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: Thursday, November 16th, 2017

1. The annual mean concentration of sulfur dioxide in an industrialized region of Bulgaria was 31.8 $\mu g/m^3$. Calculate the pH of rainwater in equilibrium with this $\mathbf{SO_2}$.

K_H ($\mathbf{SO_2}$) = 1.2×10^{-5} M Pa^{-1}
K_{a1} ($\mathbf{H_2SO_3}$) = 1.7×10^{-2}
K_{a2} ($\mathbf{H_2SO_3}$) = 6.4×10^{-8}

2. In an effort to compare the water solubility of two atmospheric sulfur containing gases, you manage to track down the following Henry's law constants from two independent sources (both reported at 25°C). K_H for methane thiol (methyl mercaptan) is reported as 830 Pa m^3 mol^{-1} whereas the K_H given for dimethyl sulfide was reported as 0.41 M atm^{-1}. Which gas is more water soluble? (Note that the reaction used to define K_H in these two sources is reversed).

3. Derive each of the following.

a) The equilibrium vapour pressure of water in the atmosphere is given by;

P_{H2O} = [$\mathbf{H_2O}$(g)] RT, where [$\mathbf{H_2O}$(g)] is the molar concentration of water vapour.

b) The fractional abundance (α_x) for a species 'x' in an aqueous phase aerosol (partitioning between the gas and aqueous phases) is given by;

$$\alpha_x = \frac{P_x K_H v_L}{P_x K_H v_L + (P_x / RT)}$$

where K_H is the Henry's law constant for x and v_L is the volume of the liquid aerosol per volume of air.

4. At the high temperatures of exhaust gases that are emitted from automobiles, the reaction below has an equilibrium constant of 1×10^{-13} atm.

$$2\,\mathbf{CO_2}(g) \;===\; 2\,\mathbf{CO}(g) + \mathbf{O_2}(g)$$

a) If the percentages by volume of the exhaust gases are 0.30, 13 and 4.0 for **CO**, $\mathbf{CO_2}$, and $\mathbf{O_2}$ (respectively), what is the reaction quotient for the above reaction and which products will be produced as the reaction proceeds towards equilibrium?

b) Provide balanced chemical reactions and catalysts that help reduce the amount of carbon monoxide in automobile exhaust.

5. The elementary reaction below is a possible source of cloud water nitrate. If the rate coefficients for the forward and reverse reactions are 1.5 x 10^{-12} M^{-1} s^{-1} and 5.0 x 10^{-2} s^{-1}, respectively, what is the value of the equilibrium constant in units of M?

$$\mathbf{NO_2}(g) \quad + \quad \mathbf{NO_3}(g) \quad === \quad \mathbf{N_2O_5}(g)$$

6. Under very humid conditions, $\mathbf{SO_2}$ oxidation has been observed to occur at rates up to 30% per hour. Under these conditions the following is the major reaction pathway.

$$\mathbf{SO_2}(aq) \quad + \quad \mathbf{H_2O_2}(aq) \rightarrow \mathbf{H_2SO_4}(aq) \qquad k = 1 \text{ x } 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$$

Assuming that $\mathbf{SO_2}$(g) and $\mathbf{SO_2}$(aq) are at all times equilibrated, what does this suggest about the concentration of $\mathbf{H_2O_2}$(aq) under these conditions?

7. Consider two clouds in which 5 x 10^{-4} kg m^{-3} of water condenses. The CCN concentration in each cloud is 100 and 1000 cm^{-3}, respectively. Assuming that the liquid water is equally distributed amoung the CCN, what is the droplet size (diameter in μm) in each cloud? What might the different concentrations of CCN indicate about the locations of the clouds?

8. A coal burning power station burns 10,000 tonnes of coal per day. The coal is 2.35% sulfur by mass (assume the remaining mass is carbon). The stack gases contain $\mathbf{CO_2}$, $\mathbf{SO_2}$ from the coal plus 150 ppm_v of $\mathbf{NO_x}$ and unreacted $\mathbf{N_2}$. Using an average molar mass of 38 g mol^{-1} for $\mathbf{NO_x}$, calculate the total amount (tonnes) of acidic gases $\mathbf{CO_2}$, $\mathbf{SO_2}$ and $\mathbf{NO_x}$ from the plant per day as well as the mole ratio of $\mathbf{SO_2}/\mathbf{NO_x}$ in the flue gas.

9. A fly ash aerosol with a density of 1.8 g mL^{-1} consists of particles averaging 10. μm in diameter and a concentration of 800. μg/m^3. Use this information to calculate the average settling velocity (cm s^{-1}) and deposition rate (g m^{-2} s^{-1}) of particles in still air.

10. The homogeneous gas phase reaction of $\mathbf{SO_2}$ with **OH** is represented by the following mechanism, where $\mathbf{HOSO_2}$* represents an electronically excited state.

$$\mathbf{SO_2} \quad + \quad \mathbf{OH} \rightarrow \mathbf{HOSO_2}^* \qquad\qquad k_1$$
$$\mathbf{HOSO_2}^* \rightarrow \mathbf{SO_2} \quad + \quad \mathbf{OH} \qquad\qquad k_{-1}$$
$$\mathbf{HOSO_2}^* \quad + \quad M \rightarrow \mathbf{HOSO_2} \quad + \quad M \qquad\qquad k_2$$

a) Write an expression for the rate of formation of $\mathbf{HOSO_2}$
b) Modify the answer to part (a) by applying the steady state approximation to $\mathbf{HOSO_2}$*
c) Does your answer to (b) change if you consider the first two steps above as a pre-equilibrium step (Note: $K_{eq} = k_1/k_{-1}$)