Exercises- Kinetics and Stratospheric Chemistry

Bring your answers to class on Thursday, September 21
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 O₂ at 20 km (that is, treating [O₂] as constant)?
   (Treat O + O₂ → O₃ reaction as elementary with k = 2.6 × 10⁻¹⁵ cm³/(molecule sec).)
What is the lifetime of O₂ with respect to reaction with O at 20 km (that is, treating [O] as constant)?

B. Calculate pseudo-1ˢᵗ order rate constants for F reacting with O₃, H₂O, and CH₄ at 25 km.
   What is the ratio of k’ O₃ to k’ CH₄?

C. Calculate pseudo-first ¹ˢᵗ rate constants for Cl reacting with O₃ with CH₄ at 25 km.
   What is the ratio of k’ O₃ to k’ CH₄?
   The overall lifetime of Cl is determined by t = (1/k’ total) where k’ total = k’ O₃ + k’ CH₄
   Calculate the overall lifetime of Cl at 25 km.
   Is the overall lifetime smaller or larger than the lifetime for loss by any one reaction? You should be able to figure out the answer by logic without doing any math. But you should also do the math!

D. Compute ΔHᵣ°(θ K) for gas phase reactions X + CH₄ → HX + CH₃ 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, NO₂, OH, and O at 30 km (consider only these reactions. Treat the reaction ClO + NO₂ → ClONO₂ as elementary with k = 9.0 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹).

F. Compute the steady state concentration of O atom at 40 km from the following mechanism:
   O₂ + hv → O + O       J₀₂
   O₃ + hv → O + O₂       J₀₃
   O + O₂ → O₃         treat as an elementary reaction with k₃ = 9.1 × 10⁻¹⁷ cm³/(molecule sec).
   O + ClO → Cl + O₂      k₄

G. What is the largest Arrhenius pre-exponential factor for the reaction of Cl or OH with another species in Table 1 of Burkholder?

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Homework #03 Problems

I. Which will destroy more ozone, an atom of F or Cl? Note that the answer to this question is related to the question of why HFCs have lower ODPs than CFCs, so an answer in terms of ODP is not valid.
   Base your answer on:
   1) The two types of processes controlling the efficiency of O₃-destroying catalytic cycles
   2) Answers to Exercise B and C

II. Why is k(Cl + H₂O) so small that it is not relevant in the stratosphere (and not listed in Burkholder)?
   Base your answer on:
   1) Enthalpy of reaction for Cl + H₂O → HCl + OH
   2) Relationship between reaction enthalpy and activation energy on a reaction coordinate diagram (aka reaction progress diagram)
   3) An estimate of the upper limit to k(Cl + H₂O)

III. What does your answer to Exercise E imply about how much (a lot versus a little) null cycles and termination reactions (together) limit the efficiency of the ClOₓ cycle?

IV. Is the [O]ₘₙ determined in Exercise F consistent with the value in DeMore at 40 km?
   What fraction of [O] reacts with O₂ in this mechanism?
   Pick one of OH, HO₂, O₃, or NO₂: Compute whether the reaction of O with that one radical will add more than 1% to the destruction of O atom at 40 km?

V. Compute the rate at which NOₓ cycle 1 destroys odd oxygen at 20 km and at 40 km.
   (Assume the NO₂ + O reaction is rate limiting)
   Which factor, the rate constant or [O], changes the most with altitude? (You only need to consider 20 and 40 km)
   What do these results imply about how the rate of X/XO cycles changes with altitude?

VI. 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.