CLEANING EXAM

WUCT 2019

Grading Technology
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Instructions & Rules

Clearly write your name and ID number above. Your exam will not be graded if these cannot be read. Write darkly on your exam, and box your answers. Two students will work on this exam for 60 minutes; a copy of the test will be provided to each student, but only one copy of the exam will be graded. Only work written on the front pages of this copy will be graded. No electronics of any kind can be used during the exam, except for a non-programmable scientific calculator. Cell phones must be turned off, and watches must be removed. The time will be projected and/or announced in the exam rooms. Necessary equations, constants, and a periodic table will be provided. Explanations must be in complete sentences, diagrams must be labeled, and units must be shown throughout calculations for full credit. Partial credit will be awarded where appropriate. Proctors may answer procedural questions, but they will not answer content-specific problems. Cheating will NOT be tolerated. Refer to proctor(s) for further questions.

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Question 1 (26 points)
The alkaline battery is a ubiquitous device used to power many household cleaning devices like vacuum cleaners, Roombas, and much more. This question will give you an idea of how these simple batteries produce electric currents and provide the energy for these cleaning devices to work.

a. **(5 points)** The alkaline battery consists of MnO_2(s) (MW = 86.94 g/mol) at the positive electrode and Zn (s) (65.38 g/mol) powder at the negative electrode. At the positive electrode, a substance with molecular weight of 157.9 g/mol is generated while at the negative electrode, a substance with molecular weight of 81.4 g/mol is generated through the redox reaction. The electrodes are immersed in a potassium hydroxide solution, hence the name "alkaline." Write out the net reaction.

+1 for both statements
The MnO_2 is at the positive electrode, or cathode, so it must be getting reduced
The Zn is at the negative electrode, or anode, so it must be getting oxidized.

+1 for half-reaction
At the cathode, a substance with a molecular weight of 157.9 g/mol is produced through the reduction. Because in reduction reactions, the Mn and O will typically be in the products, we can use a linear combination of the masses of Mn and O to determine the identity of the reduction product.

54.93 g/mol * x + 16 g/mol *y = 157.9 g/mol
Solving the equation yields Mn_2O_3 (s)

Half reaction at cathode:
$2MnO_{2(s)} + H_2O_{(l)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)}$

+1 for half reaction
At the anode, a similar process can be carried out to determine that the final product is ZnO. Students may recognize the difference between the MW of the product and Zn is 16, hinting at an oxygen.

Half reaction at anode:
$Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$

+2 for net reaction or +5 if they got net reaction but went about it a different way.
Balancing and adding: Net reaction
$Zn_{(s)} + 2MnO_{2(s)} \rightleftharpoons ZnO_{(s)} + Mn_2O_{3(s)}$

b. **(5 points)** The free energy released at the negative electrode is -0.247 MJ while the free energy released at the positive electrode is -0.0289 MJ. What voltage does the battery produce between the two electrodes?

+1 point for statement of equation
$dG = -nFE_{ox/red}$

+1 point for reduction potential at cathode
At the cathode, reduction occurs, so we will be finding the E of reduction.
E_{red}=dG/(-nF) = -0.0289*10^6 J/(-2 mol e * 96485 C/mol e) = 0.15 V

+1 point for reduction potential at anode
At the anode, oxidation occurs, so we will be finding the E of oxidation
E_{ox}=dG/(-nF) = -.247*10^6 J/(-2 mol e * 96485 C/mol e) = 1.28 V

Each reaction increases the voltage of a charge carrier by the amounts above, so the total voltage of the battery is the sum,

+2 for correct answer
1.43 V

Or +5 overall if they went about it a different way and got the right answer

c. **(1 point)** Are both reactions spontaneous?

+1 all or nothing
Both reactions are spontaneous since the free energy releases are negative/the potentials of reaction are positive.

d. **(3 points)** Draw a diagram describing the flow of electrons and electrolytes in the battery.

Must include electrons going from anode to cathode, OH^- ions going to the anode, K^+ ions going to the cathode.
+1 for correct direction of electrons
+1 for correct direction of hydroxide ions
+1 for correct direction of potassium ions.

e. **(2 points)** Batteries run out of charge when the solid at one electrode is used up. How would you recharge the battery?

+2 all or nothing

Connect a power supply of at least 1.43 V with the negative electrode connected to the cathode and the positive electrode connected to the anode and run the electrons essentially in the opposite direction to regenerate the solids that were initially in the battery.

f. **(5 points)** If you started with a battery containing 10 moles of MnO_2 and 5 moles of Zn (s), how long would it take for the battery to die if you run it circuit with a vacuum cleaner that draws 10 A?
+1 for identifying electron stoichiometry
Looking at the half reactions, for every mol of electrons pushed through the circuit, 1 mol of MnO_2 is used up. For Zn, 1 mol of Zn is used up for 2 mol of electrons.
+1 for implicitly or explicitly arriving at this conclusion
So neither is technically the limiting reagent, both solids will run out when 10 moles of electrons have been pushed through the circuit.
+3 for calculation
The total charge that gets pushed in 10 moles
Q=n(e)*F = 10 mole e * 96485 C/mol = 964850 C
I = Q/t => t = Q/I = 964850 C/10A = 96485 seconds or 1600 minutes
Note: can still get full credit if they do the full calculation and don't necessarily state what the electron stoich./limiting reagent. They can "embed" those steps in the calculation. But if they get the calculation wrong, then give 1 point for the stoich and 1 point for the limiting reagent.

g. **(5 points)** Suppose you managed to poke a hole in the battery to allow all of the alkaline solution to escape and you replaced it with 100 mL of a 10 M solution of $HBrO_3$ (aq). Write the new redox reaction, and explain any changes you would notice in the battery's voltage. Note the following half reactions:

$$\mathbf{MnO_2\,(s) + 4\,H^+(aq) + 2\,e^- \rightarrow Mn^{2+}(aq) + 2\,H_2O\,(l)\ E_{red} = 1.23\ V}$$

$$\mathbf{BrO_3^-\,(aq) + 6\,H^+(aq) + 5\,e^- \rightarrow Br_2\,(l) + 3\,H_2O\,(l)\ E_{red} = 1.52\ V}$$

$$\mathbf{Zn^{2+}(aq) + 2\,e^- \rightarrow Zn\,(s)\ in\ acid\ E_{red} = -.76\ V}$$

+2 for recognizing this
Now you have 1 mol of BrO_3^- sitting in the battery. At the cathode, it is actually more likely to get reduced than MnO_2, so it will undergo the reduction. Also, note the reaction is now in an acidic medium, so the above half reactions that were given should be used.

To get the new overall reaction, the Zn half reaction should be flipped and added to the second half reaction to yield:

+2 for correct net equation

$5\ Zn\ (s) + 2\ BrO_3^-\ (aq) + 12\ H^+(aq) + 2\ Br_2\ (l) + 6\ H_2O\ (l) + 5\ Zn^{2+}(aq)$

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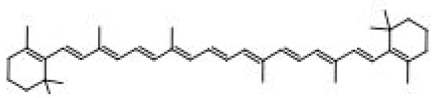
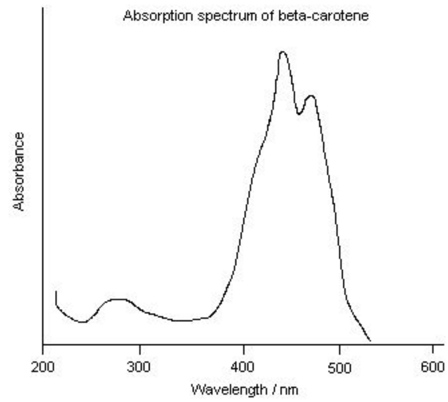
+1 for correct voltage
The voltage would be the difference of the reduction potentials, yielding 2.28 V
So the voltage, compared to the alkaline case would increase.

Question 2 (24 points)
On the left is beta carotene, a common organic molecule found in many foods (like carrots!) that can stain your teeth and make them appear orange. Pictured below is the absorption spectrum for beta carotene. Note: the max absorption lies at 410 nm.





a. **(3 points)** What color of light does beta carotene reflect?

+3 all or nothing
Orange, it's stated in the problem

b. **(3 points)** What color of light does beta carotene primarily absorb?

+3 all or nothing
Blue/green

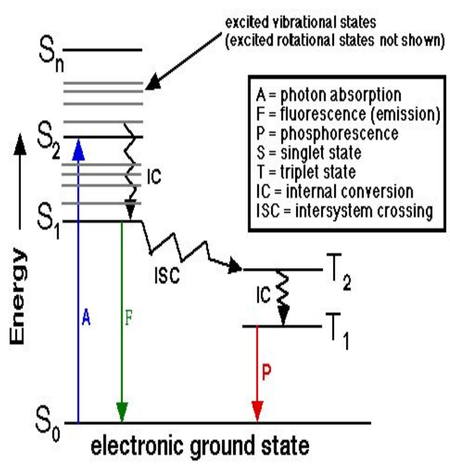
c. **(3 points)** Light is absorbed when a photon excites an electron in a particular orbital to a higher energy orbital. Looking at the spectrum's max absorption peak, what is the energy gap between the electron's pre-excitation orbital and the post-excitation orbital in eV?

+3 points all or nothing
E = hv = hc/wv = 1240 nm-eV/410 nm = 3.02 eV

d. **(3 points)** These energy gaps between orbitals that match well with the visible light spectrum arise because of the double bonds in beta carotene. Assuming that you cannot simply wipe the beta carotene off your teeth, how would you get rid of the color? Give your answer in terms of oxidation/reduction of carbons.

+3 points all or nothing
Reduce the carbons with a strong reducing agent. Carbons with double bonds are in a higher oxidation state that carbons with single bonds in beta carotene. Reducing the carbons would remove the double bonds and weaken the absorption intensity, getting rid of the color.

e. **(4 points)** Absorption spectroscopy is a very useful technique for determining the identity and structure of a compound through studying the various allowed transitions of electrons. Alongside absorption spectroscopy, many chemists use fluorescence spectroscopy, a technique that measures emitted light from a molecule after excitation. As you can see in the following diagram, the electron is excited by a photon to the S_2 "orbital level" through a process known as internal conversion (IC). IC occurs when some energy is converted into thermal energy before relaxing down to the S_1 "orbital level." It turns out that any excitation of an electron to levels above S_1 always results in this relaxation back to the S_1, where the electron then returns to the ground state (S_0) in a process called fluorescence, emitting a photon of energy corresponding to the energy gap between S_0 and S_1. Say photons of 500 nm, 600 nm, and 750 nm excite the ground state electron in some molecule. How many different wavelengths of fluorescence would you expect? Note: this is known as Kasha's rule.



+4 points all or nothing; only need to state a number of wavelengths
Based on the description in the problem, you would only expect one major fluorescence wavelength, or, more correctly, one profile of emission (weaker fluorescence transitions can occur, but all will be from the S_1). This is because irrespective of the initial absorption energy, the electron always makes its way back down to the S_1 before fluorescing, so you would really only see one major fluorescence peak corresponding to the $S_1 \rightarrow S_0$ transition.

f. **(8 points)** If I had a mixture of two unknown molecules that fluoresce, how could I use Kasha's rule to identify which compound is which? Assume you have access to the absorption spectrum of the mixture, the tools to generate any fluorescence emission spectrum, and references for the absorption spectra of every known fluorescent molecule known. *Hint*: fluorescence emission spectra are generated by exciting the molecule at a fixed wavelength (normally the wavelength at which absorbance of the specific molecule is at a maximum and at which nothing else with it is excited) and detecting all of the resulting fluorescence wavelengths from the molecule. Assume the two molecules do not have the same S_1-S_0 gap.

+3 for incorporating absorption spectrum of the mixture
+3 for stating that fluorescence emissions are needed
+2 for tying everything together
Based on the absorption spectrum, pick the peaks with the most absorbance and excite the mixture at that wavelength. Then measure the fluorescence from that excitation. If you only get one major peak, then you know you're only exciting one molecule in that mixture, and you can assign that peak in the absorption spectrum to one molecule. Do this for every peak and dissect the absorption spectrum. Then compare the dissections to known spectra and identify the compounds.

Question 3 (28 points)
Rust is a pesky reddish substance we find on many iron appliances. Growing up, you may have heard of the Coca-Cola method for cleaning off rust. In this question, we will explore why it works.

a. **(3 points)** Rust is a mixture of metal oxides, primarily Fe_2O_3. What would you expect if you try washing off the rust with water? Why?

   + 3 points all or nothing; must state a solubility argument
   Nothing would happen. Fe_2O_3 is insoluble so the water would just run off. If anything it may make it worse by providing a path for the redox reaction that creates rust to occur.

b. **(5 points)** The pH of coca cola is about 3.4. The main acid in the soda syrup is phosphoric acid. Draw the Lewis structure for fully protonated phosphoric acid.

   +5 all or nothing

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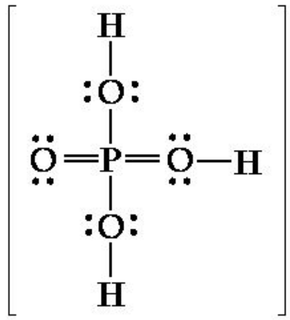


c. **(5 points)** What would be the most effective way to create the strongest possible 1 L buffer of phosphoric acid and monobasic phosphoric acid?

+5 points all or nothing; could use any strong base or also start with monobasic phosphoric acid and add a strong acid

Take 667 mL of phosphoric acid solution with any concentration, add 333 mL of NaOH of the same concentration.

d. **(3 points)** Phosphoric acid is the main active reagent in Coca-Cola. Write the balanced reaction between Fe_2O_3 and phosphoric acid and explain whether or not this would effectively solve the problem. (*Hint*: it is similar to a double displacement reaction).

+3 points all or nothing
$Fe_2O_3 + 2\ H_3PO_4 \rightarrow 2\ FePO_4 + 3\ H_2O$

e. **(5 points)** Calculate the enthalpy change and entropy change of the reaction at 298 K and 1 bar using the following information:

At 298 K: S(Fe_2O_3) = 87.404 J/mol K, S(H_3PO_4) = 150.77 J/mol K, S($FePO_4$) = 171.3 J/mol K, S(H_2O) = 69.95 J/mol K

At 298 K: H(Fe_2O_3) = 824.2 KJ/mol, H(H_3PO_4) = -1271.66 KJ/mol, H($FePO_4$) = -1888 KJ/mol, H(H_2O) = -285.83 KJ/mol

+2.5 for dH; 1 for eq, 1 for correct value of answer, 0.5 for correct units
dHrxn = 3(-285.93 KJ/mol) + 2(-1888 KJ/mol) – 2(-1271.66 KJ/mol) – 824.2 KJ/mol = -2914.67 KJ/mol rx

+2.5 for dS; 1 for eq, 1 for correct value of answer, 0.5 for correct units
dS = 3(69.95 J/mol K) + 2(171.3 J/mol K) – 2(150.77 J/mol K) – 87.404 J/mol K = 163.5 J/mol K

f. **(1 point)** Is the reaction spontaneous?

+1 point all or nothing; no need for explanation
Yes, with an increase in entropy and negative enthalpy, the reaction will have a negative change in free energy, making it spontaneous.

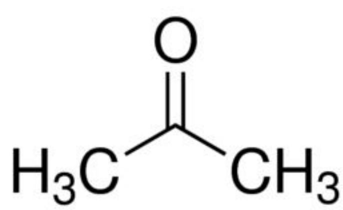
g. Can you definitively conclude that the reaction will occur quickly? If not, what extra information would you need?

+3 points; +1 for saying no; +2 for correct extra information
Spontaneity does not imply it will occur quickly. You would need the activation energy of the transition states to calculate the kinetics of the reaction. Spontaneous reactions like the conversion of diamond to graphite can occur very slowly because of the activation energy.

h. **(3 points)** If we increased the temperature of the reaction from standard temperature conditions, which way would the equilibrium shift?

+3 points all or nothing
Since the reaction is exothermic, increasing the temperature would shift the reaction to the left.

Question 4 (22 points)
Pictured below is a common cleaning agent known as acetone. If you've ever taken off nail polish or thinned paint, you've utilized acetone. This question will help you explore some chemical properties of acetone.



a. **(4 points)** Would you expect acetone to be miscible with water? If yes, what are the primary intermolecular forces contributing to this mixing?

+4 points; 2 for the first question, 2 for the statement of hydrogen bonds/dipole-dipole interactions must state both!
Yes, the CO dipole can interact through dipole-dipole interactions and form Hydrogen bonds with the water molecules.

b. **(4 points)** Would you expect acetone-acetone interactions or water-acetone interactions to be lower in energy? Why?

+4 points; 2 for correct prediction; 2 for the explanation
Water-acetone interactions, given that the CO dipole can work into hydrogen bond networks which are stronger than the dipole-dipole interactions of acetone-acetone interactions. Stronger bonds → lower energy.

c. **(4 points)** If an acetone-acetone interaction is broken in favor of forming a water-acetone reaction, what would be the sign of the enthalpy change?

+4 points all or nothing
It would be negative

d. **(5 points)** Would you expect the boiling point of acetone to be higher or lower than that of water? Why?

+5 points; 2 for correct prediction; 3 for explanation
The boiling point should be lower given that dipole-dipole interactions are easier to break than hydrogen bonds. It would therefore take less heat to free acetone molecules into the gas phase.

e. **(5 points)** Behind water, acetone is often referred to as the second universal solvent. What features make it so versatile as a solvent?

+5 points; some statement about intermolecular forces that make sense
It has a polar CO dipole but also hydrophilic methyl groups making it versatile in dissolving both polar and non polar substances.