Oxygen
Stratosphere and Mesosphere
Part-2b

- Chemical Rate Equations
- Ozone Density vs. Altitude
- Stratospheric Heating
- Thermal Conductivity
- Thermospheric Structure
- Temperature Structure on other planets

Rate Equations for Oxygen Chemistry

Simple Model: Two Reactions, Production + Loss; No Ozone!

$$O_2 + h\nu \rightarrow O + O \quad ; \quad J_2$$

$$O + O + M \rightarrow O_2 + M \quad ; \quad k_{11}(T)$$

k_{11} = rate constant

M = all species, O_2, N_2, etc.

$$\frac{dn_2}{dt} = \text{Production - Loss} \quad : n_2 \rightarrow \text{density of } O_2$$

$$= n_1^2 n_M k_{11} - n_2 J_2$$

$$\frac{dn_1}{dt} = \text{Production - Loss} \quad : n_1 \rightarrow \text{density of } O$$

$$= 2 n_2 J_2 - 2 n_1^2 n_M k_{11}$$

Steady State: $dn_i/dt = dn_2/dt = 0$

Solve these equations:

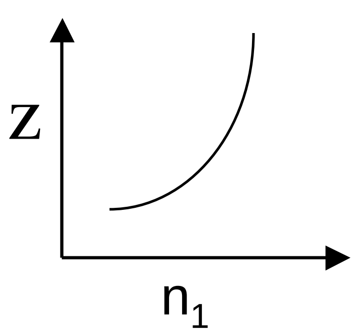
$$n_1^2 = \frac{n_2}{n_M} \frac{J_2(z)}{k_{11}},$$

where $J(z) = \sigma_{abs}[F_{s\nu}(z)/h\nu]$

$$n_1 = \sqrt{0.21 \frac{J_2(z)}{k_{11}}} \qquad O_2 \sim 21\% \; ; n_2/n_M \sim 0.21$$

no transport

no diffusion



Formation and destruction of Ozone all equations

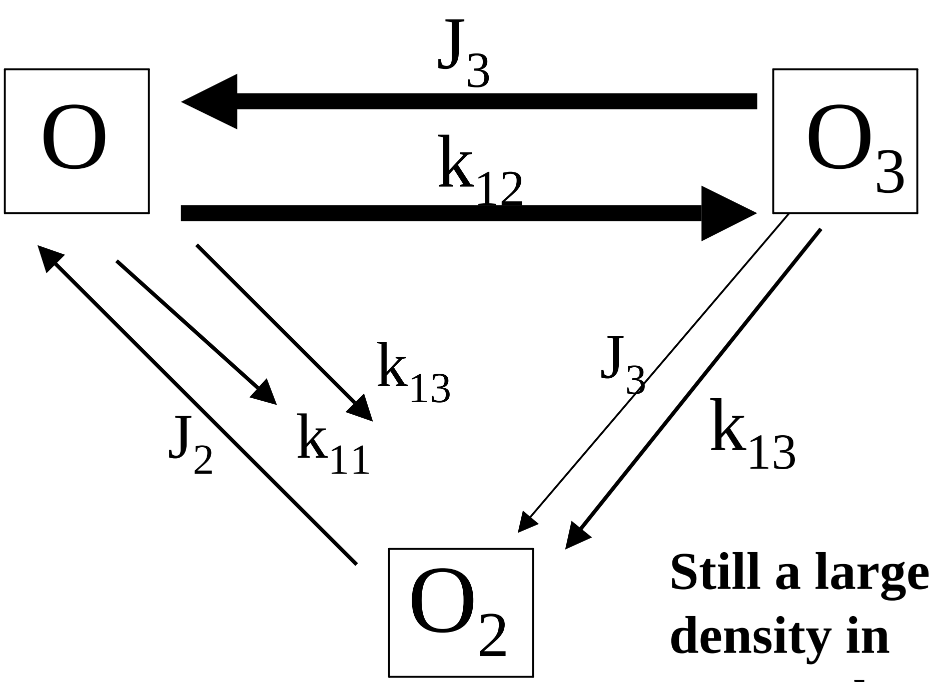
$$O_2 + h\nu\ (EUV) \rightarrow O + O \ : \ J_2$$

$$O_3 + h\nu\ (UV) \rightarrow O_2 + O \ : \ J_3$$

$$O + O + M \rightarrow O_2 + M \ : \ k_{11}$$

$$O + O_2 + M \rightarrow O_3 + M \ : \ k_{12}$$

$$O + O_3 \rightarrow O_2 + O_2 \ : \ k_{13}$$



Still a large density in stratosphere

Introduce Ozone

$$[\mathrm{O}] = n_1, \quad [\mathrm{O_2}] = \mathrm{n_2}, \quad [\mathrm{O_3}] = \mathrm{n_3}$$

Rate of Change = Production - Loss

Molecular Oxygen Eq.

$$\dot{\mathrm{n}}_2 = \mathrm{n_1}^2\, \mathrm{n_M}\, \mathrm{k_{11}} + 2\, \mathrm{n_3}\, \mathrm{n_1}\, \mathrm{k_{13}} + \mathrm{n_3}\, \mathrm{J_3} - \mathrm{n_2}\, \mathrm{J_2} - \mathrm{n_2}\, \mathrm{n_1}\, \mathrm{n_M}\, \mathrm{k_2}$$

Atomic Oxygen Eq.

$$\dot{\mathrm{n}}_1 = 2\, \mathrm{n_2}\, \mathrm{J_2} + \mathrm{n_3}\, \mathrm{J_3} - 2\, \mathrm{n_1}^2\, \mathrm{n_M}\, \mathrm{k_{11}} - \mathrm{n_1}\, \mathrm{n_2}\, \mathrm{n_M}\, \mathrm{k_{12}} - \mathrm{n_1}\, \mathrm{n_3}\, \mathrm{k_{13}}$$

Ozone Eq.

$$\dot{\mathrm{n}}_3 = \mathrm{n_1}\, \mathrm{n_2}\, \mathrm{n_M}\, \mathrm{k_{12}} - \mathrm{n_3}\, \mathrm{n_1}\, \mathrm{k_{13}} - \mathrm{n_3}\, \mathrm{J_3}$$

Sum: $\mathbf{O_3}$ + O ('odd' oxygen: fast processes)

$$\frac{\mathrm{d(n_1 + n_3)}}{\mathrm{dt}} = 2\, \mathrm{n_2}\, \mathrm{J_2} - 2\, \mathrm{n_1}^2\, \mathrm{n_M}\, \mathrm{k_{11}} - 2\, \mathrm{n_3}\, \mathrm{n_1}\, \mathrm{k_{13}}$$

Ozone continued

$[O] = n_1, \quad [O_2] = n_2, \quad [O_3] = n_3$

Steady State (for 'odd' oxygen)

$$\frac{d(n_1 + n_3)}{dt} = 0 = 2\, n_2\, J_2 - 2\, n_1^{\,2}\, n_M\, k_{11} - 2\, n_3\, n_1\, k_{13}$$

$$[-\, 2\, n_1^{\,2}\, n_M\, k_{11} \quad : \text{ if slow then-}]$$

$$n_3 n_1 \approx \left[\frac{n_2\, J_2}{k_{13}}\right] \qquad (1)$$

Steady State for O_3

$$dn_3/dt = 0 = n_1\, n_2\, n_M\, k_{12} - n_3\, n_1\, k_{13} - n_3\, J_3$$

$$[-\; n_3\, n_1\, k_{13} \;\text{,if slow then-}]$$

$$n_3 \approx \frac{n_1\, n_2\, n_M\, k_{12}}{J_3} \qquad (2)$$

Combine (1) and (2): get O and O_3 separately

$$n_1 \approx \left[\frac{J_2}{k_{13}} \frac{J_3}{k_{12} n_M}\right]^{1/2} \propto n_M^{-1/2} \propto n_2^{-1/2}$$

Same trend but somewhat different from the earlier result for n_1 because O_3 is a sink and source

$$n_3 \approx n_2 \left[\frac{J_2}{J_3}\left(\frac{k_{12} n_M}{k_{13}}\right)\right]^{1/2} \propto n_2^{3/2}\left[\frac{J_2}{J_3}\right]^{1/2}$$

(below ~ 100km, mixed $n_2 \sim 0.2 n_M$)

Densities of O_2,O_3 and O

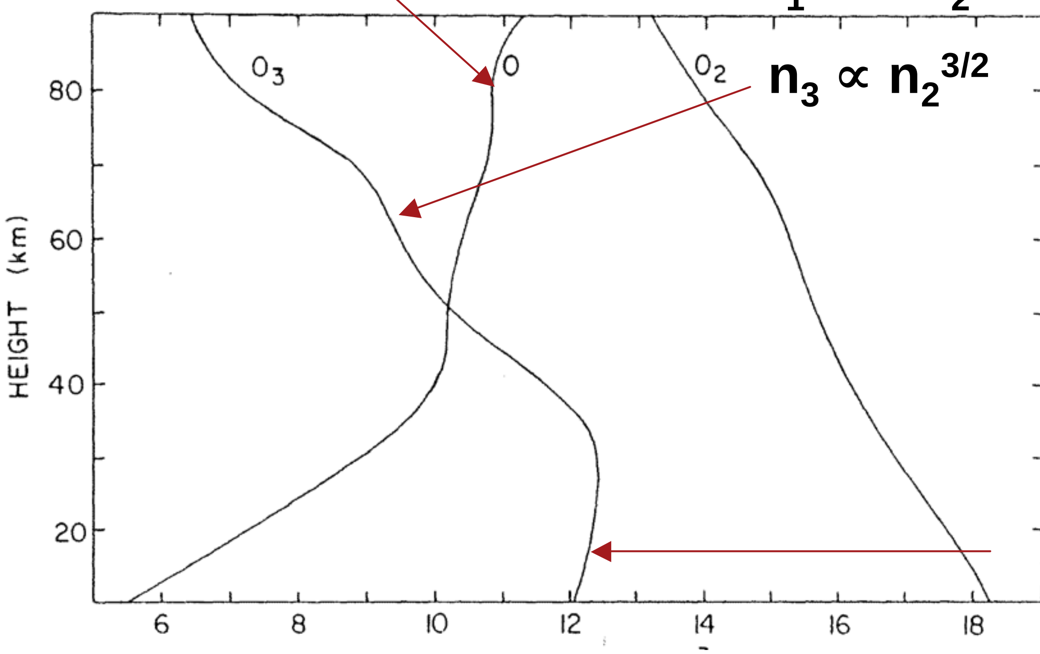
High up

J_2, J_3 slowly varying

$n_1 \propto 1/n_2^{1/2}$

$n_3 \propto n_2^{3/2}$

n_1 grows until it Dominates O_2 >120km



Lower z
J_2 and J_3 decrease

$Log_{10}n(mol/cm^3)$

Fig. 1.10 Daytime equilibrium of oxygen allotropes according to the Chapman theory. The abscissa is $\log_{10} N$. [Calculations by D. R. BATES (1954) *in* "The Earth as a Planet," (G. P. Kuiper, ed.), p. 581, Univ. Chicago Press, Chicago.]

Diffusive separation in the upper regions

At night: $J_2(z)$ and $J_3(z)$ --> 0

'slow' reactions become important

Dependence on z

Remember:

EUV absorption

$J_2(z) = J_2^o \exp[-\tau_2(z)/\mu]$

where $\mu = \cos\theta$

$\tau_2(z) = \sigma_{abs} \int_z^\infty n_2 \, dz$

$n_2(z) \approx 0.21 \, n_M$

$n_M(z) = n_M(0) \exp(-z/H)$

in mixed region

UV absorption

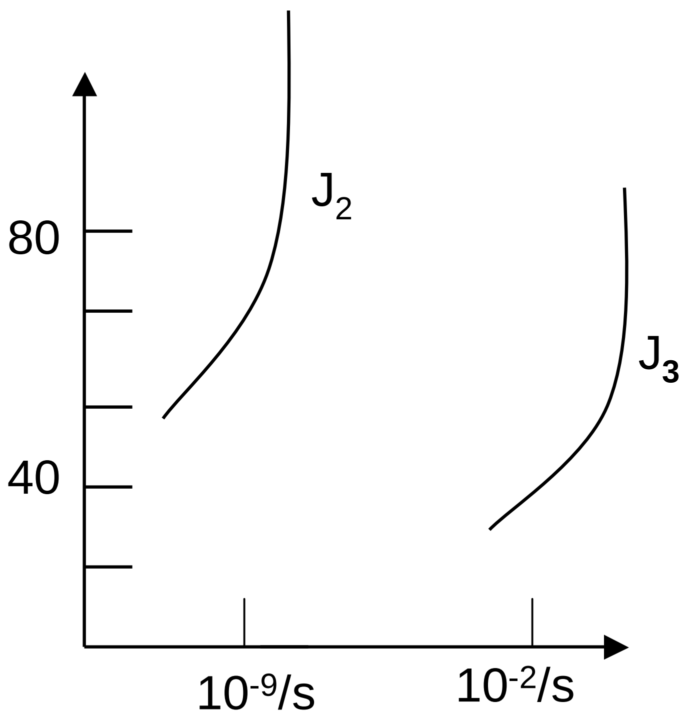
$J_3(z) = J_3^o \exp[-\tau_3(z)/\mu]$

For $\tau_3(z)$ need $n_3(z)$

which we are solving for.

Rough Vertical Profiles

$$J_2 = [\sigma_{abs} F_s / h\nu]_{EUV} \quad ; \quad J_3 = [\sigma_{abs} F_s / h\nu]_{UV}$$



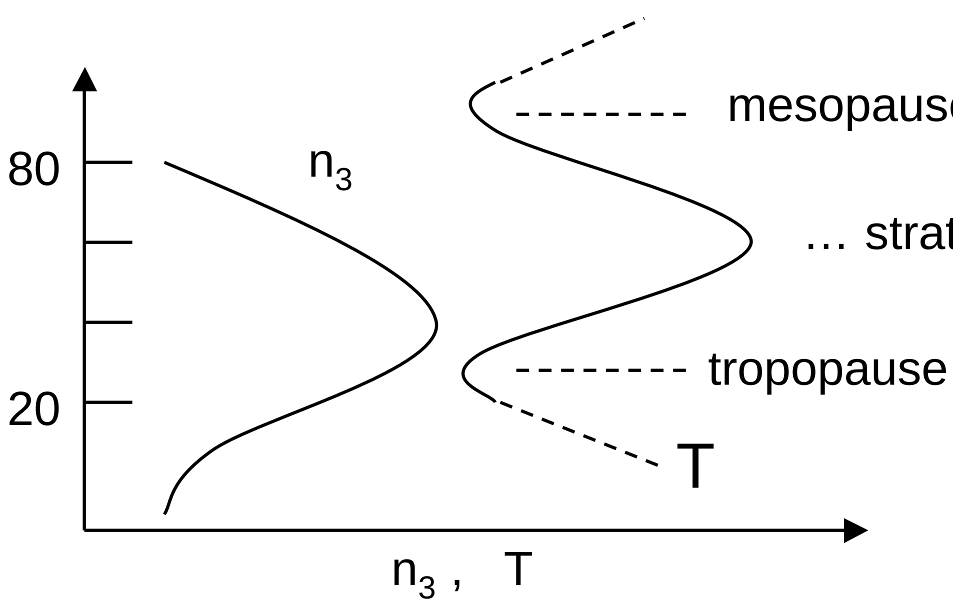
High z

J_2/J_3 =constant $\sim 10^{-7}$

Low z

J_2/J_3 --> 0

$$n_3 \propto n_M^{3/2} \left[\frac{J_2}{J_3}\right]^{1/2}$$

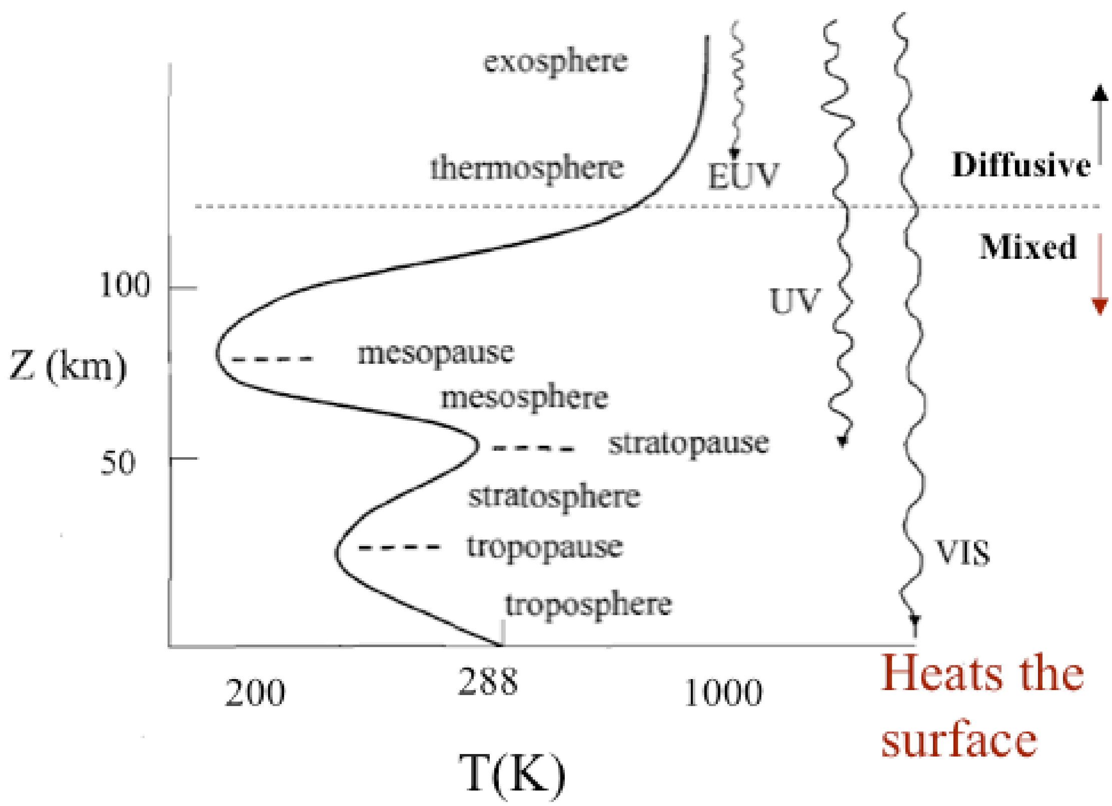


$$c_p \frac{dT}{dt} \propto J_3 n_3 \propto n_M^{3/2} \left[J_3 J_2\right]^{1/2}$$

Temperature vs. Altitude
Earth's Atmosphere

Stratospheric Heating peak and Ozone Peak related

$$J_3(z) = J_3^o \exp[-\tau_3(z)/\mu]$$
$$dT/dt \propto h\nu_3 \, J_3(z) \, n_3(z)$$



Summary

Start

$$O_2 + h\nu \xrightarrow{J_2} O + O$$

Form Ozone

$$O + O_2 + M \xrightarrow{k_{12}} O_3 + M$$

Heat Stratosphere

$$O_3 + h\nu \xrightarrow{J_3} O + O_2$$

Ozone Loss

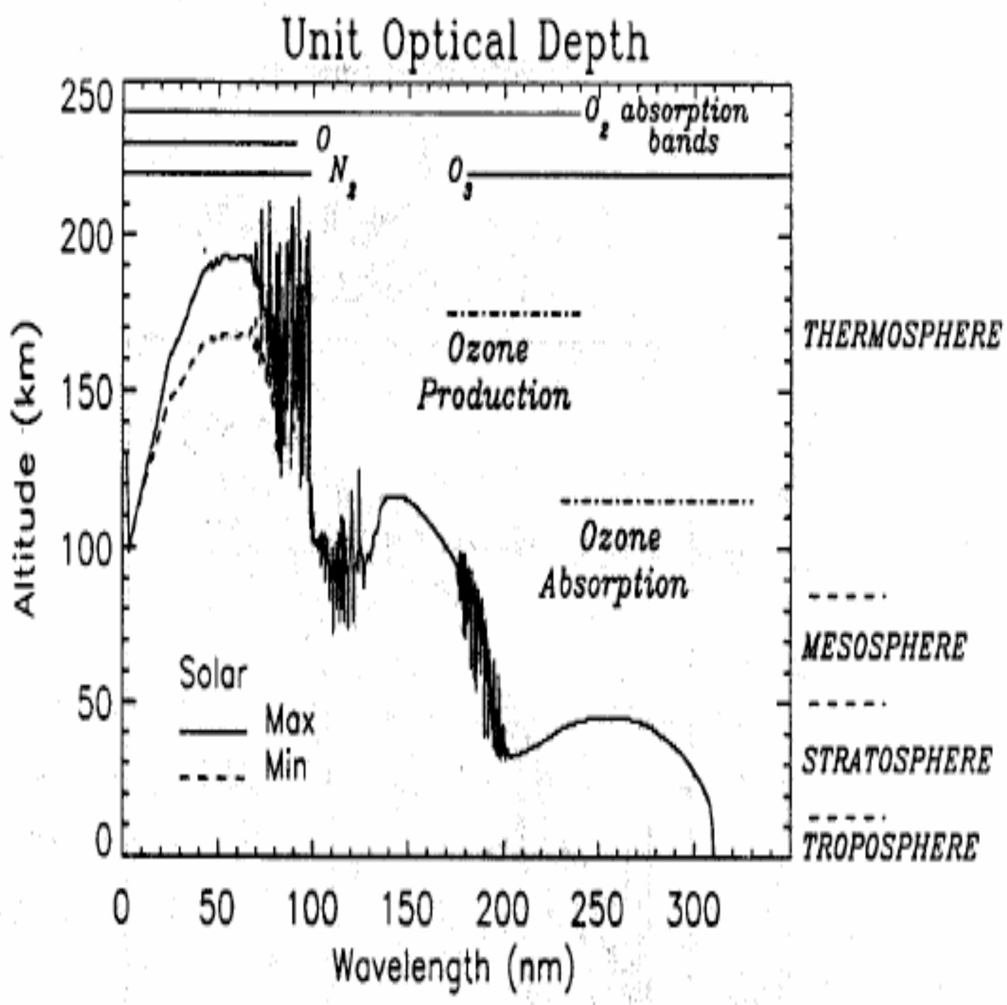
$$O + O_3 \xrightarrow{k_{13}} 2\,O_2$$

Radiate Heat Away (not discussed yet)

CO_2 in IR (15 μm)

J2 and J3

In the stratosphere 0_2 and 0_3 are the primary absorbers. The 'stratospheric window' of significant flux at 190-210 nm is particularly important in photochemistry of the lower atmosphere. Close to the Earth's surface the UV radiation has been removed completely by absorption at higher altitudes, and only radiation at wavelengths greater than ~290 nm is present. Since the chemistry of the troposphere is defined by radiation at wavelengths greater than -290 nm, molecules that absorb in the UV region live longer at these altitudes than those that absorb in the visible region.



Ozone (cont)

Night: Turn sun off

O and O_3 rapidly recylce between each other

But net decreases:

O_3 + O ('odd' oxygen: gradually decreases)

$$\frac{d(n_1 + n_3)}{dt} = -2 n_1^2 n_M k_{11} - 2 n_3 n_1 k_{13}$$

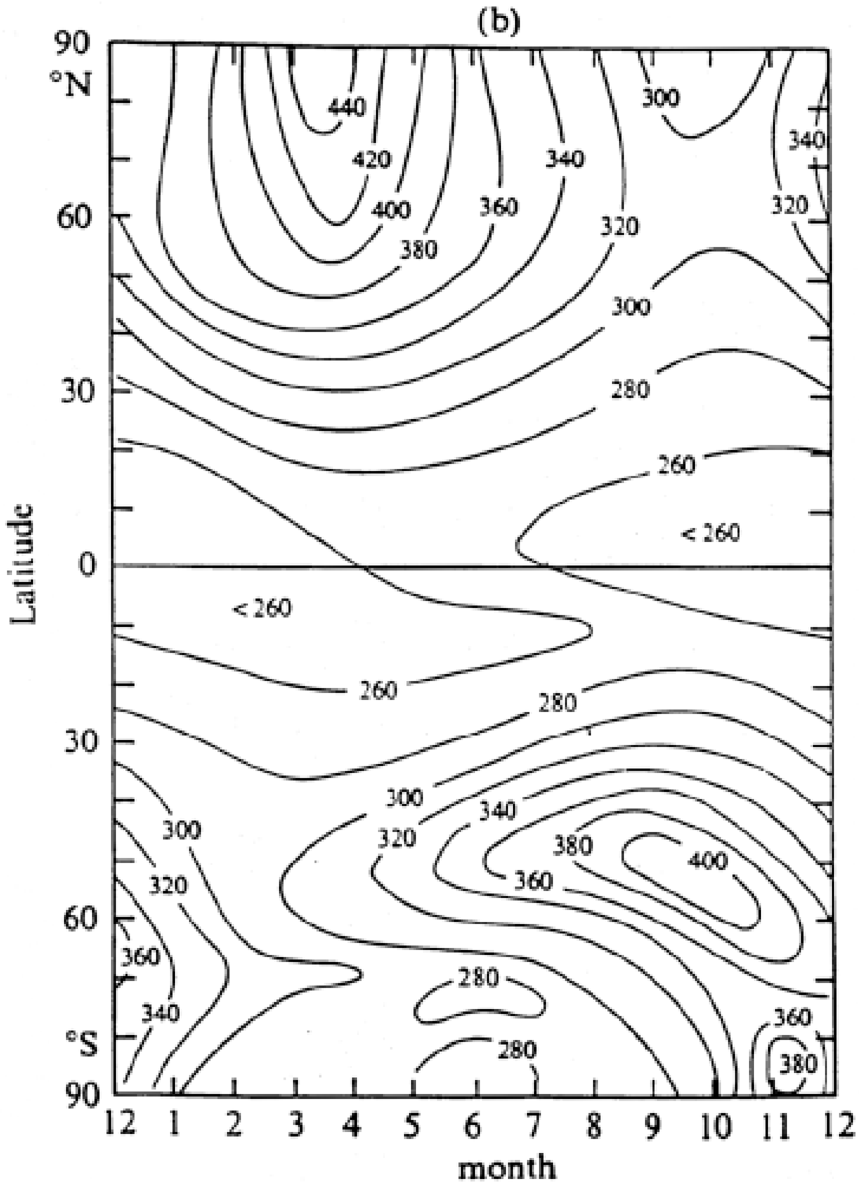
time constant: initially when there is still some O3

use second term--finally use first term

time constant $\sim (n_1 n_M k_{11})^{-1} \sim$ 10 days at $\sim$ 40 km

A result of Horizontal Transport

Ozone column density in ppm



Tropopause higher near equator and lower in T
Drives upper atmospheric flows
Will treat horizontal transport soon

Noctilucent Clouds

(night shining clouds, ~85km, ice grains)
(polar mesospheric clouds)
over a lake in northern Sweden

Possibly produced by climate change and space shuttle exhaust

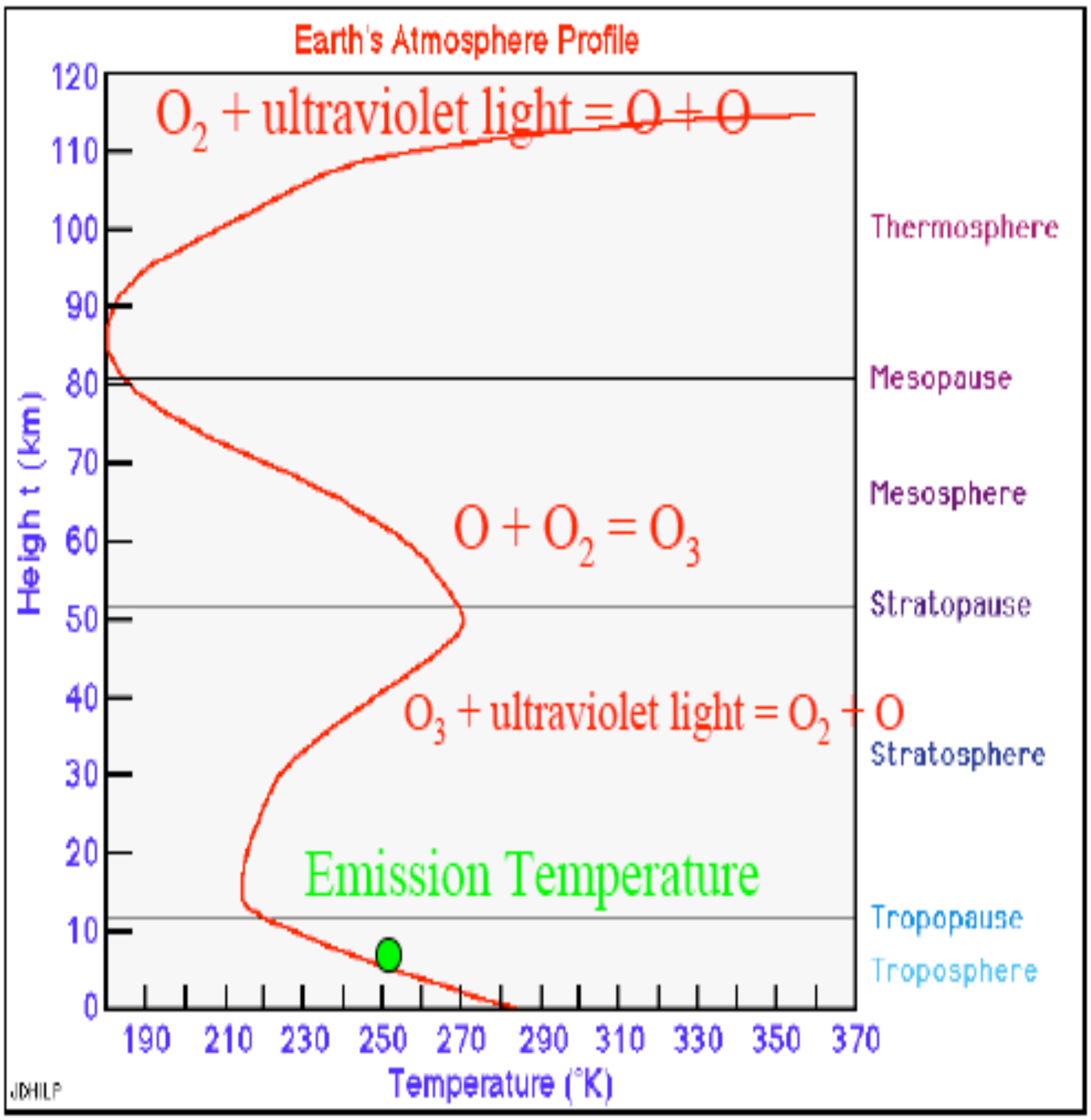
O_3 and be turned into O_2 on an ice grain

Polar Stratospheric (nacreous)Clouds

Polar Stratospheric (nacreous)Clouds
~15-25km: ice, nitric and sulfuric acids
Implicated in ozone holes

Oxygen Summary

Absorption by trace gases influences the atmosphere's temperature



#3 Summary

Things you should know

Earth's thermal structure
Rate equations
Oxygen reactions
Ozone layer
Stratospheric Heating
Stratopause
Mesosphere