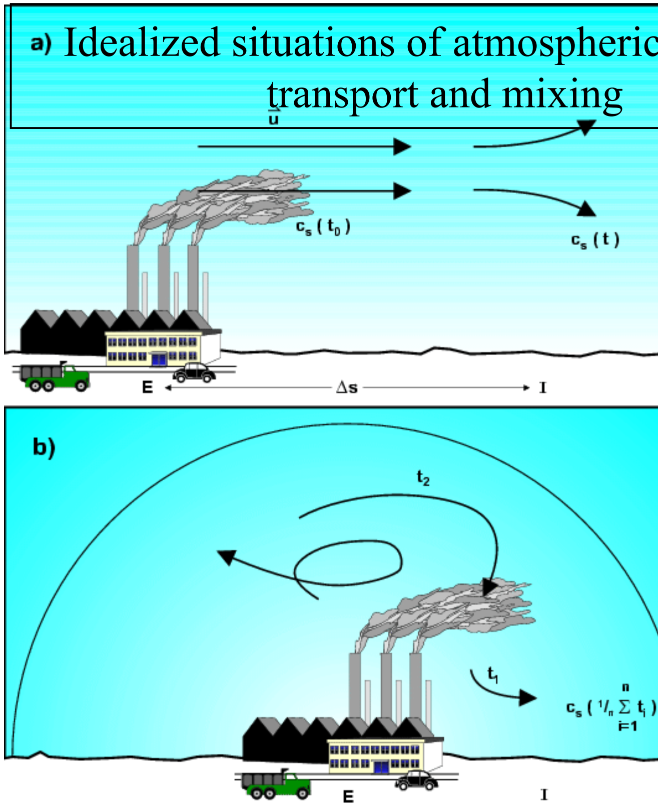
0. Introduction – 0.1 Concept

The air / environment (geosphere): Is it a reactor ?

It‘s a matter of reactions <u>and</u> transports and mixing !

mixing times:

- vertically lower few kilometers (boundary layer) 1h-1d, mixing with free troposphere 2-10 days
- around the globe on the same latitude (zonal transport) within a few weeks
- from mid latitudes to the pole (meridional transport) within days to weeks, hemispheric mixing 2-6 months
- Between hemispheres about 1 year
- troposphere-stratosphere 1-3 years



Conceptually / knowledge to understand:

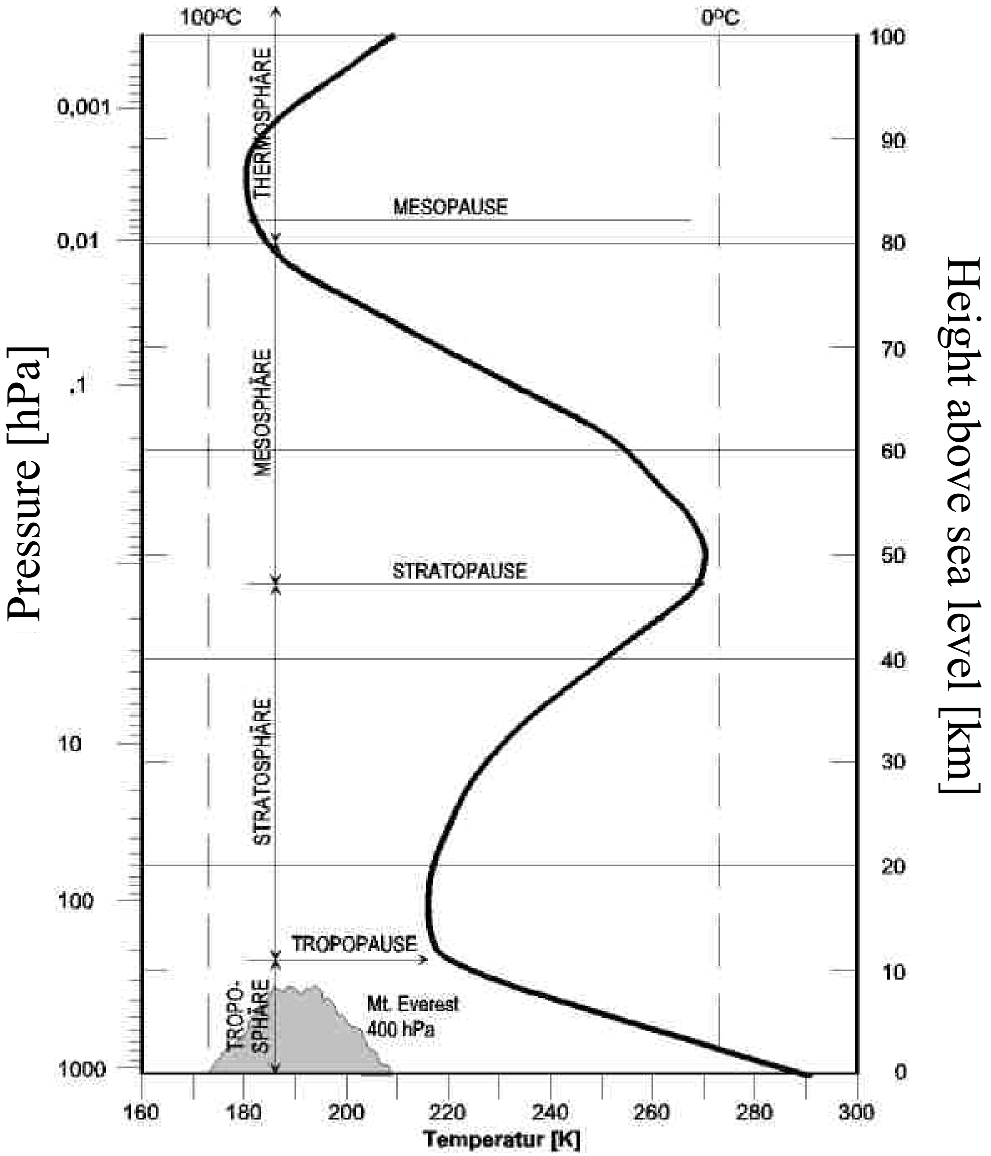
- (chemical) reactions
- (meteorological) transports and mixing

Tools to understand:

- 3D transport models
- model parameters isolated in laboratory experiments
- significant ‚ingredients‘ identified in the ‚field‘

0.2 Atmospheric pressure and composition

Pressure and temperature profiles in the atmosphere



Pressure declin

$\Delta p = -g\ \rho\ \Delta z$

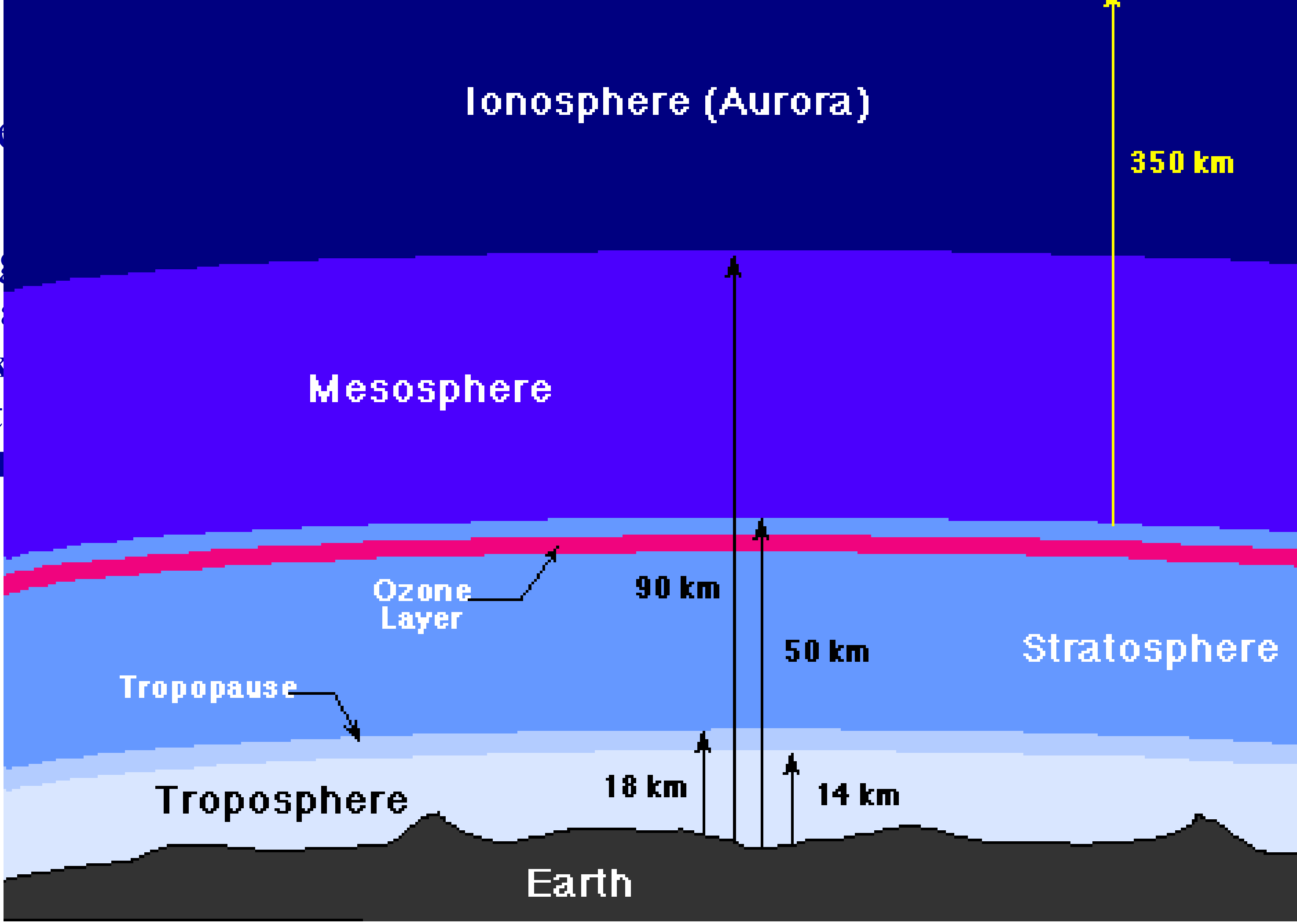
ρ = 1.225 mg/cm,

→ $\Delta z/\Delta p$ = 8 m/hP

16 m/hPa in 6k

„barometric st

$p(h) = p_0\ e^{-hg/RT}$



,Standard'

km	T[°C]			
0	0			
0	15			
0	25			
3	- 4.4	700	28.964	$1.76\text{x}10^{19}$
10	-49.9	265	28.964	$6.67\text{x}10^{18}$
20	-56.5	55	28.964	$1.38\text{x}10^{18}$
30	-46.6	12	28.964	$0.30\text{x}10^{18}$
100	-63	.00021	28.5	$5.29\text{x}10^{12}$

0.3 Units for quantification of atmospheric trace substances

Ideal gas law: $pV = nRT = mRT/M_g$

Universal gas constant $R = 8206$ Pa L/(mol K) = 8.314 J/(mol K) = $N_a k_B$

Avogadro's number $N_A = 6.023 \times 10^{23}$

Boltzmann constant $k_B = 1.38 \times 10^{-23}$ J/K

1 Pa = 1.013 N/m² = 1.013 J/m³

Molar mass $M_{g\ air} \approx 28.8$ g/mol

Molar volume at T_0=273 K and p_0=101325 Pa: V = 22.414 L/mol

Concentration $c_i = m_i/V$ [µg/m³] (for gases: = density)

Mass mixing ratio $\mu_{m\ i} = c_i/c$ [, %, ppmm, ppbm]

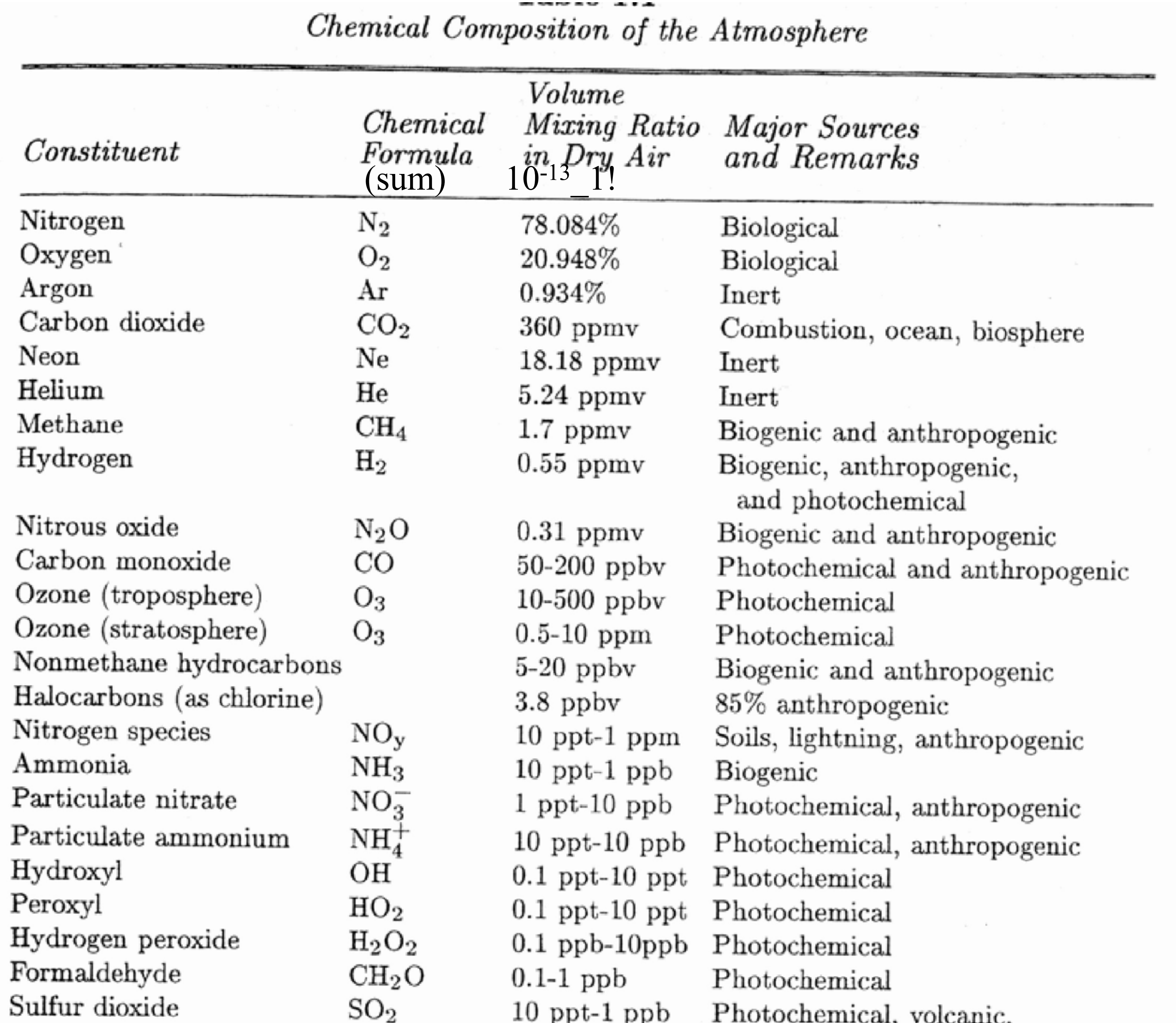
Partial pressure $p_i = n_i RT/V_i$ [Pa]

Volume mixing ratio $\mu_{V\ i} = p_i/p = V_i/V$ [, %, ppmV, ppbV]

Number density $N_i/V = n_i N_A/V = p_i N_A/RT$ [molec/cm³]

Avogadro's number $N_A = 6.022 \times 10^{23}$ molec/mol

More details: Schwartz & Warneck (1995): Units for use in atmospheric chemistry, Pure Appl. Chem. 67, 1377-1406



Chemical Composition of the Atmosphere

Constituent	Chemical Formula (sum)	Volume Mixing Ratio in Dry Air 10^{-13}_1!	Major Sources and Remarks
Nitrogen	N_2	78.084%	Biological
Oxygen	O_2	20.948%	Biological
Argon	Ar	0.934%	Inert
Carbon dioxide	CO_2	360 ppmv	Combustion, ocean, biosphere
Neon	Ne	18.18 ppmv	Inert
Helium	He	5.24 ppmv	Inert
Methane	CH_4	1.7 ppmv	Biogenic and anthropogenic
Hydrogen	H_2	0.55 ppmv	Biogenic, anthropogenic, and photochemical
Nitrous oxide	N_2O	0.31 ppmv	Biogenic and anthropogenic
Carbon monoxide	CO	50-200 ppbv	Photochemical and anthropogenic
Ozone (troposphere)	O_3	10-500 ppbv	Photochemical
Ozone (stratosphere)	O_3	0.5-10 ppm	Photochemical
Nonmethane hydrocarbons		5-20 ppbv	Biogenic and anthropogenic
Halocarbons (as chlorine)		3.8 ppbv	85% anthropogenic
Nitrogen species	NO_y	10 ppt-1 ppm	Soils, lightning, anthropogenic
Ammonia	NH_3	10 ppt-1 ppb	Biogenic
Particulate nitrate	NO_3^-	1 ppt-10 ppb	Photochemical, anthropogenic
Particulate ammonium	NH_4^+	10 ppt-10 ppb	Photochemical, anthropogenic
Hydroxyl	OH	0.1 ppt-10 ppt	Photochemical
Peroxyl	HO_2	0.1 ppt-10 ppt	Photochemical
Hydrogen peroxide	H_2O_2	0.1 ppb-10ppb	Photochemical
Formaldehyde	CH_2O	0.1-1 ppb	Photochemical
Sulfur dioxide	SO_2	10 ppt-1 ppb	Photochemical, volcanic,

1 Reaction types, kinetics

1.1 Reaction rate coefficient k (dt.: Reaktionsgeschwindigkeitskoeffizient)

Temperature dependence:

$-dc_i/dt = k_T\ c_i$

$k_T = A(T)\ e^{[\Delta E/(RT)]}$

Universal gas constant $R = k_B\ N_A = 1.38\text{x}10^{-23}$ J/K x $6.023\text{x}10^{23}$/mol

Providing the energy is sufficiently large, the temperature dependence of A
is unimportant, and k_T follows the Arrhenius expression:

$k_T\ = A\ e^{[E_a/(RT)]}$

with activation energy E_a

Frequently used, too: van t‘Hoff expression:

$k_T = B\ e^{[-\ E_a/R\ (1/T - 1/T_{ref})]}$,

The two expressions are equal via: $A = B\ e^{[E_a/(RT_{ref})]}$

Rate coefficient from gas kinetic theory

= effective reactions per unit of time =

= collision frequency x likelyhood of reaction per collision

1) Molecules need to collide ($\approx 10^9$ /s at 10^5 Pa).

They are close enough to collide during $\approx (10^{-13} - 10^{-12}) \times 10^9$/s

Collision frequency

$$\boxed{Z_{ij} = \left(\frac{8kT}{\pi m_{ij}}\right)^{1/2} \sigma_{ij}^2 N_i N_j \qquad \mathrm{cm}^{-3}\mathrm{s}^{-1}}$$

$\left(\frac{8kT}{\pi m_{ij}}\right)^{1/2}$ root-mean-square relative speed of molecules i and j

$m_{ij} = \frac{m_i m_j}{m_i + m_j}$ reduced mass

N_i : number density (cm^{-3})

$k = 1.381 \cdot 10^{-23}\ \mathrm{JK}^{-1}$ Boltzmann constant

σ_{ij}^2 : collision cross section

Speed, collisions in absolute terms:

from Maxwell-Boltzmann distribution function of molecular velocities (gas kinetic theory):

$dN/N = c^{(m <v_i>^2 / 2kT)}$; with $c = (m / 2\pi kT)^{0.5}$

$<v_i>$ = mean absolute velocity of molecules

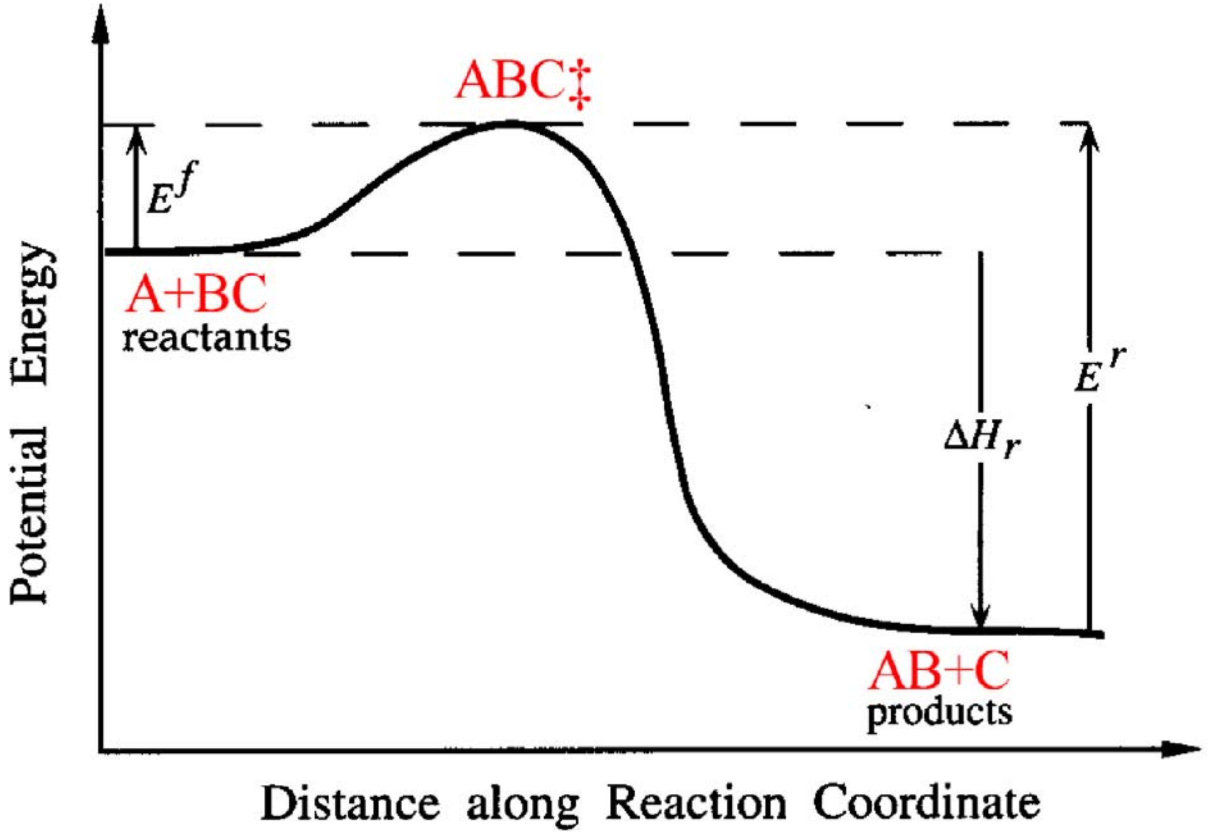
corresponding mean free path λ with regard to collisions

$\lambda_i = 1 / [(N_A/V)(\sqrt{2}\ \pi\sigma_i^2)]$,
$N_A/V = 6.022\text{x}10^{23} / 0.0224 = 2.46 \text{ x } 10^{25}$ molec/m^3

N_2 : $<v> = 0.51$ m/s = 1840 km/h, $\lambda = 65$ nm
CO_2: $<v> = 0.41$ m/s = 1490 km/h, $\lambda = 44$ nm

2) Extra energy is needed to overcome the transition state

As molecules approach each other they have to overcome an energy barrier because of electronic repulsion. The energy they absorb leads to a loosening of the intramolecular bonds until a transition state is reached, which can then either fall back into the original molecules or proceed to yield the products of the reaction. Reaction enthalpy ΔH_r.



Likelyhood: collision cross section, σ_{ij}

In the transition state, usually the energy provided from bond formation is less than the energy consumption from bond breaking.

The collision cross section takes into account that a minimum amount of energy is needed. It is not necessarily provided with every orientation of the molecules during approach (steric factor).

$$\sigma_{ij} = \pi\left(r_i + r_j\right)^2\left(1 - \frac{E_0}{E}\right) \qquad \text{for } E \geq E_0,\ 0 \text{ elsewhere}$$

Integrated over all total energies from 0 to ∞, the frequency of reactive collisions becomes

$$Z_{ij}^R = \underbrace{\pi\left(r_i + r_j\right)^2\left(\frac{8kT}{\pi m_{ij}}\right)^{1/2} e^{-E_0/kT}}_{k} N_i N_j$$

Theoretical maximum
at 1000 hPa, 293 K
(for r_i, r_j = 0.2 nm, $E_0 = 0$ and no steric hindrance): $k \approx 2 \times 10^{-10}$ cm³/molec/s

1.2 Homogeneous gas-phase reactions

Reactions can be unimolecular, bi- or termolecular.

The rate law of a reaction of the general form

$$aA + bB \rightarrow cC + dD$$

Is defined as

Rate (dt.: Rate) $= -dc_A/dt/a = -dc_B/dt/b = dc_C/dt/c = dc_D/dt/d$

example:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

Rate $= -dc_{NO}/dt/2 = -dc_{O2}/dt = dc_{NO2}/dt/2$

Second order

Usually: bimolecular

$$A + B \rightarrow C + D$$

$$A + B \rightarrow C$$; A, B, C, D molecules or radicals

example:

$$O + O_2 \rightarrow O_3$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$dc_C/dt = -dc_A/dt = -dc_B/dt = k^{(2)}\, c_A{}^1\, c_B{}^1$

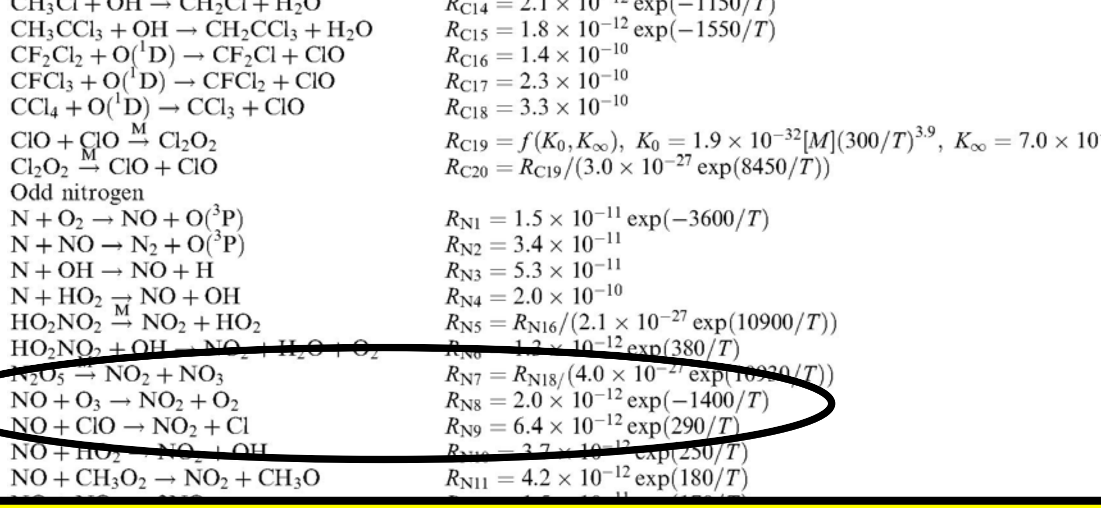
Reaction rate: second order (1+1=2)

Reaction rate coefficient (denoting the order): $k^{(2)}$

The reaction order is given by the sum of the exponentials, n+m+..., of the concentration terms in the rate law of the form $-dc_A/dt = k\, c_A{}^n\, c_B{}^m$ (n = zero or integer or fraction*)

It is determined empirically.

* ‚overall‘ reactions only



$CH_3Cl + OH \rightarrow CH_2Cl + H_2O$	$R_{C14} = 2.1 \times 10^{-12} \exp(-1150/T)$
$CH_3CCl_3 + OH \rightarrow CH_2CCl_3 + H_2O$	$R_{C15} = 1.8 \times 10^{-12} \exp(-1550/T)$
$CF_2Cl_2 + O(^1D) \rightarrow CF_2Cl + ClO$	$R_{C16} = 1.4 \times 10^{-10}$
$CFCl_3 + O(^1D) \rightarrow CFCl_2 + ClO$	$R_{C17} = 2.3 \times 10^{-10}$
$CCl_4 + O(^1D) \rightarrow CCl_3 + ClO$	$R_{C18} = 3.3 \times 10^{-10}$
$ClO + ClO \xrightarrow{M} Cl_2O_2$	$R_{C19} = f(K_0, K_\infty),\ K_0 = 1.9 \times 10^{-32}[M](300/T)^{3.9},\ K_\infty = 7.0 \times 10$
$Cl_2O_2 \xrightarrow{M} ClO + ClO$	$R_{C20} = R_{C19}/(3.0 \times 10^{-27} \exp(8450/T))$
Odd nitrogen	
$N + O_2 \rightarrow NO + O(^3P)$	$R_{N1} = 1.5 \times 10^{-11} \exp(-3600/T)$
$N + NO \rightarrow N_2 + O(^3P)$	$R_{N2} = 3.4 \times 10^{-11}$
$N + OH \rightarrow NO + H$	$R_{N3} = 5.3 \times 10^{-11}$
$N + HO_2 \rightarrow NO + OH$	$R_{N4} = 2.0 \times 10^{-10}$
$HO_2NO_2 \xrightarrow{M} NO_2 + HO_2$	$R_{N5} = R_{N16}/(2.1 \times 10^{-27} \exp(10900/T))$
$HO_2NO_2 + OH \rightarrow NO_2 + H_2O + O_2$	$R_{N6} = 1.3 \times 10^{-12} \exp(380/T)$
$N_2O_5 \xrightarrow{M} NO_2 + NO_3$	$R_{N7} = R_{N18}/(4.0 \times 10^{-27} \exp(10930/T))$
$NO + O_3 \rightarrow NO_2 + O_2$	$R_{N8} = 2.0 \times 10^{-12} \exp(-1400/T)$
$NO + ClO \rightarrow NO_2 + Cl$	$R_{N9} = 6.4 \times 10^{-12} \exp(290/T)$
$NO + HO_2 \rightarrow NO_2 + OH$	$R_{N10} = 3.7 \times 10^{-12} \exp(250/T)$
$NO + CH_3O_2 \rightarrow NO_2 + CH_3O$	$R_{N11} = 4.2 \times 10^{-12} \exp(180/T)$

k_T

Example

$NO + O_3 \rightarrow NO_2 + O_2$

$k = A\, e^{[-(E_a/R)T]}$

Arrhenius expression, preexponential factor A, activation energy E_a

$k(T^{-1}) \rightarrow$ slope $m = -E_a/R$, intercept ln A, $E_a/R > 0 \leftrightarrow$ faster at higher T

$A = 2 \text{x} 10^{-12}$ cm³/molec/s

$E/R = -1400$ K

→

$k_{298\ K} = 1.8 \text{ x} 10^{-14}$ cm³/molec/s

$k_{230\ K} = 0.45 \text{x} 10^{-14}$ cm³/molec/s

2. Exception:

First order (but not unimolecular):

$$A + M \rightarrow C + D + M$$

or if $c_B >> c_A$

$$A + B + M \rightarrow C + D + M$$

Here, M stands for any molecule or atom (i.e. N_2, O_2,...), not transformed but required to absorb excess energy, e.g. of an activated intermediate state:

$$A + B = AB^* \xrightarrow{+M} C + D$$

$$A \xrightarrow{+M} C + D$$

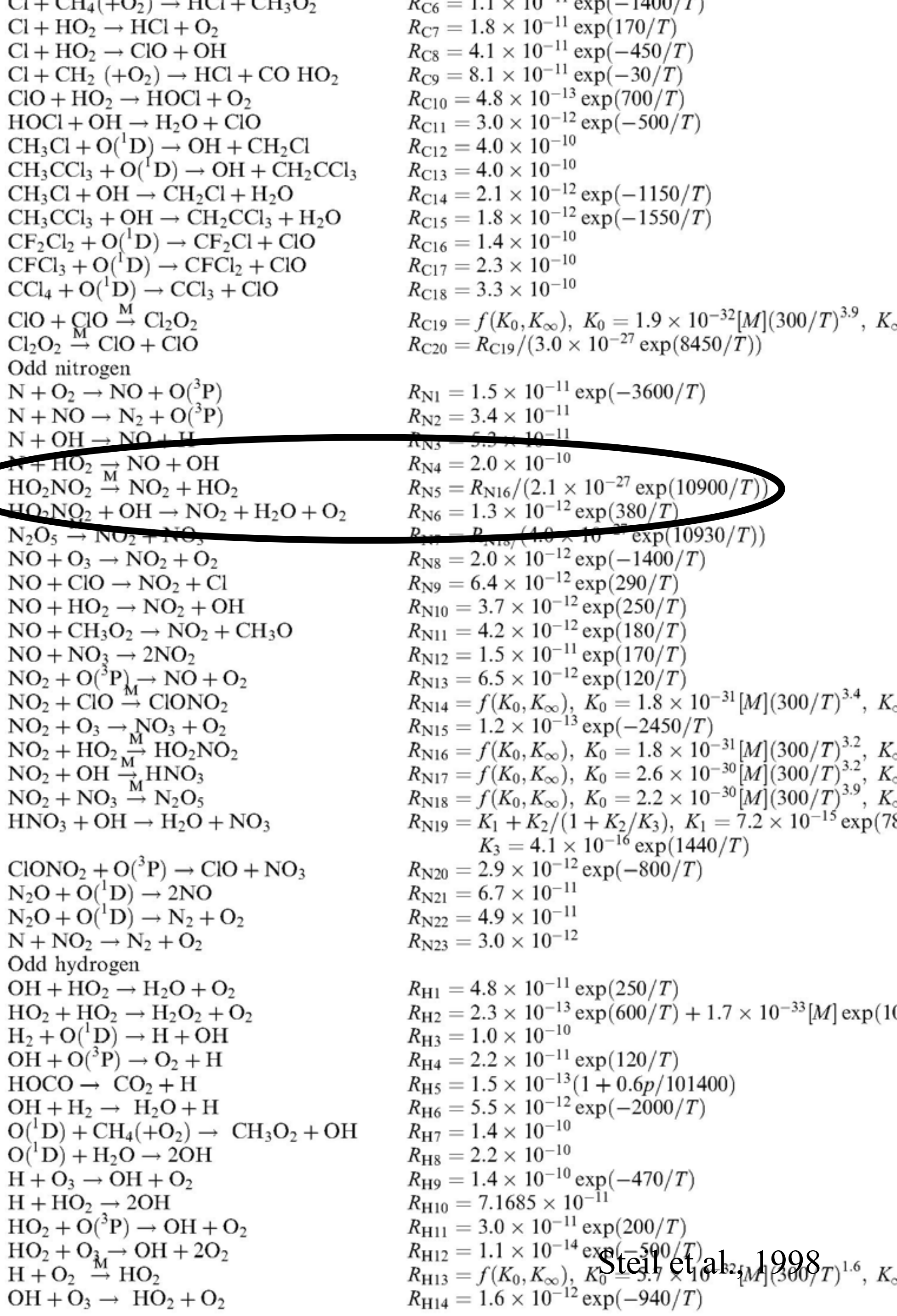
Example: thermic dissociation

$$HOONO_2 \rightarrow HO_2 + NO_2$$

Reaction rate

$$dc_C/dt = -dc_A/dt = k^{(1)} c_A^{\,1}$$

$$k^{(1)} = k^{(2)} c_M^{\,1} \; (c_M^{\,1} \text{ constant})$$



$Cl + CH_4(+O_2) \rightarrow HCl + CH_3O_2$	$R_{C6} = 1.1 \times 10^{-11} \exp(-1400/T)$
$Cl + HO_2 \rightarrow HCl + O_2$	$R_{C7} = 1.8 \times 10^{-11} \exp(170/T)$
$Cl + HO_2 \rightarrow ClO + OH$	$R_{C8} = 4.1 \times 10^{-11} \exp(-450/T)$
$Cl + CH_2\ (+O_2) \rightarrow HCl + CO\ HO_2$	$R_{C9} = 8.1 \times 10^{-11} \exp(-30/T)$
$ClO + HO_2 \rightarrow HOCl + O_2$	$R_{C10} = 4.8 \times 10^{-13} \exp(700/T)$
$HOCl + OH \rightarrow H_2O + ClO$	$R_{C11} = 3.0 \times 10^{-12} \exp(-500/T)$
$CH_3Cl + O(^1D) \rightarrow OH + CH_2Cl$	$R_{C12} = 4.0 \times 10^{-10}$
$CH_3CCl_3 + O(^1D) \rightarrow OH + CH_2CCl_3$	$R_{C13} = 4.0 \times 10^{-10}$
$CH_3Cl + OH \rightarrow CH_2Cl + H_2O$	$R_{C14} = 2.1 \times 10^{-12} \exp(-1150/T)$
$CH_3CCl_3 + OH \rightarrow CH_2CCl_3 + H_2O$	$R_{C15} = 1.8 \times 10^{-12} \exp(-1550/T)$
$CF_2Cl_2 + O(^1D) \rightarrow CF_2Cl + ClO$	$R_{C16} = 1.4 \times 10^{-10}$
$CFCl_3 + O(^1D) \rightarrow CFCl_2 + ClO$	$R_{C17} = 2.3 \times 10^{-10}$
$CCl_4 + O(^1D) \rightarrow CCl_3 + ClO$	$R_{C18} = 3.3 \times 10^{-10}$
$ClO + ClO \xrightarrow{M} Cl_2O_2$	$R_{C19} = f(K_0, K_\infty),\ K_0 = 1.9 \times 10^{-32}[M](300/T)^{3.9},\ K$
$Cl_2O_2 \xrightarrow{M} ClO + ClO$	$R_{C20} = R_{C19}/(3.0 \times 10^{-27} \exp(8450/T))$
Odd nitrogen	
$N + O_2 \rightarrow NO + O(^3P)$	$R_{N1} = 1.5 \times 10^{-11} \exp(-3600/T)$
$N + NO \rightarrow N_2 + O(^3P)$	$R_{N2} = 3.4 \times 10^{-11}$
$N + OH \rightarrow NO + H$	$R_{N3} = 5.3 \times 10^{-11}$
$N + HO_2 \rightarrow NO + OH$	$R_{N4} = 2.0 \times 10^{-10}$
$HO_2NO_2 \xrightarrow{M} NO_2 + HO_2$	$R_{N5} = R_{N16}/(2.1 \times 10^{-27} \exp(10900/T))$
$HO_2NO_2 + OH \rightarrow NO_2 + H_2O + O_2$	$R_{N6} = 1.3 \times 10^{-12} \exp(380/T)$
$N_2O_5 \xrightarrow{M} NO_2 + NO_3$	$R_{N7} = R_{N18}/(4.0 \times 10^{-27} \exp(10930/T))$
$NO + O_3 \rightarrow NO_2 + O_2$	$R_{N8} = 2.0 \times 10^{-12} \exp(-1400/T)$
$NO + ClO \rightarrow NO_2 + Cl$	$R_{N9} = 6.4 \times 10^{-12} \exp(290/T)$
$NO + HO_2 \rightarrow NO_2 + OH$	$R_{N10} = 3.7 \times 10^{-12} \exp(250/T)$
$NO + CH_3O_2 \rightarrow NO_2 + CH_3O$	$R_{N11} = 4.2 \times 10^{-12} \exp(180/T)$
$NO + NO_3 \rightarrow 2NO_2$	$R_{N12} = 1.5 \times 10^{-11} \exp(170/T)$
$NO_2 + O(^3P) \rightarrow NO + O_2$	$R_{N13} = 6.5 \times 10^{-12} \exp(120/T)$
$NO_2 + ClO \xrightarrow{M} ClONO_2$	$R_{N14} = f(K_0, K_\infty),\ K_0 = 1.8 \times 10^{-31}[M](300/T)^{3.4},\ K$
$NO_2 + O_3 \rightarrow NO_3 + O_2$	$R_{N15} = 1.2 \times 10^{-13} \exp(-2450/T)$
$NO_2 + HO_2 \xrightarrow{M} HO_2NO_2$	$R_{N16} = f(K_0, K_\infty),\ K_0 = 1.8 \times 10^{-31}[M](300/T)^{3.2},\ K$
$NO_2 + OH \xrightarrow{M} HNO_3$	$R_{N17} = f(K_0, K_\infty),\ K_0 = 2.6 \times 10^{-30}[M](300/T)^{3.2},\ K$
$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	$R_{N18} = f(K_0, K_\infty),\ K_0 = 2.2 \times 10^{-30}[M](300/T)^{3.9},\ K$
$HNO_3 + OH \rightarrow H_2O + NO_3$	$R_{N19} = K_1 + K_2/(1 + K_2/K_3),\ K_1 = 7.2 \times 10^{-15} \exp(78$ $K_3 = 4.1 \times 10^{-16} \exp(1440/T)$
$ClONO_2 + O(^3P) \rightarrow ClO + NO_3$	$R_{N20} = 2.9 \times 10^{-12} \exp(-800/T)$
$N_2O + O(^1D) \rightarrow 2NO$	$R_{N21} = 6.7 \times 10^{-11}$
$N_2O + O(^1D) \rightarrow N_2 + O_2$	$R_{N22} = 4.9 \times 10^{-11}$
$N + NO_2 \rightarrow N_2 + O_2$	$R_{N23} = 3.0 \times 10^{-12}$
Odd hydrogen	
$OH + HO_2 \rightarrow H_2O + O_2$	$R_{H1} = 4.8 \times 10^{-11} \exp(250/T)$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$R_{H2} = 2.3 \times 10^{-13} \exp(600/T) + 1.7 \times 10^{-33}[M] \exp(1$
$H_2 + O(^1D) \rightarrow H + OH$	$R_{H3} = 1.0 \times 10^{-10}$
$OH + O(^3P) \rightarrow O_2 + H$	$R_{H4} = 2.2 \times 10^{-11} \exp(120/T)$
$HOCO \rightarrow CO_2 + H$	$R_{H5} = 1.5 \times 10^{-13}(1 + 0.6p/101400)$
$OH + H_2 \rightarrow H_2O + H$	$R_{H6} = 5.5 \times 10^{-12} \exp(-2000/T)$
$O(^1D) + CH_4(+O_2) \rightarrow CH_3O_2 + OH$	$R_{H7} = 1.4 \times 10^{-10}$
$O(^1D) + H_2O \rightarrow 2OH$	$R_{H8} = 2.2 \times 10^{-10}$
$H + O_3 \rightarrow OH + O_2$	$R_{H9} = 1.4 \times 10^{-10} \exp(-470/T)$
$H + HO_2 \rightarrow 2OH$	$R_{H10} = 7.1685 \times 10^{-11}$
$HO_2 + O(^3P) \rightarrow OH + O_2$	$R_{H11} = 3.0 \times 10^{-11} \exp(200/T)$
$HO_2 + O_3 \rightarrow OH + 2O_2$	$R_{H12} = 1.1 \times 10^{-14} \exp(-500/T)$
$H + O_2 \xrightarrow{M} HO_2$	$R_{H13} = f(K_0, K_\infty),\ K_0 = 5.7 \times 10^{-32}[M](300/T)^{1.6},\ K$
$OH + O_3 \rightarrow HO_2 + O_2$	$R_{H14} = 1.6 \times 10^{-12} \exp(-940/T)$

Steil et al., 1998

Reaction orders

$A + B \rightarrow C + D$

is 2nd order or – in case $dc_B/dt \approx 0$ - pseudo-1st order

$A + B + M \rightarrow C + D + M$

is 2nd order or – in case $dc_B/dt \approx 0$ - pseudo-1st order or
– if $p \ll 1000$ hPa - between 2nd and 3rd order

The unit of a homogeneous gas-phase rate is $[\text{molec/cm}^3\text{/s}]$.

A 1st or pseudo-1st order rate law reads:

$-dc_A/dt = dc_C/dt = k^{(1)}\, c_C$, with $k^{(1)}$ [1/s].

A 2nd order rate law reads:

$-dc_A/dt = dc_C/dt = k^{(2)}\, c_C\, c_D$, with $k^{(2)}$ $[\text{cm}^3\text{/molec/s}]$.

A 3rd order rate law reads e.g.:

$-dc_A/dt = k^{(3)}\, c_C^{\,2}\, c_D$, with $k^{(3)}$ $[\text{cm}^6\text{/molec}^2\text{/s}]$.

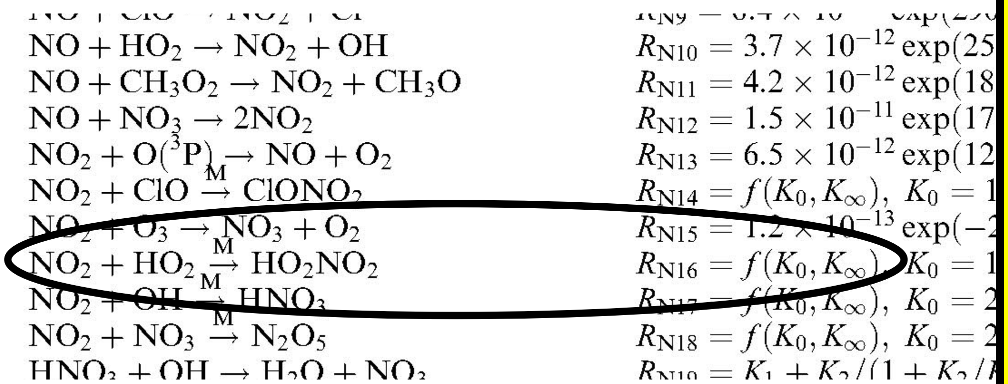
3. **between 2nd and 3rd order:** In the range of pressures and temperatures in the upper troposphere and stratosphere (c_M small) many reactions are in the region between 2nd and 3rd order reactions:

$$k = \frac{k_0 M}{1 + k_0 M / k_\infty} F_C^{\left(1+\log(k_0 M/k_\infty)^2\right)^{-1}} \qquad F_C \approx 0.6$$

$$k_0(T) = k_0^{300K}\left(\frac{T}{300K}\right)^{-n}, \qquad k\infty(T) = k_\infty^{300K}\left(\frac{T}{300K}\right)^{-m}$$

k_0, k_∞ = low, high pressure limiting rate constant *(Troe, 1979)*

F_C = broadening factor of falloff curve between 2nd and 3rd order in the range of atmospheric pressures



$NO + ClO \rightarrow NO_2 + Cl$	$R_{N9} = 6.4 \times 10$ exp(29
$NO + HO_2 \rightarrow NO_2 + OH$	$R_{N10} = 3.7 \times 10^{-12}$ exp(25
$NO + CH_3O_2 \rightarrow NO_2 + CH_3O$	$R_{N11} = 4.2 \times 10^{-12}$ exp(18
$NO + NO_3 \rightarrow 2NO_2$	$R_{N12} = 1.5 \times 10^{-11}$ exp(17
$NO_2 + O(^3P) \rightarrow NO + O_2$	$R_{N13} = 6.5 \times 10^{-12}$ exp(12
$NO_2 + ClO \xrightarrow{M} ClONO_2$	$R_{N14} = f(K_0, K_\infty),\ K_0 = 1$
$NO_2 + O_3 \rightarrow NO_3 + O_2$	$R_{N15} = 1.2 \times 10^{-13}$ exp(−2
$NO_2 + HO_2 \xrightarrow{M} HO_2NO_2$	$R_{N16} = f(K_0, K_\infty),\ K_0 = 1$
$NO_2 + OH \xrightarrow{M} HNO_3$	$R_{N17} = f(K_0, K_\infty),\ K_0 = 2$
$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	$R_{N18} = f(K_0, K_\infty),\ K_0 = 2$
$HNO_3 + OH \rightarrow H_2O + NO_3$	$R_{N19} = K_1 + K_2/(1 + K_2/$

$NO_2 + HO_2 + M \rightarrow HO_2NO_2 + M$

$K_0 = k_0(T)c_M$, $n = 3.2$

$K_\infty = k_\infty(T)$, $m = 1.4$ →

$k_{288\ K/1000\ hPa} = 1.9 \times 10^{-12}\ cm^3/molec/s$

$k_{288\ K/500\ hPa} = 1.5 \times 10^{-12}\ cm^3/molec/s$

$k_{230\ K/500\ hPa} = 2.3 \times 10^{-12}\ cm^3/molec/s$

$k_{230\ K/1000\ hPa} = 3.0 \times 10^{-12}\ cm^3/molec/s$

1.3 Combinations of thermic reactions- Quasi steady state approximation

Second order

Usually: bimolecular

$$A + B \rightarrow C + D$$

$$A + B \rightarrow C$$

A, B, C, D molecules or radicals

example:

$$O + O_2 \rightarrow O_3$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

Reaction rate: second order (1+1=2)

$dc_C/dt = -dc_A/dt = -dc_B/dt = k\ c_A^{\ 1}\ c_B^{\ 1}$

Reaction rate coefficient: $k^{(2)}$

$k = A \exp [-(E_a/R)T]$

Arrhenius expression, preexponential factor A, activation energy E_a

$k(T^{-1}) \rightarrow$ slope $-E_a/R$, intercept ln A, $E_a/R > 0 \leftrightarrow$ faster at higher T

1.3 Combinations of thermic reactions- Quasi steady state approximation

Second order

Usually: bimolecular

$$A + B \rightarrow C + D$$

$$A + B \rightarrow C$$

A, B, C, D molecules or radical

example:

$$O + O_2 \rightarrow O_3$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

Reaction rate: second order (1+

$dc_C/dt = -dc_A/dt = -dc_B/dt = k\ c$

Reaction rate coefficient: $k^{(2)}$

$k = A \exp [-(E_a/R)T]$

Arrhenius expression, preexpone

$k(T^{-1}) \rightarrow$ slope $-E_a/R$, intercept ln A,

Very frequent:

(1) $A + B \rightarrow C^*$

(-1) $C^* \rightarrow A + B$

(2) $C^* + M \rightarrow C$

Intermediate C*:

$dc_{C^*}/dt = k_1\ c_A\ c_B - k_{-1}\ c_{C^*} - k_2\ c_{C^*}\ c_M$

Lifetime of C* short $\rightarrow dc_{C^*}/dt = 0$

Hence:

$k_1\ c_A\ c_B = k_{-1}\ c_{C^*} + k_2\ c_{C^*}\ c_M$

$k_1\ c_A\ c_B = c_{C^*}\ (k_{-1} + k_2\ c_M)$

$c_{C^*} = k_1\ c_A\ c_B\ /(k_{-1} + k_2\ c_M)$

Example

(1) $O + O_2 = O_3^*$

(2) $O_3^* + M \rightarrow O_3$

Example

(1) $O + O_2 = O_3^*$

(2) $O_3^* + M \rightarrow O_3$

$$c_{O3*} = k_1\, c_O\, c_{O2} / (k_{-1} + k_2\, c_M)$$

$$dc_{O3}/dt = k_2\, c_{O3*}\, c_M$$

$$dc_{O3}/dt = k_1\, k_2\, c_O\, c_{O2}\, c_M / (k_{-1} + k_2\, c_M) = [\underbrace{k_1\, k_2\, c_M / (k_{-1} + k_2\, c_M)}_{k}]\, c_O\, c_{O2}$$

High pressure limit: $k_{-1} \approx 0 \rightarrow \quad k_\infty = k_1$

Low pressure limit: $c_M \rightarrow 0 \qquad \rightarrow k_0 = k_1\, k_2 / k_{-1}$

Reaction rate compilations

Compilations are considered the state-of-the-art description of atmospheric chemistry, because

- complete knowledge is summarized and assessed, and
- laboratory kineticists from around the world are involved

However,

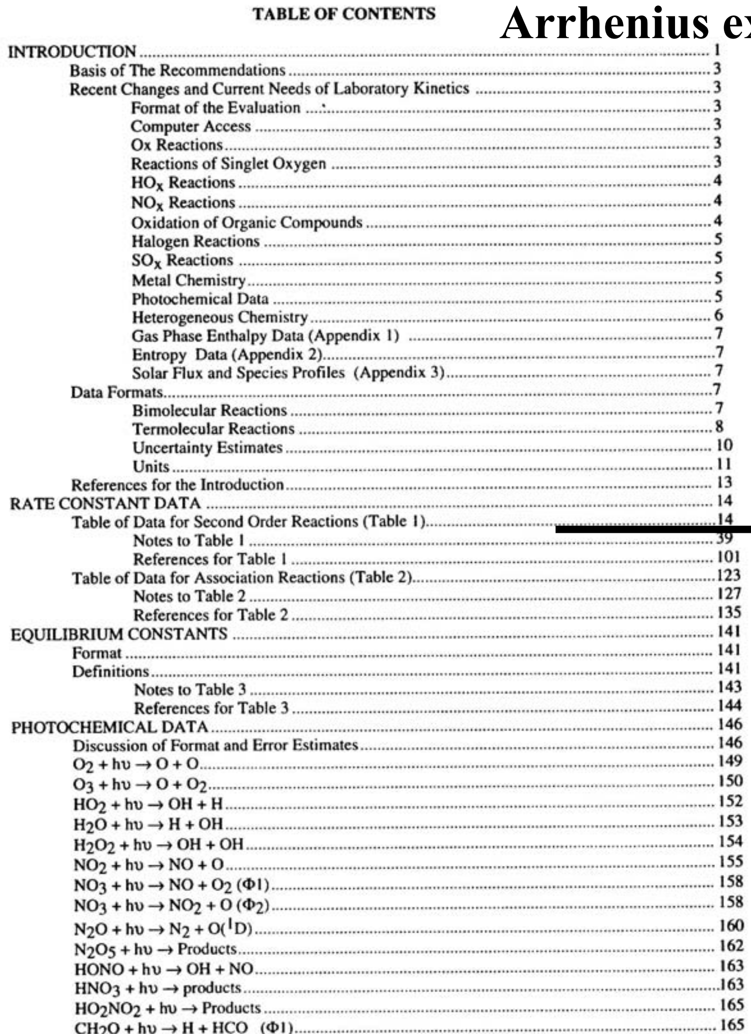
- there is no guarantee for completeness, and
- some rate constants are very uncertain, but uncertainty is quantified

- Chemical kinetics and photochemical data for use in stratospheric modeling Eval. No. 12 (JPL-Publ-97-4; NAS 1.26112606; NASA CR-97-112606), 1997 (updated 2005, http://ntrs.nasa.gov/search.jsp

- Hydrocarbon reactions: Atkinson et al., Atmos. Chem. Phys. 6 (2006) 3625-4055

Chemical kinetics and photochemical data for use in stratospheric modeling
Eval. No. 12 (JPL-Publ-97-4; NAS 1.26112606; NASA CR-97-112606), 1997 (updated 2005)
http://ntrs.nasa.gov/search.jsp

$k = A \exp(-E_a / RT)$
Arrhenius expression



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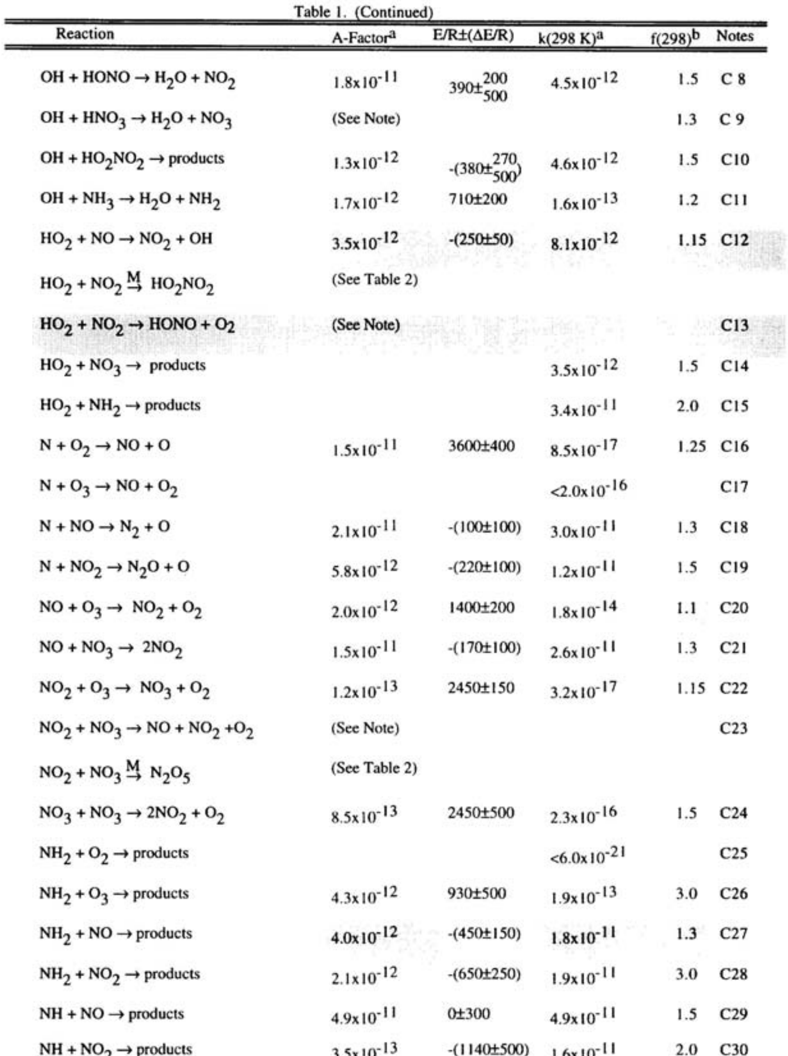


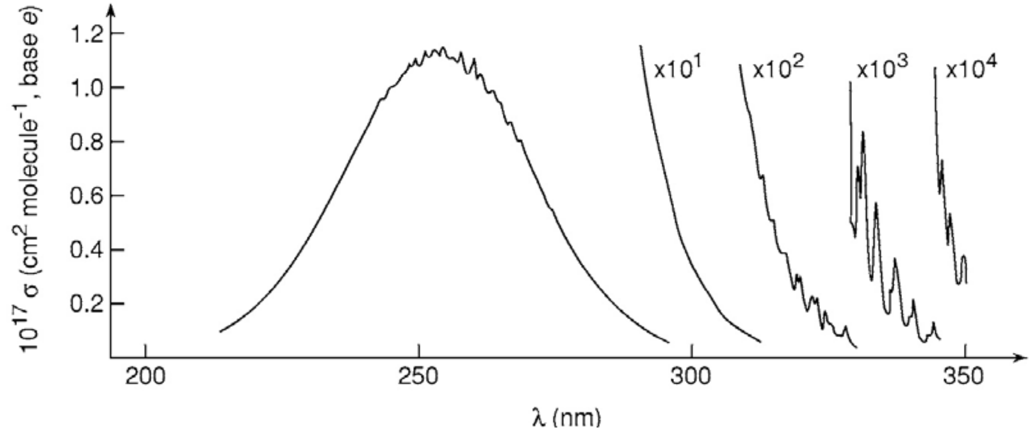
Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes
$OH + HONO \rightarrow H_2O + NO_2$	1.8×10^{-11}	$390\pm^{200}_{500}$	4.5×10^{-12}	1.5	C 8
$OH + HNO_3 \rightarrow H_2O + NO_3$	(See Note)			1.3	C 9
$OH + HO_2NO_2 \rightarrow$ products	1.3×10^{-12}	$-(380\pm^{270}_{500})$	4.6×10^{-12}	1.5	C10
$OH + NH_3 \rightarrow H_2O + NH_2$	1.7×10^{-12}	710±200	1.6×10^{-13}	1.2	C11
$HO_2 + NO \rightarrow NO_2 + OH$	3.5×10^{-12}	-(250±50)	8.1×10^{-12}	1.15	C12
$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(See Table 2)				
$HO_2 + NO_2 \rightarrow HONO + O_2$	(See Note)				C13
$HO_2 + NO_3 \rightarrow$ products			3.5×10^{-12}	1.5	C14
$HO_2 + NH_2 \rightarrow$ products			3.4×10^{-11}	2.0	C15
$N + O_2 \rightarrow NO + O$	1.5×10^{-11}	3600±400	8.5×10^{-17}	1.25	C16
$N + O_3 \rightarrow NO + O_2$			$<2.0 \times 10^{-16}$		C17
$N + NO \rightarrow N_2 + O$	2.1×10^{-11}	-(100±100)	3.0×10^{-11}	1.3	C18
$N + NO_2 \rightarrow N_2O + O$	5.8×10^{-12}	-(220±100)	1.2×10^{-11}	1.5	C19
$NO + O_3 \rightarrow NO_2 + O_2$	2.0×10^{-12}	1400±200	1.8×10^{-14}	1.1	C20
$NO + NO_3 \rightarrow 2NO_2$	1.5×10^{-11}	-(170±100)	2.6×10^{-11}	1.3	C21
$NO_2 + O_3 \rightarrow NO_3 + O_2$	1.2×10^{-13}	2450±150	3.2×10^{-17}	1.15	C22
$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$	(See Note)				C23
$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(See Table 2)				
$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$	8.5×10^{-13}	2450±500	2.3×10^{-16}	1.5	C24
$NH_2 + O_2 \rightarrow$ products			$<6.0 \times 10^{-21}$		C25
$NH_2 + O_3 \rightarrow$ products	4.3×10^{-12}	930±500	1.9×10^{-13}	3.0	C26
$NH_2 + NO \rightarrow$ products	4.0×10^{-12}	-(450±150)	1.8×10^{-11}	1.3	C27
$NH_2 + NO_2 \rightarrow$ products	2.1×10^{-12}	-(650±250)	1.9×10^{-11}	3.0	C28
$NH + NO \rightarrow$ products	4.9×10^{-11}	0±300	4.9×10^{-11}	1.5	C29
$NH + NO_2 \rightarrow$ products	3.5×10^{-13}	-(1140±500)	1.6×10^{-11}	2.0	C30

1.4 Photochemical reactions

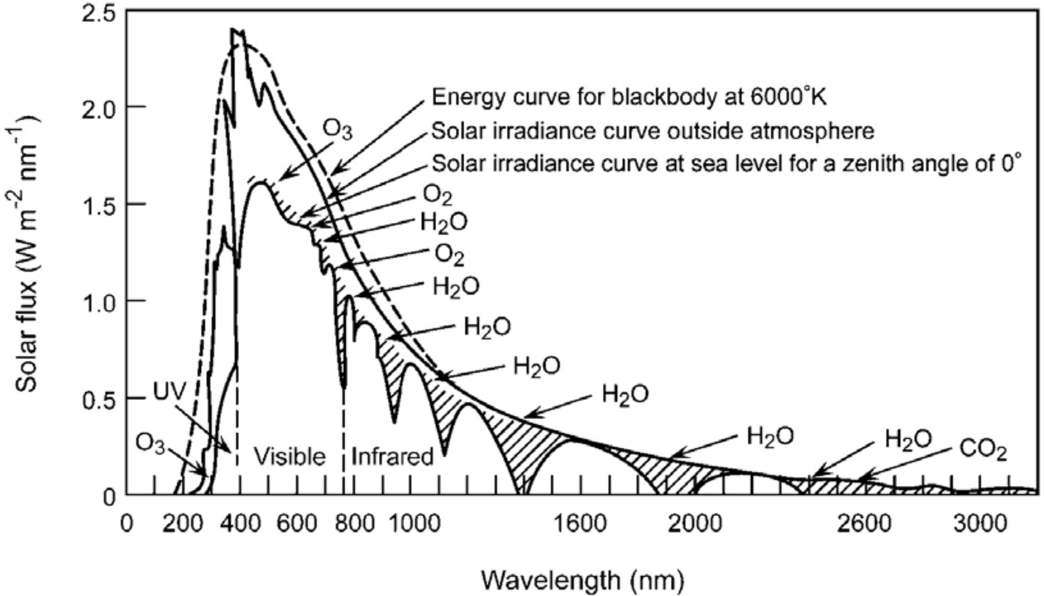
Radiation absorption in the atmosphere

Gaseous molecules absorb ultraviolet, visible and infrared light: O_3



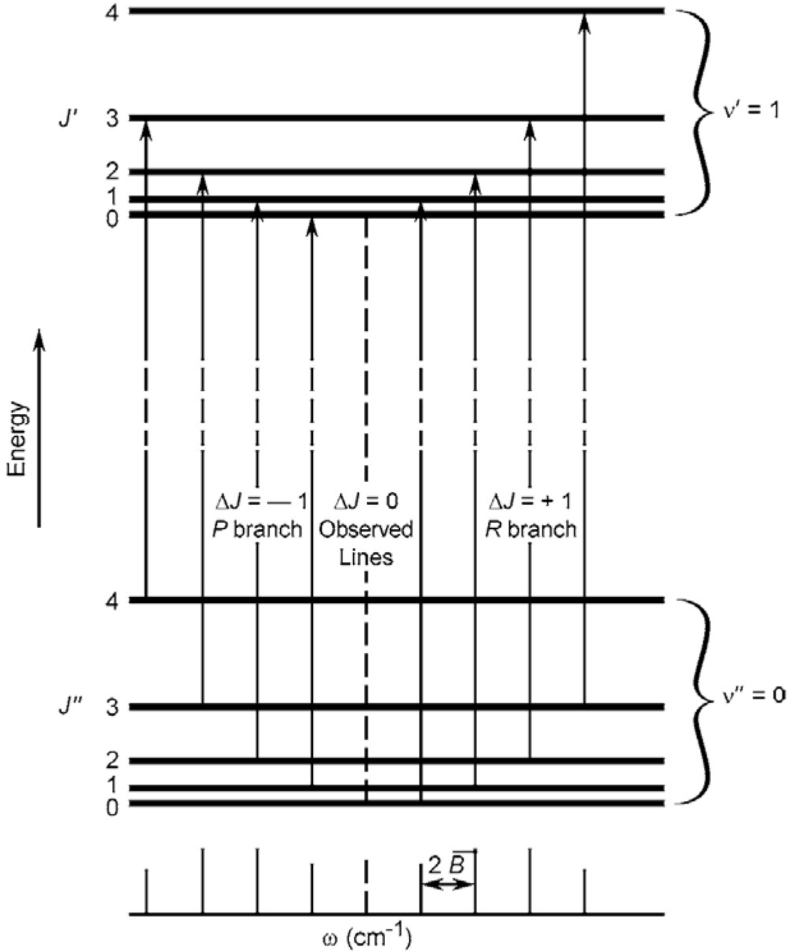
Consequences:

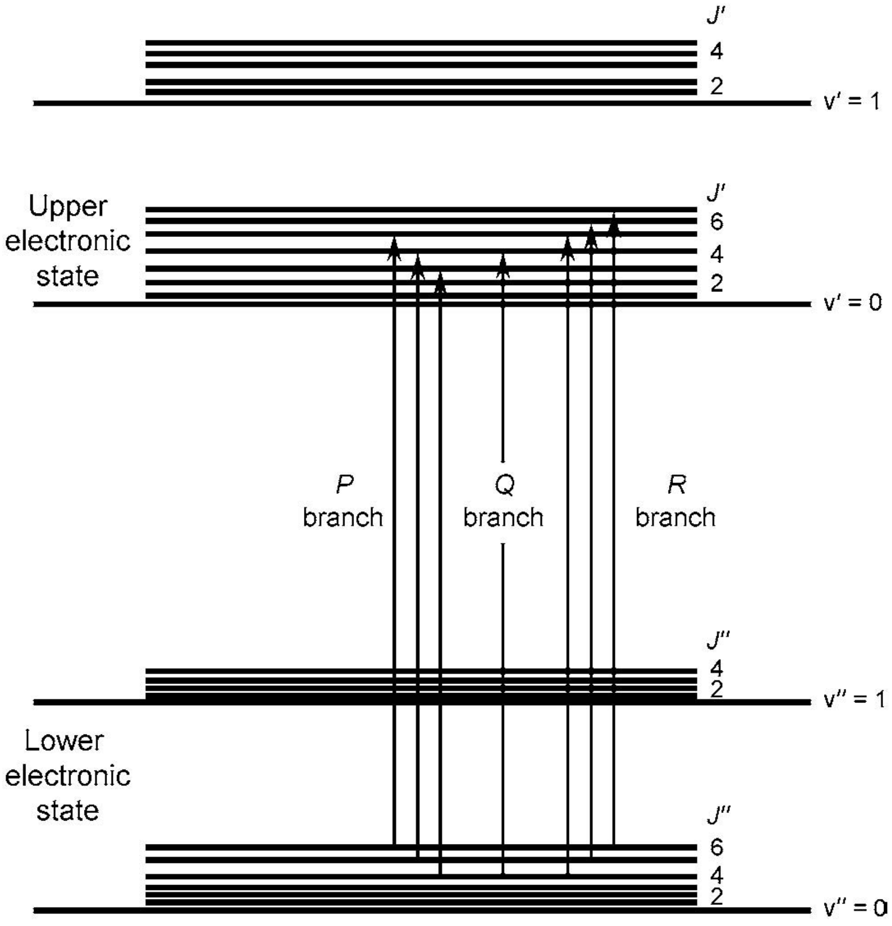
- photophysical and photochemical molecular processes
- change of spectrum:



Specific because of vibrational-rotational and electronic transitions:

A series of vibrational-rotational states are populated (temperature dependent, Boltzmann) within electronic states. Vibrational-rotational (P, Q, R branches of change of J) and electronic transitions follow quantum rules (selection rules, ‚allowed‘ or not allowed). These correspond to characteristic spectroscopic patterns. Therefore, emission and absorption spectroscopy allows for unambiguous identification of molecules.

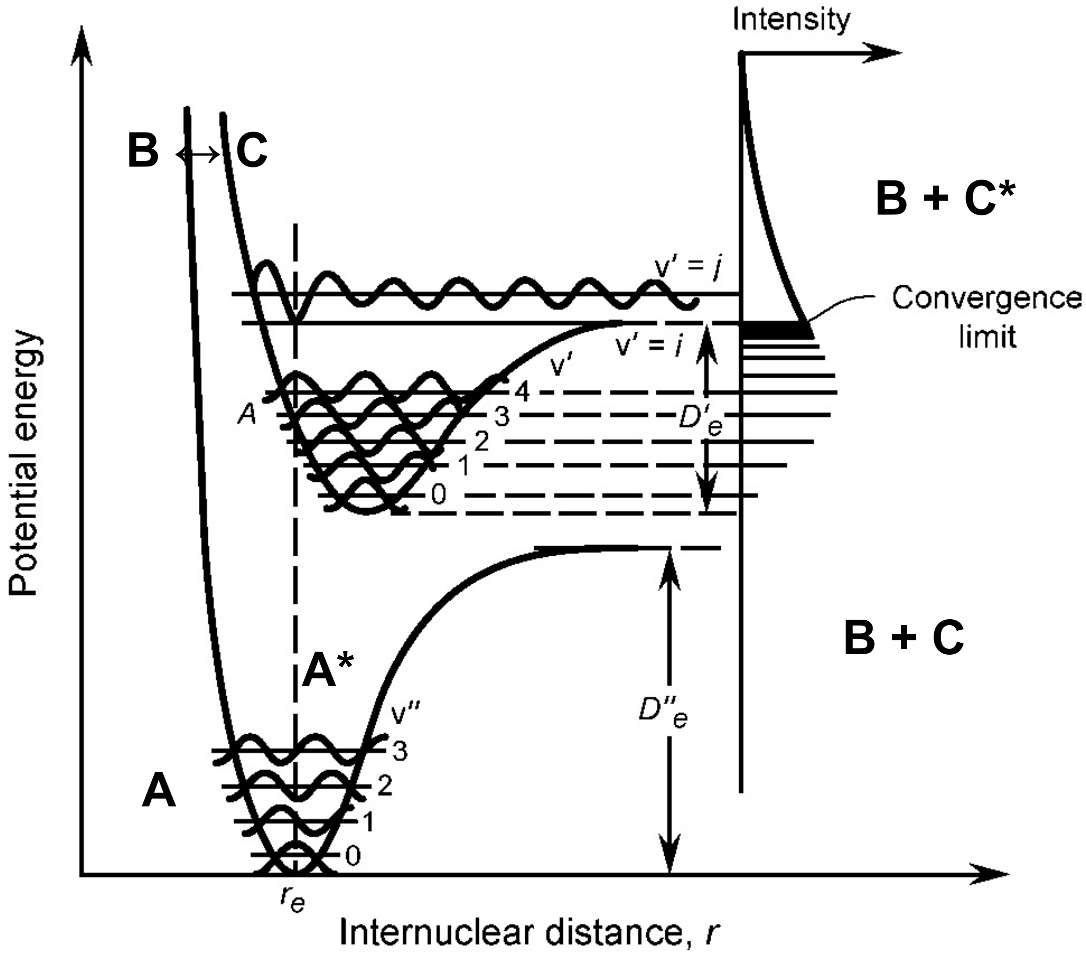




Electronic excitation:

$A \rightarrow B + C$

The energy barrier will be smaller and the distance between atoms will be larger for the excited molecule.



Fates of electronically excited molecules:

Photophysical primary processes: emission (fluorescence, phosphorescence), nonradiative energy transition into heat

Photochemical primary processes: dissociation, isomerization, re-arrangement, reaction

Example for photophysical process: $A^* + B \rightarrow A + B^*$*:*

$SO_2\,(^3B_1) + O_2\,(^3\Sigma_g) \rightarrow SO_2\,(^1A_1) + O_2\,(^1\Sigma_g)$

Example for photochemical process:

$NO_2\,(X^2A) + h\nu\,(290 < \lambda < 430\ \mathrm{nm}) \rightarrow NO\,(X^2\Pi) + O\,(^3P)$

Def.:

Efficiency of a primary photochemical process i is given by ist quantum yield ϕ_i:= number of excited molecules by process i divided by total number of photons absorbed.

The sum of the ϕ_i of all the photochemical primary processes = 1.

Photodissociations

Unimolecular

$$A + h\nu \rightarrow B + C$$

A, B, C, D molecules or radicals

example:

$$O_3 + h\nu \rightarrow O_2 + O\ (^3P)$$

Reaction rate coefficient j (photolysis rate):

$$dc_C/dt = -dc_A/dt = j\ c_A$$

Ground state, A /excitation state, A*:

$$A + h\nu \rightarrow A^*$$

Example:

$$O + h\nu \rightarrow O^*$$

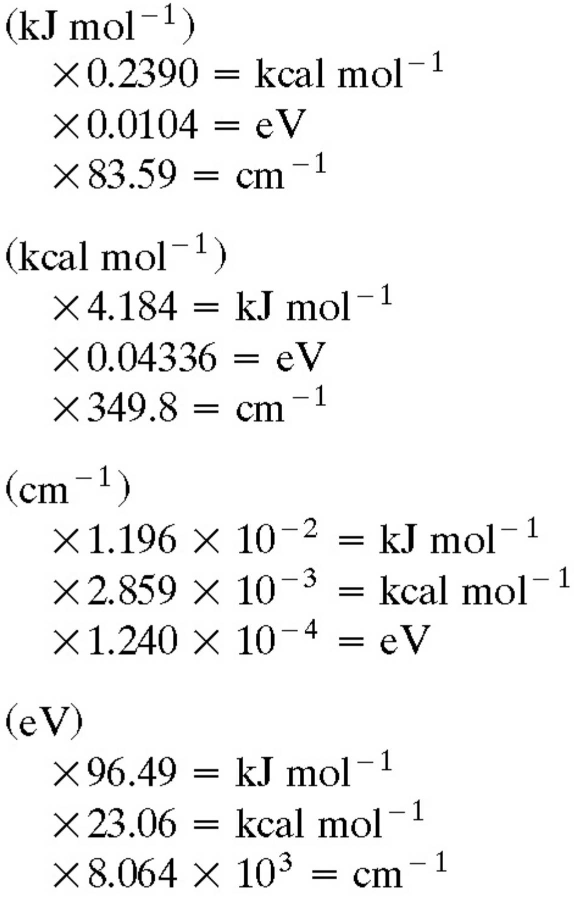
i.e. $O(^3P) + h\nu \rightarrow O(^1D)$

Energy ranges, correspondence between energy and wavelength

$\lambda = c/\nu$ with frequency ν

$\Delta E = hc/\lambda = hc\omega$ Planck relationship (wavelength λ, wavenumber ω, Planck‘s constant $h = 6.626 \times 10^{-34}$ Js)

Commonly used energy units:



(kJ mol^{-1})
$\times 0.2390$ = kcal mol^{-1}
$\times 0.0104$ = eV
$\times 83.59$ = cm^{-1}

(kcal mol^{-1})
$\times 4.184$ = kJ mol^{-1}
$\times 0.04336$ = eV
$\times 349.8$ = cm^{-1}

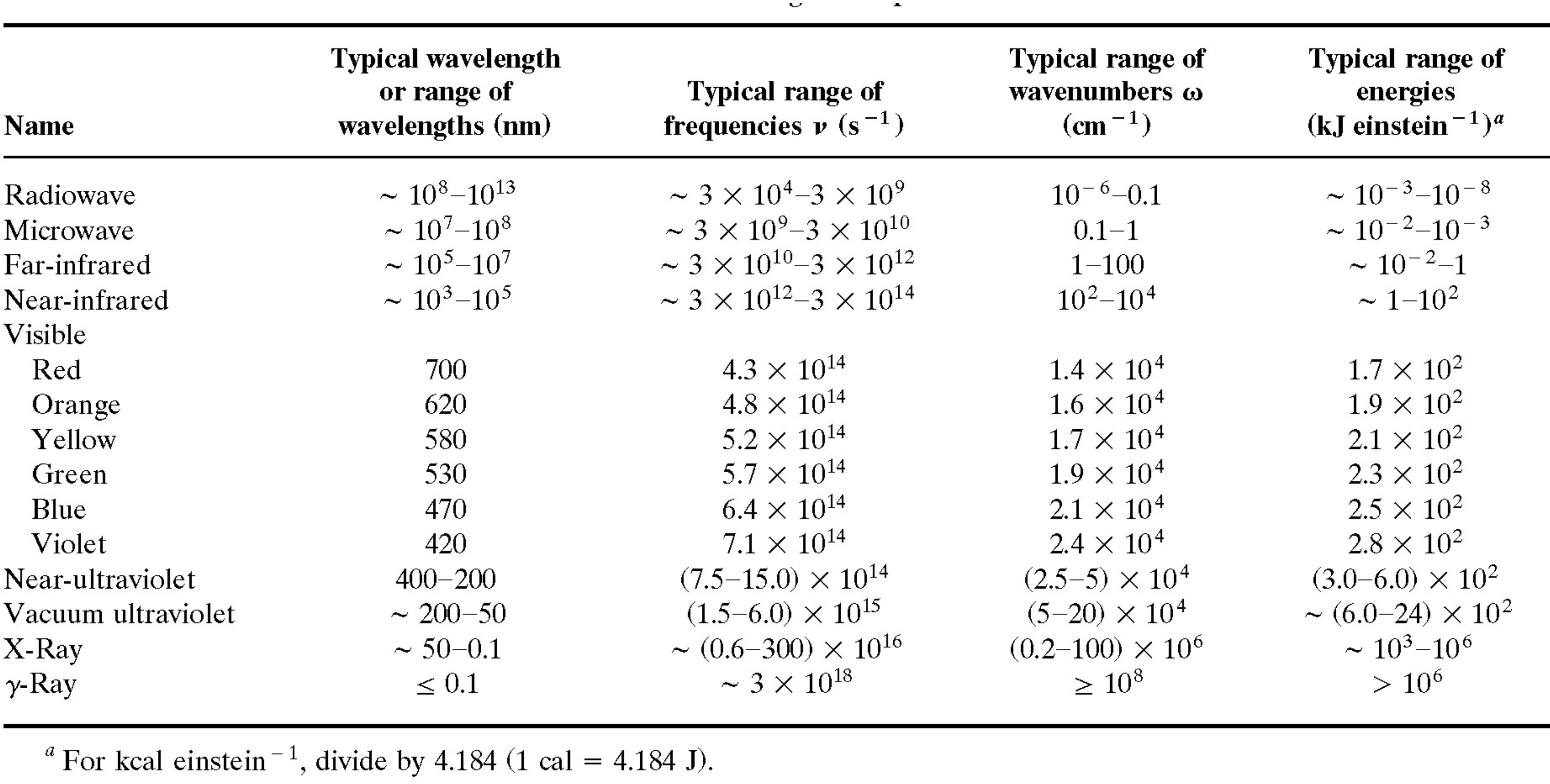
(cm^{-1})
$\times 1.196 \times 10^{-2}$ = kJ mol^{-1}
$\times 2.859 \times 10^{-3}$ = kcal mol^{-1}
$\times 1.240 \times 10^{-4}$ = eV

(eV)
$\times 96.49$ = kJ mol^{-1}
$\times 23.06$ = kcal mol^{-1}
$\times 8.064 \times 10^{3}$ = cm^{-1}

Energy ranges, correspondence between energy and wavelength

$\lambda = c/\nu$

$\Delta E = hc/\lambda = hc\omega$ Planck relationship (wavelength λ, wavenumber ω, Planck‘s constant $h = 6.626 \times 10^{-34}$ Js)



Name	Typical wavelength or range of wavelengths (nm)	Typical range of frequencies ν (s^{-1})	Typical range of wavenumbers ω (cm^{-1})	Typical range of energies (kJ $einstein^{-1}$)[a]
Radiowave	$\sim 10^8$–10^{13}	$\sim 3 \times 10^4$–3×10^9	10^{-6}–0.1	$\sim 10^{-3}$–10^{-8}
Microwave	$\sim 10^7$–10^8	$\sim 3 \times 10^9$–3×10^{10}	0.1–1	$\sim 10^{-2}$–10^{-3}
Far-infrared	$\sim 10^5$–10^7	$\sim 3 \times 10^{10}$–3×10^{12}	1–100	$\sim 10^{-2}$–1
Near-infrared	$\sim 10^3$–10^5	$\sim 3 \times 10^{12}$–3×10^{14}	10^2–10^4	~ 1–10^2
Visible				
Red	700	4.3×10^{14}	1.4×10^4	1.7×10^2
Orange	620	4.8×10^{14}	1.6×10^4	1.9×10^2
Yellow	580	5.2×10^{14}	1.7×10^4	2.1×10^2
Green	530	5.7×10^{14}	1.9×10^4	2.3×10^2
Blue	470	6.4×10^{14}	2.1×10^4	2.5×10^2
Violet	420	7.1×10^{14}	2.4×10^4	2.8×10^2
Near-ultraviolet	400–200	$(7.5$–$15.0) \times 10^{14}$	$(2.5$–$5) \times 10^4$	$(3.0$–$6.0) \times 10^2$
Vacuum ultraviolet	~ 200–50	$(1.5$–$6.0) \times 10^{15}$	$(5$–$20) \times 10^4$	$\sim (6.0$–$24) \times 10^2$
X-Ray	~ 50–0.1	$\sim (0.6$–$300) \times 10^{16}$	$(0.2$–$100) \times 10^6$	$\sim 10^3$–10^6
γ-Ray	≤ 0.1	$\sim 3 \times 10^{18}$	$\geq 10^8$	$> 10^6$

[a] For kcal $einstein^{-1}$, divide by 4.184 (1 cal = 4.184 J).

The rate of photochemical reactions
Absorption

$\ln(I_0/I) = \sigma N d$ Beer-Lambert law

$I/I_0 = e^{(-\sigma N d)}$

absorption cross section σ (cm^2, default: base e)

molecule concentration N (cm^{-3}), depth of absorptive layer d (cm)

optical depth $OD = \sigma N d$

Caution: Most measurements are made to the

base 10 ($\log(I_0/I) = \sigma_{10} N d$) → x 2.303 to reach base e

The photolysis rate

The photolysis rate, j (s^{-1}), is given by:

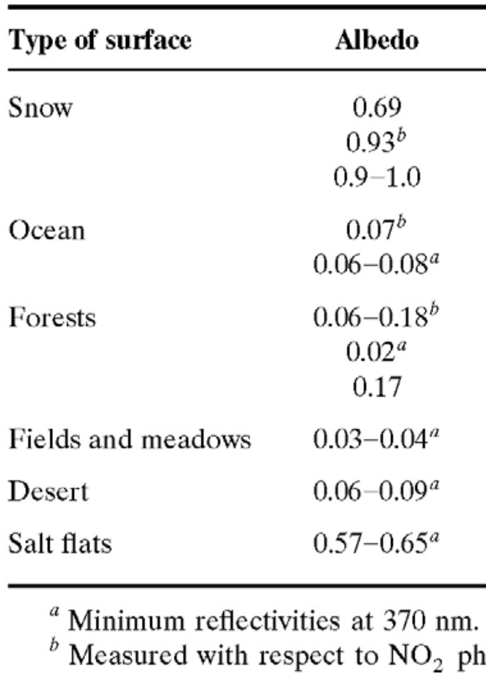
$$j = \int_{\lambda} \phi(\lambda)\ \sigma(\lambda)\ L(\lambda)\ d\lambda$$

- quantum yield $\phi(\lambda)$ ( ),
- absorption cross section σ (cm^2),
- actinic flux, $L(\lambda)$ ($cm^{-2}\ s^{-1}$)

  L is the total intensity of effective light (direct + scattered + reflected, spherically integrated).

The photolysis rate

L(λ) is a function of the solar zenith angle, cloudiness, aerosol concentration, and surface albedo*.



*

Type of surface	Albedo
Snow	0.69 0.93^b 0.9–1.0
Ocean	0.07^b $0.06–0.08^a$
Forests	$0.06–0.18^b$ 0.02^a 0.17
Fields and meadows	$0.03–0.04^a$
Desert	$0.06–0.09^a$
Salt flats	$0.57–0.65^a$

[a] Minimum reflectivities at 370 nm.
[b] Measured with respect to NO_2 ph

$$\frac{dn_A}{dt} = -n_A \underbrace{\int_\lambda \phi(\lambda)\sigma(\lambda)\left(\int_0^{2\pi}\int_0^{\pi} L(\lambda,\theta,\varphi)\sin\theta \, d\theta \, d\varphi\right) d\lambda}_{j_A}$$

Typical j-values for midlatitude noontime equinox conditions range from ~1 · 10^{-5} s-1 for $j_{O(1D)}$ to ~0.2 s^{-1} for j_{NO3}. The actinic flux under these conditions is about $2 \cdot 10^{14}$ photons cm^{-2} s^{-1} at 315-320 nm, and $7 \cdot 10^{14}$ photons cm^{-2} s^{-1} at 360-365 nm.

The photolysis rate

L is measured using a (2π) radiometer or by measuring the photolytic decay (so-called chemical actinometry).
Its value can be estimated via tabulated values of ϕ and σ for intervals of λ and estimates of L(λ) for given conditions.

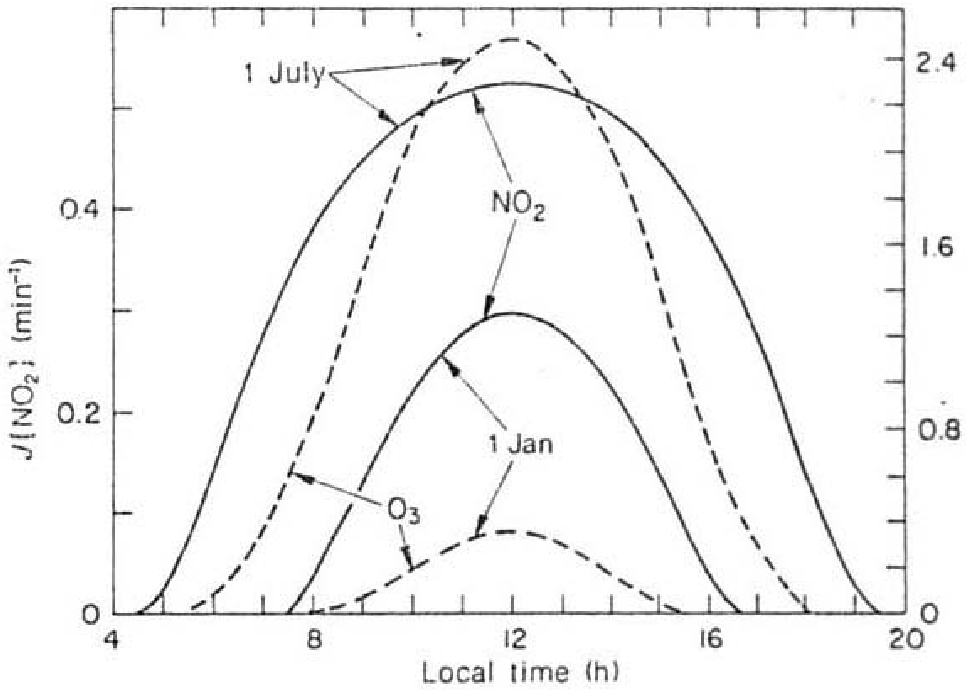


Fig. 3 Theoretical diurnal variation of the $J[NO_2]$ and $J[O_3]$ values for midsummer and midwinter at 40° N latitude near sea level.

(Calvert, 1985)

Example j_{O3}: Quantum yield $\phi_i(\lambda)$ for $i = O_3 + h\nu \rightarrow O(^1D) + O_2(^3\Sigma_g^-)$

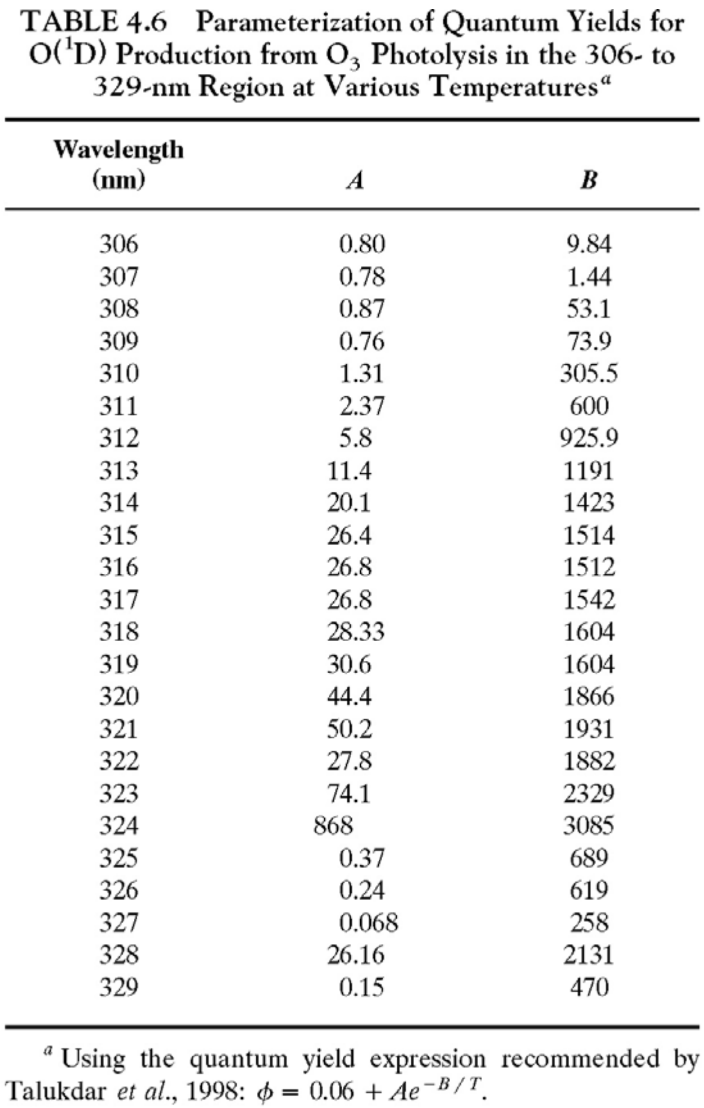
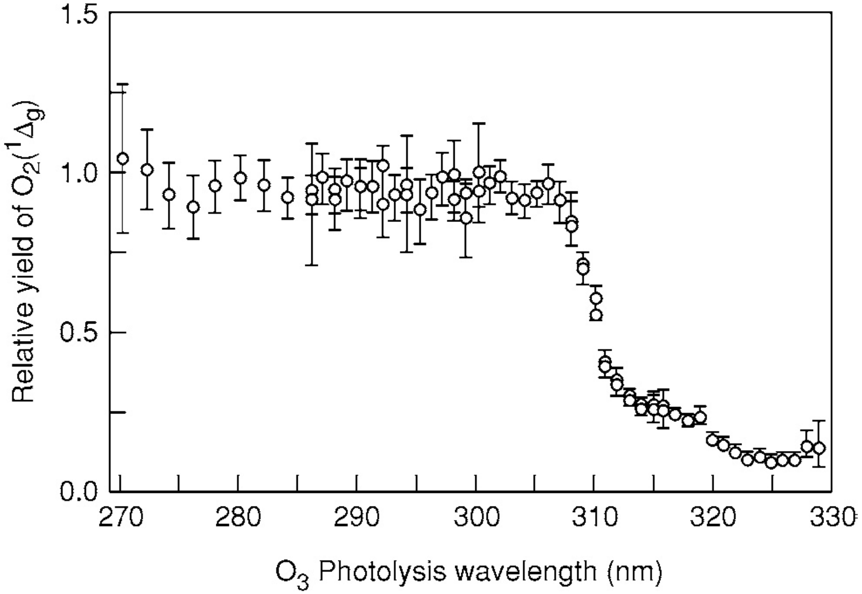


TABLE 4.6 Parameterization of Quantum Yields for $O(^1D)$ Production from O_3 Photolysis in the 306- to 329-nm Region at Various Temperatures[a]

Wavelength (nm)	***A***	***B***
306	0.80	9.84
307	0.78	1.44
308	0.87	53.1
309	0.76	73.9
310	1.31	305.5
311	2.37	600
312	5.8	925.9
313	11.4	1191
314	20.1	1423
315	26.4	1514
316	26.8	1512
317	26.8	1542
318	28.33	1604
319	30.6	1604
320	44.4	1866
321	50.2	1931
322	27.8	1882
323	74.1	2329
324	868	3085
325	0.37	689
326	0.24	619
327	0.068	258
328	26.16	2131
329	0.15	470

[a] Using the quantum yield expression recommended by Talukdar *et al.*, 1998: $\phi = 0.06 + Ae^{-B/T}$.



$\phi_{O3\rightarrow O(^1D)}(310\text{-}320\ \text{nm}) \approx 0.2$

Data src.: Finlayson-Pitts & Pitts, 1998

Example j_{O3}: Absorption cross section $\sigma(\lambda,T)$ of O_3

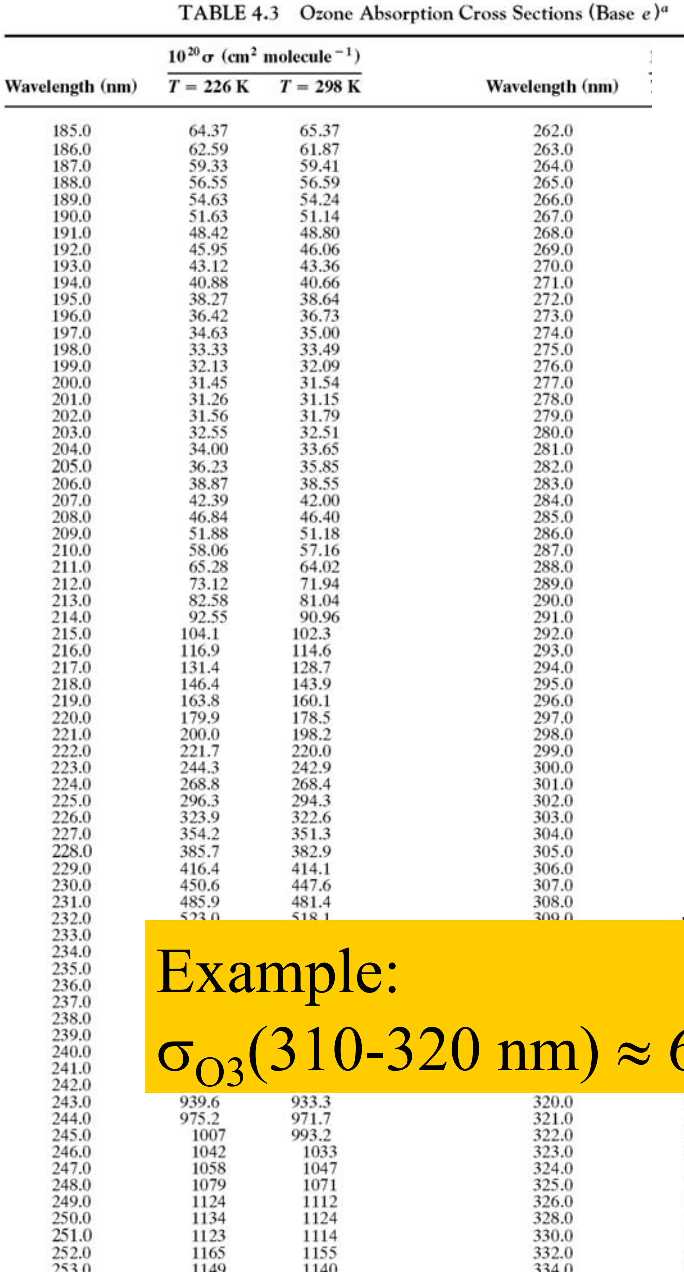


TABLE 4.3 Ozone Absorption Cross Sections (Base e)[a]

Wavelength (nm)	$10^{20}\sigma$ (cm^2 molecule^{-1}) T = 226 K	$10^{20}\sigma$ (cm^2 molecule^{-1}) T = 298 K	Wavelength (nm)		
185.0	64.37	65.37	262.0		
186.0	62.59	61.87	263.0		
187.0	59.33	59.41	264.0		
188.0	56.55	56.59	265.0		
189.0	54.63	54.24	266.0		
190.0	51.63	51.14	267.0		
191.0	48.42	48.80	268.0		
192.0	45.95	46.06	269.0		
193.0	43.12	43.36	270.0		
194.0	40.88	40.66	271.0		
195.0	38.27	38.64	272.0		
196.0	36.42	36.73	273.0		
197.0	34.63	35.00	274.0		
198.0	33.33	33.49	275.0		
199.0	32.13	32.09	276.0		
200.0	31.45	31.54	277.0		
201.0	31.26	31.15	278.0		
202.0	31.56	31.79	279.0		
203.0	32.55	32.51	280.0		
204.0	34.00	33.65	281.0		
205.0	36.23	35.85	282.0		
206.0	38.87	38.55	283.0		
207.0	42.39	42.00	284.0		
208.0	46.84	46.40	285.0		
209.0	51.88	51.18	286.0		
210.0	58.06	57.16	287.0		
211.0	65.28	64.02	288.0		
212.0	73.12	71.94	289.0		
213.0	82.58	81.04	290.0		
214.0	92.55	90.96	291.0		
215.0	104.1	102.3	292.0		
216.0	116.9	114.6	293.0		
217.0	131.4	128.7	294.0		
218.0	146.4	143.9	295.0		
219.0	163.8	160.1	296.0		
220.0	179.9	178.5	297.0		
221.0	200.0	198.2	298.0		
222.0	221.7	220.0	299.0		
223.0	244.3	242.9	300.0		
224.0	268.8	268.4	301.0		
225.0	296.3	294.3	302.0		
226.0	323.9	322.6	303.0		
227.0	354.2	351.3	304.0		
228.0	385.7	382.9	305.0		
229.0	416.4	414.1	306.0		
230.0	450.6	447.6	307.0		
231.0	485.9	481.4	308.0		
232.0	523.0	518.1	309.0		
233.0					
234.0					
235.0					
236.0					
237.0					
238.0					
239.0					
240.0					
241.0					
242.0					
243.0	939.6	933.3	320.0	2.859	3.243
244.0	975.2	971.7	321.0	1.368	2.041
245.0	1007	993.2	322.0	2.117	2.435
246.0	1042	1033	323.0	1.529	1.983
247.0	1058	1047	324.0	0.7852	1.250
248.0	1079	1071	325.0	1.486	1.727
249.0	1124	1112	326.0	0.7276	1.105
250.0	1134	1124	328.0	1.158	1.300
251.0	1123	1114	330.0	0.2854	0.4923
252.0	1165	1155	332.0	0.2415	0.4347
253.0	1149	1140	334.0	0.3788	0.5343

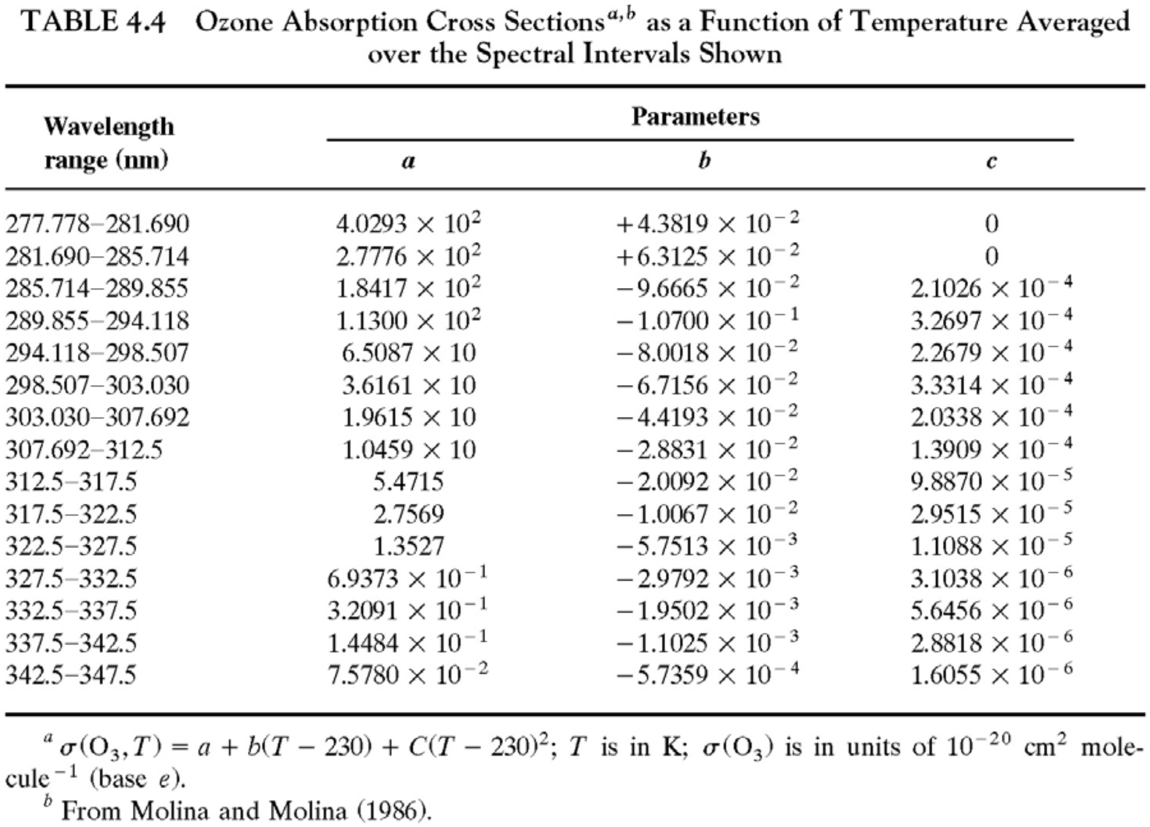


TABLE 4.4 Ozone Absorption Cross Sections[a,b] as a Function of Temperature Averaged over the Spectral Intervals Shown

Wavelength range (nm)	Parameters a	Parameters b	Parameters c
277.778–281.690	4.0293×10^2	$+4.3819 \times 10^{-2}$	0
281.690–285.714	2.7776×10^2	$+6.3125 \times 10^{-2}$	0
285.714–289.855	1.8417×10^2	-9.6665×10^{-2}	2.1026×10^{-4}
289.855–294.118	1.1300×10^2	-1.0700×10^{-1}	3.2697×10^{-4}
294.118–298.507	6.5087×10	-8.0018×10^{-2}	2.2679×10^{-4}
298.507–303.030	3.6161×10	-6.7156×10^{-2}	3.3314×10^{-4}
303.030–307.692	1.9615×10	-4.4193×10^{-2}	2.0338×10^{-4}
307.692–312.5	1.0459×10	-2.8831×10^{-2}	1.3909×10^{-4}
312.5–317.5	5.4715	-2.0092×10^{-2}	9.8870×10^{-5}
317.5–322.5	2.7569	-1.0067×10^{-2}	2.9515×10^{-5}
322.5–327.5	1.3527	-5.7513×10^{-3}	1.1088×10^{-5}
327.5–332.5	6.9373×10^{-1}	-2.9792×10^{-3}	3.1038×10^{-6}
332.5–337.5	3.2091×10^{-1}	-1.9502×10^{-3}	5.6456×10^{-6}
337.5–342.5	1.4484×10^{-1}	-1.1025×10^{-3}	2.8818×10^{-6}
342.5–347.5	7.5780×10^{-2}	-5.7359×10^{-4}	1.6055×10^{-6}

[a] $\sigma(O_3,T) = a + b(T - 230) + C(T - 230)^2$; T is in K; $\sigma(O_3)$ is in units of 10^{-20} cm^2 molecule^{-1} (base e).

[b] From Molina and Molina (1986).

Example:

σ_{O3}(310-320 nm) ≈ 60 x 10^{-20} cm²/molecule for T = 298 K

Data src.: Finlayson-Pitts & Pitts, 1998

Radiation absorption in the atmosphere

Actinic flux L(λ) - Example:

For z = 15 km and solar zenith angle of 40°:

$L(310\text{-}320\ nm) = (1.69+2.08+2.35+2.88+2.95) x 10^{14v} cm^{-2}\ s^{-1}$

Order of magnitude estimate of $j_{O3\rightarrow O(^1D)}$ for a selected wavelength interval:

$j_{O3\rightarrow O(^1D)}(310\text{-}320\ nm) \approx 0.2\ x\ 60\ x\ 10^{-20}\ x\ 12\ x\ 10^{14}\ s^{-1} \approx 10^{-4}\ s^{-1}$