CHAPTER 1

Stratospheric Chemistry: The Ozone Layer

Problem 1-1

From the text, \( E = \frac{119627}{\lambda} \) where \( \lambda \) is in nm and the units of the constant are nm kJ mol\(^{-1}\)

(a) \( E = \frac{119627 \text{ nm kJ mol}^{-1}}{280 \text{ nm}} = 427 \text{ kJ mol}^{-1} \)
    From Figure 1-2, 280 nm lies in the UV region, at the junction between UV-B and UV-C

(b) \( E = \frac{119627 \text{ nm kJ mol}^{-1}}{400 \text{ nm}} = 299 \text{ kJ mol}^{-1} \)
    Junction of UV(-A) and visible regions

(c) \( E = \frac{119627 \text{ nm kJ mol}^{-1}}{750 \text{ nm}} = 160 \text{ kJ mol}^{-1} \)
    Junction of visible and infrared regions

(d) \( E = \frac{119627 \text{ nm kJ mol}^{-1}}{4000 \text{ nm}} = 29.9 \text{ kJ mol}^{-1} \)
    Beginning of thermal IR region

Problem 1-2

Rearrange the formula from Problem 1-1 to obtain \( \lambda \):

\[ \lambda = \frac{119627}{E} = \frac{119627 \text{ nm kJ mol}^{-1}}{105 \text{ nm}} = 1140 \text{ nm}, \text{i.e., IR light.} \]

Problem 1-3

Obtain \( E \) as \( \Delta H^\circ \) of the reaction

\[
\begin{align*}
\text{NO}_2 & \rightarrow \text{NO} + \text{O} \\
\Delta H^\circ &= \Delta H^\circ (\text{NO}) + \Delta H^\circ (\text{O}) - \Delta H^\circ (\text{NO}_2) \\
&= 90.2 + 249.2 - 33.2 \\
&= 306.2 \text{ kJ mol}^{-1}
\end{align*}
\]

\[ \lambda = \frac{119627}{E} = \frac{119627 \text{ nm kJ mol}^{-1}}{306.2 \text{ kJ mol}^{-1}} = 390.7 \text{ nm} \]
For the complete dissociation, we need $\Delta H^\circ$ for

$$
\text{NO}_2 \longrightarrow \text{N} + 2 \text{O}
$$

$$
\Delta H^\circ = \Delta H^\circ_\text{f} (\text{N}) + 2 \Delta H^\circ_\text{f} (\text{O}) - \Delta H^\circ_\text{f} (\text{NO}_2)
$$

$$
= 472.7 + 2 \times 249.2 - 33.2
= 937.9
$$

$$
\lambda = \frac{19627}{937.9} = 127.5 \text{ nm}
$$

Box 1-1 Problem 1

Labelling the reactions given in the text as 1, 2, and 3, then the expression for the rate of change of the concentration of $\text{O}^\circ$ with time is

$$
d [\text{O}^\circ] / dt = k_1 [\text{O}_2] - k_2 [\text{O}^\circ] [\text{M}] - k_3 [\text{O}^\circ] [\text{H}_2\text{O}]
$$

But $d [\text{O}^\circ] / dt = 0$ at steady state.

Thus, setting the right-hand side of this equation to zero, and collecting terms involving $\text{O}^\circ$ on the left, we obtain

$$
[\text{O}^\circ] (k_1 [\text{M}] + k_3 [\text{H}_2\text{O}]) = k_1 [\text{O}_2]
$$

and thus

$$
[\text{O}^\circ] = \frac{k_1 [\text{O}_2]}{k_1 [\text{M}] + k_3 [\text{H}_2\text{O}]}
$$
Box 1-3, Problem 2

Since Cl is formed in steps 1 and 3 and destroyed in step 2, we obtain

\[ \frac{d [Cl]}{dt} = 2 k_1 [Cl]_1 - k_2 [Cl] [O_3] + 2 k_3 [ClO]^2 = 0 \text{ at steady state} \]

where the coefficients of 2 are needed since two Cl's are formed, and the square of ClO is required since two of them are reactants in the step.

Similarly, 

\[ \frac{d [ClO]}{dt} = k_4 [Cl] [O_3] - k_5 [ClO]^2 - k_6 [ClO] [NO_2] = 0 \]

If we add the two equations together, the middle two terms will cancel out, leaving the simple equation

\[ 2 k_1 [Cl]_1 - k_5 [ClO] [NO_2] = 0 \]

which we can use to solve for [ClO]:

\[ [ClO] = \frac{2 k_1 [Cl]_1}{k_5 [NO_2]} \]

Since the equation for \( \frac{d [Cl]}{dt} \) contains only one term for [ClO], we can substitute this expression into it to obtain an equation in [Cl]:

\[ 2 k_1 [Cl]_1 - k_2 [Cl] [O_3] + 2 k_3 [ClO]^2 / k_5 [NO_2]^2 = 0 \]

The rate of destruction of O_3 is simply the middle term, \( k_2 [Cl] [O_3] \), of this equation, so by rearrangement we obtain for its net rate of change (\( = -k_1 [Cl] [O_3] \)):

\[ \text{Rate of change in } [O_3] = -2 k_1 [Cl]_1 - 8 k_2 k_5 [ClO]^2 / k_5 [NO_2]^2 \]

Alternatively, the equation for [Cl] can be obtained by solving the equation for the middle term:

\[ k_1 [Cl] [O_3] = 2 k_1 [Cl]_1 + 8 k_2 k_5 [ClO]^2 / k_5 [NO_2]^2 \]

\[ [Cl] = 2 k_1 [Cl]_1 / k_2 [O_3] + 8 k_2 k_5 [ClO]^2 / k_5 [O_3] [NO_2]^2 \]

Problem 1-7

Since \( X = OH \) here, we obtain by substituting it for X in the two steps of Mechanism 1,

\[ \text{OH} + \text{O}_3 \rightarrow \text{HOO} + \text{O}_2 \]

\[ \text{HOO} + \text{O} \rightarrow \text{OH} + \text{O}_2 \]

Adding these two reactions, and cancelling the common OH and HOO terms, we obtain

\[ \text{O}_3 + \text{O} \rightarrow 2 \text{O}_2 \]
a. An equilibrium system is a closed system in which the forward and reverse processes are occurring at the same time and at equal rates. A steady-state system is an open system in which an intermediate is formed and destroyed at the same rate in separate reactions.

Equilibrium system (A = B)

\[ \text{Reactants} \xleftrightarrow{A \rightarrow B} \text{Products} \]

Steady-state system (A = B)

\[ \text{Reactants} \xrightarrow{A} \text{Intermediate} \xrightarrow{B} \text{Products} \]

Problem 2

a. \( p(\text{Ar sea level}) = (1.5 \text{ atm})(0.0093) \)
   \[ = 1.4 \times 10^{-2} \text{ atm} \]

   \( p(\text{Ar 38km}) = (0.045 \text{ atm})(0.0093) \)
   \[ = 4.2 \times 10^{-4} \text{ atm} \]

b. \( \text{ppmv} = \frac{p(\text{Ar}) \times 10^6}{p(\text{total})} \)

   \( p(\text{Ar sea level}) = \frac{p(1.4 \times 10^{-2} \text{ atm}) \times 10^6}{p(1.5 \text{ atm})} = 9.3 \times 10^3 \text{ ppmv} \)

   \( p(\text{Ar 38 km}) = \frac{p(4.2 \times 10^{-4} \text{ atm}) \times 10^6}{p(0.045 \text{ atm})} = 9.3 \times 10^3 \text{ ppmv} \)

c. Air becomes thinner with increasing altitude. If the "mixing ratio" of a gas remains the same at different altitudes, the relative concentrations are constant, the Argon ppmv in Part (b); however, the partial pressure and therefore the absolute concentration of a gas may vary as shown in Part (a).

Problem 3
a. Knowing that $\lambda = \frac{hc}{E}$, for $h$ being Plank’s constant and $c$ being the speed of light, you must first calculate the bond energy, $E$.

For C-F bond:

$$E_{C-\text{F}} = \frac{423 \text{ kJ mol}^{-1} \times 1000 \text{ J}}{6.022 \times 10^{23} \text{ molecules mol}^{-1}} = 7.02 \times 10^{-19} \text{ J}$$

$$\lambda_{C-\text{F}} = \frac{hc}{E_{C-\text{F}}} = \frac{(6.625 \times 10^{-34} \text{Js})(3.00 \times 10^8 \text{ ms}^{-1})}{7.02 \times 10^{-19} \text{ J}} = 2.83 \times 10^{-7} \text{ m} = 283 \text{ nm}$$

For C-Cl bond:

$$E_{C-\text{Cl}} = \frac{544 \text{ kJ mol}^{-1} \times 1000 \text{ J}}{6.022 \times 10^{23} \text{ molecules mol}^{-1}} = 9.03 \times 10^{-19} \text{ J}$$

$$\lambda_{C-\text{Cl}} = \frac{hc}{E_{C-\text{Cl}}} = \frac{(6.625 \times 10^{-34} \text{Js})(3.00 \times 10^8 \text{ ms}^{-1})}{9.03 \times 10^{-19} \text{ J}} = 2.20 \times 10^{-7} \text{ m} = 220 \text{ nm}$$

b. Figure 1-5 (pg 9, 5th and pg 33 4th) in the textbook, shows that there is not much light intensity below the wavelength of 305 nm. Therefore there is not sufficient energy to break the C-Cl or the C-F bonds.

c. There is not enough photon energy in the troposphere to break the C-F or C-Cl bonds. The nature of sunlight absorption by CFCs generally requires wavelengths of less than 220 nm for photolysis to occur.

Problems 4

The slow decline and lagged response can be attributed to:

a. CFC molecules are slow to migrate from ground level to the stratosphere

b. once in the stratosphere, chlorine and bromine removal is slow; and

c. there is continued release of some chlorine and bromine into the atmosphere.