CHEM 302
Assignment #3

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.
Attempt all questions. *<u>Submit even number questions only for grading</u>.*
Due Tuesday, Nov 10th, 2015

1. The pH of suspended water droplets is sensitive to the amount of covalent oxide gases present in the atmosphere.
a) Derive a general expression for the pH of rainwater in equilibrium with a monoprotic gas and explain if this will apply to common atmospheric gases like $\mathbf{CO_2}$ and $\mathbf{SO_2}$?
b) Using Excel, plot a graph of pH (y-axis) versus partial pressure of $\mathbf{CO_2}$ (0-1000 ppm_v) and $\mathbf{SO_2}$ (0-1000 ppb_v).
c) Why is the pH of rain much more sensitive to P_{SO2} than P_{CO2}?

2. Peroxyacetyl nitrate (PAN) decomposes thermally with a temperature dependent unimolecular rate constant of $k = 1.95 \times 10^{16}\, e^{-\{13540/T\}}\, s^{-1}$.

a) Suggest the products of the decomposition reaction.
b) Calculate the activation energy of this reaction using the Arrhenius relation.
c) Calculate the half-life of PAN in the atmosphere at 25 and -10 ^oC?

3. The ionic composition (in units of ng m^{-3}) of an atmospheric aerosol in a tropical rain forest is $\mathbf{SO_4^{2-}}$, 207; $\mathbf{NO_3^-}$, 18; $\mathbf{NH_4^+}$, 385; $\mathbf{K^+}$, 180; $\mathbf{Na^+}$, 247. The pH is 5.22. Use these data to calculate the total positive and negative charge 'concentration' (in units μmol m^{-3}) in the aerosol and suggest reasons, which might account for a discrepancy in the charge balance. (Note a mole of charge is referred to as an equivalent, therefore μmol charge m^{-3} is equal to μequiv m^{-3})

4. The least volatile oxidation products of hydrocarbons are usually the corresponding carboxylic acid. The following transformations have been observed and the corresponding vapour pressures are given in the table below.

Compound	1-decene →	nonanoic acid	Cyclohexene →	1,6-hexandioic acid
Vapour Pressure (torr)	1.7	6×10^{-4}	89	6×10^{-8}

a) What concentration (ppm_v) of each of the hydrocarbon (separately) would be needed to cause the formation of haze, if 1% is converted to the corresponding carboxylic acid? Are these concentrations likely to occur?
b) Look up the structure of α-pinene (emitted from coniferous trees). Do you think it could be responsible for the summer haze in remote BC valleys.

5. A coal burning power station burns 10,000 tonnes of coal per day. The coal is 1.25% sulfur by mass (assume the remaining mass is carbon).

a) Calculate the mass of $\mathbf{CO_2}$ and $\mathbf{SO_2}$ produced per day, assuming complete combustion.

b) Estimate the mixing ratios of $\mathbf{N_2}$, $\mathbf{CO_2}$ and $\mathbf{SO_2}$ in the stack gases, assuming all the oxygen has been consumed in the combustion process.

c) Calculate the mass of lime ($\mathbf{Ca(OH)_2}$) needed per day to react with 95% of the $\mathbf{SO_2}$ produced.

$$\mathbf{Ca(OH)_2} + \mathbf{SO_2} + \tfrac{1}{2}\,\mathbf{O_2} \rightarrow \mathbf{CaSO_4}$$

6. Soot particles have a density close to 2.2 g cm^{-3}.

a) Use Stokes Law to estimate the rate of settling of particles having the diameters below using the viscosity of air to be 182 μpoise (1 poise = 1 g cm^{-1} s^{-1});

i) 15 μm

ii) 0.3 μm

b) How long will it take particles of these sizes to settle out of the atmosphere from a height of 5 km assuming the air is still?

c) Under highly polluted conditions, concentrations of particulates up to 4000 μg/m^3 have been recorded. Assuming the density given above and the average particle diameter of 1 μm, estimate the number of particles inhaled per hour by a person breathing this polluted air.

7. Nitrogen dioxide is oxidized to nitric acid in the presence of a third body according the reaction below.

$$\mathbf{NO_2}(g) + \mathbf{OH}(g) \rightarrow \mathbf{HNO_3}(g) \qquad k = 2.0 \times 10^{-11}\ cm^3\ molec^{-1}\ s^{-1}$$

If in a laboratory experiment, [**OH**] is maintained at a constant concentration of 2.4 x 10^6 molec cm^{-3} and 10.0 L of air initially containing 3.5 ppm_v of $\mathbf{NO_2}$ is maintained in contact with 0.010 L of liquid water, calculate the pH of the water after 4.5 hr.

8. Suppose the only reactions important in oxidizing $\mathbf{SO_2}$ are the two given below with the second order rate constants reported at 300 K.

$$\mathbf{SO_2}(g) + \mathbf{OH}(g) \rightarrow \mathbf{HSO_3}(g) \qquad k = 9 \times 10^{-13}\ cm^3\ molec^{-1}\ s^{-1}$$
$$\mathbf{SO_2}(aq) + \mathbf{H_2O_2}(aq) \rightarrow \mathbf{H_2SO_4}(aq) \qquad k = 1 \times 10^{3}\ L\ mol^{-1}\ s^{-1}$$

a) Given the information below at 300K and assuming a constant [OH] = 5 x 10^6 molec cm^{-1}, calculate the amount of liquid water in the atmosphere (expressed g L^{-1}) for the rate of the aqueous phase reaction to equal the rate of the gas phase reaction.

K_H (SO_2)	P_{SO2}	K_H (H_2O_2)	P_{H2O2}
1.2 mol L^{-1} atm^{-1}	1.0 ppm_v	1 x 10^5 mol L^{-1} atm^{-1}	1.0 ppb_v

b) How does the half-life of $\mathbf{SO_2}$ in the atmosphere vary as the water content increases?