Unit 14

Atmospheric chemistry – basic concepts

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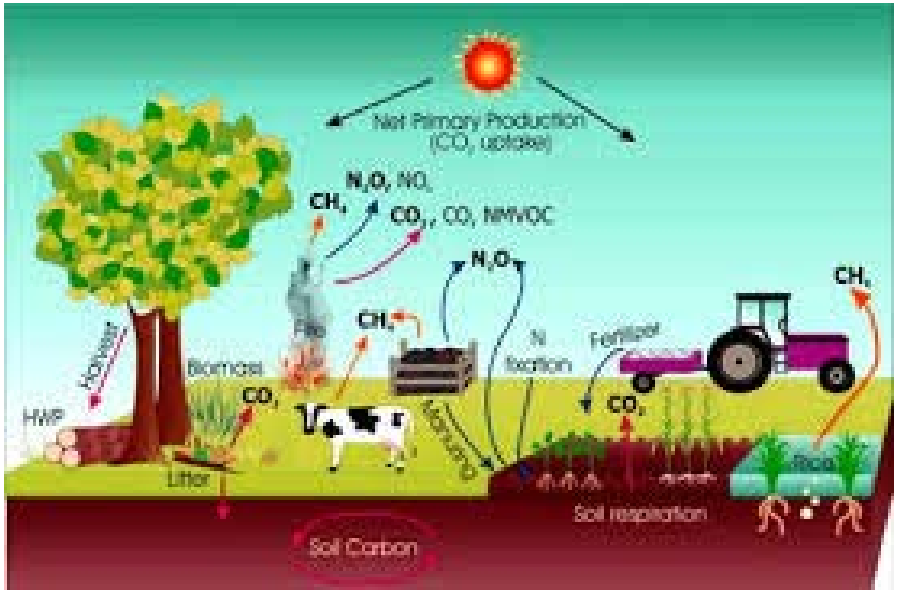
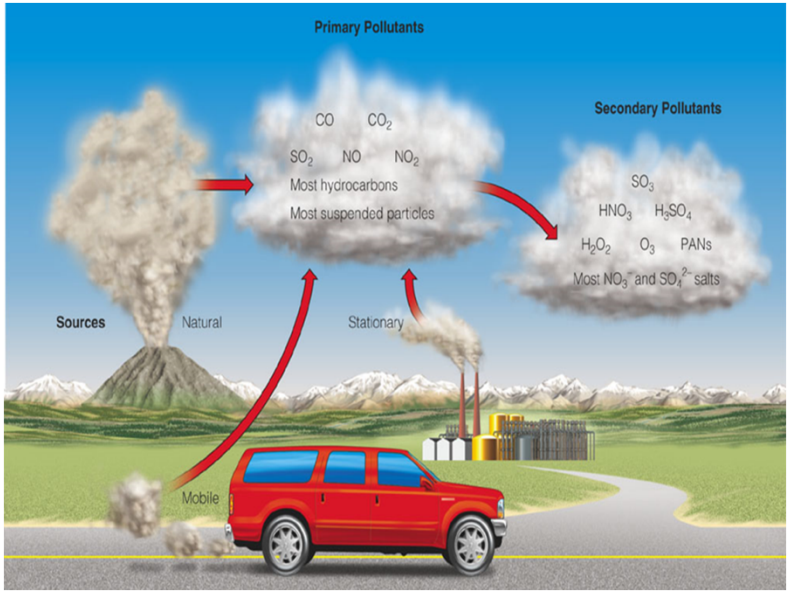
Natural and anthopogenic emissions



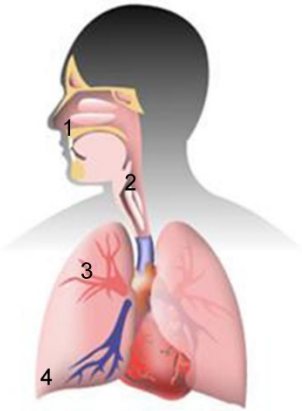
http://www.nature-education.org/cart/air-carbon-graphic.jpg

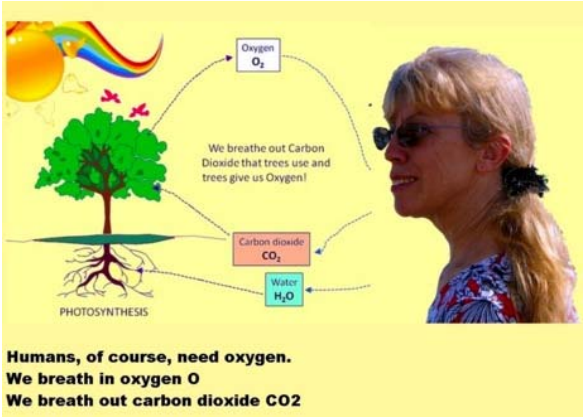


Mexico City: Example for reduction of visibility

From: Don Wuebble

Impacts of air pollution





Definitions

$$-\frac{d[A]}{dt} = k[A]$$

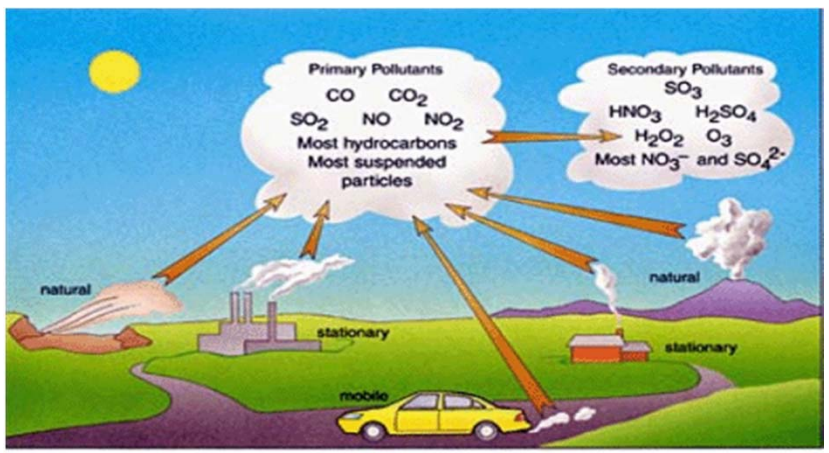
Reaction rate
[A] concentration of A
k reaction rate coefficient

$$t_{1/2} = \frac{0.693}{k}$$

half-live time

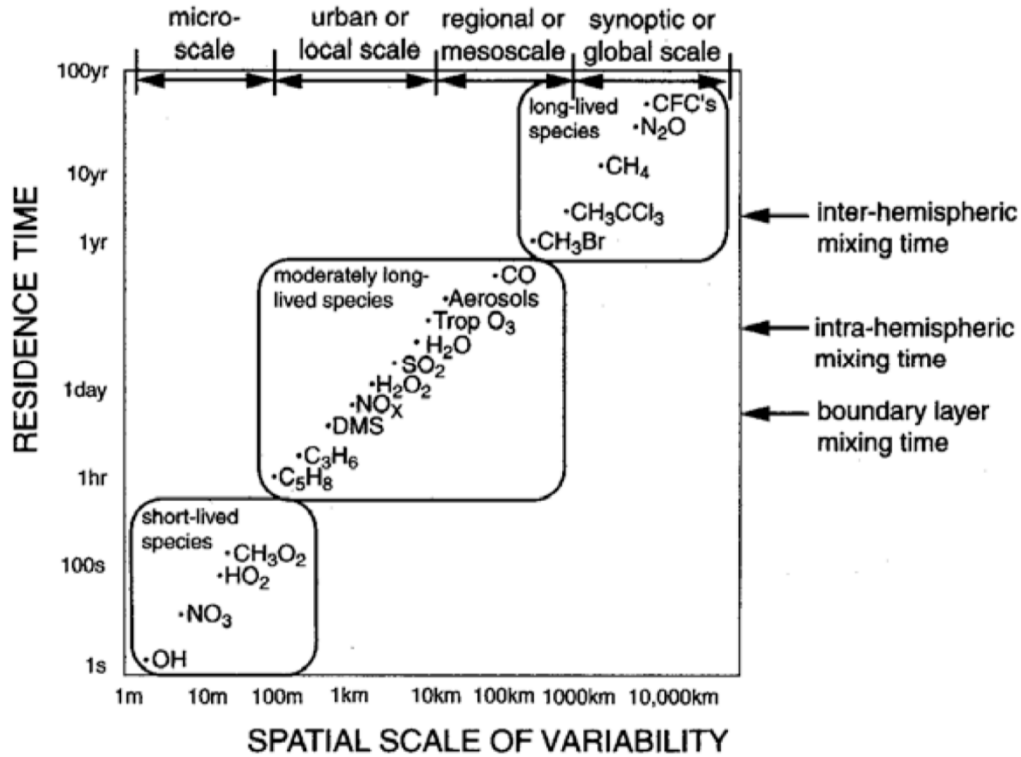
$$\tau = \frac{M(t)}{F(t)}$$

residence time, life-time
M amount, F efflux



Types and sources of air pollutants

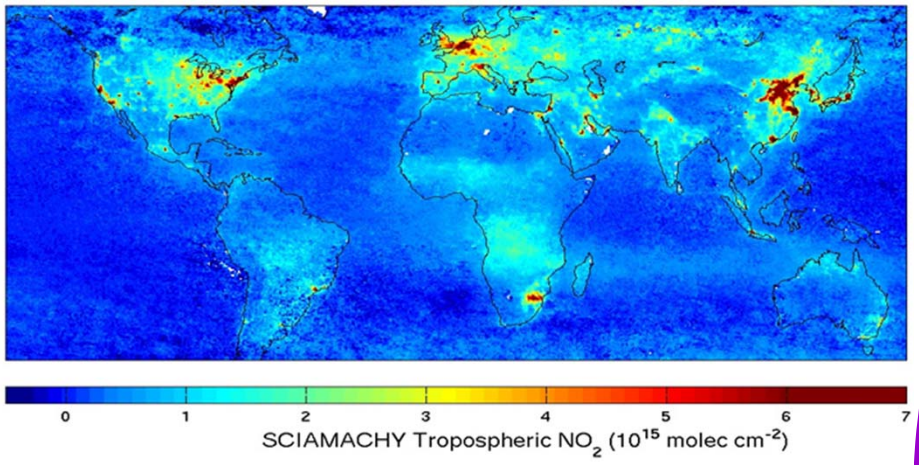
http://nptel.ac.in/courses/Webcourse-contents/IIT-Delhi/Environmental%20Air%20Pollution/air%20pollution%20(Civil)/Module-1/images1/35.gif

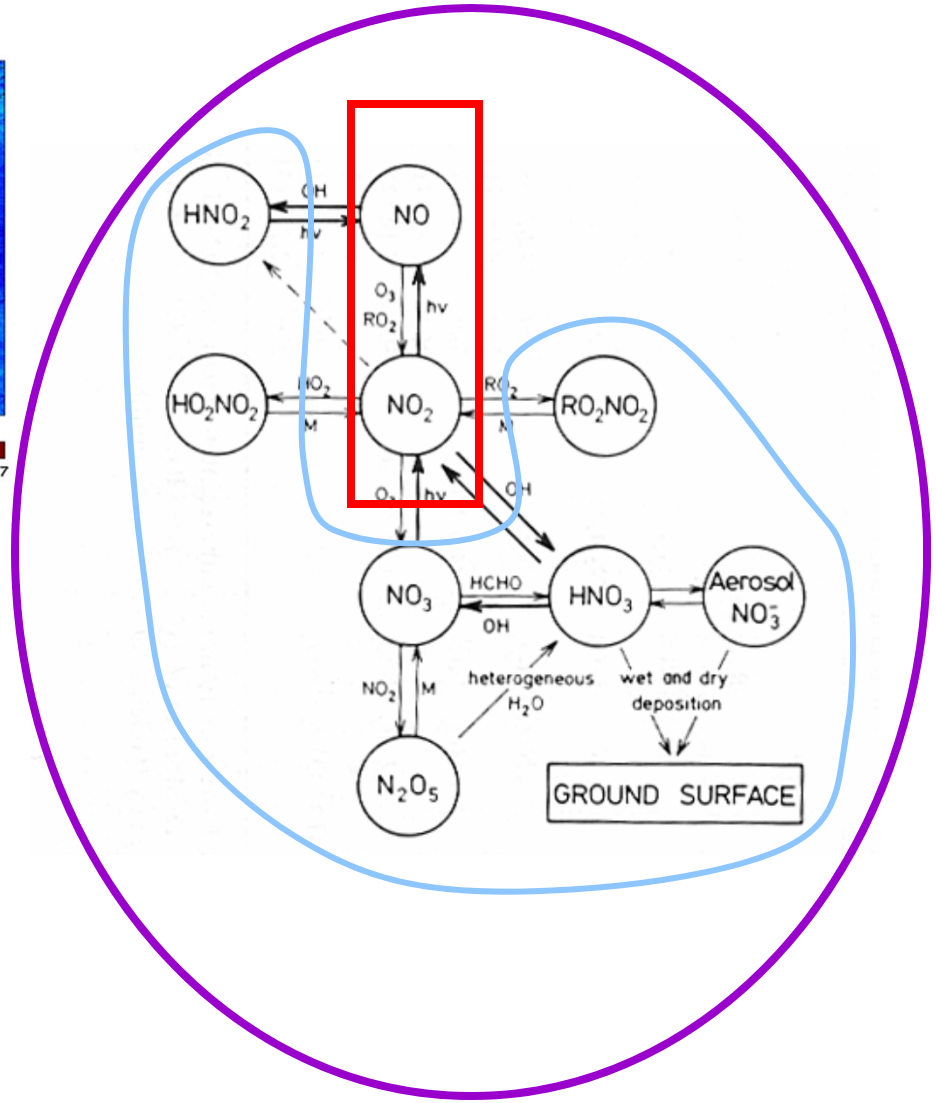


Definition of NO_y

NO_x
NO_y
NO_z

NO_2 columns observed from the SCIAMACHY satellite instrument





Equilibrium constants depend on reactants

$$aA + bB \leftrightarrow cC + dD$$

$$\longrightarrow \quad \text{forward rate} = k_f\,[A]^a[B]^b$$

$$k_f\,[A]^a[B]^b = k_b\,[C]^c[D]^d \qquad \longleftarrow \quad \text{backward rate} = k_b\,[C]^c[D]^d$$

$$K_{eq} = \frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Equilibrium constant

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Reaction quotient

$pV = nR^*T = n_o kT$

n number of moles, $k = 1.3806503 \times 10^{-23}\ m^2 kg\ s^{-2} K^{-1}$ Boltzmann constant

$R^* = 8.31\ J\ mole^{-1}\ K^{-1}$ universal gas constant

$$[A] = \frac{n}{V_A} = \frac{p_A}{R_c^* T}$$

$$k_c = \frac{[p_C/(R_c^*T)]^c[p_D/(R_c^*T)]^d\ldots}{[p_A/(R_c^*T)]^a[p_B/(R_c^*T)]^b\ldots} = \frac{p_C^c p_D^d\ldots}{p_A^a p_B^b\ldots}(R_c^*T)^{\Delta m} = k_p(R_c^*T)^{\Delta m}$$

Gibbs free energy determines reaction behavior

$$Q = \frac{[\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}}}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}}$$ if not at equilibrium

$$\Delta\overline{G}_r^o = \Delta\overline{G}_{f\ \mathrm{products}}^o - \Delta\overline{G}_{f\ \mathrm{reactants}}^o$$ Gibbs free energy of reaction

$$\Delta\overline{G}_r = \Delta\overline{G}_r^o + RT\ln Q$$ with $$\Delta\overline{G}_r^o = -RT\ln K_{eq}$$

Frequency factor

$\Delta\overline{G}_r < 0$ forward reaction

$\Delta\overline{G}_r > 0$ backward reaction

$\Delta\overline{G}_r = 0$ @ equilibrium

$$K_{eq} = \exp\left(-\frac{\Delta\overline{G}_r^o}{RT}\right)$$

Reaction-rate constant is not a real constant!
R ideal gas constant
T absolute temperature (plug in in K)

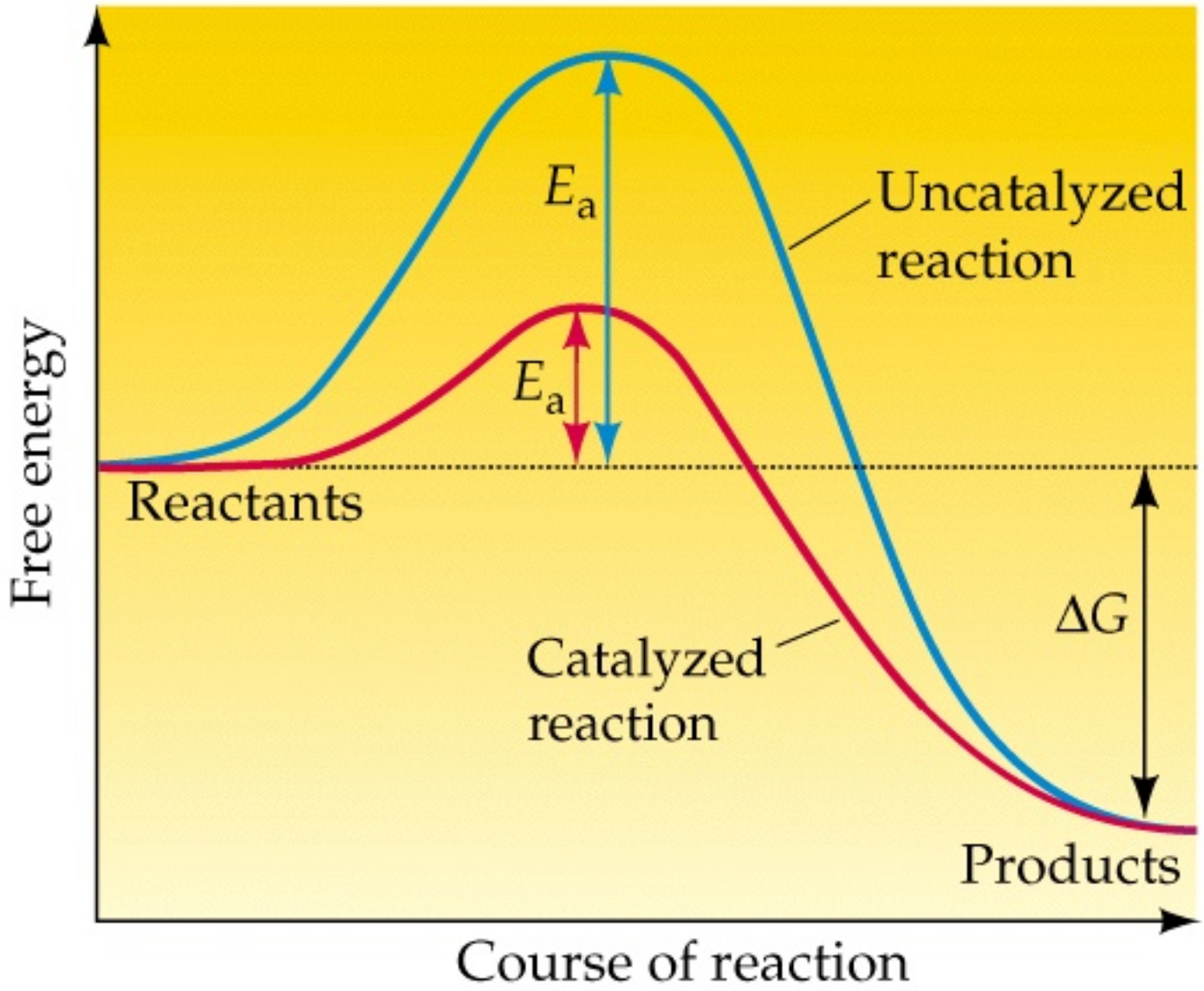
Temperature affects K_{eq}

van't Hoff's equation

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta\overline{H}_r^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

with $\Delta\overline{H}_r^o$ enthalpy of reaction

Activation energy E_a and catalysis



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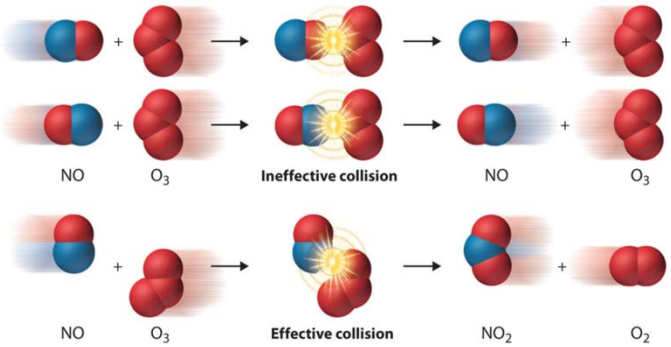
Kinetics



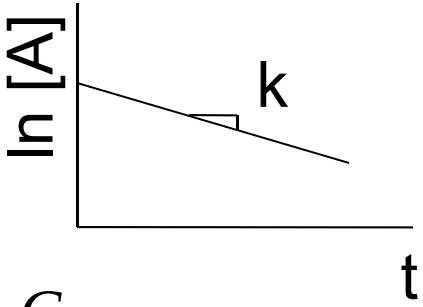
Order of reaction

$$aA + bB + cC + \cdots \rightarrow \text{Products}$$

$$\text{Reaction rate} = k[A]^a[B]^b[C]^c \qquad \text{Reaction order} = a + b + c + \cdots$$

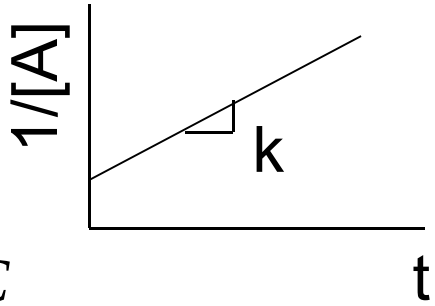
1st-order reaction $\quad A \rightarrow B$

$$\frac{d[A]}{dt} = -k[A] \qquad [A] = [A]_0 e^{-kt}$$



2nd-order reaction $\quad A + A \rightarrow C \qquad A + B \rightarrow C$

$$\frac{d[A]}{dt} = -k[A]^2 \qquad \frac{1}{[A]} - \frac{1}{[A]_0} = kt$$



Pseudo 1st-order reaction $\quad A + B \rightarrow C$

$$\frac{d[A]}{dt} = -k[B][A] = -k'[A]$$

When [B] >> [A]

Kinetic treatment of combination and dissociation

$$A + B + M \longrightarrow AB + M$$

$$A + B \rightleftharpoons^{k_1}_{k_{-1}} AB^*$$

$$AB^* + M \longrightarrow^{k_2} AB + M$$

Intermediate steps

$$\frac{d[AB]}{dt} = k[A][B]$$

Overall reaction rate

This is what we use!

Photolysis and quantum yield

$$A + h\nu \longrightarrow^{j} A^*$$

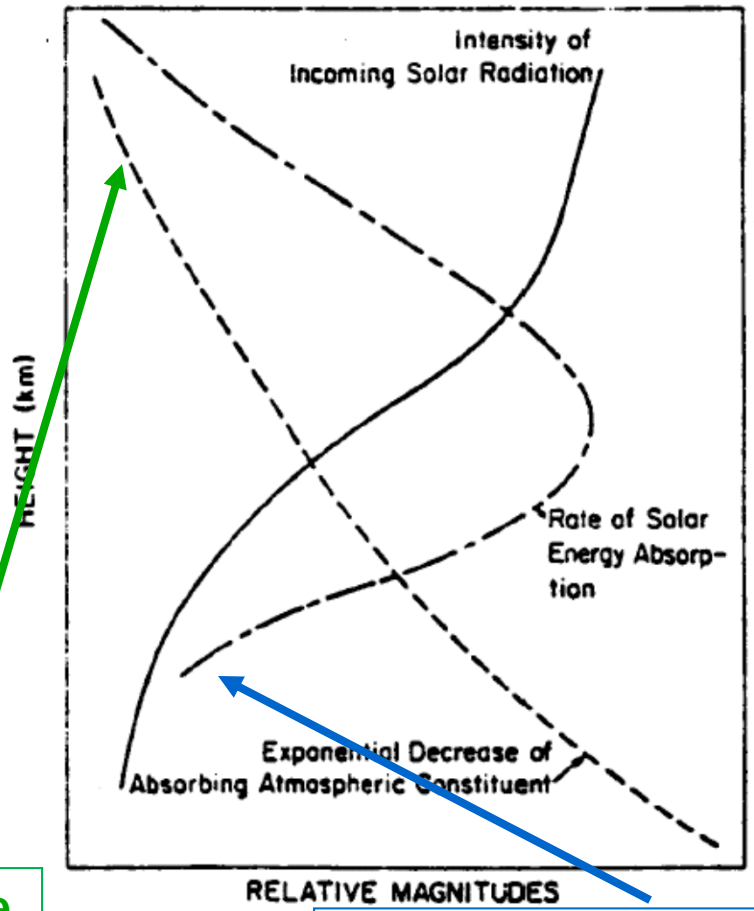
- dissociation: $A^* \longrightarrow^{k_1} B_1 + B_2 + B_3....$
- direct reaction: $A^* + B \longrightarrow^{k_2} C_1 + C_2 + C_3....$
- fluorescence: $A^* \longrightarrow^{k_3} A + h\nu$
- or collisional deactivation: $A^* + M \longrightarrow^{k_4} A + M$

$$\boxed{\sum_{i=1}^{4} \Phi_i = 1}$$

$$j = \int_{\lambda_1}^{\lambda_2} \sigma(\lambda, T)\Phi(\lambda, T)F(\lambda)d\lambda$$

$$j = \sum_i \overline{\sigma}(\lambda_i, T)\Phi(\lambda_i, T)\overline{F}(\lambda_i)\Delta\lambda_i$$

Atmospheric attenuation of solar radiation



Absorbing gas is thin here
⇒little absorption

Few photons left here
⇒little absorption

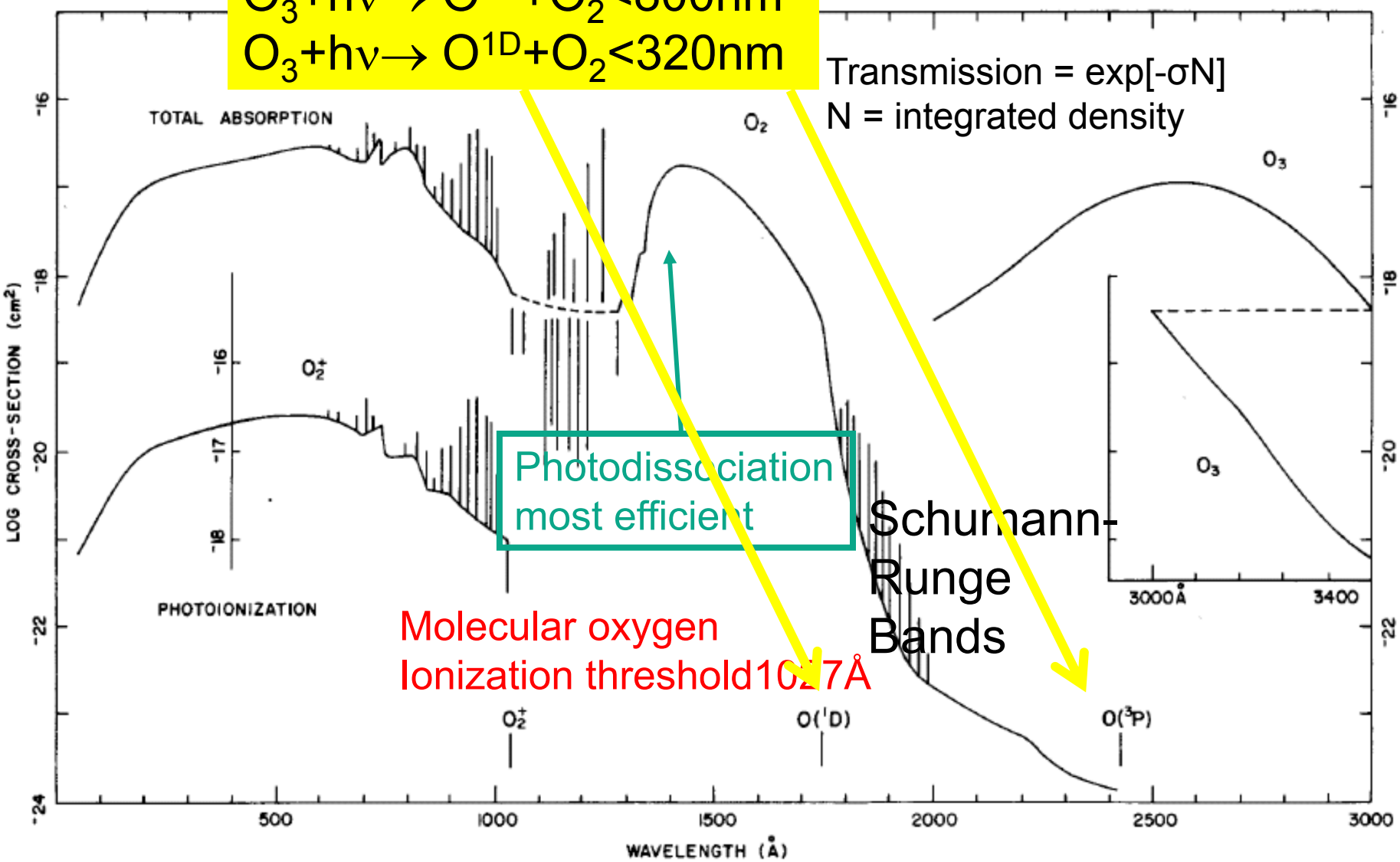
Absorption cross-sections σ for O_2 & O_3

$O_3 + h\nu \rightarrow O^{3P} + O_2 < 800nm$

$O_3 + h\nu \rightarrow O^{1D} + O_2 < 320nm$

Transmission = exp[-σN]

N = integrated density



Photodissociation most efficient

Schumann-Runge Bands

Molecular oxygen Ionization threshold1027Å

photoionization

photodissociation

References

Material shown here partly stems from:

- www.atmos.uiuc.edu/courses/atmos348.../Atmos348Lecture17.pdf
- www.ees.ufl.edu/homepp/cywu/.../Equilibrium%20&%20Kinetics.ppt
- http://ua.acd.ucar.edu/Presentations/lecture2.pdf
- http://www.atmos.uiuc.edu/courses/atmos348-sp04/documents/Atmos348Lecture5.pdf
- www.authorstream.com/.../aSGuest8996-131504-smog-chemistry-project-science-technology-ppt-powerpoint/
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