Name (Last, First): ____________________ ID Number: ________________________

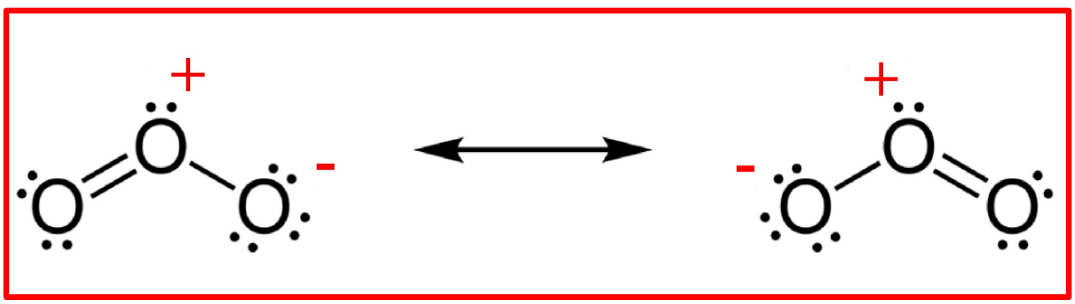
Sample Question Solutions for the Chemistry of Environment Topic Exam

1. The earth's stratosphere contains a region of high ozone (O3) concentration called the ozone layer. The ozone layer is very important in protecting the earth and its organisms from the harmful UV radiation of the sun. It does so by absorbing ultraviolet light and undergoing various chemical reactions, thus preventing the rays from passing through the Earth's atmosphere. However, due to certain man-made pollutants, it was found that the amount of ozone was depleting at an alarming rate.

a. Ozone is produced by the combination of an oxygen atom (O) with oxygen gas (O2) through the following reaction:

$$O + O_2 \rightarrow O_3 \qquad \text{(Equation 1)}$$

Using this information and the knowledge of the charge of ozone, draw two resonance structures for the molecule ozone (O3).



b. Oxygen radicals, aka oxygen atoms, are formed by the following reactions:

$$O_2 \rightarrow 2\,O \qquad \text{(Equation 2)}$$
$$O_3 \rightarrow O + O_2 \qquad \text{(Equation 3)}$$

Photolysis, or photodissociation, is the chemical reaction in which the bonds in a chemical compound are broken down by the absorption of high-energy photons. The equations 2 and 3 can thus be modified:

$$O_2 + h\nu \rightarrow 2\,O \qquad \text{(Equation 2.5)}$$
$$O_3 + h\nu \rightarrow O + O_2 \qquad \text{(Equation 3.5)}$$

Considering this information, along with the function of the ozone layer and the structure of oxygen radicals (O), explain why there is a high concentration of ozone in the ozone layer as compared to on the earth's surface. Use chemical reactions in your explanation if appropriate.

Oxygen radicals are very unstable (incomplete octet) thus have low concentrations normally. However, in the high atmosphere regions aka the ozone layer, there is more UV radiation and the following reactions can occur, generating more oxygen radicals:

$O_2 + h\nu \rightarrow 2\ O$ (Equation 2.5)
$O_3 + h\nu \rightarrow O + O_2$ (Equation 3.5)

These oxygen atoms can then react and form ozone:

$O + O_2 \rightarrow O_3$ (Equation 1)

c. Before the oxygen atom can react with an O_2 molecule and make ozone, it must lose some energy and go to a more stable electronic configuration. It does this by colliding with another molecule, which will leave with excess kinetic energy (E_K).

i. (1) Write the initial electronic configuration of unimolecular oxygen and (2) the more stable electronic configuration of oxygen following its collision with another molecule and subsequent energy loss.

Oxygen goes from:

$[He]2s^2 2p_x^2 2p_y^2 2p_z^0$ to $[He]2s^2 2p_x^2 2p_y^1 2p_z^1$

Minimize electron-repulsion

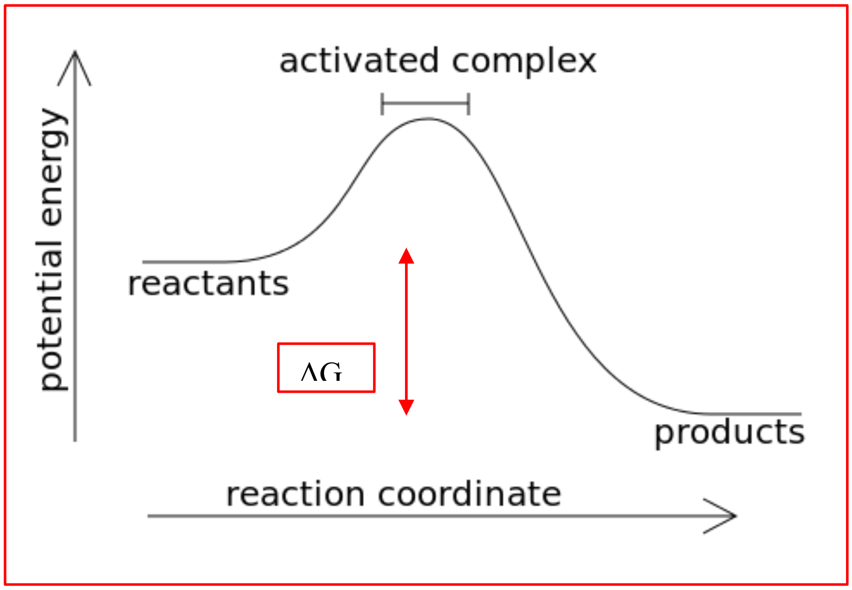
ii. Equation 1 from above of ozone production can then be modified by the following addition

$$O + O_2 \rightarrow O_3 + E_K$$

where E_K stands for the excess energy of the reaction which is converted to kinetic energy of molecules, or heat. (1) Is this reaction endothermic or exothermic? (2) Draw reaction coordinate diagram of this reaction. Label the energies of the reactants, the energies of the products, and ΔG clearly on the diagram.

Name (Last, First): ______________________ ID Number: __________________________

Exothermic



d. The concentration of ozone in the stratosphere is constant. This means that there is a dynamic equilibrium between the rate of ozone formation and the rate of ozone destruction. The reaction mechanism, named the Chapman Cycle, is categorized by the following four steps:

1. $O_2 \rightarrow 2\ O$
2. $O_3 \rightarrow O + O_2$ (fast)
3. $O + O_2 \rightarrow O_3$ (fast)
4. $O + O_3 \rightarrow 2\ O_2$ (slow)

i. Manmade pollution has increased the rate of ozone destruction relative to formation, causing a decrease in overall ozone levels. The proposed reaction mechanism for ozone destruction is defined by steps 2-4 above. Using those equations, write the overall reaction for the destruction of ozone.

Step 2 and 3: $O_3 \leftrightarrow O_2 + O$
Step 4: $O_3 + O \rightarrow 2\ O_2$

Overall reaction is $2\ O_3\ (g) \rightarrow 3\ O_2\ (g)$

ii. Determine the rate law for ozone destruction. What order of reaction is this?

Step 2 and 3: $O_3 \leftrightarrow O_2 + O$ (equilibrium)

$r_1 = k_{1+}[O_3] - k_{1-}[O_2][O\cdot] = 0$

Solve for

$[O\cdot] = (k_{1+}/k_{1-})[O_3]/[O_2]$

and plug into

Step 4: $O_3 + O \rightarrow 2\ O_2$ (rate-determining step)

$r = r_2 = k_2[O_3][O\cdot]$

$r = k[O_3]^2/[O_2]$ **with $k = k_2(k_{1+}/k_{1-})$**

overall first order reaction

e. Ozone depletion is caused by chemicals found in refrigerators and air conditioners which are called chlorofluorocarbons (CFCs). They contain chlorine atoms which are released from the compounds after encountering UV radiation. These Cl atoms (aka Cl radicals) can then destroy ozone molecules via the following reactions:

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O. \rightarrow Cl + O_2$$

i. Write the overall reaction of this reaction mechanism. Which species acts like a catalyst?

$O_3 + O. \rightarrow 2\ O_2$

Cl radical is a catalyst.

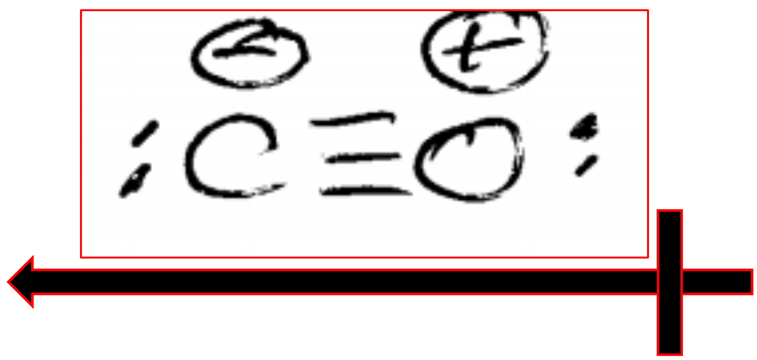
ii. This reaction can also occur with other halogen radicals, such as bromine which is actually more efficient at destroying ozone than Cl. However, on the other hand, fluorine atoms are not very efficient at destroying ozone. Using your prior knowledge and the information provided in this question, explain why this may be. It is important to note that Cl atoms can be removed from the atmosphere through reactions that form reservoir species such as hydrogen chloride (HCl).

F atoms are removed more efficiently from the atmosphere since they react to form strongly bound HF in the Earth's stratosphere. The other reservoir species, such as HCl and HBr, have weaker bonds. Thus, Cl and Br radicals are more likely to exist in the atmosphere than F radicals.

2. In 2015 about 29% of the United States energy came from the combustion of natural gas. Overall natural gas is composed of a range of hydrocarbons, while containing trace amount of nitrogen, carbon dioxide, and many other compounds. With a much higher energy value than other substitutes including coal many see the use of natural gas as a good transition towards a more renewable energy source. However, natural gas is still known to have negative impacts on the environment releasing large quantities of CO_2 and carbon monoxide (CO) into the atmosphere.

a. Carbon monoxide is a colorless, odorless gas that is toxic to humans in concentrations above 35ppm and a constant product of incomplete combustion.

i. Draw the most stable Lewis dot structure of this molecule. Resonance and non-zero formal charges must be included for full credit.

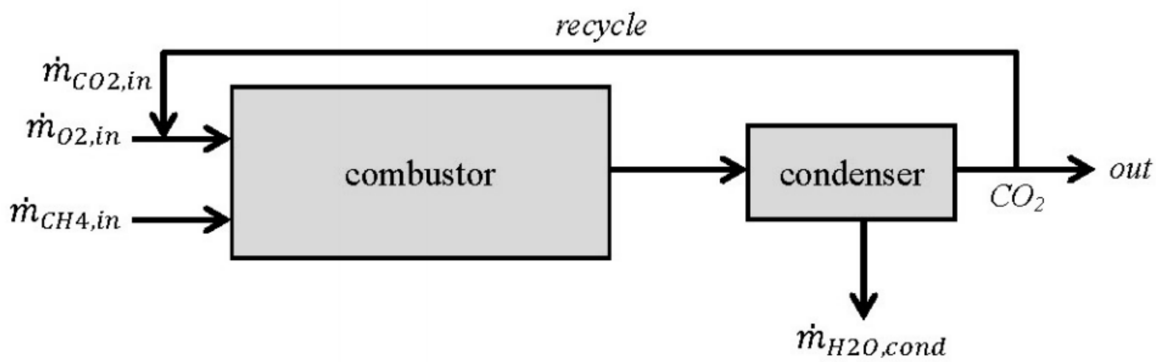


ii. On the Lewis structure above use an arrow to draw the general direction of the net dipole, indicating which end represents the negative end of the dipole.

iii. Explain if the Lewis structure you drew agree with an electronegativity argument?

No this does not agree with electronegativity since the oxygen is more electronegative than carbon and therefore should have a partial negative charge if relying only on electronegativity values.

b. For part b, you will be operating a steady state oxy-combustion process. In this process natural gas which we are assuming for simplicity to be only methane and pure oxygen are combined and combusted resulting in CO_2 and water vapor. While oxy-combustion has many benefits it unfortunately burns at a much higher temperature than regular combustion with air. As a result, there is a recycled stream of CO_2 present to prevent the excessively high temperatures which could potentially melt the process equipment. Remember the system below is at **steady state** meaning that all the mass entering the system is equal to all the mass exiting the system i.e. no accumulation of mass within the system. For this problem assume that the mass flow rate of CH_4 is entering the combustor is 1.73 kg/s. Assume that the combustion of the reaction is perfectly stoichiometric and that the only products are CO_2 and water vapor. All answers involving calculations should be given with units (**kg/s**).



i. Determine $\dot{m}_{O2,in}$ (mass flow rate of O_2) into the stoichiometric combustor.

RXN: $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$$\frac{1.73\ kg\ CH_4}{s} \cdot \frac{2\ mol\ O_2}{1\ mol\ CH_4} \cdot \frac{32g/(gmol)}{16g/(gmol)} = \frac{6.92kg\ O_2}{s}$$

ii. Determine $\dot{m}_{CO2,in}$ (mass flow rate of CO_2) into the combustor so that the inlet gas (carbon dioxide and oxygen mixture) has an oxygen mole fraction of 0.2.

$$\frac{6.92kg\ O_2}{s} \cdot \frac{kgmol}{32kg} = 0.21625 \therefore \frac{0.21625}{0.21625 + CO_{2,\,IN}} = 0.2$$

$$CO_{2,\,IN} = \frac{0.865kgmol}{s} \cdot \frac{44kg}{1kgmol} = 38.06\frac{kg\ CO_2}{s}$$

iii. Determine the fraction of CO_2 in the product stream must be recycled in order to achieve this 0.2 mole fraction of oxygen in the inlet stream.

Use SS assumption:

$$CO_{2,\,IN} = 38.06\frac{kg\ CO_2}{s}$$

$$CO_{2,\,Out} = CO_{2,\,IN} + CO_{2,\,RXN}$$

$$CO_{2,\,out} = 38.06\frac{kg\ CO_2}{s} + CO_{2,\,RXN}$$

$$\frac{1.73\ kg\ CH_4}{s}\cdot\frac{1\ mol\ CO_2}{1\ mol\ CH_4}\cdot\frac{44g/(gmol)}{16g/(gmol)} = \frac{4.7575kg\ CO_2}{s}$$

$$CO_{2,\,out} = 38.06\frac{kg\ CO_2}{s} + \frac{4.7575kg\ CO_2}{s} = \frac{42.8175kg\ CO_2}{s}$$

$$\%_{recycled} = 38.06\frac{kg\ CO_2}{s} \div \frac{42.8175kg\ CO_2}{s}\cdot 100 = 88.89\%$$

iv. An alternative combustor used for the combustion of natural gas is an air blown combustor which uses air instead of pure oxygen as it is much cheaper since air is free. While the oxy-combustor above needed a recycle stream of CO_2 to prevent excessively high temperatures, why would an air blown combustor not need one?

There are molecules other than O_2 in air such as N_2 which absorbs a lot of the heat released.

c. A serious problem with natural gas is fugitive methane emissions. Once in the atmosphere methane is said to be 30 times better at trapping heat than CO_2 but luckily has a much shorter life span. The biggest sink for these methane molecules are in atmosphere where they can react with various radicals such as OH· or Cl· which can abstract hydrogens.

i. Write two separate reactions of methane with a OH· and a Cl· radical.

OH· Rxn: $CH_4 + OH\cdot \rightarrow CH_3\cdot + H_2O$

Cl· Rxn: $CH_4 + Cl\cdot \rightarrow CH_3\cdot + HCl$

Single Bond Energies (kJ/mol of bonds)

	H	C	N	O	S	F	Cl	Br	I
H	436								
C	413	346							
N	391	305	163						
O	463	358	201	146					
S	347	272	—	—	226				
F	565	485	283	190	284	155			
Cl	432	339	192	218	255	253	242		
Br	366	285	—	201	217	249	216	193	
I	299	213	—	201	—	278	208	175	151

Multiple Bond Energies (kJ/mol of bonds)

C=C 602 C=N 615 C=O 799

Photo credit: University of Texas Chemistry Department

ii. Calculate the change in enthalpy for both reactions above

$\Delta\text{H} = \sum \textit{Bonds Broken} - \sum \textit{Bonds Formed}$

OH· **RXN:** ΔH = -50kJ/mol
Cl· **RXN:** ΔH = -19kJ/mol

iii. Which reaction is more exothermic? Explain?

The hydroxyl radical rxn is more exothermic due to it releasing more heat than the chlorine radical reaction. (ΔH OH· < ΔH Cl·**)**

iv. For these reactions above does the entropy of the universe increase or decrease?

The entropy of the universe is always increasing.

Name (Last, First): ______________________ ID Number: __________________________

3. A radiation worker walks down a half way to find that drops from a uranium fuel rod have melted through the ceiling. He is 50 meters away from the nasty pool of radioactive death. The uranium pool has a decay rate of 10 curies (assume 1 curie=$3.7*10^{18}$decays per second). For simplicity's sake assume that only gamma rays get to the worker, and that the gamma decay rate is the same as the uranium decay rate.

a. Calculate how many gamma rays hit the radiation worker per second. You can model the radiation worker as a 1 by 1 by 1-meter cube. You may also assume that the uranium pool acts like a point source of radiation. To calculate the angler correction all you need to do is divide the amount of gamma rays emitted by the source that reaches the same distance as the radiation worker by 4pi*distance squared, and then multiple by the area of interest.

$$\frac{1}{4\pi d^2}$$

$$10 * 3.7 * 10^{18}\frac{d}{s} * \frac{1}{4\pi * 50^2 m^2} * (1m * 1m) = 11.8 * 10^{15} gamma\ rays\ per\ second$$

b. Calculate how much energy is deposited into the radiation worker per second. Assume for now that all gamma rays have energies of $1.6*10^{-13}$J. Also assume that if they hit the radiation worker all of their energy will be deposited in the radiation worker.

$$11.8 * 10^{15}\frac{gamma\ ray}{s} * \frac{1.6 * 10^{-13} J}{1\ gamma\ ray} = 18.9 * 10^2 J$$

c. Calculate the Rads per second that the radiation worker is exposed to (1 Rad=90ergs/g of material, 1 erg=$1*10^{-7}$ joules) (assume the density of humans are 1g/cm^3).

$$1\ meter = 100cm$$

$$Mass\ of\ human = Volume * Density$$

$$Mass\ of\ human = 100cm * 100cm * 100cm * \frac{1g}{1cm^3}$$

Name (Last, First): ____________________ ID Number: ________________________

$$Mass\ of\ human = 10^6 g$$

$$\frac{1890J}{human\ cube * s} * \frac{1 * 10^7 ergs}{1\ J} * \frac{1g}{90ergs} * \frac{1\ human\ cube}{10^6 g} = 210 \frac{Rads}{s}$$

d. Calculate the Rems (Rad equivalent man) per second. Rem is calculated by multiplying the Rads by the quality factor, the purpose of this conversion is to take into account the differences in tissue damage done by different forms of radiation. A table of quality factors is placed below.

Radiation type	Quality factor
$X-, \gamma-$rays	1
e^-, or e^+	1
n ($E_n < 10$ keV)	3
n ($E_n > 10$ keV)	10
p	$1 - 10$ depends on E
α	$1 - 20$
Heavy Ions	20

$$210 Rads * 1 = 210 Rems$$

e. Calculate how long a person would have to be exposed to a 1 Curie neutron flux (assume all neutrons have $1*10^{-13}$ J and 1 J=$6.42*10^{15}$ keV) in order to accumulate the same number of Rems as the radiation worker received if he stayed in the hallway for 1 hour.

$$210 \frac{Rems}{s} * \frac{60s}{1min} * \frac{60min}{1\ hr} * 1hr = 75600 Rems$$

$$\frac{10 Curies\ before}{1\ Curie\ now} * \frac{1\ (Q\ factor\ before)}{10 (Q\ factor\ now)} * 1hr (time\ it\ took\ before) = 1hr$$