CHEM 302
Assignment #1

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, September 28th, 2017

1. Each of the following gases are known atmospheric contaminants with both natural and anthropogenic sources. Identify gaseous species in lower oxidation that may act as sources and higher oxidation states that may act as sinks for each of the following.

Carbon monoxide, **CO**

Nitrogen dioxide, **NO_2**

Chlorine monoxide, **C*l*O**

2. The ground electronic state of both atomic and molecular oxygen are said to be diradical 'triplet' states. Use your knowledge of atomic and molecular orbital theory to explain why 'singlet' (spin paired) states are electronically excited.

3. Exhaust gases from internal combustion engines can contain as much as 200 ppm_v of nitric oxide (**NO**). Express this concentration in (a) mg m^{-3} and (b) molecules per cm^3.

4. 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 ^oC. It is soluble in water, and photochemically active with an estimated outdoor half-life of 1 day. The 8 hour workplace exposure limit is 250 $\mu g/m^3$.

a) Identify at least one indoor and 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 room at 17^{o}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 residence time is around 35 hours.

5. The mass of the atmosphere is roughly 5.2 x 10^{15} tonnes. Carbonyl sulfide (**COS**) is present as a trace gas at a concentration of 0.51 ppb_v and it's major source is from the oceans; 6 x 10^8 kg yr^{-1}. Estimate the total mass and the residence time of **COS** in the atmosphere.

6. The average North American car is driven 20,000 km per year and travels ~ 500 km on a 60 L tank.

a) Assuming gasoline has a composition of $\mathbf{C_8H_{18}}$ and a density of 0.8 kg/L, estimate the mass of carbon dioxide produced by the average NA vehicle per year.

b) Assuming no atmospheric losses, estimate the number of car – years required to increase the mass of $\mathbf{CO_2}$ in the Earth's atmosphere by 100 ppm_v.

7. Consider the typical altitude number density profile for ozone (attached).

a) Calculate the mixing ratio of $\mathbf{O_3}$ at ground level (z = 0 km, P = 101,300 Pa, T = 300 K) and 25 km (P = 3500 Pa, T = 220 K). Why does the mixing ratio fall off more dramatically than the number density?

b) The stratospheric ozone layer is actually a fairly diffuse distribution of $\mathbf{O_3}$ that spans ~20 – 60 km in altitude, peaking at about 8 ppm_v around 35 km above sea-level. The total number of $\mathbf{O_3}$ molecules in a column above a unit area of the Earth's surface is measured often measured and reported in Dobson units (DU, where 1 DU corresponds to a layer of $\mathbf{O_3}$ that would be 10 μm thick at STP). Estimate the number of $\mathbf{O_3}$ molecules in a $1m^2$ column if there are 200 DU of ozone. Would this be considered 'ozone hole' conditions?

8. Using the enthalpy of formation data given in Appendix B2 of your textbook, calculate the maximum wavelength of electromagnetic radiation which would have sufficient energy to effect the dissociation of nitrous oxide. In what regions of the atmosphere would such radiation be available?

$$\mathbf{N_2O} + h\nu \rightarrow \mathbf{N_2} + \mathbf{O(^1D)}$$