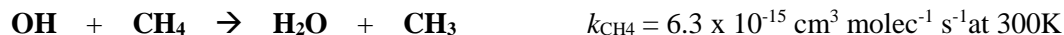# CHEM 302
Assignment #2

Provide solutions to the following questions in a neat and well organized manner, including dimensional analysis, where appropriate.
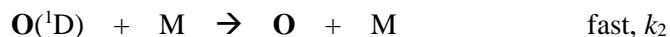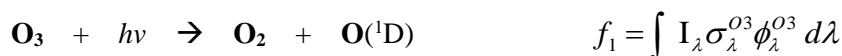*Reference data sources for any constants and state assumptions, if any.*
Due: **Tuesday, October 13th, 2015**

1. The mesopause is occurs roughly at 85 km altitude and is the point where a second large scale inversion in the atmospheric temperature profile occurs.
a) Explain why the percentage of atomic oxygen to total oxygen increases above the mesopause.
b) Calculate the atmospheric pressure and air number density at this altitude.
c) Consider a cubic meter of air at the mesopause, what volume would it occupy at STP?

2. The ground electronic state of both atomic and molecular oxygen are diradicals in a 'triplet' electronic state. Use your knowledge of atomic and molecular orbital theory to explain why 'singlet' (spin paired) states are electronically excited for these two oxygen species.

3. Acrolein (2-propenal) is a volatile organic compound with a disagreeable odour and physiological effects (lachymator). It has a reported vapour pressure of 200. torr at 17 °C. It is soluble in water, and photochemically active with an estimated outdoor half-life of 1 day in the troposphere. The 8 hour workplace exposure limit is 250 μg/m^3.
a) Identify at least one indoor and one outdoor source of atmospheric acrolein (properly citing your reference/s).
b) Determine the mixing ratio of acrolein in the air if a spill were to occur in a closed non-ventilated room at 17°C. How does this compare to the 8 hour workplace exposure limit?
c) Assuming the loss of acrolein follows *psudeo* first order kinetics, show that the outdoor residence time is around 35 hours.

4. The PCB concentration in the air inside a typical 600 m^3 home is 400 ng/m^3 and the ventilation is such that the residence time of the indoor air is 10 hr. If the PCBs are coming from a source within the house, estimate how much (in mg) leaks per year?

5. For the reaction;
$$NO \ + \ O_3 \ \rightarrow \ NO_2 \ + \ O_2$$
The *second order* rate constant has a value of 1.8 x 10^{-14} molecules^{-1} cm^3 s^{-1} at 25°C. The concentration of **NO** in a relatively clean atmosphere is 0.10 ppb$_v$ and that of **O$_3$** is 15 ppb$_v$.
a) Calculate the rate of the **NO** oxidation using units of molecules cm^{-3} s^{-1}.
b) Show how the rate law may be expressed in *pseudo* first order terms and calculate the corresponding *pseudo first order* rate constant.
c) Calculate the apparent atmospheric residence time of **NO** under these conditions, assuming this to be the only loss process.

6. Two important sinks for **OH** in the troposphere are reaction with **CH₄** and **CO**, respectively. Calculate the lifetime of hydroxyl radical against chemical loss in the troposphere using typical concentrations of 4.6 ppm$_v$ for **CO** and 1.7 ppm$_v$ for **CH₄**.

$$OH \; + \; CO \; \rightarrow \; H \; + \; CO_2 \qquad\qquad k_{CO} = 2.7 \text{ x } 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ at } 300K$$

$$OH \; + \; CH_4 \; \rightarrow \; H_2O \; + \; CH_3 \qquad\qquad k_{CH4} = 6.3 \text{ x } 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{at } 300K$$

7. Hydroxyl radicals (**OH**) are reactive react species in the atmosphere, particularly in **H**-atom abstraction reactions whereby it is converted to **H₂O**. The production of **OH** occurs by reaction of 'singlet' oxygen with water vapour in both the troposphere and stratosphere. Singlet oxygen is produced by the photolysis of ozone. Considering only the reactions below, derive the expression for the production rate of **OH** by assuming *steady state* for **O(^{1}D)**.

$$O_3 \; + \; hv \; \rightarrow \; O_2 \; + \; O(^1D) \qquad\qquad f_1 = \int I_\lambda \sigma_\lambda^{O3} \phi_\lambda^{O3} \, d\lambda$$

$$O(^1D) \; + \; H_2O \; \rightarrow \; 2\,OH \qquad\qquad \text{slow, } k_3$$

$$O(^1D) \; + \; M \; \rightarrow \; O \; + \; M \qquad\qquad \text{fast, } k_2$$

$$\text{Rate of production of OH} \approx \frac{2\,k_3\,[O_3][H_2O]}{k_2\,[M]} \int I_\lambda \sigma_\lambda \phi_\lambda$$

8. The chlorofluorocarbon CFC-12 is removed from the atmosphere solely by photolysis (occurring mostly in the stratosphere)*. Its atmospheric lifetime is ~100 years. In the early 1980's (prior to the Montreal protocol), the mean atmospheric concentration of CFC-12 was 400 ppt$_v$ and was increasing at a rate of 4% yr^{-1}.
a) Show the structure of CFC-12 illustrating the photolysis reaction occurring in the stratosphere.
b) Using the residence time and the mean concentration, estimate the rate constant for the chemical loss of CFC-12 and its total mass in the atmosphere in the 1980's.
c) Use the mass balance equation below, to estimate the CFC-12 emission rate during the 1980's.

$$\text{Rate of change = Emission rate – Loss rate;} \quad \frac{d\text{m}}{d\text{t}} = E - k\,\text{m}$$

Where $d\text{m}/d\text{t}$ is the rate of change in mass (kg/yr), m is the mass (kg), E is the emission rate (kg/yr) and k is the rate constant for loss (yr^{-1}).
d) The initial Montreal protocol called for a 50% reduction of CFC emissions by 1989 and a stabilization henceforth. Consider a scenario whereby emissions are held constant at 50% of the value calculated in part c (above). Show that the mass of CFC-12 in the atmosphere would eventually approach a steady state value of ~2 x 10^{10} kg, which is higher than the value estimated in part b (above).

The Montreal protocol was amended in London (1990) and again in Copenhagen (1992) to respond to the increased urgency created by the appearance of the Antarctic ozone hole.