

Environmental Chemistry
Problem Set 2
Due Thursday, October 15, 2009 (due by the start of class)

Report all final numerical results to the correct number of significant figures.

1. Baird and Cann, Additional Problem 3 (on p. 57)

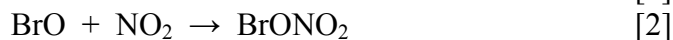
(Meta-comment: Hey, isn't ClONO₂ supposed to be a photochemically inactive reservoir species? It is—for the most part. The mechanism you are considering in this problem is a minor pathway that requires significant solar flux to drive both ClONO₂ and NO₃ photolysis. This requirement makes the pathway negligible at the polar latitudes, where solar flux is relatively low.)

2. Consider the kinetics of forming the chlorine reservoir species HCl:
 - (a) Calculate the lifetime of Cl atom with respect to reaction with CH₄ at 25 km. Use the following data in your calculation:
 1. The U. S. Standard Atmospheric temperature and pressure data on the ozone depletion handout from September 24
 2. The typical mixing ratio (or relative concentration) of CH₄ at 25 km is 1.5 parts per million (ppm)
 3. For the Cl + CH₄ reaction, the Arrhenius pre-exponential factor is $A = 7.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and the activation energy is $E_a = 2.5 \text{ kcal/mol}$.
 - (b) Compare your answer to the lifetime of Cl atom with respect to reaction with O₃ at 25 km (which we probably calculated in class on September 29). If your calculation in part (a) was correct, something should not make sense here. What is it?
 - (c) HCl formation becomes especially important when the ambient O₃ is very low. (It is therefore a key mechanism for the recovery of O₃.) Explain how this makes the comparison in part (b) make more sense.
3. (Inspired by Baird and Cann, Additional Problem 1(b), on p. 88) Calculate the total mass of ozone (in kg) present in the atmosphere if the average column abundance is 350 Dobson Units (DU). Assume (or remember) the following:
 - a. The earth is a sphere with surface area $4\pi r^2$.
 - b. The radius of the earth is 6380 km.
 - c. Reporting column abundances in DU assumes that $[\text{O}_3] = 2.688 \times 10^{19} \text{ molecule cm}^{-3}$.

Problem Set 2 concludes on the back.

4. The same kind of ozone-depleting chemistry driven by chlorine can be driven by bromine as well.

(a) Calculate the equilibrium constants (at 222 K) for these competing reactions:



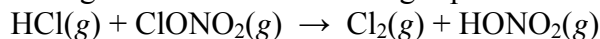
Use the following data in your calculations:

Species	$\Delta_f H^\circ$ (kcal mol ⁻¹)	S° (cal mol ⁻¹ K ⁻¹)
BrO	29.6	55.6
NO ₂	7.9	57.4
BrOOBr	41	76.3
BrONO ₂	10.1	74.9

Show all your work explicitly for one of the reactions; for the other reaction, you may just write down $\Delta_r H^\circ$, $\Delta_r S^\circ$, and K .

- (b) Based on your results in part (a), and our results in class, does bromine or chlorine pose more of a threat to stratospheric ozone? Explain your answer.
5. In the stratosphere, 5 ppm of H₂O vapor in the presence of HNO₃(g) will condense at around 195 K. In contrast, the same mixing ratio of H₂O vapor in the presence of H₂SO₄(g) will condense at temperatures as high as 220 K. (The ability of sulfuric acid aerosols to form at significantly higher temperatures leads to enhanced ozone depletion at lower latitudes.) Explain this difference in behavior. Draw Lewis structures as part of your explanation.
6. Provide qualitative, but specific, answers (including Lewis structures, when appropriate) to the following questions:

(a) Why is the following reaction so slow in the gas phase?



(b) Which reaction would happen more quickly on Polar Stratospheric Clouds, and why?

