Exercises- Kinetics and Stratospheric Chemistry

Bring your answers to class on Thursday, September 20
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).

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.1 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?
C.2 The overall lifetime of Cl is determined by τ = (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 H₂O, but for Cl we neglected this. Compute the enthalpy of reaction for Cl + H₂O → HCl + OH

D. Compute ΔH°(0 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, 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. 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:
O₂ + hν → O + O  \( J_{O₂} \)
O₃ + hν → O + O₂  \( J_{O₃} \)
O + O₂ → O₃  \( k₃ = 9.1 \times 10⁻¹⁷ \) cm³/(molecule sec).
O + ClO → Cl + O₂  \( k₄ \)

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.