

- I 1) (B) 2) (A) 3) (B) 4) (C) 5) (C) 6) (A)

II (a)



M absorbs the energy excess increasing T in the upper layer of the stratosphere



One molecule of O_3 is produced, one is destroyed
So the concentration remains constant according to the Chapman cycle.

~~10~~

~~$$\frac{d[O]}{dt} = 2j_1[O_2] - k_2[O][O_2][M] + j_3[O_3] - k_4[O][O_3]$$~~

~~$$\frac{d[O_3]}{dt} = k_2[O][O_2][M] - j_3[O_3] - k_4[O][O_3]$$~~

~~After a time $\frac{d[O]}{dt} = \frac{d[O_3]}{dt} = 0$~~

~~$$[O] = \frac{2j_1[O_2] + j_3}{k_2[O_2][M] + k_4[O_3]}$$~~

II (b)



As Y (that can be Cl, NO_x, HO_x) regenerates again in the second reaction it can react and destroy a large number of O₃ molecules.

III (a)

Solar radiation passes through the atmosphere

Part is absorbed by the Earth surface and warms it

IR radiation is emitted from the Earth surface.

Some passes through the atmosphere and some is absorbed and re-emitted in all directions by greenhouse gases molecules. The effect of this is

to warm the Earth surface and lower atmosphere. Earth Temperature as followed the cycles of the Sun for millennia, but in the beginning

of the industrial revolution it started to increase continuously, an increase that was also present in the concentration of gases like CO₂, ~~methane~~ methane and N₂O.

If there was no natural Greenhouse effect the temperature of the Earth would be about -18°C

III

T-3

① When the residence time of a GHG is smaller than the residence time of CO_2 , as in CH_4

$$\text{GWP}_{20} > \text{GWP}_{100}$$

The opposite

$$\text{GWP}_{100} > \text{GWP}_{20}$$

occurs when the residence time of the gas is larger than that of CO_2 , like for SF_6

② CFC's and Hydrocarbons, or any other polyatomic gases present in the atmosphere because they absorb radiation in the IR.

③ This is a "debate" question.

Some people say that water, as a polyatomic molecule, absorbs radiation in the IR, so it should be considered a GHG, specially because it is present in very large amounts in the atmosphere

Other people say that because of its small residence time its effect should not count for the calculation of Greenhouse effect.

The aim was for you to develop your own point of view in this subject.

(IV)

$$F = 598 \text{ Tg y}^{-1}$$

$$J = \frac{m}{F}$$

$$X_{\text{CH}_4} = \frac{n^{\circ} \text{ mol of CH}_4}{n^{\circ} \text{ mol of air}} = \frac{\frac{m_{\text{CH}_4}}{M_{\text{CH}_4}}}{\frac{m_{\text{air}}}{M_{\text{air}}}} = \frac{m_{\text{CH}_4} \times M_{\text{air}}}{m_{\text{air}} \times M_{\text{CH}_4}}$$

$$M_{\text{air}} = (0,78 \times 28) + (0,21 \times 36) + (0,01 \times 40) = 29,8 \text{ g/mol}$$

$$m_{\text{CH}_4} = X_{\text{CH}_4} \times \frac{m_{\text{air}} \times M_{\text{CH}_4}}{M_{\text{air}}}$$

$$= 1,7 \times 10^{-6} \times \frac{5 \times 10^{18} \times 16}{29,8}$$

$$= 4,564 \times 10^{12} \text{ Kg} = 4,564 \times 10^3 \text{ Tg}$$

$$J = \frac{4564}{598} = 7,6 \text{ y}$$

IV (b)

$$\Delta X_{\text{CH}_4} = \frac{M_{\text{air}}}{m_{\text{air}} \times M_{\text{C}}} \Delta m_{\text{C}}$$

$$(1,7 - 0,722) \times 10^{-6} = \frac{29,8}{5 \times 10^{18} \times 12} \Delta m_{\text{CH}_4}$$

$$\Delta m_{\text{CH}_4} = 1,97 \times 10^{12} \text{ Kg}$$

V (a)

$$X = \frac{\# \text{ mol SO}_2 / \text{m}^3}{\# \text{ mol air} / \text{m}^3}$$

$$\# \text{ mol SO}_2 / \text{m}^3 = \frac{50 \times 10^{-6} \text{ g}}{64 \text{ g}} = 7,8 \times 10^{-7} \text{ mol} / \text{m}^3$$

$$\# \text{ mol air} / \text{m}^3 = \frac{PV}{RT} = 42,3 \text{ mol} / \text{m}^3$$

$$P = 1 \text{ atm}$$

$$V = 1 \text{ m}^3 = 10^3 \text{ l}$$

$$R = 0,082 \text{ l} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$T = 288 \text{ K}$$

$$X = 1,8 \times 10^{-8} = 18 \text{ ppb}$$

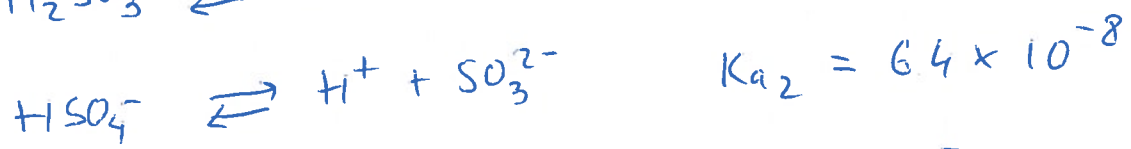
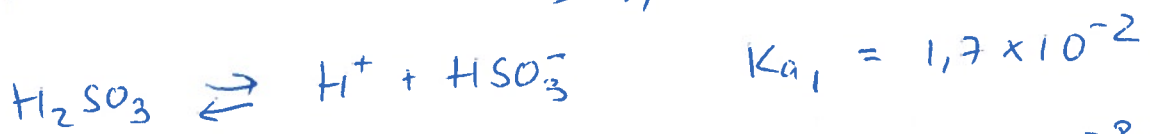
V(b)

$$K_H = 5.4 \text{ M atm}^{-1}$$

$$C_g = K_H P_g$$

$$P_{\text{SO}_2} = 18 \times 10^{-9} \times 1 \text{ atm} = 18 \times 10^{-9} \text{ atm}$$

$$C_g = [\text{SO}_2]_{\text{aq}} = [\text{H}_2\text{SO}_3] = 5.4 \times 18 \times 10^{-9} \\ = 9,72 \times 10^{-8} \text{ mol/l}$$



$K_{a1} \gg K_{a2}$, so the second dissociation does not affect the $[\text{H}^+]$

$$K_{a1} = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]} = \frac{[\text{H}^+]^2}{[\text{H}_2\text{SO}_3]}$$

$$[\text{H}^+] = [\text{HSO}_3^-]$$

$$[\text{H}^+]^2 = 1,7 \times 10^{-2} \times 9,72 \times 10^{-8} = 1,65 \times 10^{-9}$$

$$[\text{H}^+] = 4,1 \times 10^{-5} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = 4,4$$

① Outfluxes = 9 Tg/year

$$\tau = \frac{1300 \text{ Tg}}{9 \text{ Tg/year}} = 144,4 \text{ y}$$

Long residence time \rightarrow substance well mixed in the atmosphere

② Influxes = $2 + 0.5 + 4 + 6 = 12.5 \text{ Tg/year}$

Accumulation rate = $12.5 - 9 = 3.5 \text{ Tg/year}$

③
$$X_{\text{N}_2\text{O}} = \frac{m_{\text{N}_2\text{O}}}{m_{\text{air}}} = \frac{M_{\text{air}}}{M_{\text{N}_2\text{O}}} \times \frac{m_{\text{N}_2\text{O}}}{m_{\text{air}}}$$

$$m = \# \text{ moles}$$

$$= \frac{m}{M}$$

$$\Delta X_{\text{N}_2\text{O}} = \frac{M_{\text{air}}}{M_{\text{N}_2\text{O}} \times m_{\text{air}}} \times \Delta m_{\text{N}_2\text{O}}$$

$$\Delta m_{\text{N}_2\text{O}} = \Delta X_{\text{N}_2\text{O}} \times m_{\text{air}} \times \frac{M_{\text{N}_2\text{O}}}{M_{\text{air}}}$$

$$= 5 \times 10^{18} \times \frac{44 \times 10^{-3}}{29 \times 10^{-3}} \times 80 \times 10^{-9}$$

$$= 6 \times 10^{11} \text{ Kg}$$

~~6×10^{11} kg / 65 years~~

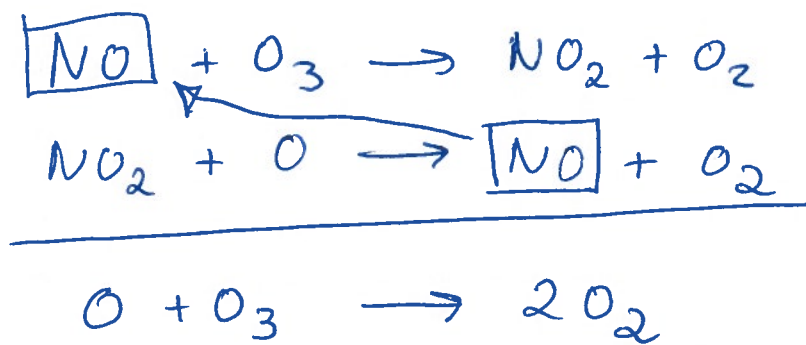
E1 - (2)

$$6 \times 10^{11} \text{ kg} / 65 \text{ years} = 9.3 \times 10^9 \text{ kg/y}$$

$$3.5 \text{ Tg/y} = 3.5 \times 10^9 \text{ kg/y} \quad (\text{data from } b) \\ \text{y 2000})$$

Since the year 2000 the rate of accumulation of N_2O has increased substantially

(d)



This is a catalytic process because one molecule of NO can react with various molecules of O_3 (see arrow)

(e)

$$\frac{d[\text{NO}_2]}{dt} = k_3 [\text{O}_3][\text{NO}] - j_1 [\text{NO}_2] = 0$$

$$k_3 [\text{O}_3][\text{NO}] = j_1 [\text{NO}_2]$$

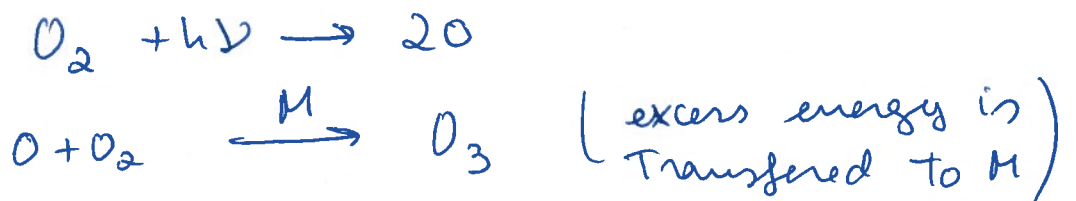
$$[\text{O}_3]_{ss} = \frac{j_1}{k_3} \frac{[\text{NO}_2]}{[\text{NO}]}$$

Exam 2

① In the stratosphere and thermosphere T increases with altitude.

In the stratosphere T remains constant between 10-20 km and increases between 20-50 km, reaching 273 K in the stratopause.

Temperature increase results from the photochemical reactions of O_2 and O_3



M - any molecule existing in the stratosphere
(N_2, O_2, O_3 , etc)



Temperature is higher close to the stratopause because of greater energy absorption (despite the smaller number of molecules). Temperature decreases as it gets close to Earth because most of the photons have already been absorbed.

In the Thermosphere a similar phenomenon occurs but this time involving absorption of radiation by O_2 and N_2



②

$$X_{O_2} = 0,21$$

$$P_{\text{Troposphere}} = 100 \text{ hPa}$$

$$T = 0^\circ\text{C}$$

$$R = 8,314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$N_A = 6.023 \times 10^{23} \text{ particles/mol}$$

$$V = 1 \text{ m}^3$$

$n_a = \text{number density} = \text{number of molecules per volume (m}^3 \text{ or cm}^3)$

$$n_a = \frac{N_A PV}{RT}$$

$$n_{\text{air}} = \frac{6.023 \times 10^{23} \times 100 \times 1}{8.314 \times 273} = 2,654 \times 10^{22} \text{ molecules/m}^3$$

$$n_{O_2} = 2.65 \times 10^{22} \times 0,21 = 5.57 \text{ molecules/m}^3$$

(3)

$$J = \frac{m}{\text{Influxes}}$$

$$\begin{aligned} \text{Influxes} &= 75 + 10 + 3 + 7 + 0,5 + 25 \\ &= 120,5 \text{ Tg/y} \end{aligned}$$

$$m = 1,2 \text{ Tg}$$

$$\begin{aligned} J &= 9,958 \times 10^{-3} \text{ y} \\ &= 3,6 \text{ days} \end{aligned}$$

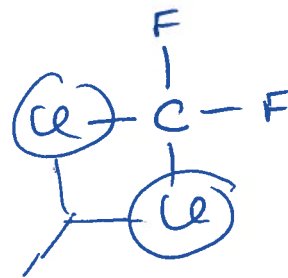
Acid Rain caused by SO_2 is a local phenomenon

4 a) CFC-12 = CF_2Cl_2

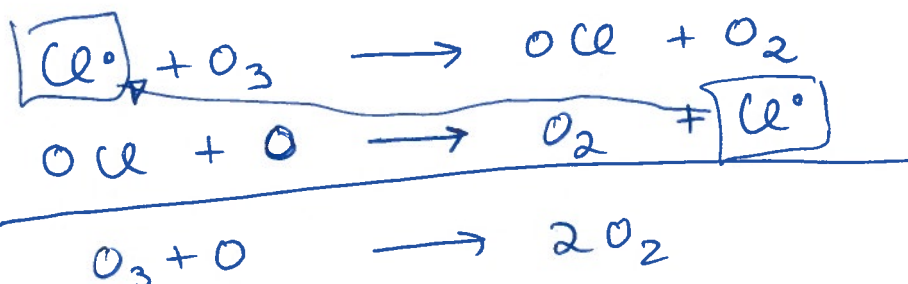
Rule of 90

$$12 + 90 = 102$$

$\downarrow \downarrow \downarrow$
 C H F



The atoms left are Cl



It is a catalytic process because the initial Cl^\bullet is recovered at the end of the cycle, becoming able to react with another O_3 molecule.

(b) The destruction of O_3 by CFC's involves breaking a C-Cl bond



With halons it is the breaking of a C-Br bond that is involved and this bond is considerably weaker (and therefore easier to break) than C-Cl, which makes halons much more reactive than CFC's in forming radicals that will destroy ozone.

Hydrocarbons don't have C-Cl or C-Br bonds to break so they don't form radicals and they don't destroy ozone.

(c) Both HFC's and hydrocarbons are polyatomic molecules, so they absorb IR radiation. Therefore they participate in Global Warming because they are Greenhouse gases.