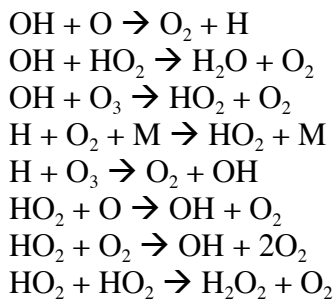


Chem/ATOC 5151
Homework #5

1. In the following, we compare some features of the Chapman mechanism at 20 and 45 km. Assume temperatures of 200 K and 270 K at 20 and 45 km, respectively. Assume number densities of 1.8×10^{18} molecules/cm³ and 4.1×10^{16} molecules/cm³ at 20 and 45 km, respectively. Also assume the ozone photolysis occurs with a rate constant $J = 10^{-2} \text{ s}^{-1}$. Assume ozone formation is in the low-pressure limit with $k_0 = 10^{-33} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$. Finally assume the reaction of O with O₃ occurs with a rate constant $k(\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}) = 8 \times 10^{-12} \exp(-2030/T)$.

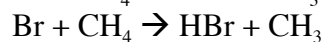
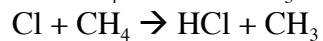
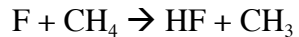
- Using the Chapman mechanism, calculate the lifetime of O atoms at 20 and 45 km. Can O atoms be assumed to be in steady state throughout the stratosphere?
- Now assuming O and O₃ are in steady state, calculate the ratio O/O₃ at 20 and 45 km. Can it be assumed that [O₃] = [Ox] throughout the stratosphere?
- Following the procedure discussed in class, calculate the lifetime of Ox at 20 and 45 km. In what part of the stratosphere do you expect Ox to be in chemical steady state?

2. Consider the following reactions involving HOx=(H + OH + HO₂):



- Find four different catalytic ozone loss cycles starting with reaction of OH.
- Which reactions above represent a loss of HOx?

3. Use enthalpy tables to determine the heat of reaction for the three reactions:



Use this information to comment on why.....

(a) Br is more damaging to ozone than is Cl.

(b) F does not destroy ozone. You may need to include other reactions in addition to the above to support this claim!

4. Problem 10.8 in Daniel Jacob text, "Introduction to Atmospheric Chemistry." Pages from text attached below.

degradation of methyl bromide (see problem 6. 4) and a number of industrial gases. Consider the following ensemble of reactions involved in the cycling of Br_y :



1. Draw a diagram of the Br_y cycle.
2. Identify three catalytic cycles for O_3 loss involving bromine.

10. 8 Limitation of antarctic ozone depletion

High concentrations of chlorine radicals ($\text{ClO}_x = \text{Cl} + \text{ClO}$) in the antarctic spring stratosphere cause rapid destruction of O_3 . Recent observations indicate that the extent of O_3 depletion in antarctic spring is ultimately limited by conversion of ClO_x to the long-lived HCl reservoir as O_3 concentrations fall to very low levels. Consider an air parcel in the antarctic spring stratosphere containing 0.8 ppmv

CH_4 , 0.6 ppmv O_3 , 0.3 ppbv NO_x , and 1.0 ppbv ClO_x , with an air density $n_a = 3.5 \times 10^{18}$ molecules cm^{-3} . The following reactions cycle the ClO_x and NO_x radicals:



Rate constants are $k_1 = 7.9 \times 10^{-12}$ cm^3 molecule $^{-1}$ s $^{-1}$, $k_2 = 2.7 \times 10^{-11}$ cm^3 molecule $^{-1}$ s $^{-1}$, $k_3 = 1.8 \times 10^{-15}$ cm^3 molecule $^{-1}$ s $^{-1}$, and $k_4 = 1 \times 10^{-2}$ s $^{-1}$.

1. Assuming steady state for ClO_x and NO_x radicals, show that $[\text{Cl}] \ll [\text{ClO}]$ and $[\text{NO}] \ll [\text{NO}_2]$.
2. What are the lifetimes of Cl and NO? Is the steady state assumption in question 1 realistic?
3. Conversion of ClO_x to HCl takes place by:



with rate constant $k_5 = 1.0 \times 10^{-14}$ cm^3 molecule $^{-1}$ s $^{-1}$. Show that the lifetime τ of ClO_x against conversion to HCl is

$$\tau \approx \frac{k_1 [\text{O}_3] [\text{ClO}_x]}{k_4 k_5 [\text{NO}_x] [\text{CH}_4]}$$

Calculate the numerical value of τ as a function of the O_3 concentration. Conclude regarding the eventual limitation of O_3 depletion by reaction (5) in the antarctic stratosphere.

[Source: Mickley, L.J., et al., Evolution of chlorine and nitrogen species in the lower stratosphere during Antarctic spring: use of tracers to determine chemical change, *J. Geophys. Res.*, 102, 21,479-21,491, 1997]

10. 9 Fixing the ozone hole

Ozone depletion over Antarctica is catalyzed by chlorine radicals. An early theoretical study proposed that this depletion could be prevented by the injection of ethane (C_2H_6) into the antarctic stratosphere. Ethane reacts quickly with Cl, converting it to HCl.