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, $\gamma$, becomes dependent on particle size:

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{3\sigma}{4R_pHRTk_{aq}}$$  \hspace{1cm} (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 $k_{aq}$ 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$_2$SO$_4$ by O$_3$:

- $\text{SO}_2(g) \Leftrightarrow \text{H}_2\text{SO}_3(aq)$
- $\text{H}_2\text{SO}_3(aq) \Leftrightarrow \text{H}^+(aq) + \text{HSO}_3^-(aq)$, $K_1 = 1.3 \times 10^{-2}$ M
- $\text{HSO}_3^-(aq) \Leftrightarrow \text{H}^+(aq) + \text{SO}_3^{2-}(aq)$, $K_1 = 6.3 \times 10^{-8}$ M
- $\text{O}_3(g) \Leftrightarrow \text{O}_3(aq)$, $K_{O_3} = 1.1 \times 10^{-2}$ M atm$^{-1}$
- $\text{SO}_3^{2-}(aq) + \text{O}_3(aq) \rightarrow \text{SO}_4^{2-} + \text{O}_2(aq)$, $k^{II} = 1 \times 10^3$ M$^{-1}$ 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, $\gamma$, is unity.

5. Repeat the calculations assuming $\gamma = 0.1, 0.01, \text{and } 0.001$. 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 $\gamma$ must be 1, and cannot be 0.1. To which size range of particles is this species being lost?