ITINERIS

“Anthropogenic activities and effects on the living environment and human health.”

Atmosphere chemistry and physics

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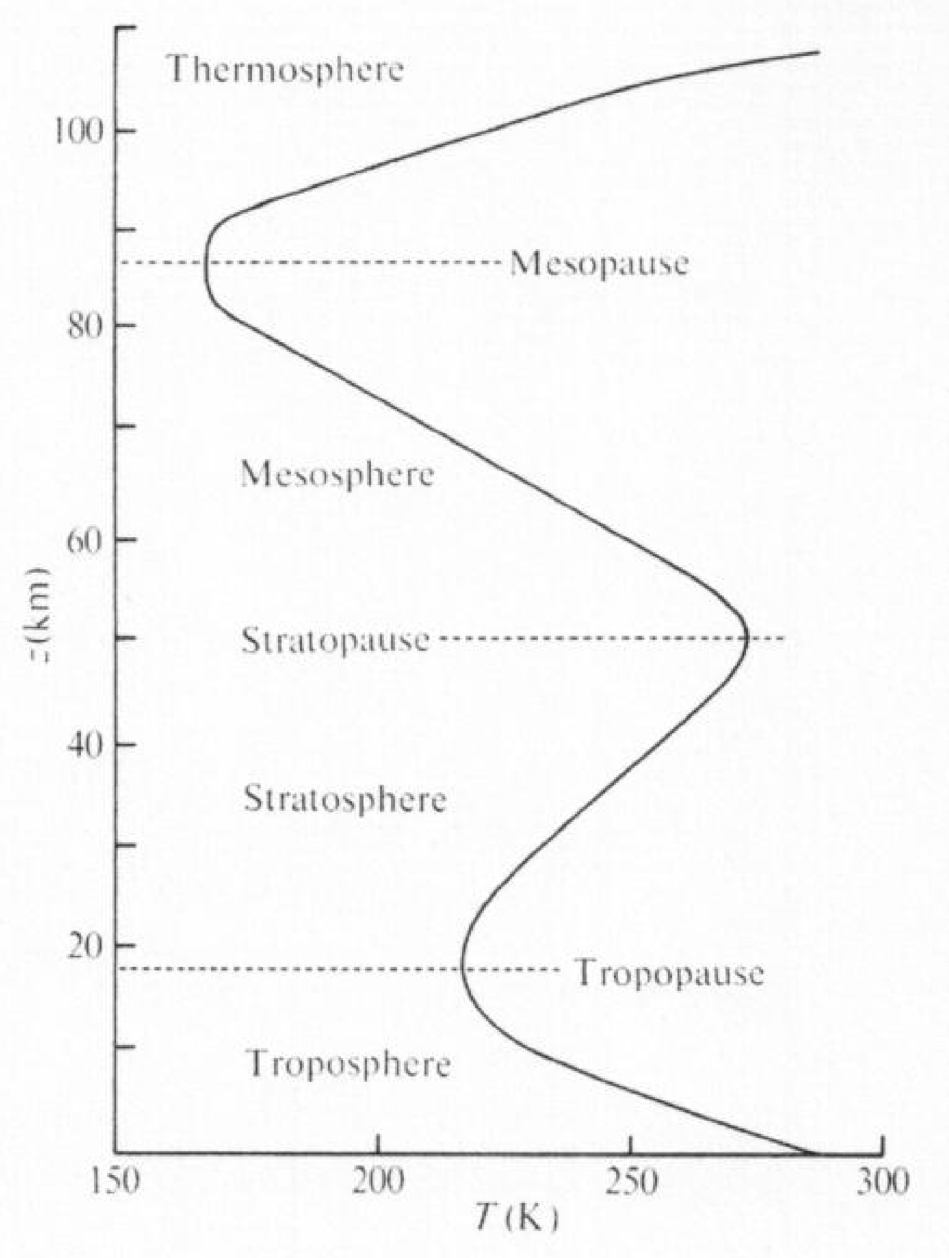
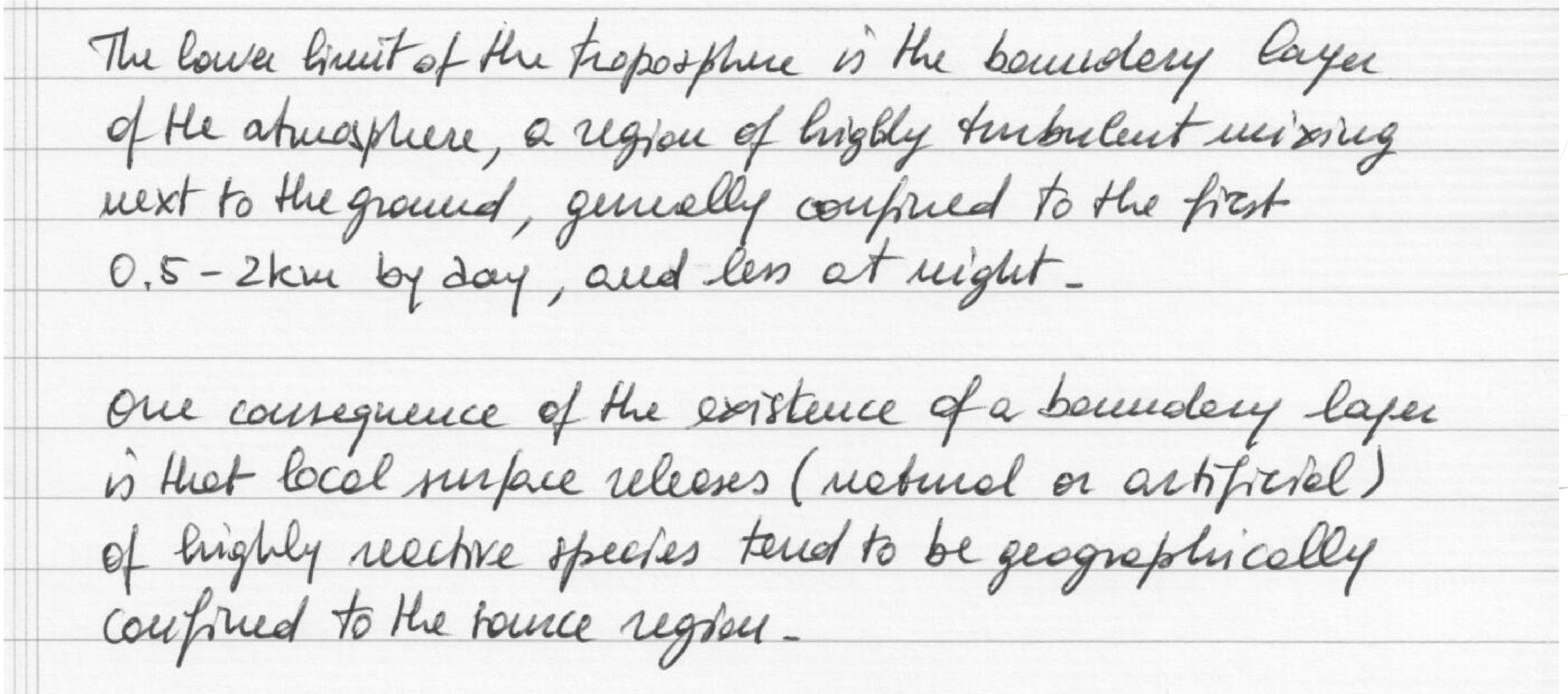
Earth Atmosphere



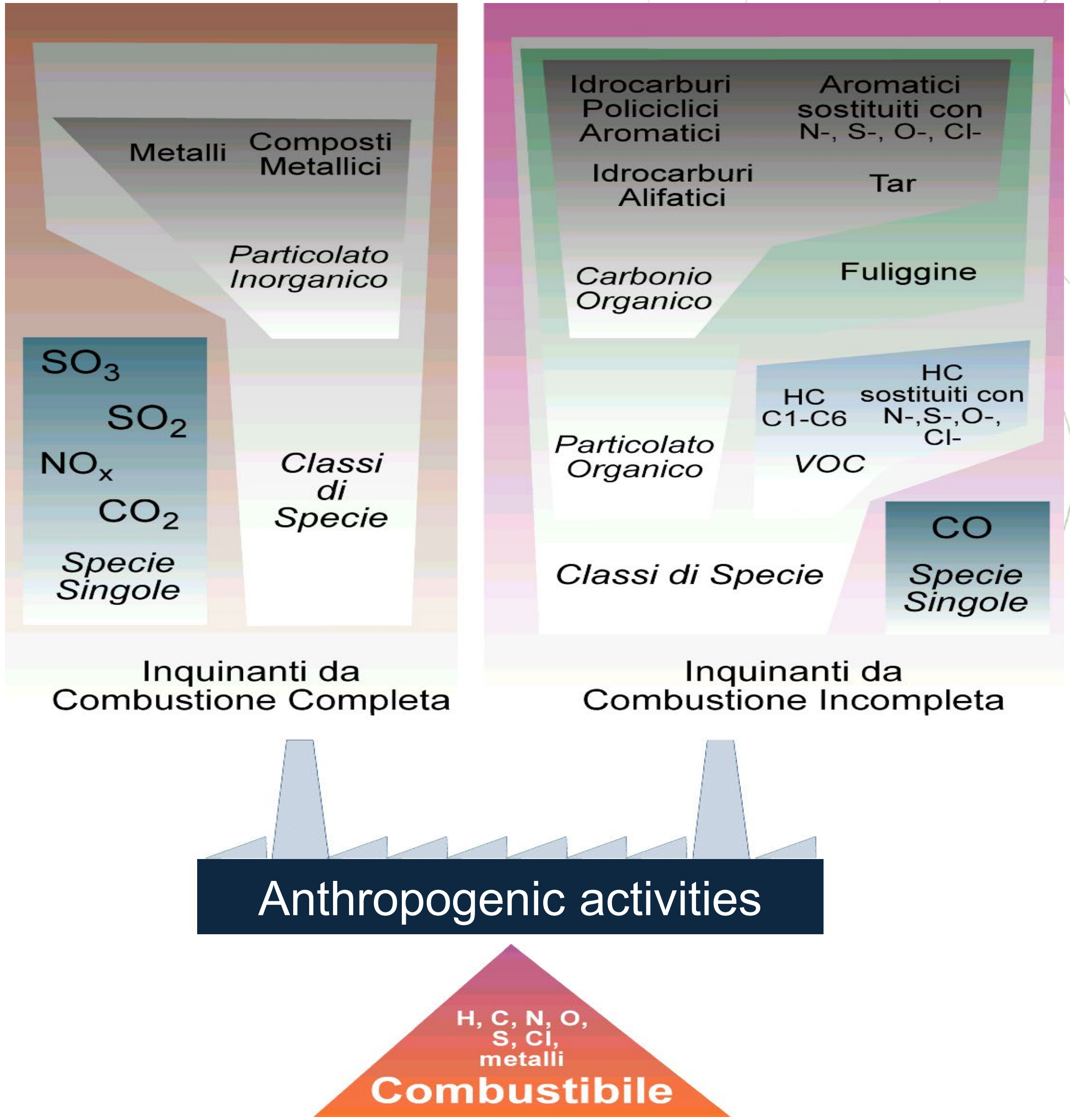
Earth Atmosphere



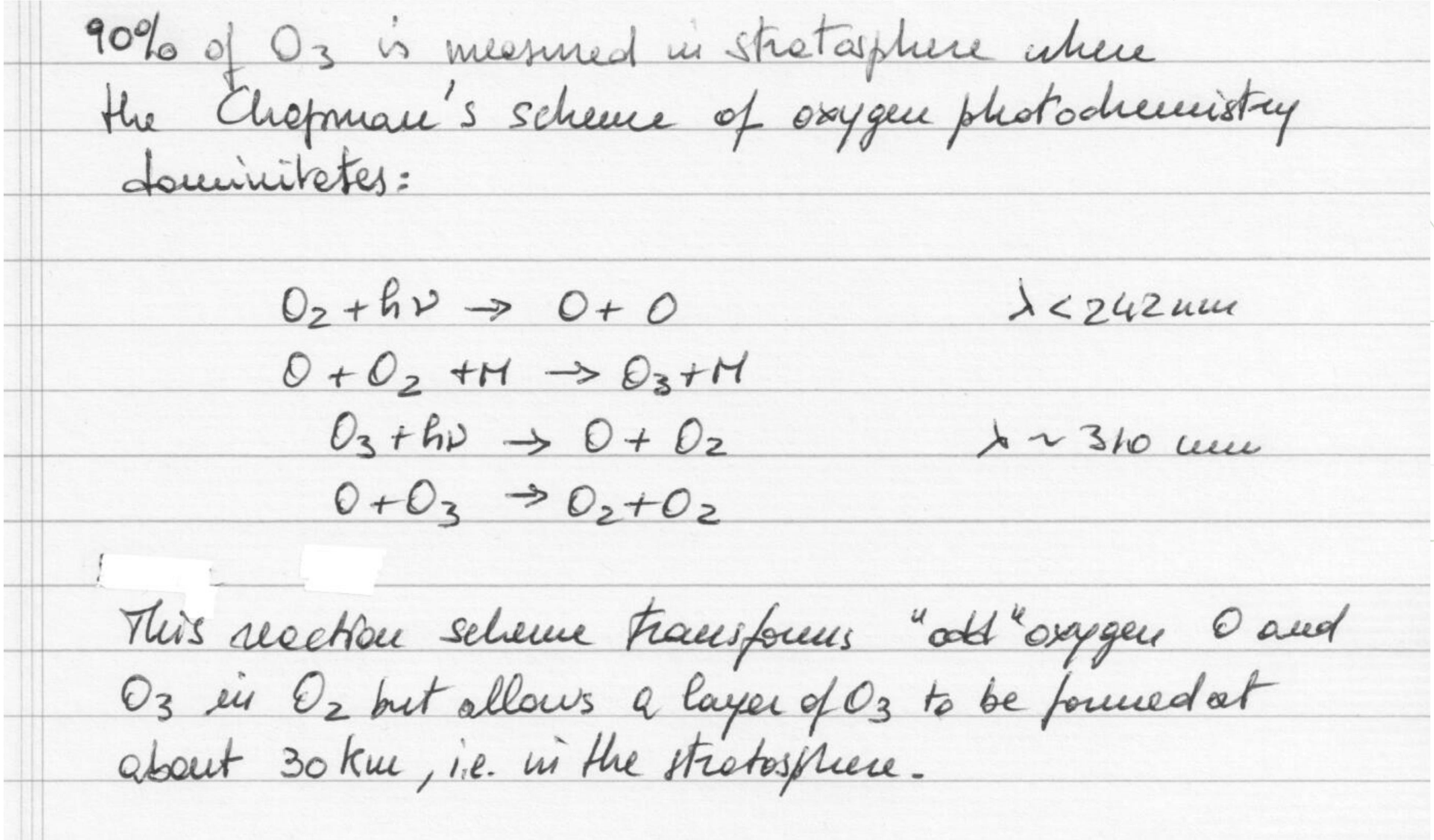
The lower limit of the troposphere is the boundary layer of the atmosphere, a region of highly turbulent mixing next to the ground, generally confined to the first 0,5 - 2km by day, and less at night.

One consequence of the existence of a boundary layer is that local surface releases (natural or artificial) of highly reactive species tend to be geographically confined to the source region.

Pollutant emission



Ozone in the atmosphere



90% of O_3 is measured in stratosphere where the Chapman's scheme of oxygen photochemistry dominitates:

$$O_2 + h\nu \rightarrow O + O \qquad \lambda < 242\,nm$$

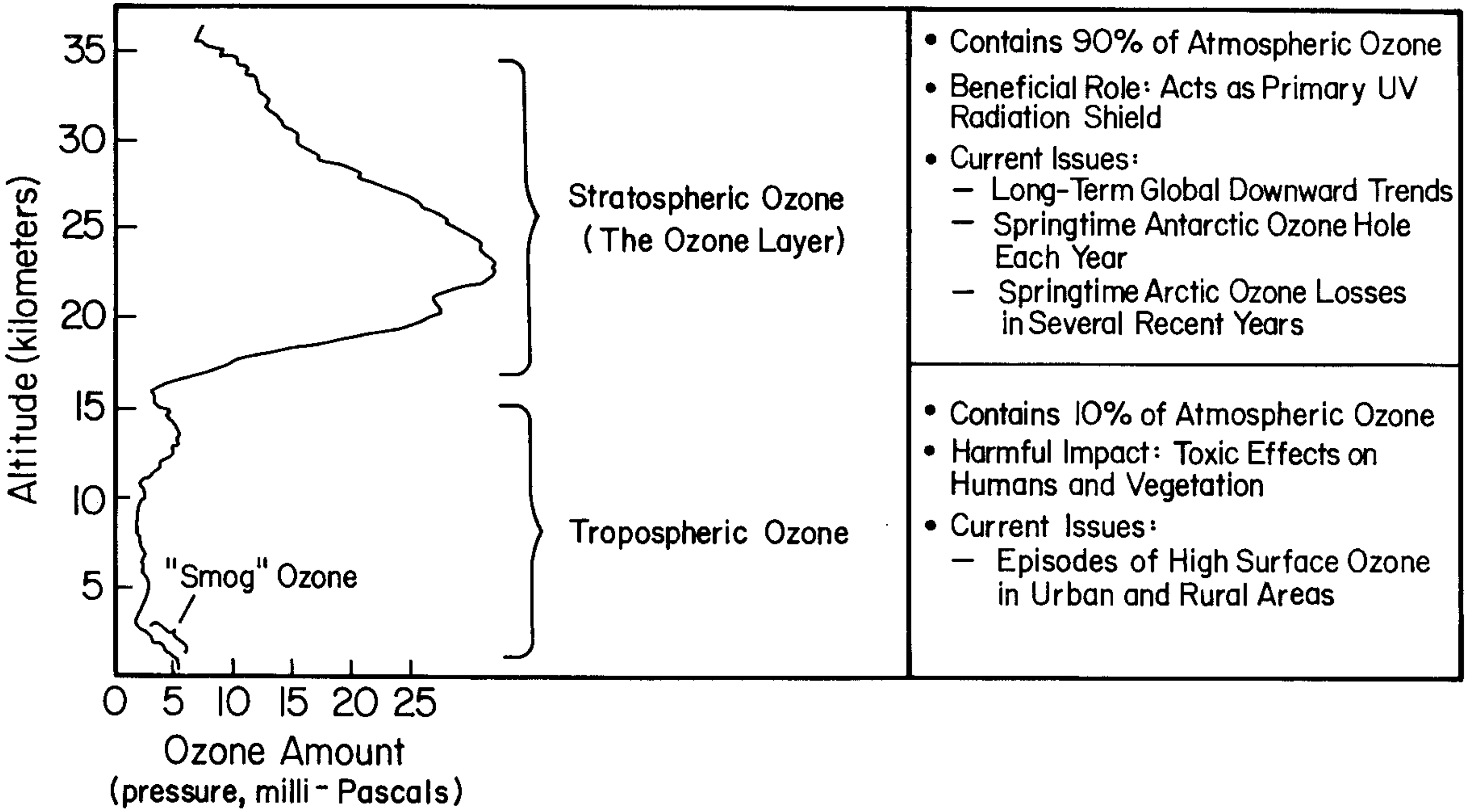
$$O + O_2 + M \rightarrow O_3 + M$$

$$O_3 + h\nu \rightarrow O + O_2 \qquad \lambda \sim 310\,nm$$

$$O + O_3 \rightarrow O_2 + O_2$$

This reaction scheme transforms "odd" oxygen O and O_3 in O_2 but allows a layer of O_3 to be formed at about 30 km, i.e. in the stratosphere.

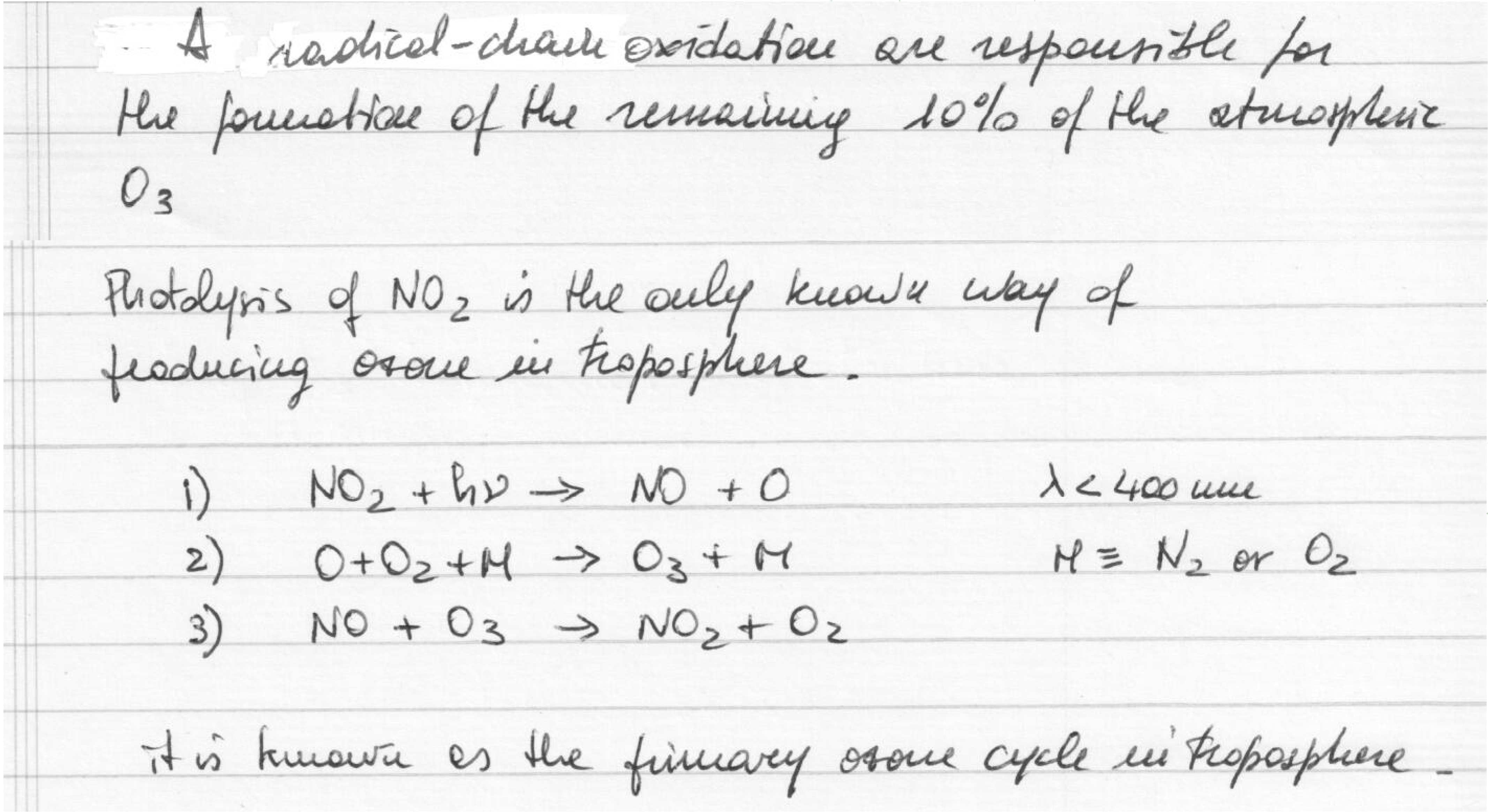
Ozone in the atmosphere



- Contains 90% of Atmospheric Ozone
- Beneficial Role: Acts as Primary UV Radiation Shield
- Current Issues:
  - Long-Term Global Downward Trends
  - Springtime Antarctic Ozone Hole Each Year
  - Springtime Arctic Ozone Losses in Several Recent Years

- Contains 10% of Atmospheric Ozone
- Harmful Impact: Toxic Effects on Humans and Vegetation
- Current Issues:
  - Episodes of High Surface Ozone in Urban and Rural Areas

Ozone in the atmosphere



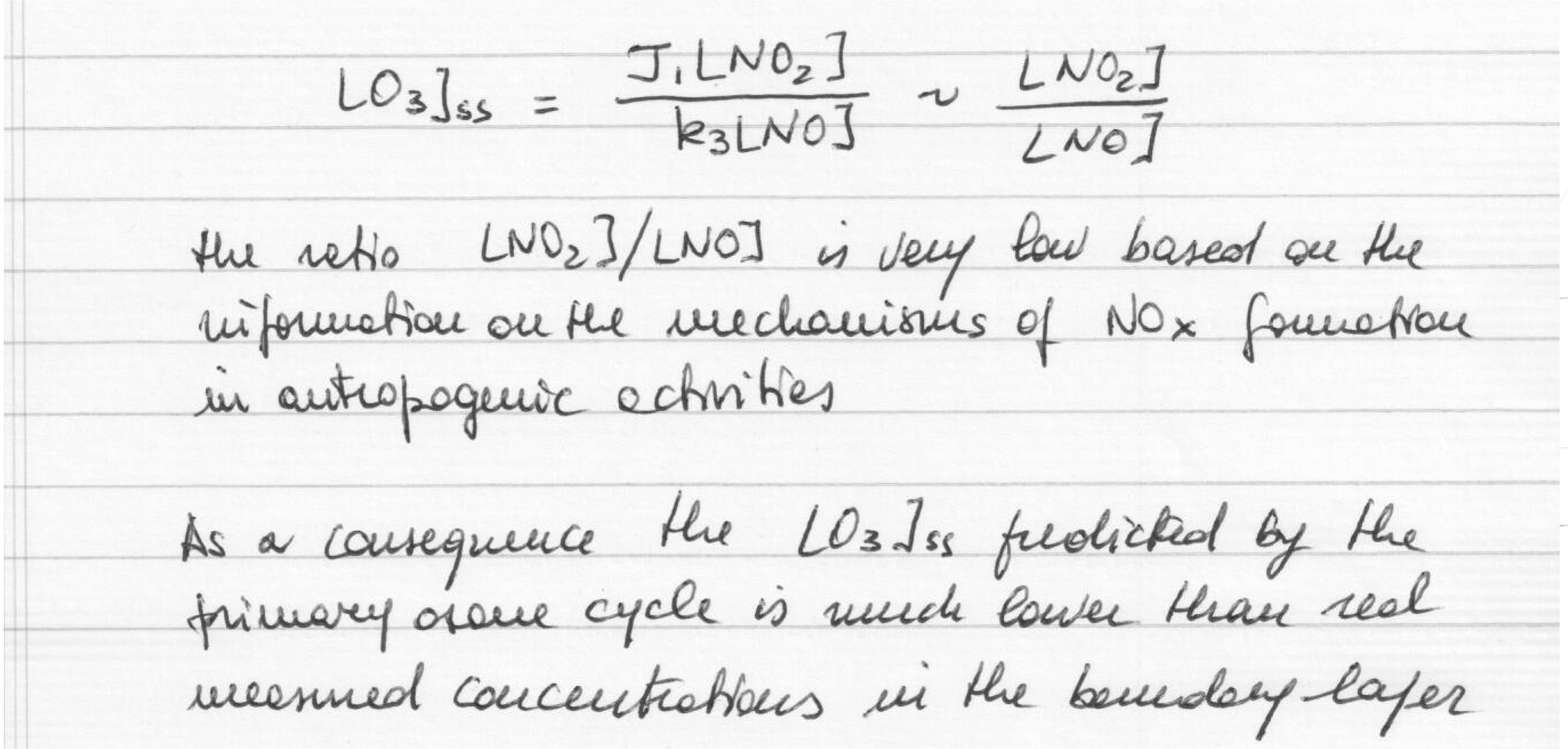
A radical-chain oxidation are responsible for the formation of the remaining 10% of the atmospheric O_3

Photolysis of NO_2 is the only known way of producing ozone in troposphere.

1) $NO_2 + h\nu \rightarrow NO + O$ $\lambda < 400$ nm
2) $O + O_2 + M \rightarrow O_3 + M$ $M \equiv N_2$ or O_2
3) $NO + O_3 \rightarrow NO_2 + O_2$

It is known as the primary ozone cycle in troposphere.

Ozone in the atmosphere

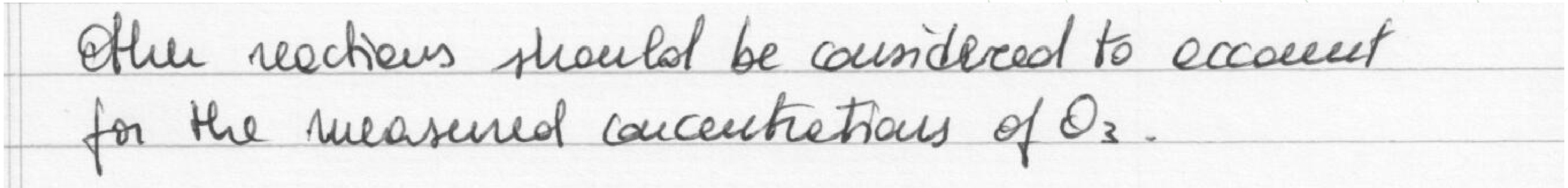


$$[O_3]_{ss} = \frac{J_1[NO_2]}{k_3[NO]} \sim \frac{[NO_2]}{[NO]}$$

the ratio $[NO_2]/[NO]$ is very low based on the information on the mechanisms of NO_x formation in antropogenic activities

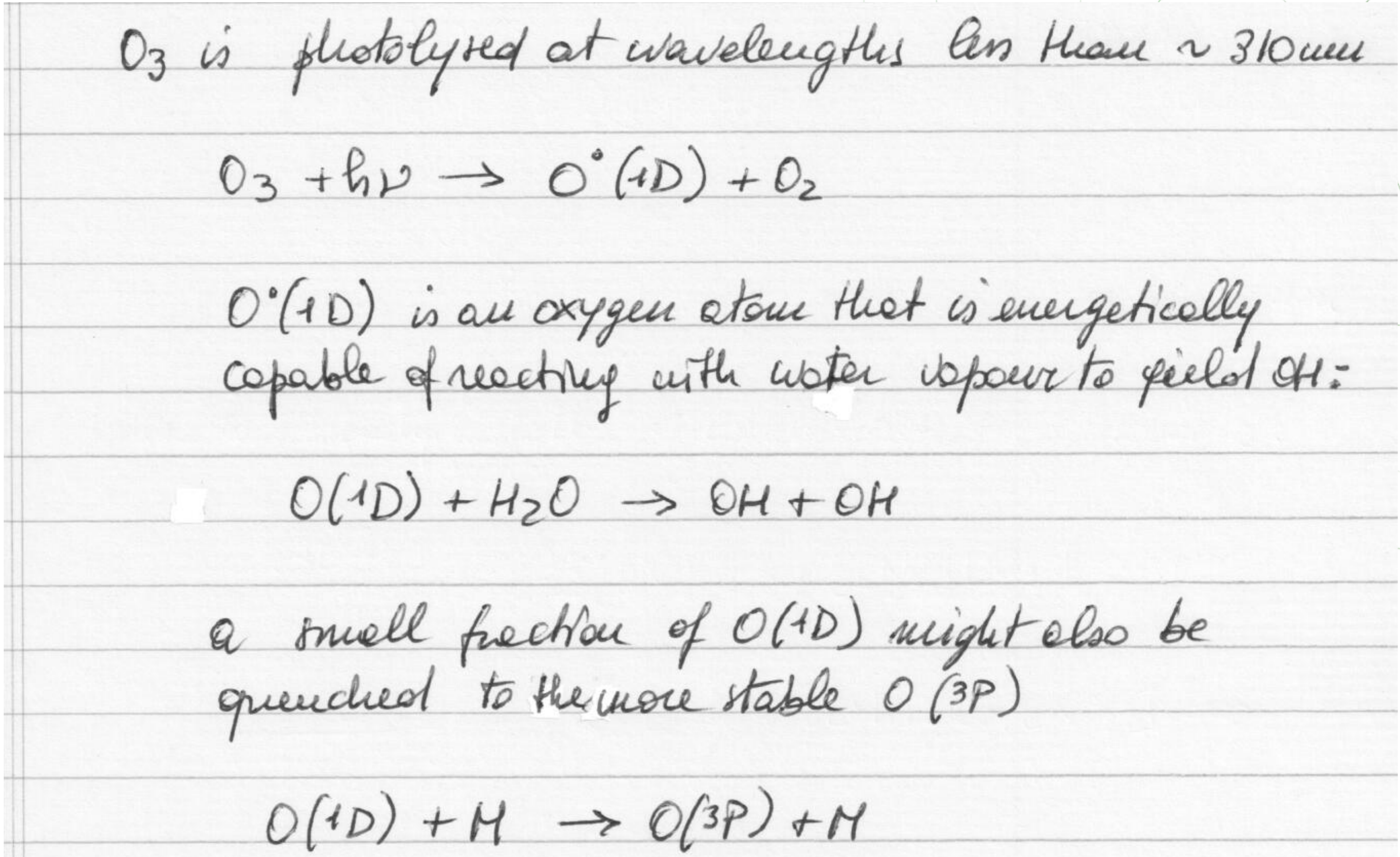
As a consequence the $[O_3]_{ss}$ predicted by the primary ozone cycle is much lower than real measured concentrations in the boundary layer

Ozone in the atmosphere



Other reactions should be considered to account for the measured concentrations of O_3.

Ozone in the atmosphere



O_3 is photolysed at wavelengths less than ~ 310nm

$$O_3 + h\nu \rightarrow O^{\circ}(^1D) + O_2$$

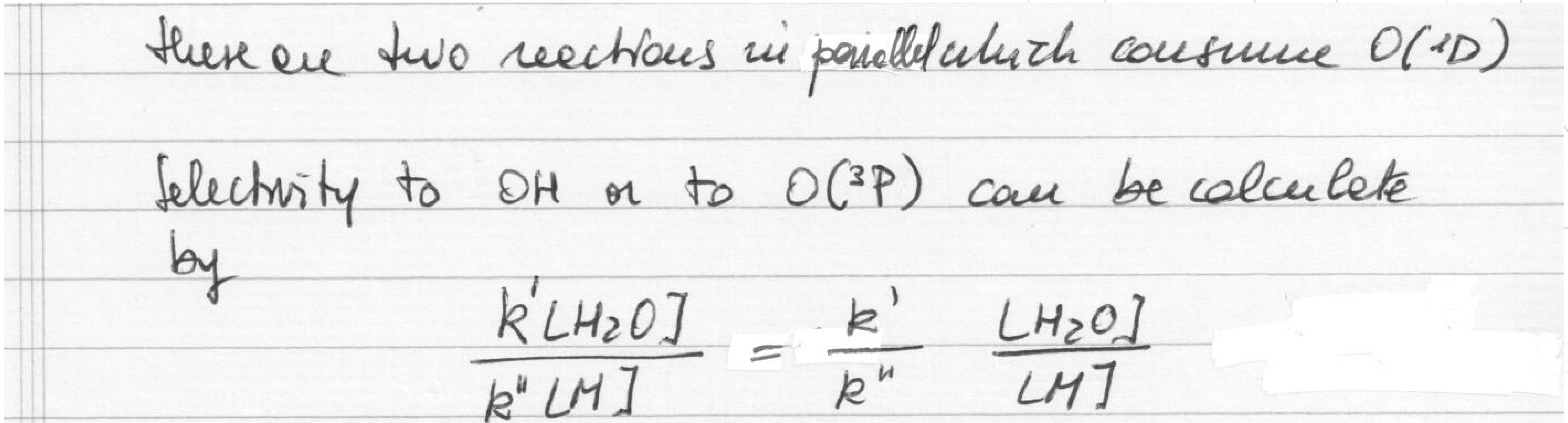
$O^{\circ}(^1D)$ is an oxygen atom that is energetically capable of reacting with water vapour to yield OH:

$$O(^1D) + H_2O \rightarrow OH + OH$$

a small fraction of $O(^1D)$ might also be quenched to the more stable $O(^3P)$

$$O(^1D) + M \rightarrow O(^3P) + M$$

Ozone in the atmosphere

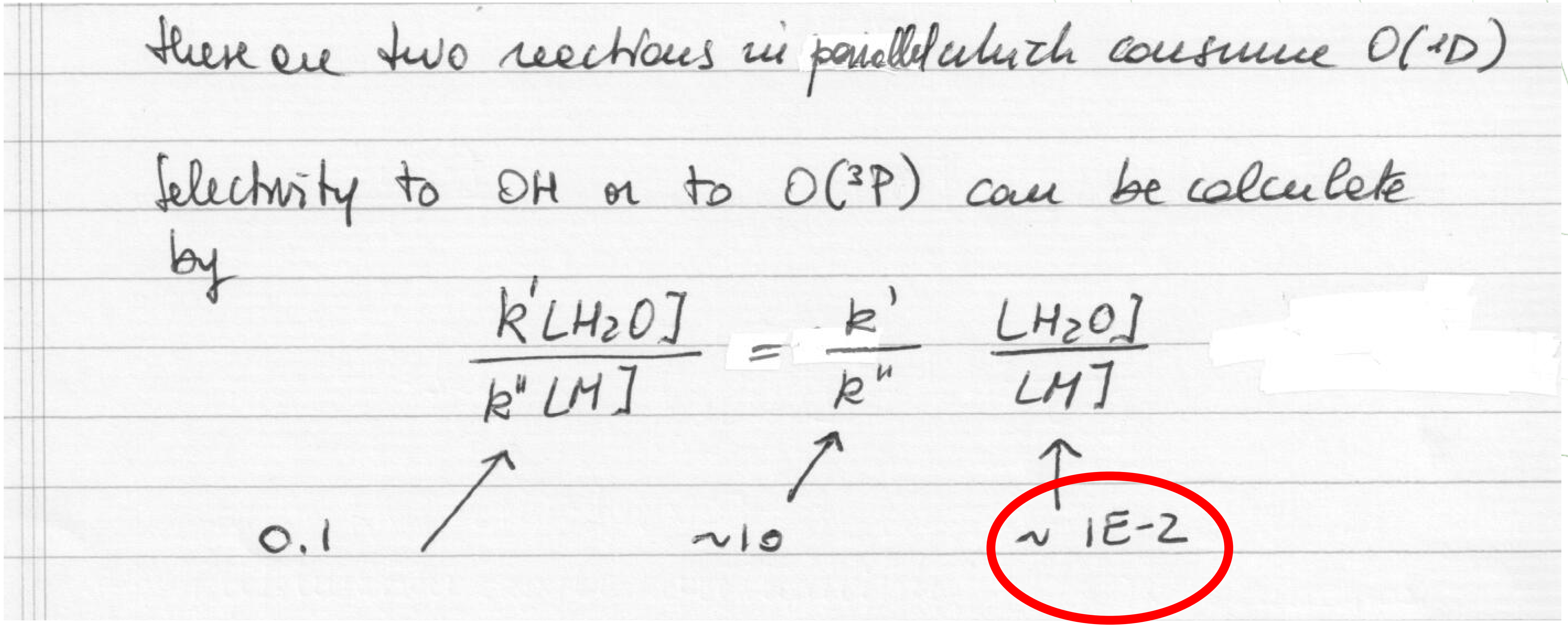


there are two reactions in parallel which consume $O(^1D)$

Selectivity to OH or to $O(^3P)$ can be calculate by

$$\frac{k'[H_2O]}{k''[M]} = \frac{k'}{k''} \frac{[H_2O]}{[M]}$$

Ozone in the atmosphere



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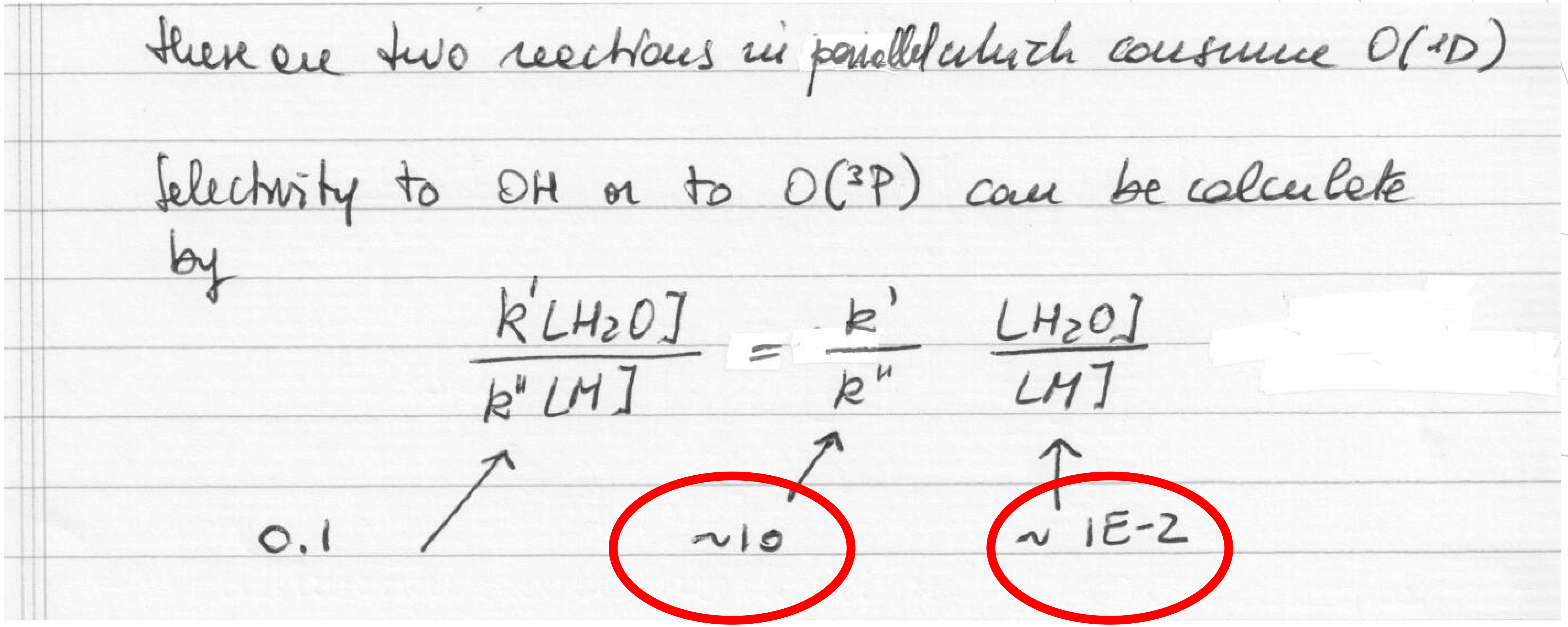
0.1 ↗ ~10 ↗ ↑ ~ 1E-2

Ozone in the atmosphere



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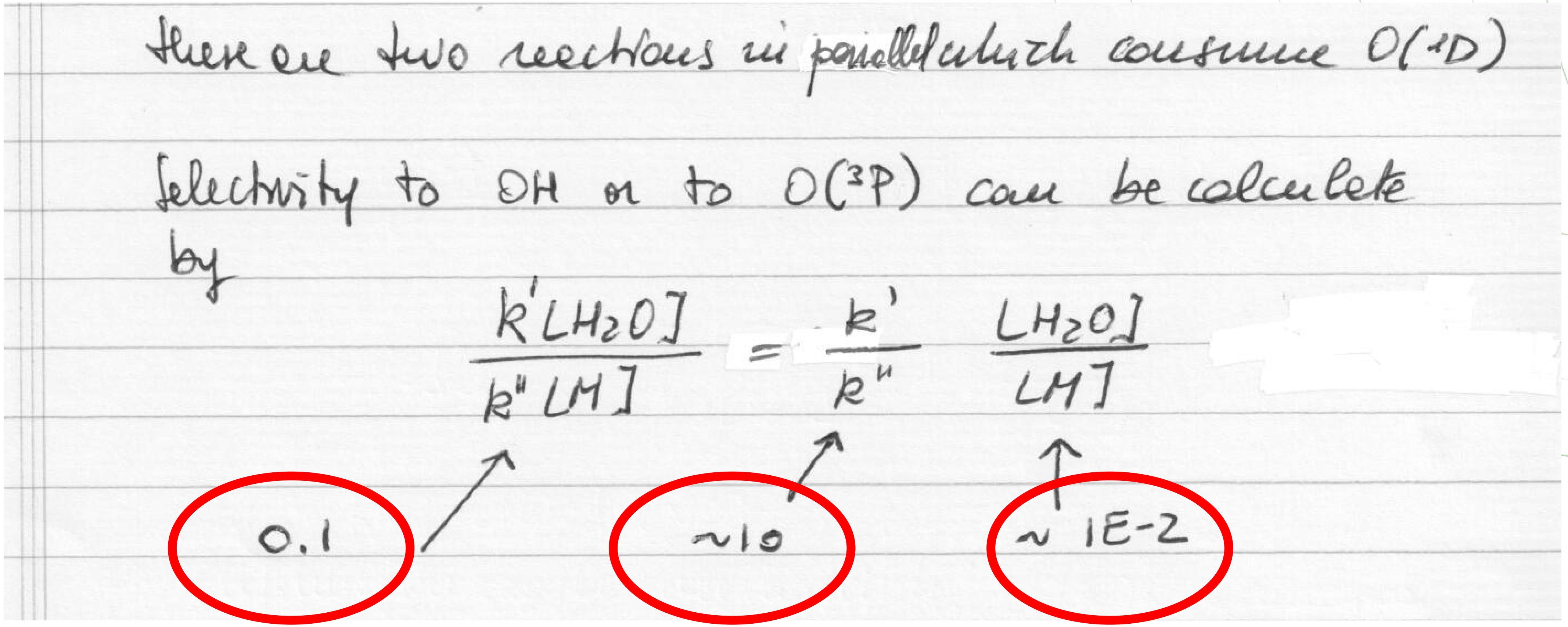
Ozone in the atmosphere



there are two reactions in parallel which consume $O(^1D)$

Selectivity to OH or to $O(^3P)$ can be calculate by

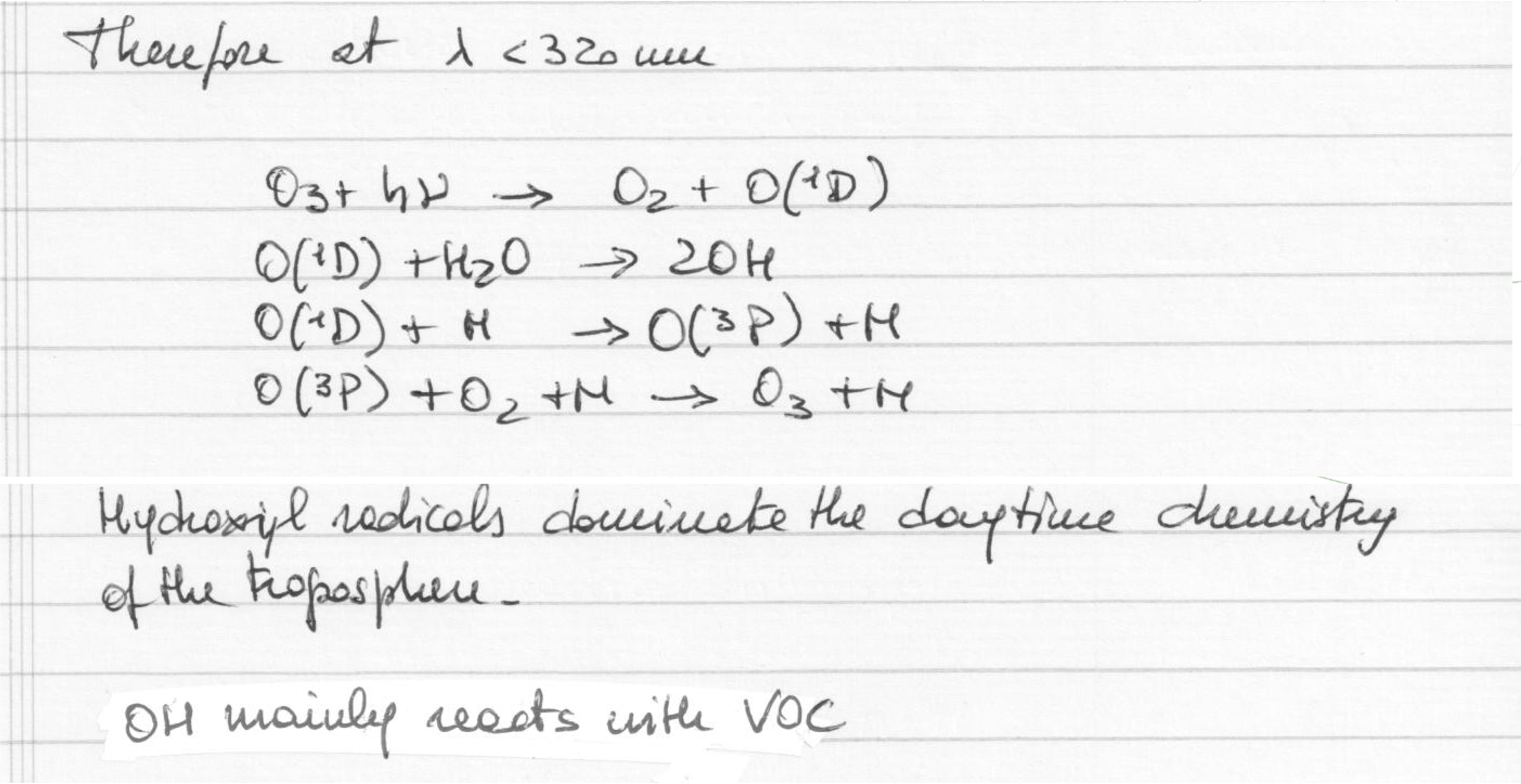
$$\frac{k'[H_2O]}{k''[M]} = \frac{k'}{k''} \frac{[H_2O]}{[M]}$$

0.1

~10

~ 1E-2

Ozone in the atmosphere



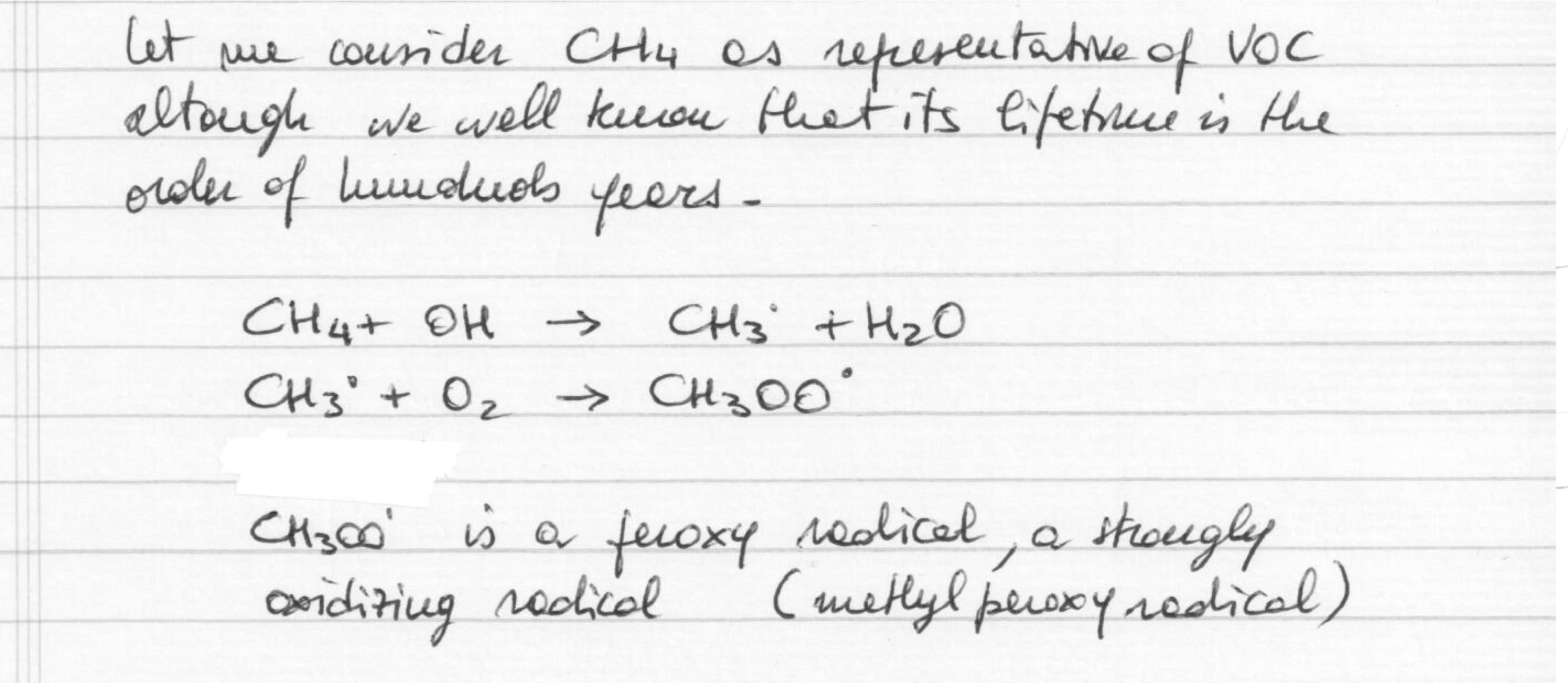
Therefore at $\lambda < 320$ nm

$$O_3 + h\nu \rightarrow O_2 + O(^1D)$$
$$O(^1D) + H_2O \rightarrow 2OH$$
$$O(^1D) + M \rightarrow O(^3P) + M$$
$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

Hydroxyl radicals dominate the daytime chemistry of the troposphere.

OH mainly reacts with VOC

Ozone in the atmosphere



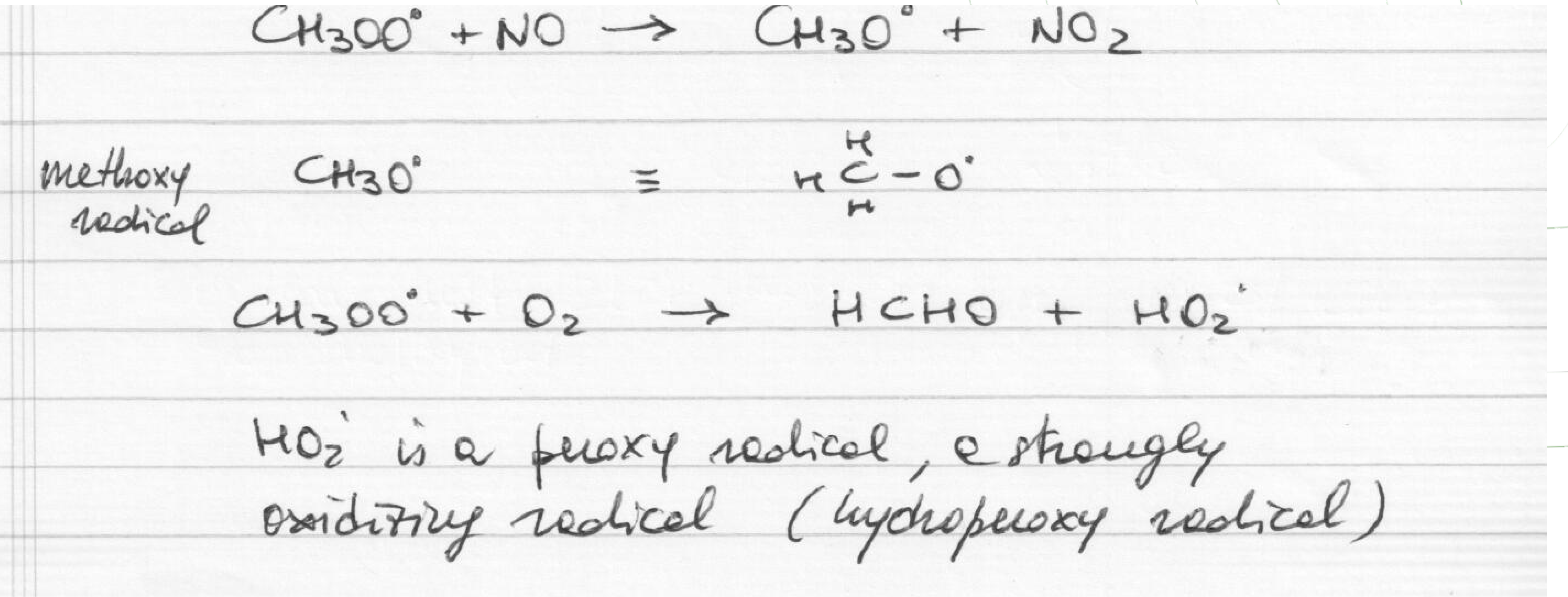
Let me consider CH_4 as representative of VOC altough we well know that its lifetime is the order of hundreds years.

$$CH_4 + OH \rightarrow CH_3^{\circ} + H_2O$$

$$CH_3^{\circ} + O_2 \rightarrow CH_3OO^{\circ}$$

CH_3OO° is a peroxy radical, a strongly oxidizing radical (methyl peroxy radical)

Ozone in the atmosphere



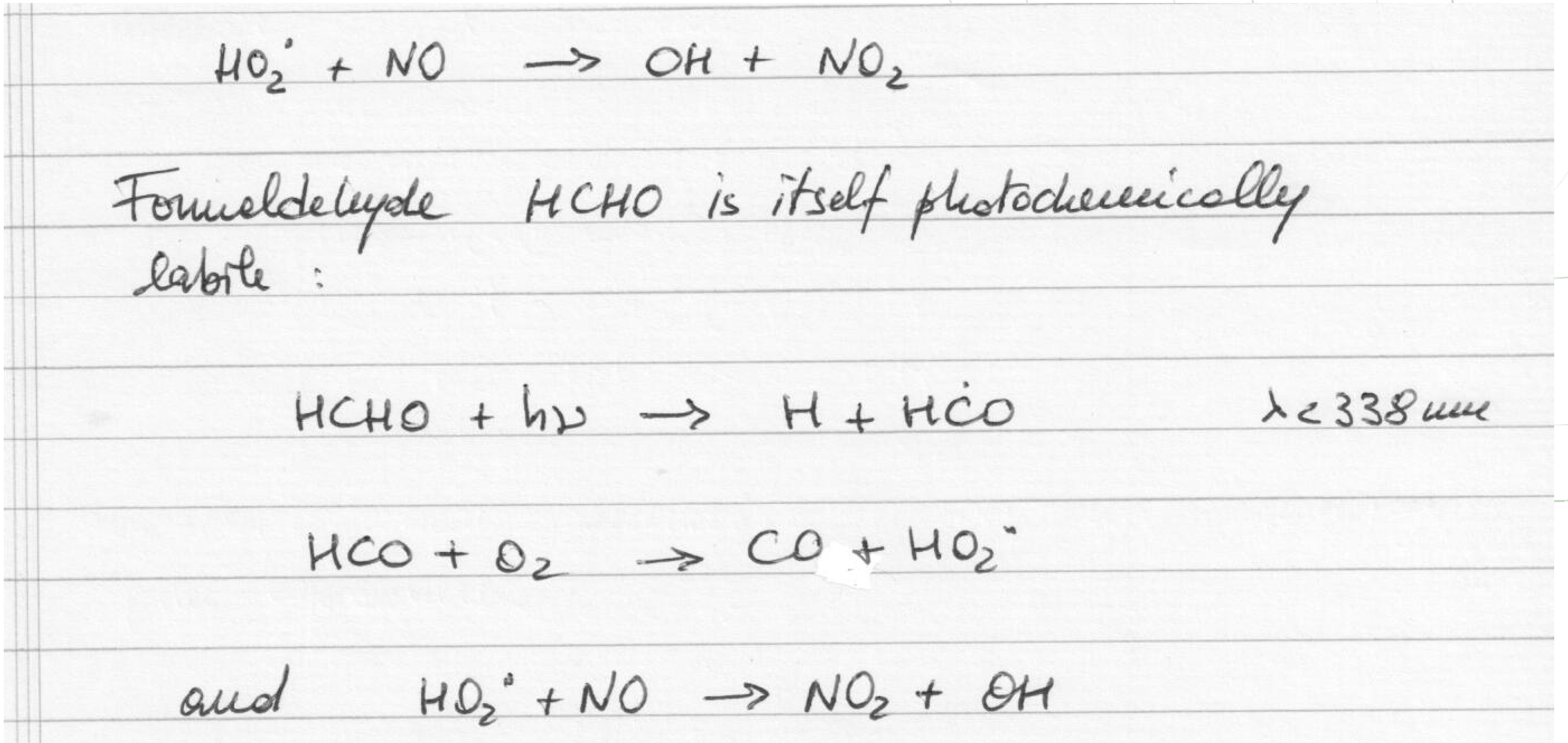
$CH_3OO^\circ + NO \rightarrow CH_3O^\circ + NO_2$

methoxy radical $CH_3O^\circ \equiv H-\overset{H}{\underset{H}{C}}-O^\circ$

$CH_3OO^\circ + O_2 \rightarrow HCHO + HO_2^\circ$

HO_2° is a peroxy radical, a strongly oxidizing radical (hydroperoxy radical)

Ozone in the atmosphere



$$HO_2^{\cdot} + NO \rightarrow OH + NO_2$$

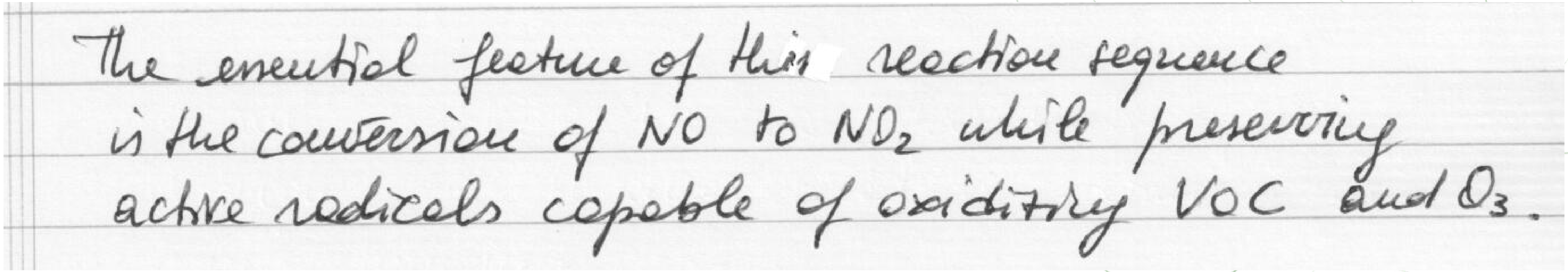
Formaldehyde HCHO is itself photochemically labile :

$$HCHO + h\nu \rightarrow H + H\dot{C}O \qquad \lambda < 338\,nm$$

$$HCO + O_2 \rightarrow CO + HO_2^{\cdot}$$

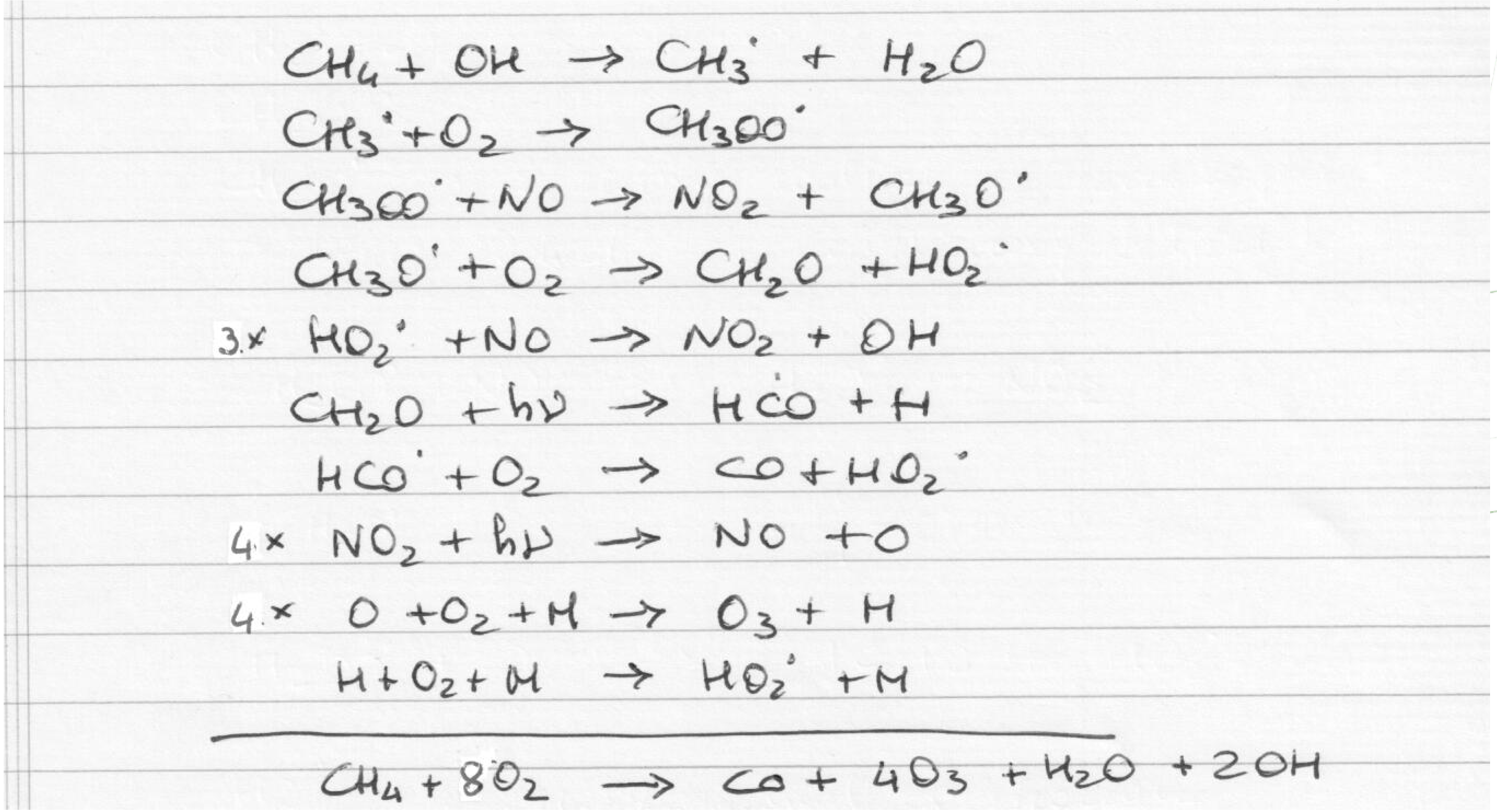
and $HO_2^{\cdot} + NO \rightarrow NO_2 + OH$

Ozone in the atmosphere



The essential feature of this reaction sequence is the conversion of NO to NO_2 while preserving active radicals capable of oxidizing VOC and O_3.

Ozone in the atmosphere



$$CH_4 + OH \rightarrow CH_3^{\cdot} + H_2O$$

$$CH_3^{\cdot} + O_2 \rightarrow CH_3OO^{\cdot}$$

$$CH_3OO^{\cdot} + NO \rightarrow NO_2 + CH_3O^{\cdot}$$

$$CH_3O^{\cdot} + O_2 \rightarrow CH_2O + HO_2^{\cdot}$$

$$3\times \quad HO_2^{\cdot} + NO \rightarrow NO_2 + OH$$

$$CH_2O + h\nu \rightarrow H\dot{C}O + H$$

$$HCO^{\cdot} + O_2 \rightarrow CO + HO_2^{\cdot}$$

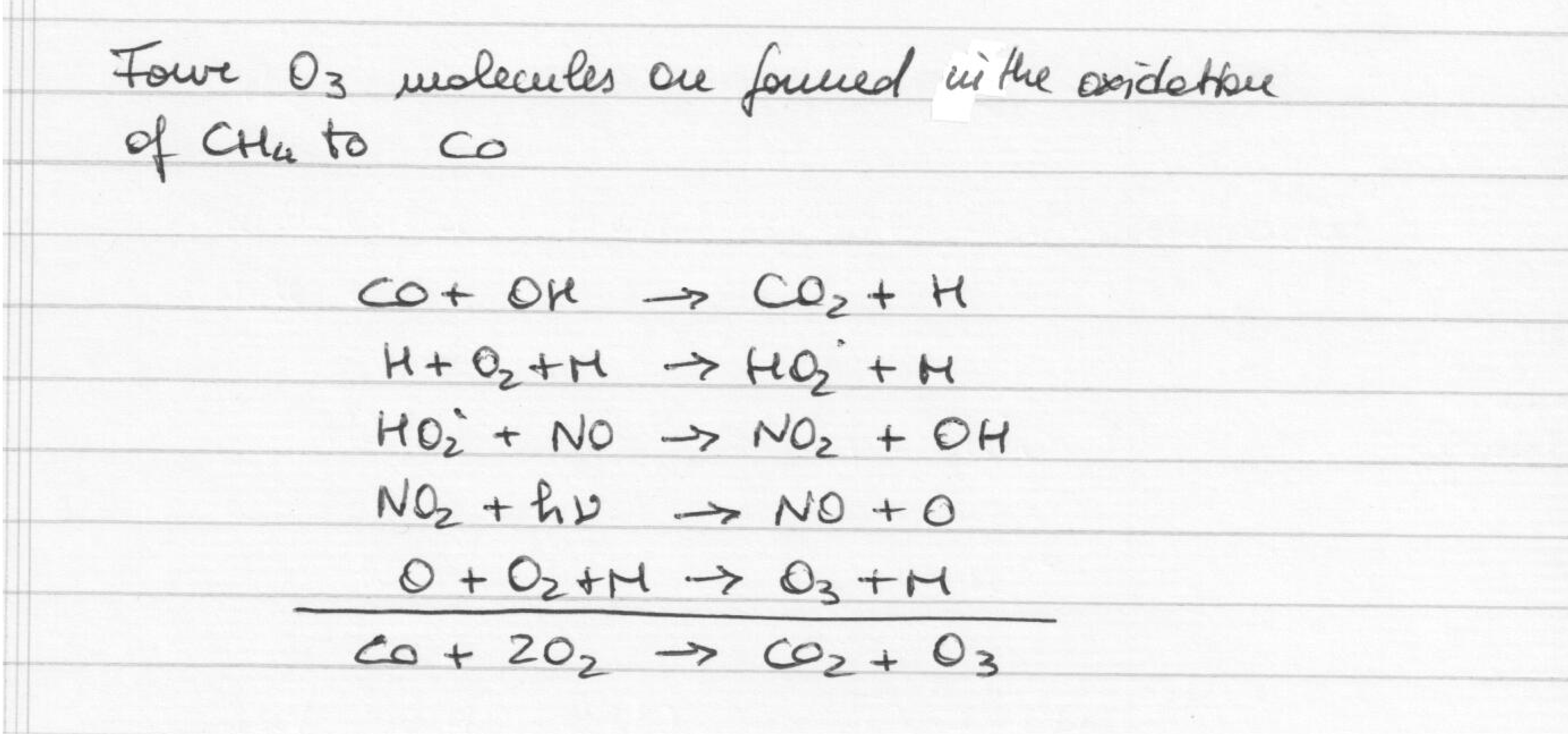
$$4\times \quad NO_2 + h\nu \rightarrow NO + O$$

$$4\times \quad O + O_2 + M \rightarrow O_3 + H$$

$$H + O_2 + M \rightarrow HO_2^{\cdot} + M$$

$$CH_4 + 8O_2 \rightarrow CO + 4O_3 + H_2O + 2OH$$

Ozone in the atmosphere



Four O_3 molecules are formed in the oxidation of CH_4 to CO

$$CO + OH \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2^{\cdot} + M$$

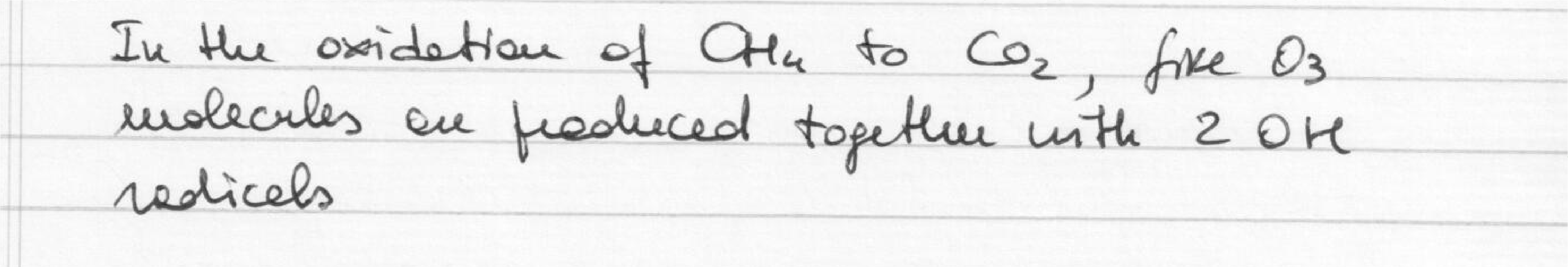
$$HO_2^{\cdot} + NO \rightarrow NO_2 + OH$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

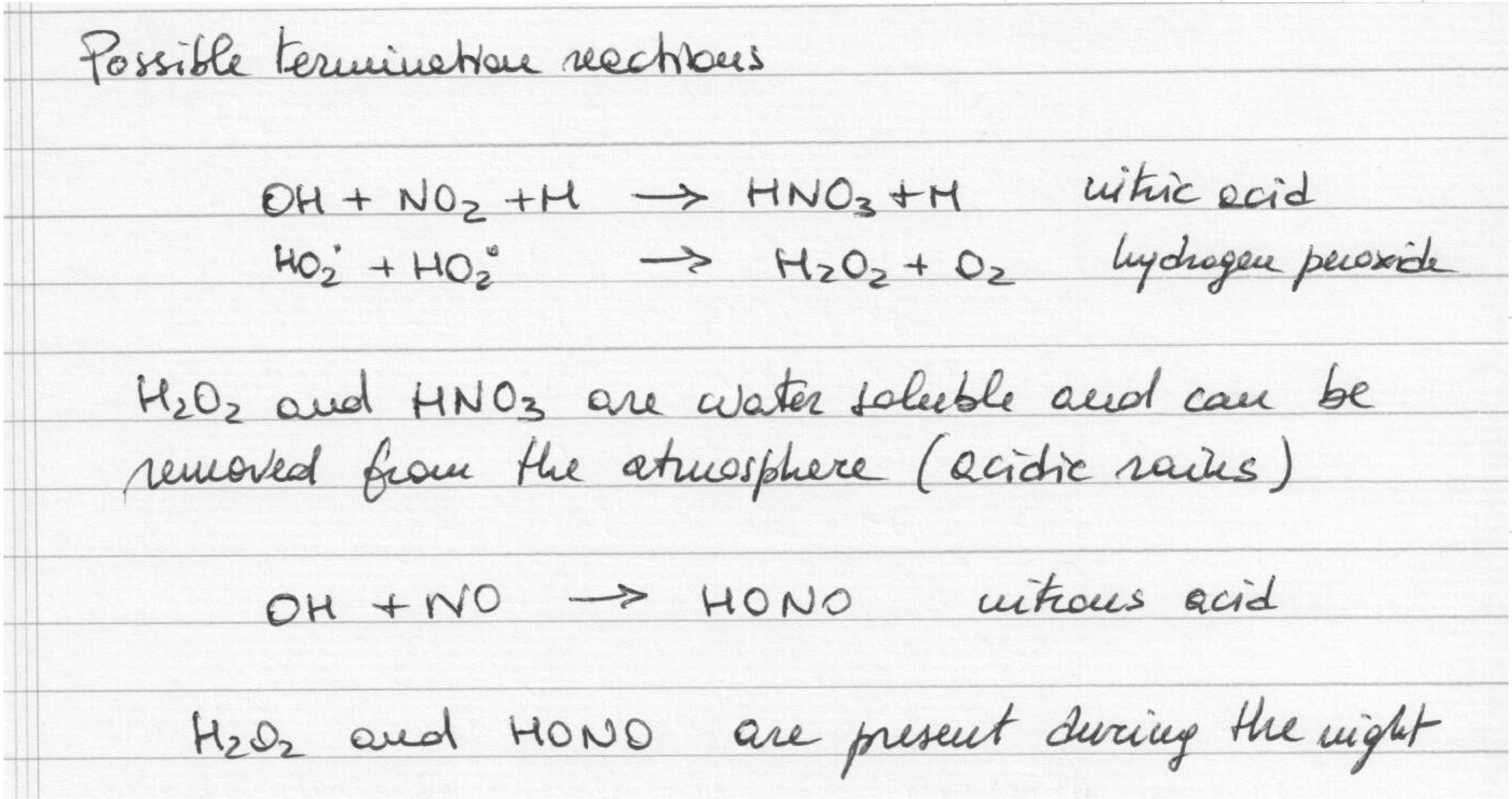
$$CO + 2O_2 \rightarrow CO_2 + O_3$$

Ozone in the atmosphere



In the oxidation of CH_4 to CO_2, five O_3 molecules are produced together with 2 OH radicals

Ozone in the atmosphere



Possible termination reactions

$OH + NO_2 + M \rightarrow HNO_3 + M$ nitric acid

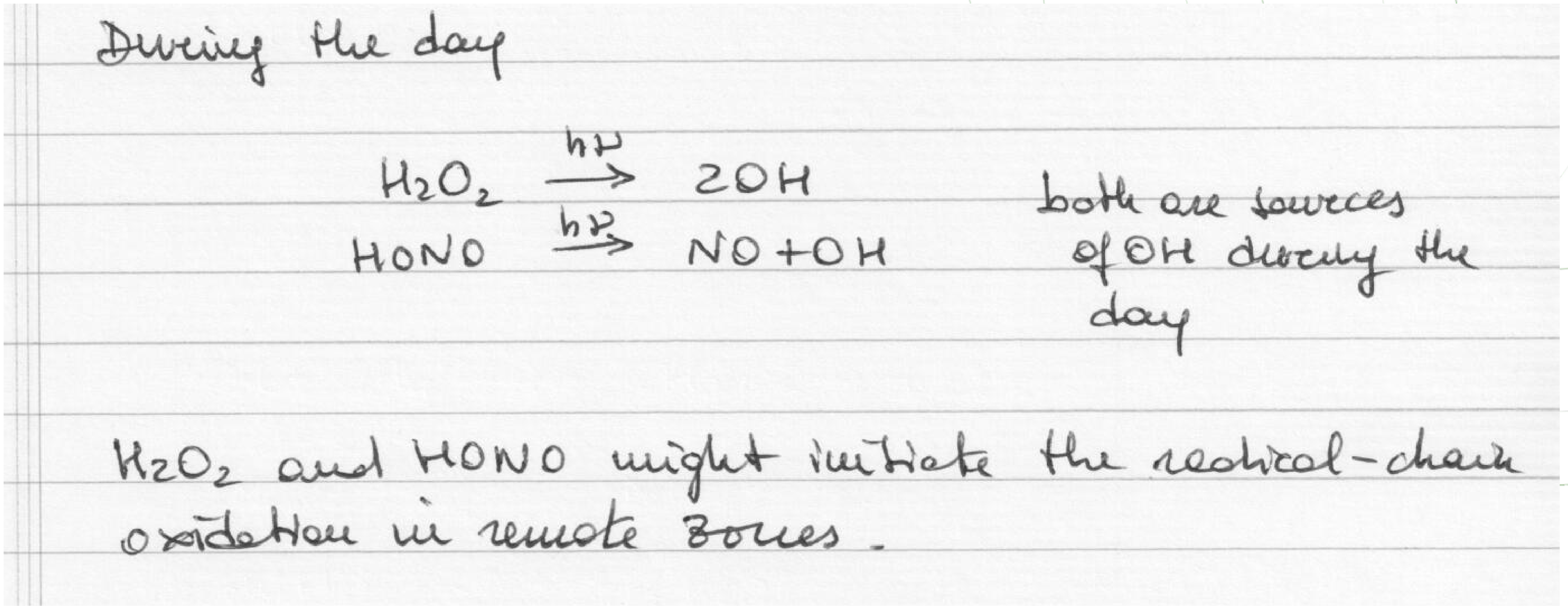
$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$ hydrogen peroxide

H_2O_2 and HNO_3 are water soluble and can be removed from the atmosphere (acidic rains)

$OH + NO \rightarrow HONO$ nitrous acid

H_2O_2 and HONO are present during the night

Ozone in the atmosphere



During the day

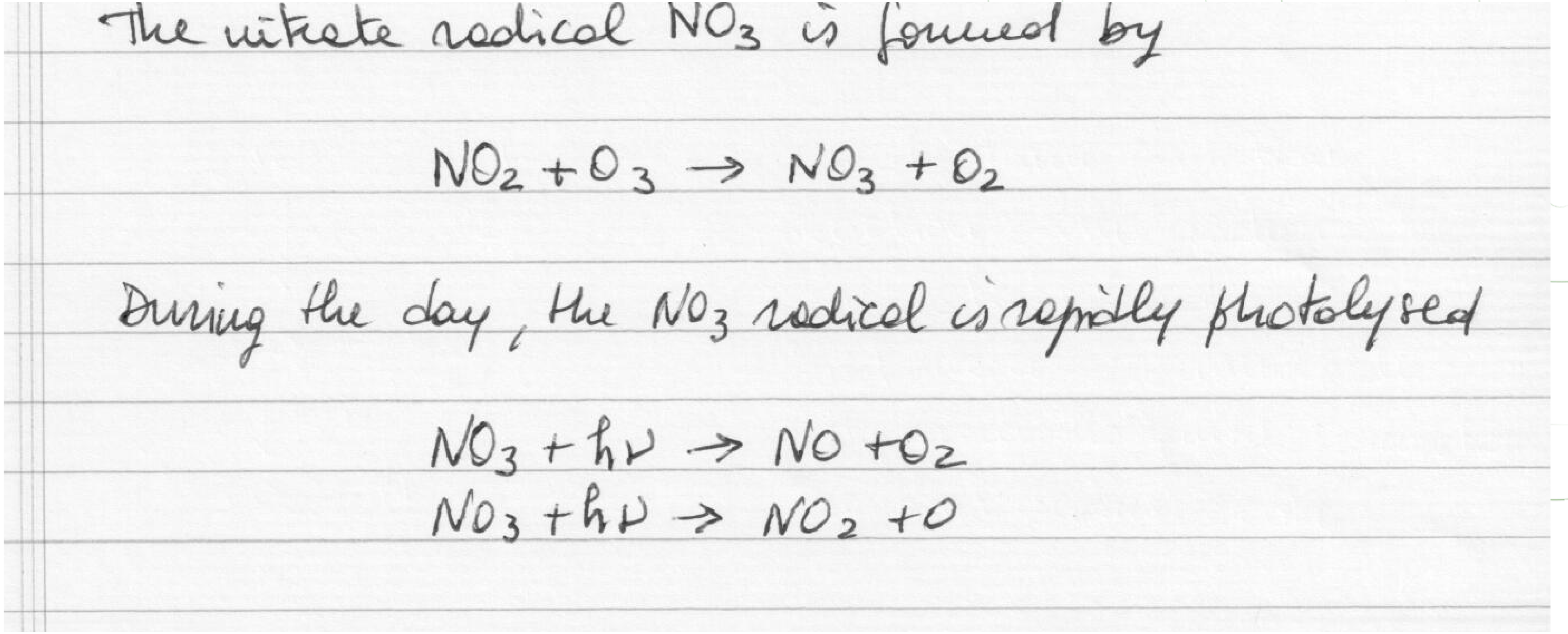
$$H_2O_2 \xrightarrow{h\nu} 2OH$$

$$HONO \xrightarrow{h\nu} NO + OH$$

both are sources of OH during the day

H_2O_2 and HONO might initiate the radical-chain oxidation in remote zones.

Ozone in the atmosphere



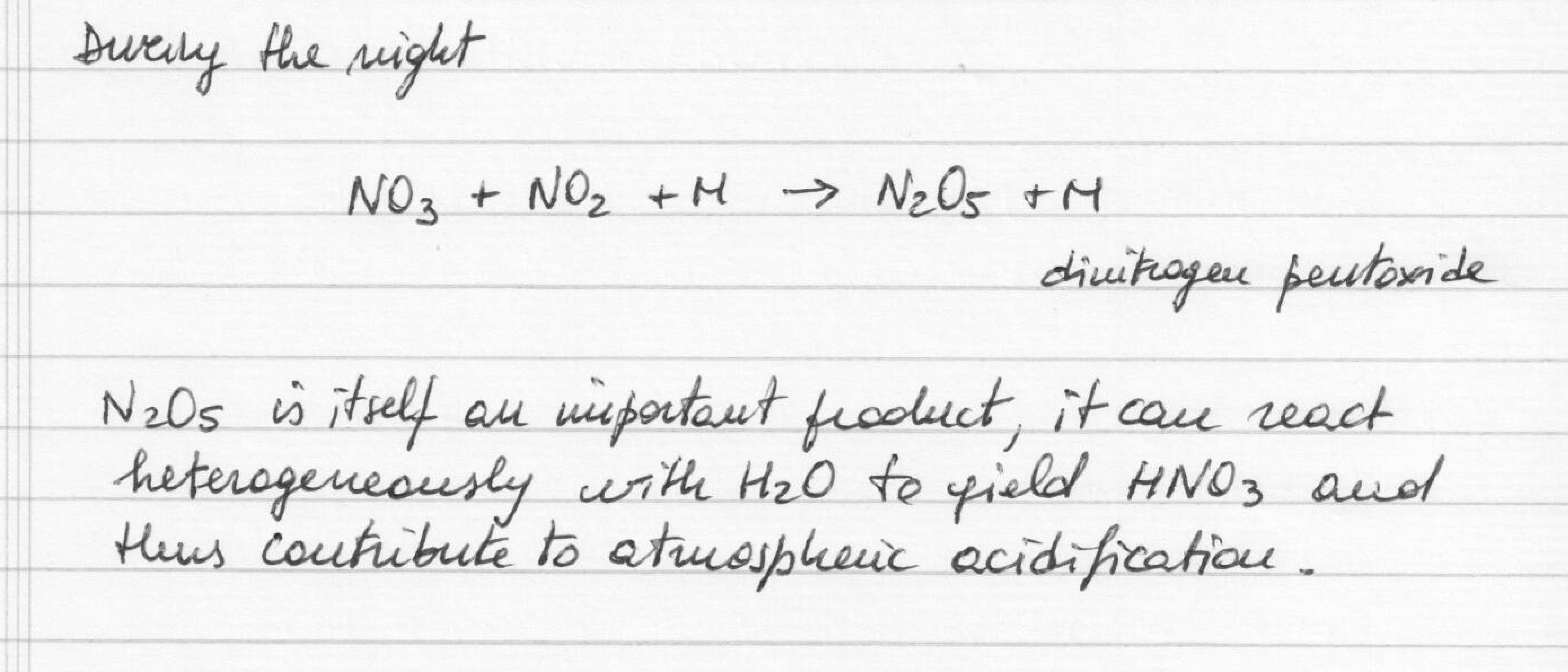
The nitrate radical NO_3 is formed by

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

During the day, the NO_3 radical is rapidly photolysed

$$NO_3 + h\nu \rightarrow NO + O_2$$
$$NO_3 + h\nu \rightarrow NO_2 + O$$

Ozone in the atmosphere



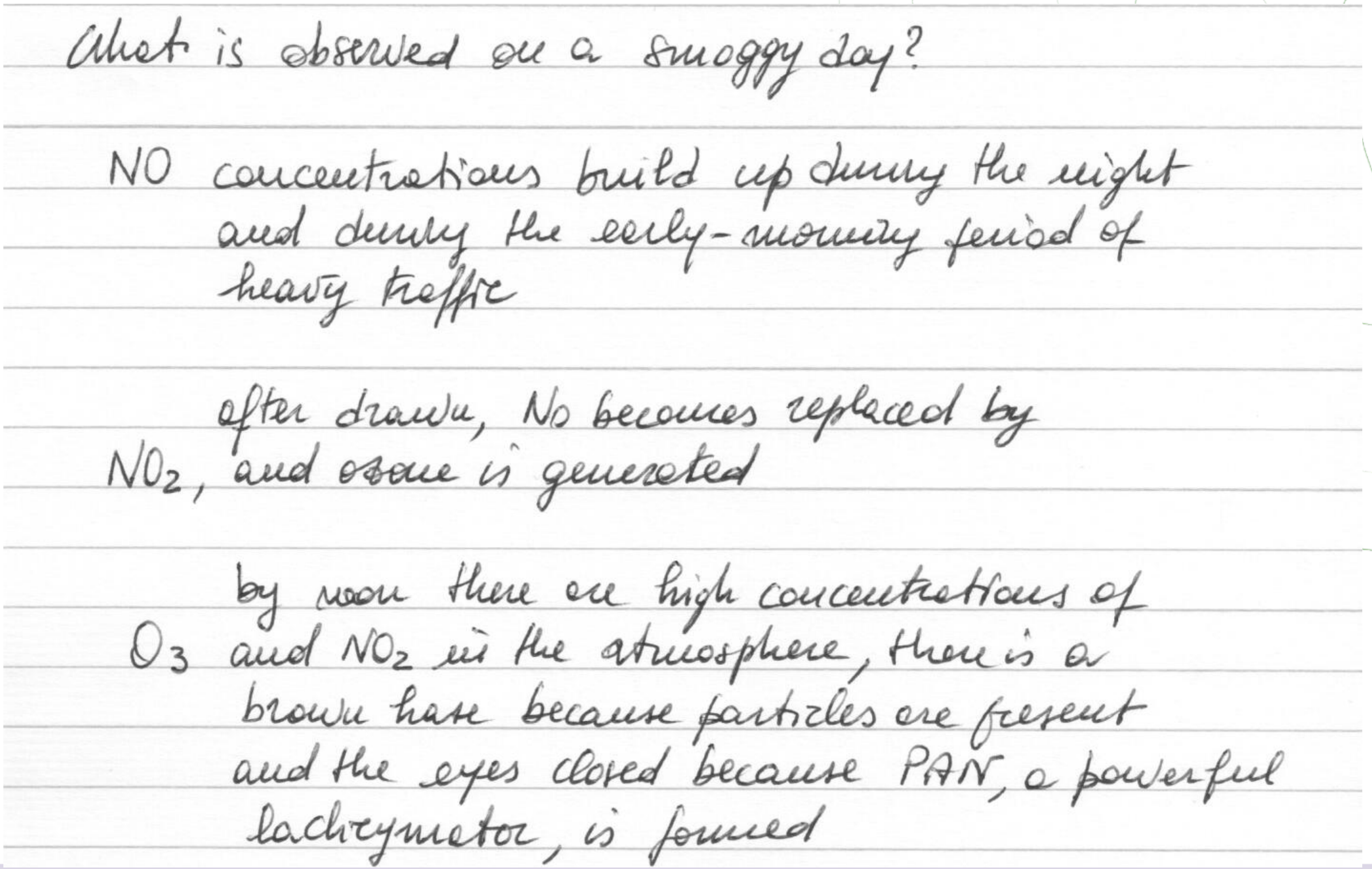
During the night

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$$

dinitrogen pentoxide

N_2O_5 is itself an important product, it can react heterogeneously with H_2O to yield HNO_3 and thus contribute to atmospheric acidification.

Ozone in the atmosphere



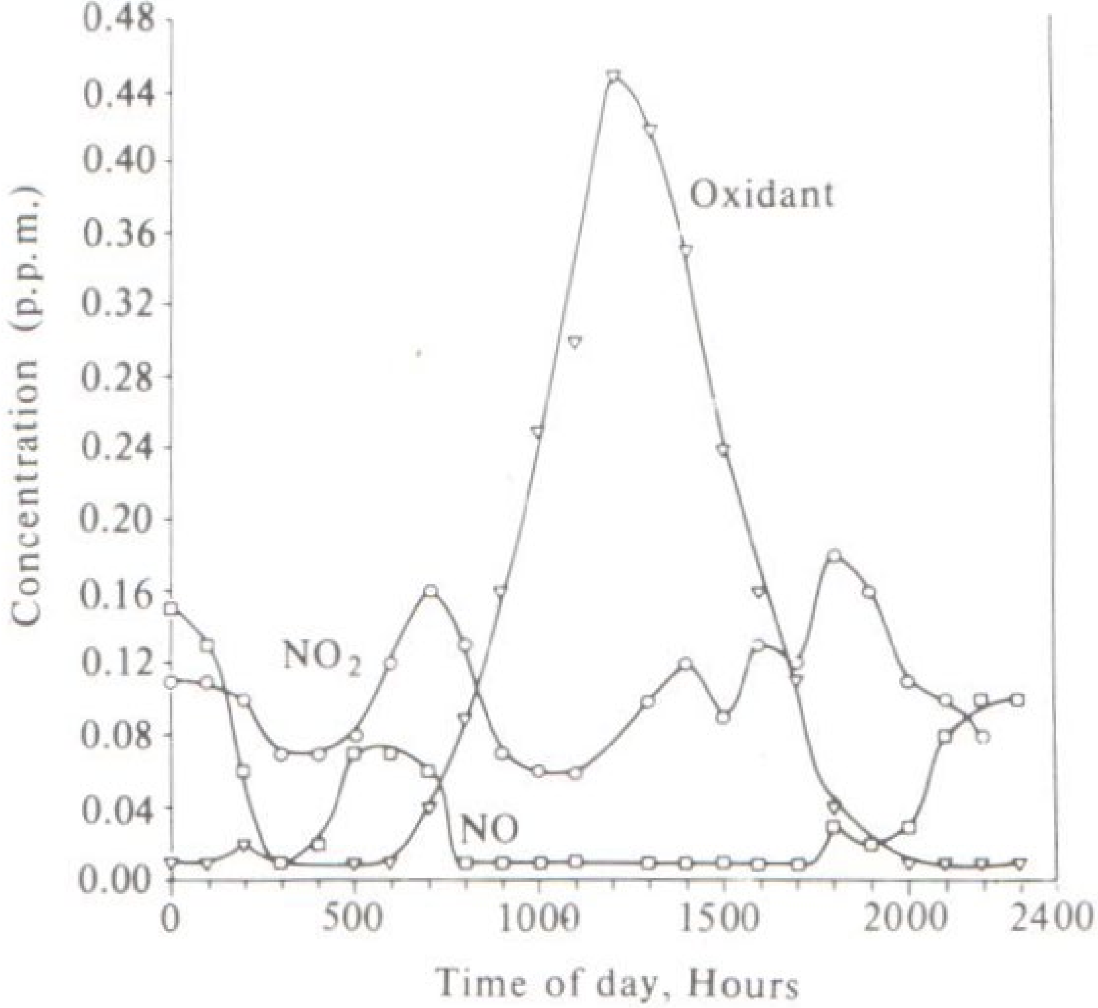
What is observed on a smoggy day?

NO concentrations build up during the night and during the early-morning period of heavy traffic

after drawn, NO becomes replaced by NO_2, and ozone is generated

by noon there are high concentrations of O_3 and NO_2 in the atmosphere, there is a brown haze because particles are present and the eyes closed because PAN, a powerful lachrymator, is formed

Ozone in the atmosphere



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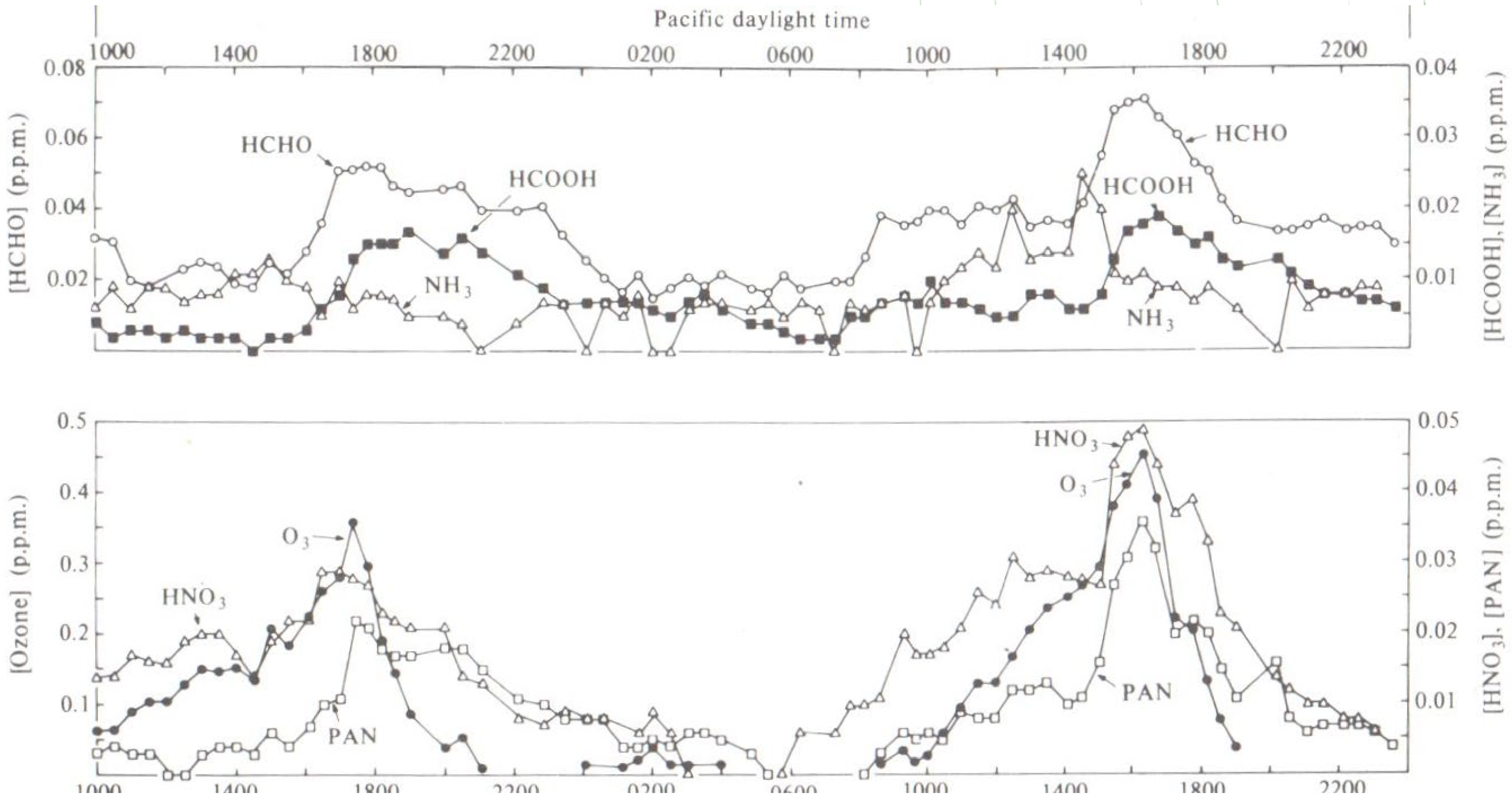

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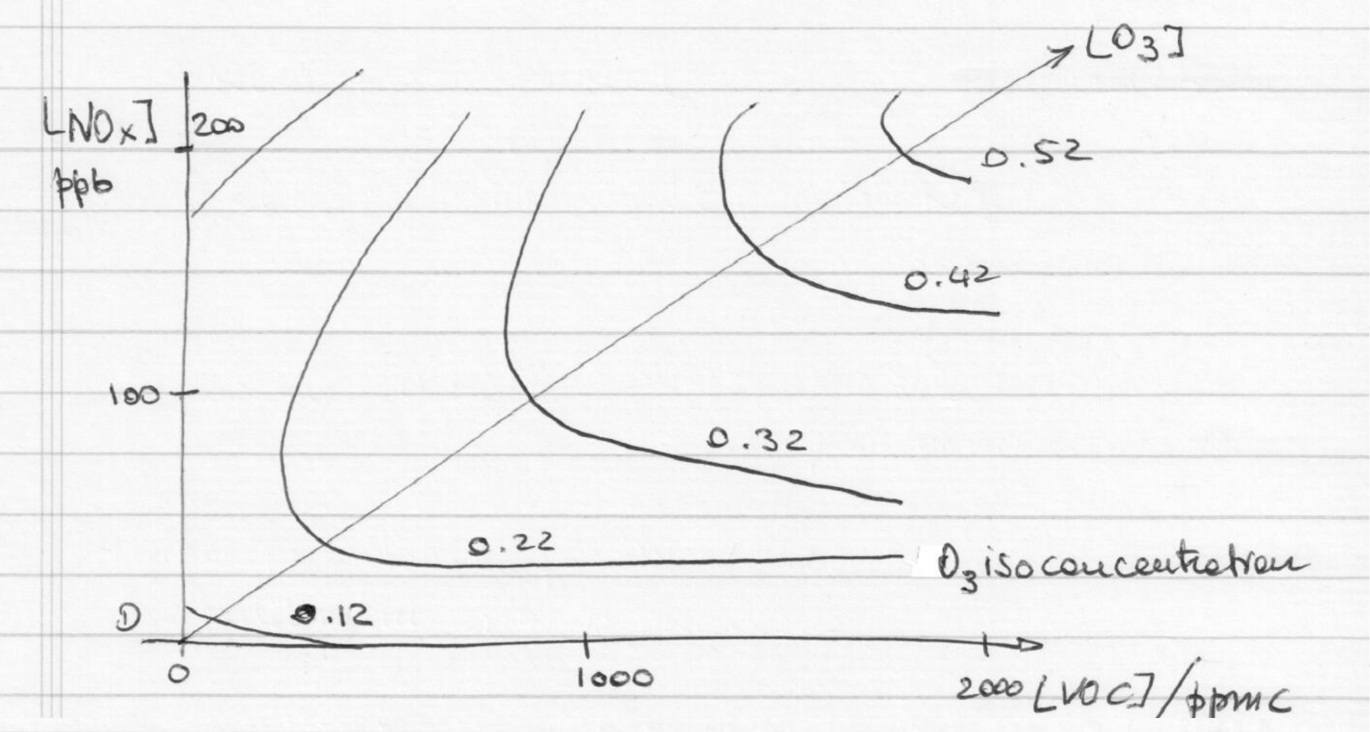
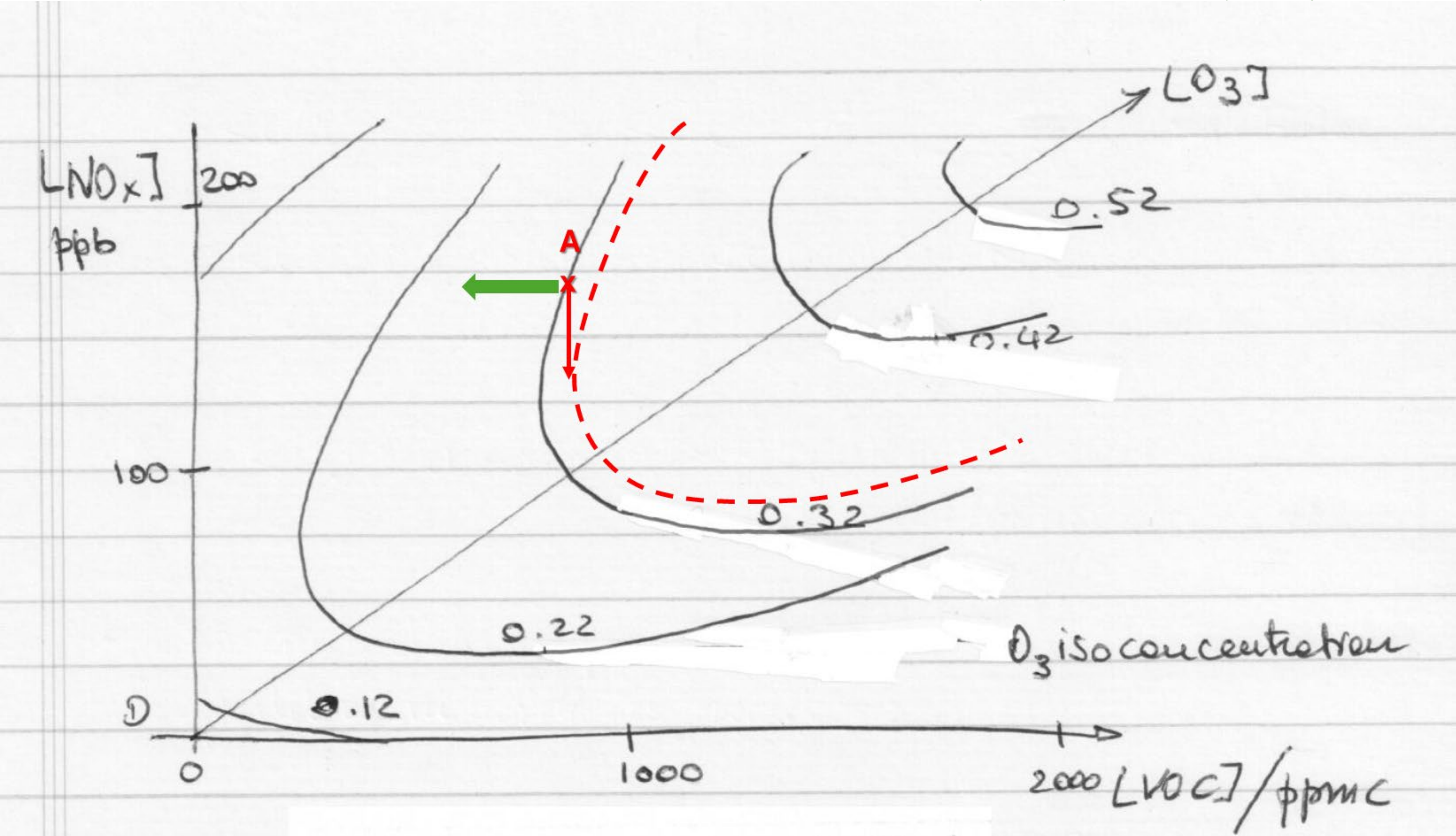


A is VOC - controlled

B is NOx - controlled

C depends on both VOC and NOx

Ozone in the atmosphere



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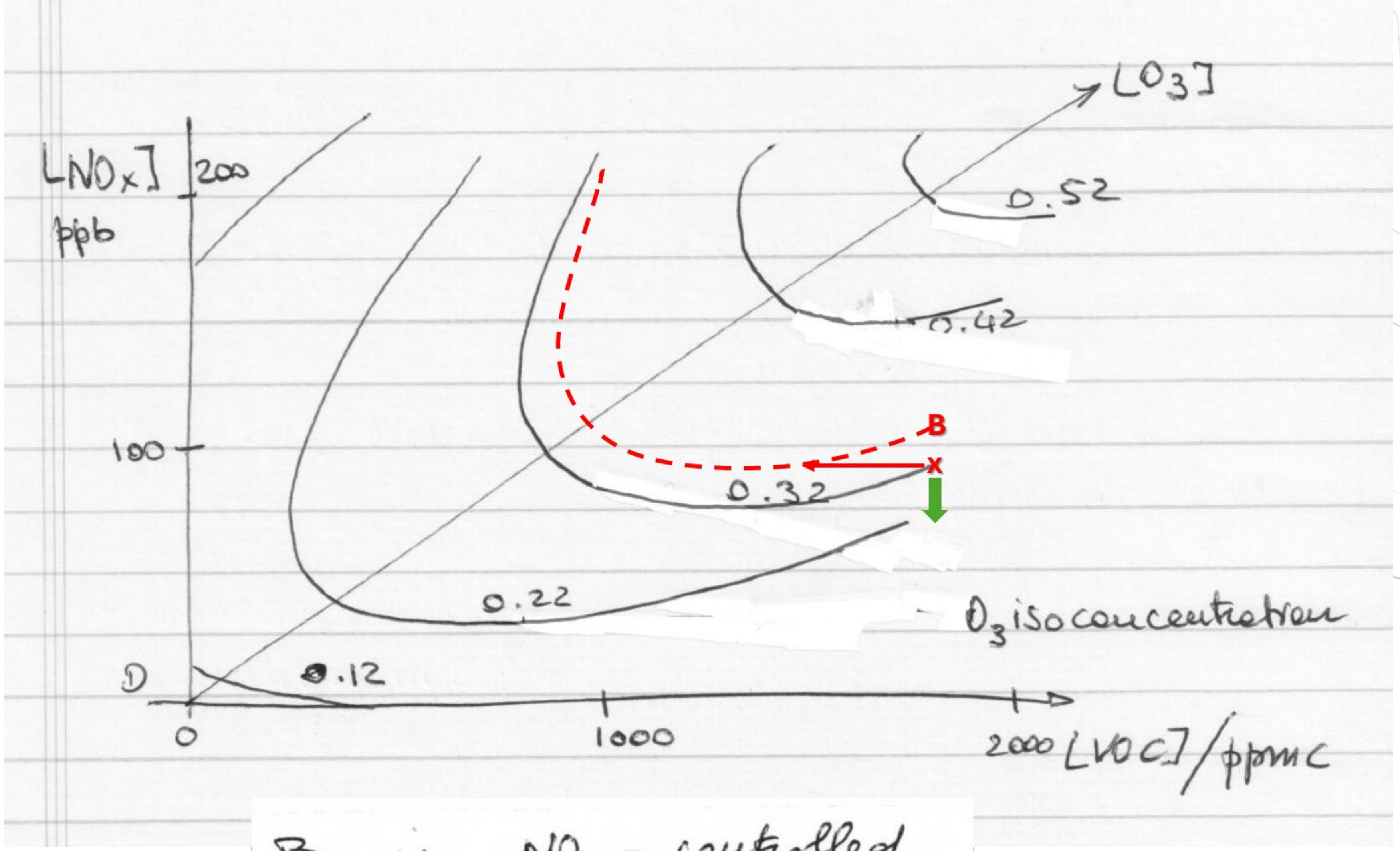
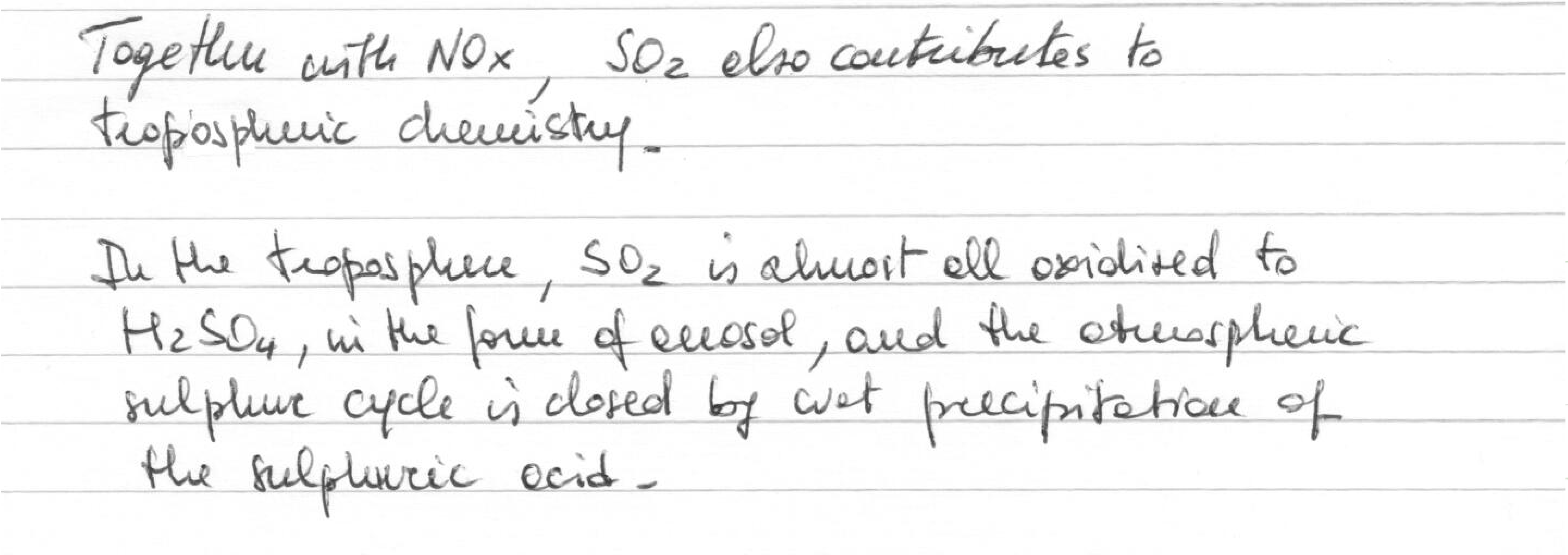
Ozone in the atmosphere



B is NOx - controlled

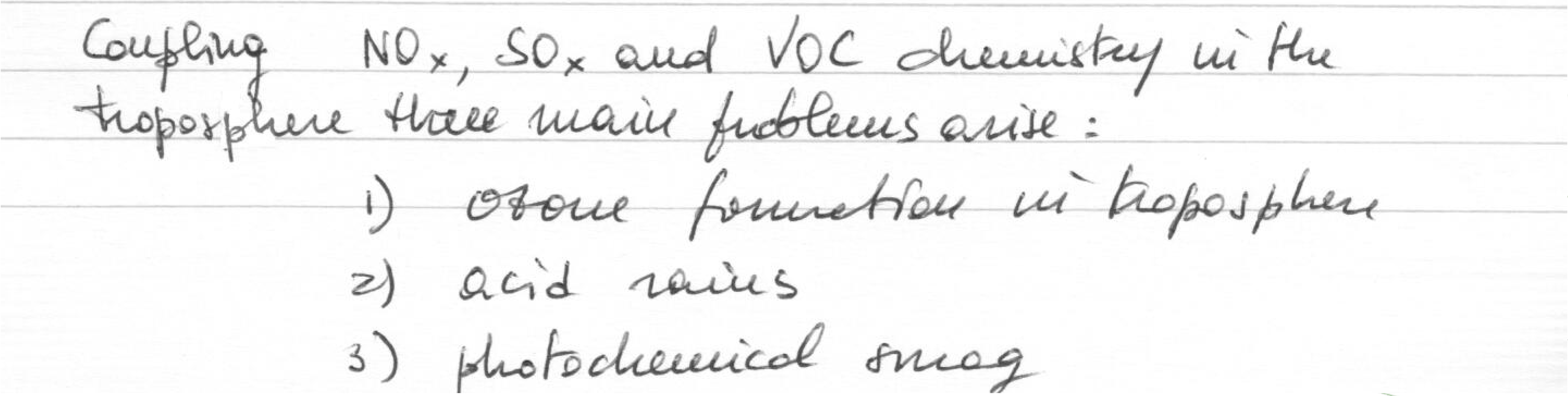
Ozone in the atmosphere



Together with NOx, SO_2 also contributes to tropospheric chemistry.

In the troposphere, SO_2 is almost all oxidized to H_2SO_4, in the form of aerosol, and the atmospheric sulphur cycle is closed by wet precipitation of the sulphuric acid.

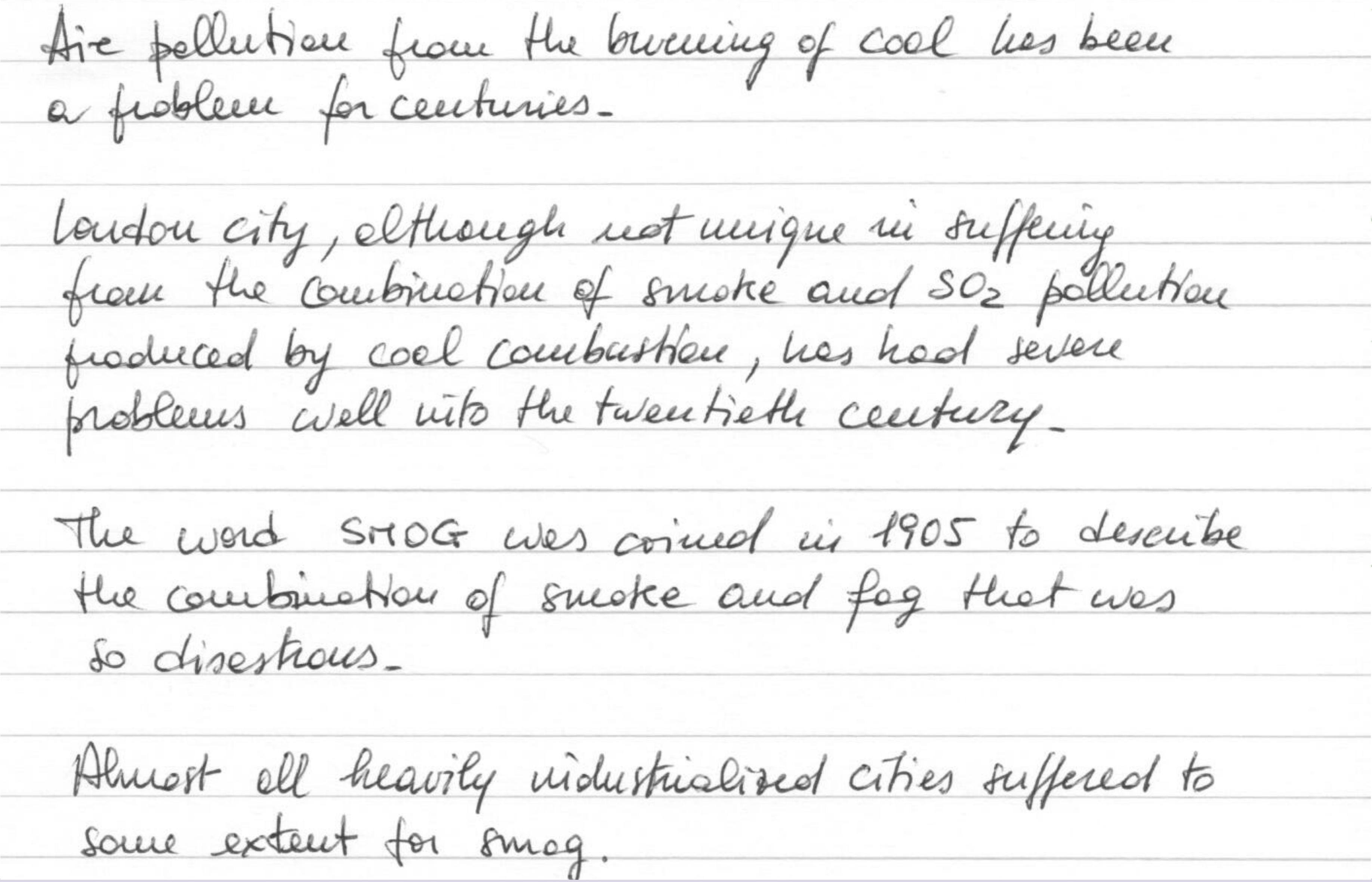
Ozone in the atmosphere



Coupling NO_x, SO_x and VOC chemistry in the troposphere three main problems arise:

1) ozone formation in troposphere
2) acid rains
3) photochemical smog

Ozone in the atmosphere



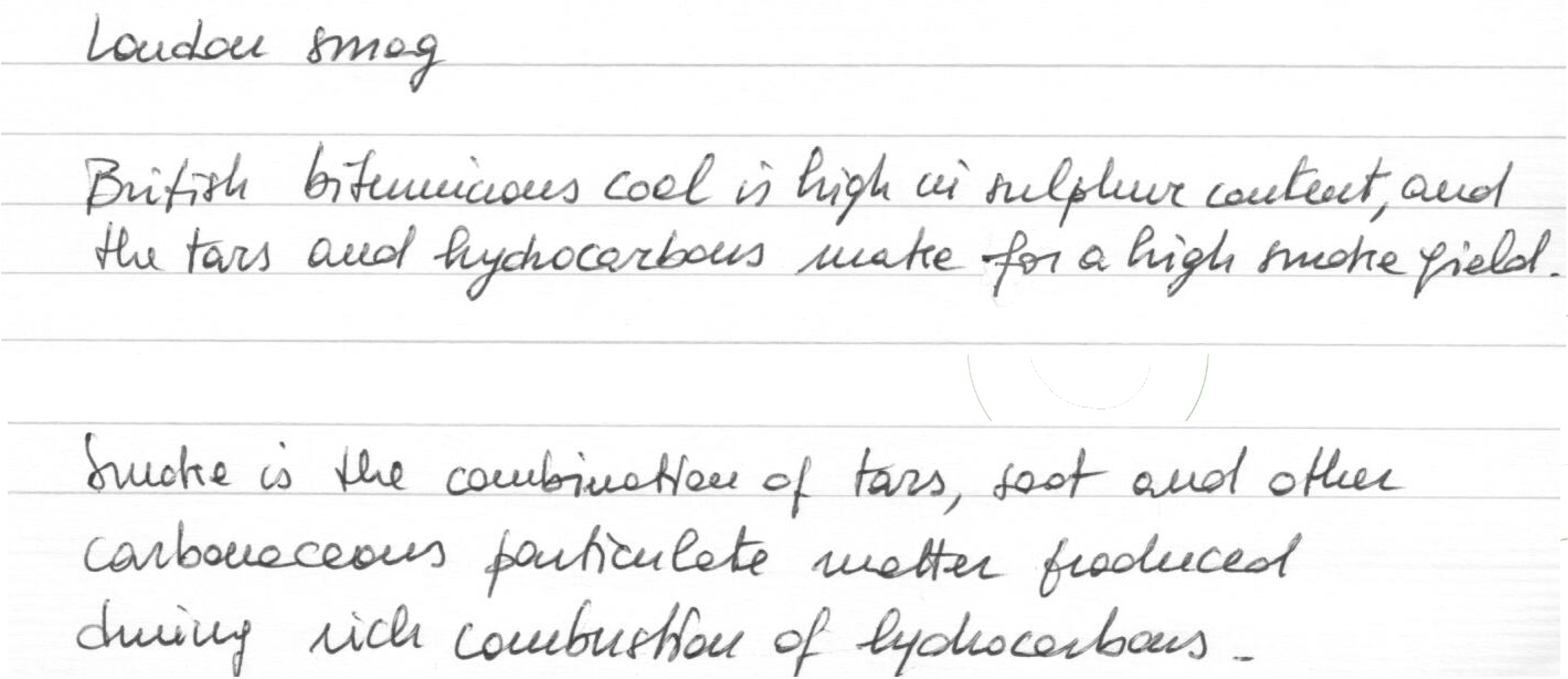
Air pollution from the burning of coal has been a problem for centuries.

London city, although not unique in suffering from the combination of smoke and SO_2 pollution produced by coal combustion, has had severe problems well into the twentieth century.

The word SMOG was coined in 1905 to describe the combination of smoke and fog that was so disastrous.

Almost all heavily industrialized cities suffered to some extent for smog.

Ozone in the atmosphere

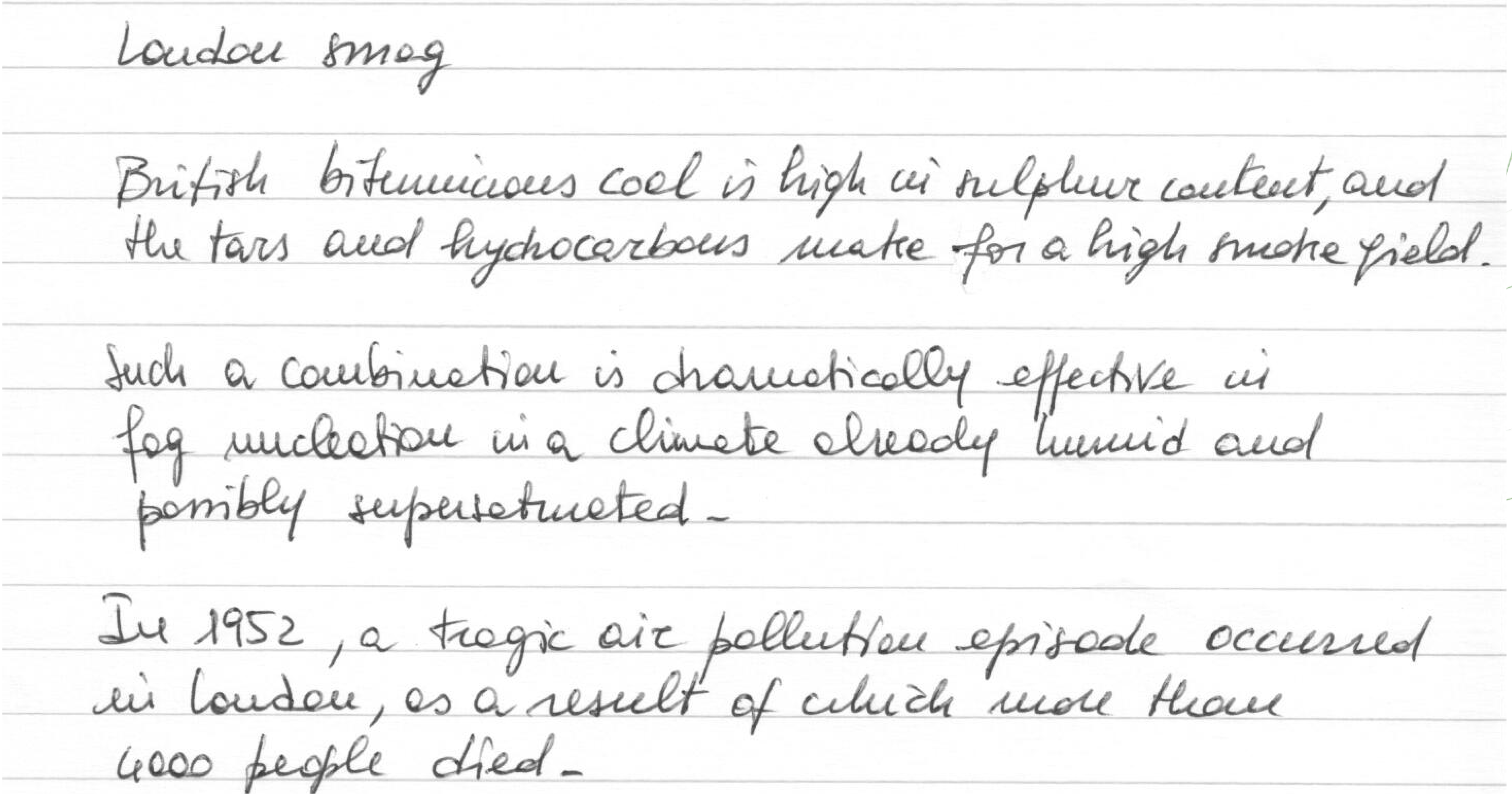


London smog

British bituminous coal is high in sulphur content, and the tars and hydrocarbons make for a high smoke yield.

Smoke is the combination of tars, soot and other carbonaceous particulate matter produced during rich combustion of hydrocarbons.

Ozone in the atmosphere



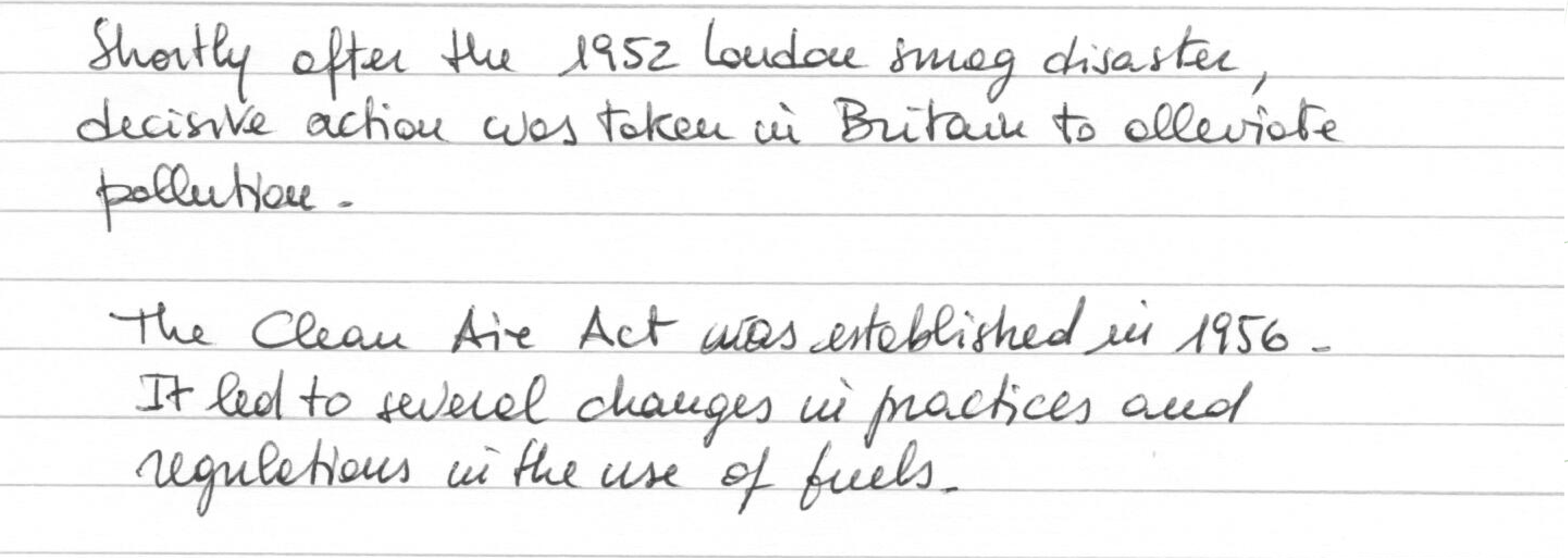
London smog

British bituminous coal is high in sulphur content, and the tars and hydrocarbons make for a high smoke yield.

Such a combination is dramatically effective in fog nucleation in a climate already humid and possibly supersaturated.

In 1952, a tragic air pollution episode occurred in London, as a result of which more than 4000 people died.

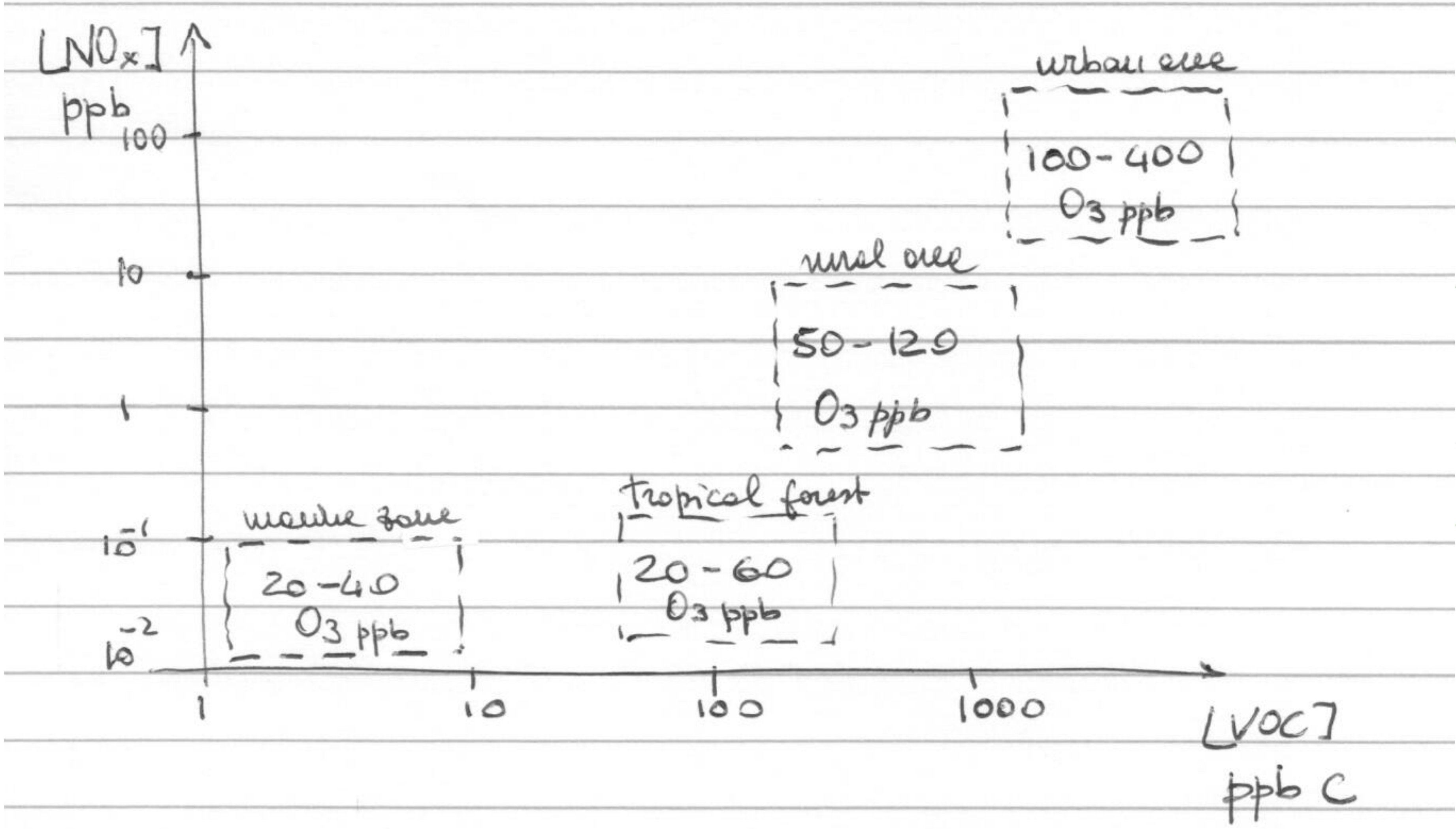
Ozone in the atmosphere



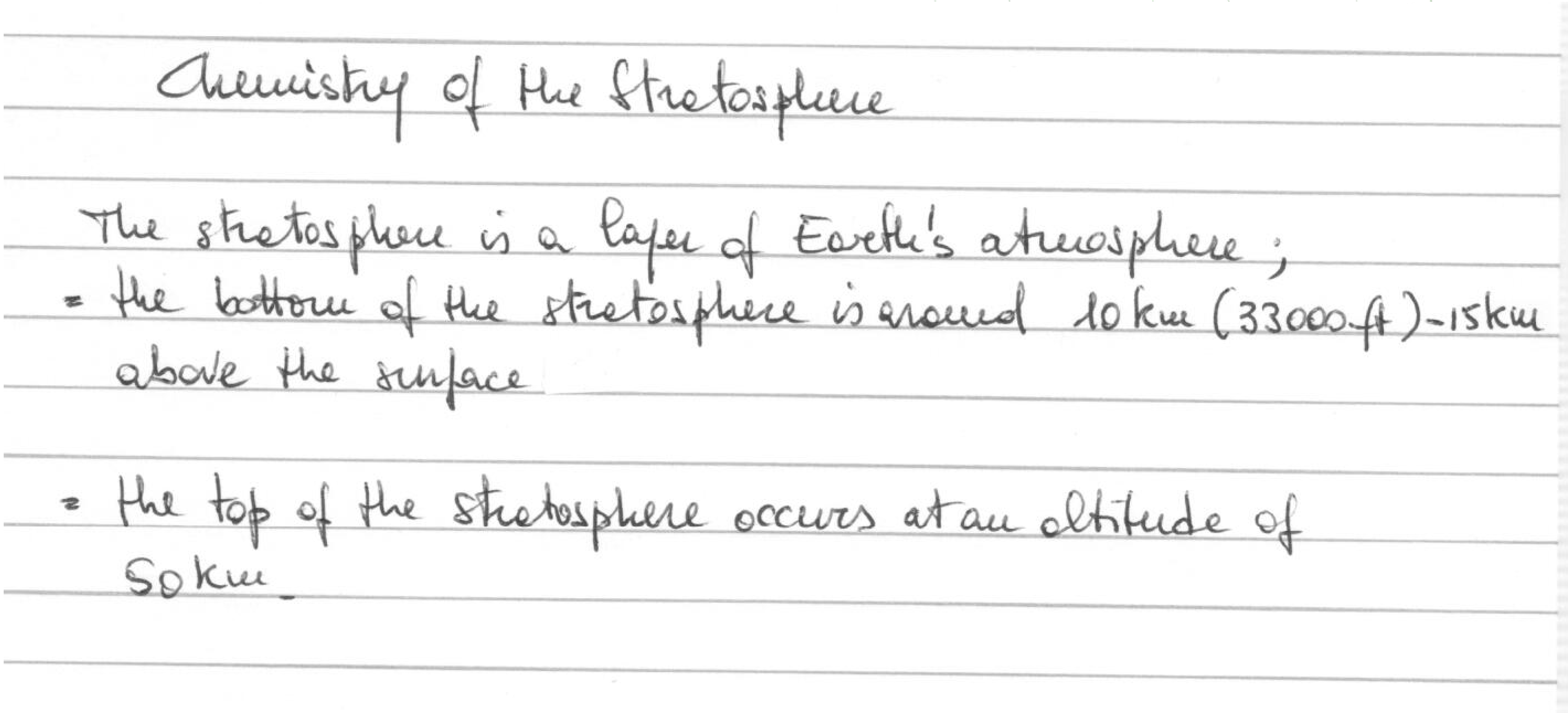
Shortly after the 1952 London smog disaster, decisive action was taken in Britain to alleviate pollution.

The Clean Air Act was established in 1956. It led to several changes in practices and regulations in the use of fuels.

Ozone in the atmosphere



Ozone in the stratosphere

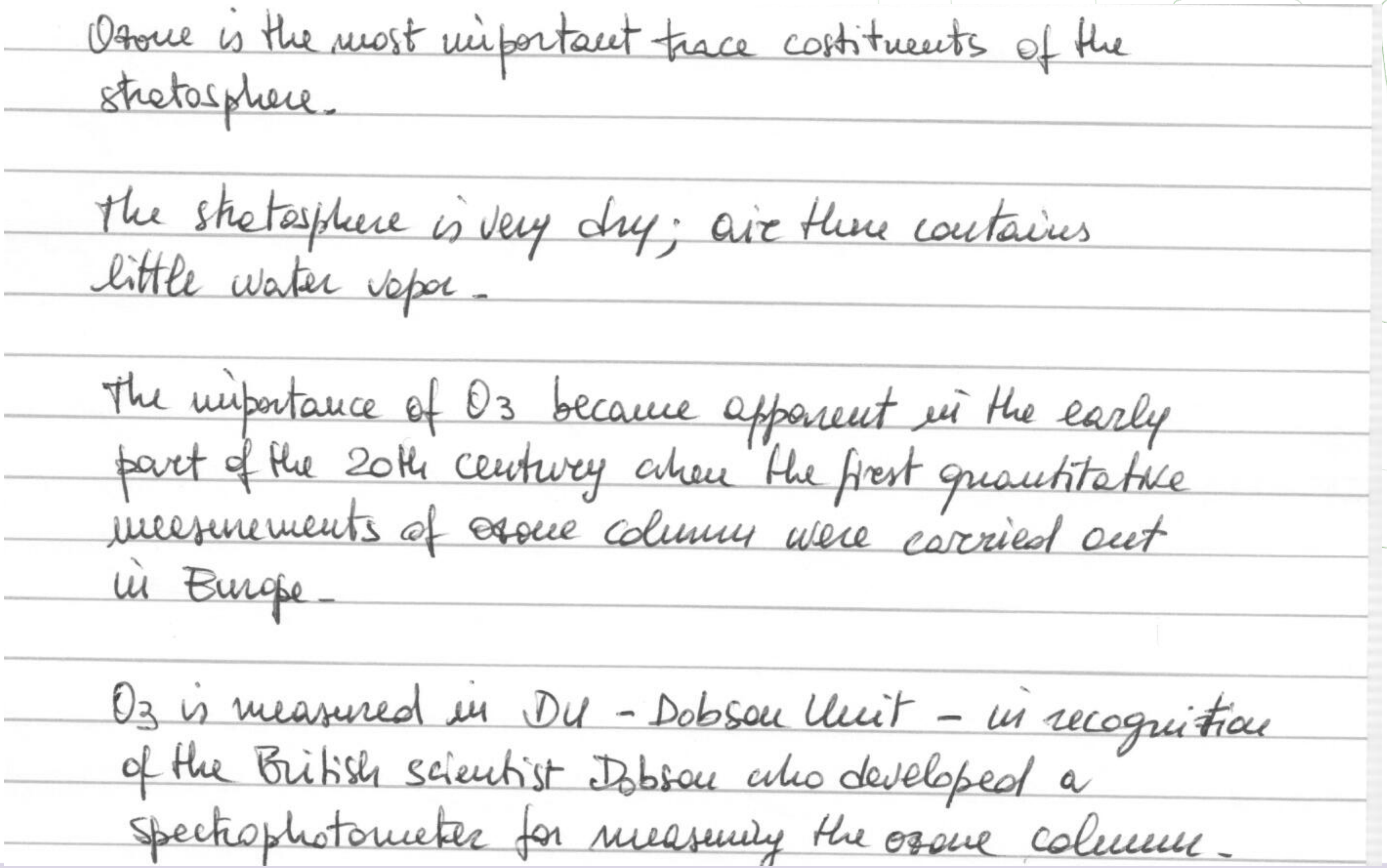


Chemistry of the Stratosphere

The stratosphere is a layer of Earth's atmosphere;

- the bottom of the stratosphere is around 10 km (33000 ft) - 15 km above the surface
- the top of the stratosphere occurs at an altitude of 50 km

Ozone in the stratosphere



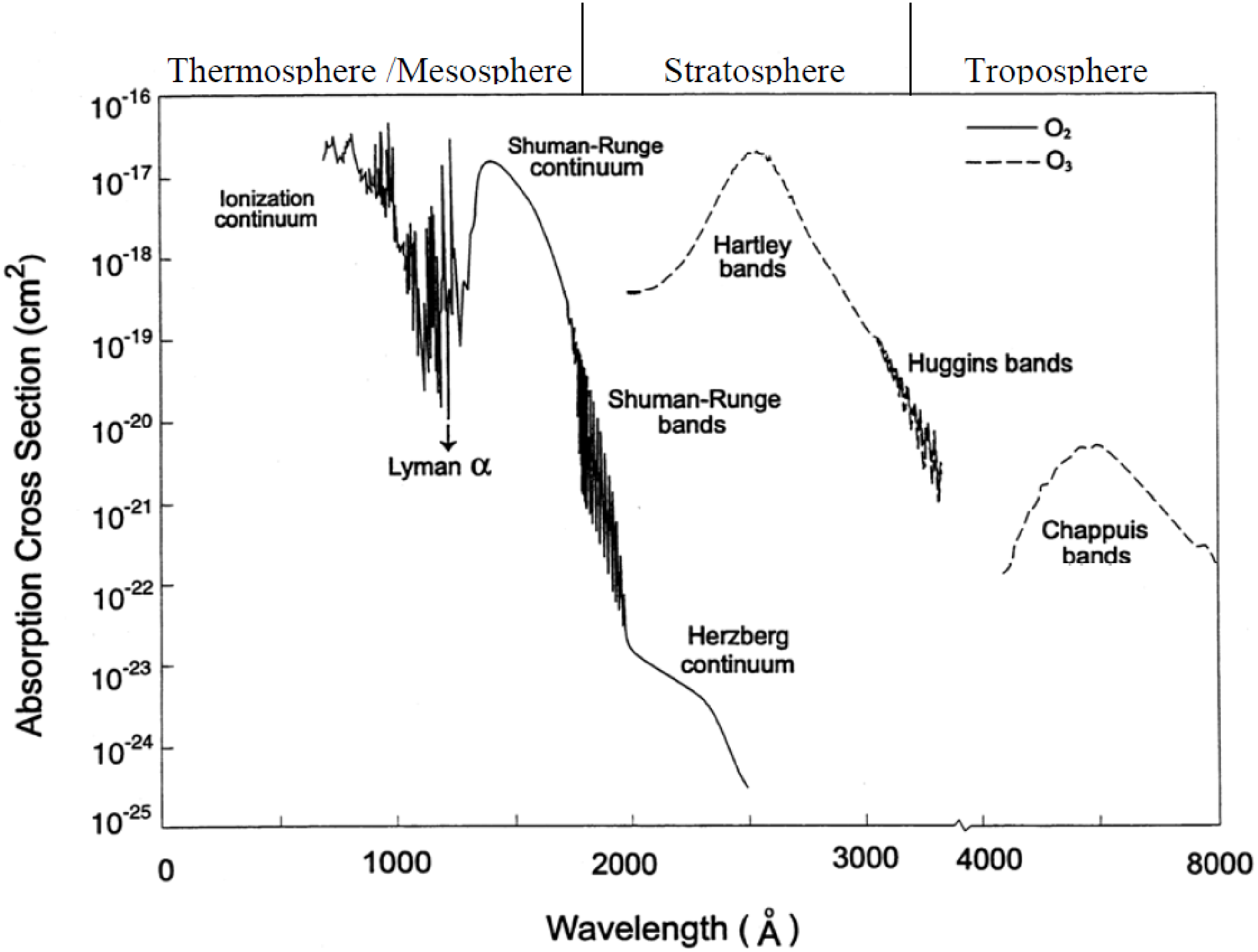
Ozone is the most important trace costituents of the stratosphere.

The stratosphere is very dry; air there contains little water vapor.

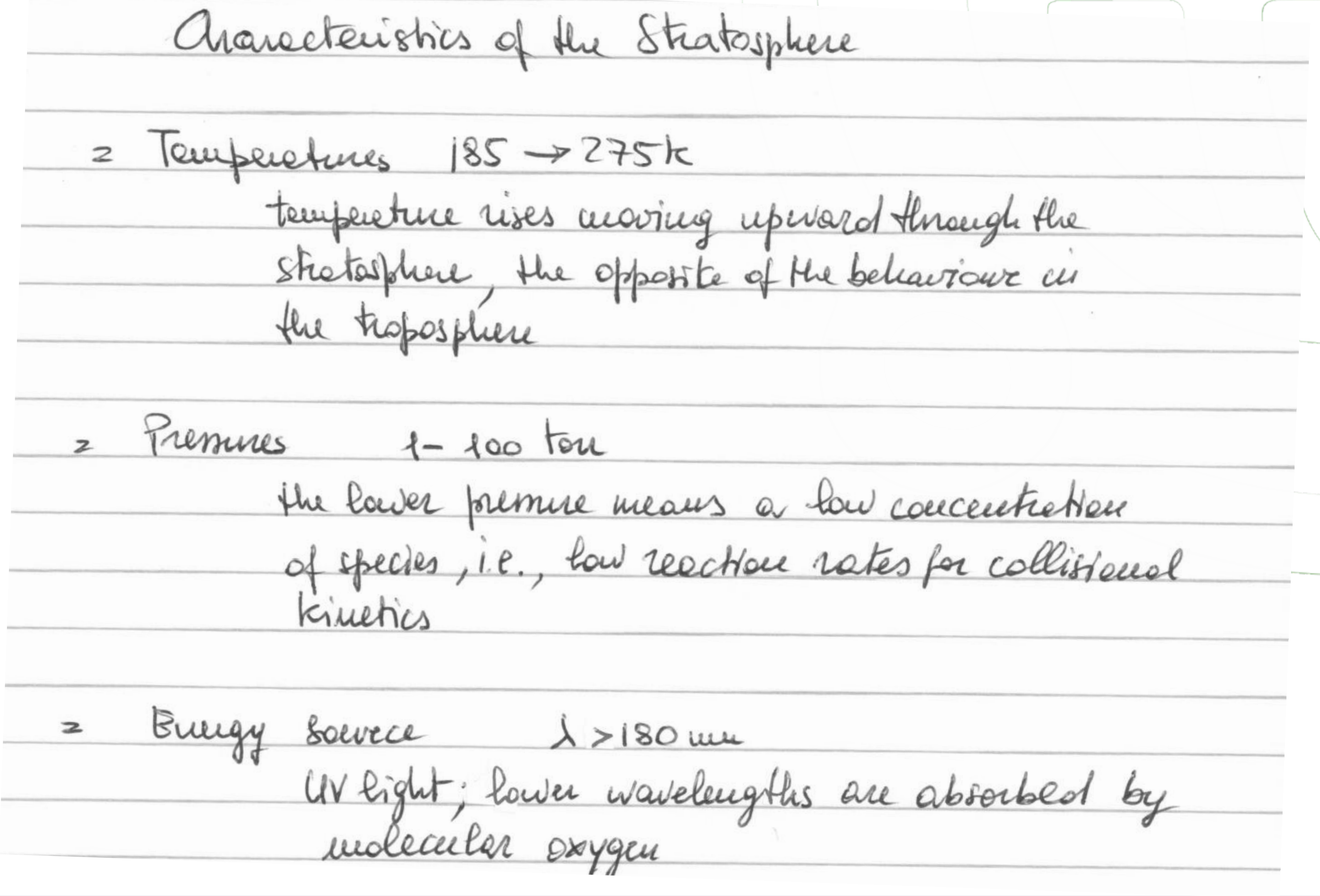
The importance of O_3 became apparent in the early part of the 20th century when the first quantitative measurements of ozone column were carried out in Europe.

O_3 is measured in DU - Dobson Unit - in recognition of the British scientist Dobson who developed a spectrophotometer for measuring the ozone column.

Ozone in the stratosphere



Ozone in the stratosphere



Characteristics of the Stratosphere

- Temperatures 185 → 275 k

  temperature rises moving upward through the stratosphere, the opposite of the behaviour in the troposphere

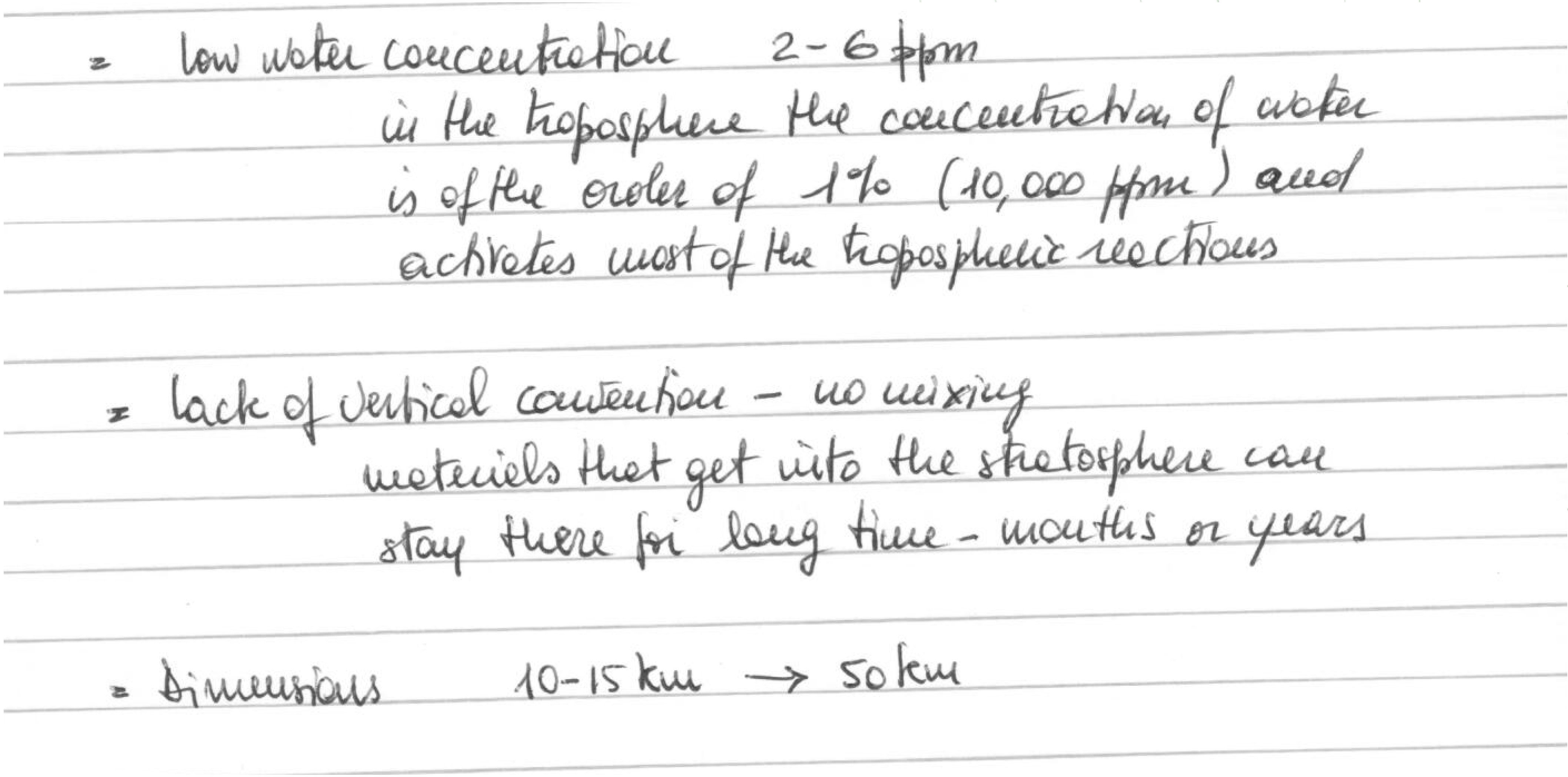
- Pressures 1– 100 torr

  the lower pressure means a low concentration of species, i.e., low reaction rates for collisional kinetics

- Energy source $\lambda > 180$ nm

  UV light; lower wavelengths are absorbed by molecular oxygen

Ozone in the stratosphere

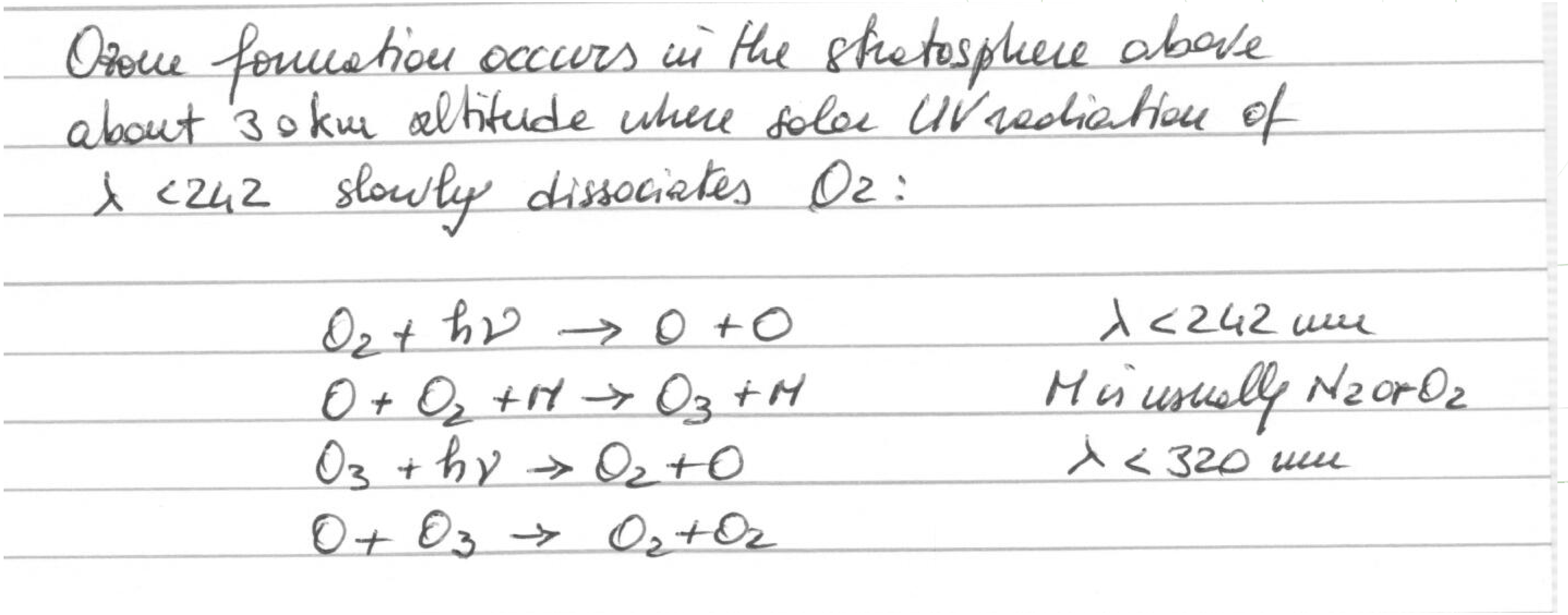


- low water concentration 2-6 ppm
  in the troposphere the concentration of water is of the order of 1% (10,000 ppm) and activates most of the tropospheric reactions

- lack of vertical convection – no mixing
  materials that get into the stratosphere can stay there for long time – months or years

- Dimensions 10-15 km → 50 km

Ozone in the stratosphere



Ozone formation occurs in the stratosphere above about 30km altitude where solar UV radiation of $\lambda < 242$ slowly dissociates O_2:

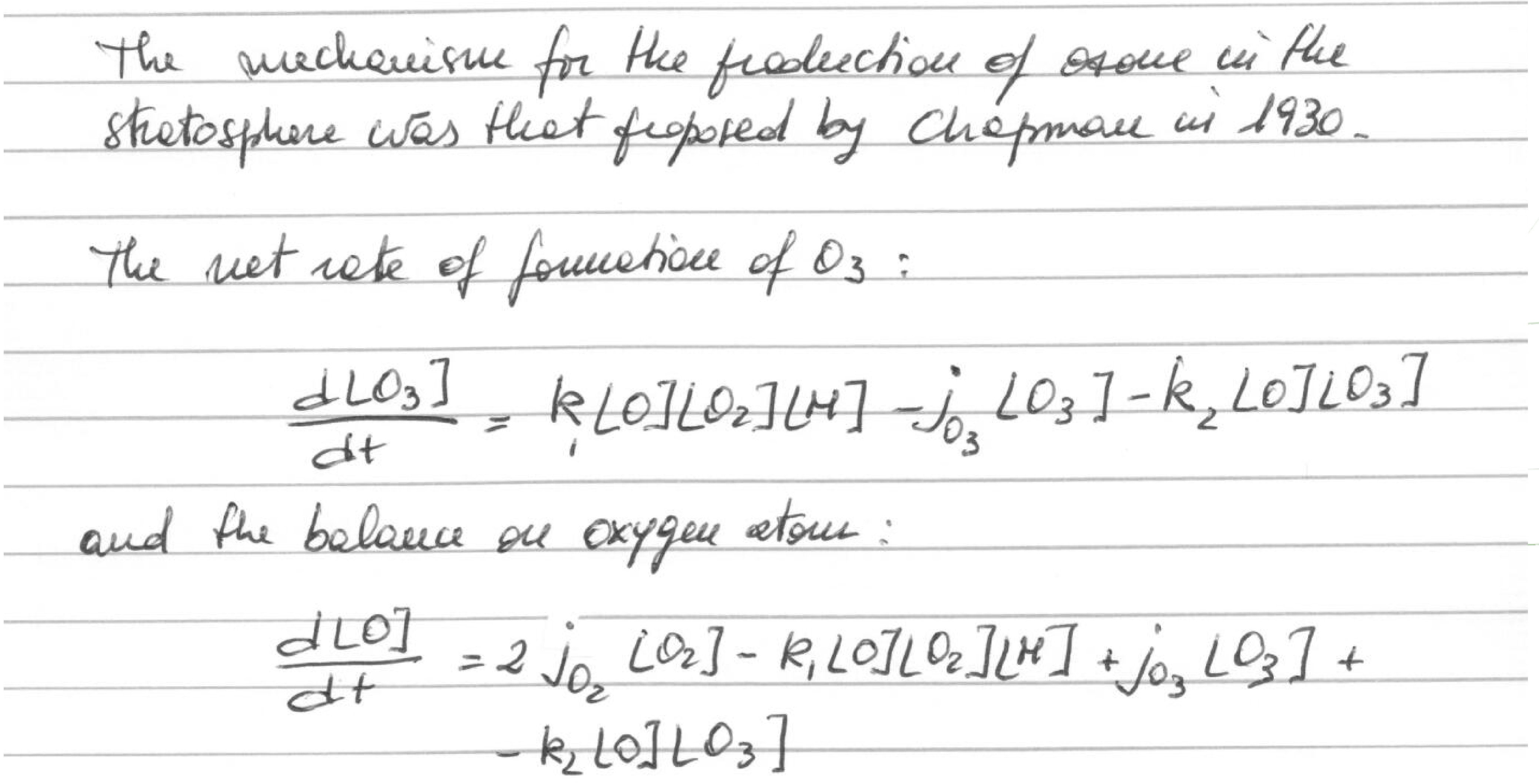
$O_2 + h\nu \rightarrow O + O$ $\lambda < 242$ nm

$O + O_2 + M \rightarrow O_3 + M$ M is usually N_2 or O_2

$O_3 + h\nu \rightarrow O_2 + O$ $\lambda < 320$ nm

$O + O_3 \rightarrow O_2 + O_2$

Ozone in the stratosphere



The mechanism for the production of ozone in the stratosphere was that proposed by Chapman in 1930.

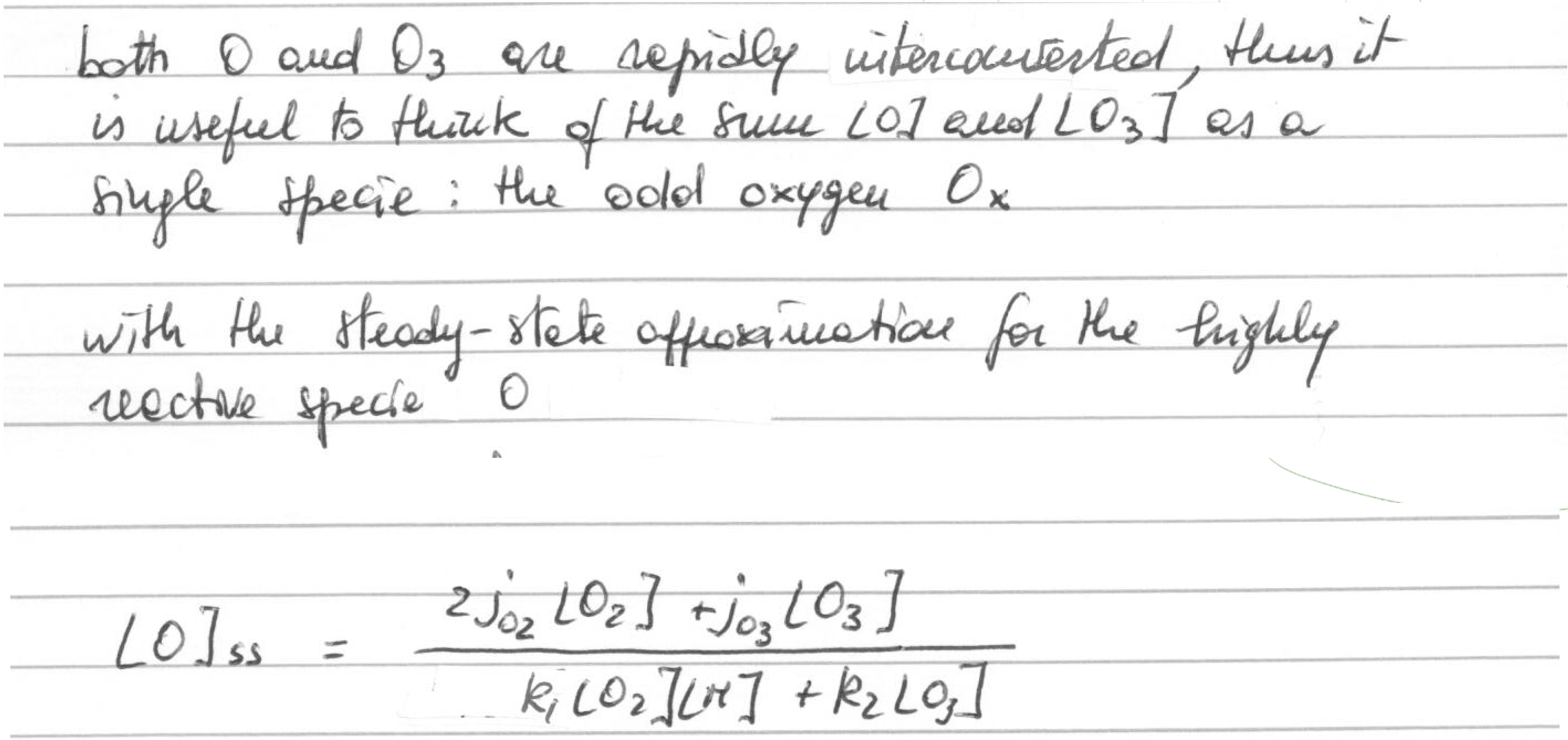
The net rate of formation of O_3 :

$$\frac{d[O_3]}{dt} = k_1[O][O_2][M] - j_{O_3}[O_3] - k_2[O][O_3]$$

and the balance on oxygen atom :

$$\frac{d[O]}{dt} = 2\,j_{O_2}[O_2] - k_1[O][O_2][M] + j_{O_3}[O_3] + \\ - k_2[O][O_3]$$

Ozone in the stratosphere

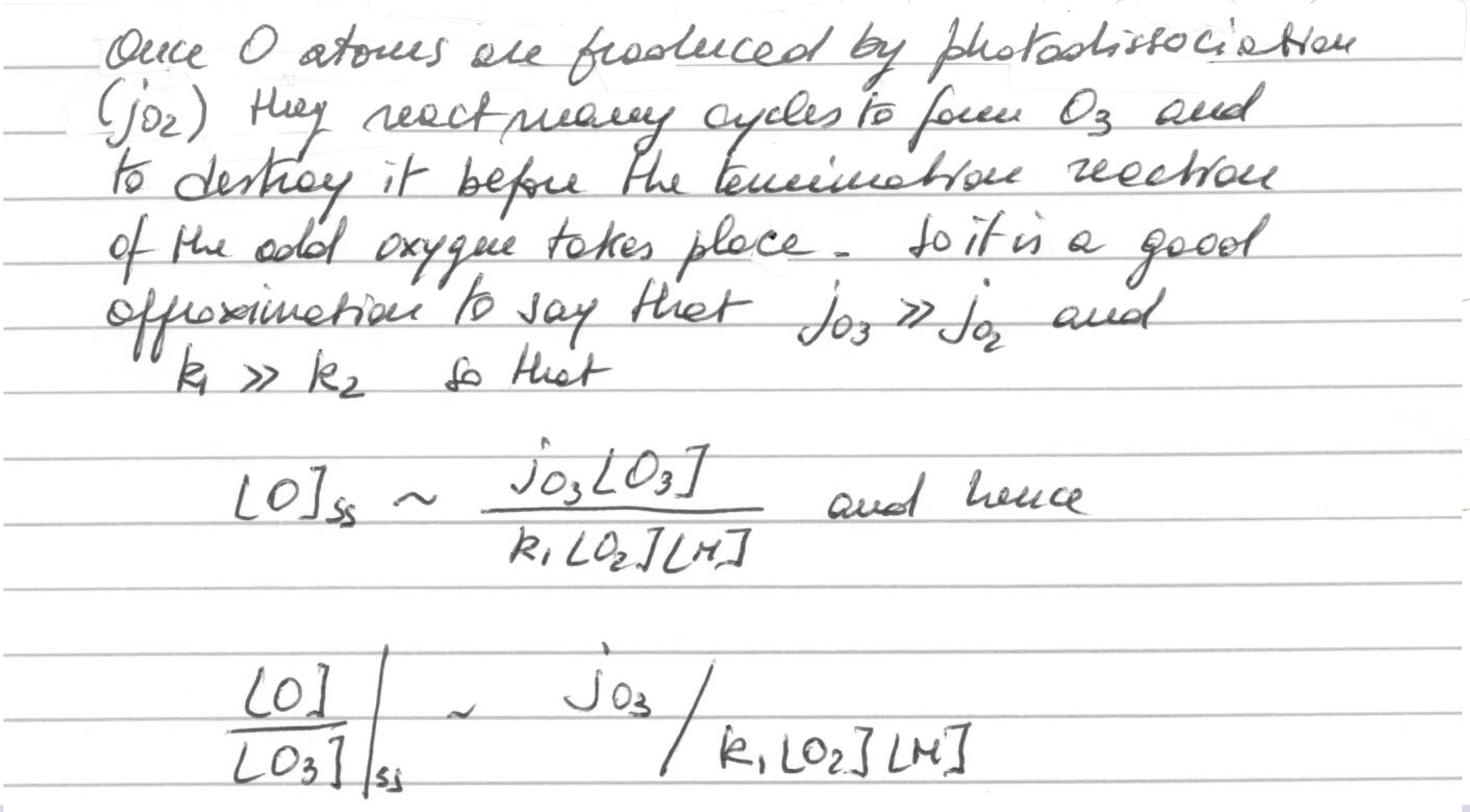


both O and O_3 are rapidly interconverted, thus it is useful to think of the sum [O] and [O_3] as a single specie: the odd oxygen O_x

with the steady-state approximation for the highly reactive specie O

$$[O]_{ss} = \frac{2 j_{O_2} [O_2] + j_{O_3} [O_3]}{k_1 [O_2][M] + k_2 [O_3]}$$

Ozone in the stratosphere

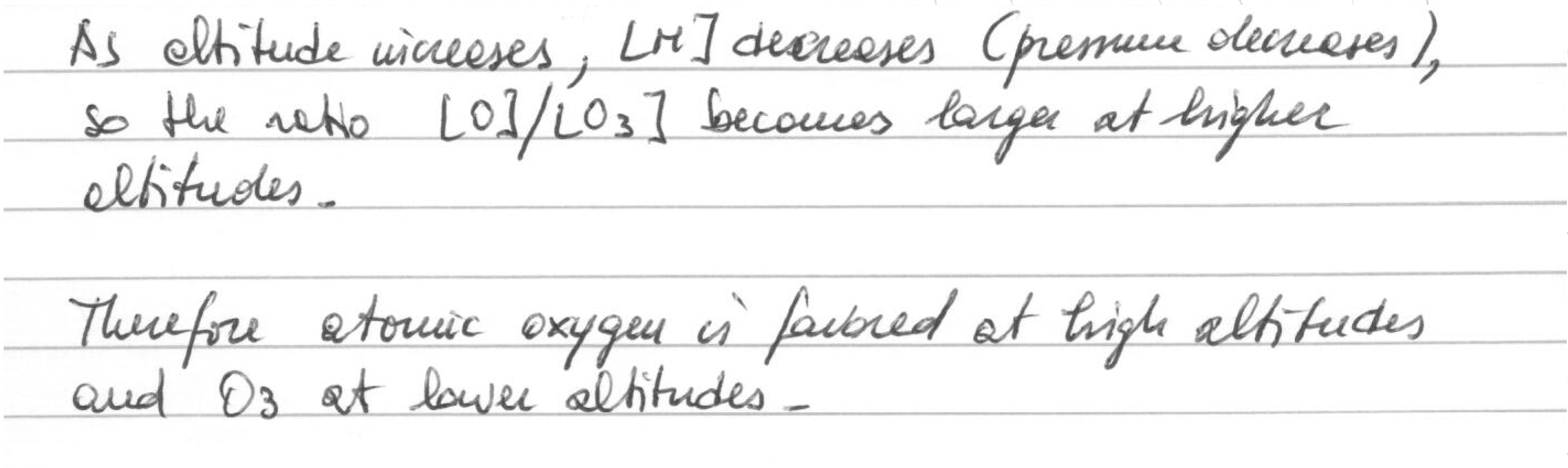


Once O atoms are produced by photodissociation (j_{O_2}) they react many cycles to form O_3 and to destroy it before the termination reaction of the odd oxygen takes place. So it is a good approximation to say that $j_{O_3} \gg j_{O_2}$ and $k_1 \gg k_2$ so that

$$[O]_{ss} \sim \frac{j_{O_3}[O_3]}{k_1[O_2][M]}$$ and hence

$$\left.\frac{[O]}{[O_3]}\right|_{ss} \sim j_{O_3} / k_1[O_2][M]$$

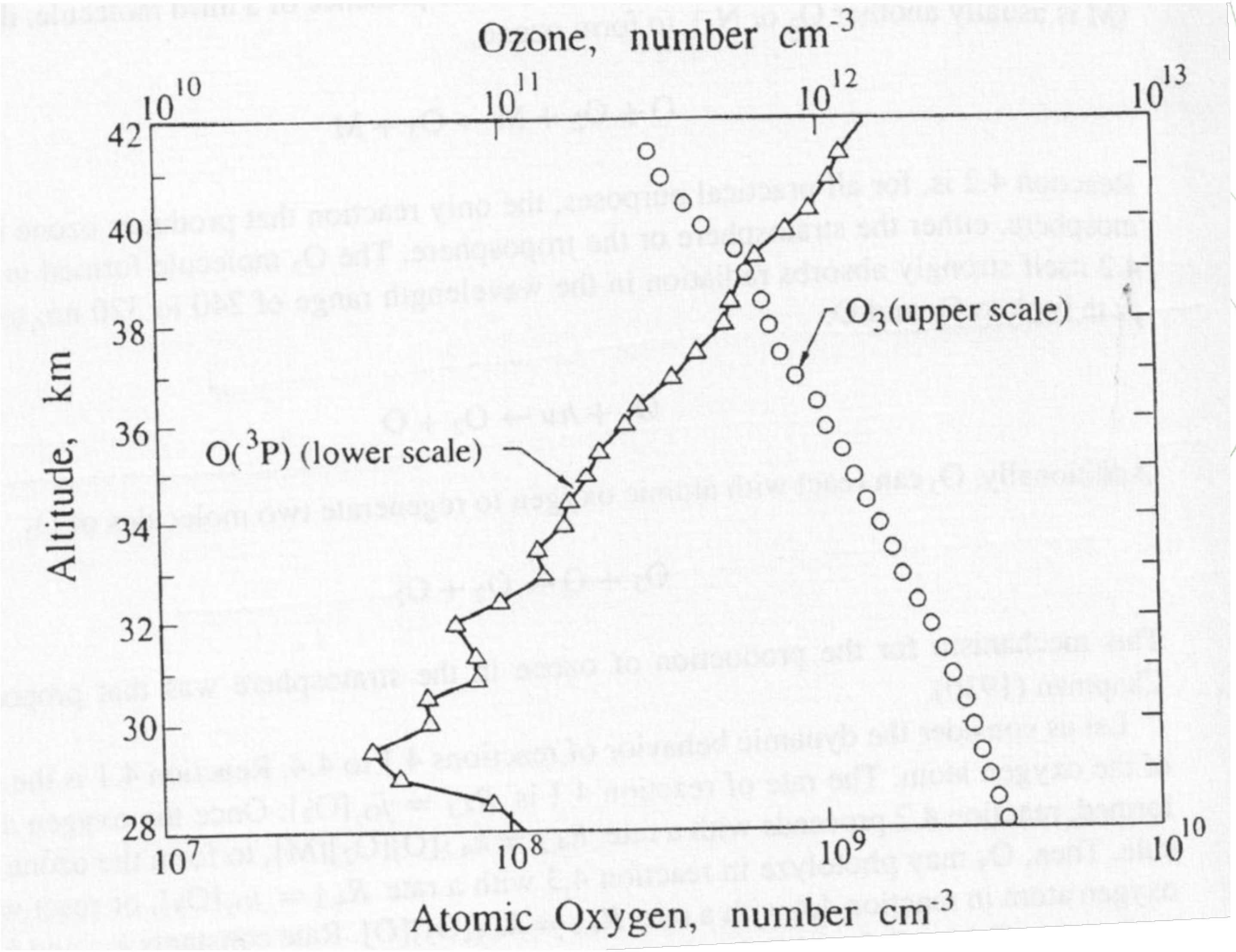
Ozone in the stratosphere



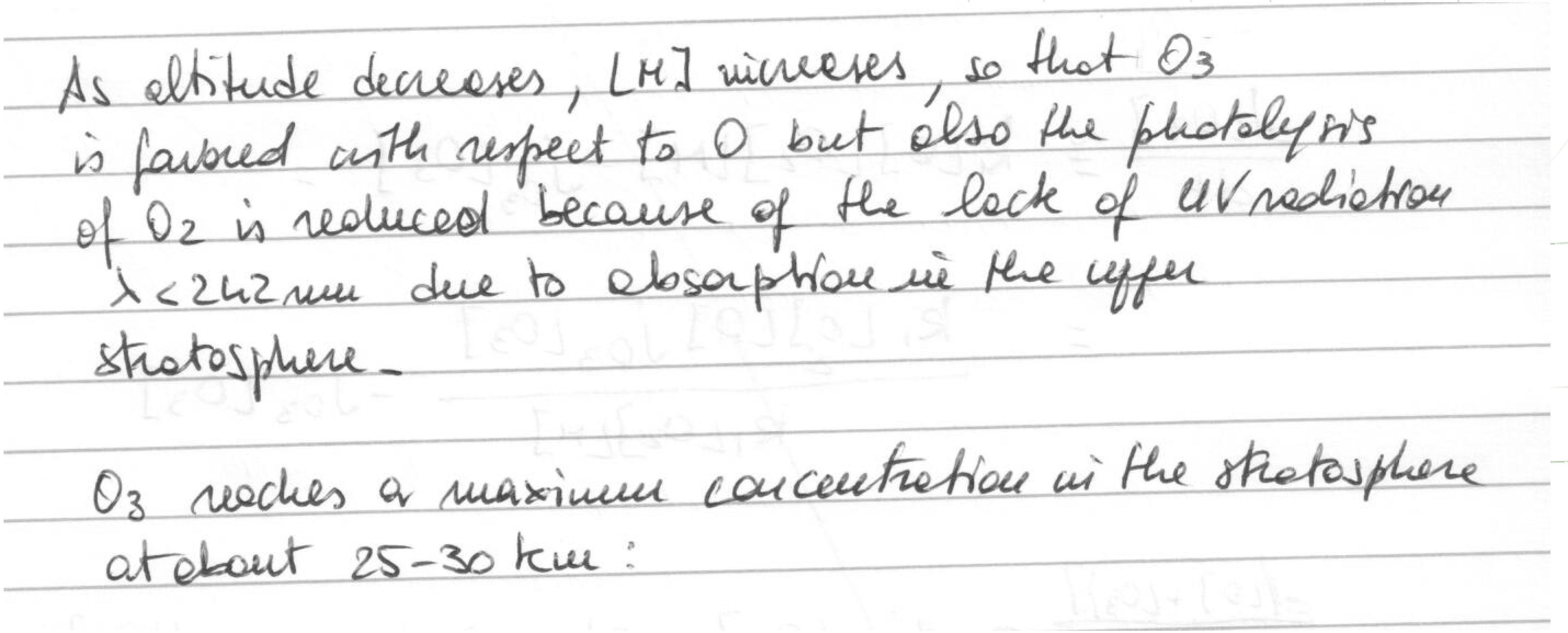
As altitude increases, $[M]$ decreases (pressure decreases), so the ratio $[O]/[O_3]$ becomes larger at higher altitudes.

Therefore atomic oxygen is favored at high altitudes and O_3 at lower altitudes.

Ozone in the stratosphere



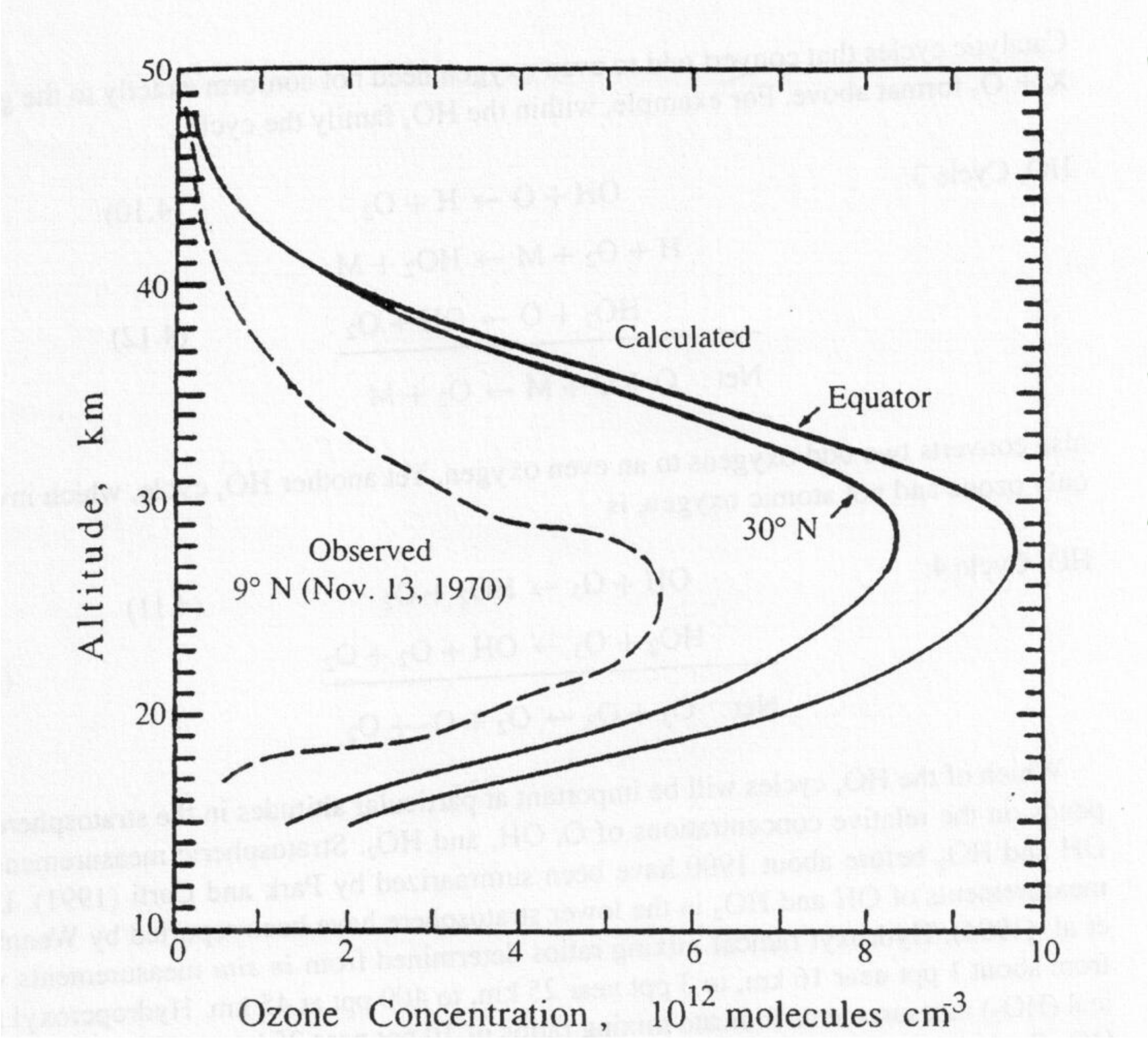
Ozone in the stratosphere



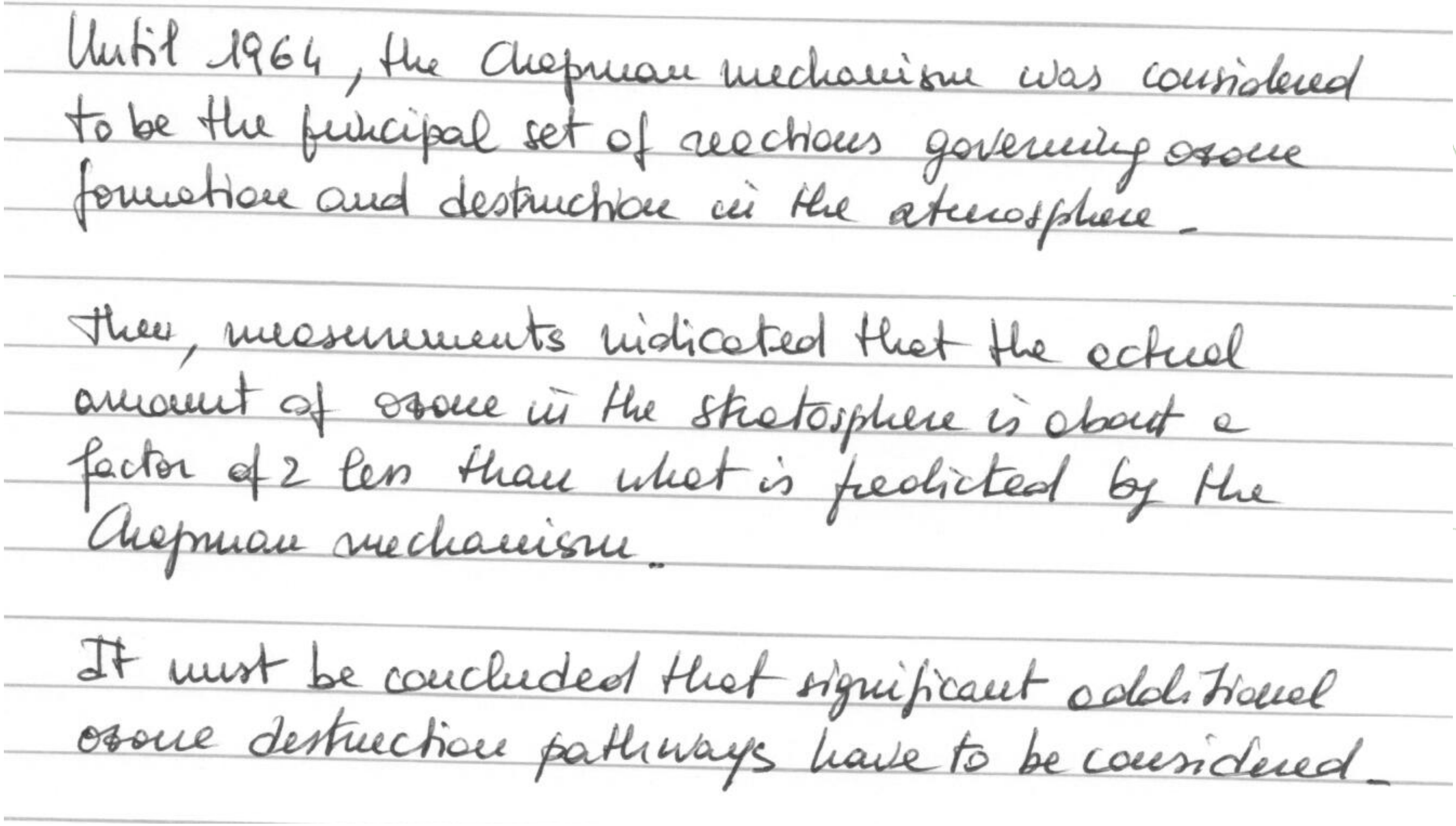
As altitude decreases, [M] increases, so that O_3 is favored with respect to O but also the photolysis of O_2 is reduced because of the lack of UV radiation $\lambda < 242$ nm due to absorption in the upper stratosphere.

O_3 reaches a maximum concentration in the stratosphere at about 25-30 km:

Ozone in the stratosphere



Ozone in the stratosphere

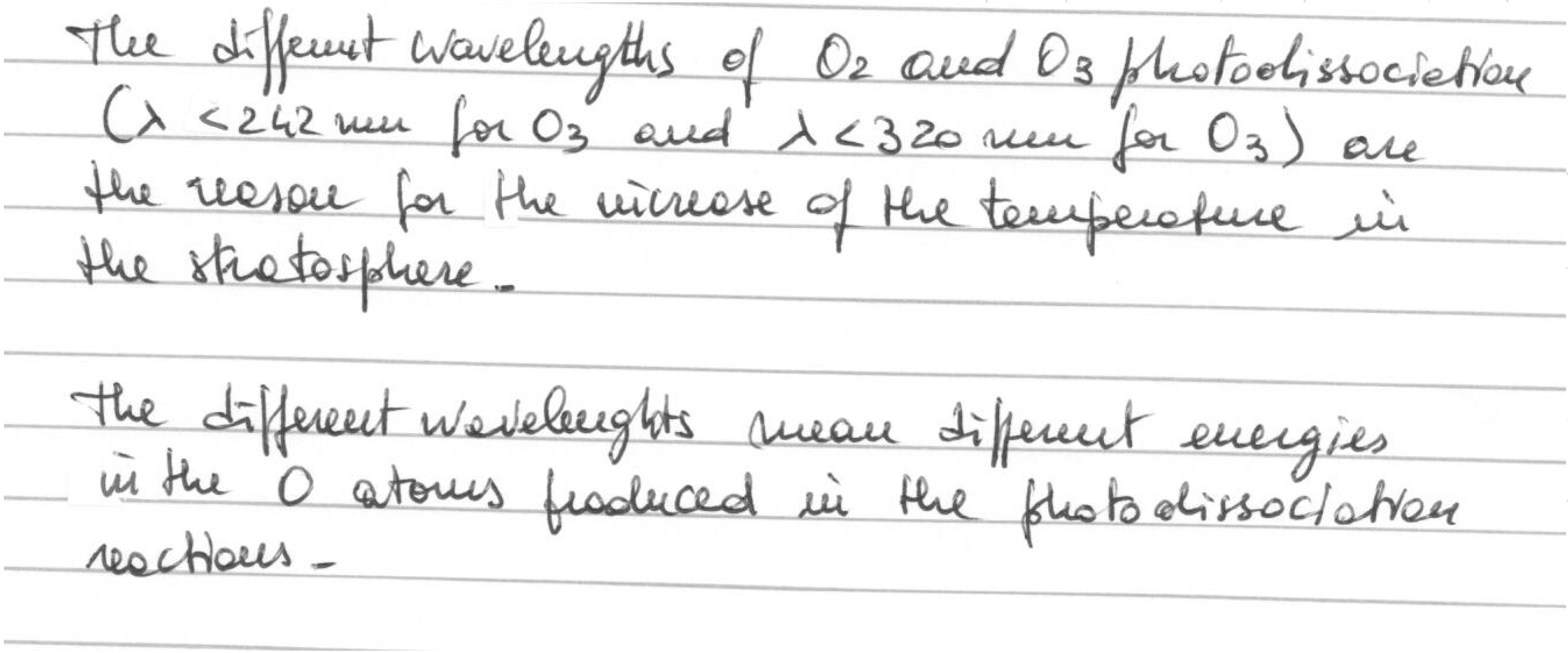


Until 1964, the Chapman mechanism was considered to be the principal set of reactions governing ozone formation and destruction in the atmosphere.

Then, measurements indicated that the actual amount of ozone in the stratosphere is about a factor of 2 less than what is predicted by the Chapman mechanism.

It must be concluded that significant additional ozone destruction pathways have to be considered.

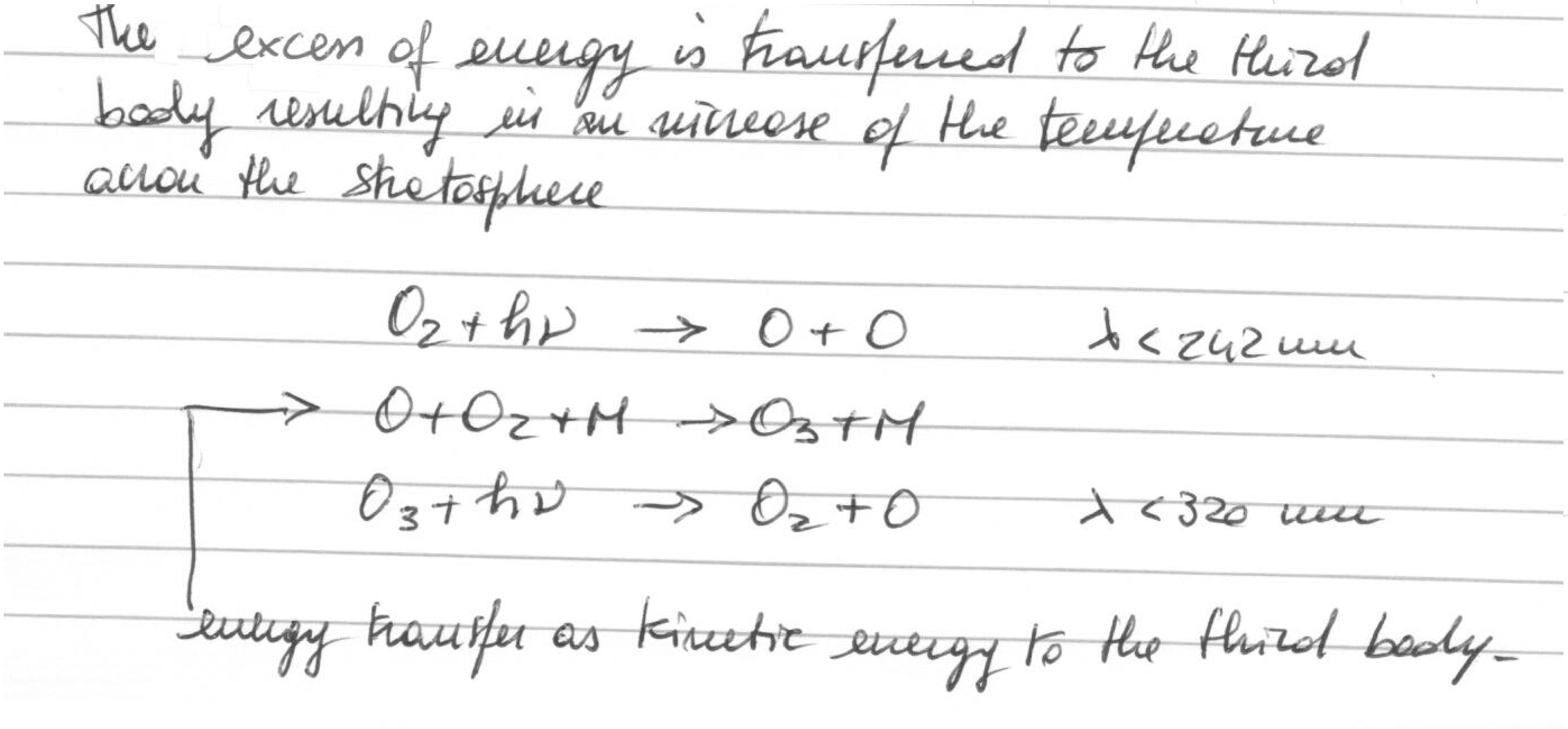
Ozone in the stratosphere



The different wavelengths of O_2 and O_3 photodissociation ($\lambda < 242$ nm for O_3 and $\lambda < 320$ nm for O_3) are the reason for the increase of the temperature in the stratosphere.

The different wavelengths mean different energies in the O atoms produced in the photodissociation reactions.

Ozone in the stratosphere



The excess of energy is transferred to the third body resulting in an increase of the temperature across the stratosphere

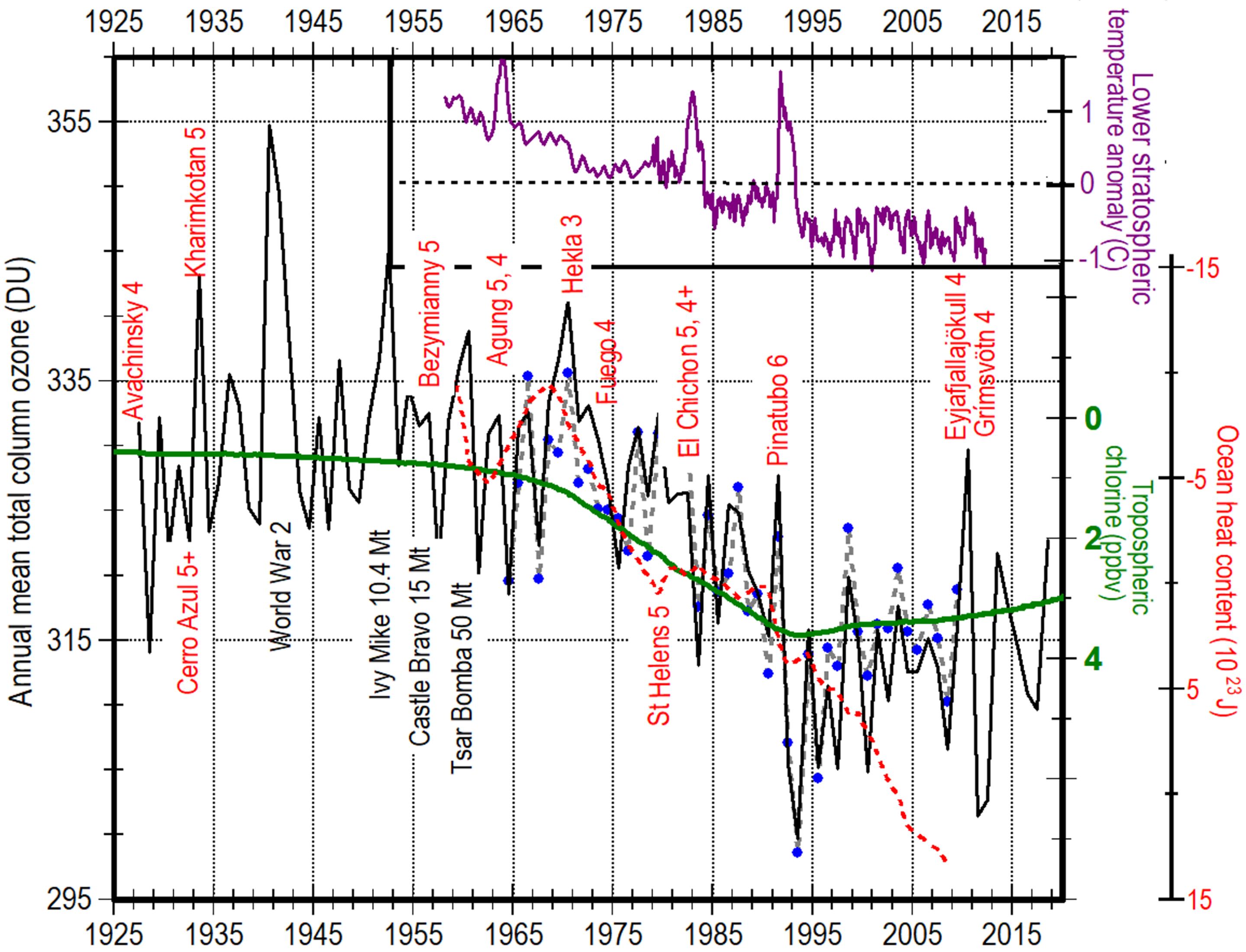
$O_2 + h\nu \rightarrow O + O$ $\lambda < 242$ nm

$O + O_2 + M \rightarrow O_3 + M$

$O_3 + h\nu \rightarrow O_2 + O$ $\lambda < 320$ nm

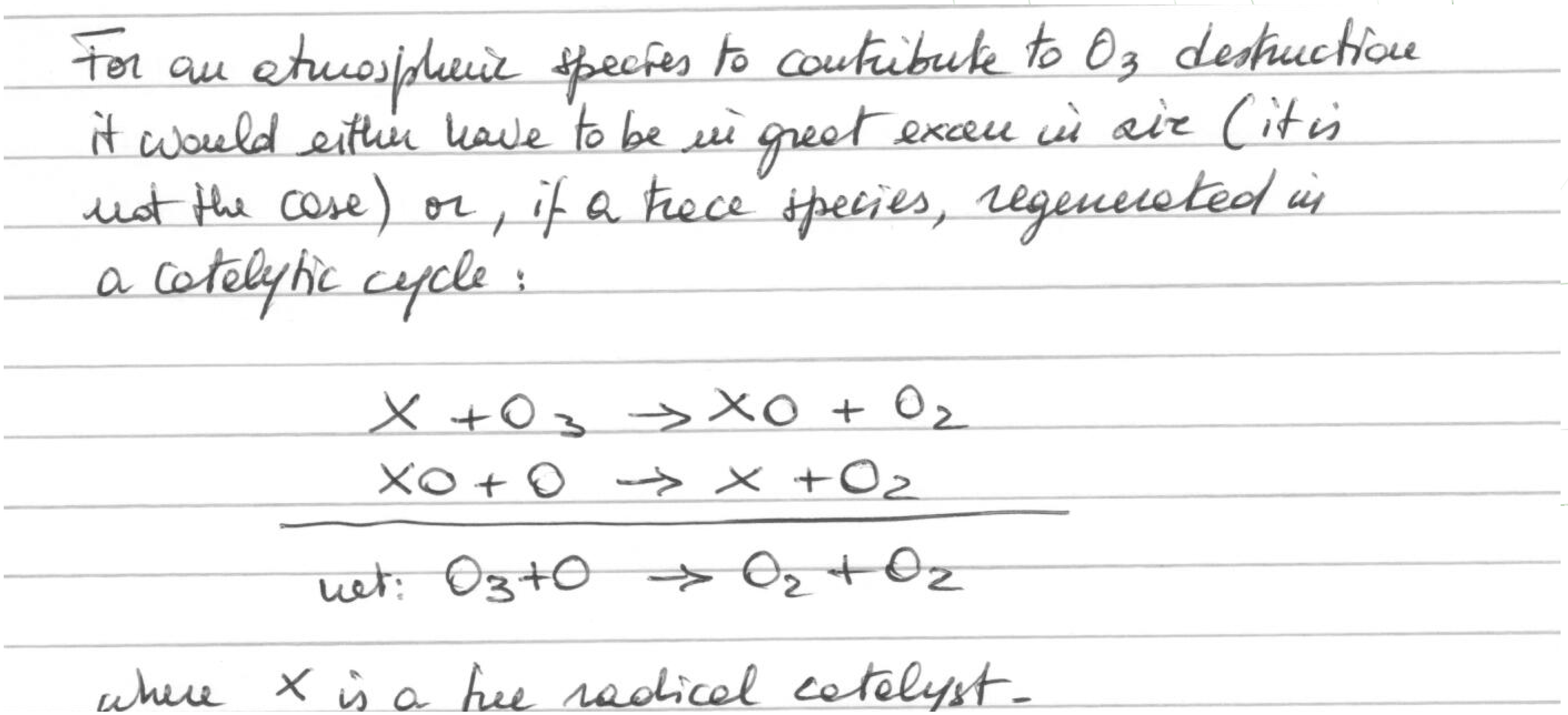
energy transfer as kinetic energy to the third body.

Ozone in the stratosphere



The long-term decrease in ozone has been reliably associated with an increase in the concentration of anthropogenic tropospheric chlorine (green line, **y-axis inverted**)

Ozone in the stratosphere



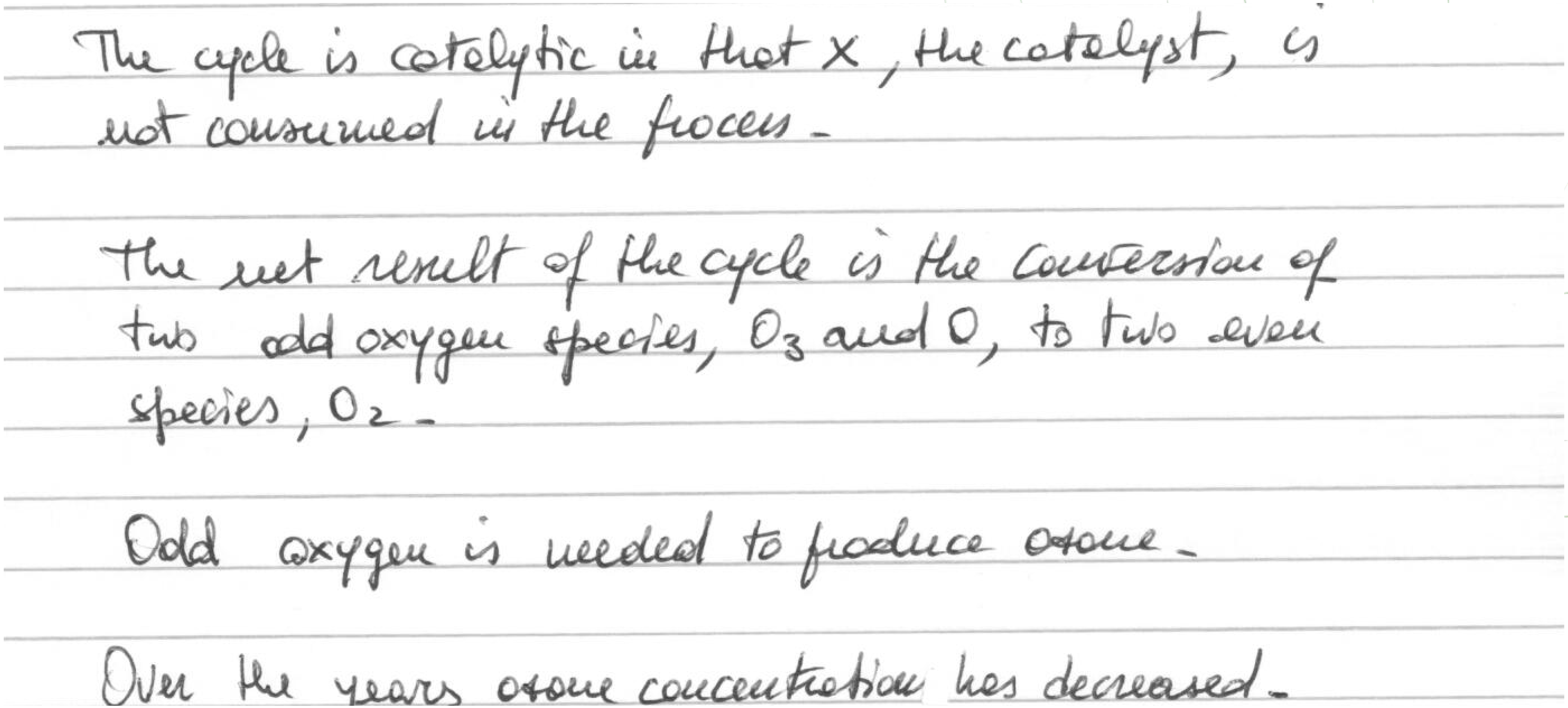
For an atmospheric species to contribute to O_3 destruction it would either have to be in great excess in air (it is not the case) or, if a trace species, regenerated in a catalytic cycle:

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O \rightarrow X + O_2$$

net: $O_3 + O \rightarrow O_2 + O_2$

where X is a free radical catalyst.

Ozone in the stratosphere



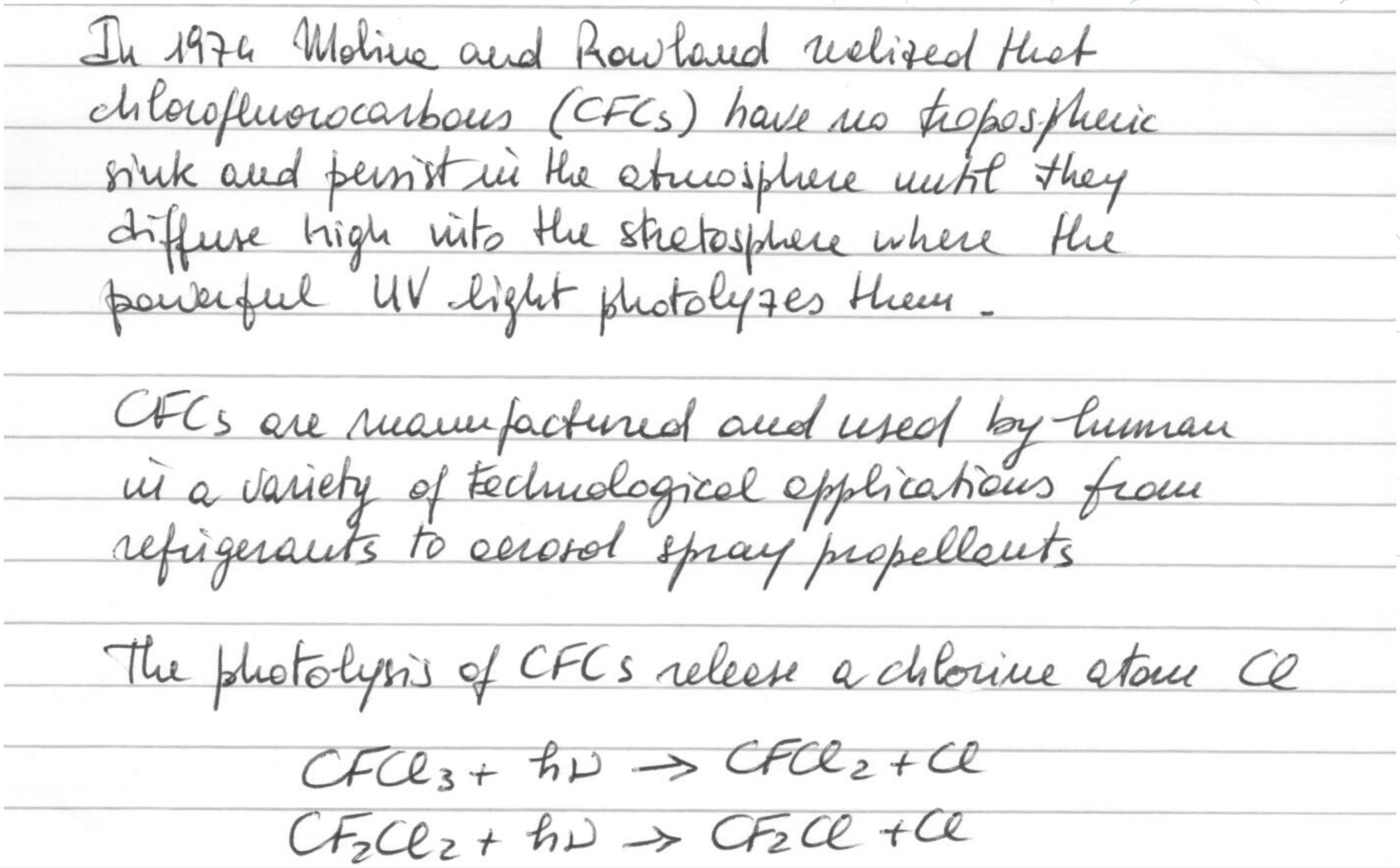
The cycle is catalytic in that X, the catalyst, is not consumed in the process.

The net result of the cycle is the conversion of two odd oxygen species, O_3 and O, to two even species, O_2.

Odd oxygen is needed to produce ozone.

Over the years ozone concentration has decreased.

Ozone in the stratosphere



In 1974 Molina and Rowland realized that chlorofluorocarbons (CFCs) have no tropospheric sink and persist in the atmosphere until they diffuse high into the stratosphere where the powerful UV light photolyzes them.

CFCs are manufactured and used by human in a variety of technological applications from refrigerants to aerosol spray propellants

The photolysis of CFCs release a chlorine atom Cl

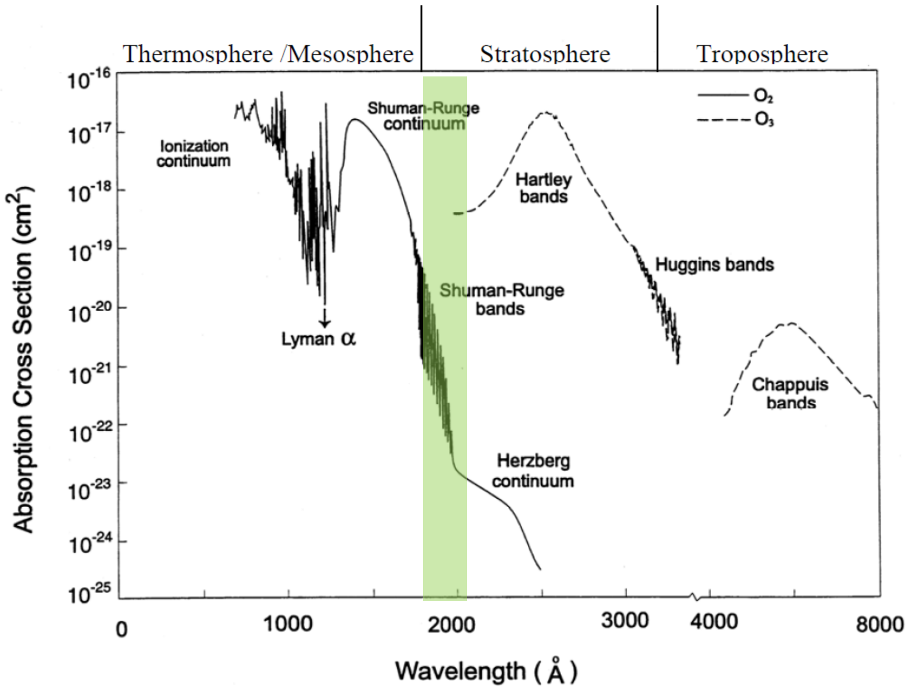
$$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$$

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$$

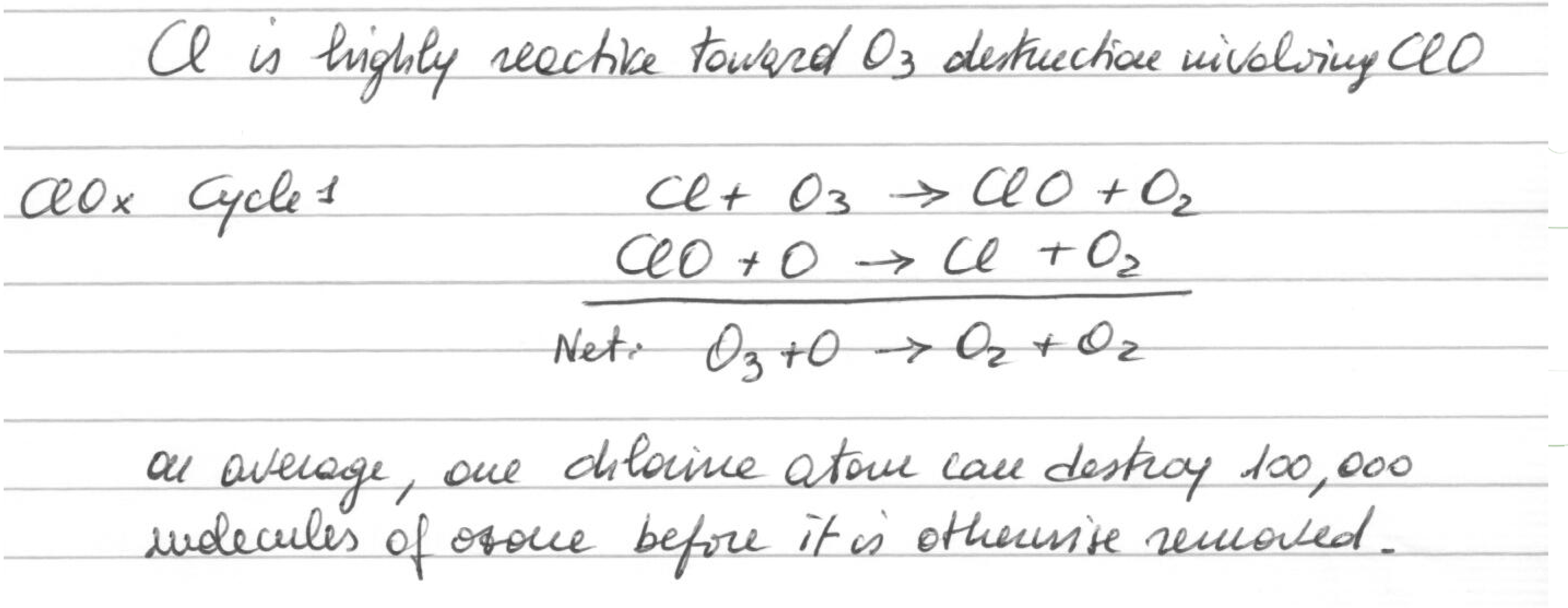
Ozone in the stratosphere

To photodissociate CFCs need to rise above most of the atmospheric O_2 and O_3.

CFCs photodissociate at wavelengths in the 185 - 210 nm spectral window between O_2 absorption at shorter wavelengths and O_3 absorption of longer wavelengths.



Ozone in the stratosphere



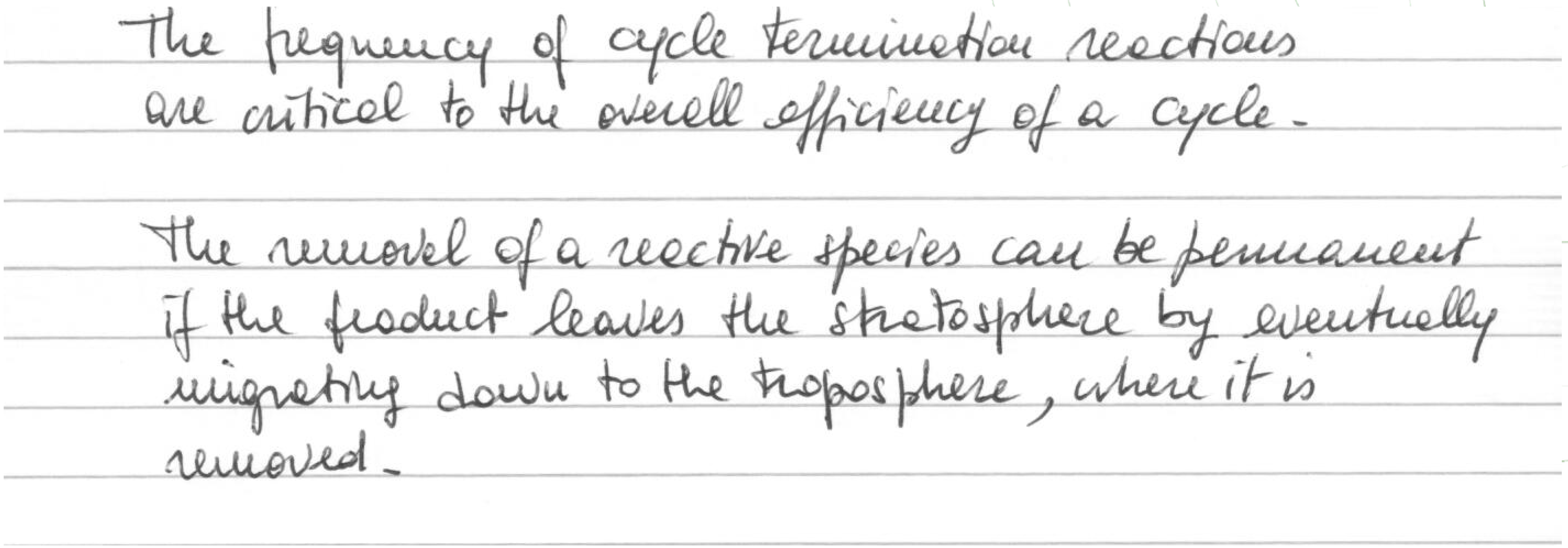
Cl is highly reactive toward O_3 destruction involving ClO

ClO_x Cycle 1

$$\begin{aligned} Cl + O_3 &\rightarrow ClO + O_2 \\ ClO + O &\rightarrow Cl + O_2 \\ \hline \text{Net: } O_3 + O &\rightarrow O_2 + O_2 \end{aligned}$$

on average, one chlorine atom can destroy 100,000 molecules of ozone before it is otherwise removed.

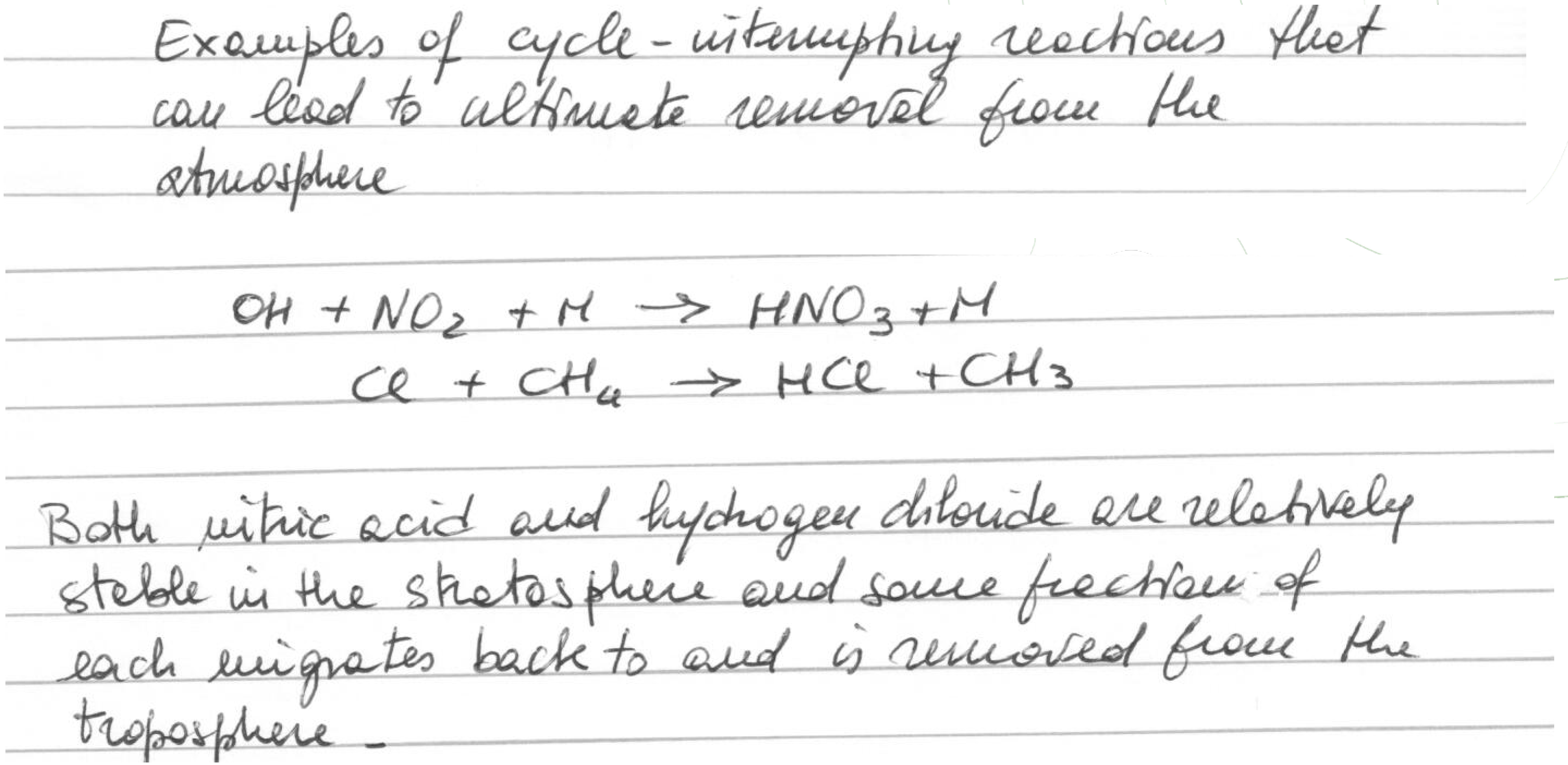
Ozone in the stratosphere



The frequency of cycle termination reactions are critical to the overall efficiency of a cycle.

The removal of a reactive species can be permanent if the product leaves the stratosphere by eventually migrating down to the troposphere, where it is removed.

Ozone in the stratosphere



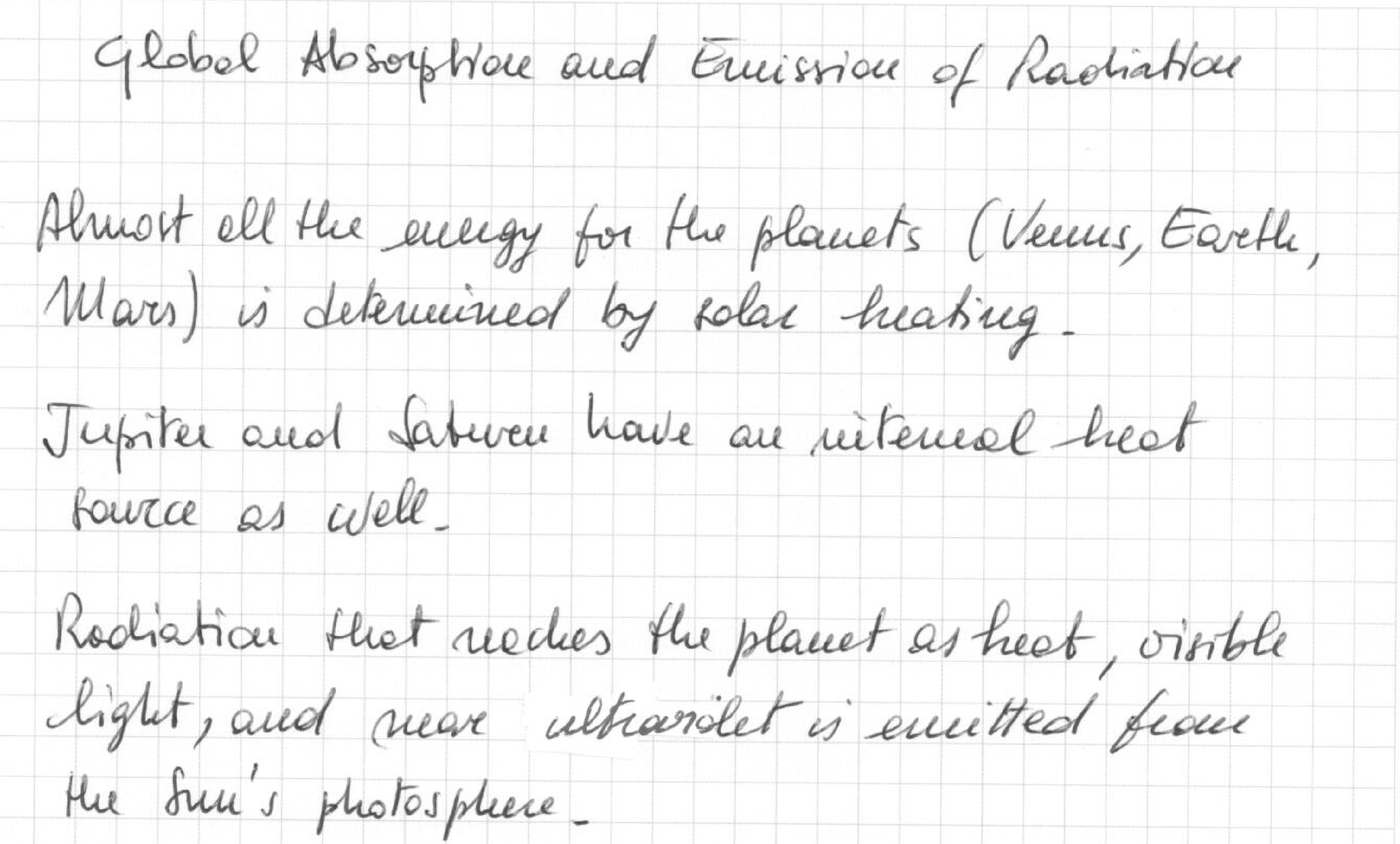
Examples of cycle-interrupting reactions that can lead to ultimate removal from the atmosphere

$$OH + NO_2 + M \rightarrow HNO_3 + M$$

$$Cl + CH_4 \rightarrow HCl + CH_3$$

Both nitric acid and hydrogen chloride are relatively stable in the stratosphere and some fraction of each migrates back to and is removed from the troposphere.

Radiative balance in the atmosphere



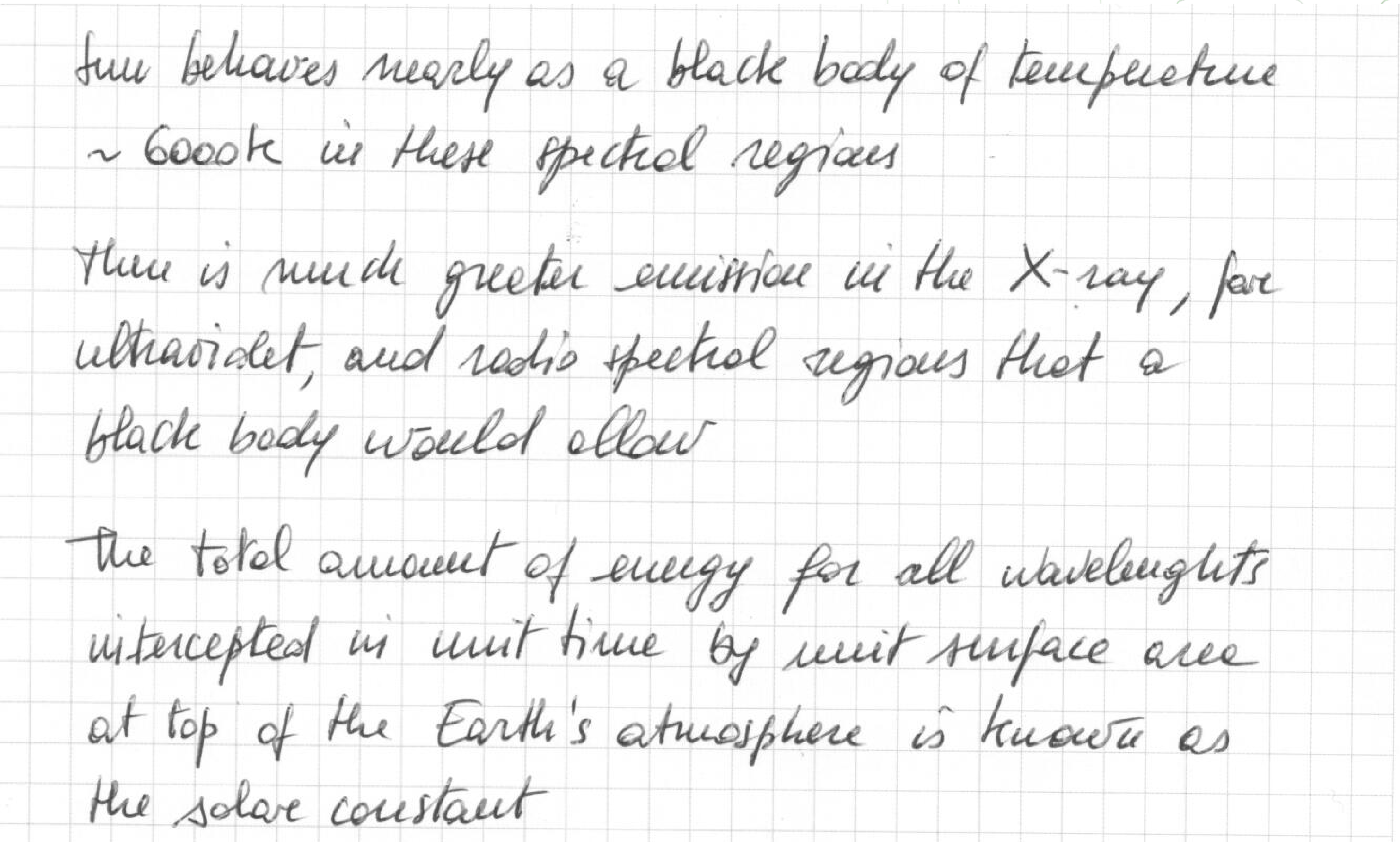
Global Absorption and Emission of Radiation

Almost all the energy for the planets (Venus, Earth, Mars) is determined by solar heating.

Jupiter and Saturn have an internal heat source as well.

Radiation that reaches the planet as heat, visible light, and near ultraviolet is emitted from the sun's photosphere.

Radiative balance in the atmosphere

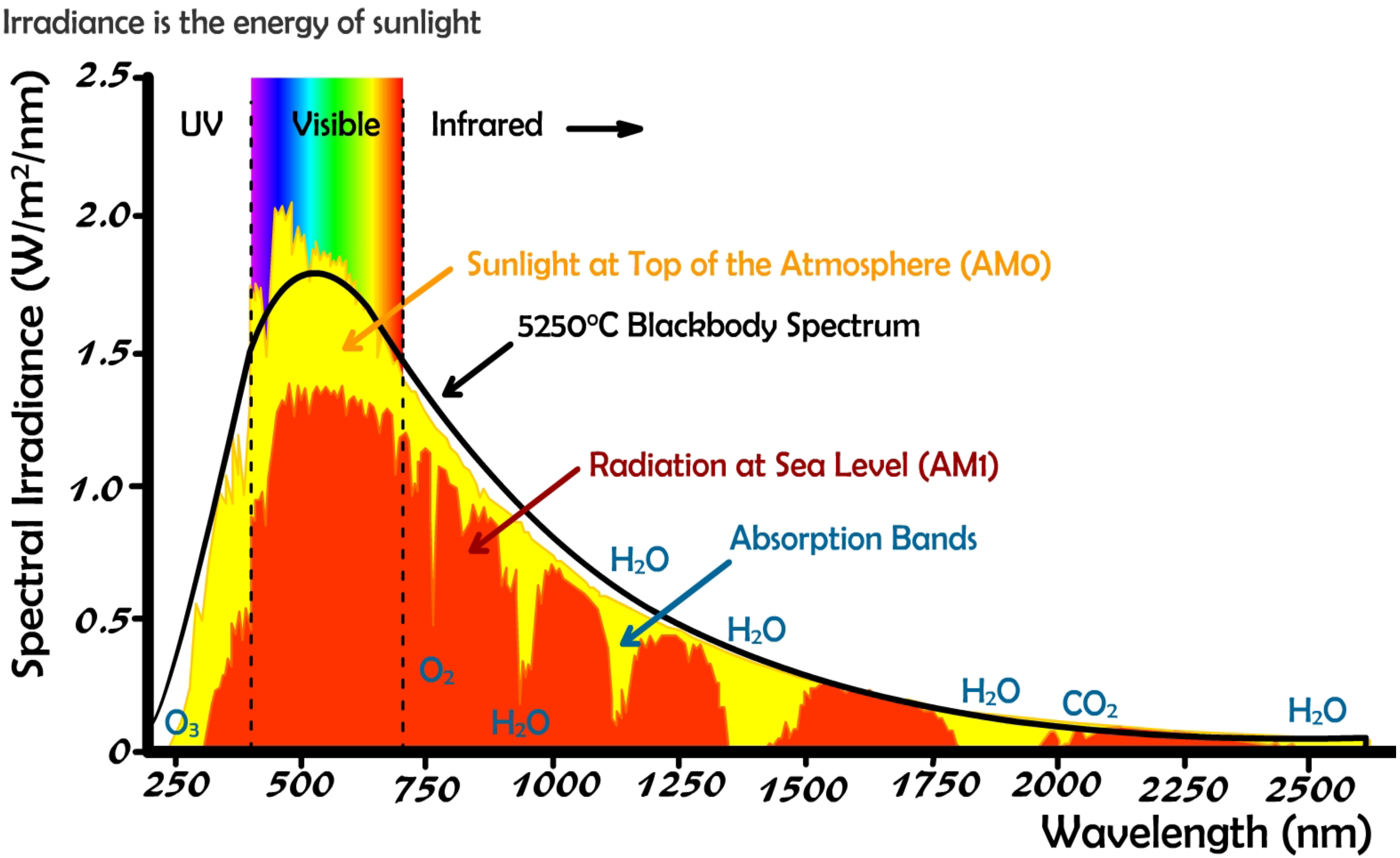


Sun behaves nearly as a black body of temperature ~ 6000K in these spectral regions

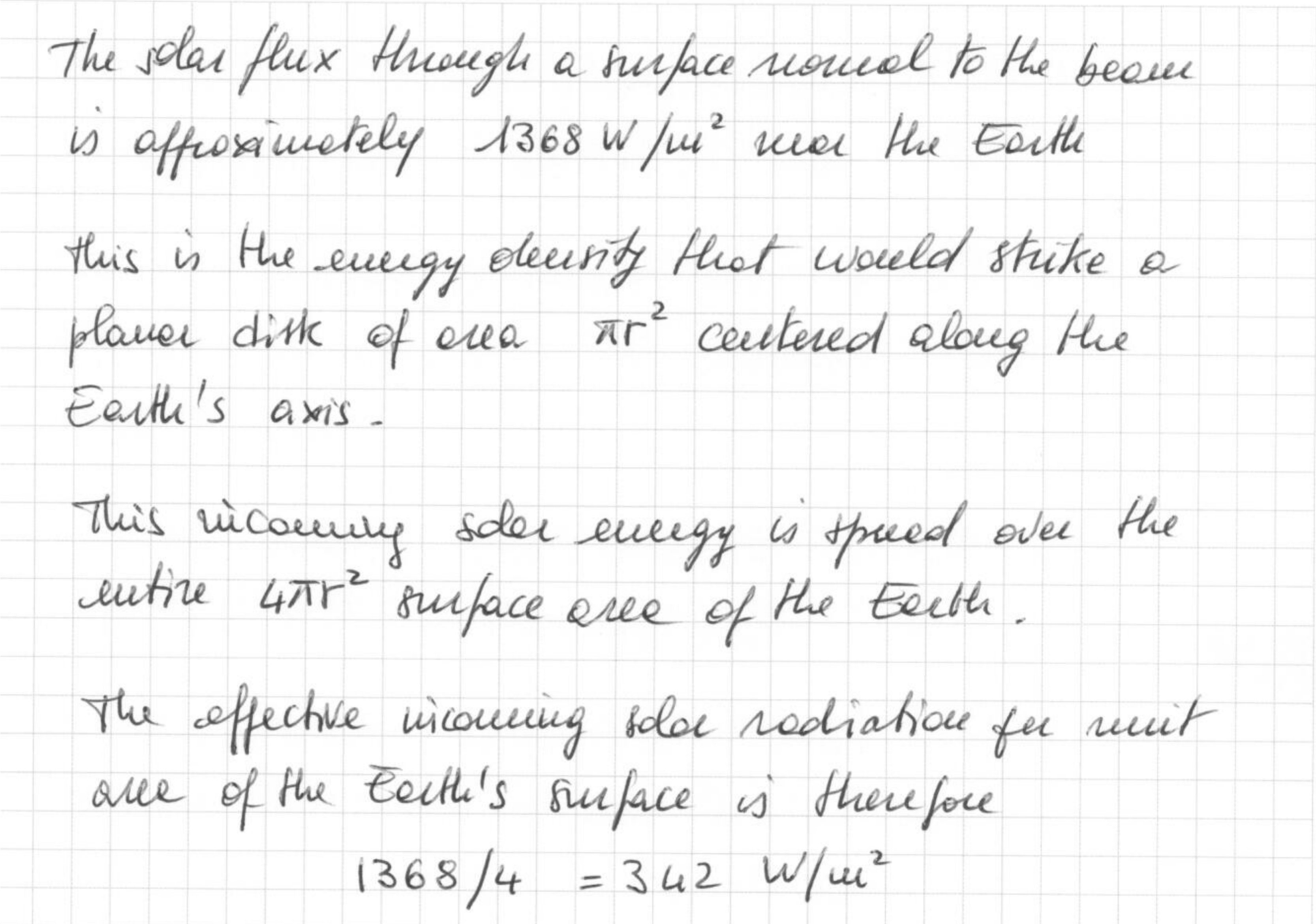
There is much greater emission in the X-ray, far ultraviolet, and radio spectral regions that a black body would allow

The total amount of energy for all wavelenghts intercepted in unit time by unit surface area at top of the Earth's atmosphere is known as the solar constant

Radiative balance in the atmosphere



Radiative balance in the atmosphere



The solar flux through a surface normal to the beam is approximately 1368 W/m^2 near the Earth

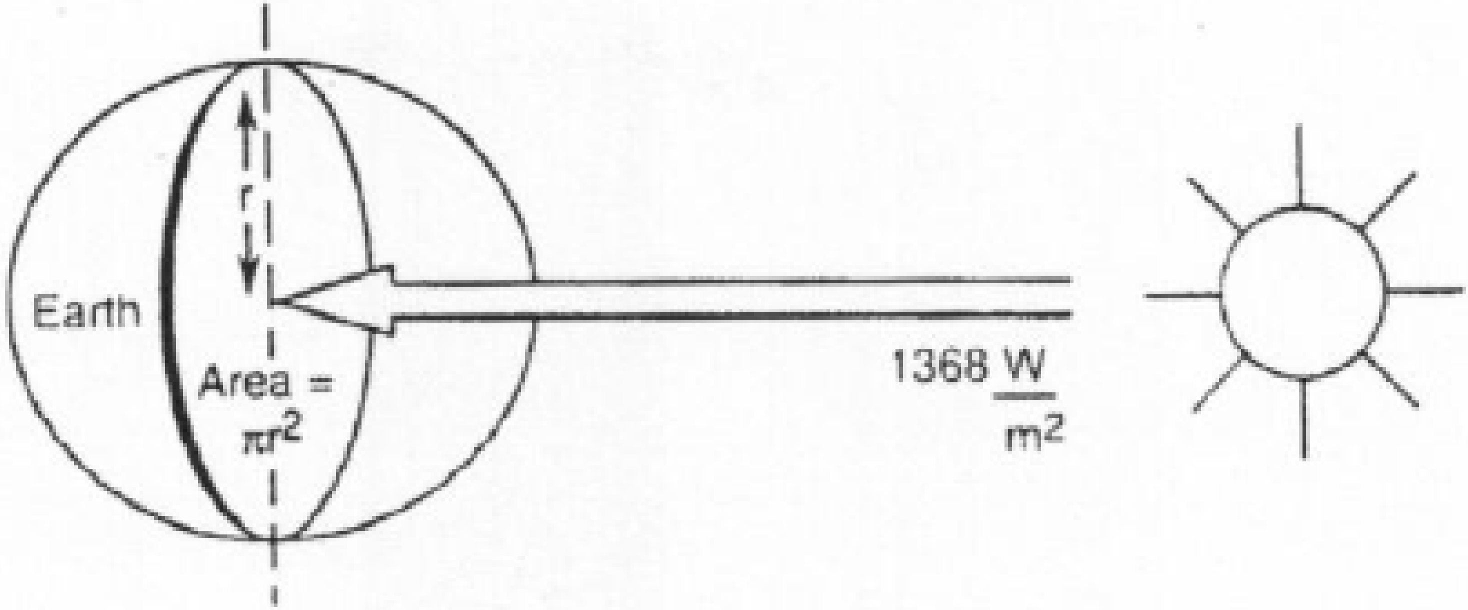
this is the energy density that would strike a planar disk of area πr^2 centered along the Earth's axis.

This incoming solar energy is spread over the entire $4\pi r^2$ surface area of the Earth.

The effective incoming solar radiation per unit area of the Earth's surface is therefore

$$1368/4 = 342 \text{ W/m}^2$$

Radiative balance in the atmosphere



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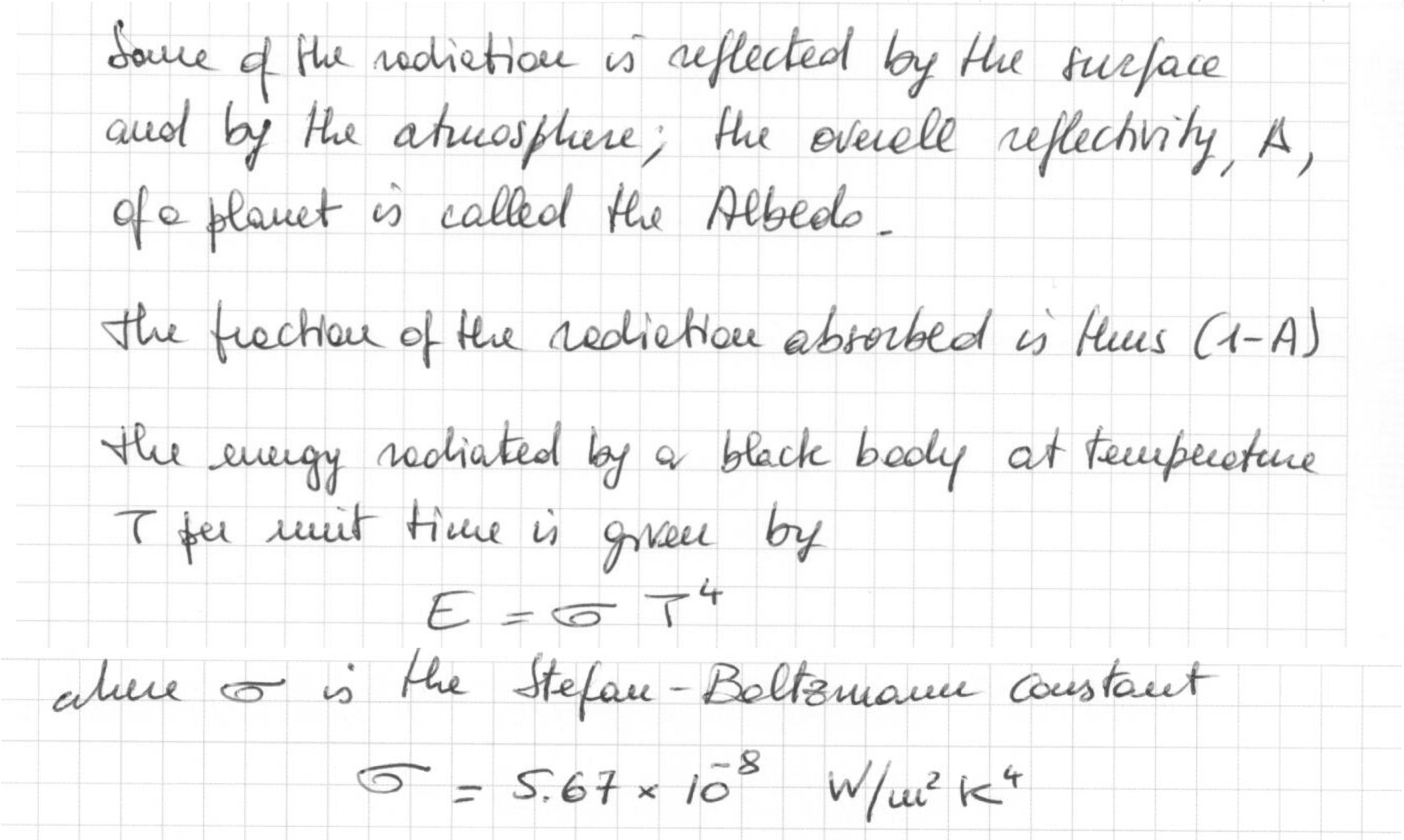
Radiative balance in the atmosphere



Some of the radiation is reflected by the surface and by the atmosphere; the overall reflectivity, A, of a planet is called the Albedo.

the fraction of the radiation absorbed is thus (1-A)

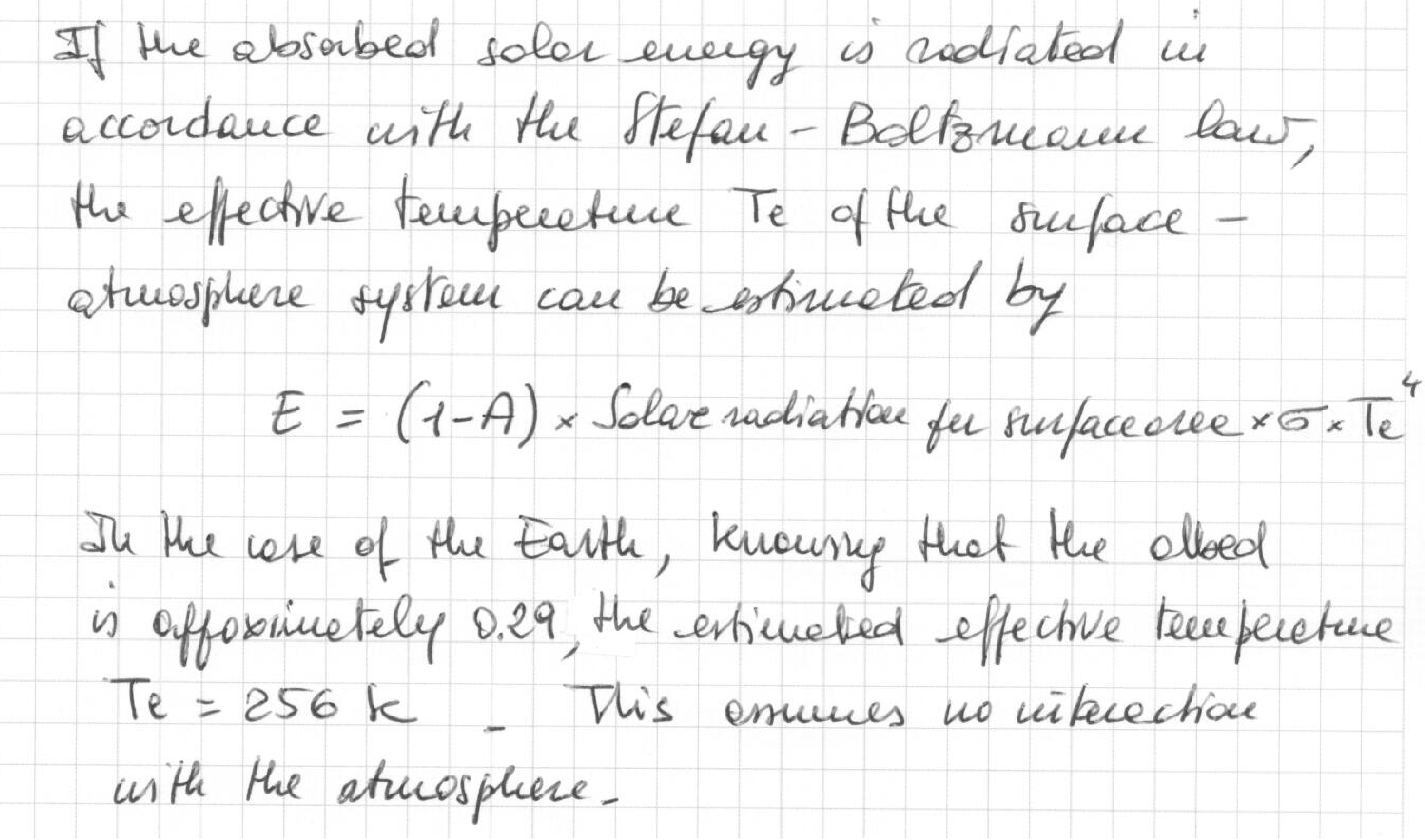
the energy radiated by a black body at temperature T per unit time is given by

$$E = \sigma T^4$$

where σ is the Stefan-Boltzmann constant

$$\sigma = 5.67 \times 10^{-8} \quad W/m^2 K^4$$

Radiative balance in the atmosphere

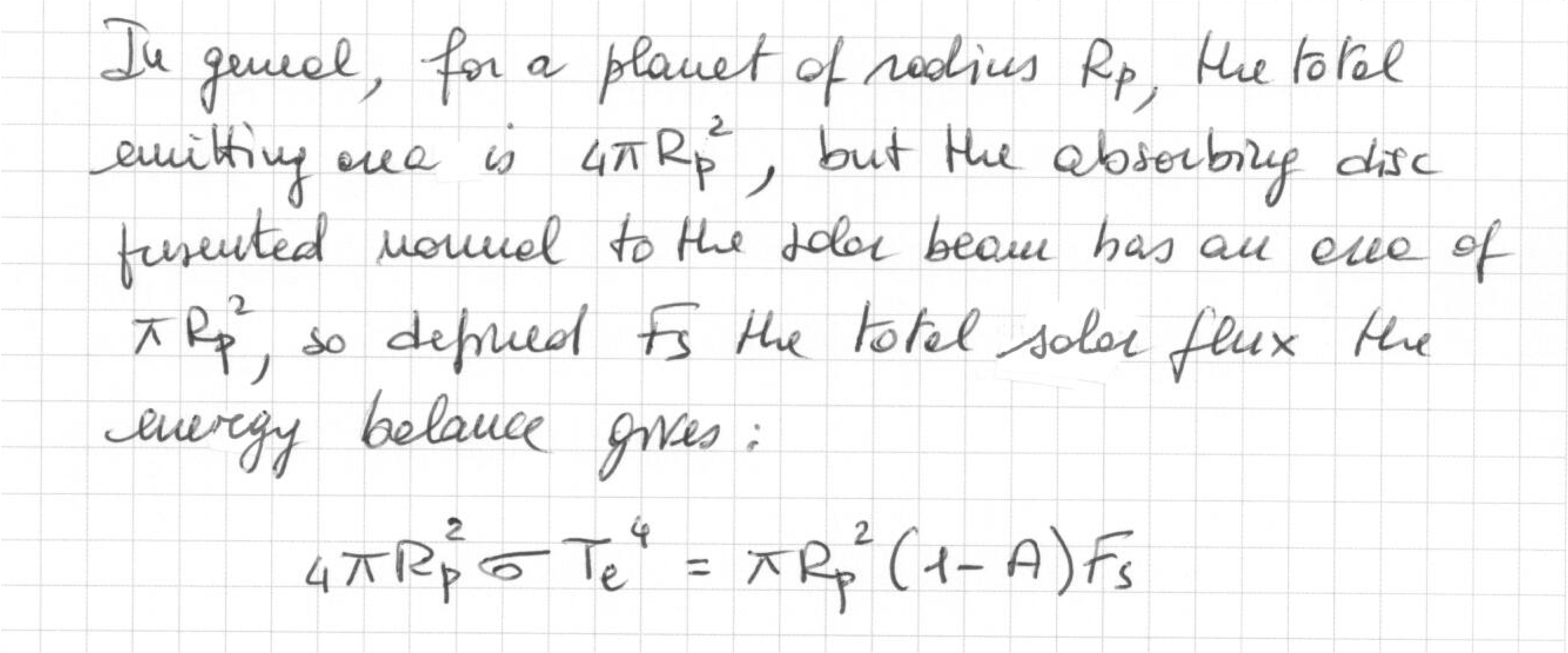


If the absorbed solar energy is radiated in accordance with the Stefan-Boltzmann law, the effective temperature Te of the surface-atmosphere system can be estimated by

$$E = (1-A) \times \text{Solar radiation per surface area} \times \sigma \times Te^4$$

In the case of the Earth, knowing that the albedo is approximately 0.29, the estimated effective temperature Te = 256 K. This ensures no interaction with the atmosphere.

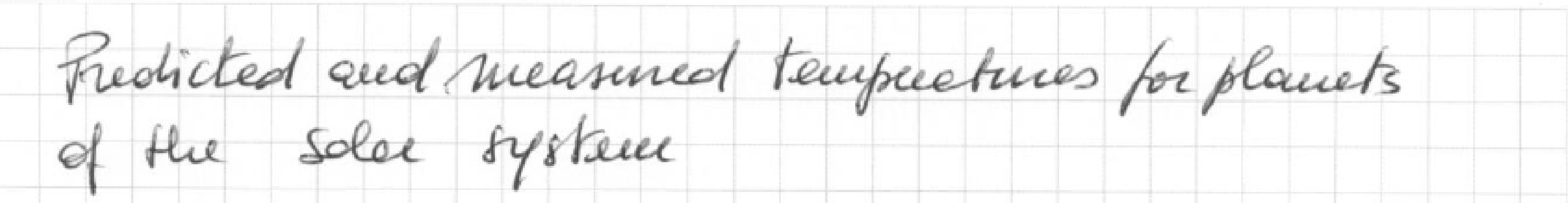
Radiative balance in the atmosphere



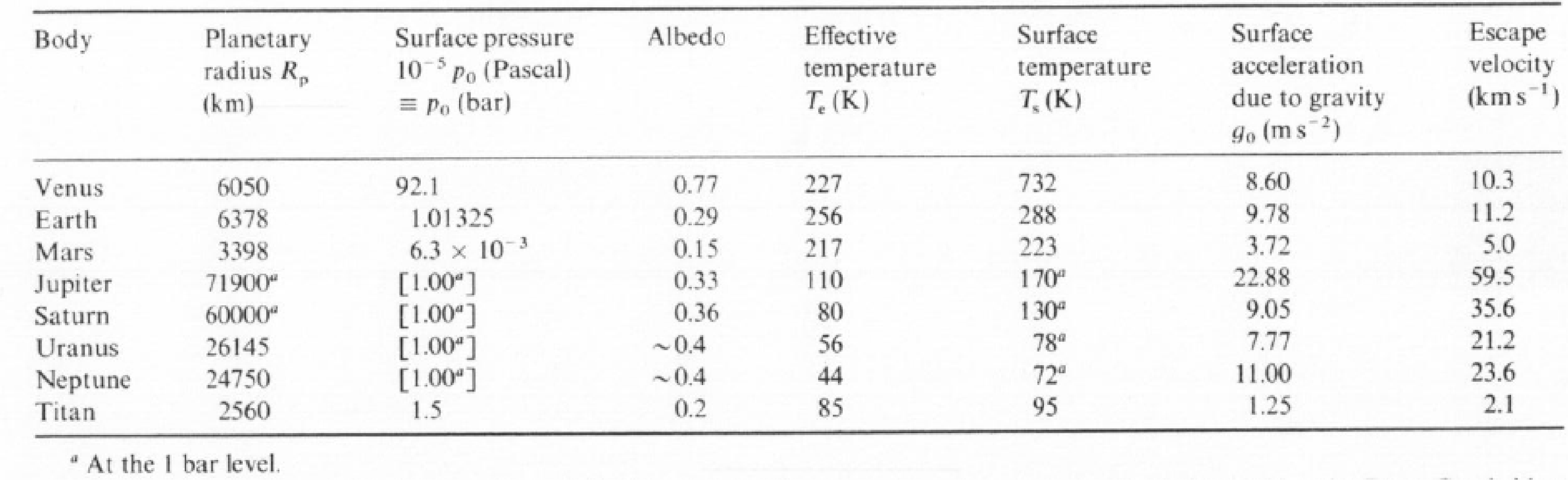
In general, for a planet of radius R_p, the total emitting area is $4\pi R_p^2$, but the absorbing disc presented normal to the solar beam has an area of πR_p^2, so defined F_s the total solar flux the energy balance gives:

$$4\pi R_p^2 \sigma T_e^4 = \pi R_p^2 (1-A) F_s$$

Radiative balance in the atmosphere



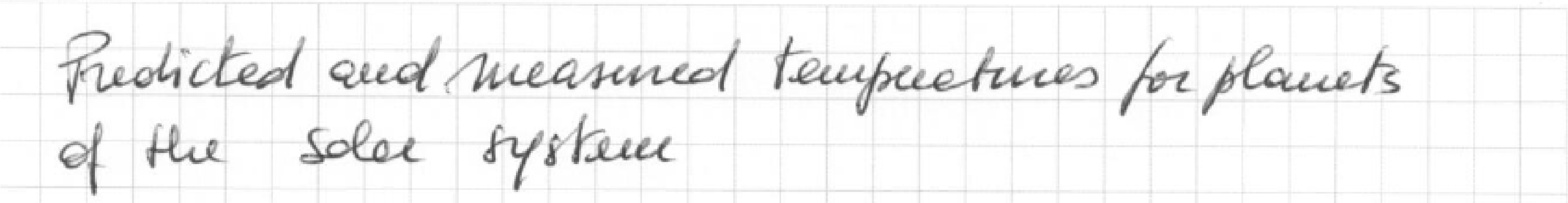
Predicted and measured temperatures for planets of the solar system



Body	Planetary radius R_p (km)	Surface pressure $10^{-5} p_0$ (Pascal) $\equiv p_0$ (bar)	Albedo	Effective temperature T_e (K)	Surface temperature T_s (K)	Surface acceleration due to gravity g_0 ($\mathrm{m\,s^{-2}}$)	Escape velocity ($\mathrm{km\,s^{-1}}$)
Venus	6050	92.1	0.77	227	732	8.60	10.3
Earth	6378	1.01325	0.29	256	288	9.78	11.2
Mars	3398	6.3×10^{-3}	0.15	217	223	3.72	5.0
Jupiter	71900[a]	[1.00[a]]	0.33	110	170[a]	22.88	59.5
Saturn	60000[a]	[1.00[a]]	0.36	80	130[a]	9.05	35.6
Uranus	26145	[1.00[a]]	~0.4	56	78[a]	7.77	21.2
Neptune	24750	[1.00[a]]	~0.4	44	72[a]	11.00	23.6
Titan	2560	1.5	0.2	85	95	1.25	2.1

[a] At the 1 bar level.

Radiative balance in the atmosphere



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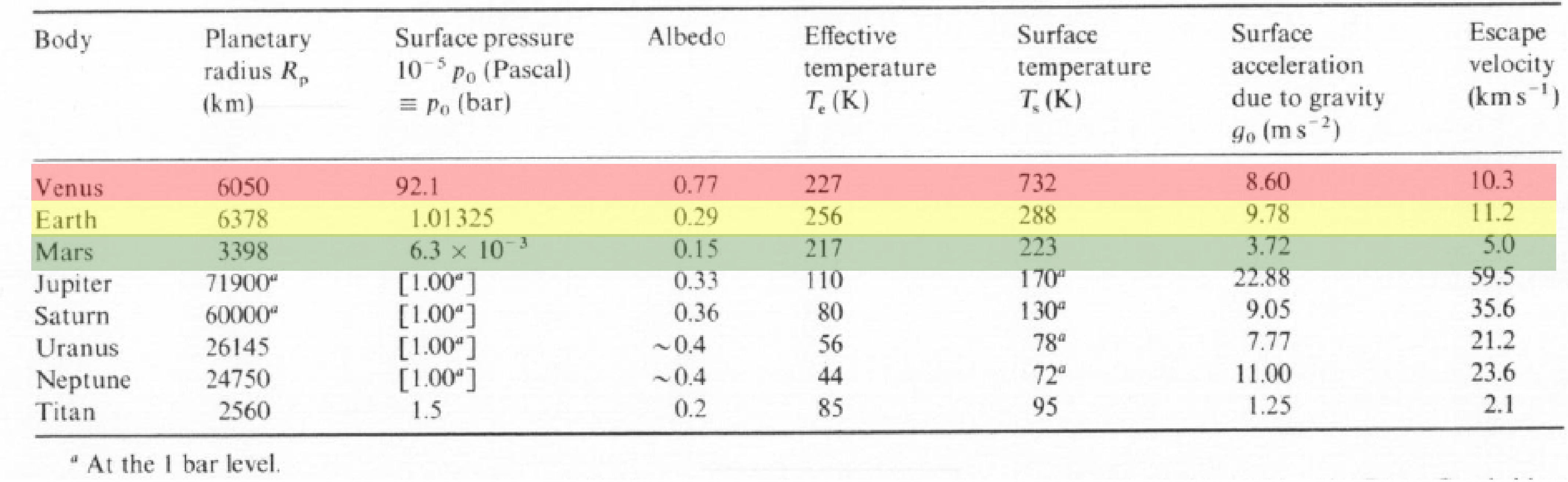

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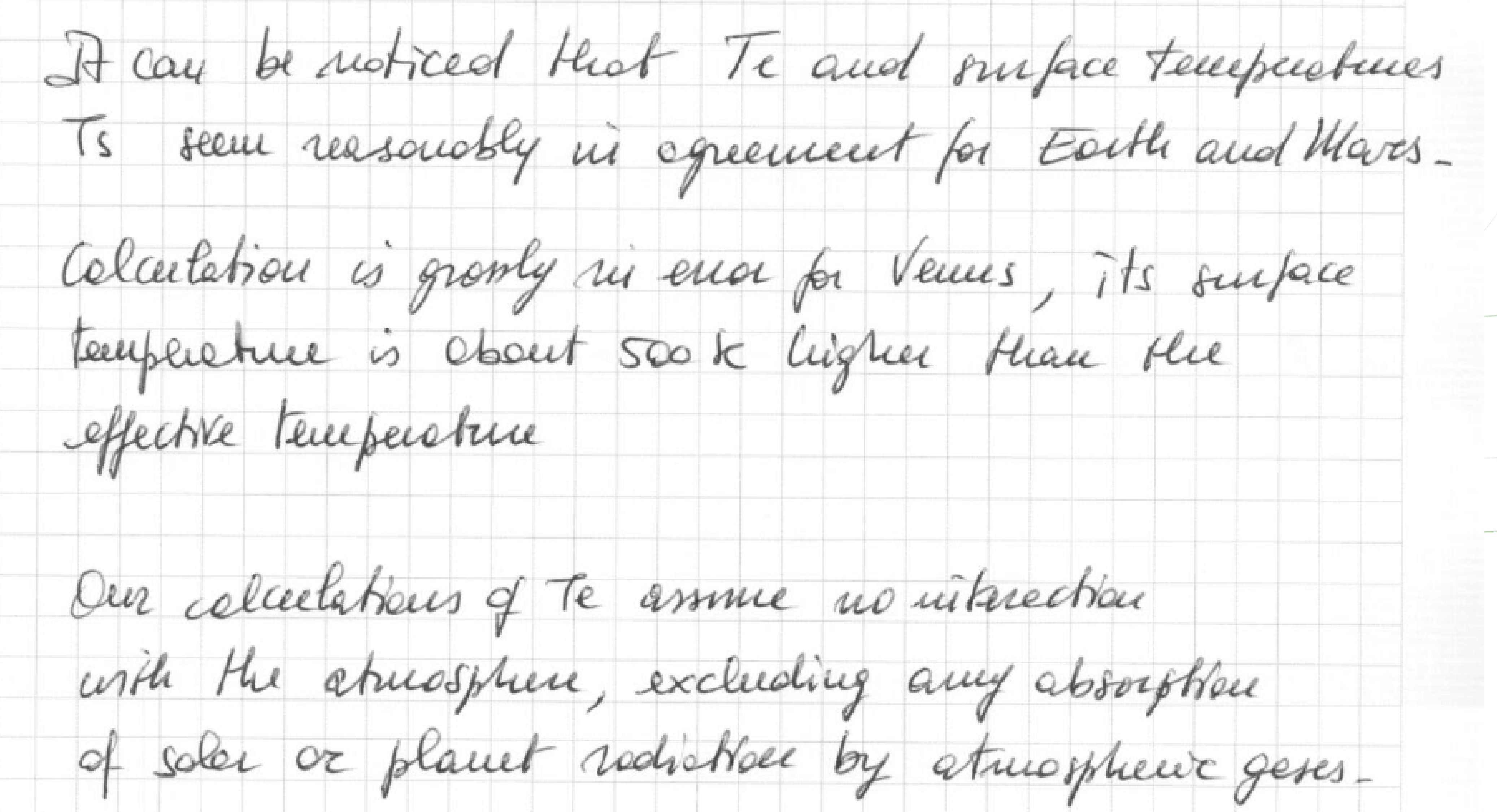
Radiative balance in the atmosphere

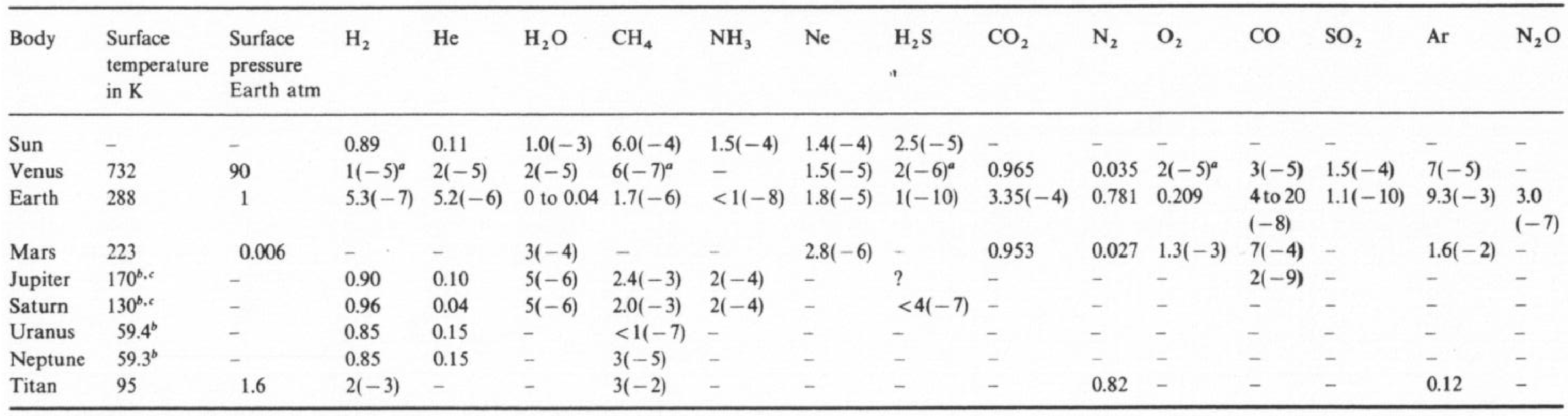


It can be noticed that T_e and surface temperatures T_s seem reasonably in agreement for Earth and Mars.

Calculation is grossly in error for Venus, its surface temperature is about 500 K higher than the effective temperature

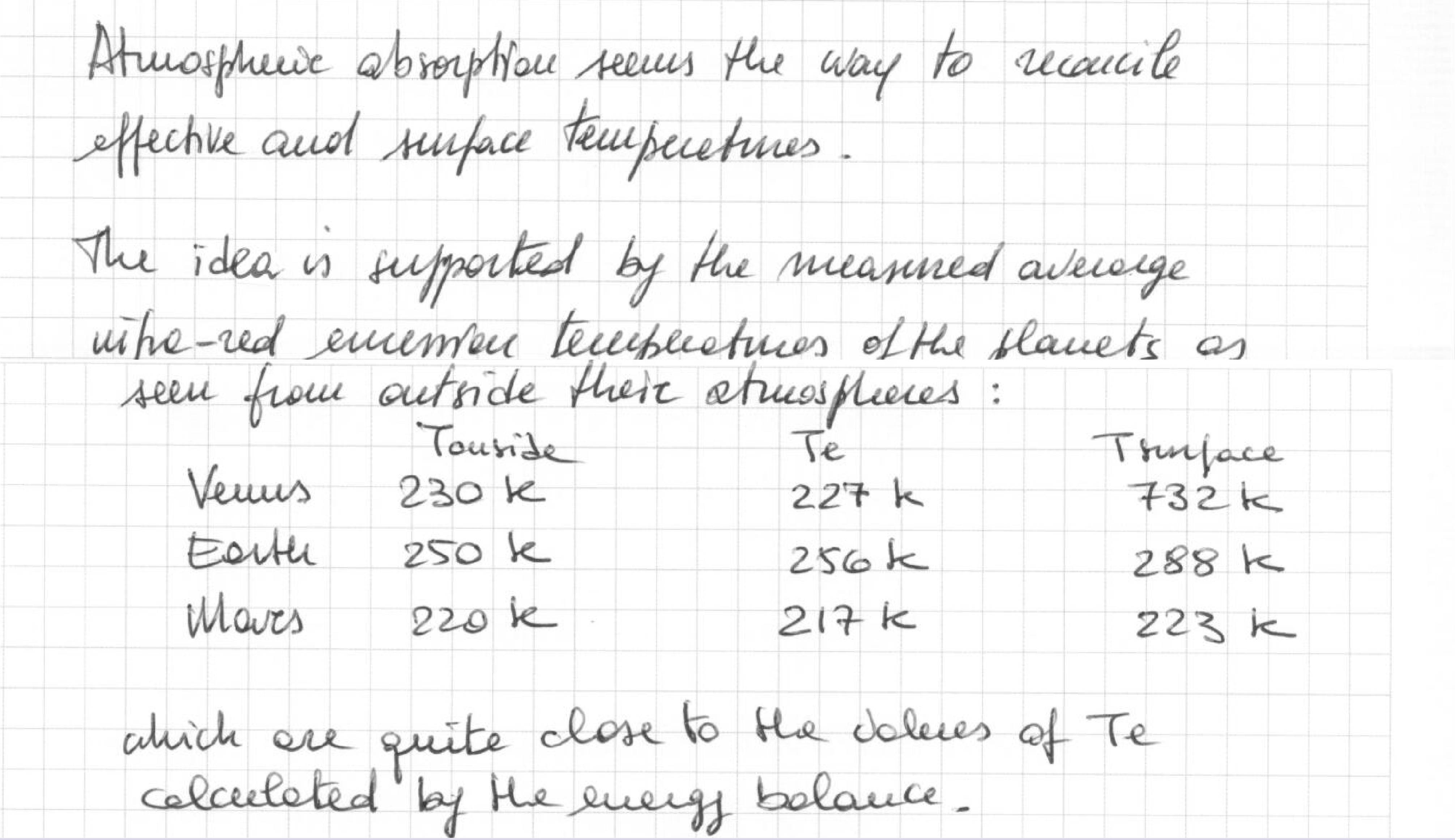
Our calculations of T_e assume no interaction with the atmosphere, excluding any absorption of solar or planet radiation by atmospheric gases.

Radiative balance in the atmosphere



Body	Surface temperature in K	Surface pressure Earth atm	H_2	He	H_2O	CH_4	NH_3	Ne	H_2S	CO_2	N_2	O_2	CO	SO_2	Ar	N_2O
Sun	–	–	0.89	0.11	1.0(–3)	6.0(–4)	1.5(–4)	1.4(–4)	2.5(–5)	–	–	–	–	–	–	–
Venus	732	90	$1(-5)^a$	2(–5)	2(–5)	$6(-7)^a$	–	1.5(–5)	$2(-6)^a$	0.965	0.035	$2(-5)^a$	3(–5)	1.5(–4)	7(–5)	–
Earth	288	1	5.3(–7)	5.2(–6)	0 to 0.04	1.7(–6)	<1(–8)	1.8(–5)	1(–10)	3.35(–4)	0.781	0.209	4 to 20 (–8)	1.1(–10)	9.3(–3)	3.0 (–7)
Mars	223	0.006	–	–	3(–4)	–	–	2.8(–6)	–	0.953	0.027	1.3(–3)	7(–4)	–	1.6(–2)	–
Jupiter	$170^{b,c}$	–	0.90	0.10	5(–6)	2.4(–3)	2(–4)	–	?	–	–	–	2(–9)	–	–	–
Saturn	$130^{b,c}$	–	0.96	0.04	5(–6)	2.0(–3)	2(–4)	–	<4(–7)	–	–	–	–	–	–	–
Uranus	59.4^b	–	0.85	0.15	–	<1(–7)	–	–	–	–	–	–	–	–	–	–
Neptune	59.3^b	–	0.85	0.15	–	3(–5)	–	–	–	–	–	–	–	–	–	–
Titan	95	1.6	2(–3)	–	–	3(–2)	–	–	–	–	0.82	–	–	–	0.12	–

Radiative balance in the atmosphere



Atmospheric absorption seems the way to reconcile effective and surface temperatures.

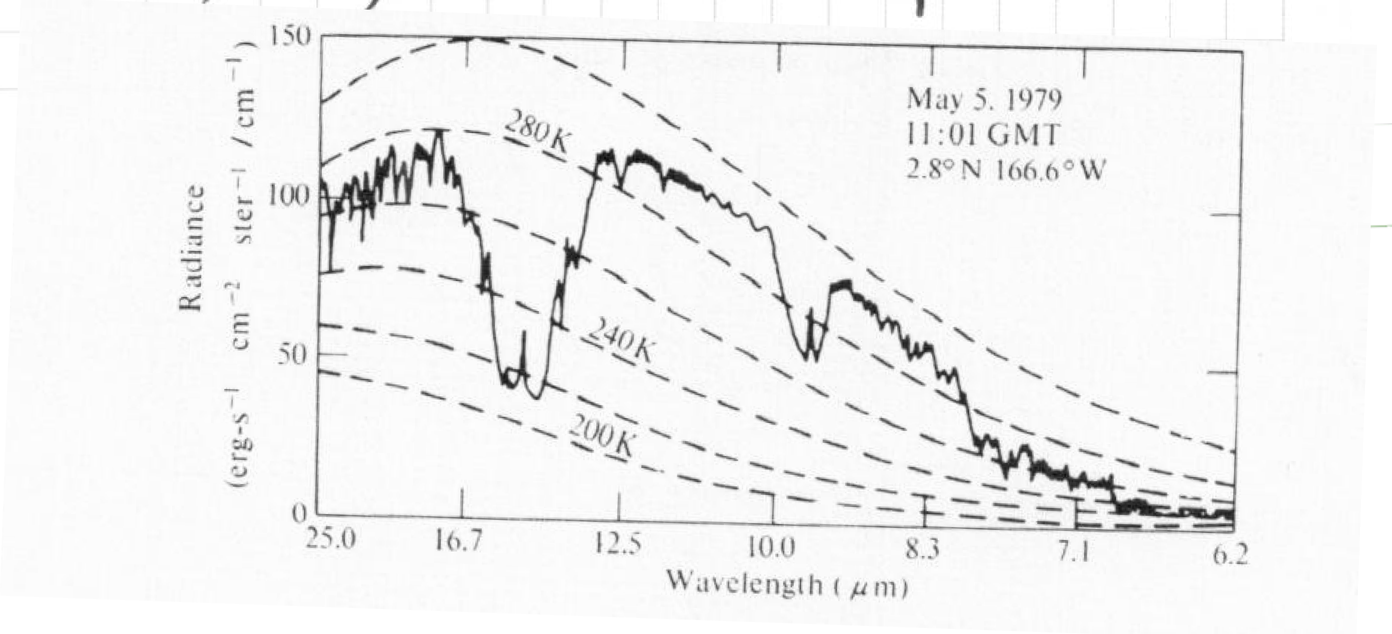
The idea is supported by the measured average infra-red emission temperatures of the planets as seen from outside their atmospheres :

	$T_{outside}$	T_e	$T_{surface}$
Venus	230 K	227 K	732 K
Earth	250 K	256 K	288 K
Mars	220 K	217 K	223 K

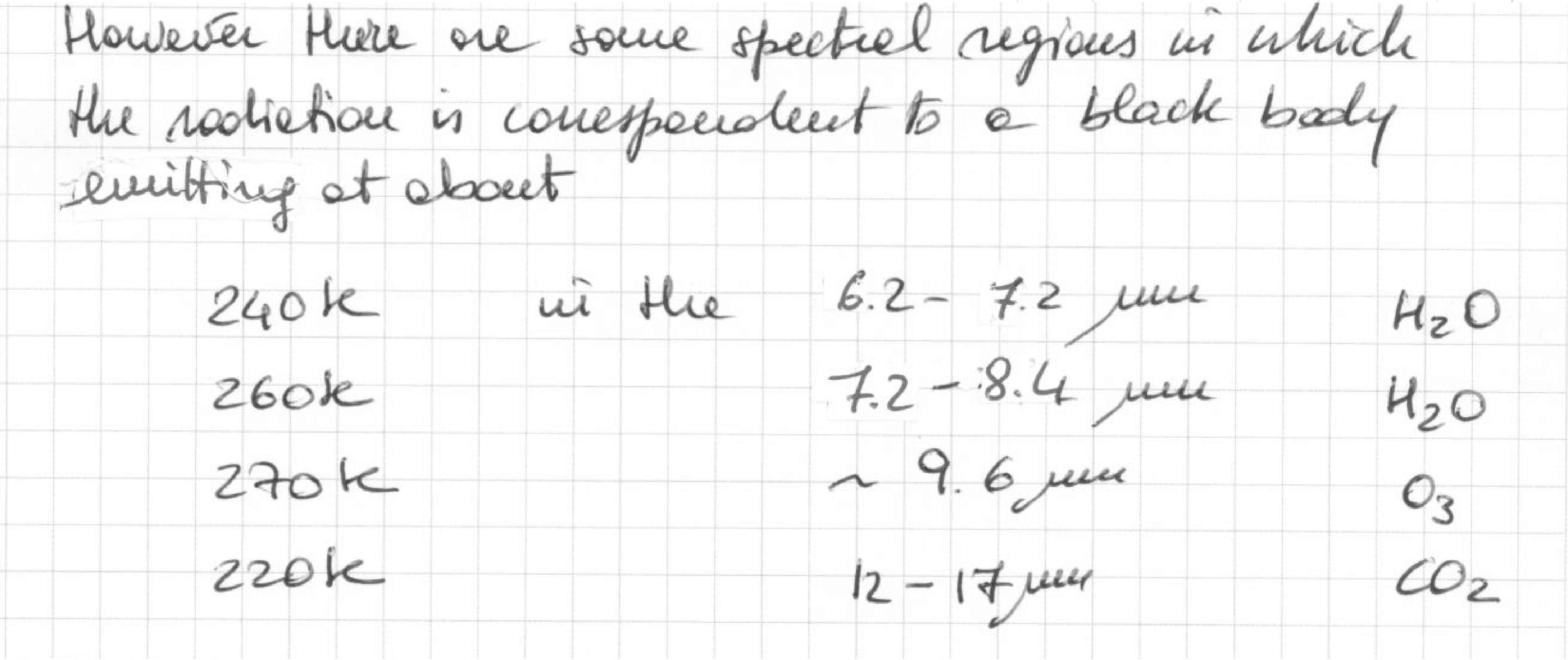
which are quite close to the values of Te calculated by the energy balance.

Radiative balance in the atmosphere

Looking at the low-resolution spectrum obtained by a satellite in a cloud-free field of view we observe that over some of the spectral region, the temperature of the black body emitting a similar radiation is approximately 288K, i.e., the near-surface temperature.



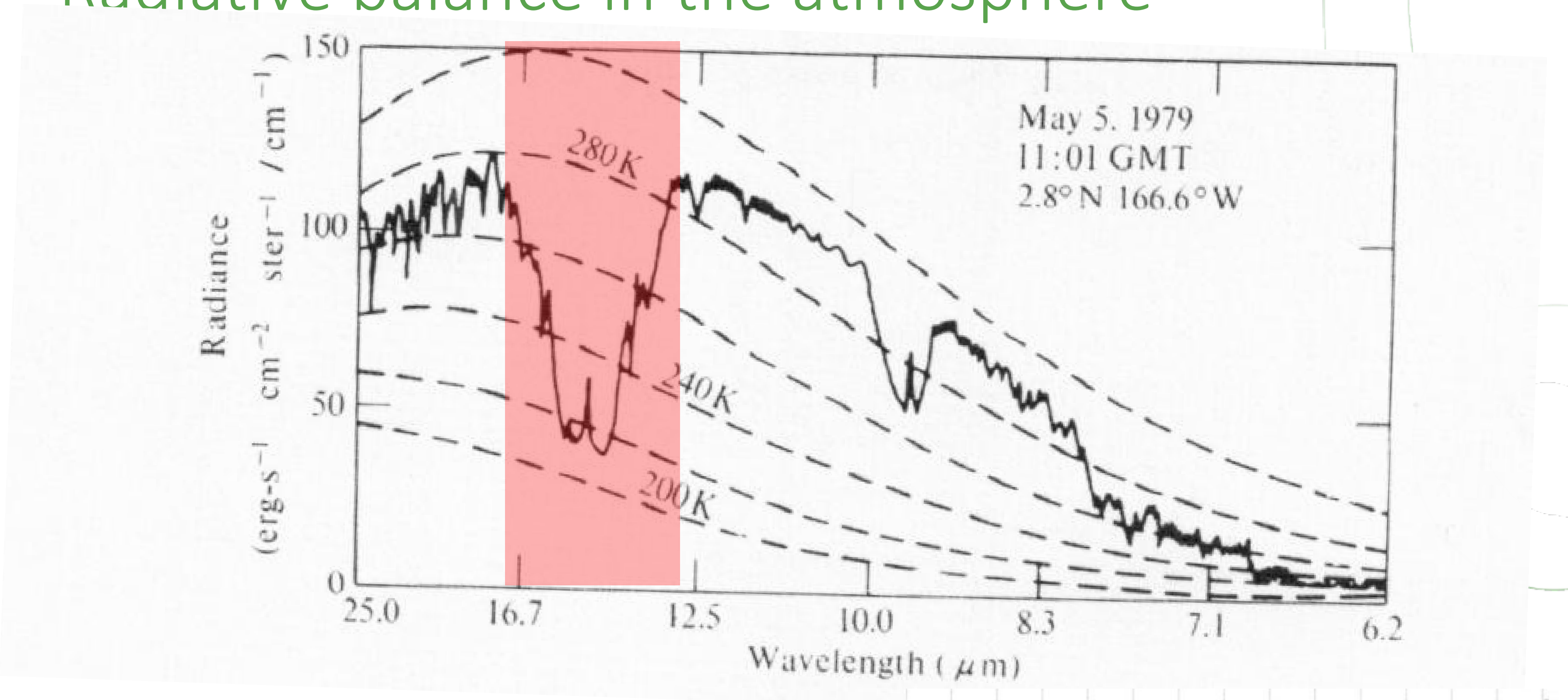
Radiative balance in the atmosphere



However there are some spectral regions in which the radiation is correspondent to a black body emitting at about

240 K	in the	6.2 – 7.2 μm	H_2O
260 K		7.2 – 8.4 μm	H_2O
270 K		~ 9.6 μm	O_3
220 K		12 – 17 μm	CO_2

Radiative balance in the atmosphere



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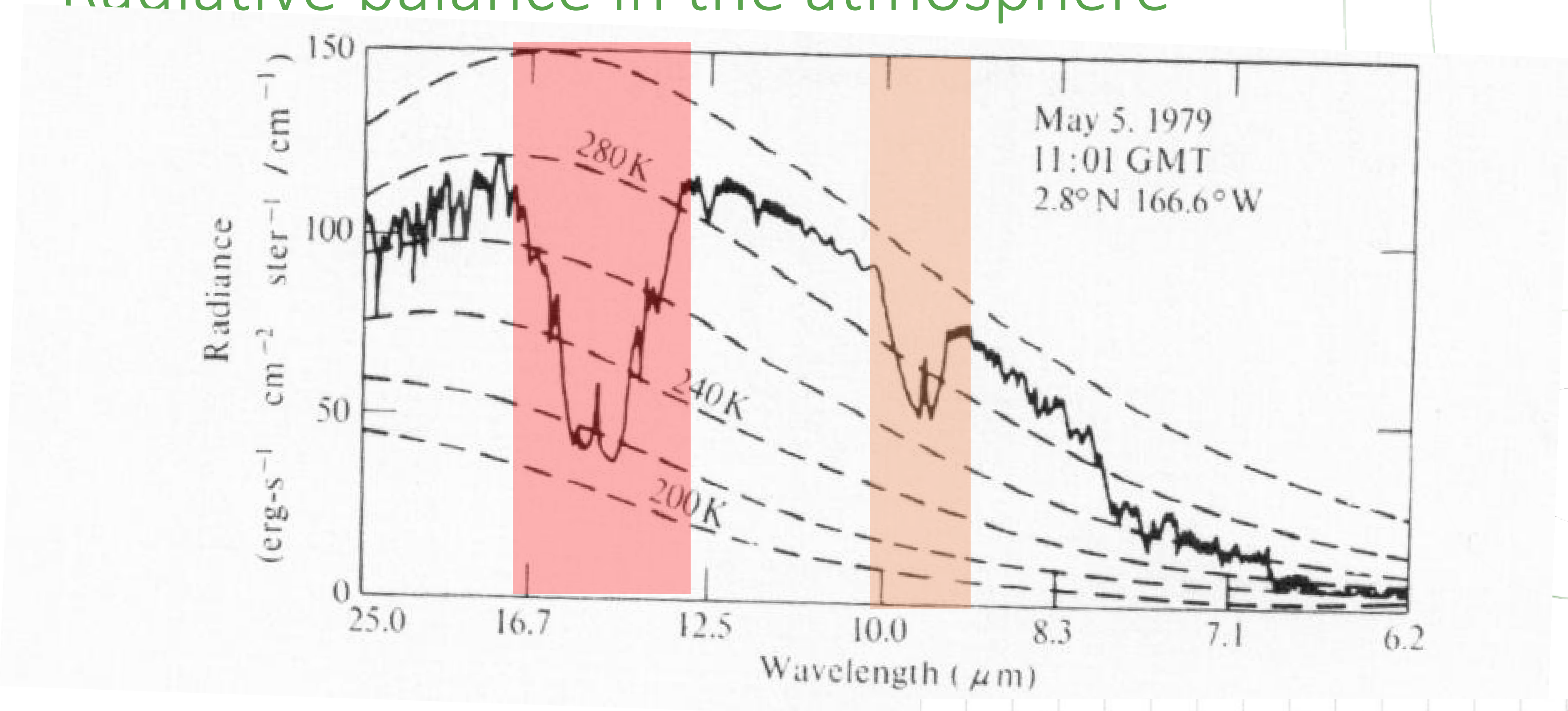

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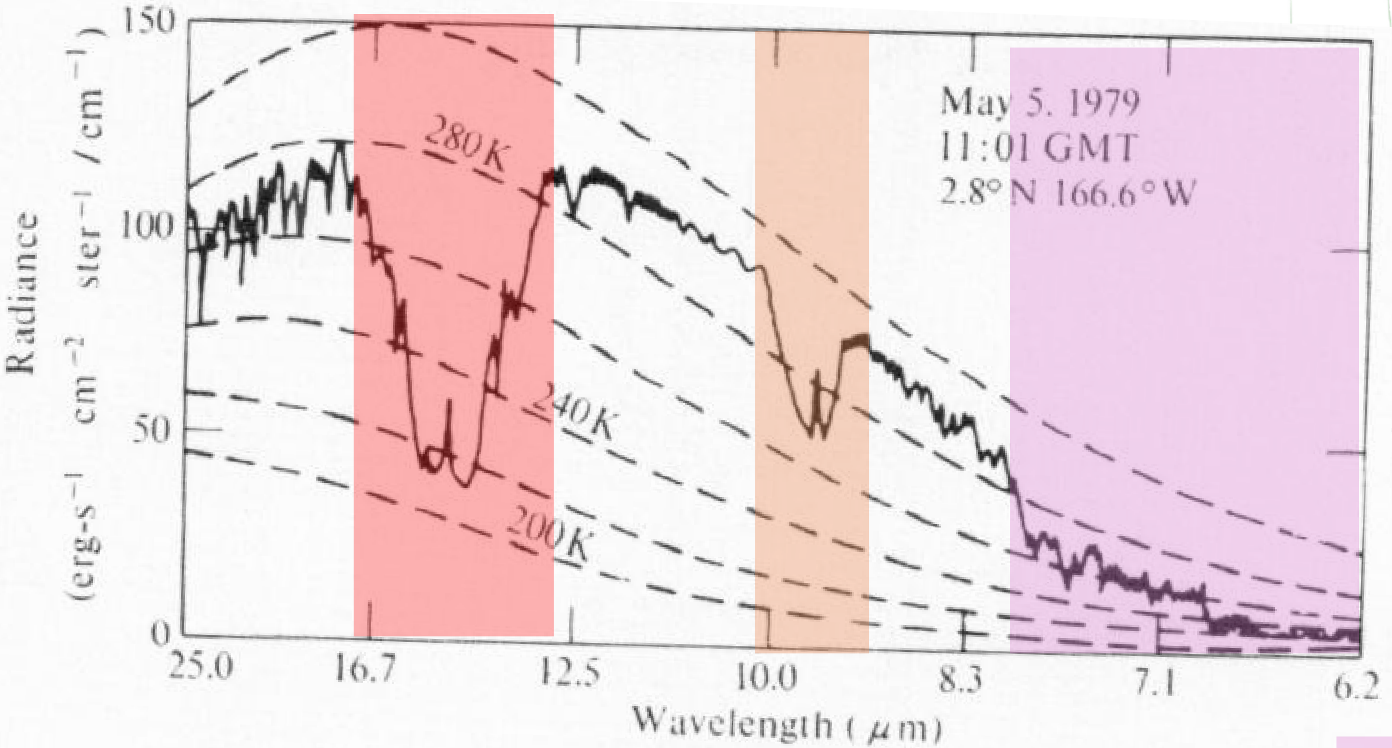
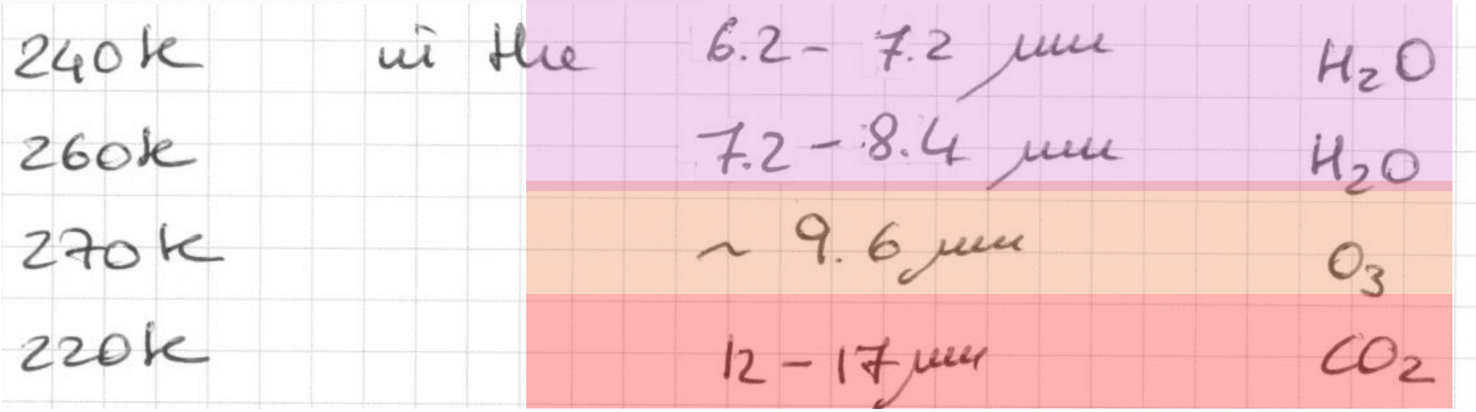


May 5. 1979
11:01 GMT
2.8° N 166.6° W



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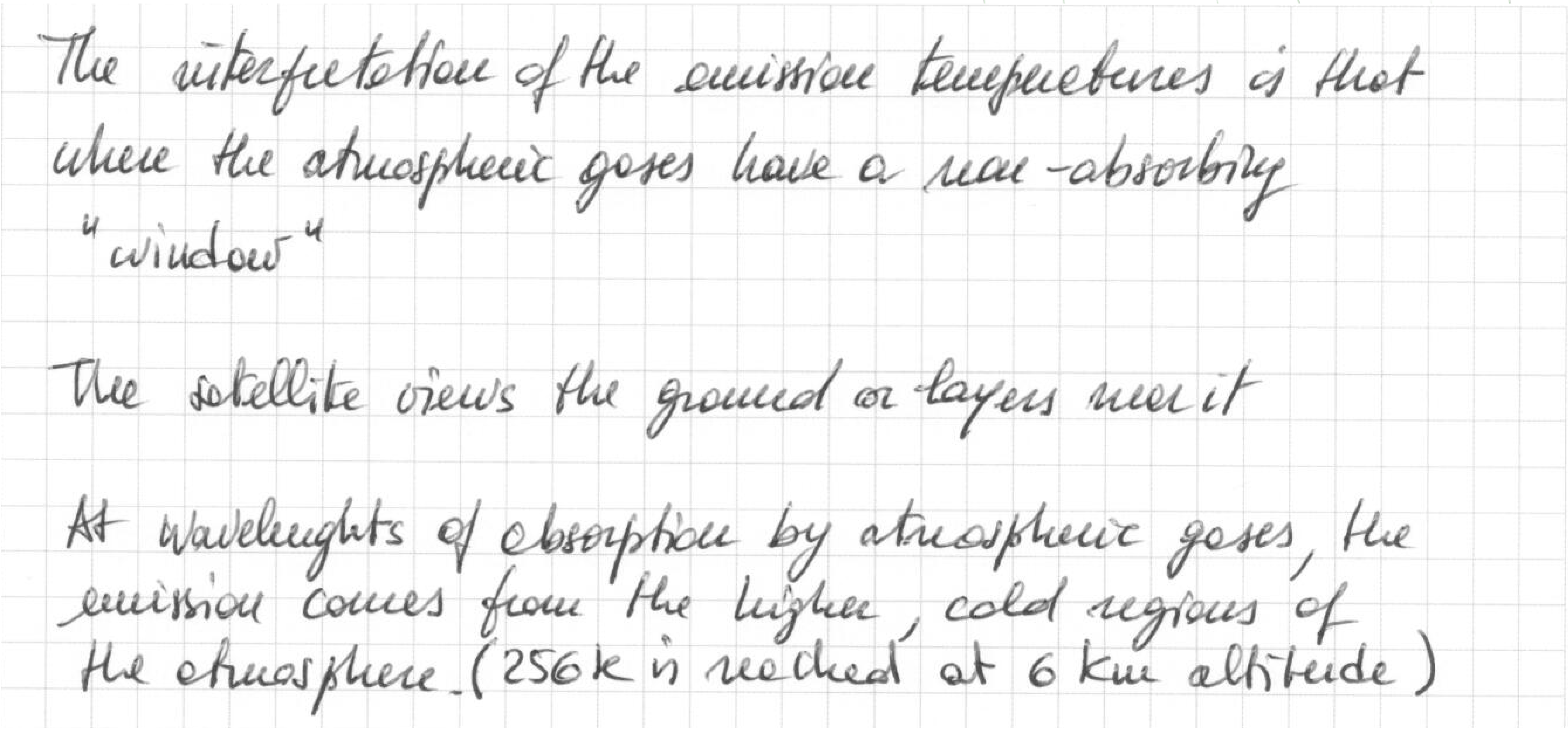
Radiative balance in the atmosphere

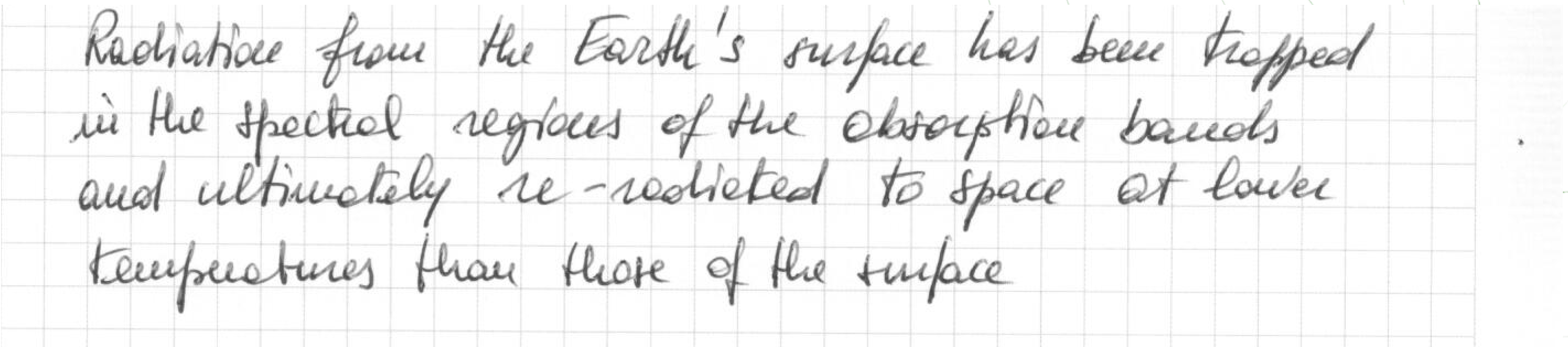


The interpretation of the emission temperatures is that where the atmospheric gases have a non-absorbing "window"

The satellite views the ground or layers near it

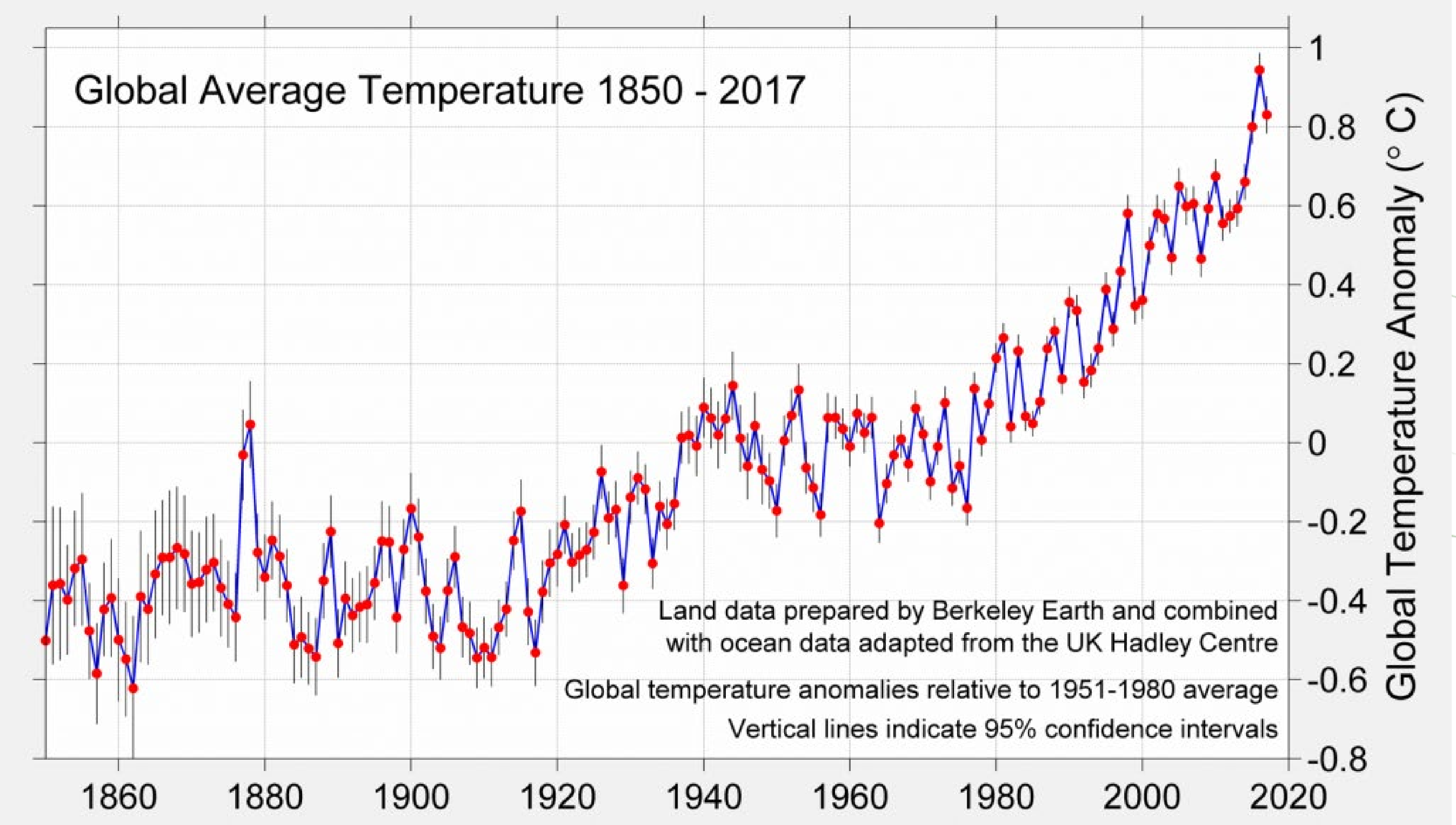
At wavelengths of absorption by atmospheric gases, the emission comes from the higher, cold regions of the atmosphere. (256k is reached at 6 km altitude)

Radiative balance in the atmosphere

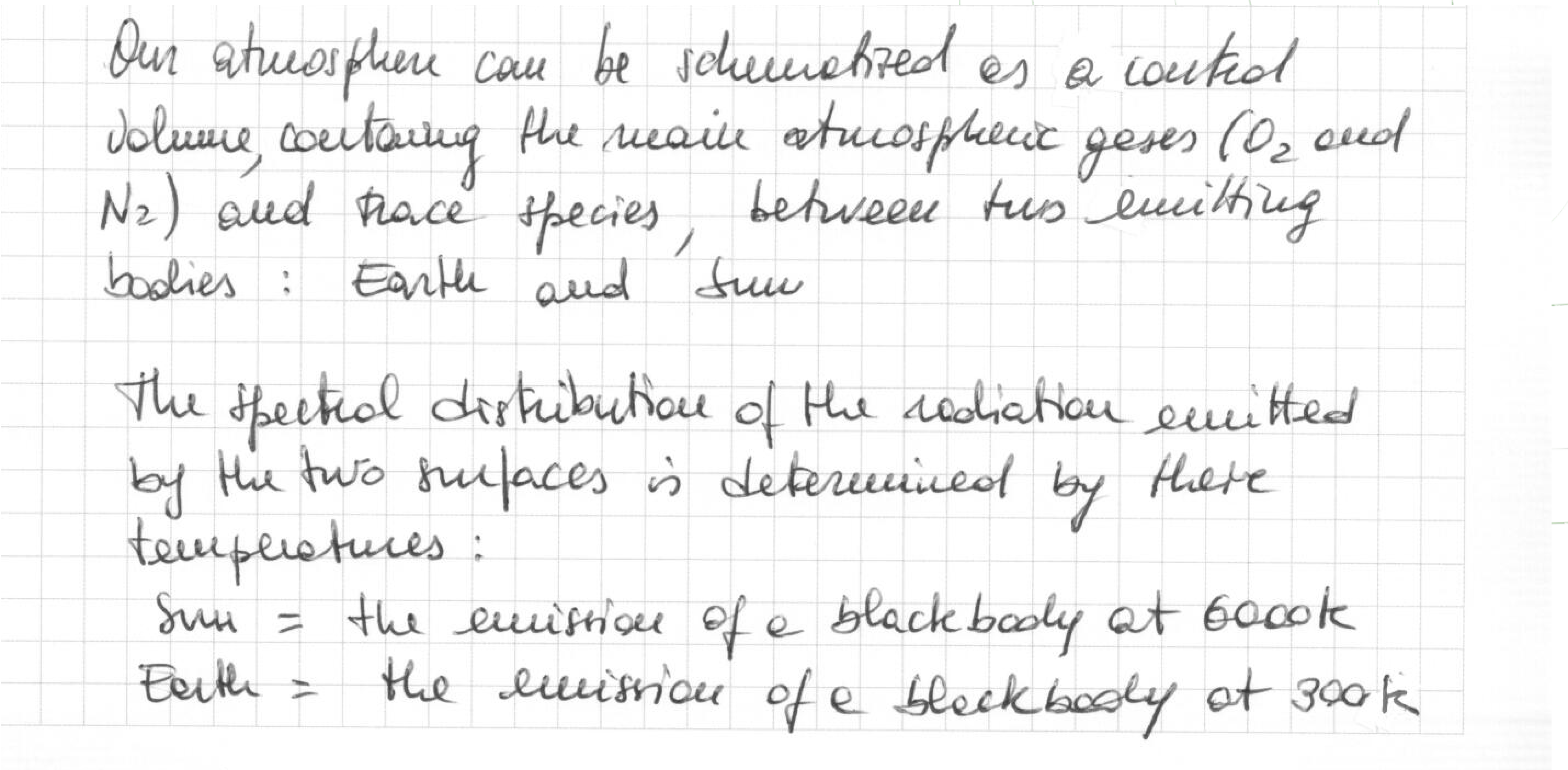


Radiation from the Earth's surface has been trapped in the spectral regions of the absorption bands and ultimately re-radiated to space at lower temperatures than those of the surface

Radiative balance in the atmosphere



Radiative balance in the atmosphere



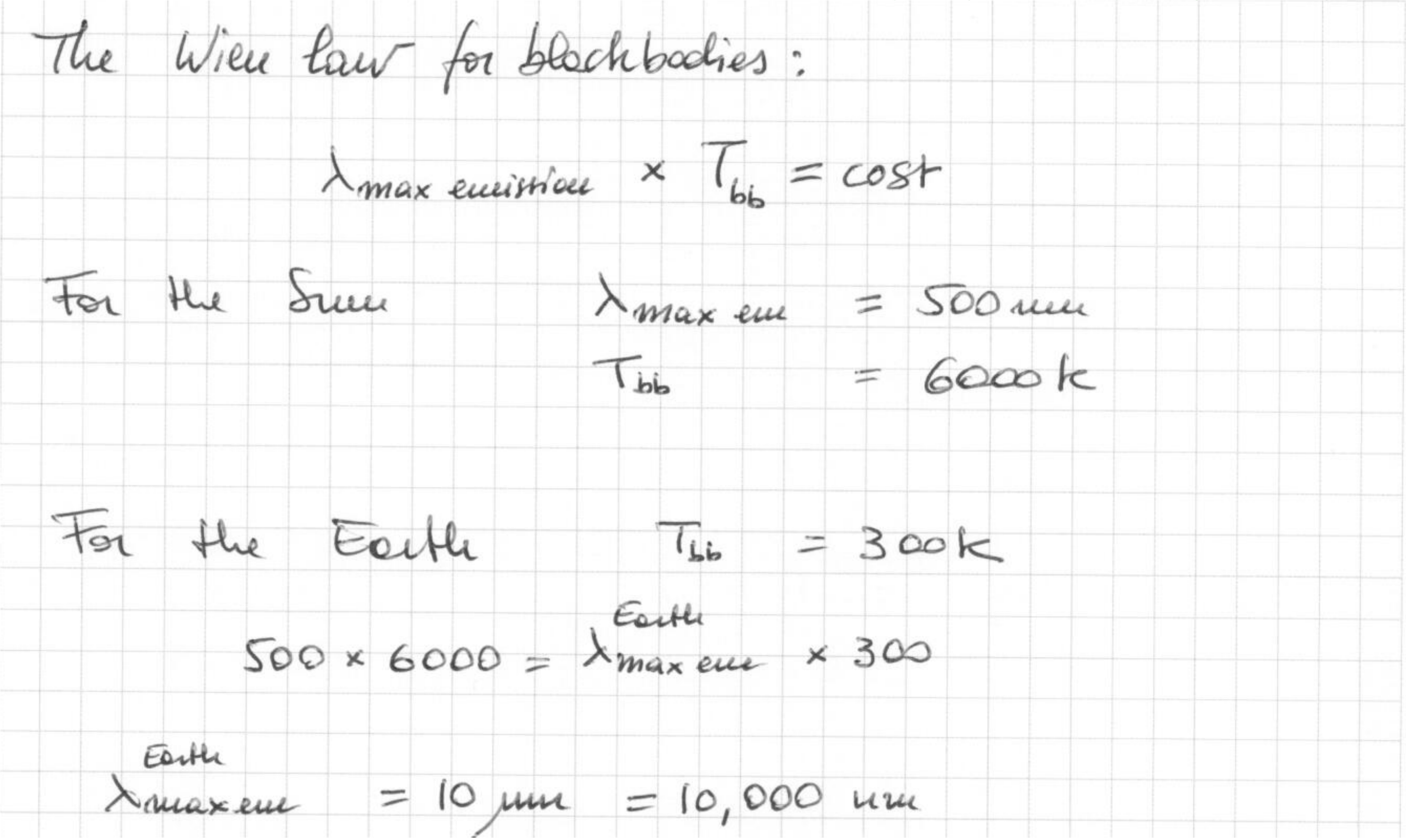
Our atmosphere can be schematized as a control volume, containing the main atmospheric gases (O_2 and N_2) and trace species, between two emitting bodies : Earth and Sun

The spectral distribution of the radiation emitted by the two surfaces is determined by there temperatures :

Sun = the emission of a blackbody at 6000K

Earth = the emission of a blackbody at 300K

Radiative balance in the atmosphere



The Wien law for blackbodies :

$$\lambda_{max\ emission} \times T_{bb} = cost$$

For the Sun $\lambda_{max\ em} = 500\ nm$

$T_{bb} = 6000\ k$

For the Earth $T_{bb} = 300\ k$

$$500 \times 6000 = \lambda^{Earth}_{max\ em} \times 300$$

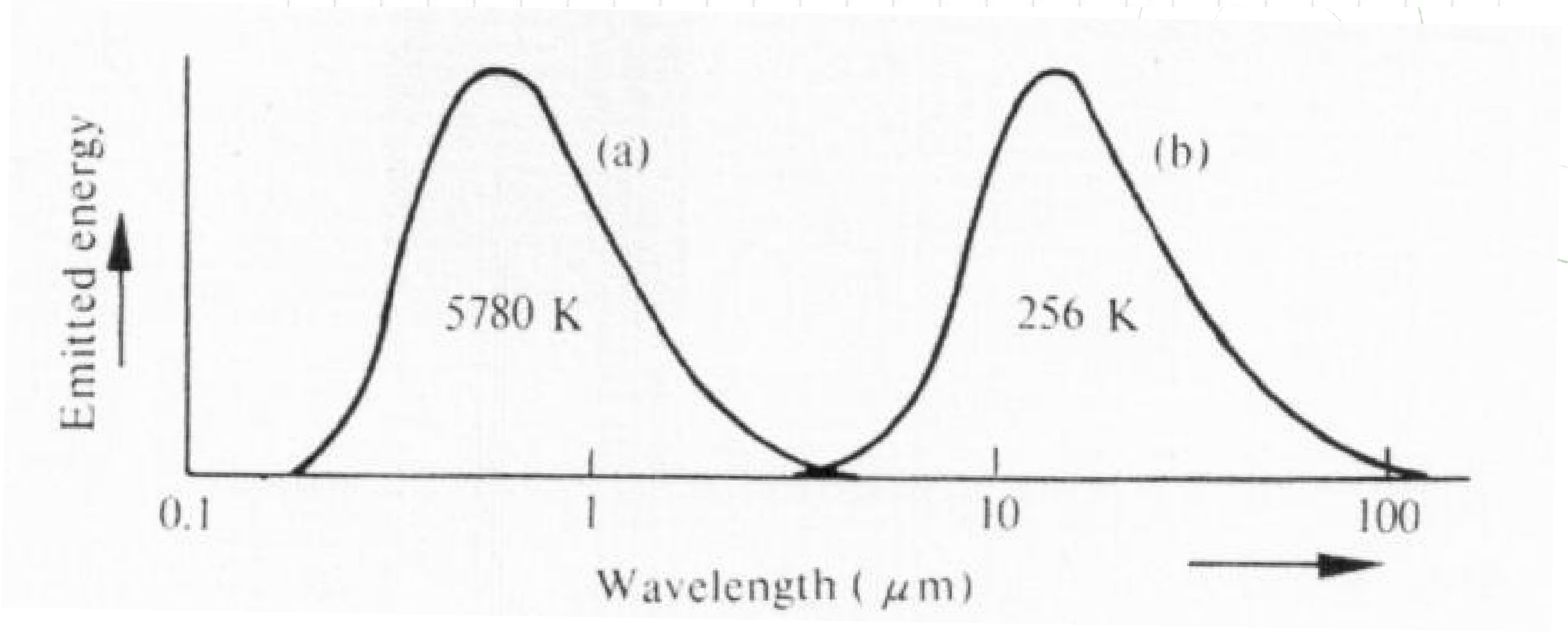
$$\lambda^{Earth}_{max\ em} = 10\ \mu m = 10{,}000\ nm$$

Radiative balance in the atmosphere

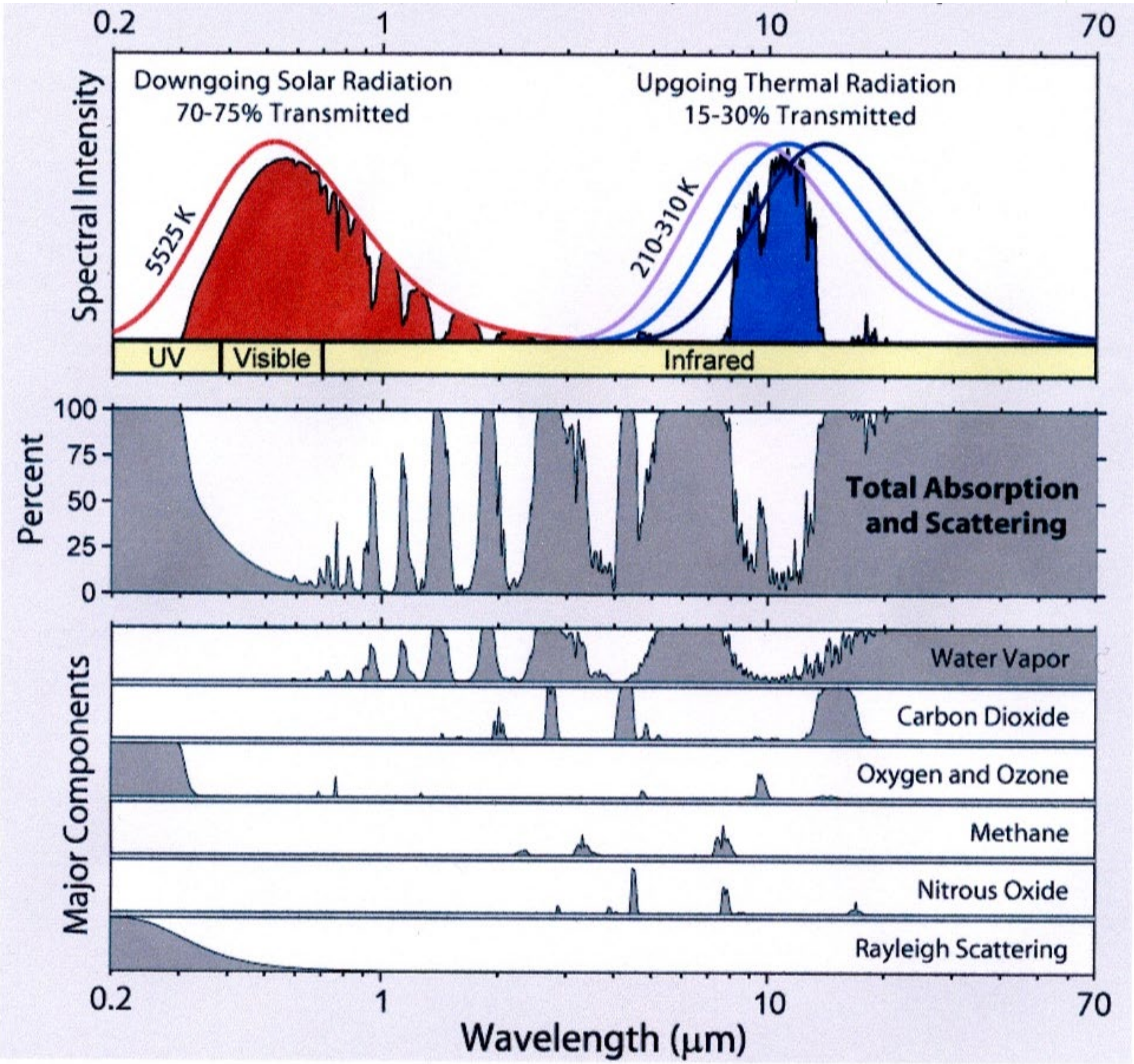
For the Sun $\lambda_{max\ em} = 500$ nm

$T_{bb} = 6000$ k

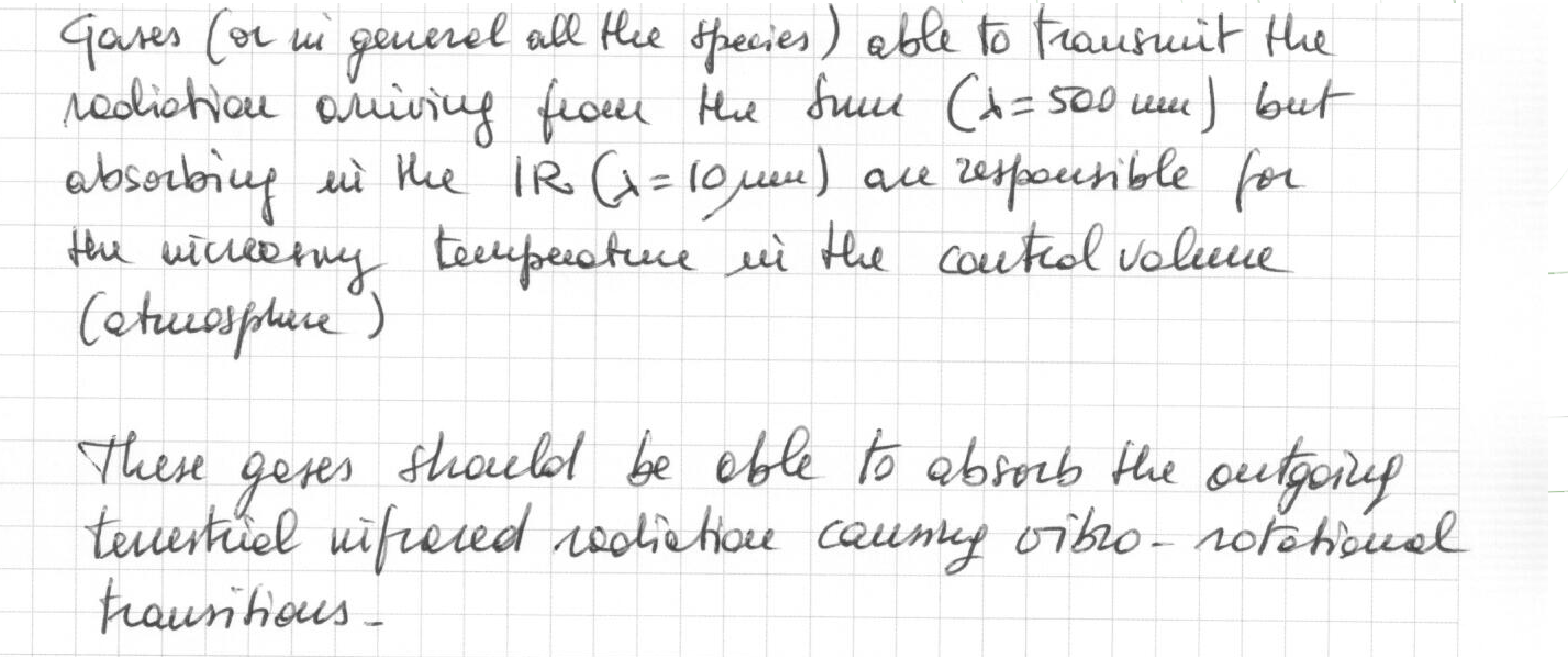
For the Earth $T_{bb} = 300$ k



Radiative balance in the atmosphere



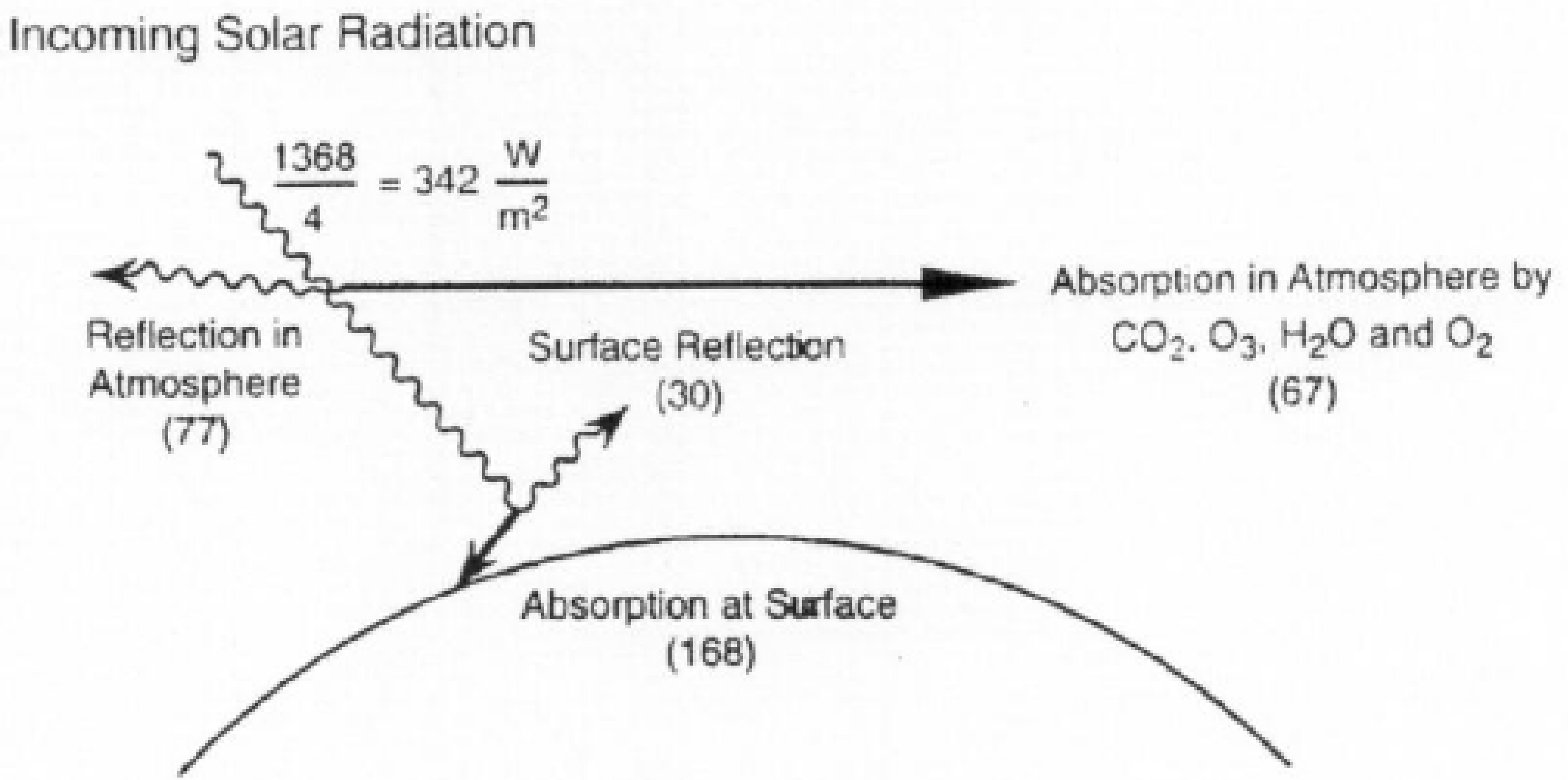
Radiative balance in the atmosphere



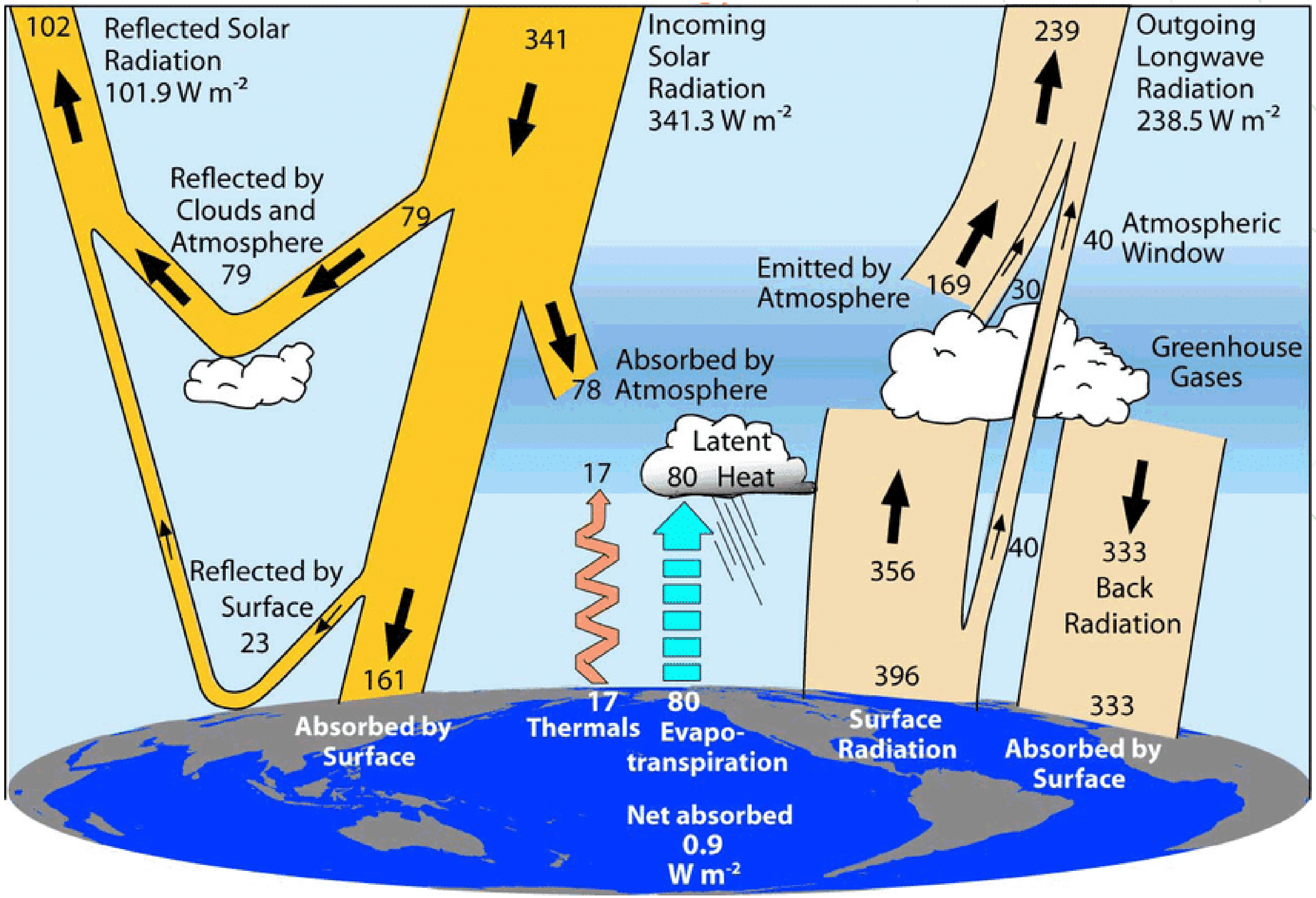
Gases (or in general all the species) able to transmit the radiation arriving from the Sun ($\lambda = 500$ nm) but absorbing in the IR ($\lambda = 10\ \mu m$) are responsible for the increasing temperature in the control volume (atmosphere)

These gases should be able to absorb the outgoing terrestrial infrared radiation causing vibro-rotational transitions.

Radiative balance in the atmosphere

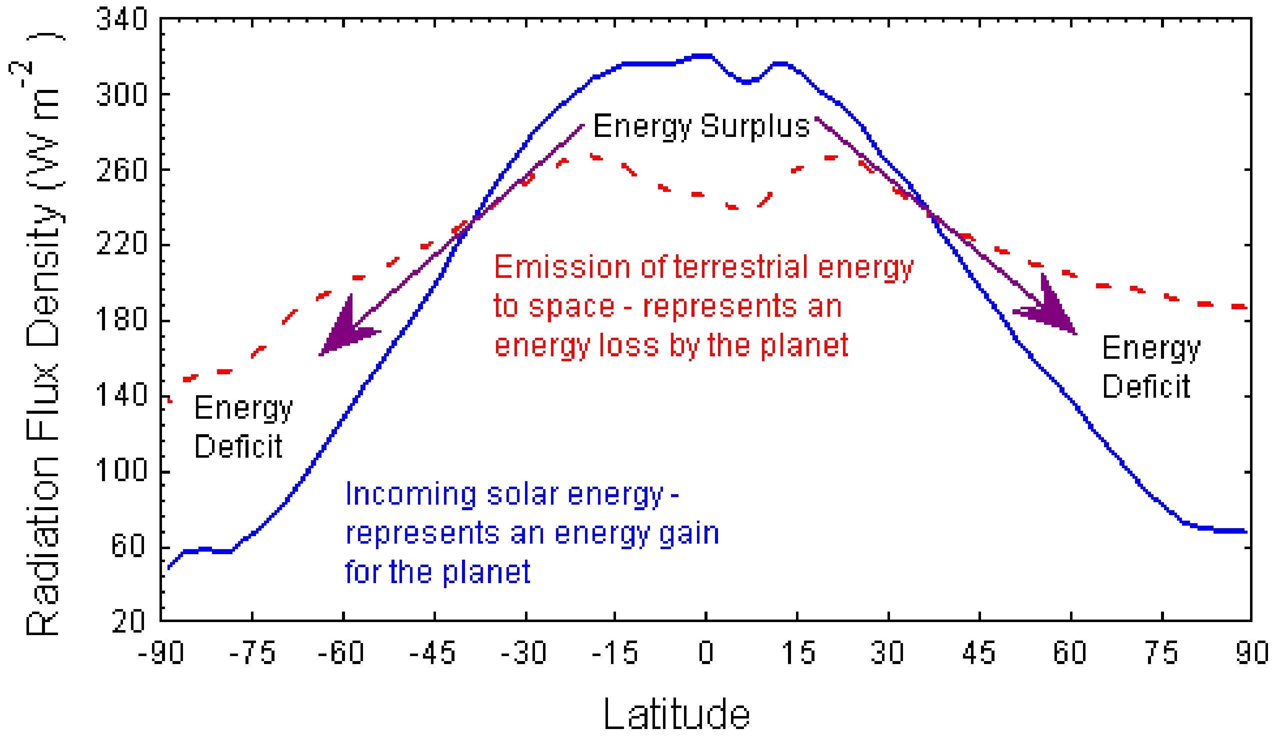


Radiative balance in the atmosphere

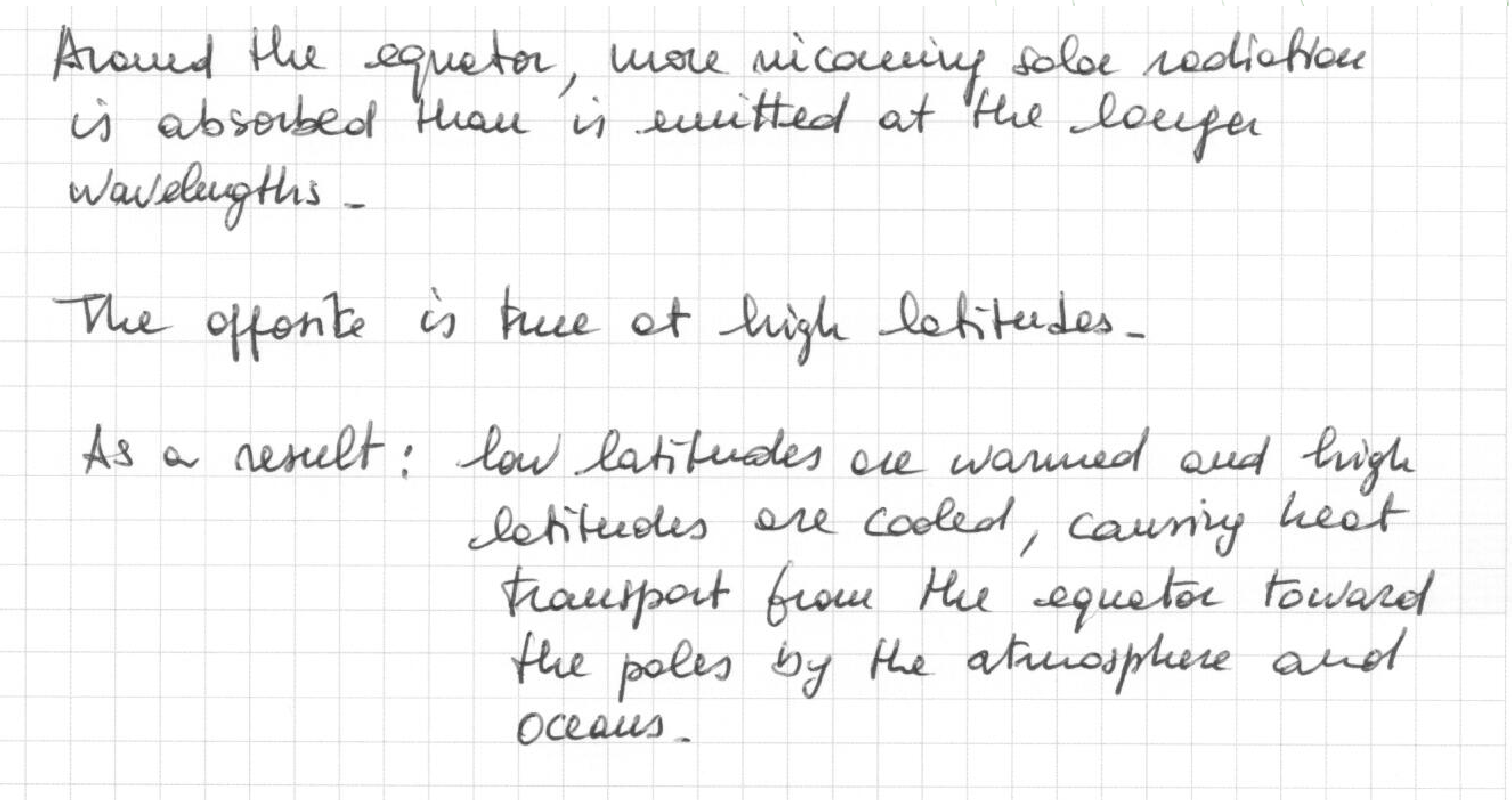


Radiative balance in the atmosphere

The processes of incoming solar radiation and
outcoming infrared radiation from Earth surface
are not homogeneous on a global scale -



Radiative balance in the atmosphere



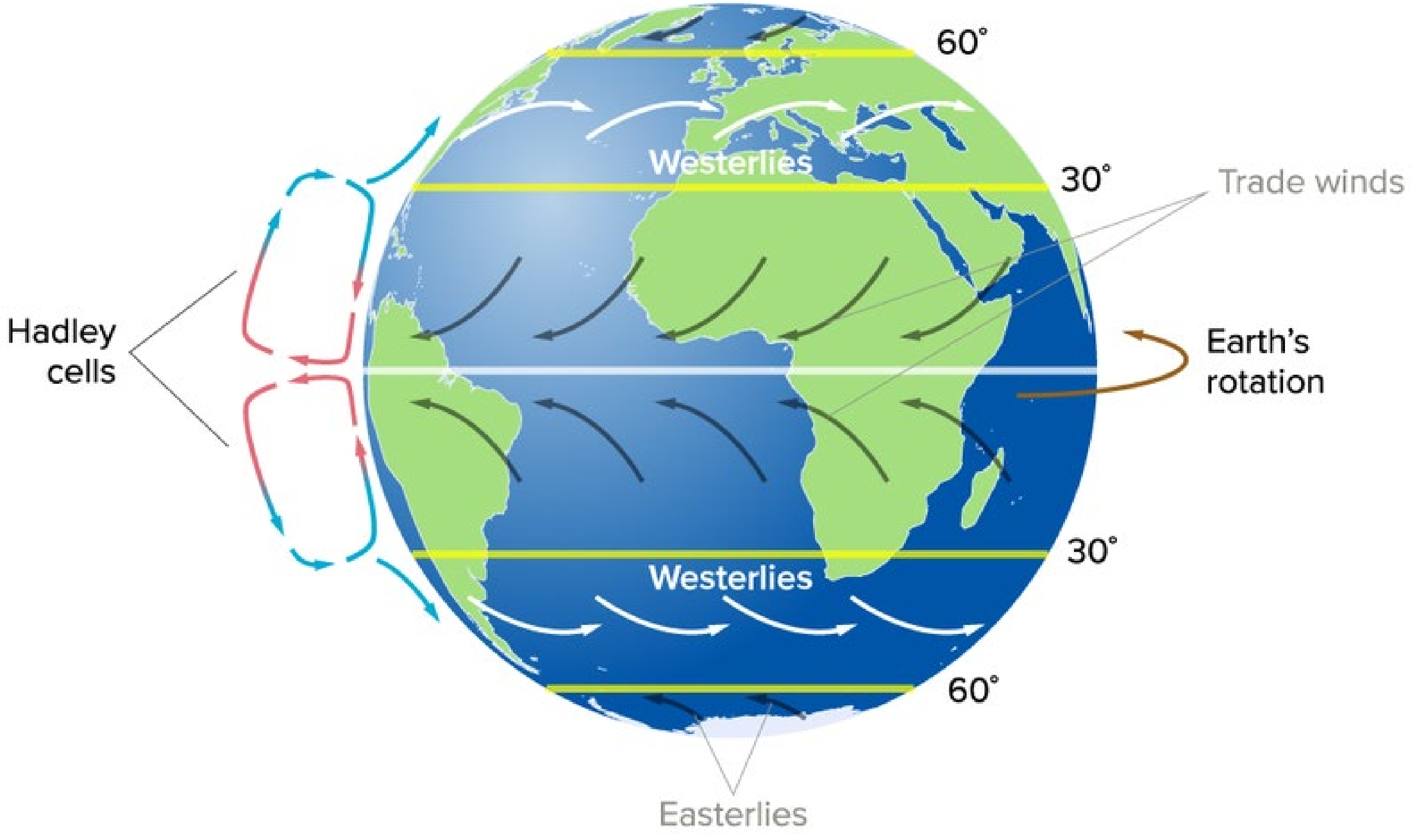
Around the equator, more incoming solar radiation is absorbed than is emitted at the longer wavelengths.

The opposite is true at high latitudes.

As a result: low latitudes are warmed and high latitudes are cooled, causing heat transport from the equator toward the poles by the atmosphere and oceans.

Radiative balance in the atmosphere

The two hemispheres are completely separated
because of the air transport from the equator
towards poles in the upper part of the atmosphere



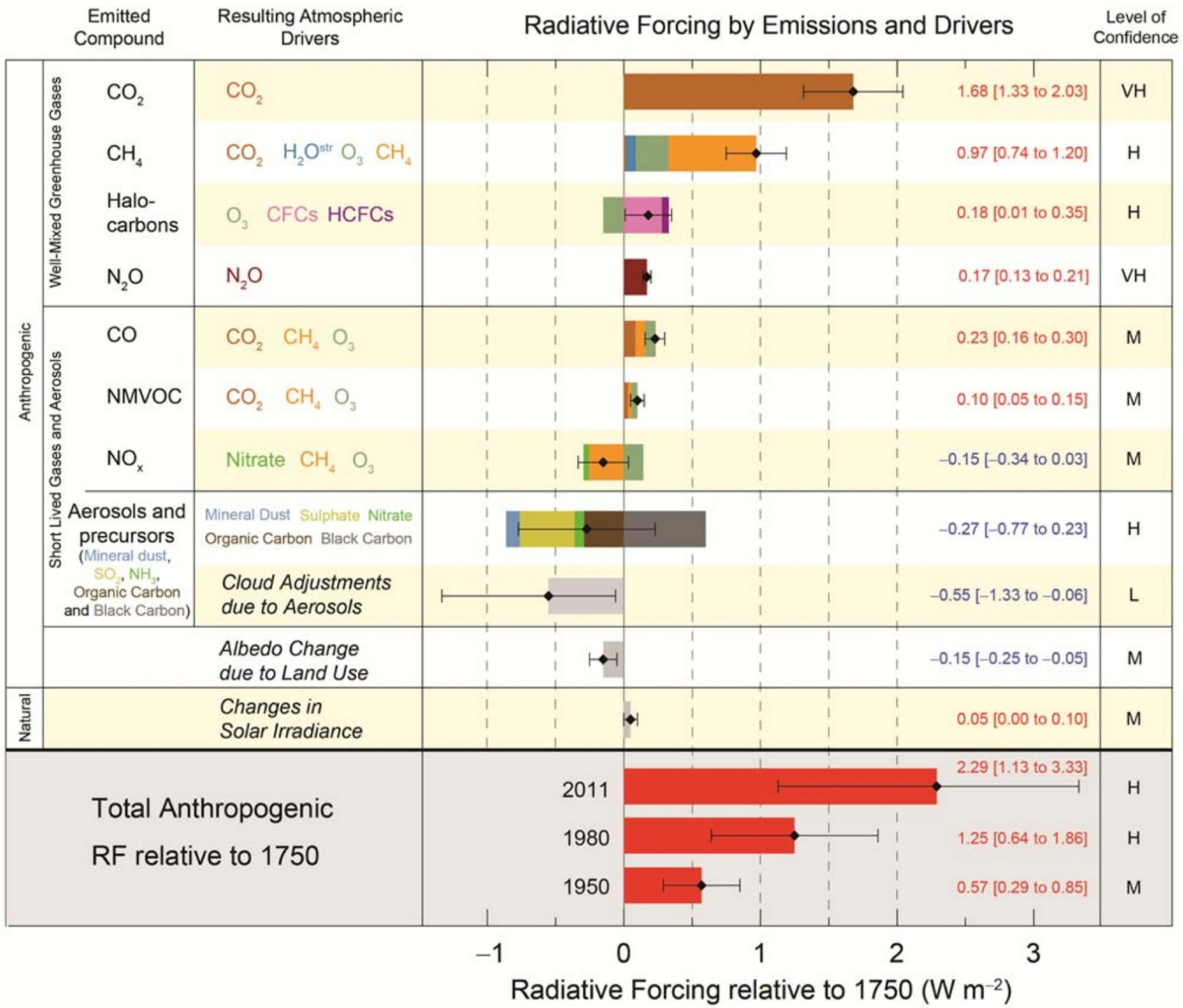
Radiative forcing

Radiative forcing is the change imposed on the planetary heat balance that alters global temperature.

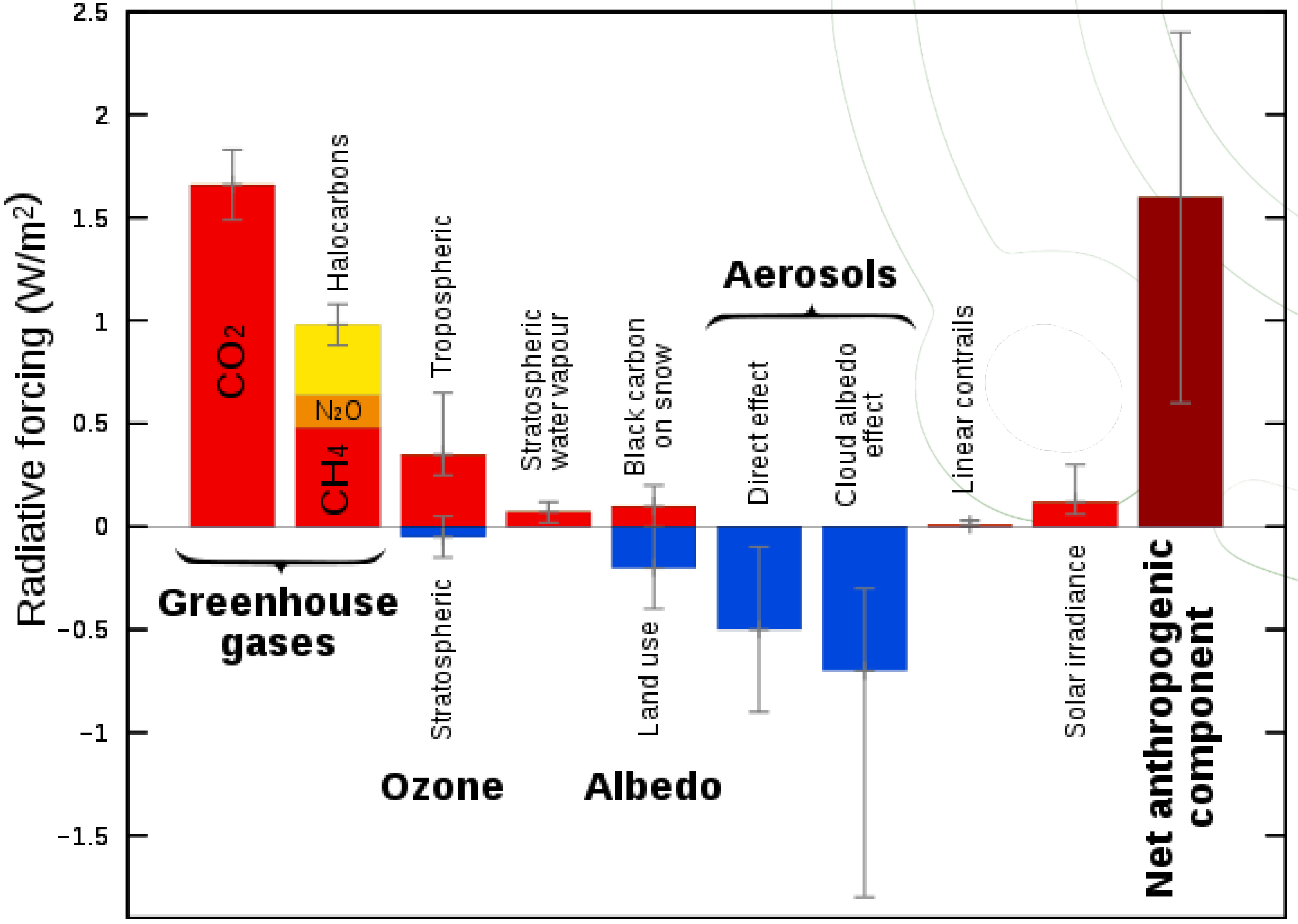
Such changes are measured in watts per square meter, and they allow direct comparison of forcing from different atmospheric constituents.

The current, global mean forcing from anthropogenic increases in GHGs [including CO_2, CH_4, N_2O, and chlorofluorocarbon (CFC)] is estimated to be approximately +2.5 W/m^2.

Radiative forcing



Radiative forcing



THANKS!

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