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.
Not all questions will necessarily be graded.
Due: Tuesday, September 29th

1. Use Lewis dot structures to aid in your answer to each of the following.
a) Indicate formal charges, if any and determine which of the following chemical species are radicals?

NO_3 **C*l*O** **CO** **H_2O_2** **C*l*NO_2**

b) For the following atmospheric reactions, indicate the oxidation states on each atom and identify the species being oxidized and reduced.

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$CH_3 + O_2 \rightarrow CH_3O_2$$

c) A number of reduced sulfur compounds, such as hydrogen sulfide, methanethiol and dimethylsulfide are released to the atmosphere from both anthro- and bio-genic sources. Ultimately, these sulfur compounds are exported from the atmosphere either through *dry* or *wet* deposition. Explain what is meant by the term 'sink' in relation to this example using chemical structures to illustrate to the 'sink' species.

2. Calculate each of the following concentrations,
a) Carbon monoxide in $\mu g/m^3$ in polluted urban air containing 200 ppb_v at STP
b) Methane mixing ratio at altitude when P_{CH4} = 10. Pa (T=250K, P_T = 0.50 atm)
c) Water vapour as molecules cm^{-3} at RTP (298K, 1.00atm) and 50.% humidity

3. Estimate an answer of the following, making reasonable assumptions, if needed.
a) The average sea salt aerosol in surface air over the ocean is 10 $\mu g/m^3$. Estimate the average number of 10 μm diameter aerosol particles in a cubic meter of sea air.
b) Propane will burn in air if its *mixing ratio* is between 2 and 10%. My camping propane tank contained 50 mL of liquid propane before it completely leaked into my garage. Determine if the air in my 10^2 m^3garage is explosive.

4. The mean global concentrations of **CO**, **CH_4** and **C_5H_8** (isoprene) are 100 ppbv, 1800 and 2 ppbv, respectively. Removal rates from the atmosphere by reaction with hydroxyl radical has been estimated to be 2400, 480 and 513 Tg/yr, respectively. Assuming that hydroxyl radical reaction accounts fro 90% of the removal process, estimate the atmospheric residence times for **CO**, **CH_4** and **C_5H_{12}**. What do the results imply about the geographic variability and global distribution of these gases.

5. The barometric pressure of the Earth's atmosphere drops exponentially with increasing altitude approximately according to the barometric law below, where (z) is in altitude and (H) is the characteristic scale height.

$$P_z = P_o \ e^{-\left\{\frac{z}{H}\right\}} \quad \text{where, } H = \frac{R\,T}{MW_{air}\ g}$$

a) Using a mean atmospheric temperature of 220 K for Earth, calculate the H and the factor the atmospheric pressure will have dropped at z = H.
b) Using a spreadsheet to carry out repetitive calculations, plot a graph of the atmospheric pressure in atmospheres (x-axis) as a function of altitude in km (y-axis) up to 100 km.
c) At what altitude, will 90% of the Earth's atmosphere be below?

6. 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 chloromethane. In what regions of the atmosphere would such radiation be available?

$$\mathbf{CH_3C}\boldsymbol{l} \; + \; h\nu \; \rightarrow \; \mathbf{CH_3} \; + \; \mathbf{C}\boldsymbol{l}$$

7. In an article titled *The Cleansing Capacity of the Atmosphere*, R.G. Prinn (Annu Rev Environ Resources. 2003 (28), 29-57), the author describes important atmospheric conditions that affect the concentration of hydroxyl radicals in the troposphere. Briefly explain how each of the following conditions lowers **OH** concentrations, using chemical reactions to illustrate your answer. (See in particular Fig 2 and the text describing tropospheric reactions pp 33-38).
a) Night-time, winter and/or cloudy conditions
b) Lower nitric oxide emission concentrations
c) Dry atmospheres

8. The stratospheric ozone layer is actually a fairly diffuse distribution of $\mathbf{O_3}$ that spans ~20 – 60 km in altitude, peaking at about 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).
a) Estimate the number of $\mathbf{O_3}$ molecules in a 1 m^2 column by approximating the attached $\mathbf{O_3}$ distribution profile with the linear function shown as the thin solid line. Express your answer in Dobson units.
b) Compare the number density of $\mathbf{O_3}$ at 35 km in the stratosphere to that of polluted urban air at 100 ppb_v at STP.