

1. Despite the imagery, Ima's whiskey still is a very good approximation of a "Magic Syringe." (Her beer still is anything but.)
- a. If the reaction is carried out under a constant pressure and meets the other requirements discussed in class and in the book, then  $\Delta H = q$  and the heat flow associated with the reaction is  $-67$  kJ per mole. Because we take the point of view of the system,  $-67$  kJ of heat means  $67$  kJ of energy *leaves* the system, i.e. heat energy is released. That's exactly what exothermic means.

The fermentation reaction is exothermic, because  $\Delta H_{\text{rxn}}$  is negative.

- b. Ima's garbage bag still is nearly frictionless and nearly massless, but it manages to keep a clear dividing line between the "system" (the fermenting corn mash and the products of the fermentation reaction) and the "surroundings" (Ima's basement and the other things outside the garbage bag). So it's about as close to a "Magic Syringe" as we are likely to get in anything approaching real life. That means that as  $\text{CO}_2$  is generated by the fermentation reaction, the system's volume increases against a constant pressure (the pressure in Ima's basement). Because fermentation does not give off substantial amounts of radiation, all the requirements are met for us to employ the handy relationship  $\Delta H = q$ . So the amount of heat exchanged with Ima's basement will be

$$\text{Molecular mass of glucose} = 6 \text{ C} + 12 \text{ H} + 6 \text{ O} = 6 \cdot 12.01 + 12 \cdot 1.008 + 6 \cdot 16.00 = 180.156 \frac{\text{g glucose}}{\text{mol glucose}}$$

$$200. \text{ g glucose} \left[ \frac{1 \text{ mol of glucose}}{180.156 \text{ g glucose}} \right] \left( \frac{-67 \text{ kJ}}{\text{mol of reaction}} \right) \left( \frac{1 \text{ mol of reaction}}{1 \text{ mol of glucose}} \right) = -74.38 \text{ kJ} = \Delta H = q$$

With our sign convention, and as discussed in part (a), this means heat leaves the system, so the fermentation reaction will act to heat up Ima's basement. Heat is transferred from the system to the surroundings.

74 kJ of heat energy will be released into Ima's basement as a result of the fermentation reaction.

- c. The  $\text{CO}_2$  released by the fermentation reaction will expand pretty much like an ideal gas. We can calculate how much  $\text{CO}_2$  will be generated, and then from the ideal gas law determine how much space it will occupy:

$$200. \text{ g glucose} \left( \frac{1 \text{ mol glucose}}{180.156 \text{ g glucose}} \right) \left( \frac{2 \text{ mol CO}_2}{1 \text{ mol glucose}} \right) = 2.22 \text{ mol CO}_2 \quad P = 1.0 \text{ atm} \quad T = 25^\circ\text{C} = 298 \text{ K}$$

$$2.22 \text{ mol of CO}_2 \left( \frac{24.45 \ell \text{ (at } 25^\circ\text{C and } 1 \text{ atm)}}{1 \text{ mol of ideal gas}} \right) = 54.3 \ell \text{ using the hint at the end of the problem...or, from the ideal gas law}$$

$$PV = nRT \quad \Rightarrow \quad V = \frac{nRT}{P} = \left[ \frac{(2.22 \text{ mol}) \left( 0.08206 \frac{\ell \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (298 \text{ K})}{1.0 \text{ atm}} \right] = 54.32 \ell$$

So the  $\text{CO}_2$  gas released by the fermentation reaction will occupy  $54 \ell$ ; this is the volume change of the system ( $\Delta V$ ) because the liquid components of the system don't undergo an appreciable volume change. We could calculate that volume change, but it would be negligible compared to  $54 \ell$ ...in every case where have you have seen a condensed-phase reaction take place, have you ever seen the volume change notably? Put more numerically, based on the densities in the trusty CRC Handbook of Chemistry and Physics (73<sup>rd</sup> Ed.), the volume of  $200. \text{ g}$  of glucose is about  $130 \text{ mL}$  (think of about a cup of sugar, sort of) and the volume of  $2.22 \text{ mol}$  (about  $100 \text{ g}$ ) of ethanol is  $80 \text{ mL}$ : their difference, on the order of  $50 \text{ mL}$ , is miniscule when compared with  $54 \ell$ . Since the  $\text{CO}_2$  gas is generated and expands against a constant opposing pressure of  $1.0 \text{ atm}$  (the pressure of the atmosphere pushing in on the garbage bag),

$$w = -P\Delta V = -(1.0 \text{ atm})(54.32 \ell) = -54.32 \ell \cdot \text{atm} \left( \frac{101325 \text{ Pa}}{1 \text{ atm}} \right) \left( \frac{1 \text{ m}^3}{1000 \ell} \right) \left( \frac{1 \frac{\text{kg}}{\text{m} \cdot \text{s}^2}}{1 \text{ Pa}} \right) = -55.04 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} \left( \frac{1 \text{ J}}{1 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}} \right) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) = -5.504 \text{ kJ}$$

This means, according to our "system's point of view" sign convention, that

Still A did  $5.5 \text{ kJ}$  of work on the atmosphere as it expanded.

- d. Internal energy is a state function, so the internal energy change for a system is the same no matter what path is used to get from the initial to the final state. Because the initial and final states in the two stills are identical in this scenario, the internal energy change of the two stills must be identical. Heat, however, is not a state function! It depends critically on the path taken in getting from the initial to the final state. The sequence of events that took place in Still A was very

different from the sequence that unfolded in Still B, and so the paths were different. This does not, in and of itself, guarantee that the heat flow in the two cases is different, but it means that we have no reason to expect that it is.

However, with a bit more thought we can state pretty confidently that the heat released from Still B was less than that released from Still A. Recall that  $\Delta E = q + w$ . Since  $\Delta E$  is the same for the two stills, what might differ is the distribution of the energy released between heat and work. It's pretty clear that the work done by Still B is more than that done by Still A; here are the two best explanations for this that I can come up with:

1. After it's all said and done, there are twisted bits of keg everywhere. It took work to bend the metal in that keg!
2. Stating the same thing a bit more numerically, remember that work =  $-P_{\text{opposing}}\Delta V$ . In the end both stills generated the same amount of  $\text{CO}_2$ , and it ended up expanding to occupy an equal volume. So the volume change of the system was the same in each case. However, as the keg sat there and built up pressure, it may have swelled up a bit...and certainly just before it blew up, some part of it must have deformed, allowing the pressurized  $\text{CO}_2$  inside to expand a bit. That expansion would have taken place against a pressure of more than one atmosphere, and so that portion of the volume change would have involved more work than did the same portion of the volume change in Still A. If Still B did more work than Still A, it must have released less heat, because the work and heat must add up to the same sum in both cases.

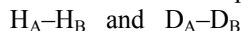
Because the contents of Still B must have done some work on the keg while expanding inside of it, Still B must have actually released less heat into Ima's basement than did Still A.

Note that if we really wanted to, we could figure out what  $\Delta E$  is for both distillation apparatus, because we calculated both  $q$  and  $w$  for Still A. ( $\Delta E = q + w = -74 \text{ kJ} + -5.5 \text{ kJ} = -79.5 \text{ kJ}$  = total energy released as a result of fermentation) But that really isn't important as far as answering the question goes, because we can't get a number for how much energy went into smashing up Still B; we just know that it took some work to do so, and that's all we need to know.

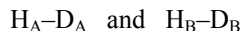
2. Since we are asked about spontaneity under standard conditions (25°C and 1 atm), we don't need to use  $\Delta H$  and  $\Delta S$ , we can just add and subtract  $\Delta G^\circ_f$  values from Appendix 2, just as we would with  $\Delta H^\circ_f$  values:
  - a.  $\Delta G^\circ_{\text{reaction}} = \Delta G^\circ_f[\text{products}] - \Delta G^\circ_f[\text{reactants}] = \Delta G^\circ_f[\text{C}_{(\text{s}), \text{graphite}}] - \Delta G^\circ_f[\text{C}_{(\text{s}), \text{diamond}}] = 0 \text{ kJ}\cdot\text{mol}^{-1} - 2.900 \text{ kJ}\cdot\text{mol}^{-1}$   
 $\Delta G^\circ_{\text{diamond to graphite}} = -2.900 \text{ kJ}\cdot\text{mol}^{-1}$  and therefore this reaction is spontaneous at 25°C and 1 atm.
  - b.  $\Delta G^\circ_{\text{reaction}} = \Delta G^\circ_f[\text{products}] - \Delta G^\circ_f[\text{reactants}] = (2 \Delta G^\circ_f[\text{Fe}_{(\text{s})}] + 3 \Delta G^\circ_f[\text{CO}_{2(\text{g})}]) - (\Delta G^\circ_f[\text{Fe}_2\text{O}_{3(\text{s})}] + 3 \Delta G^\circ_f[\text{CO}_{(\text{g})}])$   
 $= 2(0 \text{ kJ}\cdot\text{mol}^{-1}) + 3(-394.36 \text{ kJ}\cdot\text{mol}^{-1}) - [(-742.2 \text{ kJ}\cdot\text{mol}^{-1}) + 3(-137.17 \text{ kJ}\cdot\text{mol}^{-1})]$   
 $= -29.37 \text{ kJ}\cdot\text{mol}^{-1}$  and so this one is also spontaneous. A lot of you were shocked at this...how can you reverse rust?!? Well, you can with a strong reducing agent, like carbon monoxide. Not that I recommend locking your car in a garage with the engine running in the hopes of reversing all the rust damage! Rust is actually a hydrate,  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , and that actually makes it much more difficult to turn back into iron. Plus, rusting causes migration of metal ions; so even if you manage to reverse it (turn rust back into iron) you don't get back the coherent metal part you started with. See pp. 822-3 of your book for the juicy (if a bit advanced) details!
  - c.  $\Delta G^\circ_{\text{reaction}} = \Delta G^\circ_f[\text{products}] - \Delta G^\circ_f[\text{reactants}] = 2 \Delta G^\circ_f[\text{NH}_{3(\text{g})}] - (\Delta G^\circ_f[\text{N}_{2(\text{g})}] + 3 \Delta G^\circ_f[\text{H}_{2(\text{g})}])$   
 $= 2(-16.45 \text{ kJ}\cdot\text{mol}^{-1}) - [3(0) + 3(0)] = -32.90 \text{ kJ}\cdot\text{mol}^{-1}$  Whaddayaknow, this one is spontaneous too.
  - d.  $\Delta G^\circ_{\text{reaction}} = \Delta G^\circ_f[\text{products}] - \Delta G^\circ_f[\text{reactants}]$   
 $= (\Delta G^\circ_f[\text{C}_6\text{H}_{12}\text{O}_{6(\text{s})}] + 3 \Delta G^\circ_f[\text{O}_{2(\text{g})}]) - (6 \Delta G^\circ_f[\text{CO}_{2(\text{g})}] + 6 \Delta G^\circ_f[\text{H}_2\text{O}_{(\text{l})}])$   
 $= -910. \text{ kJ}\cdot\text{mol}^{-1} + 3(0) - [6(-394.36 \text{ kJ}\cdot\text{mol}^{-1}) + 6(-237.13 \text{ kJ}\cdot\text{mol}^{-1})] = -910. \text{ kJ}\cdot\text{mol}^{-1} - [-3788.94 \text{ kJ}\cdot\text{mol}^{-1}]$   
 $= +2879 \text{ kJ}\cdot\text{mol}^{-1}$  so this reaction is most definitely *not* spontaneous and a substantial input of energy is required to drive it in the "forward" direction. Plants get this energy from sunlight! Note that the reverse reaction, the combustion of glucose, *is* spontaneous, and this is why we can eat sugars and harvest energy by doing so.

3. The possible microstates for a system include all the possible final states that constitute “different” ways to generate one of the *relevant* arrangements for that system. It’s hard to put that in plain English, so hopefully this problem will clarify what it means. Your book is full of sample problems focusing on positional entropy: different arrangements of atoms in space. This problem is about associative entropy: different ways that atoms can be connected to each other. *In this problem we do not care about where the atoms are located in space, we care about how they are connected (bonded) to each other.* The relevant microstates in this problem relate to what is bonded to what, not where the pairs of atoms are located. (Analogously, in the “Set Up” Your Roommate example from class, we care about who’s paired up with who, not where they go on their date.)

- a. Because we want to count the different ways of getting a given arrangement (pairing) of atoms (these are the microstates), we label each atom in our system. We start the problem by adding an  $H_{2(g)}$  molecule and a  $D_{2(g)}$  molecule to the vacuum chamber. So let’s label these atoms with A and B subscripts, so we can tell the two H and the two D atoms apart:

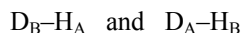


This is our initial condition, and also one possible microstate. To generate the other possible microstates, we ask what other possible pairings can be generated. Well, the  $H_A$  atom could be bonded to  $D_A$  rather than  $H_B$ :

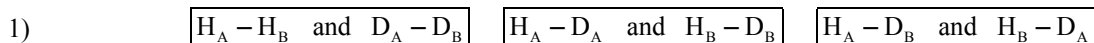


$H_A$  could also be connected to  $D_B$ :  $H_A-D_B \text{ and } H_B-D_A$

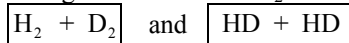
One might be tempted to think that this is different from the arrangement



but all that’s happened here is that we have rotated each molecule  $180^\circ$ . This is not a different way to generate  $2HD_{(g)}$ , and thus not a distinct microstate with respect to the question being investigated in this problem. Thus the three possible microstates relevant to the question of associative entropy are:



As with Jesse Helms, we aren’t really interested in who’s paired up with whom, we just want to know about how many  $H_2$ ,  $D_2$ , and HD molecules we are likely to have. We don’t know the atoms personally and don’t really care about their personal lives. We just want to know if we will get HD if we mix  $H_2$  and  $D_2$  together. The two possible arrangements are



If you look at the three microstates above, you see that one falls under the heading of  $H_2 + D_2$ , while the other two are two distinct ways of getting 2 HD, or  $(HD + HD)$ . Each of the microstates is equally probable, so there is a 1 in 3 chance that we’ll end up with the  $H_2 + D_2$  arrangement, and a 2 in 3 chance of getting one of the 2 HD outcomes. By following the instructions in the problem set, I arrived at approximately the same results without using statistics. Here are the outcomes of twenty draws of pairs of cards from a deck consisting of 2 aces and 2 deuces:

(A2, A2) (A2, A2) (A2, A2) (A2, A2) (AA, 22) (A2, A2) (AA, 22) (A2, A2) (A2, A2) (A2, A2) (AA, 22) (A2, A2) (AA, 22) (A2, A2) (AA, 22) (A2, A2) (A2, A2) (A2, A2) (A2, A2) (AA, 22)

I got 14 mixed pairs and 6 matched pairs. This method correctly predicts mixed pairs as the most likely outcome, and gets amazingly close to the mathematically-predicted 1:3 vs. 2:3 probability ratio. 1:3 is 0.333333, while 6:20 is 0.3.

2) The most probable arrangement for this system is  $2HD_{(g)}$ .

3) The statistically predicted probability of  $(H_2 + D_2)$  is 1:3 or 0.333; experimentally I got 6:20 or 3:10: in other words 0.3.  
The statistically predicted probability of (2 HD) is 2:3 or 0.666; experimentally I got 14:20 or 7:10: in other words 0.7.

- b. If you tried to do this one mathematically, using statistics, rather than using cards, you are either really good at statistics or you got it wrong. It’s very easy to fall into the trap of assuming that 4 HD will be the most probable outcome; it is not! Here are the outcomes of my 40 trials with cards (there are still only three arrangements in this case; I present only arrangement outcomes, not microstate outcomes, which is to say I do not label the cards!):

(AA AA 22 22) – I got this 8 times      (AA A2 A2 22) – I got this 25 times      (A2 A2 A2 A2) – I got this 7 times

My statistics experiment predicts the most probable outcome to be  $(H_2 + 2HD + D_2)$ , which suggests the reaction would not go to completion. My attempt at the “real statistics” predicts  $(2H_2 + 2D_2)$  8.6% of the time,  $(4HD)$  22.9% of the time, and  $(H_2 + 2HD + D_2)$  the remaining 68.6% of the time. The statistical experiment I carried out with cards came sort of close: 8:40 is 20%, 25:40 is 62.5%, and 7:40 is 17.5%. This is reassuring to me, because I’m horrible at statistics!

The most probable arrangement is  $H_2 + 2HD + D_2$ , which indicates that in an 8-atom system the reaction  $H_2 + D_2 \rightarrow 2HD$  would not go to completion.

There are actually 105 possible microstates for this four-card system...you can see why statistics become necessary for dealing with systems containing any realistic number of molecules! I don’t mean to scare any math majors out there, but many people from the mathematical field of applied probability find work in the statistical mechanics branch of chemistry. It is pretty heavy-duty stuff, and it’s of non-trivial importance in the advancement of scientific theory.

4. The key relations used in this problem are  $E_{\text{photon}} = h \cdot \nu$  and  $\lambda \cdot \nu = c$ , where  
 $h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$        $E_{\text{photon}} = \text{the energy of a single photon}$   
 $\nu = \text{frequency [=} \text{s}^{-1} \text{ or Hz}$        $\lambda = \text{wavelength [=} \text{m (or any length)}$   
 $c = \text{the speed of light} = 2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$  (we use the value of  $c$  in vacuum for everything...close enough!)

a. Frequency =  $\nu = 88.1 \text{ MHz} \left( \frac{10^6}{\text{M}} \right) \left( \frac{\text{s}^{-1}}{\text{Hz}} \right) = 8.81 \times 10^7 \text{ s}^{-1}$        $\lambda \nu = c \Rightarrow \lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}}{8.81 \times 10^7 \text{ s}^{-1}} = 3.40_3 \text{ meters}$

The wavelength of a 88.1 MHz radio wave is 3.40 meters.

b. Frequency =  $\nu = 68_0 \text{ kHz} \left( \frac{10^3}{\text{k}} \right) \left( \frac{\text{s}^{-1}}{\text{Hz}} \right) = 6.8_0 \times 10^5 \text{ s}^{-1}$

$$\lambda \nu = c \Rightarrow \lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}}{6.8_0 \times 10^5 \text{ s}^{-1}} = 4.4_{087} \times 10^2 \text{ meters}$$

The wavelength of a 68<sub>0</sub> kHz radio wave is 44<sub>1</sub> meters.

Note: This big wavelength difference is why FM radio tends to be line-of-sight (it bounces off of buildings, but for the most part you have to be able to see the transmitter to pull in an FM station) while AM is not (it can diffract around buildings!).

c. Wavelength =  $454 \text{ nm} \left( \frac{10^{10} \text{ \AA}}{10^9 \text{ nm}} \right) = 4540 \text{ \AA}$

$\Rightarrow$  Using the chart included with the problem set, it can be seen this falls between blue and violet.

The flame would be blue-violet in color.

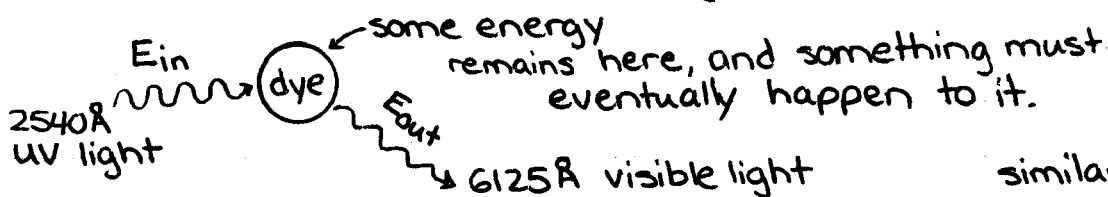
- d. Electrons conserve energy as they move from one energy level to another by emitting or absorbing a single photon at the very instant they make the "jump." The energy of this photon is equal to the difference in energy between the two energy

levels:  $|\Delta E_{\text{electron}}| = E_{\text{photon}} = h\nu = 4.9 \times 10^{-19} \text{ Joules} \Rightarrow \lambda \nu = c \Rightarrow \lambda = \frac{c}{\nu} \Rightarrow \nu = \frac{|\Delta E_{\text{electron}}|}{h}$

$$\lambda = \frac{c}{\nu} = \frac{hc}{|\Delta E_{\text{electron}}|} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})}{4.9 \times 10^{-19} \text{ J}} = 4.0_{54} \times 10^{-7} \text{ m} \times \left( \frac{10^9 \text{ nm}}{1 \text{ m}} \right) = 40_{.54} \text{ nm} \times \left( \frac{10^{10} \text{ \AA}}{10^9 \text{ nm}} \right) = 40_{.54} \text{ \AA}$$

This light clearly falls in the violet portion of the visible spectrum, with  $\lambda = 410 \text{ nm}$ .

e. The process can be diagrammed like this:



similarity

$$E_{in} = h\nu_{in} \quad \lambda_{in}\nu_{in} = c \quad \nu_{in} = \frac{c}{\lambda_{in}} \Rightarrow E_{in} = \frac{hc}{\lambda_{out}} \quad E_{out} = \frac{hc}{\lambda_{out}}$$

$$\lambda_{in} = 2540 \text{ \AA} \times \frac{1 \text{ m}}{10^{10} \text{ \AA}} = 2.54 \times 10^{-7} \text{ m}$$

$$\lambda_{out} = 6125 \text{ \AA} \times \frac{1 \text{ m}}{10^{10} \text{ \AA}} = 6.125 \times 10^{-7} \text{ m}$$

$$E_{in} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})}{2.54 \times 10^{-7} \text{ m}} = 7.82_{08} \times 10^{-19} \text{ J}$$

$$E_{out} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})}{6.125 \times 10^{-7} \text{ m}} = 3.243_{22} \times 10^{-19} \text{ J}$$

Electron volts (eV) are a convenient unit to use for photon energies. One eV is the energy needed to move an

Note: A Coulomb is a measure of electrical charge. The charge on a single electron is far far less than one Coulomb.

electron through a potential difference of one volt:

$$1 \text{ eV} = (e)(1 \text{ volt}) = 1.602 \times 10^{-19} \text{ Coul} \cdot 1 \text{ Volt} = 1.602 \times 10^{-19} \text{ Coul}\cdot\text{Volt} = 1.602 \times 10^{-19} \text{ Joules}$$

It will be helpful for you to know  $1 \text{ Coul} \cdot 1 \text{ Volt} = 1 \text{ Joule}$ .

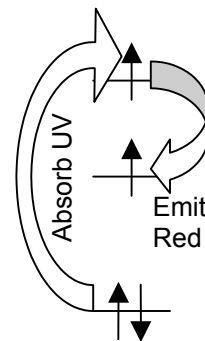
$$E_{in} = 7.82_{08} \times 10^{-19} \text{ J} \cdot \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} = 4.88_{14} \text{ eV}$$

$$E_{out} = 3.243_{22} \times 10^{-19} \text{ J} \cdot \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} = 2.024_{26} \text{ eV}$$

The coating absorbed a photon with 4.88 eV of energy, then emitted one with 2.024 eV of energy. Thus it is left with

$$4.88 \text{ eV} - 2.024 \text{ eV} = 2.86 \text{ eV}$$

2.86 eV of energy are left over after one absorption and emission event.



5. The amount of energy required to form a typical C–C bond is called the C–C bond energy; Zumdahl has a big table of bond energies on p. 373. The value listed for an average C–C bond is 347 kJ per mole. That means it takes 347 kJ of energy to break one mole of typical C–C bonds. We are interested here in whether a single 420 nm photon has enough energy to break a single C–C bond, so we just need to figure out the energy required to break just one bond. Easier than it might seem!

$$\frac{347 \text{ kJ}}{1 \text{ mol of C-C bonds}} \times \frac{1 \text{ mol of C-C bonds}}{6.022 \times 10^{23} \text{ C-C bonds}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = \frac{5.76_2 \times 10^{-19} \text{ J}}{\text{single C-C bond}}$$

Now we want to figure out how much energy a single 420 nm photon can provide. That's pretty simple too:

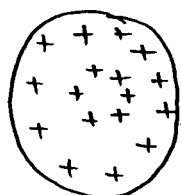
$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})}{420 \text{ nm} \left( \frac{10^{-9} \text{ m}}{1 \text{ nm}} \right)} = 4.7_3 \times 10^{-19} \text{ J}$$

So a single 420 nm photon carries  $4.73 \times 10^{-19}$  J of energy, but it requires  $5.76 \times 10^{-19}$  J of energy to break a typical C–C bond. That means a 420 nm photon can't break a typical C–C bond. (But photons in the UV, with shorter  $\lambda$ 's and higher energies, can!)

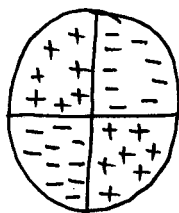
A 420 nm photon does not have enough energy to break a typical C–C bond.

Question 6 – This question was meant to educate rather than test you. The hope was that after working through this problem, you would come to understand wavefunctions much better. I hope it had that effect for some of you.

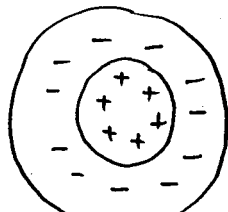
- a. The + and – signs are a simple way of indicating whether the surface of the drum is closer or farther from you than the rim of the drum is. + signs indicate the drum head is actually bubbled out of the page, toward you, while – signs indicate that the drum head is situated below the level of the page. Since each drum head oscillates with time, at a given instant in time the same spot on the drum might be + or -. The important thing is that when a given part of the drum is toward you, the surrounding region will also be toward you...until you cross a node. **Whenever you cross a node, the sign must change.** This does not require planning on your part, the wave mechanics ensure that it is possible. You just draw the drum head with the nodes on it as indicated by the black powder in the pictures...the black powder shows you the nodes. Then you arbitrarily draw a sign somewhere, + or -, your choice. Then keep drawing the same sign until you cross a node. When you do cross a node, change sign. That's it, the rest is automatic.



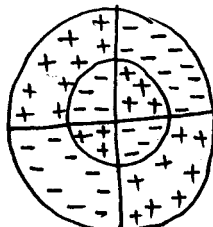
I (1s)



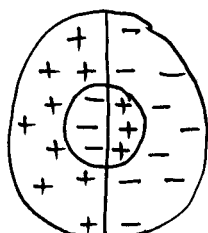
II (3d)



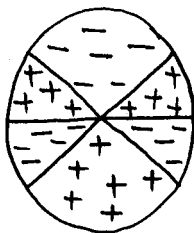
III (2s)



IV (4d)



V (3p)



VI (4f)

If all your signs in a given picture are opposite those shown here, your answer is still correct!

b. The answers appear next to the drum pictures in (a), but the explanation is key. Two simple rules are at work here:

1) The principal quantum number,  $n$ , is equal to one more than the total number of nodes

2) The angular quantum number,  $\ell$ , is equal to the number of linear nodes

Since in this two dimensional system there are two and only two possible types of nodes, linear and circular,

$$\text{Total number of nodes} = n + 1 = \text{circular} + \text{linear nodes} = \# \text{ of circular nodes} + \ell$$

$$\# \text{ of circular nodes} = n + 1 - \ell$$

The linear nodes run all the way across the drum head, not halfway. A line across the drum counts as one node, not two.

The rim of the drum does not count as a node, even though it does not oscillate with time, just as the ends of a string are not counted as nodes in the case of a one-dimensional wave on a string. The wavefunction doesn't change sign there!

Example of determining  $n$ : in image IV, there are two linear nodes and there is one circular node. (Note subject-object agreement. -Ed.) So the total number of nodes is  $(2 + 1)$ , or 3. This must be equal to  $n + 1$ , so  $n$  must be 4 in image IV.

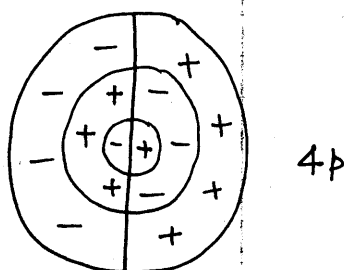
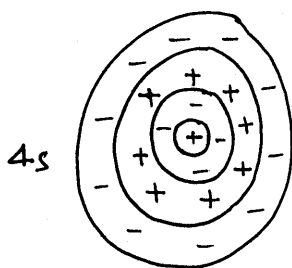
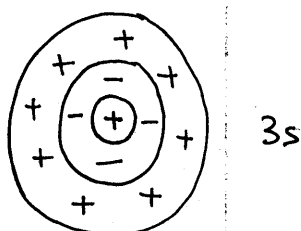
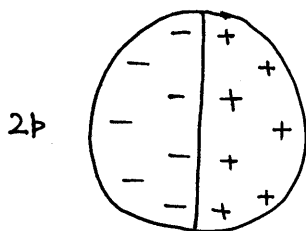
Rather than saying " $n = 2, \ell = 1$ " we use the shorthand "2p" where the "p" indicates  $\ell = 1$ . The letters used for this are

$\ell$	Letter used for $\ell$	# of linear nodes
0	s	0
1	p	1
2	d	2
3	f	3
4	g	4
5	h	5
6	i	6
...	...	...

This table summarizes the logic behind the assignments:

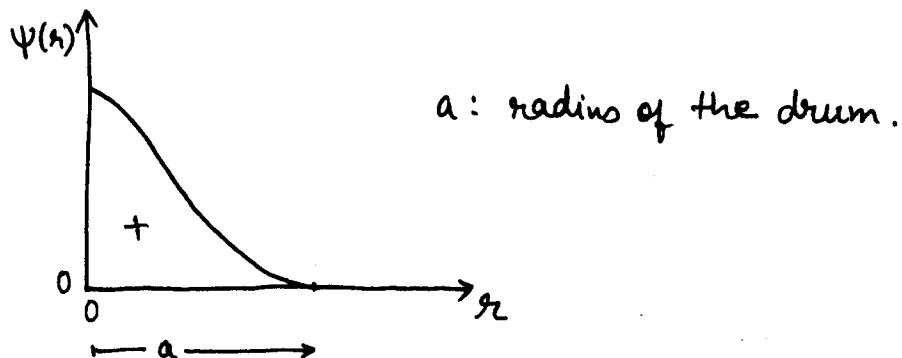
Image #	# of Linear Nodes ( $\ell$ )	# of Circular Nodes	Total # of nodes ( $n - 1$ )	$n$	$\ell$	Name
I	0	0	0	1	0	1s
II	0	1	1	2	0	2s
III	1	1	2	3	1	3p
IV	2	0	2	3	2	3d
V	2	1	3	4	2	4d
VI	3	0	3	4	3	4f

c. The rules delineated in (b), above, limit the possible orbitals to a subset of all the  $n, \ell$  combinations. For example, there can be no 2d orbital, because d implies  $\ell = 2$ , but if  $n = 2$  then the total number of nodes must be  $(n - 1) = 2 - 1 = 1$ . The allowed orbitals are therefore as follows: 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d, 5f, 5g, etc... Of the allowed states with  $n \leq 4$ , the images above exclude 2p, 3s, 4s, and 4p. Here's what their images would look like:



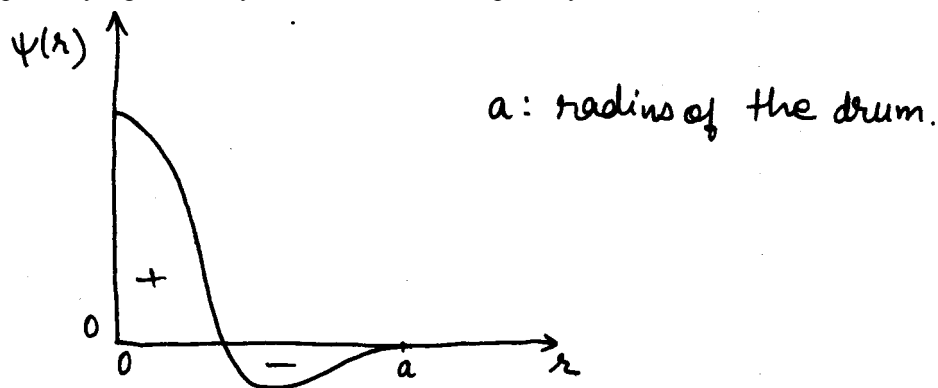
(Again, if all your signs are opposite in a given picture, it means the same thing.)

- d. The 1s state (Image I) corresponds to the lowest energy state because it has zero nodes and the energy of a state increases with the number of nodes. You can't have less than zero nodes, so that's got to be the lowest-energy state.
- e.  $\Psi$  just corresponds to the amplitude of the wave – in this case, the displacement of the skin of the drum away from the plane in which the rim of the drum rests. The only really tricky part of this question is that you are asked to plot the answer in cylindrical coordinates, that is, in terms of  $r$  rather than  $x$  and  $y$ .  $r$  is just the distance away from the center of symmetry, in this case the center of the drum. To draw  $\Psi(r)$ , imagine you are an ant on the surface of the drum head. Freeze the motion of the drum head when it reaches its maximum amplitude, then walk along the surface of the drum from the center toward the rim. Your position relative to the plane in which the rim of the drum rests is  $\Psi$  at that  $r$ . For the 1s state, the entire drum head is either above or below the rim at maximum amplitude. If  $a$  is the value of  $r$  at the rim,



If you multiply  $\Psi$  by  $-1$ , the resulting picture is the other possible answer. The important thing is that the wavefunction does not change sign. (Additionally,  $\Psi$  and  $\Psi$ 's slope must be continuous, if that means anything to you.)

- f. The 2s state has one circular node, where  $\Psi$  changes sign. Where that happens is not important in this plot, and again it is perfectly legitimate if your  $\Psi$  is this one multiplied by  $-1$ .



(Don't worry if your amplitude differs!)