1.725 Fate + Transport   Problem set #11 Solutions

26.

a) $\cdot OH + NO_2 \rightarrow HNO_3$ $k = 1.1 \times 10^{-11}$ cm³/molec·sec

$k' = k[\cdot OH]$

$$= 1.1 \times 10^{-11} \frac{cm^3}{molec \cdot sec} \left(3 \times 10^{6} \frac{molec}{cm^3}\right) = 3.3 \times 10^{-5}\ sec^{-1}$$

$$t_{1/2} = \frac{\ln 2}{k} = 2.1 \times 10^{4}\ sec = \boxed{5.8\ hours}$$

b) also consider $NO_2 \xrightarrow{h\nu} NO + O$ $k = 0.53\ min^{-1}$

$k_{total} = k_{OH} + k_{photo}$

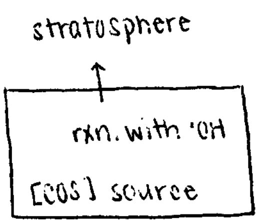
$$= 3.3 \times 10^{-5}\ sec^{-1} + 0.53\ min^{-1}\ (min/60\ sec) = 8.87 \times 10^{-3}\ sec^{-1}$$

$$t_{1/2} = \frac{\ln 2}{k_{total}} = 78\ sec = \boxed{1.3\ min}$$

note: this is so much shorter that reaction with ·OH can be neglected

c) NO_2 is regenerated through reactions with O_3 and $RO_2^\cdot / HO_2^\cdot$

28.



assumptions.
- can be treated as steady-state
- no input from stratosphere
- treat as well-mixed

$$\text{input} - \text{output} + \Sigma\,\text{sources} - \Sigma\,\text{sinks} = V\frac{dC}{dt}$$

$$\Sigma\,\text{sources} = \text{output} + \Sigma\,\text{sinks}$$

$$= V \cdot C \cdot (k_{mix} + k_{OH}[\cdot OH])$$

b) find Σsources for V = 1 L

[COS] = 500 ppt (trillion)

$$\frac{500\ \text{parts COS}}{10^{12}\ \text{parts troposphere}} = \frac{P_{COS}}{0.5\ atm} \Rightarrow P_{COS} = 2.5 \times 10^{-10}\ atm$$

↑ assumption of avg. pressure

$$\frac{n}{V} = \frac{P}{RT} = \frac{2.5\times10^{-10}\text{ atm}}{(.08206\text{ L atm/mol K})(253\text{ K})} = 1.2\times10^{-11}\text{ mol/L}$$

↑ assumption of avg temp.

$$\Sigma\text{ sources} = V\cdot C\,(k_{mix} + k_{OH}[\cdot OH])$$

$$= 1\text{ L}\times\frac{1.2\times10^{-11}\text{ mol}}{\text{L}}\left[0.04\text{ yr}^{-1}\times\frac{\text{yr}}{86400\cdot365\text{ sec}} + 9\times10^{-15}(10\times10^{6})\text{ sec}^{-1}\right]$$

$$= 1.2\times10^{-11}\text{ mol}\,(1.3\times10^{-9}\text{ sec}^{-1} + 9.1\times10^{-8}\text{ sec}^{-1})$$

$$= 1.1\times10^{-18}\text{ mol/sec} = \boxed{3.5\times10^{-11}\text{ mol/yr (per liter)}}$$

30. expected concentration = 2 ng/m³ travel time = 1 hr

actual conc. = 0.2 ng/m³

$$C = C_0 e^{-k't}$$

$$\frac{0.2\text{ ng/m}^3}{2\text{ ng/m}^3} = e^{-k'(3600\text{ s})} \qquad k' = \frac{2.3}{3600\text{ s}} = 6.4\times10^{-4}\text{ s}^{-1}$$

$$k' = k[\cdot OH]$$

$$k = \frac{6.4\times10^{-4}\text{ s}^{-1}}{3\times10^{5}\text{ molec/cm}^3} = \boxed{2.1\times10^{-9}\frac{\text{cm}^3}{\text{molec}\cdot\text{sec}} = 7.7\times10^{-6}\frac{\text{cm}^3}{\text{molec}\cdot\text{hr}}}$$