CHEM 202040

Assignment 1

Solve the problems from the textbook (same for both 4th and 5th editions). You can refer to specific questions in the textbook using the pages and questions number given.

PROBLEM 1 [(Pg 39 4th Ed., Pg 15 5th Ed.) Problem 1-1]

What is the energy, in kilojoules per mole, associated with photons having the following wavelengths?

What is the significance of each of these wavelengths? [*Hint*: See Figure 1-2.]

(a) 280 nm (b) 400 nm (c) 750 nm (d) 4000 nm

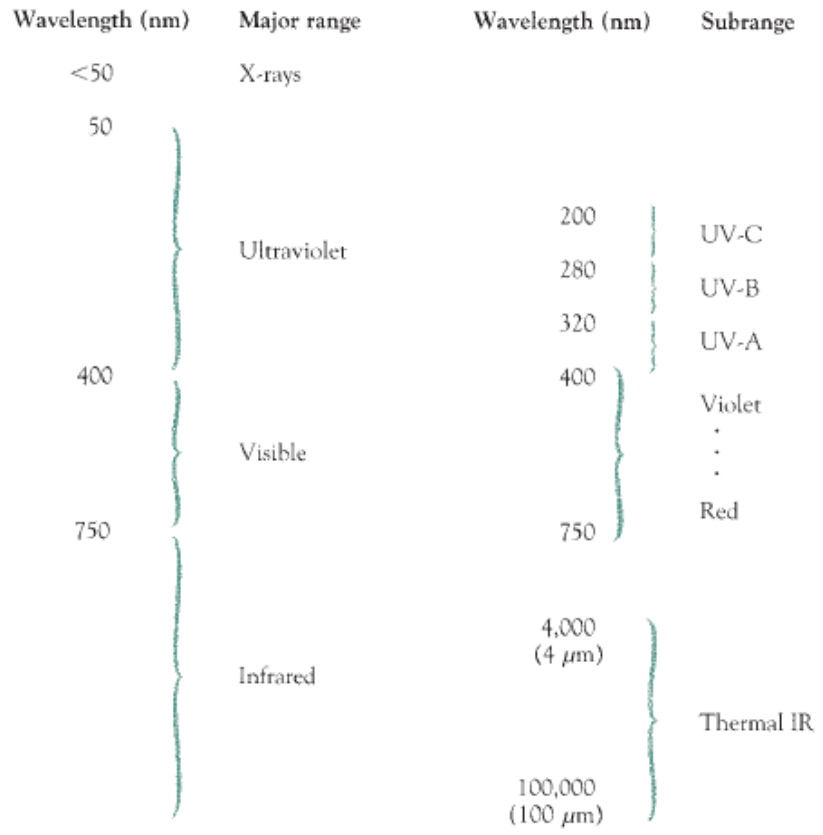

FIGURE 1-2 The electromagnetic spectrum. The ranges of greatest environmental interest in this book are shown.

PROBLEM 2 (Pg 39 4th Ed., Pg 15 5th Ed.) Problem 1-2]

The $\Delta H°$ for the decomposition of ozone into O2 and atomic oxygen is +105 kJ mol^{-1}:

$$O_3 \longrightarrow O_2 + O$$

What is the longest wavelength of light that could dissociate ozone in this manner? By reference to Figure 1-2, identify the region of sunlight (UV, visible, or infrared). Does O_3 absorb in this region?

PROBLEM 3 [(Pg 39 4th Ed., Pg 15 5th Ed.) Problem 1-3]

Using the enthalpy of formation information given below, calculate the maximum wavelength that can dissociate NO_2 to NO and atomic oxygen. $NO_2 \longrightarrow NO + O$

Recalculate the wavelength if the reaction is to result in the complete dissociation into free atoms (i.e., N + 2O). $NO_2 \longrightarrow N + O_2$

Is light of these wavelengths available in sunlight?

$\Delta H_f°$ values (kJ mol^{-1}): NO_2: +33.2; NO: +90.2; N: +472.7; O: +249.2

PROBLEM 4 [Pg 44 4th Ed., Pg 30 5th Ed.) Box 1-1 4th Ed. , Box 1-3 5th Ed. 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 5 [(Pg 44 4th Ed., Pg 30 5th Ed.) Box 1-1 4th Ed., Box 1-3 5th Ed. Problem 2]

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

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

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

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

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

PROBLEM 6 [(Pg 51 4th Ed., Pg 25 5th Ed.) Problem 1-7]

Write out the two-step mechanism by which the hydroxyl free radical catalytically destroys ozone by Mechanism I. By adding together the steps, deduce the overall reaction.

Additional Problems (Not in Textbook)

Problem 7

Explain the difference between an equilibrium system and a steady-state system.

Problem 8

Argon makes up 0.93% of the air in the atmosphere. Assume the atmospheric pressure (temperature) is 1.5 atm (25°C) at sea level and 0.045 atm (-10°C) at 38 km high in the stratosphere.

a. Calculate the partial pressure of Ar (in atm) at each altitude.

b. Convert these partial pressures to units of ppmv.

c. Compare your values in Parts (a) and (b). What is the limitation of reporting relative concentrations in ppmv as compared to partial pressures?

Problem 9

Assume the average bond enthalpies of C-F and C-Cl are 417 and 537 kJ mol^{-1}, respectively.

a. Calculate the maximum wavelength of light required to break each of these bonds.

b. In each case, are photons available in the troposphere energetic enough to break that carbon-halogen bond through photodissociation?

c. Why do CFCs not photodissociate to an appreciable extent in the troposphere?

Problem 9

Despite the rapid phase-out of CFC use and production with the Montreal Protocol (1987) and subsequent amendments in London, Copenhagen, Vienna and Montreal, the stratosphere chlorine equivalent level is projected to start decreasing slowly only by 2005. (see Figure 2-21 textbook). Suggest reasons why this projection predicts both a lag in response and the slow rate of decline of chlorine equivalent levels in the stratosphere.