Exercises- Kinetics and Stratospheric Chemistry

Bring your answers to class on Thursday, September 19. The Problems will be given out in class that day to be done in class.

You will be lost if you have not worked through the Exercises and understood them!

A. What is the lifetime of O with respect to reaction with O_2 at 20 km (that is, treating $[O_2]$ as constant)? Treat $O + O_2 \rightarrow O_3$ reaction as elementary with $k = 2.6 \times 10^{-15}$ cm^3/(molecule sec).

B. Calculate pseudo-1st order rate constants for F reacting with O_3, H_2O, and CH_4 at 25 km.

What is the ratio of k'_{O3} to k'_{CH4}?

C.1 Calculate pseudo-first 1st rate constants for Cl reacting with O_3 with CH_4 at 25 km. What is the ratio of k'_{O3} to k'_{CH4}?

C.2 The overall lifetime of Cl is determined by $\tau = (1/k'_{total})$ where $k'_{total} = k'_{O3} + k'_{CH4}$. Calculate the overall lifetime of Cl at 25 km.

C.3. For F you considered reaction with H_2O, but for Cl we neglected this. Compute the enthalpy of reaction for $Cl + H_2O \rightarrow HCl + OH$

D. Compute $\Delta H_r°(\mathbf{0}\ K)$ for gas phase reactions $X + CH_4 \rightarrow HX + CH_3$ for X = F, Cl, and Br.

Can the rate constant for X=Br be as high as that for X=Cl (see Exercise C)? Answer in terms of the relationship between reaction enthalpy and activation energy on a reaction coordinate diagram (aka reaction progress diagram).

E. Calculate the fraction of ClO reacting with NO, NO_2, and O at 30 km (consider only these reactions. Treat $ClO + NO_2 \rightarrow ClONO_2$ as elementary with $k = 9.0 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.

Which of these reactions is a propagation reaction, termination reaction, or part of a null cycle?

F. Compute the steady state concentration of O atom at 40 km from the following mechanism:

$O_2 + h\nu \rightarrow O + O$ $\quad J_{O2}$

$O_3 + h\nu \rightarrow O + O_2$ $\quad J_{O3}$

$O + O_2 \rightarrow O_3$ $\quad$ treat as an elementary reaction with $k_3 = 9.1 \times 10^{-17}$ cm^3/(molecule sec).

$O + ClO \rightarrow Cl + O_2$ $\quad k_4$

G. Look at the A-factors for reactions of Cl in Table 1.F of *Burkholder* (pp. 1-196 to 1-203). What is the highest value of an A-factor?

How does this value relate to the rate constant for collision ($k_{collision}$) of Cl with small molecules?

The goal of this Homework is for you to develop the tools (and to realize you have the tools) to derive your own conclusions about the importance of various atmospheric processes.

Homework #03 Problems

1. At 25 km, which will destroy more ozone, an atom of Cl or F? Note that the answer to this question is related to the question of why HCFCs have higher ODPs than HFCs, so **an answer in terms of ODP is not valid**.

Base your answer on: The answers to Exercise B and C, particularly the relationship of the ratio k'_{O3} / k'_{CH4} with the efficiency of ozone-depleting catalytic cycles.

2. What does your answer to Exercise E imply about whether null cycles and termination reactions, combined, have a large or small effect on the efficiency of the ClO_x cycle?

3. Estimate an upper limit to $k(Cl + H_2O)$ at 298 K based on $A \leq k_{collision}$ and the relationship between reaction enthalpy (from *Exercise* C.3) and activation energy as the minimum value implied by Exercise C.3.

Based on this rate constant and the other reactions of Cl, is it worth worrying about the $Cl + H_2O$ reaction?

4. a) Is the $[O]_{ss}$ determined in Exercise F consistent with the value in *DeMore* at 40 km?

b) Under the conditions of Exercise F, what fraction of [O] reacts with O_2?

c) Pick **any one** of OH, HO_2, O_3, or NO_2: Compute whether the reaction of O with that one radical will add more than 1% to the destruction of O atom at 40 km?

5. a) Compute the **rate** at which NO_x cycle 1 destroys odd oxygen at 20 km and at 40 km. (Assume the NO_2 + O reaction is rate limiting at both altitudes)

b) Which factor, the rate constant or [O], changes the most between these two altitudes?

c) What do these results imply about how the rate of X/XO cycles changes with altitude?

6. Chapter 2, Question 1. A qualitative answer is satisfactory, but an approximate calculation would be great.

Helpful Information: The lifetime of methane in the atmosphere is roughly 10 years. Other useful information is in section 2.4.5.

7. For each Problem, identify the parts for which you are confident of your answers and explain why you are not sure of other parts of your answers.