How are our lives influenced by atmospheric chemistry?

Positive effects:

- **UV Protection (stratospheric ozone layer)**
- **Removal of toxic substances from the atmosphere (the OH radical)**

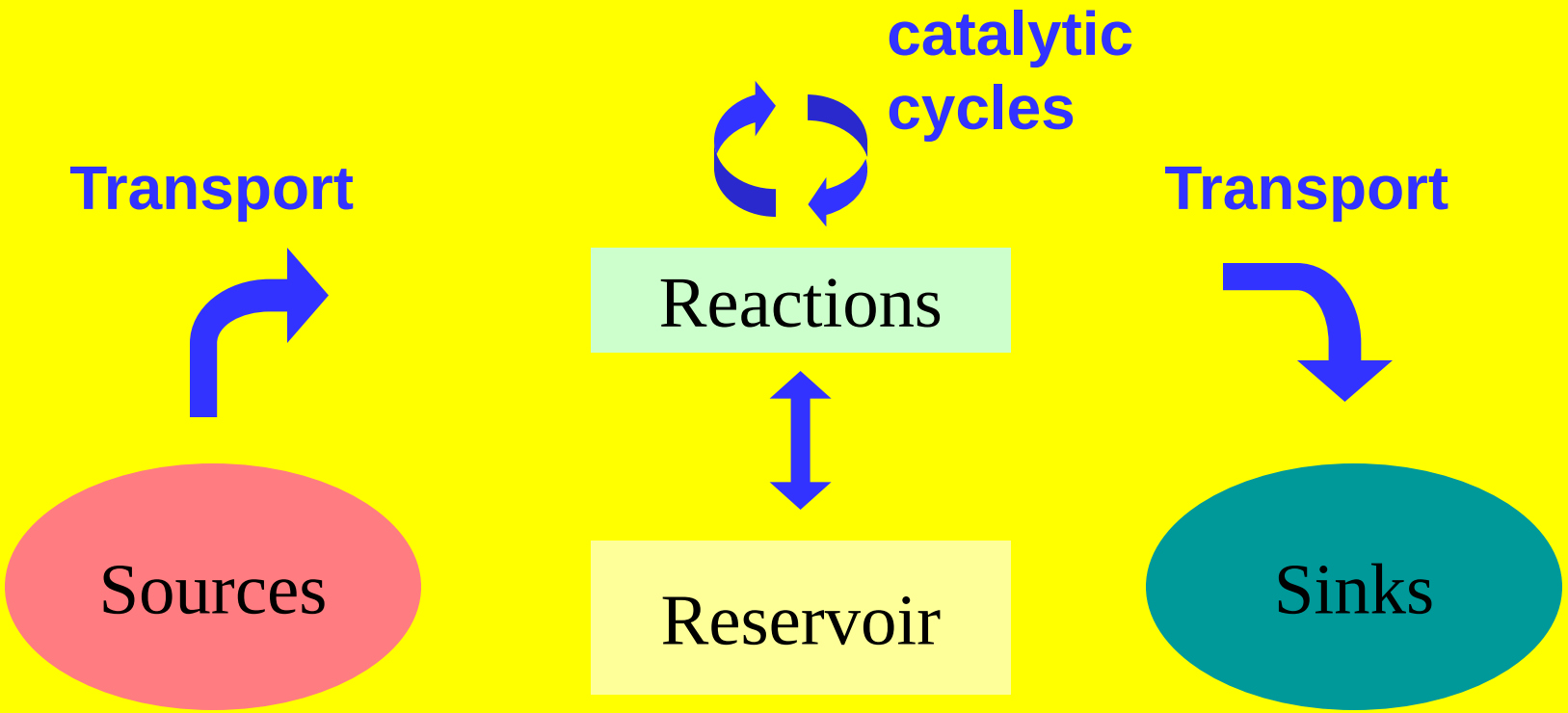
Negative effects:

- **Production of toxic substances (e.g. tropospheric ozone)**
- **Damage to humans, animals, plants, and buildings**

Indirect effects:

- **Feedbacks with climate system**
- **Fertilization of ecosystems (e.g. eutrophication)**

The system atmospheric chemistry



Chemical reactions

- gas-phase reactions
  $A+B \rightarrow C+D$
  $A+B \rightarrow C$
  $C \rightarrow A+B$ } often $A+B \leftrightarrow C$
  $A+B+M \rightarrow C+D+M$
- photodissociation reactions
  $A+h\nu \rightarrow B+C$
- heterogeneous (aerosol-, liquid-phase) reactions
  surface reactions
  bulk reactions

(Homogeneous: same phase) gas-phase reactions

Let us concentrate on a reaction of type A+B $\rightarrow$ C+D.

Then

$$-\frac{dA}{dt} = -\frac{dB}{dt} = \frac{dC}{dt} = \frac{dD}{dt}$$

$$\frac{dC}{dt} = k \cdot A \cdot B$$

k **is called reaction rate constant.**

Note: ***k*** **is often dependent on temperature and pressure.**

Quasi (Pseudo) steady state approximation

Several reactions proceed via the formation of an activated complex, which needs to get rid of excess energy in order to stabilize ("quenching"). Example:

$$O + O_2 \leftrightarrow O_3^*$$

$$O_3^* + M \rightarrow O_3$$

The rate equation for the intermediate complex is:

$$\frac{dO_3^*}{dt} = k_1^{\rightarrow} \cdot O \cdot O_2 - k_1^{\leftarrow} \cdot O_3^* - k_2 \cdot O_3^* \cdot M$$

If the lifetime of the complex O_3^* is <u>sufficiently short</u>, then

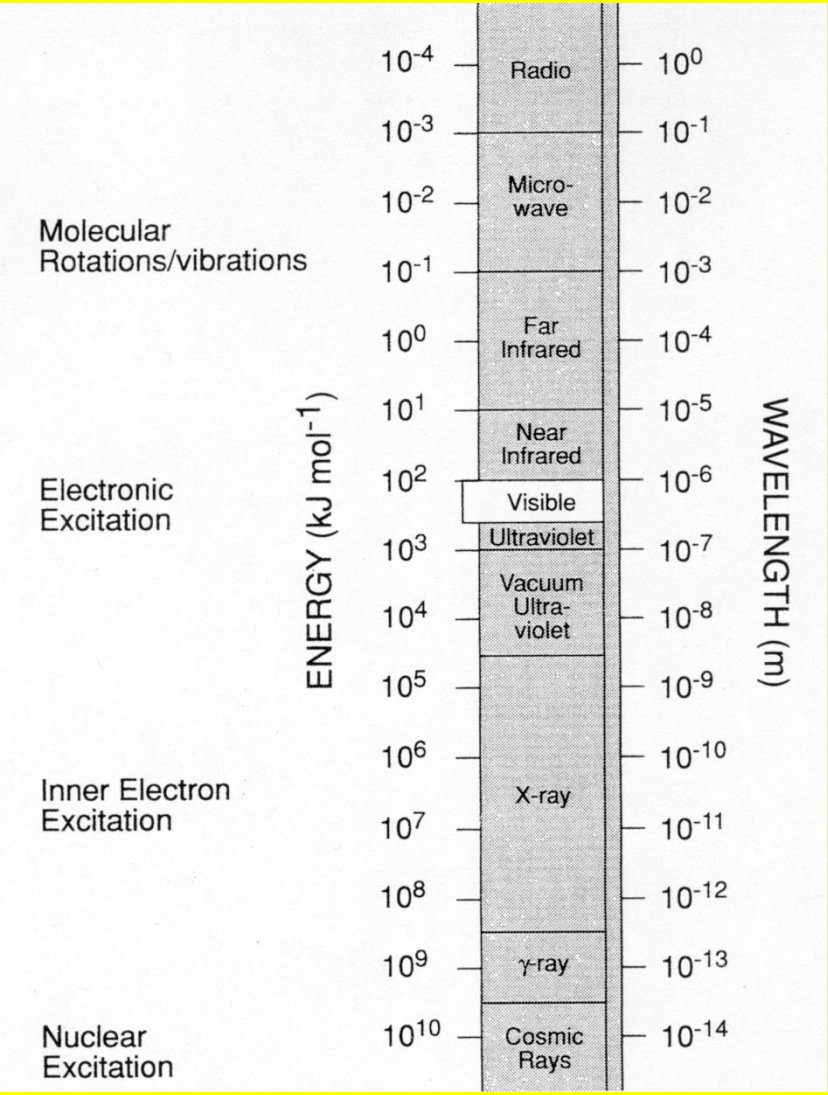
$$\frac{dO_3^*}{dt} = 0 \qquad \textbf{thus} \qquad O_3^* = \frac{k_1^{\rightarrow} \cdot O \cdot O_2}{k_1^{\leftarrow} + k_2 M}$$

All in moles/Vol

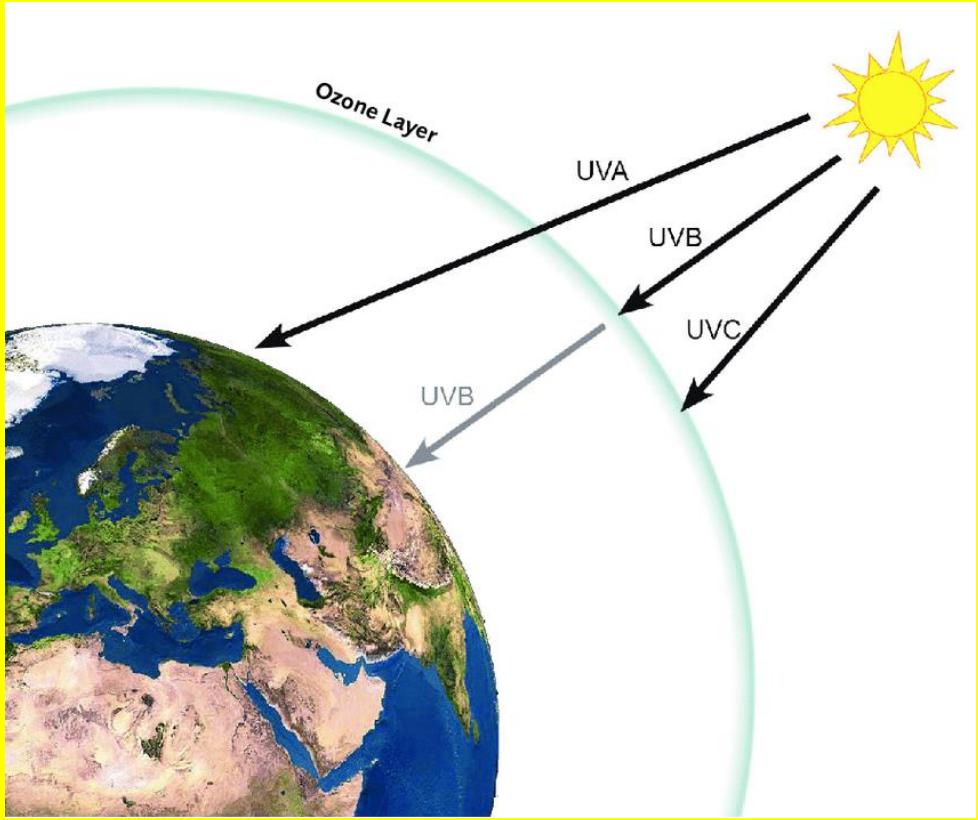
Photodissociation reactions

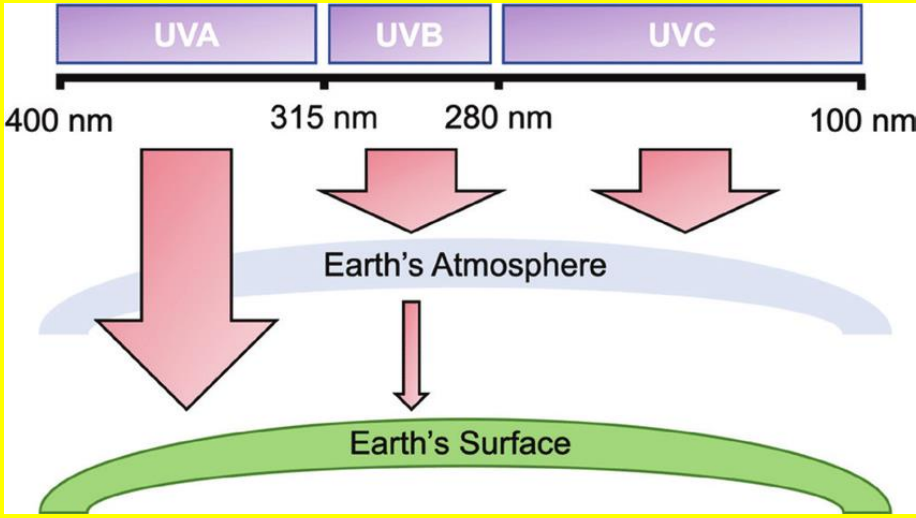
The energy of a photon absorbed by an atmospheric molecule is transformed to the breaking of a chemical bond, so that the molecule is dissociated.

For most molecules, photodissociation requires radiation in the UV wavelength range (< 380 nm).



Sun's Energy on Earth Surface





Ozone photolysis

$$O_3 + h\nu \rightarrow O + O_2, \quad \lambda < 800 \text{ nm (O –ground state)}$$

$$O_3 + h\nu \rightarrow O(^1D) + O_2, \lambda < 320 \text{ nm (O(1D) – excited state)}$$

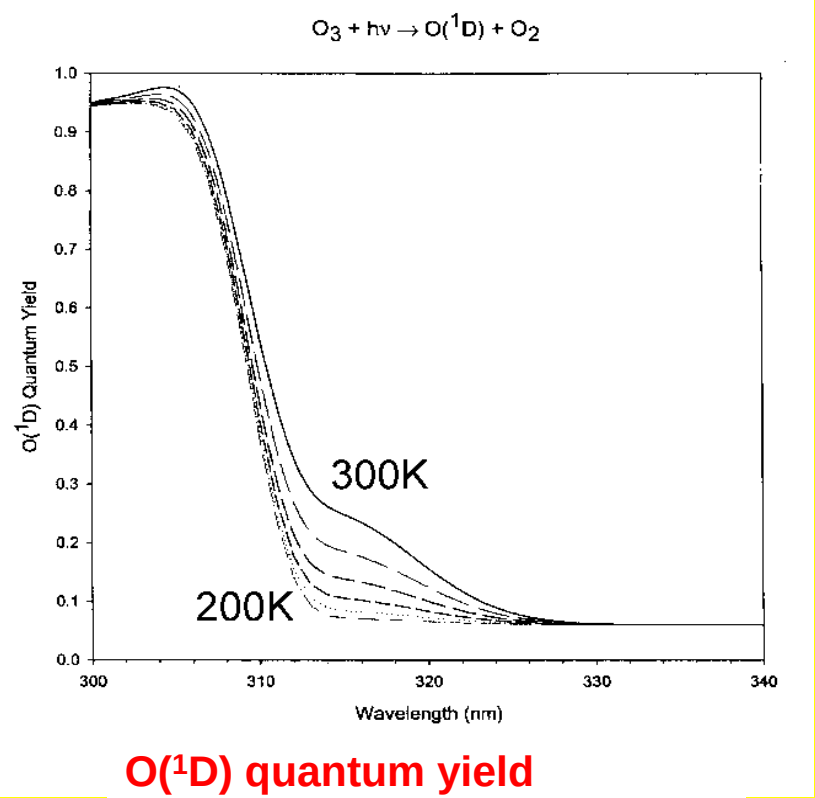
$O(^1D)$ formation is important for the formation of OH, which is the cleansing agent of the atmosphere:

$$O(^1D) + H_2O \rightarrow 2\ OH$$

Only a fraction of the O(1D) radicals react with water vapour, because:

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

and $$O + O_2 \rightarrow O_3$$



$O(^1D)$ quantum yield

Pseudo steady state approximation for O(^{1}D)

In the troposphere, the rate of change for the O(^{1}D) concentration is given by

$$\frac{d\mathrm{O}\left(^1D\right)}{dt} = \underbrace{j_{O^1D} \cdot \mathrm{O}_3}_{\text{production}} \underbrace{- k_1 \cdot \mathrm{M} \cdot \mathrm{O}\left(^1D\right) - k_2 \cdot \mathrm{H_2O} \cdot \mathrm{O}\left(^1D\right)}_{\text{loss}}$$

Under equilibrium conditions $\frac{d\mathrm{O}\left(^1D\right)}{dt} = 0$, thus

$$\mathrm{O}\left(^1D\right) = \frac{j_{O^1D} \cdot \mathrm{O}_3}{k_1 \cdot \mathrm{M} \cdot \mathrm{O}\left(^1D\right) + k_2 \cdot \mathrm{H_2O} \cdot \mathrm{O}\left(^1D\right)}$$

Basic Photochemical Cycle of NO_2, NO and O_3

$NO_2 + h\nu \rightarrow NO + O$ ---------- (1)
($h\nu \rightarrow \lambda < 424nm$)

$O + O_2 + M \rightarrow O_3 + M$ ---------- (2)

[M → N_2 or O_2 or another molecule that absorbs the excess vibrational energy and thereby stabilizes the O_3 molecule formed. There are no significant source of ozone in the troposphere other than reaction (2)]

$O_3 + NO \rightarrow NO_2 + O_2$ ---------- (3)

Lets assume that that known concentration of known initial concentrations of NO and NO_2, $[NO]_0$ and $[NO_2]_0$, in air are paced in a reactor of constant volume at constant temperature and irradiated.

$$\frac{d[NO_2]}{dt} = -k_1 [NO_2] + k_3 [O_3][NO] \qquad (4)$$

$$\frac{d[O]}{dt} = k_1[NO_2] - k_2[O][O_2][M] \qquad (5)$$

The oxygen atom is so reactive that it disappear by reaction 2 virtually as fast as it is formed by reaction 1. In dealing with highly reactive species such as the oxygen atom, it is customary to invoke the pseudo-steady state approximation (PSSA).

So,

$k_1[NO_2] = k_2 [O][O_2][M]$

i.e. the rate of formation = the rate of disappearance

The steady-state oxygen atom concentration in this system is then:

$$[O] = \frac{k_1[NO_2]}{k_2[O_2][M]} \qquad (6)$$

From eqs. (2) and (3), it is clear that these three reactions will reach a point where NO_2 is destroyed and reformed so fast that a steady-state cycle is maintained. The steady-state concentration of NO, NO_2 and O_3 are calculated as follows:

From eq(4), the steady state ozone concentration is given by:

$$[O_3] = \frac{k_1[NO_2]}{k_3[NO]} \qquad (7)$$

The steady-state concentration of ozone concentration is proportional to the $[NO_2]/[NO]$ ratio. We now need to compute $[NO_2]$ and [NO]. These are obtained from conservation of nitrogen,

$[NO] + [NO_2] = [NO]_0 + [NO_2]_0$

stoichiometric reactions of O_3 with NO,

$[O_3]_0 - [O_3] = [NO]_0 - [NO]$

Contd…

Solving for $[O_3]$ by using eq(7) and the two conditions as described earlier, The concentration of ozone is given by:

$$[O_3] = -\frac{1}{2}\left([NO]_0 - [O_3]_0 + \frac{k_1}{k_3}\right) + \frac{1}{2}\left\{\left([NO]_0 - [O_3]_0 + \frac{k_1}{k_3}\right)^2 + \frac{4k_1}{k_3}([NO_2]_0 + [O_3]_0)\right\}^{1/2} \qquad (8)$$

If $[O_3]_0 = [NO]_0 = 0$, then eq(8) reduces to:

$$[O_3] = \frac{1}{2}\left\{\left[\left(\frac{k_1}{k_3}\right)^2 + \frac{4k_1}{k_3}[NO_2]_0\right]^{1/2} - \frac{k_1}{k_3}\right\} \qquad (9)$$

Most observed value of k_1/k_3 = 0.01 ppm, So ozone concentration attained as a function of the initial concentration of NO_2 with $[O_3]_0=[NO]_0=0$:

$[NO_2]_0$, ppm	$[O_3]$, ppm
0.1	0.027
1.0	0.095

Conclusions:

- When $[NO_2]_0= [O_3]_0=0$ $\rightarrow[O_3]_0=0 \rightarrow$ With no NO_2, there is no means to produce ozone.

The concentration of ozone attained in urban and regional atmospheres are often greater than those sample calculation from the model.

Since most of the NO_x emitted is in the form of NO and not NO_2, the concentration of ozone observed can be calculated accurately, if the reactions governed by eqs(1 – 3) only.

It must be concluded that reactions other than 1- 3 are important in the tropospehere air in which relatively high concentration occurs.