## 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:

$$O + O_2 \rightarrow O_3$$
 (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:

$$O_2 \rightarrow 2 O$$
 (Equation 2)  
 $O_3 \rightarrow O + O_2$  (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:

$$\begin{array}{ll} O_2 + hv \rightarrow 2 \ O & (Equation \ 2.5) \\ O_3 + hv \rightarrow O + O_2 & (Equation \ 3.5) \end{array}$$

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.

- c. Before the oxygen atom can react with an O2 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.

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  $\Delta G$  clearly on the diagram.

**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.

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

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:

$$\begin{array}{l} Cl+O_3 \rightarrow ClO+O_2 \\ ClO+O_{\cdot} \rightarrow Cl+O_2 \end{array}$$

- i. Write the overall reaction of this reaction mechanism. Which species acts like 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).

- 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<sub>2</sub> 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?

**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<sub>4</sub> 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<sub>2</sub> 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<sub>2</sub>) into the stoichiometric combustor.

ii. Determine  $\dot{m}_{CO2,in}$  (mass flow rate of CO<sub>2</sub>) into the combustor so that the inlet gas (carbon dioxide and oxygen mixture) has an oxygen mole fraction of 0.2.

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.

- 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<sub>2</sub> to prevent excessively high temperatures, why would an air blown combustor not need one?
- 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<sub>2</sub> 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.

	н	С	Ν	0	$\mathbf{S}$	$\mathbf{F}$	Cl	$\mathbf{Br}$	Ι	
Н	436									-
С	413	346								
Ν	391	305	163							
0	463	358	201	146						
$\mathbf{S}$	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=0 799

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Photo credit: University of Texas Chemistry Department

ii. Calculate the change in enthalpy for both reactions above

- iii. Which reaction is more exothermic? Explain?
- iv. For these reactions above does the entropy of the universe increase or decrease?

- 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<sup>18</sup> 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.



**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.

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).

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
$X-,\gamma-\mathrm{rays}$	1
$e^-$ , or $e^+$	1
$n (E_n < 10 \text{ keV})$	3
$n (E_n > 10 \text{ keV})$	10
p	1-10 depends on E
α	1 - 20
Heavy Ions	20

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<sup>15</sup> keV) in order to accumulate the same number of Rems as the radiation worker received if he stayed in the hallway for 1 hour.