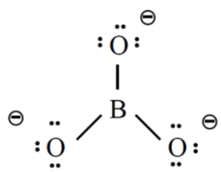
Name (Last, First): ____________________________ ID Number: _______________________

Solutions – Chemistry of Coffee Topic Test

1. When you gaze into the perfection that is a Pumpkin Spiced Latte, it is easy to forget that the coffee, started its journey as a plant, Coffea arabica, - technically a “woody perennial evergreen dicotyledon.”

a. When coffee plants are deficient in certain nutrients, there are characteristic patterns that appear. For each of the ions mentioned below, draw the most-preferred Lewis structure and give the geometry about the central atom. Resonance and non-zero formal charges must be included for full credit.

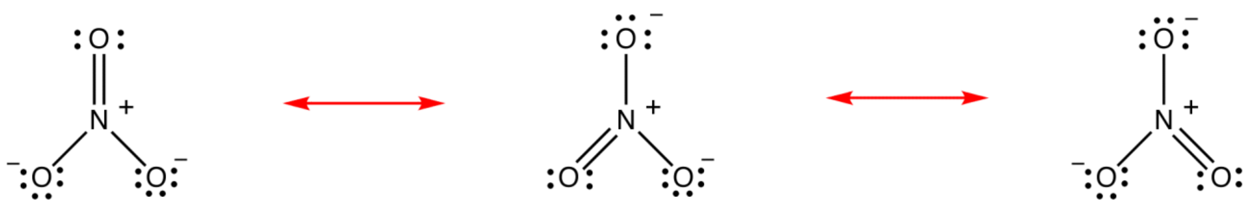
i. BO_3^{3-} is the source of boron. With low boron, the base of coffee leaves turns yellow, and holes form on the edges of the leaves.



Geometry is trigonal planar

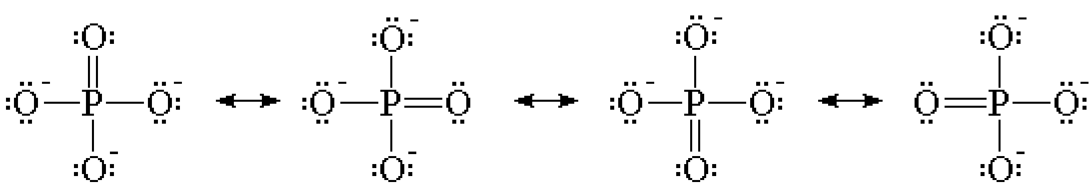
If the Lewis structure is drawn such that one of the oxygen atoms has a double bond to boron, giving boron a negative charge and that oxygen a formal charge of 0, the answer will also be accepted.

ii. NO_3^- is one source of nitrogen. Plants deficient in nitrogen have leaves that are much paler.



Geometry is trigonal planar

iii. PO_4^{3-} is a source of phosphorus. Phosphorus deficiency is marked by teardrop-shaped leaves with brown spots on the leaf.



Geometry is tetrahedral. Single Lewis structure where phosphorus is +1 charge and all oxygen atoms are -1 is also accepted for full points.

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b. Metals are also crucial to plant growth. They are crucial as cofactors for proteins. Each of the following metals is crucial for growth of the coffee plant. For each, give the ground state electronic configuration. Noble gas configuration may be used.

i. Manganese: $[Ar]3d^5\ 4s^2$
ii. Zinc(II): $[Ar]3d^{10}$
iii. Molybdenum: $[Kr]4d^5\ 5s^1$
iv. Copper(II): $[Ar]3d^9$

2. Another *scientific* method of brewing coffee involves using a vacuum apparatus, pictured below. In this brewing method, a bulb is filled with (purified of course) water and set over a heat source. On top of the bulb is a sealed chamber containing the coffee grounds, which is connected to the water vessel via a tube. The conditions in this upper chamber can be approximated as 298 K and 1 atm.

a. As the water heats and boils, it will vaporize and enter the grounds chamber. Using phase changes, explain how the coffee is brewed from this point on in 3 sentences or less.

Once the water is in its vapor phase, it will pass through the chamber containing the coffee grounds, where it extracts the flavor molecules from the coffee grounds. Once the heat is turned off, the water will condense back to its liquid phase and drop back into the main chamber.

b. Consider a beaker of water at 298 K and 1 atm. If $\Delta H_{vap} = 44.0 \frac{kJ}{mol}$ and $\Delta S_{vap} = 118.89 \frac{J}{mol \cdot K}$, calculate the vapor pressure of water in atmospheres under these conditions using the equations $\Delta G° = \Delta H° - T\Delta S°$ and $\Delta G° = -RT\ln K_p$.

$$\Delta G° = \left(44000 \frac{J}{mol}\right) - (273.15\ K)\left(118.89 \frac{J}{mol \cdot K}\right) = 11525 \frac{J}{mol}$$

$$11525 \frac{J}{mol} = -\left(8.314 \frac{J}{mol \cdot K}\right)(273.15\ K) \ln K_p$$

$$K_p = 0.00625$$

Since liquid water is not included in the equilibrium expression, the partial pressure of water is 0.00625 atmospheres.

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c. How does the pressure calculated in part (b) compare to that of H_2O in the lower chamber of a vacuum apparatus during heating? Explain your answer.

The vapor pressure of water from part b will be lower than that in the lower chamber. In the lower chamber, the water is being heated which causes its vapor pressure to be greater.

d. Use your answer to (b) to explain below why water is a liquid in the upper chamber. Remember that the upper chamber's conditions are approximately the same as those in part (b).

The water is liquid in the upper chamber because under standard temperature and pressure, the value of K for the vaporization of water is less than 1 (equilibrium lies more towards liquid than the vapor phase).

e. Let's say you have the idea to add a mystery substance to the water to add flavor to your coffee. Unfortunately, by doing this, you are making the coffee-brewing process less efficient by lowering the vapor pressure of water. You have 150 grams of water and the original vapor pressure in the chamber at 100 ℃ before adding the mystery substance is 1.00 atm. The vapor pressure at the same temperature drops to 0.857 atm after adding 83.5 g of the substance. Calculate the molar mass of the mystery substance in grams per mole, assuming ideal behavior.

$\Delta P = P_A^* \cdot X_B$ where P_A^* is the vapor pressure of the pure liquid and X_B is the mole fraction of the solute

$$0.143\ atm = (1.00\ atm)X_B$$
$$X_B = 0.143$$

We have 150 g of water (8.32 mol) and we now know that the mole fraction of the water is equal to $1 - 0.143 = 0.857$. Therefore the total moles of compounds = 8.32/0.857= 9.71 mol, and the number of moles of the mystery compound must therefore equal 1.39 moles.

$$\frac{83.5\ g}{1.39\ mol} = 60.1\frac{g}{mol}$$

3. According to coffeeresearch.org, the 3 chemicals that contribute most to the acidic flavor of coffee are citric acid, malic acid, and acetic acid, and the quantity of these acids varies based on where the coffee was grown, grind size, brewing time, and brewing temperature. The "Wash U Blend" coffee served at various locations around campus has a reputation for tasting very burnt and acidic.

Suppose that dining services decides to remove some of the acidic compounds from its coffee to make it more appealing. Once the acid is extracted, it will need to be processed to a safe pH before disposal. Dining services has 4 L of coffee with a citric acid ($MW = 192.1\frac{g}{mol}$) concentration of $461.00\frac{\text{mg}}{\text{L}}$. They extract 80% of the citric acid and re-dissolve it in 50 mL of water. Calculate the number of grams of NaOH ($MW = 40.1\frac{g}{mol}$) that will be required to obtain a solution with a pH of 4.00

Note: citric acid is a triprotic acid, but we will only consider its first pKa value, which is 3.14.

$$4L * 461\frac{mg}{L} = 1844\ mg = 1.844\ g$$

$$0.80 * 1.844\ g = 1.475\ g\ citric\ acid = 7.68 \times 10^{-3}\ mol\ citric\ acid$$

$$\frac{7.68 \times 10^{-3}\ mol}{0.050\ L\ H_2O} = 0.154\ M\ \ citric\ acid$$

Using the Henderson-Hasselbalch equation: $pH = pK_a + log\frac{[\text{A}^-]}{[HA]}$

$4 = 3.14 + log(\frac{x}{0.00768-x})$ where x is the number of moles of NaOH

Solve for x to obtain $(0.006755\ mol\ NaOH)\left(\frac{40\ g\ NaOH}{1\ mol\ NaOH}\right)$ = 0.270 g NaOH

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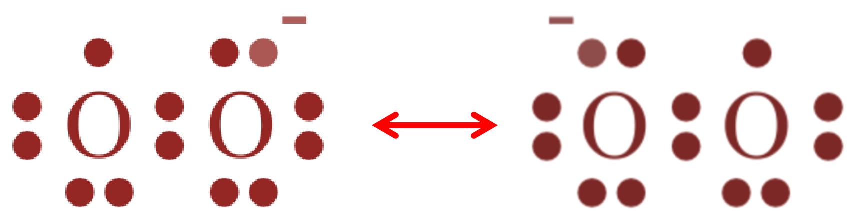
4. Coffee is one of the world's biggest sources of antioxidants. Antioxidants are an important part of a healthy diet because they stabilize free radicals formed in the body as a byproduct of metabolism. <u>A radical is an atom, ion, or molecule that contains unpaired valence electrons</u>. Some examples of radical species are neutral halogen atoms (F, Cl, Br, I), NO_2, and NO.

a. Explain below why radicals can be harmful to long chained molecules.

The unpaired electrons of radicals are extremely reactive, and when they react with long chained molecules, the result can be damage to a part of the molecule that will disrupt the chain and cause it to break apart.

b. One common radical found in cells is the O_2^- radical species, also called a superoxide. Draw the most-preferred Lewis structure for this molecule. Hint: the octet rule is not fulfilled for both atoms.



c. The enzyme Superoxide Dismutase (this is a great band name, by the way), converts superoxides to hydrogen peroxide (H_2O_2).
In an acidic medium, hydrogen peroxide then is converted to water and oxygen gas. Write both the oxidation and reduction half-reactions for this second conversion of H_2O_2 to H_2O and O_2. What species is being oxidized? What species is being reduced?

$$\text{oxidation: } H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$

$$\text{reduction: } H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

$$\text{overall: } 2H_2O_2 \rightarrow 2H_2O + O_2$$

Hydrogen peroxide is being oxidized and reduced in this process

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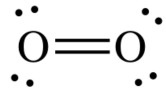
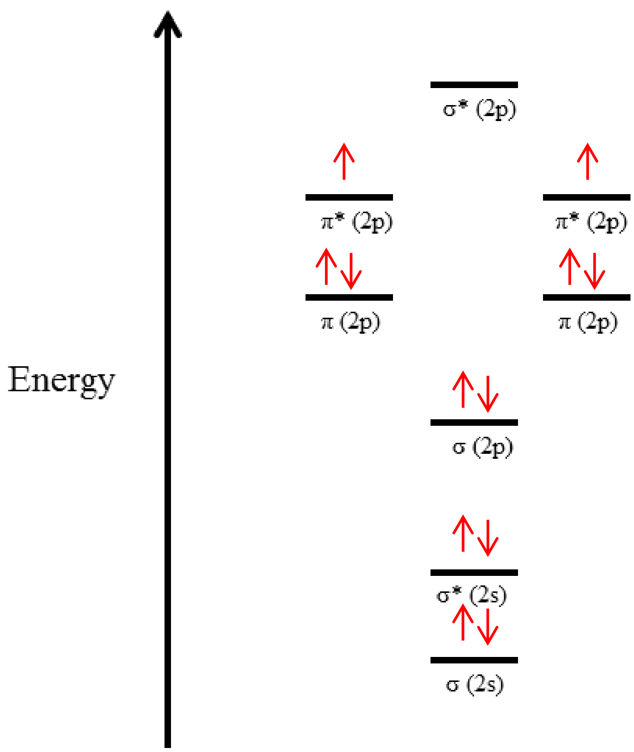
d. Oxygen gas is very reactive and is largely responsible for the rapid degradation of quality in coffee after it has been ground. The most-preferred Lewis structure for oxygen gas is shown below:



However, it does not explain experimental results in which O_2 is paramagnetic, meaning that it contains unpaired electrons. The diagram below depicts the organization of valence electrons in valence molecular orbitals (don't have to know exactly what these are, they follow the same rules as atomic orbitals) of the O_2 molecule. Use the diagram and your knowledge of electron filling rules to explain why O_2 is paramagnetic.



There are 12 total valence electrons in the oxygen gas molecule. Electrons fill from the lower energy orbitals (ground state rule), so the first 5 orbitals will receive an electron pair. The next two orbitals have the same energy (degenerate), which means that the remaining two electrons will be split between the two orbitals (Hund's rule). This means that oxygen gas has two molecular orbitals that only have a single unpaired electron, making it paramagnetic.

5. As a heterocyclic purine derivative, caffeine has interesting spectroscopic properties.

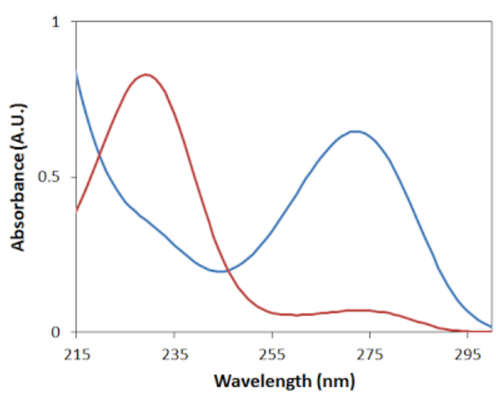
a. With an extinction coefficient of 875 $M^{-1}cm^{-1}$ at 270 nm, caffeine (MW = 194.19 g/mol) concentration can be determined by UV-vis spectrophotometry. One morning in the lab, you accidentally spill your coffee on the lab bench (even though your PI has told you several times NOT to drink coffee in the lab) and decide you want to see what the caffeine concentration is. You prepare a 1 mL sample in a cuvette and measure the absorbance to be 0.676 at 270 nm with a path length of 1 cm. If your cup of coffee was originally 300. mL, calculate the number of milligrams (mg) of caffeine in the cup?

$$A = \varepsilon bc$$

$$c = \frac{A}{\varepsilon b} = \frac{0.676}{875\ M^{-1}cm^{-1} \cdot 1\ cm} = 0.0007726\ M$$

$$\left(0.0007726 \frac{mol}{L}\right)(0.300\ L)\left(194.19 \frac{g}{mol}\right) = 45.00\ mg$$

b. The UV-vis spectrum obtained is shown below:



What does this suggest about the composition of your coffee? Use the spectrum to explain below, in 2 sentences or less.

The absorbance line with a peak around 270 nm is likely that of caffeine, but the additional peak indicates that the cup of coffee contains other compounds that absorb uv-vis light.

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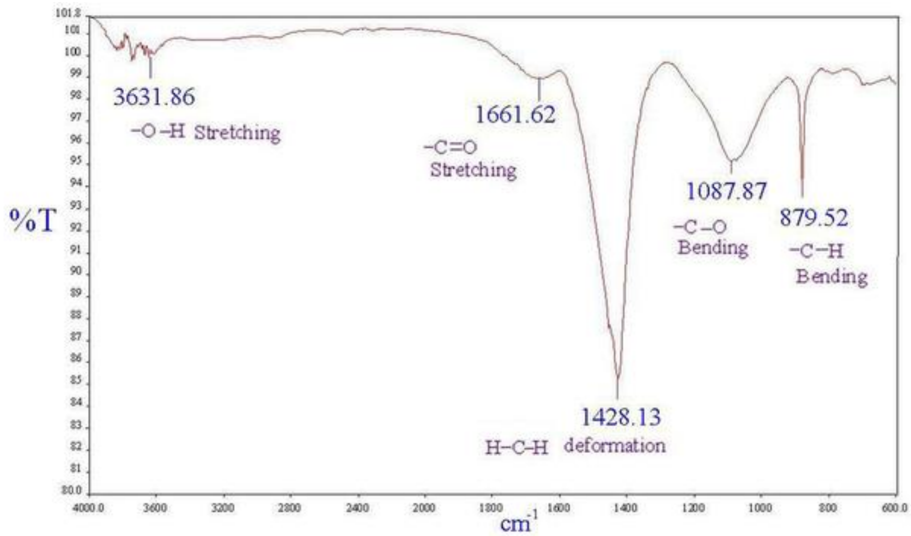
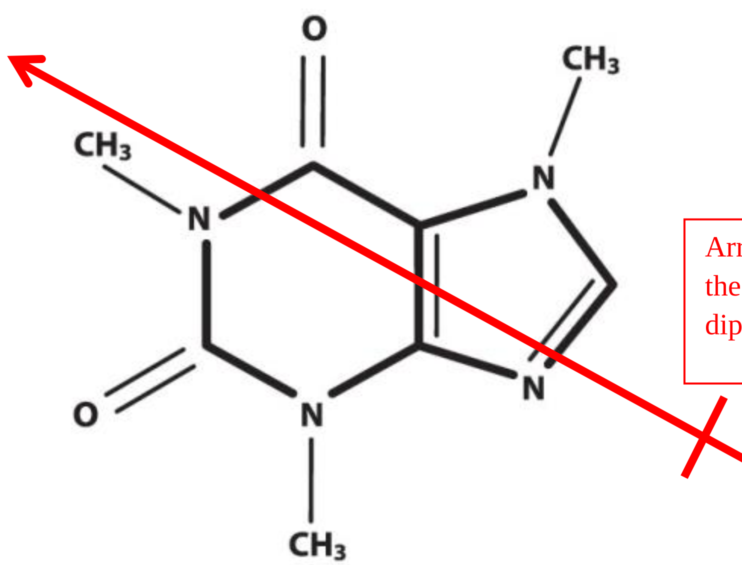
c. Each signal on the infrared (IR) spectrum of caffeine below represents a feature of the molecule based on wavenumber (the frequency of vibrational mode measured) and the intensity (larger peaks = stronger signal). IR depends on having a changing bond dipole to measure molecular features.
This, however, is out of the scope of this competition. We will consider the caffeine molecule as a whole. **On the structure of the caffeine molecule given below, please use an arrow to draw the general direction of the net dipole, indicating which end represents the negative end of the dipole.**



Infrared (IR) absorption spectrum of caffeine



Arrow is pointing towards the more negative end of the dipole.

Caffeine molecule structure

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d. Since IR spectroscopy measures the different vibrational modes (such as rocking, stretching, scissoring and more), it takes into account the strength of bonds. Which types of bonds are less likely to “vibrate?” Please circle an example on the caffeine molecule structure in part c.

Stronger bonds will take more energy to cause to vibrate, because more force is needed to get the atoms moving. Any of the double bonds circled on the diagram will count as full credit.