

$$Q1 \ a) \quad TLV = 55 \text{ mg/m}^3 \times \frac{1 \text{ mol}}{28.019} \times \frac{19}{10^3 \text{ mg}} = 1.96 \times 10^{-3} \frac{\text{mol}}{\text{m}^3}$$

for CO

$$\frac{n_{\text{air}}}{V} = \frac{P}{RT} = \frac{101,300 \text{ Pa}}{(8.314 \frac{\text{J}}{\text{mol K}})(273 \text{ K})} = 44.63 \frac{\text{mol}}{\text{m}^3}$$

$$\therefore \chi_{\text{CO}} = \frac{1.96 \times 10^{-3}}{44.63} = 4.39 \times 10^{-5} \quad \text{or} \quad 43.9 \text{ ppm}_v$$

$$b) \quad P_g = P_0 e^{\left\{ \frac{-g M_{\text{air}} z}{RT} \right\}}$$

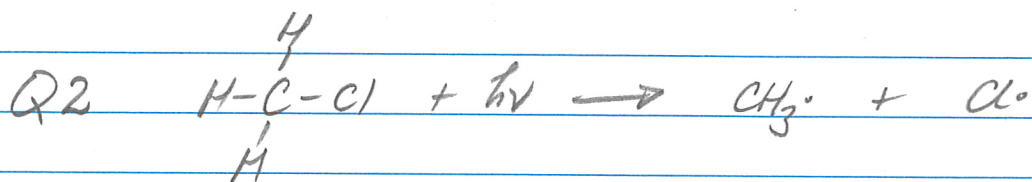
$$= 101,300 \text{ Pa} e^{\left\{ \frac{-(9.81 \frac{\text{m}}{\text{s}^2})(0.02896 \frac{\text{kg}}{\text{mol}})(5000 \text{ m})}{(8.314 \frac{\text{J}}{\text{mol K}})(273 \text{ K})} \right\}}$$

$$= 101,300 \text{ Pa} e^{-(0.6258)}$$

$$= 54,180 \text{ Pa} \quad \text{or} \quad 0.5348 \text{ atm}$$

$$n_{\text{O}_2}^* = (0.2095)(0.5348)(2.69 \times 10^{19} \frac{\text{molec}}{\text{cm}^3})$$

$$= 3.014 \times 10^{18} \frac{\text{molec}}{\text{cm}^3}$$



$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

$$\therefore \lambda = \frac{hc}{E_{\text{photon}}}$$

and

$$E_{\text{photon}} = \frac{\text{BDE} \left( \frac{\text{J}}{\text{mol}} \right)}{N_A \left( \frac{1}{\text{mol}} \right)} = \frac{338,000}{6.023 \times 10^{23}} = 5.612 \times 10^{-19} \text{ J}$$

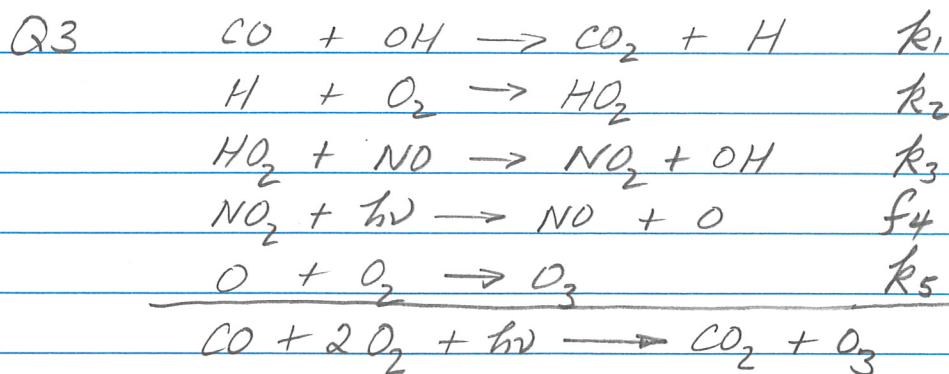
$$\therefore \lambda = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{5.612 \times 10^{-19} \text{ J}}$$

$$= 3.54 \times 10^{-7} \text{ m} \quad \text{or} \quad 354 \text{ nm}$$

$$f = \int_{\lambda_1}^{\lambda_2} \underbrace{\Phi_{\lambda}}_{\substack{\text{pdt quantum} \\ \text{yield}}} \cdot \underbrace{J_{\lambda}}_{\substack{\text{photon} \\ \text{flux}}} \cdot \underbrace{\sigma_{\lambda}}_{\substack{\text{absorption cross section}}} d\lambda$$

Photons less than 354 nm are required to photochemically break C-Cl in  $\text{CH}_3\text{Cl}$ . However, the magnitude of the rate constant for this reaction depends on three factors integrated over some wavelength range

- 1) product quantum yield
- 2) photon flux
- 3) absorption x-section



a) each mol of CO oxidized by this reaction yields one mol of CO<sub>2</sub> and one mol of O<sub>3</sub>

b) catalysts are consumed in one reaction and re-generated in subsequent reaction  
OH & NO are catalysts in this sequence

c) rate prod<sup>n</sup> of HO<sub>2</sub> =  $k_2 [\text{H}][\text{O}_2]$

rate destruction of HO<sub>2</sub> =  $k_3 [\text{HO}_2][\text{NO}]$

at steady state of HO<sub>2</sub>, these are equal

$$k_2 [\text{H}][\text{O}_2] = k_3 [\text{HO}_2][\text{NO}]$$

$$\therefore [\text{HO}_2] = \frac{k_2 [\text{H}][\text{O}_2]}{k_3 [\text{NO}]}$$



$$k = 1.2 \times 10^{-14} \frac{\text{cm}^3}{\text{molec} \cdot \text{s}}$$

$$\therefore \text{rate} = k [\text{OH}] [\text{CH}_3\text{CCl}_3]$$

and if  $[\text{OH}]$  is constant, we can write

$$\text{rate} = k' [\text{CH}_3\text{CCl}_3], \text{ where } k' = k [\text{OH}]$$

$$\therefore k' = 1.2 \times 10^{-14} \left( \frac{\text{cm}^3}{\text{molec} \cdot \text{s}} \right) \cdot 1 \times 10^6 \left( \frac{\text{molec}}{\text{cm}^3} \right)$$

$$= 1.2 \times 10^{-8} \text{ s}^{-1} \quad (\text{pseudo 1}^{\text{st}} \text{ order rate constant})$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.2 \times 10^{-8} \text{ s}^{-1}} = 5.8 \times 10^7 \text{ s}$$

↑  
for 1<sup>st</sup> order  
processes

or  
 $6.7 \times 10^2 \text{ days}$

or  
 $1.8 \text{ yrs}$

With a half-life of nearly 2 yrs, we expect  $\text{CH}_3\text{CCl}_3$  to be well mixed in the troposphere.

$$Q5 \quad \tau_{\text{trap}} = 11 \mu\text{s} = 1.1 \times 10^{-5} \text{ s}$$

$$\tau = \frac{1}{k'} \quad \text{for 1st order process}$$

$$\therefore k' = \frac{1}{\tau} = 9.1 \times 10^4 \text{ s}^{-1}$$

$$\text{overall rate} = k_3 [\text{O}][\text{O}_2][\text{M}]$$

where  $k_3$  is third order rate constant

and  $[\text{O}_2]$  and  $[\text{M}] \gg [\text{O}]$ .

$$\text{Therefore, rate} = k' [\text{O}]$$

$$\text{where } k' = k_3 [\text{O}_2][\text{M}]$$

$$\text{and at STP } [\text{M}] = 2.69 \times 10^{19} \frac{\text{molec}}{\text{cm}^3}$$

$$\text{and } [\text{O}_2] = (0.2095) \left( 2.69 \times 10^{19} \frac{\text{molec}}{\text{cm}^3} \right) \\ = 5.64 \times 10^{18} \frac{\text{molec}}{\text{cm}^3}$$

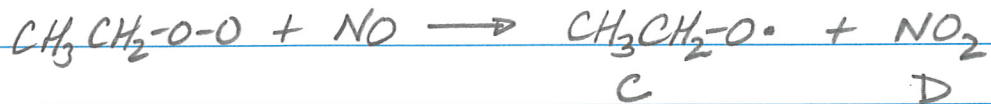
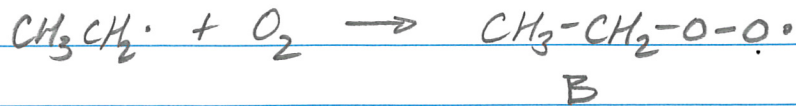
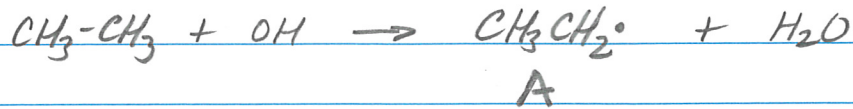
$$\text{So } k_3 = k' / [\text{O}_2][\text{M}]$$

$$= 9.1 \times 10^4 \text{ s}^{-1}$$

$$\left( 2.69 \times 10^{19} \frac{\text{molec}}{\text{cm}^3} \right) \left( 5.64 \times 10^{18} \frac{\text{molec}}{\text{cm}^3} \right)$$

$$= 6.0 \times 10^{-34} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$$

Q6



Q7 a) troposphere is heated from long wavelength infrared<sup>(IR)</sup> radiation from Earth's surface.

e.g. CO<sub>2</sub>  
and H<sub>2</sub>O

Certain tropospheric gases ('greenhouse' gases) absorb on-going IR. As altitude increases, more of IR has already been absorbed and all gases (including 'greenhouse' gases) are becoming less concentrated.

e.g. O<sub>3</sub>  
and O<sub>2</sub>

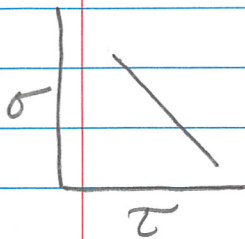
stratosphere is heated from short wavelength ultraviolet (UV) radiation from Sun. Certain stratospheric gases (such as ozone) absorb this in-coming UV. Temperature increases with altitude in stratosphere as short wavelength photons become more plentiful closer to sun.

b) atmospheric gases with long residence times are well mixed in atmosphere meaning that their concentrations do not vary much over time and space. On the other hand, gases with short residence times are not well mixed and their concentrations will vary widely over time and space.

e.g.  
 $\text{CH}_2\text{Cl}_2$   
 $\tau \sim 2 \text{ yrs}$

e.g.  
 $\text{NO}$   
 $\tau \sim 2 \text{ hr}$

Consequently, if one calculated the statistical variability of gas concentration (i.e. standard deviation), it would be observed that these correlate with residence time. (i.e.  $\tau = -m\sigma + b$  where  $m$  and  $b$  are the slope and intercept of linear correlation).

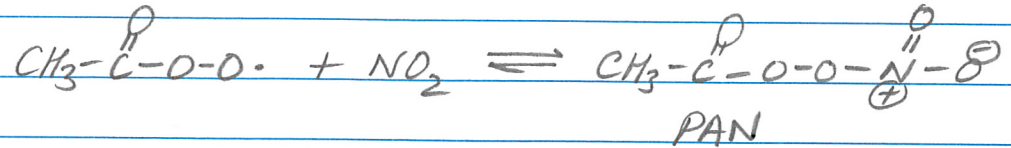


c) ozone depletion potential is an important criteria in setting regulation to mitigate the thinning ozone layer in the stratosphere.

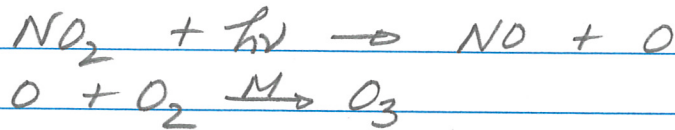
It takes into account a comp's residence time, ability to produce ozone depleters and the type of ozone depleter on a per kg basis.

However, it does not take into account the net production or release into the atmosphere. As we saw in the case study on dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), a compd with a small ODP can still have a significant impact if it is released on a large scale.

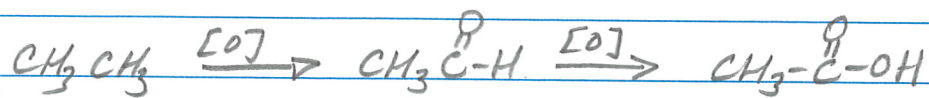
d) Peroxyacetyl nitrate is formed by the combination of peroxyacetyl radical and nitrogen dioxide



Its formation is reversible and temperature dependent. Therefore, PAN can hold ground level ozone precursors, such as  $\text{NO}_2$ .



e) Volatile organic compounds (VOCs) released to the atmosphere will be oxidized over time under the influence of oxidizing agents, such as  $\text{OH}$ ,  $\text{O}_3$  and  $\text{O}_2$ . As this occurs, hydrocarbons become oxygenated to yield less volatile alcohols, aldehydes and carboxylic acids. These more polar compounds will condense and form micro droplets of liquid phase. This results in secondary organic aerosols (SOA).



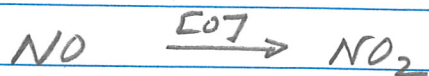
↑  
more polar ∴ less volatile  
⇒ SOA's



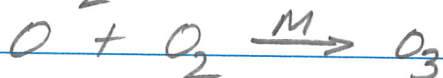
f) Forest fires create high temperatures that result in formation of nitric oxide



Nitric oxide is oxidized to nitrogen dioxide



Nitrogen dioxide is photolyzed to yield atomic oxygen in the troposphere.



Ozone has a tropospheric residence time of several days-week, therefore can travel thousands of kilometers away from source. This was observed to occur in 2016 after Alberta fires created  $\text{O}_3$  that appeared on eastern coast of N. America.

Q8. see Chap. 3 (textbook)

Bonus Two step catalytic cycle that results in ozone destruction. Overall, the net reaction can only proceed as fast as the rate limiting step.

$$\begin{aligned}\text{step 1; Rate} &= k_1 [\text{NO}] [\text{O}_3] \\ &= (5 \times 10^{-15} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}) (5 \times 10^8 \frac{\text{molec}}{\text{cm}^3}) (2 \times 10^{12} \frac{\text{molec}}{\text{cm}^3}) \\ &= 5 \times 10^6 \frac{\text{molec}}{\text{cm}^3 \cdot \text{s}}\end{aligned}$$

$$\begin{aligned}\text{step 2; Rate} &= k_2 [\text{NO}_2] [\text{O}] \\ &= (1 \times 10^{-11} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}) (5 \times 10^9 \frac{\text{molec}}{\text{cm}^3}) (1 \times 10^9 \frac{\text{molec}}{\text{cm}^3}) \\ &= 5 \times 10^7 \frac{\text{molec}}{\text{cm}^3 \cdot \text{s}}\end{aligned}$$

$$\therefore \text{Overall rate} = \text{Rate step 1} = 5 \times 10^6 \frac{\text{molec}}{\text{cm}^3 \cdot \text{s}}$$