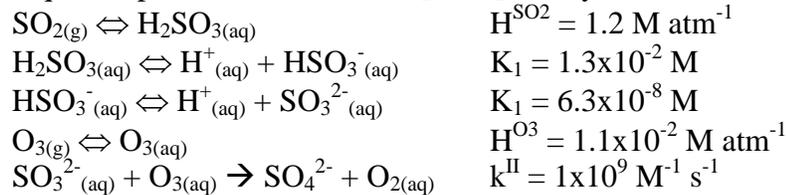**ATMS 564 Problem Set #3: Due In Class March 6, 2005**

Material for problem 4 will be sent in an email.

1. Show that for an aqueous phase reaction which occurs much slower than aqueous phase diffusion, the reaction probability, γ becomes dependent on particle size:

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{3\varpi}{4R_p HRTk_{aq}^I} \qquad (1)$$

2. The conditions in problem 1 imply that there is no aqueous phase mass transport limitation to the reactive processing of the gas by the aerosol. If a rate constant k_{aq}^I for pseudo-first order reaction in solution, and aqueous phase diffusivity, D_{aq}, are known show mathematically how you could predict whether an aqueous phase mass transport limitation would exist.

3. Consider the aqueous-phase oxidation of SO_2 to H_2SO_4 by O_3:

$$SO_{2(g)} \Leftrightarrow H_2SO_{3(aq)} \qquad H^{SO2} = 1.2 \text{ M atm}^{-1}$$
$$H_2SO_{3(aq)} \Leftrightarrow H^+_{(aq)} + HSO_3^-_{(aq)} \qquad K_1 = 1.3 \times 10^{-2} \text{ M}$$
$$HSO_3^-_{(aq)} \Leftrightarrow H^+_{(aq)} + SO_3^{2-}_{(aq)} \qquad K_1 = 6.3 \times 10^{-8} \text{ M}$$
$$O_{3(g)} \Leftrightarrow O_{3(aq)} \qquad H^{O3} = 1.1 \times 10^{-2} \text{ M atm}^{-1}$$
$$SO_3^{2-}_{(aq)} + O_{3(aq)} \rightarrow SO_4^{2-} + O_{2(aq)} \qquad k^{II} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

Calculate the rate of sulfate formation as a function of pH from pH 3 – 7 neglecting mass transport limitations and assuming $SO_2 = 1$ ppbv and $O_3 = 50$ ppbv. Is this a significant source of acidity to cloud drops? (Explain). Is this reaction limited by aqueous phase diffusion under any conditions for typical cloud droplet sizes from 10 – 100 microns in size? Assume T = 298 and P = 1 atm.

4. Using the size distributions measured during NAMBLEX, calculate the overall, pseudo-first order mass transfer rate coefficient using the Fuchs-Sutugin approach to the transition regime. The rate coefficient should have units of s^{-1} and represents the total (integrated) transfer rate of a generic gas-phase molecule to the population of particles being considered. It will be easiest to calculate a k_{mt} for each size distribution (i.e. DMA, FSSP, GRIMM) which vary as a function of time of day. Compare the Fuchs-Sutugin approach to the alternative method also developed in class known as the "timescale comparison" mass transfer rate constant. For each calculation you will need to assume a molecular mass (e.g. ~ 60 g/mol), a temperature, and diffusivity (e.g. 0.1 $cm^2 s^{-1}$). Assume for these calculations that the reaction probability of the gas, γ, is unity.

5. Repeat the calculations assuming $\gamma = 0.1$, 0.01, and 0.001. Describe differences in k_{mt} that result between the different size distributions. For example, suppose measurements of a gas-phase species imply that it's reaction probability γ must be 1, and cannot be 0.1. To which size range of particles is this species being lost?