

CHEM 302
Assignment #2

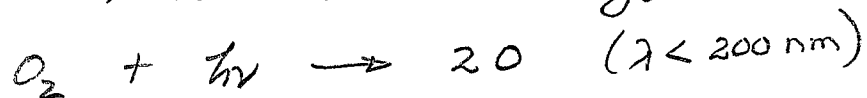
Provide solutions to the following questions in a neat and well organized manner, including dimensional analysis, where appropriate.

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

Due: Tuesday, October 13th, 2015

1. The mesopause is occurs roughly at 85 km altitude and is the point where a second large scale inversion in the atmospheric temperature profile occurs.
- Explain why the percentage of atomic oxygen to total oxygen increases above the mesopause.
 - Calculate the atmospheric pressure and air number density at this altitude.
 - Consider a cubic meter of air at the mesopause, what volume would it occupy at STP?

a) The relative abundance of atomic oxygen increases above the mesopause as the flux of short wavelength (high energy) photons $\lambda < 200$ nm increases. (Fig. 2.1) Molecular oxygen (O_2) absorbs photons between 130-180 nm which leads to dissociation into oxygen atoms.



b) Using barometric pressure law ($P_z = P_0 e^{-z/H}$) and a typical scale height $H = 6500$ m, the pressure at 85 km is given by $P_0 e^{-(85/6.5)} = 2.1 \times 10^{-6}$ atm.

Number density (n_{air}^*) is given by $\frac{n}{V} \cdot N_A$ where n is #mols air, V is typically expressed as 1 cm^3 and N_A is Avagadro's number.

Since $PV = nRT$, we can write $\frac{n}{V} \cdot N_A = \frac{P}{RT} \cdot N_A$

$$\therefore n_{air}^* = \frac{(2.1 \times 10^{-6} \text{ atm}) (6.02 \times 10^{23} \text{ mol}^{-1})}{\left(\frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol K}} \right) \left(\frac{10^3 \text{ cm}^3}{1 \text{ L}} \right) (180 \text{ K})} = 8.6 \times 10^{13} \frac{\text{molecules}}{\text{cm}^3}$$

(Fig 2.1) \uparrow

c) Let's approach this by determining n (#moles) of air in 1m^3 at 85 km ($P = 2.1 \times 10^{-6}\text{ atm}$, $T = 180\text{ K}$) and then calculate the volume of this number of moles of air at STP ($P = 1\text{ atm}$, $T = 273\text{ K}$).

At $z = 85\text{ km}$ (mesopause)

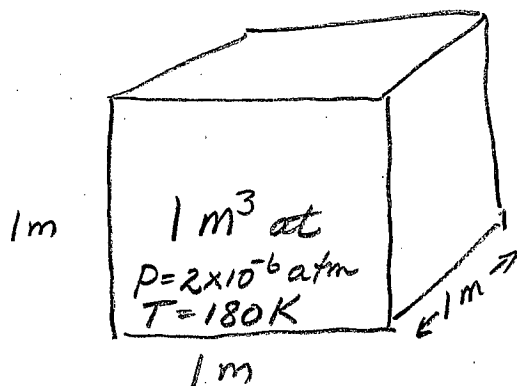
$$n = \frac{PV}{RT} = \frac{(2.1 \times 10^{-6}\text{ atm})(1\text{ m}^3) \left(\frac{10^3\text{ L}}{1\text{ m}^3}\right)}{\left(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(180\text{ K})} = 1.42 \times 10^{-4}\text{ mols}$$

At $z = 0$ (STP)

$$V = \frac{nRT}{P} = \frac{(1.42 \times 10^{-4}\text{ mols}) \left(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right) (273\text{ K})}{(1.00\text{ atm})}$$

$$= 3.18 \times 10^{-3}\text{ L} \quad \text{or} \quad 3.2\text{ mL}$$

$$\text{or} \quad 3.2 \times 10^{-6}\text{ m}^3$$

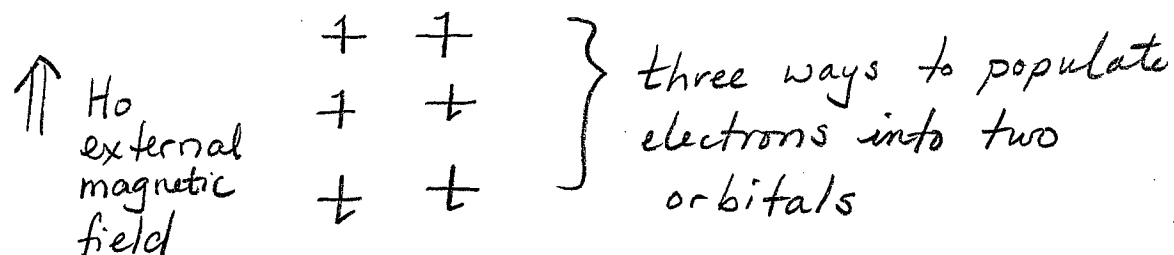


or 1.5 cm cubed

$\approx 300,000 \times$ smaller volume at STP

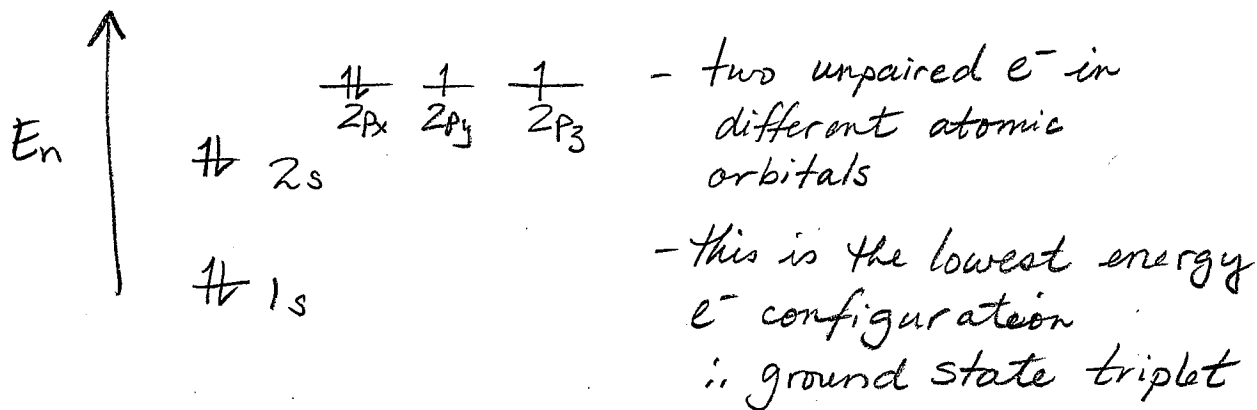
2. The ground electronic state of both atomic and molecular oxygen are diradicals in a 'triplet' electronic state. Use your knowledge of atomic and molecular orbital theory to explain why 'singlet' (spin-paired) states are electronically excited for these two oxygen species.

Triplet electronic states have two unpaired electrons
In the presence of an external magnetic field,
triplets will exhibit three distinct energy levels.

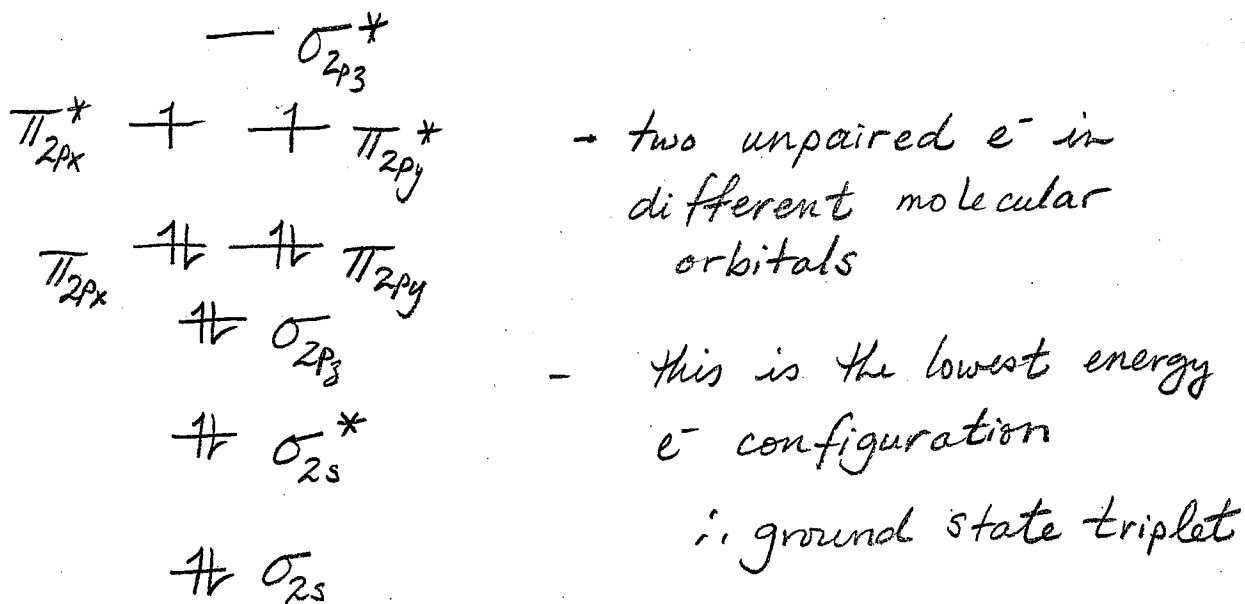


Atomic oxygen has a total of $8e^-$ (6 valence e^-) which are distributed into atomic orbitals from lowest energy to highest energy in accordance with Pauli exclusion principle (no two electrons in given atom can have same four quantum numbers) which means electrons in the same orbital must have opposite spin states and Hund's rule (lowest energy configuration of electrons in a degenerate orbital set involves maximum total spin) which means degenerate orbitals are singly occupied before electron spins are paired in same orbital. (This has the effect of spreading electrons over different regions of space)

Atomic orbitals for oxygen atom



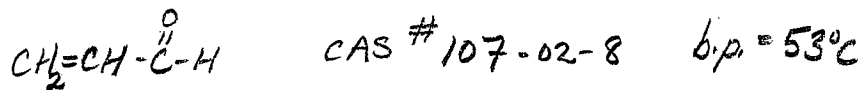
Molecular orbitals for O_2 molecule (considers valence e^- only). Total of $6 + 6 = 12$ valence e^-



Note: Most stable molecules are 'spin paired' and have ground state singlets.
 Radicals with one unpaired e^- are ground state doublets.

3. Acrolein (2-propenal) is a volatile organic compound with a disagreeable odour and physiological effects (lachrymator). It has a reported vapour pressure of 200. torr at 17 °C. It is soluble in water, and photochemically active with an estimated outdoor half-life of 1 day in the troposphere. The 8 hour workplace exposure limit is 250 µg/m³.

- Identify at least one indoor and one outdoor source of atmospheric acrolein (properly citing your reference/s).
- Determine the mixing ratio of acrolein in the air if a spill were to occur in a closed non-ventilated room at 17°C. How does this compare to the 8 hour workplace exposure limit?
- Assuming the loss of acrolein follows *pseudo* first order kinetics, show that the outdoor residence time is around 35 hours.



a) indoor - second hand smoke
cooking

out door - biocide for aquatic weeds and algae

- b) Assuming that the spill is of sufficient size to saturate the room air with acrolein (i.e. there is liquid acrolein on the floor after some has evaporated), we can use the vapour pressure to determine the conc. in air in units µg/m³.

$$P = 200. \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.263 \text{ atm}$$

$$\therefore X = \frac{0.263}{1.0} = 0.263$$

Converting to mass/volume ratio using $PV = nRT$ calculate n in 1 m³, then use molar mass to calculate mass.

$$n = \frac{P \cdot V}{R \cdot T} = \frac{(0.263 \text{ atm})(10^3 \text{ L})}{(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(290 \text{ K})} = 11.0 \text{ mols}$$

$$\text{mass} = 11.0 \text{ mols} \times 56.0 \text{ g/mol} = 619 \text{ g/m}^3$$

$$\text{or } 6.2 \times 10^8 \text{ } \mu\text{g/m}^3 \text{ (way high)}$$

c) outdoor half life \sim 1 day



assuming first order loss processes

$$\tau = \frac{\text{stock}}{\text{flux}} = \frac{[\text{acrolein}]}{k [\text{acrolein}]} = \frac{1}{k}$$

Integrated rate equation for 1st order process is given by;

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

$$\text{at } t = t_{1/2}, [A]_t = \frac{1}{2} [A]_0$$

$$\text{and } \ln\left(\frac{\frac{1}{2} [A]_0}{[A]_0}\right) = -k t_{1/2}$$

$$\therefore \frac{\ln(0.500)}{-t_{1/2}} = k$$

$$\text{and } k = 0.693 \text{ day}^{-1}$$

$$\therefore \tau = \frac{1}{k} = 1.4 \text{ day}$$

$$\text{or } \approx 35 \text{ hrs}$$

4. The PCB concentration in the air inside a typical 600 m^3 home is 400 ng/m^3 and the ventilation is such that the residence time of the indoor air is 10 hr. If the PCBs are coming from a source within the house, estimate how much (in mg) leaks per year?

$$\begin{array}{l} V = 600 \text{ m}^3 \\ \text{stock} = 400 \frac{\text{ng}}{\text{m}^3} \cdot 600 \text{ m}^3 \\ \uparrow \text{source} \quad \tau_{\text{air}} = 10 \text{ hr} \end{array}$$

$$\tau = \frac{\text{stock}}{\text{flux}}$$

Assuming PCB's are persistent (which they are) and only loss mechanism is by ventilation of indoor air, we can say

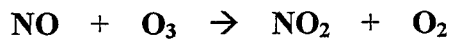
$$10 \text{ hr} = \frac{0.240 \text{ mg PCB}}{\text{flux}}$$

$$\therefore \text{flux} = \frac{0.240 \text{ mg PCB}}{10 \text{ hr}} = 0.024 \frac{\text{mg}}{\text{hr}}$$

On an annual basis, this amounts to;

$$0.024 \frac{\text{mg}}{\text{hr}} \times \frac{24 \text{ hr}}{\text{day}} \times \frac{365 \text{ day}}{\text{yr}} = 210 \text{ mg/yr}$$

5. For the reaction;



The *second order* rate constant has a value of $1.8 \times 10^{-14} \text{ molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$ at 25°C . The concentration of **NO** in a relatively clean atmosphere is 0.10 ppb_v and that of **O₃** is 15 ppb_v .

- Calculate the rate of the **NO** oxidation using units of $\text{molecules cm}^{-3} \text{ s}^{-1}$.
- Show how the rate law may be expressed in *pseudo* first order terms and calculate the corresponding *pseudo first order* rate constant.
- Calculate the apparent atmospheric residence time of **NO** under these conditions, assuming this to be the only loss process.

a)
$$\text{rate} = k_2 [\text{NO}] [\text{O}_3]$$

\uparrow $1.8 \times 10^{-14} \text{ molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$

\swarrow $15 \text{ ppb}_v \rightarrow \text{convert to molecules/cm}^3$
 \searrow $0.10 \text{ ppb}_v \rightarrow \text{ " " "}$

Number density (n_{NO}^* and $n_{\text{O}_3}^*$) use $n^* = \frac{PV}{RT} \cdot N_A$

and partial pressure of each gas is given by

$$P_i = \chi_i P_T \quad \therefore P_{\text{NO}} = \left(\frac{0.10}{10^9}\right) (1.00 \text{ atm}) = 1.0 \times 10^{-10} \text{ atm}$$

$$P_{\text{O}_3} = \left(\frac{15}{10^9}\right) (1.00 \text{ atm}) = 1.5 \times 10^{-8} \text{ atm}$$

$$\begin{aligned} \text{So } n_{\text{NO}}^* &= \frac{(1.0 \times 10^{-10} \text{ atm})(1 \text{ cm}^3)(10^{-3} \text{ L/cm}^3)(6.02 \times 10^{23} \text{ mol}^{-1})}{(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(298 \text{ K})} \\ &= 2.46 \times 10^9 \text{ molecules/cm}^3 \end{aligned}$$

$$\text{and } n_{\text{O}_3}^* = 3.70 \times 10^{11} \text{ molecules/cm}^3$$

$$\begin{aligned} \therefore \text{rate of NO oxidation by this rxn under these} \\ \text{conditions} &= (1.8 \times 10^{-14} \frac{\text{molec}^{-1} \text{ cm}^3 \text{ s}^{-1}}{\text{molec}})(2.46 \times 10^9 \frac{\text{molec}}{\text{cm}^3})(3.70 \times 10^{11} \frac{\text{molec}}{\text{cm}^3}) \\ &= 1.64 \times 10^7 \frac{\text{molec}}{\text{cm}^3} / \text{sec} \end{aligned}$$

b) Since $[O_3] \gg [NO]$, we can say that its conc will not change appreciably during the course of this reaction. Hence we can rewrite the rate expression as pseudo first order

$$\text{rate} = k'[NO]$$

$$\text{where } k' = k [O_3]$$

$$= \left(1.8 \times 10^{-14} \frac{\text{cm}^3}{\text{molec. s}} \right) \left(3.70 \times 10^{11} \frac{\text{molec}}{\text{cm}^3} \right)$$

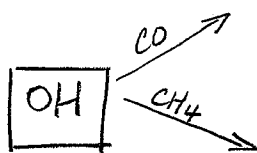
$$= 6.7 \times 10^{-3} \text{ s}^{-1}$$

c) residence time, $\tau = \frac{1}{k}$ for first order processes

$$\therefore \tau = \frac{1}{6.7 \times 10^{-3} \text{ s}^{-1}} = 150 \text{ s}$$

or 2.5 mins

6. Two important sinks for OH in the troposphere are reaction with CH₄ and CO, respectively. Calculate the lifetime of hydroxyl radical against chemical loss in the troposphere using typical concentrations of 4.6 ppm_v for CO and 1.7 ppm_v for CH₄.



two independent
bimolecular (2nd order)
processes.

Given that [OH] conc in atmosphere is exceedingly small ($\sim 2 \times 10^6$ molec/cm³, textbook sec. 2.2.4), we can say that [CO] \gg [OH] and [CH₄] \gg [OH]

Therefore, both of these second order reactions can be expressed as pseudo first order reactions where the conc of CO and CH₄ are essentially constant.

$$k'_{\text{CO}} = \left(2.7 \times 10^{-13} \frac{\text{cm}^3}{\text{molec} \cdot \text{s}} \right) [\text{CO}]$$

↖ 4.6 ppm_v → convert to n_{CO}^*

and

$$k'_{\text{CH}_4} = \left(6.3 \times 10^{-15} \frac{\text{cm}^3}{\text{molec} \cdot \text{s}} \right) [\text{CH}_4]$$

↖ 1.7 ppm_v → convert to $n_{\text{CH}_4}^*$

$$n^* = n N_A = \frac{P V}{RT} N_A \text{ where } V = 1 \text{ cm}^3$$

assuming $P_T = 1.0 \text{ atm}$ and $T = 300 \text{ K}$ (temp. at which rate constants given)

$$n_{CO}^* = \frac{(4.6 \times 10^{-6} \text{ atm})(1 \text{ cm}^3 \cdot \frac{1 \text{ L}}{10^3 \text{ cm}^3})(6.02 \times 10^{23} \text{ mol}^{-1})}{(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(300 \text{ K})}$$

$$= 1.13 \times 10^{14} \text{ molecules/cm}^3$$

$$n_{CH_4}^* = 4.16 \times 10^{13} \text{ molecules/cm}^3$$

$$\therefore k'_{CO} = 30.5 \text{ s}^{-1}$$

$$\& k'_{CH_4} = 0.262 \text{ s}^{-1}$$

$$\tau = \frac{1}{\sum k} \text{ for first order processes}$$

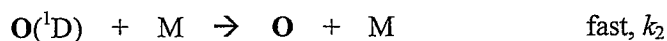
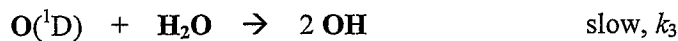
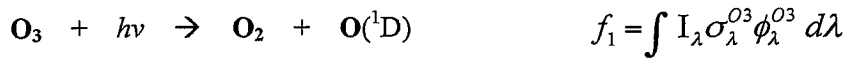
$$\therefore \tau = \frac{1}{(30.5 \text{ s}^{-1}) + (0.262 \text{ s}^{-1})}$$

$$= \frac{1}{30.77 \text{ s}^{-1}} = 0.0325 \text{ sec}$$

$$\text{or } \approx 32 \text{ msec}$$

with the predominant loss by CO under these conditions.

7. Hydroxyl radicals (**OH**) are reactive react species in the atmosphere, particularly in **H**-atom abstraction reactions whereby it is converted to **H₂O**. The production of **OH** occurs by reaction of 'singlet' oxygen with water vapour in both the troposphere and stratosphere. Singlet oxygen is produced by the photolysis of ozone. Considering only the reactions below, derive the expression for the production rate of **OH** by assuming *steady state* for **O(¹D)**.



$$\text{Rate of production of OH} \approx \frac{2k_3 [\text{O}_3][\text{H}_2\text{O}]}{k_2 [\text{M}]} \int I_\lambda \sigma_\lambda \phi_\lambda d\lambda$$

S.S.A. for **O(¹D)**

\therefore rate of **O(¹D)** prodⁿ = rate of **O(¹D)** loss

$$\text{rate of prod}^n = f_1 [\text{O}_3]$$

$$\text{rate of loss} = k_3 [\text{O}][\text{H}_2\text{O}] + k_2 [\text{O}][\text{M}]$$

$$\therefore f_1 [\text{O}_3] = k_3 [\text{O}][\text{H}_2\text{O}] + k_2 [\text{O}][\text{M}] = (k_3 [\text{H}_2\text{O}] + k_2 [\text{M}]) [\text{O}]$$

$$\therefore [\text{O}] = \frac{f_1 [\text{O}_3]}{k_3 [\text{H}_2\text{O}] + k_2 [\text{M}]}$$

$$\text{rate of prod}^n \text{ of OH} = k_3 [\text{O}][\text{H}_2\text{O}] \times 2$$

$$\therefore \text{rate prod}^n \text{ of OH} = \frac{k_3 f_1 [\text{O}_3][\text{H}_2\text{O}] \times 2}{k_3 [\text{H}_2\text{O}] + k_2 [\text{M}]}$$

where this takes into account that OH is produced at twice the rate of **O(¹D)**

$$= \frac{2k_3 [\text{O}_3][\text{H}_2\text{O}] \int I_\lambda \sigma_\lambda \phi_\lambda d\lambda}{k_3 [\text{H}_2\text{O}] + k_2 [\text{M}]}$$

$$\text{where } f_1 = \int I_\lambda \sigma_\lambda \phi_\lambda d\lambda$$

if $k_2 [\text{M}] \gg k_3 [\text{H}_2\text{O}]$ then this reduces to

$$\approx \frac{2k_3 [\text{O}_3][\text{H}_2\text{O}] \int I_\lambda \sigma_\lambda \phi_\lambda d\lambda}{k_2 [\text{M}]}$$

since $k_2 > k_3$ (above) and $[\text{M}] \gg [\text{H}_2\text{O}]$, this is reasonable

8. The chlorofluorocarbon CFC-12 is removed from the atmosphere solely by photolysis (occurring mostly in the stratosphere)*. Its atmospheric lifetime is ~100 years. In the early 1980's (prior to the Montreal protocol), the mean atmospheric concentration of CFC-12 was 400 ppt_v and was increasing at a rate of 4% yr⁻¹.

- Show the structure of CFC-12 illustrating the photolysis reaction occurring in the stratosphere.
- Using the residence time and the mean concentration, estimate the rate constant for the chemical loss of CFC-12 and its total mass in the atmosphere in the 1980's.
- Use the mass balance equation below, to estimate the CFC-12 emission rate during the 1980's.

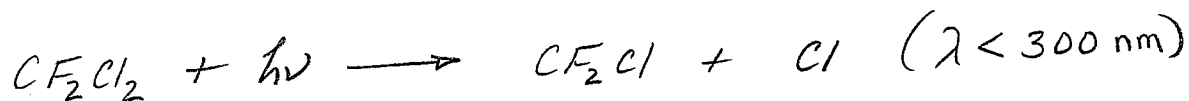
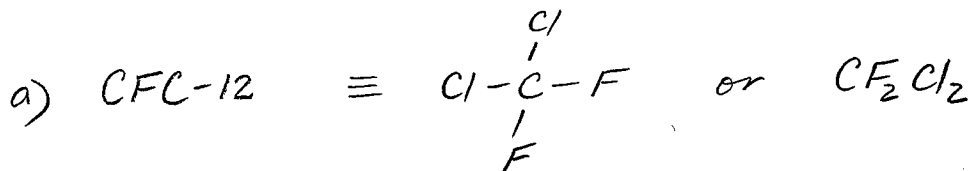
$$\text{Rate of change} = \text{Emission rate} - \text{Loss rate}; \quad \frac{dm}{dt} = E - k m$$

Where dm/dt is the rate of change in mass (kg/yr), m is the mass (kg), E is the emission rate (kg/yr) and k is the rate constant for loss (yr⁻¹).

- The initial Montreal protocol called for a 50% reduction of CFC emissions by 1989 and a stabilization henceforth. Consider a scenario whereby emissions are held constant at 50% of the value calculated in part c (above). Show that the mass of CFC-12 in the atmosphere would eventually approach a steady state value of $\sim 2 \times 10^{10}$ kg, which is higher than the value estimated in part b (above).

The Montreal protocol was amended in London (1990) and again in Copenhagen (1992) to respond to the increased urgency created by the appearance of the Antarctic ozone hole.

* *Nature*, 249, 810-812 (1974). This was a ground breaking paper that contributed to the Nobel prize in Chemistry awarded in 1995.



b) $\tau \cong 100 \text{ yrs}$ $[\text{CF}_2\text{Cl}_2] = 400 \text{ ppt}_v$

$$\tau = \frac{\text{stock}}{\text{flux}} = \frac{1}{k} \quad \text{assuming steady-state and first order loss processes}$$

$$\therefore k = \frac{1}{\tau} = \frac{1}{100 \text{ yrs}} = 0.010 \text{ yr}^{-1}$$

$$\text{mass in atmosphere} = \frac{400}{10^{12}} \cdot \left(\begin{array}{c} \text{total number moles} \\ \text{in atmosphere} \end{array} \right) \cdot \frac{121 \text{ g}}{1 \text{ mol}}$$

$$= \left(\frac{400}{10^{12}} \right) (5.27 \times 10^{18} \text{ kg}) \left(\frac{1 \text{ mol}}{28.96 \text{ g}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(\frac{121 \text{ g}}{1 \text{ mol}} \right)$$

$$= 8.81 \times 10^{12} \text{ g} \quad \text{or} \quad 8.81 \times 10^9 \text{ kg}$$

$$c) \quad \frac{dm}{dt} = E - km$$

$$\text{where } m = 8.81 \times 10^9 \text{ kg}$$

$$k = 0.010 \text{ yr}^{-1}$$

$$\frac{dm}{dt} = \text{rate of change in kg/yr}$$

$$= (8.81 \times 10^9 \text{ kg})(0.04) = 3.52 \times 10^8 \text{ kg/yr}$$

↑
4% increase per yr

$$E = \frac{dm}{dt} + km$$

$$= \left(3.52 \times 10^8 \frac{\text{kg}}{\text{yr}}\right) + (0.010 \text{ yr}^{-1})(8.81 \times 10^9 \text{ kg})$$

$$= 4.40 \times 10^8 \text{ kg/yr}$$

d) if E were reduced by 50%

$$E' \text{ (new emission rate)} = 2.2 \times 10^8 \text{ kg/yr}$$

at steady state, rate of change = 0

$$\therefore E = km$$

$$\uparrow \quad \quad \quad \uparrow$$
$$\text{use } E' = 2.2 \times 10^8 \frac{\text{kg}}{\text{yr}}$$

$$k = 0.010 \text{ yr}^{-1}$$

$$\therefore m = \frac{E'}{k} = \frac{2.2 \times 10^8 \text{ kg/yr}}{0.010 \text{ yr}^{-1}} = 2.2 \times 10^{10} \text{ kg}$$

