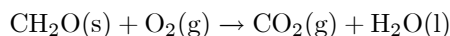


## Chapter 5

- 5.12** (a) As discussed in Section 5.2.1(a), the earth's atmosphere is strongly affected by biota (i.e., plants). For example, VOCs and HCs are emitted by plants. Therefore, statement has some truth.
- (b) (See Section 5.3.5.)  $O_3$  production is enhanced by  $NO_x$  from industrial and car emissions (eqns. (5.15)–(5.16) and (5.22)).
- (c) Residence time of  $CO_2$  is 3–4 years, whereas for  $H_2S$  it is 1–5 days (Table 5.1).
- (d) OH production requires  $h\nu$  (see eqn. (5.6)), and OH has very short residence time ( $\sim 1$  s).
- (e) OH,  $HO_2$ ,  $H_2O_2$ ,  $NO_x$  (Note:  $O_2$  and  $O_3$  have large bond energies and are therefore relatively unreactive except with radicals— $O_2$  is reactive only with highly unstable radicals).
- (f) Since  $O_3$  is involved in production of OH (eqn. (5.6)), and  $O_3$  is increasing due to emissions of  $NO_2$ , source of OH could be increasing. However some of the maximum sinks of OH are oxidation by CO (to form  $CO_2$ ) and HC, and concentrations of CO and HC are increasing due to industrial activities. Hence, concentration of OH may not be changing much. (Prinn et al. (1995) derived an OH trend of  $0 \pm 0.2\%$   $yr^{-1}$  based on model analysis of  $CH_3CCl_3$  data for the period 1978–1994.)
- (g) Because of scattering of sun's rays by particles in the air (compare with scattering from the beam of a slide projector).
- (h) Because of less attenuation of light by pollutants.
- (i) Due to flow around collectors, which biases against the collection of smaller particles.
- (j) Due to salt particles and humidity.
- (k) Due to thermal phoretic effect.
- (l) Due to g-to-p conversion.
- (m) If rate at which chemical is emitted is less than rate of removal, the amount of the chemical in the atmosphere would eventually decrease to essentially zero.
- (n) Clouds and precipitation (sinks for water vapor) are much more common in tropics than in polar regions.
- (o) Because at high temperatures  $N_2$  is oxidized to NO (thermal NO)—see Section 5.5.1.
- (p) Because most of UV radiation is absorbed in the stratosphere.
- (q) At very high altitudes  $h\nu$  is intense but the concentration of  $O_2$  is too low to produce much atomic oxygen via eqn. (5.47). At low altitudes there is plenty of  $O_2$ , but  $h\nu$  is reduced. At some intermediate height  $O_3$  will peak.

- (r) The sink reactions for atomic oxygen (5.48) and (5.50) remain, but the source reactions (5.47) and (5.49) are removed.
- (s) More stratospheric O<sub>3</sub> would lower  $h\nu$  in the troposphere. With less  $h\nu$  there would be less OH and therefore higher concentrations of tropospheric pollutants.
- (t) Because NaCl particles are relatively large and therefore confined to lower troposphere.
- (u) Because of lack of sunlight and isolation of polar vortex.
- (v) ClO (chlorine monoxide)—see eqns. (5.88).
- (w) ClO is formed by photolysis of Cl<sub>2</sub> when sun rises (only weak sunlight is needed) via eqns. (5.83) and (5.86).
- (x) In lower stratosphere of the polar vortex HCl condenses onto PSCs which sediment.
- (y) In the lower stratosphere HCl condenses to form PSCs. CH<sub>4</sub> is transported into stratosphere, hence it is present in higher concentrations in lower stratosphere. (CH<sub>4</sub> is depleted in low stratosphere by OH, and in upper stratosphere by O(<sup>1</sup>D) and Cl. Oxidation of CH<sub>4</sub> is the main source of H<sub>2</sub>O(g) in the stratosphere.
- (z) Because low temperatures might cause more PSCs.

**5.13** The reverse of the photosynthesis reaction (5.2) in this chapter is



which is the respiration reaction. If  $x$  is the oxidation number of C in CH<sub>2</sub>O we have

$$x + 2(+1) + (-2) = 0$$

Therefore,

$$x = 0$$

If  $y$  is the oxidation number of C in CO<sub>2</sub> we have

$$y + 2(-2) = 0$$

Therefore,

$$y = 4$$

**Change in oxidation number of C for the above reaction is +4.** Since the oxidation number of C is increased, C is *oxidized*. (NOTE: "burning" = "oxidation").

**5.14** Molecular weight of NH<sub>3</sub> is  $14 + 3(1.01) = 17.03$ . Therefore, the number of moles of NH<sub>3</sub> in 1 m<sup>3</sup> of air at 0°C and 1 atm is  $\frac{0.456 \times 10^{-6}}{17.03}$ , and

number of molecules of  $\text{NH}_3$  in  $1 \text{ m}^3$  of air is  $\frac{0.456 \times 10^{-6}}{17.03}$  (Avogadro's number)

$$= \left( \frac{0.456 \times 10^{-6}}{17.03} \right) (6.022 \times 10^{23}).$$

The total number of molecules in  $1 \text{ m}^3$  of air at 1 atm and  $0^\circ\text{C}$  is Loschmidt's number which, from Ex. 5.1, is  $2.687 \times 10^{25}$  molecules  $\text{m}^{-3}$ . Therefore, the fraction of  $\text{NH}_3$  molecules in air (and therefore the fraction of  $\text{NH}_3$  by volume in air) is

$$\begin{aligned} & \frac{\frac{0.456 \times 10^{-6}}{17.03} (6.022 \times 10^{23})}{2.687 \times 10^{25}} \\ &= 6.00 \times 10^{-10} \\ &= \underline{\underline{\mathbf{0.600 \text{ ppbv}}}} \end{aligned}$$

**5.15** Since it is an adiabatic expression, we have for the air in the chamber

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

and

$$p_1 v_1^\gamma = p_2 v_2^\gamma$$

Therefore

$$T_2 = \left( \frac{v_1}{v_2} \right)^{\gamma-1} T_1$$

with  $\frac{v_2}{v_1} = 1.2$  and  $T_1 = 288^\circ\text{K}$

$$\begin{aligned} T_2 &= (0.8333)^{1.4-1} 288 \\ &= (0.8333)^{0.4} 288 \\ &= 0.9297 \times 288 \\ &= 267.74 \text{ K} = -5.26^\circ\text{C} \end{aligned}$$

$$\text{Maximum saturation ratio} = \frac{e(T_2)}{e_s(T_2)}$$

For the water vapor itself

$$\frac{e_s(T_1) v_1}{T_1} = \frac{e(T_2) v_2}{T_2}$$

Therefore,

$$\begin{aligned} e(T_2) &= \frac{T_2 v_1}{T_1 v_2} e_s(T_1) \\ &= \frac{267.74}{288} \frac{1}{1.2} 17 \text{ hPa} [e_s(15^\circ\text{C}) = 17 \text{ hPa from Fig. 3.9}] \\ &= 13.17 \text{ hPa} \end{aligned}$$

Therefore,

$$\begin{aligned}
\text{Maximum saturation ratio} &= \frac{13.17}{e_s(-5.26^\circ\text{C})} = \frac{13.17}{4} [e_s(-5.26^\circ\text{C}) = 4 \text{ hPa from Fig. 3.9}] \\
&= 3.29 \\
\text{Maximum supersaturation (\%)} &= (\text{saturation ratio} - 1)100 \\
&= (3.29 - 1)100 \\
&= \underline{\underline{229\%}}
\end{aligned}$$

**5.16** (a) If particles are spherical

$$dS = \pi D^2 dN$$

Therefore,

$$\frac{dS}{d(\log D)} = \pi D^2 \frac{dN}{d(\log D)}$$

Hence, using (5.31),

$$\frac{dS}{d(\log D)} = \pi C D^{2-\beta}$$

(b) For spherical particles,

$$dV = \frac{\pi}{6} D^3 dN$$

Therefore,

$$\frac{dV}{d(\log D)} = \frac{\pi}{6} D^3 \frac{dN}{d(\log D)}$$

Hence, using (5.31),

$$\frac{dV}{d(\log D)} = \frac{\pi}{6} C D^{3-\beta}$$

From the expression derived in (a) we see that  $dS/d(\log D)$  is an increasing function of  $D$  for  $\beta < 2$  and a decreasing function of  $D$  for  $\beta > 2$ . Hence, the surface area distribution will reach a peak value when  $\beta$  passes through a value of 2. Similarly, from the expression derived in (b) above, we see that the volume distribution will attain a peak value when  $\beta$  passes through a value of 3.

**5.17**

$$m \frac{dv}{dt} = 6\pi\eta r v$$

Therefore,

$$\frac{dv}{v} = -\frac{6\pi\eta r}{m} dt$$

and,

$$\int_{v_o}^v \frac{dv}{v} = -\frac{6\pi\eta r}{m} \int_o^t dt$$

$$\ln \frac{v}{v_o} = -\frac{6\pi\eta r}{m} t$$

or,

$$v = v_o \exp\left(-\frac{6\pi\eta r}{m} t\right)$$

Therefore,

$$\frac{dx}{dt} = v_o \exp\left(-\frac{6\pi\eta r}{m} t\right)$$

$$\int_0^L dx = v_o \int_0^\infty \exp\left(-\frac{6\pi\eta r}{m} t\right) dt$$

or,

$$L = v_o \frac{m}{6\pi\eta r}$$

**5.18** The residence time  $\tau$  is given by

$$\tau = \frac{M}{F}$$

where  $M$  is the quantity of chemical in the atmosphere, and  $F$  the efflux. For  $\text{NH}_3$ ,

$$M = \frac{1 \times 10^{-8}}{100} (5 \times 10^{18}) \text{ kg}$$

and  $F = 5 \times 10^{10}$  kg per year, therefore,  $\tau_{\text{NH}_3} = 0.01\text{a} = \mathbf{4 \text{ days}}$ . For  $\text{N}_2\text{O}$ ,

$$M = \frac{(3 \times 10^{-5})}{100} (5 \times 10^{18}) \text{ kg}$$

and  $F = 1 \times 10^{10}$  kg per year, therefore,  $\tau_{\text{N}_2\text{O}} = \mathbf{150 \text{ years}}$ . For  $\text{CH}_4$ ,

$$M = \frac{(7 \times 10^{-5})}{100} (5 \times 10^{18}) \text{ kg}$$

and  $F = 4 \times 10^{11}$  kg per year, therefore,  $\tau_{\text{CH}_4} = \mathbf{9 \text{ years}}$ .

**5.19** We can imagine the deposition velocity as the rate at which a column of gas is deposited onto the ground. Hence, the time required to deplete a 5 km high column at  $0.4 \text{ cm s}^{-1}$  is

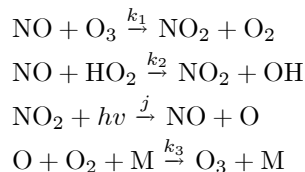
$$\frac{5 \text{ km}}{0.40 \times 10^{-5} \text{ km s}^{-1}} = 12.5 \times 10^5 \text{ s}$$

$$= 14.47 \text{ days}$$

$$\simeq \underline{\underline{\mathbf{14 \text{ days}}}}$$

This calculation gives an upper limit to the residence time of  $O_3$  because other (*in situ*) removal mechanisms have not been considered. Compare this estimate to "days to weeks" for the residence time of  $O_3$  given in Table 5.1.

5.20 (a)



(b)

$$\begin{aligned} \frac{d[\text{NO}]}{dt} &= -k_1[\text{NO}][\text{O}_3] - k_2[\text{NO}][\text{HO}_2] + j[\text{NO}_2] \\ \frac{d[\text{O}_3]}{dt} &= -k_1[\text{NO}][\text{O}_3] + k_3[\text{O}][\text{O}_2][\text{M}] \\ \frac{d[\text{NO}_2]}{dt} &= -\frac{d[\text{NO}]}{dt} \\ \frac{d[\text{HO}_2]}{dt} &= -k_2[\text{NO}][\text{HO}_2] \\ \frac{d[\text{HO}]}{dt} &= k_2[\text{NO}][\text{HO}_2] \\ \frac{d[\text{O}]}{dt} &= j[\text{NO}_2] - k_3[\text{O}][\text{O}_2][\text{M}] \end{aligned}$$

(c) Under steady-state conditions

$$\frac{d[\text{NO}]}{dt} = 0$$

and, if  $[\text{HO}_2] = 0$ , the first equation in (b) above becomes

$$[\text{O}_3] = \frac{j[\text{NO}_2]}{k_1[\text{NO}]}$$

5.21 Some of the increase in atmospheric  $\text{CO}_2$  over, say, the past 50 years may be due to an increase in the average temperature of the oceans, which would cause a decrease in the solubility of  $\text{CO}_2$  in the oceans and therefore release  $\text{CO}_2$  into the atmosphere. Estimate the percentage change in the  $\text{CO}_2$  content of the atmosphere due to an average warming of  $0.5^\circ\text{C}$  in the upper (mixed) layer of the world's oceans over the past 50 years. (Assume that the average temperatures of the mixed layer of all the oceans has increased from  $15.0^\circ\text{C}$  to  $15.5^\circ\text{C}$ . You may treat the ocean water as pure water.)

Based on your calculation, does it appear likely that the measured increase in atmospheric CO<sub>2</sub> over the past 50 years (~20%) is due to warming of the oceans?

You will need to use the following information. The solubility,  $C_g$ , of a gas in a liquid is given by Henry's law:

$$C_g = k_H p_g$$

where  $k_H$  is the Henry's law constant, and  $p_g$  the partial pressure of the gas over the solution. For CO<sub>2</sub> in pure water,  $k_H = 4.5 \times 10^{-2} \text{ M atm}^{-1}$  at 15°C. The temperature dependence of  $k_H$  is given by

$$\ln \frac{k_H(T_2)}{k_H(T_1)} = \frac{\Delta H}{R^*} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

where for CO<sub>2</sub> in water  $\Delta H = -20.4 \times 10^3 \text{ J mol}^{-1}$ , and  $R^*$  is the universal gas constant ( $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ ). The total mass of carbon in the form of CO<sub>2</sub> in the mixed layer of the world's oceans is  $\sim 6.7 \times 10^5 \text{ Tg}$ , which is about the same as the mass of CO<sub>2</sub> in the atmosphere.

*Answer* +7.5% of the observed increase in CO<sub>2</sub>. No.

**Solution:**

$$C_g = k_H p$$

Therefore,

$$\Delta C_g = p \Delta k_H$$

We can determine  $\Delta k_H$  from

$$\begin{aligned} \ln \frac{k_H(288.5^\circ\text{K})}{k_H(288^\circ\text{K})} &= \frac{-20.4 \times 10^3}{8.3} \left( \frac{1}{288} - \frac{1}{288.5} \right) \\ &= -2.459 (3.472 - 3.466) \end{aligned}$$

Therefore,

$$\begin{aligned} \ln \frac{k_H(288.5 \text{ K})}{k_H(288 \text{ K})} &= (-14.7 \times 10^{-3}) \\ &= -0.0147 \end{aligned}$$

Therefore,

$$\frac{k_H(288.5^\circ\text{K})}{k_H(288^\circ\text{K})} = 0.985$$

or,

$$\begin{aligned} k_H(288.5^\circ\text{K}) &= 0.985 [k_H(288^\circ)] \\ &= 0.985 (4.5 \times 10^{-2}) \\ &= 4.433 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1} \end{aligned}$$

Therefore,

$$\Delta k_H = (4.433 - 4.5) 10^{-2} = -6.7 \times 10^{-4} \text{ mol L}^{-1} \text{ atm}^{-1}$$

Hence,

$$\Delta C_g = -6.7 \times 10^{-4} \text{ mol L}^{-1} \text{ (at 1 atm for } T \text{ changing from 288 K to 288.5 K)}$$

Therefore,

$$\text{Percentage change in } C_g = \frac{-6.7 \times 10^{-4}}{4.5 \times 10^{-2}} \times 100 = -1.5\%$$

Therefore, percentage decrease in  $\text{CO}_2$  in mixed layer of oceans is 1.5%. Since the  $\text{CO}_2$  capacity of the atmosphere is about the same as the mixed layer of the oceans, the percentage increase in  $\text{CO}_2$  in atmosphere due to  $0.5^\circ\text{C}$  warming of oceans will be  $\sim 1.5\%$ .

The above calculation shows that percentage increase in  $\text{CO}_2$  in atmosphere due to  $0.5^\circ\text{C}$  increase in the average temperature of the mixed layers of the world's oceans over the past 50 years is  $\sim 1.5\%$ . However, measured percentage increase in atmospheric  $\text{CO}_2$  over past 50 years is  $\sim 20\%$ . Therefore, warming of oceans can account for only  $\sim 7.5\%$  of observed increase in  $\text{CO}_2$  content of atmosphere.

*Answer:* No.

**5.22** This exercise is a follow-on to Exercise 5.8.

- (a) In reality, combustion in cars converts most of the hydrogen in the fuel to  $\text{H}_2\text{O}$  and most of the carbon in the fuel to varying amounts of  $\text{CO}_2$  and  $\text{CO}$  depending on the availability of oxygen.

If a fraction  $f$  of the  $\text{C}_x\text{H}_y$  fuel is provided in excess of that required for ideal combustion, derive an expression in terms of  $f$ ,  $x$ , and  $y$  for the mole fraction of  $\text{CO}$  in the emissions (i.e., the ratio of the number of moles of  $\text{CO}$  to the total number of moles in the emissions). Assume that oxygen is made available to the fuel at the rate required for ideal combustion (even though ideal combustion is not achieved), and that the only effect of the excess  $\text{C}_x\text{H}_y$  is to add  $\text{CO}$  to the emissions and to change the amount of  $\text{CO}_2$  emitted.

- (b) Assuming that  $\text{CH}_2$  is a reasonable approximation for a general hydrocarbon fuel, use the result from (a) to determine the concentrations (in ppmv and percent) of  $\text{CO}$  in the emissions from an engine for the following values of  $f$ : 0.0010, 0.010, and 0.10.

$$\text{Answer (a) } \frac{f \left( 2x + \frac{y}{2} \right)}{x(4.7 + f) + \frac{y}{2}(2.85 + f)}$$

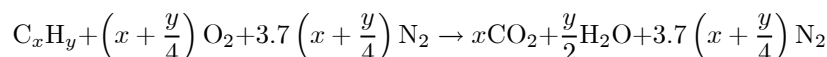
$$\text{(b) } 397 \text{ ppmv } (= 0.0397\%); 3960 \text{ ppmv } (0.396\%); 38700$$



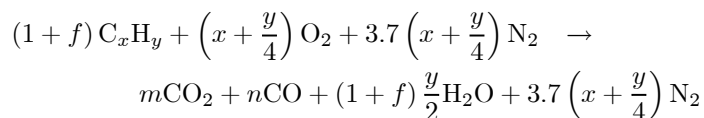
ppmv (3.87%). (The last concentration of CO would kill you in a closed garage in  $\sim 17$  mins.)

**Solution:**

- (a) If we include the (unreacting) nitrogen in the balanced chemical equation for *complete* combustion, we have from an extension of eqn. (5.34) in Chapter 5



However, if a fraction  $f$  of fuel is provided in excess of that needed for complete combustion and, as a consequence,  $m$  moles of  $CO_2$  and  $n$  moles of  $CO$  are contained in the emissions, the chemical equation for combustion becomes



Balancing the carbon atoms for this reaction yields

$$x(1+f) = m + n \tag{1}$$

and, balancing the oxygen atoms, gives

$$2x + \frac{y}{2} = (1+f)\frac{y}{2} + 2m + n \tag{2}$$

Solving (1) and (2) for  $m$  and  $n$  yields

$$m = x - xf - f\frac{y}{2}$$

and,

$$n = f\frac{y}{2} + 2fx$$

Therefore, the mole fraction of  $CO$  in the emissions is

$$\frac{f\frac{y}{2} + 2fx}{\underbrace{\left(x - xf - f\frac{y}{2}\right)}_{CO_2} + \underbrace{\left[3.7 \left(x + \frac{y}{4}\right)\right]}_{N_2} + \underbrace{\left(f\frac{y}{2} + 2fx\right)}_{CO} + \underbrace{\left(1+f\right)\frac{y}{2}}_{H_2O}}$$

$$= \frac{f \left(2x + \frac{y}{2}\right)}{x(4.7+f) + \frac{y}{2}(2.85+f)}$$

- (b) If the fuel is  $\text{CH}_2$ ,  $x = 1$  and  $y = 2$ . Therefore, from the answer to (a) above, the mole fraction of CO in the emissions is

$$\frac{3f}{7.55 + 2f}$$

**Therefore, for  $f = 0.001$  the mole fraction of unburned CO is  $3.97 \times 10^{-4}$  or 397 ppmv (= 0.0397%). For  $f = 0.01$  it is  $3.96 \times 10^{-3}$  or 3960 ppmv (= 0.396%). For  $f = 0.1$  it is  $3.87 \times 10^{-2}$  or 38700 ppmv (= 3.87%).** This last concentration of CO is enough to kill you in a closed garage in about 17 minutes!

- 5.23** (a) Write down the rate law for the production of  $\text{NO}_2$  by reaction (5.36). Does this rate law explain why the production of  $\text{NO}_2$  by (5.36) increases sharply with increasing concentration of NO? (b) Another route for the production of  $\text{NO}_2$  from NO is reaction (5.17). If the rate coefficients for the production of  $\text{NO}_2$  by (5.36) and (5.17) are  $\sim 2 \times 10^{-38} \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $\sim 2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, and the concentrations of NO,  $\text{O}_3$  and  $\text{O}_2$  are 80 ppbv, 50 ppbv, and 209460 ppmv, respectively, compare the rates of production of  $\text{NO}_2$  by these two reactions.

*Answer* (a)  $\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_1 [\text{NO}]^2 [\text{O}_2]$ . Yes, because production of  $\text{NO}_2$  varies at  $[\text{NO}]^2$ .

(b) Reaction (5.17) produces  $\text{NO}_2$  at a rate  $5.8 \times 10^4$  faster than reaction (5.36).

**Solution:**

- (a) From (5.36)

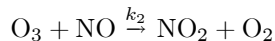
$$\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_1 [\text{NO}]^2 [\text{O}_2]$$

Production of  $\text{NO}_2$  increases sharply with increasing concentration of NO because it varies as the square of [NO].

- (b) For reaction (5.36) we are given that  $k = 2 \times 10^{-38} \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $[\text{NO}] = 80 \text{ ppbv}$  and  $[\text{O}_2] = 309460 \text{ ppmv}$ . However, the gas concentrations need to be converted to molecules  $\text{cm}^{-3}$  by multiplying them by Loschmidt's number which, from Exercise 5.1 is  $2.687 \times 10^{25} \text{ molecules m}^{-3} = 2.687 \times 10^{19} \text{ molecules cm}^{-3}$ . Therefore, from (a) above

$$\begin{aligned} \frac{1}{2} \frac{d[\text{NO}_2]}{dt} &= (2 \times 10^{-38}) \times \\ &\quad (80 \times 10^{-9} \times 2.687 \times 10^{19})^2 \times \\ &\quad (209460 \times 10^{-6} \times 2.687 \times 10^{19}) \text{ molecules cm}^{-3} \text{ s}^{-1} \\ \frac{d[\text{NO}_2]}{dt} &\simeq \underline{10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}} \end{aligned}$$

For reaction (5.17)



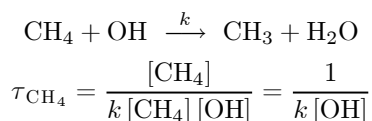
$$\begin{aligned} \frac{d[\text{NO}_2]}{dt} &= k_2 [\text{O}_3] [\text{NO}] \\ &= (2 \times 10^{-14}) (50 \times 10^{-9} \times 2.687 \times 10^{19}) \\ &\quad (80 \times 10^{-9} \times 2.687 \times 10^{19}) \\ &= \underline{5.8 \times 10^{10} \text{ molecules cm}^{-3} \text{ s}^{-1}} \end{aligned}$$

Therefore, reaction (5.17) produces  $\text{NO}_2$  at a rate  $\frac{5.8 \times 10^{10}}{10^6} = \underline{5.8 \times 10^4 \text{ times as fast}}$  as reaction (5.36).

5.24

$$\tau_{\text{CH}_4} = \frac{\text{Abundance of CH}_4}{\text{Removal rate of CH}_4}$$

Since



$$\begin{aligned} \therefore \tau_{\text{CH}_4} &= \frac{1}{(3.5 \times 10^{-15} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}) \times (1 \times 10^6 \text{ molecule cm}^{-3})} \\ &= 0.29 \times 10^9 \text{ s} \\ &= \underline{\mathbf{9 \text{ years}}} \end{aligned}$$

5.25 (a) As in Exercise (5.24) above,

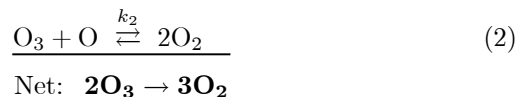
$$\begin{aligned} \tau_{\text{C}_3\text{H}_8} &= \frac{1}{k [\text{OH}]} \\ &= \frac{1}{(6.1 \times 10^{-13}) (1 \times 10^6)} \\ &= 0.16 \times 10^7 \text{ s} \\ &= \underline{\mathbf{19 \text{ days}}} \end{aligned}$$

(b) **NMHC**, because their residence time is so much shorter so that they react much quicker before dispersion than does  $\text{CH}_4$ .

(c) **Because of its relatively long residence time in troposphere.**

5.26 (a) Adding the two reaction steps we get





which is the overall reaction.

- (b) The intermediate is  $\text{O}(\text{g})$ .
- (c) **Rate law for step (i) is: Rate =  $k_1[\text{O}_3]$ .**  
**Rate law for step (ii) is: Rate =  $k_2[\text{O}_3][\text{O}]$ .**
- (d) If overall rate law is: Rate =  $k[\text{O}_3]^2[\text{O}_2]^{-1}$ , step (1) cannot be rate controlling because it depends only on  $[\text{O}_3]$ . Therefore, **step (2) must be rate controlling.**
- (e) If step (2) is rate controlling:

$$[\text{O}_3][\text{O}] \propto [\text{O}_3]^2[\text{O}_2]^{-1}$$

Therefore,

$$[\text{O}] \propto [\text{O}_3][\text{O}_2]^{-1}$$

### 5.27

$$k = 8.0 \times 10^{-12} \exp\left(-\frac{2060}{T}\right)$$

At  $T = -20^\circ\text{C} = 253\text{ K}$

$$k_{253} = 8.0 \times 10^{-12} \exp\left(-\frac{2060}{253}\right)$$

At  $T = -30^\circ\text{C} = 243\text{ K}$

$$k_{243} = 8.0 \times 10^{-12} \exp\left(-\frac{2060}{243}\right)$$

Therefore,

$$\begin{aligned} \frac{k_{253}}{k_{243}} &= \frac{\exp\left(-\frac{2060}{253}\right)}{\exp\left(-\frac{2060}{243}\right)} \\ &= \exp\left[-2060\left(\frac{1}{253} - \frac{1}{243}\right)\right] \\ &= \exp[-2060(0.00395 - 0.00412)] \\ &= \exp(2060 \times 0.00017) \\ &= \exp(0.3502) \\ &= 1.419 \end{aligned}$$

So, the rate of depletion of  $O_3$  will increase by 42% if temperature falls from  $-20$  to  $-30^\circ C$

$$\begin{aligned}\therefore k_{243} &= k_{253}/1.420 \\ &= 0.704 k_{253}\end{aligned}$$

**Therefore, rate of depletion of  $O_3$  will decrease by  $\sim 30\%$  if temperature falls from 253 K to 243 K.**

**5.28** In the middle and upper stratosphere,  $O_3$  concentrations are maintained at roughly steady values by a number of chemical reactions. Assume that at around a temperature of 220 K

$$\frac{dX}{dt} = k_1 - k_2 X^2$$

where

$$X = \frac{\text{concentration of } O_3 \text{ molecules}}{\text{concentration of all molecules}}$$

$$k_1 = (\text{constant}) \exp\left(\frac{300}{T}\right) \text{ s}^{-1}$$

$$k_2 = 10.0 \exp\left(\frac{-1,100}{T}\right) \text{ s}^{-1}$$

- (a) Doubling the concentration of  $CO_2$  in the atmosphere is predicted to cool the middle stratosphere by about  $2^\circ C$ . What fractional change in  $X$  would you expect from this temperature perturbation?
- (b) If  $X$  were temporarily raised by 1.0% above its steady-state value of  $5.0 \times 10^{-7}$ , how long would it take for this perturbation to fall to  $\exp(-1)$  of 1.0% at 220 K? ( $\exp 1 = 2.7$ )

*Answers* (a) 2.9%, (b) 172 days

**Solution:**

(a)

$$\frac{dX}{dt} = k_1 - k_2 X^2 \tag{1}$$

At steady-state,  $X = X_{ss}$  and

$$\frac{dX}{dt} = 0$$

Therefore,

$$X_{ss} = \left(\frac{k_1}{k_2}\right)^{\frac{1}{2}} = (\text{constant}) \exp\left[\frac{1}{2}\left(\frac{300}{T} + \frac{1100}{T}\right)\right]$$

and,

$$\ln X_{ss} = \text{constant} + \frac{1}{2} \left( \frac{300}{T} + \frac{1100}{T} \right)$$

Hence,

$$\begin{aligned} \frac{1}{X_{ss}} \frac{dX_{ss}}{dT} &= \frac{d}{dT} \left( \frac{700}{T} \right) \\ \frac{dX_{ss}}{X_{ss}} &= \frac{-700}{T^2} dT \end{aligned}$$

For  $dT = -2^\circ\text{C}$ ,

$$\frac{dX_{ss}}{X_{ss}} = \frac{1400}{(220)^2} = 0.029 \text{ or } \mathbf{2.9\%}$$

(b) Substitute  $Y = X - X_{ss}$  into (1) yields

$$\begin{aligned} \frac{dY}{dt} &= k_1 - k_2 (Y + X_{ss})^2 \\ &= X_{ss}^2 k_2 - k_2 (Y + X_{ss})^2 \\ &= -(2k_2 X_{ss} Y) + \text{term in } Y_2 \text{ (which is small)} \end{aligned}$$

Therefore,

$$\frac{dY}{Y} = -(2k_2 X_{ss}) dt$$

and,

$$\begin{aligned} [\ln Y]_{Y_o}^Y &= -2k_2 X_{ss} \int_0^t dt \\ \ln \left( \frac{Y}{Y_o} \right) &= -2k_2 X_{ss} t \end{aligned}$$

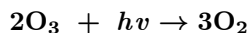
or,

$$Y = Y_o \exp(-2k_2 X_{ss} t)$$

The relaxation time ( $\tau$ ) is the time for  $y$  to decline to  $\exp(-1)$  of an initial value  $Y_o$ . Therefore, from the last expression

$$\begin{aligned} \tau &= \frac{1}{2k_2 X_{ss}} = \frac{1}{2 \left\{ 10 \exp \left( \frac{-1100}{220} \right) (5 \times 10^{-7}) \right\}} = 1.48 \times 10^7 \text{ s} \\ &= \underline{\mathbf{172 \text{ days}}} \end{aligned}$$

**5.29** (a) If (iia) dominates net effect is



If (iib) dominate there is no net effect (ClO never gets to Cl).

$$\begin{aligned}
\text{(b)} \quad \frac{d[\text{O}_3]}{dt} &= -k_4 [\text{Cl}] [\text{O}_3] \\
\frac{d[\text{Cl}]}{dt} &= j_2 [(\text{ClO})_2] + k_3 [\text{ClOO}] [\text{M}] - k_4 [\text{Cl}] [\text{O}_3] \\
\frac{d[(\text{ClO})_2]}{dt} &= k_1 [\text{ClO}]^2 [\text{M}] - j_2 [(\text{ClO})_2] \\
\frac{d[\text{ClOO}]}{dt} &= j_2 [(\text{ClO})_2] - k_3 [\text{ClOO}] [\text{M}] \\
\text{(c)} \quad \text{If } \frac{d[\text{Cl}]}{dt} &= \frac{d[(\text{ClO})_2]}{dt} = \frac{d[\text{ClOO}]}{dt}
\end{aligned}$$

in (b) above, then

$$[\text{Cl}] = \frac{2k_1 [\text{M}] [\text{ClO}]^2}{k_4 [\text{O}_3]}$$

$$\begin{aligned}
\text{(d)} \quad \text{From (b)} \\
\frac{d[\text{O}_3]}{dt} &= -k_4 [\text{Cl}] [\text{O}_3] \\
\frac{d[\text{O}_3]}{dt} &= -2k_1 [\text{M}] [\text{ClO}]^2
\end{aligned}$$

(e) If  $[\text{ClO}] \propto t$

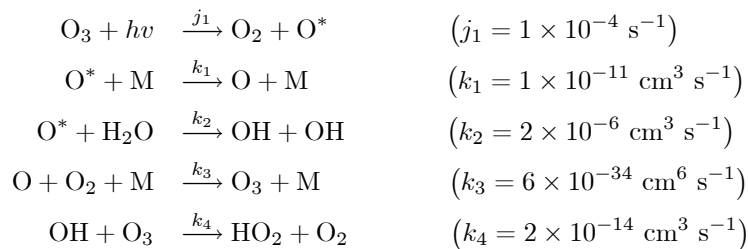
From (d)

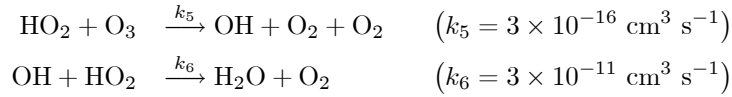
$$\frac{d[\text{O}_3]}{dt} \propto t^2$$

Therefore,

$$[\text{O}_3] \propto t^3$$

**5.30** In the atmosphere at altitudes near and above 30 km the following reactions significantly affect the chemistry of ozone





where  $\text{O}^*$  is an electronically excited metastable state of atomic oxygen. The free radical species  $\text{OH}$  and  $\text{HO}_2$  are collectively labeled "odd hydrogen." At 30 km the molecular density of the atmosphere is about  $5 \times 10^{17} \text{ cm}^{-3}$ , and the molecular fractions of water vapor and  $\text{O}_3$  are each about  $2 \times 10^{-6}$  and that of oxygen is 0.2.

- What are the approximate steady-state molecular fractions of  $\text{O}^*$ ,  $\text{HO}_2$ , and  $\text{OH}$ ?
- What is the approximate mean residence time of odd hydrogen under steady-state conditions?
- For every  $\text{O}_3$  molecule that is destroyed under steady-state conditions, how many odd-hydrogen species are produced by the reaction associated with  $k_2$ ?

(Hint: The steps associated with  $k_4$  and  $k_5$  occur many times for each formation or loss of odd hydrogen.)

- Answer* (a)  $4 \times 10^{-17}$ ,  $2 \times 10^{-8}$  and  $3 \times 10^{-10}$   
 (b) 11 sec  
 (c)  $\sim 15$

**Solution:**

- 

$$\frac{d[\text{O}^*]}{dt} = j_1 [\text{O}_3] - k_1 [\text{O}^*] [\text{M}] - k_2 [\text{O}^*] [\text{H}_2\text{O}] = 0 \text{ (at steady state)}$$

Therefore,

$$\begin{aligned} [\text{O}^*] &= \frac{j_1 [\text{O}_3]}{k_1 [\text{M}] + k_2 [\text{H}_2\text{O}]} \\ &\simeq \frac{j_1 [\text{O}_3]}{k_1 [\text{M}]} \end{aligned}$$

Hence, the molecular fraction of  $\text{O}^*$ , say  $f(\text{O}^*)$ , is

$$f(\text{O}^*) \simeq \frac{j_1 f [\text{O}_3]}{k_1 [\text{M}]} = \frac{10^{-4} (2 \times 10^{-6})}{10^{-11} (5 \times 10^{17})} = \underline{\underline{4 \times 10^{-17}}}$$

Also,

$$[\text{HO}] + [\text{HO}_2] = [\text{odd hydrogen}]$$

Therefore,

$$\frac{d[\text{odd hydrogen}]}{dt} = 2k_2 [\text{O}^*] [\text{H}_2\text{O}] - 2k_6 [\text{HO}] [\text{HO}_2] \quad (\text{i})$$



If the  $k_4$  and  $k_5$  steps occur often compared with the steps associated with  $k_2$  and  $k_6$ , they determine the concentrations of HO and HO<sub>2</sub>. Therefore, at steady state

$$k_4 [\text{HO}] [\text{O}_3] \simeq k_5 [\text{HO}_2] [\text{O}_3] \quad (\text{ii})$$

or,

$$\frac{[\text{HO}_2]}{[\text{HO}]} \simeq \frac{k_4}{k_5} \simeq \frac{2 \times 10^{-14}}{3 \times 10^{-16}} \simeq 70 \quad (\text{iii})$$

From (i) and (iii), and with  $\frac{d[\text{odd hydrogen}]}{dt} = 0$ ,

$$k_2 [\text{O}^*] [\text{H}_2\text{O}] - k_6 \frac{k_5}{k_4} [\text{HO}_2]^2 = 0$$

Therefore,

$$[f(\text{HO}_2)]^2 = \frac{k_2 k_4}{k_5 k_6} f(\text{O}^*) f(\text{H}_2\text{O})$$

$$f(\text{HO}_2) = \left\{ \frac{(2 \times 10^{-6})(2 \times 10^{-14})}{(3 \times 10^{-16})(3 \times 10^{-11})} (4 \times 10^{-17})(2 \times 10^{-6}) \right\}^{\frac{1}{2}} \simeq \underline{\underline{2 \times 10^{-8}}}$$

Using (iii),

$$f(\text{HO}) = \frac{f(\text{HO}_2)}{70} \simeq \underline{\underline{3 \times 10^{-10}}}$$

(b) The mean lifetime of odd hydrogen is

$$\tau_{\text{hyd}}^{\text{odd}} \simeq \left\{ \frac{\text{loss rate of odd hydrogen}}{\text{concentration of odd hydrogen}} \right\}^{-1}$$

Or, since  $[\text{HO}_2] \simeq 70 [\text{HO}]$

$$\tau_{\text{hyd}}^{\text{odd}} \simeq \left\{ \frac{2k_6 [\text{HO}] [\text{HO}_2]}{[\text{HO}_2]} \right\}^{-1}$$

Therefore,

$$\begin{aligned} \tau_{\text{hyd}}^{\text{odd}} &= \{2k_6 [\text{HO}]\}^{-1} \\ &= \{2k_6 f(\text{HO}) [\text{M}]\}^{-1} \\ &= \{2(3 \times 10^{-11})(3 \times 10^{-10})(5 \times 10^{17})\}^{-1} = \underline{\underline{111 \text{ secs}}} \end{aligned}$$

(c) Let

$$N = \frac{\text{number of odd hydrogen species produced by } k_2 \text{ per sec}}{\text{number of O}_3 \text{ molecules destroyed per sec}}$$

Since the steps associated with  $k_4$  and  $k_5$  are fast

$$N \simeq \frac{\{[\text{HO}] + [\text{HO}_2]\} / \tau_{\text{hydrogen}}^{\text{odd}}}{k_4 [\text{HO}] [\text{O}_3] + k_5 [\text{HO}_2] [\text{O}_3]}$$

Using (ii) and (iii) from (a) above

$$N \simeq \frac{\{[\text{HO}_2] / 70 + [\text{HO}_2]\} / \tau_{\text{hydrogen}}^{\text{odd}}}{2k_5 [\text{HO}_2] [\text{O}_3]}$$

or,

$$\begin{aligned} N &\simeq \frac{1}{2k_5 [\text{O}_3] \tau_{\text{hydrogen}}^{\text{odd}}} \\ &\simeq \frac{1}{2k_5 f(\text{O}_3) [\text{M}] \tau_{\text{hydrogen}}^{\text{odd}}} \\ &\simeq \frac{1}{2(3 \times 10^{-16})(2 \times 10^{-6})(5 \times 10^{17})} \text{ 111} \\ N &\simeq \mathbf{15} \end{aligned}$$


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**5.31** Let

$$C = C_o \exp\left(-\frac{t}{\tau}\right)$$

Then  $\tau$  = e-folding time for removal of chlorine. But for a 1st order reaction (from eqn. 2.9 in Hobbs' "Introduction to Atmospheric Chemistry")

$$\begin{aligned} t_{1/2} &= -0.69 \tau \\ (\text{half-life}) \end{aligned}$$

Therefore,

$$\begin{aligned} C &= C_o \exp\left(-\frac{t \cdot 0.69}{t_{1/2}}\right) \\ &= C_o \exp\left(-\frac{0.69}{35} t\right) \end{aligned}$$

where  $t$  is in years. For

$$\begin{aligned} C &= 1.5 \text{ ppbv} \\ C_o &= 5 \text{ ppbv} \\ 1.5 &= 5 \exp(-0.0197 t) \\ \therefore \ln 0.3 &= -0.0197 t \\ -1.2 &= -0.0197 t \\ \therefore t &= 60.9 \text{ years} \simeq 61 \text{ years or in year } \mathbf{2057} \end{aligned}$$


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