But this is very likely a transition state for the proton transfer from the N to the O atom!

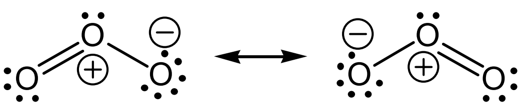


B. Draw the complete Lewis structure of the $[O_2P–NO_2]^{2-}$ molecular ion, which contains no O–O bonds. (The shorthand used here indicates that P is bonded to N, but not necessarily by a single bond.)

I apologize to any of you whom I led into temptation with this, but it was the best way to really test your understanding of Lewis structures and resonance. The best Lewis structure for this little monster is the single structure at right. Yep, no resonance. To get resonance you have to add a substantial amount of formal charge, make nitrogen hypervalent, or move atoms around between putative "resonance structures." None of those are good choices. Recall that nitrogen is not allowed to be hypervalent, realize that oxygen is the most electronegative element of this bunch, and note that the nitrogen atom in this structure is a tetrahedral center: it can't resonate with structures in which it's a trigonal planar center.

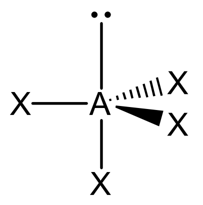


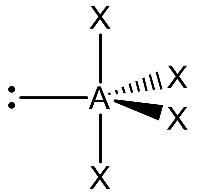
C. Based on Lewis structures and VSEPR, would you expect ozone (O_3) to be IR active, in other words, a greenhouse gas? Back up your answer with Lewis structures and a careful explanation of your logic.



We actually talked about this in class, and the Lewis structure of ozone is in your book, but I decided the key concepts were worth re-hashing. Ozone is a resonant, bent molecule with a formal +1 charge on the central oxygen atom and an effective -½ formal charge on the each of the end oxygen atoms. As a result, it has a positively charged end (the "top," in my diagram at right) and a negatively charged end (the "bottom" in my picture at right), even though it is made up entirely of oxygen atoms. That gives it a net molecular dipole moment, and what's more that dipole moment changes when the molecule vibrates in just about any vibrational mode. As a result, ozone is able to interact with infrared radiation in undergoing vibrational state transitions, and it's a powerful greenhouse gas. (One ozone molecule has the same greenhouse warming power as 2000 CO_2 molecules, in fact!)

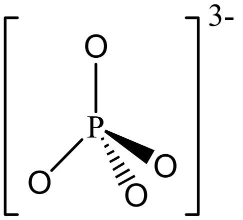
D. Why is the molecular structure shown at right never observed in nature? Explain fully.

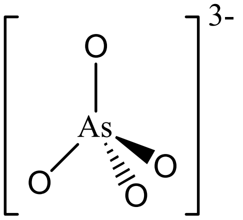




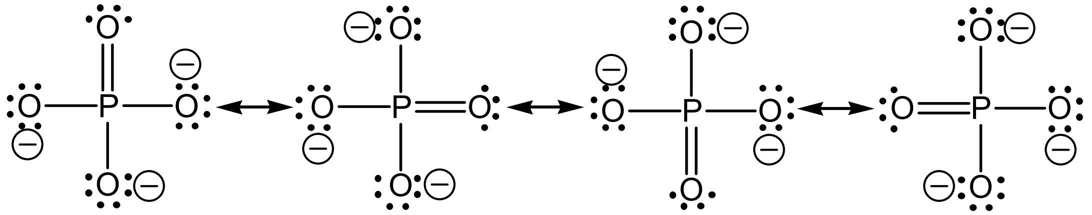
In order to answer this question, we have to consider the options available to a molecule with this sort of Lewis structure. There are two "types" of positions in a trigonal bipyramidal VSEPR structure: axial and equatorial positions, two of the former and three of the latter. The molecule at right has the lone pair in one of the axial positions. Moving it to the other axial position yields the exact same thing, but moving it to any one of the three equivalent equatorial positions yields the other distinct possibility, which is shown below, at right. So we want to size up the relative merits of these two possibilities and decide which is better. Recalling that lone pairs are "fat" and desire more elbow more room than do bonding pairs, we focus on the relative comfort or discomfort of our friend the lone pair in these two structures. In the putative structure up top, the lone pair is involved in three 90º interactions with bonded atoms. In the lower structure, the lone pair experiences two 90º interactions with bonded atoms, and two 120º interactions with the same. Here we have to recall that there's only so much elbow room a lone pair cares about, and that once you get out to a 120º separation, a lone pair no longer cares who's sitting there, or if anyone is sitting there at all. So the two 120º interactions are moot, and it becomes a simple matter of choosing between two and three 90º interactions. The lone pair has no trouble whatsoever in doing that sort of math, and quickly finds itself an equatorial position to sit in.

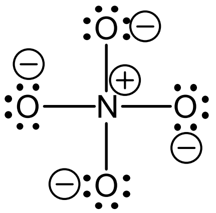
E. Shown at right are the VSEPR-predicted shapes of the phosphate (PO_4^{3-}) and arsenate (AsO_4^{3-}) ions, which are important constituents in many rocks and minerals. The equivalent nitrogen-centered ion, NO_4^{3-}, is so unstable that it is not found in nature. Explain why, basing your justification on the Lewis structures of these ions. (Note that this does *not* mean you have to draw out all the Lewis structures for all of these ions!)





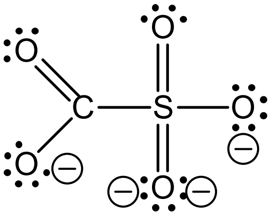
The best Lewis structures for the phosphate and arsenate ions are highly resonant beasties that reduce formal charge by invoking hypervalency, as in this set of four nifty resonance structures:



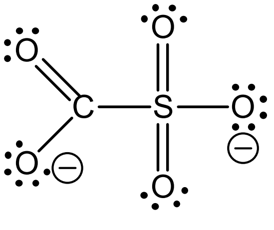


While nitrogen *is* capable of forming a Lewis structure with the appropriate geometry, nitrogen can't be hypervalent, and that hurts. The NO_4^{3-} ion has only one workable structure, the one at left, and this structure has a whopping-big formal charge count. So what makes it appreciably less stable? According to our bonding rules, let us count the ways! First and most damaging, it has more total formal charge than do the phosphate and arsenate ions. Second, it has less bonding. Third, it can not resonate. As a result, a consideration of Lewis structures would lead us to expect orthonitrate (the fancy name for the NO_4^{3-} ion) to be appreciably less stable than its P and As analogs, and indeed so it is. NO_4^{3-} salts have been synthesized in research labs, but they are very reactive, and unstable in the presence of moisture and carbon dioxide.

F. Shown below are three valid and three invalid resonance structures for the $[O_2C–SO_3]^{2-}$ molecular ion. Rank the valid resonance structures from best to worst, explaining your rationale. Cross out the three structures that can't possibly be resonance contributors, briefly stating what makes each of them completely ineligible.



Crud crud crud (crud)^{1000}. I drew too many dots on one of the structures for this problem, and it messed everything up. A few of you missed it just like I did, a few caught it but found three good structures anyway (ooops), and one of you even crossed out four structures and kept two! (Yet nobody asked me about this question…alas!) My policy for dealing with my mistake was to give you 6 extra points if you caught my error, 3 to make up for points this error likely led you to lose elsewhere in this problem and 3 to make up for the likely collateral damage to the rest of your exam caused by frustration and time spent on this problem. The erroneous structure is shown at right; the specific problem is the doubly bonded oxygen with three lone pairs. As drawn, it has a formal charge of -2, and is hypervalent to boot. That makes this structure completely unworkable – it has too many electrons to be $[O_2C–SO_3]^{2-}$ and violates a cardinal rule. I actually wanted this option to look like the structure at right, with nothing funky about that oxygen. I've written up the answer on the subsequent page based on this corrected structure. If you caught my boo-boo, chances are you rationalized one of the other illegitimate structures into plausibility, and you lost points for that. But the extra points you got for catching the problem with the incorrect structure should (more than) make up for those lost points – I hope this is a fair remedy for my error.



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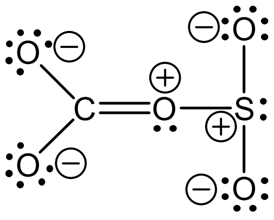
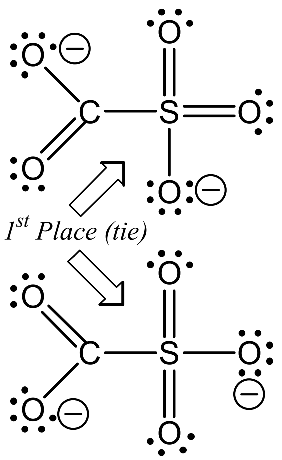
Answer continued from previous page: see note there about an error in one of the structures and how it was dealt with.



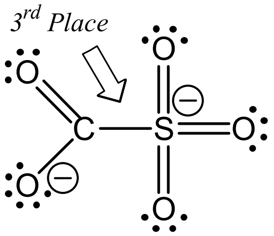
True, this structure has a formal positive charge on a centrally located electronegative oxygen atom. But what really knocks it out is that it can't resonate with any of the other possibilities - it has its atoms located in different positions, and atoms can not move between resonance structures! Thus it is **completely invalid.**

In three dimensions, these two structures are geometrically equivalent. With minimum formal charge, the negative formal charge all on the most electronegative element (oxygen) with well-separated charges to boot, and plenty-o-bonding, these two structures are in an easy two-way tie for the best resonance contributors shown.

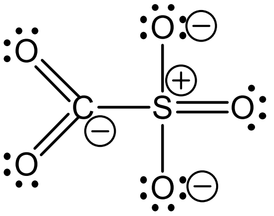


1st Place (tie)

3rd Place

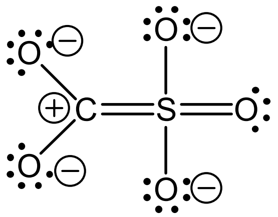


This isn't a pretty structure, because there is a negative formal charge on the less-electronegative sulfur atom. But it does have a lot of bonding, and the correct number of electrons, and doesn't break any natural laws. That makes it the second (third) best resonance contributor of those shown here.



This structure contains hypervalent carbon, and is **completely invalid**. (Its formal charge is also excessive and distributed poorly: groady to the max.)

Once you figure out the formal charges, it becomes clear this structure is actually $[O_2C\text{-}SO_3]^{4-}$; it has too many electrons to be the structure we are working on, and is thus **completely invalid**.



Problem 3: Kinetics and Equilibria

A. Silver chloride (AgCl) is a pretty darn insoluble solid: it has a K_{sp} of 1.5×10^{-16} M^2 at 25ºC. It does dissolve a little, though, via the reaction $AgCl_{(s)} \rightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$. Suppose you have a huge tank containing 1000. liters of pure water, in a room at 25ºC, and you add 12.04 milligrams of solid silver chloride to it.

a) How much solid silver chloride will be left at the bottom of the tank once equilibrium is attained?

Equilibrium will be attained when (and if) the equilibrium condition $K_{sp} = [Ag^+][Cl^-]$ is satisfied. Since in this case the dissolution of solid AgCl is the only source of Ag^+ and Cl^- ions in the solution, we can define a handy variable, say, x:

x ≡ moles per liter of AgCl that can dissolve at equilibrium = $[Ag^+]$ at equilibrium = $[Cl^-]$ at equilibrium

We then know that $K_{sp} = 1.5 \times 10^{-16}\ M^2 = \left[Ag^+\right]\left[Cl^-\right] = x \cdot x = x^2$, and thus that $x = \sqrt{1.5 \times 10^{-16}\ M^2} = 12.{}_{247} \times 10^{-9}$ M. So once $12._{25}$ nanomoles of AgCl per liter of solution dissolve, bang, that's it. That's all that will dissolve. How much is that in terms of mass? That's not so tough to figure out: $\tilde{m}_{AgCl} = \tilde{m}_{Ag} + \tilde{m}_{Cl} = 107.9\,\frac{g}{mol} + 35.45\,\frac{g}{mol} = 143.3_5\,\frac{g}{mol}$

$$\Rightarrow \quad 12.{}_{247} \times 10^{-9}\ \frac{\text{mol AgCl}}{\ell \text{ of solution}} \left(\frac{143.3_5 \text{ g AgCl}}{\underline{1} \text{ mol AgCl}} \right) = \frac{1.7_{556} \times 10^{-6} \text{ g AgCl}}{\ell \text{ of solution}} \left(\frac{10^6\ \mu g}{\underline{1}\ g} \right) = \frac{1.7_{556}\ \mu\text{g AgCl}}{\ell \text{ of solution}}$$

Since we have 1000 ℓ of solution in this ExtraValueMeal-Sized tank, we should be able to dissolve

$$\frac{1.7_{556}\ \mu\text{g AgCl}}{\ell \text{ of solution}} \left(\frac{1000.\,\ell \text{ of solution}}{\text{the tank}} \right) \left(\frac{10^3 \text{ mg}}{10^6\ \mu g} \right) = \frac{1.7_{556} \text{ mg AgCl}}{\text{the tank}} \quad \Rightarrow \quad 1.7_{556} \text{ mg of AgCl can dissolve in the tank}$$

We actually added more than that, so the rest will remain in solid form at the bottom of the tank:

12.04 mg of AgCl added - 1.7_{556} mg of AgCl can dissolve = 10.2_{844}, or 10.3, mg of AgCl will remain in solid form

Note that if we'd actually added less than 1.7_{556} mg of AgCl to the tank, then it would all dissolve, and the concentration of Ag^+ and Cl^- in the tank would equal the "molarity" of AgCl added. The product $[Ag^+][Cl^-]$ would be less than K_{sp}, the system would not be at equilibrium, and more solid would dissolve if I were to add more solid AgCl. But x would still be a useful number to know, and it would not change unless we changed the temperature.

b) What would happen to the amount of solid AgCl in the tank if you were to dump in a bunch of (very soluble) table salt (NaCl), which dissolves completely to give $Na^+_{(aq)}$ and $Cl^-_{(aq)}$? Why?

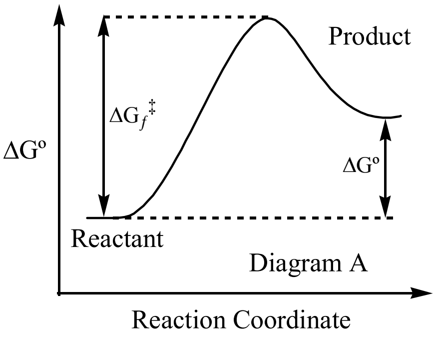
The NaCl would dissolve, releasing Na^+ and Cl^- ions into the solution. That means that $[Cl^-]$ would go up, and the product $[Ag^+][Cl^-]$ would become larger than K_{sp}. Then the system would not be at equilibrium, and would reduce the concentrations of Ag^+ and Cl^- to compensate: it would do so by causing some of the dissolved AgCl to turn back into the solid. You can also look at this in terms of LeChâtelier's Principle. We started out with the following reaction at equilibrium:

$$AgCl(s) \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

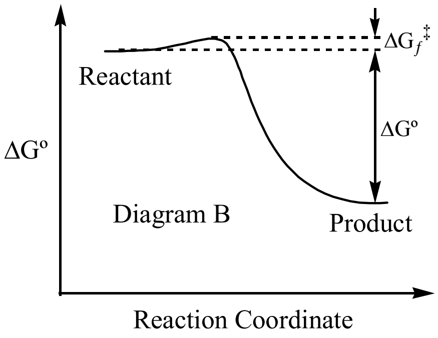
We then perturbed the system by increasing the concentration of Cl^- ions. The system would respond by shifting the equilibrium toward the left, the direction that reduces the concentration of Cl^-, and thus it would increase the amount of solid AgCl present (though what matters to LeChâtelier is really the reduction in the two ion concentrations!).

B. Shown below are three reaction coordinate diagrams, each representing one of the following reactions. Match up each diagram with the reaction it represents, explaining your logic.

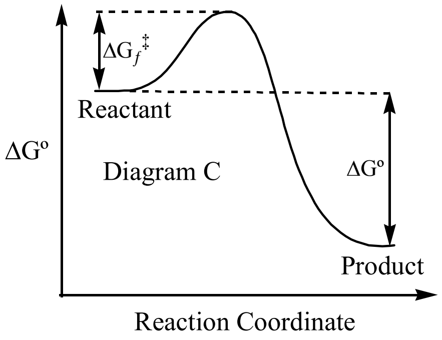
1) The detonation of ammonium nitrate, a common fertilizer: $NH_4NO_{3(s)} \rightarrow N_{2(g)} + 2\ H_2O_{(g)} + \frac{1}{2}\ O_{2(g)}$ Ammonium nitrate is extremely stable and safe in routine handling; it requires incredible heat and pressure to cause it to detonate. (But it is an explosive commonly used by terrorists - it ***is*** very powerful.)
2) The detonation of nitrogen triiodide, an extremely touchy explosive powder: $2\ NI_{3(s)} \rightarrow N_{2(g)} + 3\ I_{2(g)}$ Nitrogen triiodide can be caused to detonate by merely touching it with a feather. It detonates ***very*** fast.
3) The formation of glucose from carbon dioxide and water, performed by plants during photosynthesis: $6\ CO_{2(g)} + 6\ H_2O_{(\ell)} \rightarrow C_6H_{12}O_{6(aq)} + 6\ O_{2(g)}$ This reaction is ***not spontaneous*** (in the least!) under either standard or atmospheric conditions, which is why plants have to capture photons to make it occur.



(3) ***Photosynthesis***



(2) ***NI_3 Detonation***



(1) ***NH_4NO_3 Detonation***

I'll explain these in the order they appear. The leftmost reaction coordinate diagram depicts a reaction in which the transition from reactants to products involves a positive ΔG°, meaning a reaction that is not spontaneous under standard conditions, which can only be option (3) of those presented above. In the middle we have a reaction that is spontaneous, and has an extremely small $\Delta G^\ddagger$ value. That means the reaction is very easily activated, and thus happens quickly, with little provocation, because the forward rate of a reaction depends exponentially on $\Delta G_f^\ddagger$, getting slower as $\Delta G_f^\ddagger$ grows larger. That would make the middle reaction coordinate diagram appropriate for the detonation of NI_3, which occurs readily and very quickly. That leaves the detonation of ammonium nitrate as the reaction coordinate diagram on the right. This is a spontaneous reaction as well, (and as we would generally expect, a very large, negative ΔG° value is indeed indicative of a large, negative ΔH° and thus a highly exothermic reaction) but it has a much larger $\Delta G_f^\ddagger$ and is therefore harder to start and slower at any given temperature.

C. Does it make sense to store an activated lightstick (Assignment 6, problem 6) in a cool place when you go to bed, if you hope to have it glow for you when you wake up again the next morning? Explain carefully.

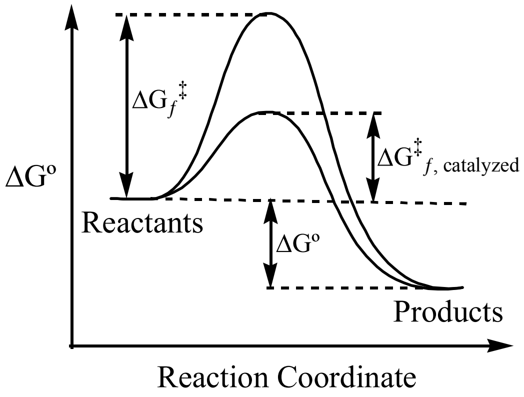
Yes indeedy, it sure does! But it won't look like it until you remove it from the fridge and let it warm up! If you take it out, look at while it's still cold, and throw it away because it's not glowing, your Dad is likely to panic and call in the nuclear (pronounced "nuke-u-laar") hazmat team when he finds the finds the garbage glowing a few minutes later! See, lowering the temperature of the lightstick causes the reaction taking place inside of it to occur more slowly: any reaction moves toward equilibrium more slowly as the temperature is reduced. The lightstick is most definitely *not* at equilibrium, in fact, when it gets to equilibrium it goes out. But in order for it to give off a photon, the chemical reaction inside of it has to occur in such a way as to move it *toward* equilibrium. So the more the lightstick glows, the faster it is dying. Putting it in a cool place will save up the reactants for later, but also make it stop glowing. [Notes: Freezing a lightstick may seem like the ultimate good idea, but it's not: hydrogen peroxide, one of the critical ingredients in these things, is incredibly unstable in a matrix of frozen water. Note too that when the lightstick reaches equilibrium, the light-producing reaction does occur in both the forward and reverse directions: but it only occurs in the forward direction, giving off a photon, as often as it occurs in the reverse direction, absorbing a photon. So it no longer glows.]

Note: In order to save paper, the pagination of the key does not match that of the exam.

D. Enzymes are proteins (often incorporating metal atoms into their structure) absolutely essential to our daily internal chemical operations. They act to speed up and direct chemical reactions that would otherwise be very slow (kinetically disfavored) or would lead to unwanted (often dangerous) side products. Cyanide ion (CN^-) is a powerful poison because it binds tightly to an enzyme critical to your body's use of stored energy, cytochrome oxidase:

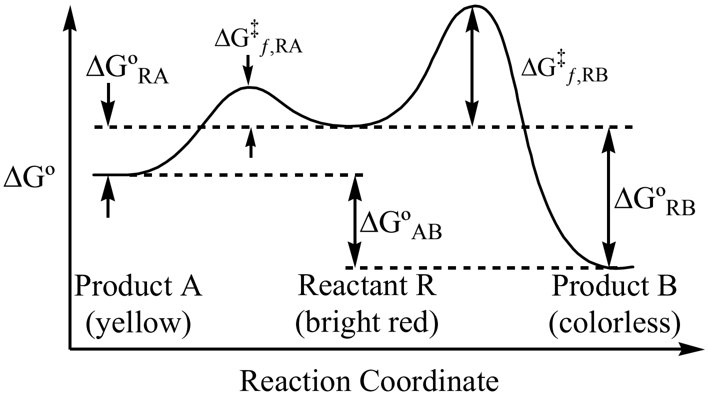
$$\begin{matrix}\text{Hydrogen itching to be pulled out of someplace} \\ \text{+ oxygen attached to hemoglobin}\end{matrix} \xrightarrow[\text{cytochrome oxidase}]{} \text{liquid water} \quad (\Delta G^{o}_{rxn} < 0)$$

If too much CN^- gets into your system, you will quickly die. In terms of either a reaction coordinate diagram or the terminology we have learned for kinetics, describe the role of cytochrome oxidase and cyanide ion in the reaction above. [Terminologically, liquid water is the *product* of the above reaction, while two hydrogen atoms and an oxygen atom are *reactants* in the above reaction. What are cytochrome oxidase and CN^-?]



Terminologically, cytochrome oxidase functions as a **catalyst** for the reaction in question, whereas CN^- functions as an **inhibitor**. That was all this question was really after, though many of you did a nice job of explaining these concepts using reaction coordinate diagrams rather than terminology. As shown on the reaction coordinate diagram at right, we can consider two of the many paths for the reaction above, one being that with the lowest transition state (activation) energy in the absence of a catalyst, ΔG_f^{o}, and the other the path with the lowest transition state (activation) energy in the presence of functioning cytochrome oxidase, $\Delta G^{\ddagger}_{f,\text{ catalyzed}}$. The enzyme provides a "comfy couch" for the dysfunctional and agitated transition state, so that the transition state isn't so high in energy, and the reaction can happen more quickly. The specifics of how this happens may vary: for example, the enzyme might instead facilitate a two-step mechanism in which an intermediate (an enzyme-substrate complex) is formed, and this then goes on to form the products. But the bottom line is that with the enzyme there and functioning, the reaction has a lower $\Delta G_f^{\ddagger}$ pathway to follow in getting from reactants to products, and can therefore happen more quickly. With the enzyme missing, or knocked out of commission by CN^-, the reaction can only follow the uncatalyzed pathway, with a much larger $\Delta G_f^{\ddagger}$, and thus a much slower rate at body temperature – too slow, in fact, for the body's metabolic needs.

E. At right is the reaction coordinate diagram for a system in which an unstable solid reactant can decompose to yield two possible solid products, A and B. (You'll see a lot of diagrams like these if you take organic chemistry!) Suppose that the reactant is bright red, product A is yellow, and product B is colorless.



a) If you observe a dry sample of pure reactant over a long period of time, what color changes will you observe, and why?

I think this problem does a nice job tying-together kinetics and equilibrium. We start with pure **R**, which is a high-energy material. We can extract ΔG^{o}'s for the following reactions from the given reaction coordinate diagram:

$\mathbf{R} \rightarrow \mathbf{A}$ $\Delta G^{o} = \Delta G^{o}_{RA}$ is negative, so this reaction is spontaneous
$\mathbf{R} \rightarrow \mathbf{B}$ $\Delta G^{o} = \Delta G^{o}_{RB}$ is negative, so this reaction is spontaneous
$\mathbf{A} \rightarrow \mathbf{B}$ $\Delta G^{o} = \Delta G^{o}_{AB}$ is negative, so this reaction is spontaneous

Thermodynamically, we expect **R** to be spontaneously transformed into both **A** and **B**, but we also expect A to be spontaneously transformed into **B**. Thus **B** is thermodynamically favored over both **A** and **R**, and given enough time we should have more **B** than **A** or **R**. In fact, because **A**, **B**, and **R** are all solids, there's no equilibrium expression for these transitions. At equilibrium we will end up with only one material: we'll have nothing but solid **B**. But that's only half of the story: what about kinetics? How fast does each product form? Here we need to look at the $\Delta G^{\ddagger}$ values for the transformations of **R** into **A** or **B**. Since $\Delta G^{\ddagger}_{f,RA}$ is a smaller value than $\Delta G^{\ddagger}_{f,RB}$, we expect **A** to form more quickly from **R** than does **B**. (One might even argue that since **A** is a solid, it will not spontaneously turn back into **R**: but that's not a problem; though it is not shown, the diagram above in no way precludes a pathway wherein **A** transforms directly into **B** without going through **R**. However, without knowing more about that pathway we can't be sure about how *quickly* **A** might turn into **B**.) Thus **A** is the ***kinetically favored*** product, while **B** is ***thermodynamically favored***. We should find **A** forming early in the game, but eventually turning into **B**; and since we are dealing with solids, at equilibrium the conversion will be utter and complete. We should see our bright red starting material quickly turn orange (as some converts to **A**), then yellow (once almost all the **R** has changed into **A**), much more slowly (or quickly, if there is a low $\Delta G^{\ddagger}$ pathway connecting **A** and **B**) fading to colorless (as **A** transforms into **B**).

b) Suppose the reactant and both products are highly soluble in water, but none of them react with water. In fact, in aqueous solution the reaction coordinate diagram looks qualitatively identical to the one above. If you observe an aqueous solution of the reactant over time, what color changes will you observe, and why?

The critical change here is that of a change of phase, such that we are no longer dealing with condensed phases. **A** will still be the kinetically favored product, and **B** the thermodynamically favored product, but now the equilibrium expressions will be markedly different, including the concentrations of **A**, **B**, and **R**. In fact, in solution we will need to have a non-zero concentration of each of these, in order for the following equilibrium expressions to be simultaneously satisfied:

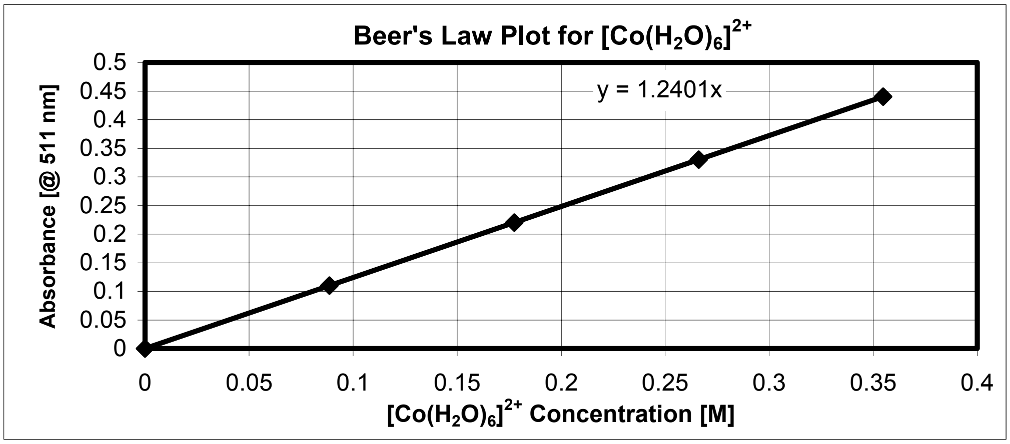
$$e^{\left(\frac{-\Delta G^o_{RA}}{RT}\right)} = \frac{[A]}{[R]} \qquad \text{and} \qquad e^{\left(\frac{-\Delta G^o_{RB}}{RT}\right)} = \frac{[B]}{[R]}$$

Note that these require that at equilibrium $e^{\left(\frac{-\Delta G^o_{AB}}{RT}\right)} = e^{\left(\frac{\left[-\Delta G^o_{RB}\right]-\left[-\Delta G^o_{RA}\right]}{RT}\right)} = \frac{e^{\left(\frac{-\Delta G^o_{RB}}{RT}\right)}}{e^{\left(\frac{-\Delta G^o_{RA}}{RT}\right)}} = \frac{\left(\frac{[B]}{[R]}\right)}{\left(\frac{[A]}{[R]}\right)} = \frac{[B][R]}{[A][R]} = \frac{[B]}{[A]}$

Thus the solution will start out bright red, and will quickly turn orange and then almost yellow; but it will never completely lose its red tint. Similarly, as **A** turns into **B**, the solution will become progressively less colored, but will never completely lose its yellow tint. At equilibrium we will have mostly **B**, with a little **A** and a small but non-zero concentration of **R**. The solution will fade to a light yellow tainted with a hint of bright red: possibly not visible with the naked eye, but most likely well within the reach of a UV/Vis spectrometer to detect!

Problem 4: Goodies From Lab

A. Using a rather old, beat-up spectrometer and a 1.00 cm pathlength cuvette, you prepared a Beer's Law plot for a cobalt complex at 511 nm, its wavelength of maximum absorbance. It looked like this:



The spreadsheet you used to prepare the plot above performed a linear regression for you and calculated the optimum slope – but as a scientist, you know better than to trust a spreadsheet with significant figures! When you repeatedly measured the absorbance of your most concentrated standard, the machine spat out 0.44835, 0.45201, 0.44933. You prepared your standards from $Co(H_2O)_6Cl_2$ using the same equipment and technique we employed in the Ni lab. Considering only ***relevant*** factors, and based on the sig. fig. method of error estimation, how many sig figs should the slope of this plot have, and why? Also, give the units of the slope.

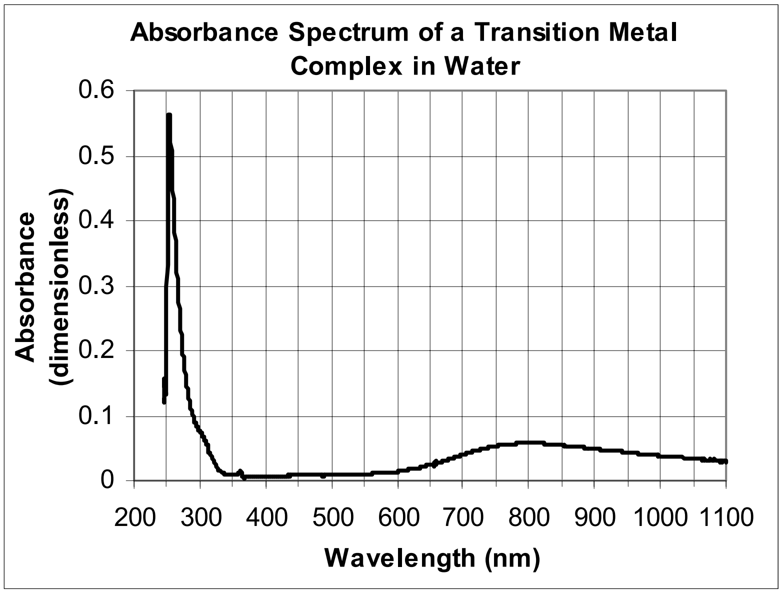
The given absorbance measurements indicate that the spectrometer is reading to ***two*** significant figures: not one, not three! In each reading, the value in the tenths place was a four, so that digit is significant, at least on the basis of precision. The hundredths digit varies, being a 4 in two cases and a 5 in the third, but this is still a variation of less than ±1, so this digit is also significant. The thousandths digit, on the other hand, varies wildly, and must clearly be considered insignificant on the basis of instrumental and methodological precision. (Note that the given values all round off to 0.45, but even if they rounded off to 0.44, 0.45, and 0.46 the hundredths digit would still be significant if the numbers were all still clustered within a range of ± 0.01 around their average!) The concentration of the stock solution you prepared in lab was known to a dazzling four or five significant figures, but that dropped to three (possibly two) with the uncertainty introduced by the autopipetters used to carry out the dilutions. In any case that still makes the concentration axis good to at least two sig figs, and since the slope is equal to

$$\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\Delta\text{Absorbance}}{\Delta\text{Concentration}} = \frac{\text{2 signficant figures}}{\geq \text{2 significant figures}} = \text{2 significant figures}[=]\frac{\text{dimensionless}}{\text{M}}[=]\text{M}^{-1},$$

we know it should have units of inverse molarity (M^{-1}) and be known to two significant figures ($1.2_4\ M^{-1}$).

Note: In order to save paper, the pagination of the key does not match that of the exam.

B. Shown at right is the absorption spectrum of a dilute aqueous solution of a copper salt. What color would this solution appear to the human eye, and why? Be quantitative. Be careful!



This solution absorbs strongly in the ultraviolet portion of the spectrum, below 400 nm, but our eyes can't see down there at all. The color of a solution hinges on its absorbance in the visible potion of the spectrum, and it this solution absorbs most strongly in the visible spectrum (between 400 and 800 nm) over in the red end of the spectrum, above 700 nm. According to the various references provided, a solution absorbing in the red/purple portion of the visible spectrum will appear green to blue-green to the human eye. Specifically, if we base our answer on Harris, since this solution absorbs most strongly in the visible spectrum at wavelengths between 680 and 780 nm, this solution absorbs purple light and will appear green to the human eye. (Note: our eyes actually become more sensitive toward the center of the visible spectrum, so in fact this solution has more of a blue tint than one might otherwise expect, because our eyes notice the weak absence of photons around 600 nm more than the strong absorbance above 700 nm.)

C. Megatron and his evil Decepticons (or possibly the boys of NSYNC, we aren't sure) are once again threatening the galaxy with their sinister plots - and this time the locus of their evil intent is focused right here in Minnesota! Using their powers of deception, they have secretly replaced the contents of a set of gas cylinders bound for the Mayo Clinic with gases other than those listed on the labels. They have done so in the knowledge that these cylinders are bound for an operating room in which the Saudi crown prince is undergoing an urgent, but otherwise routine, prostate operation involving anesthesia. With the gas substitutions the Decepticons have made, the crown prince will die in the hands of U.S. doctors, at a time when such an event could push an already unstable world over the edge. Optimus Prime (a.k.a. Paul Letendre) has discovered the evil plot and learned what he can about it, but he is too far from the Mayo Clinic to get there in time to remedy the situation. He calls upon you, his trusted lieutenant, to save the day.

The Mayo Clinic is set up with analytical equipment much like that we used in the mystery gas lab: an infrared spectrometer with a gas cell, a mass spectrometer, and an analytical balance are all readily available, as are vacuum pumps, gas bulbs, and some big balloons. There aren't any manometers around, though. Being a Transformer yourself, you can't taste or smell gases, and you don't have vocal chords. The gases are needed in the operating room immediately, so you can't afford to bring in new cylinders; you will have to very quickly identify gases that can be substituted for use in this critical operation. Most of the questions below have several possible answers, but some answers are better than others.

a) Optimus knows that the cylinder marked "oxygen" actually contains either argon (Ar) or Helium (He). What is the fastest and most reliable way you could determine which of these two it contains?

Best answer: fill up a balloon with the gas. If it floats it is He, if it sinks it is Ar. Not terrible: Compare the mass of a bulb full of room air to the mass of the gas. If it is lighter, it is He, if it is heavier, it is Ar. Or inject a sample into the mass spectrometer, looking for a *larger* peak at 40 or 4 vs. that seen for an air sample. Not workable: Inject a sample into the mass spectrometer and look for a peak at 40 or 4. (Both of these gases are present in an air sample, and there is no way to completely exclude air given the sampling system available. Any gas will show a peak of some size at both 4 and 40.) IR spectroscopy will not help in the least, because neither gas is infrared active. (They are monatomic gases with no dipole moment, so they can't vibrate and do not interact with infrared radiation and would both appear as "nothing" on an FTIR.)

b) The cylinder marked "neon" actually contains either nitrogen monoxide (NO) gas, which is very unstable and breaks apart into N and O when ionized, or nitrogen (N_2) gas. What's the fastest and most reliable means by which you could discriminate between these two gases using the equipment available?

The best way to do this is with infrared spectroscopy, because NO is IR active whereas N_2 is not. NO is a heteronuclear diatomic gas and has a static dipole moment, so it is definitely able to interact with infrared radiation. N_2 is a heteronuclear diatomic gas, and though it can vibrate, that vibration does not lead to any change in molecular dipole, and thus N_2 can not interact with infrared radiation. If a sample of the unknown gas shows an IR absorption spectrum appreciably different from that of air, it is NO; if it shows a weak air trace (due to air contamination) or no trace at all, it is N_2. Because NO and N_2 have such similar molar masses (30 and 28 g/mol, respectively), molar mass measured with the gas bulb would be a horrible way to try to differentiate these two gases. The uncertainty of such measurements was easily ±1 g/mol with the instrumentation we used for the mystery gas lab, no matter how careful you were. Mass spectrometry would also be a very dicey bet, because we are told that NO fragments upon ionization (so there would be no NO peak at 30 to look for) and because N and O, the two expected fragments, are bountifully present in air. It would be very difficult to differentiate between air contamination and a sample of NO.

c) Optimus knows the cylinder marked "chlorine" actually contains a pure polyatomic molecular gas, but nothing more than that. Which one technique (gas density, mass spectrometer, or the IR spectrometer) would be the best tool for getting a good first guess as to what the mystery gas might be, and why?

Mass spectrometry would be the best one-shot tool for this task. Gas density is vague, in that many different gases can have molar masses that vary by no more than the uncertainty in the measurement. Infrared spectroscopy is very specific, but not terribly diagnostic in that even in the hands of an expert it does a very poor job of narrowing down a list possibilities that includes a large number of possibilities. A mass spectrum might not tell you exactly what you have, but it would give you a good idea of what elements are present in the material, and possibly some idea of how the atoms are interconnected.

d) The final cylinder is marked "acetylene," but Optimus believes it contains nitrous oxide (N_2O). It is absolutely critical that this gas actually be nitrous oxide, because the anesthesiologist is going to have to use it as her anesthetic. She has a small sample of pure nitrous oxide in a lecture bottle, but not enough for the surgery. How could you quickly and most reliably verify that the "acetylene" tank actually contains nitrous oxide, given a sample of pure nitrous oxide to compare it against? Explain.

As alluded to above, this task plays to the strengths of infrared spectroscopy. An IR spectrum is very much like a molecular fingerprint, in that the whole of an IR spectrum is very particular to a given molecule, and that portions of the IR spectra of two different molecules should be appreciably different, even if the two molecules are quite similar. Given we have a sample of pure N_2O, we could readily compare its IR spectrum to that of the unknown gas and look for a spectral match. This would provide a reliable confirmation/rejection of the identity of the gas. Neither mass spectroscopy nor molar mass measurements would provide the same level of identity confirmation, because it is possible to have two molecules with very similar molar masses and/or mass spectra. (What makes mass spectroscopy useful in (c), in fact, works against it here…while we can make a pretty good guess as to what the mass spectrum of N_2O will look like without actually running it, we can also anticipate any $N_{2x}O_x$ compound will show very similar features; and with the 0-50 m/z window we used in our experiment, it would be all too easy to miss the presence of the heavier fragments which would indicate that x was greater than one.)