

ENVIRONMENT

CHEMISTRY OF ENVIRONMENTAL SCIENCE WUCT 2018

This is the Environmental Science Topic Exam. A group of two students will work together on this exam. A copy of the test will be provided to each student, but only one copy of the exam will be graded. You may split up the exam between the two of you or solve the problems together however you wish. Make sure all work and solutions are in the exam packet that you submit for grading. No work on scrap paper will be graded. Please answer the questions in the space provided, or use the back of the same page if needed. You have 60 minutes to complete this exam. Cheating will NOT be tolerated.

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Team: _____

Team ID: _____

Student 1: _____

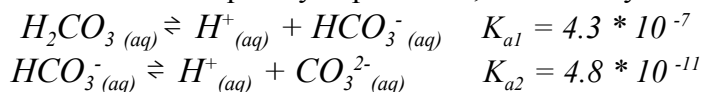
Student 2: _____

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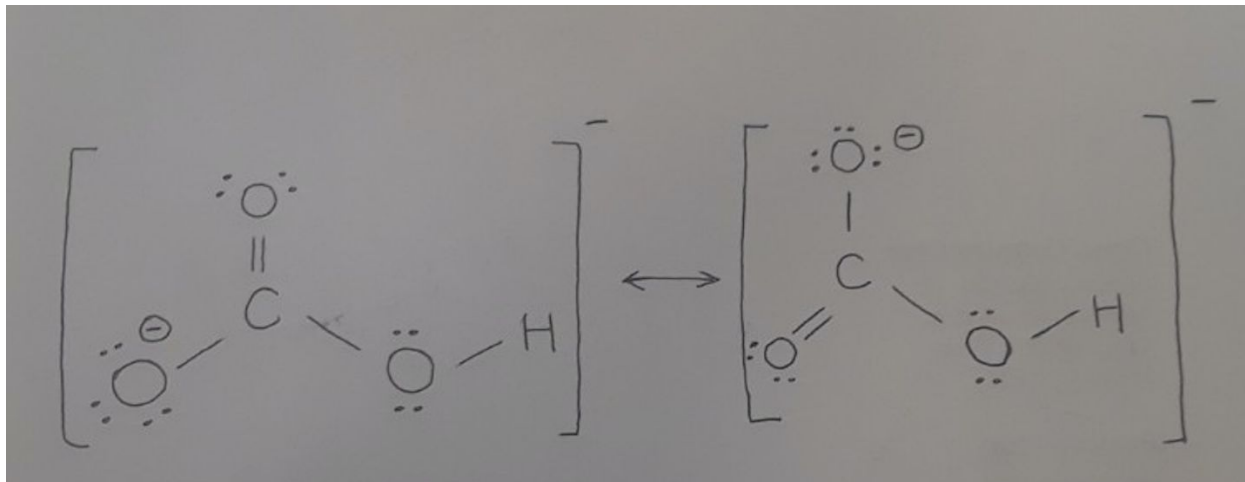
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Question 1: (18 points)

When carbon dioxide (CO_2) is absorbed by seawater (H_2O), a chemical reaction occurs that results in the formation of carbonic acid (H_2CO_3). This process is commonly known as ocean acidification. Carbonic acid can subsequently deprotonate, modeled by the equations:



- a. (5 points) Draw the most preferred Lewis structure of the HCO_3^- ion below. If equivalent resonance forms exist for the most-preferred Lewis structure, draw each of them. Circle your final answer(s).



1 point for correct connectivity, **3 points** for correct placement of bonds/charges (0.5 points deducted for each wrong formal charge, number of bonds. Don't need to show lone pairs), **1 point** for having correct resonance structure.

- b. (2 points) Write the equilibrium-constant expressions for the two reactions above. Make sure to clearly label K_{a1} and K_{a2} .

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

1 point for each correct equilibrium-constant expression

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- c. (9 points) Calculate the pH of a 0.3M diprotic carbonic acid (H_2CO_3) and the equilibrium concentrations of the species H_2CO_3 , HCO_3^- , CO_3^{2-} , and H^+ . Use 2 significant figures in your final answers. Show all your work to receive full credit.

<i>ICE Table #1</i>	$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$		
<i>Initial Concentration (M)</i>	0.3	0	0
<i>Change (M)</i>	-x	+x	+x
<i>Equilibrium Concentration (M)</i>	0.3 - x	x	x

$$K_a = 4.3 * 10^{-7} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{x*x}{0.3-x} \approx \frac{x*x}{0.3}$$

$$\text{Solve for } x \\ x = 3.59 * 10^{-4}$$

<i>ICE Table #2</i>	$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$		
<i>Initial Concentration (M)</i>	$3.59 * 10^{-4}$	$3.59 * 10^{-4}$	0
<i>Change (M)</i>	-y	+y	+y
<i>Equilibrium Concentration (M)</i>	$3.59 * 10^{-4} - y$	$3.59 * 10^{-4} + y$	y

$$K_a = 4.8 * 10^{-11} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{y * (3.59 * 10^{-4} + y)}{(3.59 * 10^{-4} - y)} \approx \frac{y * (3.59 * 10^{-4})}{(3.59 * 10^{-4})} = y$$

$$y = 4.8 * 10^{-11}$$

$$\text{Final concentration of } H^+ \text{ ions: } [H^+] = 3.59 * 10^{-4} + 4.8 * 10^{-11} = 3.59 * 10^{-4}$$

$$pH = -\log[H^+] = -\log[3.59 * 10^{-4}] = 3.4$$

Final Equilibrium Concentrations

H_2CO_3	HCO_3^-	CO_3^{2-}	H^+
$3.0 * 10^{-1} M$	$3.6 * 10^{-4} M$	$4.8 * 10^{-11} M$	$3.6 * 10^{-4} M$

2 points for using ICE Tables (If no ice tables but correct answer with reasonable work is shown, give 2 points)

2 points for setting up the problem correctly using equilibrium expressions from part B.

1 point awarded for having the correct final pH value. (sig figs are not counted for pH answer)

4 points awarded for having correct Final Equilibrium Concentrations (1 point deducted for each wrong answer, 0.5 points deducted for each right answer with wrong sig figs).

- d. (2 points) In 1-2 complete sentences, explain how the ocean is an excellent chemical buffer system.

SAMPLE ANSWER: A buffer is simply a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid. The presence of H_2CO_3 , a weak acid, with its conjugate base, HCO_3^- , allows ocean to be an excellent buffer system.

2 points are given if a weak acid-conjugate base pair is mentioned. Must show understanding of what a buffer is.

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Question 2: (19 points)

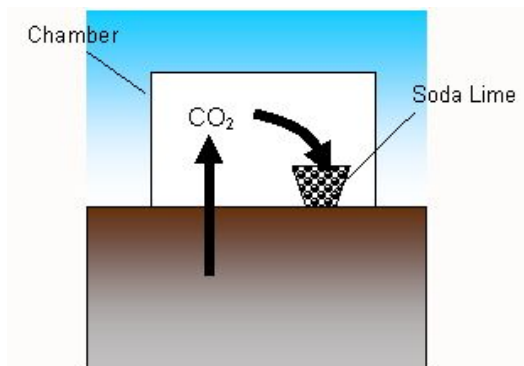
The carbon cycle is the cyclical movement of carbon atoms between the atmosphere and the biosphere.

- a. (2 points) Decomposition is an important part of the carbon cycle. Decomposers break down dead organic matter into carbon dioxide, water, and nutrients. This chemical process, termed soil respiration, is similar to combustion reactions that burn fuel. Write down the balanced chemical equation for the combustion of methanol (CH_3OH).



1 point for correct chemical reaction skeleton; **1 point** for correct stoichiometry numbers

- b. (2 points) Most of the organic carbon on this planet is found in the soil, with 1600 gigatons ($\text{Gt} = 10^9$ tons) stored in soils worldwide as compared to just 750 Gt found in the atmosphere, mainly in the form of CO_2 . If just 5% of the world's soil organic carbon pool was decomposed, by what percent would atmospheric CO_2 concentrations increase?



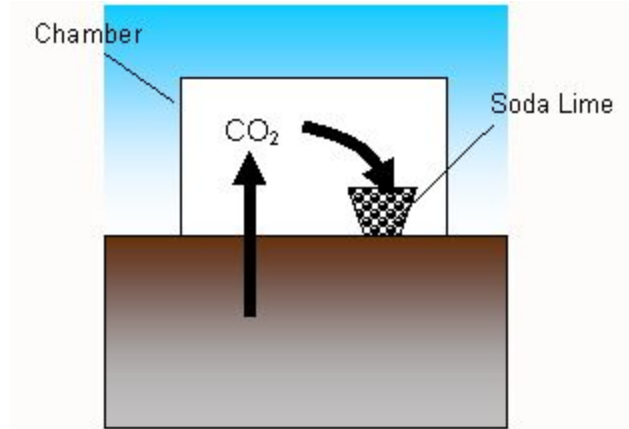
$$(1600) \times (.05) / (750) \times (100) = 10.7\%$$

2 points for correct answer (-1 if minor math error)

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- c. (3 points) The soda-lime method is one of the most common ways for measuring soil respiration. Soda lime is composed of a mixture of sodium hydroxide and calcium hydroxide; it's used to efficiently remove carbon dioxide from the atmosphere. The soda-lime method requires placing a pre-weighed, open dish of soda lime on the ground and covering it with a cylindrical chamber of known diameter. As CO_2 diffuses from the soil into the chamber, it is removed by the soda lime. After 24 hours, the soda lime dish is dried at 105°C to evaporate the water and weighed again. (see diagram of setup below)



https://www.esa.org/tiee/vol/v6/experiment/soil_respiration/description.html

You're doing an experiment on soil respiration on a certain plot of land, Area A. The diameter of the chamber you used was 18.0 cm. The initial mass of the soda lime dish was 5.000 grams. The final mass of the dish weighed after one day is 5.005 grams. Calculate the CO_2 emission rate (E), which is the rate at which soil CO_2 diffuses from a given area of ground. (Hint: units of E are $\frac{\text{grams of } \text{CO}_2}{\text{m}^2 * \text{day}}$)

$$\begin{aligned}\text{Soil CO}_2 \text{ Absorbed (g)} &= \text{Final Mass} - \text{Initial Mass} = 5.005 \text{ g} - 5.000 \text{ g} = 0.005 \text{ g} \\ E &= (\text{Soil CO}_2 \text{ Absorbed}) / (\text{Area of ground covered by chamber} * \text{Days of incubation}) \\ E &= 0.005 \text{ g} / ((.09^2\pi) \text{ m}^2 * 1 \text{ day}) \\ E &= 0.196 \text{ grams}/(\text{m}^2 * \text{day})\end{aligned}$$

1 point for finding mass of CO_2 , **1 point** for plugging into correct E equation, **1 point** for correct final answer with units

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d. In the soda-lime method, sodium hydroxide reacts with gaseous carbon dioxide to form water and sodium carbonate; calcium hydroxide undergoes a similar reaction with CO_2 to form calcium carbonate and H_2O . You are doing another soil respiration experiment on a different plot of land, Area B. You have a 2.00 g container of soda-lime that is 60.0% sodium hydroxide and 40.0% calcium hydroxide by weight. You leave it in a chamber (that covers an area of 1 m^2) on the ground for a week.

- i. (2 points) Write an equation for the reaction of sodium hydroxide with CO_2 and another equation for calcium hydroxide with CO_2 .



- ii. (2 points) The CO_2 emission rate for Area B is found to be $0.200 \frac{\text{grams of CO}_2}{\text{m}^2 * \text{day}}$. Based on this emission rate, calculate the amount of water (in grams) that is produced over the week if all of the CO_2 emitted was removed by the soda-lime.

$$0.2 \frac{\text{grams of CO}_2}{(\text{m}^2) * (\text{day})} \times (1 \text{ m}^2) \times (7 \text{ days}) \times \left(\frac{1 \text{ mol CO}_2}{44.01 \text{ g}}\right) \times \left(\frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol CO}_2}\right) \times \left(\frac{18.02 \text{ g}}{1 \text{ mol H}_2\text{O}}\right) = 0.573 \text{ g H}_2\text{O}$$

2 points for correct answer (-1 if minor math error)

- iii. (6 points) With the given setup, does your experimental design accurately measure the amount of carbon dioxide emission from the soil? Show all supporting work.(hint: what is the limiting reactant?)

$$2\text{g} \times 0.6 \times \left(\frac{1 \text{ mol NaOH}}{39.997 \text{ g}}\right) \times \left(\frac{1 \text{ mol H}_2\text{O}}{2 \text{ mol NaOH}}\right) \times \left(\frac{18.02 \text{ g}}{1 \text{ mol H}_2\text{O}}\right) = 0.270 \text{ g H}_2\text{O}$$

2 points for g of H_2O from NaOH (does not need to be in grams, -1 if minor math error)

$$2\text{g} \times 0.4 \times \left(\frac{1 \text{ mol Ca(OH)}_2}{74.093 \text{ g}}\right) \times \left(\frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol Ca(OH)}_2}\right) \times \left(\frac{18.02 \text{ g}}{1 \text{ mol H}_2\text{O}}\right) = 0.195 \text{ g H}_2\text{O}$$

2 points for g of H_2O from Ca(OH)_2 (does not need to be in grams, -1 if minor math error)

$$0.270\text{g} + 0.195\text{g} = 0.465 \text{ g of H}_2\text{O} < 0.573 \text{ g H}_2\text{O}$$

1 point for combining the NaOH and Ca(OH)_2 answers to compare with answer from part ii.

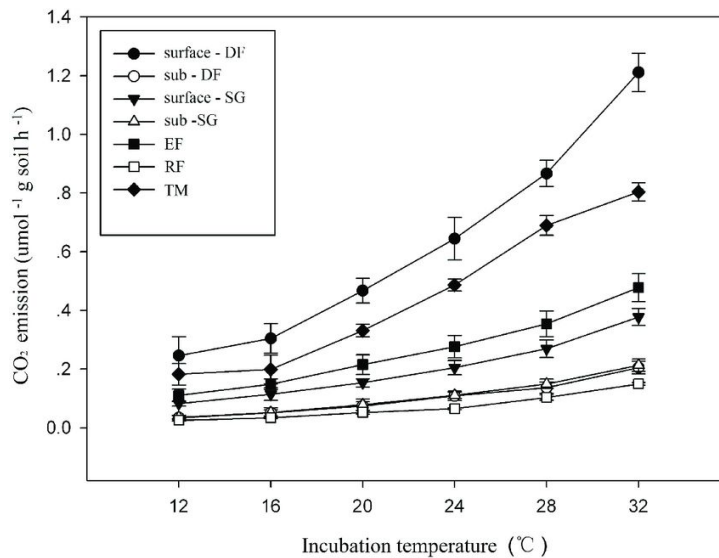
Since CO_2 was not the limiting reactant, the experimental design did not accurately measure the amount of CO_2 emission from the soil.

1 point for answering question correctly based on their work

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- e. (2 points) Since decomposition is a biological process carried out by enzymes in bacteria and fungi, it is temperature sensitive. Below is a graph of soil CO₂ emission rates of different soil conditions at various temperatures. Based on this information, determine whether global warming will increase or decrease the production of CO₂ gases. Circle your answer and briefly explain your choice in 1-2 sentences.



<https://www.researchgate.net/publication/320821816/figure/fig1/AS:556502097371136@1509691847128/fig-1-Relationship-between-SOC-decomposition-rates-and-incubating-temperatures-for-soil.png>

Increase

Decrease

As temperatures increase due to global warming, soil decomposition rates will increase. This will increase the amount of CO₂ in the atmosphere and thus, increase the greenhouse effect.

2 points for correct answer and justification

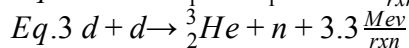
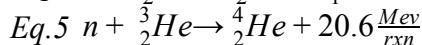
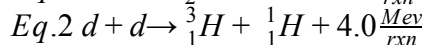
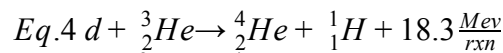
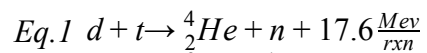
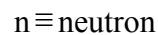
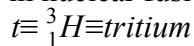
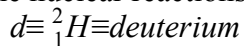
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Question 3: (18 points)

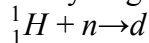
Fusion is a powerful potential energy source. Unlike nuclear fission it does not produce nearly the same amount of nuclear waste and holds the potential for producing more energy.

Here are some nuclear reactions of interest in nuclear fusion:

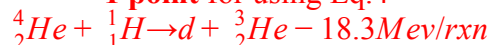


Given: 1 ev = 1.6x10⁻¹⁹ J

- a. (6 points) From this data, calculate the energy released (in Mev) by the formation of deuterium from the neutron capture of Hydrogen-1.

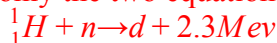


1 point for using Eq.4



1 point for using Eq.5

1 point for using only the two equations above in answer



ANSWER: 2.3 Mev

2 points for having the right magnitude (-1 if minor math error)

1 point for having the right sign

- b. (4 points) One of the reactions of great interest to fusion is $d + t \rightarrow {}^4_2\text{He} + n + 17.6 \frac{\text{Mev}}{\text{rxn}}$. Calculate the energy released from reacting 1 mole of deuterium and tritium in units of kJ.

$$17.6 \frac{\text{Mev}}{\text{rxn}} * \frac{6.02 * 10^{23} \text{rxn}}{1 \text{ mole rxn}} * 1 \text{ mole rxn} = 1.06 * 10^{25} \text{Mev}$$

2 points for having the correct energy amount in Mev (not required to show the actual answer in Mev-- instead look for correct work, -1 if minor math error)

$$1.06 * 10^{25} \text{Mev} * \frac{1 * 10^6 \text{ev}}{1 \text{Mev}} * \frac{1.6 * 10^{-19} \text{J}}{1 \text{ev}} * \frac{1 \text{KJ}}{1000 \text{J}} = 1.7 * 10^9 \text{KJ}$$

ANSWER: 1.7 x 10⁹ kJ

2 points for correct energy in KJ (-1 if wrong units/minor math error)

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- c. (8 points) Coal is an important source of energy in the world. Consumption in 2013 was 8,701,070 U.S tons (around 7,900,000,000 kg) Its primary chemical reaction is as follows:



Assuming that coal is pure carbon, calculate how many kg of deuterium and tritium you would need to burn in order to replace the current world coal energy output in a year. If you didn't get an answer for part b, you can use the incorrect value of 1×10^8 kJ per mole.

$$7.9 * 10^9 Kg * \frac{1000g}{1Kg} * \frac{1 mole C}{12g} * \frac{394 KJ}{1 mole C} = 2.59 * 10^{14} KJ$$

2 points for correct energy amount (not required to show the actual answer in KJ-- instead look for correct work, -1 if minor math error)

$$2.59 * 10^{14} KJ * \frac{1 mole tritium or deuterium}{1.7 * 10^9 KJ} = 1.53 * 10^5 moles$$

2 points for correct mole amount (not required to show the actual answer in moles-- instead look for correct work, -1 if minor math error)

ANSWER:

Kg deuterium:

$$1.53 * 10^5 moles * \frac{2 grams d}{1 mole d} * \frac{1 kg}{1000} = 305 Kg d$$

2 points for correct answer in Kg (-1 if wrong units/minor math error)

Kg tritium

$$1.53 * 10^5 moles * \frac{3 grams t}{1 mole t} * \frac{1 kg}{1000} = 458 Kg t$$

2 points for correct answer in Kg (-1 if wrong units/minor math error)

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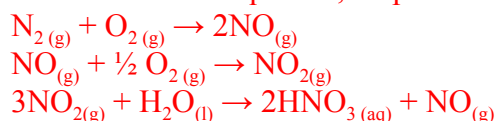
Question 4: (20 points)

Acid rain (or acid deposition) is defined by the United States Environmental Protection Agency (EPA) as “any form of precipitation with acidic components, such as sulfuric or nitric acid that fall to the ground from the atmosphere in wet or dry forms.”

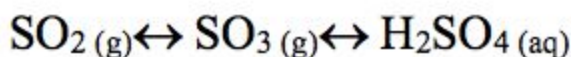
- a. (3 points) Nitrous oxide is formed during lightning storms when the nitrogen and oxygen in the atmosphere interact with one another. Firstly, nitrogen gas and oxygen gas combine to form nitrous oxide. Then, nitrous oxide combines with oxygen gas to form nitrogen dioxide, which can then react with water to form nitric acid (which contributes to about 25% of the acidity in acid rain) and nitrous oxide. Write balanced equations for all three steps outlined above.

(phases are not required for correct answer)

1 point for each correct equation, no partial credit



- b. (7 points) The other 75% of the acidity in acid rain can be attributed to sulfuric acid. The process in which sulfuric acid is created from sulfur dioxide is seen in the equation below.



Find the mole fraction and molarity of SO_2 , given that a mole of air fills up a 50.0 L container, and the starting $[\text{SO}_2]$ is 2.0ppm.

More important information:

- the density of air is $1.22 \times 10^{-6} \text{g/mL}$
- the molar mass of SO_2 is 64.06g/mol .
- $1 \text{ ppm} = \frac{\text{mass of component}}{\text{total mass}} \times 10^6$

$$\text{Mass of air} = 50.0 \text{ L} * \frac{1.22 * 10^{-6} \text{g}}{\text{mL}} * \frac{1000 \text{mL}}{1 \text{L}} = 0.061 \text{ g of air}$$

1 point to find mass of air

$$\text{Mass of SO}_2 = \frac{2.0 \text{ g SO}_2}{10^6 \text{ g air}} * 0.061 \text{ g air} = 1.22 * 10^{-7} \text{ g SO}_2$$

1 point to find mass of SO_2

$$\text{Moles of SO}_2 = 1.22 * 10^{-7} \text{ g SO}_2 * \frac{1 \text{ mol SO}_2}{64.06 \text{ g SO}_2} = 1.904 * 10^{-9} \text{ mol SO}_2$$

1 point to find moles of SO_2

Mole fraction = moles of component / total moles

$$= \frac{\text{mol SO}_2}{\text{mol SO}_2 + \text{mol air}} = \frac{1.904 * 10^{-9} \text{ mol SO}_2}{1 \text{ mol air} + 1.904 * 10^{-9} \text{ mol SO}_2} = 1.904 * 10^{-9}$$

2 points for correct mole fraction

$$\text{Molarity of SO}_2 = \frac{\text{mol SO}_2}{\text{L of air}} = \frac{1.904 * 10^{-9} \text{ mol SO}_2}{50.0 \text{ L air}} = 3.809 * 10^{-11} \text{ M}$$

2 points for correct molarity

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- c. (2 points) If the concentration of H_2SO_4 in the equation from part (b) were to increase, in which direction would the equilibrium shift? Explain briefly in one sentence why the equilibrium shifts to that direction.

2 points for correct direction and explanation. Must show understanding of Le Châtelier's Principle.

Equilibrium would shift to the left. Le Châtelier's Principle states that if an external stress is applied at chemical equilibrium, then the equilibrium position will change in such a way to counteract the effects of that stress. Using $Q = [\text{products}]/[\text{reactants}]$, Q would now be $> K$, so the reverse reaction is favored.

- d. Acid rain not only ruins trees, but also has been proven to deplete soil calcium, which in turn further stunts tree growth. Calcium can help the growth of trees by neutralizing soil acidity. As a result, compounds such as calcium carbonate (lime), as well as calcitic limestone, are often used as part of fertility programs.
- i. (4 points) Calcium carbonate can react with sulfuric acid to form calcium sulfate, carbon dioxide, and water. Calcium sulfate is only slightly soluble, whereas a compound like barium sulfate is insoluble. Determine the solubility (g/L) of CaSO_4 , given that $K_{\text{sp}}(\text{CaSO}_4)$ is 4.93×10^{-5} , and the molar mass of CaSO_4 is $136.14 \text{ g} \cdot \text{mol}^{-1}$.

	$\text{CaSO}_{4(s)}$	$\text{Ca}^{2+}_{(aq)}$	$\text{SO}_4^{2-}_{(aq)}$
I	excess	0	0
C		+s	+s
E		s	s

$$K_{\text{sp}}(\text{for } \text{CaSO}_4) = 4.93 \times 10^{-5} = s^2, s = 7.021 \times 10^{-3} \text{ mol/L}$$

$$\text{Solubility} = \frac{7.021 \times 10^{-3} \text{ mol}}{\text{L}} * \frac{136.14 \text{ g}}{\text{mol}} = 0.956 \text{ g/L}$$

1 point for using ice table (if no ice tables but correct answer with reasonable work is shown, give 1 point)

1 point for setting up problem correctly using K_{sp} value

1 point for correct solubility

1 point for correct units of g/L

- ii. (4 points) 500 mL of 0.05M H_2SO_4 and 500mL of 0.12M $\text{Ca}(\text{OH})_2$ are mixed in a container. Using the same reaction as part i, determine which direction the reaction will proceed. Assume H_2SO_4 and $\text{Ca}(\text{OH})_2$ completely dissociates.

$$0.500 \text{ L} * 0.05 \text{ M } \text{H}_2\text{SO}_4 = 0.025 \text{ mol } \text{SO}_4^{2-}$$

$$0.500 \text{ L} * 0.12 \text{ M } \text{Ca}(\text{OH})_2 = 0.06 \text{ mol } \text{Ca}^{2+}$$

Immediately after mixing (before reaction): $[\text{Ca}^{2+}] = 0.06\text{M}$, and $[\text{SO}_4^{2-}] = 0.025\text{M}$

$Q = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (0.06\text{M})(0.025\text{M}) = 1.5 \times 10^{-3} > K_{\text{sp}}$, so reaction will proceed in the reverse direction (aka precipitate).

1 point for using correct Ca^{2+} and SO_4^{2-} concentrations

2 points for finding Q correctly

1 point for correct direction based on work

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Question 5: (20 points)

The following questions will involve the analysis of three of the six “criteria air pollutants” which are found all over the United States and can cause damage to physical health, property, and the environment.

- a. (6 points) The first criteria air pollutant you will be evaluating is sulfur dioxide (SO_2). This molecule is just one of a group of gases called sulfur oxides (SO_x) where the x can be various numbers. Sulfur dioxide can undergo a chemical reaction with oxygen and be converted into sulfur trioxide which can be a contributor to acid rain. For simplification we can assume this reaction to be first order.

If the reaction has a first order rate constant at 25°C that is twice its value at 0°C , what is the activation energy of the reaction? Give answer in ($\text{kJ} \cdot \text{mol}^{-1}$).

Potentially Useful Information

Arrhenius Equation : $k = Ae^{-\frac{E_a}{RT}}$

A = Frequency Factor (constant)

E_a = Activation Energy

k = rate constant

T = Temperature

R = 8.314 J/mol-K

Natural Log/ e^x Rules:

$\ln(e^x) = x$

$e^{x-y} = e^x/e^y$

$$k_{25^\circ\text{C}} = 2k_{0^\circ\text{C}}$$

$$\frac{k_{25^\circ\text{C}}}{k_{0^\circ\text{C}}} = 2 = \frac{Ae^{-\frac{E_a}{R(25^\circ\text{C})}}}{Ae^{-\frac{E_a}{R(0^\circ\text{C})}}} = e^{-\frac{E_a}{R}\left(\frac{1}{25^\circ\text{C}} - \frac{1}{0^\circ\text{C}}\right)}$$

$$\ln(2) = -\frac{E_a}{R}\left(\frac{1}{25^\circ\text{C}} - \frac{1}{0^\circ\text{C}}\right)$$

$$E_a = -\frac{\ln(2) \cdot R}{\left(\frac{1}{298.15\text{K}} - \frac{1}{273.15^\circ\text{C}}\right)}$$

$$E_a = 18750 \text{ J/mol} = 18.75 \text{ kJ/mol}$$

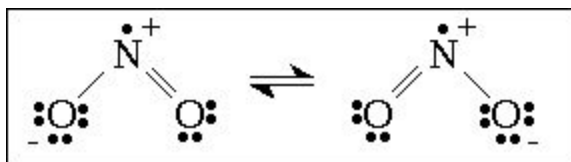
1 point for $k_{25} = 2k_0$ relationship, **1 point** for attempting to use $\ln()$ function, **1 point** for correct E_a equation, **2 points** for correct answer with correct units. (1 point deduction for correct answer with incorrect units)

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ENVIRONMENT

b. The second criteria air pollutant is nitrogen dioxide (NO_2). This is a highly reactive molecule and is primarily introduced to the air from the burning of fuel. In addition to nitrogen dioxide being harmful to health when inhaled it is also known to react and form other criteria air pollutants such as particulate matter and tropospheric ozone.

i. (3 points) Draw the most stable lewis structure for nitrogen dioxide making sure to include all non-zero formal charges and resonance structures if applicable.



1 point for correct connectivity. **1 point** for correct resonance. **1 point** for correct formal charges.

ii. (3 points) Is the O-N-O bond angle in nitrogen dioxide greater than, less than or equal to the O-S-O bond angle in sulfur dioxide? Please explain your choice in 1-2 sentences.

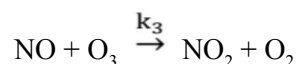
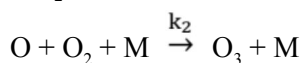
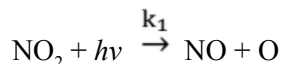
Sulfur dioxide has two unpaired electrons on the central sulfur atom which cause more repulsion than the 1 unpaired electron on nitrogen in nitrogen dioxide. The sulfur dioxide O-S-O bond angle is less than the O-N-O bond angle.

1 point for correct answer. **2 points** for correct explanation. Must mention number of unpaired electrons on central atom relating to repulsion (VSEPR). No Lewis structure for SO_2 is required, but it is probably necessary)

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ENVIRONMENT

- c. The third “criteria air pollutant” that you will be analyzing is tropospheric ozone. This pollutant is not emitted directly into the air, but is created via the reactions between oxides of nitrogen, volatile organic compounds, and sunlight. A starting point for examining the “bad” ozone dynamics in the troposphere is the following mechanism which includes the three elementary reactions: The k values are rate constants, M represents particulate matter and $h\nu$ is sunlight.



- i. (6 points) Assume that the atomic oxygen (O) and ozone (O_3) are consumed as fast as they form. This is called a pseudo steady state approximation (PSSA). Derive a relationship for $[\text{O}_3]$ in terms of the rate constants, NO and NO_2 concentrations. This expression is called the Leighton relationship.

$$d[\text{O}]/dt = k_1[\text{NO}_2] - k_2[\text{O}][\text{O}_2][\text{M}] = 0 \rightarrow [\text{O}] = k_1[\text{NO}_2] / k_2[\text{O}_2][\text{M}]$$

$$d[\text{O}_3]/dt = k_2[\text{O}][\text{O}_2][\text{M}] - k_3[\text{NO}][\text{O}_3] = 0 \rightarrow [\text{O}_3] = k_2[\text{O}_2][\text{O}][\text{M}] / k_3[\text{NO}]$$

$$[\text{O}_3] = k_2[\text{O}_2][\text{O}][\text{M}] / k_3[\text{NO}] = (k_1 k_2 [\text{O}_2][\text{M}][\text{NO}_2]) / (k_3 k_2 [\text{O}_2][\text{M}][\text{NO}])$$

$$[\text{O}_3] = k_1[\text{NO}_2] / k_3[\text{NO}]$$

1 point for attempting to use rates to describe the quantity of O and O_3 , **1 point** for setting $d[\text{O}_3]/dt$ and $d[\text{O}]/dt$ relationships = 0; **1 point** for correct $[\text{O}]$ relationship, **1 point** for correct $[\text{O}_3]$ relationship, **2 point** for correct simplification

- ii. (2 points) A key assumption that the Leighton relationship makes is that NO only reacts with O_3 when in reality it can react with other molecules. Would you expect the Leighton relationship to overpredict or underpredict the concentration of ozone in the troposphere? Circle one of the options below and give a 1-2 sentence justification.

Overpredict

Underpredict

There is competition with the third reaction and thus the Leighton relationship predicts $[\text{NO}]$ to be higher than it really is and since it is in the denominator makes the $[\text{O}_3]$ lower than it actually is.

2 points for correct answer with reasonable explanation

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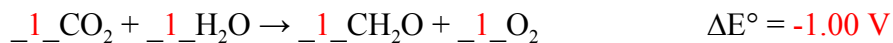
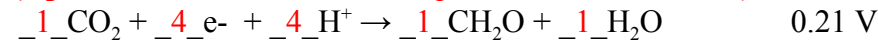
ENVIRONMENT

Question 6: (5 points)

- a. (4 points) Micro-organisms control the redox status of soils by reducing carbon to store energy, and oxidizing carbon to release energy.

Balance the following redox reactions and find the ΔE .

(2 points: .5 for each chemical equation + .5 for the ΔE°)



Is the above reaction spontaneous or not? Why?

Not spontaneous b/c negative delta E

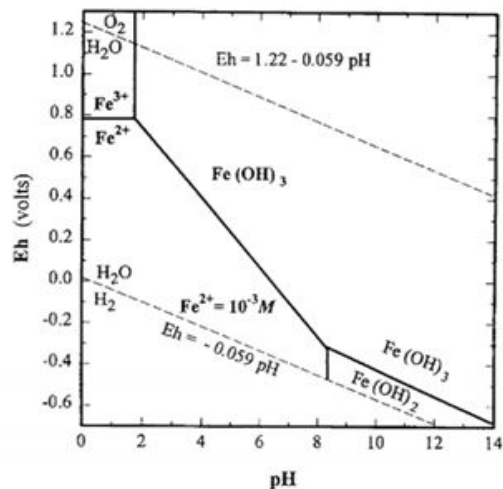
(1 point)

Cellular respiration releases energy by oxidizing carbon. What is the ΔE° of this reaction?

$\Delta E^\circ = 1.00 \text{ V}$

(1 point)

- b. (1 point) Using the Nernst equation, a relationship between the reaction potential and pH of various soil reactions can be found. This can be visualized in a Pourbaix diagram shown below. (Eh is another way of denoting ΔE)



At a pH of 2, the ferric ion is stable at potentials (Eh) above... (Circle correct answer)

- (a) -0.2 V
- (b) 0.0 V
- (c) 0.2 V
- (d) 0.4 V
- (e) 0.8 V

1 point for correct answer

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