

CHEM 302 Assignment #1

Provide solutions to the following questions in a neat and well organized manner, including dimensional analysis, where appropriate.

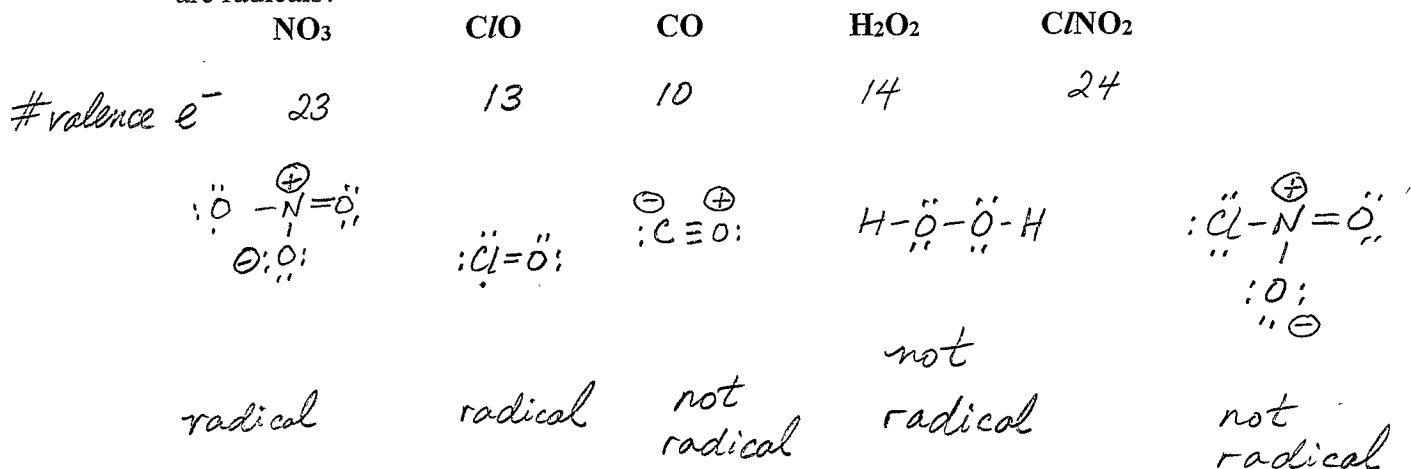
Reference data sources for any constants and state assumptions, if any.

Not all questions will necessarily be graded.

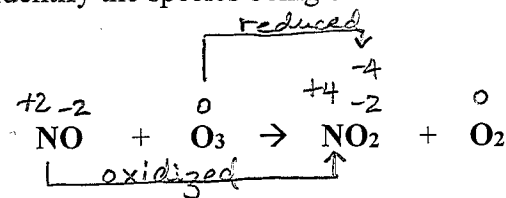
Due: Tuesday, September 29th

1. Use Lewis dot structures to aid in your answer to each of the following.

a) Indicate formal charges, if any and determine which of the following chemical species are radicals?

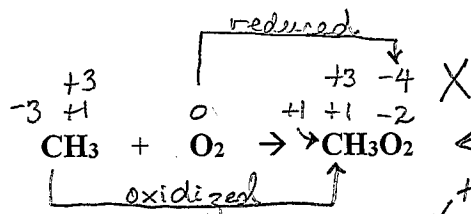


b) For the following atmospheric reactions, indicate the oxidation states on each atom and identify the species being oxidized and reduced.

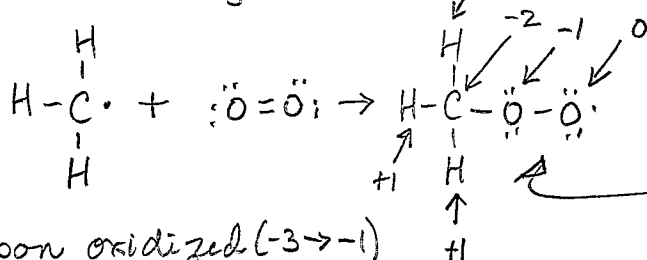


N in NO is oxidized from +2 → +4 in NO₂

one O in O₃ is reduced from zero to -2 in NO₂



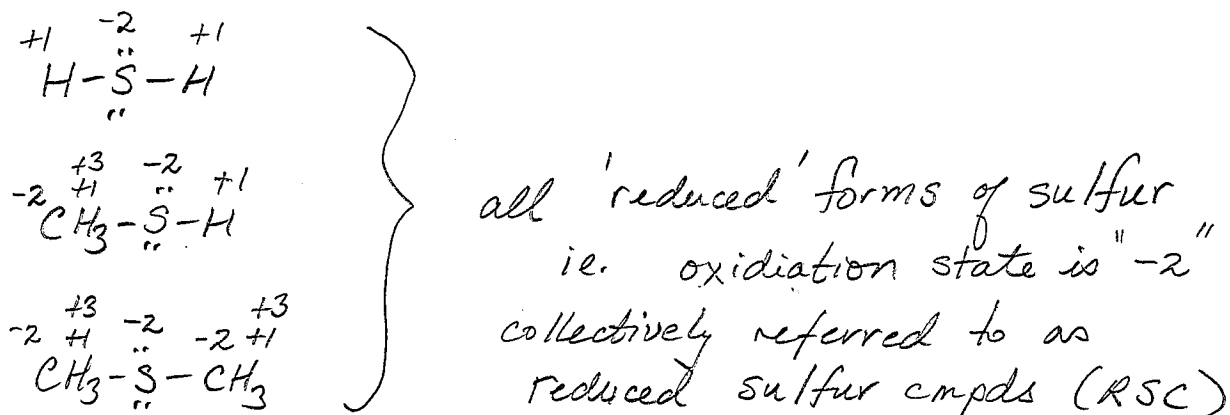
CAREFUL
this compd is a peroxide (-O-O-)
∴ oxidation is NOT '-2'



this is CORRECT

carbon oxidized (-3 → -1)
oxygen reduced (0 → -1)

c) A number of reduced sulfur compounds, such as hydrogen sulfide, methanethiol and dimethylsulfide are released to the atmosphere from both anthro- and bio-genic sources. Ultimately, these sulfur compounds are exported from the atmosphere either through *dry* or *wet* deposition. Explain what is meant by the term 'sink' in relation to this example using chemical structures to illustrate to the 'sink' species.



Sources: RSC are naturally produced micro-organisms in anaerobic sediments and released by volcanic activity. They are also released by some industrial activities, such as pulp and paper mills.

Sinks: Are processes that remove a chemical species from an environmental compartment.

All RSC will ultimately be oxidized in the atmosphere becoming SO_2 and SO_3 gases. As these covalent oxides dissolve in water (rain droplets) they form H_2SO_3 (sulfurous) and H_2SO_4 (sulfuric) acids. Removal by 'wet' deposition occurs as acid rain. Dry deposition occurs if H_2SO_3 or H_2SO_4 (g) react with a base in the atmosphere (ie. NH_3) thus forming a salt particle which may settle out of atmosphere by gravity.

2. Calculate each of the following concentrations,

- a) Carbon monoxide in $\mu\text{g}/\text{m}^3$ in polluted urban air containing 200 ppbv at STP
 b) Methane mixing ratio at altitude when $P_{\text{CH}_4} = 10. \text{ Pa}$ ($T=250\text{K}$, $P_T = 0.50 \text{ atm}$)
 c) Water vapour as molecules cm^{-3} at RTP (298K , 1.00atm) and 50.% humidity

a) $200 \text{ ppbv} = \frac{200 \text{ molecules of CO}}{10^9 \text{ molecules air}}$ ← convert to mass in μg
← convert to volume in m^3

or use Loschmidt's number for air at STP = $2.69 \times 10^{19} \text{ molecules}/\text{cm}^3$.

$$\frac{200}{10^9} \times 2.69 \times 10^{19} \frac{\text{molecules}}{\text{cm}^3} \times \frac{1 \text{ mol}}{6.023 \times 10^{23} \text{ molecules}} \times \frac{28 \text{ g}}{1 \text{ mol}} \times \frac{10^6 \mu\text{g}}{1 \text{ g}}$$

$$\times \frac{10^6 \text{ cm}^3}{\text{m}^3} = \boxed{250 \mu\text{g}/\text{m}^3}$$

b) $P_{\text{CH}_4} = 10. \text{ Pa}$ ← mixing ratio $\frac{n_{\text{CH}_4}}{n_{\text{air}}} = \frac{P_{\text{CH}_4}}{P_T^{\text{air}}}$

$$P_T^{\text{air}} = 0.50 \text{ atm} \times \frac{101,300 \text{ Pa}}{1 \text{ atm}} = 50,650 \text{ Pa}$$

$$\chi_{\text{CH}_4} = \frac{10. \text{ Pa}}{50,650 \text{ Pa}} = \boxed{1.97 \times 10^{-4}} \text{ or } 197 \text{ ppm}_v$$

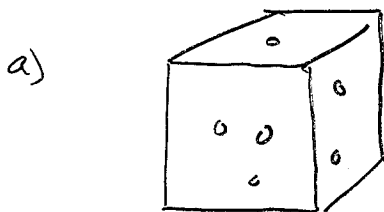
c) 50.% humidity = 0.50 vapour of water at 298K
 where vapour pressure of H_2O at 298 = 23.8 torr
 \therefore @ 50% humidity $P_{\text{H}_2\text{O}} = 11.9 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.0157 \text{ atm}$

$$n_{\text{H}_2\text{O}} = \frac{P \cdot V}{R \cdot T} = \frac{(0.0157 \text{ atm})(10^{-3} \text{ L})}{(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(298 \text{ K})} = 6.42 \times 10^{-7} \frac{\text{mol}}{\text{cm}^3}$$

$$\therefore n_{\text{H}_2\text{O}}^* = 6.42 \times 10^{-7} \frac{\text{mol}}{\text{cm}^3} \times 6.02 \times 10^{23} \frac{\text{molec}}{\text{mol}} = \boxed{3.87 \times 10^{17} \text{ molecules}/\text{cm}^3}$$

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3. Estimate an answer of the following, making reasonable assumptions, if needed.
- a) The average sea salt aerosol in surface air over the ocean is $10 \mu\text{g}/\text{m}^3$. Estimate the average number of $10 \mu\text{m}$ diameter aerosol particles in a cubic meter of sea air.
- b) Propane will burn in air if its *mixing ratio* is between 2 and 10%. My camping propane tank contained 50 mL of liquid propane before it completely leaked into my garage. Determine if the air in my 10^2 m^3 garage is explosive.



sea aerosol made up of small suspended water droplets. Given an average size of $10 \mu\text{m}$ diameter

assuming aerosols are $\text{H}_2\text{O}(\text{l})$ $\rho \approx \frac{10^3 \text{ kg}}{\text{m}^3}$

$$V_{\text{aerosol}} = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi (5 \times 10^{-6} \text{ m})^3 = 5.2 \times 10^{-16} \text{ m}^3$$

$$\therefore m_{\text{aerosol}} \approx 5.2 \times 10^{-16} \text{ m}^3 \times \frac{10^3 \text{ kg}}{\text{m}^3} \times \frac{10^3 \text{ g}}{1 \text{ kg}} \times \frac{10^6 \mu\text{g}}{1 \text{ g}} = 5.2 \times 10^{-4} \mu\text{g}$$

$$\therefore \text{Number of aerosols} = \frac{10 \mu\text{g}}{\text{m}^3} \times \frac{1 \text{ particle}}{5.2 \times 10^{-4} \mu\text{g}} = \boxed{19,000/\text{m}^3}$$

b) 50 mL evaporates into 10^2 m^3

$$X_{\text{propane}} = \frac{n_{\text{propane}}}{n_{\text{air}}} = \frac{50 \text{ mL} \times \text{density} \times \frac{1}{\text{MW}} = \# \text{ mols propane}}{10^2 \text{ m}^3 \times \frac{10^3 \text{ L}}{\text{m}^3} \times \frac{1 \text{ mol}}{22.4 \text{ L}} = \# \text{ mols air}}$$

$$= \frac{0.56 \text{ mol propane}}{4,500 \text{ mol air}} = 1.3 \times 10^{-4}$$

$$\times 10^2 \Rightarrow \boxed{0.013 \%}$$

↖ mixing ratio

∴ NOT EXPLOSIVE

when!

4. The mean global concentrations of CO , CH_4 and C_5H_8 (isoprene) are 100 ppbv, 1800 and 2 ppbv, respectively. Removal rates from the atmosphere by reaction with hydroxyl radical has been estimated to be 2400, 480 and 513 Tg/yr, respectively. Assuming that hydroxyl radical reaction accounts for 90% of the removal process, estimate the atmospheric residence times for CO , CH_4 and C_5H_{12} . What do the results imply about the geographic variability and global distribution of these gases.

$$\tau = \frac{\text{stock amount (mass)}}{\text{flux use removal rates prorated to account for 100\% of loss (mass/yr)}}$$

Carbon monoxide - 100 ppbv

$$\text{mass of CO in atmosphere} = n_{\text{CO}} \times 28 \text{ g/mol}$$

$$\uparrow$$

$$\chi_{\text{CO}} \cdot n_{\text{air}}^{\text{atmosphere}}$$

$$\uparrow$$

$$\text{mass atmos} \times \frac{1}{M_{\text{air}}}$$

$$\uparrow$$

$$5.27 \times 10^{18} \text{ kg} \quad 0.0289 \frac{\text{kg}}{\text{mol}}$$

(textbook App. A1) mol

$$\therefore \text{mass CO} = \frac{100}{10^9} \cdot 5.27 \times 10^{18} \text{ kg} \cdot \frac{1 \text{ mol}}{0.0289 \text{ kg}} \times \frac{28 \text{ g}}{\text{mol}}$$

$$= 5.1 \times 10^{14} \text{ g} \quad \text{or} \quad 510 \text{ Tg}$$

$$\therefore \tau_{\text{CO}} = \frac{510 \text{ Tg}}{(2400 \text{ Tg/yr} / 0.9)} = \frac{510 \text{ Tg}}{2700 \text{ Tg/yr}} = 0.19 \text{ yr}$$

Similarly; $\tau_{\text{CH}_4} = \frac{5250 \text{ Tg}}{530 \text{ Tg/yr}} = \boxed{9.8 \text{ yr}}$ ← global

or $\boxed{70 \text{ days}}$ ← intra hemisphere

and $\tau_{\text{C}_5\text{H}_8} = \frac{25 \text{ Tg}}{570 \text{ Tg/yr}} = 0.044 \text{ yr}$ or $\boxed{16 \text{ days}}$ ← regional

5. The barometric pressure of the Earth's atmosphere drops exponentially with increasing altitude approximately according to the barometric law below, where (z) is in altitude and (H) is the characteristic scale height.

$$P_z = P_0 e^{-\frac{z}{H}} \quad \text{where, } H = \frac{RT}{M_{\text{air}} \cdot g}$$

- a) Using a mean atmospheric temperature of 220 K for Earth, calculate the H and the factor the atmospheric pressure will have dropped at z = H.
 b) Using a spreadsheet to carry out repetitive calculations, plot a graph of the atmospheric pressure in atmospheres (x-axis) as a function of altitude in km (y-axis) up to 100 km.
 c) At what altitude, will 90% of the Earth's atmosphere be below?

$$\begin{aligned} \text{a) } H &= \frac{RT}{M_{\text{air}} \cdot g} = \frac{(8.314 \text{ J/mol K})(220 \text{ K})}{(0.02896 \text{ kg/mol})(9.8 \text{ m/s}^2)} \\ &= 6.45 \times 10^3 \text{ m} \\ &\text{or } \boxed{6.45 \text{ km}} \end{aligned}$$

$$\begin{aligned} &\text{J} \\ &\downarrow \\ &\text{N} \cdot \text{m} \\ &\downarrow \\ &\left[\frac{\text{kg m}^2 / \text{s}^2 / \text{mol K} \cdot \text{K}}{\text{kg/mol} \cdot \frac{\text{m}}{\text{s}^2}} \right] \\ &\Downarrow \\ &[\text{m}] \end{aligned}$$

b) see attached

c) 90% of atmosphere will be below altitude at which Pressure has dropped to $P_0/10$ (ie. 0.10 atm or 10.1 Pa, etc)

$$P_3 = P_0 e^{-z/H}$$

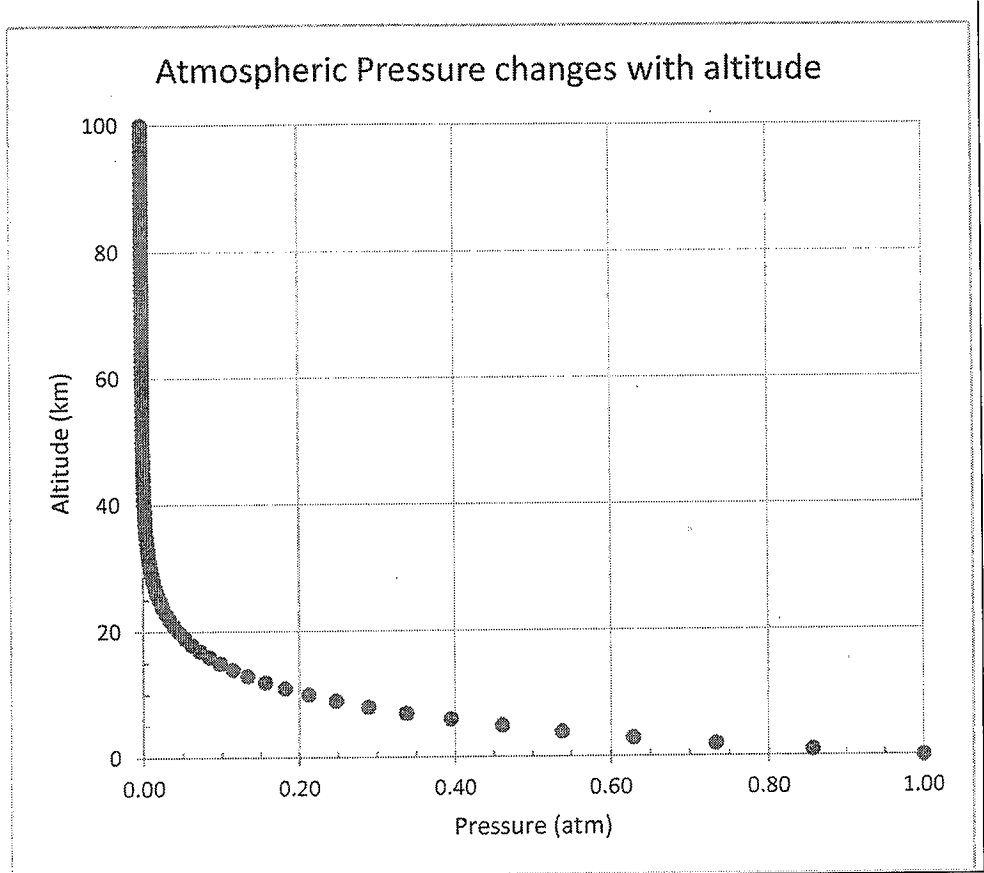
$$\therefore \ln\left(\frac{P_3}{P_0}\right) = -\frac{z}{H}$$

$$\begin{aligned} \text{and } z &= -\ln\left(\frac{P_3}{P_0}\right) \cdot H = -\ln(0.10) \cdot 6.45 \times 10^3 \text{ m} \\ &= 14,850 \text{ m or } \boxed{14.9 \text{ km}} \end{aligned}$$

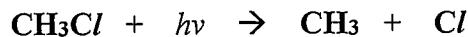
z (km)	P _z (atm)
0	1.000
1	0.856
2	0.733
3	0.628
4	0.538
5	0.461
6	0.394
7	0.338
8	0.289
9	0.248
10	0.212
11	0.182
12	0.156
13	0.133
14	0.114
15	0.098
16	0.084
17	0.072
18	0.061
19	0.053
20	0.045
21	0.039
22	0.033
23	0.028
24	0.024
25	0.021
26	0.018
27	0.015
28	0.013
29	0.011
30	0.010

P ₀ (atm)	H (km)
1.00	6.45

$$P = P_0 e^{-z/H} = 1.00 \cdot \text{EXP}(-z/6.45)$$



6. Using the enthalpy of formation data given in Appendix B2 of your textbook, calculate the maximum wavelength of electromagnetic radiation, which would have sufficient energy to effect the dissociation of chloromethane. In what regions of the atmosphere would such radiation be available?



In general, $E_{\text{photon}} = \frac{hc}{\lambda}$ (individual photon)

and for 1 mol of photons $E = \frac{hc}{\lambda} N_A$

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= \sum \Delta H_f^{\circ} (\text{products}) - \sum \Delta H_f^{\circ} (\text{reactants}) \\ &= [\Delta H_f^{\circ} (\text{CH}_3) + \Delta H_f^{\circ} (\text{Cl})] - \Delta H_f^{\circ} (\text{CH}_3\text{Cl}) \leftarrow \begin{array}{l} \text{opps} \\ \text{not in App B.2} \\ -81.9 \text{ kJ/mol} \\ (\text{nist. webbook}) \end{array} \\ &= (145.69 + 121.68) - (-81.9) \frac{\text{kJ}}{\text{mol}} \\ &= 349.3 \text{ kJ/mol} \end{aligned}$$

or use bond dissociation energy (App. B.3)

$$\text{BDE} = 338 \text{ kJ/mol} \cong \Delta H_{\text{rxn}}^{\circ} (\text{above})$$

$$E_{\text{photon}} \cdot N_A \geq \Delta H_{\text{rxn}}^{\circ} (\text{or BDE})$$

$$\lambda = \frac{hc N_A}{\text{BDE}} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})(6.02 \times 10^{23} \text{ mol}^{-1})}{338,000 \text{ J/mol}}$$

$$= 3.54 \times 10^{-7}$$

$$= \boxed{354 \text{ nm}}$$

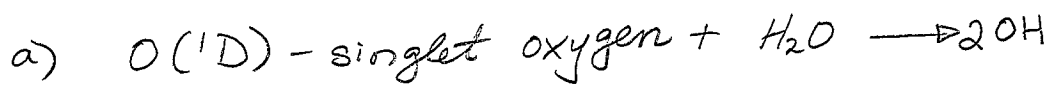
$$\left[\frac{\text{J}\cdot\text{s} \cdot \frac{\text{m}}{\text{s}} \cdot \frac{1}{\text{mol}}}{\text{J} \cdot \frac{1}{\text{mol}}} \right] \Rightarrow [\text{m}]$$

Photons of this wavelength are available throughout the atmosphere, however CH_3Cl does not absorb photons $> 300 \text{ nm}$ \therefore does not photolyze in troposphere

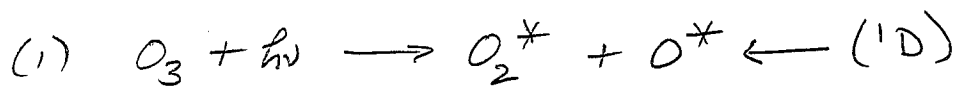
7. In an article titled *The Cleansing Capacity of the Atmosphere*, R.G. Prinn (Annu Rev Environ Resources. 2003 (28), 29-57), the author describes important atmospheric conditions that affect the concentration of hydroxyl radicals in the troposphere. Briefly explain how each of the following conditions lowers **OH** concentrations, using chemical reactions to illustrate your answer. (See in particular Fig 2 and the text describing tropospheric reactions pp 33-38).

- a) Night-time, winter and/or cloudy conditions
- b) Lower nitric oxide emission concentrations
- c) Dry atmospheres

OH radicals are produced by the following reactions in the atmosphere



where $O(^1D)$ is produced from photolysis of O_3



$\therefore [OH]$ will be lower in the absence of photons
(ie. night, winter, cloudy)

b) NO - nitric oxide reacts with hydroperoxide (HO_2)
to form NO_2 and OH



$\therefore [OH]$ will be lower if $[NO]$ is lower

c) dry conditions means less $H_2O(g)$ in atmosphere

\therefore step (2) in part a) (above) will not happen
and $[OH]$ will be lower

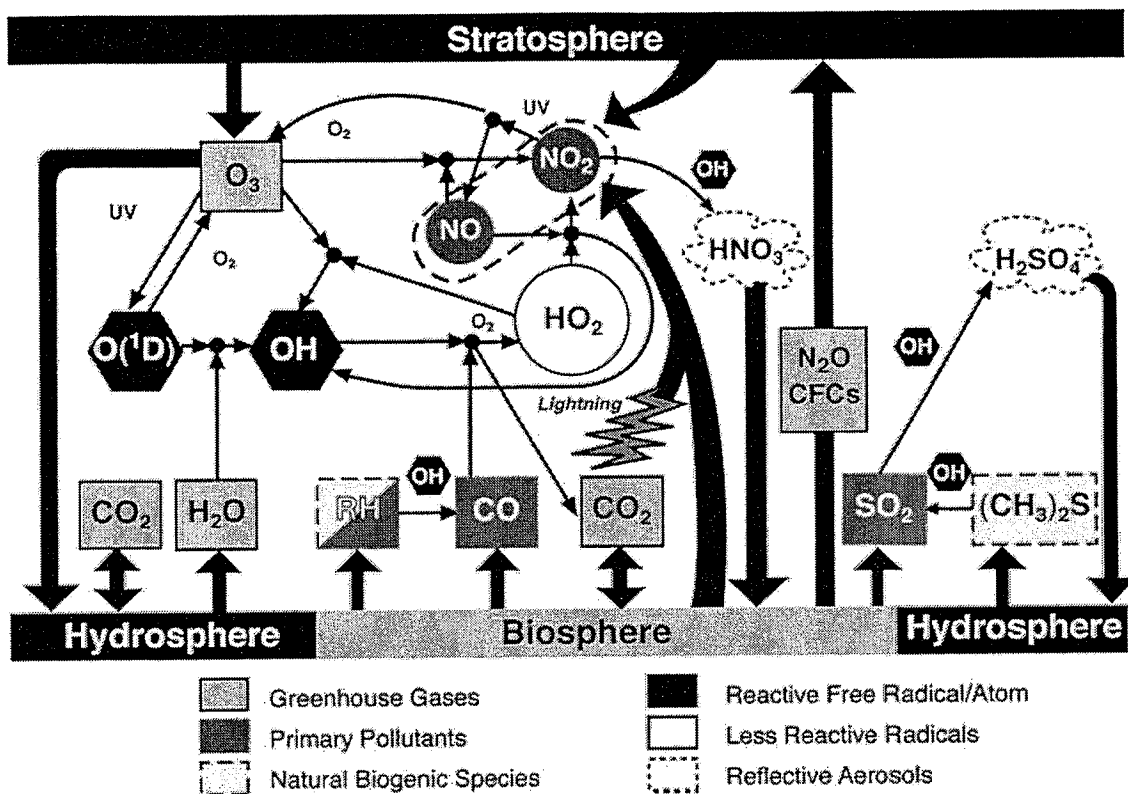
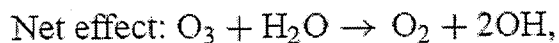
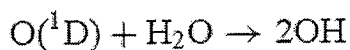
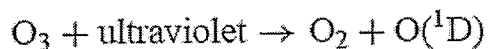


Figure 2 Summary of the main oxidation processes in the troposphere in NO_x -rich air (12). In NO_x -poor air (e.g., remote marine air), recycling of HO_2 to OH is achieved by reactions of O_3 with HO_2 to form OH and 2O_2 or by conversion of 2HO_2 to H_2O_2 followed by photodissociation of H_2O_2 . Note also that nonmethane hydrocarbons (RH) also react with OH to form acids, aldehydes (e.g., CH_2O) and ketones in addition to CO .

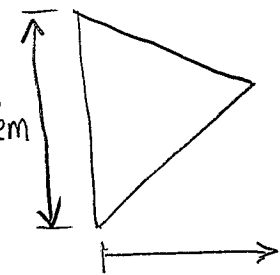


8. The stratospheric ozone layer is actually a fairly diffuse distribution of O_3 that spans ~20 – 60 km in altitude, peaking at about about 8 ppm_v around 35 km above sea-level. The total number of O_3 molecules in a column above a unit area of the Earth's surface is measured often measured and reported in Dobson units (DU, where 1 DU corresponds to a layer of O_3 that would be 10 μm thick at STP).

- a) Estimate the number of O_3 molecules in a 1 m² column by approximating the attached O_3 distribution profile with the linear function shown as the thin solid line. Express your answer in Dobson units.
 b) Compare the number density of O_3 at 35 km in the stratosphere to that of polluted urban air at 100 ppb_v at STP.

a) integrating area under the O_3 profile on the attached figure gives

Area = $\frac{1}{2} \cdot \text{base} \times \text{height}$



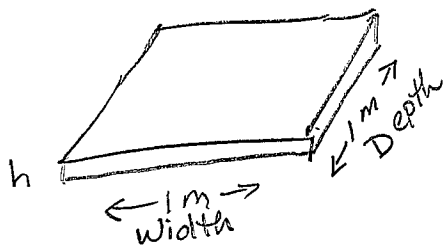
$$= \frac{1}{2} \cdot (30 \times 10^3 \text{ m}) \left(5 \times 10^{12} \frac{\text{molec}}{\text{cm}^3} \times \frac{10^6 \text{ cm}^3}{1 \text{ m}^3} \right) \left[\text{m} \cdot \frac{1}{\text{cm}^3} \cdot \frac{\text{cm}^3}{\text{m}^3} \right]$$

$$= 7.5 \times 10^{22} \frac{\text{molecules}}{\text{m}^2}$$

1 Dobson unit corresponds to 10 μm thick layer at STP

Since $PV = nRT$,

$$V = \frac{nRT}{P}$$



$$= \frac{\left(\frac{7.5 \times 10^{22} \text{ molecules}}{6.023 \times 10^{23} \text{ molecules/mol}} \right) \left(\frac{8.314 \text{ J}}{\text{mol K}} \right) (273 \text{ K})}{101,300 \text{ Pa}}$$

$$V = h \times W \times D$$

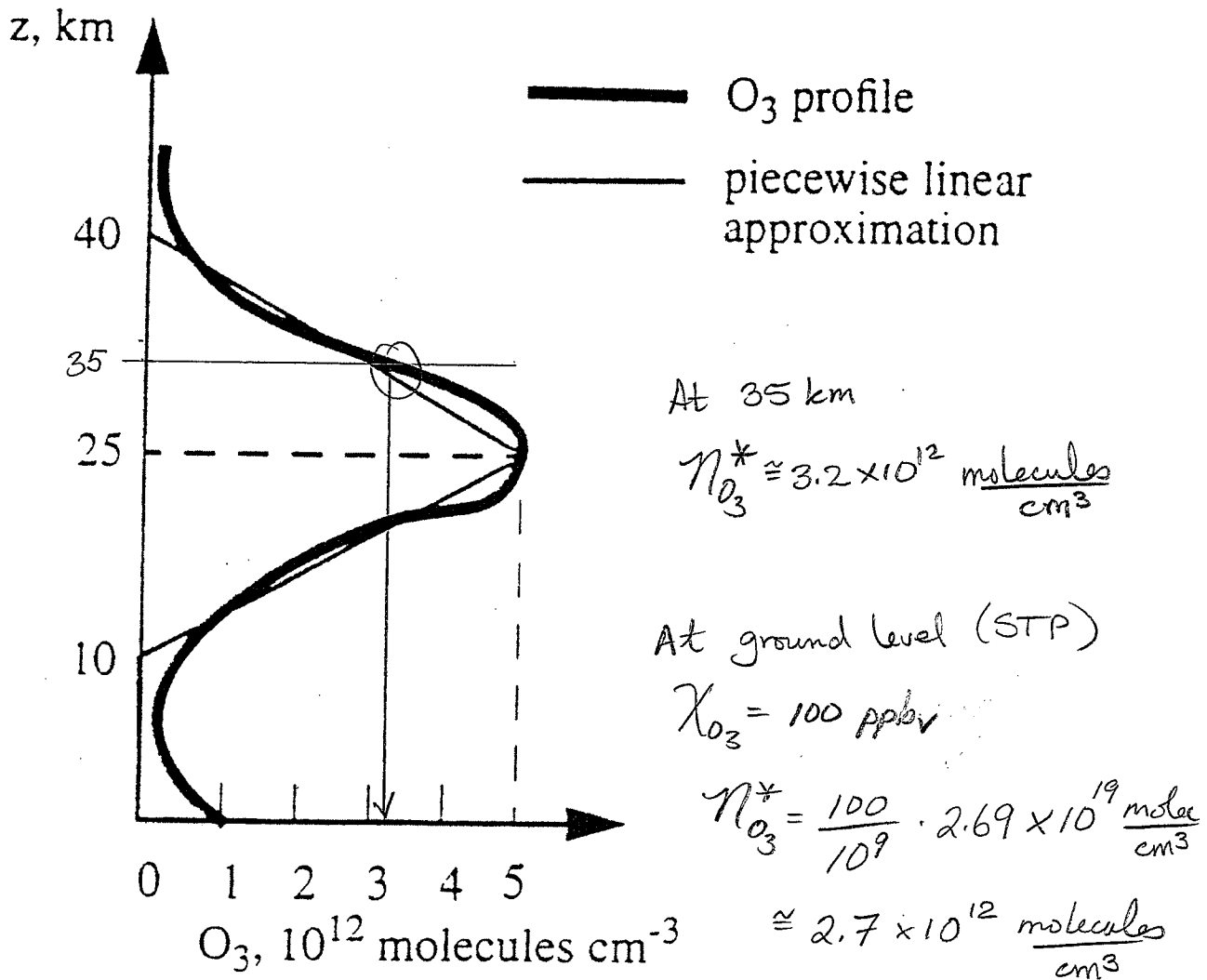
$$= 2.79 \times 10^{-3} \text{ m}^3$$

$$\therefore h = \frac{V}{W \cdot D} = \frac{2.79 \times 10^{-3} \text{ m}^3}{1 \text{ m}^2} = 2.79 \times 10^{-3} \text{ m} \Rightarrow 2790 \mu\text{m}$$

$$= 2.79 \times 10^{-3} \text{ m} \Rightarrow 2790 \mu\text{m}$$

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Since 1 DU = 10 μm, then 279 DU



Therefore the absolute number of ozone molecules present is roughly the same. However, the mixing ratio of O_3 at 35 km is much higher ($\approx 7 \text{ ppmv}$, See Fig. 3.1 textbook)