PROBLEM 1

Consider the following 3-step mechanism for the production and destruction of excited oxygen atoms, O*, in the atmosphere:

$$O_2 \xrightarrow{\text{light}} O + O^*$$

$$O^* + M \longrightarrow O + M$$

$$O^* + H_2O \longrightarrow 2\ OH$$

Develop an expression for the steady-state concentration of O* in terms of the concentrations of the other chemicals involved.

PROBLEM 2

Perform a steady-state analysis for d(Cl]/dt and for d[ClO]/dt in the following mechanism:

$$Cl_2 \longrightarrow 2\ Cl \qquad (1)$$

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (2)$$

$$2\ ClO \longrightarrow 2\ Cl + O_2 \qquad (3)$$

$$ClO + NO_2 \longrightarrow ClONO_2 \qquad (4)$$

Obtain expressions for the steady-state concentrations of Cl and ClO, and hence for the rate of destruction of ozone.

PROBLEM 3

Perform a steady-state analysis on the 3-step reaction mechanism below. Assume that both ozone and atomic oxygen are in a steady state, and derive an expression for the ratio $[NO_2]/[NO]$.

$$NO_2 \longrightarrow NO + O$$

$$O + O_2 \longrightarrow O_3$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

Review Questions

Test your knowledge of some of the factual information in this chapter. If the answer to a question is not obvious to you, use the Index to find the subtopic involved and review that material.

1. Which three gases constitute most of the Earth's atmosphere?

2. What range of altitudes constitutes the troposphere? the stratosphere?

3. What is the wavelength range for visible light? Does ultraviolet light have shorter or longer wavelengths than visible light?

4. Which atmospheric gas is primarily responsible for filtering sunlight in the 120–220-nm region? Which, if any, gas absorbs most of the Sun's rays in the 220–320-nm region? Which absorbs primarily in the 320–400-nm region?

5. What is the name given to the finite packets of light absorbed by matter?

6. What are the equations relating photon energy E to light's frequency ν and wavelength λ?

7. What is meant by the expression *photochemically dissociated* as applied to stratospheric O_2?

8. Write the equation for the chemical reaction by which ozone is formed in the stratosphere. What are the sources for the different forms of oxygen used here as reactants?

9. Write the two reactions that, aside from the catalyzed reactions, contribute most significantly to ozone destruction in the stratosphere.

10. What is meant by the phrase *excited state* as applied to an atom or molecule? Symbolically, how is an excited state signified?

11. Explain why the phrase *ozone layer* is a misnomer.

12. Define the term *free radical*, and give two examples relevant to stratospheric chemistry.

13. What are the two steps, and the overall reaction, by which X species such as ClO catalytically destroy ozone in the middle and upper stratosphere via Mechanism I?

14. What is meant by the term *steady state* as applied to the concentration of ozone in the stratosphere?

15. Explain why, atom for atom, stratospheric bromine destroys more ozone than does chlorine.

16. Explain why ozone destruction via the reaction of O_3 with atomic oxygen does not occur to a significant effect in the lower stratosphere.

Additional Problems

The problems given within the chapter, and the more elaborate ones given here, are designed to test your problem-solving abilities.

1. A possible additional mechanism that could exist for the creation of ozone in the high stratosphere begins with the creation of (vibrationally) excited O_2 and ground-state atomic oxygen from the absorption of photons with wavelengths less than 243 nm. The O_2* reacts with a ground-state O_2 molecule to produce ozone and another atom of oxygen. What is the net reaction from these two steps? What do you predict is the fate of the two oxygen atoms, and what would be the overall reaction once this fate is included?

2. In the nonpolluted atmosphere, an important mechanism for ozone destruction in the lower stratosphere is

$$OH + O_3 \longrightarrow HOO + O_2$$
$$HOO + O_3 \longrightarrow OH + 2\,O_2$$

Does this pair of steps correspond to Mechanism I? If not, what is the overall reaction?

3. A proposed mechanism for ozone destruction in the late spring over northern latitudes in the lower stratosphere begins with the photochemical decomposition of $ClONO_2$ to Cl and NO_3, followed by photochemical decomposition of the latter to NO and O_2. Deduce a catalytic ozone destruction cycle, requiring no atomic oxygen, that incorporates these reactions. What is the overall reaction?

4. Deduce possible reaction step(s), none of which involve photolysis, for Mechanism II following the $X + O_3 \longrightarrow XO + O_2$ step such that the sum of all the mechanism's steps does not destroy or create any ozone.

5. As will be discussed in Chapter 2, atomic chlorine is produced under ozone-hole conditions by the dissociation of diatomic chlorine, Cl_2. Given that diatomic chlorine gas is the stablest form of the element, and that the ΔH_f° value for atomic chlorine is $+121.7$ kJ mol^{-1}, calculate the maximum wavelength of light that can dissociate diatomic chlorine into the monatomic form. Does such a wavelength correspond to light in the visible or the UV-A or the UV-B region?

6. Under conditions of low oxygen atom concentration, the radical HOO can react reversibly with NO_2 to produce a molecule of $HOONO_2$:

$$HOO + NO_2 \longrightarrow HOONO_2$$

(a) Deduce why the addition of nitrogen oxides to the lower stratosphere could lead to an *increase* in the steady-state ozone concentration as a consequence of this reaction.

(b) Deduce how the addition of nitrogen oxides to the middle and upper stratosphere could *decrease* the ozone concentration there as a consequence of other reactions.

(c) Given the information stated in parts (a) and (b), in what regions of the stratosphere should supersonic transport airplanes fly if they emit substantial amounts of nitrogen oxides in their exhaust?

7. At an altitude of about 35 km, the average concentrations of O* and of CH_4 are approximately 100 and 1×10^{11} molecules cm^{-3}, respectively, and the rate constant k for the reaction between them is approximately 3×10^{-10} cm^3 $molecules^{-1}$ s^{-1}. Calculate the rate of destruction of methane in molecules per second per cubic centimeter and in grams per year per cubic centimeter under these conditions. [*Hint:* Recall that the rate law for a simple process is its rate constant k times the product of the concentrations of its reactant concentrations.]

8. The rate constants for the reactions of atomic chlorine and of hydroxyl radical with ozone are given by $3 \times 10^{-11}\, e^{-250/T}$ and $2 \times 10^{-12}\, e^{-940/T}$, where T is the Kelvin temperature. Calculate the ratio of the rates of ozone destruction by these catalysts at 20 km, given that at this altitude the average concentration of OH is about 100 times that of Cl and that the temperature is about −50°C. Calculate the rate constant for ozone destruction by chlorine under conditions in the Antarctic ozone hole, when the temperature is about −80°C and the concentration of atomic chlorine increases by a factor of one hundred to about 4×10^5 molecules cm^{-3}.

9. The Arrhenius equation (see Box 1-2, and note that in energy terms, $R = 8.3$ J K^{-1} mol^{-1}) relates reaction rates to temperature via the activation energy. Calculate the ratio of the rates at −30°C (a typical stratospheric temperature) for two reactions having the same Arrhenius A factor and initial concentrations, one of which is endothermic and has an activation energy of 30 kJ mol^{-1} and the other which is exothermic with an activation energy of 3 kJ mol^{-1}.