

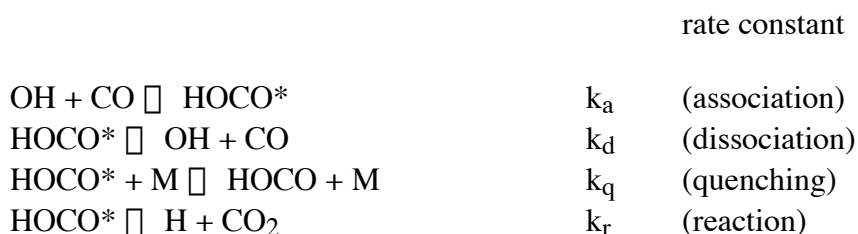
Atmospheric Chemistry

Homework #4

- Using the formal definition of the activation energy, determine the activation energy, E_a , and Arrhenius A factor for a gas phase bimolecular rate constant derived from collision theory.
- Some reactions that appear to be simple bimolecular processes exhibit pressure-dependent rate constants that are not consistent with a direct concerted reaction. A classic example of great atmospheric importance is the reaction:

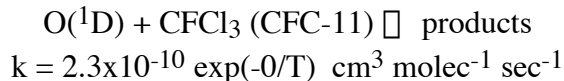
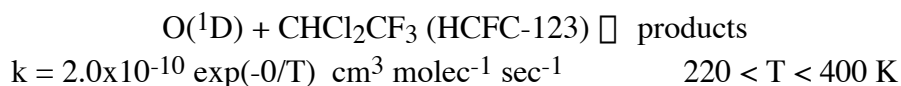
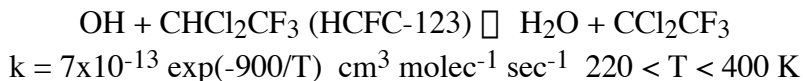


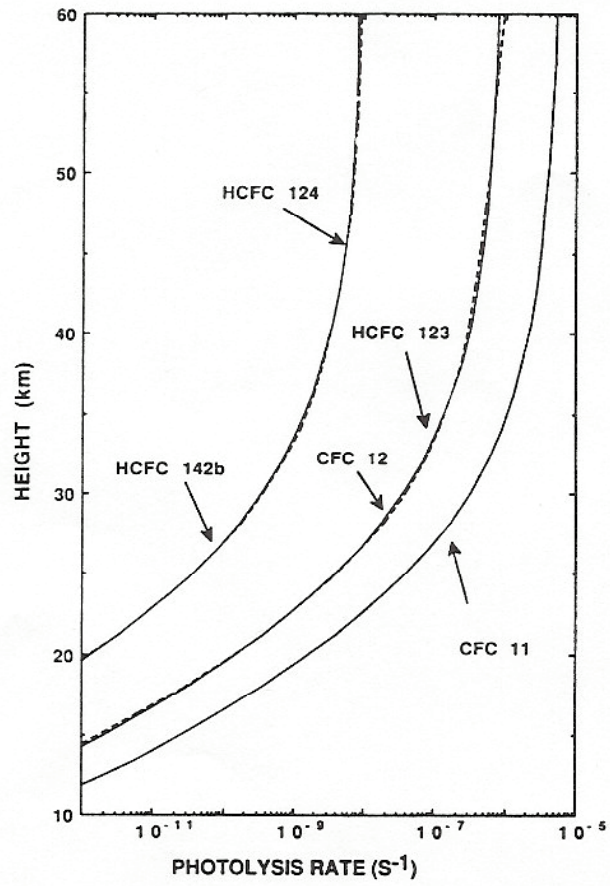
where k_{II} is the effective second order rate constant for loss of CO, i.e. $-d[\text{CO}]/dt = k_{\text{II}} [\text{CO}][\text{OH}]$. It is now believed that this reaction is not a simple bimolecular process but rather a combination of several elementary steps in which a bound adduct, HOCO^* , is formed as an intermediate: (the * indicates an energetically excited molecule)



- Assume that the excited adduct, HOCO^* , is in steady state, and solve for k_{II} in terms of the rate constants for the four elementary reactions above. Your answer should have k_{II} as a function of rate constants and $[\text{M}]$ only.
- Sketch out how this rate constant should vary with pressure, from the low pressure limit to the high pressure limit.
- For atmospheric applications, the rate constant for this reaction is often parameterized as $k_{\text{II}} = A \exp(-E_a/RT)$ where $A = 1.5 \times 10^{-13}(1 + 0.6P_{\text{atm}}) \text{ cm}^3/\text{molec-sec}$ (where P_{atm} is the total pressure in atmospheres) and $E_a/R = 0 \text{ kcal/mol}$. Assuming an OH concentration of $8 \times 10^5 \text{ molec/cm}^3$, calculate the lifetime of CO with respect to reaction with OH at $T=298 \text{ K}$ and $P=1 \text{ atm}$.

3. Hydrochlorofluorocarbons (HCFCs) are being used as replacements for chlorofluorocarbons (CFCs) because of the shorter atmospheric lifetimes of the HCFCs. The atmospheric lifetime of an HCFC is determined by its reaction with the OH molecule, by reaction with atomic O(¹D), and by photolysis. Photolysis rate constants (i.e. J values) for a number of CFCs and HCFCs are shown in the figure below as a function of altitude. Calculate the lifetime of CFC 11 and HCFC 123 at 5, 15 and 30 km. The relevant reaction rate constants are given below. Get any additional information necessary from Brasseur and Solomon Appendix. Briefly discuss how your answers are consistent with shorter atmospheric lifetimes for HCFCs than for CFCs.





4. There are many important termolecular reactions that occur in the atmosphere.
- a. Show that the pseudo-second order rate constant for a termolecular reaction can be written:

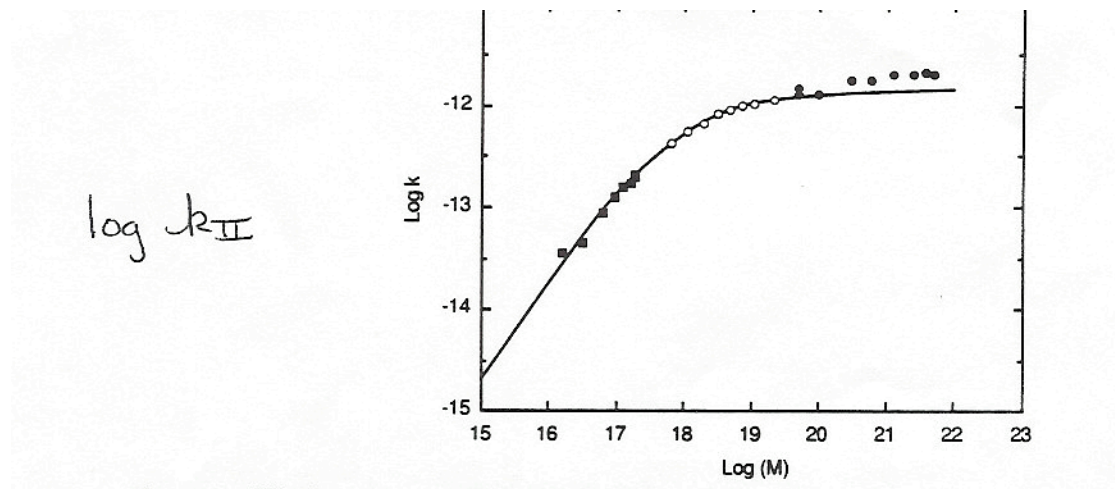
$$k_{II} = \frac{k_0[M]k}{(k_0[M] + k)}$$

where k_0 and k^∞ are the low- and high-pressure limiting rate constants, respectively.

- b. One of the most important termolecular reaction of atmospheric interest is:



The pseudo-second order rate constant, k_{II} , for this reaction at 298 K is given below as a function of $[M]$ in a log-log plot. What are approximate values for k_0 and k^∞ at 298 K?



- c. The equilibrium constant, K , for the above reaction can be parameterized as K ($\text{cm}^3 \text{ molec}^{-1}$) = $4.0 \times 10^{-27} \exp(10,930/T)$ for ($200 < T < 300 \text{ K}$). What is the approximate rate constant for the unimolecular thermal decomposition of N_2O_5 at 298 K and 1 atm pressure? What is the lifetime of N_2O_5 with respect to thermal decomposition under these conditions?

- d. Assuming a temperature dependence for k_0 and k^∞ of:

$$k_0(T) = k_0(300)\{T/300\}^{-4.3} \text{ and } k^\infty(T) = k^\infty(300)\{T/300\}^{-0.5}$$

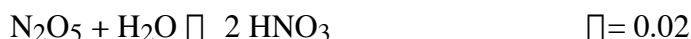
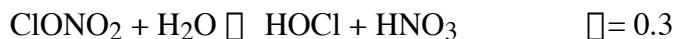
determine the lifetime of N_2O_5 with respect to thermal decomposition under temperature and pressure conditions present at an altitude of 20 km.

5. As discussed in class, heterogeneous reactions can occur on both solid and liquid particles. An important liquid particle in the stratosphere is sulfuric acid. Sulfuric acid particles are found globally, and increase in abundance after major volcanic eruptions. The “background” aerosol is thought to have a surface area density $A = 1 \times 10^{-8} \text{ cm}^2/\text{cm}^3$. After a volcanic eruption, the aerosol density can increase to $A = 50 \times 10^{-8} \text{ cm}^2/\text{cm}^3$.

- a. Assuming $\alpha = 0.1$, calculate the lifetime for the heterogeneous reaction of $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$ on sulfuric acid aerosols under background and volcanic conditions at 20 km.
- b. How does the above heterogeneous reaction compare to the gas phase reactions for N_2O_5 loss in the stratosphere? Assume the above reaction in the gas phase has a rate constant of $k = 1 \times 10^{-21} \text{ cm}^3/\text{molecule}\cdot\text{sec}$ and that water is present at 5 ppmv at 20 km. Also compare the heterogeneous pathway with thermal unimolecular decomposition in the stratosphere.

6. Some surface reactions are limited by saturation of the available number of surface sites on the particle.

- a. Estimate the number of sites per cm^2 on a typical surface composed of ice.
- b. The heterogeneous reactions of ClONO_2 and N_2O_5 on ice clouds:



can saturate because the product HNO_3 remains condensed on the ice surface, and converts the surface into a less reactive HNO_3/ice surface. Given the above α values and data in the Brasseur and Solomon Appendix, estimate how long it would take for the surface of an ice particle at 20 km to saturate to a pure HNO_3 surface via reaction with i) ClONO_2 and ii) N_2O_5 . (Assume the α values stay constant until saturation is reached.)

7. Problem 1 in your text on page 174 of Chapter 5.

8. Problem 2 in your text on page 174 of Chapter 5.