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: Thursday, October 12th, 2017

1. Use the barometric pressure equation below to calculate the pressure and number density in the upper stratosphere at 35 km altitude. Why is the relative abundance of atomic oxygen greater in the upper stratosphere relative to the lower stratosphere? What impact does this have on the residence time of O_3 in the upper stratosphere?

$$P_h = P^o e^{-\left(\frac{\overline{M}_{air} g h}{RT}\right)}$$

2. In 1974, Rowland and Molina suggested that the only environmental *sink* for CFC compounds was transport to the stratosphere*. The refrigerant known as Freon 12 (dichlorodifluoromethane) has an atmospheric *residence time* of ~ 200 yrs. Using the bond dissociation energies given in your text, calculate the maximum wavelength of light capable of photolyzing this compound. What additional information is required in order to predict rate of a photochemical reaction?

3. HCFC-22 is one of the compounds recommended as a replacement for CFCs. Its current tropospheric concentration is about 0.10 ppb_V. It is known to react with tropospheric hydroxyl radical with a rate constant of 4.0 x 10^{-15} cm^3 $molec^{-1}$ s^{-1}.
a) Using a constant value for the hydroxyl radical concentration of 6.6 x 10^5 molec cm^{-3}, determine the rate of tropospheric oxidation via hydroxyl radical and estimate the tropospheric residence time of HCFC-22.
b) Draw the structure of HCFC-22 and suggest a reaction sequence consistent with its oxidation in the troposphere.

4. The following atmospheric reaction behaves as if it were first order with respect to $\mathbf{NO_2}$ with a *pseudo*-first order rate constant of 2.2 x 10^{-5} s^{-1} at 25^{o}C.

$$\mathbf{NO_2 + O_2 \rightarrow NO + O_3}$$

a) Determine the second order rate constant ($molec^{-1}$ cm^3 s^{-1}) at 25^{o}C and P_T= 1.00 atm.
b) Assuming no new inputs of $\mathbf{NO_2}$ and no other loss processes, what percentage of $\mathbf{NO_2}$ remains after 60 mins?

* *Nature*, **249**, 810-812 (1974). This was a ground breaking paper that contributed to the Nobel prize in Chemistry awarded in 1995.

5. Explain what is meant by a 'holding cycles' and explain how these reactions can be related to polar stratospheric ozone depletion events. Illustrate your answer with examples from your textbook.

6. Applying the *steady state approximation* to **O** and **O_3** in the Chapman reactions, it can be shown that; $k_2[\mathbf{O_2}][\mathbf{O}][M] \cong f_3[\mathbf{O_3}]$ and $f_1[\mathbf{O_2}] \cong k_4[\mathbf{O}][\mathbf{O_3}]$
Given the information below about the temperature dependence of the rate constants, predict the ozone concentration at 60 km altitude. The rate constants k_2 and k_4 vary with temperature as follows;

$$k_2 = 6.0 \times 10^{-34}\left(\frac{T}{300}\right)^{-2.3} \text{cm}^6 \text{ molec}^{-2} \text{ s}^{-1} \quad k_4 = 8.0 \times 10^{-12} e^{\left\{\frac{-2060}{T}\right\}} \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

The photochemical rate constants f_1 and f_3 do not vary appreciably with temperature and are given by 1×10^{-11} s^{-1} and 1×10^{-3} s^{-1}, respectively.

7. An important reaction in the destruction of ozone is

$$\mathbf{Cl} + \mathbf{O_3} \rightarrow \mathbf{ClO} + \mathbf{O_2}$$

The rate constant for this reaction as a function of temperature is given as
$k(T) = 2.9 \times 10^{-11} e^{-260/T}$, in units of molecules^{-1} cm^3 s^{-1}.
a) What is the rate of ozone destruction by this reaction at an altitude of 30 km near the Earth's equator, where the average atomic chlorine concentration is about 4×10^3 molecules cm^{-3}?
b) How does this compare to the atmosphere above the Antarctic, where the temperature is about -80°C, the ozone concentration is 2×10^{11} molecules cm^{-3} and the atomic chlorine concentration is about 4×10^5 molecules cm^{-3}.

8. An individual who hasn't taken CHEM 302 is running their old lawnmower in their garage (don't ask). The lawnmower is spewing carbon monoxide at a rate of 11 g/hr and the garage (which has a volume of 90 m^3) is being ventilated such that the residence time of the air in the garage is 3.3 hr. Let us assume that the **CO** is lost from the garage by two processes: first, by simple flushing as it mixes with the clean ventilated air and second by some unspecified decay process with a rate constant of 5.6×10^{-5} s^{-1}. Under these conditions estimate the *residence time* (in hrs) and *steady state concentration* (ppm$_v$) of **CO** in the garage.